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Part A-1: Polymer Chemistry

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Professor C. S. Marvel

FOREWORD

With this issue of the *Journal of Polymer Science*, the editors, publishers, friends, and colleagues of Professor C. S. Marvel wish to extend to him our most sincere good wishes on the occasion of his 75th birthday.

Every chemist in this country is well aware of the enormous contribution that "Speed" Marvel has made to macromolecular chemistry. An academic pioneer in the field, he has trained most of my generation of organic chemists currently working in the macromolecular area. His drive and energy, his ability to communicate easily with students, and his dedication to teaching and research have made their mark on the American scientific community. He published 68 papers in Organic Chemistry before his first polymer paper which appeared with C. S. Gibbs as a co-author in 1933. It took a great deal of courage in those times to carry out thesis work in the field of polymer structure.

He has probably influenced more students to study in the area of macromolecules than any other one person in the United States and possibly the world. His students have entered both teaching and industrial research, the latter being the largest recipient. A cursory glance at his co-authors on many of his papers reveals that they are now in leading positions in the industrial community. Many of his students have become successful teachers who work in the polymer field.

Perhaps the most remarkable thing of all has been his creative research in the past ten years. An alleged retirement and an appointment as a Research Professor at The University of Arizona has resulted in an amazing record of scientific achievement. His interests in high temperature polymers, which started at the University of Illinois, was carried with him to The University of Arizona. There is no one who has contributed as much in a creative synthetic way to the development of new polymers useful at high temperatures than Professor Marvel. Most of this has been done after retirement. How many people have been this active in the period of age between 65 and 75! The outstanding contribution in creative research in the past ten years constitutes a legacy which will be indeed hard to surpass.

Speed, I speak for all of your former students, postdoctoral people, colleagues and friends when I say that we wish you continued good health and the opportunity to continue to work on significant chemical problems. Man has a short time to make a significant impact on a few and you have clearly done this.

C. G. Overberger

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 1923–1938 (1970)

Thermal Analyses of Polymers. III. Influence of Isocyanate Structure on the Molecular Interactions in Segmented Polyurethanes*,†

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Synopsis

The thermal responses of various polyurethane elastomers in the form of changes in heat capacity, linear expansion, and tensile strain have been examined. Most of the changes which can be attributed to the backbone of polyethylene adipate, found in several modes of thermal analysis, are still apparent, though shifted somewhat, among most of the diisocyanate extended elastomers used in this study. Tolylene diisocyanate extension changes the modulus properties markedly, low modulus properties being observed at ambient temperatures. Both hydrogenated MDI and MDI elastomers show comparable expansion and modulus response, whereas the hydrogenated TDI elastomer does not have the same characteristics as TDI-based elastomers. The thermal properties of the hydrogenated TDI elastomer resemble more those exhibited by the polyol mixture extended with hexamethylene diisocyanate, and in addition this latter elastomer exhibits more crystallinity, as shown by the large endotherm in the specific heat measurement. The structure of the diisocyanate naturally changes the behavior of the hard segment.

INTRODUCTION

Measurements of the modulus of tolylene diisocyanate (TDI)-based urethane elastomers show that the use of this diisocyanate causes a lower modulus than the diphenylmethane diisocyanate (MDI)-based elastomers. The large torsional modulus drop occurring in the vicinity of −40°C for the MDI-based elastomer shifts to the region of −20°C for TDI-based elastomers,[1] other components of the polymers remaining constant.

Polymer softening for these TDI-based polyurethanes occurs at lower temperatures than for these MDI-based polyurethanes, presumably because of the better crystalline fit of the MDI-extended segments than with TDI extension.[2] There have been no data of this type published which indicate the effect of ring hydrogenation on either TDI- or MDI-based elastomers (STDI and SMDI). Studies have been reported on the prema-

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

† Presented at the Polymer Division Symposium on Polyurethanes, American Chemical Society, Atlantic City, September 1968.

ture softening of hexamethylene diisocyanate (HMDI)-based elastomers.[3] The low-temperature properties have been shown to be dependent to a large extent upon the type of backbone which is extended by the diisocyanate.[4] Polyurethanes from poly(tetramethylene glycol) exhibit better low-temperature properties than those from poly(propylene glycol), presumably due to the more favorable molecular fit of the poly(tetramethylene glycol) residues one with another.[5] For the most part, all the polyether and polyester backbones investigated here, save poly(propylene glycol), under the same conditions of extension with diisocyanate, exhibit similar high-temperature modulus behaviors.[6]

This study illustrates the thermal response of selected polyurethane elastomers by changes in heat capacity, linear expansion, and tensile strain upon varying the diisocyanate structure. The effects of hydrogenation of the diisocyanates are examined to illustrate their influence on the molecular fit of the soft and hard blocks of the polyurethane elastomers.

EXPERIMENTAL

Materials

The polyester portion of all the polyurethane elastomers used in this study was hydroxyl-terminated poly(ethylene adipate) ($M_n = 2000$). All of the isocyanates used in this work were obtained from within the company. The 1,4-butanediol was purchased from GAF (anhydrous grade).

Preparation of Elastomers

The elastomers in this study were made according to the formulations: (A) 220 g. polyol, 139.5 g MDI; (B) 220 g. polyol, 95.7 g TDI; (C) 220 g. polyol, 144.0 g SMDI; (D) 220 g. polyol, 101.3 g HMDI; (E) 220 g. polyol, 100.0 g STDI. The polyol was a mixture of poly(ethylene adipate) and 1,4-butanediol in the proportions 1070 :219 (by weight), respectively. The NCO/OH ratio was maintained at 1.1.

The elastomers were prepared by heating the polyol mixture to 150°C, followed by degassing for 1 hr at this temperature at 50 mm Hg. This mixture was then cooled to 85°C, and the particular diisocyanate used for extension of the polymer mix was added after it had been heated to the same temperature. After thorough mixing, the polymer was cast into slabs of about 0.05″ thickness, followed by a post cure for 16 hr at 110°C. Formulation B had a particularly fast cast time and was difficult to cast without bubbles.

Characterization Methods

Thermogravimetric Analyses (TGA). The TGA characteristics of the polyurethanes of this study were measured on a Du Pont 950 TGA instrument at a heating rate of 20°C/min in an air atmosphere flowing at the rate of 40ml/min.

Differential Scanning Calorimetry. The DSC data were obtained on the DSC module for the Du Pont 900 Thermal Analyzer, with heating at a rate of 5°C/min.

Thermomechanical Analyses. Measurements of the expansion and tensile characteristics of the polyurethane elastomers were carried out on the Du Pont 941 TMA instrument as previously described,[7,8] a 10-g load being used for the tensile measurements. The heating rate for the expansion measurements was 5°C/min and that for the tensile measurements, 10°C/min.

RESULTS

Expansion Characteristics

Morphological interpretations can often be made very clearly with the aid of linear expansion measurements, and it has been adequately demonstrated that increasing the crystalline content of a polymer or in other cases increasing molecular ordering of the polymer causes the coefficient of expansion to decrease.[9] For example, polyethylene exhibits the characteristic that the linear coefficient of expansion decreases as the density increases, and the density can be directly related to the amount of crystallinity or molecular ordering within the polymer.[10] So too, one can use this type of correlation for listing the relative crystallinities of any homologous series of polymers merely by examining the linear coefficient of expansion. The temperature range in which the coefficient of expansion is measured must also be considered. If there is a need for determining the amount of molecular ordering within a polymer, that molecular ordering will usually affect the fusion characteristics of the polymer and consequently must be measured in the temperature range just prior to the fusion endotherm which has been determined from some calorimetric measurement. This is particularly true of substances such as Neoprene, where the linear coefficient of expansion at ambient temperatures is truly indicative of the amount of crystallinity, whereas measuring the coefficient of expansion near -40°C, where another phase transition occurs, does not necessarily relate to the amount of crystallinity present in the Neoprene. The transition occurring at -40°C has been reported to be the T_g of Neoprene.[11]

In Table I are listed the temperatures at which a change in the coefficient of expansion occurs for these polyurethanes, as well as changes in the heat capacity and the tensile strain. It has been shown that changes of expansion of pure polyethylene adipate have occurred at temperatures from -100°C to $+42$°C, at which temperature the polyethylene adipate apparently melts.[4] The values for the phase transitions occurring in elastomers from all of the diisocyanates in this study tend to decrease an initial transition as present in the poly(ethylene adipate) from -110°C to some temperature in the range of −130° to −140°C, with the exception of the HMDI-extended polyester, where the transition remains at about the same temperature as that of the poly(ethylene adipate) backbone. Initially this would indicate that the diisocyanate extension of the polyester backbone

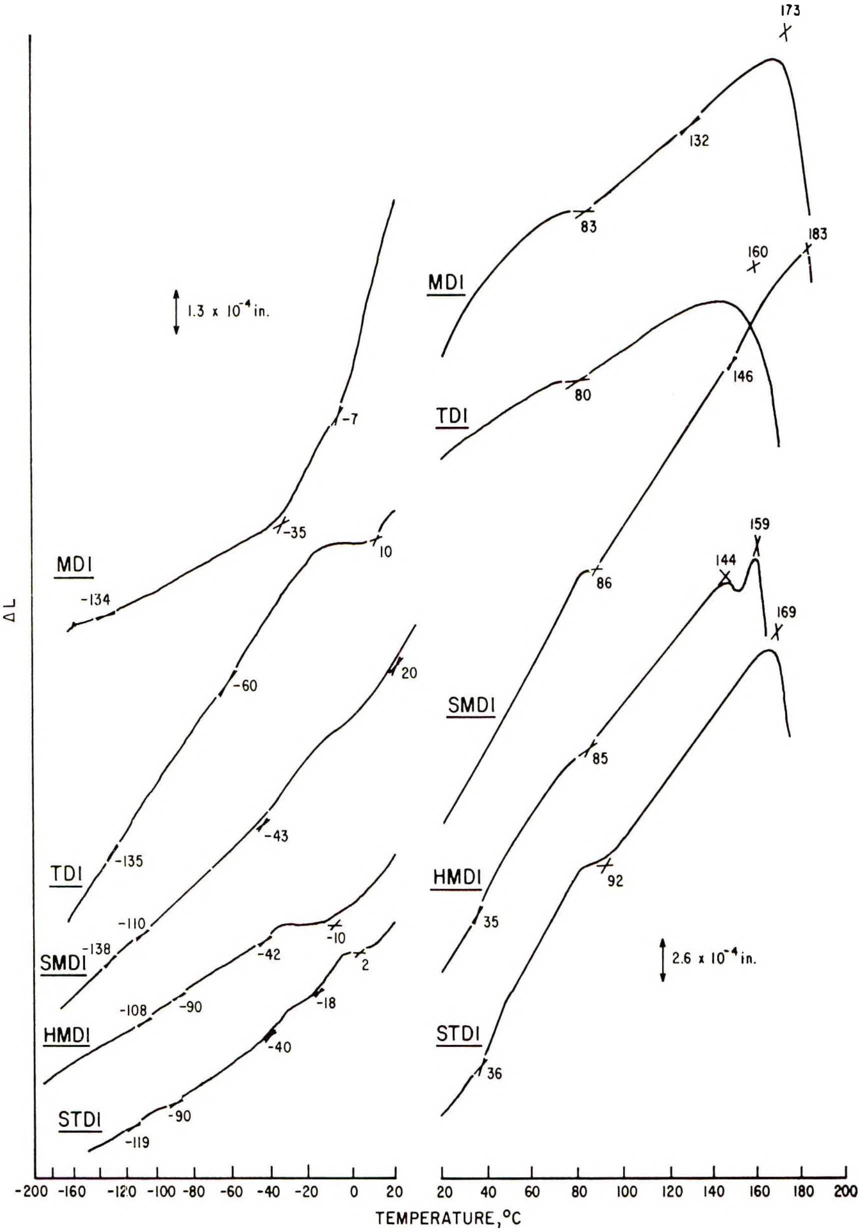

Fig. 1. Expansion characteristics as a function of temperature for poly(ester–urethane) elastomers of differing diisocyanate structure.

TABLE I
Transition Temperatures for Polyurethane Elastomers with Varying Diisocyanate Structure

Polymer	Transition Temperature, °C		
	DSC	Expansion	Tensile
Poly(ethylene adipate)	−110	−110	—
	−90	—	—
	−54	−55	—
	−24	−26	—
	4	3	—
	29	15	—
	36	34	—
MDI elastomer	−124	−134	−135
	−39	−35	−36
	—	−7	—
	48	83	37
	164	132	170
	185	173	—
TDI elastomer	−142	−135	−121
	—	−60	−90
	−18	−16	−12
	10	10	—
	—	80	—
	182	160	170
SMDI elastomer	−132	−138	−129
	−90	−110	—
	−39	−43	−39
	—	20	43
	81	86	—
	141	146	—
	165	183	169
HMDI elastomer	—	−108	−125
	−93	−90	—
	−40	−42	−42
	−31	−10	—
	79	35	46
	134	85	62
	—	144	—
	—	159	158
STDI elastomer	−141	−119	—
	−88	−90	−104
	−38	−40	−32
	—	−18	—
	—	2	—
	37	36	37
	77	92	65
	148	—	152
	175	169	—

decreases the apparent glass transition when using MDI, TDI, and SMDI, and to a lesser extent with STDI, whereas in using HMDI there is little apparent change of the glass transition. However, in the case of the −55 and −26°C transitions for the poly(ethylene adipate) backbone, all of the diisocyanate-extended elastomers except that from TDI exhibit a change near −40°C. This change has been considered to be a first-order transition[4] and is readily apparent from the expansion curves shown in Figure 1. Clough and Schneider[12] have also reported regions of small structural ordering in elastomers of MDI, butanediol, and poly(butylene adipate) or poly(tetramethylene glycol).

The TDI-extended poly(ethylene adipate) shows two first-order transitions: a small one occurring at −60°C and a much larger one at −16°C. For semicrystalline polymers, as the degree of molecular ordering increases, the first-order transitions tend to increase in temperature or at times merge with other first-order transitions. For example, Trick and Ryan[5] have shown that in the crystallization of poly(tetramethylene glycol), the melting phenomenon occurring in the region of 37°C increases to a maximum of 51°C as the degree of crystallinity is increased, as observed by x-ray diffraction measurements. From this it would seem that TDI extension of the polyester glycol tends to increase the degree of molecular ordering of the polyester backbone at subambient temperatures (probably an ordering of some polyester segments with some polyurethane segments, as discussed later), whereas the other diisocyanates result in a reduction of this ordering. Consequently, extension of poly(ethylene adipate) and most likely other polyesters with MDI, SMDI, HMDI, and STDI would tend to have the same effect on the first-order transition in the polyester backbone near −40°C.

On the contrary, properties above the temperature of the fusion of the poly(ethylene adipate) backbone must be largely dependent upon the interaction of urethane hard blocks, both with the poly(ethylene adipate) backbone and with each other. All of the diisocyanate-extended elastomers in this study show a transition occurring in the range 70–83°C as well as a fusion phenomenon occurring in the range 160–183°C.

Since the fusion temperature of the poly(ethylene adipate) is 42°C, all of the transition temperatures above this point will be due, at least in part, to the hard block sequences. Hence, it is probable that the 70–83°C transition could arise from hydrogen bonding between the urethane linkages in the hard block with the random polyester segments of the elastomer. Clough and Schneider[12] have published this interpretation for polyester and PTMG urethanes.

The fusion occurring in the 160–183°C range is due primarily to the disordering of the glycol-diisocyanate hard block. It has been demonstrated that a hard block formed from MDI and BD melts in the range 275–300°C, and a polyester extended with an equimolar quantity of MDI softens at 45°C.[4] However, an equimolar mixture of polyester–MDI–BD softens near 170°C.[4] Hence, the interference of the polyester segment in preventing a high degree of molecular ordering in the hard block reduces the fusion temperature of the hard block. Nonetheless, this order is probably brought about by intermolecular hydrogen bonding among urethane hard blocks.

In each case an NCO/OH ratio of 1.1 was used, causing an excess of NCO groups which will normally react with the urethane groups to form allophanate linkages. These may tend to crosslink the elastomer and in some cases increase its thermal stability, depending upon the amount of crosslinking induced.

In assessing the fusion behavior of the urethane elastomers used in this work, it is apparent that the SMDI-based elastomer exhibits the greatest thermomechanical stability (expansion mode) followed by the MDI-based elastomer itself. The elastomers exhibit stability toward softening in the order SMDI > MDI > STDI > TDI > HMDI. The HMDI-extended polymer shows a double fusion peak in expansion, with one maximum occurring at 145°C and the second at 159°C. This is contrasted to the single expansion peak representing fusion at 173°C for the MDI-extended and 183°C for the SMDI-extended polyester.

TABLE II
Linear Coefficients of Expansion and Enthalpy Values of Different Polyurethanes

Polyurethane	Coefficient of expansion $\times 10^4$, in./in./°C	ΔH, mcal/mg
HMDI	1.45	8.43
MDI	1.90	3.60
STDI	1.80	0.90
SMDI	2.16	0.17
TDI	2.25	0.23

While the SMDI exhibits the greatest thermomechanical stability before fusion occurs, the approach to fusion as the temperature is increased for this elastomer is accompanied by a greater thermal expansion than the corresponding MDI and HMDI-extended elastomers. Reference to Table II shows that the linear coefficient of expansion for the HMDI-extended polymer is less than that for the STDI, MDI, SMDI, and TDI-extended elastomers in that order. The linear coefficient of expansion results correlate generally with the increase in enthalpy needed to melt the ordered areas of the polymers, and it can be used to relate the crystallinities of an homologous series of polymers, particularly where the fusion endotherm is diffuse (as with TDI, STDI, and SMDI). More data will be reported at a later date to show the correlation of crystallinity with structures in polyurethane elastomers.

Calorimetric Studies

Figure 2 shows the calorimetric response of the five elastomers in this study, for all of the samples were examined by differential scanning calorimetry. The first change in the specific heat of each elastomer is very sharp, readily confirming the presence of a very low temperature transition

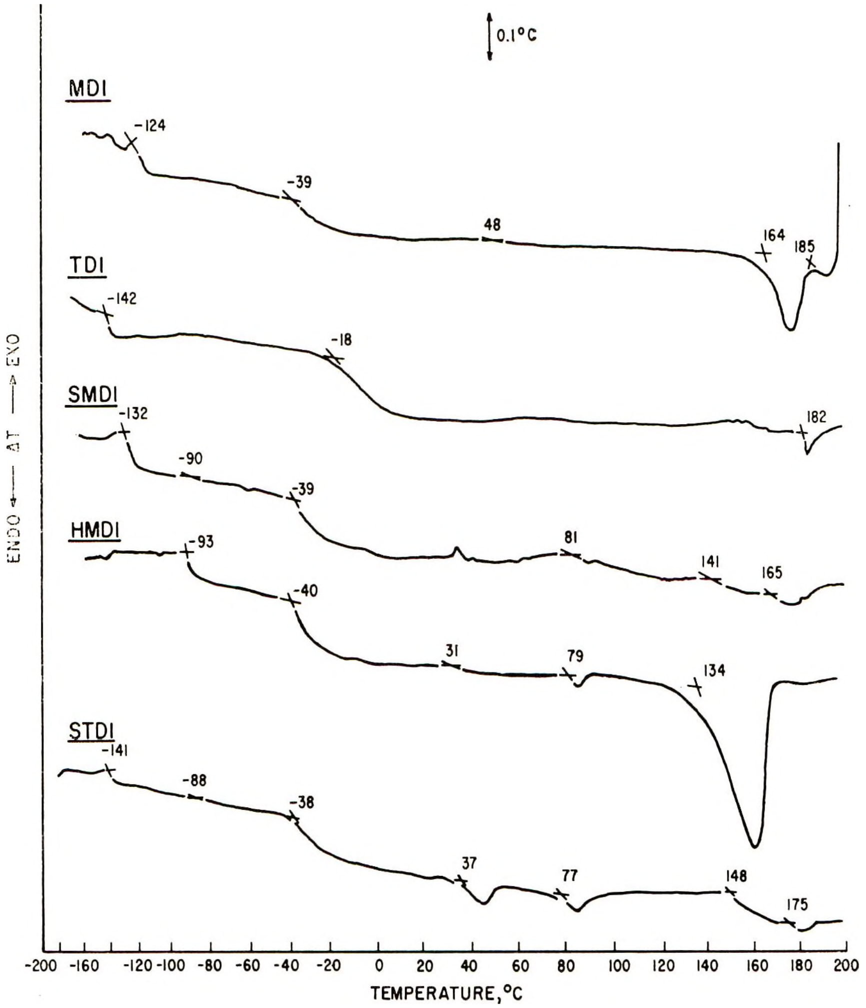

Fig. 2. Differential scanning calorimetric response of poly(ester–urethane) elastomers of differing diisocyanate structure.

for these polymers. In all of the elastomers, save that extended by HMDI, the low temperature transition occurs in the region −130 to −141°C, and those extended with the SMDI and STDI exhibit a small change in specific heat at the same temperature at which the HMDI-extended elastomer exhibits a very marked change in specific heat, −90°C. This transition for the HMDI-extended polymer is probably the mechanical glass transition.

The DSC and expansion data will usually correspond, but the tensile data can often be different. This is due, for the most part, to the stress placed upon the sample during the test. The 10-g load could strain the sample enough to shift some of the transitions, probably to lower temperatures.

Most of these elastomers have transitions occurring in the region of −35 to −45°C, save the TDI-extended elastomer, which occurs at −18°C; these data correlate with the expansion behavior. Hydrogenation of TDI appears to cause the major differences in thermal response in this homologous series of elastomers, and it appears that the cyclohexane ring more nearly approximates the behavior of the MDI and HMDI polymers. While the TDI-extended elastomer has a very small but sharp endotherm at 182°C, the STDI exhibits the lower premelting behavior at 148°C with a diffuse endotherm at 175°C. In the same way, hydrogenation of MDI causes an apparent decrease in crystallinity as well as premelting at a somewhat lower temperature than the MDI elastomer; it would be expected, *a priori*, that aromatic diisocyanate which is extended with a glycol would have a better fit than that which is nonaromatic, especially where a mixture of *cis*- and *trans*-cyclohexane-derived isomers is used, as in the SMDI example. This effect is very marked here as the effects from molecular fit on the high temperature behavior of the elastomers in this study readily show in the HMDI-extended polyurethane, wherein the linear chains cause better molecular fit similar to the crystallization of nylon. Consequently, we see, in Figure 2, a very broad endotherm and high enthalpy value for the fusion of the HMDI- and a smaller endotherm for the crystalline MDI-based polyurethane. The order of increasing crystallinity is evidenced by the expansion measurements shown in Table II (lower value for the more crystalline elastomer).

The enthalpy values in Table II readily affirm the large amounts of crystallinity in HMDI- and MDI-extended polyurethanes, with the increase in ΔH being inversely proportional to the linear coefficient of expansion. While in Table II discrete differences are apparent for the HMDI- and MDI-extended elastomers, the others which show very little crystallinity have similar ΔH values. When there is no appreciable enthalpy measurement, such as we have here for STDI-, SMDI- and TDI-extended elastomers, the linear coefficient of expansion readily relates the relative degree of ordering.

Tensile Measurements

All of the temperatures for each elastomer in this study at which there is a change in tensile strain are listed in Table I. The low temperature values are generally increased compared to DSC values because of the 10-g stress

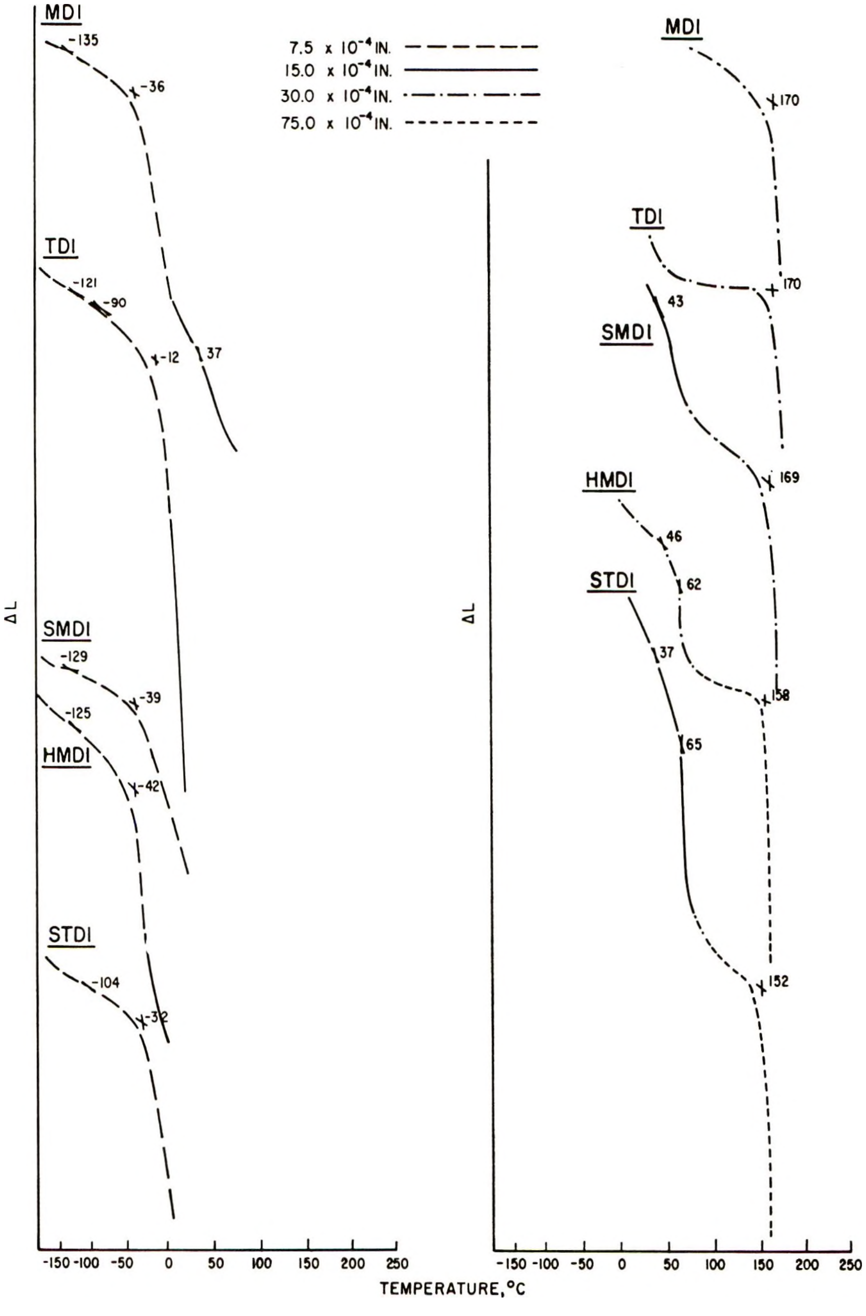

Fig. 3. Changes in strain as a function of temperature for poly(ester–urethane) elastomers of differing diioscyanate structure.

load on the 0.030 in. diameter fiber. Figure 3 shows some of the tensile strain curves as a function of temperature for the polymers of this study. A 10-g load was selected because it was found that it caused no observable creep over this temperature range while running the experiment (Fig. 4).

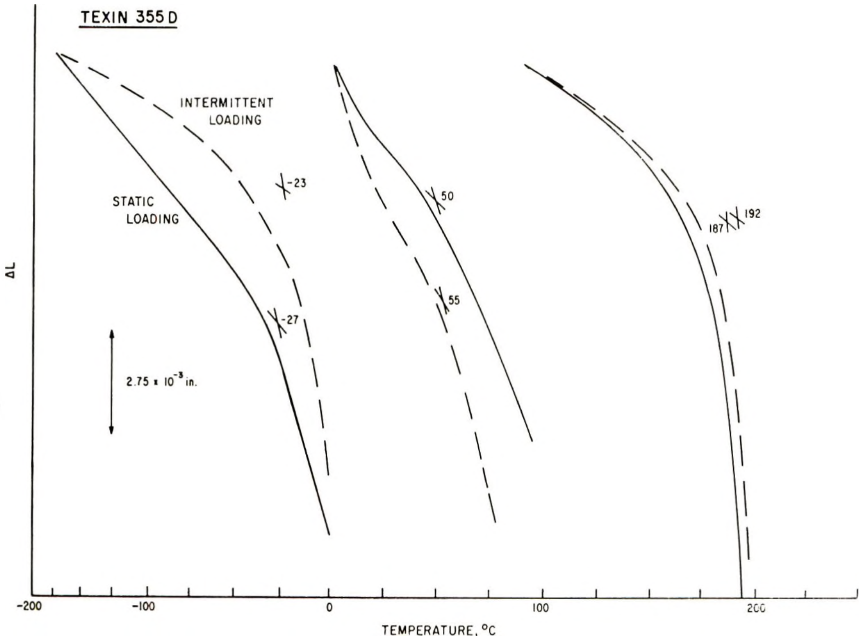

Fig. 4. Static and intermittent loading of Texin 355D as a function of temperature.

Figure 4 is included herein to demonstrate the small changes in the transitions when statically and intermittently loaded. The intermittent loading of twenty grams on the sample, recording its return to the baseline, tends to make the appearance of the low temperature transitions diffuse. The measurement also tends to show a small amount of induced strain at low temperatures under static loading. However, at higher temperatures (greater than 100°C) where creep might be expected, there is essentially no difference between intermittent and static loading; hence, there is no appreciable creep during the time span of the measurement.

Thermogravimetric Analyses

Figure 5 shows the thermogravimetric traces for MDI, SMDI, and STDI polyurethane elastomers. It was found that the TGA traces for SMDI, HMDI, and TDI elastomers were identical, whereas those for the STDI and MDI differed from these three. While the STDI elastomer appears to be distinctly less thermally stable than the others and the MDI elastomer slightly so; the STDI elastomer develops very little char between 400 and 500°C, whereas the MDI develops a considerable amount of char at 450°C (35%). This amount of char is considerably higher than that from the SMDI and other elastomers in this study. It is likely that this increased char formation may be propagated by crosslinking through the methylene bridge on the two aromatic rings or trimerization of the MDI. This might also indicate that the MDI-extended urethane elastomers exhibit less flammability than the rest of the elastomers.

DISCUSSION

The glass transition in all the polyurethane elastomers in this study, except the HMDI-extended urethane elastomer, occurred at lower temperatures than the glass transition of the poly(ethylene adipate) itself. Extension of poly(ethylene adipate) with 1,4-butanediol and HMDI moved the glass transition to a higher temperature (−93°C), and this effect corresponds with the expected changes in glassy behavior that accompany increases in crystallization of a bulk elastomer. The HMDI-extended elastomers were more crystalline than the other urethane elastomers, as shown by the large enthalpy change and the smaller linear coefficient of expansion in the temperature range near fusion.

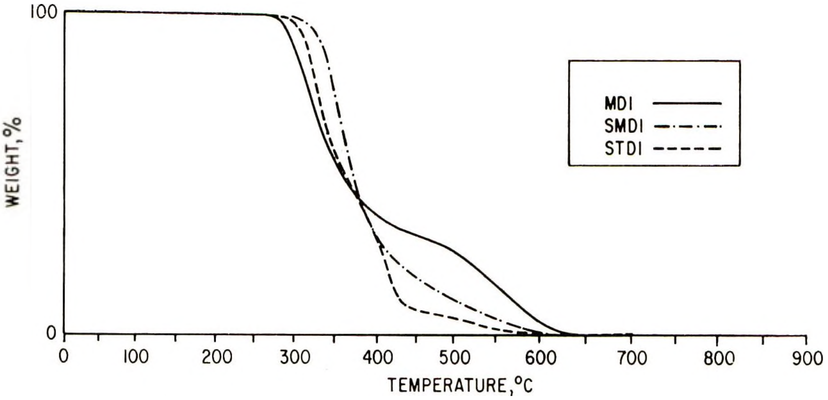

Fig. 5. TGA Scans of MDI-, SMDI-, and TDI-extended poly(ester–urethane) elastomers.

The major elastomer transition occurring near −40°C, attributed primarily to a first-order transition in the polyester soft segment, was nearly the same for all of these elastomers except that from TDI; in that case the transition was raised to about −18°C. This suggests that TDI extension of the poly(ethylene adipate) resulted in a molecular association of the polyester backbone with urethane segments which was greater than that of the other elastomers.

Similarly, the minor transitions occurring in the range of about 70–80°C may be due to a polyester segment–polyurethane interaction, visible primarily by TMA. Tensile measurements may wipe out this interaction and hence not show it. The DSC is apparently not as sensitive in this case as the TMA measurement.

The TDI-based elastomer presents an interesting feature in that the TDI system both raises the major low temperature transition (to −18°C) and also lowers the major high-temperature transition compared to the other isocyanates used here. This apparent anomaly can be explained if one assumes rather poor fit in the TDI-glycol hard segment, due to the 80/20 isomer ratio of the TDI, the *meta* orientation on the ring, the methyl substituent on the ring, and the opportunity for both "head-to-tail" and "head-to-head" polymerization of the unsymmetrical TDI. Thus, the poor fit would lead to inefficient use of the potential hydrogen bonding within the hard segment (giving poor high-temperature resistance), at the same time, leaving considerable hydrogen-bonding potential available for association with the polyester segment (raising the major low-temperature transition). Other diisocyanates giving a better fit in the hard segments should cause a higher major transition in the 150–180°C range and a lower major transition in the −40°C range compared to TDI. It is not clear as yet, prior to further experiments, what one should predict regarding either the explanation or the performance, in complicated cases such as those involving the geometric isomers of STDI or SMDI.

One additional observation is noteworthy. Both the HMDI- and MDI-based elastomers can exhibit dual expansion peaks, depending on annealing conditions; the dual expansion peaks, as well as the double endotherm occurring for the MDI- and HMDI-extended polyurethane elastomers at

TABLE III
Structural Assignments for Phase Changes in Block Polyurethanes

Polyester	Segmented polyurethane elastomers				
PEA	MDI	SMDI	HMDI	TDI	STDI
−110	−134 (b)	−138 (b)	−108 (a)	−135 (b)	−119 (b)
			−90 (c)		−90 (c)
−55				−60 (b)	
−26	−35 (b)	−43 (b)	−42 (b)	10 (c)	−40 (b)
					−18 (c)
3	−7 (b)		−10 (b)		2 (a)
15		20 (a)			
34			35 (a)		36 (a)
42	83 (c)	86 (c)	79 (c)	80 (c)	92 (c)
	132 (d)	146 (d)	144 (d)		
	173 (e)	183 (e)	159 (e)	160 (e)	169 (e)

temperatures near the melt, indicate two modes of molecular orientation within the hard block sequence of the polymer. This behavior is similar to that shown by Slade et al.[13] for nylon 66.

At this time it appears logical to consider that the phase transitions occurring in block copolymers, such as these polyurethanes, may be the result of transitions due to each block acting independently, and also due to interactions between blocks. In the particular case of these polyurethanes, the following effects seem reasonable.

(a) Polyester segment transitions resulting from regions of polyester–polyester order are unaffected by copolymerization and should be essentially the same as the transitions in pure polyester.

(b) Polyester segments may also experience some disturbance of molecular fit due to copolymerization with the urethane segment, leading to a reduction of transition temperatures compared to pure polyester.

(c) Polyester segments may be more extensively dislocated from other polyester segments than in (b), to the extent that they associate with urethane segments by hydrogen bonding and other van der Waals attractions, thus raising transition temperatures compared to pure polyester.

(d) Urethane segments may suffer a large loss in fit with other urethane segments, due to copolymerization with ester segments, so that transitions occur at much lower temperatures than in the pure polyurethane.

(e) Urethane segments may achieve a considerable degree of order, but because of short segment length or small crystallite impurities due to copolymerization or branching, they will show transitions somewhat below those of the pure polyurethane.

(f) Urethane segments of sufficient length may form ordered zones comparable to those in the pure polyurethane and show transitions similar to those of the pure polyurethane. (This was not achieved in the polymers of this study, due in part at least to the short urethane segments used.)

To illustrate, the transitions in each of the elastomers in this study from linear expansion measurements could be defined as arising from the six probable modes of molecular interaction listed above (Table III). (For reference, pure MDI/BD melts in the range 270–300°C, whereas pure HMDI/BD melts at 183°C.)

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Photocycloaddition Polymerization. I. Preparation and Characterization of Poly-*N*,*N*′-polymethylenebisdichloromaleimides*

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Synopsis

The benzophenone-sensitized solution-phase photocycloaddition polymerization of *N*,*N*′-polymethylenebisdichloromaleimides has been investigated. It is shown that a polymer can be obtained by repeated $2\pi + 2\pi$ photocycloaddition process. The intrinsic viscosity of the products varies from 0.1 to 0.6 when the link between the two maleimide moieties contains more than six and simultaneously an uneven number of methylene units. The polymeric materials form transparent, flexible, noninflammable films and decompose at 310°C.

INTRODUCTION

Although the term photopolymerization occurs frequently in the literature of polymer chemistry,[1,2] application of photochemistry to the synthesis of polymers is limited almost exclusively to the photochemical initiation of vinyl polymerization. We were attracted by the possibility of using photochemical reactions in forming the bonds of the polymer chain, during the propagation reaction; such an application of photochemistry to polymer synthesis has been reported recently.[3–5] However, previous investigators have studied photocycloaddition polymerization in the solid state, mainly in suspension, whereas we chose to study the solution-phase process.

The photochemical dimerization of olefins to cyclobutanes is a well known reaction,[6] of which the dimerization of maleimides is a specific example. The solution-phase photochemistry of *N*-substituted maleimides is well established[7,8] and since synthetic routes to *N*,*N*′-polymethylene-*bis*-maleimides are available,[9,10] the polymer synthesis formulated in Figure 1 (path b), seemed to be a good system with which to start an investigation on photocycloaddition polymerization.

The results of the investigation of the solution photochemistry of *N*,*N*′-polymethylene-*bis*-maleimides have been reported, in part, previously.[11] A novel photocyclomerization reaction giving diazatetracyclotetraones was observed (Fig. 1, path a, R = H, n = 3–7). In the case where polymers were obtained ($n > 7$) they were largely insoluble because of second-

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

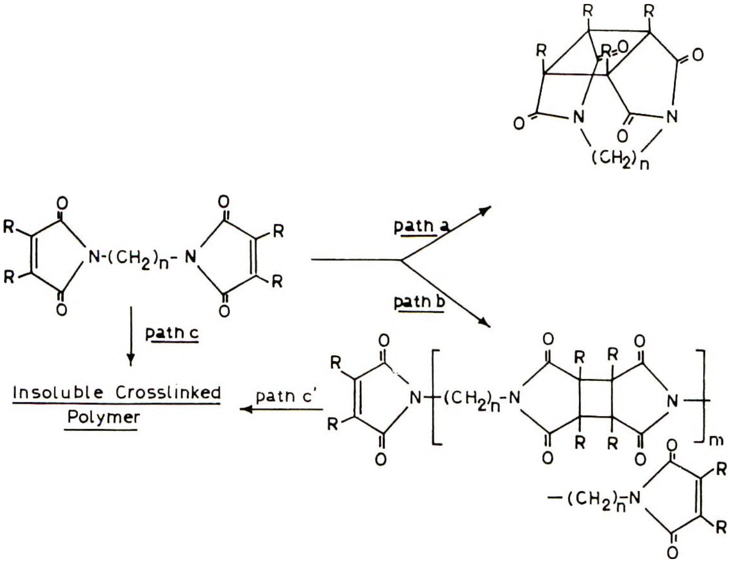

Fig. 1. Photochemical behavior of *N*,*N*′-polymethylene-bismaleimides.

ary crosslinking reactions (Fig. 1, paths c,c′) due to the relative ease with which maleimides undergo vinyl polymerization.[12,13] The photocyclomerization reaction was very rapid, unsensitized, and was not inhibited by oxygen, in contrast to the photodimerization of *N*-alkylmaleimides which is a slow reaction in the absence of a sensitizer. The yield of cyclized products decreased with increasing distance between the maleimide groups for $n \geq 7$ or where the maleimide moieties are linked by a *m*-phenylene group, only polymer is formed. Clearly from this work three reaction paths exist in the solution phase photochemistry of *N*,*N*′-polymethylene-*bis*-maleimides (Fig. 1).

In order to select path b and consequently in order to eliminate possible competition from reaction paths a and c the following major conditions must be satisfied: (1) the maleimide units should not be susceptible to vinyl polymerization in order to prevent crosslinking reactions; (2) cyclomerization reactions should be minimized by keeping the polymethylene chain longer than six units.[11]

Also to obtain an appreciable rate of polymerization the reaction should be carried out with a sensitizer.

With these considerations in mind we chose to study the benzophenone-sensitized photochemical reactions of *N*,*N*′-polymethylenebisdichloromaleimides.

EXPERIMENTAL

Synthesis of Monomers

The method of Martin, Dickinson, and Rolands[10] was used. ω,ω′-Polymethylenediamine (0.5 *M*) and 2,3-dichloromaleic anhydride (1.0 *M*)

TABLE I
Analytical Data for *N*,*N'*-Polymethylenebisdichloromaleimides

	Melting	Calculated						Found					
n	pt, °C	C, %	H, %	N, %	O, %	Cl, %	MW	C, %	H, %	N, %	O, %	Cl, %	MW
7	120.3	42.08	3.30	6.55	14.95	33.13	428	42.04	3.55	6.56	14.76	32.98	431
8	133.5	43.46	3.65	6.43	14.48	32.08	442	43.44	3.68	6.15	14.47	31.87	431
9	85.3	44.76	3.98	6.14	14.03	31.09	456	44.78	4.13	6.12	14.15	30.93	452
10	134.5	45.98	4.29	5.96	13.61	30.16	470	45.85	4.25	5.95	—	30.35	470
11	84.5	47.13	4.58	5.79	13.22	29.29	484	47.25	4.60	5.75	—	29.00	482
12	126.2	48.17	4.86	5.62	12.85	28.47	498	47.95	5.30	5.85	—	28.40	505

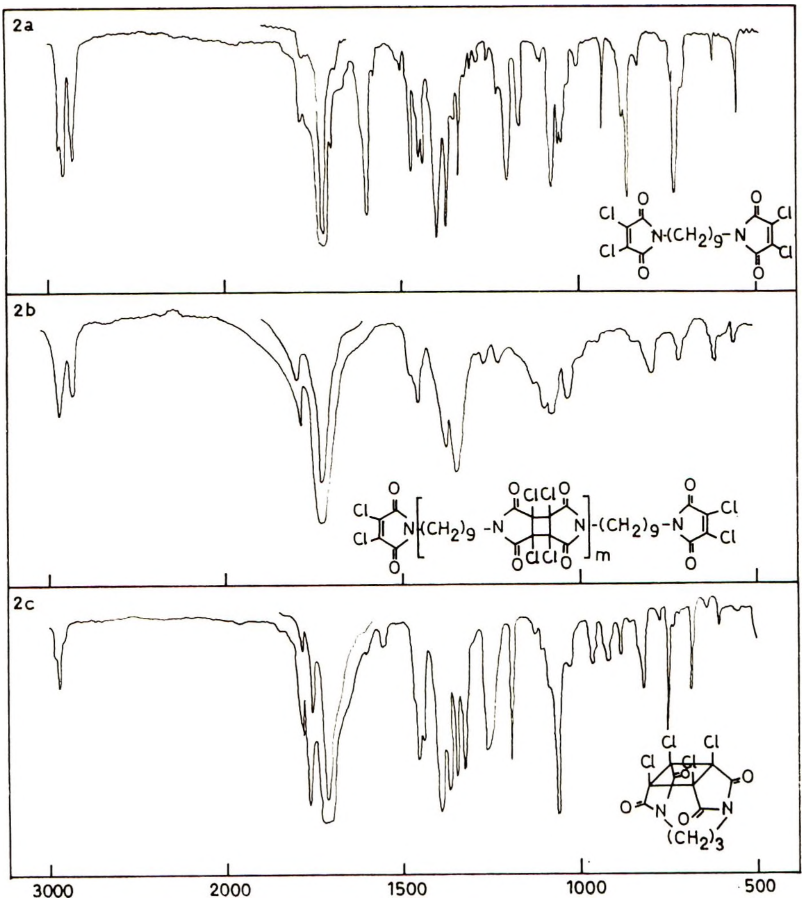

Fig. 2. Infrared spectra: (*a*) *N*,*N'*-nonamethylene *bis* dichloromaleimide; (*b*) Poly-*N*,*N'*-nonamethylene*bis*dichloromaleimide; (*c*) cyclomer from *N*,*N'*-trimethylenebis-dichloromaleimide.

were separately dissolved at room temperature in the minimum volume of glacial acetic acid; the solutions were mixed and heated slowly to reflux temperature. After refluxing for 2 hr, the mixture became dark brown. On cooling, impure *N*,*N'*-polymethylenebisdichloromaleimide generally crystallized; when it did not, it was precipitated by addition of water. The product was filtered off and washed with cold water until free of acetic acid. After drying *in vacuo*, the product was dissolved in chloroform and purified by column chromatography on Florisil (Fluka, 60–100 mesh). These bismaleimides are white crystalline solids. Yields after purification were 80–90%, with the exception of *N*,*N'*-heptamethylenebisdichloromaleimide which was difficult to purify and was obtained colorless in somewhat reduced yield (57%) by chromatography on alumina (Merck, active neutral grade, activity 1) by using toluene as eluent. Melting points, molecular weights, and analytical data are recorded in Table I. The infrared spectra (Perkin-Elmer 521 grating infrared spectrophotometer) were consistent with the assigned structures; all the compounds showed absorptions at 2920 and 2850 (C—H); 1785 and 1720 (imide C=O); and 1615 (C=C) cm^{-1} and multiple absorptions in the region 1500–700 cm^{-1}. The infrared spectra obtained in chloroform solution and with KBr disks were the same, except that in the solid state the absorptions at 2920, 2850, and 1720 cm^{-1} were split into doublets, whereas in all the solution spectra these absorptions were single peaks. Figure 2*a* shows a typical monomer spectrum.

The importance of the extreme purity of the monomers should be stressed. Initially the monomers were purified by recrystallization, although they were sharp-melting materials with satisfactory elemental analyses they did not polymerize on irradiation; purification by column chromatography overcame this difficulty.

Method of Polymerization

N,*N*′-Polymethylenebisdichloromaleimide and benzophenone (Schuchardt, Laboratory reagent grade) were dissolved in dichloromethane (Merck, analytical reagent grade) in cylindrical Pyrex reaction vessels. Dry, oxygen-free nitrogen was bubbled through the solutions for 30 min, and the reaction vessels were then stoppered with ground glass stoppers. The colorless, or occasionally pale yellow, solutions were irradiated in a Rayonet Type RS preparative photochemical reactor fitted with RUL-3500 Å lamps; the temperature of reaction varied in the range 30–40°C. After irradiation the solution was filtered and the solvent removed by rotary evaporation under vacuum. The products precipitated during irradiation, and those recovered after evaporation of the solvent were separately extracted with ether in a Soxhlet apparatus to remove the benzophenone. The quantities and concentrations of reagents, irradiation times and product yields are recorded in Table II.

All the *N*,*N*′-polymethylenebisdichloromaleimides with an even number of methylene units gave precipitates during irradiation, thereby removing the growing polymer from solution and reducing the supply of light to the reactants. On the contrary, the monomers with an odd number of methylene units gave polymers which remained in solution during irradiation.

Characterization of Products

Products were characterized by elemental analysis, infrared spectrometry, molecular weights, viscosities, and their thermal properties. (Tables III and IV.)

All the products were completely soluble in one or several of the following solvents: methylene chloride, chloroform, dimethylformamide, dimethyl sulfoxide, and *N*-methylpyrrolidone. The products with an even number of methylene units were least soluble, generally only in the latter three solvents at their boiling points; they tended to give gels on cooling.

TABLE II
Photocycloaddition Polymerization of N,N'-Polymethylenebisdichloromaleimides

Run	n	N,N'-Polymethylene-bismaleimide		Benzophenone, mole/l.	Irradiation time, hr	Recovered materials		Total, %
		g	mole/l.			Precipitated during irradiation, %	By solvent evaporation, %	
A	7	11.1[a]	0.052	0.033	112	None	51	51
B	7	5.2[b]	0.049	0.026	114	None	73	73
C	7	1.0	0.195	0.137	121	None	100	100
D	8	15.0	0.068	0.055	112	43	43	86
E	9	3.6[b]	0.039	0.027	113	None	75	75
F	9	20.0	0.044	0.027	117	None	100	100
G	9	4.6	0.20	0.12	120	None	98	98
H	10	20.0	0.043	0.007	111	11	37	48
I	10	12.0	0.051	0.036	118	22	60	82
J	10	3.0	0.127	0.165	115	Mostly precipitated		90
K	11	4.0	0.16	0.11	118	None	98	98
L	11	5.8	0.12	0.10	74	None	76	76
M	12	11.0	0.183	0.183	115	Mostly precipitated		63

[a] Starting material was bright yellow.
[b] Starting solution was pale yellow.

TABLE III

Analytical Data for Poly-N,N'-polymethylenebisdichloromaleimides

			Calculated					Found				
Run	n	m	C, %	H, %	N, %	O, %	Cl, %	C, %	H, %	N, %	O, %	Cl, %
A	7	4	42.08	3.30	6.55	14.95	33.13	42.51	3.40	6.64	14.95	33.13
C	7	10						42.22	3.44	6.42	14.78	32.97
D	8	5	43.46	3.65	6.34	14.48	32.08	44.00	3.65	6.24	14.00	31.50
D[a]	8	—						43.43	3.49	6.21	14.59	31.96
E	9	8	44.76	3.98	6.14	14.03	31.09	45.17	3.83	6.09	14.11	31.30
F	9	14						44.90	4.03	6.08	13.97	30.89
G	9	66						44.69	4.15	5.97	14.09	30.92
H	10	6	45.98	4.29	5.96	13.61	30.16	46.20	4.69	5.96	13.77	30.12
H[a]	10	—						45.93	4.37	5.85	13.52	30.03
L	11	—	47.13	4.58	5.79	13.22	29.29	46.94	4.69	5.78	13.35	29.22
M[a]	12	—	48.17	4.86	5.62	12.85	28.47	48.40	4.96	5.46	12.98	28.29

[a] Samples precipitated during irradiation.

On account of their solubility in the solvents mentioned above, appreciable crosslinking can be excluded and it can be reasonably assumed that the reaction follows path b (Fig. 1), as required. On the other hand, since under our experimental conditions all the light energy is absorbed by benzophenone sensitizer it is assumed that the reaction proceeds by way of attack of the benzophenone triplet on a maleimide unit in its ground state.

The infrared spectra provide further support for the assigned product structures. Thus, a typical product spectrum (Fig. 2*b*) shows characteristic broad bands of a polymeric material; in particular, comparison with the monomer spectrum (Fig. 2*a*) shows that the double-bond stretching frequency at 1615 cm^{-1} has disappeared, and the antisymmetric stretching frequency of the imide system at 1720 cm^{-1} has been displaced to 1735 cm^{-1}. Cyclomerization (path a, Fig. 1) can also be excluded, since cyclomers commonly show three absorptions in the region 1700–1800 cm^{-1}, as is illustrated in the spectrum of the cyclomer from *N*,*N*′-trimethylenebisdichloromaleimide.[14]

TABLE IV
Molecular Weights and Thermal Characteristics of Poly-*N*,*N*′-polymethylenebisdichloromaleimides

Run	n	MW[a]	DP	$[\eta]$[b]	DSC melting range, °C[c]	TGA onset of decomposition, °C[d]
A	7	1600	4	—	130–155	—
B	7	4130	10	—	198–220	334
C	7			0.25	222–280	332
D	8	2000[e]	5	—	201–247	—
E	9	3800	8	—	130–150	—
F	9	6300	14	—	137–200	—
G	9	30000[f]	66	0.45	None	330
H	10	2700	6	—	200–216	—
I	10	—	—		200–247	314
J	10	—	—	—	194–224	—
K	11	—	—	0.65	None	314
L	11	7000	15	0.11	—	—
M	12	—	—	—	185–237	294

[a] Measured by Mechrolab vapor-pressure osmometer in chloroform solution. For n even, measured on nonprecipitated fraction.

[b] Measured with an Ostwald viscometer at 25°C in dimethylformamide.

[c] Obtained with a Perkin-Elmer differential scanning calorimeter DSC-IB, under N_2 atmosphere at a heating rate of 8°C/min. For n even, the precipitated fraction was used.

[d] Obtained with a Perkin-Elmer TGS-1 thermobalance, under N_2 atmosphere, at a heating rate of 8°C/min.

[e] Dimethylformamide as solvent.

[f] Osmometry in chloroform.

Elemental analysis of the products indicated that they were simple polyaddition products without any detectable incorporation of benzophenone or solvent, regardless of whether the product was of low or high degree of polymerization, or whether or not it precipitated during irradiation (Table III).

The thermal characteristics and molecular weight data for the products are presented in Table IV, from which it is clear that at least two monomers having respectively nine and eleven methylene units between the dichloromaleimide units produce high polymeric addition products. From Tables III and IV (runs K and L) it can be seen that the degree of polymerization is strongly influenced by the time of irradiation, as would be expected in a polyaddition polymerization. The two genuine polymers (runs G, K) do not melt below their decomposition temperature, whereas oligomers from the same monomer (compare runs E, F, and G) show well defined melting ranges; thus, the observation of well defined melting ranges for the materials from monomers with *n* even (for which solubility problems precluded the possibility of measuring molecular weights or $[\eta]$) is support for the view that these materials are of low degree of polymerization. The thermal stability of these materials, as measured by thermogravimetric analysis under nitrogen, seems not to be sensitive to the degree of polymerization, and a polymer of degree of polymerization 66 (run G) begins to degrade at the same temperature as an oligomer of degree of polymerization 10 (runs B and C). These polymeric products formed tough, flexible, transparent films, which owing to their high chlorine content do not burn.

CONCLUSIONS

The solution-phase photochemical polyaddition of bisdichloromaleimide can be used in the synthesis of polymers containing structural units which are inaccessible by other methods. The further generalization of this polymerization method to other systems will be described in the near future.

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Polymerization and Processability of Poly(vinyl Chloride)*†

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Synopsis

The processability of rigid poly(vinyl chloride) can be improved by adding trichloroethylene as chain-transfer agent, increasing the polymerization temperature, and especially by combining the two effects together. The resulting synergistic interaction is best expressed by an equation of the form, $P = (A + B[\mathrm{TCE}])e^{C/T}$, where P is thermal plasticity, $Ae^{C/T}$ is the combined effect of chain transfer to initiator and monomer and termination through combination and disproportionation, and $B[\mathrm{TCE}]e^{C/T}$ represents the chain-transfer action of trichloroethylene.

INTRODUCTION

Poly(vinyl chloride) has properties which make it promising for use as a rigid plastic, but the high melt viscosity of the stiff polymer molecules makes processability very difficult. Conventional homopolymerization in aqueous suspension at 50°C produces polymer of molecular weight too high to be of practical value in rigid applications. Thus it is common practice to add chain-transfer agents such as trichloroethylene and/or to increase the polymerization temperature, in order to lower the molecular weight and improve the processability.[1-3]

When the two effects are combined together, the improvement in processability is greater than expected by an additive process, i.e., synergistic. This synergism has been conveniently expressed by an equation of the form

$$P = 2195 + 439[\mathrm{TCE}] + 75(\Delta T) + [\mathrm{TCE}](\Delta T)^2 \qquad (1)$$

where P is thermal plasticity, measured by pressing 0.5 g of powdered polymer between cellophane sheets in a Carver laboratory press for 30 sec at 190°C and 9000 psi and measuring the area of the fused polymer in square millimeters with a planimeter; [TCE] is the concentration of trichloroethylene chain-transfer agent in parts per hundred of vinyl chloride

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monomer; and ΔT is the increase in polymerization temperature beyond the usual 50°C. This equation was convenient because it expresses in simple form the fact that increase of either chain-transfer agent or polymerization temperature alone would increase processability and that combined use of the two together would produce a further synergistic increase as well. It does not, however, represent or explain the fundamental mechanisms involved. An improved mathematical treatment has now been developed to accomplish this.

DEVELOPMENT OF AN EQUATION TO REPRESENT THE MECHANISM

The use of chain-transfer agent and increased polymerization temperature to improve processability depends upon their ability to decrease the molecular weight of the polymer and thus decrease its melt viscosity and increase its thermal plasticity. In the conventional polymerization reaction, molecular weight M is inversely controlled by chain transfer to initiator and to monomer and by termination through combination and disproportionation, all of which increase with temperature T:[5a]

$$dM/dT \propto 1/T^2 \qquad (2)$$

Integration of eq. (2) yields

$$1/M = k_1 e^{k_2/T} \qquad (3)$$

Molecular weight is also inversely controlled by concentration of added chain-transfer agent [TCE]:[5b]

$$1/M = k_3[\text{TCE}] \qquad (4)$$

Here, however, the proportionality constant k_3 for reactivity of the chain-transfer agent also increases with temperature, and might best be expressed by an Arrhenius-type function:

$$1/M = k_4[\text{TCE}]e^{k_5/T} \qquad (5)$$

The combined effects of such a series of chain-transfer and termination mechanisms upon molecular weight is additive,[5c] and can thus be expressed in the form:

$$1/M = k_1 e^{k_2/T} + k_4[\text{TCE}]e^{k_5/T} \qquad (6)$$

If the relative effect of temperature upon these mechanisms were uniform, eq. (6) could further be factored into the simplified form:

$$1/M = (k_1 + k_4[\text{TCE}])e^{k_6/T} \qquad (7)$$

The effect of molecular weight M upon melt viscosity V is generally an exponential function:[6]

$$V \propto M^{3.4} \qquad (8)$$

The effect of melt viscosity V upon thermal plasticity P is probably a simple inverse function,

$$P \propto 1/V \tag{9}$$

or at most an inverse exponential function:

$$P \propto 1/V^n \tag{10}$$

Thus combining these equations should yield a direct relationship for the effects of trichloroethylene concentration and polymerization temperature upon thermal plasticity:

$$P = (A + B[\mathrm{TCE}])e^{C/T} \tag{11}$$

Here, according to conventional Arrhenius-type interpretation,[5a] A represents the combined frequency factor for chain transfer to initiator and monomer and for termination through combination and disproportionation, B represents the frequency factor for chain transfer to trichloroethylene, and C represents the combined activation energy for all of these chain-transfer and termination processes. All three of these constants of course contain invariant quantities such as monomer and initiator concentrations and the gas constant; individual rate constants, frequency factors, and activation energies; and their magnitude is rationalized to convert from parts per hundred of trichloroethylene and °K into square millimeters at 30 sec, 190°C, and 9000 psi. Thus they are expressed in form for maximum practical utility; but they could as well be subdivided to identify these individual components for further theoretical analysis.

DETERMINATION OF THE CONSTANTS

Data from the original study[4] (Table I) were used directly for the present calculations. A natural log plot of thermal plasticity P against the inverse of temperature $1/T$°K (Fig. 1) gave a straight line with intercept $\ln A =$

TABLE I
Effect of Trichloroethylene and Polymerization Temperature upon Thermal Plasticity of Rigid Polyvinyl Chloride[a]

Trichloroethylene, parts per hundred (phm) of vinyl chloride monomer	Thermal plasticity at various polymerization temperatures, mm²[b]		
	50°C	60°C	70°C
0.0	2195	2860	3700
1.0	2540	3300	4950
2.5	3120	4050	5960
5.0	4450	6250	7400
7.5	5610	7160	—
10.0	6470	8230	—

[a] Experimental data of Deanin.[4]

[b] Thermal plasticities at 30 seconds, 190°C, and 9000 psi.

16.73, or $A = 1.91 \times 10^7$, and slope $C = -2910$. Then, rearranging the equation into the form

$$P/e^{C/T} = A + B[\mathrm{TCE}] \tag{12}$$

and plotting $P/e^{C/T}$ against trichloroethylene concentration [TCE] in parts per hundred of vinyl chloride monomer (Fig. 2) gave a narrow bundle of straight lines with average intercept $A = 1.78 \times 10^7$ (agreeing quite well with the value from Fig. 1) and slope $B = 0.358 \times 10^7$. Combining the two values for intercept A gave an average value of $A = 1.85 \times 10^7$. Thus the entire equation was as follows:

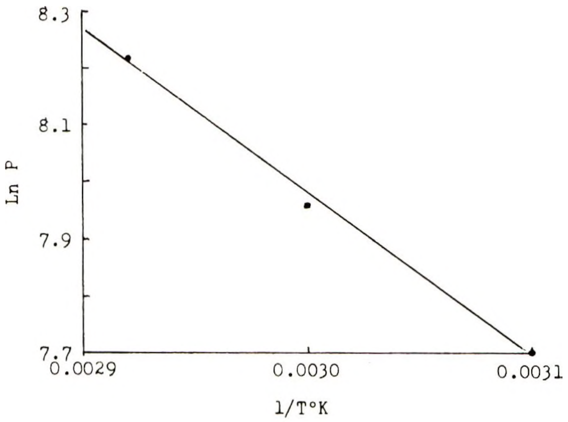

Fig. 1. Determination of constants A and C.

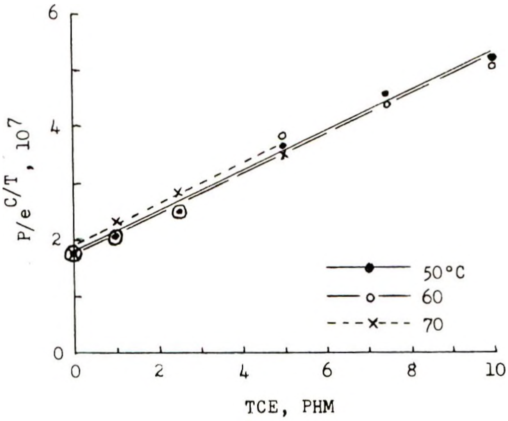

Fig. 2. Determination of constants A and B.

$$P = [1.85 \times 10^7 + 0.358 \times 10^7[\mathrm{TCE}]]e^{-2910/T} \tag{13}$$

VERIFICATION OF THE EQUATION

To verify the equation developed in this way, the experimental values for trichloroethylene concentration and polymerization temperature were fed back into the final equation and the resulting calculated values for thermal plasticity were compared with the values originally measured experimentally (Table II). These agreed within an average deviation of only 4.7%. Thus the equation conformed closely to the experimental data.

TABLE II
Verification of Equation

Polymerization Temperature, °C	Trichloroethylene, phm	Thermal plasticity, mm²	
		Calculated	Observed
50	0.0	2280	2195
	1.0	2720	2540
	2.5	3380	3120
	5.0	4480	4450
	7.5	5570	5610
	10.0	6690	6470
60	0.0	3000	2860
	1.0	3580	3300
	2.5	4450	4050
	5.0	5900	6250
	7.5	7350	7160
	10.0	8800	8230
70	0.0	3870	3700
	1.0	4630	4950
	2.5	5750	5960
	5.0	7610	7400

CONCLUSIONS

The present equation was developed by assuming that processability is inversely related to melt viscosity and molecular weight, which in turn are inversely related to the sum of incidental chain transfer and termination reactions plus purposeful chain-transfer agent; and that both incidental and purposeful effects are Arrhenius-type functions of polymerization temperature. The equation was further simplified by assuming that both incidental and purposeful effects were the same function of polymerization temperature. Success of the ensuing calculations justified these assumptions, particularly for practical work. For further theoretical study, the combined constants in the present equation should of course be separated into their individual components.

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Synthesis and Preliminary Evaluation of Ordered Aliphatic Poly(benzoxazole Amides)*†

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Synopsis

Slightly modified conventional techniques were successfully applied to prepare aliphatic benzoxazolediamines and the corresponding high molecular weight polyamides, which could be spun into excellent fibers. Compared to regular aliphatic polyamides, these products showed higher transition temperatures, improved thermal and light stability, and increased affinity for acid dyes. In addition—quite unexpectedly—these fibers were highly crystalline and oriented after drawing at elevated temperatures.

INTRODUCTION

Aromatic heterocyclic materials have been used for many years as additives to different polymers in order to increase their stability towards light, heat, and oxidation. More recently, polymer chemists have devoted considerable effort to research in the field of incorporating these heterocycles into the polymer backbone in order to improve different properties. Fully aromatic heterocycle polymers and copolymers were investigated in a search for tractable thermally stable materials.[1] Several authors have also studied aliphatic heterocyclic polymers[2] and aliphatic heterocyclic copolymers, such as poly(benzimidazole amides),[3] poly(oxadiazole amides),[4] poly(pyrazole amides),[5] in attempts to increase the thermal and oxidative stability of the aliphatic materials, or in order to increase their rigidity (T_g), dyeability,[6] etc. In very few cases has the fine structure (crystallinity, etc.) of these polymers been determined, and where this has been done, the polymers are claimed to be amorphous materials.[3,7]

It is an object of this paper to describe the synthesis of ordered aliphatic benzoxazole amide copolymers, and their spinning into fibers, which, unexpectedly, showed a high degree of crystallinity and orientation. It is another object of this paper to show the influence of the incorporation of

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the bezoxazole unit on the thermal and light stability of the resulting polymers and on their dye affinity and transition temperature.

EXPERIMENTAL

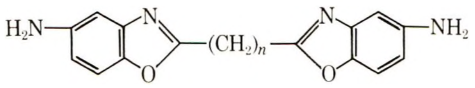
Preparation and Properties of the Monomers

The synthesis by a one-step reaction of aromatic benzoxazole containing diamines has been previously reported.[8] This method has now been modified to prepare aliphatic benzoxazole containing diamines; the synthesis of analogous compounds by a three- or four-step reaction has been reported earlier,[9] but no analytical data on these materials were available up to now. The data on the chemical structure and on the physical properties of the benzoxazole diamines are summarized in Table I.

The diamines were synthesized directly from an aliphatic diacid and a diaminophenol, by using polyphosphoric acid as solvent and condensing agent.[10] The products obtained by precipitating the polyphosphoric acid solution into water were the diamine dihydrates; they were purified by recrystallization from an ethanol–water mixture.

The free diamines were prepared by heating the diamine dihydrates at reflux temperature in butyl alcohol, followed by distillation of the formed azeotrope. The chemical structure of the benzoxazole containing diamines was proven by infrared analysis, by titration of the amino groups, and by elementary analysis. The water content of the dihydrates was determined by the Karl Fisher method and by vapor-phase chromatographic analysis on the azeotrope distillate.

TABLE I
Benzoxazole Diamines[a]



	UV spectrum,[b] λ_{max}, mμ	Molecular formula	Melting point, °C		Elementary Analysis	
			Reichert[c]	DTA[d]	Calcd.	Found
$n = 4$	—	$C_{18}H_{18}N_4O_2 \cdot 2H_2O$	153–155	153	N, 15.6	15.38
$n = 6$	213 $\epsilon = 5.68 \times 10^4$	$C_{20}H_{22}N_4O_2 \cdot 2H_2O$	136–137	138	C, 62.2	62.36
	305 $\epsilon = 7.19 \times 10^3$				H, 6.7	6.86
					N, 14.5	14.54
					O, 16.6	16.41
$n = 8$	306 $\epsilon = 7.3 \times 10^3$	$C_{22}H_{26}N_4O_2$	115–117	116	C, 70.0	70.42
					H, 6.9	7.09
					N, 14.8	14.5

[a] All the materials are white crystalline products.

[b] Measured in solution in methanol.

[c] Melting points (uncorrected) measured on a Reichert melting point apparatus.

[d] Melting point determined from differential thermal analysis.

TABLE II

Poly(benzoxazole Amides)

	Monomers			Polymer properties					
					DTA				
Polymer	Diamine,[a] A-Bx-R-Bx-A	Diacid Derivative	Polymerization Method[b]	TGA, °C[c]	T_g, °C	T_m, °C	Softening temp, °C[d]	η_{inh}[e]	Crystallinity[f]
I	m-C_6H_4[g]	Sebacyl chloride	Solution	450	120	350	Chars	0.99	Moderate
II	—$(CH_2)_6$—	Suberic acid	Melt, 230°C	--	77	230	>230	0.31	Moderate
III	—$(CH_2)_6$—	Sebacyl chloride	Solution	450	86	ND[h]	170–180	1.78	Amorphous
IV[j]	—$(CH_2)_8$—	Adipyl chloride	Solution	375 (in air, 360)	85	234	230–235	1.37	Crystalline (DTA); amorphous (x-ray)
V	—$(CH_2)_8$—	Sebacic acid	Melt, 210°C	450	72	177, 180	172–174	0.34	Moderate
VI	—$(CH_2)_8$—	Sebacyl chloride	Solution	450 (in air, 450)	93	184	170–180	1.48	Amorphous (x-ray); slightly crystalline (DTA)

[a] A = amine, Bx = benzoxazole ring, R is given in the column.

[b] Solution, in dimethylacetamide; melt, using a dibutyltin catalyst.

[c] Onset of severe degradation; determined on a Du Pont 900 Thermal Analyzer in nitrogen; rate 20°C/min. T_g = glass transition temperature, T_m = crystalline melting point.

[d] Softening temperatures (uncorrected) were measured on a Reichert melting point apparatus.

[e] Measured in a 0.5% m-cresol solution.

[f] From DTA and x-ray measurements.

[g] Data of Preston et al.[8]

[h] Not detectable.

[j] Elementary analysis for polymer IV: Calcd: C, 68.85%; H, 6.8%; N, 11.5%. Found: C, 68.84%; H, 7.46%; N, 11.37%.

Preparation and Properties of the Polymers

The polymers were synthesized by the "ordered copolymer" approach, which consists of condensing preformed blocks (the benzoxazole diamines) with other monomers under such conditions that no rearrangement of bonds occurs.[11] To accomplish this the low-temperature solution polycondensation method was used[12] starting from the block diamine and a diacid chloride. For the purpose of comparison some analogous polymers were prepared by a melt condensation method from the same diamines and the free acids with the use of different catalysts.[13] The properties of the polymers are given in Table II.

The polycondensation in solution results in polymers of high molecular weight. Melt polycondensation produced only low molecular weight materials. Without any thermal pretreatment, the polymers obtained by the melt polycondensation method were more crystalline than analogous structures prepared in solution; this can be explained by the crystallization behavior upon cooling. All the polymers were soluble in the common organic polyamide and polyheterocycle solvents, such as *m*-cresol and dimethylacetamide.

Film Casting and Fiber Spinning

Due to the low molecular weight of the products prepared in the melt, only the polymers prepared in solution could be cast into good films or spun into useful fibers.

Films of these polymers were cast from solutions in formic acid; they were colorless, transparent, and tough. They could be drawn over a hot shoe at 100°C.

TABLE III
Poly(benzoxazole amide) Fibers

			Fiber properties				
Polymer[a]	Spinning conditions	Drawing conditions	Titer, den	Tenacity, gpd	Elongation, %	T_m, °C (DTA)	X-ray
III	Melt (242–243°C)	100°C, 3.8×	20	2.47	7.2	175	Oriented, crystalline
IV	Melt (265–270°C)	100°C, 4×	50	2.61	6.8	234[b] 250	Highly crystalline, oriented
VI	Melt (237–244°C)	100°C, 4.3×	77	2.76	13	185	Highly crystalline, oriented
VI	Wet (20–25°C)	100°C, 3.5×	97	0.9	3.1	186	Highly crystalline, oriented

[a] See Table II.

[b] Two peaks.

Wet spinning of these polymers from a dimethylacetamide solution into a water–dimethylacetamide coagulation bath yielded lustrous, colorless fibers of low tenacity; drawing increased the tenacity and resulted in highly crystalline and oriented fibers, as indicated by x-ray analyses and DTA measurements (Table III).

Melt spinning of the polymers at 235–270°C yielded lustrous, slightly yellowish, crystalline, nonoriented fibers, which became oriented after drawing over a hot shoe at 100°C. The properties of the fibers are also given in Table III. The mechanical properties of these fibers were only moderate; optimization of the spinning conditions should result in improved fiber properties. Noteworthy are the high elastic modulus values of the fibers (particularly fiber III), when compared to that of a "regular" polyamide reference fiber (Table VI).

PRELIMINARY EVALUATION OF THE PRODUCTS AND DISCUSSION

Physical Properties

The results of the x-ray analyses are summarized in Table IV.

The x-ray diffractometer measurements on polymers prepared in solution and on solution-cast films show the pattern of completely amorphous materials. Forward reflection x-ray diffraction analysis of these materials yields only a diffuse halo.

TABLE IV
X-Ray Analysis on the Polymers

	Polymer IV	Polymer VI
Polymer from melt	—	25–42% crystallinity, *d* spacings at 4.69, 4.06, 3.72 Å
Polymer from solution	Amorphous, nonoriented	Amorphous, nonoriented
Film		
Solution-cast	Very weakly crystalline, nonoriented	Amorphous, nonoriented (diffuse halo 4.06–4.13 Å)
Solvent-treated (dimethyl acetamide)	—	25% crystallinity; *d* spacings at 4.67, 3.98, 3.71 Å
Annealed (4 hr, 100°C)	—	Crystalline, nonoriented; *d* spacings at 4.66, 3.94, 3.51 Å
Drawn	Slightly crystalline and oriented, *d* spacings at 4.54, 3.80, 3.46 Å	Crystalline, slight orientation in direction of drawing
Fiber		
Melt-spun	Crystalline, slightly oriented	Very crystalline, scarcely oriented
Drawn	Highly crystalline and oriented; calculated for length of repeat unit: 31.5 ± 0.5 Å	Highly crystalline and oriented; calculated for length of repeat unit: 36 ± 0.5 Å

TABLE V
Differential Thermal Analysis

	Polymer IV			Polymer VI		
	T_g, °C	Crystallization exotherm, °C	T_m, °C	T_g, °C	Crystallization exotherm, °C	T_m, °C
Polymer						
From melt	—	—	—	72	None	177–180[a]
From solution	85	None	234	93	None	184[a]
Film						
Solution-cast	95	160	220	93	None	None
Drawn	92	150	220	98	None	None
Fiber						
Melt-spun						
Undrawn	73	130	233; 250[b]	90	150	183[a]
Drawn	91	160	234; 250[b]	92	160	185
Wet spun						
Undrawn	—	—	—	94	None	187[a]
Drawn	—	—	—	95	None	186

[a] Very small peak.
[b] Two peaks.

When these films are treated for 60 hr in a dimethylacetamide atmosphere (in a desiccator at room temperature)[14] or annealed for 4 hr at 100°C the diffuse halo resolves into three clear rings, corresponding to the three peaks of the diffractometer measurements. On using lateral-order parameters,[15] a degree of crystallinity of approximately 25% was found for these materials; orientation was completely absent.

The pattern of a drawn film indicates a slight orientation in the drawing direction, but the diffuse halo has not disappeared completely. An alignment of the molecular chains has occurred, without the production of real crystallinity. Polymers prepared in the melt and melt-spun fibers are

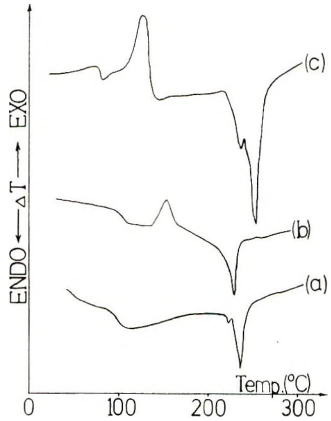
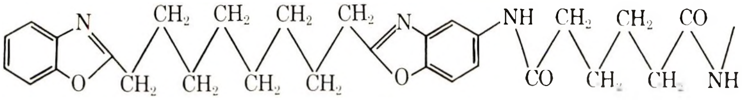


Fig. 1. DTA thermograms of polymer IV: (*a*) polymer from solution polycondensation; (*b*) drawn film; (*c*) undrawn fiber.

crystalline; the fibers, in addition, are scarcely oriented in the drawing direction. The forward reflection x-ray diffraction analysis of the drawn fiber shows a high degree of crystallinity and orientation. From these pictures the length of the repeat unit could be calculated. DTA results (Tables II and V) indicate that the glass transition temperatures of the different polybenzoxazoleamides are in the same range; the melting temperatures, however, range from 170 to 250°C, depending on the length of the methylene chains.

The glass transition temperatures for all the polymers are higher than those of regular aliphatic polyamides; this is compatible with the more rigid backbone of the poly(benzoxazole-amides).

Quite generally, all samples of polymer IV, which has probably the most symmetrical structure, show definite crystalline melting points.



Polymer IV

The x-ray analysis of the solution-polymerized polymer IV, however, shows an amorphous structure and deviates in this respect from the DTA results; this behavior is unexplained at present. The twin peaks appearing in the melt spun samples indicate that the spinning process and the subsequent drawing have induced a certain degree of orientation (confirmed by x-ray analysis), this orientation resulting in a higher degree of order, as is shown by the higher melting temperature at 250°C. This behavior could be compared to the melt process frequently observed in drawn polyamide[16,17] and polyester[18] fibers. The clear crystallization exotherms observed (Fig. 1) on heating of the samples are compatible with a chain structure sufficiently flexible for thermal crystallization to occur.

The x-ray analysis of the solution-polymerized polymer VI again differs from the DTA results; the difference is unexplained at present. Here, the DTA results for all four fibers indicate that the spinning process itself induces some orientation, this orientation inducing, in its turn, some degree of order into the fiber, translated by a clear, though small, melting peak.

Thermal and Light Stability

The poly(benzoxazole amides) are stable far above their melting temperatures, as shown by the results of the thermogravimetric analyses (Table II). The degradation in oxidative and in inert atmosphere is not very different. The polymers outperform the regular, nonstabilized aliphatic polyamides by more than 50°C, as shown on Figure 2.

The light stability in air of the poly(benzoxazole amides) is outstanding; after 5 months exposure to fluorescent light the tenacity of the fibers remained practically unchanged, while the elongation had increased sub-

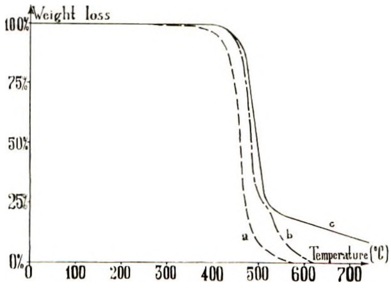


Fig. 2. TGA diagrams: (*a*) nonstabilized nylon 66, in air; (*b*) polymer VI, in air; (*c*) polymer VI, in nitrogen.

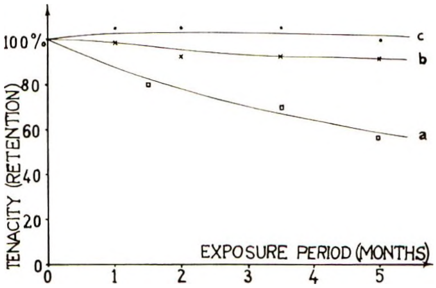


Fig. 3. Fluorescent light exposure tests: (*a*) non stabilized nylon 66; (*b*) polymer IV; (*c*) polymer VI.

stantially. Nonstabilized nylon 66 fibers treated under the same conditions had lost 50% of their original tenacity and elongation. The results of these experiments are summarized in Table VI and graphically presented in Figure 3.

TABLE VI
Light Exposure Results

	Nylon 66 (nonstabilized), 20 den			Polymer III, 20 den			Polymer IV, 50 den		
Exposure	Tenacity, gpd	Elongation, %	Modulus, gpd	Tenacity, gpd	Elongation, %	Modulus, gpd	Tenacity, gpd	Elongation, %	Modulus, gpd
Fluorescent light									
Not exposed	4.2	24	48.6	2.5	7.2	86.3	2.4	6.8	58.7
1 month	—	—	—	2.7	18.9	—	2.5	8.3	60.5
3/2 months	3.4	17	—	—	—	—	—	—	—
2 months	—	—	—	2.66	18	96.1	2.1	10.1	61
7/2 months	3.1	10.2	47.5	2.7	19.1	92.4	2.0	10.9	59.8
5 months	2.3	7.1	41.1	2.4	16.4	95.7	2.1	10.8	59.1
Xenotest, 60 hr	3.3	12.8	46.9	2.9	26.1	85	—	—	—

Dyeing Behavior

Dyeing of the poly(benzoxazole amide) fibers with an acid dye (Alizarine Blue) at pH 4.5–6 shows a dye uptake equivalent to the number of amine end groups in the polymers (approximately 10 meq/kg). A regular nylon 66 fiber behaves in the same way. When the dyeing experiments are carried out at lower pH values (2–2.5), however, the degree of "overdyeing" is greater for the benzoxazole-containing fibers than for the nylon 66 standard.

MATERIALS AND METHODS

The preparation of the diamines is illustrated by a simple example, representing the product of Table I where $n = 6$.

A 500-ml three-necked round-bottomed flask, equipped with a Drierite tube, a nitrogen inlet, and a Trubore type stirrer, was charged with 19.7 g of 2.4-diaminophenol dihydrochloride (0.1 mole), 8.7 g of suberic acid (0.05 mole), and 140 g of polyphosphoric acid. The viscous mixture was heated for 1 hr at 110°C under nitrogen flow and under continuous stirring. Then the temperature was raised slowly (to prevent excessive foaming) to 150°C, where it was kept for an additional 2 hr. The hot solution was poured into 600 ml of water, and the precipitate was filtered off, washed with 600 ml of a 10% sodium carbonate aqueous solution and dried. The product was recrystallized twice from a 50:50 ethanol–water solution. Infrared absorptions were at 3200–3400 and 1615 cm^{-1} (NH_2), 2800–3000 cm^{-1} (—CH_2—), and 1570, 1445, and 1480 cm^{-1} (C=C, C=N).

Solution polymerization, was as detailed by Morgan.[12]

Melt polycondensation was also by a literature method.[13]

Films were cast from clear viscous polymer solutions (20% solids in formic acid) onto a glass plate, leveled with a Gardner knife, and treated in a ventilated oven at 40°C, then in a vacuum oven at room temperature, to evaporate the solvent. Preferably the films were removed from the glass plate while still plasticized with a little solvent to prevent adhesion to the glass plate. Transparent, colorless, tough films were obtained.

The solution spinning was carried out on a micro wet-spinning apparatus similar to the one described by Temin.[19] The polymer solution (25–30% solids in pure dimethylacetamide) was extruded in a 50:50 dimethylacetamide–water coagulation bath at 25°C. The resulting continuous fiber was washed with water, taken up at a speed of 20 m/min, and dried in a vacuum oven at room temperature overnight.

The various polymers were melt-spun at 240–250°C in a piston-driven melt-spinning apparatus at constant speed through a one hole (diameter 230 μ) spinneret. The solidified fibers were passed over a spin-finish roll and taken up at a speed of 100 m/min. After storage for 24 hr at 65% RH, the melt- or solution-spun fibers were drawn over a preheated "hot finger" at 50°C and subsequently over a hot-plate (length 20 cm) at 100°C and wound on a bobbin at a speed of 100 m/min.

The DTA measurements were carried out on a Dupont 900 Thermal Analyzer under standard scanning conditions (nitrogen flow, scanning speed 20°C/min). No particular thermal treatment was applied to the samples prior to the analysis. Some scatter in the T_g values could probably be ascribed to incomplete dehydration of the samples.

The x-ray diagrams were recorded on a Philips diffraction unit; CuKα radiation was obtained by filtration with a Ni filter. Analysis was performed according to the conventional diffractometer techniques with a proportional counter. Also the forward reflection technique was applied to obtain flat photographs. The distance between sample and camera was calibrated with MoS_2-containing fibers. Optimal exposure times were found to be between 30 and 60 min.

In the "long term" light stability tests the samples were exposed at a distance of 18 cm to a battery of eight fluorescent light tubes (daylight spectrum, Philips TL 55) mounted in an air-filled box which was kept at room temperature. Accelerated tests were carried out in a standard Xenotest apparatus with the use of a light source without filter.

In a standard dyeing experiment, 2 g of fiber was dyed at 60°C for 5 hr in a dyebath composed of 18% of Alizarine Blue (Solide R), 15% of Alkanol LN, and 10 ml of a 1% aqueous sodium acetate solution; the bath was adjusted to pH 5 by adding acetic acid. The quantity of dye adsorbed by the fiber was calculated from the final concentration of dye in the bath, measured by spectrophotometry.

CONCLUSIONS

From the academic point of view the most interesting result of this study was the fact that highly crystalline and oriented poly(benzoxazole amides) were obtained, in spite of the presence of the bulky heterocyclic units into the polymer backbone. When practical usefulness is concerned, attention should be drawn to the high thermal stability, the elevated glass transition temperature, and the high modulus of the fibers; even more important, however, was the outstanding light stability, when compared to regular aliphatic polyamide fibers. This property could be put to profit by preparing copolymers containing small amounts of the diamines in the polymer chain; further investigation along this line may prove desirable.

The authors wish to express their appreciation to Mr. W. Gouwy for excellent technical assistance.

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N,N′-(Disubstitutedmethylene)bisacrylamides: Preparation and Polymerization*

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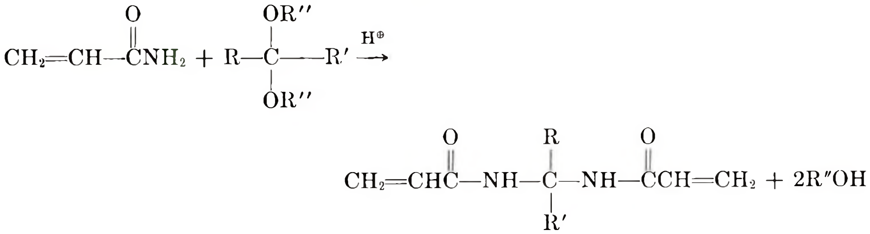
Synopsis

Preparative methods for the previously unreported *N,N′*-(disubstitutedmethylene)-bisacrylamides are presented. The solubility and thermal stability of these new bisamides are compared to the well known *N,N′*-methylenebisacrylamide. *N,N′*-Isopropylidenebisacrylamide, one of these new compounds, readily copolymerizes with a variety of vinyl monomers. It forms high molecular weight copolymers by the conjugate polyaddition of alkanedithiols or piperazine.

INTRODUCTION

The reaction of aldehydes with amides or nitriles gives good yields of *N,N′*-alkylidenebisamides.[1,2] For example, formaldehyde reacts with acrylonitrile in sulfuric acid to give *N,N′*-methylenebisacrylamide in 86% yield. Ketones react with nitriles in sulfuric acid to give *N*-oxoalkylamides.[3,4] No bisamides have been reported by the reaction of a ketone or a ketone derivative with either an amide or a nitrile.

We have found that under acidic catalysis, acrylamide will react with ketone acetals to give *N,N′*-(disubstitutedmethylene)bisacrylamides.



$$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}NH_2 + R{-}\underset{OR''}{\overset{OR''}{C}}{-}R' \xrightarrow{H^{\oplus}} CH_2{=}CH\overset{O}{\overset{\|}{C}}{-}NH{-}\underset{R'}{\overset{R}{C}}{-}NH{-}\overset{O}{\overset{\|}{C}}CH{=}CH_2 + 2R''OH$$

The copolymerization of one of these new compounds, where R=R′= CH_3 has been explored. We have found that *N,N′*-isopropylidenebisacrylamide undergoes radical-initiated copolymerization with vinyl monomers as well as conjugate addition polymerization with alkanedithiols or piperazine.

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

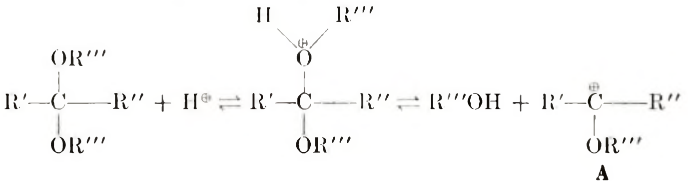
RESULTS AND DISCUSSION

Monomer Preparation

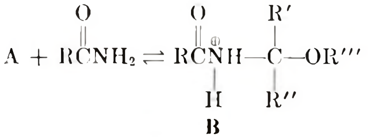
The reaction of acrylamide with ketone acetals is catalyzed by protonic acids such as *p*-toluenesulfonic acid or sulfuric acid and a variety of Lewis acids, including aluminum chloride, boron fluoride and ferric chloride. To obtain appreciable yields, the product must precipitate from the reaction mixture, or the by-product alcohol must be removed as it is formed.

Only the dialkyl acetals of ketones have been shown to react in this manner. The 1,3-dioxolanes of 3-pentanone, methyl isobutyl ketone, acetophenone, and benzophenone did not react.

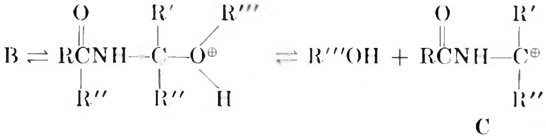
A variety of these new bisamides were prepared (Table I). The ketone acetal precursors were prepared by published procedures.[5–7] *N,N'*-Isopropylidenebispropionamide (II), prepared from acetone dimethyl acetal and propionamide was identical with hydrogenated *N,N'*-isopropylidenebisacrylamide(I). The yields of I and II show that the reaction proceeds well for a saturated amide and the more reactive acrylamide. The lower yields for the other bisamides do not indicate that the reaction goes poorly for acetals other than acetone acetal. For the most part, these reactions were not developed to achieve maximum yields. Often there was some by-product polymer formed. Compound VIII shows that even for the bulky diphenyl derivative, a reasonable yield of bisamide was obtained. A potential pathway for this reaction is shown with eqs. (1)–(4).



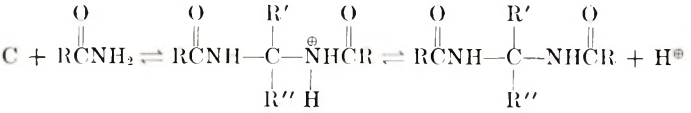
$$R'-\underset{OR'''}{\overset{OR'''}{C}}-R'' + H^{\oplus} \rightleftharpoons R'-\underset{OR'''}{\overset{\overset{H\quad R'''}{\overset{\oplus}{O}}}{C}}-R'' \rightleftharpoons R'''OH + R'-\underset{\underset{\mathbf{A}}{OR'''}}{\overset{\oplus}{C}}-R'' \qquad (1)$$



$$\mathrm{A} + R\overset{O}{\overset{\|}{C}}NH_2 \rightleftharpoons R\overset{O}{\overset{\|}{C}}\underset{H}{\overset{\oplus}{N}}H-\underset{\underset{\mathbf{B}}{R''}}{\overset{R'}{C}}-OR''' \qquad (2)$$



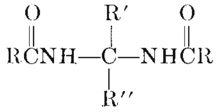
$$\mathrm{B} \rightleftharpoons R\overset{O}{\overset{\|}{C}}NH-\underset{R''}{\overset{R'}{C}}-\overset{R'''}{\underset{H}{O^{\oplus}}} \rightleftharpoons R'''OH + R\overset{O}{\overset{\|}{C}}NH-\underset{\underset{\mathbf{C}}{R''}}{\overset{R'}{C^{\oplus}}} \qquad (3)$$



$$\mathrm{C} + R\overset{O}{\overset{\|}{C}}NH_2 \rightleftharpoons R\overset{O}{\overset{\|}{C}}NH-\underset{R''}{\overset{R'}{C}}-\underset{H}{\overset{\oplus}{N}}H\overset{O}{\overset{\|}{C}}R \rightleftharpoons R\overset{O}{\overset{\|}{C}}NH-\underset{R''}{\overset{R'}{C}}-NH\overset{O}{\overset{\|}{C}}R + H^{\oplus} \qquad (4)$$

It has been shown[8] that in acid-catalyzed reactions of ketone acetals, the rate-determining step is the cleavage of a carbon–oxygen bond of the protonated acetal to give an alcohol and an alkoxy carbonium ion. The

TABLE I

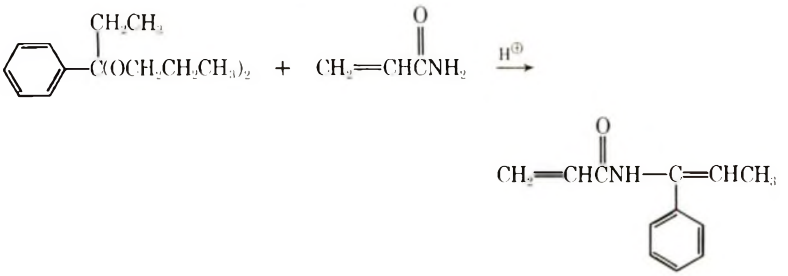


$$\mathrm{R\overset{\overset{O}{\|}}{C}NH{-}\underset{\underset{R''}{|}}{\overset{\overset{R'}{|}}{C}}{-}NH\overset{\overset{O}{\|}}{C}R}$$

Compound	R	R′	R″	Yield, %	Melting point, °C	Analyses, (calculated) and found C, %	H, %	N, %
I	$CH_2{=}CH$	CH_3	CH_3	70	210–212	(59.32)	(7.74)	(15.37)
						59.45	7.81	15.39
II	CH_3CH_2	CH_3	CH_3	60	173.5–175	(58.03)	(9.74)	(15.04)
						58.10	9.81	15.09
III	$CH_2{=}CH$	CH_3	CH_3CH_2	33	191–193	(61.20)	(8.22)	(14.28)
						61.60	8.34	14.13
IV	$CH_2{=}CH$	CH_3	C_9H_{19}	21	149.5–150	(69.34)	(10.27)	(9.52)
						69.29	10.21	9.56
V	$CH_2{=}CH$	CH_3	$C_{17}H_{35}$	28	130–133	(73.84)	(11.40)	(6.89)
						73.64	11.28	6.83
VI	$CH_2{=}CH$	CH_3	C_6H_5	6	182–188	(68.83)	(6.60)	(11.47)
						69.28	6.47	11.39
VII	CH_3	C_6H_5	C_6H_5	10	167–170	(72.32)	(6.43)	(9.92)
						72.10	6.50	10.08
VIII	$CH_2{=}CH$	C_6H_5	C_6H_5	47	229–231	(74.49)	(5.92)	(9.15)
						74.60	6.01	9.22
IX	$CH_2{=}CH$	$—(CH_2)_5—$		28	166–168	(64.84)	(8.16)	(12.60)
						64.92	8.25	12.55

remainder of the sequence then proceeds rapidly. Intermediate B may deprotonate to give the *N*-alkoxyalkylamide. However, the *N*-alkoxyalkylamide is not isolable, even when the reaction is carried out in the acetal as solvent.

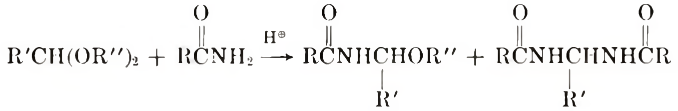
The reaction of acrylamide with propiophenone di-*n*-propyl acetal followed a different pathway. When this acetal was treated with excess acrylamide, no bisamide was obtained. The only product isolated was 1-acrylamido-1-phenylpropene in 77% yield.



(5)

In this case the intermediate carbonium ion (**C**) preferentially lost a proton. In contrast, the di-*n*-propyl acetal of acetophenone gave only the bisacrylamide VI and no other amide.

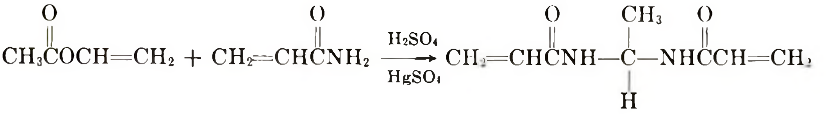
The analogous reaction of aldehyde acetals with amides to give *N*,*N*′-alkylidenebisamides has been reported:[9]



$$R'CH(OR'')_2 + R\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{H^\oplus} R\overset{O}{\overset{\|}{C}}NH\underset{R'}{\underset{|}{C}}HOR'' + R\overset{O}{\overset{\|}{C}}NH\underset{R'}{\underset{|}{C}}HNH\overset{O}{\overset{\|}{C}}R \quad (6)$$

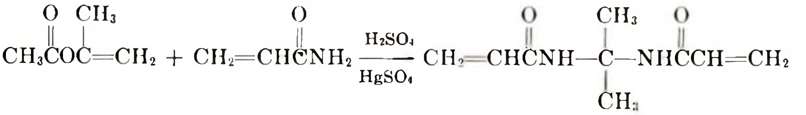
It is interesting to note that in this case, when the molar ratio of acetal to amide is unity, the *N*-alkoxyalky amide is obtained in good yield. This contrasts directly with ketone acetals which even in large excess react with amides to give only the bisamides. It should be noted that aldehyde derived bisamides are more easily prepared by the reaction of an aldehyde with a nitrile or amide in the presence of a strong acid.

Another route to bisamides starts with a vinyl ester. With acrylamide and vinyl acetate, *N*,*N*′-ethylidenebisacrylamide is formed in 82% yield.[10]



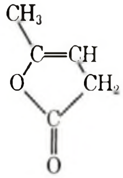
$$CH_3\overset{O}{\overset{\|}{C}}OCH{=}CH_2 + CH_2{=}CH\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow[HgSO_4]{H_2SO_4} CH_2{=}CH\overset{O}{\overset{\|}{C}}NH{-}\overset{CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}{-}NH\overset{O}{\overset{\|}{C}}CH{=}CH_2 \quad (7)$$

We extended this reaction to isopropenyl acetate, which with acrylamide, gave *N*,*N*′-isopropylidenebisacrylamide in 16% yield. This reaction is markedly sluggish in comparison with that starting with the ketone acetal.



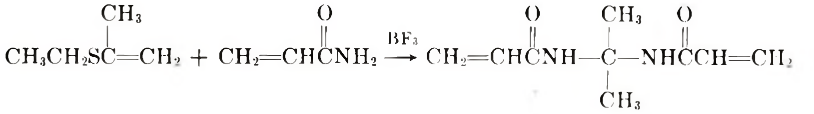
$$CH_3\overset{O}{\overset{\|}{C}}O\overset{CH_3}{\overset{|}{C}}{=}CH_2 + CH_2{=}CH\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow[HgSO_4]{H_2SO_4} CH_2{=}CH\overset{O}{\overset{\|}{C}}NH{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}NH\overset{O}{\overset{\|}{C}}CH{=}CH_2 \quad (8)$$

We tried this reaction with the related α-angelicalactone



but were not able to obtain a bisamide.

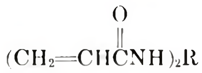
The previous reactions all involve oxygen-containing ketone derivatives. We were interested in determining if some of the sulfur derivatives would undergo similar reactions. It has been reported that ethyl vinyl ether will react with amides under acidic conditions to give the corresponding *N,N'*-ethylidenebisamides.[11] Under various conditions we were not able to duplicate this reaction with ethyl vinyl sulfide. The vinyl sulfide polymerized rapidly under the cationic conditions which were employed. However, isopropenyl ethyl sulfide, prepared via the pyrolysis of acetone ethyl mercaptole,[12] gave an 89.5% yield of *N,N'*-isopropylidenebisacrylamide based upon the acrylamide charged.


$$CH_3CH_2S\overset{CH_3}{\overset{|}{C}}{=}CH_2 + CH_2{=}CH\overset{O}{\overset{\|}{C}}NH_2 \xrightarrow{BF_3} CH_2{=}CH\overset{O}{\overset{\|}{C}}NH{-}\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}NH\overset{O}{\overset{\|}{C}}CH{=}CH_2 \quad (9)$$

Properties of the Bisacrylamides

We compared the solubilities of the new bisacrylamides with *N,N'*-methylenebisacrylamide (Table II).

TABLE II
Solubilities of Bisacrylamides


$$(CH_2{=}CH\overset{O}{\overset{\|}{C}}NH)_2R$$

Solvent	Solubility, g/100 ml solvent[a] R = CH_2	R = $C(CH_3)_2$	R = 	R = $C(CH_3)C_9H_{19}$	R = $C(C_6H_5)_2$
H_2O	3.0	0.6	<0.1	0	0
CH_3OH	8.2	5.7	—	8.3	0.4
CH_3CH_2OH	5.4	2.1	2.4	5.7	0.2
$CHCl_3$	0.3	0.7	1.3	12.1	5.5
C_6H_6	<0.1	0.2	<0.1	1.1	0.2

[a] At 30°C.

N,N'-Isopropylidenebisacrylamide showed no appreciable difference in solubility from *N,N'*-methylenebisacrylamide in any of the five solvents. This was also the case with the *N,N'*-cyclohexylidenebisacrylamide. As

TABLE III
Differential Thermal Analysis of Bisacrylamides[a]

Bisacrylamide	Thermal polymerization range, °C	Thermal decomposition range, °C
N,N'-Methylene-	182–187	>365
N,N'-Isobutylidene[b]	222–225	>230
N,N'-Cyclohexylidene-	167–187	246–266
N,N'-Isopropylidene-	212–218	271–293
N,N'-Diphenylmethylene-	230–235	275–330

[a] In a nitrogen atmosphere by use of the DuPont 900 Differential Thermal Analyzer.

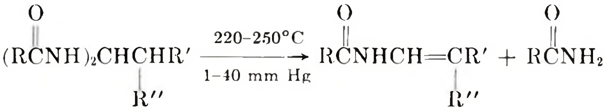
[b] *N,N'*-Isobutylidenebisacrylamide[13] was prepared from acrylonitrile and isobutyraldehyde in sulfuric acid.

the chain length in the ketone was increased to methyl nonyl, the solubilities in organic solvents increased. The diphenyl derivative again exhibited low solubilities.

The thermal stabilities of some of the new bisacrylamides are compared with the corresponding aldehyde derivatives in Table III.

In all cases, these compounds melt and undergo thermal polymerization consecutively at high temperatures. *N,N'*-Methylenebisacrylamide is clearly the most thermally stable. The isobutyraldehyde-derived bisacrylamide degrades at the lowest temperature. Thus, it is reasonable to propose that a ketone derived bisacrylamide, having the same solubilities as an aldehyde derived bisacrylamide, would be more thermally stable. This could be important if the compounds were to be used as crosslinking agents.

One of the primary routes for thermal degradation of bisamides was reported in 1965 [eq. (10)]:[14]



$$(\mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NH})_2\mathrm{CH}\underset{\underset{\displaystyle \mathrm{R''}}{|}}{\mathrm{C}}\mathrm{HR'} \xrightarrow[\text{1–40 mm Hg}]{220\text{–}250^\circ\mathrm{C}} \mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHCH{=}}\underset{\underset{\displaystyle \mathrm{R''}}{|}}{\mathrm{C}}\mathrm{R'} + \mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NH_2} \qquad (10)$$

R = Me, C_6H_5

R', R'' = H, Me

The yield was 40–70%.

This shows that bisamides derived from aldehydes degrade thermally to give enamides. We believe that the bisamides prepared from ketone derivatives also degrade by the same route, although this has not been proved. *N,N'*-Diphenylmethylene- and *N,N'*-methylenebisacrylamides are special cases, in that they have no hydrogen atom β to the amide nitrogen and hence cannot degrade by this path.

Polymerization

N,N'-Isopropylidenebisacrylamide was used in the polymerization studies since the starting acetone acetal is readily available. This monomer homopolymerized in methanol with benzoyl peroxide as initiator to give a hard, colorless, insoluble product. It also copolymerized under a variety of conditions with a range of commercial vinyl monomers which included styrene, acrylonitrile, methyl methacrylate, acrylic acid, acrylamide, diacetone acrylamide, and vinyl acetate. When the monomer feed contained more than 10% bisacrylamide, the polymers formed were insoluble and probably crosslinked.

To obtain more quantitative data on the copolymerizability of *N,N′*-isopropylidenebisacrylamide, its copolymerization reactivity ratios were determined with acrylonitrile and styrene. These copolymerizations were carried out in methanol in ampoules at 60°C. with 2,2′-azobis(2-methylpropionitrile) as the initiator. The compositions of the purified copolymers were calculated from the elementary analyses. The reactivity ratios were determined by the method of Fineman and Ross.[15] The reactivity ratios are summarized in Table IV. The data for the copolymerizations with acrylonitrile and styrene are given in Table V and Table VI.

We were also interested in the conjugate addition reactions of bisacrylamides with dithiols or diamines. Marvel and co-workers were the first to report the formation of a linear polymer by polyconjugate addition: the

TABLE IV
Reactivity Ratios of *N,N′*-Isopropylidenebisacrylamide (M_1) with Acrylontrile and Styrene[a]

Monomer M_2	r_1	r_2
Acrylonitrile	2.44	0.57
Styrene	0.565	1.57

[a] For the copolymerization of acrylamide (M_1) with acrylonitrile (M_2), the reactivity ratios are reported as $r_1 = 1.357$ and $r_2 = 0.875$.[16]

TABLE V
Copolymerization Parameters for *N,N′*-Isopropylidenebisacrylamide (M_1) with Acrylonitrile (M_2)

N,N′-Isopropylidene-bisacrylamide, g	Acrylonitrile, g	*N,N′*-Isopropylidene-bisacrylamide in monomer mixture, mole-%[a]	Methanol, ml	Conversion, %	Nitrogen, %	*N,N′*-Isopropylidene-bisacrylamide in copolymer, mole-%[a]
1.040	9.362	6.08	30	2.5	24.63	10.05
1.940	8.248	12.06	30	5.1	23.13	19.74
4.012	6.091	27.6	30	4.0	20.33	41.6
5.072	5.187	36.2	50	2.4	18.78	56.5
6.076	4.018	46.8	60	7.2	17.78	72.8
7.046	3.260	55.7	60	10.4	17.33	67.6

[a] The mole percentages here are vinyl equivalent percentages. One mole of *N,N′*-isopropylidenebisacrylamide contains two vinyl equivalents.

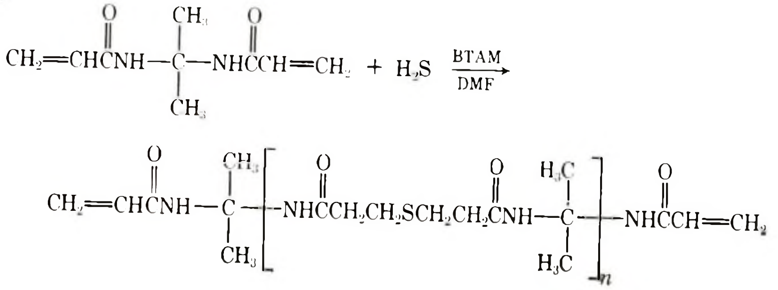
TABLE VI
Copolymerization Parameters for the *N,N'*-Isopropylidenebisacrylamide (M_1) with Styrene (M_2)

N,N'-Isopropylidene-bisacrylamide, g	Styrene, g	*N,N'*-Isopropylidene-bisacrylamide in monomer mixture, mole-%[a]	Methanol, ml	Conversion, %	Carbon, %	*N,N'*-Isopropylidene-bisacrylamide in copolymer, mole-%[a]
1.027	9.195	11.3	50	1.0	90.36	6.59
2.066	8.222	22.3	50	8.0	86.99	17.98
3.035	7.155	32.6	50	1.3	84.46	26.1
4.036	6.193	42.8	50	1.9	82.57	32.3
5.105	5.149	53.1	50	1.9	78.58	44.7
7.079	3.100	72.3	75	4.8	73.19	61.1
9.047	1.068	90.7	75	4.3	64.83	85.1

[a] The mole percentages here are vinyl equivalent percentages. One mole of *N,N'*-isopropylidenebisacrylamide contains two vinyl equivalents.

base-catalyzed addition of 1,6-hexanedithiol to dibenzalacetone.[17,18] Hulse prepared polymers of this type by the conjugate addition of amines, dithiols and other compounds with acidic hydrogen atoms to bisacrylates, bismethacrylates, *N,N'*-methylenebisacrylamide and bismaleates.[19] He obtained a high molecular weight polymer by the reaction of piperazine with the bisacrylamide. Danusso and co-workers, in a series of papers, report the polyaddition of diamines to bisacrylamides prepared by the reaction of acrylyl chloride to α,ω-diamines.[20] Erickson has prepared a series of high molecular weight polymers by the addition of hydrogen sulfide to bisacrylates and bismethacrylates.[21] This paper described the reaction of hydrogen sulfide with *N,N'*-methylenebisacrylamide, but the product was of low molecular weight. Finally, Imoto and co-workers[22] and Minoura and co-workers[23] found that the polyaddition reaction of dithiols with *N,N'*-methylenebisacrylamide gave low molecular weight polymers.

The reaction of *N,N'*-isopropylidenebisacrylamide with hydrogen sulfide was carried out in dimethylformamide (DMF) with benzyltrimethylammonium methoxide (BTAM) as catalyst [eq. (11)]



$$CH_2{=}CH\overset{\overset{O}{\|}}{C}NH-\underset{CH_3}{\overset{CH_3}{C}}-NH\overset{\overset{O}{\|}}{C}CH{=}CH_2 + H_2S \xrightarrow[DMF]{BTAM}$$

$$CH_2{=}CH\overset{\overset{O}{\|}}{C}NH-\underset{CH_3}{\overset{CH_3}{C}}-\left[NH\overset{\overset{O}{\|}}{C}CH_2CH_2SCH_2CH_2\overset{\overset{O}{\|}}{C}NH-\underset{H_3C}{\overset{H_3C}{C}}\right]_n-NH\overset{\overset{O}{\|}}{C}CH{=}CH_2 \qquad (11)$$

$n = 4$–5

TABLE VII
Polyaddition Reactions of Bisacrylamides with Alkanedithiols

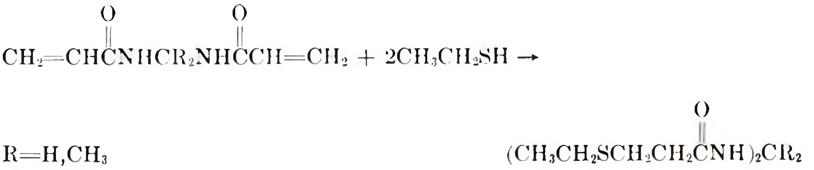
N,N′-Alkylidene-bisacrylamide	Dithiol $HS(CH_2)_nSH$, n	Polymerization solvent	Yield, %	Polymer melt temperature, °C	η_{sp}/c[a]	Elementary analysis[b] Calcd. N, %	Calcd. S, %	Found N, %	Found S, %
Isopropylidene	6	DMF	89	150–153	1.05	8.43	19.25	8.33	19.51
Isopropylidene	5	DMSO	86	149–151	0.74	8.80	20.10	8.42	20.06
Isopropylidene	10	DMSO	96	125–128	0.99	7.21	16.47	6.97	16.96
Methylene	6	DMF	85	ca. 200 (dec.)	0.11	9.21	21.03	9.53	19.57
Methylene	10	DMSO	93	ca. 200 (dec.)	0.12	7.78	17.79	7.58	18.08

[a] Measured at a concentration of 0.500 g/100 ml *m*-cresol at 30°C.

[b] Corresponding formulas: $(C_{15}H_{28}O_2S_2N_2)_n$; $(C_{14}H_{26}O_2S_2N_2)_n$; $(C_{19}H_{36}O_2S_2N_2)_n$; $(C_{13}H_{24}O_2S_2N_2)_n$; $(C_{17}H_{32}O_2S_2N\ )_n$.

During the reaction, the product precipitated to give only oligomeric products. From elemental sulfur analysis and NMR, we deduce that for the repeating unit, $n = 4$ or 5, on the average, for two different runs. The oligomers were only sparingly soluble in ethanol or DMF, but did dissolve in *m*-cresol. They were recrystallized from large volumes of ethanol. The insolubility of these products and the unbalanced stoichiometry due to the volatility of the hydrogen sulfide probably led to the formation of low molecular weight products.

Ethyl mercaptan readily added to both *N,N'*-methylenebisacrylamide and *N,N'*-isopropylidenebisacrylamide in DMF with potassium-*tert*-butoxide as the catalyst. Quantitative yields were obtained in both cases.



$$CH_2{=}CH\overset{O}{\overset{\|}{C}}NHCR_2NH\overset{O}{\overset{\|}{C}}CH{=}CH_2 + 2CH_3CH_2SH \rightarrow (CH_3CH_2SCH_2CH_2\overset{O}{\overset{\|}{C}}NH)_2CR_2 \qquad R{=}H,CH_3 \tag{12}$$

There is a major difference between the two adducts. The adduct from *N,N'*-methylenebisacrylamide is soluble only in hot ethanol, DMF, and dimethyl sulfoxide (DMSO). The adduct from *N,N'*-isopropylidenebisacrylamide is soluble at room temperature in alcohols, chloroform, benzene, DMF, and DMSO.

The addition of the alkanedithiols to the bisacrylamides was next investigated. The additions were catalyzed by potassium *tert*-butoxide in DMF or DMSO. The results are summarized in Table VII.

The polymers were insoluble in most solvents but were soluble in *m*-cresol. Tough, flexible films could be cast from solutions of the polymers in which the bisamide contained two methyl groups on the central carbon. This is the first example of a high molecular weight polymer by the addition of a dithiol to a bisacrylamide. Due to the greater insolubility of the *N,N'*-methylenebisacrylamide adducts, they precipitated at an earlier stage and hence were of lower molecular weight. The polymers (as dry powders) were crystalline by x-ray diffraction. A loss of crystallinity occurred in the films possibly due to retained solvent.

The polyaddition reaction of *N,N'*-methylenebisacrylamide and piperazine gives a high molecular weight polymer.[19] We repeated this reaction and obtained a polymer which had a higher reduced viscosity ($\eta_{sp}/c = 8.81$ at a concentration of 1 g/100 ml in 2% acetic acid at 30°C.) than the value reported (3.81). This polymer is water-soluble and forms a tough film when cast from solution. It behaves as a typical polyelectrolyte in aqueous acetic acid. *N,N'*-Isopropylidenebisacrylamide formed a similar polymer with piperazine but of lower molecular weight and decreased solubility. All of these amide-amine polymers are noncrystalline by x-ray diffraction.

EXPERIMENTAL

Monomers

N,N′-Isopropylidenebisacrylamide from 2,2-Dimethoxypropane. To a solution of 50 ml of methanol in 2000 ml of *n*-hexane were added 213 g (3.0 mole) of acrylamide, 312 g (3.0 mole) of 2,2-dimethoxypropane and a solution of 24 g (0.14 mole) of anhydrous *p*-toluenesulfonic acid in 140 ml of benzene. Upon heating the mixture, the *n*-hexane–methanol azeotrope distilled at 54°C. When the distillation temperature reached 57°C, the mixture was cooled to room temperature. The solids were collected on a suction filter and washed with dilute aqueous ammonia. The filter cake was recrystallized from isopropyl alcohol to give 191.1 g (70% based upon acrylamide charged) of colorless product, mp 210–212°C. The other *N,N′*-disubstitutedmethylenebisacrylamides were prepared in a similar manner. The yields, melting points, and elementary analyses of these products are given in Table I.

N,N′-Isopropylidenebisacrylamide from Isopropenyl Acetate. To a solution of 142 g (2.0 moles) of acrylamide and 100 g (1.0 mole) of isopropenyl acetate in 800 ml of isopropyl alcohol were added 5 g of mercuric acetate and 10 g of concentrated sulfuric acid. The mixture was stirred at room temperature for 18 hr. The white, crystalline precipitate was collected on a suction filter and washed with isopropyl alcohol. The filter cake was recrystallized from isopropyl alcohol to give 29.8 g (16.3%) of product which was identical to the product obtained from 2,2-dimethoxypropane.

N,N′-Isopropylidenebisacrylamide from Isopropenyl Ethyl Sulfide.[12] To a solution of 14.2 g (0.2 mole) of acrylamide and 20.4 g (0.2 mole) of isopropenyl ethyl sulfide in 50 ml of acetone was added 0.5 ml of boron trifluoride etherate. The mixture was stirred at room temperature for 24 hr. The white, crystalline precipitate was collected on a suction filter, washed with acetone and recrystallized from isopropyl alcohol to give 16.3 g (89.5% based upon acrylamide charged) of product which was identical to the product obtained from 2,2-dimethoxypropane.

1-Acrylamido-1-phenylpropene. A solution of 106.5 g (1.5 mole) of acrylamide, 105 g (0.5 mole) of propiophenone di-*n*-propyl acetal,[5] and 1 g of anhydrous *p*-toluenesulfonic acid in 1200 ml of benzene was heated until the propyl alcohol–benzene distilled slowly at 78–79°C. After 36 hr of slow distillation, the solution was cooled to room temperature and washed with dilute aqueous ammonia. The benzene was removed by distillation under reduced pressure on a rotary evaporator. The residual solid was recrystallized from cyclohexane to give 41.7 g (77% based upon acetal charged) of colorless product, mp 128–130°C.

ANAL. Calcd for $C_{12}H_{13}NO$: C, 76.97%; H, 7.00%; N, 7.48%. Found: C, 77.05%; H, 7.06%; N, 7.47%.

Model Compound

In preparation of *N*,*N*′-Isopropylidenebis(2-ethylthiopropionamide), approximately 50 mg of potassium *tert*-butoxide was added to a solution of 9.1 g (0.05 mole) of *N*,*N*′-isopropylidenebisacrylamide and 6.2 g (0.10 mole) of ethanethiol in 100 ml of dry dimethylformamide. There was a moderate exotherm. After standing at room temperature overnight, the reaction mixture was concentrated under reduced pressure. The residual oil solidified upon cooling. It was recrystallized from 300 ml of cyclohexane to give 11.2 g (73.4%) of colorless needles; mp 115.5–116.5°C.

ANAL. Calcd for $C_{13}H_{26}N_2O_2S_2$: C, 50.94%; H, 8.55%; N, 9.14%; S, 20.92%. Found: C, 51.1%; H, 8.67%; N, 9.1%; S, 21.03%.

Polymers

Reactivity Ratios of *N*,*N*′-Isopropylidenebisacrylamide with Styrene and with Acrylonitrile. Mixtures of monomers as shown in Tables V and VI were placed in 100-ml Pyrex ampoules. To these mixtures, methanol and approximately 50 mg of 2,2′-azobis(2-methylpropionitrile) were added. The ampoules were cooled to Dry Ice–acetone bath temperature under nitrogen and sealed. They were then placed in a bath maintained at 60 ± 0.1°C. Rapid copolymer formation occurred after an induction period of 5 to 40 min. The reactions were stopped at about 10% conversion. The copolymers were washed repeatedly with large volumes of methanol and dried. All of the copolymers thus obtained were colorless, insoluble materials. Data necessary for calculating the copolymerization ratios are given in Tables V and VI.

_N_,_N_′-Isopropylidenebisacrylamide with Hydrogen Sulfide. To a solution of 1.88 g (0.0553 mole) of hydrogen sulfide and 10.07 g (0.0533 mole) of *N*,*N*′-isopropylidenebisacrylamide in 35 ml of dry dimethyl sulfoxide, was added approximately 50 mg of potassium *tert*-butoxide. The mixture was stirred at 60°C for 20 hr under a positive pressure of nitrogen. Upon cooling the entire mixture solidified. It was poured into water, separated on a suction filter and the product filter cake was washed with water and methanol. The product was a pale yellow powder which weighed 5.9 g (49.3%). Upon recrystallization from 800 ml of ethanol the product was colorless. The elemental sulfur analysis was 12.40% which corresponds to $n = 4.5$ the product of eq. (11). The ratio of olefinic protons to the *gem*-dimethyl protons was 1:5 in the NMR spectrum determined in $DCCl_3$ solution. This ratio corresponds to $n = 4$.

_N_,_N_′-Isopropylidenebisacrylamide with Dithiols. All of these polyaddition reactions followed essentially the same procedure. Table VII summarizes the results. A typical procedure is given for the reaction with 1,6-hexanedithiol. To a stirred solution of 4.402 g (0.0293 mole) of 1,6-hexanedithiol and 5.334 g (0.0293 mole) of *N*,*N*′-isopropylidenebisacrylamide in 50 ml of anhydrous dimethylformamide under a nitrogen atmosphere, was added 50 mg of potassium *tert*-butoxide. A moderate exotherm occurred. The viscosity of the solution increased. After 1$^1/_2$ hr the mixture was a jellylike mass. It was transferred to a large volume of acetone to precipitate a solid which was separated on a filter, washed repeatedly with acetone and dried. The polymer was a colorless powder, 8.7 g (89%); PMT, 150–153°C. The reduced viscosity (η_{sp}/c) was 1.05 dl/g, calculated from the viscosity of a solution of 0.500 g/100 ml of *m*-cresol at 30°C. A tough film was cast from a *m*-cresol solution.

***N,N'*-Methylenebisacrylamide with Piperazine.** A mixture of 4.76 g (0.0553 mole) of piperazine, 8.53 g (0.0553 mole) of *N,N'*-methylenebisacrylamide and 28.0 ml of water was stirred under nitrogen at room temperature. As reaction occurred, the exotherm elevated the temperature of the mixture to 50°C. The viscosity increased rapidly and the solution climbed the stirrer shaft. Stirring was continued overnight and then the mixture was transferred to a large volume of acetone. The precipitate which formed was washed with acetone in a Waring Blendor. The polymer was a colorless, fibrous material which weighed 13.6 g (100%). Reduced viscosities (η_{sp}/c) were measured at 30°C in 2% aqueous acetic acid. The concentrations (g/100 ml solvent) and the corresponding η_{sp}/c are: 1.00, 8.81; 0.504, 11.6; 0.223, 17.0; 0.115, 22.4, 0.074, 27.4; and 0.056, 28.9 dl/g.

***N,N'*-Isopropylidenebisacrylamide with Piperazine.** A stirred mixture of 2.51 g (0.0292 mole) of piperazine and 5.33 g (0.0292 mole) of *N,N'*-isopropylidenebisacrylamide in 25 ml of water was heated under nitrogen to 40°C. The starting bisamide, which was initially insoluble, dissolved gradually to give a homogeneous solution. Stirring was continued at 40°C for a total of 24 hr. The resultant solid mass was transferred to a large volume of acetone. The solid precipitate was separated on a filter, washed with acetone and dried. The product was a colorless powder, 5.0 g (64%).

ANAL. Calcd for ($C_{13}H_{24}O_2N_4$): C, 58.18%; H, 9.02%; N, 20.88%. Found: C, 58.76%; H, 8.92%; N, 21.08%.

Viscosities of solutions in 2% acetic acid were measured at 30°C. The concentrations (g/100 ml solvent) and the η_{sp}/c dl/g. are: 0.500, 0.99; 0.333, 1.12; 0.250, 1.22; and 0.167, 1.32.

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Polymerization of Acrylonitrile Catalyzed by Methoxo-β-diketone Nickel Chelates*

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Synopsis

The polymerization of acrylonitrile initiated by methoxo-β-diketone nickel chelates of the $[Ni(L)(CH_3O)(CH_3OH)]_n$ type and pyridine was studied. Chelating agents L employed included acetylacetone, ethylacetoacetate, and salicylaldehyde. These systems could initiate the polymerization of acrylonitrile at -40°C. The polymerization is thought to occur by an anionic coordination mechanism.

INTRODUCTION

The initiation of radical polymerization of vinyl monomers with metal acetylacetonates has been investigated by many authors.[1-4]

Recently Kennedy[5] and Otsu[6] found that $MoO_2(acac)_2$ could initiate the polymerization of some vinyl monomers and some cyclic ethers by a cationic mechanism and Otsu[7] found that Mn(II) and Co(II) acetylacetonate could induce the polymerization of chloral by an anionic coordination mechanism.

In the course of studies on the oxidative coupling polymerization of 2,6-xylenol with methoxo-β-diketone copper chelates,[8] we have found that methoxo nickel chelates of the $[Ni(L)(CH_3O)(CH_3OH)]_n$ type and pyridine could initiate the polymerization of acrylonitrile at -40°C. This polymerization is thought to occur by an anionic coordination mechanism.

EXPERIMENTAL

Reagents

Methoxo nickel chelates were synthesized by the method of Bertrand,[9] that is, the nickel chelate NiL_2 was allowed to react with potassium hydroxide in methanol to produce the methoxo complexes $[Ni(L)(CH_3O)(CH_3OH)]_n$. Chelating agents L employed included acetylacetone (acac), ethylacetoacetate (EAA) and salicylaldehyde (SA).

Acrylonitrile and solvents used were purified by usual methods.

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

Polymerization Conditions

The polymerization of acrylonitrile with $[Ni(L)(CH_3O)(CH_3OH)]_n$ was carried out in a three-necked flask equipped with thermometer, nitrogen-inlet tube, and condenser. Nickel chelates were dissolved in pyridine–DMF mixed solvent. An acrylonitrile monomer was added to the catalyst solution under a nitrogen atmosphere at the prescribed temperature. After a given time, the reaction mixture was poured into a large excess of methanol containing 10% hydrogen chloride. The precipitated polyacrylonitrile was reprecipitated by a DMF–CH_3OH system and dried under vacuum.

Intrinsic Viscosity

The intrinsic viscosity, $[\eta]$ of the polymer was measured viscometrically in DMF at 25°C.

RESULTS AND DISCUSSION

Temperature Dependence of the Conversion

The nickel chelate (0.002 mole) was dissolved in 40 ml of pyridine–dimethylformamide (3:1) mixed solvent. Acrylonitrile was added to this solution and kept at prescribed temperature for 10 hr in the case of Ni(acac)OCH_3 or 5 hr in the case of Ni(SA)OCH_3. Conversion and intrinsic viscosity are shown in Figure 1.

Maximum conversion was obtained below 0°C. For a fixed reaction time at 10 hr at 0°C, acetylacetone was the most active ligand. The order of conversion was the following: Ni(acac)OCH_3, 58.9%; Ni(SA)OCH_3,

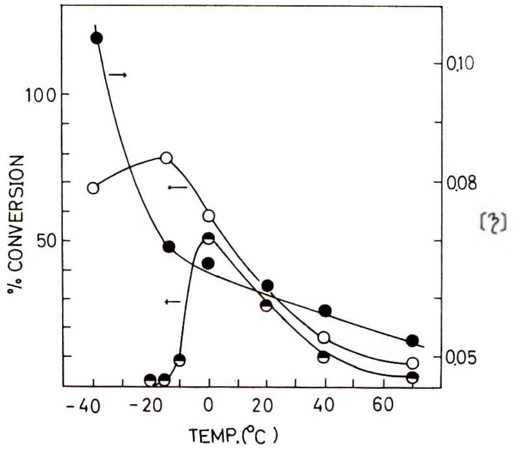

Fig. 1. Temperature dependence of the conversion: (○) [Ni(acac)(OCH_3)(CH_3OH)] catalyst, 10 hr; (◓) [Ni(SA)(OCH_3)(CH_3OH)] catalyst, 5 hr; (●) $[\eta]$ of the polyacrylonitrile prepared with [Ni(acac)(OCH_3)(CH_3OH)] at Ni complex/AN ratio of 0.002/0.1, in pyridine–DMF (30:10).

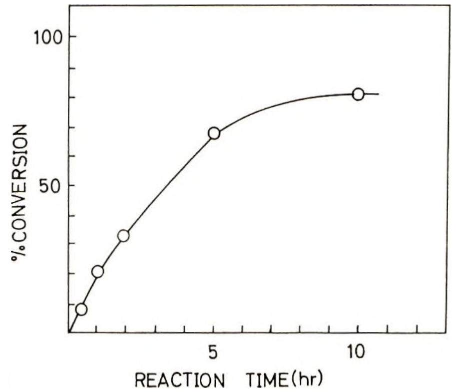

Fig. 2. Relationship between conversion and reaction time; [Ni(acac)(OCH_3)(CH_3OH)] catalyst, −15°C, pyridine-DMF (30:10), 1 hr.

48.0%; Ni(EAA)OCH_3, 45.2%. For a reaction temperature of −15°C, the relationship between conversion and reaction time is shown as Figure 2. If the reaction temperature was higher than 0°C, the yielded polymer was yellow-brown. The coloration should be due to the cyclic structures, as shown in radical oligomerization of acrylonitrile in amine.[10]

Dependence of the Conversion on Catalyst Concentration

For a reaction temperature at −15°C and different Ni(acac)OCH_3 concentrations and a constant acrylonitrile concentration of 0.1 mole, the conversion in 1 hr is shown in Figure 3. In this reaction, a mixed solvent of pyridine (30 ml) and DMF (10 ml) was used.

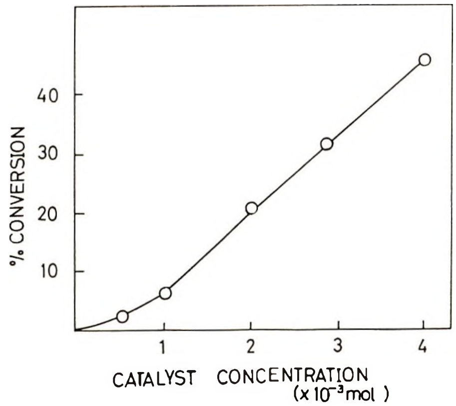

Fig. 3. Catalyst concentration dependence of the conversion; [Ni(acac)(OCH_3)(CH_3OH)] catalyst, 0°C, Ni complex/AN ratio = 0.002/0.1, 3 hr.

Dependence of the Conversion on Solvent Composition

Ni(SA)OCH_3 (0.002 mole) was dissolved in 40 ml of the mixed solvent described above. The conversion at 0°C is shown in Figure 4. (reaction

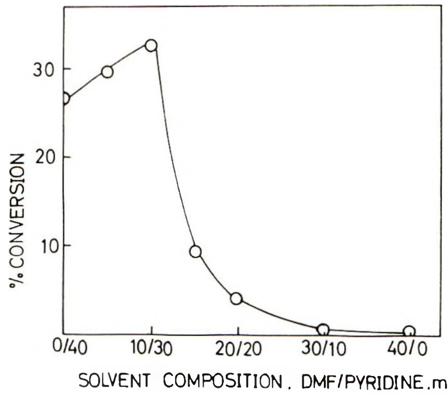

Fig. 4. Solvent composition dependence of the conversion; $[Ni(SA)(OCH_3)(CH_3OH)]$ catalyst, 0°C, Ni complex/AN ratio = 0.002/0.1, 3 hr.

time 3 hr) The solvent composition is shown on the abscissa. The maximum conversion was obtained at DMF/pyridine = 1:3, and the polymer yield decreased with an increase of the DMF concentration. This fact shows that the DMF concentration may contribute to the weakening of the coordinating ability of acrylonitrile on the catalyst.

Reaction Mechanism

In the course of the study described above, we noticed that both pyridine and methoxo nickel chelates are essential for the polymerization of acrylonitrile. Normal nickel acetylacetonate having no methoxo-bridge was inactive even in the presence of pyridine.

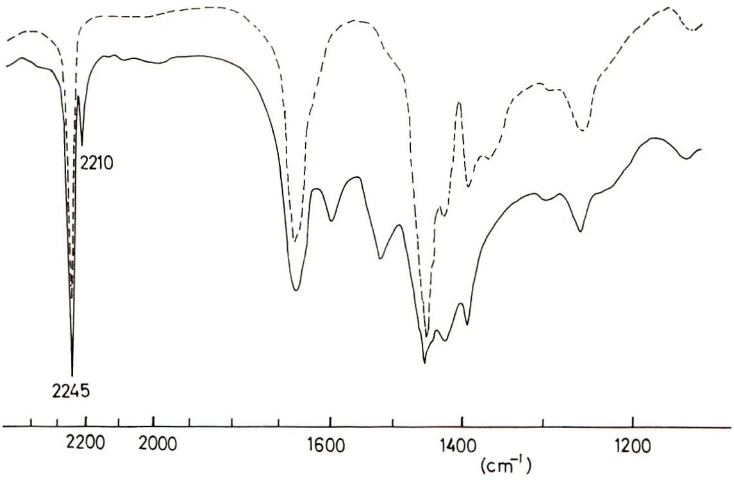

Fig. 5. Infrared spectrum of polyacrylonitrile prepared with the use of $[Ni(acac)(OCH_3)(CH_3OH)]$ catalyst: (——) polymer precipitated by pouring the reaction mixture into CH_3OH; (– –) after washing with $CH_3OH \cdot HCl$.

The infrared spectrum of the polymer precipitated by pouring the reaction mixture into methanol is shown in Figure 5 (solid line). The dashed line shows the polymer after washing with hydrochloric methanol. The solid line spectrum shows two $\nu_{C\equiv N}$ absorption bands at 2245 and 2210 cm^{-1}, and a remaining characteristic band of the chelate in the 1500–1600 cm^{-1} region. The splitting of the $\nu_{C\equiv N}$ band seems to be due to the coordination of acrylonitrile to the nickel atom of the growing polymer chain end. Shimomura[10] found that acrylonitrile polymerized by a radical mechanism in amine solution has two absorption bands at 2240 and 2180 cm^{-1}.

The 2180 cm^{-1} band was assigned to the cumulative double bonds of the imino group which is located at the β carbon atom of the nitrile group in cyclic structures. As for the 2000 cm^{-1} region, the absorption band at 2210 cm^{-1} of the polyacrylonitrile obtained at −40°C seems to be due to the nitrile group coordinated to the nickel atom.

TABLE I
Absorption Maxima in the Electronic Spectra of Ni(SA)OCH$_3$

Solvent	Absorption maximum, mμ
Pyridine	402
Pyridine–chloroform (2:8)	395
Pyridine–chloroform (1:9)	391
Chloroform	385
Dimethylformamide	392

Table I shows the pyridine coordinated species. When the polymerization was carried out in air the same results as under nitrogen were obtained.

Methyl vinyl ketone showed low polymerizability with this catalyst system and methyl methacrylate did not polymerize. From the above facts, polymerizations of acrylonitrile are thought to occur by an anionic coordination mechanism.

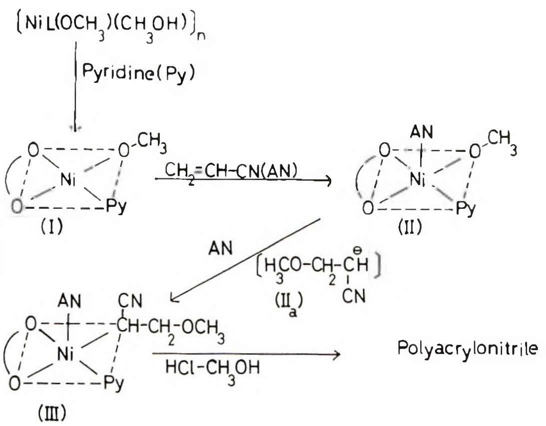

Fig. 6. Reaction mechanism: L = acetylacetone, ethylacetoacetate, and salicylaldehyde.

The polymer endgroup may be methoxyl, but this was not confirmed. The number n of the $[Ni(L)(OCH_3)(CH_3OH)]_n$ was close to 2 in chloroform solution as found (L = acac) by molecular weight determination with vapor-pressure osmometry. In pyridine, the molecular weight was in good agreement with the pyridine coordinated chelate(I).

Acrylonitrile is believed to coordinate to the nickel atom (as shown in Fig. 6) on the basis of the facts that (1) the oxidation number of the nickel atom was +2 during the reaction; (2) splitting of the $\nu_{C\equiv N}$ band at 2245 and 2210 cm^{-1} occurred; (3) the washed polymer was free from nickel metal and showed a single $\nu_{C\equiv N}$ band at 2245 cm^{-1}. The Ni–acrylonitrile coordination weakens the methoxy-nickel bond which may lead to its fission. The methoxy anion thus initiates the polymerization to form the anion IIa which recoordinates and propagates the reaction.

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Polybenzopinacols. I. Photolytic Coupling of Aromatic Diketones*

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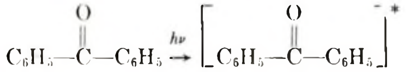
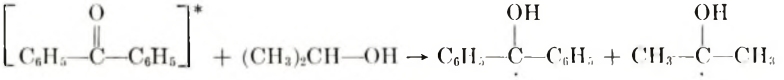
Synopsis

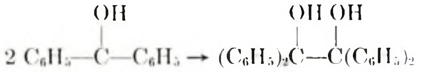
Low molecular weight polybenzopinacols were obtained by the photolytic coupling of *m*- and *p*-dibenzoylbenzene and 4,4′-dibenzoyldiphenyl ether in isopropanol, tetrahydrofuran–isopropanol, benzene–isopropanol, and benzene–ethanol solutions. The polypinacols were soluble in common organic solvents such as tetrahydrofuran, ether, and benzene. The inherent viscosities ranged from 0.06 to 0.14. Average molecular weight ($\bar{M}_n$) data indicated that the polymers were mostly dimers and trimers.

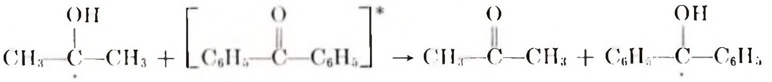
INTRODUCTION

The photochemical reduction and subsequent coupling of ketones to form pinacols has been known for some time.[1] The suggested mechanism involves a $n \rightarrow \pi^*$ excitation process in which one of the unshared electrons on a carbonyl oxygen is promoted to a π antibonding orbital followed by reduction and coupling.[2] In the case of benzophenone–isopropanol, the mechanism can be represented schematically by eqs. (1)–(4).


$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \xrightarrow{h\nu} \left[C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5\right]^* \quad (1)$$


$$\left[C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5\right]^* + (CH_3)_2CH-OH \rightarrow C_6H_5-\underset{\cdot}{\overset{\overset{\displaystyle OH}{|}}{C}}-C_6H_5 + CH_3-\underset{\cdot}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 \quad (2)$$


$$2\ C_6H_5-\underset{\cdot}{\overset{\overset{\displaystyle OH}{|}}{C}}-C_6H_5 \rightarrow (C_6H_5)_2\overset{\overset{\displaystyle OH}{|}}{C}-\overset{\overset{\displaystyle OH}{|}}{C}(C_6H_5)_2 \quad (3)$$


$$CH_3-\underset{\cdot}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 + \left[C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5\right]^* \rightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + C_6H_5-\underset{\cdot}{\overset{\overset{\displaystyle OH}{|}}{C}}-C_6H_5 \quad (4)$$

Thus the overall reaction results in the bimolecular reduction-coupling of the ketone and oxidation of isopropanol to acetone. The yield of benzopinacol in this reaction is essentially quantitative.[3]

Since this reaction seems to have great potential importance as a polymer-forming reaction, the present study deals with the application of this

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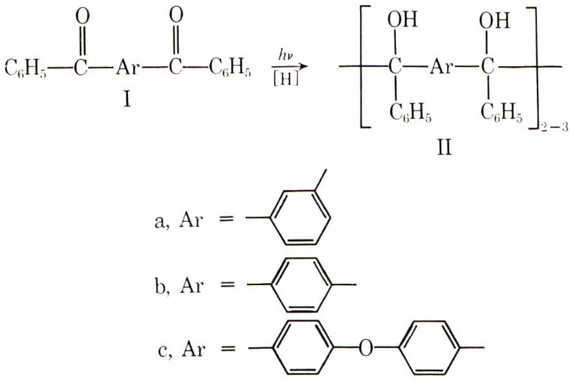
* In honor of C. S. Marvel on the occasion of his 75th birthday.

reaction as a possible synthetic route for the preparation of polypinacols from *m*-dibenzoylbenzene (Ia), *p*-dibenzoylbenzene (Ib), and 4,4′-dibenzoyldiphenyl ether (Ic).

Structures of the low molecular weight polymers were determined by comparison of NMR and infrared data with those of benzopinacol. Average molecular weights ($\bar{M}_n$) were obtained by vapor pressure osmometry and the average degrees of polymerization were calculated to be 2–3 in the solvents used for this study.

RESULTS AND DISCUSSION

Monomers Ia, Ib, and Ic were photolyzed in oxygen-free isopropanol, tetrahydrofuran–isopropanol, benzene–isopropanol, and benzene–ethanol solutions for periods of 5–7 days [eq. (5)]. In each case the products isolated consisted of dimers and trimers with inherent viscosities ranging from 0.06 to 0.14 (benzene). The low molecular weights of polymers IIa, IIb, and IIc (Table I) have been attributed to the complete reduction of some of the ketone groups by the alcohol solvents. The NMR spectra of the polymers showed a small peak at 5.3 δ which corresponds to benzhydryl protons. The infrared spectra of the polymers showed a small peak remaining at 1650 cm^{-1} (C=O) indicating that some unreacted ketone groups were present (Fig. 1). The small amount of unreacted ketone may be due to structures such as III and/or unreacted monomer in the mixtures.



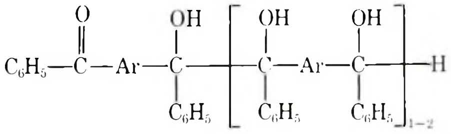
$$C_6H_5-\overset{\overset{O}{\|}}{C}-Ar-\overset{\overset{O}{\|}}{C}-C_6H_5 \xrightarrow[\text{[H]}]{h\nu} \left[\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{C}}-Ar-\underset{\underset{C_6H_5}{|}}{\overset{\overset{OH}{|}}{C}} \right]_{2-3} \quad (5)$$

TABLE I
Polymer Properties

Polymer	Viscosity (η_{inh})[a]	Melting point, °C	$\bar{M}_n$[b]	$\overline{DP}$
IIa	0.12	140	825	2.91
IIb	0.06	135	435	1.89
IIc	0.14	160	805	2.80

[a] 0.25 g/100 ml benzene solvent.

[b] Benzene solvent.



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-Ar-\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-\left[\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-Ar-\underset{\underset{\displaystyle C_6H_5}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}\right]_{1-2}-H$$

III

Benzophenone gives a quantitative yield of benzopinacol while some reduction occurs with monomers Ia, Ib, and Ic under the same reaction conditions. This suggests that the reactivities of the radical intermediates of the monomers are different from that of benzophenone. Thus, the solvents used in this study may be too strongly reducing to form higher

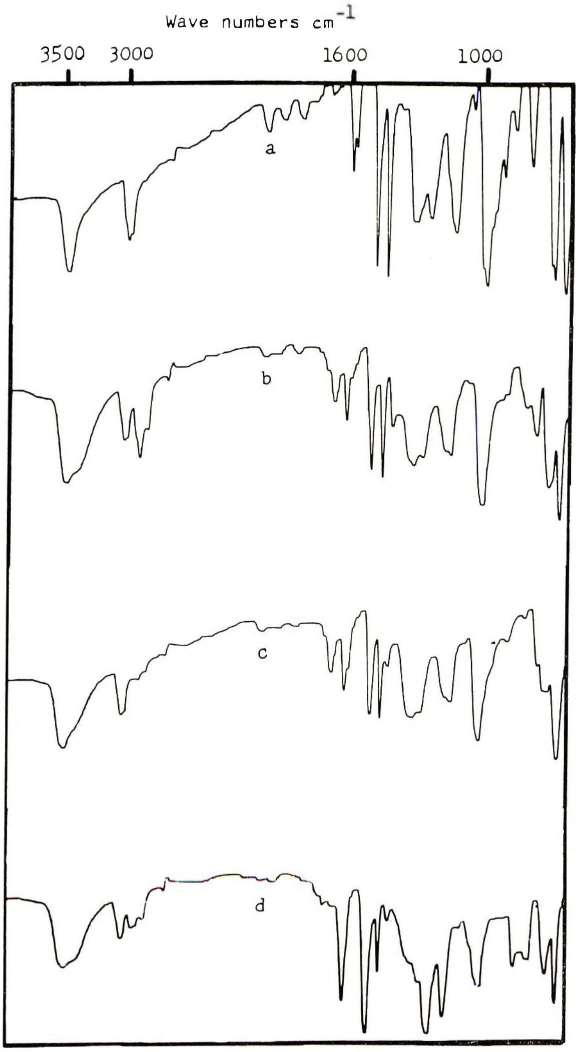


Fig. 1. Infrared spectra (KBr): (*a*) benzopinacol; (*b*) polymer IIa; (*c*) polymer IIb; (*d*) polymer IIc.

molecular weight polymers. Perhaps weaker reducing solvents, as well as other diketone monomers, would effect a corresponding increase in molecular weights. With this in mind we are presently expanding our investigations to include other monomers and a variety of reducing solvents.

EXPERIMENTAL

Instruments

Polymerizations were performed by use of a Fisher Blak-Ray long-wavelength ultraviolet lamp. Vapor-pressure measurements were taken on a Hewlett-Packard Model 302 Vapor Pressure Osmometer. Infrared spectra were taken on Beckman IR-8 and Perkin-Elmer Model 700 instruments. Nuclear magnetic resonance spectra were obtained with a Hitachi Perkin-Elmer R-20 instrument.

Preparation of Monomers

Preparation of 4,4′-Dibenzoyldiphenyl Ether from Diphenyl Ether and Benzoyl Chloride. A 30-g portion (0.176 mole) of diphenyl ether and 66.5 g (0.5 mole) of anhydrous aluminum chloride were dissolved in 300 ml of carbon disulfide and then 59 g (0.42 mole) of benzoyl chloride was added dropwise to the solution. After spontaneous refluxing stopped, the solution was refluxed for an additional 2 hr and cooled. The reaction mixture was digested for 1 hr in a 10% ice water–HCl solution. The crude product was washed thoroughly with a 5% aqueous solution of sodium carbonate, a 5% aqueous solution of HCl, and finally with water. The yield was 66 g (99.5%) of crude product. The crude product was recrystallized from carbon tetrachloride to a constant melting point of 163–164°C (lit.[4] mp, 163–164°C). Approximately 30 g (50%) of pure product was obtained.

Preparation of *m*-Dibenzoylbenzene from Isophthaloyl Dichloride and Benzene. A 50-g portion (0.197 mole) of isophthaloyl dichloride was dissolved in 400 ml of benzene and to this solution was added 80 g (0.70 mole) of anhydrous aluminum chloride in small portions. After spontaneous refluxing was complete, the solution was refluxed for an additional 2 hr. After cooling, the solution was hydrolyzed in a 10% ice water–HCl solution. The benzene was allowed to evaporate overnight and the crude product was filtered. The yield of crude product was 58.3 g (99.5%). The crude product was washed thoroughly with a 5% aqueous solution of sodium carbonate, a 5% solution of HCl, and finally with water. The crude product was recrystallized from cyclohexane to a constant melting point of 109–110°C (lit.[5,6] mp, 99.5–100°C) and dried in a vacuum desiccator overnight. The yield of purified product was 25 g (45%).

Preparation of *p*-Dibenzoylbenzene from Terephthaloyl Dichloride and Benzene. Terephthaloyl dichloride (50 g, 0.197 mole) was dissolved in 400 ml of benzene and to this solution was added 80 g (0.70 mole) of anhydrous aluminum chloride in small portions. After spontaneous refluxing was complete, the reaction mixture was refluxed for an additional 2 hr. The solution was allowed to cool and then hydrolyzed in a 10% ice water–HCl solution. The excess benzene was allowed to evaporate overnight and the crude product was filtered. The yield of crude product was 57 g (99%). The crude product was washed thoroughly with a 5% aqueous solution of sodium carbonate, a 5% aqueous solution of HCl, and finally with water. The crude product was recrystallized from carbon tetrachloride to a constant melting point of 161–162°C (lit.[7] mp, 160–161°C). The yield of purified product was approximately 15 g (25%).

Preparation of Benzopinacol

Benzophenone (20 g, 0.11 mole) was dissolved in 250 ml of hot isopropanol and to this solution was added one drop of glacial acetic acid. The reaction solution was placed in a 250 ml round-bottomed flask and purged with nitrogen at reflux for 5 min, tightly stoppered, and irradiated with ultraviolet light. After 24 hr the solution was chilled and the crystals were filtered, yielding 17.8 of benzopinacol. The filtrate was then irradiated 48 yield hr longer and again filtered to yield an additional 1.8 g of product. The total yield after 4 days was quantitative (0.055 mole), mp, 189–190°C (lit.[1] mp, 188–189°C).

Preparation of Polymers

Preparation of Polymer IIa from *m*-Dibenzoylbenzene. A 5-g portion (0.017 mole) of *m*-dibenzoylbenzene was dissolved in 125 ml of benzene, and to this solution was added 125 ml of isopropanol and one drop of acetic acid. The reaction solution was placed in a 250 ml round-bottomed flask, deoxygenated with nitrogen at reflux, tightly stoppered, and irradiated with ultraviolet light for one week. Removal of the solvent under vacuum yielded a light yellow solid. The solid was washed with hot isopropanol and dried at 62°C for 24 hr under vacuum yielding 4.6 g of polymer (94%). The inherent viscosity in benzene was 0.12. The polymerization was also carried out in isopropanol, a 50–50 solution of THF–isopropanol, and in a 50–50 solution of benzene–ethanol. In all cases the results were similar to those obtained in isopropanol.

ANAL. Calcd for $C_{20}H_{16}O_2$: C, 83.33%; H, 5.56%. Found: C, 83.13%; H, 5.38%.

Preparation of Polymer IIb from *p*-Dibenzoylbenzene. A 5-g portion (0.017 mole) of *p*-dibenzoylbenzene was dissolved in 125 ml of benzene, and to this solution was added 125 ml. of isopropanol and one drop of acetic acid. The reaction mixture was placed in a 250-ml round-bottomed flask, deoxygenated with nitrogen at reflux, tightly stoppered, and irradiated with ultraviolet light for one week. Removal of the solvent under vacuum yielded a light yellow solid. The solid was washed with hot isopropanol and dried at 62°C for 24 hr under vacuum, yielding 4.6 g of polymer (94%). The inherent viscosity in benzene was 0.06. This polymerization was also carried out in isopropanol, a 50–50 THF–isopropanol solution, and in a 50–50 benzene–ethanol solution.

ANAL. Calcd for $C_{20}H_{16}O_2$: C, 83.33%; H, 5.56%. Found: C, 82.02%; H, 6.49%.

Preparation of Polymer IIc from 4,4′-Dibenzoyldiphenyl Ether. 4,4′-Dibenzoyldiphenyl ether (5 g, 0.013 mole) was dissolved in 125 ml of benzene, and to this solution was added 125 ml of isopropanol and one drop of acetic acid. The reaction mixture was placed in a 250-ml round-bottomed flask, deoxygenated with nitrogen at reflux, tightly stoppered, and irradiated with ultraviolet light for one week. Removal of the solvent under vacuum yielded a light yellow solid. The polymer was washed with hot isopropanol and dried at 62°C for 24 hr under vacuum, yielding 4.5 g of polymer (92%). The inherent viscosity in benzene was 0.14. This polymerization was also carried out in isopropanol, a 50–50 THF–isopropanol solution, and in a 50–50 solution of benzene–ethanol.

ANAL. Calcd for $C_{26}H_{20}O_3$: C, 82.11%; H, 5.26%. Found: C, 82.10%; H, 5.36%.

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Equimolecular Binary Polydienes. V. Equibinary Poly(*cis*-1,4–trans-1,4)butadiene from Bis(π-allyl Nickel Trifluoroacetate)*

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Synopsis

The preparation of equibinary poly(*cis*-1,4–trans-1,4)butadiene was investigated in the presence of bis(π-allyl nickel trifluoroacetate) modified with suitable additional ligands. The behavior of the catalytic species in the polymerization reaction as well as the specific basic properties of the equibinary polybutadiene produced support obviously a regular distribution of the *cis* and *trans* isomers in the polymer chains.

INTRODUCTION

In order to improve our knowledge of the stereospecific polymerization of conjugated diolefins, particular attention was given to the study of the nature of the catalytic active centers and of the origin of their stereospecific behavior. The correlations gathered in the course of these investigations now become more and more significant, owing to the ability of inducing a highly stereospecific polymerization of 1,3-butadiene by means of well characterized and relatively stable monometallic catalysts.

Systematic structural modifications of the transition metal complexes change their catalytic behavior drastically: in this way, it becomes possible to control very closely their activity for both the structural and the geometrical isomerism of the polymers formed.

Moreover, use of specific additional ligands led to a new type of stereoregular polymers, named "equibinary" polydienes,[1] which contain two of the possible isomers in equimolecular amounts.

This new type of controlled propagation mechanism appeared to be rather general, since several equibinary polydienes were synthesized by modifying different catalysts in a similar way.[2] For example, the preparation of equibinary poly(*cis*-1,4–3,4) or (1,2–3,4) isoprenes was carried out by means of cobalt catalysts and alcohols[1,3] and equibinary poly(*cis* 1,4–

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

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trans-1,4)butadiene was prepared in the presence of a catalytic system obtained from 2,6,10-dodecatriene-1,12-diyl nickel and trifluoroacetic acid.[4]

Furthermore, an interesting peculiarity recently reported[5] of the nickel catalyst promoting the formation of equibinary polybutadiene is the reversibility of the modification of the catalytic species; the binary selectivity appears to enjoy some of the versatility observed with the monoisomeric stereospecificity. In fact, the addition of an electron donor such as triphenyl phosphite to the catalyst recipe yielding the equibinary poly-(*cis*-1,4–*trans*-1,4)-butadiene oriented the reaction towards the formation of crystalline *trans*-1,4-polybutadiene, while the addition of a strong electron acceptor, such as chloranil, promotes the formation of high-*cis*-1,4 polymer (96%).

The present paper is devoted to the preparation of equibinary poly-(*cis*-1,4–*trans*-1,4)butadiene, with a new catalyst obtained by modifying, with suitable ligands, bis(π-allyl nickel trifluoroacetate) which otherwise yields pure *cis*-1,4-polybutadiene.[6,7]

Besides the technical interest of the equibinary polybutadiene produced, the study of its formation mechanism in the presence of a modified π-allyl nickel trifluoroacetate seems interesting as the catalytic complex appears most suitable for a more detailed structural investigation by different physical methods.

EXPERIMENTAL

Materials

The reaction or polymerization solvents as well as the reagents were anhydrous purified products.

Gaseous butadiene was purified over potassium hydroxide pellets and dried successively on 4 Å molecular sieves and calcium hydride.

Bis(π-allyl nickel trifluoroacetate) was synthesized according to the procedure described elsewhere,[8] by reacting at room temperature a benzene solution of bis(1,5-cyclooctadiene) nickel (0) with a stoichiometric amount of the allylic ester of trifluoroacetic acid. The product was isolated as an orange powder by lyophilization of the reaction medium.

Cryoscopic determinations were performed, under argon atmosphere, on cyclohexane or benzene solutions of the complexes, by means of a thermometer graduated to 0.01°C. The addition of ligands to a suitable ligand/nickel ratio (α_L) was carried out by means of an hypodermic syringe through self-sealing caps.

NMR measurements were performed on benzene or chlorobenzene solutions with a A60 Varian apparatus.

Polymerization

The polymerization runs were performed under an argon atmosphere in sealed Pyrex tubes, according to a previously reported procedure.[5] The reagents were usually transferred in the following order: the catalytic solution, the additional ligand, the complementary amount of solvent to get the suitable nickel concentration, and then injection at low temperature of liquid-1,3-butadiene to reach the usual concentration of 3.2 mole/l.

Kinetic data on the polymerization reaction were obtained either by dilatometry on a 1*M* benzene solution, the volume contraction being graphically recorded by means of a level recorder, or by weighting the polymer produced at various reaction times.

Properties of the Polymers

The polybutadiene microstructure was determined by infrared spectrophotometry according to the method of Morero et al.[9] on a 1% CS_2 solution.

The number-average molecular weight, was determined on toluene solutions with a Mechrolab 502 membrane osmometer; relatively low molecular weights were obtained with Hewlett Packard VPO 502 Tonometer at 37°C on benzene solutions. The weight-average molecular weight was determined with a Sofica light-scattering photometer on cyclohexane solutions; the modifications of the Zimm plot as a function of the temperature were studied in a thermostatted bath regulated to ±0.05°C.

Differential thermal analyses were conducted on a CNRS model 2 microanalyzer with a 5 mg polymer sample rapidly cooled to −130°C under helium and then heated at a rate of about 2°C/min to room temperature.

The crystallinity of polymer samples stretched 400% was determined at −40°C under an anhydrous atmosphere by means of x-ray diffraction with a PW 1010 Philips apparatus. The percentage of crystallinity was evaluated as the ratio of the crystalline peak area to the amorphous area.

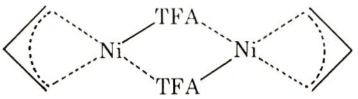
RESULTS AND DISCUSSION

The Catalyst and Its Behavior in the Polymerization Reaction

As previously reported,[6] both the NMR spectrum and the elemental analysis of the reaction product between biscyclooctadiene nickel (0) and allyl trifluoroacetate were found to be in good agreement with the expected π-allyl nickel trifluoroacetate complex.

ESR spectra of the solid complex showed a very broad signal (ΔH = 400 gauss) similar to that of nickel (II) derivatives; no signals were observed from a benzene solution of the compound, the complex being diamagnetic.

Cryoscopic measurements carried out on benzene or cyclohexane solution of the complex supported a binuclear association of π-allyl nickel trifluoroacetate,[8] as for many other π-allylic metal halides derivatives.



Bis(π-allyl nickel trifluoroacetate) induces the stereospecific polymerization of 1,3-butadiene in saturated hydrocarbons to yield polymers with *cis*-1,4 contents as high as 95% of the total unsaturation.[6,7] However, the addition of various ligands to the catalytic recipe was found to modify the microstructure of the polymer produced; in particular, equibinary poly(*cis*-1,4-*trans*-1,4)butadiene is obtained in the presence of benzene, nitrobenzene, or trifluoroacetic acid, while triphenyl phosphite or alcohols promote the formation of a pure *trans*-1,4 crystalline polymer.

In considering the influence of these additional ligands, it appeared of interest to investigate the corresponding transformations involved in the catalytic species.

Cryoscopic Determination of the Ligand–catalyst Association

Cryometry performed on catalyst solution in the presence of a ligand L, is used to determine the number of species in the solution, after the reaction of the ligand on the transition metal.

The basic relationship, according to Raoult's law, $\Delta T = k_s[\Sigma Ci]$ where Ci is the concentration of species i and k_s is the solvent constant, will become

$$\Delta T = k_s(C/2)$$

where C is the number of gram-atoms of metal per liter of solution for a solution of binuclear complex.

If a ligand L is added to the complex solution to reach a ligand/nickel molar ratio equal to α_L and if there is no interaction of the ligand with the binuclear complex, the cryoscopic relationship will be:

$$\Delta T = k_s[(C/2) + \alpha_L C]$$

Since the slope of the cryoscopic curves is defined by $P = \Delta T/C$, the measurements would be, in this case, characterized by $P/k_s = \alpha_L + {}^1/_2$.

Hypothesis (a). When the additional ligand is bonded to a nickel atom owing two unshared coordination positions without changing the binulcear association of the complex, the reaction scheme will be represented by the equilibria (1):

$$\begin{gathered} C_2 + L \overset{K_1}{\rightleftharpoons} C_2L \\ \underline{C_2L + L \overset{K_2}{\rightleftharpoons} C_2L_2} \\ C_2L_3 + L \overset{K_4}{\rightleftharpoons} C_2L_4 \end{gathered} \tag{1}$$

The study of this case implies very elaborate calculations.[10]

Hypothesis (b). However, if the bonding of the additional ligand results in a complete dissociation of the binuclear complex,

$$C_2 + 2\,L \overset{K}{\rightleftharpoons} 2\,CL$$

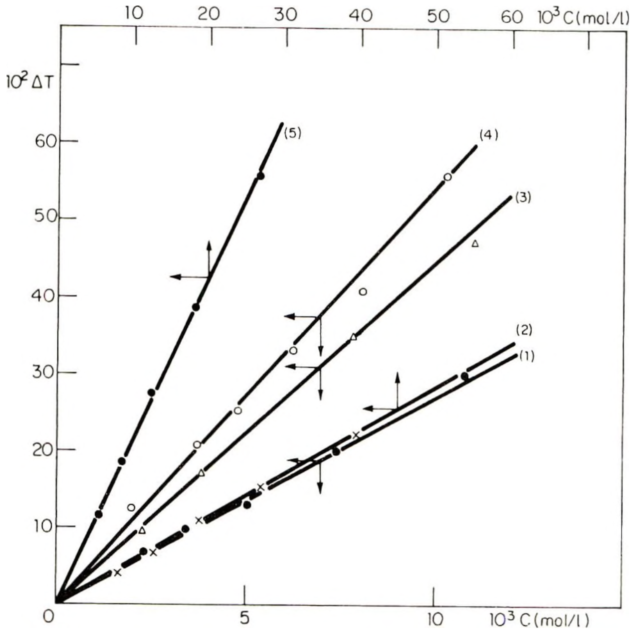


Fig. 1. Cryoscopic curves of bis(π-allyl nickel trifluoroacetate) in cyclohexane solutions in the presence of (*1*) nitrobenzene, (*3*) benzene, and (*4*) butadiene, and in benzene solutions in the presence of (*2*) triphenylphosphite and (*5*) butadiene as additional ligands.

the concentration of the different species in solution will be expressed respectively by μC for the species CL, $(C/2)(1 - \mu)$ for species C_2, and $(\alpha_L - \mu)C$ for species L, where μ is the molar fraction of the species CL.

Then, the cryoscopic relationship will become:

$$\Delta T = k_s(\alpha L + {}^1/_2 - \mu/2)C$$

and thus

$$P/k_s = \alpha_L + {}^1/_2 - \mu/2$$

As μ is determined experimentally, the equilibrium constant K may be calculated. In fact, from only one cryoscopic determination, giving the ratio P/k_s, it is not possible to distinguish between hypotheses (a) and (b). However, the calculation of the constant K from several cryoscopic determinations for various α_L values may be indicative of the existence of either scheme (a) or scheme (b).

Data calculated from the cryoscopic curves shown in Figure 1 and gathered by adding various ligands to the binuclear complex $(\pi\text{-}C_3H_5NiOOCCF_3)_2$, are summarized in Table I.

It must be noted that some of the information gathered in the polymerization study tends to reject the most elaborate forms which are theoretically possible; in fact, the interaction of the additional ligands should yield essentially the species CM, C_2B_2, CN, CBM, and CT, as indicated by the

TABLE I
Influence of Additional Ligands on π-Allyl Nickel Trifluoroacetate

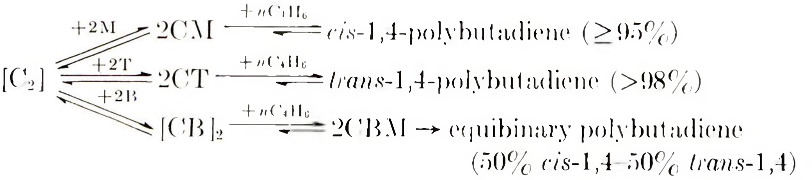
Solvent	Ligand	α_L	P/k_s	Species in solution
Cyclohexane (k_s = 26.4)	Butadiene (M)	0.93	1.17	$C_2 + 2M \rightleftharpoons 2CM$
		2.00	2.00	K # 8
	Benzene (B)	1.00	1.25	$C_2 + B \rightleftharpoons C_2B$
		2.20	1.67	$C_2B_3 + B \rightleftharpoons 3_2B_4$
	Nitrobenzene (N)	1.00	1.05	
		4.00	3.96	$C_2 + 2N \rightleftharpoons 2CN$
Benzene (k_s = 5.8)	Butadiene (M)	1.00	1.47	$C_2B_2 + 2M \rightleftharpoons 2CBM$
		2.20	2.65	
		3.14	3.36	
		3.65	3.62	
	Triphenyl phosphite (T)	1.00	0.97	$C_2B_2 + 2T \rightleftharpoons 2CT.(B)$

comparison discussed later on, of the competition curves and the changes of microstructure with the ratio α_L.

It appears from the cryoscopic measurements that a stoichiometric amount of a strong electron-donating ligand such as triphenyl phosphite, or an excess of butadiene converts the binuclear complex into a mononuclear species on which the ligands are coordinated; the new complexes formed might tentatively represent the catalytic species involved in the *trans*-1,4 and *cis*-1,4 propagation.

On the other hand, by adding benzene to a cyclohexane solution of bis(π-allyl nickel trifluoroacetate), this additional ligand was also found to be coordinated on the nickel atom, in this case, however, the complex remains binuclear and complete dissociation occurs only in the presence of an excess of butadiene, to yield a catalytic species inducing the equibinary *cis–trans* polymerization.

In fact, by adding appropriate amounts of suitable ligands to bis(π-allyl nickel trifluoroacetate), it was possible to obtain with a good overall rate three kinds of 1,4 stereoregulation through a chain growth on mononuclear catalytic species.

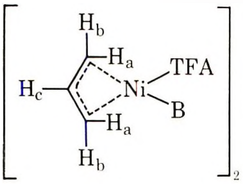
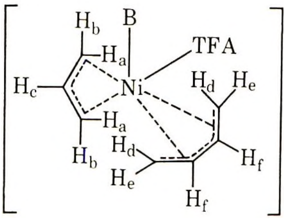


(2)

NMR Spectra of the Catalytic Complexes

The NMR spectrum of the catalytic complex CBM in benzene solution at 6°C (α_M = 2) suggests that the monomer molecule, before its insertion into the π-allylic group, is coordinated on the nickel atom by both its

TABLE II
NMR Spectra of π-Allyl Nickel Trifluoroacetate before and after Addition of Butadiene

Complex	Chemical shift δ ppm	Relative intensity	Assignment[a]
	1.8–1.95 2.5–2.65	2 2	H_a H_b
	1.8–1.95 2.5–2.65	3 2	$H_a + X(H_d.H_e)$ H_b

[a] The resonances due to the H_c and H_f protons are masked by the aromatic protons of the benzene used as solvent.

double bonds, the shape of the π-allylic signal being apparently slightly disturbed. Indeed, as shown in Table II, the relative intensity of the resonance at 1.8 ppm is larger in the CBM complex than in the $[C]_2$ complex. Since no other new signal is observed in the CBM spectrum besides those attributed to free butadiene molecules, the enhanced relative intensity at 1.80–1.95 ppm must be due to identical H_d and H_e protons of the coordinated monomer molecule.

This hypothesis is consistent with the cryoscopic data; indeed, by applying the equilibrium constant K determined by cryometry ($[C] = 10^{-2}$ mole/l.) to the concentration conditions used for the NMR determinations ($[C] = 0.2$ mole/l.), we were able to evaluate the molar fraction μ of

TABLE III
NMR Spectrum of π-Allyl Nickel Trifluoroacetate Reacted at 40°C with Butadiene ($\alpha_M = 2$)

Chemical shift δ, ppm	Relative intensity	Assignment
1.5	2	H_a and H_a'
2.0	8	H_d
2.7	1	H_b
5.0	2	H_f
5.4	4	$H_c + H_e$

the CM species formed in the course of the reversible reaction $C_2 + 2M \rightleftharpoons 2CM$, the respective concentrations for $\alpha_M = 2$, being $C/2(1 - \mu)$, $(2 - \mu)C$, and μC. The cryoscopic value of μ was found equal to 0.30.

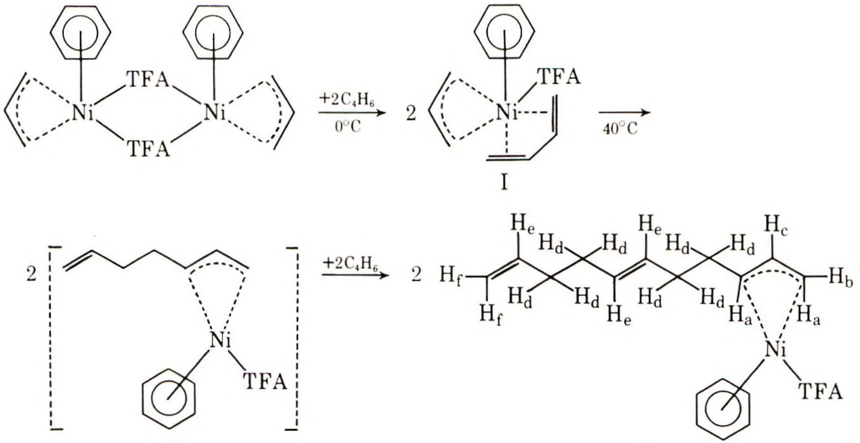
Since the π-allylic group affords two H_a protons per metal atom, the relative intensity due to the protons at 1.8 ppm in the NMR spectrum is proportional to $2C$; the complement of relative intensity, being due to the butadiene coordinated on the metal atom, must be proportional to $2\mu C$ if only one double bond per molecule interacts and to $4\mu C$ if both the two double bonds are coordinated. Thus the relative intensities ratios must give the following molar fraction μ values:

$2\mu C/2C = 3\text{–}2/2 \rightarrow \mu = 0.50$ for one double bond coordinated per molecule

$4\mu C/2C = 3\text{–}2/2 \rightarrow \mu = 0.25$ for two double bonds coordinated per molecule

The 0.25μ value (implying the coordination of both the double bonds of the butadiene molecule) appears to be in satisfactory agreement with the μ value (0.30) calculated by means of the cryoscopic data.

Furthermore, the reaction of butadiene with the π-allylic terminal group was followed also by NMR measurements performed on a solution during polymerization, with a butadiene content of $\alpha_M = 2$. The NMR spectrum recorded at 40°C and shown in Table III, is clearly representative of the species (III), with a *syn* configuration of the π-allyl group and a terminal vinyl group.



(3)

In fact, the NMR spectrum of species III is quite similar to the spectrum of 2,6,10-dodecatriene-12-yl nickel chloride reported elsewhere,[5] which was obtained by reacting 2,6,10-dodecatriene-1,12-diyl nickel with hydrochloric acid.

The chemical shift of the H_b proton rules out the exclusive existence of a stable π-σ complex in spite of the observed shift of the H_a and H_a' protons near the highest field (from 1.8 to 1.5 ppm); however this observation does not exclude the intermediary formation of such a bonding in the transition complex prior the monomer insertion, as previously suggested.[11]

The structure of a butadiene tetramer resulting from hydrolysis of the corresponding nickel complex, as determined by infrared spectrometry, further indicates that the reaction of butadiene with the terminal π-allylic group arises mostly on the less substituted carbon atom; moreover, the isomeric composition found (23% *cis*-1,4, 60% *trans*-1,4, and 18% 1,2) suggests on the basis of the equibinary structure obtained ultimately, the formation of a *trans* isomer by hydrolysis of the π-allylic group in the *syn* configuration.[12]

Influence of Additional Ligands on the Course of the Polymerization

As shown on Figure 2, depending on the nature of the additional ligand used and on the ligand/nickel molar ratio (α_L), the microstructure of the polymers produced is modified, i.e., by adding a suitable ligand to a catalytic complex yielding pure *cis*-1,4-polybutadiene, it is possible to increase the *trans*-1,4 content of the polymers, keeping the high 1,4 selectivity, until the equibinary composition (50% *cis*-1,4, 50% *trans*-1,4) is reached. Such a gradual change of microstructure is due to the competition for the monomer between two catalytic sites, i.e., CM and CML, the relative amount of these sites varying according to the α_L and K_f values. In fact, the shape of the competition curves given in Figure 2 are representative of the respective coordination constants for between nickel, butadiene, and additional ligands; for example, the equibinary *cis–trans* microstructure appears to be reached at 0°C, for α_N around 15 in the presence of nitrobenzene and for α_B up to 500, in the presence of benzene, the observed difference being presumably due to the influence of the electron-attracting substituent of the aromatic derivative.

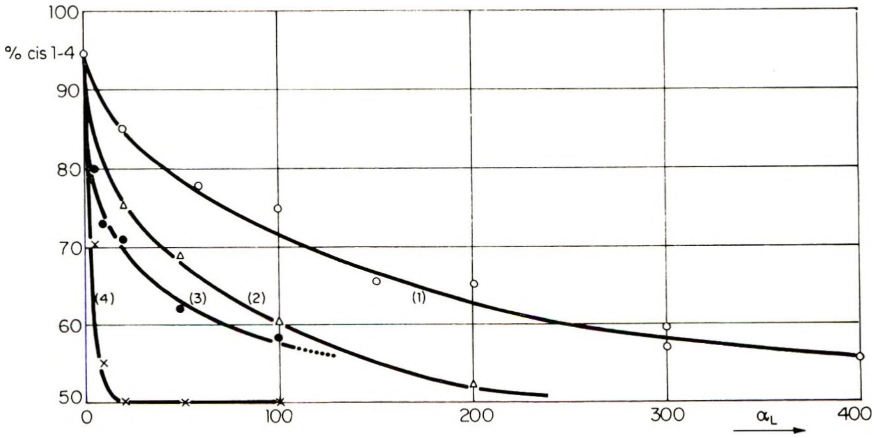


Fig. 2. Variation of microstructure of the polymers obtained vs the ligand/nickel ratio α_L in the presence of additional ligands: (*1*) benzene at 30°C; (*2*) styrene at 30°C; (*3*) nitrobenzene at 56°C; (*4*) nitrobenzene at 0°C. [Ni] = 1.33×10^{-2} mole/l., $[C_4H_6]_0 = 3.2$ mole/l.; solvent, *n*-heptane.

Variations in the microstructure of the polymers obtained may be explained by the reaction scheme (4)–(5),

$$C_2 + 2M \rightleftharpoons 2CM \qquad (4)$$

$$CM + L \rightleftharpoons CML \qquad (5)$$

the CM species inducing the *cis*-1,4 propagation and the modified CML species being responsible for the equibinary *cis–trans* polymer formation.

Considering the experimental polymerization conditions used ($\alpha_M = 240$), the equilibrium (4) is completely displaced towards CM formation and then, the *cis*-1,4 content of the polymers obtained is controlled essentially by the equilibrium (5), for which it is possible to determine the constant K_5, from the polymer microstructure. Indeed, the 1,4-*cis* content of the polymers is given by the relationship:

$$\%\ cis\text{-}1{,}4 = (95m_c + 50m_{eq})/(m_c + m_{eq})$$

where m_c and m_{eq} are respectively the amounts of *cis*-1,4 in pure (95%) and equibinary (50% *cis*/50% *trans*) polymers. From the kinetic determinations shown below, the respective formation rates of the polymers are given by:

$$R_c = k_c[CM][M]$$

and

$$R_{eq} = k_{eq}[CML][M]$$

Thus

$$\frac{m_c}{m_{eq}} = \frac{R_c}{R_{eq}} = \frac{\%\ cis - 50}{95 - \%\ cis} = \frac{k_c[CM]}{k_{eq}[CML]}$$

the k_c/k_{eq} ratio being determined as 1.9, at 30°C from the experimental conversion–time curves.

TABLE IV
Influence of the Ligand/Nickel Ratio on K_5

Ligand	α_L	*cis*-1,4, %	$K_5 \times 10^{-2}$ l./mole
Nitrobenzene[a]	2	85	0.35
	5	80	0.33
	10	75	0.30
	20	70	0.26
	35	65	0.26
	70	60	0.27
Benzene[b]	10	86	0.06
	20	84	0.05
	40	80	0.05
	70	76	0.05
	100	72	0.06
	160	67	0.07

[a] Solvent, *n*-heptane; 56°C; [C] = 1.33×10^{-2} mole/l.

[b] Solvent, *n*-heptane; 30°C; [C] = 1.33×10^{-2} mole/l.

Accordingly, from the *cis*-1,4 contents of the polymers, as determined by infrared spectrometry, it is possible to calculate the CML/CM ratio, and thus the value of the constant in the equilibrium (5). Experimental values of this constant K_5 are given in Table IV.

In spite of wide variation of α_L, K_5 values remain satisfactorily constant, considering the experimental difficulties encountered. Furthermore the K_B value determined for the benzene ligand (K_B around 6) appears to be in good agreement with the value found from the cryoscopic measurements (K_B = 7 l./mole).

Kinetics of the Equibinary Polymerization

The kinetic curves (Fig. 3) giving the variation of log [M] versus time (where [M] is the residual monomer concentration) indicate a first-order reaction versus monomer.

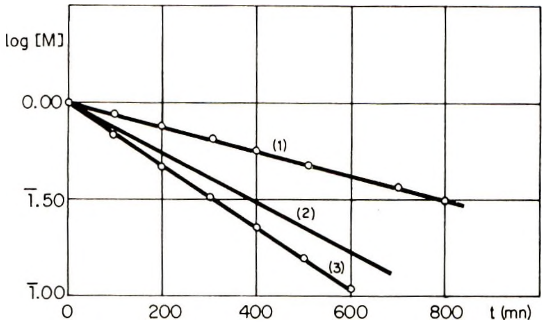


Fig. 3. Overall polymerization rate of butadiene in the presence of bis(π-allyl nickel trifluoroacetate) (dilatometric curves) at various [Ni]: (*1*) 1.33 × 10^{-2} mole/l.; (*2*) 2.7 × 10^{-2} mole/l.; (*3*) 3.3 × 10^{-2} mole/l. $[C_4H_6]_0$ = 1.0 mole/l.; solvent, benzene; 30°C.

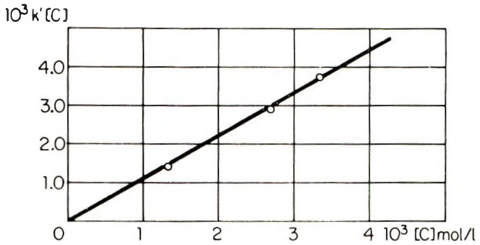


Fig. 4. Influence of the catalyst concentration on the overall polymerization rate. $[C_4H_6]_0$ = 1.0 mole/l.; solvent, benzene; 30°C.

The polymerization rate is directly proportional to the catalyst concentration (Fig. 4), this type of dependence being in good agreement with the complete dissociation, observed by cryometry, of the starting binuclear complex into a mononuclear catalytic species, in the presence of even a slight excess of butadiene.

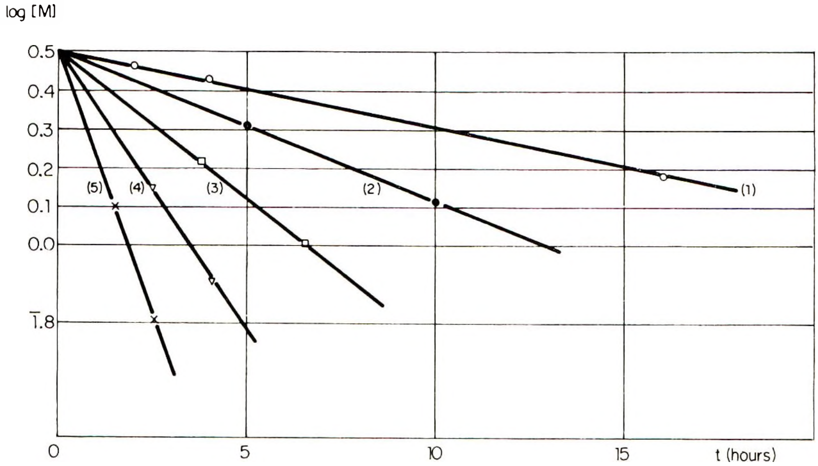


Fig. 5. Influence of the reaction temperature on the polymerization rate constant k: (*1*) 30°C; (*2*) 40°C; (*3*) 50°C; (*4*) 60°C; (*5*) 70°C. $[\mathrm{Ni}] = 1.33 \times 10^{-2}$ mole/l. $[C_4H_6]_0 = 3.2$ mole/l.

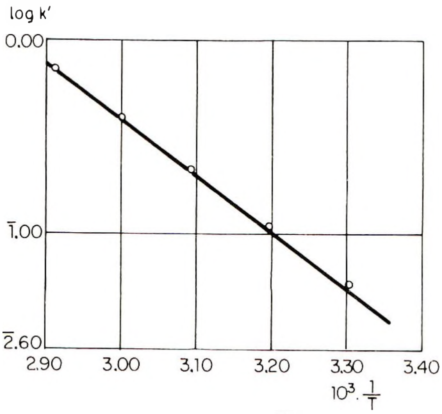


Fig. 6. Energy of activation for the formation of equibinary poly(*cis*-1,4-*trans*-1,4)-butadiene.

The overall rate of the polymerization process induced by bis (π-allyl nickel trifluoroacetate), in benzene solution, is thus given by

$$-dM/dt = k[\mathrm{C}][\mathrm{M}]$$

the k value being independent of the initial monomer concentration (at least in the range from 1 to 3 moles/l.).

The dependence of the k values on the reaction temperature has been calculated from the experimentally determined half-reaction times ($t_{1/2}$), using the relationship $k = 0.69/t_{1/2}[\mathrm{C}]$ for a first-order reaction. The evolution of log [M] as a function of reaction time at several temperatures ranging from 30 to 70°C, is shown in Figure 5.

The linear relationship between the logarithm of the constant k and the $1/T$ values led, according to the Arrhenius law, to an overall activation energy of 13 ± 0.5 kcal/mole (Fig. 6).

The variation with the conversion of the mean molecular weights of the polymers obtained suggests the absence of important transfer reactions for a suitable ligand/nickel molar ratio α_L during the chain growth, all the nickel atoms being apparently catalytically active.

Characteristic Properties of the Equibinary Poly(*cis*-1,4-*trans*-1,4)-Butadienes

The intrinsic viscosities measured at 30°C on toluene solutions, ranged from 0.2 to 0.5 dl/g for the equibinary polybutadienes (50% *cis*-1,4–50% *trans*-1,4) produced in the presence of benzene as additional ligand. When nitrobenzene is used as ligand, an increase of the mean molecular weights ($1 < [\eta] < 2$) and of the vinyl contents (up to 7%) of the polymers results.

The rubbery unvulcanized gum shows some enhanced strength under stress around 500% elongation; such behavior of the equibinary polybutadiene is reminiscent of the reinforcing properties observed in the elongation crystallization of natural rubber.

Relative narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n$ from 1.5 to 2.5) were observed by osmometry and light-scattering determinations performed at 45°C, but, as shown on Figure 7, at lower temperature (24°C) dissymmetry shows up in the Zimm plot, indicative of the formation of aggregates in the solution. Increased weight-average to number-average molecular weight ratios were found, i.e., for a polymer sample with $\bar{M}_n$ =

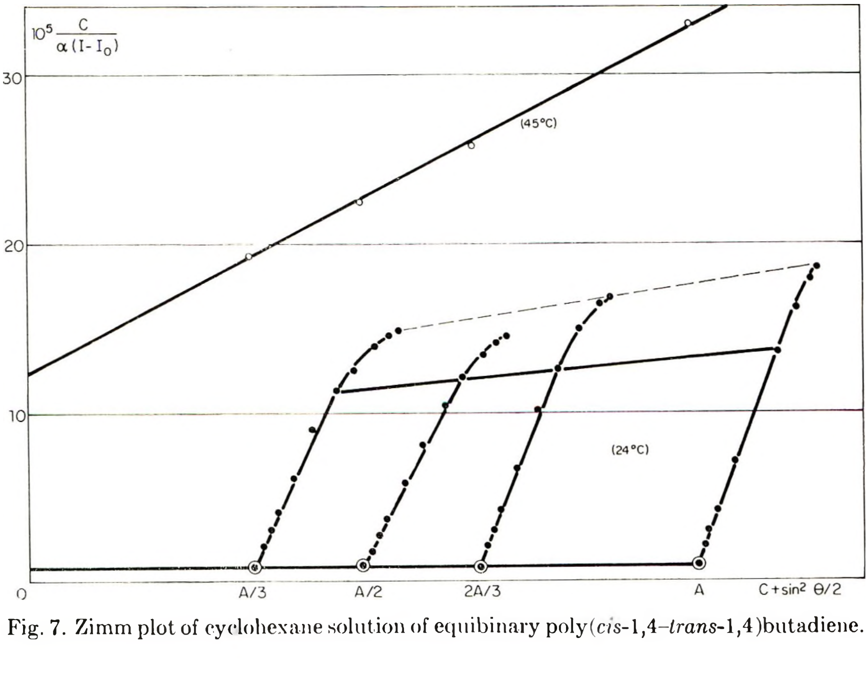


Fig. 7. Zimm plot of cyclohexane solution of equibinary poly(*cis*-1,4–*trans*-1,4)butadiene.

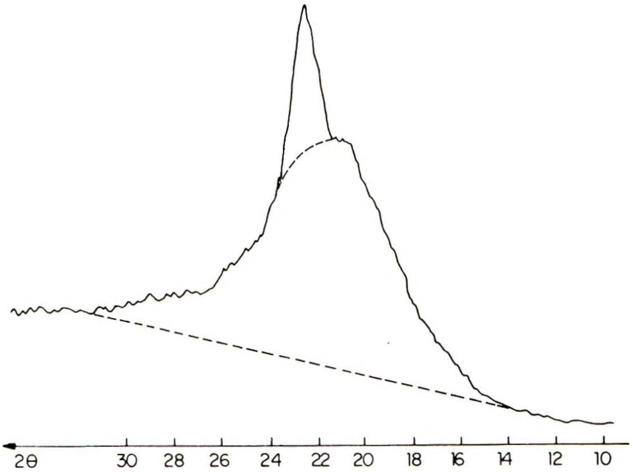


Fig. 8. The x-ray diffraction pattern of equibinary poly(*cis*-1,4–*trans*-1,4) butadiene elongated at about 400% at −40°C.

4600, a $\bar{M}_w$ value of 11 000 was found at 45°C, while a $\bar{M}_w$ value of 17 000 was determined at 24°C.

Differential thermal analysis of the equibinary polymer indicates a glass transition temperature around −105°C, compared to a T_g of −110°C for pure *cis*-1,4-polybutadiene under similar experimental conditions.

Low-temperature (−40°C) x-ray diffraction studies on polymer samples ([η] up to 2 dl/g) elongated at about 400% have shown after 2 hr the appearance of a crystalline peak located at an angle (2θ) of 22.8° (Fig. 8). The crystallinity observed after 4 hr reached 11% and did not increase further. For comparison, crystalline peaks located at 19° and 22.8° are observed at −20°C with an unelongated high-*cis*-1,4 polybutadiene (19% crystallinity), while only one peak located at 22.8° is observed at room temperature with a *trans*-1,4-polybutadiene (40% crystallinity) prepared by means of the π-allyl nickel trifluoroacetate–triphenyl phosphite catalyst complex. The presence of long sequences of *cis*-1,4 or *trans*-1,4 units in the equibinary polymer chains can be ruled out from these x-ray diffraction patterns, in spite of the common peak at 22.8°. Indeed, the crystallization of the equibinary poly(*cis-trans*)butadiene is a reversible phenomenon, the single peak disappearing when the sample is heated to 0°C and reappearing after cooling at −40°C. The presence of *trans*-1,4 sequences should give a crystalline peak at room temperature, while the presence of *cis*-1,4 sequences should give rise to two peaks, since the elongation of the sample does not modify the position of the peak located originally at 19°. Crystallizing under stretching a mixture of equibinary polybutadiene with 10% by weight of pure *cis*-1,4-polybutadiene, we did indeed observe under the same experimental conditions a crystalline peak at 19° (Fig. 9).

The specific partial crystallinity observed in the equibinary poly(*cis*-1,4–*trans*-1,4)butadiene, although relatively low, strongly suggests a

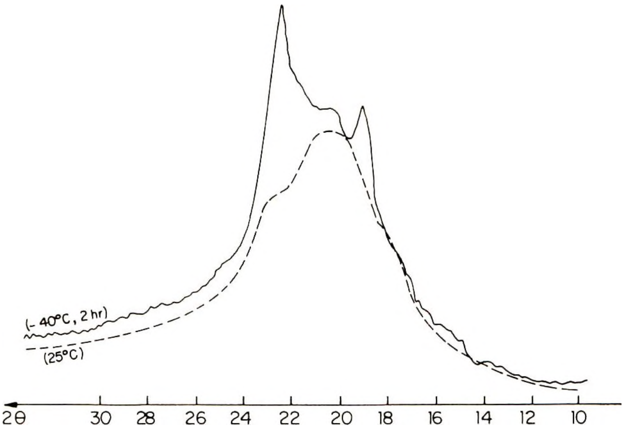


Fig. 9. The x-ray diffraction patterns of equibinary poly(*cis*-1,4-*trans*-1,4) butadiene mixed with 10 wt.-% of high-*cis*-1,4 polybutadiene and elongated at about 400 %: (- -) 25°C; (——) −40°C, 2 hr.

regular repartition of the *cis* and *trans* isomers, at least along significant sequences of the polymer chain. This result confirms the regular alternation previously proposed[2] on the basis of kinetic and structural data.

CONCLUSIONS

Appropriate modifications of bis(π-allyl nickel trifluoroacetate) catalyst, by the binding of various additional ligands, led to some interesting correlations between the nature of the catalytic species and the structure of the polymers obtained.

Starting from a well defined and relatively stable monometallic complex, three different types of 1,4-polybutadienes (high-*cis*-1,4, high-*trans*-1,4, and equibinary *cis* 1,4-*trans*-1,4 polybutadienes) were synthesized with good overall polymerization rates.

The information obtained on factors influencing the course of the equibinary polybutadiene formation, as well as on the specific properties of the polymer confirm a regular distribution of the *cis* and *trans* isomers in the polymer chain, implying a specific alternate propagation scheme, presumably on an unsymmetrical catalytic complex.

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Copolymers of 1-Methylcyclopropene*

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Synopsis

1-Methylcyclopropene (MCP) copolymerizes rapidly with acrylic and vinyl monomers to form soluble, high molecular weight products containing enchained cyclopropane rings. The high electron availability in the cyclopropene double bond promotes one-to-one alternating copolymerization with sulfur dioxide, maleic anhydride, acrylic acid, acrylonitrile, dialkyl fumarates and acrylic esters. Nonalternating copolymers are obtained with vinyl chloride and vinyl acetate, and attempted copolymerization fails entirely with styrene, α-methylstyrene and isoprene. This pattern of copolymerization reactivity resembles that of highly compressed ethylene. Methylcyclopropene copolymers have high glass temperatures in spite of the small size of the MCP unit. The combination of high T_g and small size allows preparation of copolymers with high T_g having a wide range of ductilities and cohesive energy densities.

INTRODUCTION

The preparation of a polymer containing cyclopropane rings in the main chain was first accomplished by Marvel, Sample, and Roy by treating poly(vinyl chloride) with zinc dust.[1] That work established the head-to-tail ordering in PVC and was also the first synthesis of a thermoplastic containing enchained rings. Such ring-in-chain polymers are now of great interest because of their high softening temperatures, high moduli, and high thermal stability.[2,3] The discovery of a simple route to 1-methylcyclopropene[4] has permitted preparation of several new polymers containing enchained cyclopropane rings, the properties of which are reported on below.

COPOLYMERIZATION

Sulfur Dioxide

The report of Iwatsuki, Kokubo, and Yamashita[5] that 1-methylcyclopropene copolymerizes rapidly and spontaneously with sulfur dioxide prompts us to report our own results with these monomers. The copolymer formed in excess SO_2 at 0°C as in Table I, like most sulfur dioxide–olefin copolymers, has a one-to-one alternating structure. Ungelled polymer is soluble in cresol, trifluoroacetic acid, hexafluoroisopropanol, or sulfuric

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

TABLE I
Copolymerization of 1-Methylcyclopropene

1-Methyl-cyclo-propene, g	Comonomer, g	Solvent, ml	Initiator, g	Temp, °C	Reaction time, hr	Polymer product, g	Intrinsic viscosity, dl/g	MCP content, mole-%[a]	Tensile modulus, (23°C), psi
5	Sulfurdioxide, 15	Pentane, 25	None	0	0.2	7.5 sol 1.5 gel	0.71[b]	51	c
0.9	Maleic anhydride, 2.0	Ether 10	None	25	18	0.75	0.80[d]	49	e
6	Acrylonitrile, 8.0	None	UV + AIBN, 0.2	5	2	8.7	1.2[f]	49	270,000
1.2	Diethyl fumarate, 3.4	*tert*-Butanol, 25	0.02, DEPC[h]	5	52	1.7	0.74[g]	44	89,000
1.5	Acrylic acid, 1.7	None	0.01, DEPC	5	15	1.5 sol 1.5 gel	1.8[g]	50	i
1.0	Methacrylic acid, 1.5	None	0.01, DEPC	5	17	1.5	High	43	i
1.7	Ethyl acrylate, 2.5	None	0.1, DEPC	5	16	2.9	1.2[f]	48	130,000
1.9	Methyl methacrylate, 2.5	None	0.025, DEPC	5	43	2.3	0.82[f]	39	272,000
0.2	Vinyl chloride, 4.5	None	0.05, DEPC	5	68	0.7	0.9	18	
2.0	Vinyl acetate, 4.3	None	UV + AIBN, 0.05	5	21	—	Low	20	e
3.0	None	None	0.02, DEPC	10	25	0.20	ca 0.1	100	e,j

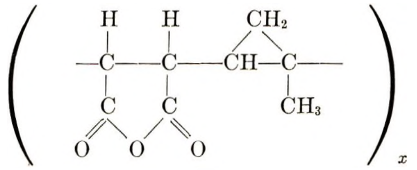
[a] Methylcyclopropene content of polymer as determined by elemental analysis. [b] In cresol, 25°C. [c] Decomposes in molding. [d] In acetone, 25°C. [e] Too brittle to test. [f] In chloroform, 25°C. [g] In tetrahydrofuran, 25°C. [h] Diethyl peroxydicarbonate. [i] Thermosetting resin. [j] IR absorption at 1.65, 1.605, 1.70 μ; density 1.03 g/ml; softens 120°C.

acid and is insoluble in sulfur dioxide, dimethylformamide, dimethyl sulfoxide, acetone, cyclohexanone, or hydrocarbons. Presence of some gel suggests that cyclopropane rings are in part opened during the 0°C polymerization to form crosslinking points. The most striking properties of the copolymers are that they are not decomposed by boiling 5% aqueous sodium hydroxide and upon pyrolysis in nitrogen leave a 25% residue stable at 500°C. Propylene–sulfur dioxide copolymer on the other hand is easily hydrolyzed by bases and reverts to monomers when heated to 200°C.[6]

Maleic Anhydride

1-Methylcyclopropene and maleic anhydride copolymerize spontaneously in bulk or in solution at 25°C. A 70% conversion is reached in 18 hr in ether solution; acetone and ethanol give slower rates, while tetrahydrofuran and dimethoxyethane are faster. The yield of nonpolymeric adducts is minimized by using ethereal solvents.

Elemental analyses indicate a one-to-one composition for the copolymer. Neither monomer polymerizes rapidly alone under the conditions used for the copolymerization, and since NMR and infrared spectra show little unsaturation, the structure must be I.



I

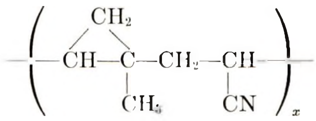
Intrinsic viscosity of 0.8 dl/g was reached; this is considerably higher than that attained in other cycloolefin–maleic anhydride reactions.[7] The polymer is fully soluble at room temperature in acetone, dimethyl sulfoxide, dimethylformamide, pyridine, or aqueous sodium carbonate and is insoluble in ether, chloroform, carbon disulfide, hydrocarbons, isopropyl alcohol or water. Cast films form a rigid glass which softens near 300°C with decomposition. No transitions were detected in the DTA plot between room temperature and 300°C.

At 300°C in nitrogen the thermogravimetric curve shows a 10% weight loss. Pyrolysis–GLC shows a broad spectrum of products with no predominance of C_4 fragments; unzipping is not a preferred decomposition path. The copolymer may be heated in air at 150°C for 1 hr with no apparent discoloration; this probably reflects the low hydrogen content of the polymer and the resistance of cyclopropane hydrogens to abstraction by free radicals.[8,9]

Acrylonitrile

Acrylonitrile and 1-methylcyclopropane copolymerize rapidly in bulk or in emulsion when initiated with radicals at 5–25°C. Polymer precipitates from the monomers as a water white transparent mass. At 5°C, in bulk, 60% conversion was obtained in 2 hr. Although 20% methylene cyclopropane was present during the preparation of the sample of Table I, this olefin is much less reactive than methylcyclopropene and may be recovered at the end of the polymerization.

Elemental analyses of the copolymer indicate a 44–57% acrylonitrile content. The usual polyacrylonitrile solvents (dimethylformamide and *m*-cresol) are solvents for the copolymer but so also are acetone, chloroform and tetrahydrofuran; acrylonitrile homopolymer is therefore absent. The 13.9 μ infrared band of polyacrylonitrile is present only as a weak shoulder; acrylonitrile sequences are also essentially absent. No olefinic protons are detected by NMR and strong infrared bands are found at 9.65, 3.28 and 1.640 μ, which are data consistent with a cyclopropane structure. Pyrolysis at 500°C leaves $<5\%$ of nonvolatile residue. A fairly high density (1.1 g/ml) and refractive index also ($n^{25} = 1.501$–1.504) appear consistent with the structure II.



II

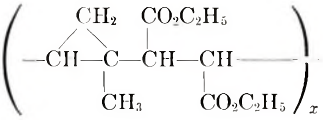
Intrinsic viscosities of the polymer (0.7–1.2 dl/g in tetrahydrofuran at 25°C) suggest a molecular weight near 10^5.

No crystallinity is detectable by x-ray diffraction. The glass temperature (Perkin-Elmer DSC-1) occurs at 136°C and clear, flexible, faintly yellow films may be pressed at 150°C. Strains generated in molding are not relaxed by heating several hours at 125°C. Prolonged heating at 150°C causes severe discoloration. The light color of films pressed at 150°C is further evidence for alternating structure; the chromophore in polyacrylonitrile arises from adjacent acrylonitrile units.[10]

Mechanical properties of the compression-molded copolymer are remarkable. Tensile yield (23°C) is 11 000–12 000 psi, elongation at yield 6–7%, elongation at break 25–30%, tensile modulus 2.5×10^5 psi, and Rockwell M hardness 85–86; this is a good combination of strength with ductility. Samples always draw without crazing or crystallizing and the fracture surface is rough rather than conchoidal.

Dialkylfumarates

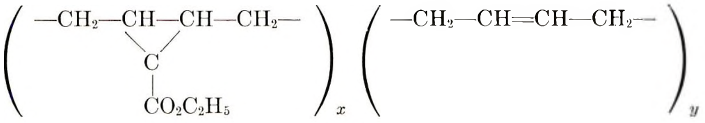
1-Methylcyclopropene and diethylfumarate copolymerize in bulk, in solution or emulsion to give soluble, high molecular weight copolymers. In bulk at 5°C, 62% conversion is obtained in 24 hr, again a rate much faster than polymerization of either monomer alone. Elemental analyses, infrared (3.25, 25.4 μ), NMR (no olefinic protons), and high density (1.12 g/ml) confirm the structure to be the alternating one-to-one copolymer with ring intact (III).



III

Highest molecular weight is obtained with AIBN plus ultraviolet light as initiator rather than with diethyl percarbonate; the latter is probably a chain transfer agent.

Soft, clear, colorless, void-free moldings of the copolymer are easily obtained at 140°C. The pendant ester units clearly plasticize the material and contribute to its softness. The monomer diethyl fumarate is known to be a powerful plasticizer and, indeed, samples of copolymer containing free monomer can be elongated 10 000% without break. Even the highest molecular weight samples have low modulus and low hardness (intrinsic viscosity 1.7 dl/g, modulus 81 000 psi, elongation at break 102%). There is no visible crazing or crystallization even at full elongation, and tensile failure clearly proceeds by a viscous mechanism. The most ductile polymer known to us at present[11] also contains cyclopropane and carboxyethyl units (IV).



IV

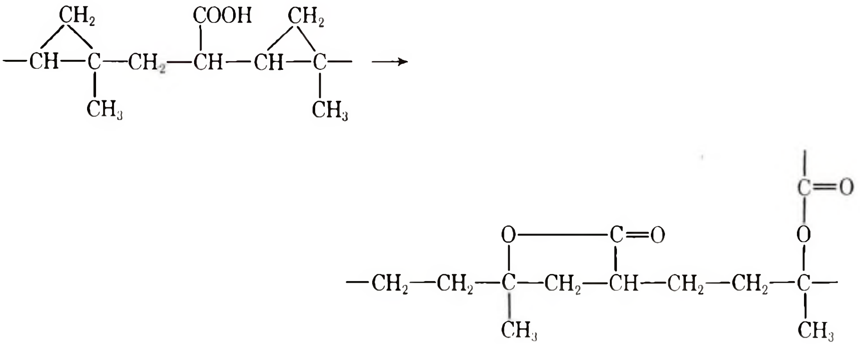
Stability of the copolymer appears quite adequate for many uses. In a thermogravimetric test under nitrogen, 3% weight loss was reached at 300°C and a catastrophic weight loss occurred at 360°C. When heated in air, no discoloration occurred until 250°C was reached. Exposures to a medium-pressure 250-W mercury arc for 24 hr produced no discoloration.

The mechanical loss modulus (100 cps vibrating reed) is nearly flat over the region -100 to $+60$°C, an unusual situation. The (Perkin-Elmer DSC-1) calorimetric T_g is only 10–15°C below the calorimetric T_g of poly-(methyl methacrylate) (110°C) but the polymer is mechanically far more lossy at room temperature than PMMA.

Dimethyl fumarate and dibutyl fumarate also copolymerize with methylcyclopropene in 1:1 proportions. The dimethyl derivative is a brittle, high-softening (T_g = 152°C) glass, while the dibutyl derivative is a low-softening glass which has still lower modulus and higher elongation than the diethyl derivative. Magnitude of the copolymer specific heat change at T_g decreases in the order dimethyl > diethyl > dibutyl fumarate. The specific heat change is undetectable in the dibutyl fumarate copolymer, which shows that the butyl side chains make a much larger contribution to the total specific heat than does the backbone.

Acrylic Acid and Methacrylic Acid

Polymerization of an equimolar mixture of MCP and acrylic acid in tetrahydrofuran at 5°C yields 1:1 copolymer. Infrared absorption at 3.28, 9.2 and 9.7 μ (no 6.1 μ band) suggests that rings are retained in the copolymerization. The polymer is soluble in dioxane, tetrahydrofuran, dimethyl sulfoxide, or aqueous sodium carbonate and is insoluble in acetone or water. Films cast from solution adhere tightly to metals or to glass. When heated to 190°C, polymer thermosets with <10% weight loss, with disappearance of both the carboxyl (2.9, 5.85 and 7.8 μ) and the cyclopropane infrared bands and with appearance of a new absorption at 5.65 μ. It is concluded that the thermosetting process involves an esterification and lactonization of the cyclopropane rings by the carboxylic acid units:

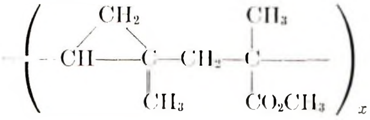


Methacrylic acid copolymerizes vigorously with methylcyclopropene at 5°C in bulk. The product contains no gel, is soluble in aqueous sodium carbonate, dioxane, or tetrahydrofuran and is insoluble in acetone, water, or chloroform. When heated at 160°C for 2 hr an endothermic dehydration reaction sets in and the polymer becomes insoluble in tetrahydrofuran. It quickly redissolves in aqueous sodium carbonate solution, however, indicating the absence of ester crosslinks.

Fumaric acid and monoethyl fumarate also copolymerize with methylcyclopropene. These polymers adhere less strongly to glass or metal, however.

Methyl Methacrylate and Ethyl Acrylate

When an equimolar mixture of 1-methylcyclopropene and methyl methacrylate is initiated in bulk at 5°C, a high polymer containing 60 mole-% methyl methacrylate is formed. This product is soluble in acetone and chloroform, and is precipitated by methanol. The infrared spectrum (1.64, 3.28, 9.65 μ) and the NMR (no olefin) indicate the rings to be intact. The polymethacrylate band at 13.3 μ was not observed; there are therefore few methacrylate sequences and the polymer is evidently rich in alternating sequences (V).



V

This product is similar in mechanical and optical properties to PMMA; T_g is slightly higher, however.

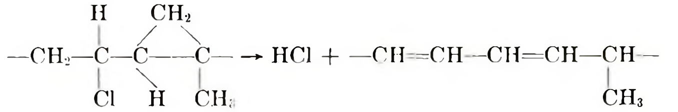
Ethyl acrylate and methylcyclopropene also copolymerize in nearly equimolar proportions forming copolymer containing no olefin units (NMR) and few acrylate sequences (strong 9.6 μ band, weak 23 μ acrylate band). Its glass temperature (37°C) is sharply higher than that of polyethyl acrylate (−13°C). Its room temperature mechanical properties include a high elongation but rather low modulus and strength, as expected for a material with T_g near 25°C.

Vinyl Chloride, Vinylidene Chloride, and Vinyl Acetate

At 5 to −20°C, vinyl chloride copolymerizes with methylcyclopropene in bulk. The polymers are soluble in chloroform and tetrahydrofuran and polymer prepared from a 1:1 charge does not display the 14.5 μ absorption of poly(vinyl chloride) sequences. The bands at 3.28 and 9.7 μ characteristic of cyclopropane rings are present; double bonds are absent from the NMR spectrum. Molecular weight of the polymer is low unless the methylcyclopropene charge is limited to about 5%. Since conversions are also low, the chain transfer may be of the degradative type.

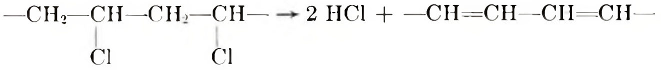
Methylcyclopropene enters the polymer chain faster than vinyl chloride. No other olefins are reported to do this. It is suspected that methylcyclopropene undergoes side reactions (ene reactions, or grafting reactions) either with vinyl chloride monomer or with its polymer and that these reactions obscure the actual reactivity of the monomer in the propagation step. Copolymerization of the thermal dimer of 1-methylcyclopropene, i.e., 3-(2-methylcyclopropyl)-1-methylcyclopropene, may also contribute to the apparently high reactivity of MCP.

When heated to 100°C the copolymer evolves HCl, discolors, and the cyclopropane rings disappear with a half-life of about 1 hr. Thermogravimetric curves show that the stability of the polymer decreases with increasing olefin content, as in the case of isobutylene–vinyl chloride copolymers.[12] Plateaus appear in the thermogravimetric curve at weight losses corresponding to the reactions



(15% weight loss)

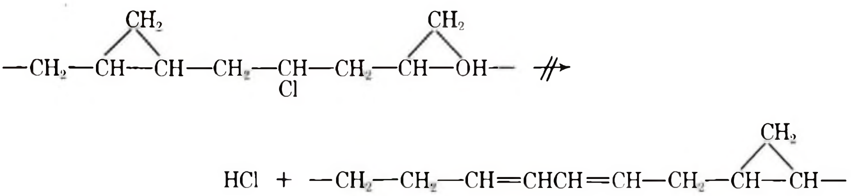
and



$$-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- \rightarrow 2\,HCl + -CH{=}CH-CH{=}CH-$$

(55% weight loss)

Poly(vinyl chloride) dehalogenated with zinc has a thermal stability (DSC exotherm 350°C) far higher than that of either methylcyclopropene copolymer (exotherm 130°C) or of poly(vinyl chloride) itself (exotherm 175°C). The chlorine atoms in dehalogenated PVC are one carbon further removed from the cyclopropane ring and this apparently deactivates them:



Vinyl acetate also copolymerizes with methylcyclopropene to give a brittle, low molecular weight, cyclopropene-rich copolymer. Its NMR spectrum shows a cyclopropyl hydrogen content lower than that calculated from the elemental analysis. It is therefore suspected that here, too, the vinyl monomer or its polymer adds to methylcyclopropene in side reactions. The complexity of the NMR spectrum in the cyclopropane region ($\delta = 0.25$, 0.3, 7.6, 0.85 ppm) give some support to this speculation.

Inactive Comonomers

Equimolar mixtures of methylcyclopropene with either styrene, α-methylstyrene, or isoprene did not give polymers when initiated with diethyl percarbonate at 5°C. These monomers lie near the bottom of the *e*-scale[13] and their failure to copolymerize suggests that methylcyclopropene also has a large negative e value. Attempted homopolymerizations of 1-methylcyclopropene gave ca. 10% yields of methanol-insoluble polymer, $[\eta] \leq 0.1$ dl/g. Black color (charge transfer) developed when tetracyanoethylene or benzoquinone were mixed with methylcyclopropene but no high polymer was obtained. Hexafluoroacetone at 5°C did not give high polymer; it is suspected that a temperature above 5°C is required for copolymerization of this monomer.

EXPERIMENTAL

1-Methylcyclopropene was prepared by dehydrohalogenating methallyl chloride with sodamide essentially according to the method of Fisher and Applequist.[4] It was found necessary first to ball mill the sodamide (under nitrogen) for several hours in order to obtain reasonable conversions in the reaction with methallyl chloride. Mineral oil is preferred over tetrahydrofuran as reaction medium because it is not lost from the reactor by entrainment in the nitrogen stream. The product methylcyclopropene contains

5–30% methylenecyclopropane, depending on the conversion of sodamide. Methylenecyclopropane may be detected by its infrared spectrum, NMR spectrum or by gas–liquid chromatography on a 500 ft. squalane capillary.

1-Methylcyclopropene is easily freed of methallyl chloride by three bulb-to-bulb distillations at −78°C on a high vacuum manifold. The half-life of the liquid monomer is only two days at room temperature but it may be stored several months at −78°C with negligible polymerization (ene reactions). Alternatively the monomer may be stored at room temperature as its lithium salt. Monomer of >99% purity may be obtained by treating the methylcyclopropane + methylenecyclopropane mixtures with butyllithium, distilling out the resulting butane and methylenecyclopropane, then regenerating the methylcyclopropene from its lithium salt by adding t-butanol in mineral oil.

Polymerizations were conducted in glass ampoules charged on a high vacuum manifold and sealed under vacuum with a torch.

CONCLUSIONS

Methylcyclopropene contains an electron-rich double bond which reacts rapidly with electron-deficient monomers to give high molecular weight, alternating copolymers. The reactivity is higher than in previously investigated strained systems: bicycloheptadiene, cyclobutene, and cyclopentene. The copolymerization competes well with the thermal homopolymerization of the cyclopropene. Side reactions of methylcyclopropene become important when copolymerization with electron-rich monomers (vinyl chloride, vinyl acetate) is attempted.

Sulfur dioxide and maleic anhydride, the most electron-deficient monomers, copolymerize spontaneously with methylcyclopropene when mixed. The low ionization potential and planarity of the cyclopropene combined with the large electron affinity of sulfur dioxide or maleic anhydride is evidently sufficient to generate charge transfer complexes with these monomers. It is significant that visible colors develop in these two polymerization systems but that those which do not spontaneously polymerize remain colorless throughout the reaction. Comonomers which are themselves electron-rich (styrene, isoprene) fail to copolymerize with methylcyclopropene at 5°C, even with radical generators present; evidently the charge-transfer phenomenon contributes to the rapid cross-propagation rates. Tetrachlorocyclopropene, a derivative with electron-withdrawing substituents, copolymerizes with styrene and vinyl acetate but fails with methyl methacrylate and acrylonitrile[14]—nearly the reverse of the methylcyclopropene pattern. Tetrafluorocyclopropene likewise forms high molecular weight alternating copolymers with methyl vinyl ether but is less reactive toward electron-deficient monomers.[15]

Although a high molecular weight, completely alicyclic homopolymer of 1-methylcyclopropene has never been prepared, extrapolation of the T_g of copolymers as in Figure 1 indicates the hypothetical homopolymer has a

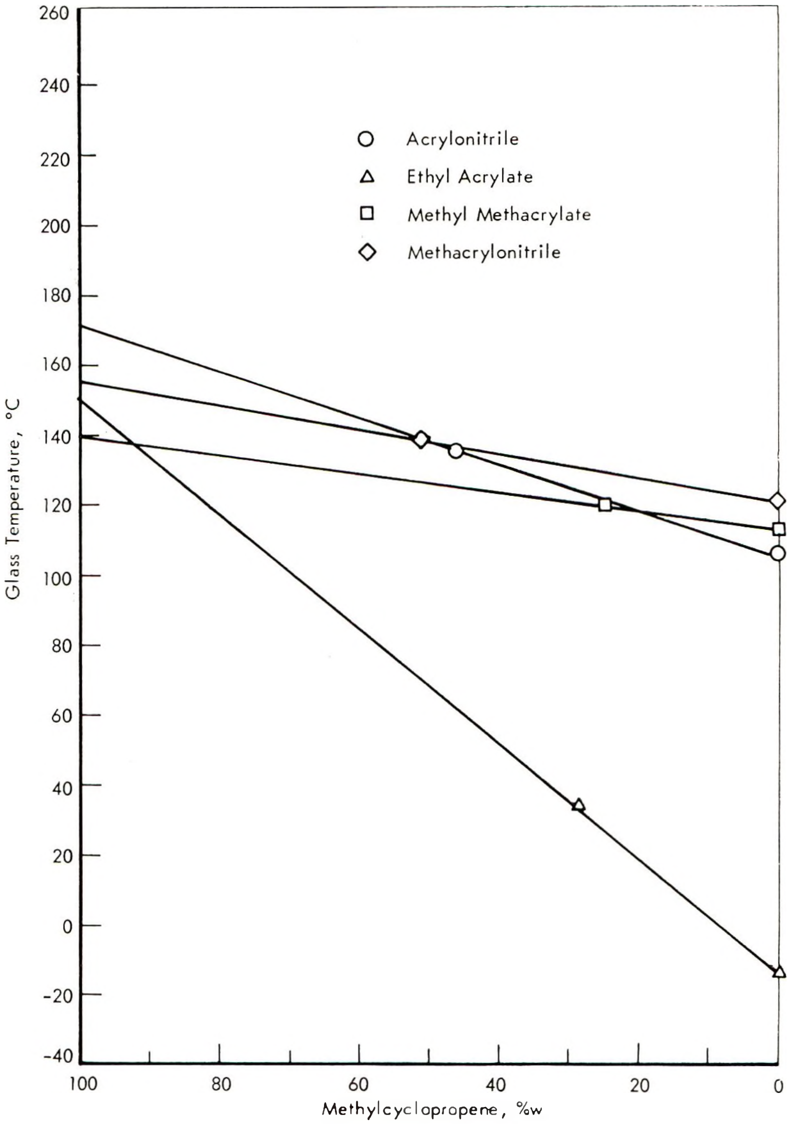


Fig. 1. Glass temperature of methylcyclopropene copolymers vs. composition.

T_g of at least 150°C. This value is considerably higher than the T_g of the known C_4 olefin homopolymers. The low molecular weight (54) and high T_g of methylcyclopropene allows preparation of copolymers of high T_g which have either high (acrylonitrile) or low (diethyl fumarate) cohesive energy densities.

The pattern of methylcyclopropene reactivities closely resembles that of ethylene at high pressure. Slow homopolymerization at room temperature, very rapid alternating copolymerization with sulfur dioxide and maleic anhydride, slower copolymerization with acrylic and fumaric monomers, copolymerization to low molecular weight products with vinyl chloride or vinyl acetate, and inhibition of polymerization by styrenes or conjugated dienes are characteristic of both ethylene at 2000 atm and of MCP. Structural features which MCP and compressed ethylene have in common are a shortened double bond and strained bond angles.[16] The enhanced electron availability in the double bond is a reasonable interpretation of the similar reactivities of these two olefins. The behavior of 1-methylcyclopropene in free-radical reactions at one atmosphere is therefore suggested as a convenient index to the behavior of ethylene in the same reactions at high pressure.

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Radical Polymerizations and Copolymerizations of Dimethylstannyl Dimethacrylate and Trimethylstannyl Methacrylate*

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Synopsis

The radical polymerizations and copolymerizations of dimethylstannyl dimethacrylate (DSM) and trimethylstannyl methacrylate (TSM) in dimethylformamide (DMF) were studied. These monomers did not polymerize thermally, but easily underwent polymerization in the presence of α,α'-azobisisobutyronitrile and on irradiation with ultraviolet light. The polymer obtained from TSM was soluble in DMF and methanol, but that from DSM was insoluble in any organic solvents; this polymer probably consists of a network structure. These polymers were converted to poly(methyl methacrylate) (PMMA) by means of acid hydrolysis and then methylation with diazomethane. The content of syndiotactic triad was determined from infrared spectra of PMMA derived from the polymers of DSM and TSM. It was noted that the content of syndiotactic triad was greater in the radical polymerization of TSM than those of DSM at every temperature investigated. The differences in the activation enthalpy($\Delta\Delta H\ddagger$) and in the activation entropy ($\Delta\Delta S\ddagger$) between isotactic and syndiotactic additions were determined as follows: for DSM, $\Delta\Delta H\ddagger = \sim 0$ cal/mole, $\Delta\Delta S\ddagger = -0.856$ eu; for TSM, $\Delta\Delta H\ddagger = 229$ cal/mole, $\Delta\Delta S\ddagger = -1.09$ eu. From the radical copolymerizations of DSM and TSM with styrene at 60°C, the copolymerization parameters, Q and e, were evaluated as follows: for DSM, $Q = 1.36$, $e = 0.41$; for TSM, $Q = 0.45$, $e = -0.37$. These results were compared with the reported effects of stannic chloride and zinc chloride on the radical polymerization of methyl methacrylate.

INTRODUCTION

Recently the effects of Lewis acid–base interaction on radical polymerizations of some polar vinyl monomers have been observed with a great deal of interest. Methyl methacrylate (MMA), ethyl acrylate, acrylonitrile (AN), and vinylpyridine were used as polar monomers which act as Lewis bases, and zinc chloride,[1-5] lithium chloride,[6] and alkylaluminum chloride[7] were used as Lewis acids. It was concluded from these studies that the inherent copolymerization reactivities of polar vinyl monomers were changed by a suitable Lewis acid–base interaction.

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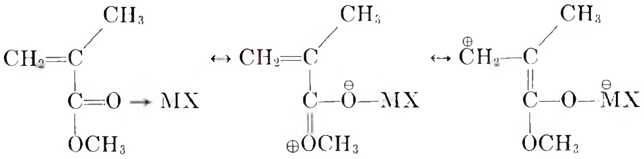
* In honor of C. S. Marvel on the occasion of his 75th birthday.

However, detailed studies on the reactivities of the complexed monomers with Lewis acids are not sufficient. In a previous paper,[8] we investigated the effect of some Lewis acids (MX) such as zinc chloride, zinc bromide, stannic chloride, aluminum chloride, and boron trifluoride on the radical polymerization and copolymerization of MMA. On the basis of the results, it was concluded that the Lewis acids formed complexes with the carbonyl oxygen of MMA, and that these complexes could be described in terms of three resonance structures.



Accordingly, it was possible to explain that the electron-accepting nature of MMA monomer, i.e., the observed e value increased with the complex formation.[2,9] However, the source of an increase in the Q value could not be explained.

On the other hand, such an interaction between polar monomers and Lewis acids was expressed by the equilibria:[9]

$$\text{Monomer} + \text{MX} \overset{K_1}{\rightleftharpoons} (\text{Monomer})\,\text{MX}$$

$$(\text{Monomer})\text{MX} + \text{Monomer} \overset{K_2}{\rightleftharpoons} (\text{Monomer})_2\text{MX}$$

The equilibrium constants for the complex formation of stannic chloride with MMA and AN were evaluated in benzene at room temperature as follows: $K_1 = 1.5$, $K_2 = 0.1$ for MMA; $K_1 = 2.0$, $K_2 = 1.0$ for AN.[9] Considering the values of these equilibrium constants, the Q and e values for the complexes of polar vinyl monomers with stannic chloride from the results of the copolymerizations in the presence of an excess molar quantities of stannic chloride were determined to be as follows: $Q = 2$–4, $e = 0.4$–1.0 for MMA–$SnCl_4$ (1:1 molar ratio); $Q = 2.64$, $e = 2.22$ for AN–$SnCl_4$ (1:1 molar ratio); and $Q = 3.58$, $e = 1.92$ for ethyl acrylate–$SnCl_4$ (1:1 molar ratio).[9]

It was also found that the syndiotacticities of PMMA obtained from the radical polymerization of the complexed MMA with zinc chloride were lower than those of PMMA obtained from free MMA under the same conditions.[8,10] However, owing to the existence of equilibrium in the complex formation, the effect of the complex formation with Lewis acids other than zinc halides on the tacticities of PMMA could not be estimated.

In the present paper, trimethylstannyl methacrylate (TSM) and dimethylstannyl dimethacrylate (DSM) were prepared as model compounds of the 1:1 and 2:1 complexes of MMA with stannic chloride in order to clarify the effect of the 1:1 and 2:1 complex formation on the radical polymerization reactivity of MMA and the syndiotacticity of the resulting PMMA.

Studies on the polymerizations of metal salts such as sodium,[11] calcium,[12] barium,[13] lead,[14,15] silyl,[16,17] germanium,[18] tin,[19–23] and zinc[24] of methacrylic acid have been reported. However, the polymerizations of these monomers in solution have been little investigated. The present paper discusses this effect from the viewpoint of the effect of substituents in TSM and DSM as well as that of ester alkyl substituents in alkyl methacrylate.[25]

EXPERIMENTAL

Dimethylstannyl Dimethacrylate (DSM)

Dimethyltin oxide was added to an *n*-hexane solution of methacrylic acid with stirring at 0°C. During the reaction, the resulting DSM precipitated. The crude DSM was collected and recrystallized twice from *n*-hexane. The yield was 75%; mp 151.0–152.0°C.

ANAL. Calcd for $C_{10}H_{16}OSn$: Sn, 37.23%. Found: Sn, 37.48%.

On the basis of the determination of double bond via bromination, the purity was established to be 99.9%. DSM monomer was soluble in dimethylformamide (DMF), methanol, ethanol, tetrahydrofuran, and carbon tetrachloride, but insoluble in water and benzene. The properties of DSM are shown in Table I.

TABLE I
Properties of Dimethylstannyl Dimethacrylate (DSM) and Trimethylstannyl Methacrylate (TSM)

	DSM	TSM
Appearance	Colorless scaly crystal	Colorless trichite crystal
Melting point, °C	151.0–152.5	113.0–113.5
Stability in air	Very stable	Stable
λ_{max}, mμ in methanol	206.0	205.0
ϵ_{max} in methanol	2.6×10^4	2.4×10^4
λ_{max}, mμ in *n*-hexane	205.0	202.5
ϵ_{max} in *n*-hexane	2.5×10^4	1.1×10^4
Equivalent conductivity in DMF, cm²/ohm-mole	0.0176 (0.266 mole/l.)[a]	0.202 (0.677 mole/l.)[a]
Thermal polymerizability in DMF	Does not polymerize at 60°C for 50 hr	Does not polymerize at 60°C for 50 hr
Photopolymerizability in DMF with UV irradiation at room temperature	Very high	High

[a] Monomer concentration.

Trimethylstannyl Methacrylate (TSM)

TSM was obtained via the reaction of trimethyltin hydroxide with methacrylic acid in *n*-hexane at 20°C. Trimethyltin hydroxide was prepared by alkaline hydrolysis of trimethyltin chloride which was obtained by a dropwise addition of stannic chloride to tetramethyltin at 100°C. The TSM which precipitated in the reaction mixture was separated by filtration and was then purified by twice recrystallization from *n*-hexane. The yield was 73%; mp 113.0–113.5°C.

ANAL. Calcd for $C_7H_{14}O_2Sn$: Sn, 47.69%. Found: Sn, 46.90%.

The TSM obtained in this manner was soluble in most of the organic solvents which dissolved also DSM; in addition it was soluble in water and benzene. The properties of TSM are also summarized in Table I.

Polymerization Procedure

The required amounts of monomer, α,α'-azobisisobutyronitrile (AIBN), and solvent were charged into a hard glass ampoule. After degassing of the contents by the usual freezing and thawing method, the ampoule was sealed off under vacuum. Polymerizations were carried out in a thermostat maintained at given temperatures. At −78, −40, and 0°C, the polymerizations were effected via irradiation with a high-pressure mercury lamp. After a given polymerization time, the contents of the ampoule were poured into large amounts of methanol and diethyl ether containing a small amount of hydroquinone to isolate the polymers of DSM and TSM, respectively. The conversion was calculated from the weight of the dried polymer obtained.

Conversion of Poly(DSM) and Poly(TSM) to Poly(MMA)

The polymers and copolymers of DSM and TSM were hydrolyzed with hydrochloric acid in methanol at 90°C for 3 hr to polymers of methacrylic acid. The resulting polymers and copolymers were then converted to the corresponding polymers and copolymers of MMA with diazomethane in benzene, followed by reprecipitation from the benzene–methanol system.

Copolymer Composition

The resulting copolymers of DSM and TSM with styrene were converted to MMA–styrene copolymers by the method described above. The copolymer compositions were subsequently determined from elementary analysis for carbon. The composition of the copolymers of TSM with maleic anhydride was determined gravimetrically from tin content. Monomer reactivity ratios were evaluated by a curve-fitting method and those of DSM were evaluated with respect to one double bond.

Syndiotacticity

The syndiotacticities of the polymers of DSM and TSM were determined from those of MMA obtained by acid hydrolysis. The content of syndiotactic triad (P_s) of the resulting PMMA was determined from the infrared spectra by use of the method reported in a previous paper.[10]

Degree of Polymerization

The number-average degree of polymerization $\bar{P}_n$ of the PMMA was determined from the intrinsic viscosity $[\eta]$ in benzene, by use of the following equation:[27]

$$\log \bar{P}_n = 3.42 + 1.13 \log [\eta]$$

RESULTS AND DISCUSSION

Properties of DSM and TSM Monomers

Table I summarizes some of the properties of DSM and TSM monomers prepared. It is to be noted that these monomers do not polymerize thermally, but are easily polymerized in the presence of a radical initiator (see Tables III and IV) and in DMF on irradiation.

TABLE II
Infrared Vibrational Frequencies of Dimethylstannyl Dimethacrylate (DSM) and Trimethylstannyl Methacrylate (TSM)

	Frequency, cm^{-1}	
Assignment	DSM	TSM
$—COO^-$		
Symmetric stretching	1400, 1370	1400, 1361
Asymmetric stretching	1570	1590, 1570
Scissoring deformation	630	628
CH_3		
Symmetric stretching	1380	1380
Asymmetric stretching	1452	1452
Rocking deformation	1005	1005
$CH_2{=}C\langle$		
C–H out of plane deformation	832	828
C—H in plane deformation	1225	1232
C=C stretching	1646	1645
$Sn–CH_3$		
Sn—C symmetric stretching	527	513
Sn—C asymmetric stretching	578	547
C—H rocking deformation	794	783
C—H symmetric deformation	—	1190

Figure 1 shows the infrared spectra of DSM and TSM monomers. The assignments of the characteristic absorption bands of these monomers are listed in Table II. Okawara and Rochow[27] found that the infrared spectra of the carboxy derivatives of methyltin compounds could be calculated as the sum of the absorptions of the carboxylate anion and the methyltin cation. The assignments according to these authors of the characteristic bands for DSM and TSM are shown in Table II. The bands at 527 cm^{-1}

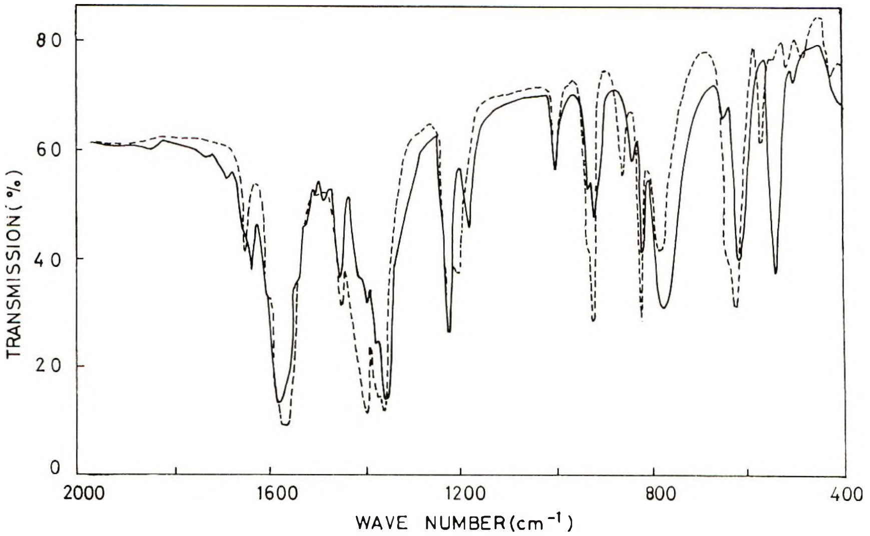


Fig. 1. Infrared spectra of (- -) DSM and (——) TSM; KBr disks.

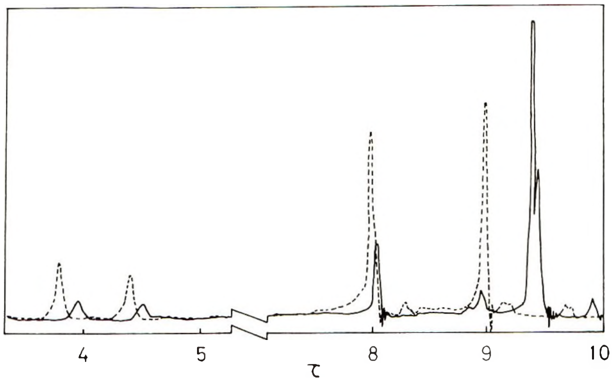


Fig. 2. NMR spectra of (- -) DSM and (—) TSM at 60 MHz in carbon tetrachloride.

for DSM and at 513 cm^{-1} for TSM were assigned to a Sn-C symmetric stretching vibration which is normally infrared-inactive for symmetric linear and planar configurations of dimethyltin and trimethyltin cations, respectively. Therefore, it seems that the Sn—O bonds in DSM and TSM were not sufficiently ionic in character to result in linear and planar configurations.

A similar conclusion was arrived at from the NMR spectra. The coupling constant of Sn^{119}-H was reported to be a useful measure for the *s* character of a Sn-CH$_3$ bond.[28] From the NMR spectra of DSM and TSM in carbon tetrachloride shown in Figure 2, the coupling constants were estimated to be 84.0 and 57.6 cps, respectively. By use of the reported calibration curve, the *s* characters of the Sn-CH$_3$ bonds in DSM and TSM were calculated to be 37 and 27%, respectively, close to values for sp^2 and sp^3 hybridizations, respectively. Since the configurations of free dimethyltin and trimethyltin cations are assumed to be sp and sp^2 hybridizations, respectively, the ionic character of the Sn-O bonds might not be complete.

The equivalent conductivities of these monomers in DMF at the monomer concentration similar to the present polymerization conditions were found to be quite small as compared with those of acetic acid.[29] Accordingly, it can be reasonably concluded that the dissociations of DSM and TSM can be ignored under the present polymerization conditions. A similar argument was also applicable to the zinc methacrylate.[30] Infrared absorption bands of the compound at 1615, 1560, and 1530 cm^{-1} were assigned to the asymmetric stretching vibrations of carboxylate anion and these data indicated that zinc methacrylate monomer is also hardly dissociated into zinc and methacrylate ions.

It was reported that two vinyl groups in some divinyl monomers interacted with each other.[31] However, the characteristic absorption bands in the ultraviolet spectrum of DSM were essentially the same as TSM.

Homopolymerization of DSM and TSM

Tables III and IV show the results of the homopolymerizations of DSM and TSM initiated by AIBN in DMF at various temperatures. Both monomers were rapidly polymerized under the conditions. The resulting polymers of DSM and TSM were colorless powders and did not melt up to 300°C. The polymer of TSM was soluble in methanol, ethanol, DMF and methyl chloride; but that of DSM was not soluble in any organic solvents. Accordingly, the polymer of DSM was considered to consist of a network structure. Figure 3 shows the infrared spectra of these polymers.

After the polymers of DSM and TSM are converted to PMMA by acid hydrolysis and then methylation with diazomethane, the syndiotactic triad (P_s) and the number-average degree of polymerization of the derived PMMA were determined as shown in Tables III and IV. If the configura-

TABLE III
Results of Polymerization of DSM Initiated by AIBN in DMF[a]

Temperature, °C	Time, hr	Conversion, %	P_s, %[b]	σ[b]	$\bar{P}_n$[b]
−40[c]	29	29.4	36	0.400	1900
0[c]	2	52.0	37	0.392	1500
30	104	60.0	38	0.384	3100
60	29	32.9	36	0.400	1700
100	0.5	69.0	35	0.408	1000
150	1	50.2	38	0.384	500

[a] Polymerization conditions: DSM, 1.50 g; AIBN, 0.3 mg; DMF, 1.05 ml.

[b] Determined from the derived PMMA.

[c] Polymerization initiated by a high-pressure mercury lamp.

TABLE IV
Results of Polymerization of TSM Initiated by AIBN in DMF[a]

Temperature, °C	Time, hr	Conversion, %	P_s %[b]	σ[b]	$\bar{P}_n$[b]
−40[c]	148	50.9	55	0.258	1300
0[c]	92	67.6	53	0.272	1800
30	72	68.9	52	0.279	4500
60	54	100	51	0.285	1100
100	32	67.7	48	0.307	400
150	4.5	8.8	—	—	—

[a] Polymerization conditions: TSM 1.50g, AIBN 0.6 mg, and DMF 5.5ml.
[b] Determined as the derived PMMA.
[c] Polymerization initiated by a high pressure mercury lamp.

tion of the polymer chain did not change during hydrolysis, the competitive reaction between isotactic and syndiotactic additions in the radical polymerization of DSM and TSM would be possible to analyze.

The plots of P_s against polymerization temperature in the polymerizations of DSM and TSM are shown in Figure 4. Similar plots in the polymerizations of zinc methacrylate and 1:1 MMA–$ZnCl_2$ complex are also indicated. It is noted that the P_s values for both monomers did not change with polymerization temperature, but these values for TSM are higher than those for DSM at every temperature.

The stereochemistry of the propagation reaction in vinyl polymerization has been treated by Bovey et al.,[32] who stated that the contents of isotactic, syndiotactic, and heterotactic triads in the resulting polymer are expressed by a single parameter σ, which denotes the probability of iso-

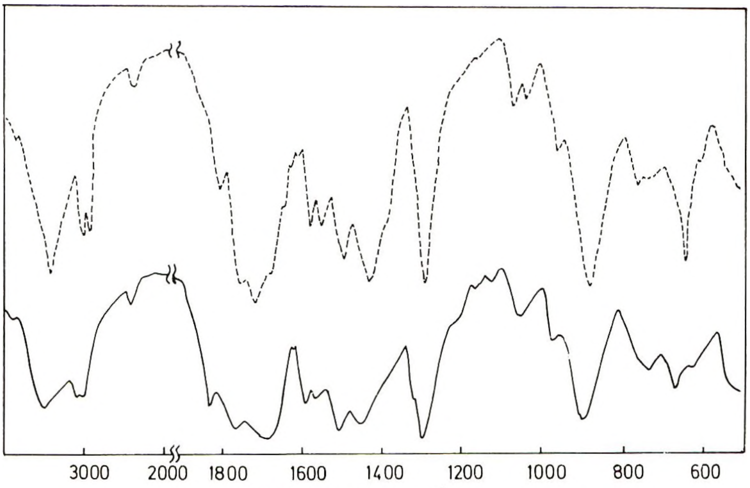


Fig. 3. Infrared spectra of (——) poly(DSM) and (- -) poly(TSM) prepared at 0 and 100°C, respectively; KBr disks.

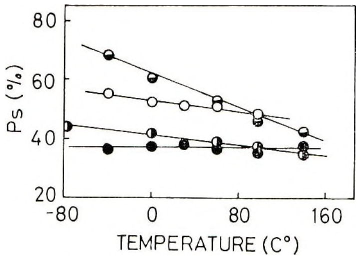


Fig. 4. Plots of P_s vs. polymerization temperature: (○) TSM; (◒) MMA-ZnCl$_2$ (1:) complex; (◑) MMA; (●) DSM.

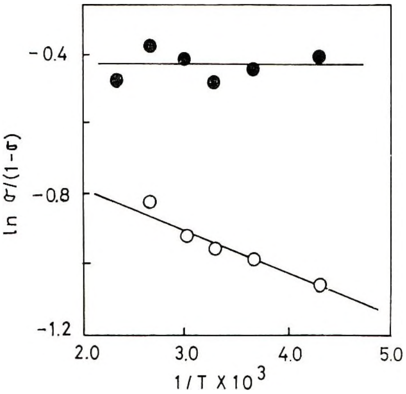


Fig. 5. Plots of ln $[\sigma/(1 - \sigma)]$ vs. $1/T$: (●) DSM; (○) TSM.

tactic addition in the propagation reaction. Thus the σ values calculated from P_s values are also shown in Tables III and IV.

Since $(1 - \sigma)$ denotes the probability of syndiotactic addition, the relationship (1) was reached:

$$\sigma/(1 - \sigma) \equiv k_i/k_s = \exp\{-\Delta\Delta H\ddagger/RT\} \exp\{\Delta\Delta S\ddagger/R\} \tag{1}$$

where k_i and k_s are rate constants for isotactic and syndiotactic additions, respectively. Accordingly the differences in activation enthalpies $[\Delta\Delta H\ddagger = (\Delta H_i\ddagger - \Delta H_s\ddagger)]$ and in activation entropies $[\Delta\Delta S\ddagger = (\Delta S_i\ddagger - \Delta S_s\ddagger)]$ between isotactic and syndiotactic additions are determined from the plots of log $[\sigma/(1 - \sigma)]$ against the reciprocal absolute temperature. The plots are shown in Figure 5, and the resulting activation parameters are summarized in Table V. The results for related monomers are also indicated.

As can be seen from Table V, the differences in activation enthalpy and entropy for DSM and TSM were smaller than those for MMA. They were close to those for zinc methacrylate and 1:1 MMA-ZnCl$_2$ complex and also for *tert*-butyl[33] and methyl methacrylates[28] which have bulky ester alkyl groups. In general, the isotactic addition in methacrylate monomers was favored with an increase in bulkiness of the ester alkyl group,[33,34] contrary to the preference of syndiotactic addition in MMA.[32] Accordingly,

TABLE V
Differences in the Activation Parameters Between Isotactic and Syndiotactic Additions

Monomer	$\Delta\Delta H\ddagger$ (= $\Delta H_i\ddagger - \Delta H_s\ddagger$), cal/mole	$\Delta\Delta S\ddagger$ (= $\Delta S_i\ddagger - \Delta S_s\ddagger$), eu	Reference
DSM	~0	−0.856	Present work
TSM	229	−1.09	Present work
MMA	960	0.94	10
Zinc methacrylate	119	−0.735	30
MMA–$ZnCl_2$ (1:1) complex	100	−0.70	10
tert-Butyl methacrylate	690	−0.16	33
Menthyl methacrylate	230	−0.14	34

in the radical polymerizations of DSM and TSM, the isotactic addition is favored by the presence of the bulky trimethylstannyl or dimethylmethacroylstannyl group and approaches the random addition value ($\sigma = 0.5$).

Copolymerizations of DSM and TSM

The radical copolymerizations of DSM and TSM (M_1) with styrene (M_2) were carried out at 60°C in DMF. The resulting copolymerization composition curves are shown in Figure 6, from which the monomer reactivity ratios were determined as is shown in Table VI. It was clear that the copolymerization reactivities of DSM and TSM toward styrene were quite different.

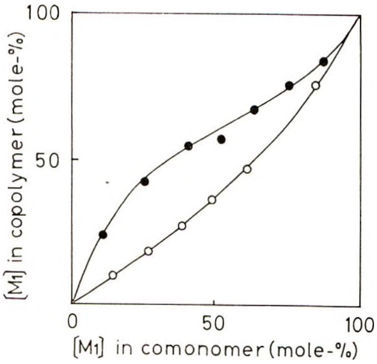


Fig. 6. Monomer–copolymer composition curves for the copolymerizations of (○) TSM and (●) DSM (M_1) with styrene (M_2).

The Q_1 and e_1 values for DSM and TSM are summarized in Table VII, in which the results for other related monomers are also indicated. DSM had larger Q_1 value than MMA, but its positive e_1 value was identical. However, it was noted that the Q_1 value of TSM was smaller than that of MMA, and its e_1 value was negative. Such a difference in the e_1 values between

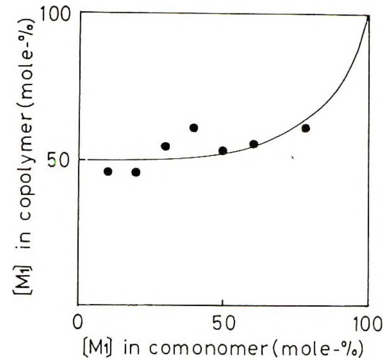


Fig. 7. Monomer–copolymer composition curve for the copolymerization of TSM (M_1) with maleic anhydride (M_2).

DSM and TSM was substantiated by their respective NMR spectra (Fig. 2), i.e., chemical shift of the methylene protons for DSM (3.75 and 4.38 τ) was larger than that for TSM, (3.92 and 4.50 τ), suggesting that the electron density of the carbon-carbon double bond of TSM was higher than that for DSM.[35] The negative e_1 value for TSM was also confirmed from the co-

TABLE VI

Monomer Reactivity Ratios for the Copolymerizations of DSM and TSM

M_1	M_2	Temperature, °C	r_1	r_2
DSM	Styrene	60	0.83	0.28
TSM	Styrene	60	0.53	1.57
TSM	Maleic anhydride	50	0.20	0.00

TABLE VII

Comparison in Copolymerization Parameters of Some Methacrylates

M_1	M_2	Temperature, °C	Q_1	e_1	Reference
DSM	Styrene	60	1.36	0.41	Present work
TSM	Styrene	60	0.45	−0.37	Present work
Zinc methacrylate	Styrene	60	1.45	0.68	30
MMA–$SnCl_4$ (1:1) complex	Vinyl chloride	60	2–4	0.4–1.0	9
MMA	Styrene	60	0.74	0.40	37
Methacrylic acid (pH 1.2)	DEAEMA[a]	70[b]	3.0	0.7	35
Methacrylic acid (pH 7.2)	DEAEMA[a]	70[c]	0.9	−1.0	35
Methacrylyl triethylgermanium	—	—	0.84	−0.64	36

[a] Diethylaminoethyl methacrylate.

[b] About 99.9% of methacrylic acid is not ionized.

[c] About 99% of methacrylic acid is ionized.

polymerization data with maleic anhydride: The resulting copolymers had a high alternating tendency (Fig. 7, Table VI).

A negative e_1 value was found for TSM, methacrylyltriethylgermanium,[36] and ionized methacrylic acid[37] (Table VII). A weaker electron-withdrawing nature of the COO^- group than for COOR and COOH groups would lead to a negative e_1 value. Similarly, the difference in Q_1 value between DSM and TSM might be explained from the ionic nature of the Sn-O bond.

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Polyarylsulfones, Synthesis and Properties*†

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Synopsis

A new class of high molecular weight polyarylsulfones is described. Polymer synthesis and structure-property relationships are discussed. The polymers are prepared by Friedel-Crafts type polycondensation of aromatic sulfonyl chlorides with aromatic hydrocarbons. A number of Lewis acids in small quantities are useful as catalysts for the polymerization. The polymerization reaction is carried out at elevated temperatures in the melt or in solution. Inert, nonbasic solvents which are compatible with the Lewis acid catalysts such as nitrobenzene and dimethyl sulfone are useful for conducting the polymerization. Many of the polyarylsulfones are amorphous, rigid thermoplastics with unusually high softening points, having glass transition temperatures in the range of 200-350°C. Outstanding resistance to air oxidation at high temperatures is derived from incorporation of the deactivating sulfone groups in the aromatic polymer backbone. Melt stability and solubility in selected solvents are emphasized as basis for processibility by conventional solution casting and molding techniques. The combination of properties, which in addition to thermal stability includes a high level of mechanical and electrical properties, chemical inertness, and hydrolysis resistance makes these new arylsulfone polymers useful over a wide temperature range and in severe and corrosive environments.

INTRODUCTION

Intensive research has been devoted within the last ten to fifteen years to the development of plastics stable at high temperatures. Advanced design concepts have created new demands and pushed the temperature requirements into ever higher regions. The need for more thermally stable materials in the aerospace industry is well known. To meet this challenge polymer research is aimed at providing new polymeric materials serviceable in the 200-500°C range.

The first high-temperature polymers were, of course, the fluorocarbons and silicones. The more recent materials to appear have been based mainly on heterocyclic and aromatic building blocks, as, e.g., the polybenzimidazoles and polyimides.[1-3] Most of these heteroaromatic polymers, however, are difficult to process because of inherent high rigidity and intractability. Their behavior and properties are often similar to those of

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

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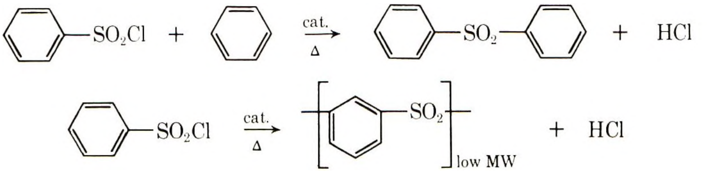
the thermosetting resins. Many of the polymers in the heterocyclic class are "B" stage materials which are converted to their final polymer structure during fabrication to the end product. This reaction usually involves elimination of a volatile by-product and in certain applications this presents serious problems to the processor.

This paper describes the synthesis and properties of a series of new high molecular weight polymers, called polyarylsulfones, which possess exceptional thermal and oxidative stability, and which can be processed as *bona fide* thermoplastics by conventional molding and solution casting techniques.

DISCUSSION

Adaptation of the well known Friedel-Crafts condensation of aromatic sulfonyl chlorides with aromatic compounds to polymer formation has provided a practical and versatile route to a series of new aromatic sulfone polymers.[4–8] The general reaction involved is illustrated by eqs. (1)–(4).

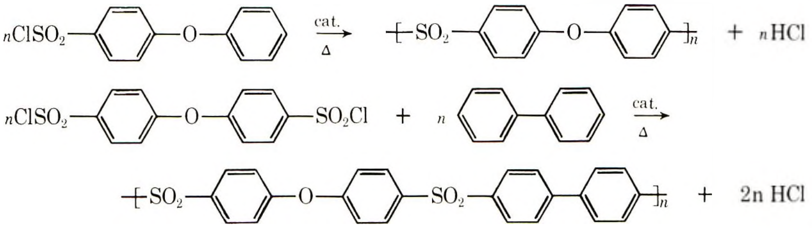
Model Compound Reaction:



(1)

(2)

Polymer-Forming Reactions:



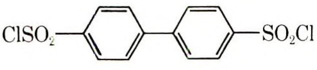
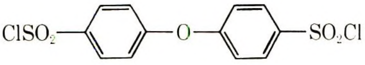
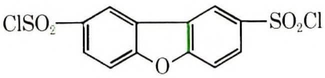
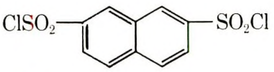
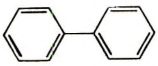
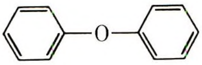
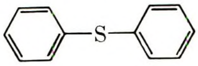
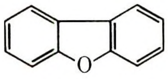
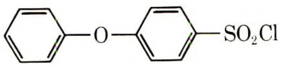
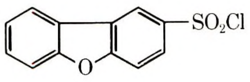
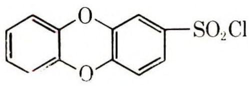
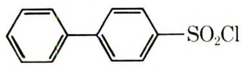
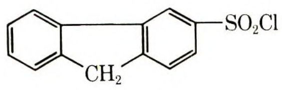
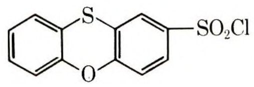
(3)

(4)

Monomers

The underlying principle in the polymer forming reactions which dictates the choice of operable monomers and provides the basis for achieving high molecular weight linear polymers is the deactivating effect of the sulfone group on the aromatic ring to which it is attached or becomes attached during the course of polymerization. With proper choice of reaction temperature and stoichiometric balance of reactants, this deactivation is sufficient to prevent higher than monosulfonylation in any one aromatic ring. Chain branching or crosslinking thus can be prevented. To provide for chain growth on the other hand, it is necessary that the terminal arylsulfone unit provide a reactive aromatic ring which can participate in the propagating reaction step. This requirement is conveniently met by the use of dinuclear aromatic structures such as biphenyl or related bridged diaryl compounds having two aromatic nuclei more or less independent of each other. A representative list of suitable monomers is shown in Table I.

TABLE I
Monomers

Monomer	Mp, °C
	212–213
	131–132
	219–220
	159–160
	69.5–70.5
	27–28
	
	82.5–83.5
	42–43
	140–141
	95–96
	115–116
	158.5–160
	128–129

Catalysts and Solvents

Much of the success in this new polymer synthesis is due to a unique catalytic activity of certain Friedel-Crafts catalysts. In contrast to the acylation with carboxylic acid chlorides, which requires molar amounts of Friedel-Crafts catalysts,[9] the sulfonylation with sulfonyl chlorides has been reported to proceed in high yield in the presence of only small, catalytic quantities of anhydrous ferric chloride.[10,11] This true catalytic nature of the sulfonylation reaction with sulfonyl chlorides seems to have received little general attention by investigators from either the synthetic or the kinetic viewpoint.

Other Lewis acid catalysts which we have found to be highly active and useful in the polymerization reaction are antimony pentachloride, molybdenum pentachloride, indium trichloride, and trifluoromethanesulfonic acid. At reaction temperatures of about 100–250°C these compounds are sufficiently active in concentrations of 0.1–1.0 mole-%.

Although the polymerization reaction can be carried out in the melt, it is preferable to use a diluent as reaction medium. Melt polymerizations require unduly high reaction temperatures in order to provide adequate mobility for the growing polymer chains. The choice of suitable solvents is rather narrow, however, due to the limited solubility of the arylsulfone polymers, and the particular nature of the Friedel-Crafts type condensation reaction. The polymerization solvent must be compatible with the strong Lewis acid catalysts and be stable towards electrophilic attack by the sulfonyl chloride. Several classes of inert solvents that have been employed in the polymerization are: chlorinated hydrocarbons [$Cl_2HC\text{-}CHCl_2$, Arochlor (Monsanto)]; nitro compounds ($C_6H_5NO_2$, *m*-chloronitrobenzene, $CH_3CH_2NO_2$); and sulfones [$CH_3SO_2CH_3$, $CH_2CH_2CH_2CH_2\text{-}SO_2$, $(CH_3\text{-}C_6H_4)_2SO_2$]. Nitrobenzene and dimethyl sulfone are the most practical and preferred polymerization solvents. For best results, high purity is essential in the solvents, as well as in the monomers. This includes the absence of water contamination and operation under a dry atmosphere.

Polymer Structure and Properties

A wide range of structural modifications and "tailor-made" properties are available through proper choice of monomers and various comonomer combinations. The solubility and softening temperature of the polymers, for example, can be varied considerably with a change in the ratio of the sulfone groups to the other heteroatom linkages. As a rule, every aromatic ring is connected to at least one sulfone group. If the heteroatom bridges, such as oxygen and sulfur, are replaced by directly joined aromatic nuclei or by condensed heterocycles, more rigid and successively higher softening and less soluble polymers are obtained. An illustration of this structure-property relationship and the range of properties available in this class of polymers are given in Table II.

In addition to exceptional thermal and oxidative stability the polyarylsulfones are resistant to hydrolysis, even in contact with strong acids and bases. They are basically colorless materials, since no chromophoric groups are present in the polymer chain. They have high softening points, with glass transition temperatures ranging from 200°C to over 350°C. Most of the polymers are noncrystalline; the high glass transitions therefore provide the basis for their utility at elevated temperatures. A significant structural feature of the polyarylsulfones is that they contain no aliphatic C—C bonds. They are thereby set apart from other engineering thermoplastics which have a mixed aromatic-aliphatic structure such as the polycarbonates and the recently introduced polysulfone and poly(phenylene oxide) products. These latter materials show excellent properties up to 150°C and in some instances up to 200°C but at higher temperatures they are either unstable or become soft and therefore lose their utility.

Thermal Stability

Evaluation of the high temperature stability of the polyarylsulfones has been carried out under various temperature conditions and environments.

An established method of measuring thermal stability in polymers is thermogravimetric analysis (TGA). This method measures the weight loss of a sample with increasing temperatures in controlled atmospheres. The exposure times usually are short (temperature increase approximately 5°C/min) and therefore only major changes are recorded. The characteristic inflection temperature in TGA curves indicates the onset of rapid thermal degradation.

The polyarylsulfones show a uniform behavior when tested by TGA (see Fig. 1). Modifications of the backbone structure within the scope discussed previously produce no significant change in the decomposition temperature. Catastrophic failure consistently occurs in the range of 520–540°C (950°F). The curves show roughly the same pattern both in air (oxidizing) and in nitrogen (inert) atmosphere, demonstrating the exceptional resistance of the arylsulfone polymers against oxidative degradation.

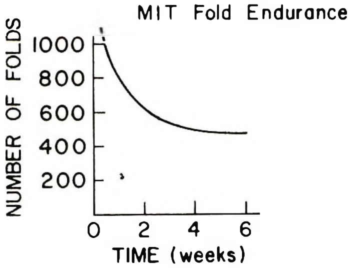
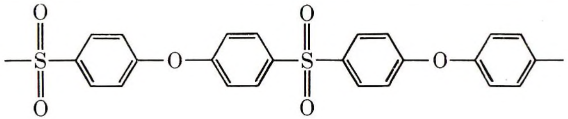
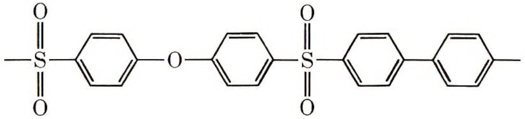
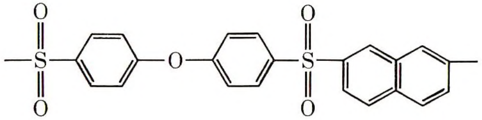
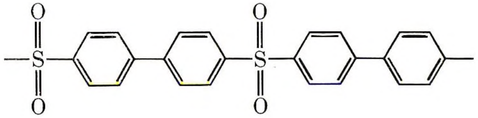
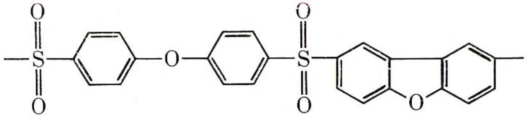
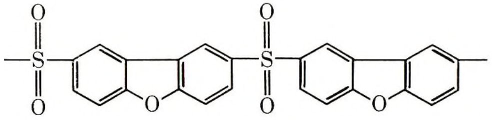


Fig. 1. Thermogravimetric analysis (TGA) for Polymer 380.

TABLE II
Polymer Structure and Properties

Polymer chain	η_{inh}[a]	T_g, °C	Solvents[b]	Morphology[c]	Compression molding temp., °F
	0.3–1.0	220	CH_2Cl_2, DMF, DMSO	Amorphous	550–600
	0.3–0.7	275	DMF, DMAC, BL	Slightly crystalline	650–700
	0.3–0.5	250	DMF, DMAC	Amorphous	650–700

	0.2	(mp >400)	Hot phenol, NMP	Crystalline	—
	0.3–0.5	290	DMF, DMAC	Amorphous	700–750
	0.3–0.5	360	NMP	Amorphous	800–830

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[a] Inherent viscosity measured in DMAC or NMP (1% conc., 25°C)

[b] DMF = dimethylformamide; DMAC = dimethylacetamide; DMSO = dimethylsulfoxide; BL = γ-butyrolactone; NMP = *N*-methylpyrrolidone.

[c] Determined by x-ray diffraction studies.

This behavior should receive particular note since most of the high temperature stable polymers in the heterocyclic-aromatic class show lower stability in air than in inert environments. It appears, therefore, that by incorporating the sulfone groups into the aromatic backbone, a significant enhancement of polymer stability has been achieved. The sulfone groups act as so-called "electron sinks" and deactivate the aromatic chain units. This results in chemical stabilization and an advantageous balance of polymer properties which is particularly evident in the resistance to thermooxidative degradation.

A more realistic picture of the thermal stability of the polyarylsulfones under temperature conditions of actual use is shown in Figure 2. Here are summarized weight loss data during prolonged aging at 260°C (500°F), 315°C (600°F), and 370°C (700°F) in air. The weight losses after 1000 hr aging at 260 and 315°C are 1–2% and 4–8%, respectively. At 370°C, approximately 15% weight loss occurs after 100 hr. The 15% level of weight loss usually represents the upper limit as far as retention of mechanical strength and practical utility of the material is concerned.

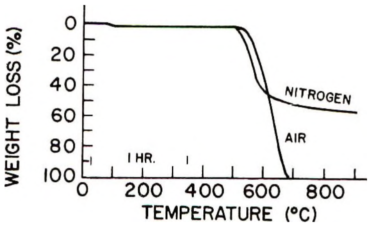

Fig. 2. High temperature aging in air for Polymer 380.

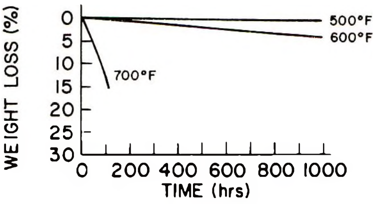

Fig. 3. Aging in air at 600°F for Polymer 380; MIT fold endurance.

Certain mechanical properties, e.g., the toughness and flexibility of a film, are sensitive to much smaller changes in the chemical composition of the polymer than can be measured by weight loss tests. Two major processes known to occur in thermooxidative degradation are chain scission and crosslinking. Both lead to embrittlement of the polymer. The effect of long-term aging at 315°C (600°F) in air on the film properties of a representative polyarylsulfone (Polymer 380) is shown in Figure 3 which summarizes data on MIT fold endurance (number of folding cycles over an angle of 270° under a load of 1.5 kg, film thickness 1–1.5 mil; ASTM D2176-63T) of film aged over a period of six weeks.

Although the number of folds after six weeks decreased to about one third of the initial value, the material was still tough and flexible. The tensile properties remained practically unchanged during this period.

300 Series Polymers

Several members of the polyarylsulfone family have been evaluated in modifications tailored to specific applications. Chemically these are copolymers composed of phenylene and biphenylene units linked by sulfone and ether oxygen groups. They are called the 300 series polymers. Within this designation fall the Polymer 380 film and coating formulations, and the Polymer 360 molding resin.[12–14]

General physical properties of Polymer 380 film are shown in Table III. In addition to the outstanding thermal and aging characteristics (see Figs. 1, 2, and 3), Polymer 380 film also has excellent electrical insulating properties. The dielectric constant is 3.85 at 23°C/100$^{\mathrm{Hz}}$ and remains flat up to 200°C. The dissipation factor increases from 0.004 at room temperature to 0.009 at 200°C/100$^{\mathrm{Hz}}$. The dielectric strength is 3200 V/mil at room temperature and 2800 at 260°C. The combination of thermal, mechanical, and electrical properties, including hydrolytic resistance, chemical inertness and abrasion resistance makes this polyarylsulfone film useful over a wide temperature range and in severe and corrosive environments.

The inherent properties of the polyarylsulfones also adapt them to use as base resins for high temperature resistant protective and decorative coating formulations. They possess attractive solution properties and allow fast and convenient application by conventional brush, spray, and dip coating

TABLE III
Properties of Polyarylsulfone Film (Polymer 380, 2 mil, 23°C)

Property	Value	Test method
Color	Clear, light beige	
Specific gravity, g/cc	1.35	ASTM D1505-63T
Tensile strength, psi	13,000	ASTM D882-64T
Tensile strength (oriented), psi	18,000	
Elongation, %	10	ASTM D882-64T
Elongation (oriented), %	50	
Tensile modulus, psi	300,000	ASTM D882-64T
Glass transition temp, °C	310	Differential thermal analysis
Heat distortion temp, °C	315	400 psi, 2% elongation
Morphology	Amorphous	X-ray
Flammability	Self-extinguishing	1/2 in. gas flame, 60 sec impingement time
Moisture absorption (50% R H), %	2.1	

techniques. No chemical curing reactions are required during the drying cycle. A solvent mixture of *N*-methylpyrrolidone (60%) and toluene (40%) has been used in most spray coating formulations with air pressure application. These formulations have been evaluated as clear, semigloss and flat lacquers. Table IV shows some typical physical properties of a semigloss spray coating on 16 gauge aluminum panel. The rigid, aromatic backbone structure of the polyarylsulfone is reflected in the excellent abrasion resistance and hardness of the coating. The impact resistance is outstanding.

TABLE IV
Physical Properties of Polyarylsulfone Coatings
(Polymer 380C, on 16-gauge aluminum)

Property	Value	Test method
Adhesion, %	100	Tape pull, $^1/_{16}$ in. × hatch
Hardness (73°F)	7H	Pencil scratch
Abrasion resistance, g/1000 cl	0.030	Taber, CS-17, 1 kg
Impact resistance, in./lb	120–160	Gardner, face and reverse
Flexibility		
73°F	$^1/_{32}$ in. (passes)	Mandrel bend
−273°F	$^1/_4$ in. (passes)	Mandrel bend

Since the base resin does not contain any hydrolyzable linkages it is not affected by steam or acids and bases in general. Solvent resistance is also excellent towards the nonpolar hydrocarbons, alcohols, fuels, Freons, silicone oils, etc. Chlorinated hydrocarbons, ketones, and other polar solvents tend to swell or in specific cases dissolve the polymer. Weather-ometer exposure data indicate relatively poor stability of the clear Polymer 380C coatings against ultraviolet radiation. With high pigment loadings, however, the weathering stability can be improved to an acceptable level for outdoor applications.

Since the polyarylsulfones generally are true thermoplastics, a molding grade polyarylsulfone has been developed called Polymer 360 (commercially available as Astrel Brand 360 Plastic). Polymer 360 has been tailored to combine high temperature serviceability with optimum moldability permitting fabrication by compression, extrusion, and injection molding. The high glass transition temperature of this polymer requires substantially higher processing temperatures than are normally employed for thermoplastics. The high fabrication temperatures, however, do not pose a degradation problem to the polymer. A list of the general physical and mechanical properties of Polymer 360 is shown in Table V. The properties of this polymer are obviously advantageous for uses at elevated temperatures. It extends the temperature capability of molded structural and electrical components from the current limit of about 180°C to above 250°C

TABLE V

Properties of Polyarylsulfone Molding Resin (Polymer 360)

Property	Value	Test method
Specific gravity	1.36	
Tensile strength, psi		
Room temperature	13,000	ASTM D-1708
500°F	4300	
Elongation, %		
Room temperature	10–20	ASTM D-1708
500°F	7–10	
Tensile modulus (room temperature), psi	370,000	ASTM D-638
Notched Izod impact strength, ft/lb	2–4	ASTM D-256
Glass transition temperature, °F	550	Differential thermal analysis
Heat deflection temperature, °F	525	ASTM D-648-56 (air oven) at 264 psi
Compression molding temperature, °F	700–750	
Extrusion temperature, °F	650–700	
Injection molding temperature, °F		
Cylinder	700–800	
Mold	450–500	
Hardness	M 110	Rockwell
Water absorption (24 hr), %	1.4	
Flammability	Self-extinguishing	ASTM D-635-56T

(350–500°F). The polymer essentially moves the usage of thermoplastics into the thermosetting resin and metals range.

EXPERIMENTAL

Materials

Hydrocarbons

Hydrocarbon monomers, such as biphenyl, diphenyl, ether, etc. were purchased from commercial sources (Matheson, Coleman & Bell, Dow Chemical Company, Monsanto) and purified by vacuum distillation through a short fractionating column or recrystallized from petrol ether–heptane with application of decolorizing charcoal.

Monosulfonyl Chlorides

The monosulfonyl chlorides of diphenyl ether and biphenyl were prepared according to known procedures[15–17] from the corresponding sulfonic acids by treatment with thionyl chloride in the presence of dimethylformamide, and purified by recrystallization from petrol ether–chloroform.

Disulfonyl Chlorides

The disulfonyl chlorides were prepared by chlorosulfonation with excess chlorosulfonic acid[18] or, alternatively, by chlorination of the disulfonic acids or their sodium salts with thionyl chloride or phosphorus pentachloride[15–17] and purified by recrystallization from chloroform or benzene.

Solvents

Nitrobenzene (Matheson, Coleman & Bell, National Aniline) was dried over phosphorus pentoxide and vacuum-distilled. Dimethyl sulfone (Crown-Zellerbach) was recrystallized from chloroform, mp 109–110°C. Arochlor 1248 was purchased from Monsanto Chemical Company.

Polymerization

A typical polymerization was carried out as follows. A dry, round-bottomed three-necked flask or glass-lined reactor equipped with a stirrer, nitrogen inlet, and temperature-control system was charged with stoichiometric quantities of the disulfonyl chloride and hydrocarbon monomers or the self-condensable monosulfonyl chloride. Nitrobenzene was added to obtain a solids concentration of about 30–50%. The reactor contents were heated to 120°C and 0.3–1.0% of catalyst (w/w based on polymer) was added. The reactor temperature was then raised to 130°C over a period of 1 hr (higher reaction temperatures may be necessary if other solvents are used) and maintained at this temperature for about 20 hr or until a sample taken from the reactor showed an inherent viscosity of at least 0.3 (dimethylacetamide, 1%, 25°C). The polymer was then diluted further with dimethylformamide or *N*-methylpyrrolidone to 20% solids content and used as such for the casting of films or directly precipitated into a bath of methanol or acetone with high shear agitation. The precipitated polymer crumb was extracted in boiling methanol and dried at temperatures up to 500°F to remove residual solvent.

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1,2-Dinitrile Polymers. III. Number-Average Molecular Weight by Pulsed NMR Technique*

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Synopsis

In studies of various polymers in the solid state by pulsed and wide-line NMR, a relationship between the spin-lattice relaxation time and the fraction of mobile protons in the polymer sample was observed. This effect has been used to determine the degree of polymerization of a series of fumaronitrile homopolymers. The technique should have wide applicability in the direct determination of the number-average molecular weight $\bar{M}_n$, especially for polymers that may be insoluble and/or infusible though not crosslinked.

INTRODUCTION

Molecular weight and its distribution are of fundamental importance for all polymers. Common methods for determining these properties require that the polymers are soluble in suitable solvents at ordinary conditions. If the polymer is insoluble and/or infusible there is little in the way of determining these properties today. High temperature polymers, particularly those containing heterocyclic nitrogen, have shown poor solubility and/or fusibility properties. As a result, direct molecular weight determinations have been few.

Polymerization of a variety of 1,2-dinitriles[1–3] leads to thermally stable, intensely colored materials which do not fuse, but are soluble in strong acids upon heating. Direct molecular weight determination by osmometry, light scattering, or sedimentation velocity determinations in the ultracentrifuge can not be performed on such dark colored acidic solutions. However, investigations of these polymers in the solid state by pulsed and wide-line NMR techniques showed differences in the structures of the respective spectra which varied uniformly with the change in the molecular weight of the polymers. As a result, we would like to propose a new technique for direct determination of the number-average molecular weight, especially, for polymers that may be insoluble and/or infusible though not crosslinked.

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

EXPERIMENTAL

Materials

Fumaronitrile, mp 96–97°C, was used as received from K and K Laboratories. Di-*tert*-butyl peroxide, 99 ± 1%, from Lucidol Division of Wallace and Tiernan was used as the initiator; *tert*-butanol, mp 24.5–25.5°C, was used as received from Matheson, Coleman and Bell.

Homopolymerization

The polymerizations were conducted in bulk in specially made glass tubes ($^3/_8 \times 11$ in.) that fitted the sample holder of the NMR instrument. Fumaronitrile (1.0 g) and subsequently di-*tert*-butyl peroxide (0.04 g) were charged under nitrogen into the tubes; the tubes were closed with a cork and then placed in a constant temperature bath at 160°C for different periods of time. The initially water clear liquid turned brown and finally black within about 10 min. The polymers were obtained as a mixture of black solid particles. Next, the tubes were attached to a high-vacuum (10^{-5} Torr) system and evacuated at 110°C for a minimum of 8 hr to remove unreacted monomer along with any other low molecular weight materials if formed. The high-vacuum sublimation was used in preference to methanol extraction to insure that no extraneous sources of protons would be introduced in the polymers. The polymers were kept under nitrogen at all times during preparation.

Relaxation Time Measurements

The pulsed NMR equipment has been described previously.[4] Relaxation time measurements were made at 38 MHz, and the sample temperature could be controlled from −175 to +150°C. Approximately 0.2–0.3 cm^3 of the polymer was transferred to a 8-mm Pyrex tube under nitrogen, then thoroughly degassed ($<10^{-5}$ Torr) and sealed under 0.5 atm helium to facilitate thermal equilibration. The *tert*-BuOH was degassed by the freeze-thaw technique, then sealed under helium.

As all the materials exhibited exponential relaxations, the t_{null} technique of Carr and Purcell was used to measure the spin-lattice relaxation time T_1.[5] All values were perfectly reversible with respect to temperature.

RESULTS

Fumaronitrile Homopolymers

All of the free-radical-initiated fumaronitrile polymers with $\eta_{\text{inh}} > 0.12$ dl/g have been found to be infusible and soluble only in such strong acids as concentrated sulfuric, phosphoric, methanesulfonic, or fuming sulfuric acid. Ultraviolet spectra of the homopolymers in sulfuric acid changed as the acid was diluted. The behavior was typical of a polybase in strong acid and similar to many other compounds that undergo protonation.[6]

Early in the work, fractionation of these polymers was unsuccessfully attempted from concentrated sulfuric acid or methanesulfonic acid by the addition of water or methanol. With neither nonsolvent could gradual precipitation be induced; instead the solution became turbid over a period of hours and finally almost complete precipitation of the polymer occurred. This behavior indicates some sort of strong molecular aggregation tendency which is different from the dilute solution properties of "ordinary" polymers. Homopolymers which were scarcely soluble in methanesulfonic acid were dissolved in fuming sulfuric acid, however, with irreversible changes in the polymer. The polymer which was reprecipitated from fuming sulfuric acid solution contained sulfone and sulfate groups according to the infrared spectra and was readily soluble in methanesulfonic acid. This led us to a more detailed investigation of the sulfuric and methanesulfonic acid-treated materials, which showed that with heating in these solvents both sulfone and sulfate groups were introduced and the molecular weight was decreased. The extent of degradation in hot methanesulfonic acid is illustrated in Table I. As a result, all our inherent viscosity values on 1,2-dinitrile polymers determined in hot methanesulfonic acid are probably low.

TABLE I
Degradation of Fumaronitrile Homopolymer in Methanesulfonic Acid at 132°C[a]

Heating time, min	η_{inh}, dl/g
0	0.203
2	0.191
30	0.090
150	0.063

[a] For degradation studies, 0.10 g samples in 10 ml of methanesulfonic acid were used.

The x-ray powder-scattering pattern for the polymers showed them to be noncrystalline. Only one diffuse ring centered at a Bragg spacing of 3.5–3.6 Å was prominent which is characteristic of the interplanar separation of aromatic molecules with nearly planar symmetry.[7] This spacing is evidence for short-range packing of the repeat units of neighboring polymer chains giving the polymer characteristics of a crosslinked network. The mobility of such a molecular arrangement would be low. Differential scanning calorimetry on a fumaronitrile homopolymer (η_{inh} = 0.34 dl/g) gave only a smooth specific heat curve up to a temperature of 600°C, indicating no transitions in the room temperature to 600°C range. The lack of both the transition temperatures and crystallinity and the presence of the diffuse ring centered at a Bragg spacing of 3.5–3.6 Å is typical of other high-temperature heterocyclic polymers.

A preliminary investigation of the fumaronitrile polymers showed that the low-temperature spin-lattice relaxation times of this material were probably determined by motion of methyl protons. The only source of such protons is the di-*tert*-butyl peroxide initiator, which on decomposition yields *tert*-butoxy endgroups for the polymer chains. Thus, relaxation times observed would be expected to be sensitive to the concentration of end groups, and therefore to the number-average molecular weight of the polymer.

In order to investigate this effect, a series of polyfumaronitrile samples was prepared with the use of the di-*tert*-butyl peroxide initiator. The molecular weight was controlled by varying the polymerization time as indicated in Table II. The inherent viscosity of the samples increased with polymerization time, though this trend is only qualitative because of the degradation of the material referred to previously. All the polymers were obtained as black powders which were infusible (except for sample I) and soluble in hot methanesulfonic acid.

TABLE II
Fumaronitrile Homopolymers[a]

Sample no.	Polymerization time, hr	Conversion, %	η_{inh}, dl/g[b]
1	4	10	0.101
2	8	40	0.118
3	16	57	0.203
4	32	71	0.246
5	64	83	0.340
6	124	88	0.340

[a] Samples (1.0 g) containing 0.04 g di-*tert*-butyl peroxide polymerized in bulk at 160°C. The analytical data on samples 2–6 was essentially the same (60.9 ± 0.2% C, 2.9 ± 0.1% H, 34.6 ± 0.2% N); compared to calculated values (61.51% C, 2.56% H, 35.9% N) the C and N contents were low with these polymers; however, the ratio of C to N in the polymers is the same as in the monomers, (1.76 versus 1.72, respectively).

[b] Sample 1 was dissolved in cold methanesulfonic acid; all the other samples were heated; viscosities were determined on solutions from 0.334 to 0.489 g/100 ml methanesulfonic acid at 30.0°C.

Relaxation Times

The temperature dependence of the spin-lattice relaxation rate ($1/T_1$) for five polymer samples is shown in Figures 1 and 2. The pronounced feature of the experimental curves is the peak at $-94°$C ($5.6 \times 10^{-3}/°$K). The most important point is the decrease in peak height with increasing polymerization time of the polymers, with a slight inversion for the last two samples. It should be noted that the slopes of these peaks also decrease with polymerization time. In addition there is a high-temperature relaxation process in these polymers, as seen by the upturn of the experimental points shown for samples 2 and 6. As this relaxation process has a relatively large temperature coefficient, it does not appreciably affect the low-temperature peak which is the focus of this work.

This low temperature relaxation peak is attributed to the reorientation of methyl protons on the *tert*-butoxy end groups of the polymer. As this

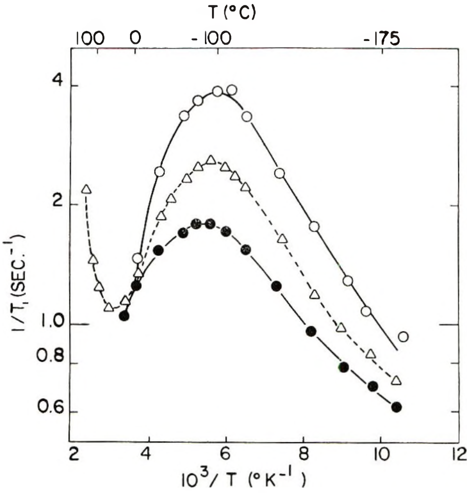


Fig. 1. Temperature dependence of the relaxation rate $1/T_1$: (○) sample 1; (△) sample 4; and (●) sample 3.

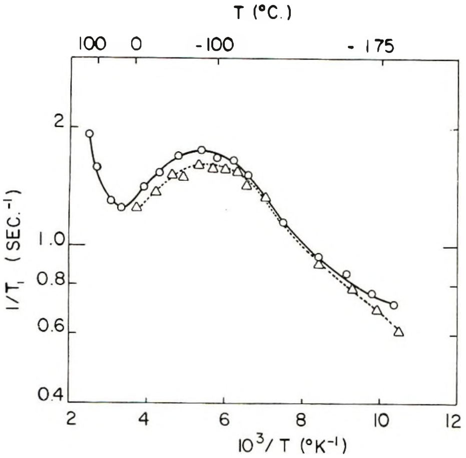


Fig. 2. Temperature dependence of the relaxation rate $1/T_1$: (△) sample 4; and (○) sample 6.

methyl relaxation is centered some 30°C lower in normal alkanes,[11,14] *tert*-butanol was investigated as a model compound for the spin-lattice relaxation associated with the end groups in question. Figure 3 shows the relaxation curve for *tert*-butanol, which exhibits a slightly asymmetric peak at -80°C (5.2×10^{-3}/°K). This is sufficiently near the -94°C peaks in Figures 1 and 2 to confirm that the relaxation in these polymers results from motion of the methyl protons. The 45°C temperature shift of the relaxation peak in *tert*-butyl groups (-80°C) with respect to that in normal alkanes (-125°C) undoubtedly reflects steric hindrance to rotation of the methyl groups in the alcohol. Comparison of Figure 3 with Figures

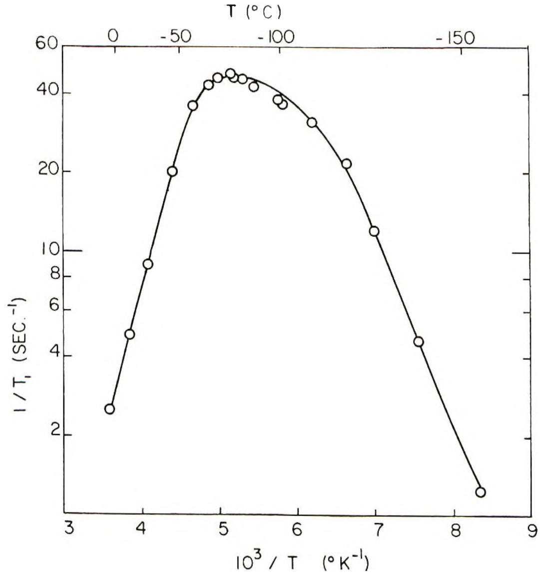


Fig. 3. Temperature dependence of the relaxation rate $1/T_1$ for *tert* butanol.

1 and 2 shows that the slopes for the peak in *tert*-butanol are some four times those for the polymer samples. This "broadening" indicates that a distribution of correlation times is present in the motion of the polymer methyl groups, as will be discussed below.

In addition, the slopes of the methyl peaks vary slightly within the polymer series itself. This is thought to result from the presence of unpaired electron spins in a concentration of about 10^{17} spins/cm^3 in these materials.[1-3] These spins give a temperature-independent contribution to the relaxation rate of about 0.25 sec^{-1} [9,10] and cause the 30% decrease in slope with increasing polymerization time mentioned above. This relaxation effect of the unpaired spins has been empirically subtracted from the experimental curves so as to obtain peaks with slopes equal to those of sample 1. The resulting peak heights, which are the net relaxation rates attributed to the terminal methyl groups, are given as $(1/T_1)_{\text{corr}}$ in Table III. This rough correction has a maximum effect of 30% on the relaxation rates, and in no way affects the validity of the present results.

TABLE III
Relaxation Rates and DP for Fumaronitrile Polymers

Sample no.	$(1/T)_{\max}$, sec^{-1}	$(1/T_1)_{\text{corr}}$, sec^{-1}	DP
1	3.90	3.90	53
2	2.60	2.40	87
3	1.80	1.45	153
4	1.57	1.13	197
6	1.75	1.25	180

DISCUSSION

Spin-Lattice Relaxation Rate

The macroscopic magnetic moment of an ensemble of nuclear spins usually approaches its equilibrium value exponentially with a time constant $1/T_1$, where T_1 is defined as the spin-lattice relaxation time. The relaxation rate $1/T_1$ depends on the effectiveness of local time-dependent magnetic fields, such as those arising from the thermal motion of neighboring spins, in inducing transitions between the nuclear spin states. For a system of protons the relaxation rate is given by an expression of the form[8]

$$\frac{1}{T_1} = k\left(\frac{\tau_c}{1 + \omega_0^2\tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2\tau_c^2}\right) \tag{1}$$

The constant k is strongly dependent on the distance between the neighboring magnetic dipoles and to a smaller extent reflects the nature of the relative motion of the spins. The correlation time describing the frequency of this motion is given by τ_c, and ω_0 is the NMR frequency. The expression in parentheses, and hence the relaxation rate, has a maximum when $\tau_c \approx \omega_0^{-1}$. If the thermal motion responsible for the relaxation can be described by an Arrhenius rate equation, a plot of ln $(1/T_1)$ versus reciprocal temperature will yield a symmetric V-shaped peak with slopes proportional to the activation energy for τ_c.

Relatively complex molecules contain certain protons which are much more mobile than others, especially in the solid state. It has been found, however, that all the spins in many such materials relax at the same rate, though according to eq. (1) the relaxation times of the mobile and immobile spins should be remarkably different. In these systems the mobile protons, which have a short relaxation time, act as "heat sinks" or relaxation sites for the immobile protons. The two groups of spins are coupled by a spin diffusion mechanism which relies on spin-spin exchange accompanying static dipolar interactions.[9,10] In the limit when this spin diffusion is much faster than the relaxation rate of the mobile protons, the observed relaxation rate of all the spins is given by:[11,12]

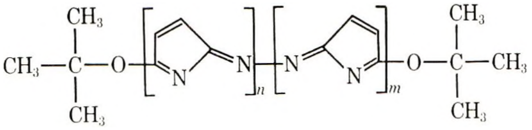
$$(1/T_1)_{\text{obs}} = X_{\text{m}}/T_1^{\text{m}} \tag{2}$$

Here X_{m} is the fraction of mobile protons in the sample, and T_1^{m} is the relaxation time of these protons as given by eq. (1).

The reorientation of a methyl group about its threefold axis is one of the most easily activated large-scale thermal motions in large molecules. The methyl protons generally exhibit a $1/T_1$ maximum ($\tau_c \approx 10^{-8}$ sec) below -100°C and can thus act as relaxation sites for the remaining protons in the molecule which are usually quite immobile at these temperatures. Perhaps the best example of this type of relaxation is the work of Anderson and Slichter,[11] which demonstrates that eq. (2) applies to normal alkanes up to n-$C_{40}H_{82}$. Connor reported a qualitatively similar effect in methoxy-terminated polyethylene oxides of different molecular weights.[13] Recent experiments in this laboratory on linear and branched polyethylenes have shown[14] that eq. (2) is valid in these materials for methyl proton concentrations (X_m) between 0.5 and 3×10^{-3}. Consequently, we propose to use this effect to determine the fraction of endgroups, and thus the degree of polymerization.

Degree of Polymerization

Before the spin-lattice relaxation data can be used to estimate the degree of polymerization in a sample, the following conditions must be assumed. (1) The polymer has essentially the structure I, where m = 0 or an integer.



I

The polymer would be expected to terminate predominantly by coupling of the growing chains or by combination with the initiator radical. Termination by disproportionation to monomer or chain transfer to polymer in this polymerization would be expected to be negligible. (2) The only source of methyl protons is the *tert*-butoxy endgroups. These are conditions that the previous structural work[1-3] and the present polymer workup and analytical data permit one to assume.

With this model the fraction of end group (methyl) protons is given by

$$X_m = \frac{N_m}{N_p(\mathrm{DP} - 2) + N_m} \tag{3}$$

In this expression N_m is the number of mobile protons per polymer molecule (18 for the two *tert*-butoxy endgroups, in this instance) and N_p is the number of protons per polymerized monomer unit (2 in this case). The degree of polymerization, DP, is the number of structural units in the polymer, and thus includes the two endgroups.

Still to be evaluated is T_1^m, which is the proportionality constant between the net relaxation rate $(1/T_1)_{\mathrm{corr}}$ and X_m. This was accomplished by applying eq. (2) to the methyl proton relaxation in *tert*-butanol, using the peak height in Figure 3. Substituting X_m = 0.9 (9 methyl protons in the molecule containing 10 protons), one obtains T_1^m = 19 msec. This is in excellent agreement with the value of 21 msec calculated from eq. (1). Before using such a value for the polymer samples, it should be realized that the small slopes found in these materials reflect a broad distribution of correlation times; such a distribution has the effect of raising T_1^m by as much as 100%.[15,16] In view of the large difference in slopes (apparent E_a = 3.4 kcal/mole for *tert*-butanol, apparent E_a = 0.8 kcal/mole for the polymers), the reasonable assumption that T_1^m is 38 msec will be used.

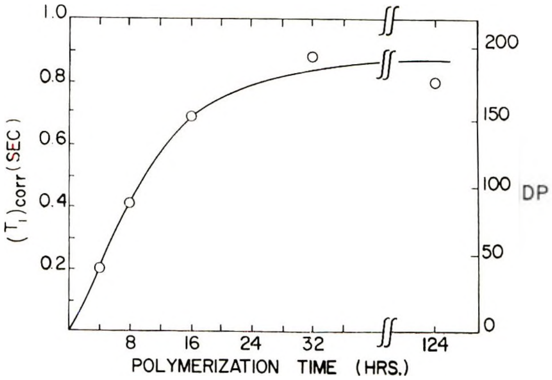


Fig. 4. Dependence of the reciprocal corrected peak height $(T_1)_{corr}$ on polymerization time for the fumaronitrile polymers. The DP ordinate on the right is calculated from eq. (3).

It is a simple matter at this point to solve for X_m for the polymer samples by using eq. (2) with $T_1{}^m = 38$ msec and the $(1/T_1)_{corr}$ values from Table III. This fraction of endgroup protons can be used to evaluate the degree of polymerization (DP) by eq. (4), which was derived from eq. (2) and (3):

$$\mathrm{DP} = \frac{N_m}{N_p}\left[\frac{(T_1)_{corr}}{T_1{}^m} - 1\right] + 2 \tag{4}$$

The results of eq. (4) are given in Table III and plotted in Figure 4. The left ordinate in Figure 4 is $(T_1)_{corr}$, the reciprocal of the corrected peak heights $(1/T_1)_{corr}$ in Table III. Note that the DP ordinate on the right is not quite linear, being expanded at low DP. In view of the assumptions made in the calculation, especially in the evaluation of $T_1{}^m$, the absolute DP values may be as much as 50% low, though this is thought unlikely. The relative values are accurate to within ±10%.

The DP values derived from the relaxation time measurements are corroborated by wide-line NMR studies in which the second moments of the absorption spectra of samples 2–6 were measured at −196°C. Because of the low yield at the shortest polymerization time, not enough material was available for obtaining a good wide line NMR spectrum of sample 1. In Figure 5 the observed second moments are plotted versus the degree of polymerization as noted in Table III. The curves shown in Figure 5 are theoretical estimates of second moment as a function of DP. The bottom curve is obtained for a random chain conformation; the two upper curves were calculated for a zigzag conformation of the conjugated polymer backbone, where the difference between these curves corresponds to the uncertainty of bond angles in the polymer chain. The curves start at a DP value of 2, i.e., pure di-*tert*-butyl peroxide, for which a second moment of 28.0 G^2 was measured at −196°C. The experimental second moments in Figure 5 indicate the zigzag conformation, which is consistent with extensive conjugation suggested by the black appearance of the material. The measured second moment shows no significant variation from one sample to

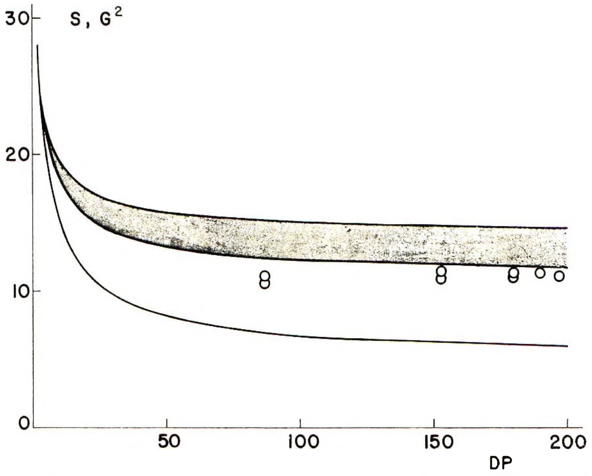


Fig. 5. The second moment S of the wide-line NMR absorption spectrum as a function of the degree of polymerization DP. Experimental values (○) were determined at $-19\,^\circ C^6$ for samples 2–6. The curves represent theoretical estimates (see text).

another, which is in good agreement with the degree of polymerization estimated above.

In concluding, two points should be made regarding the utility of the T_1 method. Ideally there should be no interfering relaxation mechanisms present (for this reason molecular oxygen, which is paramagnetic, should be rigorously excluded from the sample). In these fumaronitrile homopolymers, the high-temperature relaxation process (Figs. 1 and 2) creates no problem, but the relaxation from the unpaired electron spins does interfere slightly with the desired effect. The corrections applied above are necessarily approximate, but are small enough to not significantly affect the conclusions. Of more general interest is the sensitivity of the method. This depends primarily on the chemical constitution of the polymer, as this determines the concentration of methyl protons, and hence the relaxation strength, for a given degree of polymerization. For instance, letting DP = 150, the fumaronitrile polymer has $X_m = 5.7 \times 10^{-2}$, and $(1/T_1)_{corr} = 1.45$ sec^{-1}. A Phillips-type linear polyethylene of the same DP would have $X_m = 5.0 \times 10^{-3}$ and $(1/T_1)_{corr} \simeq 0.14$ sec^{-1}. The relaxation in the polyethylene is an order of magnitude less intense, and correspondingly more susceptible to any interfering relaxation mechanisms or other uncertainties. In addition, the fast spin-diffusion mechanism assumed in eq. (2) is not valid for very small values of X_m, though the lower limit has not yet been established. Other systems are being investigated to determine the generality of this method.

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Synthesis and Polymerization Studies of* 1,2-Dimethyleneoctafluorocyclohexane

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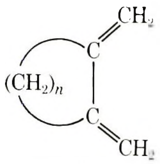
Synopsis

1,2-Dimethyleneoctafluorocyclohexane has been prepared by the pyrolysis of 2-chloromethyl-1-methyloctafluorocyclohexane. Free radicals initiate the polymerization of the diene in both bulk and emulsion systems to give a highly crystalline (mp 214–218°C) polymer that has an all-*cis* 1,4-structure. The polymer is insoluble in common laboratory solvents, but will dissolve in perfluorokerosene above 175°C and in 2,5-dichlorobenzotrifluoride above 150°C. This diene is not polymerized by cationic, anionic, or Ziegler-Natta catalysts. The diene is readily copolymerized with many common monomers to give soluble, high molecular weight polymers. Relative reactivity ratios have been measured with styrene by the Fineman and Ross method and Q–e parameters for the diene have been calculated.

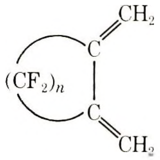
INTRODUCTION

Syntheses of several 1,2-dimethylenecycloalkanes (I) as precursors to *cis*-1,4-addition polymers have been reported.[1–11] Interest in the thermal and oxidative stability of fluorinated polymers prompted the synthesis of a series of highly fluorinated 1,2-dimethylenecycloalkane (II) monomers.[12–14] This report describes the synthesis and polymerization studies of one member of the latter series, 1,2-dimethyleneoctafluorocyclohexane (IIc).



I

(a) $n = 2$
(b) $n = 3$
(c) $n = 4$



II

(a) $n = 2$
(b) $n = 3$
(c) $n = 4$

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

EXPERIMENTAL

Analytical Methods

Infrared spectra were obtained with a Perkin-Elmer Infracord instrument. The NMR spectra were recorded with a Varian Associates A-60 spectrometer. Membrane osmometry and vapor-pressure osmometry measurements were made with a Hewlett Packard instrument and a Mechrolab vapor pressure osmometer, respectively. Viscosity measurements were made with Cannon-Oswald-Fenske and Cannon-Ubbelohde viscometers. Gas–liquid phase chromatography (GLPC) was carried out on an Aerograph A-90-P gas chromatograph by using 20% SF-96 on 30/60 mesh firebrick for all analytical work. Preparative GLPC was done with both 20% SF-96 on 60/80 mesh Chromosorb-P and 20% silver nitrate cyano-B tetraethylene glycol on 60/80 mesh Gas Chrom RA. Melting points of homopolymers were taken in open capillaries and those of copolymers on a flatiron.

Materials

All starting materials, catalyst components, and comonomers were used as received from commercial sources. Perfluorocyclohexene was obtained from Imperial Smelting Corp., Ltd., Avonmouth, England.

1,2-Dimethyloctafluorocyclohexene (IV). To a flask fitted with two Dry Ice condensers were added 2 l. of anhydrous ether and 40 g of lithium wire (0.5-in. sections) under nitrogen. Methyl bromide was condensed into the ether at 25°C until all the lithium had reacted. The methyllithium solution was cooled to −25°C, and 252 g of decafluorocyclohexene (III)in 170 ml of ether was slowly added. After stirring for 1 hr, the solution was warmed to room temperature and 10% hydrochloric acid was added to give a clear solution. The solution was washed with 5% aqueous sodium bicarbonate and then with water; the ether was removed after drying. The residue comprised 65% of the product IV, 15% 1-methylnonafluorocyclohexene, 5% starting material, and 10% of higher boiling materials. The residue was distilled and the compound IV collected at 92°C/190 mm. The pure alkene IV has bp 139°C/760 mm; NMR, τ 8.06 (t, J = 2.7 Hz); infrared, $\lambda_{\max}^{\text{neat}}$, 6.72, 7.83, 8.51, 9.07, 9.63, 10.75, 10.88, and 11.07 μ.

ANAL. Calcd for $C_8H_6F_8$: C, 37.81%; H, 2.38%; F, 59.81%. Found: C, 37.98%; H, 2.58%; F, 60.06%.

2-Chloromethyl-1-methyloctafluorocyclohexene (V). To 600 ml of carbon tetrachloride that contained 77.2 g of the olefin IV, was slowly added, through a Dry Ice condenser, 24.9 g of chlorine while irradiating with a commercial sun lamp. The solution was irradiated for 1 hr after the addition was complete, then washed with sodium bisulfite solution, water, and finally dried with calcium chloride. After removal of the solvent, the residue was distilled to give a main fraction that had bp 70–75°C/33 mm. The reaction gave 55% of the product V, 10% of 1,2-bis(chloromethyl)-

octafluorocyclohexene, and 20% of the starting material. The product V showed: NMR, τ 5.82 (s, 2.03) and 7.84 (t, 2.96, $J = 3.5$ Hz); infrared, $\lambda_{\max}^{\text{neat}}$, 8.49, 9.57, 10.25, and 10.81 μ; bp 169°C/760 mm.

ANAL. Calcd for $C_8H_5ClF_8$: C, 33.29%; H, 1.75%; Cl, 12.29%; F, 52.67%; MW 288.5. Found: C, 33.19%; H, 1.71%; Cl, 12.32%; F, 52.27%; MW 295 (Rast, carbon tetrachloride).

1,2-Dimethyleneoctafluorocyclohexane (IIc). Low-pressure, fast-flow pyrolysis was done in a vertically arranged 500 × 25 mm Vycor tube heated to 750°C in an electric oven. The low-pressure (20 mm) system consisted of a pear-shaped flask with a nitrogen inlet leading into the Vycor tube (containing a thermocouple) and then into two liquid nitrogen traps. The traps were attached to a vacuum system to maintain the pressure. A slow nitrogen stream was bubbled through 30 g of the chloride V in the pear-shaped flask, and the system was evacuated to 20 mm. The nitrogen stream was so adjusted that about 5–10 g/hr of the compound V was carried through the furnace. The trap residue was washed with aqueous sodium bicarbonate, water, and then dried. The pyrolyzate was then distilled from calcium carbonate, activated charcoal, and a small amount of hydroquinone to give a pale yellow fraction collected at 62°C/80 mm. The yield of recovered product was 70%. The diene was purified by preparative GLPC by using a 20% silver nitrate cyano-B tetraethylene glycol on 60/80 mesh Gas Chrom RA column at 50°C and a helium flow of 120 ml/min. The diene IIc showed: NMR, τ 4.02 (s, 1.02, half-height width 4 Hz) and 4.13 (s, 0.99, half-height width 2 Hz); infrared, $\lambda_{\max}^{\text{neat}}$, 5.28, 5.81, 7.60, 8.50, 8.98, 9.45, 9.91, 10.40, 10.82, and 11.03 μ; ultraviolet, $\lambda_{\max}^{\text{EtOH}}$ 207.5 mμ (log ϵ 3.85 ± 0.05); n_{D}^{20} 1.4637; d^{20} 1.618; bp 132°C/760 mm.

ANAL. Calcd. for $C_8H_4F_8$: C, 38.11%; H, 1.60%; F, 60.30%; MW, 252.11. Found: C, 37.86%; H, 1.70%; F, 60.09%; MW, 254 (Rast, carbon tetrachloride).

Hydrogenation of the Diene IIc. To a micro hydrogenation apparatus was added 15 ml of glacial acetic acid, 0.20 g of Adams catalyst, and 1.00 g of the diene IIc. In 75 min, 1.75 mole-equivalent of hydrogen was absorbed. The solution was filtered, neutralized, and extracted with carbon tetrachloride. About 10% of the theoretical yield of the dimethyl compound IV was obtained as indicated by GLPC analysis and by infrared and NMR spectra.

Hydrobromination of the Diene IIc. Into a Carius tube was added 0.25 g of the diene IIc and 4 ml of hydrogen bromide. The sealed tube was kept at room temperature for 12 hr, and heated on a steam bath for 4 hr, opened at −80°C, and warmed to room temperature. The liquid residue was washed with 5% aqueous sodium bicarbonate and dried. Analysis by GLPC, NMR, and infrared methods indicated a 46% yield of 2-bromomethyl-1-methyloctafluorocyclohexene (IX).

2-Bromomethyl-1-methyloctafluorocyclohexene (IX). To 2.0 g (7.90 mmole) of the alkene IV in 10 ml of carbon tetrachloride was added over a 15-min period 1.28 g (8.00 mmole) of bromine in 5 ml of carbon tetrachloride while being irradiated with a sun lamp. After 30 hr of irradiation the reaction mixture was washed with sodium bisulfite solution, water, and then dried. Removal of solvent and distillation gave 33% of the desired compound IX in addition to some 1,2-*bis*(bromomethyl)octafluorocyclohexene. The monobromo product IX showed: NMR, τ 4.98 (s, 2) and 7.90 (t, 3, J = 3.5 Hz); infrared $\lambda_{\text{max}}^{\text{neat}}$, 7.76, 8.50, 9.00, 9.45, 10.40, and 10.75 μ.

ANAL. Calcd for $C_8H_5BrF_8$: C, 28.68%; H, 1.50%; Br, 23.85%; F, 45.37%. Found: C, 28.90%; H, 1.68%; Br, 23.81%; F, 45.61%.

Preparation of the Mono-Adduct VI. To 10 ml of refluxing benzene was added 0.93 g (3.7 mmole) of the diene IIc and 1.65 g (7.2 mmole) of benzoyl chloride phenylhydrazone. Triethylamine (3 ml) was added over a 0.75 hr-period, and the refluxing was continued for 1.75 hr. The dark red solution was filtered, the benzene removed, and the thick red oil frozen in Dry Ice. The resulting solid was recrystallized once from absolute ethanol and 3 times from 95% ethanol to give 0.43 g (27%) of a compound that had mp 139.5–140°C; NMR, τ 2.40–2.73 (m, 5), 3.63 (s, 1), 4.02 (s, 1), and 6.26 (A-B quartet, J = 17 Hz, area 2); infrared, $\lambda_{\text{max}}^{\text{KBr}}$ 6.28, 6.71, 7.28, 7.63, 7.98, 8.38, 8.60, 8.99, 9.27, 9.72, 10.15, 10.72, 13.30, and 14.50 μ.

ANAL. Calcd. for $C_{21}H_{14}N_2F_8$: C, 56.73%; H, 3.16%; N, 6.28%; F, 34.05%. Found: C, 56.51%; H, 3.17%; N, 6.25%; F, 34.20%.

Preparation of the Di-adduct VII. To a stirred solution of 20 ml of ether that contained 1.10 g (4.37 mmole) of the diene IIc and 1.24 g (8.1 mmole) of benzaldoxime chloride cooled to 0°C there was added slowly 20 ml of 15% aqueous sodium hydroxide. The two-phase system was stirred for 1 hr, and the ether layer was washed with water and allowed to stand overnight. Long white needles (mp 253.5–254.5°C) crystallized from the ether, and more were obtained by concentrating the solution. The product showed: NMR, τ 2.26–2.50 (m, 10) and 5.83 (s, 4.3); infrared, $\lambda_{\text{max}}^{\text{KBr}}$ 6.90, 7.35, 7.56, 8.20, 8.51, 8.68, 9.64, 9.90, 10.35, 10.92, 11.41, 13.07, and 14.51 μ.

ANAL. Calcd. for $C_{22}H_{14}N_2O_2F_8$: C, 53.93%; H, 2.88%; N, 5.71%; F, 30.99%. Found: C, 53.69%; H, 2.79%; N, 5.53%; F, 30.95%.

Emulsion Polymerization of the Diene IIc. Polymerizations were carried out in 15-ml polymer tubes. To the polymer tube, while being flushed with nitrogen, was added freshly distilled water. The tube was cooled in Dry Ice and freshly distilled monomer IIc, emulsifier, and the chosen initiation system were added. The tube was frozen in liquid nitrogen and attached to a vacuum line with a nitrogen bleed. After being pumped out and refilled with nitrogen six times the tube was sealed at about 350 mm. After thawing, the sealed tube was rotated end-over-end in a constant temperature bath.

At the conclusion of the polymerization, the emulsion was poured slowly into rapidly stirred 95% ethanol that contained some hydrochloric acid and 2,6-di-*t*-butyl-4-methylphenol. The polymer was filtered and extracted in a Soxhlet with 95% ethanol for 24 hr after which it was dried *in vacuo* at 50–60°C.

Bulk Polymerization of the Diene IIc. The bulk polymerization was set up as described above except that the initiator was added before the monomer. At the conclusion of the polymerization the block of polymer was broken up and then stirred in 95% ethanol containing some 2,6-di-*t*-butyl-4-methylphenol and purified as above.

The best recipes based on yield and molecular weight for the bulk and emulsion polymerizations of the diene IIc are given in Table I.

TABLE I

	Parts (weight)
Bulk Polymerization	
Diene IIc	100
Azobisisobutyronitrile (AIBN)	0.5
Temp, 50°C	
Emulsion Polymerization	
Diene IIc	100
Water	500
Sodium stearate	5
Ferrous sulfate heptahydrate	0.4
Dihydroxyacetone	1
Cumene hydroperoxide	1
Temp, 50°C	

Homopolymer VIII. The polymer, obtained as described above, gave the following analytical data: NMR, τ 6.75 (s); infrared, $\lambda_{\max}^{\mathrm{KBr}}$ 7.43, 7.70, 8.02, 8.16, 8.31, 8.59, 9.12, 9.56, and 10.71 μ; mp 214–218°C.

ANAL. Calcd. for $C_8H_4F_8$: C, 38.11%; H, 1.60%; F, 60.30%. Found: C, 38.68%; H, 1.70%; F, 59.63%.

Copolymerization of the Diene IIc. All copolymerizations in both bulk and emulsion systems were carried out with the use of the same techniques described for the homopolymerizations. The comonomers were purified by distillation under nitrogen before use.

Emulsions: At the end of the reaction, the emulsion was slowly dropped into acidic 95% ethanol containing a few mg of 2,6-di-*t*-butyl-4-methylphenol. After washing with ethanol the copolymer was dissolved in acetone and precipitated with 95% ethanol containing 2,6-di-*t*-butyl-4-methylphenol. It was then dried *in vacuo* at 50–60°C.

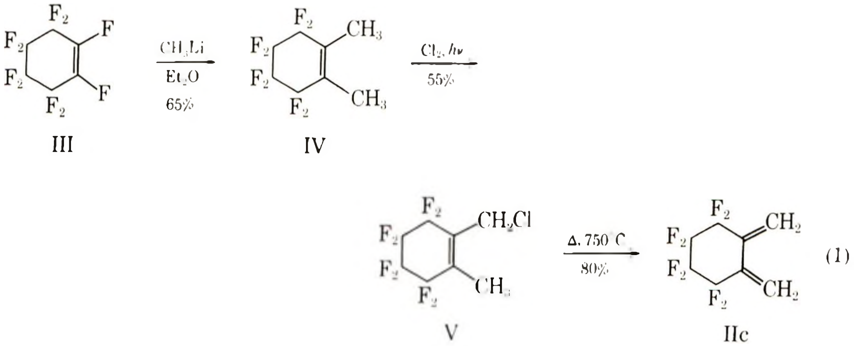
Bulk: At the end of the polymerization, the contents of the tube were dissolved in a few ml of acetone and precipitated as described for the emulsion copolymers.

Relative Reactivity Ratio Measurements. The various polymerizations were carried out by weighing into a 10-ml polymerization tube containing 1 mg (ca. 0.1% by weight of total monomers) of AIBN, both the diene IIc and styrene. The tubes were sealed under vacuum and rotated end-over-end in a 50°C bath until the first increase in viscosity of the monomers was observed (3–6 hr). About 2–3 ml of acetone was added to the contents of the tube, and the resulting solution was dropped slowly into stirred 95% ethanol. The precipitated copolymer was stirred in the ethanol for 0.5 hr and collected by centrifugation. The copolymers were washed once with 95% ethanol, centrifuged, and dried *in vacuo* at 50°C for 24–36 hr. The composition of the copolymers was determined by elemental analysis.

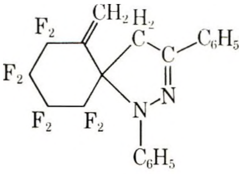
DISCUSSION

Synthesis of the Diene IIc

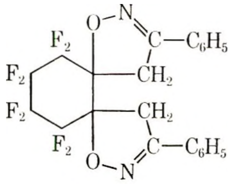
Sayers, Stephens, and Tatlow,[15] as part of a broad study of highly fluorinated cycloalkenes, have reported the preparation of the diene IIc by the dehydrochlorination of 2-chloromethyl-1-methyloctafluorocyclohexene (V) with alkali. The scheme shown as eq. (1), which was used to synthesize the dienes IIa, IIb, and IIC,[12,13] differs from that of Sayers, et al. mainly in the final step of the synthetic sequence. This represents the more favorable method for preparation of the diene IIc because the pyrolysis of the chloro derivative V affords the diene IIc in higher yield (80%) than does the chemical dehydrochlorination (28%) via reaction with a strong base.



The spectral data, elemental analysis, and physical constants of the diene are consistent with the postulated structure IIc and with the data published by Sayers et al. Catalytic hydrogenation and hydrobromination of IIc gave the known dimethyl compound IV and 2-bromomethyl-1-methyloctafluorocyclohexene IX, respectively. The bromo compound IX was also prepared by the allylic bromination of compound IV. As observed for the hydrocarbon members of this series, dienes IIa and IIb, the diene IIc failed to react with dienophiles, including tetracyanoethylene. The diene IIc reacts *via* 1,3-dipolar addition with both diphenylnitrilimine and benzonitrile oxide to give, respectively, a monoadduct (VI) and a di-adduct (VII). A di-adduct with diphenylnitrilimine could not be prepared; presumably it is too sterically crowded to be formed.



VI



VII

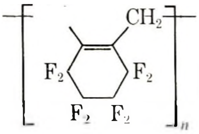
Polymerization of the Diene IIc

The diene IIc is polymerized by free radical initiators in bulk systems to give a 45% yield of the homopolymer VIII. The bulk polymerizations are best initiated by AIBN or benzoyl peroxide. A monomer-soluble redox system that comprises cumene hydroperoxide, dihydroxyacetone, and cobaltic naphthenate successfully initiates the polymerization but offers no advantages over the initiators AIBN or benzoyl peroxide.

The diene IIc is best polymerized (90% yield) in an emulsion system with the use of a redox initiator composed of ferrous sulfate, cumene hydroperoxide, and dihydroxyacetone. Sodium stearate is the surfactant which produces the most stable emulsion. The emulsions, originally about pH 9, have a pH of 5–6 before coagulation. This suggests that hydrogen fluoride may be produced via elimination from either the monomer or the resulting polymer under the polymerization conditions. Sodium perfluorooctanoate and the β-hydroxyethyldiethylammonium salts of both perfluorooctanoic acid and stearic acid produce satisfactory emulsions.

Cationic, anionic, and Ziegler-Natta initiators fail to polymerize the diene IIc. Cationic initiators are completely inert with respect to the diene. Organolithium compounds, however, react rapidly with the diene IIc to form unidentified monomeric products. A variety of other anionic initiators including trityl sodium and sodamide are equally unsuccessful as initiators for the polymerization. The diene is unaffected by a variety of Ziegler-Natta catalysts in benzene and cyclohexane. These catalysts are not decomposed by the diene as evident by the homopolymerization of styrene in the presence of equimolar amounts of the diene IIc.

Poly-1,2-dimethyleneoctafluorocyclohexane has an all-*cis* 1,4-structure (VIII) within the limits of infrared and NMR detectability.



VIII

This is consistent with the observations noted for poly-1,2-dimethylenecyclohexane, the hydrocarbon analog.[3,8] Neither the infrared nor the NMR spectrum shows exomethylene absorption which would be indicative of appreciable amounts of 1,2 propagation. The NMR spectrum shows

TABLE II

Best Recipes for Copolymerization of the Diene IIc with Various Comonomers[a]

Comonomer	Water	Sodium stearate	AIBN	Time, days	Temp, °C	Yield, %	Mp, °C	Intrinsic viscosity at 30°	Diene in copolymer, mole-%	Diene in feed, mole-%
Styrene	500	9	0.20	4	50	70	124	0.563 (TCE)	46.4	50
Isoprene	400	10	0.10	3	50	79				33
Butadiene	400	10	0.20	2	50	85				33
Vinyl chloride	350	9	0.12	9	50	65	111–128	0.856 (THF)	36.7	27
α-Methylstyrene	400	7.5	0.05	6	50	80	146–164	1.578 (acetone)	46.1	46.1
Vinylidene chloride	500	12.5	0.09	8	50	75	184–230	0.868 (THF)	48.5	50
Acrylonitrile			0.33	6	60	28	170–211	0.160 (THF)	32.5	31.4
Methacrylonitrile	400	10	0.30	14	60	10	140–175			46
Methyl methacrylate			0.30	4	60	48	132–169	0.439 (acetone)	34.3	50
Vinyl acetate			0.20	20	50	35	139–154	0.260 (THF)	68.6	45

[a] Quantities are parts by weight based on 100 parts total weight of monomers.

only one peak at 3.25 ppm from tetramethylsilane in dimethyl sulfoxide-d_6. The integrated NMR spectra of several copolymer samples of known composition indicate 100% 1,4-propagation within experimental error. The polymer shows no noticeable tendency to crosslink and is a highly crystalline solid that melts at 214–218°C to give a clear, stable melt. The polymer melt can be fabricated by conventional methods and cools to form a hard, brittle plastic. The resin burns while in a flame but is self-extinguishing when removed.

The polymer VIII has been successfully dissolved only in perfluorokerosene above 175°C and in 2,5-dichlorobenzotrifluoride above 150°C. It will remain in solution in the latter solvent at 130° for 8–12 hr before starting to precipitate very slowly. Intrinsic viscosities of several samples of the polymer VIII measured in 2,5-dichlorobenzotrifluoride at 130°C range from 0.171 to 0.251 g/cm-sec. No data are available for correlating viscosity to molecular weight for polymers of this structure.

Copolymerization of the Diene IIc

Copolymerization of the diene IIc with ten different comonomers has been carried out in either bulk or emulsion using AIBN as the initiator. Table II presents those recipes which produced the best yields and highest molecular weights.

The diene IIc copolymerizes with most comonomers more rapidly and gives higher molecular weight polymers than it does in homopolymerization. This is a common observation with fluorinated monomers[18] and probably results in highly alternating copolymers. Acrylonitrile, methacrylonitrile, and vinyl acetate do not polymerize readily with the diene IIc. The polymers with α-olefins are amorphous solids that melt over wide ranges. These copolymers are soluble in common solvents such as acetone and tetrahydrofuran. The copolymers with butadiene and isoprene are insoluble and elastomeric. Table III presents molecular weight data for some of the copolymers.

Relative reactivity ratios (r) have been measured for the diene IIc–styrene monomer pair. If the diene IIc is designated M_1 and styrene is M_2, then $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ where the k are the four possible rate constants derived from the two possible propagating radical chain ends

TABLE III
Molecular Weight Data for Various Copolymer Samples

Comonomer	$\bar{M}_n$ (VPO)[a]	$\bar{M}_n$ (MO)[a]
Styrene		505 000
α-Methylstyrene		735 000
Methyl methacrylate		93 000
Acrylonitrile	22,500	30 000

[a] Determinations made by Dale Harmon of the B. F. Goodrich Research Center, Brecksville, Ohio.

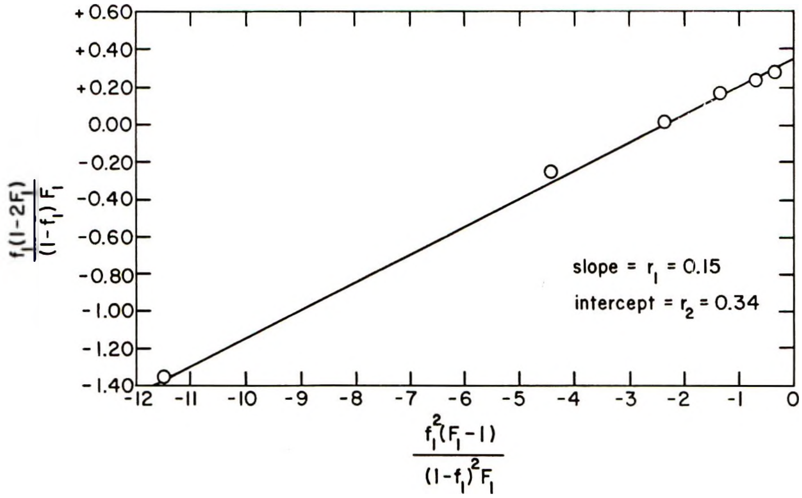


Fig. 1. Relative reactivity plot for diene IIc–styrene copolymerization.

adding to the two monomers in the copolymerization. The copolymerizations were carried out in bulk at 50°C with AIBN as the initiator. Conversion to polymer did not exceed 8.0% by weight. Table IV presents the results of these copolymerizations, where f_1 is the mole fraction of the diene IIc in the monomer feed and F_1 is the mole fraction of the diene in the resulting copolymer. Treatment of the data in Table IV by the following expression derived by Fineman and Ross[19] gives the results in Figure 1. A least-square analysis of the line in Figure 1

$$f_1(1 - 2F_1)/(1 - f_1)F_1 = r_2 + [f^2{}_1(F_1 - 1)/(1 - f_1)^2F_1]r_1$$

gives $r_1 = 0.15$ and $r_2 = 0.34$.

The Q and e parameters were calculated for the diene IIc by the method of Alfrey and Price[20] with the use of values for styrene of $Q = 1.0$ and $e = -0.8$,[21] and the relative reactivity ratios were determined for the monomer pair. This calculation gave Q(diene) = 0.73, and e(diene) = 0.93.

TABLE IV
Dependence of Copolymer Composition on Monomer Feed for the Diene IIc and Styrene

Conversion to polymer, %	Fluorine in copolymer, %	Mole fraction of diene IIc	
		Feed (f_1)	Copolymer (F_1)
1.4	35.83	0.288	0.377
8.0	38.51	0.403	0.422
0.9	39.88	0.474	0.447
2.7	42.57	0.605	0.498
3.5	44.19	0.686	0.531
0.9	47.13	0.805	0.597

The Q factor is proportional to the extent that resonance in the monomer and the resulting radical affects their reactivity. The e term is proportional to the electronic effect a polar substituent has upon the olefin double bond. The above values are consistent with published data for other monomers. The Q term for the diene IIc is less than for butadiene (2.39) or isoprene (3.33) because the two exomethylene groups in the diene are held in a conformation by the cyclohexane ring so that the π-electron systems are not in parallel planes and resonance between them is reduced. The positive e term is consistent for an electron-attaching group on a double bond. Acrylonitrile, for example, has an e value of 1.20.

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N-Vinylthiopyrrolidinone*

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Synopsis

The polymerization reactivity of *N*-vinylthiopyrrolidinone is described. This monomer readily homopolymerizes and forms copolymers with a wide variety of vinyl monomers. Reactivity ratios in the copolymerization of *N*-vinylthiopyrrolidinone with styrene and methyl methacrylate are reported and the Alfrey-Price Q and e values calculated. These results indicate the high copolymerization reactivity of this monomer in comparison with the oxo-analog, *N*-vinylpyrrolidinone. Some of the results are in conflict with previously reported data.

INTRODUCTION

The synthesis of *N*-vinylthiopyrrolidinone and a brief description of its use as a monomer in vinyl polymerization have been previously reported.[1-3] We have examined the copolymerization reactivity of this monomer, and this paper describes several new copolymer systems along with the determination of the reactivity ratios of *N*-vinylthiopyrrolidinone with styrene and methyl methacrylate. These results, which differ from the earlier literature, indicate that this monomer is considerably more reactive than *N*-vinylpyrrolidinone.

RESULTS AND DISCUSSION

Homopolymerization

N-Vinylthiopyrrolidinone was homopolymerized in benzene solution with the use of 2,2′-azobis(2-methylpropionitrile)(AIBN) as initiator to give a 97% yield of polymer which was soluble in *N*,*N*-dimethylformamide (DMF) and insoluble in ligroin, water, benzene, *n*-butanol, and methyl ethyl ketone. The polymer had an inherent viscosity of 0.26. Differential thermal analysis indicated a T_g of 80°C and two exothermic decomposition maxima at 180 and 280°C.

It is interesting to note that several attempts to prepare poly-*N*-vinylthiopyrrolidinone by use of peroxide initiators were unsuccessful. Experiments were run with the use of both benzoyl peroxide and *tert*-butyl hydroperoxide at levels from 0.5 to 2.5 wt-%. Only unreacted monomer was recovered, even after 24 hr at 75°C.

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

Copolymerization

Initial copolymerization experiments indicated that *N*-vinylthiopyrrolidinone was a more reactive monomer than *N*-vinylpyrrolidinone. Consequently, reactivity ratio determinations with styrene and methyl methacrylate were made, and the Alfrey-Price equations[4] were used to calculate *Q* and *e* values. The copolymerization data are given in Tables I and II.

TABLE I
Reactivity Ratio Data for Styrene and *N*-Vinylthiopyrrolidinone (NVT)

Mole fraction NVT in monomer	Conversion, %	Polymer analysis		Mole fraction NVT in polymer
		N, %	S, %	
0.20	8.43	1.60	3.76	0.121
0.35	6.13	2.90	6.57	0.226
0.50	8.24	4.39	10.09	0.352
0.655	11.60	6.23	14.41	0.517
0.655	1.80	5.96	14.04	0.497
0.80	14.50	8.01	18.05	0.685
0.80	1.80	7.70	17.61	0.656

TABLE II
Reactivity Ratio Data for Methyl Methacrylate and *N*-Vinylthiopyrrolidinone

Mole fraction NVT in monomer	Conversion, %	Polymer analysis		Mole fraction NVT in polymer
		N, %	S, %	
0.20	8.83	1.55	3.69	0.114
0.35	6.67	2.75	6.23	0.207
0.50	10.80	3.99	9.51	0.309
0.498	6.81	4.03	9.31	0.312
0.65	9.40	5.45	12.81	0.434
0.829	8.60	7.78	17.81	0.653

Composition curves from these experiments are shown in Figure 1. The reactivity parameters are summarized in Table III. Comparison of these results with those obtained with *N*-vinylpyrrolidinone (Table IV) reported earlier[5] confirms the increased reactivity of the thio derivative.

The literature describes the reactivity ratio determinations of *N*-vinylthiopyrrolidinone with *N*-vinylpyrrolidinone and methyl methacrylate.[2]

TABLE III
Reactivity Ratios of *N*-Vinylthiopyrrolidinone (M_2) with Styrene and Methyl Methacrylate

Monomer (M_1)	r_1	r_2	Q_1	e_1	Q_2	e_2
Styrene	1.75 ± 0.05	0.45 ± 0.03	1.0	-0.8	0.40	-0.34
Methyl methacrylate	1.85 ± 0.04	0.32 ± 0.02	0.74	$+0.4$	0.31	-0.31

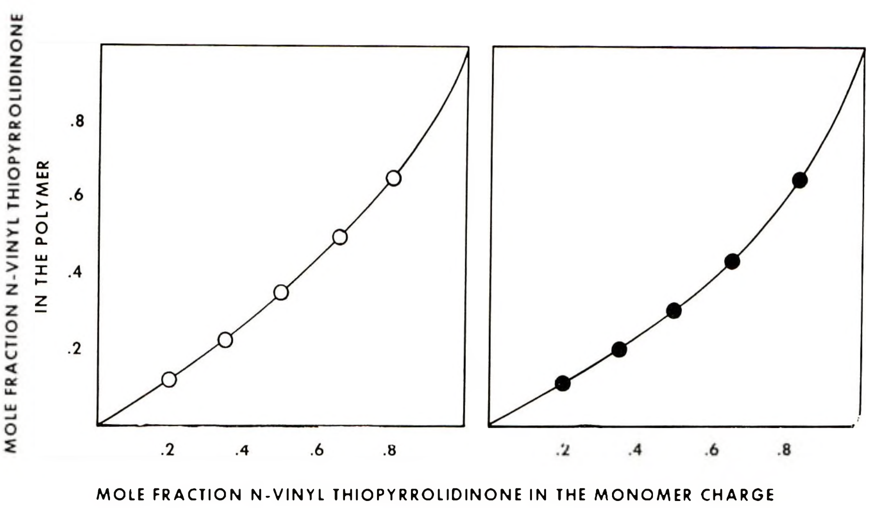

Fig. 1. Composition curves for copolymers: (○) styrene–*N*-vinyl-thiopyrrolidinone; (●) methyl methacrylate–*N*-vinylthiopyrrolidinone.

These results are summarized in Table V. It can be seen that the values differ considerably from those which we have determined. To reconcile this difference, we offer the following observations. Sividova et al.[2] used values of $Q_1 = 0.17$ and $e_1 = 0.95$ for *N*-vinylpyrrolidinone. Using average values of $Q_1 = 0.093$ and $e_1 = -1.17$ as reported elsewhere[5] and recalculating from the data of Table V, we obtained a $Q_2 = 0.23$ and $e_2 = -0.23$ which are in good agreement with our results. In the *N*-vinylthiopyrrolidinone–methyl methacrylate system, Sividova et al.[2] used just three of six experiments to determine the reactivity ratios. These three runs were all relatively high conversion (14–20%) copolymers. We found that two of the unused experiments—and the lowest conversion runs—fell on the composition curve in our Figure 1. Based on these findings, we have concluded

TABLE IV
Reactivity Ratios of *N*-Vinylpyrrolidinone (M_2) with Styrene and Methyl Methacrylate[5]

Monomer (M_1)	r_1	r_2	Q_1	e_1	Q_2	e_2
Styrene	15.7 ± 0.5	0.045 ± 0.05	1.0	−0.8	0.087	−1.22
Methyl methacrylate	4.7 ± 0.5	0.005 ± 0.05	0.74	+0.4	0.074	−1.33

TABLE V
Reactivity Ratios of *N*-Vinylthiopyrrolidinone (M_2) with *N*-Vinylpyrrolidinone and Methyl Methacrylate[2]

Monomer (M_1)	r_1	r_2	Q_1	e_1	Q_2	e_2
N-Vinyl-pyrrolidinone	0.13 ± 0.02	1.50 ± 0.3	0.74	0.4	1.36	−0.12
Methyl methacrylate	0.44 ± 0.06	1.72 ± 0.09	0.17	−0.95	1.61	−0.10

TABLE VI
Solution Copolymerizations of *N*-Vinylthiopyrrolidinone (NVT)

Comonomer	Time, hr	Conversion, %	NVT, wt-% Monomer	NVT, wt-% Polymer	Inherent viscosity	Softening point, °C
Vinyl chloride	16	10	25	80	—	>200
"	16	36	50	89	—	>200
"	16	38	75	91	—	>200
Ethyl vinyl ether	18	24	25	85	0.17	175–190
"	18	46	50	90	0.18	200–215
"	18	78	75	90	0.21	>240
1-Dodecene	18	23	25	95	0.17	>250
"	18	46	50	95	0.23	>250
"	18	73	75	95	0.25	>250
Diacetone acrylamide	16	98	25	24	0.95	135–150
"	16	98	50	50	0.85	145–160
"	16	95	75	73	0.66	175–185
Methyl vinyl ketone	18	52	25	28	0.24	70–80
"	18	88	50	48	0.26	115–125
"	18	98	75	68	0.26	125–130
Di-*n*-butyl fumarate	20	48	25	36	0.35	70–75
"	20	95	50	48	0.55	125–130
"	20	97	75	70	0.58	150–160
Di-*n*-butyl maleate	18	20	25	56	0.16	145–150
"	18	61	50	67	0.25	155–160
"	18	86	75	80	0.29	210–220
Styrene	16	41	25	16	0.27	105–110
"	16	60	50	38	0.23	120–130
"	16	72	75	62	0.29	>200

that our copolymerization parameters more nearly represent the true reactivity of *N*-vinylthiopyrrolidinone.

The published work[1–3] mentions that *N*-vinylthiopyrrolidinone forms copolymers with acrylonitrile, methyl acrylate, vinyl acetate, and *N*-vinylpyrrolidinone. Copolymers of *N*-vinylthiopyrrolidinone with a group of typical vinyl monomers are summarized in Table VI. The vinyl chloride, ethyl vinyl ether, and 1-dodecene copolymers contained significantly larger amounts of *N*-vinylthiopyrrolidinone than did the monomer charge. In these systems, the inherent viscosity of the copolymers increased with increasing incorporation of *N*-vinylthiopyrrolidinone. The copolymers were soluble in DMF and insoluble in ligroin, *n*-butanol, water, benzene, and methyl ethyl ketone. Copolymers of *N*-vinylthiopyrrolidinone with di-*n*-butyl fumarate and di-*n*-butyl maleate also contained larger amounts of *N*-vinylthiopyrrolidinone than did the monomer charge. The copolymers were soluble in DMF, benzene, and methyl ethyl ketone and insoluble in ligroin and water.

N-Vinylthiopyrrolidinone formed copolymers with diacetone acrylamide and methyl vinyl ketone in about the same ratio as charged. The copolymers were soluble in DMF and insoluble in ligroin and water. The diacetone acrylamide copolymers were soluble in benzene and methyl ethyl ketone whereas the methyl vinyl ketone copolymers were insoluble in methyl ethyl ketone and only partially soluble in benzene. The styrene copolymers contained slightly less *N*-vinylthiopyrrolidinone than charged and were soluble in DMF, benzene, and methyl ethyl ketone.

N-Vinylcarbazole and acrylic acid formed copolymers with *N*-vinylthiopyrrolidinone with polymer compositions similar to the monomer charge. Both series of copolymers were insoluble in all solvents except DMF. The *N*-vinylcarbazole copolymers all had softening points above 200°C, whereas the softening point of the acrylic acid copolymers increased from 100°C for 25% incorporation of *N*-vinylthiopyrrolidinone to 200°C for 75% incorporation.

N-Vinylthiopyrrolidinone was copolymerized with isoprene by use of a standard SB-R recipe at 60°C for 16 hr. A white rubbery solid was isolated in 20% yield. The copolymer contained 5% *N*-vinylthiopyrrolidinone from a monomer charge of 25% Attempts to prepare a copolymer with maleic anhydride using solution techniques were unsuccessful. No polymer was isolated.

EXPERIMENTAL

Monomers

The *N*-vinylthiopyrrolidinone was prepared by the reaction of *N*-vinylpyrrolidinone and P_2S_5 in a pyridine–xylene solvent according to the procedure previously reported.[1] The crude monomer was recrystallized from methanol and then ligroin giving a pure product in 22% yield, mp 68.5–69°C (lit.[2] mp 67–68°C). Only by changing the solvent to pyridine and increasing the ratio to 5 mole/mole of *N*-vinylpyrrolidinone, did yields of product (45–50%) approach the reported[1] (60%) values.

The other monomers used in this study were commercial materials and were purified before use.

Reactivity Ratio Determinations

The experimental methods were essentially those of Mayo and Lewis.[6] Solution polymerizations in benzene were run under a nitrogen atmosphere in 4-oz screw-cap bottles fitted with Teflon gaskets. Polymerization was initiated by AIBN at 0.01 wt-% based on monomer. The polymers were precipitated by pouring the benzene solution into naphtha or petroleum ether at room temperature. Purification was effected by repeated reprecipitations. The purified polymers were dried under vacuum to constant weight and the composition of the copolymers was determined by nitrogen analysis and confirmed by sulfur analysis.

Reactivity ratios were determined from the differential form of the general copolymerization equation by using both the method of intercepts[4] and the Fineman and Ross plots.[7]

Polymerizations

Copolymers of *N*-vinylthiopyrrolidinone with vinyl monomers were prepared in benzene solution under a nitrogen atmosphere. AIBN, 0.25–0.50 wt-% based on monomer, was used as initiator. Polymerization temperature was 60–65°C and monomer concentration was in the range of 33–50 wt-%. Copolymers were purified by reprecipitation from solution by a nonsolvent and dried under vacuum. Benzene, acetone, and DMF were used as solvents and methanol and ligroin were used as nonsolvents. *N*-Vinylthiopyrrolidinone incorporation was calculated from nitrogen analysis and confirmed by sulfur analysis. The inherent viscosities were determined by using 0.49 g polymer in 100 ml DMF at 30°C.

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Ladder Polymers from Tetraaminodiquinoxalpyrene*

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Synopsis

A new fused aromatic heterocyclic tetraamine 2,3,11,12-tetraaminodiquinoxal [2,3-e,2′,3′-l] pyrene has been prepared and polymerized with 1,4,5,8-naphthalenetetracarboxylic acid and pyromellitic dianhydride. The resulting ladder polymers with inherent viscosities ranging from 0.5 to 1.0 dl/g in methanesulfonic acid exhibited thermal stabilities near 600°C in nitrogen and near 450°C in air.

INTRODUCTION

Many attempts to synthesize aromatic heterocyclic ladder polymers have resulted in the formation of brick-dustlike materials, extremely stable, but infusible and intractable. The problem of intractability of this type of material has existed for some time and has limited its advancement as a candidate for high temperature applications. Recently it has been shown[1] that soluble high molecular weight ladder polymer could be obtained, namely with benzimidazobenzophenanthroline-type ladder polymer (BBL). Unfortunately, the ladder structure shows only solubility in strong acidic solvents, thereby making certain applications somewhat limited. The pyrrone ladder system,[2–4] which is of the same family of polymers, tends to produce crosslinked, insoluble materials, however, acid-soluble ladder pyrrone has been reported.[4]

This paper is concerned with structural modifications of the BBL and pyrrone systems in an attempt to render such materials soluble in solvents other than strong acids.

RESULTS AND DISCUSSION

The aromatic ladder polyquinoxalines[5,6] which have good thermal stability exhibit unusual solubility characteristics in fluorinated and aprotic solvents. It was considered that the quinoxaline reoccurring unit in the BBL and pyrrone backbone might impart solubiltiy to such systems in aprotic solvents. Since both polymer systems are prepared by the condensation of fused aromatic tetraamines and tetraacids or derivatives, the quinoxaline nucleus was built into the tetraamino monomer I. The resulting polymers

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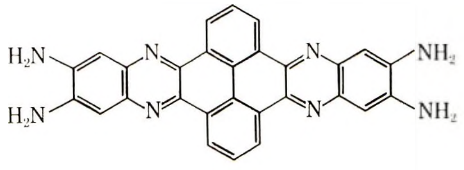
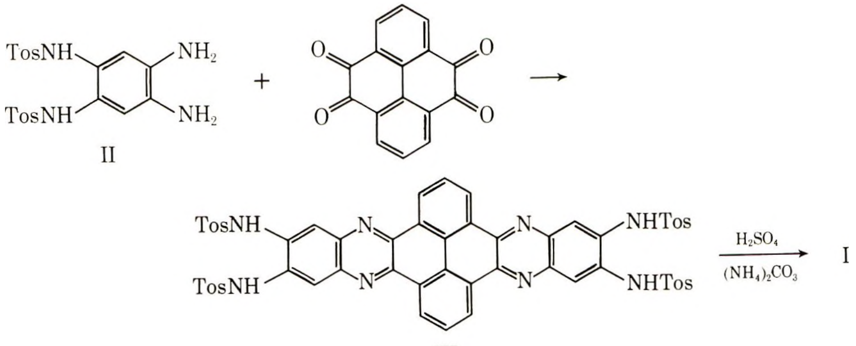
* In honor of C. S. Marvel on the occasion of his 75th birthday.

are made up of alternating sequence of quinoxalpyrene units and BBL or pyrrone units.



I

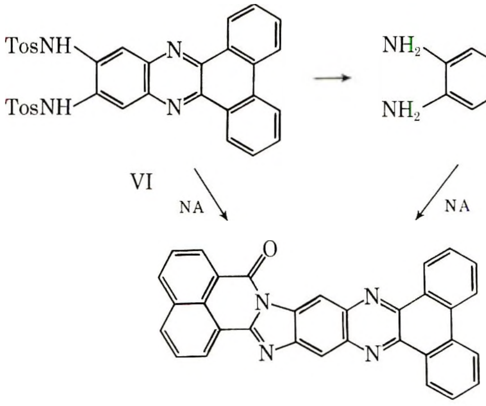
The monomer 2,3,11,12-tetraaminodiquinoxal[2,3-e,2′,3′-1] pyrene I was prepared by the reaction of 1,2-diamino-4,5-(*p*-toluenesulfamido)benzene II with 1,2,6,7-tetraketopyrene to give the fused tetratosylate III. Detosylation of III with concentrated sulfuric acid followed by an ammonium carbonate treatment gave the free amine I. The precursor II was obtained from 1,2-dinitro-4,5-(*p*-toluenesulfamido) benzene by a chemical reduction with sodium hydrosulfite in dimethylacetamide (DMAC).



III

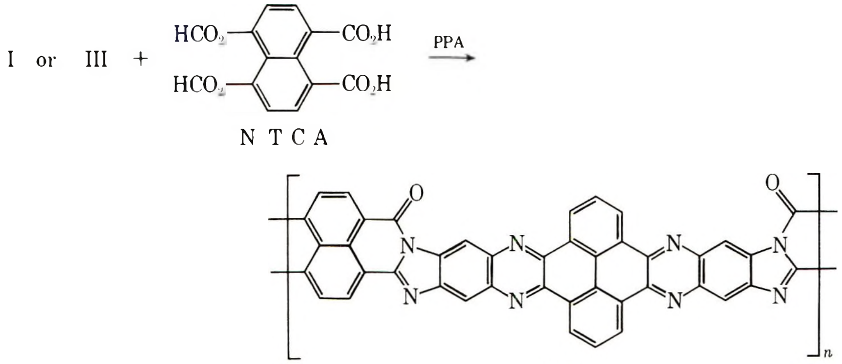
Prior to the polymerization studies, model compound IV was synthesized in order to determine the feasibility of the polycondensation and to provide a basis for interpreting polymer spectra. 11,12-Diamino[a,c]phenazine V was reacted with naphthalic anhydride (NA) in polyphosphoric acid (PPA) at 180°–190°C for 10 hrs to give IV in 75% yield. V was obtained by the condensation of II with 9,10-phenanthraquinone, followed by detosylation with sulfuric acid and ammonium carbonate treatment. The intermediate 11,12(*p*-toluenesulfamido)dibenzo[a,c]phenazine VI was also found to react with naphthalic anhydride (NA) in PPA to give IV in a 60% yield.

The tetraamine I was condensed with 1,4,5,8-naphthalenetetracarboxylic acid (NTCA) in PPA at 180°C which gave polymer VII made up of alternating bisquinoxalino-pyrene and bisimidazo-naphthaldimide structures. Since the detosylate VI could be used in the synthesis of model compound IV, the tetratosylate III was employed as a monomer in the polymerization. Polymer VII was obtained by either charging the PPA with stoichiometric amounts of NTCA and III and slowly increasing the temperature to 180°C or detosylating III at 80°C overnight and adding the NTCA thereafter.



IV

The infrared spectra of the polymer (Fig. 1) closely resembles the spectra of model compound IV (Fig. 2) in the 5.0–8.0 μ region.



VII

Polymer VII with inherent viscosities (Table I) as high as 1.0 were soluble in methanesulfonic acid; however the material showed no solubility in the aprotic solvents tested such as hexamethylphosphoramide, DMAC, dimethyl sulfoxide, and *N*-methylpyrrolidone. Fluorinated solvents such as hexafluoroisopropanol and 1,3-dichloro-1,1,3,3-tetrafluoro-2,2-dihydroxypropane, which are effective solvents for the ladder quinoxalines, had little effect on the ladder structure VII. The higher molecular weight samples were fiber-forming and could also be cast into films from methanesulfonic acid.

The reaction of I or III with pyromellitic anhydride (PMDA) in PPA afforded polymer VIII, which contained bisquinoxalinopyrene and bisimidazopyromellitimide structures. The polymer was only partially soluble in acidic solvents and showed no solubility in the various aprotic and fluorinated solvents. When the polymerization was carried out in DMAC at 30°C with I as the amino monomer, polyamide-acid-amine IX was obtained. The prepolymer IX was completely soluble in a variety of aprotic

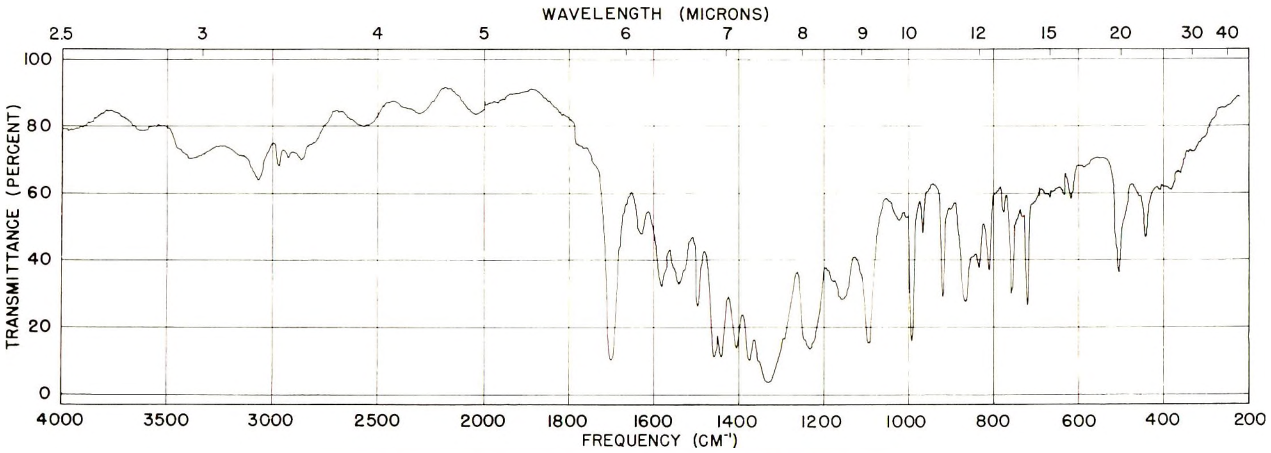


Fig. 1. Infrared spectra of polymer VII (film).

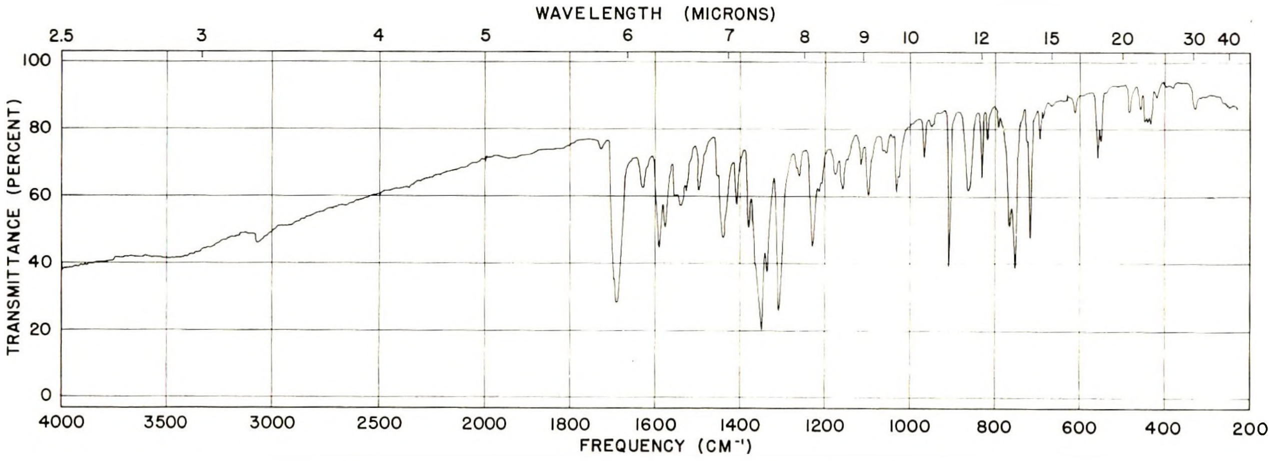


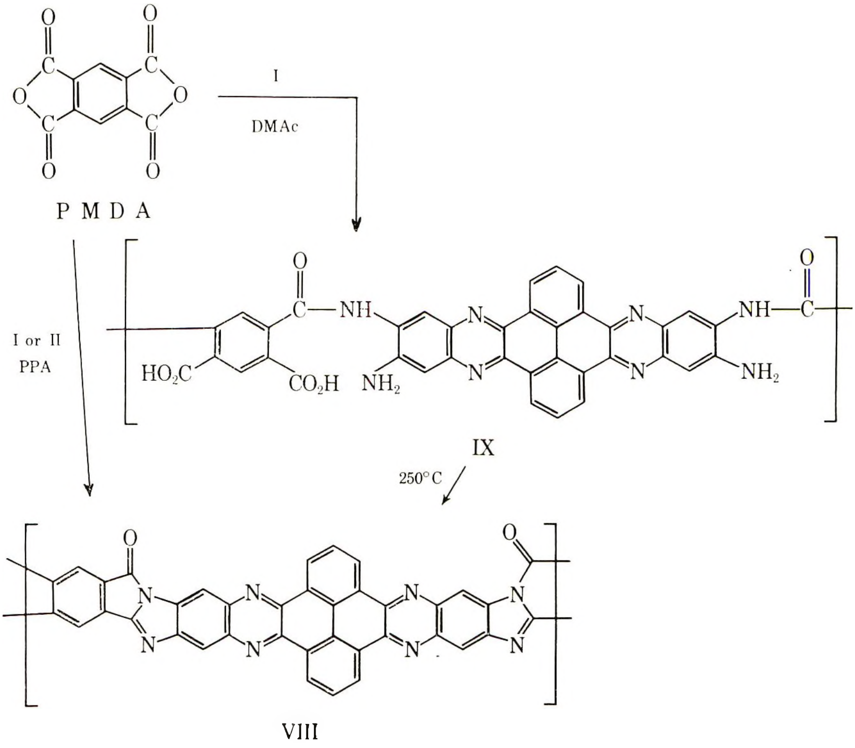
Fig. 2. Infrared spectra of model compound IV (KBr).

TABLE I
Polymers

Monomers	Solvent	Temperature, °C	Polymer	Inherent Viscosity	Solubility in $MeSO_3H$, %
NTCA + I	PPA	180	VII	1.0	100
NTCA + III	PPA	180	VII	0.70[a]	100
PMDA + III	PPA	180	VIII	0.90[a]	20
PMDA + I	PPA	180	VIII	0.50[a]	40
PMDA + I	DMAC	30	IX	0.40[b]	100
		250[c]	VIII		Insol.

[a] Inherent viscosities were obtained in 100% methanesulfonic acid (0.3 g/dl at 30°C).
[b] Inherent viscosities were obtained in DMAC (0.3 g/dl at 30°C).
[c] Temperature at which IX was second-staged.

solvents from which transparent yellow films could be cast. IX was converted to VIII by heating at 250°C under reduced pressure. The thermal cyclodehydration of IX always resulted in a completely insoluble material, both in acidic and aprotic solvents. Heat-treated films of IX turn orange in color, but no evidence of crosslinking could be detected by spectroscopic methods.



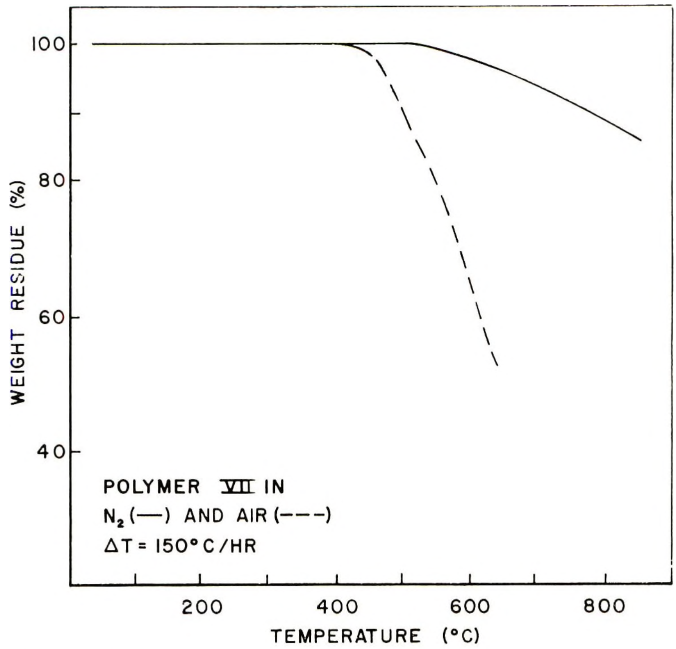


Fig. 3. TGA curve of polymer VII: (——) in N_2; (- -) in air.

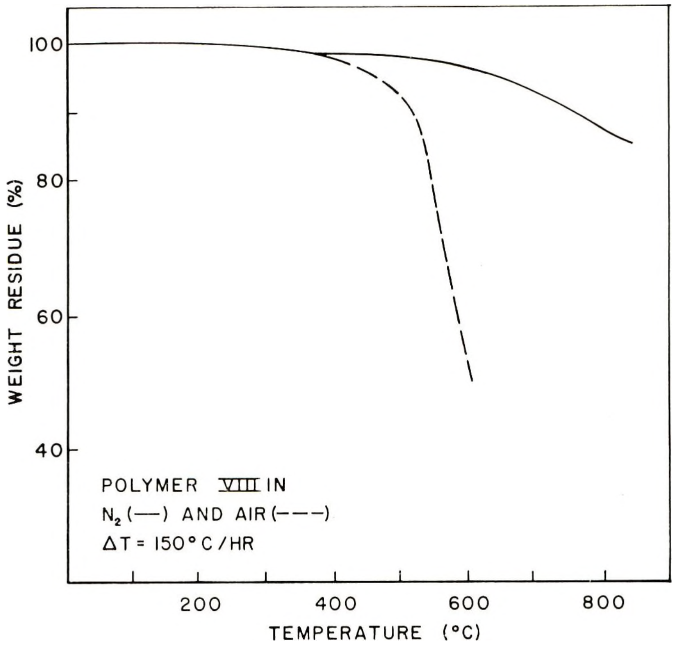


Fig. 4. TGA curve of polymer VIII: (——) in N_2; (- -) in air.

The thermal stabilities of the polymers as depicted by their TGA curves (Figs. 3 and 4) were quite good. Initial weight losses occurred in the range 550–600°C in nitrogen and 430–450°C in air.

EXPERIMENTAL

Solvents

Polyphosphoric Acid (PPA). PPA was purchased from Matheson Coleman and Bell and used as received.

N,N-Dimethylacetamide (DMAC). DMAC was purchased from Matheson Coleman and Bell and purified by distillation from calcium hydride, under reduced pressure (bp 65–66°C/30 mm).

Monomers

1,4,5,8-Naphthalenetetracarboxylic Acid (NTCA). The polymerization grade monomer was obtained through Celanese Research Co. and used as received.

Pyromellitic Dianhydride (PMDA). The monomer was obtained from Hexagon Laboratories and purified by sublimation at 220°C (0.5 mm).

2,3,11,12 - Tetra(*p* - toluenesulfamido)diquinoxal[2,3 - e,2′,3′ - 1]pyrene (III). Precursor (II) 1,2-Diamino-4,5-(*p*-toluenesulfamido)benzene. To a solution of 15.2 g (30.0 mmoles) of 1,2-dinitro-4,5-(*p*-toluenesulfamido)-benzene in 150 ml of dimethylacetamide at 90°C was added dropwise, under nitrogen, an aqueous solution 31.3 g (180.0 mmoles) of sodium hydrosulfite. After the addition was complete, the temperature was maintained at 90°C for 2 hr. The cooled reaction mixture was added to 500 ml of deoxygenated water to precipitate a white solid. The material was collected, washed with water, and recrystallized from methanol to afford 8.5 g (63%) of the product, mp 238–239°C.

ANAL. Calcd for $C_{20}H_{22}N_4O_4$: C, 53.79%; H, 4.96%; N, 12.54%. Found: C, 53.83%; H, 5.02%; N, 12.46%.

To a solution of 8.93 g (20.0 mmole) of 1,2-diamino-4,5-(*p*-toluenesulfamido)benzene in 250 ml of glacial acetic acid was added 2.62 g (10.0 mmole) of 1,2,6,7-tetraketopyrene. The solution was stirred at 60°C under a nitrogen atmosphere for 8 hr. The yellow precipitate was collected, washed with water, and recrystallized from dimethylacetamide to yield 8.90 g (82%) of the product, mp 350–400°C with decomposition.

ANAL. Calcd for $C_{56}H_{42}N_8S_4O_8$: C, 62.08%; H, 3.90%; N, 10.34%. Found: C, 62.04%; H, 3.90%; N, 10.17%.

2,3,11,12-Tetraaminodiquinoxal[2,3-e,2′,3′-1]pyrene (I). To 150 ml of concentrated sulfuric acid was added 10.8 g (10.0 mmole) of 2,3,11,12-tetra(*p*-toluenesulfamido)diquinoxal[2,3-e,2′,3′-1]pyrene. The solution was stirred at room temperature for 6 hr, cooled to 0°C, and poured over ice to precipitate a dark red solid. The red material was collected, washed with water, and added to a deoxygenated 20% ammonium carbonate solution to give a light yellow solid. The free amine was collected, washed with deoxygenated water, dried under reduced pressure, and recrystallized from dimethylacetamide to afford 4.43 g (95%), mp 300–400°C with decomposition.

ANAL. Calcd for $C_{28}H_{18}N_8$: C, 72.08%; H, 3.89%; N, 24.02%. Found: C, 71.85% H, 4.03%; N, 24.09%.

Model Reactions

Precursor (VI), 11,12-*p*-Toluenesulfamidodibenzo[a,c]phenazine. To a solution of 2.08 g (10.0 mmole) of 9,10-phenanthraquinone in 200 ml of glacial acid was added 4.46 g (10.0 mmole) of 1,2-diamino-4,5-(*p*-toluenesulfamido)-benzene. The solution was stirred at 60°C, under a nitrogen atmosphere, for 4 hr. The yellow precipitate was collected, washed with water, and recrystallized from anhydrous methanol 6.0 g (98%) of the product, mp 298–300°C.

ANAL. Calcd for $C_{34}H_{26}N_4S_2O_4$: C, 65.99%; H, 4.23%; N, 9.05%; Found: C, 65.73%; H, 4.40%; N, 9.23%.

Precursor (V), 11,12-Diaminodibenzo[a,c]phenazine. To 100 ml of concentrated sulfuric acid was added 5.0 g (8.08 mmole) of 11,12-*p*-toluenesulfamidodibenzo[a,c]phenazine. The solution was stirred overnight at room temperature, cooled to 0°C, and poured over ice to precipitate a red solid. The material was collected, washed with water, and added to a deoxygenated 20% ammonium carbonate solution to give a tan solid. The free amine was collected, washed with cold deoxygenated water, dried under reduced pressure, and recrystallized from 50% aqueous methanol to afford 1.62 g (65%), mp >300°C.

ANAL. Calcd $C_{20}H_{14}N_4$: C, 77.39%; H, 4.56%; N, 18.05%. Found: C, 77.12%; H, 4.35%; N, 17.83%.

18H-Imidazo[2,1-a]benz(d,e)isoquinolino[5,4i]dibenzo[a,c]phenazine-18-one (IV). To 100 g of polyphosphoric acid was added, under nitrogen, 0.5 g (0.16 mmole) of 11,12-diaminodibenzo[a,c]phenazine and 0.32 g (0.16 mmole) of 1,8-naphthalic anhydride. The mixture was heated to 180°C and maintained at that temperature for 10 hr. After cooling to room temperature, the mixture was poured into 1500 ml of methanol to precipitate a brown solid. The material was collected, washed with methanol, dried at reduced pressure, and recrystallized from *o*-dichlorobenzene to give 0.565 g (75%) of light yellow crystals, mp > 400°C.

ANAL. Calcd for $C_{32}H_{16}N_4O$: C, 81.34%; H, 3.41%; N, 11.84%; Found: C, 80.80%; H, 3.44%; N, 11.63%.

Model compound IV was also obtained in a 65% yield by reacting VII with 1,8-naphthalic anhydride in PPA at 180°C.

ANAL. Found: C, 81.02%; H, 3.56%; N, 11.71%.

Polymers

Polymer VII from NTCA and Free Amine I. To 50 g of deoxygenated PPA was added, under a nitrogen atmosphere, 0.1543 g (0.453 mmole) of NTCA and 0.2117 g (0.453 mmole) of 2,3,11,12-tetraaminodiquinoxal-[2,3-e,2′,3′-1]pyrene. The mixture was heated at the rate of 3°C/min to 180°C and maintained at that temperature for 10 hr. The solution was then allowed to cool to 30°C and the polymer was precipitated into 500 ml of anhydrous methanol. The dark blue solid material was dissolved in methanesulfonic acid and reprecipitated into anhydrous methanol. The product, 0.29 g (99%), had an inherent viscosity of 1.0 dl/g in methanesulfonic acid (0.3 g/100 ml at 30°C).

Anal. Calcd for $C_{42}H_{14}N_8O_2$: C, 76.12%; H, 2.12%; N, 16.91%. Found: C, 72.76%; H, 2.22%; N, 16.42%.

Polymer VII from Tetratosylate III. To 100 g of deoxygenated polyphosphoric acid was added, under nitrogen atmosphere, 2.22 g (0.212 mmole) of 2,3,11,12-tetra-(*p*-toluenesulfamido)diquinoxal[2,3-e,2′,3′-1]-pyrene. The mixture was heated to 80°C and maintained at that temperature for 8 hr. The dark blue solution was allowed to cool to room temperature and 0.64 g (0.212 mmoles) of NTCA was added. The mixture was then heated at the rate 3°C/min to 180°C and held at that temperature for 10 hr. After the mixture had cooled to room temperature, it was precipitated into 1 l. of anhydrous methanol. The material was collected, washed with methanol, dried under reduced pressure, and reprecipitated from methanesulfonic acid. The polymer 1.3 g (94%), had an inherent viscosity of 0.70 dl/g in methanesulfonic aid (0.3 g/100 ml at 30°C).

Anal. Calcd for $C_{42}H_{14}N_8O_2$: C, 76.12%; H, 2.12%; N, 16.91%. Found: C, 75.69%; H, 2.15%; N, 16.64%.

Polymer VIII from PMDA and Free Amine I. To 50 g of deoxygenated PPA was added, under a nitrogen atmosphere, 0.1291 g (0.276 mmole) of 2,3,11,12-tetraaminodiquinoxal[2.3-e,2′,3′-1]pyrene and 0.0603 g (0.276 mmoles) of PMDA. The mixture was heated at the rate of 3°C/min. to 180°C and maintained at that temperature for 10 hr. The solution was then allowed to cool to 30°C and the polymer was precipitated into 500 ml of anhydrous methanol. The resulting dark brown solid was collected, washed with methanol, and dried under reduced pressure. The crude product, 0.18 g, was 40% soluble in methanesulfonic acid. After reprecipitation of the soluble portion into anhydrous methanol it had an inherent viscosity of 0.5 dl/g in methanesulfonic acid (0.3 g/100 ml at 30°C).

Anal. Calcd for $C_{38}H_{12}N_8O_2$: C, 74.50%; H, 1.97%; N, 18.29%; Found: C, 72.69%; H, 2.15%; N, 17.65%.

Polymer VIII from Tetratosylate III. To 100 g of deoxygenated PPA was added, under a nitrogen atmosphere 2.400 g (0.224 mmole) of 2,3,11,12-tetra(*p*-toluenesulfamido)diquinoxal[2,3-e,2′,3′-1]pyrene. The mixture was heated to 80°C and maintained at that temperature for 8 hr. The dark blue solution was allowed to cool to room temperature and 0.4907 g (0.224 mmoles) PMDA was added. The mixture was then heated at the rate 3°C/min to 180° and held at that temperature for 10 hr. After the mixture had cooled to room temperature, it was precipitated into 1 l. of anhydrous methanol. The crude product 1.25 g (92%) was 20% soluble in methanesulfonic acid. After reprecipitation of the soluble portion into anhydrous methanol, it had an inherent viscosity of 0.90 dl/g in methanesulfonic acid (0.30 g/100 ml at 30°C).

ANAL. Calcd for $C_{38}H_{12}N_8O_2$: C, 74.50%; H, 1.97%; N, 18.29%; Found: C, 73.09%; H, 2.50%; N, 17.50%.

Polymer VIII with the use of *N,N*-Dimethylacetamide as a Solvent. To 100 ml of freshly distilled DMAC was added, at room temperature 0.2278 g (0.0488 mmole) of 2,3,11,12-tetraaminodiquinoxal[2,3-e,2′,3′-1]-pyrene and 0.1065 g (0.0488 mmole) of PMDA. The mixture was stirred for 12 hr, under a nitrogen atmosphere at 30°C. The DMAC was then removed under reduced pressure to afford a light yellow film which adhered to the sides of the flask. A portion of the film was redissolved in DMAC and had an inherent viscosity of 0.4 dl/g (0.3 g/100 ml at 30°C). The material that remained was heated as a solid to 250°C, under reduced pressure, (0.03 mm), whereupon it became insoluble.

ANAL. Calcd for $(C_{38}H_{12}N_2O_2)_n$: C, 74.50%; H, 1.97%; N, 18.29%; Found: C, 68.71%; H, 3.10%; N, 16.41%; res, 1.7%.

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Cyclopolymerization: Cyclization of Diallylcyanamide to Pyrrolidine Derivatives*

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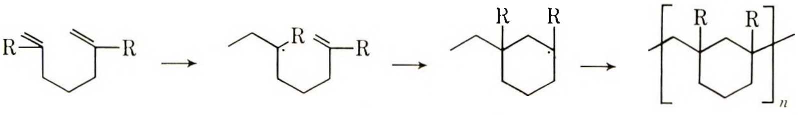
Synopsis

Free-radical addition of perfluoroalkyl iodides (R_FI) to diallylcyanamide gave *cis*- and *trans*-1-cyano-3-iodomethyl-4-(perfluoroalkyl)methylpyrrolidine (Ia,b). Five-membered ring products were preferentially formed in this reaction by other 1,6-dienes having terminal vinyl groups. This strongly suggests that cyclopolymerization of such monomers occurs in analogous fashion, instead of leading to 6-membered rings as has been previously understood. Dehydrohalogenation of Ia,b gave 3-methylenepyrrolidine derivatives as expected. Infrared and NMR spectra clearly show the exocyclic $CH_2=$ group. The influence of reaction conditions on the yield of cyclization product Ia,b and certain side products was investigated.

INTRODUCTION

One of the many contributions of Marvel and his students to polymer chemistry was the discovery of cyclopolymerization of certain dienes.[1,2] The concept of cyclopolymerization had been used by others[3-5] to explain the formation of soluble polymers from nonconjugated olefins which would be expected to give crosslinked polymer chains. In this special type of vinyl polymerization the growing free radical cyclizes by transfer to the pendant double bond, before propagation of the polymer chain takes place. Cyclization was assumed to occur by intramolecular addition to give the more stable secondary radical in the usual "head-to-tail" fashion. A six-membered ring unit connected by



(1)

$R = COOH, COOCH_3, COOC_2H_5$

methylene bridges was thus anticipated from 1,6-diolefins [eq. (1)], and a five-membered ring unit was similarly postulated from cyclopolymerization of 1,5-diolefins.[6] Marvel's work showed that in appropriate cases cyclopolymerization could be initiated by free radicals, by cationic or anionic catalysts or by Ziegler-type metal alkyl coordination catalysts,[7] and

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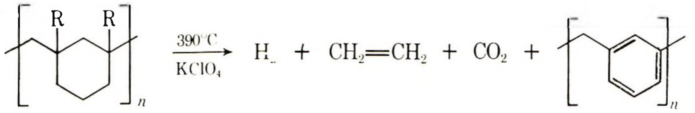
* In honor of C. S. Marvel on the occasion of his 75th birthday.

that (presumably) larger ring sizes could be obtained from higher α,ω-diolefins.[8]

Many important features of this process have since been elucidated,[9-13] but only in a few cases has the precise nature of the cyclic recurring unit been adequately demonstrated.[14-17] Here again Marvel[6] has led the way with convincing evidence that six-membered rings are present in the polymer of diethyl α,α'-dimethylenepimelate. A substance containing aromatic rings [eq. (2)], as indicated by typical properties, was obtained by heating the polymer with potassium perchlorate at 390°C for 16 hr.

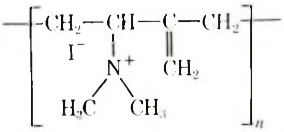


(2)

R = COOC$_2$H$_5$

As in all structure proofs by degradation reactions, there is the possibility of rearrangement; in this case there would be little reason to anticipate modification of the carbon skeleton. It was found later[18] that cyclization of free radicals similar in structure gave both six- and five-membered rings, but at the time of the original work only six-membered rings were considered for cyclopolymers from 1,6-dienes. Berlin and Butler[19] explicitly state, "A five-membered ring has never been reported in cyclic polymerization involving symmetrical 1,6-diene systems with terminal methylene groups." This general conclusion was not challenged in a recent review of cyclopolymerization.[12,20]

In the original work by Butler[21] with diallylammonium bromide, the polymer was degraded to a substance which contained $CH_2{=}C$ groups, as shown by oxidation to formic acid. From the steps used it is not clear how the proposed piperidine-like polymer structure could be distinguished from a polymer containing pyrrolidine rings. The degraded polymer would have



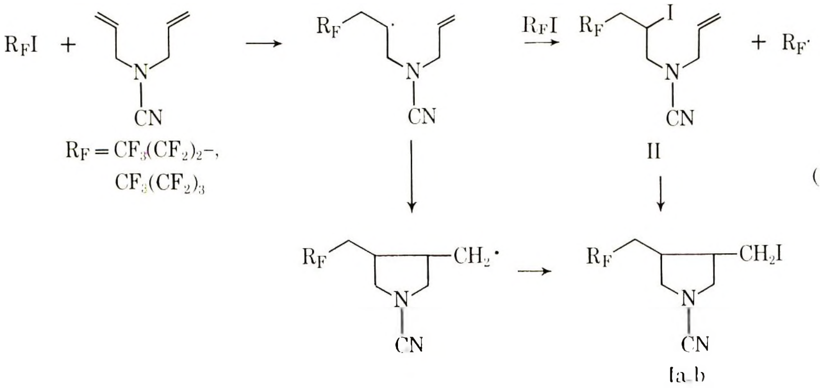
units in this latter case, and would have led to the same chemical evidence. Matsoyan et al.[22,23] also concluded that N-substituted diallylamines undergo cyclopolymerization with formation of piperidine rings. Even very recently the cyclopolymerization of diallylcyanamide was reported to give substituted piperidine rings.[24]

In a number of instances where cyclopolymerization by an intramolecular-intermolecular mechanism has been reported to give six-membered repeating units, analogous reaction of the 1,6-diene with iodoperfluoroalkanes,*[20,25] polyhalomethane,[26] or NF_2 radicals[27] has given monomeric five-membered ring products. This preference for five-membered ring structures has also been recently observed for cyclization of variously prepared olefinic radicals[28–31] and carbanions.[32]

CYCLIZATION OF DIALLYLCYANAMIDE

Cyclization of diallylcyanamide by reaction with perfluoroalkyl iodides (R_FI) was observed some time ago[20] but essential features of the work have just been completed. A careful examination of products and satisfactory proof of structures appeared to be of great significance in the light of unanimous opinion as to six-membered ring structures for the cyclopolymer from this *N*-cyanodiallylamine and related 1,6-dienes.

Many features of the cyclization reaction were described previously for analogous reaction of R_FI with 1,6-heptadiene,[20,25] diallyl ether,[20,25] diethyl diallylmalonate,[25] or ethyl diallylacetate.[25] Thus, diallylcyanamide gave *cis*- and *trans*-1-cyano-3-iodomethyl-4-(perfluorobutyl)methylpyrrolidine (Ia,b) in 95% yield, by use of azobisisobutyronitrile (AIBN) initiator.



(3)

Pure samples of Ia,b were obtained by column chromatography or by crystallization from cold solvent; a small amount of olefinic isomer (II) was present in the liquid residue as indicated by NMR and infrared spectroscopy. A sharp melting isomer Ia [$R_F = CF_3(CF_2)_3-$] was obtained by recrystallization.

Efficiency of the initiator in bringing about reaction was markedly dependent on the reactant ratio (Table I). At a 1:1 mole ratio the extent of reaction was a minimum. At a 2:1 mole ratio of R_FI to diallylcyanamide, complete conversion occurred, while the inverse ratio gave only 78% reaction. This was not merely a dilution or solvent effect, since reaction in benzene of a 1:1 mole ratio also gave a low conversion even though the

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* Gibbs and Barton[12] incorrectly state that "free radical-initiated reaction of iodoperfluoropropane with allyl ether gives a high yield of substituted six-membered ring compounds;" the cited report[20] actually stated that the cyclic product from diallyl ether had a five-membered ring similar to that obtained from 1,6-heptadiene.

amount of initiator was increased. The principal product in every case consisted of Ia,b, with less than 5% of side products.

It is likely that II would readily suffer loss of HI or disproportionate, since it is a reactive secondary iodide. II may have been the unstable substance which eliminated iodine or hydrogen iodide very readily and caused a dark red color to appear in certain reaction mixtures. This could account for loss of initiator efficiency, the presence of acidic side products, and the formation of some amide from the nitrile in these low conversion reactions. The presence of dark-colored impurities was greatest in reactions in which an excess of diallylcyanamide was used. However, chromatography of any of these product mixtures on activated alumina gave better than 90% recovery of Ia,b from ligroin, benzene and ether eluates; acetone eluted a small amount of complex mixture from which a crystalline amide, probably *N*-allyl *N*-(2-iodo-4 through 7-nonafluoroheptyl)urea, $CF_3CF_2CF_2CF_2CH_2$-$CHICH_2N(CH_2CH{=}CH_2)CONH_2$ (III) was isolated. III, of course, is a derivative of II. III readily eliminated HI and showed typical amide and $CH_2{=}CH$ bands in its infrared spectrum but was not completely characterized.

TABLE I
1-Iodoperfluorobutane and Diallylcyanamide[a]

Reactants, mole				Products		Recovered, mole	
R_FI	DAC[b]	AIBN $\times 10^{-4}$	R_FI/DAC	Conversion, %[c]	Yield, %[c]	R_FI	DAC
0.050	0.050	9.3	1.00	56.1	95	0.0306	0.0194
0.050	0.100	9.3	0.500	78.0	96	0.010	0.055
0.050	0.150	9.3	0.333	87.0	96	0.005	0.098
0.100	0.050	9.3	2.00	98	96	0.0475	0.00
0.180	0.100	18	1.80	85.5	96	0.037	0.013
0.0462[d]	0.0462[d]	22	1.00	62.5	96	—	0.016

[a] Reaction time 15–17 hr, 70.0°C in sealed tube.

[b] DAC = diallylcyanamide.

[c] Conversion calculated from moles of products/moles limiting reactant; yield from moles Ia,b/moles limiting reactant used up.

[d] Reaction in 10.0 ml benzene solution (4.62*M*); R_FI not readily recovered.

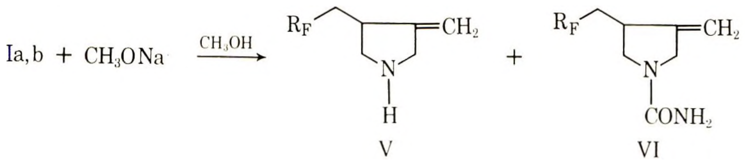
Other compounds were present in small amount in these reaction mixtures, but a careful examination of solid fractions by infrared spectroscopy or nmr spectroscopy did not indicate their presence. One crude reaction product gave a little 1-cyano-2-methylene-3-(perfluoropropyl)methylpyrrolidine (IV) as sublimed solid. This dehydrohalogenation product, mp 65–66°C, showed infrared bands for $CH_2{=}CH$ at 3090, 1660, and 900, $C{\equiv}N$ at 2200 cm^{-1}, and an NMR spectrum showed the $=CH_2$ resonance at δ 5.1. In view of the low molecular weight polymer usually obtained from diallylcyanamide,[24] it is remarkable that such high conversions to cyclic adducts were obtained with only one per cent initiator.

NMR Spectroscopy

There was very little difference in the NMR spectrum of pure isomer Ia (mp 59°C) and the crude product mixture from neat reaction or from benzene solution. Some change in the shape of resonances at δ 2.8 of methinyl protons on C_3 and C_4 was apparent, as would be expected. The protons on C_2 and C_5, adjacent to the *N*-cyanoamine group, were shifted down to δ 3.7, the $-CH_2I$ group was at δ 3.25 as in previous structures of this type,[20,25] and the R_FCH_2- protons were found at δ 2.3. Areas under the peaks agreed with the number of protons, and there was no proton resonance at δ 4.5 as would be expected for the $-CHI$ group in a six-membered ring.[25]

Conversion of Ia,b to Derivatives

Elimination of HI from adducts Ia,b gave the exocyclic olefinic amine V and amide VI in excellent combined yield. The relative amount of V and VI varied in the few experiments conducted. Formation of the single exocyclic olefin was conclusive evidence for the iodomethyl group, as demonstrated earlier in analogous cases.[25] Infrared and NMR spectra confirmed the postulated structures. 3-Methylene-4-(perfluoropropyl)-methylpyrrolidine (V) dissolved readily in dilute aqueous acid to give foamy, surface-active solutions; VI was insoluble. In acetone solution, V decolorized 1% $KMnO_4$ aqueous solution readily, and the colloidal suspension foamed in acetone when shaken. Benzene solutions of the amide VI also showed pronounced surface activity.

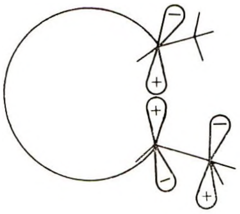


(4)

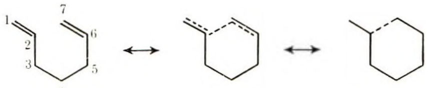
DISCUSSION OF RESULTS

Free-radical cyclization of 1,6-dienes such as diallylcyanamide and their cyclopolymerization are processes which are very closely related. Since diallylcyanamide polymerizes under the same conditions as it cyclizes with adding radicals, it seems logical to assume that the same structural units would be formed in both cases. If this assumption is accepted, it seems clear that revision of structures of cyclopolymers from diallylcyanamide, diallyl ether, 1,6-heptadiene, diethyl diallylmalonate, and other 1,6-dienes having terminal vinyl groups, is now in order. These monomers all give five-membered rings when cyclized during the addition of free radicals. It seems probable that other 1,6-dienes behave similarly.

Just why these particular 1,6-dienes prefer to cyclize to five-membered rings is a puzzling question. It cannot now be attributed to the nature of the adding radical or transfer agent, since the same size ring resulted when different radicals (NF$_2$·,[27] R$_F$·,[25] RS·,[12] Cl$_3$C·,[26] (RO)$_2$PO[25]) were added. Moreover, this observation is in accord with the more rapid cyclization of the 5-hexen-1-yl radical to cyclopentylmethyl rather than to the more stable cyclohexyl radical,[29–31] and would indicate that the process is under stereoelectronic rather than thermodynamic control. It has been suggested[31] that initial stages of addition involve approach of the radical within the plane of the π system and vertical to one of the terminal carbon atoms (VIIa) and that this would lead preferentially to five-membered rings.



VIIa



VIIb

VIIc

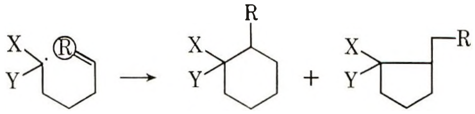
VIId

Butler and Raymond[33] anticipated this conclusion in an unexpected way, since they were convinced that six-membered rings were formed. An orientation effect of across space homoconjugation between double bonds in a monomer molecule was postulated (VIIb–VIId). These authors state, "For a strong π–π interaction the nodal planes of all of the *p*-orbitals must lie in a common plane. An examination of a molecular model of 1,6-heptadiene reveals there are two such conformations with a reasonably close approach between the double bonds. One of these conformations is with the closest approach between atoms C_2 and C_7, and this is the conformation which could act as a precursor to the formation of a six-membered ring. However, in this geometry one of the terminal hydrogens lies in the nodal plane directly between the number two and number seven carbon atoms. It seems highly unlikely that a strong π–π interaction could take place through a bonded hydrogen. The other conformation which meets the π–π interaction requirement is with the closest approach between the carbons C_2 and C_6. In this conformation, measurements on the models indicate a closest approach of approximately 2 Å (center-to-center). There is a slight steric interference at this distance from one of the internal chain hydrogens. Of course, the most serious objection to this conformation is that if it leads to ring closure, the resulting ring would be five-membered."

It is evident that seric considerations also would predict the formation of a five-membered ring. Gibbs and Barton[12] feel that steric control is the basis both for cyclization versus chain propagation (favorable k_c/k_{11}) and for variation of k_c/k_{11} with ring size within an homologous series. They suggest that electronic interaction, if it is present in these systems, may be easily overcome to such a point that the less stable five-membered rings can be formed. This suggestion has been obviated by the new proposal[31] that the addition process involves interaction of the unpaired electron with the lowest unoccupied orbital of the π system, and that this can best form a five-membered ring.

The results of Julia[28,34] are of considerable importance to this discussion, since cyclization of resonance-stabilized radicals to either or both five- and six-membered rings was observed. The more highly stabilized radicals gave a preponderance of six-membered ring compounds (Table II). This was attributed to the increased time available for bonding which allowed the more difficult six-membered ring closure to occur.[34]

TABLE II
Cyclization of Resonance-Stabilized Radicals


VIII IX

X	Y	R	VIII, %	IX, %
CN	CO_2Et	H	86	16
CN	CO_2Et	CH_3	100	0
CN	CN	CH_3	100	0
H	CN	CH_3	0	100
H	CO_2Et	H	44	56
H	CO_2Et	CH_3	0	100

Since resonance-stabilized radicals from monomers such as acrylic anhydride and diethyl α,α'-dimethylenepimelate have been shown to give six-membered ring polymer subunits, there appears to be a reasonable degree of correlation. In any event the clear implication of our results with diallylcyanamide and related 1,6-dienes is that five-membered cycles are formed in preference to six-membered rings. It appears most likely that a careful study of cyclopolymers from this type of monomer will confirm the presence of five-membered rings.

EXPERIMENTAL

Source of Reagents

Diallylcyanamide was obtained from American Cyanamid Co. and redistilled (bp 100°C/12 mm, n_D^{25} 1.4618) after passing down a 6-in. column of alumina (Woelm Activity grade No. 1, neutral used throughout this work). 1-Iodoperfluoropropane from Pierce Chemical Co., and 1-iodoperfluorobutane from Thiokol Chemical Co. were redistilled, and their physical constants agreed with the literature values.[25] Other materials used were analytical or reagent grade.

1-Iodoperfluoropropane and Diallylcyanamide

1-Iodoperfluoropropane (29.6 g, 0.10 mole), diallylcyanamide (6.1 g, 0.050 mole) and azobisisobutyronitrile (AIBN) (0.16 g, 0.0010 mole) were charged to a heavy-walled tube (Fischer-Porter aerosol tube) cooled to −78°C, evacuated, and filled with nitrogen three times. The tube was heated in an oil bath at 80 ± 4°C for 6 hr and opened. 1-Iodoperfluoropropane (17.1 g, 0.058 mole) and diallylcyanamide (0.55 g) were removed by distillation, giving adduct mixture (17.4 g, 83% conversion). Highly polar side products were removed by passing a carbon tetrachloride solution down 4 in. of alumina. The solution was evaporated to a viscous oil and used for conversion to unsaturated derivatives (see below). A second reaction was allowed to run for 18 hr at 70.0°C. In this one instance a complex mixture of products was obtained in 78% conversion which were partially separated by elution on alumina (10 by 1-in. column). Ligroin, benzene, and ether (50 ml each eluate) gave 15 fractions (7.13 g) containing Ia,b ($R_F = CF_3CF_2CF_2$), acetone gave 1.20 g of brown oil, and methanol gave 7.30 g of an amide mixture as shown by infrared analysis. Further separation of adducts Ia,b and *N*-cyano-3-methylene 4-(heptafluoropropyl)-methylpyrrolidine (IV) was achieved by sublimation of fractions 4–14 (4.35 g) in a sublimer cup apparatus at 112°C (0.05 mm). The adduct Ia,b (3.20 g) collected in the cup as an oil, and solid IV (0.40 g) was scraped off the cold finger and recrystallized from hexane, mp 66°C; the infrared showed $CH_2{=}$ at 3090, 1660, and 905 cm^{-1}; $\nu_{C \equiv N}$ 2220; δ_{CH} 1480, 1350, 1430, and 1350; heavy CF bands at 1220, 1180, and 1120 cm^{-1}, bands also at 1020, 960, 930 and 720 cm^{-1}; NMR showed δ 2.32, CF_2CH_2 (2, *t*, 20 Hz); δ 3.25, $CHCH_2$-N (2, *q*, 7 Hz); δ 3.75, *C*H-CH_2 (1, *t*, 7 Hz); δ 4.05, NCH_2-C= (2, s); δ 5.1, $CH_2{=}$ (2, *s*, with 2–3 Hz splitting). The pattern agreed well with postulated structure.

ANAL. Calcd for $C_{10}H_9F_7N_2$: C, 41.4%; H, 3.12%. Found: C, 41.48%; H, 3.25%.

A mixture of *cis*- and *trans*-1-(perfluoropropyl)methyl-2-iodomethyl *N*-cyanopyrrolidine (Ia,b) was obtained as an oil, which could not be crystallized or separated by distillation. The infrared showed $\nu_{C \equiv N}$ 2220, no $CH_2{=}CH$, but bands at 1350, 1220, 1180, 1120, 960, 930, and 730 cm^{-1}. NMR proton resonances were found at δ 2.35, CF_2CH_2 (2, *t*, J = 19 Hz); δ 2.8, CH_2CH-$CHCH_2I$ (2, *q*, J = 7 Hz); δ 3.25, $CHCH_2I$ (2, *t*, J = 7 Hz); δ 3.3–4.2, CH_2NCH_2 (4, *m*).

ANAL. Calcd for $C_{10}H_{10}F_7N_2I$: C, 28.72%; H, 2.41%. Found: C, 29.00%; H, 2.42%.

1-Iodoperfluorobutane and Diallylcyanamide

Iodoperfluorobutane (34.5 g, 0.10 mole), diallylcyanamide (6.10 g, 0.050 mole) and AIBN (0.15 g, 0.0010 mole) was heated as above for 16 hr at 70

± 0.01°C in a thermostatted oil bath. A mixture of Ia,b [$R_F = CF_3$-$(CF_2)_3$-] mp 48–53°C (25.3 g, 100% conversion) remained after 1-iodoperfluorobutane was recovered (16.4 g, n_D^{25} 1.3180, 95%). Several similar experiments are summarized in Table I. Elution chromatography showed that 90–95% of the product mixture in each case was Ia,b in contrast to the anomalous reaction of 1-iodoperfluoropropane described above. Thus, impure Ia,b (22.0 g) was dissolved in benzene (250 g) and run down 60 g (9.5 in.) of alumina. Three elutions with benzene (100 ml each) gave Ia,b (20.7 g, 94%, mp 48–52°C); acetone and methanol gave 1.2 g of a brown oil mixture which was shown by infrared data to contain amide and other groups but no nitrile. A solution in CCl_4 deposited brown gum and crystalline solid which was washed with benzene and ether leaving 0.10 g of white solid, III. On recrystallization from benzene III had mp 73–75°, and from aqueous ethanol, mp 75–76°, 0.029 g. The infrared spectra showed ν_{NH} 3450, 3340, and 3290 cm^{-1}; $CH_2{=}CH$ bands at 3020, 1660, 990 and 908: $\nu_{C=O}$ 1645 (amide I) and 1600 cm^{-1} (amide II); heavy CF bands at 1230–1130 cm^{-1}; and bands at 1060, 1040, 1020, 870, 850, 770, 730, 715, 670, 600, 590, 560, and 530 cm^{-1}: the NMR (d^6-acetone solution) showed δ 2.1, 2.8, 3.3–3.5, and 5.3 (poorly resolved spectrum). Except for bands at 3020, 1660, 990, and 908 cm^{-1} the infrared spectrum of III resembled that of VI. III was tentatively identified as *N*-allyl *N*-(2-iodo-4 through 8-nonafluoro-heptyl) urea. Hydrolysis in aqueous alkali gave iodide ion, which precipitated silver iodide and formed a dark purple layer in CCl_4.

ANAL. Calcd for $C_{11}H_{12}F_9N_2OI$: C, 27.2%; H, 2.48%; I. 26.1%. Found: C. 29.3%; H, 2.44%; I, 25.1%.

A solution of Ia,b fractions (14.8 g), 15 ml of ether and 100 ml of hexane was chilled to −78°C, the white solid Ia (11.8 g) collected and rinsed with cold ether–hexane; mp (sinter 53°C) 54–55°C. The filtrate gave 2.43 g of solid, mp 37–46°C, and 1.17 g of viscous oil Ib and II which sublimed at 100°C (0.12 mm); the infrared spectrum (CCl_4) showed bands the same as Ia, but weak bands of $CH_2{=}CH$ were also present. NMR (CCl_4) showed δ 3.2, CH_2I (as in Ia), δ 4.4, $CH_2C\mathit{H}I$-CH_2 (II), and δ 5.0–6.2, $CH_2{=}CH$—, multiplet (II). The relative areas indicated about 25% was II (2–3% of original sample). Recrystallization of Ia (11.5 g) from 350 ml of hexane gave 8.5 g, mp 56–57.5°C, and 1.6 g, mp 54.5°C. A second recrystallization gave material with mp 58–59°C; the infrared spectrum showed ν_{CH} 2950, 2880 cm^{-1}; $\nu_{C\equiv N}$ 2200; δ_{CH} 1480, 1425, 1340 cm^{-1}; ν_{CF} 1230, 1140; bands at 1120, 930, 905, 880, 720, and 590 cm^{-1}. The NMR spectrum showed δ 2.32, $C\mathit{H}_2CF_2$, (2, *t*, J = 19 Hz); δ 2.75, —*CH*—*CH*—, (2, *m*); δ 3.18, $C\mathit{H}_2I$ (2, *d*, J = 7 Hz); δ 3.2–4.2, CH_2NCH_2, (4, *m*).

ANAL. Calcd for $C_{11}F_9H_{10}IN_2$: C, 28.25%; H, 2.15%; N, 5.99%; I, 27.1%. Found: (Ia,b): C, 28.1%; H, 2.2%; N, 6.4%; I, 26.7%.

Hydrolysis of Iab to 3-Methylene-4-(heptafluoropropyl)methylpyrrolidine (V) and 1-Carboxamido-3-methylene-4-(heptafluoropropyl) methylpyrrolidine (VI)

Ia,b ($R_F = CF_2CF_2CF_2—$) mixture (11.5 g, 0.0275 mole) was added to a solution of sodium methoxide (5.4 g, 0.10 mole) in 75 ml of absolute methanol and heated at 67°C for 4 hr. The red solution was poured into 100 ml of water, the brown oil drawn off, and the aqueous layer extracted three times with 20 ml of ether. The organic layer was treated with decolorizing carbon and evaporated off, 7.4 g (100% crude yield of amine and amide), mp (sinter 57.5°C) 59–62°C. It was recrystallized from 40 ml of pentane, chilled to −5°C yielding 6.8 g, mp (sinter 60.5°C) 61–62°C, and a second crop, 0.50 g, mp (sinter 61°C) 63–65°C. The solid (6.8 g) was redissolved in pentane and chromatographed on 6 in. of alumina, with elution with 100 ml of ether, with methylene chloride (50 ml), and with methanol (50 ml). The first eluate gave 5.8 g (80% yield) of V. On recrystallization from pentane a material with mp 63–64°C was obtained. The infrared spectrum (CCl_4) showed ν_{NH} 3450 cm^{-1}; $\nu_{CH_2=}$ 3090 cm^{-1}; ν_{CH} 2980, 2950, 2890, 2850 cm^{-1}; $\nu_{C=CH_2}$ 1630 (vs) cm^{-1}; δ_{CH} 1450, 1380, 1350 cm^{-1}; ν_{CF} 1260, 1230–1180 (vs) cm^{-1}; bands at 1120, 1100, 1080, (CH_2NHCH_2), 1020, 960, and 925 cm^{-1}, $\gamma_{CH_2=}$ 890 and 720 cm^{-1}. The NMR spectrum (CCl_4) showed δ 2.35 CF_2CH_2 (*t* split further, 20 Hz × 7 Hz); δ 3.06 $CH_2CH—CH_2$ (5- line, 7 Hz); δ 3.68 $NCH_2C=$ (*s*); δ 3.82 $N—CH_2CH$ (*d* distorted, 7 Hz); δ 4.75 NH (?), (1, *s*); δ 5.0 $C=CH_2$ (2, *d* split further, 7 Hz × 1–2 Hz). The resonance at δ 4.75 was absent in VI (see below). V dissolved in 5% hydrochloric acid (foamy solution) and reprecipitated when made basic.

ANAL. Calcd for $C_9H_9F_7N$: C, 40.92%; H, 3.43%. Found: C, 41.16%; H, 3.65%.

The methylene chloride and methanol eluates gave 0.174 g and 1.35 g of amide (VI) (18% yield), mp 118–119°C, recrystallized from benzene or CCl_4. The infrared spectrum (Nujol mull on KBr plates or KBr pellet) gave ν_{NH} 3430, 3310, 3270 cm^{-1}: $\nu_{C=C}$, $\nu_{C=O}$ 1645 cm^{-1} (amide I); ν_{C-N} 1610 cm^{-1} (amide II); δ_{CH} 1480, 1450, and 1350 cm^{-1}; ν_{CF} 1270, 1230; bands at 1180, 1165, 1125, 1115, 1035, 1015 w, 980 w, 950 s, 930 s, 870 w, 790 w, 735 s, 675 w, 620 w, 570 w, and 555 w cm^{-1}. The NMR spectrum (d^5-pyridine solutions) showed δ 1.8–2.7, CH_2CF_2 (1.9, broad multiplet); δ 2.7–4.15, $(CH_2)_2N—$, $CH—CH_2$, 5.4, unresolved multiplets); δ 4.9 $C=CH_2$ (1.95, *s*); δ 6.55, NH_2 (1.7, s). The amide protons were reported at δ ca. 6.4 in propionamide.[35]

ANAL. Calcd for $C_{10}H_{11}F_7N_2O$: C, 38.97%; H, 3.60%. Found: C, 38.70%; H, 3.39%.

In similar fashion 13.4 g (0.0286 mole) of Ia,b [$R_F = CF_2[CF_2)_3-$] gave brown solid (9.8 g), which did not distill when heated to 122°C/15mm. The infrared spectrum (CCl_4) showed ν_{NH} 3360, cm^{-1}; $\nu_{CH_2=C}$ 3090 cm^{-1};

$\nu_{C=C}$ 1630 cm^{-1}; ν_{CN} 1140, 1100, and 1080 cm^{-1}; $\nu_{CH_2=}$ 895 cm^{-1}. The solid (9.0 g) on a Buchner funnel was washed three times with *n*-pentane, and the residue (5.6 g) was recrystallized from pentane and a little ether. The first two fractions contained 0.08 g of amine (VI) [$R_F = CF_3(CF_2)_3$-], mp 131°C; the remainder gave amine (V) [$R_F = CF_3(CF_2)_3$-], 4.9 g, mp 67–68°. The infrared spectrum (CCl_4, NaCl) showed ν_{NH} 3350 cm^{-1}; $\nu_{C=CH_2}$ 3080 cm^{-1}; γ_{CH} 2980, 2940, 2850 cm^{-1}; $\nu_{C=CH_2}$ 1630 cm^{-1}; δ_{CH} 1450, 1380, 1340 cm^{-1}; ν_{CF} 1240 cm^{-1}; bands at 1170, 1140, 1100, 1080, 1022, 950, 895, 882 and 720 cm^{-1}. The infrared spectrum of VI (Nujol mull, KBr plates) showed ν_{NH_2} 3430, 3320, 3270 cm^{-1}; $\nu_{CH_2=}$ 3080, $\nu_{C=C}$, $\nu_{C=O}$ 1645 cm^{-1}; ν_{C-N} 1605 cm^{-1} (amide II); ν_{CF} 1230, 1135 cm^{-1}; bands at 1050, 1020, 905, 895 ($\gamma_{CH_2=}$), 855, 775, 760, 730, 715, 665, 615, 600, 570, and 530 cm^{-1}. NMR spectra were identical with those of V and VI above.

ANAL. Calcd for $C_{11}H_{11}F_9N_2O$: C, 37.51%; H, 3.15%. Found (VI): C, 37.77%; H, 3.04%.

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Irradiation of Terephthalophenone in Isopropyl Alcohol*

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Synopsis

Irradiation of terephthalophenone in isopropyl alcohol gave a bright yellow-colored intermediate which decayed rather rapidly. The products were complex and depended upon the mode of irradiation. They ranged from a mixed polymer I to a dimer II. I consisted of about 5 terephthalophenone units capped with hydrogen or isopropyl alcohol radicals or terminated by cyclization. II, the dimer, was capped by hydrogen atoms.

INTRODUCTION

The literature[1] states that a yellow color is produced by a solution of terephthalophenone or isophthalophenone in alcohol exposed to light. When oxygen is introduced, the color disappears. Since very little further information is given in the above paper, a study was initiated to shed some light on the stoichiometry of the reaction and on the nature of the intermediate and products. It should be stated now that the stoichiometry and the product composition were variable depending on the mode of irradiation.

EXPERIMENTAL

Stock Isopropyl Alcohol

About 2.3 ml of dry ether, the internal standard, was added to 2 liters of acetone-free isopropyl alcohol, the mixture being used as a stock solution. The stock solution was protected from air by an argon atmosphere and did not change composition over a period of 3 months.

Gas Chromatography

A 6-ft 25% glycerol on Celite 545 column (Glycerol K) at 80°C with 80 ml/min He flow rate was used for acetone determination with hydrogen flame detector. The calibration curve for acetone between 64 to 400 mg/100 ml of stock isopropyl alcohol was linear. Peak area ratios, acetone/ether, were plotted versus acetone weight, mg/100 ml. The peak areas,

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

having retention time of 30 sec for ether and of 80 sec for acetone, were narrow in width, necessitating the injection of a known sample for each series of runs to set the widths. In later work, a better column was found: a 6-ft, 20% Carbowax 20 M column on Diatoport S, 80–100 mesh; retention time of acetone 125 sec.

Normal Irradiation

Most irradiations were carried out with a mercury high-pressure lamp, Philips, HPK 125 W, suspended in an open well surrounded by water-cooled jacket. The inner wall of the jacket cooled the lamp and the outer wall cooled the solution undergoing irradiation and contained in a Pyrex glass apparatus. The solution was stirred by a magnetic bar and protected from air by an argon atmosphere.

More Strenuous Irradiation

The solution to be irradiated was added to a series of 3 ml ampoules. The ampoules were flushed with argon, sealed, and mounted against the outside wall of the water jacket of the irradiation apparatus described above. Water was not circulated in the jacket but rather was allowed to boil gently from the heat generated by the lamp. The radiation from the lamp at 100°C was more intense.

Mild Irradiation

A Sylvania, 400-W, H33-ICD medium pressure mercury lamp was immersed in a circulating water bath held at 25°C. Ampoules, filled, degassed, sealed and mounted on a plastic board, were immersed in the water-bath and the distance from the lamp to the board adjusted to about 15 in. At this distance, the rate of acetone formation followed pseudo zero-order kinetics.

Terephthalophenone

The compound was recrystallized from ethyl acetate giving almost colorless plates, mp 163.5–164.5°C (Kofler), reported[2] mp 160–161°C. The ultraviolet absorption spectrum was as follows: π–π^* transition in ethanol, λ_{max} 264 mμ, $\epsilon_{max} = 3.23 \times 10^4$; n–π^* transition, λ_{max} 335 mμ, $\epsilon_{max} = 144$. An isopropyl alcohol solution of the ketone in a closed vessel exposed to sunlight turned bright yellow. The color was discharged by exposing contents to air but reappeared when the vessel was closed and irradiated. The process could be repeated a number of times but eventually the yellow color failed to appear.

The Yellow Intermediate, Y ($\lambda_{max} = 416.5$ mμ)

The molecular extinction coefficient could not be ascertained, as the optical density of the π–π^* transition band at 264 mμ and the 416.5 mμ band could not be measured simultaneously. The optical density of the

TABLE I

t, sec	OD	t, sec	OD
0	0.0	175	0.33
30	0.27	185	0.30
60	0.40	205	0.26
90	0.43	305	0.21
120	0.45	605	0.14
165	0.43	905	0.10

264 mμ band did not seem to decrease as the 416.5 mμ band increased. The rate of appearance and disappearance of the 416.5 mμ band was followed by dissolving 2.29 mg of terephthalophenone in 40 ml. of air-free isopropyl alcohol, placing an aliquot in an air-tight 1 cm. cuvet, and carrying out alternate radiation with light passing through a Brephos-Schwarz filter with alternate measurement of optical density at 416.5 mμ. Results are shown in Table I.

The yellow compound, Y, showed no ESR signals. Attempts to trap Y with butadiene failed because of the quenching action of butadiene. With furan in slight excess of 2 eq, a small amount of white powder, mp 150–152°C, was obtained in one experiment. Enough of the white powder could not be accumulated to identify.

Product I from Irradiation of Terephthalophenone

Terephthalophenone (2.334 g) in 150 ml of benzene (to solubilize substrate) and 50 ml of isopropyl alcohol was irradiated with magnetic stirring for a total of 19 hr while protected from air with argon. The bright yellow color eventually faded to a straw color. The solution was concentrated on a rotating evaporator yielding a slightly yellowish solid. It was impossible to crystallize the solid in concentrated solutions; a skin formed over the surface of the liquid, and some gel was observed in the liquid. The compound was dissolved in acetone, filtered, and allowed to evaporate. On complete evaporation a solid was obtained which looked crystalline but was not, mp 166.5–168.5°C. The sample was dried at 0.001 mm pressure at 80°C for several hours; the product had mp 162–164°C, the average molecular weight (by rise in boiling point in C_6H_6) was 1335. Further evacuation at 0.001 mm and at 120°C for 12 hr caused no change in the melting point; the average molecular weight was 1570.

Infrared examination showed the absence of a carbonyl band at 1650 cm^{-1}, the presence of a hydroxyl band at 3500 cm^{-1}, a small peak at 1600 cm^{-1}, larger sharp peaks at 1500 and 1450 cm^{-1}, broad bands at 1330, 1160, and 1030 cm^{-1}, a small peak at 800 cm^{-1}, and large peaks at 750 and 700 cm^{-1}. Nmr ($CDCl_3$):δ 1.3 (s from CH_3); 2.4 (broad s, OH); 3.0 (broad s, OH); 5.8 (s?, barely above noise, *H*COH), 7.8 (m, arom. H). The NMR singlet at 1.3 ppm cannot be from isopropyl alcohol: the methyl signals of isopropyl alcohol would have appeared as a doublet at 1.1 and 1.2 ppm.

Integration shows a ratio of aromatic to aliphatic hydrogen of 29 to 1. The molecular weight indicates that about 5 terephthalophenone units are combined which, if they were capped by isopropyl alcohol groups, would give a ratio of 5.83 aromatic to aliphatic hydrogen. Thus, only a few polymer chains terminate in isopropyl alcohol groups. The NMR signal at 5.8 ppm indicates that at least half of the polymer ends is capped with hydrogen (integration of aromatic to benzylic hydrogen: 70 to 1, approximately). The rest of the polymer must be in cyclic form.

I gave a positive Tollen's test on heating and also polymerized styrene at 130°C. Both tests were indicative of the benzpinacol structure, which dissociates in part to the free radical, $Ar_2\dot{C}OH$, at elevated temperatures. Thin-layer chromatography with Eastman Silica Gel 6060 with 10% methanol in C_6H_6 showed a single, elongated spot, $R_f = 0.7$.

Product II

Irradiation for 25 hr by the more strenuous irradiation procedure gave a stoichiometry of acetone to terephthalophenone of 1.5, 1.3, 1.5, 1.5, 1.5, 1.6, 1.5 (avg = 1.5), indicating three acetone molecules are produced for every two terephthalophenone molecules consumed. The contents of the ampoules were combined and evaporated to dryness, yielding an almost colorless, crystallike glass, mp 107–110°C.

Anal. Calcd for $C_{40}H_{34}O_4$: C, 83.04%; H, 5.93%; O, 11.03%; MW, 579. Found: C, 82.77%; H, 6.26%; O, 10.94%; MW, 698.

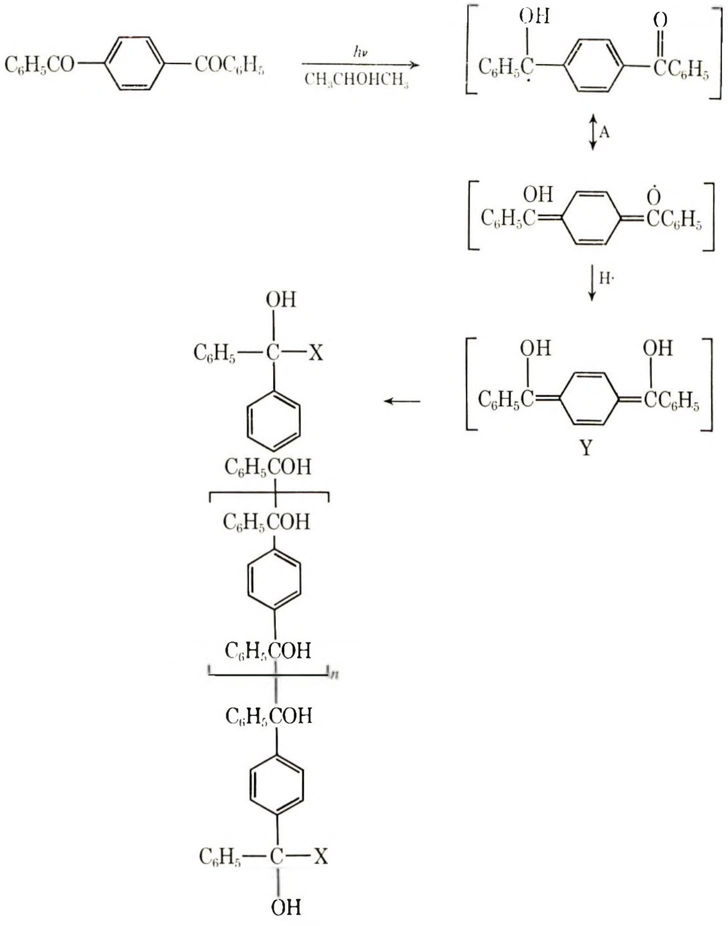
The infrared spectrum of II was almost identical to that of I. The NMR spectrum, however, differed significantly: the benzhydryl hydrogen peak at 5.7 was much more prominent; one broad hydroxyl hydrogen was at 3.0 ppm and (less certainly) a second at 2.25 ppm. Integration indicated the ratio: aromatic hydrogen 19, benzhydryl hydrogen 1, hydroxyl hydrogen 1, second hydroxyl hydrogen 1. The actual ratio should be 14:1:1:1. The difference was due to traces of isopropyl alcohol which were not removed by pumping. That it was isopropyl alcohol was confirmed by the NMR ($CDCl_3$) δ 1.1 and 1.2 (*d*, CH_3). This doublet differed considerably from the singlet at 1.3 for I.

Product III

Under mild irradiation conditions, the rate of acetone formation was found to be 1×10^{-4} mole/hr for the first 50% of reaction, the rate tailing off toward the end of the reaction. This pseudo zero-order rate is slower than that of benzophenone (2×10^{-3} mole/hr). The products of the 50% and 100% irradiation were examined only by NMR ($CDCl_3$): δ 7.5–7.0 (m, aromatic H) 3.0 (broad *s*, OH). No benzylic hydrogen nor methyl hydrogens from an isopropyl alcohol residue were present, facts which could be compatible only with a cyclic structure. Ratios of aromatic to hydroxyl hydrogen were not compared as starting material interfered with this ratio.

DISCUSSION OF RESULTS

The course of the reaction of terephthalophenone irradiated in isopropyl alcohol was found to be complex and variable. Under normal irradiation conditions (see Experimental) the course may be represented tentatively as



I, II, or III

No evidence has been gathered to eliminate the possibility that at least part of the course of the reaction proceeds via the coupling of A with itself.

Arguments for the existence of Y are the long-wavelength absorption (416.4 mμ), the nonradical nature of the intermediate, and the stability of the intermediate although it does decay with time. An argument against its existence is that a similar yellow color is produced with isophthalophenone (which could not form a quinone-dimethide structure).[1] The composition of I, to judge from molecular weight, NMR, and infrared studies, is that $n = 3$ or 4 and that X, the capping group, is partly $(CH_3)_2\dot{C}OH$, partly H, and partly where the ends of the polymer are cyclized at the X positions (see Experimental).

The indication that hydrogen partly capped the polymer suggested that more strenuous irradiation conditions would increase the amount of this hydrogen capping. Indeed, the product from intense irradiation is crystalline, mp 107–110°C, and is nearly compatible with the structure II, where $n = 0$ and $X = H$. A slight amount of isopropyl alcohol seemed to be strongly absorbed by this product as indicated by NMR and by molecular weight determination.

The implication that some cyclic polymer was formed in I suggested that a greater amount of the cyclic derivative could be obtained by milder irradiation conditions. Indeed, the NMR of the product obtained under mild irradiation was compatible only with the structure of such a cyclic derivative. Complete identification of III was postponed, however, because the cyclic product could be more assuredly synthesized by mild irradiation of terephthalophenone and the corresponding carbinol, *p*-xylene-α,α'-diphenyl-α,α'-diol in benzene. This work is in progress.

The senior author, D.P., a student of Dr. C. S. Marvel, congratulates him on the occasion of his seventy-fifth birthday. The senior author also wishes to acknowledge the support of the National Science Foundation (Grant No. GP-4414) and that of Dr. Günther O. Schenck and the Max Planck Institute für Kohlenforschung, Abt. Strahlenchemie, Mülheim, W. Germany for furnishing laboratory space, equipment, housing, consultation, and many other forms of kind assistance. The junior author, P.D.T., is indebted to the Monsanto Chemical Co. for support during part of this work.

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Synthesis of Spiro Polymers*,†

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Synopsis

Synthesis of the first totally organic spiro polymer was accomplished by the reaction of 1,4-cyclohexanedione and pentaerythritol in benzene plus a trace of *p*-toluenesulfonic acid to produce the polyspiroketal. The polymer did not melt, but began to decompose at 350°C. Although it was insoluble in most common solvents, it was found to be soluble in hexafluoroisopropanol. The x-ray diffraction indicated the polymer was very highly crystalline. A series of lower molecular weight related polymers were prepared by carrying out a similar condensation with a mixture of 1,4-cyclohexanedione containing 5–50 mole-% of cyclohexanone. In order to prepare a material with greater solubility, a polyspiroketal was prepared from 1,10-cyclooctadecanedione plus pentaerythritol. This polymer was soluble not only in hexafluoroisopropanol, but to a limited extent in dimethyl sulfoxide.

INTRODUCTION

Double-stranded polymers, such as the ladder and spiro polymers, have attracted interest because they should have extremely high melting points because of restricted rotation and should have a high degree of chemical and thermal stability, since two cleavages are required within a single ring to result in a drop in molecular weight. Although a number of workers, including Staudinger,[1,2] who reinvestigated the cyclization of natural rubber, Marvel and Levesque,[3] who studied the cyclization of poly(methyl vinyl ketone) and Houtz,[4] who studied the formation of "black orlon" from polyacrylonitrile, have postulated partial ladder structures, the first polymer with a complete ladder structure was very likely that (I) which was reported in 1954 by Bailey and Economy[5,6] by the reaction of 2-vinyl-1,3-butadiene with benzoquinone.

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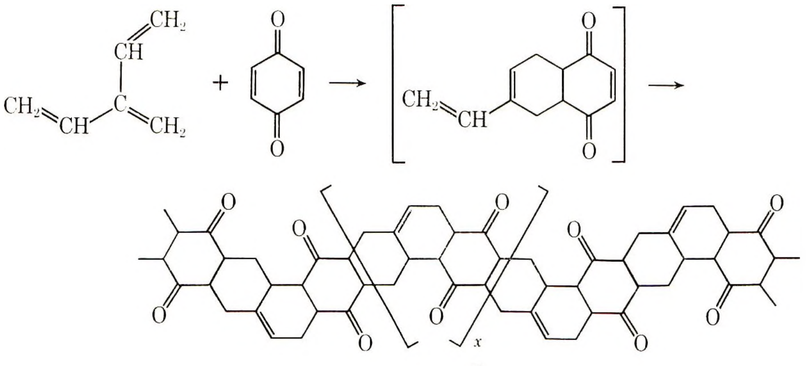
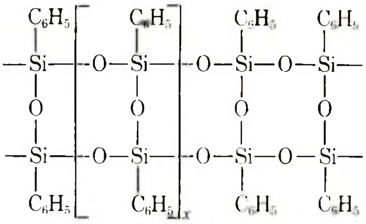


(1)

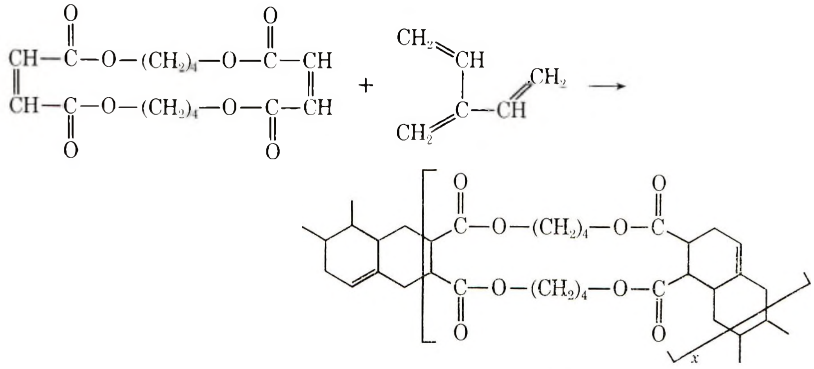
I

This polymer did not attract much attention at the time, because it was initially reported to be infusible as well as insoluble in all available solvents. More recent work has shown this material to be soluble in hexafluoroisopropanol. In contrast, the polyphenylsilsesquioxane (II) reported by



II

Brown and co-workers[7] in 1960 was soluble in a number of common solvents although it was still infusible. That the presence of a large flexible ring in a ladder polymer would increase the solubility was shown by the synthesis of a Diels-Alder polymer (III) from 2-vinyl-1,3-butadiene and a large ring bisfumarate.[8]



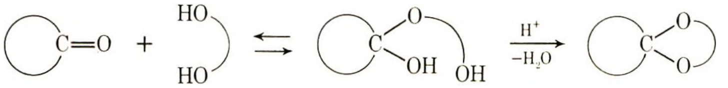
(2)

III

Although there have been many other approaches to syntheses of ladder polymers, the evidence indicated that probably no other polymers have a perfect ladder structure and thus contain some single-stranded units even though a number of these partial ladder polymers have improved thermal stability.[9]

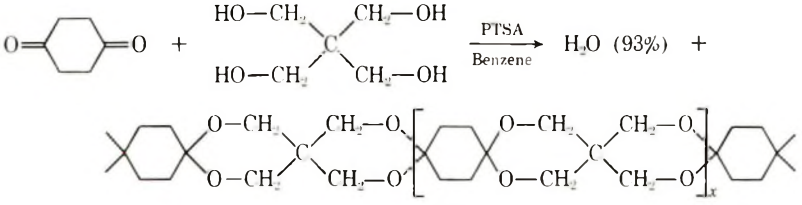
POLYMERIZATION

Although a number of inorganic polymers have been assigned the complete spiro structure,[10–12] no complete spiro polymer containing only carbon, oxygen or nitrogen in the backbone has been reported. In order to prepare such a spiro polymer we began a search for reactions that would produce either a spiro ring or form no bond at all. The reaction that appeared to meet this requirement was a ketal formation between a cyclic ketone and diol. The condensation proceeds stepwise, but since the hemiketal intermediate is unstable, no condensation would be expected to take place until the stable ketal is formed.



(3)

Since pentaerythritol forms spiro compounds very readily and gives high enough yields to be used in a polymerization reaction with dialdehydes,[13,14] it was reasoned that a similar reaction with a cyclic diketone should produce a polyspiroketal. Thus, when 1,4-cyclohexanedione was heated in benzene with pentaerythritol plus a trace of *p*-toluenesulfonic acid (PTSA) and the resulting water (93%) was removed by distillation, a white polymer (IV) precipitated.

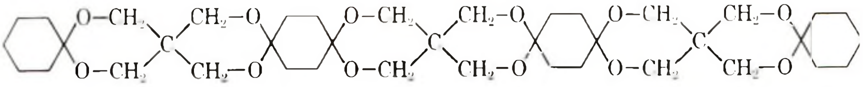


(4)

IV

This powder did not melt but began to decompose at 350°C. The polymer was insoluble in most common solvents for polymers, such as dimethylformamide, dimethyl sulfoxide, and hexamethylphosphoramide, but did dissolve in concentrated sulfuric acid with degradation. The infrared spectrum indicated the presence of the spiroketal structure with only a trace of carbonyl and hydroxyl groups still detectable. Evidence for the linear nature of the polymer was obtained from the x-ray diffraction pattern which indicated that the polymer was at least 95% crystalline with a very strong band at 5.10 Å.

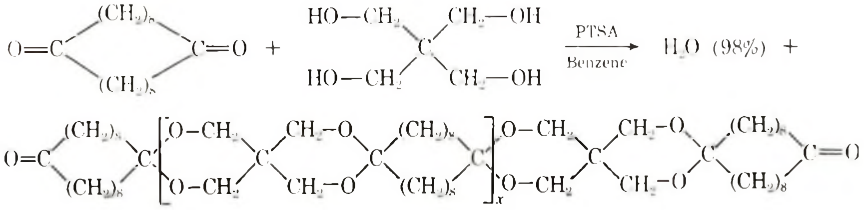
Since it was difficult to determine the structure or characterize the insoluble polymer, several approaches were made to produce soluble spiro polymers. First, the molecular weight of the spiro polymer containing the cyclohexane rings was reduced by carrying out the polymerization with a mixture of cyclohexanone and 1,4-cyclohexadione. As the amount of cyclohexanone was increased from 5 to 10 to 20 to 50 mole-%, the solubility of the resulting spiro polymer increased. The polymers containing the large amounts of cyclohexanone as a chain stopper were swollen in benzene and were soluble in dimethyl sulfoxide. The polymer (V) with 50 mole-% cyclohexanone should theoretically contain nine rings and give a molecular weight of 720.



V

Even this material did not melt but began to decompose slightly at 305°C. The x-ray diffraction studies indicated that all of these capped spiro polymers were crystalline with a diffraction pattern very similar to that of the unmodified spiroketal.

Secondly, since the introduction of a large ring increased the solubility of a ladder polymer,[8] this effect was investigated in the spiro series. Thus, 1,10-cyclooctadecanedione and pentaerythritol were condensed to form the polyspiroketal (VI).



VI

This polymer also did not melt but began to decompose at about 300°C. The x-ray diffraction studies indicated that this spiro polymer was also very highly crystalline with a very dominant peak at 4.70 Å. However, about 12% of the polymer, presumably the low molecular weight fraction, was soluble in boiling dimethyl sulfoxide. Both the soluble and the insoluble fractions had similar analyses, infrared spectra, and x-ray diffraction patterns.

Finally a copolymer was prepared from a mixture of 1,4-cyclohexadione and 1,10-cyclooctadecanedione plus pentaerythritol in order to reduce the crystallinity. However, even this mixture produced a polyspiroketal that was highly crystalline, as indicated by x-ray diffraction studied with intense bands at both 5.15 and 4.74 Å. This result would suggest that the material was a block copolymer rather than a random copolymer.

A stroke of good luck developed with the availability of Dupont's hexafluoroisopropanol. All of the spiro polymers including the polyketal from 1,4-cyclohexanedione prepared in this work were completely soluble in hexafluoroisopropanol at room temperature and all of the polymers could

TABLE I

Comonomer for pentaerythritol polymer	Intrinsic viscosity in hexafluoroisopropanol at 25°C
1,4-Cyclohexanedione	0.049
1,10-Cyclooctadecanedione	0.092
Mixture of 1,4-cyclohexanedione and 1,10-cyclooctadecanedione	0.045

be recovered from this solvent. The spiro polymers were also soluble in hexafluoroacetone sequihydrate, but some solvolysis or degradation always occurred. The complete solubility of these spiro polymers proves that they are linear and not crosslinked. Intrinsic viscosities of these materials were determined at 25°C in hexafluoroisopropanol with the results given in Table I.

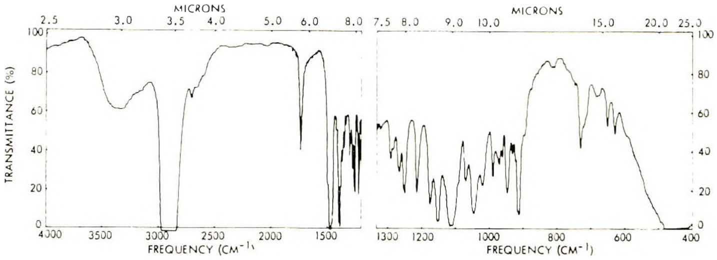


Fig. 1. Infrared spectrum of pentaerythritol–1,4-cyclohexanedione polyspiroketal, Nujol mull.

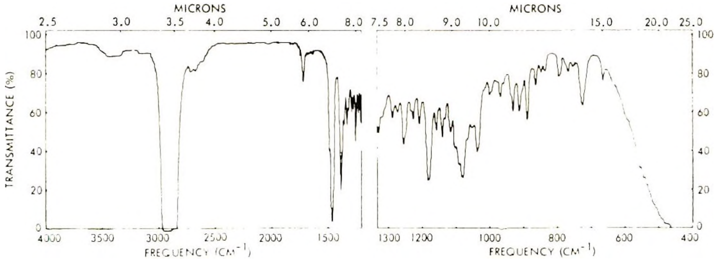


Fig. 2. Infrared spectrum of pentaerythritol–1,10-cyclooctadecanedione polyspiroketal, Nujol mull.

The constants for these polymers in the relationship $[\eta] = KM^{\alpha}$ are not yet known, but if one assumes K in the range of 1×10^{-4} and an $\alpha = 2/3$, the polymer from 1,4-cyclohexanedione would have a calculated molecular weight in the range of 10,000 while the polymer from 1,10-cyclooctadecanedione would have a calculated value of about 30,000. These values for the molecular weights are also consistent with the molecular weight calculated from endgroup analysis involving the ketone absorption band in the infrared spectra listed in Figures 1 and 2.

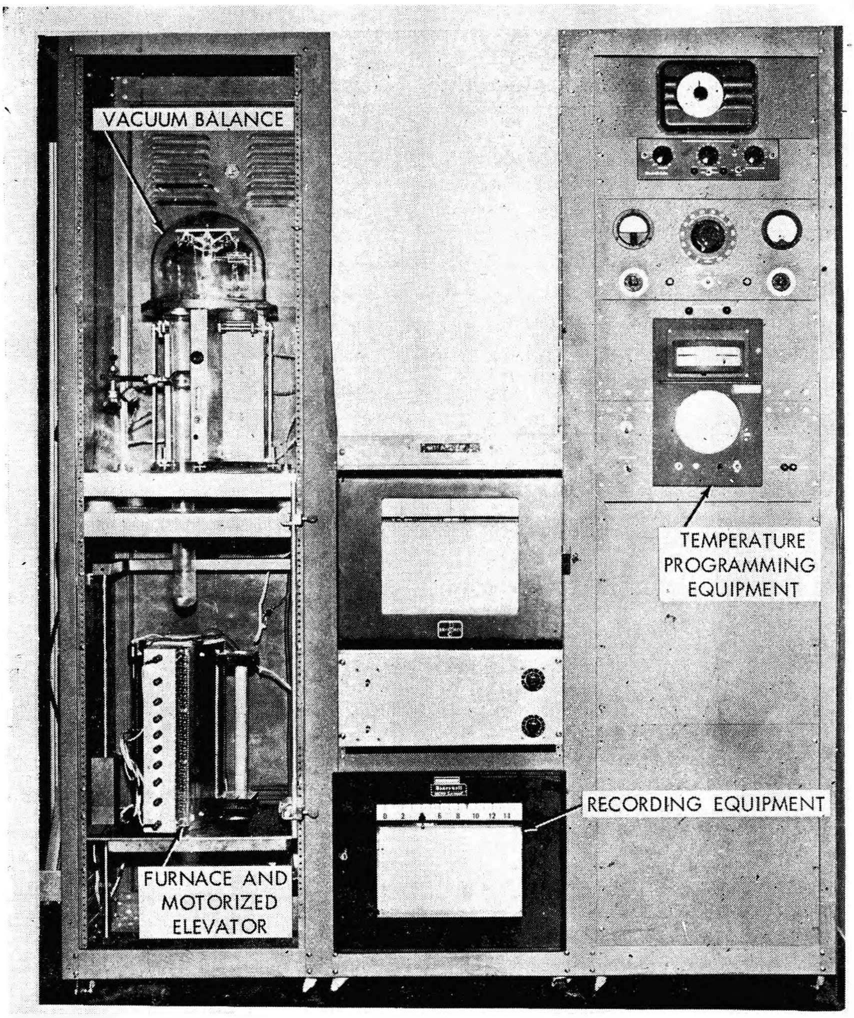


Fig. 3. Thermogravimetric analysis apparatus.

Thermogravimetric analyses (Figs. 3–6) reveal that the spiro structure does indeed confer increased thermal stability to the polymers. Madorsky[15] has shown that the introduction of oxygen into a hydrocarbon polymer generally lowers the thermal stability of the polymer because the carbon–oxygen bond is weaker than the carbon–carbon bond. For example, the T_h of polypropylene is 387°C, while that of atactic polypropylene oxide is 295°C, where T_h is Madorsky's characteristic temperature for maximum rate of decomposition. The polyspiroketals were studied in the thermogravimetric analysis apparatus,[16] and the results shown in Table II were obained, where $T^1/_2$ is the temperature in the TGA analysis required for 50% weight loss.

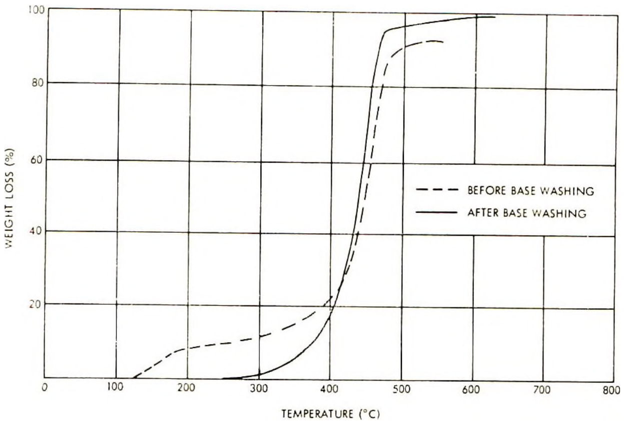


Fig. 4. Thermograms of pentaerythritol–1,4-cyclohexanedione polyspiroketal.

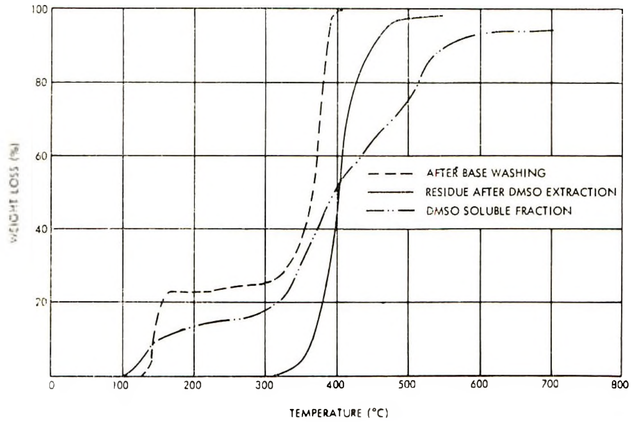


Fig. 5. Thermograms of pentaerythritol-1,10-cyclooctadecanedione polyspiroketal.

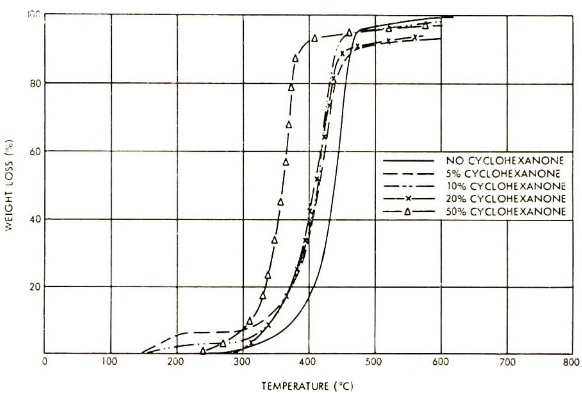


Fig. 6. Thermograms of pentaerythritol–1,4-cyclohexanedione polyspiroketals with cyclohexanone.

TABLE II

Comonomer for polymer from pentaerythritol	$T^1/_2$, °C
1,4-Cyclohexanedione	450
1,4-Cyclohexanedione and cyclohexanone (95:5)	425
1,4-Cyclohexanedione and cyclohexanone (90:10)	414
1,4-Cyclohexanedione and cyclohexanone (80:20)	407
1,4-Cyclohexanedione and cyclohexanone (50:50)	360
1,10-Cyclooctadecanedione	365
1,10-Cyclooctadecanedione (dimethyl sulfoxide-insoluble fraction)	400
1,10-Cyclooctadecanedione (dimethyl sulfoxide-soluble fraction)	400
1,4-Cyclohexanedione and 1,10-cyclooctadecanedione (50:50)	438

It can be seen from these data that the spiro structure has made these polymers much more thermally stable than one would expect from a linear aliphatic polyether.

If the proper solvent can be found for the polymerization, it appears that a large variety of organic reactions can be used to produce spiro polymers with high melting points and increased thermal and chemical stability.

EXPERIMENTAL

Source of Starting Materials

Pentaerythritol (mp 255–260°C) was obtained from Eastman Organic Chemicals, Rochester, N. Y. Benzoquinone (mp 113–115°C), acenaphthenequinone (mp 259–262°C, and 1,4-cyclohexanedione (mp 77–79°C) were supplied by the J. T. Baker Chemical Co., Phillipsburg, N. J., while the 1,2-cyclodecanedione (mp 42.5–45°C) and another sample of 1,4-cyclohexanedione (mp 77–78.5°C) were supplied by the Aldrich Chemical Company, Milwaukee, Wisconsin. The 1,10-cyclooctadecanedione used was a sample synthesized by the method of Blomquist et al.[17]

Reaction of Pentaerythritol and 1,4-Cyclohexanedione

A mixture of 6.8 g (0.05 mole) of pentaerythritol, 5.6 g (0.05 mole) of 1,4-cyclohexanedione, and 0.5 g of *p*-toluenesulfonic acid monohydrate was heated under reflux in 100 ml of benzene. After the mixture had been heated for 3 hr, 1.71 ml (93% of the theoretical amount) of water was collected a Bidwell-Sterling trap. The mixture was cooled to room temperature and allowed to stand overnight. The product was a white precipitate which was collected by filtration, washed several times with benzene, and dried in air. About 11.2 g (90%) of a white, powdery polymer was obtained which did not melt below 310°C and which did not hydrolyze in water but did hydrolyze in concentrated sulfuric acid to give back starting materials. Since a small amount of pentaerythritol was recovered, the reaction, based on unrecovered starting material, seemed to be essentially quantitative.

ANAL. Calcd for $(C_{11}H_{16}O_4)_n$: C, 62.24%; H, 7.59%. Found: C, 61.12%; H, 7.44%.

Reaction of Pentaerythritol and 1,10-Cyclooctadecanedione

To 14 g (0.05 mole) of 1,10-cyclooctadecanedione dissolved in 100 ml of benzene was added 6.8 g (0.05 mole) of pentaerythritol. After an additional 40 ml of benzene had been added to the 200-ml flask, the mixture was stirred while 0.5 g of *p*-toluenesulfonic acid monohydrate was added. While the mixture was heated under reflux, the water which was removed by azeotropic distillation was collected in a Bidwell-Sterling trap over a period of 99 hr. About 1.81 ml (98% of the theoretical amount) of water was collected, and an almost quantitative yield of polymer, which was somewhat swelled in benzene, was obtained by filtration. Since approximately 2% of the original amount of unreacted diketone was recovered from the benzene solution and since about the same amount of unreacted pentaerythritol was also recovered, the yield, based on unrecovered starting material, was essentially quantitative. The white, powdery polymer which swelled upon washing with benzene, was dried and was found to begin to discolor at 250°C and was completely black at 300°C.

ANAL. Calcd for $C_{23}H_{40}O_4$: C, 72.63%; H, 10.53%. Found: C, 72.17%; H, 10.48%.

Reaction of Pentaerythritol and 1,4-Cyclohexanedione plus 5% Cyclohexanone

To 6.66 g (0.049 mole) of pentaerythritol in 140 ml of benzene in a 200-ml flask were added 5.3 g (0.0475 mole) of 1,4-cyclohexanedione, 0.3 g (0.0025 mole) of cyclohexanone, and 0.5 g *p*-toluenesulfonic acid monohydrate. After the mixture had been heated under reflux for 30 hr, a little more than 1.6 ml of water was collected in a Bidwell-Sterling trap. In this case, a small amount of unreacted pentaerythritol was also recovered. The mixture was filtered, and the white, powdery polymer, which swelled in benzene, was washed several times with benzene and then dried in air. It did not melt or decompose below 310°C.

Reaction of Pentaerythritol and 1,4-Cyclohexanedione plus 10% Cyclohexanone

To 6.46 g (0.475 mole) of pentaerythritol in 140 ml of benzene were added 5.04 g (0.045 mole) of 1,4-cyclohexanedione, 0.49 g (0.05 mole) of cyclohexanone, and 0.5 g of *p*-toluenesulfonic acid monohydrate. After the mixture had been heated under reflux for 26 hr, 1.6 ml (91%) of water was collected, and a small amount of unreacted pentaerythritol was recovered. This polymer, which swelled in benzene, was isolated in the usual manner except that it was washed with cold water several times after drying. It did not melt below 310°C.

Reaction of Pentaerythritol and 1,4-Cyclohexanedione plus 20% Cyclohexanone

To 6.21 g (0.045 mole) of pentaerythritol in 150 ml of benzene were added 4.48 g (0.04 mole) of 1,4-cyclohexanedione, 0.98 g (0.01 mole) of cyclohexanone, and 0.5 g of *p*-toluenesulfonic acid monohydrate. After the mixture had been heated under reflux for 29 hr, 1.6 ml (96%) of water was collected, along with enough unreacted pentaerythritol so that the reaction, based upon recovered starting material, was essentially quantitative. This polymer also swelled in benzene and was isolated in the usual manner except that it was repeatedly (5–6 times) washed with cold water after drying. It also did not melt or decompose below 310°C.

Reaction of Pentaerythritol and 1,4-Cyclohexanedione plus 50% Cyclohexanone

To 5.1 g (0.0375 mole) of pentaerythritol in 160 ml of benzene were added 2.8 g (0.025 mole) of 1,4-cyclohexanedione, 2.45 g (0.025 mole) of cyclohexanone, and 0.5 g of *p*-toluenesulfonic acid monohydrate. After the mixture had been heated under reflux for 29 hr, 1.4 ml (100%) of water was collected. The low molecular weight polymer which was obtained was very highly swelled and gelatinous in benzene. It dried to a white powder which was somewhat hydrophobic, since cold water did not seem to wet the material. This polymer began to decompose slightly at 305°C.

Reaction of Pentaerythritol, 1,4-Cyclohexanedione, and 1,10-Cyclooctadecanedione

To 3.4 g (0.025 mole) of pentaerythritol in 75 ml of benzene were added 3.5 g (0.125 mole) of 1,10-cyclooctadecanedione and 0.4 g of *p*-toluenesulfonic acid monohydrate. After the mixture had been heated under reflux for 11 hr, 0.2 ml of water was collected. At this point 1.4 g (0.0125 mole) of 1,4-cyclohexanedione was added, along with an additional 25 ml of benzene. After the resulting reaction mixture had been heated under reflux for an additional 132 hr, essentially all of the water (0.94 ml, 100%) was collected. The polymer, which swelled in benzene, was collected by filtration, washed with benzene and water, and then dried in air to give a white powder which began to shrink about 260°C and decompose slightly at 310°C.

Analyses of Spiro Polymers

Polymer from Pentaerythritol and 1,4-Cyclohexanedione. The infrared spectrum of the spiro polymer indicated that this material contained a very small number of hydroxyl groups (3400 cm^{-1}) and ketone carbonyl groups (1725 cm^{-1}) which are due either to entrapped starting materials or to endgroups on the polymer. For the most part, however, the polymer seemed to consist mainly of a polyspiroketal structure, since its spectrum was similar to that of pentaerythritol dibutyral.[13,14]

The x-ray analysis of the polymer gave a diffraction pattern that contained very sharp peaks with no amorphous background which indicated that it was very highly crystalline (probably greater than 95% crystalline). The interplanar spacings to which all of its peaks corresponded and their intensities are shown in Table III.

TABLE III

Location of x-ray reflection, Å	Intensity
5.50	Low
5.10	Very high (dominates pattern completely)
4.67	Low
4.35	Medium
3.97	Very low
3.53	Very low
3.07	Very low
2.81	Very low
2.60	Very low
2.50	Very low

Polymer from Pentaerythritol and 1,10-Cyclooctadecanedione. The infrared spectrum of this polymer also indicated the presence of a very small number of hydroxyl and carbonyl groups. Its similarity to the pentaerythritol–1,4-cyclohexanedione polymer indicated that it also consisted of the polyspiroketal structure rather than a crosslinked one.

On x-ray analysis a diffraction pattern which contained very sharp peaks with no amorphous background was obtained; this indicated that this polymer also was very highly crystalline. The interplanar spacings to

TABLE IV

Location of x-ray reflections, Å	Intensity
9.82	Low
7.19	Medium
6.55	Very low
6.28	Very low
5.28	Medium
4.70	Very high (dominant peak)
4.68	Medium
4.19	Low
3.88	Low
3.57	Very low
3.03	Very low
1.87	Very low

which all of its peaks corresponded and their intensities are shown in Table IV.

A sample of this polymer was extracted with dimethyl sulfoxide and the insoluble residue, which had a decomposition point above 300°C, was submitted for analysis. Its infrared spectrum indicated the presence of only a negligible number of hydroxyl and carbonyl endgroups.

ANAL. Calcd for $C_{23}H_{40}O_4$: C, 72.63%; H, 10.53%. Found: C, 72.17%; H, 10.68%; with 0.7% noncombustible residue.

Polymer from Pentaerythritol, 1,4-Cyclohexanedione, and Cyclohexanone. Infrared spectra of the spiro polymers containing 5, 10, 20, and 50% cyclohexanone indicated that these materials contained a small number of hydroxyl and carbonyl groups. For the most part, however, these polymers seemed to consist mainly of spiro structures, since their spectra were nearly identical to the spectrum obtained from the polymer prepared from pentaerythritol and 1,4-cyclohexanedione alone.

The x-ray analyses of the polymers gave diffraction patterns which were also nearly identical to each other and to that of the spiro polymer which did not contain any cyclohexanone as a chain stopper. These diffraction patterns contained sharp peaks with no amorphous background, indicating that there was no apparent decrease in crystallinity with an increase in the amount of cyclohexanone used and the dominant peak in all cases was the one which corresponded to an interplanar spacing of 5.10 Å.

Polymer from Pentaerythritol, 1,4-Cyclohexanedione, and 1,10-Cyclooctadecanedione. The infrared spectrum of this polymer indicated the presence of a very small number of hydroxyl and carbonyl groups. However, the main absorption bands of the spectrum indicated that the polymer was a linear polyspiroketal, since these bands occurred in the 900–1250 cm^{-1} region.

The x-ray analysis of the polymer indicated that it may be a block copolymer, since it contained peaks which were present in the patterns of the individual polymers. The lack of amorphous background in this diffraction pattern indicated that, like all the other spiro polymers, this one was also highly crystalline. The interplanar spacings to which its peaks corresponded and their intensities are shown in Table V.

TABLE V

Location of x-ray reflections, Å	Intensity
10.05	Low
7.32	Low
5.15	Very high (dominant peak)
4.74	High
4.51	Low
3.24	Very low (diffuse)
2.83	Very low (diffuse)

TABLE VI

Comonomer for polymer with Pentaerythritol	Solubility			
	Soluble at room temperature	Soluble at reflux temperature	Swells	Completely insoluble
1,4-Cyclohexanedione	Sulfuric acid (hydrolyzes) Hexafluoroisopropanol			Benzene Dimethylformamide Dioxane
1,10-Cyclooctadecanedione	Hexafluoroisopropanol Hexafluoroacetone sesquihydrate (partial hydrolysis)	Dimethyl sulfoxide (about 12% soluble)	Benzene	Acetone Methanol Dimethylformamide
1,4-Cyclohexanedione with cyclohexanone	Hexafluoroisopropanol	Benzene (sl. sol.) Dimethylformamide (sl. sol.)		Acetone Methanol

Solubility of Spiro Polymers

Various solvents were tested for their effect on the polyspiroketals. In general, the procedure consisted of treating about 0.1 g of the polymer with about 20 ml of solvent. If solution did not occur, the mixture was heated under reflux and the mixture was filtered hot. After the solvent had been removed from the filtrate, the residue was examined to determine if it contained any unchanged polymer. Table VI summarizes the effect of some of these solvents on the polymers prepared.

Since all of the polymers were soluble in hexafluoroisopropanol, intrinsic viscosity studies were carried out in this solvent. When concentrations varying from 0.3426 to 0.0785 g/100 ml were used at 25°C in a Cannon-Fenske modification of an Ostwald viscometer, the intrinsic viscosity values were 0.049 for the pentaerythritol–1,4-diketone polyspiroketal, 0.045 for the block polymer from pentaerythritol, 1,4-diketone, and 1,10-diketone, and 0.092 for the pentaerythritol–1,10-diketone polyspiroketal.

Thermogravimetric Analysis of the Spiro Polymers

The apparatus used was identical to the one described by Anderson.[16] Samples of 7–25 mg (weighed to 0.1 mg on a semimicro balance) were heated in No. 0000 Coors glazed porcelain crucibles at a rate of 5 ± 0.5°C/min over temperature ranges of 25°C to as high as 700°C. All of the experiments were performed at a pressure of approximately 0.05 mm.

A 19.7-mg sample of the polyspiroketal from pentaerythritol and 1,4-cyclohexanedione was heated at the usual rate to 550°C. An initial weight loss of about 7%, which was attributed to the volatilization of *p*-toluenesulfonic acid, began at 125°C. The rate of weight loss leveled off until 325°C, when it began to increase. The temperature at which 50% of the polymer had decomposed was approximately 450°C. At 550°C there was about a 7% residue.

A portion of this polymer was stirred for several hours in a 5% aqueous solution of diethylenetriamine. Upon thermogravimetric analysis of a dried sample, it was found that the initial weight loss at 125°C found in the previous thermogram did not occur.

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Quaternary Ammonium and Sulfonium Derivatives of 2-Chloromethylbutadiene and Poly-2-Chloromethylbutadiene*

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Synopsis

2-Chloromethylbutadiene has been converted to quaternary ammonium and sulfonium monomers which have been polymerized at room temperature. They show a very great tendency to dimerize on heating in water solution. The aqueous quaternary monomer dimerized 25 times as fast as the aqueous sulfonium monomer and nearly 10^6 times as fast as neat isoprene at 50°C. The quaternary monomer dimerized with itself in a water solution to which 2-hydroxymethylbutadiene has been added as an example of a nonionic diene. The latter monomer did not dimerize rapidly in water, nor did 2-aminomethylbutadiene. The hydrochlorides of 2-aminomethylbutadiene and 2-dimethylaminomethylbutadiene dimerized at rates comparable to that of the sulfonium monomer. Poly 2-chloromethylbutadiene contains reactive chlorine except for the structure resulting from the minor extent of 1,2 addition. Water-soluble derivatives have been made from it with nucleophilic tertiary amines and sulfides. Cationic polymers are substantive to paper pulp, and the sulfonium polymers can be cured in paper to give improved wet strength.

Several derivatives of isoprene are known with polar substituents on the methyl group. These include the dimethylamino,[1] hydroxy,[2] and acetoxy.[2] Vinyl polymers of 2-hydroxymethylbutadiene have been described.[3] The acetal and biscarbamate of 2-hydroxymethylbutadiene have been added to conjugated dienophiles.[4,5] The present work concerns dienes which appear to be activated by inductive effects only. Because of previous experience with quaternary and sulfonium derivatives of other active halogen monomers and polymers,[6,7] there was interest in investigating the derivatives of 2-chloromethylbutadiene.[8] The preparation of this monomer by the chlorination of isoprene has been described by the authors[9] and by others.

The cationic monomers were made by reaction with tertiary amines and sulfides under mild conditions. Those made with trimethylamine and dimethyl sulfide were identified as picrates and could be converted to crystalline picrate salts. Other molecules such as the quaternary derived from *N*-methylmorpholine could be crystallized as chlorides. All had the charac-

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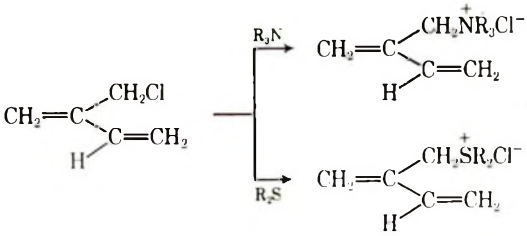
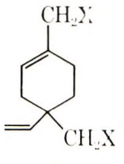
* In honor of C. S. Marvel on the occasion of his 75th birthday.

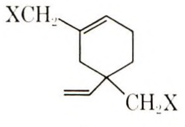


teristic ultraviolet absorption of dienes, and NMR spectra showed that no double-bond rearrangement had occurred. Sulfides reacted more slowly than amines. With especially nucleophilic sulfides, such as dimethyl sulfide or methyl β-methiopropionate, it was possible to get complete reaction without using such an excess sulfide as was necessary in the case of thiodiglycol.

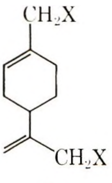
Unexpected difficulty was encountered in polymerizing the ionic monomers in water solution. At first it was suspected that isomerization might have occurred during the reaction with amine or sulfide, but it had not. It was discovered that the difficulty lay with an exceptionally high dimerization rate in water solution.[10] 2-Chloromethylbutadiene dimerized slowly. The dimer, like that of isoprene, was formed by 1,2 and 3,4 addition to approximately equal degree (contrary to reported vinyl addition at 150° C.[11]) These products were separated by distillation. The higher-boiling isomer II was the result of 3,4 addition. Both chlorines in II are allylic and could be aminated, whereas only one of structure I reacted.



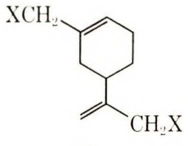
Ia



Ib



IIa



IIb

The a and b structures were not distinguished. The ratio of II/I was determined also in the case of the dimers of trimethylammonium and dimethylsulfonium monomers. The ratio was found for the former monomer to be 80:20 when dimerized in D_2O and 76:24 when dimerized in DMSO-d_6. The ratio for the sulfonium monomer was 79:21 when dimerized in D_2O. No change in ratio was apparent over the temperature range of 50-90°.

Whereas 2-dimethylaminomethylbutadiene had been reported[1] to give an open-chain dimer, the hydrochloride gave II as the main product and the same was obtained by reaction of dimethylamine with the higher-boiling dimer of 2-chloromethylbutadiene.

The rates of dimerization were followed by NMR both by observing the disappearance of terminal methylenes and the shift of $-CH_2X$ methylene. The single $-CH_2X$ line of monomer was replaced by a two-line spectrum shifted upfield in the case of the dimer. The two lines correspond to the

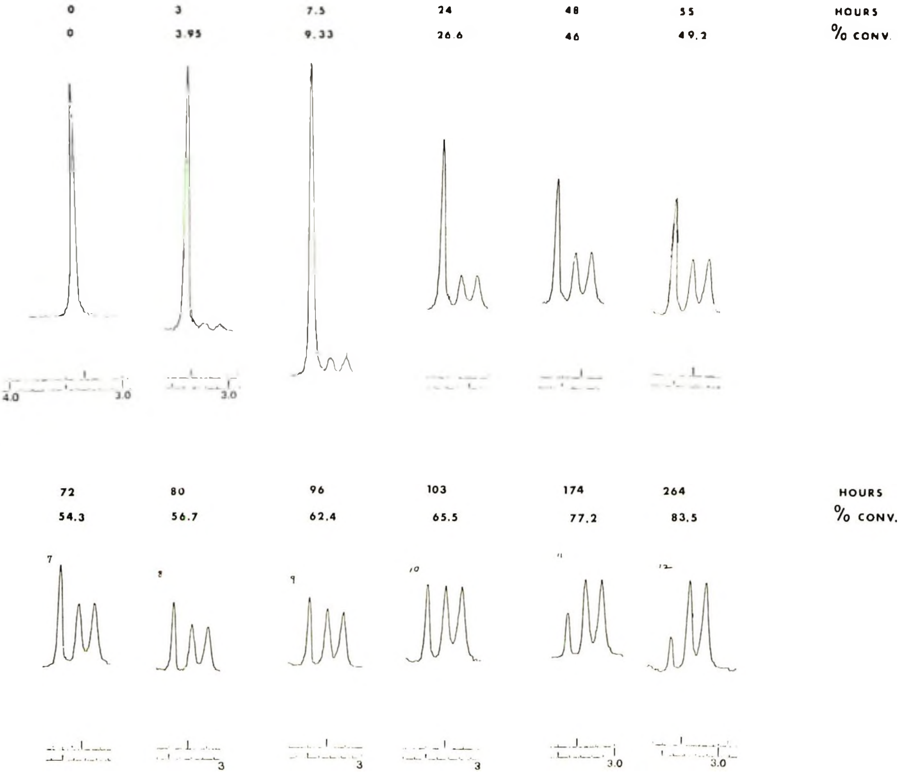


Fig. 1. Dimerization rate at 50°C of 4-aminomethylbutadiene hydrochloride (5.4 M in D_2O) as followed by disappearance of $-CH_2N$ line of monomer and appearance of corresponding lines of dimer.

two $-CH_2X$ groups of each dimer superimposed on those of the other dimers. (Fig. 1)

The dimerization reaction followed second-order kinetics, as seen in Figure 2. There was a small positive salt effect.

TABLE I
Temperature Dependence of Diels-Alder
Cycloaddition of Ionic Butadiene Derivatives

2-Substituent	Solvent	$k_r \times 10^5$, l./mole-sec 47°C	54°C	62°C	72°C	82°C	91°C
$-CH_2-\overset{+}{N}(CH_3)_3$	D_2O	6.63	19.4	25.3	37.7	76.4	121.5
$-CH_2-\overset{\oplus}{N}(CH_3)_3$	DMSO-d_6	0.45	—	1.05	2.04	3.51	—
$-CH_2-\overset{\oplus}{S}(CH_3)_2$	D_2O	—	—	1.08	1.64	5.47	11.1

Arrhenius plots of the data of Table I yielded the thermodynamic constants listed in Table II. An enthalpy effect appeared to account for rate differences between the sulfonium and ammonium derivatives and the high rate of both compared to isoprene.* The increased rate in D_2O compared to DMSO-d_6 for the quaternary salt was through the entropy term. In an equivolume solution of D_2O and DMSO-d_6 the quaternary dimerization rate was 14×10^{-5} at 80°C.

TABLE II
Thermodynamic Constants for Diels-Alder Dimerization of Ionic Butadiene Derivatives

2-Substituent	Solvent	$\Delta H‡$, kcal/mole	$\Delta S‡$, cal/mole-deg
$-CH_2-\overset{\oplus}{N}(CH_3)_3$	D_2O	13.2 ± 0.8	−36 ± 3
$-CH_2-\overset{\oplus}{N}(CH_3)_3$	DMSO-d_6	13.2 ± 0.9	−42 ± 4
$-CH_2-\overset{\oplus}{S}(CH_3)_2$	D_2O	18.5 ± 0.9	−26 ± 4

Three nonionic dienes were given cursory examination. These were 2-hydroxymethyl-, 2-aminomethyl-, and 2-dimethylaminomethylbutadiene. They dimerized slowly like the parent compound, 2-chloromethylbutadiene. They were not very soluble in water, and the dimerization did not seem to be promoted by water. A surprising discovery was that when 2-hydroxymethylbutadiene and the quaternary monomer were dissolved together in water solution, the latter monomer homodimerized, leaving the former essentially unchanged.

The protonated amino and dimethylamino derivatives dimerized fairly rapidly in water solution; the dimerization of the quaternary monomer was not catalyzed by acid. It was noted that protonation produced a downfield shift in the NMR of all of the hydrogens (Table III). The amount of the shift relative to isoprene could be correlated on an exponential scale with the rate of dimerization in water (Table IV). Both the shift and dimerization rate were less in DMSO, but the single data point fell off the water data correlation. These data were of a first-order nature and the correlation, admittedly only semiquantitative; however it seems to show that the dimerization tendency benefits from the electron deficiency in the diene.

In view of the tendency of the ionic dienes to give dimer rather than polymer on heating in water solution, even when radical catalysts were added, it seemed important to find out whether the dimer was itself a retarder of radical polymerization. To test this point a polymerization of styrene was carried out in *tert*-butyl alcohol containing the quaternary dimer in 10% amount by weight of styrene. After 3 hr at 119°C the conversion was

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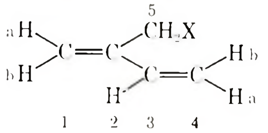
* The rate of dimerization of neat isoprene is given[12] as 4.57×10^{-9} l./mole-sec at 60°C and 2.12×10^{-8} at 75°C with $k = 7.9 \times 10^7 \exp \{24900/RT\}$.

TABLE III
Chemical Shift as Shielding from Internal Si—CH_3 Reference ($NaDSS$ in D_2O, TMS in DMSO-d_6) at Ambient Probe Temperature[a]



X	Solvent	Chemical shift, ppm				
		1a, b	3	4a	4b	5
$\overset{+}{N}(CH_3)_3$	D_2O	−5.87, −5.62	−6.56	−5.33	−5.55	−4.15
	DMSO-d_6	−5.82, −5.67	−6.54	−5.26	−5.88	−4.41
$S^+(CH_3)_2$	D_2O	−5.66, −5.57	−6.54	−5.36	−5.48	−4.26
$^+ND(CH_3)_2$	D_2O	−5.67, −5.63	−6.52	−5.37	−5.53	−4.04
$-ND_2 \cdot DCl$	D_2O	−5.46, −5.41	−6.49	−5.29	−5.37	−3.85
$-N(CH_3)_2$	DMSO-d_6	−5.13, −5.14	−6.37	−5.08	−5.40	−2.96
$—NH_2$	DMSO-d_6	−5.24, −5.10	−6.43	−5.05	−5.23	−3.31
H	CCl_4	−4.87, −4.87	−6.35	−4.95	−5.05	

[a] In all cases $J_{3-4a} = 11.0 \pm 0.1$ Hz and $J_{3-4b} = 17.8 \pm 0.1$ Hz.

TABLE IV
Comparison of $\Delta\delta$ of Hydrogens in 1 Position versus Isoprene and Dimerization Rate at 50°C[a]

K	$\Delta\delta$	10^6k	Solvent
$N^+(CH_3)_3$	1.0	100	D_2O
$N^+(CH_3)_3$	.95	5	DMSO-d_6
$N^+H(CH_3)_2$	0.8	3.9	D_2O
$S^+(CH_3)_2$	0.79	3	D_2O
$\overset{+}{N}H_3$	0.50	0.89	D_2O
OH	0.39	[b]	DMSO-d_6
H	0	0.0014	Neat

[a] Inasmuch as 1a and 1b were not distinguished, the larger δ value was selected for this comparison.

[b] No appreciable dimerization in a week in saturated water solution.

10.1%, compared to 14.5% in the control. The number-average molecular weight was 680 000 compared to 860 000 in the control. This level of retardation and transfer did not seem very great. A similar conclusion had been reached in regard to isoprene dimer added at the 1% level in the copolymerization of isoprene and styrene.[13]

Concentrated solutions of the quaternary monomer underwent spontaneous polymerization at room temperature. For example, the trimethylammonium quaternary in 75% solution thickened overnight to form a solution which by examination using Sephadex was half polymer and half dimer.

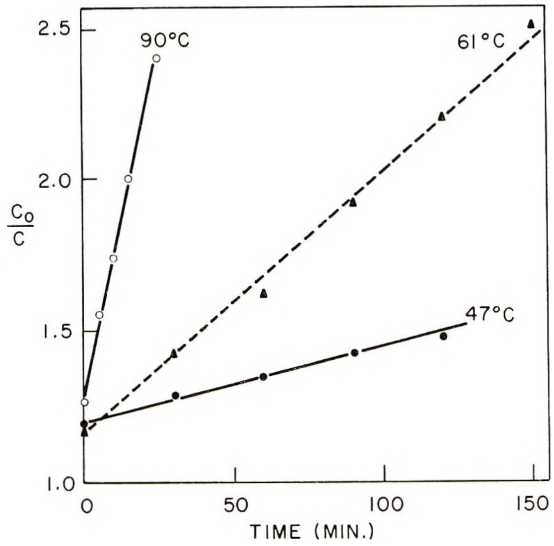


Fig. 2. Dimerization of 2-methylene-3-butenyltrimethylammonium chloride in DMSO; $[C_0] = 5\%$ wt-%.

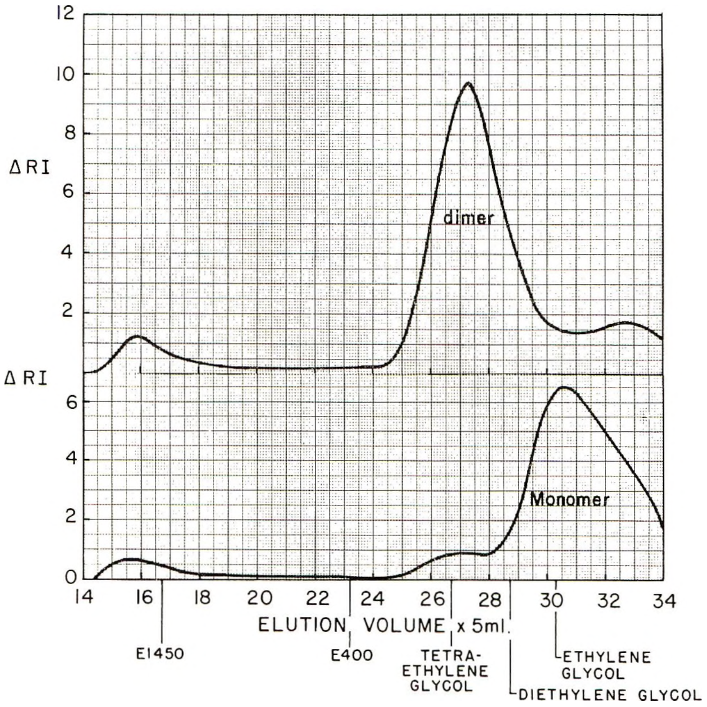


Fig. 3. Separation on Sephadex G25 of aqueous quaternary monomer, dimer, and polymer. E 400 and E 1450 are poly(ethylene oxide) samples of molecular weight 400 and 1450.

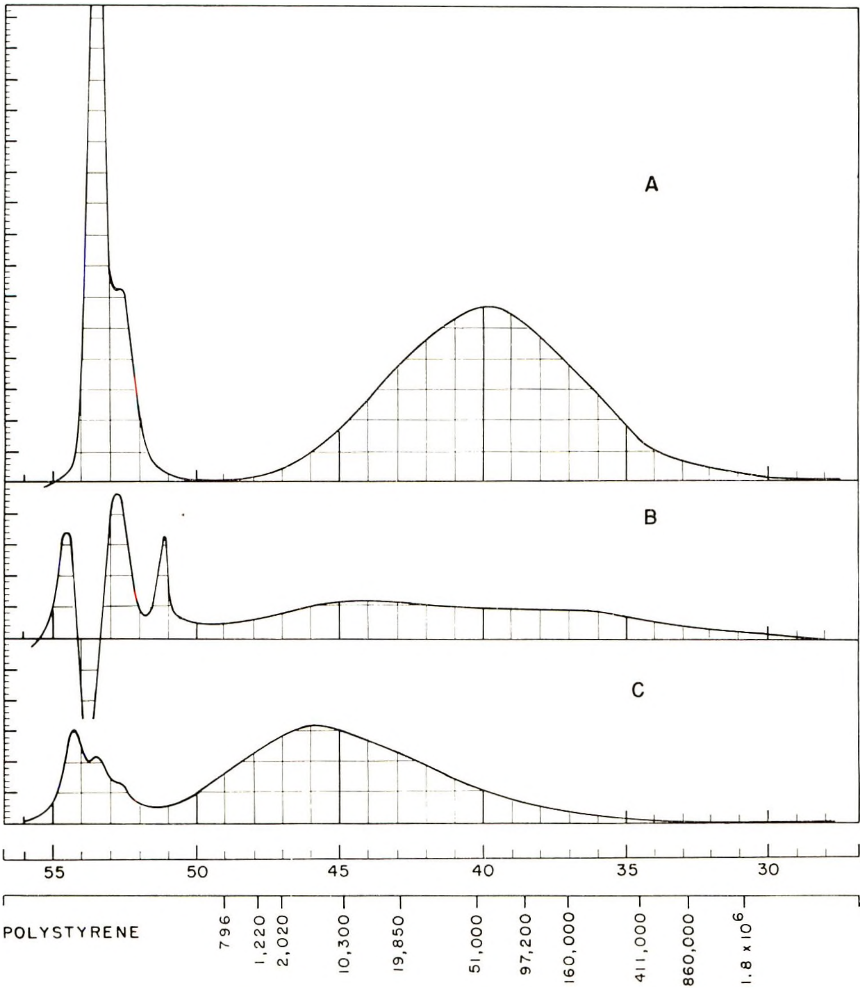


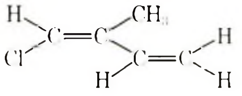
Fig. 4. Gel-phase chromatograph in tetrahydrofuran of three samples of poly 2-chloromethylbutadiene: (*A*) free-radical polymer, (*B*, *C*) cationic copolymers with 1-chloro-2-methylbutadiene, made with 60% 2-chloromethylbutadiene (*B*) and 37% 2-chloromethylbutadiene (*C*). Calibration scale is made with polystyrene of narrow molecular weight distribution.

The polymer had a reduced specific viscosity of 0.6 dl/g in 2% sodium chloride. Monomer, dimer, and polymer were clearly distinguishable on Sephadex G25, but the polymer was too large to penetrate the absorbant (Fig. 3). Similar results were obtained with the dimethylsulfonium derivative. In this case the reduced specific viscosity was 1.3. When polymerization at room temperature was accelerated by light or free-radical sources, dimerization was minimized.

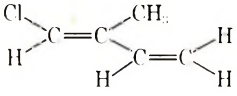
Cationic polyelectrolytes were made also by polymerization of 2-chloromethylbutadiene and post-reaction with tertiary amines and sulfides. It was not difficult to obtain emulsion polymerization of this monomer to high molecular weight polymer; in fact, it was especially necessary to use a chain-transfer agent in order to obtain soluble polymer. It was convenient to make the latex with a cationic surfactant in order that charge reversal did not occur during reaction with amine or sulfide and create the liklihood of coagulation. 2-Chloromethylbutadiene was polymerized by a radical mechanism to polymer having the same molecular size by gel-phase chromatography in tetrahydrofuran as polystyrene of molecular weight 50,000 (curve *A*, Fig. 4). Previous work has shown that the molecular weight of polybutadiene is half that of polystyrene of the same size in this solvent. The reduced specific viscosity was 0.5 in benzene.

Copolymers of butadiene and chloromethylbutadiene having more than 25 mole-% of the latter gave water-soluble derivatives upon complete reaction to quaternary or sulfonium derivatives. At lower levels of comonomer (or less complete amination), the polymer derivatives were soluble in aqueous acetone or aqueous alcohol.

The chlorination of isoprene produced as a by-product nearly equal amounts of the *cis* and *trans* isomers of 1-chloro-2-methylbutadiene. The *trans*-methyl isomer corresponds in structure to *cis*-1-chlorobutadiene and vice versa. Cationic copolymerization of 2-chloromethylbutadiene with 1-chloro-2-methylbutadiene was carried out with boron trifluoride at −78°C without a solvent. Gel-phase chromatography of the polymers showed them to be lower in molecular weight than the free-radical polymer. The monomer mixtures of 2-chloromethylbutadiene and 1-chloro-2-methylbutadiene contained 60% of the former in case *B* and 37% in case *C* (Fig. 4). Analysis of the unconverted monomer showed that the 1-chloro-2-methylbutadiene had copolymerized and that the concentration of the *cis*-methyl isomer was reduced to one-eighth of the initial value at a conversion such that the *trans* isomer was less than half consumed. The polymers were sticky. Polymer C had a reduced specific viscosity in benzene of 0.25 and gel phase chromatography in tetrahydrofuran indicated a broad range of molecular weights with the largest amount ap-



trans-methyl



cis-methyl

TABLE V

Effect of Thiodiglycol Derivative of Poly-2-chloromethylbutadiene at 0.5% Loading on Unbleached Sulfite Pulp having a Freeness of 258 CSF

	dry			wet		
	pH 4.5	pH 7.0	pH 9.5	pH 4.5	pH 7.0	pH 9.5
Control, pressure to burst	36.4	37.0	39.0	—	2.3	1.8
Treated, pressure to burst	43.7	47.0	49.6	17.7	18.1	18.1
Improvement factor	1.20	1.27	1.28	40	38	36

TABLE VI

Effect of Thioglycol Derivative of Poly-2-chloromethylbutadiene on Unbleached Hardwood Soda Pulp Beaten to 400 CSF[a]

% added	Alum, %	Final pH	Dry tensile change (vs. control, %	Wet tensile (vs. dry), %	Dry burst change (vs. control, %	Wet burst (vs. dry), %	Tear change (vs. control, %	MIT double folds (1 Kg)	KBB size, sec
0	—	5.9	—	1.0	—	3.0	—	8	0.3
0.5	—	6.1	28.6	17.3	38.7	27.9	12.0	35	0.7
1.0	—	6.4	34.6	18.1	47.3	25.8	5.7	39	0.6
2.0	—	6.5	26.5	19.6	46.6	26.5	−2.2	33	0.6
1.0	—	5.2	41.4	21.6	62.4	29.0	8.2	46	2.3
1.0	—	7.0	35.2	20.0	38.0	28.2	6.3	30	1.0
1.0	—	8.8	22.0	22.4	49.9	28.3	3.1	60	1.4
0	—	8.9	—	9.8	—	10.2	—	18	0.3
0	2	5.4	—	4.0	—	3.38	—	8	1.0
1.0	2	5.3	15.7	23.2	45.3	32.9	−1.4	35	1.2
0	4	5.3	—	11.7	—	11.5	—	11	1.0
1.0	4	5.1	18.5	22.1	27.2	30.4	7.3	29	1.0

[a] The sheets were dried for 4 min with a 115°C platten temperature.

pearing where polystyrene of molecular weight 4000 appears. The infrared absorption spectrum showed that half of the chlorine was secondary, corresponding to 1,4 polymerization of the 1-chloro-2-methylbutadiene. Chlorovinyl groups and vinyl groups were absent. The copolymers were reacted with trimethylamine, but amination occurred only to the extent of the amount of 2-chloromethylbutadiene in the copolymer.

2-Chloromethylbutadiene underwent cationic polymerization more rapidly than 1-chloro-2-methylbutadiene and gave a copolymer of higher molecular weight. When pure 2-chloromethylbutadiene was polymerized at −50°C with boron trifluoride gas only 5 ml of gas was needed to initiate the polymerization of 10 ml of the monomer. The polymerization was stopped at 18% conversion by injection of tetrahydrofuran; nevertheless a crosslinked polymer was obtained on amination with trimethylamine, whereas water-soluble derivatives had been obtained from the copolymers.

Like other cationic polymers the quaternary ammonium and sulfonium derivatives of polymers of 2-chloromethylbutadiene were substantive to paper solids when added to the beater. The adsorption was nearly quantitative at low loadings, such as 0.5% of the paper solids. At higher loadings the pick-up became increased but less quantitative, and evidently the carboxylic ion exchange capacity of unbleached paper pulp was inadequate for pick-up of much more than 1%. The sulfonium polymer conferred wet strength after curing on the paper. There was some stiffening of the paper at the highest treatment level. A still higher level of treatment, at which sizing was significant, was achieved by addition of larger amounts to the preformed paper.

The properties of the paper produced by beater addition, and by inference the substantivity, were not very pH sensitive in the pH range of 5–8. Evidently the substantivity of the polymer exceeded that of aluminum cations because the presence of alum did not alter appreciably the effect of the polymer. In addition to improving strength, the quaternary polymer produced improved freeness and filler retention when used as a beater additive and also electrical conductivity, especially at the higher loadings achievable by addition to the preformed paper (Tables V and VI).

DISCUSSION

The rate enhancement produced by an electron-withdrawing inductive effect would seem to affect the dienophilic role, and therefore preferrential codimerization with a nonionic diene had been expected. Inasmuch as it was not found, another explanation was sought. A reduction in the barrier to *cis–trans* isomerism in the diene, while probably present as reported for 2-neopentylbutadiene,[14] would account for a rate enhancement of only a single order of magnitude. The possibility of association prior to reaction was considered but no evidence found for it. The conductivity of the quaternary monomer was normal, and solutions obeyed Beer's Law. There was no evidence of charge transfer absorption. The free energy of activation was positive as expected for long range charge repulsion.

A radical mechanism seemed unlikely inasmuch as the dimerizations were carried out in the presence of antioxidant. Because there is no evidence for bond rearrangement in the dimerization of the quaternary derived from 2-chloromethylbutadiene, it is assumed that no stabilized cation radical is involved, such as appears to confer unusual stability to quaternized vinylpyridines in water.[15,16]

It is known that the trimethylammonium ion is a more potent *meta*-orienting group than the protonated amino group, even when separated from the benzene ring by a methylene. A similar charge delocalization by hydration is assumed to be responsible for lesser electron withdrawing character of the protonated aminomethylbutadiene.

No adequate explanation is offered for the high dimerization rate of the ionic dienes in water solution.

EXPERIMENTAL

Dimerization Rate Measurement

The chloride salts were dissolved as 10% solutions by weight in D_2O or 5% solutions in DMSO-d_8. The rate of dimerization was followed by using a Varian Associates A-60 NMR spectrometer equipped with a variable temperature probe. *tert*-Butylcatechol acted as an inhibitor to polymerization without affecting the dimerization. Disappearance of the four lines of the —CH= proton in the monomers, coupled with the growth of its broad isolated band in the cyclic dimer, provided means for monitoring the reaction at several temperatures. Spectra were calibrated by the side-band technique. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as an internal reference in D_2O. A constant temperature bath (±0.5°C) maintained equivalent probe temperatures for the slower reactions. Spectrum peaks were electronically integrated 10 times or more and an average taken. A least-squares treatment of all data was performed.

2-Chloromethylbutadiene

2-Chloromethylbutadiene was prepared by chlorinating isoprene at 0°C. The product mixture was separated by fractional distillation using a 4-ft column of glass helices with a 25:1 reflux ratio. Hydroquinone was added as an inhibitor. 2-Chloromethylbutadiene (98.7% pure) was distilled at 38°C 50 mm with the use of a pot temperature of 86°C. It had a molar extinction coefficient of 1.44×10^4 at 219 mμ. The product was stored with refrigeration and with the addition of a small amount of hydroquinone without which popcorn polymer formed eventually.

2-Chloromethylbutadiene (5 ml) containing 0.08% *tert*-butylcatechol was converted to dimer by heating for 16 hr at 90°C. By distillation monomer (1 ml) was recovered and dimer (3 ml) was obtained, bp 81–86C°, 0.3 mm. The dimer was fractionally distilled at 0.2 mm and the ratio of structure II:I determined by NMR on the various cuts. The boiling points and ratios were as follows: 74–78°C, 0.3; 78–82°C, 0.57; 82–83C°, 1.6; 83–87°C, 7.5. The unfractionated dimer had a ratio of nearly unity. It was aminated with triethylamine. The product contained 18.3% ionic chloride, as expected from a 50:50 blend of I and II.

The refractionated higher-boiling dimer, by 87–87.5°C 0.88 mm, 95% pure by GLC analysis, was converted to the trimethylamine and dimethylamine derivatives which were identified by NMR.

2-Methylene-3-butenyltrimethylammonium Chloride

2-Chloromethylbutadiene (96.7% pure, 29.5 g) and trimethylamine (75 g) were allowed to react for 2 hr at room temperature in 300 ml ethanol (2B). The solution was evaporated at room temperature. The NMR spectrum in D_2O of the product showed less than 5% dimer to be present. The yield was 37.3 g (84%). The ultraviolet absorption at 220.5 mμ corresponded to a molar extinction coefficient of 1.03×10^{-4}. There was an infrared absorption band at 720 cm^{-1} in the *cis*-diene region.

ANAL. Calcd for $C_8H_{16}NCl$: C, 59.4%; H, 9.98%; N, 8.66%; Cl, 21.9%. Found: C, 59.5%; H, 10.3%; N, 8.15%; Cl, 22.0%.

The monomer was stable indefinitely as a dry solid with refrigeration. If allowed to absorb traces of water it slowly changed at room temperature to a gummy polymer.

In another experiment the reaction of trimethylamine (0.4 mole) and 2-chloromethylbutadiene (0.125 mole) was carried out in a sealed ampoule without solvent. After 2.5 hr of shaking at room temperature the product was recovered by evaporation of unreacted reagents, yield 5.6 g of white solid 2-methylene-3-butenyltrimethylammonium chloride of greater than 90% purity by NMR analysis.

2-Methylene-3-butenyldimethylsulfonium Chloride

2-Chloromethylbutadiene (2.1 g) and dimethyl sulfide (4.0 ml) were dissolved in methanol (5 ml). The mixture was stirred at room temperature for 22 hr and then extracted with methylene chloride. A 57% conversion to the sulfonium chloride was shown by chloride titration (corrected for 10% hydrolysis).

ANAL. Calcd for $C_7H_{13}SCl$: C, 51.0%; H, 7.95%; S, 19.4%; Cl, 21.5%. Found: C, 50.5%; H, 8.18%; S, 18.6%; Cl, 21.3%.

The solution was treated with lithium picrate, and the yellow sulfonium picrate crystallized in 4.6 g yield after recrystallization from methanol. Two samples were titrated potentiometrically in glacial acetic acid with perchloric acid. Results of the titrations indicated molecular weights of 359 and 364; calculated, 357. The picrate showed an absorption peak at 220 mμ and also one at 360 mμ due to the picrate ion.

The sulfonium picrate was converted to the chloride by passage through a column of strong base anion-exchange resin (Dowex 21K ion exchange resin, 50–100 mesh) in the chloride form. The effluent was allowed to evaporate to 22 ml volume which is 0.38*N* in chloride ion. The sulfonium chloroplatinate was precipitated from this solution as a light orange product and recrystallized from aqueous methanol. It had strong absorption at 220 mμ. The infrared spectrum (Nujol mull) showed bands at 8.05, 9.65, 9.95, 10.10, 11.0 (strong) in common with those of chloromethylbutadiene.

ANAL. Calcd for $(C_7H_{13}S)_2PtCl_6$: C, 25.1%; H, 3.9%; residue, 29.2%. Found: C, 25.33%; H, 4.39%; residue, 28.8%. Calcd for $C_7H_{13}S.C_6H_3N_3O_7$: C, 43.7%; H, 4.2%; N, 11.8%; Found: C, 44.24%; H, 5.01%; N, 11.5%.

In another experiment, dimethyl sulfide (0.5 mole) was dissolved with 2-chloromethylbutadiene (0.125 mole) in methanol (100 ml) and after stirring four days at room temperature and evaporation there was obtained 2-methylene-3-butenyldimethylsulfonium chloride in 67% yield and greater than 90% purity by NMR analysis.

2-Chloromethylbutadiene (50 g) was also reacted with thiodiglycol (74 g) in the presence of water. After stirring at 55°C for 7 hr 85% of the oil phase had dissolved to form the sulfonium salt.

2-Hydroxymethylbutadiene

2-Chloromethylbutadiene (51.5 g) (purity 81%) was inhibited with 0.01 g *tert*-butyl catechol and stirred with 200 g 10% sodium hydroxide at 85°C overnight. The pH of the aqueous layer dropped to 10.7. There was a tendency to emulsify. By titration of consumed base it was found that hydrolysis was 83% based on the crude 2-chloromethylbutadiene. The product was salted out and distilled, bp 56–57°C/30 mm, yield 70.6%.

2-Aminomethylbutadiene

2-Chloromethylbutadiene (100 g, 85% purity, remainder 1-chloro-2-methylbutadiene) was dissolved in 500 g liquid ammonia in a stainless steel vessel and allowed to stand overnight at room temperature. (A previous test had shown 97% complete reaction in 4 hr.) The ammonia was vented slowly and benzene added to precipitate ammonium chloride. The benzene solution was distilled in a 10-plate still with 5:1 reflux rate, yield 15 g 2-aminomethylbutadiene, bp 74–75°C/200 mm, 30–33°C/30 mm. There was a higher boiling residue.

2-Aminomethylbutadiene (35 g) was dissolved in 231 ml water and 35.5 ml concentrated hydrochloric acid. Hydroquinone (0.077 g) was added and the solution heated 147 hr at 70°C. The NMR spectrum indicated 65–80% dimerization. Solid potassium hydroxide and potassium carbonate were added and the dimer layer removed and distilled. The infrared spectrum Indicated the presence of isopropenyl groups, terminal $CH_2=$ at 900 cm^{-1}, C=C stretch to 1690 cm^{-1}, and NH_2 bend at 1605 cm^{-1}. There was absorption corresponding to *antisym* NH_2 vibration.

ANAL. Calcd C, 71.4%; H, 10.8%; N, 16.6%. Found: C, 72.0%; H, 11.4%; N, 16.3%.

Like other allylamines it tended to discolor but could be kept water-white with refrigerated storage.

2-Aminomethylbutadiene (17.14 g) was neutralized with concentrated hydrochloric acid (17.43 ml) and heated for 26 hrs. at 50°C with azobisisobutyronitrile (0.17 g). The product was a pale yellow rubber.

Polymerization of 2-Methylene-3-butenyltrimethylammonium Chloride

The quaternary monomer (2.0 g) dissolved in *tert*-butyl alcohol–water (1.03 g, 1 : 1) polymerized spontaneously in the refrigerator over a period of 4 days. A white very rubbery, water-soluble polymer formed. The reduced specific viscosity in 2% sodium chloride solution was 2.34.

The polymer was applied as an 18% water solution to paper, and the electrical resistance measured at 7% RH and two levels of additive, 3.14 and 7.00% by weight of paper. Both surface and volume resistance measurements were made. The surface resistivities were 6.5 and 3.6 × 10^{10} ohms. The volume resistivities were 3.80 and 3.12 × 10^3 ohm-cm. Typical values obtained with the trimethylamine derivative of chloromethylated polystyrene are 0.26 × 10^{10} ohms and 1.18 × 10^3 ohm-cm for surface and volume resistivity at the higher concentration level.

Polymerization of 2-Methylene-3-butenyldimethylsulfonium Chloride

The sulfonium compound was copolymerized at room temperature in 10% water solution with acrylamide by use of a combination of sodium sulfite and sodium hydrosulfate as the catalyst. The solution became viscous over a period of 4 days. The polymer had a viscosity of 1.5 cP measured at 25° as a 5% solution containing 4% sodium chloride. The viscosity of a dimer solution under the same conditions was 0.91 cP.

To a solution of 2-hydroxymethylbutadiene (0.105 g) and 2-methylene-3-butenyltrimethylammonium chloride (0.150 g) in water (2.019 g) was added 0.0014 g *tert*-butylcatechol and 0.021 g glycol monomethyl ether. The ratio of 2-hydroxymethylbutadiene to glycol monomethyl ether was followed by GLC while heating at 50°C and had diminished 8% after 24 hr. In similar experiments the nearly complete dimerization of the quaternary monomer and slight disappearance of 2-hydroxymethylbutadiene was observed by NMR.

Polymerization of 2-Chloromethylbutadiene

An aqueous emulsion was prepared by vigorously agitating a mixture of 2-chloromethylbutadiene (60 g) (containing 20% 1-chloro-2-methylbutadiene) and *tert*-dodecylmercaptan (0.12 g) with 140 g water containing sodium lauryl sulfate (1.4 g), potassium persulfate (0.3 g), and sodium bicarbonate (0.3 g). The emulsion was then heated at 50°C for 40 hr and the polymer recovered as a white precipitate by pouring the emulsion into stirred methanol. The polymer was soluble in methylene chloride, toluene, or tetrahydrofuran. The molecular weight was 35,000, as determined by membrane osmometry in tetrahydrofuran.

ANAL. Calcd Cl, 34.6%. Found: Cl, 31.5%.

Nearly all of the chlorine became ionic after amination with trimethylamine.

In another experiment, 2-chloromethylbutadiene (31.4 g) was treated with 0.75 ml water, 0.3 ml of 5% ethylenediaminetetraacetic acid disodium salt, and 0.074 ml of 10% aqueous *tert*-butyl hydroperoxide and heated for 16 hr at 60°C. The polymer had a viscosity of 1.30 cP at 5% concentration in the presence of 4% sodium chloride. No monomer was visible in the NMR spectrum. A second sample prepared with 0.022 g potassium persulfate as the catalyst had a viscosity of 1.51 cP.

A solution of azobisisobutyronitrile (0.015 g) in 2-chloromethylbutadiene of 98.7% purity (15 g) was exposed through glass to ultraviolet light in the absence of oxygen for 40 hr at 30°C. A viscous pale yellow polymer had formed. The polymer was recovered as a soft solid without cross-linking by evaporation of the solution at room temperature, yield 5.3 g. The reduced specific viscosity in benzene was 0.50.

Poly 2-chloromethylbutadiene (250 g) which had been isolated by precipitation with methanol was agitated at room temperature with aqueous trimethylamine (720 g, 25%) until the polymer dissolved. The polymer derivative was precipitated by pouring into stirred acetone. The product was hydroscopic.

ANAL. Calcd for $C_8H_{16}NCl$: Cl, 22.0%; Found: Cl, 19.2%.

Cationic Copolymerization

A mixture (100 ml) of 2-chloromethylbutadiene (59%) and 1-chloro-2-methylbutadiene (39%) was cooled in a Dry Ice bath, and boron trifluoride introduced at the rate of 0.084 l./min for 45 min while the solution turned orange and then brown and viscous. There was a 56% conversion to polymer (polymer B of Fig. 1). It was stirred for a day in dioxane solution with aqueous trimethylamine and evaporated to a viscous orange polymer, 113 g, having a reduced specific viscosity in 2% salt solution of 0.09, and containing 4.2% nitrogen.

A sample (54 g) of a mixture of 2-chloromethylbutadiene and 1-chloro-2-methylbutadiene containing 37% of the former and 58% of the latter (39% of which was the *cis*-methyl isomer) and 4.9% of isoprene hydrochlorides was chilled in a Dry Ice bath; boron trifluoride was introduced at the rate of 0.038 l./min for 1 hr, at which point the solution had become viscous. The solution was purged with nitrogen while cold and found to have been 50% converted to polymer. The polymer was dissolved in tetrahydrofuran and catalyst removed with weak base anion exchange resin. The polymer was recovered as a pale yellow solid by precipitation in methanol, yield 25.8 g.

The infrared absorption of the polymer film did not show the presence of vinyl or chlorovinyl groups. The structure was evidently mainly that resulting from 1,4-addition. The methyl group derived from units of polymerized 1-chloro-2-methylbutadiene was observable. Absorption of unsaturated methinyl was of two types, consistent with equal amounts of *trans* addition of each monomer.

Contributions were made by F. Meyer and C. Humiston in paper tests, H. Heeschen in NMR, R. L. Wence in GPC and M. J. Hatch and G. Geyer in early preparative work.

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Reversible Crosslinking in Cellulose. III. Factors Controlling the Oxidation Behavior of Mercapto Groups in Cotton Derivatives*

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Synopsis

The oxidation behavior of mercaptocellulose prepared from tosylated cotton and of cellulose β-mercaptoethylaminocarboxylate (RDTC), which was prepared by reduction of a cotton derivative made by the reaction with bis-β-isocyanatoethyl disulfide, was studied, and the factors controlling the oxidation behaviors of solid polymeric mercaptans were discussed. RDTC was converted quantitatively to the corresponding disulfide by oxidation under mild conditions. Repeated oxidation–reduction cycles were applied to RDTC to demonstrate complete reversibility of disulfide crosslinking. On the other hand, only a portion of the mercaptan in mercaptocellulose could form disulfide by oxidation. It is considered that the mobility of the mercapto groups necessary for the oxidation coupling is restricted because they are attached directly to rigid cellulose chains. The oxidation of RDTC with air in alkaline medium was studied kinetically. It was found that the oxidation of the mercaptan in paired placement in the cellulose matrix proceeded more than ten times faster than that of the randomly placed mercaptan.

INTRODUCTION

Schwenker et al.[1,2] reported the preparation of 6-mercaptocellulose by the reaction of tosylated cotton fabrics and potassium thiolacetate followed by alkaline hydrolysis. The crease recovery measurement suggested that the oxidation of mercaptocellulose yielded intermolecular crosslinks which stabilize fabrics against deformation. Oxidation of mercaptan and disulfide with iodine is often used for the quantitative analysis of mercaptans of low molecular weights.[3] Schwenker et al.[1] considered that the mercapto groups in mercaptocellulose were also converted to disulfide crosslinks quantitatively by treatment with iodine.

In a previous paper[4] it was reported that the mercaptan and disulfide contents of modified cotton samples could be determined by application of Leach's polarographic method for wool, with minor modification. It was found that mercaptocellulose contained a considerable amount of disulfide in addition to the mercaptan. Iodometric titration of mercaptocellulose

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

gave a higher value of mercaptan than that obtained by the polarographic method. It was considered that the mercaptan in close proximity to another was readily oxidized to form disulfide, while the mercaptan isolated from others was converted to sulfonic acid by the iodine treatment.

Tesoro et al.[5] prepared mercaptoacetamidomethyl cellulose by the reaction of cotton with *N*-hydroxymethylacetylthioacetamide followed by hydrolysis, studied its oxidation, and determined by chemical methods, that the oxidation of mercaptan to disulfide proceeded almost quantitatively.

A classical work of Harris et al.[6] showed that the cystein residues produced by the reduction of wool were very labile and could easily be reoxidized, either by prolonged exposure to the atmosphere or by treatment with mild oxidizing agents. The stress-strain curve of the reoxidized wool fiber in water was almost identical with that of the original fiber.

Mack et al.[7] claimed, on the basis of crease recovery measurements that the reduced form of a complex cellulose derivative made by the reaction of dialdehyde cotton with acethydrazide disulfide was very susceptible to oxidation, whereby rebuilding the original disulfide crosslinks. They considered that the two mercapto groups formed by the reduction of a disulfide linkage were placed close to each other in the cellulose matrix and this paired placement of mercapto groups in this system could account for the observed readiness of disulfide formation.

The purpose of the present work is to study the oxidation of cellulose β-mercaptoethylaminocarboxylate,[8] which was produced by the reduction of a cotton derivative made by the reaction of cotton with bis-β-isocyanatoethyl disulfide, through chemical analysis, and to discuss factors controlling the oxidation behavior of solid polymeric mercaptans.

EXPERIMENTAL

Materials and Reagents

All samples were prepared from 140 × 70, bleached, scoured and unmercerized cotton print cloth kindly provided by Fuji Spinning Co. Ltd., Japan.

Bis-β-isocyanatoethyl disulfide (BIED) was synthesized from dithiodipropionyl dihydrazide.[8]

Mercaptocellulose (M)

M-1 was prepared by the reaction of tosylated cotton (sulfur content, 1.26%) with potassium thiolacetate in acetone followed by hydrolysis. M-2 was prepared by the reaction of tosylated cotton (sulfur content, 3.40%) with potassium thiolacetate in methanol followed by hydrolysis.

BIED-treated Cotton (DTC)

Cotton samples were treated in 1% BIED in dimethylformamide (DMF) with a liquor ratio of 1:100 at 80°C for fixed periods, washed with DMF, and extracted with acetone in a Soxhlet apparatus.

Reduction

Samples were treated with 1% tri-*n*-butylphosphine in methanol containing 10% water at boiling temperature for 6 hr. The reduced samples were washed and extracted with acetone in a Soxhlet apparatus.

Oxidation with Iodine

The iodine oxidation of samples in water was carried out according to Schwenker et al.[1] The iodine oxidation in methanol was performed with 0.0125 *N* iodine at room temperature for 4 hr.

Oxidation with Air

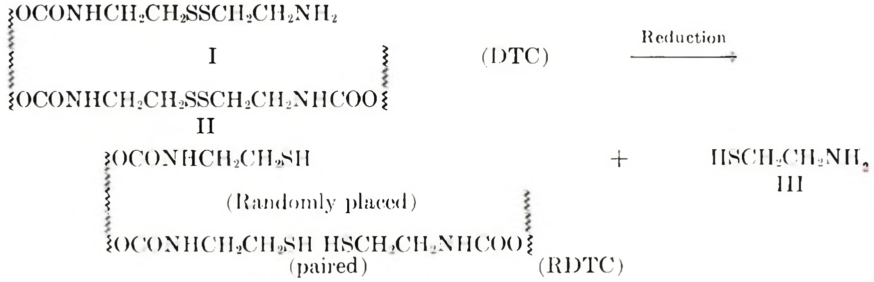
The samples were oxidized with air saturated in a Clark and Lubs buffer of pH 10.5 at 30°C for fixed periods. The treated samples were rinsed with water and with acetone and dried in *vacuo*.

Determination of Mercaptan (SH) and Disulfide (SS)

The SH and SS contents of cotton derivatives were determined by the polarographic methods.[4,8] All polarograms were recorded on a Yokogawa Polarocorder Pol-12.

RESULTS AND DISCUSSION

In the preceding paper[8] it was reported that bis-β-isocyanatoethyl disulfide (BIED) reacted with cotton both monofunctionally and bifunctionally to form branches (I) and crosslinks (II), respectively. The disulfide (SS) in the BIED-treated cotton could be almost completely reduced to mercaptan (SH) by treatment with tri-*n*-butylphosphine. The sulfur content and the SH + 2SS value decreased by the reduction because one of the two sulfur atoms in the branch was removed from cotton as a reduction fragment (III).



The mercapto groups in the reduced cotton sample (RDTC) were considered to be divided into two categories: The mercapto groups produced from the crosslinks in DTC are supposed to be in paired placement and very susceptible to oxidation to form the original disulfide crosslinks, and the mercapto groups produced from the branches in DTC were supposed to be placed randomly in the polymer matrix and less susceptible to disulfide formation. The amounts of both paired and randomly placed mercapto groups in RDTC can be calculated from the polarographic analysis[8] of DTC and the corresponding RDTC as follows:

$$\begin{aligned}\text{Paired SH} &= 2\,T_r + 2\,D_r - T_d - 2\,D_d \\ &\doteq 2\,(T_r + 2\,D_r) - (T_d + 2\,D_d)\end{aligned}$$

$$\text{Randomly placed (unpaired) SH} = (T_d + 2\,D_d) - (T_r + 2\,D_r),$$

where T_d and T_r are the SH contents (μmole/g) of DTC and RDTC, respectively, and D_d and D_r are the SS contents (μmole/g) of DTC and RDTC, respectively.

Various DTC samples were subjected to repeated alternating reduction-oxidation treatments (Tables I and II). DTC-1 (Table I) contained 344 μmole/g of SS and the SH + 2SS value decreased from 688 to 433 μmole/g by reduction with tri-*n*-butylphosphine. The reduced sample (RDTC-1) contained 172 μmole/g of paired SH and 255 μmole/g of unpaired SH in addition to a small amount of SS (3 μmole/g). It was found that RDTC was stable against air oxidation in a dry atmosphere, contrary to the observation of Mack et al.[7] mentioned in the Introduction. This difference seems to be explained by the differing reducing conditions used. Mack et al. employed sodium borohydride in water as a reducing agent. It seemed that air oxidation of mercaptan at alkalinity took place rapidly during the purification of the reduced sample. In this work the reduction was carried out with tri-*n*-butylphosphine at neutrality, so that air oxidation during preparation of the sample was kept to a minimum.

TABLE I
Repeated Alternating Reduction–Oxidation Treatments on RDTC-1: Comparison of Two Different Oxidation Conditions

	Iodine–oxidation in water			Iodine–oxidation in methanol		
Treatment	SH, μmole/g	SS, μmole/g	SH + 2SS, μmole/g	SH, μmole/g	SS, μmole/g	SH + 2SS, μmole/g
Original	0	344	688	0	344	688
1st reduction	427	3	433	427	3	433
1st oxidation	0	183	366	0	220	440
2nd reduction	413	6	425	457	4	465
2nd oxidation	6	154	314	9	216	441
3rd reduction	370	8	386	434	7	448
3rd oxidation	5	135	275	7	217	441

About 85% of the total SH in RDTC-1 was converted to SS by oxidation with iodine in water according to the procedure of Schwenker et al.[1] and the rest of the SH converted to some other oxidation states. The disulfide (180 μmole/g) formed by oxidation was far more than that (172/2 μmole/g) calculated to be produced from the paired SH in RDTC-1, indicating that both

TABLE II
Repeated Alternating Reduction-Oxidation Treatments on Various RDTC Samples

Treatment[a]	RDTC-2 SH, μmole/g	RDTC-2 SS, μmole/g	RDTC-2 SH + 2SS, μmole/g	RDTC-3 SH, μmole/g	RDTC-3 SS, μmole/g	RDTC-3 SH + 2SS, μmole/g	RDTC-4 SH, μmole/g	RDTC-4 SS, μmole/g	RDTC-4 SH + 2SS, μmole/g
Original	0	309	618	0	94	188	0	67	134
1st reduction	336	4	344	138	9	156	61	0	61
1st oxidation	0	164	328	3	67	136	3	12	27
2nd reduction	330	10	350	119	7	133	28	0	28
2nd oxidation	6	166	338	3	61	125	1	8	17
3rd reduction	330	6	342	—	—	—	—	—	—
3rd oxidation	11	160	331	—	—	—	—	—	—

[a] Oxidation was carried out with iodine in methanol.

paired and unpaired forms of mercaptans could form SS crosslinks. Some of the oxidation products, other than SS, were reduced to SH by the second reduction treatment. About 70% of the total SH was converted in both the second and the third oxidation treatments. The SS content of the oxidized cotton derivative decreased gradually as the number of cycles of the treatments increased, because the oxidation product stable to reduction accumulated after each oxidation and the concentration of SH in the reduced cotton derivative decreased as the number of cycles increased.

In an attempt to explain the observed low conversion of SH to SS, it appeared desirable to study the oxidation behavior of RDTC under milder oxidation conditions. Crewther and Dowling[9] studied the reaction of wool with iodine in various solvents and found that the decrease in the cystein and cystine residues by the treatment occurred less significantly in alcohols than in water. The oxidation of RDTC-1 with iodine in methanol was investigated to show that 100% of SH in the sample was converted to SS. The repeated alternating reduction–oxidation treatments indicated that the cleavage and re-formation of SS crosslinks by reduction and oxidation, respectively, were quantitatively reversible. Table I compares the reduction–oxidation experiments on RDTC-1 under two different oxidizing conditions (iodine in water and in methanol).

The repeated alternating reduction–oxidation treatments were carried out on three other samples of different degrees of substitution (Table II). RDTC-2 showed complete reversibility as in the case of RDTC-1. On the other hand, the conversion of SH to SS in the oxidation of RDTC-4 was only 40%, and the rest of the SH converted to some other oxidation products as in the oxidation of RDTC-1 with iodine in water. RDTC-4 contained only 61 μmole/g of SH, which were all in random placement. It seemed that the unpaired placement and the low density of mercaptan restricted the coupling of mercaptans to form disulfide, and most of the mercaptan was converted to products other than disulfide before they could come close enough for a coupling.

From the results discussed above it was concluded that RDTC of high degrees of substitution can be oxidized to the corresponding disulfide derivative quantitatively under mild oxidizing conditions. This conclusion is in accordance with the report of Tesoro et al.[5] on the initial oxidation of mercaptoacetamidomethyl cellulose, although the yield of the disulfide formation decreased, due to unknown side reactions, as the number of the cycles of the reduction–oxidation treatments increased.

In an earlier work[4] it was suggested that a large portion of SH in mercaptocellulose could not form disulfide crosslinks by the iodine treatment because of the spatial limitation. To discuss this view further in connection with the results on the oxidation of RDTC, a comparative study was undertaken on the oxidation of mercaptocellulose (M) with iodine in methanol.

Table III shows two typical examples of the repeated reduction–oxidation treatments of M. One sample, M-1, contained a considerable amount of SS as well as SH and yielded some new SS by the oxidation with iodine in

TABLE III
Repeated Alternating Reduction–Oxidation Treatments on Mercaptocellulose

	M-1			M-2		
Treatment[a]	SH, μmole/g	SS, μmole/g	SH + 2SS, μmole/g	SH, μmole/g	SS, μmole/g	SH + 2SS, μmole/g
Original	178	73	324	93	126	345
1st reduction	288	19	326	279	37	353
1st oxidation	20	90	200	20	129	278
2nd reduction	217	17	251	243	46	335
2nd oxidation	21	81	183	20	114	248
3rd reduction	182	15	212	224	41	306
3rd oxidation	19	75	169	16	106	228
Oxidation of the original	34	99	232	24	123	270

[a] Oxidation was carried out with iodine in methanol.

methanol. On the other hand, M-2 contained a higher proportion of SS and yielded no new SS by the iodine treatment. It seemed that most of the SH groups favorably placed for SS formation had already been converted to SS crosslinks in the preparative stage of M-2.

Most of the SS in M was reduced to SH with tri-*n*-butylphosphine. The reduced sample (RM) was oxidized with iodine in methanol. The net increase in SS was 71 μmole/g for RM-1 and 92 μmole/g for RM-2. The conversion of SH to SS was 49% for RM-1 and 66% for RM-2. Most of the remaining mercaptan was converted to some other oxidation products as observed in the oxidation of RDTC with iodine in water. A large proportion of the oxidation products, other than the SS was reduced to SH by the subsequent reduction. The conversion of SH to SS in the second and third oxidation treatments was about 60%. The SS content of the oxidized product decreased gradually as the number of the cycles of the reduction–oxidation treatments increased. Both RM samples contained approximately as much SH as RDTC-1 and RDTC-2. However, the conversion of SH to SS was very low for both RM samples under the oxidizing conditions in which the RDTC samples were converted quantitatively to the corresponding disulfide.

The difference between the oxidation behaviors of mercaptocellulose and RDTC probably comes from the difference in the mobilities of the mercapto groups of the two cellulose derivatives. The mercaptan in mercaptocellulose is directly attached to a rigid cellulose chain, thereby restricting its movement in the cellulose matrix to another to form a disulfide linkage. On the other hand, the mercaptan in RDTC is attached to the end of a long sidechain, thereby enabling it to move around more easily in the matrix to link with another.

The difference in the oxidation behaviors of RDTC and RM was also confirmed when they were treated with air saturated in an alkaline buffer solu-

TABLE IV
Oxidation of RDTC-5 with Air Saturated in an Alkaline Buffer of pH 10.5 at 30°C

Oxidation time, hr	SH, μmole/g	SS, μmole/g	SH + 2SS, μmole/g
0	333	10	353
24	69	124	317
48	35	165	365
72	14	168	350
96	8	170	348

TABLE V
Oxidation of RM-1 with Air Saturated in an Alkaline Buffer of pH 10.5 at 30°C

Oxidation time, hr	SH, μmole/g	SS, μmole/g	SH + 2SS, μmole/g
0	288	19	326
1	263	21	305
2	248	37	322
4	216	55	326
6	204	66	336
8	200	60	320
48	191	58	307

tion of pH 10.5 at 30°C. Table IV shows that the SH groups in RDTC were converted slowly to SS in the alkaline solution, and the oxidation proceeded almost to completion in 3 days. On the other hand, only about 30% of the mercaptan in RM-1 was converted to the disulfide in about 10 hr, and the rest of the mercaptan remained unchanged for a prolonged period of treatment (Table V). This provides a strong evidence supporting the presence of SH groups which cannot be coupled to form SS owing to the spatial limitation.

It was interesting to note that the conversion of SH to SS of RM-1 was much smaller in the oxidation with air than that in the oxidation with iodine in methanol. The reaction medium may therefore play some role on the mobility and the probability of coupling of polymeric mercaptans in the cellulose matrix.

Wallace and Schriesheim[10] studied the oxidation of *n*-butyl mercaptan to the corresponding disulfide by the action of molecular oxygen in the presence of a base, and reported that the oxidation proceeded with the first-order kinetics to mercaptan. The kinetics of the oxidation of various RDTC samples with air saturated in the alkaline buffer of pH 10.5 was investigated. Figure 1 shows plots of logarithm of the SH concentration versus reaction time. A linear relationship was observed for RDTC-6, which contained only unpaired mercapto groups, and the apparent first-order rate constant (k_2) was calculated from the slope.

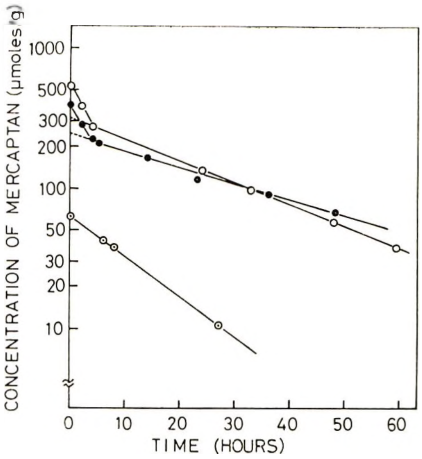


Fig. 1. Kinetics of the oxidation of mercapto groups in RDTC: (⊙) RDTC-6; (●) RDTC-7; (○) RDTC-8.

The plots for RDTC-7 and RDTC-8, which contained both paired and unpaired mercaptans, were divided into two parts: an initial rapid decrease and the following slower decrease. A linear relationship was observed for the latter part of the plots. From the extrapolation of the line to time zero, the initial concentration of the mercaptan of slower disappearance could be estimated. The estimated values for both RDTC-7 and RDTC-8 were nearly equal to the concentrations of the unpaired mercaptan, calculated from the SH and SS contents of RDTC and the corresponding DTC samples. Then, the apparent rate constant of the oxidation of the unpaired mercaptan could be obtained from the slope of the second part of the plots.

The amount of the paired mercaptan at a given time during the oxidation could be estimated from the difference of the amount of the total mercaptan observed and the amount of the unpaired mercaptan which was obtained by extrapolation of the line of the second part of the plot to the given time. The apparent first-order rate constant (k_1) for the oxidation of the paired mercaptan was obtained from the plots of the logarithm of the estimated concentration of the paired mercaptan versus the reaction time. The rate constants obtained are given in Table VI. It was found that the oxidation of the paired mercaptan proceeded more than ten times faster than that of the unpaired mercaptan. The concept of the paired and random placements of mercapto groups in modified cotton, originally proposed by Mack et al.,[7] could be successfully applied to explain the kinetics of the oxidation of RDTC.

The apparent first-order rate constant for the oxidation of the mercaptan of RM-1 was also calculated from the data in Table IV. The rate constant (5×10^{-3} min^{-1}) for the disulfide formation of RM is close to k_1 for the oxidation of the paired mercaptan of RDTC and much higher than k_2 for the oxidation of the unpaired mercaptan This suggests that only those

TABLE VI

Apparent First-Order Reaction Rate Constants for the Oxidation of Mercaptans in RDTC with Air Saturated in an Alkaline Buffer of pH 10.5 at 30°C

Sample	Initial concentration, μmole/g: Total SH	Unpaired SH	SH of slower disappearance[a]	Rate constants[b]: $k_1 \times 10^3$, min^{-1}	$k_2 \times 10^3$, min^{-1}
RDTC-6	64	64	64	—	1.1
RDTC-7	395	265	250	7.1	0.51
RDTC-8	547	325	320	7.6	0.59

[a] Estimated by extrapolation of the second part of the first-order kinetic plots.

[b] k_1, rate constant for the paired mercaptan; k_2, rate constant for the unpaired mercaptan.

mercapto groups which when introduced happened to be in proximity could form disulfide crosslinks as rapidly as the paired mercaptan in RDTC, while those considerably separated from one another could never be combined to form disulfide crosslinks under the oxidizing conditions employed.

Conclusion

The polarographic analysis of mercaptan and disulfide indicated that cellulose β-mercaptoethylaminocarboxylate (RDTC) produced by reduction of the cotton treated with bis-β-isocyanatoethyl disulfide (BIED) was converted quantitatively to the corresponding disulfide by the oxidation with iodine in methanol, the exception being RDTC of a very low degree of substitution. RDTC was subjected to repeated alternating oxidation–reduction treatments to show the complete reversibility of the disulfide crosslinking. On the other hand, only a portion of the mercaptan in mercaptocellulose was converted to disulfide by the oxidation. It seems that the mercapto group in RDTC is attached to the end of a long side-chain, so that it can move around in the cellulose matrix to find another one and form disulfide, while the mercapto group in mercaptocellulose is attached to a rigid cellulose chain and the mobility of the mercapto group is limited so that it is difficult to couple with another to form disulfide.

It is considered that the mercapto groups in RDTC, which are derived from the crosslinks in the BIED-treated cotton, are in paired placement, while the mercapto groups derived from the branches, which are produced by the monofunctional reaction of BIED with cotton, are in random placement. The kinetic study of the oxidation of RDTC with air saturated in the alkaline buffer solution revealed that the oxidation of the paired mercaptan to disulfide occurred much faster than that of the randomly placed mercaptan. A portion of mercapto groups in mercaptocellulose was oxidized to disulfide as rapidly as the paired mercaptan in RDTC, while the rest of them remained unchanged.

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Four-Center Type Photopolymerization in the Solid State. IV. Polymerization of α,α′-Dicyano-*p*-benzenediacrylic Acid and Its Derivatives*

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Synopsis

The solid-state photopolymerization of α,α′-dicyano-*p*-benzene diacrylic acid (*p*-CBA) series has been studied. *p*-CBA, its esters, amide, and a few other cyano derivatives were prepared and new polymers were obtained from *p*-CBA alkyl esters on irradiation of ultraviolet or visible light. Though the polymerization behavior differs with each monomer, polymerization proceeds in essentially the same manner as in the 2,5-distyrylpyrazine (DSP) and *p*-benzenediacrylic acid (BDA) series: the reaction proceeds topochemically forming polymer with a cyclobutane ring in the main chain. Properties of high polymer are typical of cyclobutane-containing polymer. That is, they are highly crystalline with high melting temperature and a limited solubility. The study on this series of compounds, as well as the DSP and *p*-BDA series, supports the generalization that solid-state dimerization can be extended to solid-state photopolymerization of compound having two dimerizable units in a molecule.

INTRODUCTION

The study on four-center type photopolymerization has been extended to α,α′-dicyano-*p*-benzenediacrylic acid (*p*-CBA) and its derivatives, R(CN)-C=CHC$_6$H$_4$CH=C(CN)R, and as a result several new polymers have been prepared.

It has been established from the previous studies[1-6] on this field that photodimerization in the solid state can be extended to the photopolymerization of corresponding bifunctional compounds. Baker and Howes[7] reported the photodimerization of ethyl-2-methoxybenzylidene cyanoacetate in the solid state. This result suggests another possibility of solid-state photopolymerization of *p*-CBA series of compounds. We have prepared *p*-CBA derivatives which include an acid, esters, amide and a few other cyano derivatives and surveyed their photopolymerizability.

It has been found that *p*-CBA alkyl esters from methyl to butyl and octyl polymerize into linear polymers with cyclobutane ring in the main chain.

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

The polymerization process and the properties of polymers thus obtained, were found to be typical of the poly-2,5-distyryl pyrazine (poly-DSP) and poly-*p*-benzenediacrylic acid series (poly-*p*-BDA) in several respects. For example, crystalline *p*-CBA *n*-propyl ester polymerizes as quickly as DSP by the action of ultraviolet or visible light to give highly crystalline polymer quantitatively. Poly-*p*-CBA *n*-propyl ester has high melting temperature (335°C) and dissolves only in such limited solvents as concentrated sulfuric acid. In this paper, the preparation of monomers, photopolymerization procedure, and the structure and properties of the polymers are described.

EXPERIMENTAL

Preparation of Monomers

p-CBA series of compounds was prepared by condensation of terephthalaldehyde with cyanoacetic acid, its esters, or cyanoacetamide in the presence of piperizine. As an example, preparation of *p*-CBA methyl ester is described. Terephthalaldehyde (0.075 mole, 10.05 g) was dissolved in methanol (400 ml). Methyl cyanoacetate (0.15 mole, 15 g) and a small amount of piperizine (2 ml) were added. The solution was stirred for 3 hr at room temperature and crystal formed was collected by filtration. The green-yellow needle crystals were obtained by recrystallization from xylene, yield 20 g (90%). Dicyanodistyrylbenzene, terephthalodimalononitrile and terephthalodicyanoacetophenone were prepared according to Kauffmann[8] by condensation of terephthalaldehyde with benzyl cyanide, malononitrile, or cyanoacetophenone.

Photopolymerization in the Solid State

The monomer crystal (250 mg) was dispersed in an inert solvent such as water–ethanol (19:1 v/v 100 ml) in a Pyrex flask and irradiated with a 500-W xenon lamp for 50 hr at room temperature with stirring. After irradiation the product was washed with a solvent such as ethyl acetate to remove the residual monomer and dried *in vacuo* at room temperature. The formation and the structure of the polymer were confirmed by means of infrared and NMR spectroscopy and solution viscosity.

Attempted Photopolymerization in Solution

In order to examine photopolymerizability in solution, *p*-CBA ethyl ester (300 mg) was dissolved in dioxane (50 ml) and irradiated with a 450-W high-pressure mercury lamp for 5 days. The solution became yellow gradually and the absorption peak at 348 mμ finally disappeared. The excess of dioxane was distilled off under the reduced pressure. The residue was dissolved in methanol and poured into water. White precipitate was collected by filtration and dried *in vacuo*. Characterization of the product was carried out by infrared and NMR spectroscopy and estimation of molecular weight was by a VPO method with a Mechrolab Model 301A osmometer.

RESULTS AND DISCUSSION

Monomers

All the monomers prepared are shown in Tables I and II with melting points, maximum ultraviolet absorption bands, and the results of elementary analysis. The condensation of benzaldehyde with cyanoacetic acid derivatives is known generally to lead the formation of *trans* isomer in which the benzene ring and the carboalkoxy group are on opposite sides of the carbon–carbon double bond. Therefore these monomers are also deduced to be *trans, trans* isomers. Except for *p*-CBA phenyl ester and *n*-stearyl ester, no solid phase transition was observed by differential scanning calorimeter analysis over a temperature range from room temperature to the melting point.

Polymerization

In the *p*-CBA series, *p*-CBA alkyl esters were found to photopolymerize into linear polymers in the solid state. Other compounds such as *p*-CBA phenyl ester, amide, and other cyano derivatives examined here did not polymerize under the described conditions. As is shown in Table I, the rate of polymerization, polymer yield, and the degree of polymerization differ greatly with each monomer. In general, polymerization temperature, over the range from room temperature to $-20°C$, had no effect on the yield and properties of polymers. It seems that the smaller density change during polymerization corresponds to the formation of polymer of higher molecular weight. For example, *p*-CBA, *n*-propyl ester, isopropyl ester, and ethyl ester, for which the density difference between the monomer and the polymer is about 0.03, gave linear high polymers. This fact implies that molecules align in these crystals favorably to polymerize with less atomic or molecular movement. From above observation, this type of polymerization is concluded to be a topochemical reaction. Further definite evidence for this was offered by crystallographic study.[9] The most photoreactive monomer in the present series, is *p*-CBA *n*-propylester. The plots of reaction time versus conversion (Fig. 1) show that the polymer with high molecular weight was obtained by irradiation with a 50-W high-pressure mercury lamp for 30 min. Thus the rate of polymerization is comparable with that of DSP. *p*-CBA methyl ester is the next reactive in this series. It polymerizes nearly quantitatively on irradiation with a 450-W high-pressure mercury lamp for 6–7 hr. However high molecular weight polymer ($\eta_{red} > 0.3$) was not obtained under various conditions. The phenomenon is due to partly at least the *cis–trans* isomerization occurring during polymerization.

The isomerization was confirmed by NMR spectroscopy as follows. The NMR spectrum (Fig. 2) of partially polymerized crystal shows three kinds

TABLE I
Polymerizable Monomers and Their Polymerization

Compound			Elementary analysis					Polymer				
Compound $\mathrm{R(NC)C{=}CH{-}Ar{-}CH{=}C(R)CN}$	Mp, °C	λ_{max}, mμ[a] (ϵ)	C, %	H, %	N, %	Light source	Reaction time, hr	Yield, %	Mp, °C	η_{red}[b]	Solvents	Density of polymer (monomer), g/cc[c]
R=$\mathrm{COOCH_3}$	237	348 (41,500)	64.86 64.24 64.83	4.08 3.95 3.95	9.45[d] 9.38[e] 9.33[f]	450-W high-pressure mercury lamp	6–7	Quantitative	290	0.3	Conc. H_2SO_4 CF_3COOH, $CHCl_3$ acetone	1.296 (1.348)
R=$\mathrm{COOC_2H_5}$[g]	205	348 (44,200)	66.65 67.00	4.94 5.05	8.65[d] 8.78[f]	"	144	66	340	2.6	Conc. H_2SO_4	1.303 (1.276)
R=COO-*n*-$\mathrm{C_3H_7}$	180	348 (46,400)	68.14 68.79 68.93	5.71 5.75 5.73	7.96[d] 8.01[e] 7.99[f]	50-W high-pressure mercury lamp	0.5	Qualitative	335	3.0	Conc. H_2SO_4	1.232 (1.262)
R=COO-*i*-$\mathrm{C_3H_7}$	200	348 (44,100)	68.14 69.38 67.84	5.17 5.73 5.70	7.96[d] 8.01[e] 7.47[f]	450-W high-pressure mercury lamp	120	"	320	1.8	Conc. H_2SO_4	1.226 (1.254)
R=COO-*n*-$\mathrm{C_4H_9}$	178	348 (44,700)	69.45 69.41 69.60	6.36 6.36 6.37	7.37[d] 7.39[e] 7.44[f]	"	144	88	330	0.6	Conc. H_2SO_4	1.263 (1.198)
R=COO-*n*-$\mathrm{C_8H_{17}}$	160	350 (43,700)	73.13 73.26 71.59	8.14 8.32 8.21	5.68[d] 5.52[e] 5.47[f]	"	240	Quantitative	—	—	—	—

[a] Measured in dioxane. [b] Reduced viscosity (0.36 g/100 ml in concentrated H_2SO_4 at 30°C). [c] Measured in CCl_4–*n*-hexane at 30°C. [d] Calculated.
[e] Found for monomer. [f] Found for irradiated product. [g] Data of Kaufmann.[8]

TABLE II

Nonpolymerizable Monomers

Compound $\mathrm{(R)(NC)C{=}CH{-}Ar{-}CH{=}C(R)(CN)}$	Mp, °C	λ_{max}, mμ[a] (ϵ)	Elementary analysis C, %	H, %	N, %	Reference
R=COOH	300	346 (42,400)	62.68[b] 62.98	3.01 3.05	10.44[b] 10.62[c]	New compound
R=$COOC_6H_5$	260	356 (53,700)	74.26 74.37	3.83 3.71	6.66[b] 6.77[c]	New compound
R=$CONH_2$	313	376 (49,500)	63.15 63.17	3.78 3.67	21.04[b] 21.05[c]	New compound
R=CN	268	351 (43,800)	—	—	—	8
R=COC_6H_5	224	355 (46,300)	—	—	—	8
R=C_6H_5	242	363 (45,700)	—	—	—	8
R=$COOC_6H_{37}$	137		77.68 76.58	10.43 10.67	3.64[b] 3.54[c]	New compound

[a] Measured in dioxane except for *p*-CBA and amide, which were measured in concentrated H_2SO_4.

[b] Calculated.

[c] Found for monomer.

of methyl signals: a peak at 4.2 ppm is the methyl proton of the original methyl ester, the peak at 3.85 ppm is that of attaching to cyclobutane ring. Another one at 4.1 ppm is considered to be that of *cis* isomer according to the Hayashi's assignment on the *cis–trans* isomer of α-cyanocinnamate.[10] He reported that the methyl proton of *cis* methyl α-cyanocinnamate appears at a higher field than that of the *trans* isomer by 0.1 ppm. Actually, when *p*-CBA methyl ester was irradiated with ultraviolet in benzene solution, in addition to the original methyl proton (4.2 ppm), a new peak was observed at 4.1 ppm which corresponds to the methyl proton of *cis* isomer. The NMR spectrum of this polymer also suggests the formation of *cis* isomer. It shows the two peaks for cyclobutane ring (Fig. 2, 5.45 5.15 ppm). The main peak (5.45 ppm) may originate from *trans, trans* isomer, while the smaller peak (5.15 ppm) presumably from isomerized monomer.

One probable mechanism is that the polymerization is terminated at the site where *cis* isomerization occurred, resulting in formation of a low molecular weight polymer.

p-CBA ethyl ester photopolymerizes to a high polymer. However the rate of polymerization is rather slow (66% for 144 hr irradiation) and prolonged irradiation (240 hr) was unsuccessful to raise up the polymer yield. Other monomers such as *p*-CBA isopropyl ester and *n*-butyl ester polymerize more quickly than the corresponding compounds of the *p*-BDA series.

In the *p*-BDA alkyl ester series, the rate of polymerization seems to depend on the size of ester residue. That is, the ease of polymerization is in the following order: methyl > ethyl > *n*-propyl or iso-propyl > *n*-butyl.

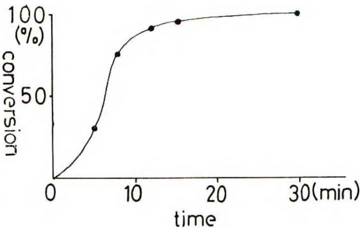


Fig. 1. Plot of reaction time vs. conversion. Polymerization conditions: room temperature, 50-W high-pressure mercury lamp, 0.250 g *p*-CBA *n*-propyl ester, 250 ml EtOH–H_2O.

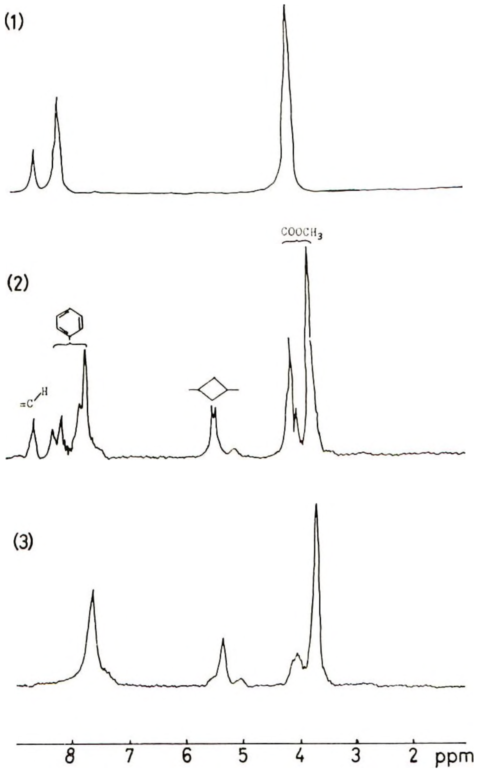


Fig. 2. NMR spectra of monomer and polymer: (*1*) *p*-CBA methyl ester; (*2*) partially polymerized *p*-CBA methyl ester; (*3*) poly(*p*-CBA methyl ester).

On the other hand, it seems in this series that the size of the alkyl ester residue has no serious effect on photopolymerizability.

The study of photopolymerizable compounds was extended to *p*-CBA alkyl esters with long paraffinic chains. For this purpose *p*-CBA *n*-octyl ester and *n*-stearyl ester were prepared. *p*-CBA *n*-octyl ester would seem to be photopolymerizable on the basis of the usual spectroscopic methods. However, it was impossible to measure solution viscosity of the product because of its poor solubility. *p*-CBA *n*-stearyl ester did not photopolymerize.

Photoirradiation of *p*-CBA ethyl ester in solution, which was carried out to check the photopolymerizability in solution led to different results depending on solvents employed. Photoirradiation of *p*-CBA ethyl ester in benzene solution resulted in the formation of *cis* isomer. On the other hand, photoirradiation of this monomer in dioxane led to another result. The infrared spectrum of this photoproduct indicated the disappearance of double bonds (1600 cm^{-1}) and the presence of ether (1130 cm^{-1}) and strong absorption of methylene (2900 cm^{-1}). The NMR spectrum showed the disappearance of olefinic proton and the presence of dioxane proton (3.8 ppm). The molecular weight, as estimated by a VPO method, was about 1000. From these data, it is reasonable to conclude that this photoreaction led to the formation of the oligomeric adduct of dioxane and *p*-CBA ethyl ester. Thus photoreaction in solution is complicated and so far no polymeric material with a cyclobutane ring has been obtained.

Structure and Properties of Polymers

The structure of the polymer was investigated by means of NMR and infrared spectroscopy. Infrared spectra of monomers and polymers are shown in Figure 3. The spectrum of the polymer shows the disappearance of C=C double bond (1600 cm^{-1}) and the shift of carbonyl group to higher wave number. The NMR spectrum of poly-*p*-CBA methyl ester is shown in Figure 2 with that of *p*-CBA methyl ester. New peaks at 5.45, and 5.15 ppm in the polymer are attributed to proton pendant from the cyclobutane ring, by analogy with spectra of poly-DSP and poly-*p*-BDA ethyl ester. The NMR data for other polymers are given in Table III.

TABLE III
NMR Spectra of Polymers[a]

	Peaks δ				
Polymer	Aromatic protons	Cyclobutane protons	Methyl protons	Methylene protons	Solvent
Poly-*p*-CBA ethyl ester	7.7	5.5	1.2	4.2	Conc. H_2SO_4
Poly-*p*-CBA *n*-butyl ester	7.8	5.5	1.1	1.3–2.2 4.3	Conc. H_2SO_4 or CF_3COOH
Poly-*p*-CBA *n*-octyl ester	7.7	5.5	0.9	1.1–2.0 4.2	Conc. H_2SO_4 or CF_3COOH

[a] NMR spectra were obtained on JNM-C-60HL high-resolution NMR spectrometer operating at 20–22°C.

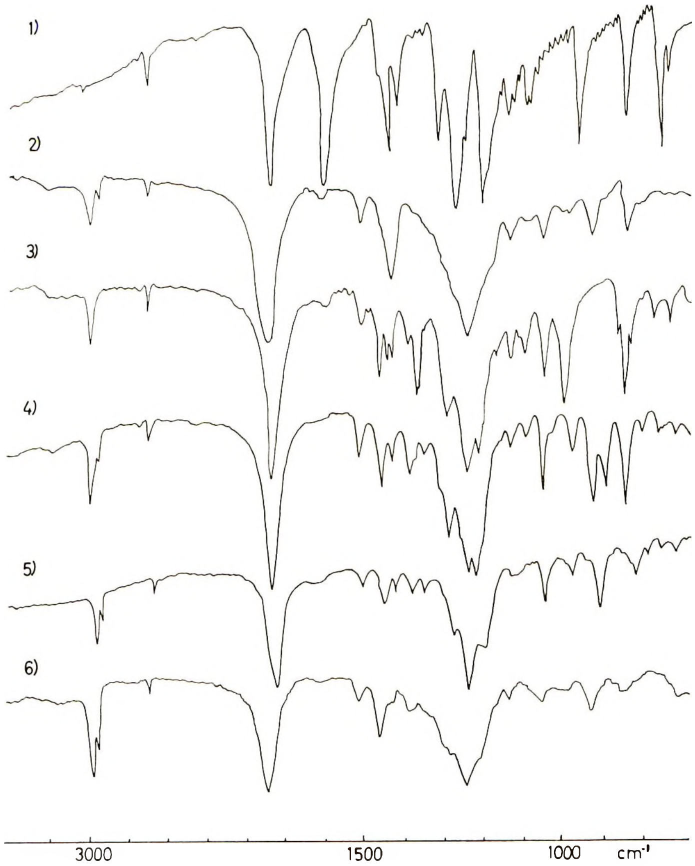
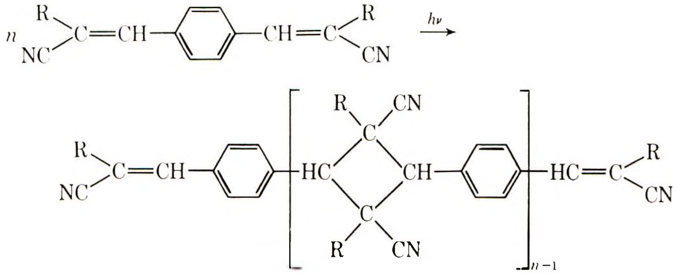


Fig. 3. Infrared spectra of monomer and polymers: (*1*) *p*-CBA methyl ester; (*2*) poly(*p*-CBA methyl ester); (*3*) poly(*p*-CBA ethyl ester); (*4*) poly(*p*-CBA *n*-propyl ester); (*5*) poly(*p*-CBA isopropyl ester); (*6*) poly(*p*-CBA *n*-butyl ester).

The results of elementary analysis of monomers and polymers (Table I) show they have same compositions. Based on these data, it is concluded that polymer consists of recurring cyclobutane and aromatic rings alternating in the main chain:



R=$COOCH_3$, $COOC_2H_5$, $COOC_3H_7$ etc.

Some properties of the polymers are shown in Table I and Figure 4. As is shown in Figure 4, poly-*p*-CBA *n*-propyl ester is highly crystalline; x-ray powder diagrams of other polymers also show crystallinity. One exception is seen: this is poly-*p*-CBA methyl ester, which is nearly amorphous (Fig. 4). This is presumably caused by formation of *cis* monomer, which will disturb the crystal structure.

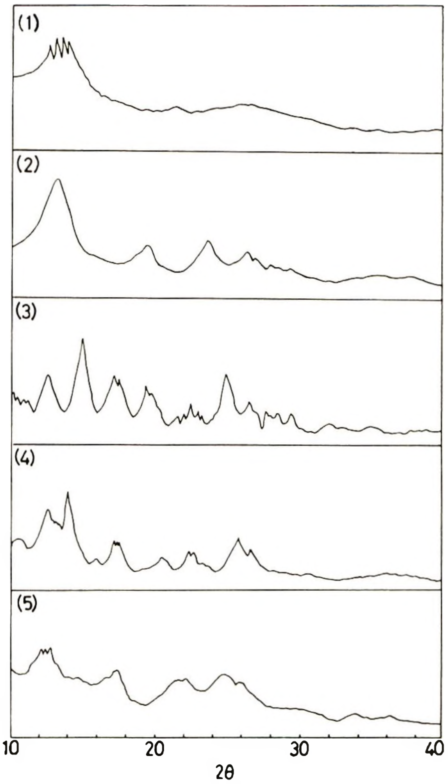


Fig. 4. X-Ray diffraction diagrams of polymers: (*1*) poly(*p*-CBA methyl ester); (*2*) poly(*p*-CBA ethyl ester); (*3*) poly(*p*-CBA *n*-propyl ester); (*4*) poly(*p*-CBA isopropyl ester); (*5*) poly(*p*-CBA *n*-butyl ester).

Because of their high crystallinity, the solubility of these polymers is very limited. Highly crystalline polymers dissolve only in concentrated sulfuric acid. The solubility of amorphous poly-*p*-CBA methyl ester ($\eta_{\text{red}} = 0.3$) is interesting. It is partially soluble in ordinary organic solvents such as chloroform, acetone, and ethyl acetate. The soluble fraction was found to be of low molecular weight ($\eta_{\text{red}} < 0.1$). Thus, the solubility of this type of polymer is governed by crystallinity and molecular weight.

Another feature of this type of polymer is high melting temperature, for example, 335°C for poly-*p*-CBA *n*-propyl ester. However, these cyclobutane-containing polymers decompose into monomer on being heated to near the melting temperature.

Conclusions

Crystalline alkyl esters of α,α'-dicyano-p-benzenediacrylic acid photopolymerize topochemically into highly crystalline linear polymers.

The photopolymerization proceeds by cycloaddition of double bonds with formation of cyclobutane ring in the main chain.

The study of the α,α'-dicyano-p-benzenediacrylic acid series of compounds confirmed that solid-state photodimerization can be extended to solid-state photopolymerization of the corresponding bifunctional compounds.

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Cyclic Amine Initiation of Polypivalolactone*

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Synopsis

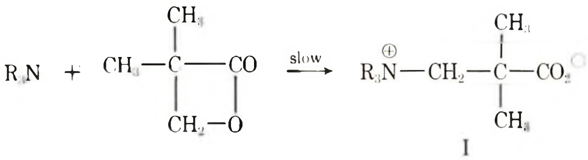
Certain monocyclic and polycyclic tertiary amines initiate polymerization of, and copolymerize with, pivalolactone. These comprise three-, four-, and five-membered monocyclic amines and 1-azapolycyclic amines. The polymerization proceeds in three steps: (a) initiation to form a cyclic amine/pivalate betaine, (b) propagation to yield a polylactone zwitterion by an anionic mechanism, and (c) interlinking by a carboxylate end attacking a cyclic amine end to incorporate amine as a comonomer in the chain. When polymerization is carried out at low temperatures, the more stable cyclic amine ring systems yield isolatable step b polymers. These polymeric zwitterions undergo step c by heating, even in the solid state. The mechanism suggests that, for the more labile cyclic amines, a lactone could be the initiator for polyamine formation by a cationic mechanism. Interlinking would lead to incorporation of lactone initiator. In intermediate cases, block copolymers would result. With a proper balance of reactivities, 1:1 alternating copolymers would be possible.

INTRODUCTION

The polymerization of pivalolactone (2,2-dimethylhydracrylic acid lactone) was first described by Reynolds and Vickers.[1] Tertiary amines were evidently the preferred initiators.

Fischer[2] explored the polymerization in detail. He showed that polymerization involved two steps.[3] With tertiary amines, for example, steps (1) and (2) were observed:

Initiation



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* In honor of C. S. Marvel on the occasion of his 75th birthday.

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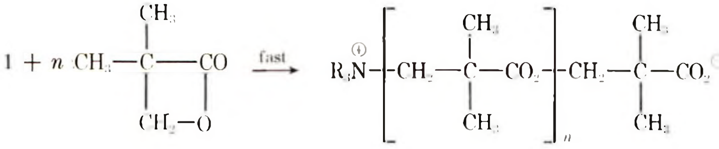
Propagation



$$1 + n\ CH_3{—}\overset{CH_3}{\underset{CH_2—O}{C}}{—}CO \xrightarrow{\text{fast}} R_3\overset{\oplus}{N}{—}\left[CH_2{—}\overset{CH_3}{\underset{CH_3}{C}}{—}CO_2\right]_n{—}CH_2{—}\overset{CH_3}{\underset{CH_3}{C}}{—}CO_2^{\ominus} \qquad (2)$$

In this paper we report our results[4] using as tertiary amine initiators both monocyclic and polycyclic amines having ring strain in their quaternary forms.

EXPERIMENTAL

Materials

Figure 1 depicts the structures of the various ring systems used as initiator-comonomers. Table I details materials used.

Pivalolactone. Pivalolactone was prepared by alkali ring closure of chloropivalic acid. It was purified by distillation from calcium hydride at reduced pressure, bp 48°C/18 mm. Purified monomer (mp −13°C, bp 161°C) was stored under nitrogen in a freezer.

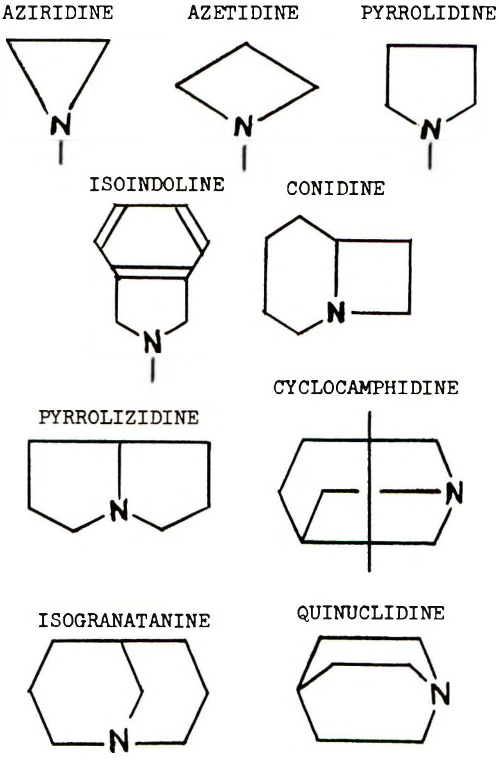


Fig. 1. Initiator-comonomer ring systems.

TABLE I
Materials Used

Compound	Boiling point, °C	Purity, %[a]
Monomer		
Pivalolactone	48 (18 mm)	99+
Solvent		
Acetonitrile	—	C.P.
Initiators		
Triethylamine	—	C.P.
N,*N*-Dimethylaniline	—	C.P.
Piperidine	—	C.P.
N-Methylpiperidine	105.5	99+
N-Ethylpiperidine	129	99+
N-Methylhexamethyleneimine	137.0–137.5	—
Initiator-Comonomers		
N-Methylaziridine	~29	97
N-Ethylaziridine	49–50	—
N-Phenylaziridine	74.5–75.5 (13.8 mm)	99+
3,3-Dimethyl-*N*-methylazetidine	78–79	—
3,3-Di-*n*-butyl-*N*-methylazetidine	94–96 (17 mm)	99+
N-Methylpyrrolidine	79.5	99+
N-Ethylpyrrolidine	104.5	99+
N-Methylisoindoline	88.0–89.5 (18 mm)	98+
Conidine	101 (209 mm)	99+
Pyrrolizidine	80–82 (96 mm)	85–90
Isogranatanine	mp 114–115	—
Cyclocamphidine	mp 172.5–174.5	—
Quinuclidine	mp 158.5–160.5	—

[a] By vapor-phase chromatography; C.P. = Chemically Pure Reagent grade.

Amines. Amines not commercially available were prepared by published literature methods. With one exception, no amine was used unless it was judged at least 97% pure. Pyrrolizidine (by hydrogenation of the oxime from diethyl 4-oxopimelate) after three distillations was only 85–90% pure by vapor-phase chromatography; but since it performed satisfactorily as an initiator, the impurities were evidently inert. The liquid amines were distilled from sodium before use to ensure against traces of water.

Polymerizations

Table II summarizes the pivalolactone polymerizations conducted.

Yields, based on pivalolactone, were generally nearly quantitative, in keeping with a nonequilibrium, ring-opening polymerization. Initiator efficiencies were low, however, in agreement with slow initiation followed by rapid propagation. (For low per cent modification, mole per cent incorporation equals approximately % N times 100/14; for example, quantitative incorporation of 3% charged should give 0.42% N whereas the observed range was 0.11–0.43).

TABLE II
Pivalolactone Polymerizations

Run no.	Initiator	Initiator, mole-%	Method	Melting point, °C	η_{inh}	N, %	No. per chain
1	Triethylamine	1	B	239	2.57	0.02	1
2	N,N-Dimethylaniline	2	B	238	3.33	0.01	1
3	Piperidine	5	S[a]	203	0.10	0.69	1
4	N-Methylpiperidine	5	S[a]	229	0.88	0.06	1
5	N-Ethylpiperidine	5	B	240	3.22	0.01	1
6	"	5	S[a]	237	2.23	0.01	1
7	N-Methylhexamethyleneimine	5	B	233	0.98	0.04	1
8	"	5	S	228	0.77	0.07	1
9	N-Methylaziridine	3	B	—	1.53	0.41	13
10	"	17	S	207	0.49	1.84	14
11	N-Ethylaziridine	3	B	226	2.87	0.26	18
12	N-Phenylaziridine	5	B	213	2.96	0.83	58
13	3,3-Dimethyl-N-methylazetidine	5	B	224	0.81	0.75	10
14	3,3-Di-*n*-butyl-N-methylazetidine	3	B	227	2.96	0.42	29
15	N-Methylpyrrolidine	5	S	—	1.04	0.16	3
16	"	5	S[a]	221	1.46	0.16	5
17	N-Ethylpyrrolidine	5	S[a]	231	2.81	0.04	3
18	N-Methylisoindoline	9	S	—	1.37	0.13	4
19	"	9	S[a]	220	1.38	0.13	4
20	Conidine	3	B	222	0.95	0.43	7
21	"	3	S	—	1.46	0.13	4
22	"	3	S[a]	231	1.41	0.13	4
23	Cyclocamphidine	3	B	217	1.23	0.22	5
24	"	3	S	—	0.37	0.36	2
25	"	3	S[a]	208	0.99	0.36	6
26	Pyrrolizidine	5	B	229	1.37	0.08	2
27	"	5	S	—	0.53	0.23	2
28	"	5	S[a]	216	1.56	0.23	7
29	Isogranatanine	5	B	224	2.41	0.08	4
30	"	5	S	—	0.26	0.25	1
31	"	5	S[a]	208	1.37	0.25	7
32	Quinuclidine	3	B	226	5.94	0.11	18
33	"	4	S	—	0.35	0.21	1
34	"	4	S[a]	—	1.50	0.21	6
35	"	5	S	—	0.31	0.31	1
36	"	5	S[a]	—	2.12	0.31	14
37	"	20	S	—	0.17	0.42	1
38	"	20	S[a]	—	1.73	0.42	15
39	"	3	MS	—	0.21	0.41	1
40	"	3	MS[a]	—	1.35	0.41	11

[a] Polymer heated at 150°C.

Bulk (Method B). To a flame-dried, thick-walled polymer tube cooled in an ice bath was added, under nitrogen, 20–30 g of monomer and initiator. The tube, cooled in Dry Ice, was sealed *in vacuo*. As a safety precaution, most bulk polymerizations were conducted with the sealed tube in a pipe autoclave pressured to 200 psi with nitrogen. This assembly was placed in a 250°C oil bath for 15 min. Recovered polymer was ground with Dry Ice in a Wiley mill for easier handling.

Nearly equivalent results were obtained in several cases by placing the cooled monomer–initiator mixture in a large (2 × 15-in.) test tube behind a safety shield. Mild warming with a flame initiated violent polymerization, accompanied by monomer refluxing in the tube. Polymerization was complete in a few minutes. *Caution:* The azetidines led to explosive decomposition, and so this method is extremely dangerous.

Solution (Method S). To a flame-dried, 500-ml flask fitted with stirrer, reflux condenser, and nitrogen inlet were added 150 ml of anhydrous (<0.01% water) acetonitrile. Monomer and initiator, ca. 15 g total, were added separately, in order. The mixture was stirred and refluxed for 2 hr. The polymer, which precipitated as formed, was collected, washed with acetonitrile, and dried *in vacuo* at room temperature.

Modified Solution (Method MS). Same as for solution method except that the mixture was stirred for 0.5 hr at room temperature before refluxing.

Characterization

Inherent Viscosity. Inherent viscosities were determined at 0.5 g/100 ml in trifluoroacetic acid at 30°C with a Cannon-Fenske viscometer.

Melting Point. The major endotherm on the second cycle in differential thermal analysis was recorded as the polymer crystalline melting point.

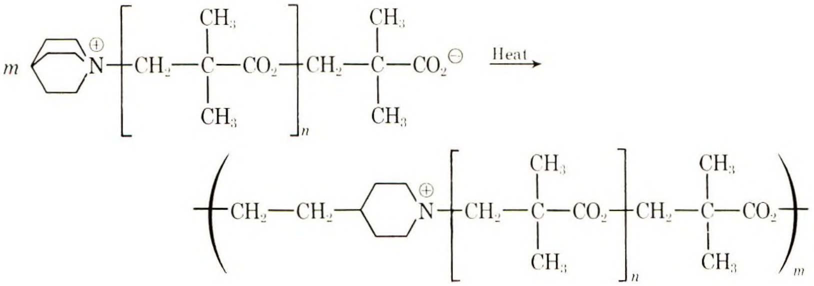
Dyeing. To a dyebath consisting of 12 ml of water, 0.08% of acid dye, 0.05% of sodium lauryl sulfate, 2% of acetic acid, with pH adjusted to 2.0 by trifluoroacetic acid, was added 0.25 g of polymer (as melt-spun, drawn fiber). Dyeing was at the boil for 2 hr.

RESULTS AND DISCUSSION

Thesis

Certain tertiary cyclic amines not only initiate pivalolactone polymerization [steps (1) and (2), above] but also are incorporated in the chain by a novel chain interlinking [step (3), below]. This is illustrated with quinuclidine.

Interlinking:



(3)

Thus, the initiator becomes a comonomer.

Theory

The relation between inherent viscosity, η_{inh}, and number-average molecular weight, $\bar{M}_n$, for polypivalolactone has been determined in these laboratories to be:

$$\eta_{\text{inh}} = 3.0 \times 10^{-4}\ \bar{M}_n^{0.8} \tag{4}$$

(Trifluoroacetic acid, $0.5 \leq \eta_{\text{inh}} \leq 2.0$)

For a polymer containing amine residues:

$$\%\ \text{N} = \frac{14\ (\text{No. per chain})}{\bar{M}_n} \times 100 \tag{5}$$

Combining eq. (4) with eq. (5) yields

$$\text{No. per chain} = 18\ (\%\ \text{N})\ (\eta_{\text{inh}})^{1.25} \tag{6}$$

For example, a polypivalolactone of DP = 250, $\bar{M}_n = 25{,}000$, $\eta_{\text{inh}} = 1.0$ would have % N = 0.06 for one nitrogen atom per chain. For the number per chain data in Table II, it was assumed eq. (6) would hold approximately for the copolymers and for $0.10 \leq \eta_{\text{inh}} \leq 5.94$.

Initiators

A series of amine initiators gave the expected results of about 1 initiator moiety per chain (Table II, runs 1–8). The tertiary amines, even in gross amounts, led to high polymers of low nitrogen contents in both bulk and solution systems. The one secondary amine tested, piperidine, was quantitatively incorporated, leading to very low polymer, but still with an estimated 1 amine moiety per chain.

Initiator—Comonomers

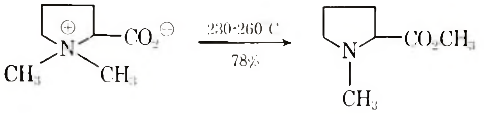
Cyclic tertiary amines having high steric strain in the quaternary form were found to be an unusual class of initiators. They produced in melt systems high polymers with higher than expected nitrogen analyses. That is to say, there was more than 1 initiator moiety per chain.

Table II, runs 9–40, describes results with 13 monocyclic and polycyclic amines behaving in this way. They comprise three-, four-, and five-membered monocyclic amines and the 1-azapolycyclic amines.

It is reasonable to presume that the polylactone zwitter ions, step (2), could react with themselves by carboxylate attack of one chain end on the quaternary cyclic amine of another chain end, opening the ring through ester formation, and thus relieving the strain and neutralizing the charges, step (3).

We were unable to find an example in organic chemistry specifically describing carboxylate ring-opening attack on quaternary rings.

The conversion of stachydrine to methyl hydrate by dry distillation[5] is the nearest analog:



(7)

Attack on methyl rather than the ring is undoubtedly favored by: (a) the ratio of two methyls to one methylene, (b) no steric hindrance around methyl, and (c) ring strain is relievable by methyl transfer as well as ring opening.

For the initiator-comonomers considered here, we may distinguish three cases. (1) The three-ring aziridines and the four-ring azetidines, having high strain even in the unquaternized forms, would have strong driving force for ring-opening attack rather than N-alkyl transfer. (2) The five-ring pyrrolidines would depend mainly on having two methylenes as opposed to one alkyl for methylene ring-opening attack. (The "neopentyl" structure of the pivalate chain should be too hindered for carboxylate attack.) (3) The polycyclics would present no alternative to ring-opening, other than the unfavored "neopentyl" pivalate.

Chain Interlinking

Six-Ring Polycyclics. The bicyclic amines containing only six-rings, isogranatanine and quinuclidine, would be expected to be the most stable, even in quaternized forms.

Indeed, solution polymerization in acetonitrile with polymer drying at room temperature yielded low-to-moderate polymers with just 1 amine moiety per chain (Table II, runs 30, 33, 35, 37, 39).

Heating these polymers at 150°C for several hours in the solid state converted them to high polymers, without loss of nitrogen (Table II, Method S[a]). The resulting polymers had from 7 to 14 copolymerized initiator fragments, proof of a separate chain interlinking step.

Five-Ring Polcyclics. The polycyclic amines containing one or more five-rings, pyrrolizidine and cyclocamphidine, yielded solution polymers averaging 2 initiator moieties per chain. Thus, these more highly strained rings led to some chain interlinking even at 82°C. Heating these polymers resulted in a threefold increase in inherent viscosities, demonstrating further chain interlinking.

Four-Ring Polycyclics. The one polycyclic containing a four-ring evaluated was conidine. The high ring strain led to complete interlinking during solution polymerization; no increase in inherent viscosity was observed after heating.

Monocyclics. The larger, strain-free, monocyclic rings, as represented by *N*-methylhexamethyleneimine and two *N*-alkylpiperidines, functioned as simple tertiary amine initiators, giving 1 initiator molecule per chain.

By contrast, the higher strained three-ring aziridines and four-ring azetidines by solution polymerization gave interlinked polymers directly.

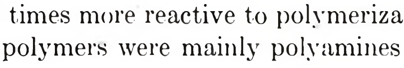
Only in the case of the five-ring *N*-methylpyrrolidine was any postinterlinking observed. A solution polymer (η_{inh} = 1.04, 3 moieties per chain) increased in molecular weight after heating (η_{inh} = 1.46, 5 moieties per chain). However, *N*-methylisoindoline, also a five-ring, gave interlinked product directly, undoubtedly influenced by the benzene ring, with no further reaction on heating.

Thesis Proof

The following evidence establishes the incorporation of cyclic initiators as eventual comonomers as depicted in steps (1)–(3). Cyclic amines acted in precisely the same way as simple amines in steps (1) and (2). The eventual polymers contained far more nitrogen than is possible from chain ends alone. Incorporated nitrogen is basic, as shown by acid dyeings. Increasing nitrogen contents led to increasing depths of dyeing. Polymer crystalline melting points decreased with increasing nitrogen content, indicative of increasing copolymer content. Ease of chain interlinking followed the expected order based on ring size and strain.

Related Polymerizations

Previous Work. In an initial paper,[6] Kagiya et al. reported the uncatalyzed copolymerization of *N*-phenylaziridine and β-propiolactone in acetonitrile solution at 0°C. The product was shown to contain aminoester units:



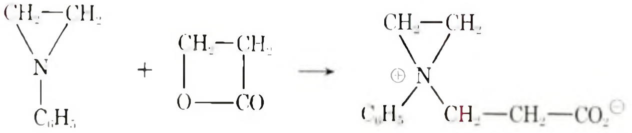
$$\text{—CH}_2\text{—CH}_2\text{—CO}_2\text{—CH}_2\text{—CH}_2\text{—}\underset{\displaystyle \text{C}_6\text{H}_5}{\underset{|}{\text{N}}}\text{—}$$

The amine was 50 times more reactive to polymerization than the lactone, and the resulting polymers were mainly polyamines with low amounts of ester.

A subsequent paper[7] on the polymerization mechanism, however, attributed catalysis to adventitious propionic acid in the lactone. For added acid catalyst, the mechanism proposed was cationic copolymerization, with the propagating chain end being imine-onium or lactone-onium.

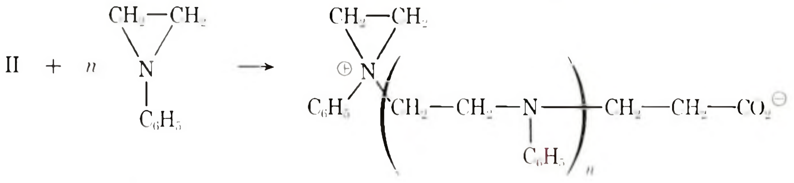
Theory. Tertiary amines are known[8] to react readily with β-propiolactone to form betaines. For example, trimethylamine and β-propiolactone in acetonitrile at 10–15°C yield 98% betaine. Further, it is known[9] that β-propiolactone is stable to polymerization at 0°C. One would then expect betaine formation but not propiolactone polymerization under the Kagiya conditions.

Hence, a mechanism for the direct copolymerization of *N*-phenylaziridine and β-propiolactone leading to polyamine containing internal ester could be as shown in eqs. (8)–(10).



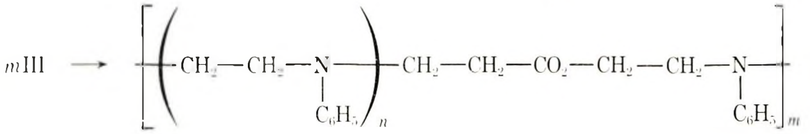
II

(8)



III

(9)



(10)

CONCLUSION

We believe uncatalyzed copolymerization of cyclic tertiary amines and β-lactones is general. Our work, particularly with the polycyclic amines, represents one extreme in which propagation is anionic polymerization of lactone. Kagiya et al. may have discovered the other extreme in which propagation is cationic polymerization of amine. Intermediate and mixed cases having simultaneous anionic and cationic propagations leading to block copolymers are then possible. In all cases, chain interlinking would effect copolymerization. Theoretically possible is an alternating 1:1 copolymer of cyclic amine and lactone by a simple charge neutralization polymerization consisting of step (1) followed by step (3).

Although our work was not detailed enough to prove the contention, in cases with very active amines we may have produced mixed cases leading to block copolymers. The quantitative incorporation and very large number per chain obtained with *N*-methylaziridine, *N*-phenylaziridine, two *N*-methylazetidines, and conidine (all higher strained) strongly suggests this.

This work was presented, in part, at the 159th National ACS Meeting in Houston, Texas, February, 1970, and at the 5th Middle Atlantic Regional Meeting in Newark, Delaware, April, 1970.

The Pioneering Research Laboratory is pleased to honor Professor Marvel with this paper; for he has been a friend and valued consultant for many years.

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Block Copolymer from α,ω-Dihydroxyl Polystyrene and Polyethylene Glycol*

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Synopsis

α,ω-Dihydroxyl polystyrene was synthesized by the addition of styrene oxide to polystyryl dianion initiated with sodium naphthalene. Diglyme was found to be an unsuitable solvent for the preparation of low molecular weight compounds. Block copolymerization of the α,ω-dihydroxyl polystyrenes ($\bar{M}_n$ = 2250, 3140, and 6200) with poly(ethylene glycols) ($\bar{M}_n$ = 404, 1960, and 5650) was pursued by introducing urethane linkages with 4,4′-diphenylmethane diisocyanate. The mechanical, thermal, and viscoelastic properties, solution viscosity, molecular weight distribution, and moisture absorption of the block copolymers obtained were examined. Incorporation of styrene blocks was found to disturb the crystallization and fusion of poly(ethylene glycol) blocks. Films cast from benzene solution were soft and elastic and absorbed up to 5.8% moisture.

INTRODUCTION

Several methods[1] have been reported for the introduction of functional groups to the ends of vinyl and diene polymers, but few are actually practical for obtaining α,ω-bifunctional polymers as a component of block copolymers. For the synthesis of α,ω-dihydroxyl polystyrene, addition of ethylene oxide to polystyryl dianion is recommended; however skilled techniques are required to obtain bifunctionality.

We have found that styrene oxide can be used to obtain α,ω-dihydroxyl compounds instead of ethylene oxide; in this case the polymer ends were closer to phenethyl alcohol. An attempt to use diethylene glycol dimethyl ether (diglyme) as a solvent for Na naphthalene to obtain low molecular weight polystyrene was unsuccessful. In spite of the good solubility of Na naphthalene in diglyme and the moderate value (ca. 4) of the dielectric constant, k_p/k_i and diffusion of styrene are not considered to be suitable to obtain uniform low molecular weight polystyrene.

Block copolymerization of α,ω-dihydroxyl polystyrene with poly(ethylene glycol) was pursued by introducing urethane linkages with 4,4′-diphenylmethane diisocyanate (MDI). Thermal and viscoelastic properties, solution viscosity, molecular weight distribution, and moisture absorp-

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

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tion of the resulting block copolymers were studied. A poly(ethylene oxide)–polystyrene–poly(ethylene oxide) sandwich-type copolymer was also synthesized by using Cs naphthalene–THF as the initiator; this material was used as a reference.

RESULTS AND DISCUSSION

Preparation of α,ω-Dihydroxyl Polystyrene

α,ω-Dihydroxyl polystyrene was prepared by the polymerization of styrene with Na naphthalene in a suitable solvent such as THF, followed by the addition of styrene oxide. For the purpose of obtaining starting materials for block polymerization, the molecular weight of the α,ω-dihydroxyl polystyrene was chosen to lie in the range of 10^3.

As was reported previously,[2] α,ω-dihydroxyl polystyrene having a molecular weight less than 1000 is not easy to prepare. A high initiator concentration is required in any solvent. In dioxane, the initiator precipitates out before sufficiently high concentrations are reached. In THF, k_p/k_i is not small enough to obtain uniform polymer. Diglyme was considered to be a good solvent because of its solvent power for Na naphthalene and its dielectric constant, but the results were negative; k_p/k_i was large and there was slow diffusion of styrene which changed the molecular weight (Table I). To avoid the possible killing of the initiator radical ion and polystyryl ion pairs by impurities, styrene and styrene oxide were added without dilution with solvent to the initiator solution in a blender running at 9000 rpm. The obtained dihydroxyl polystyrene showed distinct infrared OH absorptions at 3400 and 3560 cm^{-1} and good bifunctionality, as can be seen in the molecular weight from VPO and endgroup analysis.

Preparation of Block Copolymer

The chain extension of α,ω-dihydroxyl polystyrene with isocyanates has been already examined,[4] and extended polymer having $\bar{M}_n$ = 160 000 has been obtained from the α,ω-dihydroxyl polystyrene of $\bar{M}_n$ = 5500 and 4,4′-diphenylmethane diisocyanate.[5] Introduction of another component should bring about $(AB)_n$ type block copolymer. In this connection poly(ethylene glycols) of three different molecular weights have been taken as a component and block-polymerized by using 4,4′-diphenylmethane diisocyanate as a linking agent. To avoid the randomness of the addition of two components, two moles of the diisocyanate was added to either component in the first step; the other component was then added in the second step. The relative reactivity of the two isocyanate groups in the first and second addition is reported to be 3.2 for 4,4′-diphenylmethane diisocyanate and 25 for 2,4-tolylene diisocyanate,[6] but the latter was not used because of the tendency to produce crosslinked polymer.

The results obtained with the use of poly(ethylene glycols) having molecular weights of 404, 1960, and 5650 are listed in Table II. After 48 hr of

TABLE I

Synthesis of α,ω-Dihydroxyl Polystyrene[a]

Expt. no.	Naphthalene, mmole	Solvent		Styrene, g	Styrene oxide, g	$\bar{M}_n \times 10^3$	
		Type	Volume, ml			By VPO[b]	By endgroup analysis[c]
S-98	20.1	THF	250	23	11.5	6.20	5.75
S-100-A	25.4	"	620	32	19	3.14	3.41
S-101	39.0	"	750	33	9	2.90	3.00
S-102	46.4	Diglyme	620	65[d]	5	9.10	90.5
S-115	33.2	"	570	23	19	21.0	43.2
S-104	28.2	THF dioxane	350 410	34	8	2.25	2.18

[a] Na cation, −20°C, 9000 rpm in A atmosphere.

[b] Molecular weight measured by Mechrolab vapor pressure osmometer, Model 301-A, with benzene at 37°C.

[c] Molecular weight measured from the absorption at 442 mμ of the phenylazophenyl urethane of the polymer.[3]

[d] Styrene was diluted with 47 g of diglyme.

TABLE II
Preparation of Block Copolymers[a]

Expt. no.	α,ω-Dihydroxyl polystyrene $\bar{M}_n$	α,ω-Dihydroxyl polystyrene wt, g	MDI, g	Poly(ethylene glycol) $\bar{M}_n$	Poly(ethylene glycol) wt, g	Tri-ethylene-diamine, mg	Ben-zene, ml	$\bar{M}_n$ $\times 10^4$[b]	η_{inh}[c]	Elemental analysis C, %	Elemental analysis H, %	Elemental analysis N, %
S-104-2	2250	1.4575	0.3325	404	0.2620	9.8	16.0	4.25	0.24_5	82.80	7.36	1.76
S-104-3	"	1.4575	0.3325	1960	1.2710	9.8	16.0	5.37	0.39_0	73.80	8.16	1.19
S-104-4	"	1.4605	0.3325	5650	3.6625	9.8	21.0	5.28	0.52_1	64.47	8.73	0.78
S-100-A-9	3140	1.3725	0.2197	404	0.1750	9.0	14.0	3.00	0.21_5	86.31	7.55	1.35
S-100-A-3[d]	"	0.7465	0.1196	1960	0.4667	4.0	7.0	5.64	0.25_7	76.58	8.12	0.88
S-100-A-6[e]	"	0.7322	0.1199	"	0.4568	4.5	7.0	4.47	0.28_4	78.65	8.19	0.83
S-100-A-7[f]	"	1.4277	0.2398	"	0.8916	8.8	14.0	4.99	0.29_9	77.38	8.12	0.84
S-100-A-8	"	1.4727	0.2401	"	0.8968	20.6	15.0	6.58	0.26_6	77.87	8.00	0.99
S-100-A-10	"	1.4081	0.2249	5650	2.5316	13.0	17.0	4.43	0.81_6	66.81	8.59	0.70
S-98-3	6200	1.5035	0.1222	404	0.0980	9.0	15.0	2.11	0.24_4	88.21	7.59	0.69
S-98-4	"	1.5055	0.1222	1960	0.4745	9.0	15.0	3.22	0.32_7	83.50	7.97	0.60
S-98-5	"	1.5035	0.1222	5650	1.3730	9.0	18.0	6.25	0.64_3	74.80	8.46	0.38

[a] Reaction conditions: 50°C, 48 hr, 2.05 equivalents MDI.

[b] Molecular weight measured by a Hewlett-Packard 501 high-speed membrane osmometer in toluene at 37°C.

[c] Inherent viscosity at 0.25 g/dl in benzene at 25°C.

[d] MDI, 2.00 equivalents, first added to the solution of poly(ethylene glycol).

[e] Anisole was used instead of benzene.

[f] Anisole was used instead of benzene, 2.10 equivalents MDI used.

heating at 50°C, the molecular weight reached several tens of thousands, and elastic films could be cast from the benzene solution of the copolymer. Copolymer having long poly(ethylene glycol) segments had an affinity for methanol and swelled in it.

Reactivity of MDI with ω-Hydroxyl Polystyrene

To select conditions favorable for preparing isocyanate-terminated polystyrene, the reaction velocity of MDI was examined in benzene at 20°C with the use of a monofunctional ω-hydroxyl polystyrene, $\bar{M}_n = 6800$, prepared by living polymerization with *n*-butyllithium initiator. The isocyanate concentration in the reaction mixture was plotted against time (Fig. 1). Without catalyst, isocyanate was almost unreactive after 21 hr, but in the presence of triethylenediamine the reaction proceeded at a moderate rate. Under conditions similar to those used for the preparation of the block copolymer, half of the isocyanate was consumed within 9 hr.

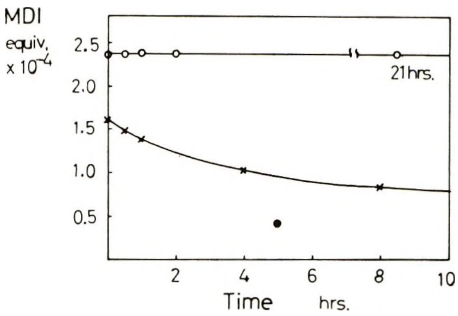


Fig. 1. Rate of reaction of MDI with ω-hydroxyl polystyrene: (○) uncatalyzed; (●) 2×10^{-5} mole triethylenediamine and 2×10^{-5} mole dibutyltin dilaurate added, initial concentration of NCO 2.36×10^{-4} equiv; (×) 2×10^{-5} mole triethylenediamine, added.

Molecular Weight and Inherent Viscosity

The molecular weights of the alternating block copolymers were measured by use of a Hewlett-Packard's 501 high-speed membrane osmometer using toluene and a Sartorius UCF membrane at 37°C. Inherent viscosities were determined at a concentration of 0.25 g/dl in benzene at 25°C. The results in Table II show that the copolymers with longer poly(ethylene glycol) blocks have higher viscosities (cf. S-104-3 and S-104-4). The relation between log $\bar{M}_n$ and log η (Fig. 2) is hard to elucidate but the plots for copolymers of S-104 and S-98 series lay on two different lines.

Molecular Weight Distribution

The molecular weight distribution was measured in THF at room temperature at a flow rate of 1 ml/min by use of a Waters Associates, gel permeation chromatograph, Model 200, equipped with four columns having permeabilities of 5×10^3, 5×10^4, 7×10^5, and 7×10^5 Å. As can be seen in

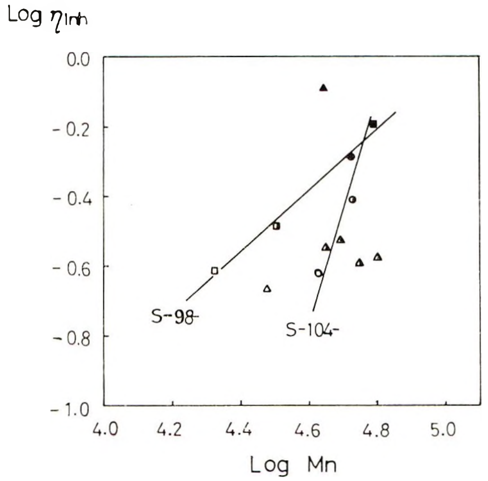


Fig. 2. Relation between log $\bar{M}_n$ and log η_{inh} of the block copolymers for various block lengths of PSt–PEG: (⊙) 2250–404; (◑) 2250–1960; (●) 2250–5650; (△) 3140–404; ◭ 3140–1960; (▲) 3140–5640; (□) 6200–404; ◧ 6200–1960; (■) 6200–5650.

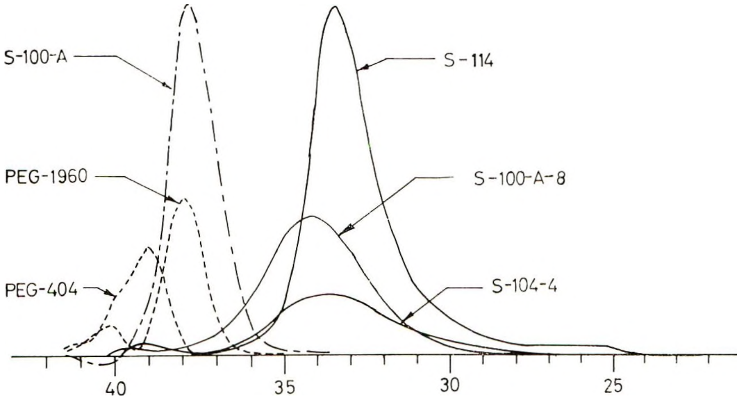


Fig. 3. Gel permeation chromatograms; room temp, 1 ml/min, 2.5–3.0 g/l THF, range 2.

Figure 3, the alternating block copolymer had a broad distribution, whereas the sandwich copolymer and starting α,ω-dihydroxyl polystyrene had narrow distributions.

Thermal Properties

Thermal behavior of the block copolymers in the range 0–150°C was measured by using a Perkin-Elmer DSC-1B differential scanning calorimeter. As is shown in Table III, a sharp heat absorption peak for the melting of poly(ethylene glycol) blocks appeared at 55–61°C (T_m) and one for the glass transition of polystyrene blocks around 90°C (T_g). Both T_m and T_g differed slightly, depending on the length of the block components.

The T_g appeared clearly in α,ω-dihydroxyl polystyrene, was somewhat indistinct in S-100-A-9, and almost impossible to measure in S-104-4. Incorporation of poly(ethylene glycol) ($\bar{M}_n$ = 1960) made the T_g unnoticeable. The T_m of the block copolymers appeared at temperatures lower than 70°C, the T_m for pure poly(ethylene glycol), and the peaks became smaller when the poly(ethylene glycol) blocks were short. The heat of fusion for the poly(ethylene glycol) blocks in the copolymer was always smaller than the value calculated from poly(ethylene glycol) content and the heat of fusion for pure poly(ethylene glycol), 40.0 cal/g. This deviation became greater as the polystyrene blocks became longer. An exothermic peak for the crystallization of poly(ethylene glycol) blocks in the block copolymer appeared only at a slow cooling rate (4°C/min), although that for pure poly(ethylene glycol) appeared at all cooling rates. The peak shifted to lower temperatures with the incorporation of polystyrene blocks, i.e., 49°C for poly(ethylene glycol) and 4°C for S-104-4 (both at the scanning rate of 4°C/min, but remained at the same temperature, 44.5°C(8°C/min) in the sandwich copolymer S-114. From these facts it is concluded that crystallization and fusion of the poly(ethylene glycol) blocks are disturbed by the existence of polystyrene blocks, while the disturbance is small in the sandwich copolymer.

TABLE III

Thermal Properties of the Block Copolymers

Expt. no.	PSt–PEG composition	T_m, °C[a]	Heat of fusion, cal/g	T_g °C[a]
S-104-2	2250–404	57	0.65	—
S-104-4	2250–5650	55	16.6	—
S-100-A-9	3140–404	60	0.09	90
S-98-3	6200–404	60	0.02	—
S-98-4	6200–1960	61	0.05	—
S-98-5	6200–5650	55	4.0	—
S-114	PEG–PSt–PEG	54	2.9[b]	—
PEG 5650	PEG 5650	70	40.0	—
S-104	PSt 2250	—	—	87

[a] Measured at a scanning speed of 16°C/min.

[b] Quenched sample at −20°C for 2 days.

Viscoelastic Properties

Viscoelastic loss E'' was measured by use of a Vibron DDV-1 viscoelastometer (Toyo Measuring Instruments Co., Tokyo) and is plotted in Figure 4. Some of the block copolymers showed a maximum in E'' at 25–35°C, while for others no maximum was in the observable range. The copolymer with long poly(ethylene glycol) blocks ($\bar{M}_n$ for PEG, 5650) was too soft for E'' to be measured at ordinary temperature ranges.

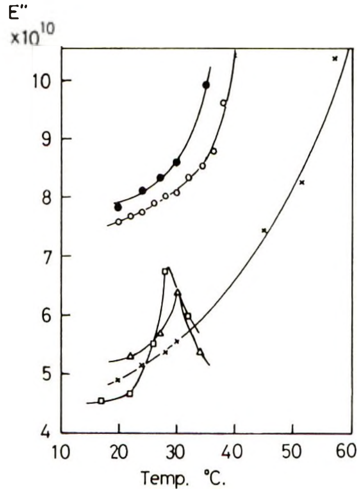


Fig. 4. Viscoelastic properties: (△) S-104-3; (⊙) S-100-A-10; (□) S-98-5; (×) PSt 860 000; (●) S-100-A-8.

Tensile Strength and Elongation

Tensile strength and elongation were measured for films of block copolymer S-100-A-7 [polystyrene block, $\overline{M}_n = 3140$, poly(ethylene glycol) block, $\overline{M}_n = 1960$] by using an Instron-type instrument (Tensilon UTM-IIIE, Toyo Measuring Instruments Co., Tokyo). The film (20×5×0.032 mm) showed a strength of 1.3 kg/mm^2 and 44% elongation at a draw rate of 4 mm/min under a load of 20 kg. at 15°C, 65% RH. These values imply that the block copolymer is soft and elastic.

Moisture Absorption

Moisture absorption at 65% RH and 20°C was measured for the samples of 0.03–0.06 mm thickness. All block copolymers showed better moisture absorption than polystyrene, and the percentage water absorption increased with increasing poly(ethylene glycol) content in the block copolymer (Fig. 5).

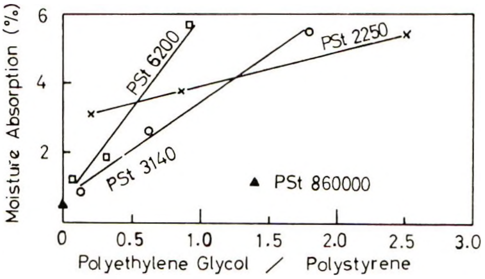


Fig. 5. Moisture absorption.

EXPERIMENTAL

Materials

All reagents and solvents were either of reagent grade or of maximum purity and treated in the following way.

Styrene was freed from stabilizer with aqueous NaOH, washed, dried and distilled under reduced pressure. After complete removal of water with calcium hydride, the styrene was distilled into a dropping funnel in a vacuum line.

Styrene oxide was distilled under reduced pressure, dried with calcium hydride, and distilled into a dropping funnel in a vacuum line.

Naphthalene was recrystallized three times from alcohol, dried thoroughly, and sublimed into the reaction system.

Sodium was freed of oxide layer and fused in a vacuum system.

Tetrahydrofuran was regenerated from Na naphthalene–THF complex previously prepared by simply adding Na and naphthalene in dried THF.

Diethylene glycol dimethyl ether (diglyme) was refluxed over sodium for 6 hr and distilled under reduced pressure. The diglyme for the reaction was regenerated from the Na naphthalene–diglyme prepared by adding sodium and naphthalene to the dried diglyme.

Dioxane was prepared in exactly the same way as diglyme.

4,4′-Diphenylmethane diisocyanate (MDI) was distilled under reduced pressure and stored at −20°C.

Triethylenediamine was distilled under reduced pressure and stored in nitrogen atmosphere.

Poly(ethylene glycols) were supplied by Nisso Yuka Co. and dried 3 hr at 100°C/10^{-3} mm Hg.

Preparation of α,ω-Dihydroxyl Polystyrene

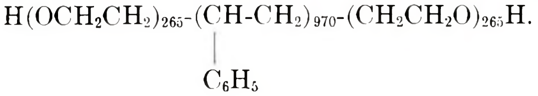
In a 1-liter flask was placed a 2-g lump of sodium which was fused in vacuo. Into this flask was distilled about 600 ml of tetrahydrofuran through a vacuum line. Naphthalene, 5.5 g, was introduced by the aid of a heating lamp. A green color developed rapidly in the mixture, and the solution was swirled for about 6 hr at room temperature. The initiator solution was then transferred to a blender equipped with dropping funnels delivering 30 g styrene and 15 g styrene oxide through a #3 glass filter under dry argon pressure. The initiator solution was cooled to −20°C in an argon atmosphere, rapidly swirled at a speed of 9000 rpm, and the styrene and styrene oxide added successively over an interval of a few minutes. The resulting polymer solution was allowed to stand for about 1 hr, acidified by addition of 12 ml of 1:1 aqueous HCl, and precipitated in methanol. The obtained polymer was purified by reprecipitation from its benzene solution. The initiator concentration was measured by introducing 25 ml to a buret, dropping it into 2 ml of methyl iodide, and titrating with 0.1*N* silver nitrate solution.

Preparation of Block Copolymer

The general procedure was to charge 1.5 g of α,ω-dihydroxyl polystyrene and 9 mg of triethylenediamine in 6 ml of benzene. To this was added 2.05 equivalents of 4,4′-diphenylmethane diisocyanate in 5 ml benzene solution. The mixture was allowed to stand for 9 hr at 20°C. An equivalent amount of poly(ethylene glycol) in benzene was then added, and the total volume was made up to 14 ml. After 48 hr at 50°C with occasional shaking, the reaction mixture was poured into methanol and was purified by repeated precipitations from benzene solution with methanol. In case of poly(ethylene glycol) of $\bar{M}_n = 5650$, the resulting block polymer solution in benzene was precipitated in petroleum ether and washed well with 50% aqueous methanol after drying the precipitate.

Preparation of Sandwich Copolymer

Poly(ethylene oxide)–polystyrene–poly(ethylene oxide) sandwich copolymer was prepared by adding ethylene oxide to polystyryl dianion initiated in Cs naphthalene–THF. The molecular weight as determined with a high-speed membrane osmometer (120 000) and elemental analysis (C, 84.82%; H, 8.13%) showed that the average structure for S-114 was



$$H(OCH_2CH_2)_{265}\text{-}(\underset{\substack{|\\ C_6H_5}}{CH}\text{-}CH_2)_{970}\text{-}(CH_2CH_2O)_{265}H.$$

Measurement of the Reaction Velocity of MDI

In each run, 0.8039 g of completely dried monofunctional ω-hydroxyl polystyrene ($\bar{M}_n = 6800$) and 5.6 mg triethylenediamine in 5 ml benzene were used. After adding 0.02029 g MDI in 2 ml benzene, the mixture was kept at 20°C with occasional shaking for time given in Figure 1. To measure the amount of unreacted isocyanate groups, 5.00 ml of 0.08*N* di-*n*-propylamine in dioxane solution and 0.020 mole/l. dibutyltin dilaurate in 1.00 ml dioxane solution were added. After shaking the mixture at 50°C for 30 min, it was titrated with 0.01*N* perchloric acid in dioxane by use of bromcresol green–methyl red mixed indicator.[7]

Thanks are given to Mrs. T. Hatakeyama of this Institute, and to Prof. Y. Iwakura and Dr. H. Katsuki of Tokyo University for valuable discussions, and also to Nisso Co. for the supply of poly(ethylene glycols).

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Polymerization of Complexed Monomers. I. Alternating Copolymers from Cyclopentene and Complexed Polar Monomers*

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Synopsis

Alternating, equimolar copolymers of cyclopentene with acrylonitrile and methyl acrylate were prepared in the presence of ethylaluminum sesquichloride. Varying conditions of monomer ratio, temperature, light, and reaction time were studied. The structures of the polymers and mechanistic implications are discussed.

INTRODUCTION

Cyclopentene copolymerizes with acrylonitrile under standard free-radical conditions revealing a penultimate effect, i.e., cyclopentene refuses to add to a growing chain when the terminal or next (penultimate) unit is cyclopentene.[1] Also, cyclopentene forms homopolymers (either with intact or opened ring) or alternating copolymers with ethylene under Ziegler-Natta conditions.[2,3]

Recent work[4,5] involving polymerization of complexed polar monomers has made possible formation of novel alternating copolymers in a variety of cases. The patent literature[6] describes the preparation of alternating copolymers from several monomers (including cyclopentene) with acrylonitrile and methyl acrylate in the presence of Lewis acids and peroxides.

This paper describes our examination of copolymerization of cyclopentene with polar monomers complexed with ethylaluminum sesquichloride (EASQ) to yield alternating copolymers under a variety of conditions. The effects of monomer ratio, reaction time, temperature, and light upon copolymerization yields have been studied. The results of these investigations are shown in Tables I and II and are discussed in the next section.

RESULTS AND DISCUSSION

Effects of Reaction Conditions

Both the cyclopentene–acrylonitrile (CP–AN) and cyclopentene–methyl acrylate (CP–MAC) systems show generally higher yields when excess CP

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

TABLE I
Copolymerizations of Cyclopentene (CP) with Acrylonitrile (AN), Methyl Acrylate (MAC), Methacrylonitrile (MAN), and Methyl Methacrylate (MMA), in the Presence of One Equivalent of Ethylaluminum Sesquichloride (EASQ) in 0.66M Toluene Solution

Run	Polar monomer	Temp., °C	Time, hr	Ratio CP/polar monomer	Yield, %	η_{inh}[a]	MW[b]	Light
1	AN	20	17	1	8	0.056	—	Ambient
2	AN	24	70	1	16	0.048	—	Ambient
3	AN	45	16	1	0	—	—	Ambient
4	AN	4	16	1	2	0.054	—	Ambient
5	AN	20	17	3	24	0.074	3300	Ambient
6	AN	21	17	3	34	0.066	3130	Sun Lamp
7	AN	18	17	3	16	0.078	3065	Darkness
8	MAC	24	21	1	33	0.031	—	Ambient
9	MAC	22	70	1	29	0.048	1710	Ambient
10	MAC	45	21	1	0	—	—	Ambient
11	MAC	3	21	1	8	0.046	—	Ambient
12	MAC	22	18	3	60	0.049	2310	Ambient
13	MAC	21	18	3	74	0.047	1850	Sun Lamp
14	MAC	21	18	3	44	0.062	2340	Darkness
15	MAN	22	21	1	0	—	—	Ambient
16	MMA	22	19	1	0	—	—	Ambient

[a] Viscosities were measured as 0.5% solutions in acetone at 30°.

[b] Molecular weights were obtained by vapor pressure osmometry in DMF for AN copolymers and in acetone or tetrahydrofuran for MAC copolymers. Determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., 37921.

is used (Table I). This is in accord with the results of Hirooka et al.[7] in the acrylonitrile–propylene system, and would lead to a larger equilibrium concentration of the CP–AN–EASQ and CP–MAC–EASQ complexes, resulting in a faster reaction rate and higher yield.[8] Increasing the reaction time from overnight to 70 hr doubled the yield of CP–AN copolymer but had little effect on the CP–MAC system. The optimum reaction temperature was near room temperature in both the CP–AN and CP–MAC cases. In both systems, no polymer was obtained at 45°C, and very low yields resulted near 0°C. This delicate balance between dissociation of the complex at high temperatures and inability to overcome activation barriers for polymer formation at low temperatures is discussed by Gaylord.[8] Neither methacrylonitrile (MAN) nor methyl methacrylate (MMA) yielded polymers with CP at room temperature. This is probably a steric effect, caused by the addition of an α-methyl group in both cases, and may involve a low ceiling temperature for copolymerization. The use of a sun lamp with Pyrex equipment increased the yields of the CP–AN and CP–MAC copolymers, and exclusion of light lowered the yields correspondingly. The absorption of light by charge-transfer complexes is known to sensitize photopolymerization in several other systems, which are discussed by Tazuke.[9] Molecular weights were close to 3000 for CP–AN copolymers and near 2000 for the CP–MAC system.

Copolymer Structures

The CP–AN and CP–MAC copolymers gave elemental analyses which would be expected for equimolar, alternating structures regardless of starting monomer ratios (Table II). The infrared and NMR spectra in each series were essentially identical from run to run. In the infrared, the CP–AN and CP–MAC copolymers showed enhanced C-H absorption over the AN and MAC homopolymers, but were otherwise similar.

TABLE II
Representative Elemental Analyses with Calculated 1:1 Compositions of AN–CP and MAC–CP Copolymers[a]

Run	C, %	H, %	N, %
Calcd AN–CP	79.29	9.15	11.56
1	78.60	9.17	11.60
2	78.38	9.23	11.31
7	79.95	9.13	11.78
Calcd MAC–CP	70.10	9.15	—
12	69.29	9.04	—
13	69.61	8.97	—
14	69.65	8.90	—

[a] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., 37921, and by Scandinavian Microanalytical Laboratories, P.O. Box 25, Herlev, Denmark 2730.

The 60 MHz NMR spectrum ($CDCl_3$ solution) of a CP–AN alternating copolymer is shown in Figure 1. The peak at 1.80 ppm represents the resonances of the AN methylene group and the CP methylene and methine protons. The broad absorption at 2.75 ppm is characteristic of the AN methine proton. The ratio of these peak areas is 10:1, corresponding to equimolar composition.

The CP–MAC shows resonances in its 60 MHz spectrum in $CDCl_3$ (Fig. 2) corresponding to methoxy (3.64 ppm), methyl acrylate methine (2.25 ppm), and methyl acrylate methylene plus cyclopentene protons (1.55), in the ratio of approximately 3:1:10, indicating an equimolar structure. The methoxy resonance is broadened in comparison to the corresponding peak

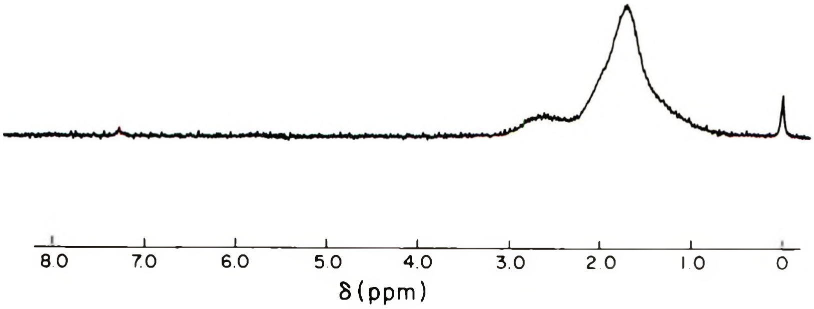

Fig. 1. NMR spectrum (60 MHz) of CP–AN copolymer in $CDCl_3$.

in the NMR spectrum of poly(methyl acrylate) from free-radical polymerization. Figure 3 shows the methoxy resonance of the alternating CP–MAC copolymer in the 100 MHz spectrum. Here four distinct peaks are observed, and possibly arise from different environments of the methoxy

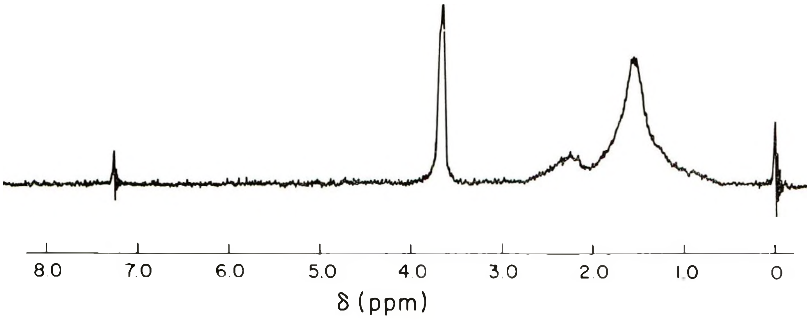

Fig. 2. NMR spectrum (60 MHz) of CP–MAC copolymer in $CDCl_3$.

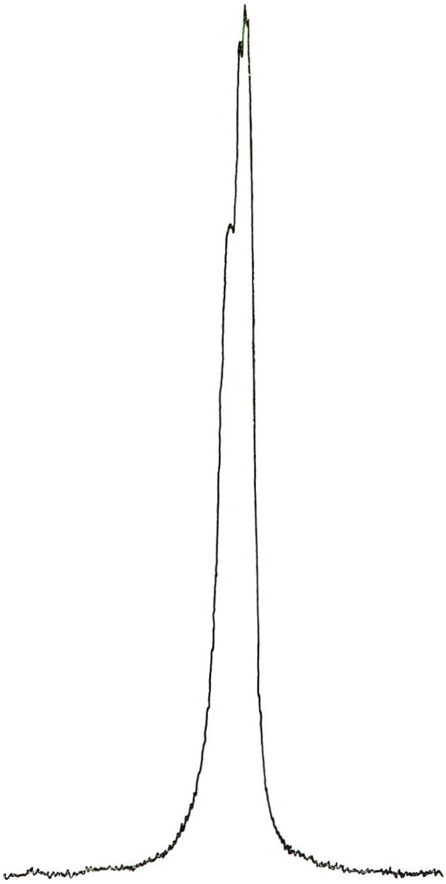

Fig. 3. Methoxy region of CP–MAC copolymer at 100 MHz.

group depending upon whether the neighboring cyclopentene units are fixed in the polymer chain in a *cis* or *trans* configuration.

EXPERIMENTAL

Materials

Cyclopentene (Aldrich Chemical Company) was shaken with saturated aqueous ferrous sulfate solution to remove peroxides, dried over molecular sieves, and distilled, bp 45–46°C. The polar monomers were dried over molecular sieves, distilled, and stored with 0.1% of 4-*tert*-butylcatechol which was removed immediately before use by passing the material through a silica gel column. Ethylaluminum sesquichloride (Texas Alkyls, Inc.) was diluted to a 25% toluene solution in an efficient dry box.

Copolymerizations

Acrylonitrile–Cyclopentene. A solution of 1.06 g (0.02 mole) of acrylonitrile in 10 ml of dry toluene was cooled to −60°C in a three-necked flask fitted with a serum cap, thermometer, and nitrogen inlet tube. A 10-ml sample of 25% ethylaluminum sesquichloride solution in toluene (0.02 mole of Al) was added with a gas tight syringe. The temperature rose quickly to −30°C. When the yellow solution had cooled again to −60°C, a solution of 1.36 g (0.02 mole) of cyclopentene in 10 ml of toluene was added. The cooling bath was removed and the mixture was then stirred at the desired temperature. As polymer formed, it coated the sides and bottom of the flask. After the reaction time had elapsed, the toluene solution was added to dry methanol (ethylaluminum sesquichloride reacts violently with water). The residue was hydrolyzed carefully with isopropyl alcohol and transferred to the methanol precipitation system. The polymer was collected, dissolved in acetone or nitromethane, reprecipitated in methanol, and dried in a vacuum oven at 100°C. The polymers soften at temperatures in the 100–125°C range. In runs where a sun lamp was used, the lamp was positioned about 6 in. from the Pyrex flask, which was cooled with a water bath. When total darkness was desired, the flask was covered with aluminum foil.

Methyl Acrylate–Cyclopentene. The same general procedure was used, 1.72 g (0.02 mole) of methyl acrylate being employed. In the precipitation step, water was added to the methanol after complete hydrolysis of the ethylaluminum sesquichloride. A small amount of concentrated hydrochloric acid could be added to aid coagulation of the product. Drying of the copolymers of methyl acrylate could be accomplished at about 60°C, since the softening points are in the range of 55–65°C.

CONCLUSIONS

Cyclopentene forms alternating copolymers with acrylonitrile and methyl acrylate when these polar monomers are complexed by ethylaluminum sesquichloride. The mechanism of polymerization is not free-radical in the ordinary sense, because under standard free-radical conditions alternating polymers are not formed, and the limiting mole fraction of cyclopentene is 0.33.[1] The nmr spectra of the CP–MAC copolymers prepared here show that the cyclopentene units are incorporated as both *cis* and *trans* 1,2-disubstituted cyclopentane rings. Thus the mechanism is not the same as that observed with Ziegler-Natta catalysis, where alternating ethylene–cyclopentene copolymers have *cis* incorporation of cyclopentene.[3]

Acceleration of the copolymerizations of cyclopentene with complexed polar monomers by light is a key factor in mechanistic interpretation and seems to support a hydrogen-transfer type of scheme such as that suggested by Gaylord.[8] Several cases of light-catalyzed hydrogen-transfer reactions are cited by Tazuke,[9] including that between the two moieties of the tetrahydrofuran–maleic anhydride complex upon photolysis.[10,11]

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Characterization and Polymerization of Thioacetone*

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Synopsis

The thioketo and thioenol tautomers of thioacetone have been separated by gas chromatography and characterized by infrared and NMR spectra at low temperatures. The pure thioketo tautomer polymerizes rapidly at room temperature, but the thioenol tautomer does not. At room temperature, the thioenol gradually disappears, probably by tautomerization to the reactive thioketo form, which then polymerizes. Attempts to copolymerize thioacetone with vinyl and diene monomers were not successful.

INTRODUCTION

Although thioacetone has been the subject of a number of investigations,[1-3] relatively little has been disclosed on the isolation and characterization of the tautomeric forms of thioacetone and their relationship either to the method of synthesis or to polymerization. Several years ago in this laboratory, we investigated the synthesis of high molecular weight polythioketals. Thioacetone received special attention, and several methods of synthesis, isolation, and polymerization were developed. Other investigators who were working in this area concurrently and independently have since reported on the syntheses and polymerization of thioacetone, agreeing substantially with our findings.[1-3]

RESULTS AND DISCUSSION

In the present investigation, thioacetone was always obtained as a mixture of the thioketone, CH_3CSCH_3, and the thioenol, $CH_2{=}CSHCH_3$, although the ratio of tautomers varied widely depending on the synthesis route and conditions. Because of the great propensity of the keto tautomer to polymerize spontaneously even at low temperatures, the equilibrium concentrations of the two tautomers or the time to attain equilibrium was not estimated. It was desired, however, to examine the pure keto tautomer because it was likely the other tautomer, an enethiol, would be an effective transfer agent via its allylic and thiol hydrogens and its presence would preclude formation of high polymer from thioacetone.

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

Separation of Tautomers

There was evidence that thioacetone could be partially separated into two fractions of somewhat different behavior by vacuum distillation at low temperatures. Each fraction was presumed to be enriched in one of the tautomers, but a nearly quantitative separation appeared unlikely. This did suggest, however, that equilibrium was not rapidly attained. Preliminary experiments with gas chromatography indicated that thioacetone could be separated into two principal components. After numerous trials, a column was developed comprising DC 200 silicone oil on Gas Chrom Z, which was found to be extraordinarily inactive in promoting polymerization and permitted use of 6-ft columns of useful capacity and life. In this way, the thioketo and thioenol tautomers were obtained in nearly pure form by gas chromatographic separation at 0°C. It was advantageous to carry out this separation at as low a temperature as possible because thioacetone polymerizes so easily. Very low temperatures were not feasible, however, because of the moderate volatility of thioacetone (bp ~70°C). A reasonable compromise was 0°C, at which temperature polymerization was slow enough in the attenuated state for most of the material to pass through the column unchanged. Two chromatograms are shown in Figure 1 illustrating the wide variation in tautomer ratio that was obtained under different synthesis conditions.

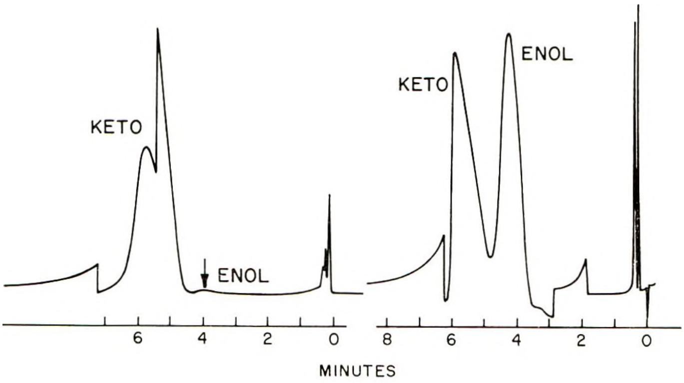
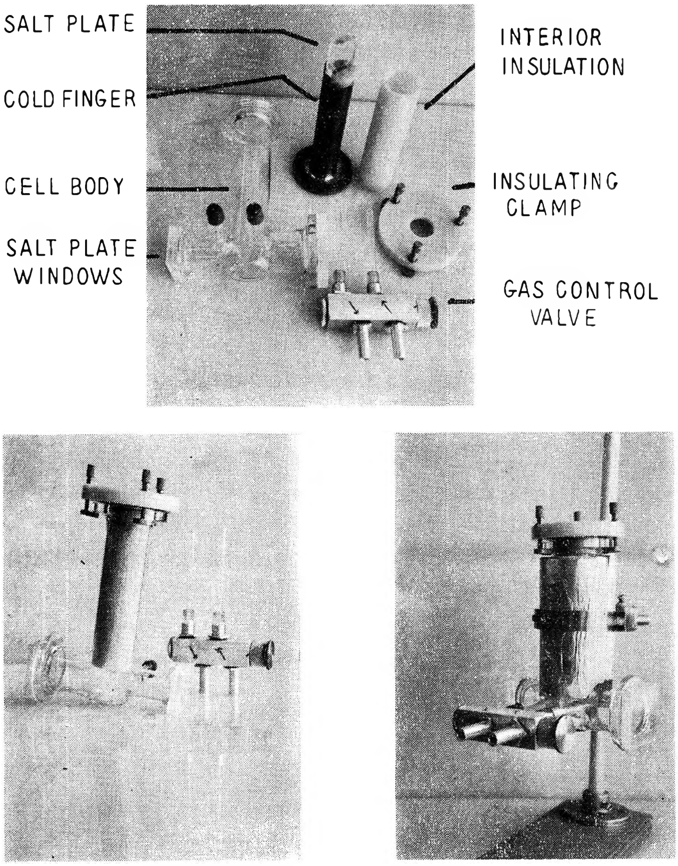


Fig. 1. Gas chromatograms for thioacetone.

Infrared Characterization

Separation of the tautomers offered the opportunity to obtain the infrared spectra of propanethione and 2-propenethiol, but the small sample size and the great lability of these compounds required the development of a special technique. A cell was designed and constructed that would serve directly as a sample-collecting device and as a low-temperature infrared transmission cell, thus obviating any material transfers. The cell is illustrated in Figure 2. Samples of the tautomers were collected directly at the outlet of the gas chromatographic columns on the cooled surface of a sodium chloride



PARTLY ASSEMBLED CELL

ASSEMBLED CELL WITH EXTERIOR INSULATION

Fig. 2. Infrared cell for direct collection and examination of GC samples.

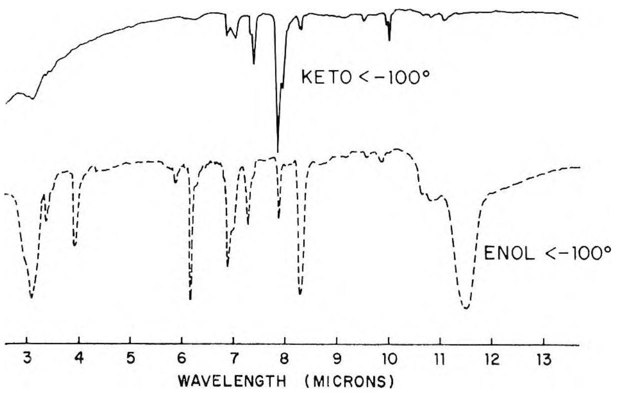


Fig. 3. Infrared spectra of thioacetone tautomers.

plate at −100°C within the cell, and the spectra were determined immediately at that temperature. In this way, it was possible to retard tautomerization or polymerization, and good spectra of the tautomers were obtained (Fig. 3). It will be noted that the principal characteristic absorptions due to —SH, C=C, and =CH_2 groups at 3.93, 6.15, and 11.55 μ were absent in the spectrum of the keto tautomer. Tentatively, the absorption at 7.85 μ is attributed to the C=S group in thioacetone, even though this is at somewhat shorter wavelength than that assigned to C=S absorption in more complex thioketones.[4,5] Neither the stable trimer nor the polymer absorbs at this wavelength.

NMR Characterization

The NMR spectra of propanethione and 2-propenethiol have proved useful in the study of thioacetone. Figure 4*A* shows the spectrum, obtained with a Varian HR 60 instrument, of a freshly distilled, enol-rich sample of thioacetone just above the melting point (∼−55°C, depending on tautomer ratio). Integration of the spectrum confirmed the expected 2:1:3 ratio for vinyl (−4.93 ppm), mercapto (−3.30 ppm), and methyl protons (−1.95

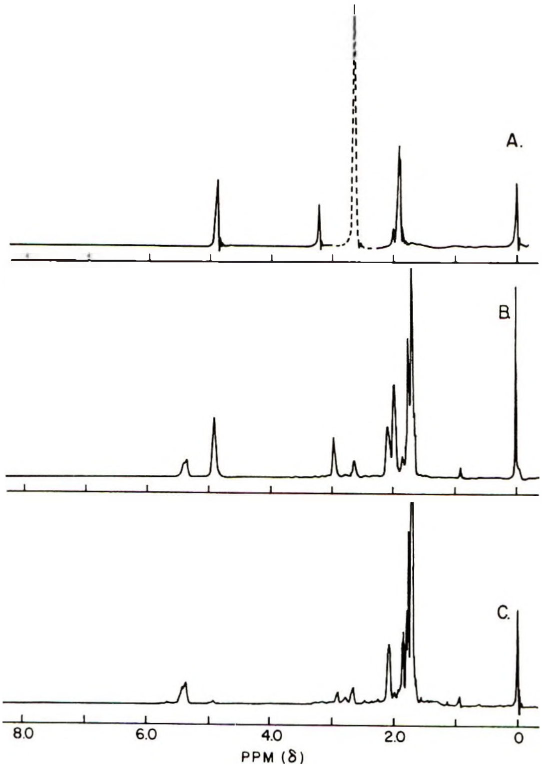


Fig. 4. NMR spectra of enol-rich thioacetone (*A*) monomer at −52°C; (*B*) after 1 min at room temperature; (*C*) after 2 days at room temperature.

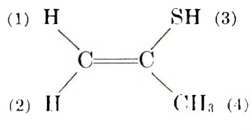
ppm) of the enol. The methyl protons of the keto tautomer absorbed at -2.67 ppm (referred to tetramethylsilane as internal standard) and comprised a little less than 50% of the total area of this spectrum.

The great sensitivity of these compounds is illustrated by the spectrum of Figure 4*B*, which was obtained immediately after the above sample was warmed to room temperature. The keto tautomer virtually disappeared, and new resonances appeared in the vinyl and methyl regions of the spectrum at about -5.4 ppm and -2.09 ppm, respectively. Much of the enol in this relatively enol-rich sample, however, was still present. After two days at room temperature, the enol tautomer also had largely disappeared (Fig. 4*C*). When the enol tautomer was present in large proportion, as in this sample, transfer and initiation of new polymer chains would occur frequently enough to permit accumulation of low molecular weight polymer containing vinyl, methyl, and mercaptan endgroups. These are most likely the sources of new vinylic and methyl resonances as well as the residual (SH?) resonance at -2.8 ppm observed in these spectra after polymerization had occurred. The strong resonances that appeared at -1.75 ppm and -1.94 ppm were due to the methyl group protons of propanethione trimer and polymer, respectively.

To assign unequivocally the specific absorptions to the protons of thioacetone, the tautomers were separated by gas chromatography and collected at low temperature directly in NMR sample tubes. The spectrum thus obtained of pure enol, 2-propenethiol, in deuterochloroform solution at -52°C showed the three proton resonances previously assigned to the enol to be present in the required ratio, although the SH resonance was shifted in the solution to about -2.8 ppm. The single resonance assigned to the keto protons was absent. The pure enol tautomer appeared to be fairly stable and failed to change rapidly under these conditions at room temperature, as indicated by the small changes in its spectrum after 1 hr. Gross changes were apparent, however, after two days.

Further confirmation was obtained from the spectrum of pure keto which, as expected, was a single peak. This tautomer was exceedingly labile and polymerized appreciably even at -78°C in a few hours or in a few seconds if the temperature was allowed to approach that of the room.

Casual inspection of the spectrum of the enol tautomer suggests that the absorption peaks are all single, unsplit peaks. However, the structure of the enol,



makes it likely that some coupling exists among the protons of this molecule. If SH and CH_3 were very similar in an electromagnetic sense, then the chemical shift of H (1) and H (2) might be similar and, indeed, this appears to be true here. Attempts were made to resolve the spectrum of thioacetone at −60°C, with moderate success. The vinylic protons, (1) and (2), were separated into a very narrow overlapping pair of multiplets, one of which appeared to be a quadruplet, the other more complex. The band width was less than 8 Hz. The mercapto proton was a closely spaced doublet with a separation of 1.5 Hz at −3.28 ppm, and the methyl protons were split into four closely spaced peaks at about −1.98 ppm with a total band width of ∼5 Hz. All the couplings were very weak, with none of the constants exceeding 1.5 Hz.

Control of Tautomer Ratio

Following this development of an assay procedure based on gas chromatography and NMR, it became possible to determine the tautomer ratio in thioacetone and, theoretically, the rate of change of either tautomer to an equilibrium mixture.

The thioketo tautomer could be kept without appreciable change for a short time at temperatures below −50°C. At higher temperatures, it polymerized quite rapidly. 2-Propenethiol polymerized much more slowly, probably because it must first tautomerize to the keto form. It was quite stable at −50°C or below.

As ordinarily prepared by low-pressure pyrolysis of hexamethyltrithiane, thioacetone was a mixture containing 85–95% of the thioketo tautomer. Below 500°C, much of the trimer was recovered unchanged. Above 600°C, thioacetone decomposed extensively. Within the range of 500–600°C, the thioketo : thioenol ratio increased with increase in pyrolysis temperature.

Pyrolysis in a tube packed with fresh quartz rings gave a product relatively rich in thioenol tautomer. Use of the tube for a number of successive runs resulted in conditioning such that each successive product was a little richer in the thioketo tautomer up to a maximum of a little over 95%. Relatively large amounts of the thioenol, 2-propenethiol, were obtained by pyrolysis of 2,2-propanedithiol over sodium fluoride pellets at about 200°C. Formation of thioketones by pyrolysis of *gem*-dithiols was studied earlier by Bleisch and Mayer,[6] but they made no mention of thioketo/thioenol tautomerism. In our hands pyrolysis at 150°C gave a deep-red product containing more than 90% of the thioketo form. However, at 250°C more than 50% of the product was the thioenol tautomer. We suggest that the relatively weak C—S and S—H bonds of the *gem*-dithiol group break first at relatively low temperatures to result in high conversions to propanethione. At higher temperatures the stronger but more numerous C—H bonds become involved, which leads to substantial quantities of 2-propenethiol.

Polymerization

It was assumed that 2-propenethiol would be an efficient chain-transfer agent for either anionic or free-radical polymerizations. Polymerization by either mechanism of the pure thioketo tautomer in the absence of the enol should lead to high molecular weight polymer. It was found that initiation of >95% purity propanethione with the triethylborane–diethyl (peroxyethyl)borane redox couple[7] at −50°C gave a product melting at 120–124°C, which is the melting temperature that Burnop and Latham gave for high molecular weight polymer. However, this polymer did not have the toughness and film- and fiber-forming characteristics that would be expected of truly high molecular weight material. Ultraviolet irradiation of the thioketo tautomer gave a somewhat lower melting product that was also weak and brittle. Both polymers appeared to be stable for at least several weeks, which was not observed for polymer prepared from thioacetone containing substantial amounts of thioenol.

Initiation of thioacetone composed of more than 95% of the thioketo tautomer by sodium hydride at −60°C led to rapid reaction as indicated by the rapid disappearance of orange-red color and formation of white, solid polymer. This white polythioacetone melted at 119–120°C and had a molecular weight of only 1500. Apparently the concentration of thioenol was not sufficiently low to permit high molecular weight polymer in anionic systems, though this product did melt higher than that prepared under similar conditions from high thioenol content monomer.

Potassium *tert*-butoxide was also used to initiate polymerization of >95% thioketo thioacetone. The result was a rapid loss of orange color followed by slow formation and precipitation of solid polymer. Unless removed and purified, the solid polymer slowly reverted to form a viscous liquid polymer. Reversibility of base-catalyzed polymerization of thioacetone was noted on a number of occasions. The highest melting point for polymers formed by potassium *tert*-butoxide initiation was 71–73°C. It is likely that the base promotes formation and stabilization of the enol form leading to low molecular weight polymer containing many thiol and vinylic groups.

Though thioacetone polymerized readily in free-radical systems, it did not copolymerize with diene or vinyl monomers. Attempts to copolymerize it with 2,3-dimethylbutadiene, methyl methacrylate, acrylonitrile, vinyl acetate, or styrene led only to thioacetone homopolymer. In this respect, thioacetone differs from thiocarbonyl fluoride, which copolymerizes readily with a large number of vinyl monomers.[7]

EXPERIMENTAL

Hexamethyl-s-trithiane and 2,2-Propanedithiol[8,9]

The cyclic trimer was prepared from acetone and hydrogen sulfide as described by Böhme et al.[10] The only modification was reaction at a lower temperature than the 10°C used by Böhme. In addition to the trimer, 2,2-propanedithiol was also obtained as a major product. At −25°C, the *gem*-dithiol comprised about 30–40% of the product mixture. The crude product was decanted from the $ZnCl_2$ catalyst, dried, and isolated by fractional distillation under reduced pressure. The dithiol was a colorless liquid, bp 40°C/43 mm, n_D^{25} 1.5068, with an intensely powerful, disagreeable odor. The trithiane distilled at 101°C/5 mm, n_D^{25} 1.5393.

Thioacetone

From Hexamethyl-*s*-trithiane. Thioacetone was prepared by pyrolyzing hexamethyl-*s*-trithiane on hot quartz rings under reduced pressure with subsequent quenching of the product as quickly as possible to −78°C.[11] The pyrolysis temperature was fairly critical. Within the pressure range of 5–20 mm, a temperature below about 500°C permitted much of the trimer to survive. Above 650°C, decomposition to simpler compounds became excessive, and allene and hydrogen sulfide became important products. Under favorable conditions, 80% yield of red-orange, clear liquid monomer could be obtained, which could be redistilled quantitatively in a vacuum system.

In a typical pyrolysis, 7 g of hexamethyl-*s*-trithiane was added dropwise over 1 hr to a vertical, quartz pyrolysis tube (1 × 12 in.) packed with 8-mm sections of quartz tubing and heated to 560°C. The pressure was maintained at 11 mm. The product was collected in a U-trap cooled to −78°C and attached directly to the pyrolysis tube. When the pyrolysis was completed, the red-orange liquid product was distilled at −20°C and under <1 mm pressure to another trap. All distilled except for approximately 1 g of trimer, which had survived the pyrolysis. The distilled monomer (4.8 ml) crystallized to an orange solid at −78°C but melted readily on slight warming. It was easily redistilled in a vacuum system.

From 2,2-Propanedithiol. The vapor of 2,2-propanedithiol was passed through a 1-in. diameter quartz tube packed over a length of 9 in. with sodium fluoride pellets heated to 150°C. The pressure was reduced to 11 mm and the product was collected in a Dry Ice-cooled trap and a liquid nitrogen-cooled trap connected in series. From 4.2 ml of the *gem*-dithiol was obtained 1.1 ml (theory, 1.3 ml) of hydrogen sulfide in the liquid nitrogen-cooled trap and a deep-red liquid product in the Dry Ice-cooled trap. The product obtained under these conditions had an unusually strong tendency to polymerize, and as a result only a small amount could be distilled before the remainder had polymerized. After trituration with methanol, the polymer thus isolated was a white solid melting at 112–115°C.

When the pyrolysis temperature was raised to 200°C, under otherwise similar conditions, the product was an orange liquid, in contrast to the deep-red product of pyrolysis at 150°C. However, nearly the stoichiometric amount of hydrogen sulfide was obtained during the pyrolysis as before. Furthermore, the orange product showed no great tendency to polymerize spontaneously at low temperatures. Free-radical initiation at −78°C yielded a solid polymer in greater than 60% yield melting at 90–92°C.

Polymerization of Thioacetone

Purified thioacetone can be polymerized to a solid polymer reproducibly simply by allowing the monomer to stand at −10 to −20°C for 20–25 hr.

At lower temperatures, the spontaneous polymerization was exceedingly slow, whereas at higher temperatures much liquid polymer was likely to be obtained. Many polymerization initiators have been scouted; of these, free-radical initiators have been most effective in giving solid polymers. Polymers obtained by radical-induced polymerization were very similar to those obtained by spontaneous polymerization but could be obtained in a very much shorter time. For example, it would take many days to get a good yield of polythioacetone by spontaneous polymerization at −50°C. With radical initiation, this time was reduced to a few minutes.

Selection of free-radical initiators was restricted by the necessity of polymerization at low temperatures. Suitable initiators included photoinitiators and reduction-activated systems.

As Table I indicates, light alone was effective in accelerating the rate of polymerization. Addition of photoinitiators to the system results in a marked increase in polymerization rate. The apparent greater efficiency of ethyl azodiisobutyrate may result from the fact that this compound is a liquid and can thus dissolve in and mix more readily with the cold monomer.

TABLE I
Photoinitiation at −50°C (>3000 Å)

Photoinitiator	Time for solid polymer, hr
None	>16
α,α'-Azobisisobutyronitrile	6
Benzoin methyl ether	2
Ethyl azodiisobutyrate	<0.5

Free-radical initiation with the triethylborane (TEB)–oxygen redox system gave rapid polymerization (Table II). Triethylborane alone, without oxygen, was ineffective. Greatest activity and control were obtained when diethyl(peroxyethyl)borane was substituted for oxygen as the oxidizing component.[7]

TABLE II
Redox Initiation

Initiator	Time for solid polymer, min	Temp, °C
TEB	None	−50
TEB/O_2	10	−80
TEB/O_2	30	−50
$TEBO_2$/TEB	4	−80

Other types of initiators were scouted. Acid catalysis appeared to favor trimerization, which proceeded rapidly even at −80°C, although some solid polymer was obtained by the action of boron trifluoride on solid thioacetone at −120°C.

Base catalysts resembled free-radical initiators, although dimethylformamide induced polymerization at a very low rate. Stronger bases, for example, tetraethylammonium cyanide, butyllithium, sodium hydride, or potassium *tert*-butoxide, caused rapid polymerization even at −50°C to solid polymers. The polymers obtained were less stable than those from free radicals and changed almost entirely to liquid polymers in 24–48 hr if the catalysts were not neutralized promptly with acetic acid.

The authors are particularly grateful to Mrs. Adah B. Richmond for her invaluable assistance in gas chromatographic separation of the thioenol and keto tautomers of thioacetone. In addition, we wish to acknowledge assistance in obtaining infrared spectra that was provided by Miss Naomi E. Schlichter.

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Cyclopolycondensation. XIII. New Synthetic Route to Fully Aromatic Poly(heterocyclic imides) with Alternating Repeating Units*

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Synopsis

Fully aromatic poly(heterocyclic imides) of high molecular weight were prepared by the cyclopolycondensation reactions of aromatic diamines with new monomer adducts prepared by condensing orthodisubstituted aromatic diamines with chloroformyl phthalic anhydrides. The low-temperature solution polymerization techniques yielded tractable poly(amic acid), which was converted to poly(heterocyclic imides) by heat treatment to effect cyclodehydration at 250–400°C under reduced pressure. In this way, the polyaromatic imideheterocycles such as poly(benzoxazinone imides), poly(benzoxazole imides), poly(benzimidazole imides) and poly(benzothiazole imides) were prepared, which have excellent processability and thermal stability both in nitrogen and in air. The poly(amic acids) are soluble in such organic polar solvents as *N,N*-dimethylacetamide, *N*-methylpyrrolidone, and dimethyl sulfoxide, and the films can be cast from the polymer solution of poly(amic acids) ($\eta_{\text{inh}} = 0.8–1.8$). The film is made tough by being heated in nitrogen or under reduced pressure to effect cyclodehydration at 300–400°C. The polymerization was carried out by first isolating the monomer adducts, followed by polymerization with aromatic diamines. On subsequently being heated, the open-chain precursor, poly(amic acid), undergoes cyclodehydration along the polymer chain, giving the thermally stable ordered copolymers of the corresponding heterocyclic imide structure.

INTRODUCTION

Earlier publications[1–3] from this laboratory reported that polymers containing benzoxazinone, quinazolone, and quinazolinedione nuclei could be prepared by the low-temperature solution polymerizations and polyphosphoric acid solution polymerizations of suitable aromatic diaminodicarboxylic acids and aromatic dicarbonyl compounds. In this paper we wish to report the successful preparation of new types of ordered hetero-

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

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cyclic copolymers containing both imides and other aromatic heterocycles which are of high molecular weight, thermally stable, and have good film- and fiber-forming properties. This work is a continuation of studies on cyclopolycondensation reactions to prepare thermally stable linear polymers using new monomer adducts, which permits a great degree of flexibility in tailoring polymers to meet specific needs.

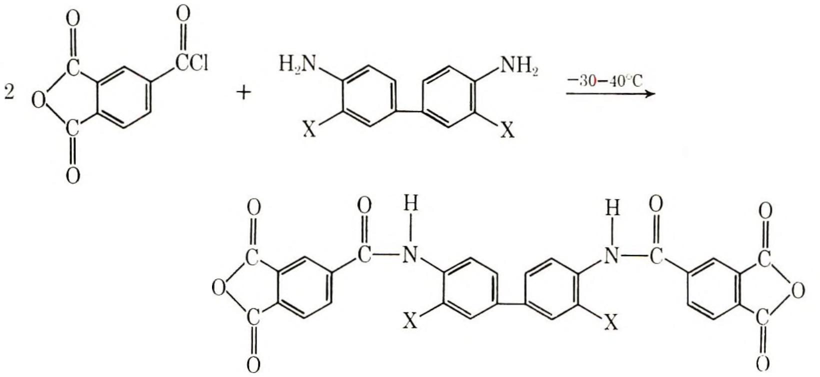
Several routes to aromatic ordered copolymers which contain two different heterocyclic rings in adjoining positions have appeared in the literature.[4,5] The regular alternation of *m*-phenylene and *p*-phenylene rings between the heterocyclic units of polyheterocycles has also been reported.[6,7] The regular alternation of ordered copolymers containing heterocyclic ring systems was accomplished by Preston et al.,[8–11] who prepared a variety of ordered heterocyclic copolymers by the polymerization of heterocyclic diamines with pyromellitic anhydride or heterocyclic dicarboxylic acids with tetramines.

In the present study, new copolymerization systems are employed by first preparing new monomer adducts from trimellitic anhydride and *o*-disubstituted aromatic diamines into which units are incorporated in a predetermined way, where one type of heterocycles and selected aromatic hydrocarbon units are involved. The adducts are then polymerized with diamine to form poly(amic acid) by low-temperature solution polymerizations under such conditions that no rearrangement of bonds occurs. The cyclodehydrations of prepolymer afford ordered polyaromatic heterocycles. Regular alternation of different aromatic heterocycles such as benzoxazinones, benzoxazoles, benzothiazoles, benzimidazoles, benzoxadiazoles, and imides in ordered sequence results in the formation of aromatic polyimide-heterocycles having the desired balance of properties such as superior mechanical properties, thermal stability, processability, and increased crystallinity, modulus, and glass transition temperatures. The use of two or more different heterocycles permits a much wider range of possibilities than the use of only one. This approach of using an open-chain adduct makes possible the preparation of thermostable polymers of high molecular weight without precipitating out of polymers which are sufficiently tractable to be useful. At the same time, the resulting polymers have high glass transition temperatures, high melting point, and increased crystallinity. In this study, benzoxazinone, benzothiazoles, benzimidazole and benzoxazole units are introduced into polyimides as to obtain ordered copolymers. Techniques for preparing poly(benzothiazole imide) by condensation of diamines containing preformed benzothiazole units with pyromellitic anhydride have recently been reported, but no means have been found to date for the preparation of high molecular weight, open-chain prepolymer of ordered copolymers as soluble precursors, which can then be transformed into a heterocyclic polymer by thermal cyclodehydration process.

In the present paper, the preparation of a variety of new adducts by reacting one mole of *o*-disubstituted aromatic diamines with two moles of 4-chloroformyl phthalic anhydride is reported, and the polymerizations of monomer adducts with aromatic diamines are described.

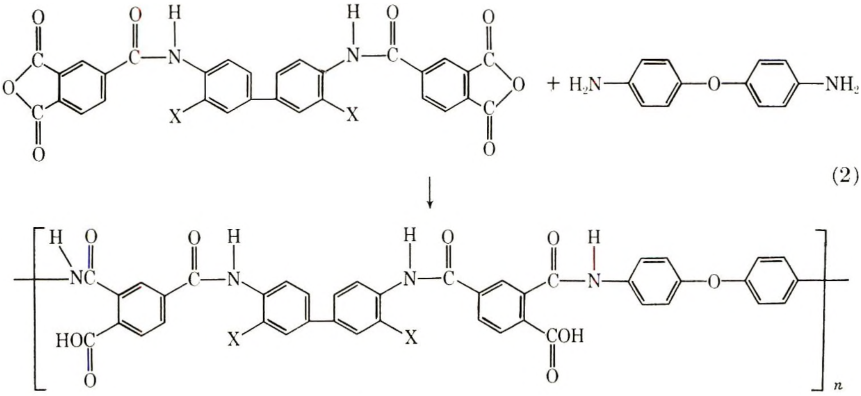
RESULTS AND DISCUSSION

Four new poly(heterocyclic imide) monomer adducts, 4,4′-[(3,3′-dihydroxy - 4,4′ - biphenylene)bis(iminocarbonyl)]diphthalic anhydride(I), 4,4′-[(3,3′-dicarboxy-4,4′-biphenylene)bis(iminocarbonyl)] diphthalic anhydride(II), 4,4′[(3,3′-diamino-4,4′-biphenylene)bis(iminocarbonyl)]diphthalic anhydride(III), and 4,4′[(3,3′-dimercapto-4,4′-biphenylene)bis(imino carbonyl)] diphthalic anhydride(IV) were synthesized for this study. The preparative route of new adducts is illustrated in eq. (1), where Ar denotes the arylene residue and X may be a carboxyl group, hydroxyl group, amino group, or mercapto group.



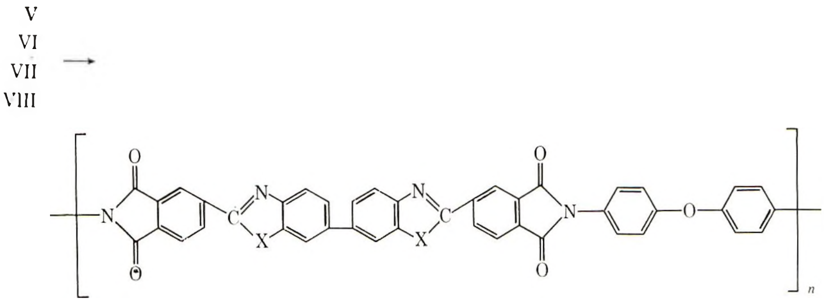
(1)

The new monomer adducts(I, II, III, and IV) were polymerized with diamines such as 4,4′-diaminobiphenyl ether, yielding the open-chain poly(amic acids)V, VI, VII, and VIII as shown in eq. (2). Poly(aromatic heterocyclic imides)IX, X, XI, and XII were obtained from V, VI, VII, and VIII, respectively, by the thermal cyclodehydration of poly(amic acids) along the polymer chain as described in eq. (3).



(2)

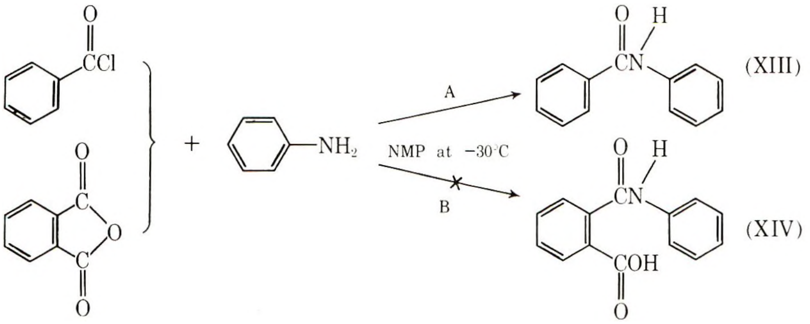
X = —OH (V)
—COOH (VI)
—NH₂ (VII)
—SH (VIII)



(3)

Syntheses of Model Compounds

It was observed that the selective reactivity of reaction between primary amine and acid chloride, or reaction between primary amine and acid anhydride was clearly different depending upon the specific reaction conditions. It strongly suggests the possibility of selecting either reaction path A or B in eq. (4) by optimizing conditions such as appropriate temperatures and monomer concentrations in such organic polar solvents as *N*-methylpyrrolidone, *N*,*N*-dimethylacetamide or *N*,*N*-dimethylformamide.



(4)

In the model reaction, aniline (1 mole) dissolved in *N*-methylpyrrolidone was added dropwise at −30°C to a solution of an equimolar mixture of benzoyl chloride and phthalic anhydride in *N*-methylpyrrolidone, and the solution was stirred at −30°C for 2 hr. As a result, *N*-benzoylaniline (XIII) was obtained quantitatively at −30°C, the formation of the other possible product(XIV) could be avoided by utilizing a low reaction temperature (−30°C). Mixed products containing XIII and XIV were obtained when the reaction was carried out above 20°C.

Under the same reaction conditions, several model compounds were synthesized by the reaction of 4-chloroformyl phthalic anhydride with *o*-substituted amines as summarized in Table I. The infrared spectra and elemental analyses support the fact that the reactivity difference of *o*-substituted amines with acid chloride and acid anhydride at −30°C in organic polar solvents is significant. It was confirmed that the dehydrochlorination products of amine and acid chloride were the sole products in these reactions. The experimental results are shown in Table II. The

TABLE I
Reaction Products of *o*-Substituted Aniline with 4-Chloroformyl Phthalic Anhydride at −30°C

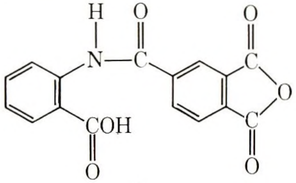
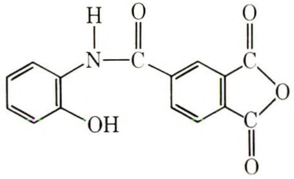
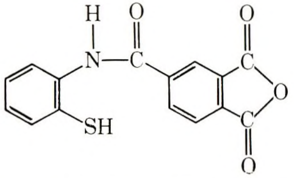
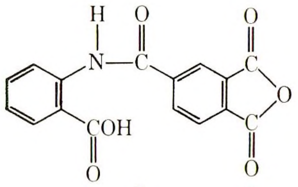
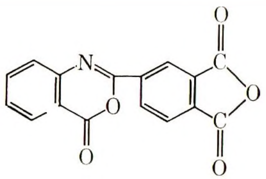
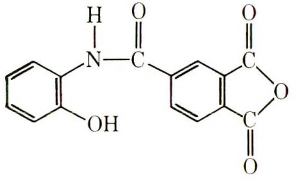
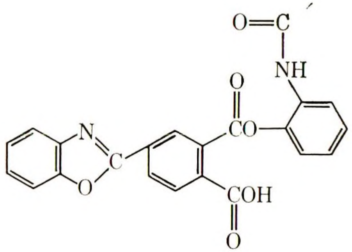
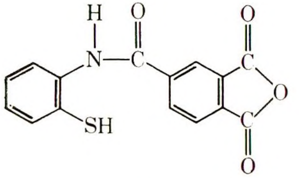
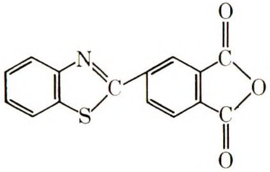
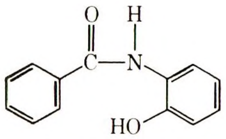
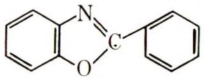
o-Substituted amine	Product	Melting point, °C	Infrared absorption band, cm^{-1}	N, % Calcd	N, % Found	S, % Calcd	S, % Found
Anthranic acid		256–257	1670 1700	4.50	4.56	—	—
o-Aminophenol		255–256	1650 3200	4.95	5.10	—	—
o-Mercaptoaniline		191–192	1650	4.42	4.24	10.01	10.02

TABLE II
Cyclodehydration Reactions of Model Compounds

Uncyclized model compounds	Cyclodehydration conditions	Cyclized products	Melting point, °C	Infrared absorption band, cm^{-1}	N, %		S, %	
					Calcd	Found	Calcd	Found
	$(Ac)_2O$/ pyridine 100°C, 1 hr		217–218	1760 1040	4.56	4.56	—	—
	$(Ac)_2O$/ pyridine or 200–250°C, vac.		>300	1730	4.94	—	—	—
	$(Ac)_2O$/ pyridine 100°C, 3 hr		—	1620	4.98	4.24	11.38	10.36
	200°C, 30 min		98–99	1620 1015	7.17	7.01	—	—

cyclodehydration of compound IV was unsuccessful, owing to the competitive nucleophilic reactions of amine and hydroxyl anions towards carbonyl groups of acid anhydride.

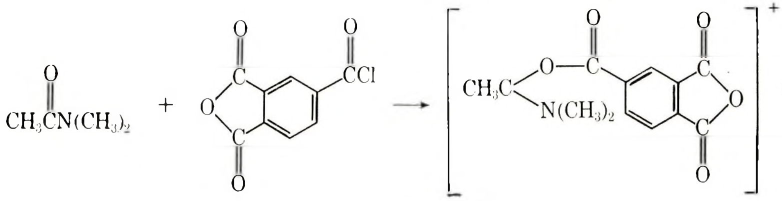
Preparation of Monomer Adducts

The four new monomer adducts were prepared, and their infrared characteristic absorption bands, melting points, and nitrogen analyses are given in Table III.

Optimum Polymerization Conditions for Low-Temperature Solution Polymerization of Poly(heterocyclic imides)

The new adducts thus obtained were polymerized with aromatic diamines, and typical data are summarized in Table IV. The highest inherent viscosity of 1.7–1.9 was obtained when poly(benzoxazole imide) was polymerized in organic polar solvents at 25°C.

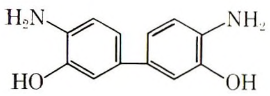
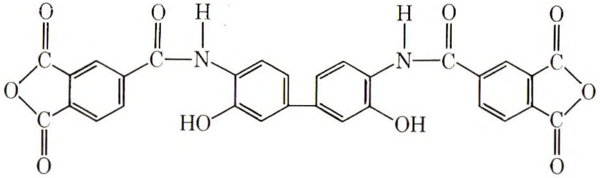
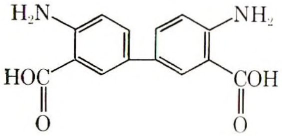
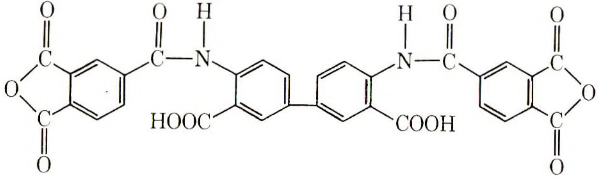
Poly(benzoxazole imide)(IX). The optimum polymerization conditions were determined for the preparation of adduct I and poly(amic acid)(V) by measuring the variation in the extent of polymerization with reaction variables. The experimental results are given in Table IV. The adduct prepared by the reaction of 3,3′-dihydroxybenzidine with 4-chloroformyl phthalic anhydride was found to have excellent solubility in organic polar solvents such as *N*,*N*-dimethylacetamide and *N*-methyl-2-pyrrolidone, and a homogeneous polymer solution of polyamic acid of high molecular weight was obtained by low-temperature solution methods. The effect of reactant mole ratio of 3,3′-dihydroxybenzidine and 4-chloroformyl phthalic anhydride on the extent of polymerization is summarized in Table V. The data in Table V indicate that the reactant equivalence is critical, and a 0.15–0.2 molar excess of 4-chloroformyl phthalic anhydride over 3,3′-dihydroxybenzidine is beneficial. It is presumed that the excess may counteract losses from hydrolysis and other side reactions such as inactivation of 4-chloroformyl phthalic anhydride by the formation of a charge-transfer complex with organic polar amide solvents such as *N*,*N*-dimethylacetamide and *N*-methylpyrrolidone. It was also reported that organic amide solvents such as *N*,*N*-dimethylacetamide form a complex salt with the acid halide under specific conditions as shown in eq. (5).[12]



(5)

The excess 4-chloroformyl phthalic anhydride is removed by washing the reaction product with solvents such as warm benzene.

TABLE III
Reaction Products of *o*-Disubstituted Benzidines with 4-Chloroformyl Phthalic Anhydride in *N*-Methylpyrrolidone

o-Disubstituted benzidine	Product	Melting point, °C	Infrared absorption band, cm^{-1}	N, % Calcd	N, % Found
	 I	>300	1650 3200	4.96	4.92
	 II a	>300	1670 1700	4.52	6.99

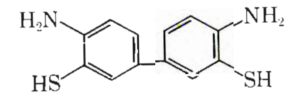
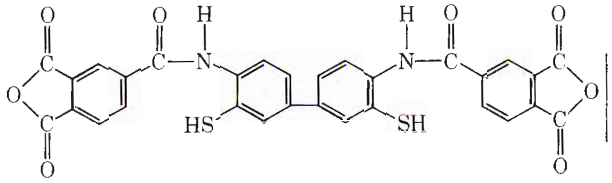
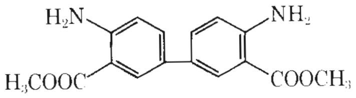
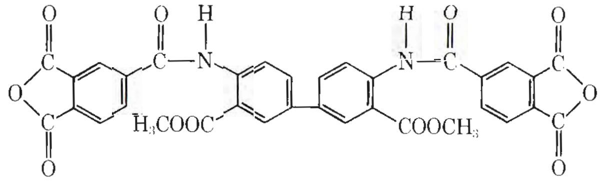
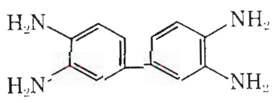
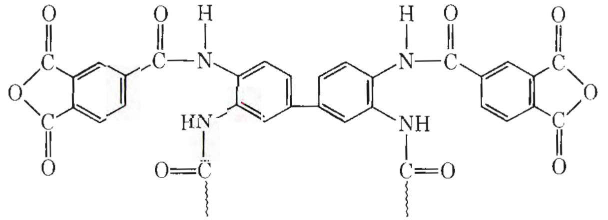
	 IV	190	1650	4.57	6.58
	 II$_b$	>300	1670 1730	4.53	6.33
	 III	>300	1650	gelled product	

TABLE IV

Polymerization of Poly(heterocyclic imides) by Low-Temperature Solution Methods

Monomer[a]			Solvents	Temp, °C	η_{inh} (0.5%, NMP, 25°C)	Polymer structure
TMC	DOB	Benzidine	DMAc	25.0	0.26	Poly(benzoxazole imide)
"	"	DPE	NMP	25.0	1.86	"
"	"	"	DMAc	25.0	1.87	"
"	"	"	DMF	25.0	1.57	"
"	"	"	DMSO	25.0	1.57	"
"	"	"	HMPA	25.0	1.20	"
"	"	"	Pyridine	25.0	0.34	"
"	BDC	Benzidine	NMP	25.0	0.18	Poly(benzoxazinone imide)
"	"	"	"	25.0	0.21	"
"	BDC Me	"	NMP–pyridine	25.0	0.20	"
"	"	DPE	NMP	25.0	0.02	Poly(benzimidazole imide)
"	"	"	"	25.0	gell	"
"	DMB	"	"	−10	"	Poly(benzothiazole imide)
"	DMA	"	"	−10	0.34	"

[a] TMC = 4-chloroformyl phthalic anhydride; BDC = 3,3′-benzidinedicarboxylic acid; BECMe = 3,3′-benzidinedicarboxylic acid dimethyl ester; DOB = 3,3′-dihydroxybenzidine; DAB = 3,3′-diaminobenzidine; DMB = 3,3′-dimercaptobenzidine; DMA = 3,3′-dimercapto-4,4′-diaminodiphenyl ether; DPE = 4,4′-diaminodiphenyl ether.

TABLE V

Effect of Mole Ratio of 4-Chloroformyl Phthalic Anhydride (TMC) and 3,3′-Dihydroxybenzidine (DOB) on Inherent Viscosity of Poly(amic acid)

Solvents	2 TMC/DOB mole ratio	η_{inh}(0.5%, NMP, 30°C)
NMP	1.00	0.36
NMP	1.05	0.41
DMAc	1.05	1.00
NMP	1.10	0.63
NMP	1.15	1.54
DMAc	1.20	1.83
NMP	1.25	2.11

An acid acceptor was usually used in the polymerization of diacid halide with diamine in the low temperature solution polymerizations.[13] In the present study, pyridine and triethylamine were employed for the polymerization. The effect of mole ratio of pyridine and 3,3′-dihydroxybenzidine on the extent of polymerization was determined. It was found (Fig. 1) that the optimum mole ratio of pyridine to 3,3′-dihydroxybenzidine was

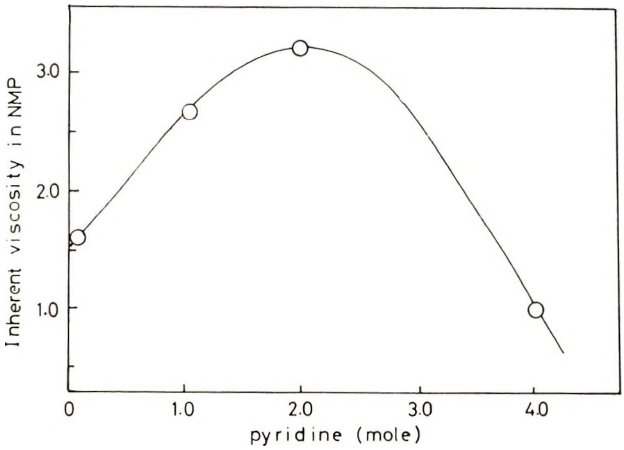


Fig. 1. Effect of pyridine on the extent of polymerization.

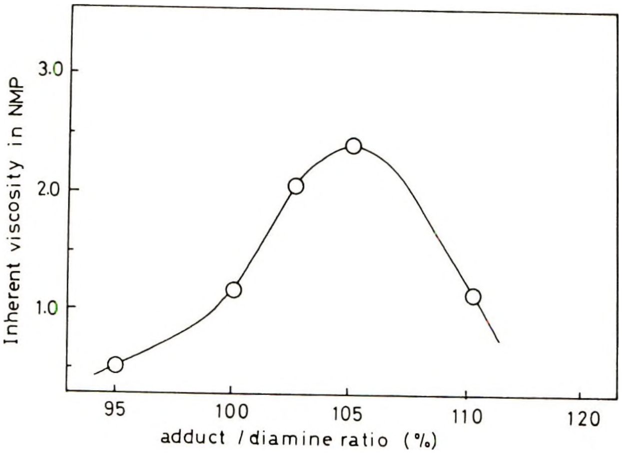


Fig. 2. Effect of reactant ratio on the extent of polymerization (inherent viscosity measured in NMP, 0.5% concentration at 25.0°C).

about 2. When triethylamine was used as an acid acceptor, the inherent viscosity of the resultant poly(amic acid) was found to be below 0.5. It is presumed that the basicity of triethylamine is higher ($pK_a = 10.74$) than that of pyridine ($pK_a = 5.26$), and hydroxyl protons of 3,3′-dihydroxybenzidine are deprotonated, followed by oxidation to form deactivated terminal units. The effects of reactant ratio of adduct and diamine on the extent of inherent viscosity of poly(amic acid) are studied and the data are given in Figure 2. It was found that 5 mole-% excess of adduct is favorable for the formation of poly(amic acid) of higher molecular weight. It is presumed that the excess may counteract losses of acid chloride from hydrolysis and other side reactions. The inherent viscosity of cast film shows maximum at the monomer ratio of 1 (Fig. 3). A tough, flexible film was obtained by casting the polymer solution on the glass plate and evaporating the solvent at 80°C for 14 hr. The measurement of inherent viscosity confirmed that depolymerization of the polymers occurred to give oligomers and monomers, followed by recoupling and crosslinking during the thermal treatment.

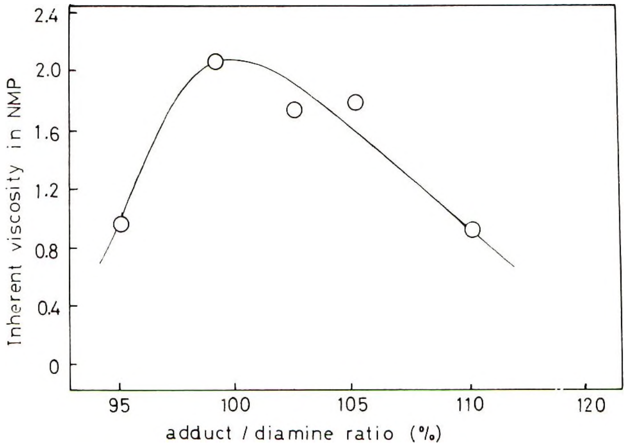


Fig. 3. Effect of reactant ratio on the inherent viscosity of cast film (inherent viscosity measured in NMP, 0.5% concentration, at 25°C).

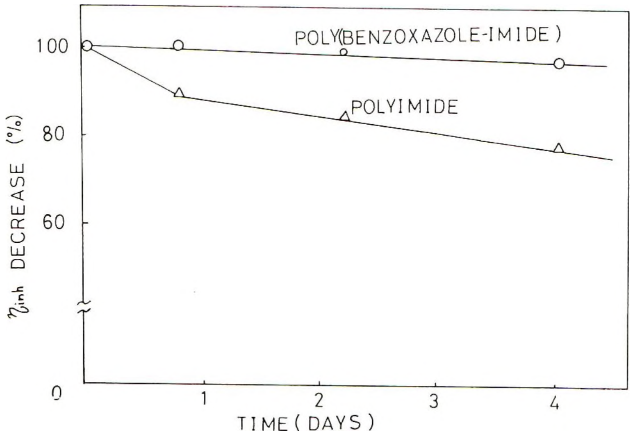


Fig. 4. Stability of poly(hydroxyamic acid) solution in N-methylpyrrolidone at 25°C (inherent viscosity measured in NMP, 0.5% concentration at 25°C).

Poly(benzoxazinone imide)(X). Since the solubility of the monomer adducts (II_a) and (II_b) in N-methyl-2-pyrrolidone is relatively low, the low monomer concentration for the low-temperature solution polymerization affords poly(benzoxazinonimide) of relatively low molecular weight. The inherent viscosity of poly(amic acid) was found to be 0.21 (in concentrated H_2SO_4, 0.5%, 25°C) under the given polymerization conditions.

Poly(benzimidazole imide)(XI). In this case, a gelled polymer was obtained, mainly because there is no difference among the amino groups of the tetraamine with respect to reactivity with acid chloride, and thus cross-linked polymer is formed. In the case of polymerization of diacid anhydride or acid ester with tetraamine, a linear polymer was obtained,[14,15] and the acid chloride of the reaction shows almost the same reactivity with the two adjacent amino groups in the aromatic nucleus.

Poly(benzothiazole imide)(XII). In order to obtain a linear polymer polymerization should be carried out at below −10°C in *N*-methyl-2-pyrrolidone. Otherwise, gelation occurs easily at 20–25°C by the side reaction of the mercapto group as well as by reaction of an amino group with acid chloride. As shown in Table V, poly(amic acids) of high molecular weight were prepared. The thermal treatment of an open-chain precursor yielded a tractable, tough film of poly(benzothiazoleimide).

Poly(amic acids)(V). The poly(amic acids)(V) are soluble in organic polar solvents such as *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, dimethyl sulfoxide, *N*-methylpyrrolidone and *N*-methyl-ϵ-caprolactam. The poly(amic acid) solution shows excellent pot-life at room temperature in contrast to poly(amic acid) of poly(pyrromellitic imide), and it is quite stable to hydrolysis as determined by inherent viscosity measurement (Fig. 4).

Properties of Poly(heterocyclic imide)

Thermal Stability. The thermal stability of the resulting poly(heterocyclic imide) was measured either in nitrogen or in air by the thermogravimetric methods, and the data are shown in Figure 5. Poly(benzoxazinone imide) and poly(benzoxazole imide) have excellent thermal stabilities which are comparable with those of aromatic polyimides,[16] polybenzoxazinone,[17] and polybenzoxazole.[18] The order of thermal stability based on the thermogravimetric method data obtained in air appears to be: poly-

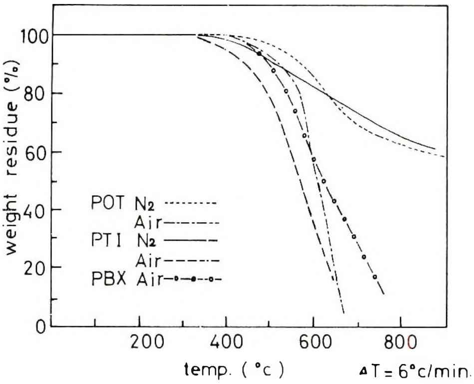


Fig. 5. Thermal gravimetric analysis curves for poly(heterocyclic imide) in nitrogen and in air. POT = poly(benzoxazole imide); PTI = poly(benzothiazole imide); PBX = poly(benzoxazinone imide).

(benzoxazole imide) > poly(benzoxazinone imide) > poly(benzothiazole imide). Poly(benzothiazole imide) is, however, more stable than poly(benzoxazole imide) above 700°C. in nitrogen.

Film Properties. The mechanical properties of the polymer are summarized in Table VI. The tenacity of the polymer is excellent and is comparable with that of the commercial product, du Pont Kapton. It was reported that several poly(heterocyclic imides) had better thermal stability than polyimide and other poly(aromatic heterocycles).[19–22]

TABLE VI
Mechanical Properties of Poly(benzoxazole imide) Film (50 μ)

Property	Value	Test method
Ultimate tensile strength (22°C), kg/mm^2	18	ASTM D 882-64T
Ultimate tensile strength (200°C), kg/mm^2	9	"
Ultimate elongation (22°C), %	21	ASTM D 882-64T
Ultimate elongation (200°C), %	48	"
Tensile modulus (22°C), kg/mm^2	353	JISL-1073
Tear strength (initial, 22°C), kg/mm	555	ASTM D-827
Tear strength, propagating (22°C), g/mm	360	JIS P-8116
Folding Endurance (MIT) (22°C), cycles	30,000	JIS P-8115
Density (25°C), g/cm^3	1.41	

TABLE VII
Electrical Properties of Poly(benzoxazole imide) Film (50 μ)

Property	Value	Test method
Dielectric constant		
1 kcps, 22°C	3.4	ASTM D 150-64T
1 kcps, 180°C	3.1	"
1 Mcps, 22°C	3.3	"
1 Mcps, 180°C	3.0	"
Dissipation factor		
1 kcps, 22°C	0.0038	ASTM D 150-64T
1 kcps, 180°C	0.0041	"
1 Mcps, 22°C	0.0068	"
1 Mcps, 180°C	0.0033	"
Dielectric strength (22°C), kV/mm	210	ASTM D 149-64
Volume resistivity, ohm-cm		
22°C	2×10^{18}	ASTM D 257-61
180°C	7×10^{17}	"
Surface resistivity (22°C), ohm	9×10^{15}	ASTM D 257-61

Poly(benzoxazole imides) in the present study have several characteristic properties. The initial modulus of elasticity is quite high, whereas elongation is relatively low. The film shows excellent flexural resistance, which is unique for poly(benzoxazole imide). The film of this polymer has the feel of gold foil. The electrical properties of poly(benzoxazole imide) are summarized in Table VII. The thermal stability of poly(benzoxazole imide) film (thickness, 50μ) was determined by measuring the thermal life of the film. The thermal life at a temperature is defined as the time required for reduction of the ultimate elongation from the initial value to 1/2. The data are given in Figure 6, and it was confirmed that the thermal stability of poly(benzoxazole imide) film is excellent, being comparable with those of polybenzoxazole and polyimide films.[16]

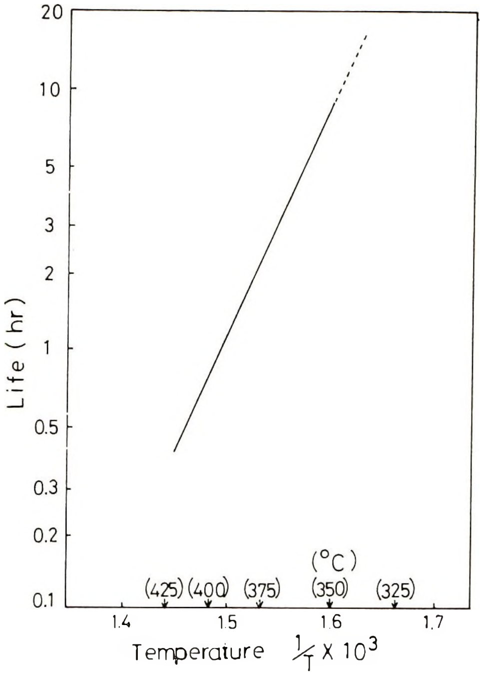


Fig. 6. Thermal life (time required for reduction of ultimate elongation from initial to 1/2) of poly(benzoxazole imide) film (50 μ).

Stability in Inorganic Reagents. Poly(benzoxazole imide) film is quite stable in alkali and acid, as shown in Table VIII. This is a unique property.

TABLE VIII
Stability of Poly(benzoxazole imide) Film (50 μ) in Inorganic Reagents

Property	Test condition	Weight loss, %
Moisture absorption	90% RH, 40°C	0.9
	Immersion for 24 hr at 22°C	2.9
Chemical resistance to:		
5% NaOH aq. soln.	Boil for 5 hr	0.44
10% NaOH aq. soln.	Boil for 5 hr	17
Conc. H_2SO_4	24 hr at 30°C	3.5
Conc. HCl	24 hr at 30°C	−0.73[a]
Organic solvents		insoluble

[a] Weight increase.

EXPERIMENTAL

Instrumentation

All melting points were taken on a Büchi melting point apparatus and were uncorrected. Microanalyses were carried out by the elemental analysis section of Basic Research Laboratories, Toray Industries, Inc. Infrared spectra were recorded with a Hitachi Model EPI-S recording spectrophotometer as in potassium bromide disks or film. Thermal gravimetric analysis (TGA) in nitrogen and air was obtained with a Shimadzu RT-3 instrument; 100-mg samples were used, and heating was at the rate of 6°C/min.

Monomers

4,4′-Diaminobiphenyl-3,3′-dicarboxylic Acid (BDC) and Its Methyl Ester. BDC was prepared in 92% yield from *o*-nitrobenzoic acid by benzidine rearrangement.[23] The monomer was carefully purified by recrystallization followed by vigorous vacuum drying.

ANAL. Calcd for free BDC, $C_{14}H_{12}O_4N_2$: C, 61.76%; H, 4.44%; N, 10.29%. Found: C, 61.31%; H, 4.52%; N, 10.19%.

BDC methyl ester was prepared in 95% yield from BDC by esterifying with methanol in the presence of concentrated sulfuric acid as catalyst. Recrystallization from tetrahydrofuran and methanol afforded crystalline powder, mp 213–214°C.

ANAL. Calcd for $C_{16}H_{16}O_4N_2$: C, 63.99%; H, 5.37%; N, 9.33%. Found: C, 64.12%; H, 5.52%; N, 9.33%.

3,3′-Diaminobenzidine (DAB). DAB was prepared in 25% yield from benzidine by nitration and reduction[24] and purified by sublimation; mp 178–179°C (lit.[24] mp 178–179°C).

ANAL. Calcd for $C_{12}H_{14}N_4$: C, 67.17%; H, 6.54%; N, 26.17%. Found: C, 67.12%; H, 6.32%; N, 26.33%.

4-Chloroformyl Phthalic Anhydride. A 1-liter flask containing 250 ml. of benzene was fitted with a condenser capped with a calcium chloride drying tube. A 100-g portion (0.51 mole) of trimellitic anhydride and 140 g (1.2 mole) of thionyl chloride was added, and the reaction mixture was refluxed for 12 hr. The resulting clear solution was distilled, the excess thionyl chloride and benzene were removed, and pure 4-chloroformyl phthalic anhydride was isolated by fractionation at 174°C/7 mm Hg, yield 85%; mp 67–68°C (lit.[25] mp 68°C).

ANAL. Calcd for $C_9H_3O_4Cl$: C, 51.4%; H, 1.43%; N, 16.8%. Found: C, 51.1%; H, 1.49%; N, 16.8%.

4,4′-[(3,3′-Dicarboxy-4,4′-biphenylene)bis(iminocarbonyl)]diphthalic Anhydride. To a solution of 2.10 g (0.01 mole) 4-chloroformyl phthalic anhydride in 20 ml of trichloroethylene was added dropwise a

1.36-g portion (0.005 mole) of 3,3′-benzidinedicarboxylic acid dissolved in 20 ml of *N*-methylpyrrolidone at −30°C. The mixture was stirred at −30°C for 3 hr and at room temperature for 1.5 hr. The precipitate was collected through a suction filter and then washed with 50 ml of benzene and dried for 3 hr under reduced pressure (1 mm Hg) at 180°C. The yield is 2.46 g (77%). The infrared spectrum shows an acid anhydride carbonyl band at 1870 cm^{-1} and an amide carbonyl band at 1670 cm^{-1}. The melting point of this compound is above 300°C. Other oligomers from 3,3′-mercaptobenzidine and 3,3′-diaminobenzidine were prepared by the same method.

4,4′ - [(3,3′ - Dihydroxy - 4,4′ - biphenylene)bis(iminocarbonyl)]di - phthalic Anhydride. A 1.08 g portion (0.005 mole) of 3,3′-dihydroxybenzidine was dissolved in 10 ml of *N*,*N*-dimethylacetamide at −30°C, and the solution was added dropwise to a solution of 2.52 g (0.024 mole) 4-chloroformyl phthalic anhydride in 10 ml of *N*,*N*-dimethylacetamide. The mixture was stirred at −30°C for 2 hr, and it was added to 200 ml of dry benzene. After filtration, the precipitate was washed with warm benzene and dried at 180°C under vacuum for 4 hr. The yield of oligomer was almost quantitative. The infrared spectrum above acid anhydride carbonyl absorption bands at 1870 and 1780 $cm.^{-1}$ and an amide carbonyl absorption band at 1670 cm^{-1}.

ANAL. Calcd for $C_{30}H_{16}O_{10}N_2$: C, 63.83%; H, 2.86%; N, 4.96%. Found: C, 63.63%; H, 3.04%; N, 4.92%.

4,4′-Diaminodiphenyl Ether. Commercially available reagent (Sumitomo Chemical Co.) was used directly without purification, mp 185°C.

Model Compounds

N-(3,4-Oxydicarbonyl benzoyl)anthranic Acid. To a solution of 1.05 g (0.005 mole) 4-chloroformyl phthalic anhydride in 10 ml of trichloroethylene was added dropwise 0.834 g (0.005 mole) of anthranic acid dissolved in 2 ml of *N*,*N*-dimethylacetamide under cooling at −30°C by a methanol–Dry Ice bath. The mixture was stirred at −30°C for 2 hr. The white precipitate was collected through a suction filter; the crystallization from *o*-dichlorobenzene afforded a white powder which melted at 256–257°C. The yield was 2.86 g (92%). The infrared spectrum showed acid anhydride bands at 1870 cm and 1780 cm^{-1} and an amide carbonyl band at 1670 cm^{-1}.

ANAL. Calcd for $C_{16}H_9O_6N$: C, 61.74%; H, 2.91%; N, 4.51%. Found: C, 61.02%; H, 3.04%; N, 4.56%.

2-(3,4-Oxydicarbonyl phenyl)benzoxazinone. A 1-g portion of *N*-(3,4-oxydicarbonyl benzoyl)anthranic acid was heated with 30 ml of acetic anhydride and 15 ml of pyridine at 100°C for 1 hr. The precipitate was collected through a filter; crystallization from benzene afforded colorless needles, melting at 217–218°C, in 87% yield. The infrared spectrum shows a new characteristic carbonyl absorption band of the benzoxazinone ring at 1760 cm^{-1}.

Anal. Calcd for $C_{15}H_7O_5N$: C, 65.5%; H, 2.38%; N, 4.78%. Found: C, 64.84%; H, 2.58%; N, 5.34%.

N-(3,4-Oxydicarbonyl benzoyl)-*o*-mercaptoaniline. To a solution of 4.21 g (0.02 mole) of 4-chloroformyl phthalic anhydride in 15 ml of *N,N*-dimethylacetamide was added over a period of 10 min 2.70 g (0.02 mole) *o*-mercaptoaniline dissolved in *N,N*-dimethylacetamide at −40°C. The mixture was stirred at −30°C for 2 hr. The reaction product was poured into 100 ml of dry benzene. The precipitate was collected through a suction filter and washed with 50 ml of benzene and dried for 2 hr under reduced pressure (1 mm Hg) at 60°C. The yield was 5.68 g (98%). The infrared spectrum had acid anhydride bands at 1870 and 1780 cm^{-1} and an amide carbonyl band at 1670 cm^{-1}; mp 191–192°C.

Anal. Calcd for $C_{15}H_9NO_4S$: C, 58.30%; H, 3.46%; N, 4.42%; S, 10.01%. Found: C, 58.36%; H, 3.38%; N, 4.42%; S, 10.02%.

3,3′-Dimercaptobenzidine.[26] This was prepared in 72% yield from benzidine and ammonium thiocyanate in the presence of bromine, followed by alkaline hydrolysis with an aqueous potassium hydroxide solution. Recrystallization with hydrochloric acid afforded 3,3′-dimercaptobenzidine as yellow crystals, mp 287°C.

Anal. Calcd for $C_{12}H_{12}N_2S_2$: C, 58.06%; H, 4.87%; N, 11.29%; S, 25.78%. Found: C, 57.84%; H, 4.67%; N, 11.44%; S, 26.05%.

3,3′-Dimercapto-4,4′-diaminodiphenyl Ether. This was prepared in 65% yield from 4,4′-diaminodiphenyl ether, ammonium thiocyanate, and bromine by the same method as used for preparation of 3,3′-dimercaptobenzidine; mp 165°C.

Anal. Calcd for $C_{12}H_{12}N_2OS_2$: C, 54.51%; H, 4.54%; N, 10.59%; S, 24.25%. Found: C, 54.48%; H, 4.57%; N, 10.72%; S, 24.05%.

Polymerization

Preparation of a Poly(amic acid). A 0.615-g portion (0.003 mole) of benzidine was dissolved in 20 ml. of *N*-methylpyrrolidone with 0.4 g of lithium chloride in a dry 100-cc three-necked flask. To this solution was added 2.07 g (0.003 mole) of powdered 4,4′-(3,3′-dicarboxyl-4,4′-biphenylene) bis(iminocarbonyl)diphthalic acid anhydride at 5°C with rapid stirring in an inert atmosphere. An exothermic reaction took place, and after 15 min a clear solution was obtained. The solution was continuously stirred for 4.5 hr at 50°C. and the resulting viscous polymer solution was quenched by pouring it into acetone. The polymer was filtered, washed thoroughly with water and acetone, and dried under vacuum at 80°C. for 2 hr. The yield of polymer was nearly quantitative (97%), and the inherent viscosity was 0.21 in concentrated sulfuric acid (0.5% concentration, 25°C.). The infrared spectrum of poly(amic acid) shows the amide carbonyl band at 1670 cm^{-1}, and the NH stretching band appears at 3400 cm^{-1}.

Conversion to Poly(benzoxazinone imide). The poly(amic acid) powder was heated in an oven at 180–360°C under vacuum (0.1 mm Hg). Dehydration began at about 180°C, followed by cyclization to form poly(benzoxazinone imide). The formation of the benzoxazinone and imide ring by intramolecular thermal dehydration of poly(amic acid) was confirmed by a comparison with infrared spectra of model compounds, and a new characteristic carbonyl absorption band of the benzoxazinone ring was observed at 1760 cm^{-1}.

Preparation of Poly(amic acid)

A 2.0012-g portion (0.001 mole) of 4,4′-diaminodiphenyl ether was dissolved in 50 ml. of *N*-methylpyrrolidone. To this solution was added at 5°C 5.6644 g (0.001 mole) of powdered 4,4′-[(3,3′-dihydroxy-4,4′-biphenylene)bis(iminocarbonyl)]diphthalic anhydride with rapid stirring in an inert atmosphere. An exothermic reaction set in immediately after

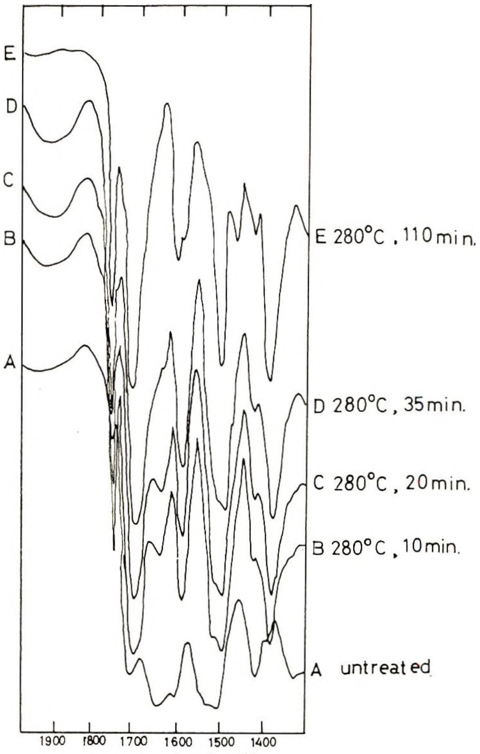


Fig. 7. Infrared spectral changes in carbonyl region of poly(hydroxyamic acid) film (V) heated in vacuum at 280°C for 110 min.

addition, and a viscous clear polymer solution was obtained. The inherent viscosity of the resultant polymer measured in *N*-methylpyrrolidone (0.5% concentration, 25°C) was found to be 1.86. The resultant polymer solution was poured onto a glass plate and dried at 120°C for 20 min. to afford a transparent, flexible, tough film.

The infrared spectrum (Fig. 7) of poly(amic acid) film shows an amide carbonyl absorption band at 1670 cm^{-1}. The NH stretching band appears at 3400 cm^{-1}, and the carbonyl absorption band of carboxyl group is observed at 1700 cm^{-1}.

Thermal Cyclodehydration of Poly(amic acid) to Poly(benzoxazole imide). The poly(amic acid) film was heated on a frame in an oven at 200–380°C. under vacuum for 1.0 hr. Dehydration began at 200°C. and a cyclized product of poly(benzoxazole imide) of high molecular weight was obtained. The formation of both benzoxazole and imide rings by intramolecular thermal dehydration of poly(amic acid) was confirmed by the comparison of infrared spectra of model compounds and polymer as shown in Figure 7. A new characteristic absorption band of the —C=N— group at 1620 cm^{-1} which is attributed to the benzoxazole ring, was observed; the carbonyl absorption bands of the imide ring were found at 1770 and 1735 cm^{-1}. The infrared spectrum in Figure 7 clearly supports the formation of both benzoxazole and imide rings along the polymer chain.

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Design of Active-Site-Directed Fluorescent Probes and Their Reactions with Biopolymers*

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Synopsis

Fluorescent probes which are active-site-directed, reversible, competitive inhibitors of serum cholinesterase (ChE) enzymes have been designed and synthesized. Reversible inhibitors of enzyme active sites have a unique importance when they act as fluorescent probes, allowing fluorescence spectroscopic detection of conformation changes and active-site dynamics. 5-Dimethylamino-naphthalene-1-sulfonamido-*N*,*N*-dimethyl-*n*-propylamine and its aliphatic quaternary derivative are fluorescent probes for serum cholinesterase. The quaternary probe forms complexes with acetylcholinesterase (AChE). The dissociation constants K_d for the two probes with serum ChE are 6.0×10^{-7} and $6.5 \times 10^{-7}M$. The inhibition constants K_i are 3.1×10^{-6} and $6.3 \times 10^{-6}M$ from the slopes of Lineweaver-Burk plots. The Michelis constant K_m for the enzyme was $8.8 \times 10^{-4}M$.

INTRODUCTION

Luminescence is the general term applied to emission of light by a molecule in an excited state. It consists of either fluorescence or phosphorescence. Phosphorescence is the emission from the triplet state while fluorescence occurs from singlet-singlet transformations. The quantum yield of fluorescence is a key factor. It is a function of the relative portion of excited state energy lost to intersystem transfer and to nonradiative processes. The importance of fluorescence in the study of biopolymers stems from the fact that fluorescence spectra are related to molecular structure, conformation, and environment. It is a sensitive method for the study of the structure and dynamics of complex molecules or molecular complexes. Instrumental sensitivity for the detection of fluorescence emission is usually several orders of magnitude greater than that possible for absorption measurements. The limitation of fluorescence spectroscopy include the fact that only a minority of organic molecules are fluorescent. We circumvent this limitation by design and synthesis of biologically active, fluorescent molecules, particularly those useful as fluorescent probes.

Fluorescent probes are defined[1-3] as fluorescent molecules whose spectral response (quantum yield, excitation, and emission) vary as a function of the physical and chemical environment with which the probe is associated.

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

Fluorescent probes are a sensitive measure of the polarity of their environment. When that environment is an enzyme active site, its polarity can be measured by the relative blue shift in the emission of the probe–enzyme complex. When fluorescent probes are reversible or irreversible inhibitors of enzyme active sites they are a part of an important new methodology in the biochemistry of enzyme systems.

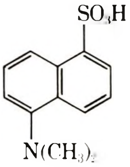
The intrinsic fluorescence of most proteins is largely a function of their tryptophan content.[4–6] The quantum yield of fluorescence and emission maximum (λ_{max}) of such proteins varies as a function of the conformation of the molecule.[7] The scope of fluorescence spectroscopy in the study of polymer conformation and dynamics is related to the fact that any intrinsic fluorescence can be supplemented, quenched, modified, or made more significant by extrinsic fluorescence.[8] Extrinsic fluorescence of a polymer system is that which is added by covalent or noncovalent bonding of a fluorescent moiety to the polymer. Laurence[9] has reviewed fluorescence techniques for polymer solutions. These include life-time of fluorescence and polarization of fluorescence. The fluorescence of proteins and the application of intrinsic and extrinsic probes have been reviewed.[1–3,7]

The design of active-site-directed irreversible inhibitors of enzyme systems has been reviewed by Baker.[10] Irreversible inhibitors can also be fluorescent.[11] An enzyme system which is irreversibly inhibited is, to a significant degree, dead. Reversible inhibitors are important because they can be used to study the dynamics of reactions occurring at active sites if a suitable analytical system is available. Reversible inhibitors are uniquely important when they act as fluorescent probes because their reactions can be detected by spectroscopic means. We synthesize and use such molecules as a key to fluorescence spectroscopy of: (1) the equilibrium dynamics of reactions at the active site, (2) the effect of chemical or physical stress on conformational changes and active site dynamics, (3) insect biochemistry *in vitro* and *in vivo*.

The design and synthesis of either active-site-directed reversible or irreversible inhibitors of enzyme systems follows many of the concepts discussed by Baker.[10] Addition of requisite fluorescence into such biologically active molecules increases the problem; however, some remarkably simple fluorescent molecules act as fluorescent probes and as reversible or irreversible inhibitors of many enzyme systems. Most enzymes have a considerable tolerance to bulk in positions exo to the active site, and even a moiety as small as the 5-dimethylaminonaphthalene-1-sulfonyl (dansyl) group has many favorable fluorescence characteristics. Other well defined fluorescent groups include anthracene carboxylic acids and sulfonic acids, as well as derivatives of flavins, acridines and pterins. All offer possible approaches to complex enzyme systems through fluorescence spectroscopy.

An optimum fluorescent probe molecule for an enzyme system containing tryptophan is one that is photolytically stable, not quenched by oxygen, and with a low or zero quantum yield in water but a very high quantum yield in organic solvents. Finally, the emission maximum should be in the range of 600 nm, and the excitation maximum should be close to that of the emission of tryptophan (λ_{max} 340 nm). Such an optimum probe molecule must include the stereochemical requirements which allow it to become coincident with the active site of the enzyme. The characteristics and reactions of several fluorescent probe molecules which are reversible inhibitors of enzyme systems are discussed. In this research, over 30 candidate fluorescent probe molecules have been synthesized, but only a minority are effective probes. Some of the effective probes contain the dansyl moiety.

5-Dimethylaminonaphthalene-1-sulfonic acid (dans acid) (I)



I

has an excitation maximum at 320 nm and an emission maximum at 515 nm. This emission is from the deprotonated excited state. I is relatively unique among aminonaphthalene sulfonic acid isomers because of its greater than expected bathochromic shift of the emission.[12] The dimethylamino group is an excellent auxochrome for fluorescent molecules. Not all normal chromophores or auxochromes are useful in fluorescent molecules since many promote intersystem transfer. Halogen and nitro groups cause quenching of fluorescence. The 1–5 disubstituted naphthalene configuration is exceptionally favorable for fluorescent probes because most of its derivatives have excellent fluorescence characteristics and because they respond to changes in environment by detectable changes in the excited state.

The protolysis kinetics of dansyl *N*-methyl sulfonamide was reported by Whidby et al.[13] from NMR spectroscopy. Protolysis was subject to acid and base catalysis, which may be significant in the biological activity of sulfonamides, as well as being a factor in reversible bonding with enzymes at esteratic sites. When a dansyl sulfonamide does become coincident with an enzyme active site it has been found to be an efficient fluorescent probe. The ease of synthesis of groups attached to the nitrogen of the sulfonamide allows a considerable variation in stereochemistry and ancillary binding moieties in dansyl sulfonamides.

Dansyl sulfonamide has been studied by Chen and Kernohan[14] as a reversible inhibitor and fluorescent probe for the active site of carbonic anhydrase. Deranleau and Neurath[15] used the dansyl sulfonamide of *d*-tryptophan ethyl ester as a reversible inhibitor and probe of the active site of α-

chymotrypsin. On the other hand, a series of dansyl sulfonamides of amino acids have been found to be ineffective as probes for acetylcholinesterase enzymes,[16] showing that proper stereochemical configuration of a molecule is of overriding importance in each specific enzyme system.

In this paper we report the reactions of active-site-directed fluorescent probes as reversible inhibitors of serum cholinesterase and a fluorescent quaternary amino derivative as the first fluorescent probe molecule designed for anionic site interaction.

EXPERIMENTAL

Synthesis of Fluorescent Probes

5-Dimethylaminonaphthalene-1-sulfonyl chloride (dansyl chloride) is a versatile synthesis reagent for introduction of significant fluorescence into designed molecules. Over thirty candidate probe molecules have been synthesized. Methods for synthesis of pure aminosulfonate or phenolic sulfonamides from dansyl chloride and aminophenols have been developed.[17] Phosphate, carbamate, and carboxyl esters interact at esteratic sites of many enzymes hence their fluorescent derivatives are potential fluorescent probe molecules.[8] Spectroscopic requirements for optimum probe characteristics have been discussed.

Reaction of dansyl chloride with a $3M$ excess of *N*,*N*-dimethyl-1,3-diaminopropane in ether gave 5-dimethylaminonaphthalene-1-sulfonamido-*N*,*N*-dimethyl-*n*-propylamine (II). The amine hydrochloride was removed by filtration. The product was recrystallized from 25/75 ethanol–water, mp 119–120°C. Microanalytical data were consistent with theoretical and the structure was verified by infrared and NMR spectra. Purity was monitored by thin layer chromatography (TLC).

Pure II was dissolved in ether containing a 50 fold excess of methyl iodide. The quaternary derivative (III) precipitated immediately. After four hours the product was removed by filtration and was recrystallized from water, mp 201–202°C. The structure was verified by infrared and NMR spectra. Purity was monitored by TLC.

A purified sample of Maretin (IV), a commercial insecticide, was obtained from Chemagro Corporation, who also supplied naphthostyril (V) and the *N*-hydroxynaphthalimide (VI) as standards. Although Maretin is a commercial insecticide and an alternate substrate for cholinesterase and acetylcholinesterase enzymes, its rate of phosphorylation is very slow. It therefore acts over extended periods of time as a reversible inhibitor of the enzyme. Although its fluorescence characteristics are marginal as a probe, it is readily available and of considerable spectroscopic interest. Kinetic, spectroscopic and equilibrium data will be reported separately.

Instrumentation and Methods

All spectra were obtained with a G. K. Turner Spectro 210. This absolute spectrofluorometer presents corrected emission spectra and excitation spectra at constant energy.[18] The fluorescence well was temperature-controlled to 25 ± 0.01°C. Water was doubly distilled from glass and found to have low intrinsic fluorescence. Enzymes used in the fluorescence studies were dissolved in $0.05M$ Tris buffer solution. One-milliliter portions of enzyme solutions were used in the fluorescence measurements with addition of microliter amounts of $10^{-3}M$ solutions of the probe in isopropanol or Tris buffer solution. Enzyme solutions were changed after irradiation times of not more than 5 min to minimize photodegradation and photooxidation.

The kinetic data with acetylcholine as substrate were obtained by using a modification of the method of Nabb and Whitfield.[19] The pH meter used was a Radiometer Model 26 equipped for automatic titration. Enzymes used were dissolved in doubly distilled water at a concentration to produce a hydrolysis rate of 0.625 μmole acetylcholine/sec/ml. The final total volume for the reaction mixture was 10 ml. The endpoint for titration was pH 7.5 and temperature was approximately 25°C. The hydrolysis product was titrated with $0.01N$ NaOH. All additions of probes to solution were carried out with Hamilton microsyringes.

Materials

Enzymes were obtained from Sigma Chemical Company, St. Louis, and included horse serum cholinesterase, Type IV, bovine erythrocyte acetylcholinesterase, Type I, and electric eel acetylcholinesterase Type III. Dansyl chloride, mp 68–70°C was obtained from Peninsular Chemresearch. The effect of purity of enzyme preparations on research data is of considerable importance. Enzymes as with other polymers where conformational states are important are subject to "conformational purity" concepts as well as classical purity concepts of molecular weight and monomer sequence. The use of fluorescent probes in the study of enzyme reactions is not a total release from purity problems, however, equilibria are less subject to nonspecific impurities than are kinetic dynamics.

RESULTS AND DISCUSSION

5- Dimethylaminonaphthalene - 1 - sulfonamido - *N*,*N* - dimethyl - *n*-propylamine (II) is a reversible, competitive inhibitor of the esteratic site of horse serum cholinesterase. The dissociation constant K_d of the probe–enzyme complex is 6.0×10^{-7}, as indicated from data in Figure 1 by the method of Chen and Kernohan.[14] Figure 2 is a Lineweaver-Burk plot indicating that the probe is a competitive inhibitor of the enzyme. The inhibition constant K_i was obtained from the slope and found to be 3.1 ×

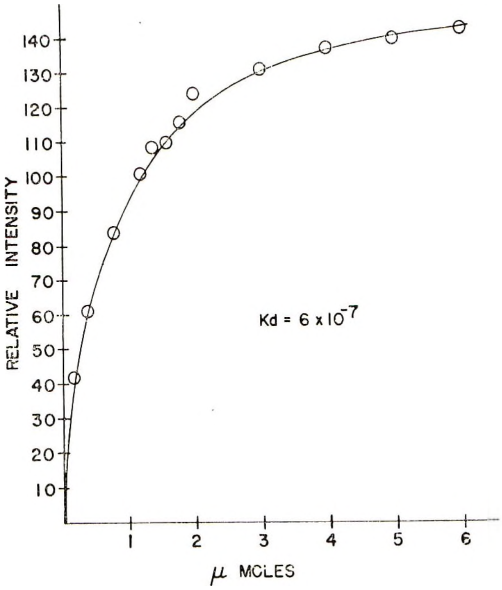


Fig. 1. Titration of dansyl-NH-(CH$_2$)$_3$-N(CH$_3$)$_2$ (II) with horse serum cholinesterase (ChE). Excitation 280 nm, emission 515 nm, BW 10 nm; ChE activity 0.675 μmole ACh/sec/ml.

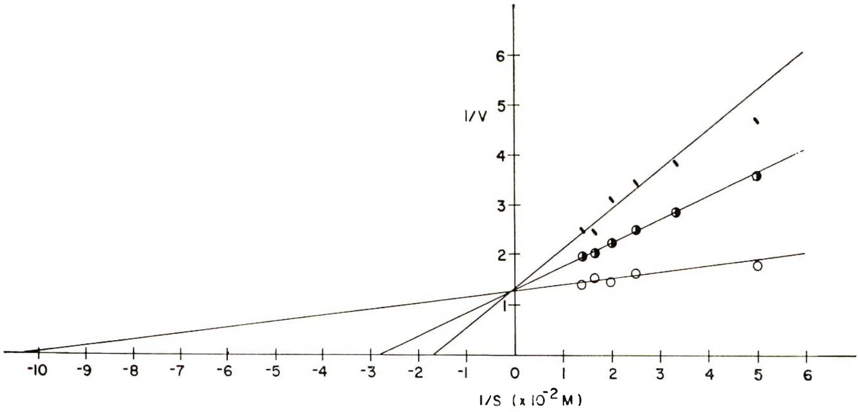


Fig. 2. Lineweaver-Burk plots of ChE with dansyl-NH-(CH$_2$)$_3$-N(CH$_3$)$_2$ (II): (\) $2 \times 10^{-5} M$; (◑) $1 \times 10^{-5} M$; (O) no inhibitor, 2 min incubation with inhibitor; $1/V = 10^4$ sec/mole.

$10^{-6} M$. An average K_m was $8.8 \times 10^{-6} M$. The data of Whidby et al.[13] indicate the potential activity of secondary sulfonamides as inhibitors of enzyme esteratic sites. When complexed, II acts as a fluorescent probe. The free probe in water has a λ_{max} of 580 nm, while the probe–enzyme complex has a λ_{max} at 515 nm. This hypsochromic shift of the emission is a measure of the polarity at the active site of this serum cholinesterase. An isopropanol solution of the probe (II) has an emission maximum at 515 nm, indicating that the relative polarity at the active site is close to that of isopropanol. Fluorescence spectra of the probe and the probe-enzyme complex at a series of concentrations are given in Figure 3. This probe is a remarkably valuable research tool for use with serum cholinesterase. It is an effective probe of the active-site dynamics of the enzyme, since it responds to conformational changes of the enzyme from physical and chemical stress. To a major extent, methods to obtain these fundamental data have not been readily available heretofor. The emission of the probe at 580 nm is well removed from that of tryptophan at 340 nm. The polarity at the active site is such that the probe–enzyme complex has an emission at 515 nm, giving a minimum of spectral overlap with tryptophan and the free probe. All data were corrected for any spectral overlap by use of data from blank runs.

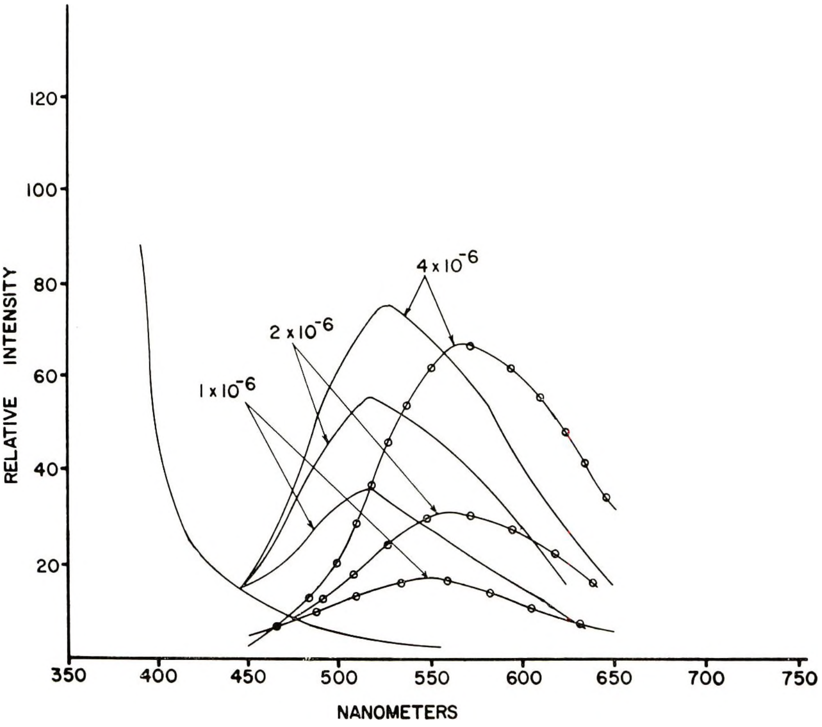


Fig. 3. Emission spectra of ChE (activity 0.45 mole ACh/ml/sec) with dansyl-NH-$(CH_2)_3$-$N(CH_3)_2$, 1×10^{-6} to 4×10^{-6} moles, BW 10 nm: (O) free probe, E_x 335 nm; (—) probe-enzyme complex E_x 280 nm.

The active site or endo area of an enzyme has critical stereochemical requirements which vary from enzyme to enzyme. Although II can become coincident with the active site of serum cholinesterase, kinetic and fluorescence data indicate that it is ineffective for acetylcholinesterase (AChE). Other candidate probe molecules are being studied with AChE.

Quaternization of II by methyl iodide in ether at room temperature goes readily to produce the aliphatic quaternary derivative (III). This fluorescent quaternary amine has excitation and emission characteristics similar to II. It is an inhibitor of bovine AChE; however, unequivocal proof

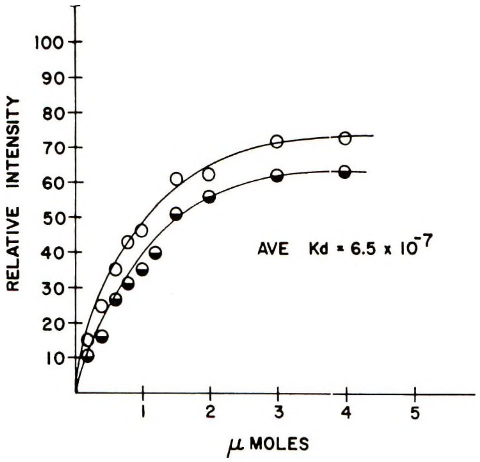


Fig. 4. Titration of dansyl-NH-$(CH_2)_3$-$\overset{+}{N}(CH_3)_3$ (III) with horse serum cholinesterase: (◒) ChE activity 0.9 μmole ACh/sec/ml; (○) ChE activity 0.675 μmole ACh/sec/ml. Excitation 280 nm, emission 515 nm; BW 10 nm.

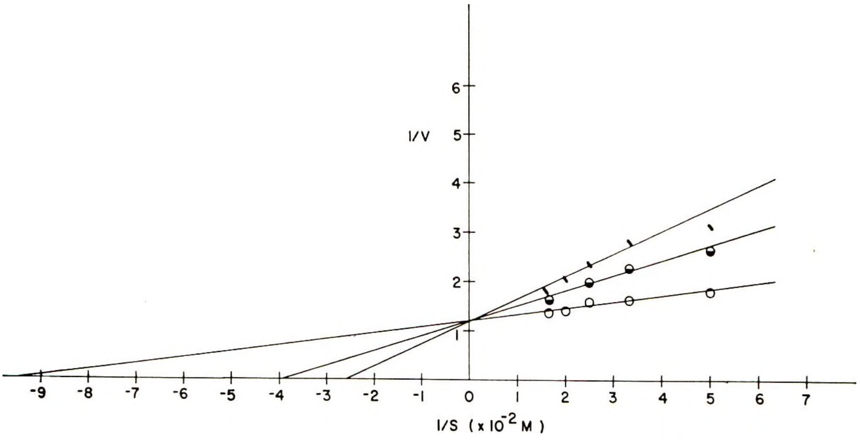
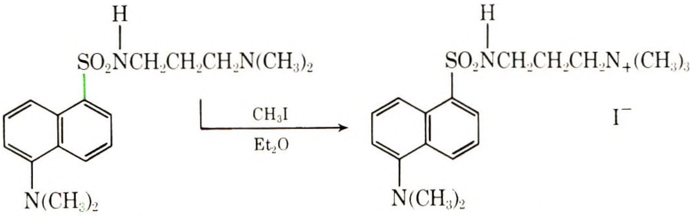


Fig. 5. Lineweaver-Burk plots of ChE with dansyl-NH-$(CH_2)_3$-$\overset{+}{N}(CH_3)_3$ (III): (╲) $2 \times 10^{-5} M$; (◒) $1 \times 10^{-5} M$; (○) no inhibitor, 2 min incubation with inhibitor; $1/V = 10^4$ sec/mole.

of competitive inhibition of the active site has not been obtained. The tryptophan emission in this AChE is quenched by III, indicating complex formation of the quaternary probe with the enzyme. No emission at or near 515 nm was observed. The energy transferred from the tryptophan appeared at 580 nm and may have been radiation emission transfer from tryptophan to the probe which then emitted this energy as 580 nm fluorescence in the absence of excited state interaction with this enzyme. The status of probe–enzyme complex formation with AChE is being determined along with a study of the energy transfer mechanism(s) and quantum yield.

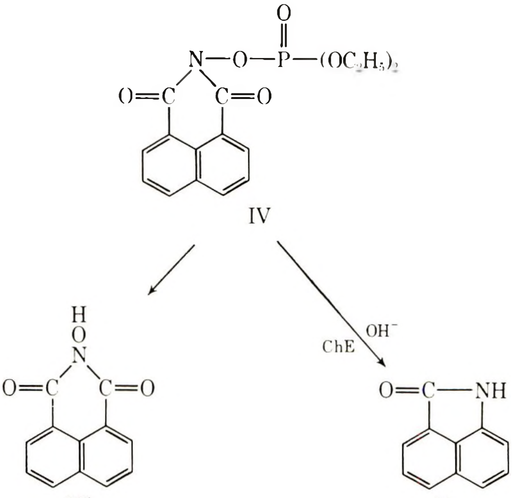
The quaternary probe III reacts with serum cholinesterase in a manner analogous with the tertiary amine II. The Lineweaver-Burk plots are given in Figure 4. K_i was found to be $6.3 \times 10^{-6} M$. As indicated in Figure 5, the K_d was $6.5 \times 10^{-7} M$, close to that of II with this enzyme. An average K_m was $8.8 \times 10^{-4} M$. Fluorescence data are given in Figure 6.

Maretin (IV) is a commercial insecticide which acts as a fluorescent probe for the active site of AChE. Its utility as a probe is marginal, since the emission wavelength of the free probe in aqueous media is 400 nm and that of the probe enzyme complex is 385 nm. Fluorescence data are given in Figure 7. Although Maretin is an alternate substrate for cholinesterase enzymes with phosphorylation of the active site, the rate of the phosphoryla-



II

III



VI

V

TABLE I
Relative Polarities of Active Sites

Enzyme	Polarity comparable to
α-Chymotrypsin[11]	Water
Serum cholinesterase	Isopropanol
Acetylcholinesterase	Benzene

tion reaction is slow and over extended periods of time Maretin acts as a reversible inhibitor of the enzyme. The kinetics of reaction of Maretin with cholinesterase enzymes and the equilibrium constant of the probe-enzyme complex will be reported separately. It is important that the fluorescence (blue) shift of the probe-enzyme complex indicates that the polarity at the active site of this "specific" enzyme is in the range of benzene. Relative polarities of the active sites of a series of esterase enzymes are given in Table I. The importance of these data is that they show that specificity of an enzyme active site is a function not only of known stereochemical requirements but also of relative polarity at the active site. As would be

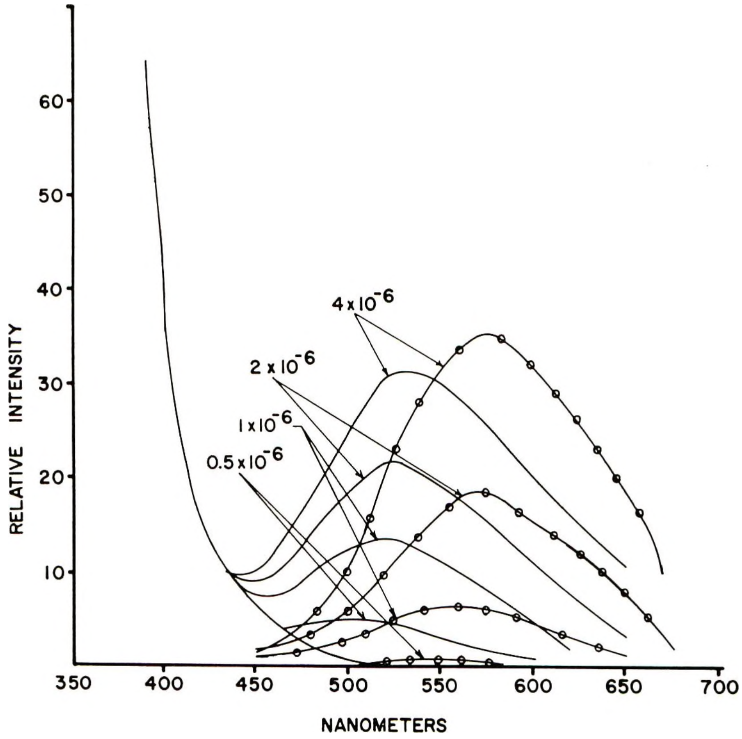


Fig. 6. Emission spectra of ChE (activity 0.45 μmole ACh/sec/ml) with dansyl-NH-$(CH_2)_3$-$N^+(CH^3)_3$, 0.5 × 10^{-6} to 4 × 10^{-6} moles, BW 10 nm; (○) free probe, E_x 335 nm; (—) probe–enzyme complex, E_x 280 nm.

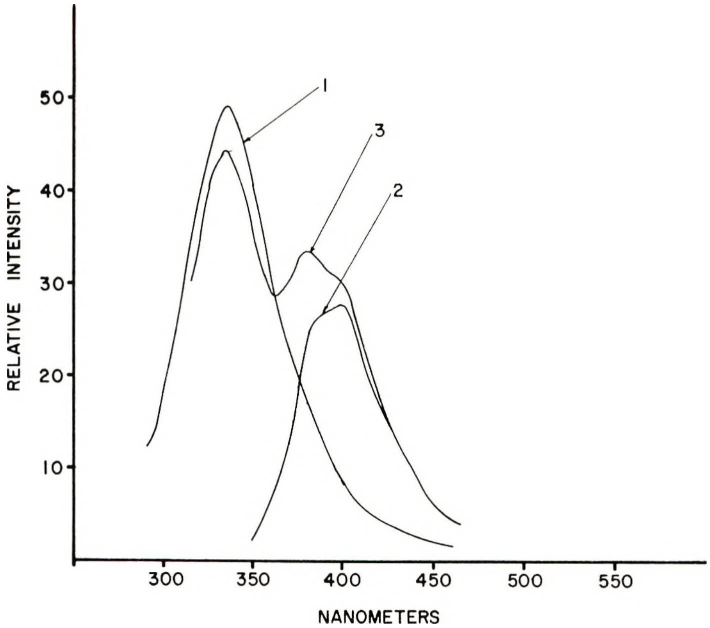


Fig. 7. Emission spectrum of Maretin and electric eel cholinesterase (AChE): (*1*) AChE, 20 μmole ACh/sec/ml; (*2*) Maretin at 1 × $10^{-6}M$, E_x 280 nm; (*3*) probe–enzyme complex, E_x 280 nm, BW 10 nm.

expected, increase in specificity of the active site is accompanied by a decrease in polarity. Stryer[2] has compiled a table of relative polarity data for a series of enzymes and proteins.

Alkaline hydrolysis of Maretin (IV) produces naphthostyril (V) rather than the expected *N*-hydroxynaphthalimide (VI). The same products are produced on enzymatic action on Maretin.

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Halatopolymers*

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Synopsis

The polymeric character of a series of salts derived from divalent metal ions and organic dibasic acids has been investigated. On melting, these salts form extremely viscous melts which cool to amorphous solids with polymerlike properties and excellent thermal stabilities. This change from a salt to a polymerlike structure appears to be novel and has been termed a halatopolymeric transformation. Halatopolymers are unique in that they have no end groups in the traditional sense. Essentially, the metal carboxylate groups undergo a rapid interchange to afford an association equilibrium of long chains. Studies of the effects of chain modifiers on a calcium sebacate melt at 386°C have indicated that on a time-average basis the association consists of approximately ten repeat units.

INTRODUCTION

A program was undertaken to establish the possible polymeric character of a series of salts derived from divalent metal ions and organic dibasic acids. In early work[1] it has been reported that Zn dimerate behaved like a resinous material. More recently Paquot[2] and co-workers ascribed molecular weights of 5000-6000 for Mg, Cd, and Pb sebacates. The idea that polymerlike structures could occur with highly ionic units spaced regularly along the chain is most intriguing, particularly since metal sebacates would be expected to crystallize in a salt like structure. Yet ionic links can act as useful primary bonds as is illustrated by the fact that polymers containing acidic pendant groups can be crosslinked with divalent metal ions e.g., Hypalon rubbers, Ionomers, and metal ion-crosslinked polyacrylates.

In this paper the preparation and characterization of a series of metal dicarboxylates is reported. Polymerlike behavior is observed when the metal dicarboxylate salt melts. This transformation during melting from a salt to an amorphous polymerlike structure is called a "halatopolymeric transition." The melt is highly viscous, and the molecular weight can be described in terms of an association (or dissociation) constant; however, there are no endgroups in the classical sense. Some insight into the structure of halatopolymers was obtained by studying the effect of chain modifiers on the melt flow.

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

EXPERIMENTAL

Preparation of Metal Dicarboxylates

Melt Reaction. In a typical melt preparation, 21.4 g (0.1 mole) of $Mg(OAc)_2 \cdot 4H_2O$ and 20.2 g (0.1 mole) of sebacic acid were placed in a 300-ml resin kettle equipped with a nitrogen inlet tube, distilling head, thermometer, and stirrer. The distilling head was connected to a liquid nitrogen trap for the collection of volatiles. After purging the system with nitrogen the reactor was slowly heated. The reaction mass melted at 85°C. At 175°C the melt began to thicken appreciably. After 3.5 hr the temperature had reached 295°C, and the melt could no longer be conveniently stirred. The system was then placed under 15 mm Hg vacuum and heated for an additional 6 hr at 320°C; 17.5 g of water and acetic acid (91% of theoretical) was obtained from the trap.

Precipitation Reaction. In a typical precipitation reaction from water, 40 g (1.0 mole) NaOH was dissolved in 500 ml of water and 101 g (0.5 mole) of sebacic acid dissolved in the NaOH solution. The solution of sodium sebacate was then filtered, the pH adjusted to pH 8 by means of 10% NaOH and a solution of 77.2 g (0.52 mole) of $CaCl_2 \cdot 2H_2O$ in 300 ml of water was added with stirring. Although a precipitate formed immediately, the mixture was allowed to stir at least 10 min. The calcium sebacate was filtered and washed successively with two 300-ml portions of distilled water and two 300-ml portions of methanol. The product was then dried in a vacuum oven at 150°C. The yield was 115.1 g, 96% of theoretical.

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) were carried out in a Chevenard Thermobalance at a heating rate of 6°C/min and a gas flow of 100 cc/min.

Differential Thermal Analyses

Differential thermal analyses (DTA) were carried out with Stone DTA equipment at a heating rate of 12°C/min and no gas flow.

Chlorine Analyses

Analyses were obtained by ashing the sample, taking the ash up in nitric acid, and titrating by the Volhard method.

Sodium Analyses

Spectrographic analyses were carried out on the ashed samples.

Infrared Spectra

All infrared curves were determined on KBr pellets containing 0.2 wt-% of the metal carboxylate. In determining the concentration of —COOH, known mixtures of calcium sebacate and sebacic acid containing 1.25–24.4

mole-% —COOH were analyzed. The absorption of the acid carbonyl group at 5.84 μ was determined using the C—H absorption at 3.49 μ as an internal standard. Under these conditions the plot of absorbency versus concentration was found to obey Beer's law. A similar approach was employed for determining the concentration of Ca—OH endgroups.

Melt Flow

All melt flow data were obtained from equipment described in ASTM-D-1238-57T and manufactured by D&R Plastic Welders, Inc. A temperature of 386 ± 1°C and pressure of 6.5 psi were employed. Extrudate was allowed to flow 5 min before sampling, and samples were generally taken at 0.5–1.0 min intervals.

X-Ray Diffraction

Powder samples were examined with a diffractometer or Debye-Scherrer camera. Single crystals were examined by the use of rotation and Weissenberg photographs. In all cases Ni filtered CuKα radiation was used.

RESULTS AND DISCUSSION

Metal Carboxylate Preparation

The two routes used for the preparation of metal carboxylates are shown in eqs. (1) and (2),

$$M(OAc)_2 + HOOCRCOOH \xrightarrow[300° \text{ C}]{\Delta} [MOOCRCOO]_x + AcOH \qquad (1)$$

$$MCl_2 + NaOOCRCOONa \xrightarrow{H_2O} [MOOCRCOO]_x + NaCl \qquad (2)$$

where R is $(CH_2)_n$ or Ar.

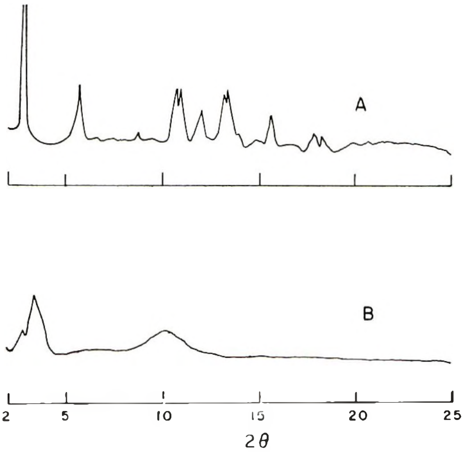

Fig. 1. X-Ray powder diagrams of calcium sebacate: (*A*) crystalline form precipitated from water; (*B*) amorphous form obtained after fusion.

Metal dicarboxylates that melt below their decomposition temperature could be prepared by either method; however, those structures melting above their decomposition temperature could only be obtained by eq. (2). Generally, with metal dicarboxylates prepared via eq. (1), a little over 90% of the acetic acid could be recovered before the reaction had to be stopped due to the high viscosity of the melt. The x-ray powder diagrams showed that structures prepared in this manner possessed a very low degree of crystallinity. Because of the simplicity of the second route most of the metal dicarboxylates used in this study were prepared in this manner. These products were obtained as highly crystalline, water insoluble precipitates. Those precipitates which could be fused formed extremely viscous melts similar to those observed in the first route and also yielded the amorphous solid on cooling. A comparison of x-ray patterns for crystalline and amorphous calcium sebacate is shown in Figure 1.

Thermal and Mechanical Properties

The melting points and thermal stabilities in air of a series of metal dicarboxylates prepared by precipitation from water are summarized in Table I. As expected, the relatively high ionic nature of the metal dicarboxylate bond leads to excellent thermal stabilities.

TABLE I
Melting Points and Thermal Stabilities of Metal Carboxylates

(OOCRCOOM)			
M	*R*	Mp, °C	Degradation temperature in air, °C[a]
Mg	$(CH_2)_8$	240	350
Ca	$(CH_2)_8$	320	380
Ba	$(CH_2)_8$	None	350
Zn	$(CH_2)_8$	315	330
Cd	$(CH_2)_8$	280	310
Pb(+2)	$(CH_2)_8$	275	320
Sn(+2)	$(CH_2)_8$	170	320
Mn(+2)	$(CH_2)_8$	275	305
Mg	-*p*-Ar	None	495
Ca	-*p*-Ar	None	525
Ba	-*p*-Ar	None	590
Sn(+2)	-*p*-Ar	None	400
Sn(+2)	-*m*-Ar	None	400
Ca	$(CH_2)_4$	None	360
Ca	$(CH_2)_7$	340	340
Ca	$(CH_2)_8$	320	380
Ca	$(CH_2)_{10}$	295	420

[a] Temperature at which 5% weight loss occurs.

Of the metal sebacates, calcium sebacate possessed the highest melting point, except for barium sebacate which did not melt below its decomposition temperature of 350°C. In all cases where fusion occurred, highly

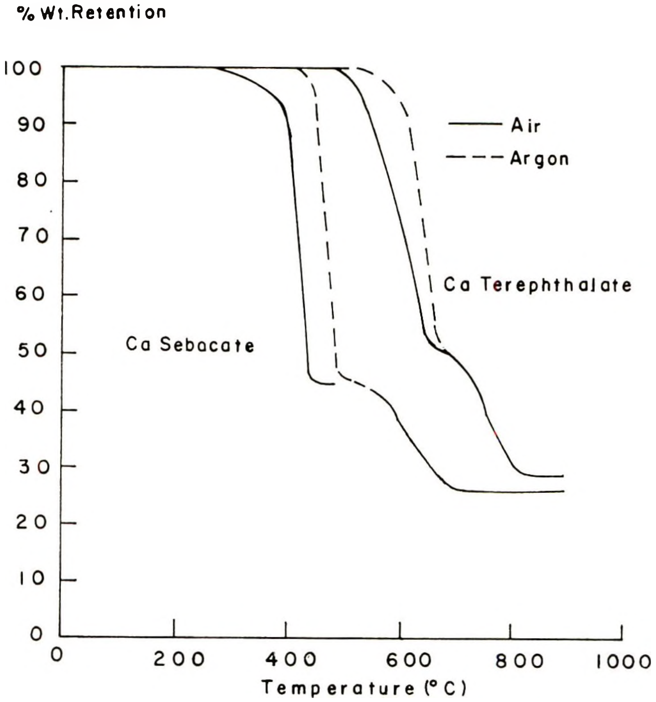

Fig. 2. Thermal gravimetric analysis curves of calcium sebacate and calcium terephthalate in air and argon.

viscous melt phases were obtained. Substituting terephthalate for sebacate led to much more thermally stable structures, e.g., barium terephthalate was stable in air up to 590°C. The effect of different dicarboxylic acids on melting point was evaluated. It was found that decreasing the number of methylene groups in the dicarboxylate led to an approximate 12–20°C increase in melting point of the polymer per methylene unit removed. Thermal gravimetric analysis curves both in air and argon are shown for calcium sebacate and calcium terephthalate in Figure 2. Calcium sebacate appears to possess substantially higher thermal stability in argon up to 445°C. The plateau observed at 58% weight loss corresponds to the formation of $CaCO_3$ and the second plateau to CaO. No ketone formation could be detected during the decomposition of calcium sebacate. On the other hand, cadmium sebacate and magnesium sebacate yielded ketone-containing products. In the case of calcium terephthalate, thermal gravimetric analysis indicates a stability in argon up to 600°C. Again, the plateaus correspond to the formation of the carbonate and oxide. Most of the metal carboxylates could be readily burned in a Bunsen flame except for magnesium sebacate and zinc sebacate. From an examination of the thermal gravimetric analysis curve for magnesium sebacate it is apparent that magnesium carbonate does not form as a stable intermediate but probably decomposes, producing CO_2 which acts as a flame retardant.

The mechanical properties of the amorphous metal dicarboxylates were examined. Test specimens of calcium sebacate containing from 50–75% asbestos filler were formed by compression molding at 350°C and 7000 psi. Tensile strengths ranged from 5000 to 7000 psi. The absestos filler was necessary to reduce the thermal stresses resulting from the high molding temperatures.

Nature of the Crystalline and Amorphous Phases

Work was carried out to better characterize the crystalline calcium sebacate produced by precipitation from water as well as the amorphous structure obtained after fusion. Paquot et al.,[2] in their earlier studies, ascribed molecular weights of 5000–6000 to the crystalline Mg, Cd and Pb sebacates on the basis of metal analyses which were slightly lower than theoretical. They also analyzed for sodium and sulfur which could be present from the reaction of the divalent metal sulfate with sodium sebacate in water. They found insufficient sodium or sulfur to account for the low metal (Mg, Pb and Cd) analyses and therefore assumed a carboxylic acid end group. They concluded that these materials contained 13–31 repeat units.

In the present study, analyses of purified crystalline calcium sebacate showed that there were negligible quantities of sodium or chlorine (<0.05% from the divalent metal chloride) and that there were no carboxylic acid or —CaOH groups detectable. This suggests that calcium sebacate is a salt and has no endgroups in the conventional polymer sense. The low metal analyses observed by Paquot et al.[2] may be attributed to either impure sample or the analytical methods. Conclusive evidence in favor of the salt nature of the crystalline metal dicarboxylate was obtained with isolation of single crystals of barium terephthalate and barium sebacate. Crystallographic data on these materials are given in Table II.

TABLE II
Crystallographic Data of Single Crystal Metal Dicarboxylates

Compound	System	a, Å	b, Å	c, Å
Barium terephthalate	Monoclinic	9.65	5.89	6.90
Barium sebacate	Tetragonal	8.64		15.42

The amorphous solid of calcium sebacate was studied and found to display a thermoplastic behavior. Differential thermal analysis of amorphous and crystalline calcium sebacate showed an almost identical melting region (see Fig. 3). Presumably, if the calcium sebacate were completely amorphous, then one should observe a differential thermogram with a minor transition spread out over a broad range. The relative sharpness of the DTA indicates retention of a localized degree of order which x-rays cannot detect. The amorphous solid could not be crystallized either by very slow

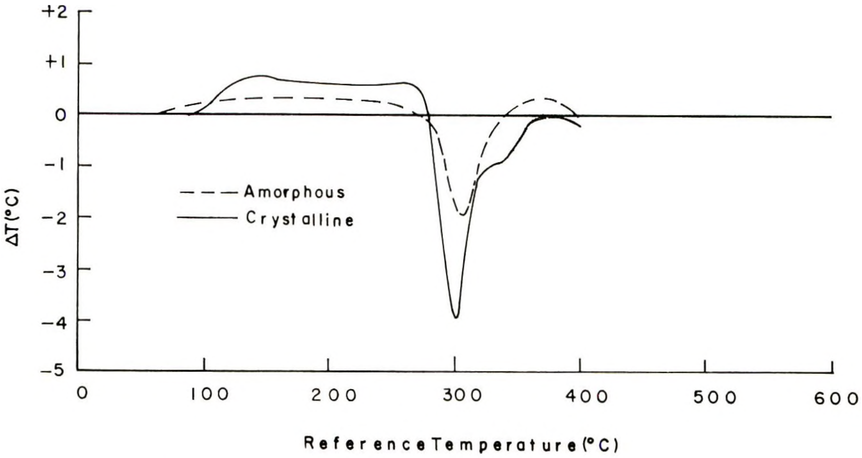

Fig. 3. Differential thermal analyses of crystalline and amorphous calcium sebacate.

cooling of the melt or annealing at elevated temperatures. Some crystallization could be induced by exposing the amorphous solid to water for 68 hr.

Melt Properties

The metal carboxylate bond has been estimated to have 70% ionic character[3] and might be expected to undergo rapid interchange reactions in the melt phase. Two approaches were used to examine this phenomenon, namely, infrared analyses of mixtures before and after melting and melt flow measurements in the presence of chain modifiers.

Infrared evidence for the interchange reaction is presented in Figure 4. Spectra *A* and *B* are those of fused calcium azelate and calcium dodecanedioate, respectively. Spectrum *C* is that of a 50–50 physical mixture of the materials used to prepare spectra *A* and *B* after re-fusing at the same temperature. As can be seen, absorptions at 735, 742, 780 and 910 cm^{-1} which are attributable to the calcium azelate can no longer be detected. The spectrum closely resembles that of the calcium dodecanediodate, except that the absorptions at 720, 1110, 1310 and 1580 cm^{-1} are shifted toward the slightly lower wave lengths at which similar absorptions are observed for calcium azelate. Spectra identical to *C* can also be obtained by fusing a 50–50 physical mixture of crystalline calcium azelate and crystalline calcium dodecanedioate or by fusing the coprecipitated calcium salt of a 50–50 mixture of sodium azelate and sodium dodecanedioate. Based on these results the calcium carboxylate bonds appear to undergo relatively rapid interchange on melting.

The rapid interchange of the metal carboxylate bonds in the molten state suggests that the polymeric behavior of the melt is due to an association equilibrium of linear metal dicarboxylate units. Thus, at any given time there is a finite concentration of dissociated metal carboxylate and groups. If this is the case materials such as $CaCl_2$, $Ca(OH)_2$, NaCl, sodium

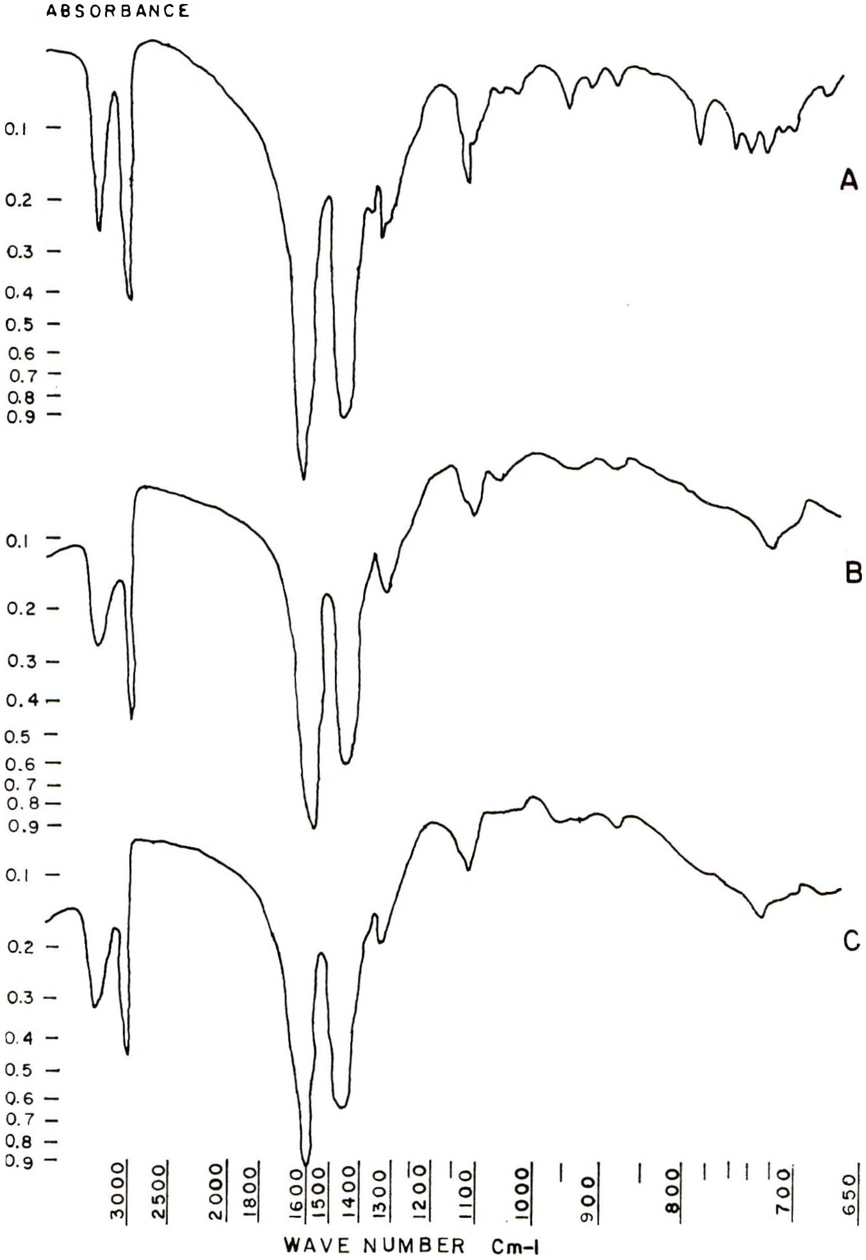

Fig. 4. Infrared absorbances of: (*A*) fused calcium azelate; (*B*) fused calcium dodecanoate; (*C*) fused 50–50 physical mixture of materials used for spectra *A* and *B*.

sebacate, and sebacic acid should interchange and act as chain modifiers. Such chain modifiers, as indicated schematically in eqs. (3)–(7) might have an effect similar to that of adding endgroups and result in marked increases in the melt flow.

$$\sim\!\sim\text{COOCaOOC}\sim\!\sim + \text{NaCl} \rightleftharpoons \sim\!\sim\text{COONa} + \text{ClCaOOC}\sim\!\sim \quad (3)$$

$$\sim\!\sim\text{COOCaOOC}\sim\!\sim + \text{CaCl}_2 \rightleftharpoons \sim\!\sim\text{COOCaCl} + \text{ClCaOOC}\sim\!\sim \quad (4)$$

$$\sim\!\sim\text{COOCaOOC}\sim\!\sim + \text{Ca(OH)}_2 \rightleftharpoons \sim\!\sim\text{COOCaOH} + \text{HOCaOOC}\sim\!\sim \quad (5)$$

$$\sim\!\sim\text{COOCaOOC}\sim\!\sim + \text{NaOOC(CH}_2)_8\text{COONa} \rightleftharpoons \sim\!\sim\text{COONa} + \text{NaOOC(CH}_2)_8\ \text{COOCaOOC}\sim\!\sim \quad (6)$$

$$\sim\!\sim\text{COOCaOOC}\sim\!\sim + \text{HOOC(CH}_2)_8\text{COOH} \rightleftharpoons \sim\!\sim\text{COOH} + \text{HOOC(CH}_2)_8\ \text{COOCaOOC}\sim\!\sim \quad (7)$$

The effects of small additions of these chain modifiers on the melt flow of calcium sebacate are summarized in Table III. Form this it can be seen that the calcium hydroxide and calcium chloride have essentially no effect on the melt flow, whereas sodium chloride, sodium sebacate and sebasic acid markedly increase the melt flow. Most likely the —COOCaCl and —COOCaOH groups are highly reactive and the equilibria illustrated by eqs. (4) and (5) lie far to the left. This would also account for the sodium sebacate being about twice as effective a chain modifier as sodium chloride on a molar basis. In other words the ClCaOOC— groups formed from NaCl would tend to react with each other according to eq. (4).

Another implication of rapidly interchanging polymer chains is that the addition of a small amount of a branched-chain modifier should lead to a higher pressure sensitivity of the melt. This effect could actually be observed by the addition of a small amount of trimesic acid to a calcium sebacate melt. The results are summarized in Table IV.

TABLE III

Effect of "Monomers" on the Melt Flow of Calcium Sebacate

Additive	Concentration, mole/mole CaSeb	Melt flow, dg/min
None	—	0.88
$CaCl_2$	0.020	0.91
$Ca(OH)_2$	0.020	0.92
NaCl	0.026	1.10
Sodium sebacate	0.010	1.04
Sebacic acid	0.020	1.30

TABLE IV

Effect of Branching on Melt Flow and Pressure Sensitivity of Calcium Sebacate

Material	Melt flow, dg/min		Pressure sensitivity factor (*P*)[a]
	325 g wt	2150 g wt	
Calcium sebacate	0.88	8.57	1.47
Calcium sebacate + 1.92×10^{-2} mole fraction trimesic acid	1.10	14.44	1.98

[a] $P = 2150\text{ g MF}/6.62 \times 325\text{ g MF}$.

It is also of interest that the trimesic acid is less effective than the sebacic acid in increasing the melt flow at the same molar concentration. Presumably the branching resulting from the trimesic acid tends to offset the higher melt flow expected on the basis of chain termination.

These data indicate that, in the melt, polymeric molecules exist, and that there is a rapid equilibrium interchange between the metal carboxylate groups. Thus, the polymer chains are present on a time-average basis and cannot be thought of in terms of discrete polymer molecules with ionic endgroups. The average molecular weight in the melt could then be expressed in terms of an association or dissociation constant. It would be expected that this constant would be a function of temperature and at higher temperatures there would be a lower time average molecular weight.

Molecular Weight

The sharp change in melt flow with certain chain modifiers provided a novel method for obtaining at least a first approximation of the time average molecular weight. The relationship between viscosity and molecular weight of a polymer can be described by the equation:

$$\log \eta = 3.4 \log Zw + K \tag{8}$$

Since melt flow (MF) is inversely proportional to the viscosity, this equation may be restated:

$$\log \mathrm{MF} = 3.4 \log M_{\mathrm{e}}/M_{\mathrm{p}} + K' \tag{9}$$

where M_{e} denotes moles of endgroups and M_{p} is moles of polymer repeat units. Expressing the molecular weight in terms of endgroups gives a number-average molecular weight, and this is approximately equal to Zw, especially if there is a normal distribution as might be expected for an equilibrium reaction.

The ionic endgroups in pure metal carboxylate are the result of an equilibrium dissociation reaction, and their concentration may be expressed by a dissociation constant D:

$$D = (M_{\mathrm{e}}/M_{\mathrm{p}})^2 \tag{10}$$

or, the moles of ionic endgroups resulting from the dissociation can be expressed as:

$$M_{\mathrm{e}} = M_{\mathrm{p}} \sqrt{D} \tag{11}$$

When a small amount of chain modifier capable of interchanging with the metal carboxylate group, as indicated in eqs. (3)–(7), is added to the metal carboxylate, the concentration of endgroups is increased by an amount proportional to the concentration of the chain modifier. Thus, eq. (9) may be rewritten:

$$\log \mathrm{MF} = 3.4 \log [(M_{\mathrm{p}}\sqrt{D} + K''M_{\mathrm{m}})/M_{\mathrm{p}}] + K' \tag{12}$$

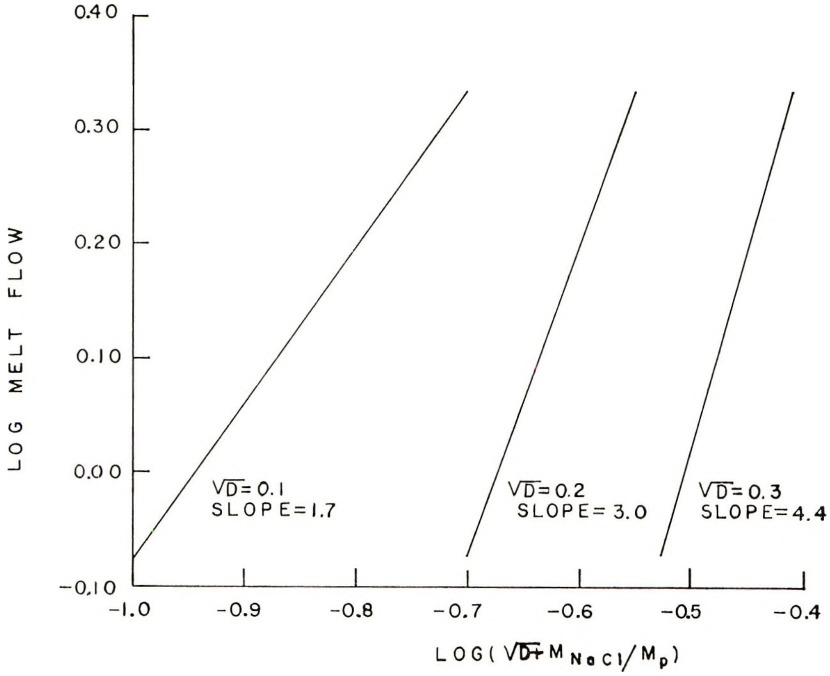

Fig. 5. Effect of sodium chloride concentration on the melt flow of calcium sebacate assuming various values for the dissociation constant of calcium sebacate.

where M_m is the moles of chain modifier. If, as is postulated in the case of sodium chloride with calcium sebacate, the interchange equilibrium of eq. (3) lies far to the right and that of eq. (4) far to the left, K'' becomes essentially equal to unity. This simplication of eq. (12) allows the determination of D for calcium sebacate by determining the melt flow of calcium sebacate containing various quantities of sodium chloride. The value of D which yields a slope of 3.4 for a plot of log MF versus log $[\sqrt{D} + (M_{\mathrm{NaCl}}/M_p)]$ was determined, and the results are summarized in Table V. Plots of log MF versus log $[\sqrt{D} + (M_{\mathrm{NaCl}}/M_p)]$ for various values of $\sqrt{D}$ are given in Figure 5. From these data it can be seen that the $\sqrt{D}$ equals approximately 0.2 (slope = 3.0) for calcium sebacate. Thus on a time-average basis, the calcium sebacate consists of approximately ten repeat units or has a time-average molecular weight of 2,000 at 386°C.

TABLE V
Effect of Sodium Chloride on the Melt Flow of Calcium Sebacate

$M_{\mathrm{NaCl}}/M_p \times 10^2$	Melt flow (MF), dg/min	log MF
0	0.85	−0.071
2.16	1.1	0.041
4.57	1.6	0.20
10.74	2.2	0.34

Similar data are given for the sodium sebacate–calcium sebacate system in Table VI and Figure 6. In this case the equilibrium shown by eq. (6) is assumed to proceed completely to the right, and each mole of sodium sebacate is twice as effective as sodium chloride. Again the data indicate a value of approximately 0.2 for $\sqrt{D}$ (slope = 3.5) and a time-average molecular weight of approximately 2000. Also, these results are comparable to the value of approximately 25 repeat units reported by Cowan and Teeter[1] for zinc dimerate in pyridine and obtained by extrapolating the viscosity of dilute solution to a high concentration.

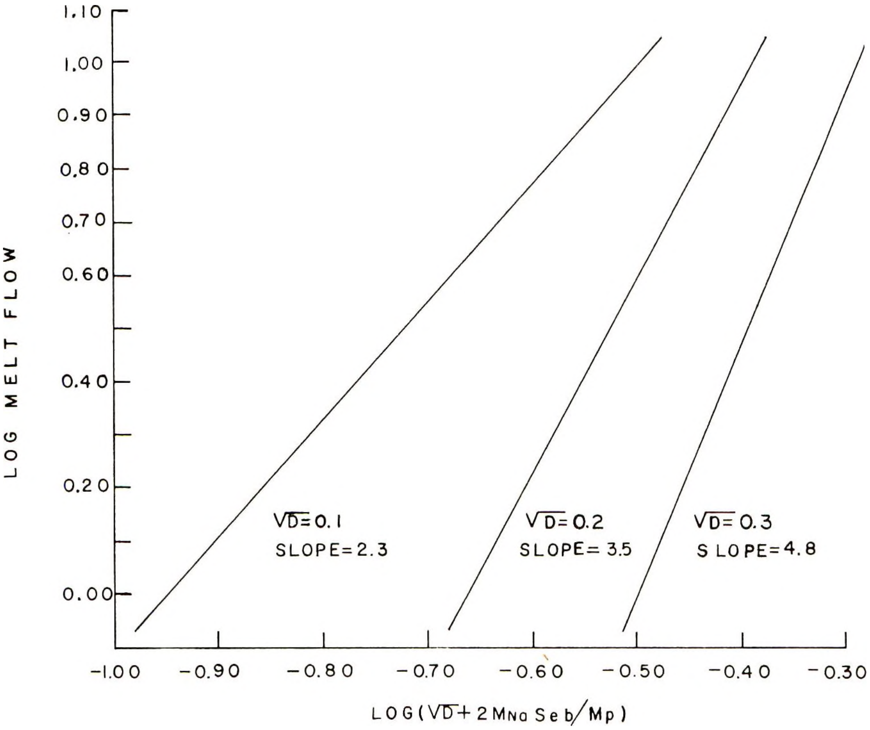

Fig. 6. Effect of sodium sebacate concentration on the melt flow of calcium sebacate assuming various values for the dissociation constant of calcium sebacate.

TABLE VI
Effect of Sodium Sebacate on the Melt Flow of Calcium Sebacate

$M_{NaSeb}/M_p \times 10^2$	Melt flow (MF), dg/min	log MF
0	0.85	−0.071
1.015	1.0	0.000
5.268	3.1	0.491
10.030	8.5	0.929
11.120	16.4	1.046

Structure

Polymeric association through the metal carboxylate bond could conceivably occur along the carboxylic acid chains or directly between two metal carboxylate groups as illustrated in Figures 7*A* and 7*B*, respectively. If the primary association is directly between metal carboxylate bonds as illustrated by Figure 7*B*, the melt flow of a monobasic metal carboxylate such as calcium dodecanoate should be sensitive to the addition of chain modifiers such as sodium chloride. That this is not the case is demonstrated by the melt flow data in Table VII. However, a pressure-sensitivity factor which decreases from 2.21 at 205°C to 1.49 to 213°C suggests there may be minor association in this direction which becomes increasingly important at lower temperatures. It is this type of secondary association that would account for the localized degree of order suggested by the DTA data.

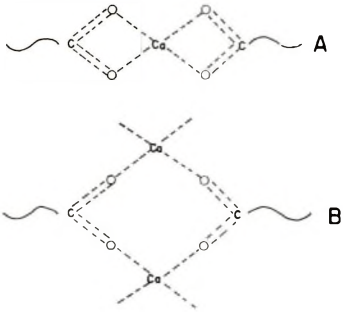

Fig. 7. Schematic diagram of two types of association possible in halatopolymers.

TABLE VII
Melt Flow of Calcium Decanoate

$M_{\mathrm{NaCl}}/M_{\mathrm{CaDec}}$	Temp, °C	Pressure	Melt flow, dg/min
0	205	1 *P* (325 g)	1.63
1.26×10^{-2}	''	''	1.66
2.62×10^{-2}	''	''	1.59

CONCLUSIONS

This work has shown that the metal dicarboxylates can exist either as salts or as amorphous, polymerlike structures, depending on the method of preparation. Fusion of the salts yields a highly viscous melt. The change from a salt to a polymerlike structure appears to be novel and has been termed a halatopolymeric transformation [from the Greek word (*halas*, *halatos*) meaning salt]. Halatopolymers are unique in that they have no endgroups in the traditional sense. In the melt, halatopolymers undergo a rapid equilibrium association. Polymer molecules of finite length are present on a time average basis and molecular weight in the melt should be thought of in terms of an association or dissociation constant.

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Hydrocarbon Ladder Aromatics from a Diels-Alder Reaction*

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Synopsis

The Diels-Alder homopolycycloaddition of 2,5-diphenyl-3,4-(5,6-acenaphthylenylene)-cyclopentadienone (VIII) affords a low molecular weight soluble ladder polymer having reduced specific viscosities between 0.17 and 0.25 dl/g in benzene and an insoluble fraction of higher molecular weight. The ladder polymers exhibited a major TGA break at 450°C in an air atmosphere and lost approximately 30% of their weight at 700°C in a nitrogen atmosphere.

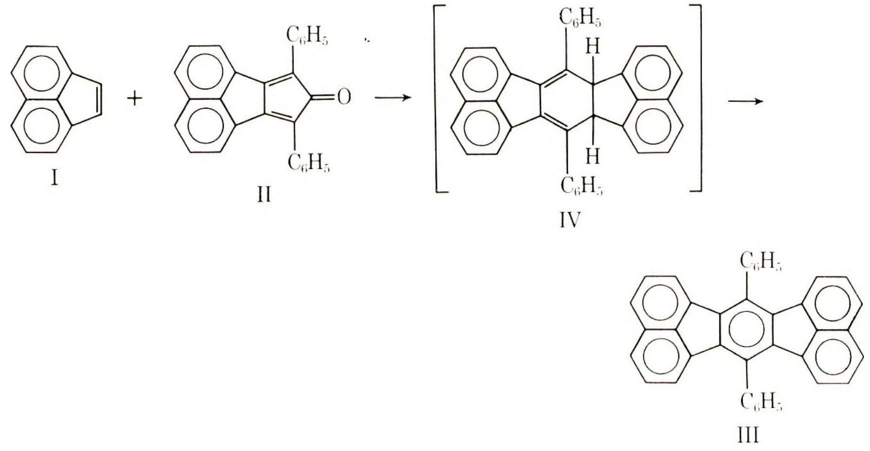
INTRODUCTION

Ladder polymers have been shown to possess enhanced thermal stability over polymers of similar structure but having a single-stranded structure.[1] The enhanced thermal stability is much more obvious in an inert atmosphere than in an oxidizing atmosphere. Many of the synthetic ladder polymers, however, are either insoluble or have limited solubility in selected solvents, either because of the rigidity inherent in their structures and/or because a certain amount of crosslinks formed during their synthesis by an imperfect polymerization reaction.

The Diels-Alder step-growth reaction of bisdiacetylenes and either biscyclopentadienones[2-6] or bispyrones[2,7] has been successfully utilized in the synthesis of several phenylated polyphenylenes. The yields of white, amorphous polyphenylenes were nearly quantitative, and the polymers were readily soluble in common organic solvents such as benzene, toluene, and chloroform. This high degree of solubility has been attributed to the presence of the pendent phenyl groups.[8]

The Diels-Alder reaction of acenaphthylene (I) with 2,5-diphenyl-3,4-(1,8-naphthylene)cyclopentadienone (II) yields 2,5-diphenyl-3,4,1,6-bis-(1,8-naphthylene)benzene (III).[9] The reaction occurs with the loss of both carbon monoxide and hydrogen, and presumably proceeds through the dihydrobenzene intermediate IV. The ladderlike structure of the product III and the previous success of the Diels-Alder reaction in the synthesis of soluble, totally aromatic polymers made the synthesis of ladder polymers with this structure a significant endeavor.

* In honor of C. S. Marvel on the occasion of his 75th birthday.

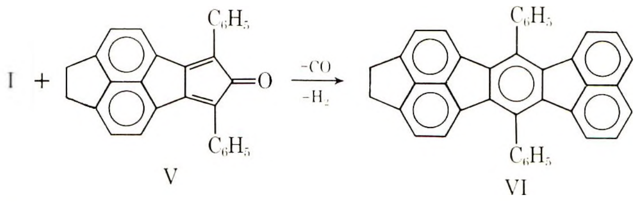


RESULTS AND DISCUSSION

Model Reactions

The Diels-Alder cycloaddition reaction of I with II served as the principal model reaction for the preparation of the ladder-type polymers. In this reaction the intermediate dihydrobenzene adduct IV was not isolated but lost hydrogen under the reaction conditions to afford the totally aromatic product. The original reaction[9] had been carried out in the melt, but for the polymerizations it was desirable that the reaction be carried out in solution. Since the reactants were soluble in aromatic solvents, the model compound studies were performed in benzene, toluene, and chlorobenzene. Benzene and toluene were found to be satisfactory solvents for the reaction in sealed tubes giving high yields of the model compound, while refluxing chlorobenzene gave considerable amounts of charred material and subsequently low yields of product III. Isolation of the dihydrobenzene intermediate IV by carrying out the reaction at lower reaction temperatures was not accomplished.

The reaction of acenaphthylene (I) with 2,5-diphenyl-3,4-(5,6-acenaphthenylene)cyclopentadienone (V) gave the polynuclear aromatic hydrocarbon, 2,5-diphenyl-3,4-(1,8-naphthylene)-1,6-[5,6-acenaphthenylene]-benzene(VI).



Both model compounds III and VI were high-melting (>350°C) yellow solids having good solubility in such solvents as benzene, toluene, chloroform, carbon tetrachloride, and hexane. Their infrared spectra revealed

TABLE I
Ultraviolet-Visible Spectra of the Model Compounds[a]

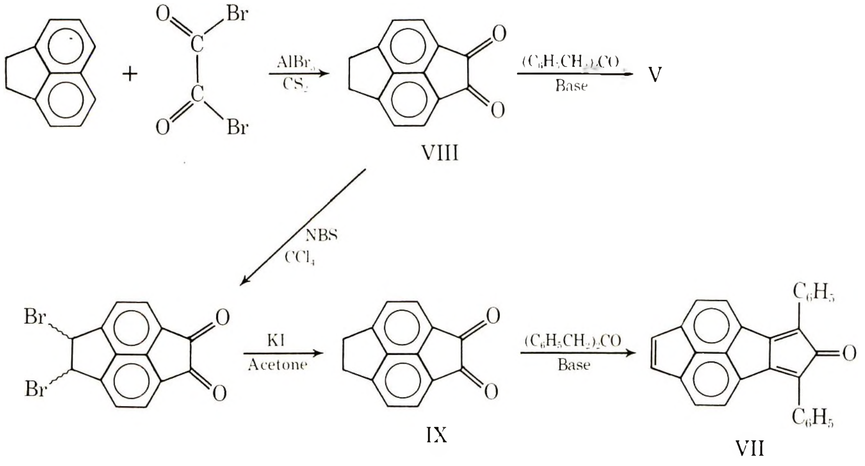
Compound	λ, mμ	ε, l./mole-cm
III	425	1.77×10^4
	400 (shoulder)	1.35×10^4
	390 (shoulder)	8.8×10^3
	338	1.09×10^4
	310	4.79×10^4
VI	443	2.63×10^4
	417	2.29×10^4
	400 (shoulder)	1.17×10^4
	340	1.35×10^4
	314	6.16×10^4

[a] Spectra were all taken in benzene on a Cary 14 spectrophotometer.

the loss of carbonyl and the presence of the characteristic aromatic hydrogens. The ultraviolet-visible spectra of the model compounds are summarized in Table I.

Monomer Synthesis

Diels-Alder polymerizations may be performed by using two monomers, one consisting of a bisdiene and the other consisting of a bisdienophile (A-A + B-B monomers) or with a single monomer incorporating the diene and the dienophile into the same molecule (A-B monomer). In order to obtain ultimate monomer balance the synthesis of the A-B monomer, 2,5-diphenyl-3,4-(5,6-acenaphthylenylene)cyclopentadienone (VII) was undertaken. The cyclization reaction of pyracyloquinone (IX) with dibenzyl ketone afforded the A-B monomer VII in a 70% yield. The physical properties of the two tetracyclones V and VII are compared with those of the known 2,5-diphenyl-3,4-(1,8-naphthalene)cyclopentadienone (II) in Table II.



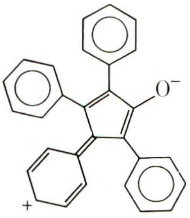
The characteristic carbonyl absorption for tetracyclones in the infrared region is in the range 5.85–5.95 μ.[11] The fused-ring tetracyclones II and V are shown to absorb at the same frequency (5.85 μ), while the fused-ring tetracyclone VII has an absorption which is shifted to a slightly higher frequency (5.92 μ). This shift can be attributed to a weak conjugative effect similar to that observed in the tetraphenylcyclopentadienone series containing *para* substituents on the 3,4-phenyl groups.[12]

TABLE II
Physical Properties of Fused-Ring Tetracyclones

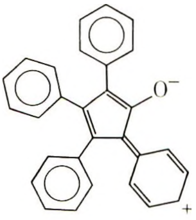
	II	V	VII
Melting point, °C	290–291	245–247	>400
Infrared carbonyl absorption frequency, μ	5.85	5.85	5.92
Ultraviolet visible spectrum[a] [λ, mμ and (ε)]	588(1,230)	580(1,050)	615(7,500) shoulder
	370(9,580) shoulder	360(10,500)	390(33,000) shoulder
	333(15,400)	333(16,800)	384(34,000)

[a] Benzene solvent on a Cary 14 spectrophotometer.

The values for the ultraviolet visible absorptions of the fused-ring tetracyclones II and V are quie similar, as expected, since the basic structures are the same, and *para* alkyl substitution has little affect on the ultraviolet-visible transitions.[11] These values are also close to the reported values for II.[11] The ultraviolet-visible spectrum of the fused-ring tetracyclone VII is somewhat different from those of II and V, but this difference can be rationalized in terms of studies on the parent compound, tetraphenylcyclopentadienone.[11] The shorter wavelength absorptions (~340 mμ) have been shown to result from excited states of the type Xa; electron-releasing substitutents in the *para* position of the 3-phenyl group produce a bathochromic shift with an accompanying hyperchromic shift. Values as high as 428 mμ have been reported for this absorption band.[13] The longer wave length band has been related to structure Xb and attributed to an $n \rightarrow \pi^*$ transition in a molecular orbital involving oxygen.[12] Since $n \rightarrow \pi^*$ transitions are known to be affected by increased conjugation it would be expected that the incorporation of the new double bond to produce VII would produce the observed bathochromic shift in the longer-wavelength band.



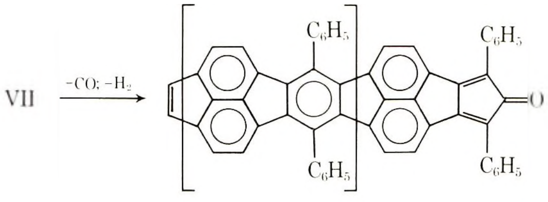
Xa



Xb

Polymers

Ladder polymers having varying molecular weights have been obtained by the Diels-Alder polycycloaddition of 2,5-diphenyl-3,4-(5,6-acenaphthylenylene)cyclopentadienone (VII) in several solvents. The polymers, which could be precipitated nearly quantitatively in *n*-hexane, were extracted with refluxing benzene for 24 hr to obtain the soluble fractions. The properties of the polymers are summarized in Table III. The benzene-soluble portions were 20–60% of the total polymer yield. The benzene solutions, which consisted of low molecular weight material, were red and gave characteristic visible spectra (Fig. 1). Comparison with the visible spectra of the model compounds and the monomer reveals a distinct bathochromic shift. A similarity exists in the relative absorbances of the characteristic double maxima at longer wave lengths and in the separation of these maxima (25–35 mμ) in both the polymers and the model compounds. The infrared spectra of the insoluble portion of the polymers show a decrease in the intensity of the aromatic double bond absorption at 6.24 μ which is very strong in the model compounds. The presence of the carbonyl absorption in the infrared suggests that the polymerization is incomplete, giving rise to the tetracyclone end groups.



XI

TABLE III

Polymerization Conditions and Properties of Ladder polymers

Solvent	Concentration, %	Time, hr	Temperature, °C	Yield, %[a]	Benzene-solubles, %	η_{sp}/c, dl/g (concn, g/100 ml)[b]
1,2,4-Trichlorobenzene[c]	0.5	48	216(reflux)	123[d]	54	0.17(0.231)
Nitrobenzene	1	24	210(reflux)	82	30	0.25(0.112)[e]
α-Chloronaphthalene	5	48	200	88	—[f]	0.18(0.231)
Toluene	5	42	200–250	85	24	0.21(0.428)

[a] Precipitated from *n*-hexane.

[b] Soluble portion of polymer in benzene. Compare to monomer η_{sp}/c of 0.03 dl/g (0.060 g/100 ml).

[c] Catalyzed by aluminum chloride.

[d] Contains residual catalyst.

[e] $\bar{M}_n$ = 1010 (vapor pressure osmometer).

[f] Not determined.

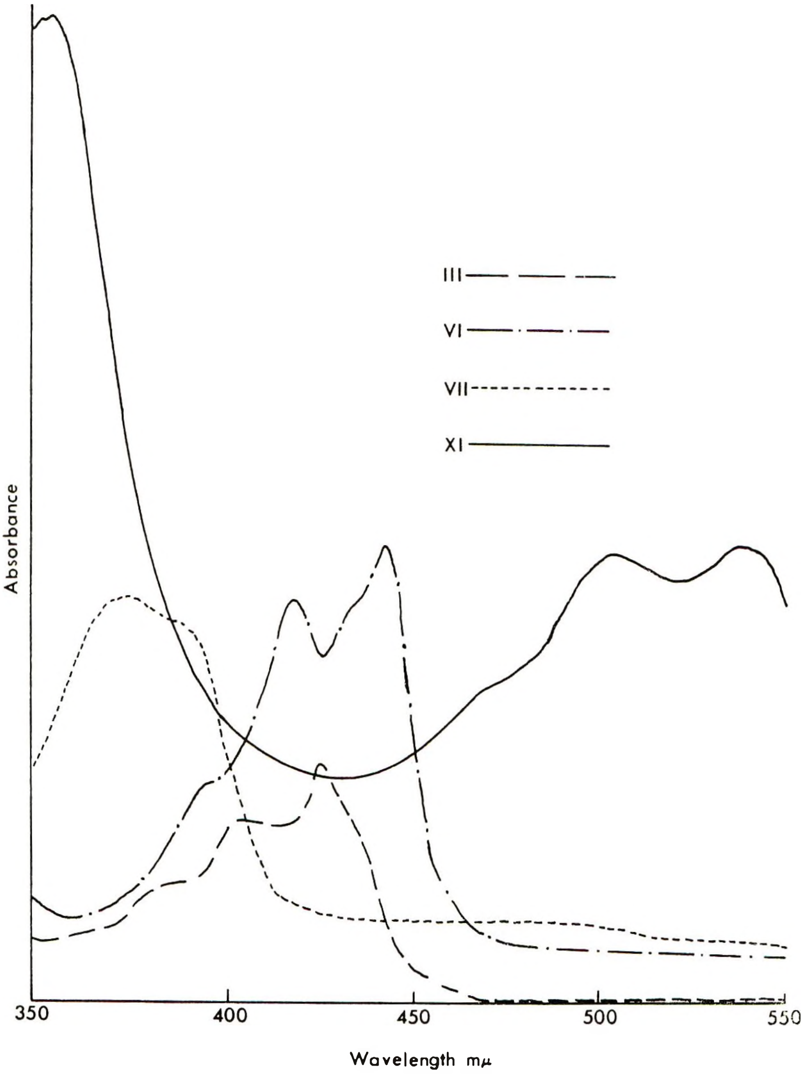


Fig. 1. Visible spectra of polymer, monomer, and model compounds.

The incomplete solubility of the polymers may be attributed either to the formation of high molecular weight materials or crosslinking. The reduced specific viscosities taken on the benzene soluble portion of the polymer range from 0.17 dl/g to 0.25 dl/g compared to a value of 0.03 dl/g for a solution of the monomer. The 0.25 viscosity corresponds to a number average molecular weight of 1010.

The thermal stability of the polymer (Fig. 2) was investigated in both air and nitrogen atmospheres. Although the polymers show good thermal stability in nitrogen it was surprising to note the major TGA break at 450°C in air. A thermogram of the monomer VII shows a sharp break at 225–

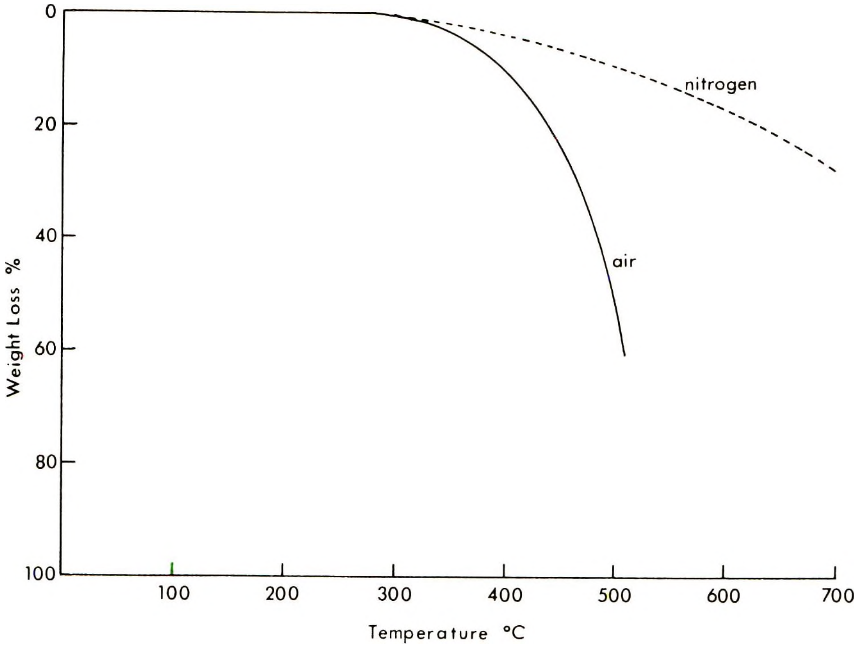


Fig. 2. Thermal gravimetric analysis of the Diel-Alder ladder polymer.

250°C, which corresponds to the loss of carbon monoxide. The low thermal stability in air may be a result of oxidation of the ladder at the end containing the cyclopentadienone moiety and subsequent oxidation down the chain.

EXPERIMENTAL

Materials

Acenaphthylene (K and K laboratories) was sublimed prior to use. 2,5-Diphenyl-3,4-(1,8-naphthalene)cyclopentadienone was prepared as described.[14]

1,2-Diketopyracene (VIII).[10] A solution of 5 g (0.037 mole) of freshly sublimed acenaphthene in 100 ml of dry carbon disulfide was prepared under nitrogen. After cooling the solution to −10°C, 10.8 g (0.05 mole) of oxalyl bromide in 40 ml of dry carbon disulfide was added. Freshly sublimed aluminum bromide (16 g, 0.06 mole) was added to the stirred reaction mixture over a period of 30–40 min, during which time the temperature was maintained between −15°C and −10°C. A black gum formed, and stirring became impossible. The mixture was allowed to warm slowly to room temperature and stand overnight, still under nitrogen. At the end of this time, the mixture was heated to the reflux temperature in a water bath for 1 hr and after it cooled to room temperature the carbon disulfide was decanted. The black residue was treated with 150 ml of 3*N* hydrochloric acid and stirred until there was no evolution of hydrogen bromide gas.

The dark-brown solid was filtered and washed thoroughly with water. The solid was suspended in 500 ml of 10% aqueous sodium bisulfite at 80°C for 2 hr and filtered hot. The filtrate was heated to 80°C and concentrated hydrochloric acid was added until the evolution of sulfur dioxide ceased. A fluffy yellow precipitate formed. The mixture was stirred at 80°C for an additional 30 min, cooled, and filtered. This sodium bisulfite extraction procedure was repeated five times on the dark-brown reaction residue to yield a total of 3.05 g (45%) of yellow solid melting at 282–292°C(dec).

2,5-Diphenyl-3,4-(5,6-acenaphthenylene)cyclopentadienone (V). A mixture of 0.6 g (2.89 mmole) of 1,2-diketopyracene and 1.0 g (4.8 mmole) of dibenzylketone in 20 ml of triethylene glycol was heated to 100°C, and 1 ml of a 40% solution of benzyltrimethylammonium hydroxide in methanol was added. The mixture immediately turned black. The mixture was heated an additional 10 min at 100°C and then was cooled to 60°C. Methanol (20 ml) was added, and the mixture was cooled to 0°C in an ice bath and filtered. The product was isolated by filtration and washed several times with cold methanol until the filtrate was clear to give 0.8 g (73%) of product melting at 240–245°C. An analytical sample was recrystallized from benzene:ethanol (5:3), mp 245–247°C.

ANAL. Calcd: C, 91.1%; H, 4.72%. Found: C, 90.8%; H, 4.63%.

5,6-Dibromo-1,2-diketopyracene.[10] A solution of 1 g (0.0048 mole) of 1,2-diketopyracene in 100 ml of carbon tetrachloride was heated to the reflux temperature for 30 min under nitrogen. *N*-Bromosuccinimide (2.60 g, 0.015 mole) and 100 mg of dibenzoyl peroxide were added to the hot solution and the mixture was heated at reflux for 5 hr. The mixture was filtered hot and the residue was washed with an additional 25 ml of hot carbon tetrachloride. The carbon tetrachloride was evaporated to yield a yellow solid. This solid was washed with methanol and then recrystallized from carbon tetrachloride to yield 0.6 g (35%) of product, mp 189–193°C (dec).

Pyracyloquinone (IX).[10] In a nitrogen atmosphere, 1.2 g (0.0033 mole) of 5,6-dibromo-1,2-diketopyracene dissolved in 90 ml of acetone was treated with 7.5 g (0.045 mole) of anhydrous potassium iodide. After the reaction mixture was heated to the reflux temperature for 20 hr it was allowed to cool to room temperature and was then poured into a cooled aqueous sodium thiosulfate solution. The aqueous mixture was extracted with chloroform. Evaporation of the chloroform layer produced a red solid. Recrystallization from ethanol gave 0.6 g (88%) of a dark red solid, mp >400°C. This material was sublimed (150°C/0.5 mm) to yield an orange solid, mp >400°C.

2,5-Diphenyl-3,4-(5,6-acenaphthylenyl)cyclopentadienone (VII). A mixture of 0.2315 (1.1 mmole) of pyracyloquinone and 0.2315 g (1.1 mmole) of dibenzylketone in 8 ml of triethylene glycol was heated to 100°C under a nitrogen atmosphere. When the solution was complete, 0.3 ml of a 40% solution of benzyltrimethylammonium hydroxide was added, and the solution turned black. Heating was continued for an additional 10 min, the mixture was cooled to 60°C and 20 ml of methanol was added. The mixture was cooled to 0°C; the solid was isolated by filtration and was washed several times with cold methanol to give 0.3000 g (70%) of product. An analytical sample was recrystallized from benzene:ethanol (7:3).

ANAL. Calcd: C, 91.5%; H, 4.25%. Found: C, 90.6%; H, 4.35%.

2,5-Diphenyl-3,4,1,6-bis(1,8-naphthylene)benzene (III). A mixture of 0.3958 g (1.11 mmole) of 2,5-diphenyl-3,4-(1,8-naphthylene)cyclopentadienone and 0.1690 g (1.11 mmole) of acenaphthylene in 7.5 ml of reagent grade benzene was sealed in a 25-ml polymerization ampoule after three freeze-thaw cycles at liquid nitrogen temperatures, placed in a Paar pressure reactor, and heated to 180°C for 48 hr. The material was then chromatographed on Woelm neutral alumina using benzene as an eluent to give a yellow solid, 0.3592 g (68%), mp >400°C.

2,5 - Diphenyl - 3,4 - (1,8 - naphthylene) - 1,6 - (5,6 - acenaphthenylene) - benzene (VI). A mixture of 0.2410 g (0.63 mmole) of 2,5-diphenyl-3,4-(5,6-acenaphthenylene)cyclopentadienone and 0.0961 g (0.63 mmole) of acenaphthylene in 3.5 ml of reagent grade benzene was sealed in a 25-ml polymerization ampoule after three freeze-thaw cycles at liquid nitrogen temperatures, and was heated to 230°C for 16 hr. The benzene was removed under reduced pressure and the resultant red oil was chromatographed on Woelm neutral alumina with benzene as an eluent. The yield of yellow solid was 0.220 g (68%), mp >350°C. An analytical sample was rechromatographed under the same conditions.

ANAL. Calcd: C, 95.3%; H, 4.78%. Found: C, 95.8%; H, 5.05%.

The reaction of I with V was carried out at the reflux temperature of chlorobenzene to give approximately a 30% yield of VI plus a considerable amount of charred material. The reaction of I with II to yield III was carried out at varying temperatures for varying times (Table IV).

TABLE IV
Effect of Reaction Temperature on the Preparation of 2,5-Diphenyl-3,4,1,6-bis(1,8-naphthylene)benzene

Reaction temperature, °C	Reaction time, hr	Yield, %
230	24	61
180	48	68
140	60	80
100	96	93

Polymers

The polymerizations were carried out in various solvents at concentrations of 0.5–5.0%. At the termination of the polymerization, the product was precipitated in *n*-hexane, filtered, and washed several times with *n*-hexane. The polymeric materials were then extracted with refluxing benzene in a Soxhlet for 24 hr. The polymerization conditions, yields, and ultraviolet-visible spectra of the benzene soluble fraction are summarized in Table III. In one case, aluminum chloride was used as a catalyst and was removed by extraction in a Soxhlet with refluxing ethanol.

ANAL. Calcd: C, 95.96%; H, 4.04%. Found: C, 93.03%; H, 4.81%.

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Telomerization by Free-Radical Mercaptan Chain Transfer. IV. Effects of Structure, Solvent and Initiator Variation on the Stereochemistry of Acrylate Ester–Mercaptan Telomers*

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Synopsis

Chain-transfer constants for radicals one to five units in length were determined for the methyl acrylate–isopropanethiol system. Effects of varying ester alkyl group, mercaptan solvent and initiator on three-unit diastereomer ratio were also investigated. It was found that the proportion of syndiotactic isomer increased as the size of either the ester alkyl group or the mercaptan increased, the latter result being equivalent to a penultimate effect. Polar solvents, on the other hand, favored the formation of the isotactic form. This effect was observed in the free-radical telomerization and to an even greater degree in the base-initiated anionic telomerization. Possible reasons for solvent effects are discussed.

INTRODUCTION

Recent studies reported from this laboratory[1] showed that chain-transfer constants of methyl acrylate with ethanethiol for radicals two to five units in length were constant and equal to values for long chains. It was therefore concluded that mercaptan telomerization processes were good models for studying individual steps in polymerization. Since it was found possible to separate the two three-unit diastereomers by gas chromatography, it was decided to investigate effects on mole ratio produced by varying reactant structures, solvents, and other factors which might influence stereospecificity of acrylate ester addition to two-unit radicals. In this way the simplest appropriate systems available could be studied.

Information on stereospecificity in polymerization has been much more limited for acrylates than for methacrylates, owing to the greater complexity of acrylate NMR spectra. Analysis of tacticity sequences in polymethacrylates by quantitative measurement of methyl and methylene proton bands has led to a number of interesting conclusions regarding factors controlling monomer addition.[2] In the case of methyl methacrylate syn-

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

diotactic placement is favored, especially at low temperature. This is not unexpected, owing to the obviously greater crowding of bulky ester groups in the isotactic configuration, which presumably exists, not only in the final polymer, but in the transition state for addition of each next unit. However, rather surprisingly, it has been reported that still bulkier ester groups give rise to more random, less syndiotactic addition rather than the reverse.[3] This has been explained by the proposal that an energy barrier exists to the rotation of substituents on the end of the radical, such rotation being necessary for a shift from the initial random conformation distribution to one which is predominantly syndiotactic. In the case of radicals bearing larger ester groups, addition of the next unit presumably tends to occur before rotation. In acrylate esters, which lack the α-methyl group, no such situation is to be expected, and some evidence for a greater degree of syndiotactic orientation with bulkier ester groups has been reported.[2]

Our initial investigation[1] of the three-unit diastereomer ratio in the methyl acrylate–ethanethiol system showed it to be almost one-to-one and unaffected by changes in mercaptan-to-monomer ratio and temperature. Such a result indicates equal activation energies and nearly equal activation entropies for both addition paths. It is also consistent with conclusions reported elsewhere[4] that the stereochemistry of free-radical addition involves no penultimate effect, ie, it is influenced only by the configuration of the last asymmetric center in the radical chain. However the failure to observe changes in diastereomer ratio under the conditions tested is no substantial positive indication that such effect can not occur. This report describes an extension of these studies to systems involving bulkier ester groups and bulkier mercaptans to test the limits of influence of nearby structures on addition steps.

Owing to their potential value in controlling the outcome of reactions, solvent effects have always been considered of interest. In 1958 Szwarc[5] proposed that variation of solvent might be made to control stereoregularity of products even in free radical polymerizations. He suggested that a *poor solvent* might have the effect of forcing a growing radical into a regular conformation such as the helical form. Once this started, the free energy of activation of addition of monomer molecules in the orientation required to continue the helix might be substantially less than for the opposite one. Thus far, poor solvents have not been shown to have any clear-cut effect on stereoregularity in free-radical systems,[6] although tacticity effects have been claimed in butyraldehyde and in solutions containing metal ions.[2] In the event that a radical chain is not linearly crystalized as it forms in the manner conceived by Szwarc, it is to be expected that it may collapse randomly around the growing end, thereby providing some of its own environment for monomer addition in a poor solvent. It would seem that such effects as a solvent can exert on an addition step might be most readily observed in a situation such as this involving very small radicals. Experiments undertaken to investigate such effects are also reported here.

EXPERIMENTAL

Telomers were prepared, purified, and characterized by procedures previously described,[1,7] their identity being confirmed by infrared and NMR spectra. Quantitative measurements were made on reaction mixtures formed by heating reactants in acid-washed Pyrex tubes sealed under nitrogen. Chromatograms were obtained either directly from reaction mixtures or from mixtures partially stripped of reactants by vacuum evaporation. Mole ratios of telomers were calculated from area ratios by a Disc Chart integrator, Model 204, on the basis of calibration using pure telomers as standards. Nmr spectra were checked on a Varian A60A spectrometer. Infrared spectra were run on a Perkin-Elmer 237B spectrometer.

Reaction mixtures for chain-transfer constant data were run without initiator for periods of about 1 hr at 60°C giving 1–3% conversion. Mixtures prepared for measuring three-unit diastereomer ratios were run with the use of about 0.005 g of azobisisobutyronitrile (AIBN) initiator and heating at 60°C for 3–5 hr periods except as otherwise noted. For chain-transfer constant data, chromatograms were run by use of a 1.5-ft × 0.25 in. column filled with 10% SE 52 phenyl silicone on Gaschrom Z at temperatures progressively varied from 100 to 300°C. For measurement of three-unit diastereomer ratios, a 4-ft column filled with 5% butanediol succinate on Gaschrom Z was used at 180–190°C. Mole ratios of diastereomers were calculated by least-squares computer simulation based on summation of two overlapping Gaussian type functions using an IBM 360-30 computer as described previously.[1]

RESULTS AND DISCUSSION

Chain transfer constant data for the methyl acrylate–isopropanethiol system are plotted in Figure 1. The resulting constants C_1–C_6 and ranges of probable error calculated as described[1] are summarized in Table I. Values for these constants indicate lower reactivity for the secondary mercaptan than in the methyl acrylate–ethanethiol system, but the same pat-

TABLE I
Chain-Transfer Constant Data on Methyl Acrylate–Isopropanethiol Telomerization at 60°C

Constant	Value from slope[a]	Estimated error[b]	Value from slope/intercept[a]	Estimated error[b]
C_1	0.544	±0.078		
C_2	0.668	±0.073	0.636	±0.154
C_3	0.700	±0.083	0.570	±0.112
C_4	0.656	±0.084	0.595	±0.110
C_6			0.563	±0.111

[a] Values are based on least-squares calculation assuming linearity.

[b] At 5% probability level.

tern of essential constancy for radicals two units and longer holds here also. Evidently, special endgroup effects are absent, and this system is likewise suitable for model reaction studies. Similar complete determinations have not been made on other systems discussed below, but there seems to be no reason to expect irregular variations of overall reactivity with chain length.

TABLE II
Three-unit Telomer Diastereomer Mole Fractions for the Methyl Acrylate–Isopropanethiol System

Run no.	Mercaptan/monomer mole ratio	Temperature, °C	Product mole fractions[a]			
			A		B	
1A	0.318	60	0.547	0.561	0.453	0.439
1B			0.576		0.424	
2A	0.955	60	0.559	0.575	0.441	0.425
2B			0.592		0.408	
3A	1.805	60	0.590	0.576	0.410	0.424
3B			0.563		0.437	
4A	2.862	60	0.554	0.557	0.446	0.443
4B			0.560		0.440	
5A	0.955	90	0.567	0.561	0.433	0.439
5B			0.554		0.446	

[a] Diastereomers are designated A and B in order of the elution as shown on the chromatogram. The second column for each set gives the average of two runs under identical conditions.

TABLE III
Three-unit Telomer Diastereomer Mole Fractions for Various Acrylate Ester Mercaptan Systems at 60°C

Run no.	Acrylate ester	Mercaptan	Mercaptan/monomer mole ratio	Product mole fractions[a]	
				A	B
1	Methyl	Ethanethiol[b]	0.81	0.536	0.464
2	Methyl	Isopropanethiol	0.96	0.561	0.439
3	Methyl	2-Methyl-2-propanethiol (*tert*-butyl)	1.27	0.719	0.281
4	Ethyl	Isopropanethiol	1.16	0.740	0.260
5	Isopropyl	Isopropanethiol	1.29	0.776	0.224

[a] Diastereomers are designated A and B in order of the elution as shown on the chromatogram.

[b] Value from ref. 1.

Data on three-unit methyl acrylate-isopropanethiol diastereomer mole fractions formed from mixtures containing varying reactant ratios and at different temperatures are listed in Table II. Table III shows variation of the same quantity as a function of mercaptan structure and acrylate ester alkyl group.

The diastereomer eluted first had previously been assigned the syndiotactic configuration on the basis of its greater yield.[1] If it is assumed that this assignment is valid, Table III indicates the expected increase in mole fractions of syndiotactic products (column A) with increased bulkiness of the ester alkyl group. A similar increase occurs with the increase in the size of the mercaptan. The increase in going from ethanethiol to isopropanethiol is small but may be real in spite of the fact that Table II gives no indication of a penultimate effect. The very pronounced increase observable with *tert*-butyl mercaptan indicates very clearly that with this structure the limit of steric interference required for a clear-cut penultimate influence has been passed.

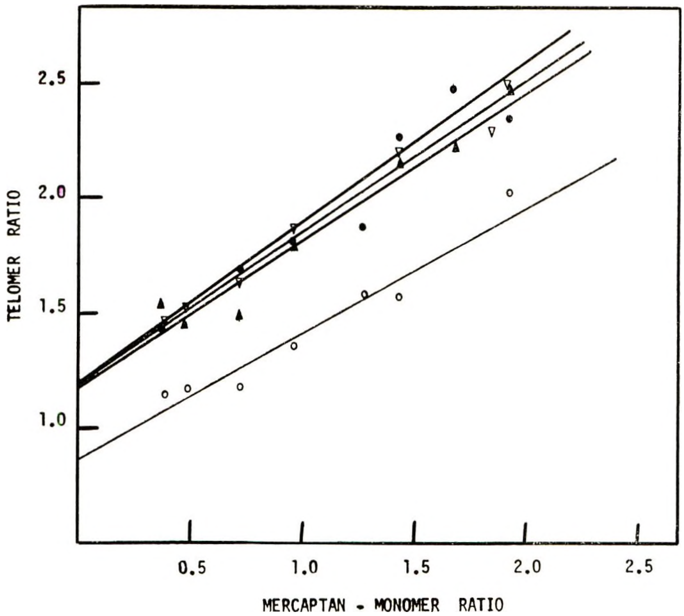


Fig. 1. Mole ratios of telomers $n/(n + 1)$ units as a function of mercaptan/monomer mole ratio at low conversion at 60°C: (○) $n = 1$; (▽) $n - 2$; (●) $n = 3$; (▲) $n = 4$.

Table IV shows the variation in methyl acrylate–isopropanethiol diastereomer mole fractions for reactions carried out in solvents of varying polarity. Typical chromatograms appear in Figure 2.

It is significant to note that increasing polarity of solvent clearly shifts the diastereomer ratio in favor of the isotactic configuration. The case of formamide, in which the isotactic form actually predominates, was found to be especially interesting. In addition to the usual telomers, three unidentified by-products were noted in the gas chromatograms of the product mixtures. These are formed by reaction of the monomer with formamide whether mercaptan is present or not, but they do not prevent the telomerization nor interfere with analysis of reaction mixtures. In preliminary

TABLE IV
Mole Fractions of Isopropanethiol–Methyl Acrylate Three-Unit Diastereomers Formed in Solvents of Varying Polarity with the Use of AIBN Initiator[a]

Run no.	Solvent	Dielectric constant	Monomer Concentration, g/100 g solvent	Product mole fractions[b]			
				A		B	
1A	Hexane	1.9	8.66	0.625	0.619	0.375	0.381
1B				0.649		0.351	
1C				0.584		0.416	
2A			4.02	0.615	0.609	0.385	0.391
2B				0.603		0.397	
3A			1.03	0.612	0.613	0.388	0.387
3B				0.614		0.386	
4A	Ethyl acetate	6.0	2.29	0.543	0.551	0.457	0.449
4B				0.558		0.442	
5	Dimethyl formamide	38	1.20	0.527		0.473	
6A	Dimethyl sulfoxide	45	2.00	0.495	0.501	0.505	0.499
6B				0.509		0.491	
7A	Formamide	109	1.12	0.443	0.429	0.557	0.571
7B				0.415		0.585	
8A	Formamide[c]	109	1.69	0.433	0.443	0.567	0.557
8B				0.446		0.554	
8C				0.450		0.550	

[a] Run at 60°C with a mercaptan/monomer mole ratio of 0.955 and 0.005 g AIBN/20 ml.

[b] Diastereomers are designated A and B in order of elution.

[c] No. 8 runs used double the specified amount of initiator.

experiments with formamide a much higher isotactic content than any reported in Table IV was noted. It was discovered, however that this was not the result of a free-radical reaction but was due to basic impurities in the formamide since this telomerization with impure formamide, unlike the others was not inhibited by hydroquinone but was prevented by purification of the solvent. As early as 1948 Kharasch and Fuchs[8] reported the formation of one-unit telomer of methyl acrylate by base-initiated reaction. However, lacking the tool of gas chromatography, they failed to detect any higher telomers and assumed that the chain transfer with the mercaptan was too rapid to allow any to form under these conditions. We have found, however, that higher telomers can form in various media presumably by anionic telomerization initiated by sodium mercaptide or even pyridine. Data on diastereomers observed in some of these reactions are reported in Table V (see also Fig. 2C).

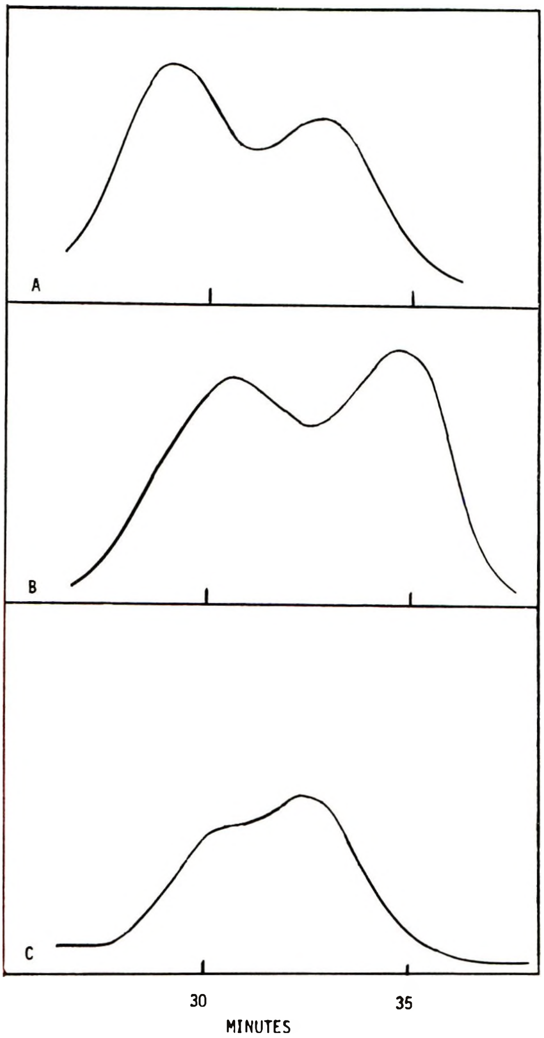


Fig. 2. Gas chromatograms of isopropanethiol–methyl acrylate three-unit diastereomers showing typical effects of solvent and initiator changes: (*A*) AIBN in hexane; (*B*) AIBN in dimethylformamide; (*C*) sodium mercaptide in formamide.

CONCLUSIONS

In spite of the fact that we still do not have independent confirmation of our previous assumption that the first-eluted diastereomer is always syndiotactic, this work seems to confirm the assignment. The results of structural variation of the monomer and mercaptan are difficult to explain on any other basis. It seems reasonable to suppose that the chromatographic column can be consistently selective in this way. Indeed analogous separations have been reported for a significant number of model compounds of proven structure,[9] and the diastereomer with syndiotactic structure is

TABLE V
Mole Fractions of Methyl Acrylate–Isopropanethiol Three-Unit Diastereomers Formed under Various Conditions with Basic Initiation[a]

Run no.	Solvent	Monomer concentration g/100 g solvent	Initiator	Product mole fractions A		Product mole fractions B	
1A	None		Pyridine[b]	0.525	0.525	0.475	0.475
1B				0.525		0.475	
2A	Dimethyl Sulfoxide	4.0	Pyridine[b]	0.418	0.429	0.582	0.571
				0.440		0.560	
3A	Formamide	4.2	Sodium mercaptide[c]	0.232	0.235	0.768	0.764
3B				0.239		0.761	

[a] Each run was carried out at 60°C at a mercaptan/monomer mole ratio of 0.955 in the presence of 0.01–0.02 g. of hydroquinone.

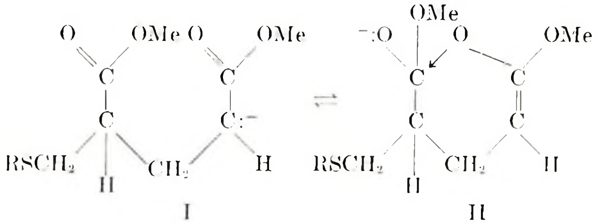
[b] Concentration, 10 μl/20 ml solvent.

[c] Mercaptide formed by adding 0.0042 NaH to the mercaptan.

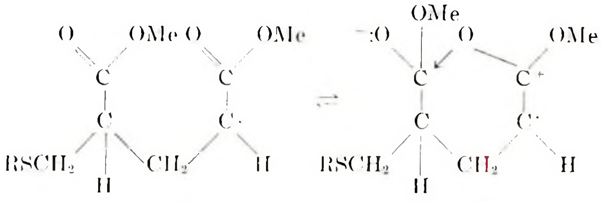
always slightly more volatile and first to elute. The straight-forward relationship between this ratio and the size of the ester group is consistent with what has been observed in polymers.[2] The penultimate effect of the *tert*-butyl thioalkyl group is less directly comparable to the polymer situation, but it suggests that such effects may be expected when substituent groups are of about this size.

Acceptance of this picture in turn leads to the conclusion that solvent polarity can control configuration in such a way that polar solvents tend to favor the isotactic form. This effect is strongest when the mechanism is anionic but is still very definitely operative in the free-radical case. Models show that such an influence can only function if the solvent somehow effectively facilitates attraction between the two ester groups. Although ester groups are somewhat polar and presumably can be mutually attractive when free to assume favorable positions, the well established polymerization behavior of methyl methacrylate shows that ester electron clouds must usually repel each other under the characteristic constraints involved in chain growth.

The data in Tables IV and V indicate that the stereochemical control involved here is probably a general effect of polar molecules rather than a geometrically selective process such as have been proposed in many cases where chelating metal ions are involved. Two possible mechanisms for such effects are suggested: (*1*) one or more polar solvent molecules may intervene between ester groups as mediating dipoles allowing attractive forces to operate in series with less geometric constraint than in a nonpolar medium; (*2*) direct reversible cyclization joining the two ester groups to form a relatively more polar species may occur. For example, structures I and II might be considered for the anionic case and structures III and IV for the free-radical case.



I II



III IV

Geometrically the ester groups are favorably placed to permit these cyclizations, and it is conceivable that polar molecules might not only tend to stabilize these ionic structures II and IV but also act catalytically to lower the transition state energy barriers so that equilibration might be more rapid than addition of the next monomer unit.

It is planned to study solvent effects on a wider variety of systems to see whether there are structural limitations on this effect which may elucidate further its mechanism.

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Preparation of Some New Polybenzimidazoquinazolines*

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Synopsis

Several new types of polybenzimidazoquinazolines with a different recurring unit have been prepared by solution polycondensation in polyphosphoric acid followed by heating at elevated temperature under reduced pressure. The polymers thus obtained were light yellow to brown powdery materials hardly soluble in common organic solvents and soluble in concentrated sulfuric acid. The inherent viscosity of the polymers ranged from 0.1 to 0.58 and showed good thermal stability.

INTRODUCTION

Various syntheses of certain 6-substituted benzimidazo-(1, 2-c) quinazolines have been well investigated.[1] Also, it is recognized that the compounds containing the benzimidazoquinazoline unit show good thermal stability. In the course of the investigations on the syntheses of thermally stable polymers, it is interesting to prepare the polymers with benzimidazo-(1, 2-c) quinazoline recurring units.

This paper deals with some studies on the preparation of benzimidazo (1, 2-c) quinazoline using anthranilic acid as starting material. Also it deals with the preparation and the properties of some new polybenzimidazoquinazolines. Several high molecular weight polymers having excellent thermal stability were obtained.

RESULTS AND DISCUSSION

Prior to the polymer synthesis, some studies on the preparation of model compounds containing the benzimidazoquinazoline unit were carried out. There are different synthetic routes to obtain benzimidazo (1, 2-c) quinazoline. In this paper, three routes have been examined based on the use of anthranilic acid as starting material (Fig. 1).

In the first method,[3] stoichiometric amounts of anthranilic acid and benzoyl chloride reacted in polyphosphoric acid (PPA) and gave 2-phenyl-4H-3,1-benzoxazine-4-one (I), which reacted with *o*-phenylenediamine to yield quinazolone (II).[4] Benzimidazo (1, 2-c) quinazoline could be obtained on heating compound II under reduced pressure (route A).

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

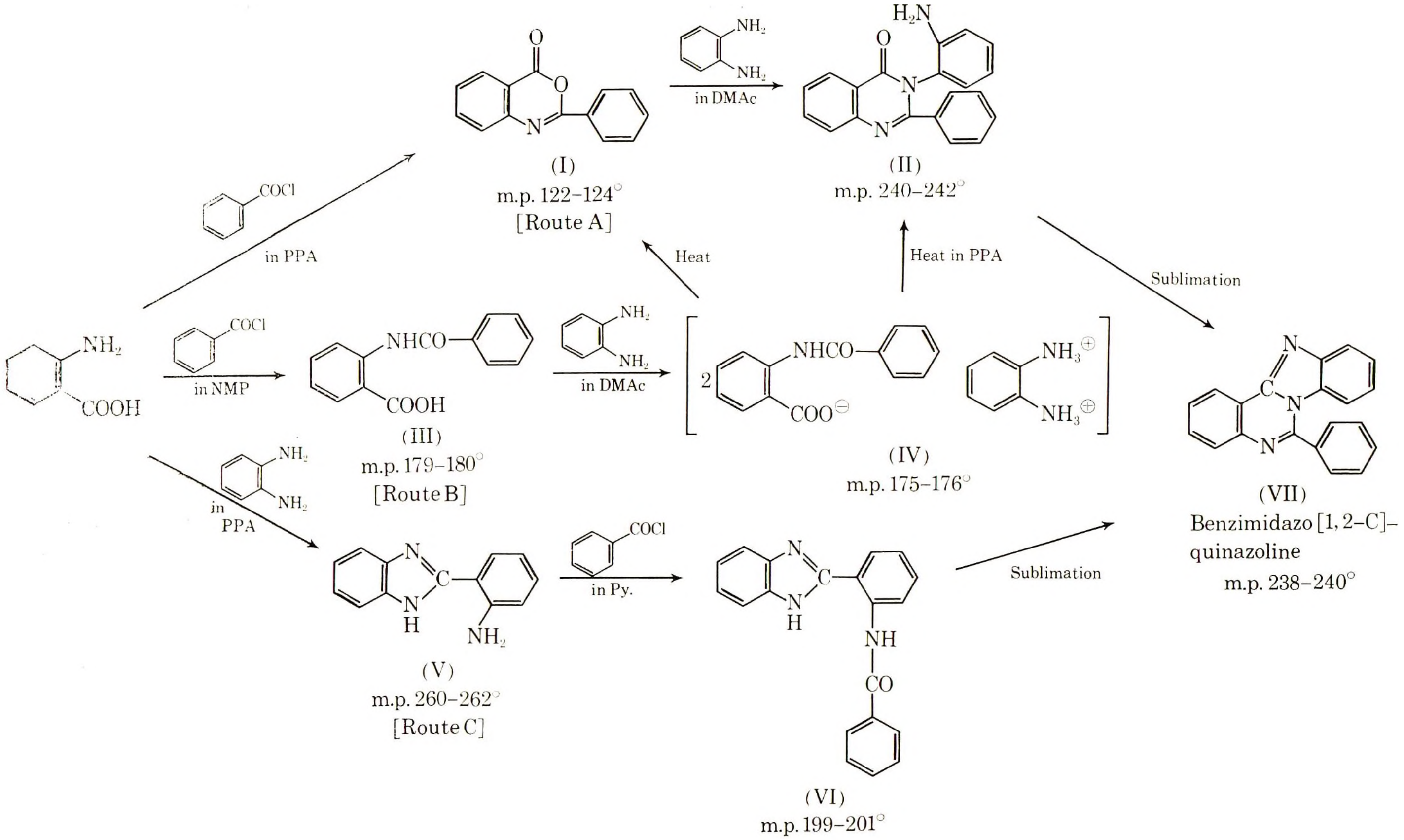


Fig. 1. Synthesis of benzimidazo(1,2-c)quinazoline.

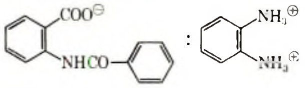
The dehydrocyclization process was confirmed by the disappearance of the characteristic ester carbonyl absorption band at 1750 cm^{-1}, and appearance of an —NH stretching band at 3290 cm^{-1} and a ketocarbonyl band at 1650 cm^{-1} in the infrared region. In a second method, *N*-benzoylanthranilic acid (III)[2] was prepared by the reaction of anthranilic acid with benzoyl chloride in *N*-methylpyrrolidone. Then this reacted with *o*-phenylenediamine to give the product. Pale yellow crystals could be obtained by the recrystallization of the crude product from ethanol.

The infrared spectrum shows a characteristic $—NH_3^+$ absorption band at 3050 cm^{-1}, and no evidence for supporting the formation of imidazole ring is found.

It was difficult to determine the molecular weight by means of mass spectrometry, because the parent peak was not clearly defined. An elemental composition of the product showed 69.34% carbon, 5.20% hydrogen, and 9.29% nitrogen. From these results, the salt of *N*-benzoylanthranilic acid and *o*-phenylenediamine is considered to be formed by the reaction.

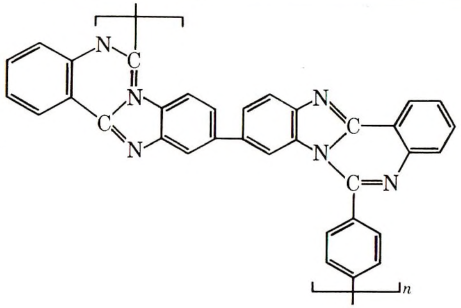
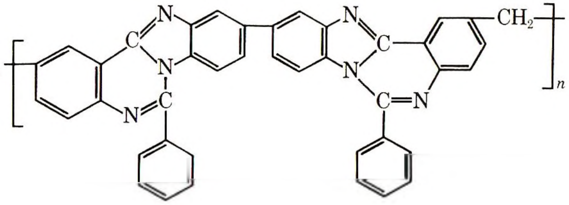
Possible structures of the salt and their calculated elemental analysis are listed in Table I. The results for our product fit best to the 2:1 salt (Table I). The salt thus obtained could be converted to benzoxazinone (I) on heating under reduced pressure. On the other hand, compound II was obtained by treating the salt in PPA at elevated temperature (route B).

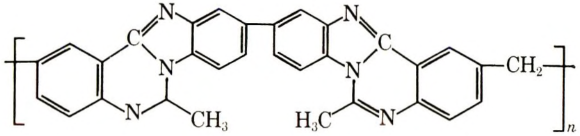
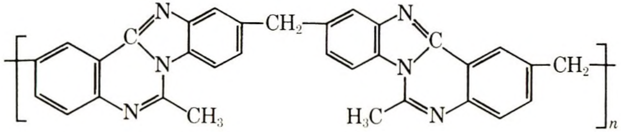
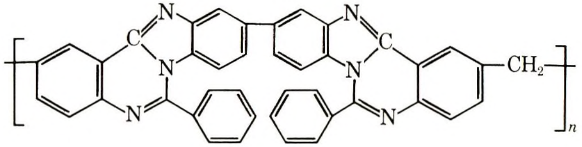
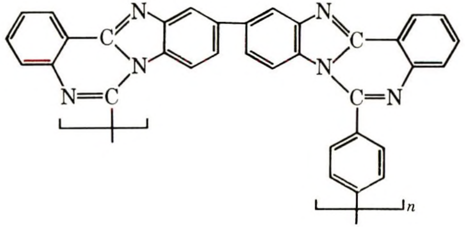
TABLE I
Salt Structures and their Calculated Elemental Analyses

	Elemental composition (calcd)		
	C, %	H, %	N, %
1:1	68.56	5.76	11.98
1:2	67.81	6.58	15.19
2:1	69.03	5.13	9.29

In a third method, 2-*o*-aminophenylbenzimidazole (V) was prepared by the condensation of anthranilic acid with *o*-phenylenediamine. This reacted with benzoyl chloride in *N*-methylpyrrolidone (route C). The product thus obtained was sublimed to give benzimidazo (1, 2-c)-quinazoline. Elemental analysis and the infrared spectrum were in good agreement with the product obtained via route A. Another three model reactions have been carried out by taking into consideration the polymer preparation method. One portion of difunctional monomer reacted with two portions of monofunctional compound in PPA at elevated temperature, followed by heating the isolated product at reduced pressure to form the expected product. Thus, model compounds containing benzimidazoquinazoline were prepared in two successive steps as shown in Figure 2. By a similar way, some new polybenzimidazoquinazolines with different

TABLE II
Polymers with Benzimidazoquinazoline Recurring Units

No.	Monomers	Structure	Reaction[a] Time, hr	Reaction[a] Yield, %	Product	η_{inh}[b]
1	2,2′-Di-*o*-aminophenyl-5,5′-bibenzimidazole Dimethylterephthalate		9	87	Light yellow powder	0.22
2	*N*,*N*′-Dibenzoyl methylene-dianthranilic acid 3,3′-Diaminobenzidine		9.5	92	Light brown powder	0.10

3	Methylene-2,2′-dimethyl-benzoxazine-4,4′-dione	“		10	98	Brown powder	0.25
4	“	Tetraamino-diphenylmethane		10	86	Brown powder	0.31[c]
5	Methylene-2,2′-diphenyl-benzoxazine-4,4′-dione	3,3′-Diaminobenzidine		8	78	Brown powder	0.21
2	Terephthaloyl-anthranilic acid	“		10	93	Light brown powder	0.58

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[a] Polycondensations have been carried out with 0.01 mole of each monomer and 50 g of PPA at 230–250°C for the time described.

[b] Determined on a solution of 0.25 g/100 ml of concentrated sulfuric acid at 30° unless otherwise noted.

[c] Obtained on a solution of 0.25 g/100 ml of *m*-cresol at 30°C.

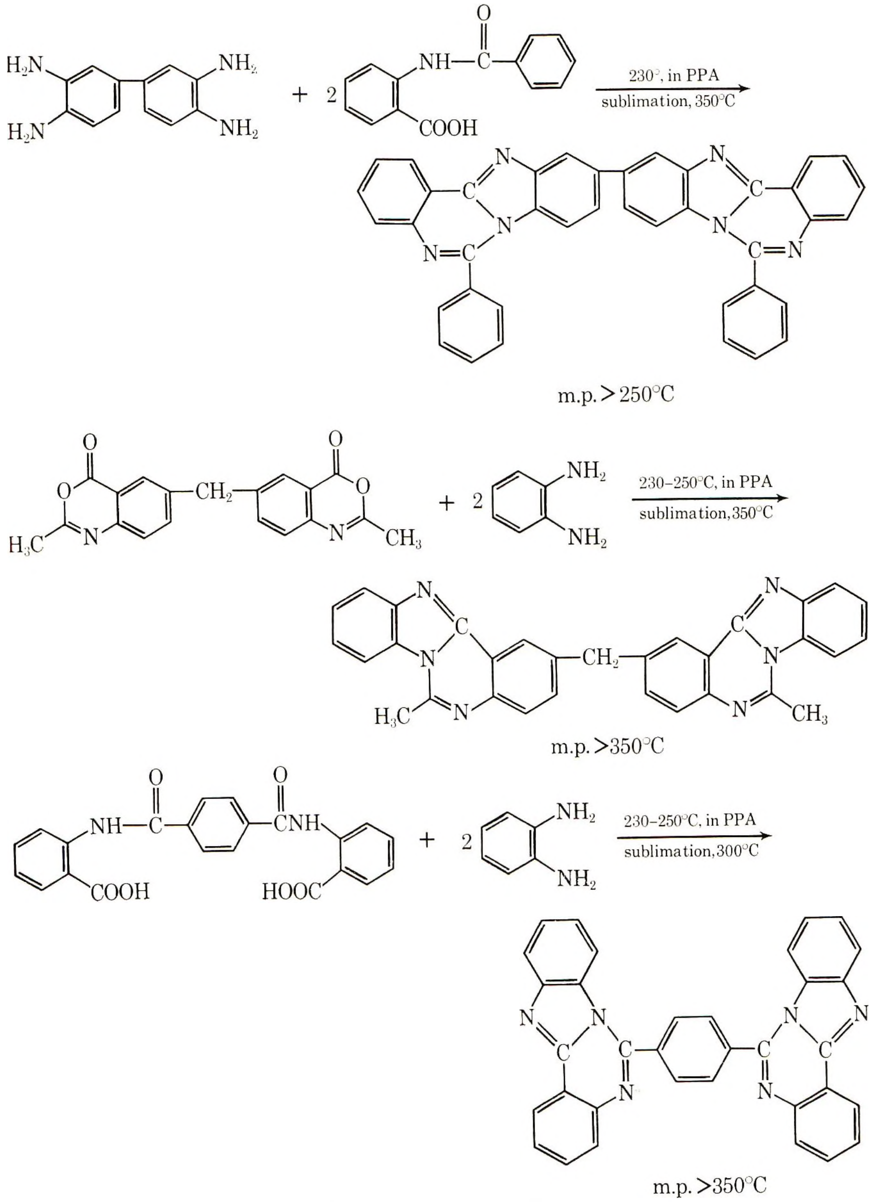

Fig. 2. Synthesis of model compounds containing benzimidazoquinazoline.

recurring units have been prepared. The results thus obtained are summarized in Table II. The inherent viscosity of the polymers ranged from 0.1 to 0.58. The thermal stability of these polymers was evaluated by thermogravimetric analysis which was run in air at the heating rate of 150°C/hr. Figure 3 shows the thermogravimetric curve of the polymers. Initial decomposition did occur at 380–420°C, and finally at 550°C the total weight loss was only 9.5–19%.

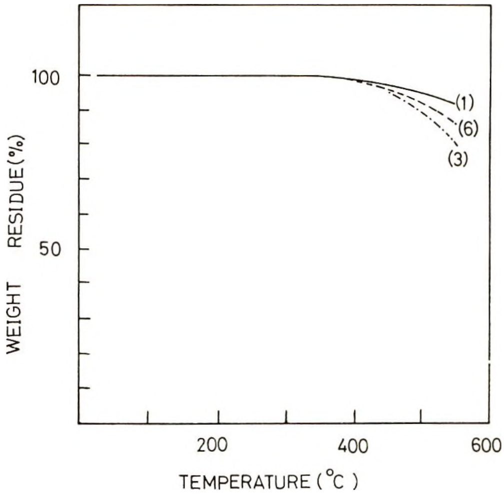

Fig. 3. TGA curves of polybenzimidazoquinazolines: (*1*) 2,2′-di-*o*-aminophenyl-5,5′-bibenzimidazole + dimethyl terephthalate; (*3*) methylene-2,2′-dimethylbenzoxazine-4-4′-dione + 3,3′-diaminobenzidine; (*6*) terephthaloylanthranilic acid + 3,3′-diaminobenzidine.

These polymers showed poor solubility in common organic solvents. Polymer IV was partly soluble in *m*-cresol, but the other polymers were insoluble in all organic solvents and the only solvent for the polymers was sulfuric acid.

From the results obtained by the preparation of model compounds, it is concluded that the formation of polybenzimidazoquinazolines was confirmed via the same synthetic route as described in model reactions. High molecular weight polymers can be expected when the preparative method of the model reaction (route B), i.e., the purified salt of two monomers followed by the solution polycondensation employing PPA as a solvent, is used.

EXPERIMENTAL

Monomers

2,2′-Di-*o*-aminophenyl-5,5′-bibenzimidazole. This compound was prepared by a minor modification of the preparation of 2,2′-di-*p*-aminophenyl-5,5′-bibenzimidazole.[5] The product obtained was recrystallized from methanol to give white crystals.

ANAL. Calcd for $C_{26}H_{20}N_6$: C, 74.98%; H, 4.84%; N, 20.18%. Found: C, 75.12%; H, 5.04%; N, 20.30%.

***N,N′*-Dibenzoylmethylenedianthranilic acid.** 5,5′-Methylenedianthranilic acid (12 g, 0.042 mole) was dissolved in 70 ml of N-methylpyrrolidone. To this solution was added dropwise 14 g (0.1 mole) of benzoyl chloride with stirring while keeping the temperature below 0°C. After the addition was completed, the reaction mixture was poured into 300 ml of water to precipitate the product. It was filtered and dried. The crude product thus obtained was reprecipitated by dissolving in dimethylformamide and pouring into water. Reprecipitation was repeated three times to yield a white powder which had a mp of 176–178°C.

ANAL. Calcd for $C_{29}H_{22}N_2O_6$: C, 70.43%; H, 4.49%; N, 5.66%: Found: C, 70.52%; H, 4.27%; N, 5.80%.

Methylene-2,2′-dimethylbenzoxazine-4,4′-dione. Methylenedianthranilic acid (10 g) and 400 ml of acetic anhydride were heated with stirring in a 1-liter round-bottomed flask and refluxed for 2 hr. After cooling, yellow crystals were filtered and recrystallized three times from acetic anhydride to give a colorless product in 70% yield. The product had mp 258–261°C.

ANAL. Calcd for $C_{19}H_{14}N_2O_4$: C, 62.30%; H, 4.31%; N, 8.42%; Found: C, 61.97%; H, 4.27%; N, 8.29%.

Methylene-2,2′-diphenylbenzoxazine-4,4′-dione. Methylene-dianthranilic acid (7.1 g, 0.05 mole) was dissolved in 30 ml of pyridine, and to this was added benzoyl chloride (14.0 g, 0.11 mole) dropwise at room temperature. After the addition was completed, the reaction mixture was stirred for 1 hr, after which it was poured into 300 ml of water to yield the product.

Recrystallization from dioxane gave colorless crystals with mp 270–274°C (decomp.).

ANAL. Calcd for $C_{29}H_{18}N_2O_4$: C, 75.98%; H, 3.95%; N, 6.11%. Found: C, 75.74%; H, 4.00%; N, 6.11%.

Terephthaloylanthranilic Acid. Anthranilic acid (13.7 g, 0.1 mole) was dissolved in 50 g of PPA and heated up to 100–110°C. To this was added terephthaloyl chloride (10.1 g, 0.05 mole) in portions with vigorous stirring. After the addition was completed, the homogeneous mixture was heated at 110°C for 12 hr. After cooling, the mixture was poured into 1 liter of water to yield a white precipitate. The precipitate was filtered, dried, and dissolved in 20% sodium hydroxide solution. The filtrate was neutralized with hydrochloric acid to give white crystals. The product thus obtained was recrystallized from dimethylformamide to give colorless crystals which had mp 350°C (decomp.).

ANAL. Calcd for $C_{22}H_{16}O_6N_2$: C, 65.35%; H, 3.98%; N, 6.93%. Found: C, 65.42%; H, 3.77%; N, 6.95%.

Model Compounds

The preparation of model compound (VII) has been made via three different synthetic routes: A, B, and C.

Route A. 2-Phenylbenzoxazine-4-one (I) was prepared by a method described previously.[6] In a 100-ml two-necked round-bottomed flask equipped with air condenser and nitrogen inlet was placed 2-phenylbenzoxazine-4-one (4.46 g., 0.02 mol), *o*-phenylenediamine (2.16 g, 0.02

mole) and 40 ml of dimethylacetamide. After stirring for 10 hr at 50°C, the resulting mixture was poured into 300 ml of water to yield a white precipitate. The product thus obtained was recrystallized from hot ethanol to give white crystals, mp 240–242°C.

ANAL. Calcd for $C_{20}H_{15}ON_3$: C, 76.70%; H, 4.79%; N, 13.41%. Found: C, 76.86%; H, 4.55%; N, 13.21%.

The molecular weight obtained from mass spectrometry showed good agreement with the structure II.

Compound II thus obtained was placed in a sublimation vessel, heated to 245°C and kept for 30 min. Then the temperature was raised to 280–300°C under reduced pressure (<1 mm Hg) and sublimation occurred.

The sublimed product was collected and recrystallized from *n*-propyl alcohol to yield colorless crystals which have a melting point of 238–240°C. Elemental analysis and mass spectrometric data of the product were in good accordance with benzimidazo-[1, 2-c] quinazoline (VII).

ANAL. Calcd for $C_{20}H_{13}N_3$: C, 81.37%; H, 4.40%; N, 14.23%. Found: C, 81.50%; H, 4.35%; N, 14.15%.

Route B. *N*-Benzoylanthranilic acid (III) (4.82 g, 0.02 mole) reacted with *o*-phenylenediamine (2.16 g, 0.02 mole) in 50 ml of dimethylacetamide. The reaction procedure and conditions were similar to those described in the preparation of compound II. Pale yellow crystals which correspond to 2:1 salt of the reactants could be obtained by the recrystallization of the crude product from hot ethanol.

Route C. Anthranilic acid (8.5 g, 0.06 mole) and *o*-phenylenediamine (6.7 g, 0.06 mole) were dissolved in 50 g of PPA. The temperature was slowly raised to 250°C with vigorous stirring and maintained for 4 hr. The resulting mixture was poured into 1 liter of water to give a dark brown precipitate, which was neutralized with a sodium bicarbonate solution and washed thoroughly with water. The product thus obtained was recrystallized from hot ethanol to yield white crystals which had a melting point of 262°C. This product changed color to pale brown on standing in the air.

ANAL. Calcd for $C_{13}H_{11}N_3$: C, 74.62%; H, 5.31%; N, 20.08%. Found: C, 74.46%; H, 4.93%; N, 19.97%.

2-*o*-Aminophenylbenzimidazole thus obtained (5 g, 0.024 mole) was dissolved in 40 ml of pyridine at 60°C, to this was added dropwise 3.5 g (0.025 mole) of benzoyl chloride.

After the addition was completed, the reaction was continued for 1 hr. The resulting mixture was poured into 50 ml of water to give a white precipitate. Colorless crystals which melted at 199–201°C were obtained by recrystallization from hot ethanol.

ANAL. Calcd for $C_{20}H_{15}ON_3$: C, 76.67%; H, 4.82%; N, 13.41%. Found: C, 76.70%; H, 4.88%; N, 13.36%.

The molecular weight obtained from mass spectrometry showed good agreement with compound VI.

Polymers

Another three model compounds from one portion of difunctional monomer and two portions of monofunctional compound and polybenzimidazoquinazolines summarized in Table II were prepared in two successive steps. In the first step, condensation reactions were conducted in PPA at elevated temperature. Dehydrocyclization of the isolated product was performed by heating at reduced pressure.

The authors wish to acknowledge the encouragement of Dr. Koichiro Shinra for his support and interest on this work. They wish to express also their deep gratitude to Miss Yuko Yamashoji for her valuable assistance.

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Synthesis of Inherently Dissymmetric Polyamides*†

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Synopsis

The preparation of polyamides from derivatives of optically active biphenic acid is described. The diacid chlorides chosen were 2,2′-dinitro-6,6′-dimethylbiphenyl-4,4′-dicarbonyl chloride and 2,2′-dichloro-6,6′-dimethylbiphenyl-4,4′-dicarbonyl chloride, the diamines were phenyldiamines (*o*-, *m*-, *p*-) piperazine, *trans*-2,5-dimethylpiperazine, and 1,2-piperaazolidine. Polymerization was carried out by the method of interfacial polycondensation. The polymers of aromatic diamines were insoluble in common organic solvents but soluble in dimethylformamide containing 5% lithium chloride, triesters of phosphoric acid, and methanesulfonic acid. The polymers of aliphatic diamines were also insoluble in common organic solvents but soluble in trifluoroethanol. All polymers had melting points higher than 280°C.

INTRODUCTION

This work was directed to the synthesis and optical rotatory study of optically active polyamides derived from optically active biphenyls. These polymers would contain one asymmetric center, but the rotation of the main chain would be restricted in such a way that the polymers may preferentially assume a particular, asymmetric conformation in solution. This paper is concerned only with the syntheses of the monomers and their subsequent polymerization. The discussion of the optical rotatory dispersion (ORD) and circular dichroism (CD) spectra of these compounds will be published in a separate paper.

In order to obtain an optically active polyamide which is suitable for the purposes mentioned above, it was necessary to introduce an asymmetric unit into a reasonably rigid polymer chain and to maintain structural homogeneity of the monomer units. This could be achieved by a polycondensation reaction of either optically active cyclic or biphenyldicarbonylic acids with acyclic and cyclic symmetrical diamines. Thus, optically active 2,2′-dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic acid and 2,2′-dichloro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic acid were chosen as the

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* In honor of C. S. Marvel on the occasion of his 75th birthday.

† This is the 20th in a series of papers concerned with the synthesis and properties of asymmetric polymers; for the previous papers in this series see C. G. Overberger et al.[1]

‡ Fellow of the Brazilian National Research Council and the National Academy of Science overseas research fellowship program.

diacid components, and as the diamine component, a series of phenylenediamines (*o*-, *m*-, *p*-) and cyclic diamines such as piperazine (PIP), trans-2,5-dimethylpiperazine (DMP), 1,2-pyrazolidine (PD) were selected, not only to maintain structural identity but also to vary the rigidity of the polymer chain.

RESULTS AND DISCUSSION

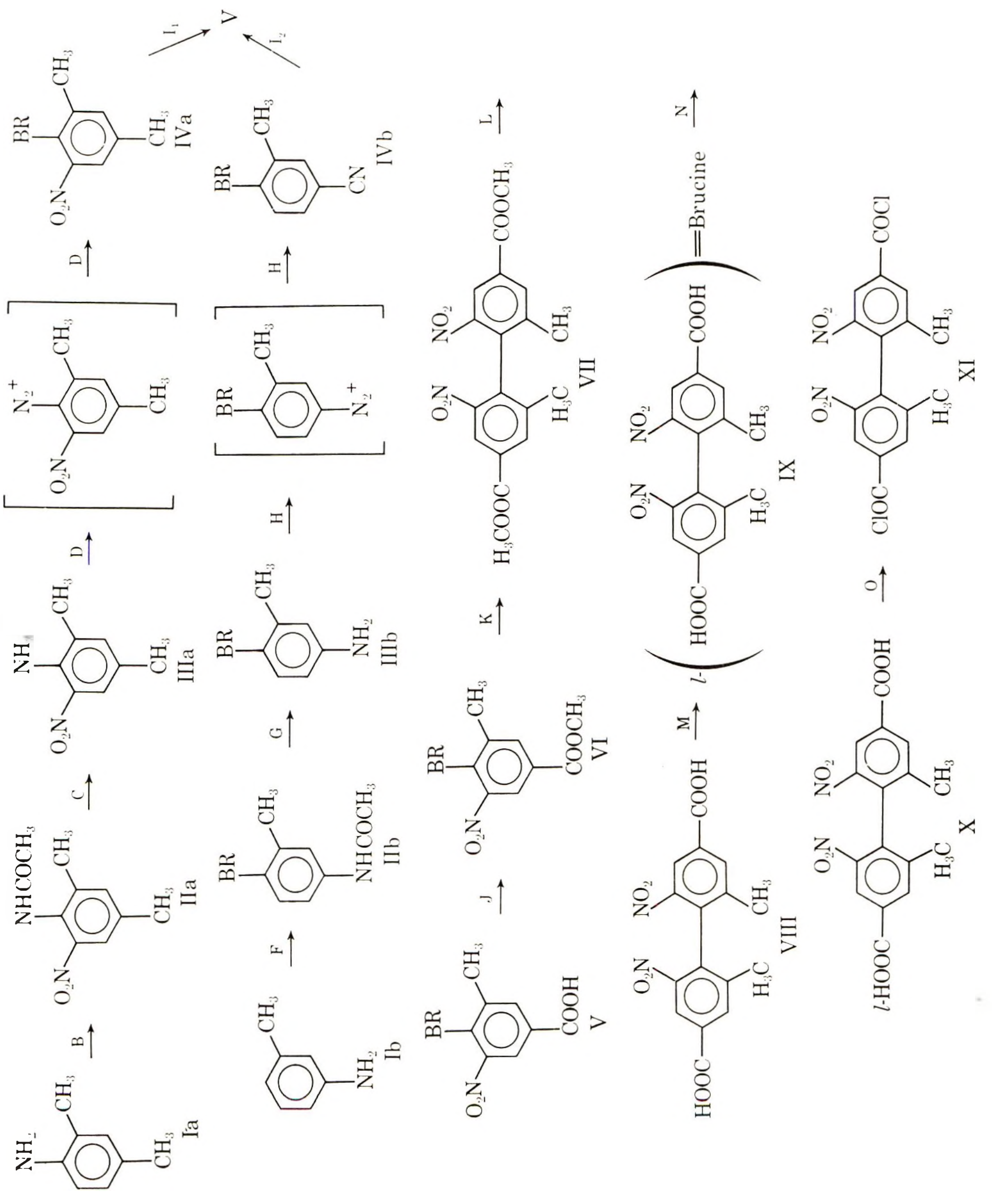
Monomer Synthesis

Synthetic Routes to *l*-2,2′-Dinitro-6,6′-Dimethylbiphenyl-4,4′-Dicarbonyl Chloride (XI). The dicarbonyl chloride XI was prepared by either of two routes.

Synthesis of 3-Methyl-4-Bromo-5-Nitrobenzoic Acid (V). The acid (V) was prepared by two different synthetic routes, A and B, to compare the overall yield. The route A is a modification and extension of the procedure of Mix[2] which was followed by Overberger and Yoshimura[3] (experimental details are not provided in reference 3). The overall yield of the acid (V) from the starting material, 2,4-dimethylaniline (Ia), was 11.6%. Among the reaction steps, the oxidation of 2,4-dimethyl-6-nitrobromobenzene (IVa) to the acid (V) by potassium dichromate and 50% sulfuric acid was very difficult. During the oxidation, the reaction product formed a very thick precipitate which caused inadequate stirring resulting in nonuniform reaction, and a yield of 34.4%.

Route B was chosen to increase the overall yield by modifying the procedure of Adams and Teeter.[4] It was expected that 3-methyl-4-bromo-5-nitrobenzonitrile would result from the nitration of 3-methyl-4-bromobenzonitrile (IVb) by treatment with an excess of mixed nitric and concentrated sulfuric acid. After the nitration was carried out at 10–16°C for 4 hr, the reaction product melted at 178°C. The expected compound is reported to melt at 103°C.[4] The infrared spectra of the product contained no absorption for a CN group at 2250 cm^{-1} and indicated the presence of NO_2 (1539, 1377 cm^{-1}), $C{=}O$ (1715 cm^{-1}), and NH_2 (3460 cm^{-1}) bands, which indicate that conversion to 3-methyl-4-bromo-5-nitrobenzoic acid amide was occurring. The reaction product was hydrolyzed with aqueous sodium hydroxide, and after the evolution of ammonia had ceased, the solution was neutralized with aqueous hydrochloric acid. The white precipitate thus obtained melted at 206–207°C. Its elemental analysis was almost identical to that of the acid (V) mentioned above. The overall yield of the acid (V) from the starting material, *m*-toluidine (Ib), was 20.3%. Thus, only the methyl group at the 4-position of 2,4-dimethyl-6-nitrobromobenzene (IVa) was converted to a carboxylic acid group.

Synthesis of 2,2′-Dinitro-6,6′-Dimethylbiphenyl-4,4′-Dicarboxylic Acid (VIII). A modified procedure used by Slocum and Mislow[5] for the hydrolysis of dimethyl-2,2′-dichloro-6,6′-dimethylbiphenyl-4,4′-dicarboxylate was attempted in the preparation of VIII from dimethyl-2,2′-dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylate (VII).

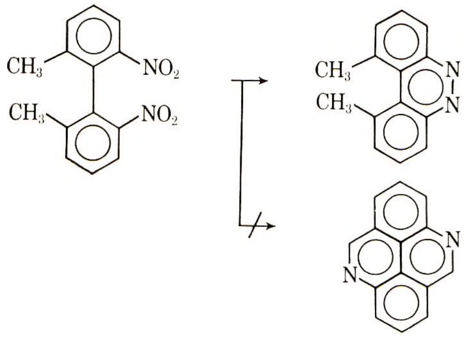

NH2
CH3
CH3
Ia
B
O2N
NHCOCH3
CH3
CH3
IIa
C
O2N
NH2
CH3
CH3
IIIa
D
O2N
N2+
CH3
CH3
D
O2N
BR
CH3
CH3
IVa
L1
V
L2
CH3
NH2
Ib
F
BR
CH3
NHCOCH3
IIb
G
BR
CH3
NH2
IIIb
H
BR
CH3
N2+
H
BR
CH3
CN
IVb
BR
O2N
CH3
COOH
V
J
BR
O2N
CH3
COOCH3
VI
K
H3COOC
O2N
H3C
NO2
CH3
COOCH3
VII
L
HOOC
O2N
H3C
NO2
CH3
COOH
VIII
M
l-
HOOC
O2N
H3C
NO2
CH3
COOH
Brucine
IX
N
l-HOOC
O2N
H3C
NO2
CH3
COOH
X
O
ClOC
O2N
H3C
NO2
CH3
COCl
XI

The ester (VII) and an 83.1 molar excess of potassium hydroxide were dissolved in 60% methanol and the mixture was refluxed for 3 hr. During the course of the reaction, the solution became dark red, and the reaction product, after the solution was neutralized with aqueous hydrochloric acid, was yellowish and decomposed at a temperature of 315°C (lit. >340°C). The elemental analysis of the crude acid was the following.

ANAL. Calcd for $C_{16}H_{12}N_2O_8$: C, 53.32%; H, 3.36%; N, 7.75%; Found: C, 55.50%; H, 3.93%; N, 8.07%.

The acid was difficult to dissolve in common organic solvents such as acetone, methanol, ethanol, acetic acid, tetrahydrofuran, and DMF. The infrared spectrum of the ester (VII) had shown, in addition to a strong band at 1732 cm^{-1} (carbonyl stretch), two strong bands at 1537 and 1353 cm^{-1} which correspond to the asymmetric and symmetric vibrations, respectively, of the nitro group. However, the acid obtained showed only a weak band at 1541 cm^{-1} beside the carbonyl band at 1699 cm^{-1}.

It is well known that 2,2′-disubstituted biphenyls undergo intramolecular cyclization reactions with particular facility by either reduction or oxidation or the action of base or acid because of the proximity of the interacting substituents. In the reduction of 2,2′-dinitrobiphenyl cyclization is almost impossible to avoid.[6] Indeed, the most widely used method of preparing benzo-[c]-cinnolines is reduction of 2,2′-dinitrobiphenyls by zinc[7] or by lithium aluminum hydride.[8] It has been observed that reduction of 2,2′-dinitro-6,6′-dimethylbiphenyl with triethyl phosphite affords only 1,10-dimethylbenzo[c]cinnoline and no 4,9-diazapyrene.[9] (eq. (1)]



Although the acid obtained here was not further investigated, it may be assumed that reduction occurred, to some extent, during the hydrolysis by an unknown process.

Therefore, the conditions of the hydrolysis were carefully investigated. When the ester VII was hydrolyzed with a tenfold molar excess of potassium hydroxide in 60% methanol, the infrared band characteristic of the carboxyl group appeared in the spectrum of the reaction product after refluxing for only 30 min. It was also found that the color and melting point of the product were darkened and decreased, respectively, according to the length of time the mixture was refluxed. No effect on the bands characteristic of nitro groups was observed under these conditions. The acid (VIII) thus obtained in 95% yield, after purification by repeating the precipitation three times, was a white powder of high melting point (>340° C) and had a satisfactory elemental analysis. Infrared spectra of the acid (VIII) showed two strong bands at 1528 and 1348 cm^{-1} (nitro groups) of intensity comparable to the carbonyl band at 1704 cm^{-1}. This acid was further checked by connecting it to its methyl ester in 69% yield by a method similar to that employed in the synthesis of methyl-3-methyl-4-bromo-5-nitrobenzoate (VI). The melting point, infrared spectra, and elemental analysis of the converted ester were almost identical with those of the ester (VII).

Optical Resolution of 2,2′-Dinitro-6,6′-Dimethylbiphenyl-4,4′-dicarboxylic Acid (VIII). Our racemic acid was resolved with brucine by using a modified method described by Mix,[2] followed by Slocum and Mislow,[5] and Overberger and Yoshimura.[3] The half brucine salt of racemic 2,2′-dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic acid was formed in absolute ethanol, followed by fractional crystallization of the *l*-half salt (IX) in 80% ethanol, and then purified by repeating the recrystallization from the same solvent. After four or five recrystallizations, the *l*-acid (X) was liberated with aqueous ammonium solution followed by neutralization with dilute hydrochloric acid. The specific rotations of the *l*-salt (IX) in dioxane obtained by Mix and Slocum and Mislow were −11.5° and −13°, respectively, and those of the liberated *l*-acid (X) were −20° in ethanol and −16.3° in 95% ethanol, respectively. Overberger and Yoshimura obtained a value of −16.1° in ethanol.

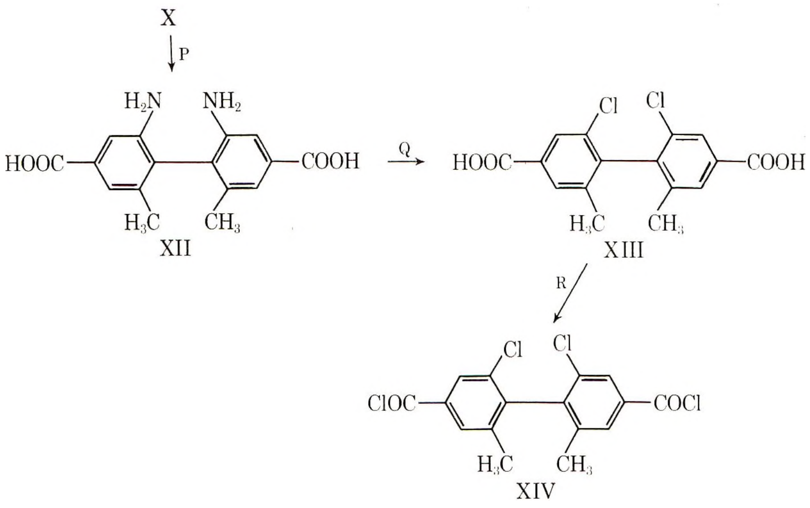
With these factors in mind, the optical resolution of the racemic acid (VIII) was attempted. Equivalent amounts of the acid and brucine were mixed in hot absolute ethanol to form the racemic brucine salt as pale yellowish crystals. The analytical data indicated the salt to be half salt. The yield was 91.5%, mp >275°C [lit.[2] 275°C (dec.)], $[\alpha]_D^{23}$ + 1.57 (0.8, dioxane). Resolution of the racemic salt was attempted by fractional crystallization from hot 80% ethanol. Pale yellowish crystals with a specific rotation of +3.23° were obtained. Upon recrystallization from hot 80% ethanol, the specific rotation of the salt was slowly increased to +4.08°, and then to +5.26°. The specific rotation of the free acid obtained on neutralization of the salt with $[\alpha]_D^{20}$ + 4.08° was +3.91° (2.5, ethanol).

To obtain an optically pure salt, the conditions of the fractional crystallization were investigated with respect to the following factors: The ratio of alcohol and water, amount of solvent used, conditions during the crystallization such as temperature and the effect of stirring. However, no improvement was observed when the preformed racemic half salt was used. It appears that, in this case, the proper choice of the initial conditions of salt formation are the most important factors.

After preliminary examination, the proper conditions for salt formation were determined. Thus, equivalent amounts of the racemic acid (VIII) and brucine were combined in hot 80% ethanol (26 ml/g of free acid). After standing at 20°C overnight, two apparently different kinds of crystals were obtained. One was a small amount of pale yellowish crystals adhering to the bottom and wall of the flask, and the other was bright yellow, long needles lying on the former crystals. They were easily separated from each other by decantation. The yield and specific rotation in dioxane were 1.2% and +4.48°, 40% and −8.75°, respectively. The salt with a negative rotation was purified further by recrystallization from hot 80% ethanol (17–18 ml/g of salt). On recrystallization, marked enhancement of the specific rotations accompanied by increasing yields was obtained, as shown in Table I.

Finally, the *l*-salt (IX) with a specific rotation of −15.7° (lit.[25] −11.5°, −13°), mp 218–221°C (lit. 220–222°C) was liberated to the free acid by the method of Mix.[2] The *l*-acid (X) thus obtained in 96.4% yield showed a specific rotation of −18.4° (lit.[2,5,3] −20°, −16.3°, −16.1°), mp 330°C (dec.) (lit.[5,3] 330–332, 350°C) and excellent agreement with the calculated data in elemental analysis. The optical and chemical purities of the *l*-acid (X) were determined as 92 and 99.9%, respectively.

Chloride (XIV). The synthetic procedure for the preparation of this monomer was essentially the same as that followed by Slocum and Mislow[5] and Overberger and Yoshimura [eq. (2)].[3]



Reduction of X with hydrogen with the use of 5% Pd/C and glacial acetic acid gave 48.8% of 2,2′-diamino-6,6′-dimethylbiphenyl-4,4′-dicarboxylic acid XII. However, the key step was the bisdiazotation of XII to obtain the 2,2′-dichloro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic acid (XIII).

Poor solubility of the bisdiazonium salt in water at low temperature, frothing caused by rapid evolution of nitrogen, and the formation of phenols and mixture of phenol and chloro compounds were observed. Combustion analyses showed the presence of such impurities in the final product. Several attempts to separate these impurities by thin layer chromotography on silica gel and alumina using several mixtures of solvents were unsuccessful. Then the procedure described by Slocum and Mislow[5] was followed. Conversion of the crude diacid (XIII) into its corresponding ester, by reaction with diazomethane was followed by column chromatography on silica gel with the use of benzene and hexane. The final yield from the initial compound X to XIV was 5.4%.

Synthesis of Model Compounds

To compare with the optical rotatory properties of the polyamides in solution, optically active low molecular weight model compounds were also synthesized. The synthetic routes for the model compounds and the designation of compounds involved in these syntheses are summarized in eqs. (3)–(4).

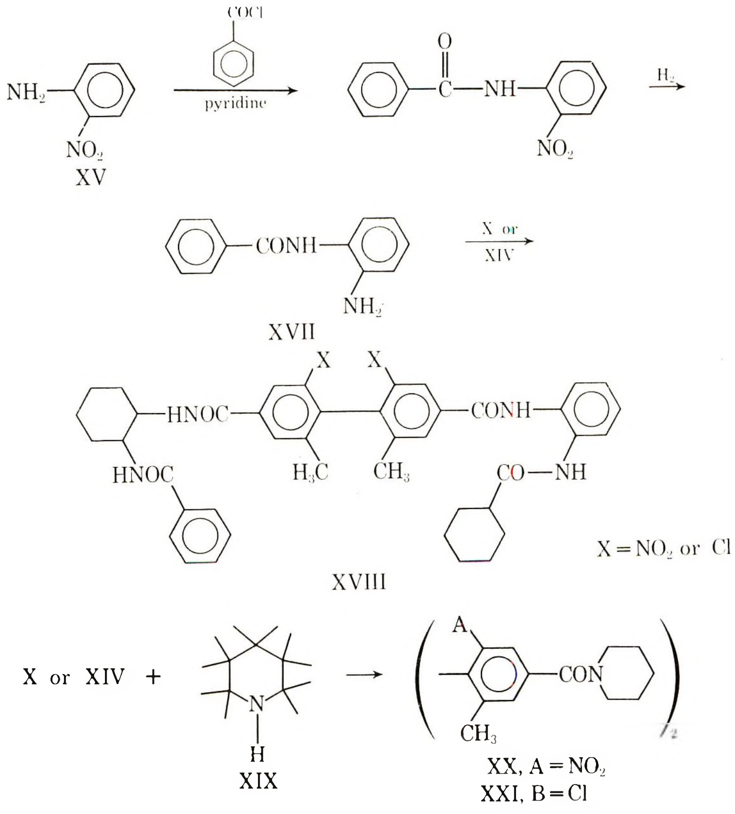


TABLE I
Purification of Brucine Salt of 2,2′-Dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic Acid from 80% Ethanol

Recrystallization	0	1	2	3	4
Brucine salt (IX)					
Recovered yield, %		79.2	85.9	89.0	91.9
$[\alpha]_D^{20}$ (1.0, dioxane)	−8.75	−12.4	−13.1	−15.3	−15.7
Liberated free acid (X)					
$[\alpha]_D^{20}$ (2.5, ethanol)			−15.1	−17.0	−18.4

Polymerization

All polymerizations were carried out by the method of interfacial polycondensation;[10] in the case of the phenylenediamines, a modified procedure was used.[3]

Thus, a modified blender flask, precooled in a refrigerator, was charged with an aqueous solution of phenylenediamine dihydrochloride (0.2 mole). To the rapidly stirred system, after nitrogen gas was introduced, were quickly added at the same time a solution of the *l*-dicarbonyl (0.05 mole) in methylene chloride and a glass tube containing an aqueous solution of sodium sulfite as acid acceptor. The reaction was carried out for 5 min. Equivalent amounts of diamine and diacid chloride were used. Each polymer was purified by threefold reprecipitation; the polymer was dissolved in DMF containing 5% LiCl and the solution was poured, with vigorous stirring, into 30% methanol.

The properties of the polymers are shown in Table II.

EXPERIMENTAL

Materials

2,4-Dimethylaniline (Ia) and *m*-toluidine (Ib), available commercially, were distilled *in vacuo* prior to use. The *trans*-2,5-dimethylpiperazine was recrystallized twice from ethyl acetate, and colorless plates were obtained, mp 118°C (lit.[11] mp, 118°C). Piperazine hexahydrate was dissolved in dilute hydrochloric acid. The solution was evaporated to dryness under reduced pressure. The product was recrystallized from absolute ethanol and dried *in vacuo* at 110°C/25 mm, mp 318–320°C (lit.[12] 322–323°C). 1,2-Pyrazolidine dihydrochloride was prepared by the method of Stetter and Spangenberger.[13] The *o*-, *m*-, and *p*-phenylenediamine dihydrochlorides were recrystallized three times for 6*N* hydrochloric acid.

2,4-Dimethyl-6-nitroacetanilide (IIa). This was prepared by the procedure described in *Organic Syntheses*, and 600 g (4.95 mole) of Ia gave 730 g (70.8%) of IIb. Recrystallization from ethanol gave yellowish needles, mp 174–174.5°C (lit.[15] 172°C).

TABLE II

	XI ($[\alpha]^{20}_{D}$ = +2.0°)						XIV ($[\alpha]^{20}_{D}$ = −18.8°)					
	o-Phenyldiamine	*m*-Phenylenediamine	*p*-Phenylenediamine	PIP	DMP	PD	*o*-Phenylenediamine	*m*-Phenylenediamine	*p*-Phenylenediamine	PIP	DMP	PD
Mp (dec) °C	330	>350	>350	—	>320	>280	330	350	>350	>330	>330	>280
$[\eta]$	0.18[a]	0.37[a]	1.13[a]	—	0.12[b]	0.09[b]	0.10[a]	0.33[a]	1.26[a]	0.41[b]	0.43[b]	0.10[b]
$[\alpha]^{20}_{D}$	−4.94[c]	0.50[c]	+6.53[c]	—	28.0[d]	+5.4[d]	−19.6[c]	−19.4[c]	−18.2[c]	−10.0[d]	−6.7[d]	−6.7[d]

[a] 0.5%, conc. H_2SO_4, 25°C.

[b] 0.5%, TFE, 25.5°C.

[c] 1.0, DMF/5% LiCl.

[d] 1.0, TFE.

2,4-Dimethyl-6-nitroaniline (IIIa). The procedure of Parkam and Strassburg[16] was used, and 728 g (3.5 mole) of IIa gave 518 g (89.1%). Recrystallization from ethanol gave red needles, mp 68°C (lit.[16] 68–70°C).

4-Bromo-5-nitro-*m*-xylene (IVa). The procedure of Parkam and Strassburg[16] was used with modification. Aniline (IIIa) (515 g, 3.1 mole) was suspended in 1400 g (8.34 mole) of 48.2% hydrobromic acid and diazotized with a solution of 222 g (3.22 mole) of sodium nitrite in 1 liter of water at 0°C; the mixture was stirred for 2 hr at room temperature and finally for 1 hr at 50°C. The reaction product was extracted with benzene and distilled at 135–145°C/4.5 mm; yield 388 g (54.4%), mp 54°C (lit.[16] 53–56°C).

ANAL. Calcd for $C_8H_8NO_2Br$: C, 41.88%; H, 3.57%; N, 6.09%; Br, 34.74%. Found: C, 41.88%; H, 3.57%; N, 6.07%; Br, 34.86%.

3-Methyl-4-bromoacetanilide (IIb). The procedure described in the literature[17] was used, and 563 g (5.25 mole) of Ib gave 962 g (80.2%) of the desired product. Recrystallization from 50% ethanol gave mp 100°C (lit.[18] 103–104°C).

3-Methyl-4-bromoaniline (IIIb). A literature procedure[17] was used, and 958 g (4.2 moles) of IIb gave 673 g (86%) of IIIb. Recrystallization from 70% ethanol gave white plates, mp 79.5°C (lit.[18] 79–81.5°C).

3-Methyl-4-bromobenzonitrile (IVb). The procedure described in the literature[19] was applied, and 670 g (3.6 mole) of IIIb gave 306 g (43.3%) of IVb, mp 53.5–54°C (lit.[4] 54–55°C).

3-Methyl-4-bromo-5-nitrobenzoic Acid (V), by Route A. The procedure of Mix[2] was used, and 385 g (1.67 mole) of IVa gave 150 g (34.4%) of V. Recrystallization from 95% ethanol gave a white powder, mp 212.5–213°C (lit.[2] 212–213°C).

V by Route B. The procedure of Adams and Teeter[4] was used with modification. A solution of 304 g (1.55 moles) of IVb in 960 ml of conc. sulfuric acid, cooled in an ice bath to 10°C, was added dropwise over a period of 1 hr, to a mixture of 1160 ml of concentrated sulfuric acid and 1160 ml of concentrated nitric acid. After the addition was completed, stirring was continued for 3 hr at 10–16°C and then the reaction was poured into ice water. The precipitated product was filtered, washed with water, and then treated with 3.5 liters of 5% sodium hydroxide on the steam bath for 2 hr. The reddish solution was cooled, filtered, and acidified with dilute hydrochloric acid. The white precipitate was filtered, washed with water, and dried; yield 277 g (68.7%). Recrystallization from 95% ethanol gave a white powder, mp 212°C (lit.[4] 212–213°C).

Methyl 3-Methyl-4-bromo-5-nitrobenzoate (VI). The procedure of Adams and Teeter[4] was used, and 422 g (1.62 mole) of the acid (V) gave 387 g (87.3%) of the desired ester, mp 82–82.5°C (lit.[4] 81–81.5°C).

Dimethyl 2,2′-Dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylate (VII). The procedure of Mix[2] was used with modification. A mixture of 304 g (1.11 mole) of the ester (VI) and 35.2 g (0.56 mole) of activated copper powder[20] was heated to 190°C in a 300-ml beaker. With constant stirring and raising the temperature, 106 g (1.67 mole) of activated copper powder was added in small portions over a period of 1.5 hr to reach a temperature of 220°C. The cooled reaction mixture was broken up and extracted for 15 hr with acetone in a Soxhlet extractor. The extract was evaporated to dryness and the residue was recrystallized from methanol; yield 167.3 g (77.8%), mp 102°C. For further purification, the product was dissolved in methanol, treated with Norit, and then allowed to recrystallize from the filtrate. Repeating the purification twice, pale yellow coarse crystals were obtained; yield 125 g (58.6%), mp 105.5°C (lit.[2] 108–108.5°C).

ANAL. Calcd for $C_{18}H_{16}N_2O_8$: C, 55.62%; H, 4.15%; N, 4.15%; N, 7.23%. Found: C, 55.62%; H, 4.03%; N, 7.22%.

2,2′-Dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic Acid (VIII). A mixture of 100 g (0.26 mole) of the ester (VII), 4.6 liters of methanol, 145 g (2.58 mole) of potassium hydroxide, and 3 liters of water was refluxed for 30 min. The cooled solution was filtered and acidified with dilute hydrochloric acid. The yellowish white precipitate was dissolved again in dilute aqueous sodium hydroxide and then acidified with dilute hydrochloric acid. By repeating the purification three times, a white precipitate was collected by filtration and dried *in vacuo;* yield 88.5 g (95.3%), mp >340°C (lit.[2,3] >340°C), infrared spectrum: 1704(s), 1528(s), 1348(s) cm^{-1}.

ANAL. Calcd for $C_{16}H_{12}N_2O_8$: C, 53.32%; H, 3.36%; N, 7.75%. Found: C, 53.38%; H, 3.40%; N, 7.71%.

The acid (VIII) obtained was further checked by esterification. A mixture of 0.72 g (0.002 mole) of the acid (VIII) and 0.02 g (0.00025 mole) of pyridine, and 14.3 g (0.12 mole) of thionyl chloride was refluxed until a clear solution was obtained. Following a similar procedure mentioned in the synthesis of the ester (VI), pale yellow coarse crystals were obtained; yield 0.62 g (69%), mp 104°C.

ANAL. Calcd for $C_{18}H_{16}N_2O_8$: C, 55.62%; H, 4.15%; N, 7.23%. Found: C, 55.83%; H, 4.13%; N, 71.6%.

***l*-2,2′-Dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic Acid Brucine Salt (IX).** To a hot solution of 45 g (0.125 mole) of the racemic acid (VIII) in 1600 ml of 80% ethanol, was added a hot solution of 49.3 g (0.125 mole) of brucine in 830 ml of 80% ethanol. The mixture was allowed to reflux for 3 hr, and then filtered when the solution temperature was around 65°C. After the filtrate was allowed to stand in a temperature-controlled room (20°C) overnight, two different kinds of crystals had formed; one was a small amount of pale yellow, hard crystals adhering to the bottom and wall of the flask, and the other was bright yellow, long needles heaped on the first crystals. They were easily separated from each other by decantation, the latter was filtered whereas the former remained in the flask. The yields and specific rotations respectively, of the crystals and the needles were 1.1 g (1.21%) and +4.48° (1.005, dioxane); 36.6 g (40%) and −8.75° (1.001, dioxane).

The needles (35.9 g, 0.048 mole) were dissolved in 650 ml of boiling 80% ethanol and the clear solution was seeded (obtained in preliminary investigation) and left to stand in the room overnight. Long yellow needles were formed (with a trace of the other type of crystals) and were filtered and dried; yield 28.4 g (recovered yield 79.2%), $[\alpha]_D^{22}$ −12.4° (1.01, dioxane), mp 219–223°C. When the second recrystallization was done by the same procedure, no trace of the impure crystals was found; yield 24.9 g (recovered 85.9%), $[\alpha]_D^{23}$ −13.1° (1.0, dioxane), mp 218–221°C. The third recrystallization produced only the needles in a yield of 21.4 g (recovered 89%), $[\alpha]_D^{23}$ −15.3° (0.995, dioxane). Finally, an additional recrystallization gave the *l*-brucine salt (IX); yield 19.1 g (recovered 91.9%), $[\alpha]_D^{23}$ −15.7° (1.0, dioxane) (lit.[5] −11.5–13°), mp 218–221°C (lit.[2] 220–222°C).

ANAL. Calcd for $C_{16}H_{12}N_2O_8.C_{23}H_{26}N_2O_4$: C, 62.05%; H, 5.06%; N, 7.44%. Found: C, 62.16%; H, 5.17%; N, 7.34%.

l-2,2′-Dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic Acid (X). The procedure of Slocum and Mislow[5] was used. To a warm dispersion of 18.7 g (0.0248 mole) of the *l*-brucine salt (IX) in 300 ml of water, was added slowly 34 ml of 7*M* aqueous ammonia. The brucine which formed was filtered, and the filtrate was cooled with seeds of brucine in the refrigerator overnight. The solution was filtered through an ultrafine fritted glass funnel, and the filtrate was acidified with dilute hydrochloric acid. The precipitate obtained was filtered and was purified by dissolving in aqueous sodium carbonate, which was filtered through an ultrafine fritted glass funnel and then acidified with dilute hydrochloric acid. The white precipitate was filtered and dried in a vacuum desiccator for 2 days; yield 8.6 g (96.4%), $[\alpha]_D^{24}$ −18.4° (2.48, ethanol) (lit.[3,5,2] −16.1°, −16.3, −20), mp 330°C (lit.[3,5] 350°C, 330–332°C).

ANAL. Calcd for $C_{16}H_{12}N_2O_8$: C, 53.32%; H, 3.36%; N, 7.77%. Found: C, 53.35%; H, 3.39%; N, 7.74%.

2,2′-Dinitro-6,6′-dimethylbiphenyl-4,4′-dicarbonyl Chloride (XI). The procedure of Overberger and Yoshimura[3] was used. A mixture of 8 g (0.0222 mole) of the *l*-acid (X), 0.16 g (0.02 mole) of pyridine which had been dried over potassium hydroxide, and 40 g of distilled thionyl chloride was cooked for 1.45 hr. After the evaporation of excess thionyl chloride, the residue was treated with 200 ml of distilled benzene. The solution was filtered and the filtrate was evaporated to dryness. The product was recrystallized from a mixture of benzene–*n*-hexane (7:3) to give a white powder; yield 7.4 g (85.3%), mp 115–116°C (lit.[3] 98°C), $[\alpha]_D^{21}$ +2.01° (0.996, DMF containing 5% LiCl), infrared spectrum: 1767–1755(s), no band at around 1705 cm^{-1}.

ANAL. Calcd for $C_{16}H_{10}N_2O_6Cl_2$: C, 48.38%; H, 2.54%; N, 7.06%; Cl, 17.86%. Found: C, 48.52%; H, 2.55%; N, 7.14%; Cl, 17.81%.

2,2′-Diamino-6,6′-dimethylbiphenyl-4,4′-dicarboxylic Acid (XII). The procedure of Mislow and Slocum[5] was used, and 24 g of X gave 11.1 g (48.8%) of the desired product (XII), mp 314–318°C (dec) (lit.[5] 314–325°C), $[\alpha]_D^{24} = -30.76$ (95% ethanol) (lit.[2] $[\alpha]_D^{20} = 41.2°$, ethanol).

2,2′-Dichloro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic Acid (XIII). The procedure of Slocum and Mislow[5] was followed, and 10 g of XII gave, after purification by column chromatography, 2.4 g (20.9%) of a white solid, mp 340–350°C (dec.) (lit.[5] 340–364°C), $[\alpha]_D^{23}$ −21° (acetone) (lit.[5] −10.6°).

ANAL. Calcd for $C_{16}H_{12}Cl_2O_4$: C, 56.56%; H, 3.57%; Cl, 20.91%. Found: 56.76%; H, 3.74%; Cl, 20.80%.

2,2′-Dichloro-6,6′-dimethylbiphenyl-4,4′-dicarbonyl Chloride (XIV). A mixture of thionyl chloride (50 ml), 2.0 g of XIII and anhydrous pyridine (2 ml) was refluxed for 2 hr. The clear yellow solution was evaporated to dryness and the residue taken up in 50 ml of dried benzene. The mixture was refluxed for 5 min and filtered. The solution was evaporated and the residue was recrystallized from 40 ml of benzene–*n*-hexane (6:4) solution by slow evaporation of the solvent with a stream of dried nitrogen. The white crystals were collected by filtration and dried *in vacuo* in a desiccator containing KOH; yield 1.4 g (63%), mp 120–122°C; $[\alpha]_D^{24} = -18.85°$ (0.87, benzene).

ANAL. Calcd for $C_{16}H_{10}O_2Cl_4$: C, 51.06%; H, 2.66%; Cl, 37.76%. Found: C, 51.08%; H, 2.61%; Cl, 37.89%.

***N*-Benzoyl-*o*-nitroaniline (XIII-o).** The procedure of Overberger and Yoshimura[3] was used with modification. To a mixture of 5.5 g (0.04 mole) of *o*-nitroaniline (XII-o), 3.2 g (0.04 mole) of dried pyridine, and 60 ml of distilled benzene, was dropped 5.6 g (0.044 mole) of benzoyl chloride at around 10°. After the addition was completed, the mixture was allowed to stand overnight at room temperature. The solution was filtered, and the filtrate was evaporated to dryness. The residue was recrystallized from 95% ethanol. The yellow needles were collected; yield 7.75 g (85%), mp 92°C (lit.[3] 92°C).

ANAL. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.45%; H, 4.16%; N, 11.57%. Found: C, 64.53%; H, 4.15%; N, 11.57%.

***N*-Benzoyl-*o*-phenylenediamine (XIV-o).** The procedure of Overberger and Yoshimura[3] was used. To a mixture of 0.81 g (0.0034 mole) of nitrobenzene XIII-o, 0.03 g of 5% Pd on charcoal, and 50 ml of ethanol charged in a 250 ml Parr bottle, was introduced hydrogen at 29 psi, initial pressure at room temperature. After the quantitative consumption of hydrogen, the catalyst was removed by filtration. The filtrate was evaporated to dryness, and the residue was recrystallized from 95% ethanol. Yellowish needles were obtained; yield 0.53 g (74.7%), mp 138.5°C (lit.[21] 140°C).

ANAL. Calcd for $C_{13}H_{12}N_2O$: C, 73.57%; H, 5.71%; N, 13.18%. Found: C, 73.45%; H, 5.61%; N, 13.13%.

2,2′-Dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic-*N*-benzoyl-*o*-phenylenediamide (XV-o). To a mixture of 0.234 g (0.0011 mole) of the phenylenediamine (XIV-o), 0.08 g (0.001 mole) of dried pyridine in 10 ml of distilled methylene chloride, was dropped a solution of 0.2 g (0.0005 mole) of the dicarbonyl chloride (XI) in 7 ml of methylene chloride at 8–9°C. After the addition, the reaction temperature was allowed to reach 20°C. A white precipitate appeared and was filtered and washed thoroughly with methylene chloride; yield 0.29 g (77.4%), mp 275–276°C (lit.[3] 285–287°C), $[\alpha]_D^{21}$ −1.34° (1.12, DMF containing 5% LiCl).

Anal. Calcd for $C_{42}H_{32}N_6O_8$: C, 67.40%; H, 4.30%; N, 11.21%. Found: C, 67.62%; H, 4.34%; N, 11.18%.

The solubility of this compound (XV-o), the model compound of the polyamide derived from *o*-phenylenediamine, was checked with respect to the measurement of optical properties in the region of the far ultraviolet. It is soluble in trifluoroethanol containing 3% LiCl, tetrafluoropropanol, trimethyl phosphate, and tributyl phosphate, but insoluble in chloroform, cyclohexane, dioxane, trifluoroethanol, and methanesulfonic acid.

2,2′-Dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylate-*N,N*′-dipiperidine (XX) and 2,2′-Dichloro-6,6′-dimethylbiphenyl-4,4′-dicarboxylate-*N,N*′-dipiperidine (XXI). In a typical procedure, XXI was prepared as follows. A solution of the acid chloride (XI), (0.3175 g; 0.8 mmole) in 15 ml of dichloromethane, was added, at once, into a well stirred solution of piperidine (0.33 ml; 3.2 mmole) in 7 ml of H_2O and 15 ml of H_2CCl_2. The final solution was further stirred for 5 min. The H_2CCl_2 was evaporated and the solid was collected by filtration and washed with water. The white solid was recrystallized from 10 ml of dichloromethane–petroleum ether (30–60°C) 1:1 solution. The white crystals were collected by filtration and dried *in vacuo;* yield 0.44 g (99%), mp 178–180°C, $[\alpha]_D^{23}$ = −14.5° (0.69, acetone).

Anal. Calcd for $C_{26}H_{30}N_2O_2Cl_2$: C, 65.95%; H, 6.38%; N, 5.91%. Cl, 14.97%. Found: C, 66.07%; H, 6.42%; N, 5.96%; Cl, 14.90%.

The model compound XX was white in color, yield 98%, mp 206–206.5°C, $[\alpha]_D^{20}$ = −18.4 (0.7, TFE).

Anal. Calcd for $C_{26}H_{30}N_4O_6$: C, 63.29%; H, 6.12%; N, 11.15%. Found: C, 63.29%; H, 6.12%; N, 11.15%.

Polymerization

Methylene chloride, 1500 ml. was washed three times with 150 ml of concentrated sulfuric, once with 150 ml of water, twice with 150 ml of 0.5N sodium hydroxide, and finally with 150 ml of water. After drying over calcium chloride overnight, it was distilled into a flask which contained phosphorous pentoxide and allowed to stand overnight. It was then distilled again and kept cold in a dark bottle.

Polymerization was carried out by the method of interfacial polycondensation.[10] In a 500-ml flask-type blender container precooled overnight in the refrigerator, was charged a solution of 0.297 g (0.00164 mole) of phenylenediamine dihydrochloride in 4.9 ml of water and 16.4 ml of methylene chloride. To the rapidly stirred system, after the introduction of nitrogen, were dropped at once a solution of 0.66 g (0.00166 mole) of the dicarbonyl chloride (XI) in 16.4 ml of methylene chloride and a glass tube containing a solution of 0.87 g (0.00691 mole) of sodium sulfite, employed as an acid acceptor, in 3.3 ml of water. The reaction occurred immediately, as evidenced by the precipitation of polymer. After the mixture was stirred for 5 min, it was poured into 300 ml of water. The polymer was collected on a Büchner funnel and was partly dried. Meanwhile, the container was washed with 25 ml of DMF containing 5% LiCl, and the solution was filtered. The polymer was dissolved in the filtrate, which was then filtered through a medium fritted glass funnel and was dropped slowly into 500 ml of 30% methanol. After standing overnight, the polymer was filtered, washed with 30% methanol and dried *in vacuo* at 80°C 80 mm. The polymer was purified by three reprecipitations, DMF containing 5% LiCl and 30% methanol being used as solvent and nonsolvent, respectively.

The polymer derived from *o*-phenylenediamine (PO) was grayish white in color, yield 0.67 g (94.4%), mp 330°C (dec), $[\eta] = 0.18$ (0.5%, conc. H_2SO_4, 25°C), $[\alpha]_D^{20} = -4.94°$ (1.1, DMF/5% LiCl).

ANAL. Calcd for $C_{22}H_{16}N_4O_6$: C, 61.12%; H, 3.74%; N, 12.94%. Found: C, 59.84%; H, 4.07%; N, 12.83%.

The polymer derived from *m*-phenylenediamine (PM) was gray in color, yield 0.68 g (95.8%), mp >350°C, $[\eta] = 0.37$, $[\alpha]_D^{20} = -0.50°$ (0.99, DMF/5% LiCl).

ANAL. Found: C, 59.57%; H, 4.06%; N, 12.33%.

The polymer derived from *p*-phenylenediamine (PP) was yellow in color, yield 0.68 g (95.8%), mp >350°C, $[\eta] = 1.13$, $[\alpha]_D^{20} = +6.53°$ (0.99, DMF/5% LiCl).

The polymer derived from *o*-phenylenediamine and 2,2′-dichloro-6,6′-dimethyl-4,4′-dicarbonyl chloride (XIV) was grayish white in color, mp 330°C (dec), $[\eta] = 0.10$ (0.5% conc. H_2SO_4, 25°C), $[\alpha]_D^{20} = -19.6°$ (1.1 DMF/5% LiCl).

ANAL. Calcd for $C_{22}H_{16}N_2O_2Cl_2$: C, 64.23%; H, 3.89%; N, 6.81%; Cl, 17.28%. Found: C, 64.01%; H, 4.12%; N, 7.03%; Cl, 17.03%.

The polymer derived from *m*-phenylenediamine and XIV was gray in color, mp 350°C (dec), $[\eta] = 0.33$, $[\alpha]_D^{20} = -19.6°$ (0.99, DMF/5% LiCl).

ANAL. Calcd for $C_{22}H_{16}N_2O_2Cl_2$: C, 64.23%; H, 3.89%; N, 6.81%; Cl, 17.28%. Found: C, 64.01%; H, 4.12%; N, 7.03%; Cl, 17.03%.

The polymer derived from *m*-phenylenediamine and XIV was gray in color, mp 350°C (dec.), $[\eta] = 0.33$, $[\alpha]_D^{20} = -19.6°$ (0.99, DMF/5% LiCl).

ANAL. Found: C, 64.05%; H, 4.06%; N, 6.52%; Cl, 16.82%.

The polymer derived from *p*-phenylenediamine and XIV was yellowish in color, mp >350°C (dec), $[\eta]$ = 1.26, $[\alpha]_D^{25}$ = −18.2° (0.98, DMF/5% LiCl).

ANAL. Found: C, 64.01%; H, 4.12%; N, 7.03%; Cl, 17.03%.

A general procedure for the polymerization of DMP, PIP and PD with XI and XIV is described below. In a Waring Blendor container (250 ml), precooled in the refrigerator, was placed 0.125 g of DMP, 10 ml of dichloromethane, 2.2 ml of 1*N* NaOH (0.0022 mole) and 3.3 ml of H_2O. Into the rapidly stirred mixture was added, all at once, a solution of 0.376 g (0.001 mole) of XIV in 10 ml of dichloromethane. The polymerization mixture was stirred for 5 min, then it was poured into 300 ml of water. Methylene chloride was evaporated in a steam bath and the crude polymer collected by filtration on a Büchner funnel, dried *in vacuo*. The polymer was dissolved in trifluoroethanol (18 ml), filtered through a medium fritted glass funnel, and was dropped slowly into 500 ml of ether. After standing overnight, the polymer was filtered, and dried *in vacuo* at 80°C (25 mm). The polymer was white in color, yield 0.37 g (92.5%), mp >330°C, $[\eta]$ = 0.43 (0.5%, TFE, 25.5°C), $[\alpha]_D^{20}$ = −6.7° (0.1, TFE).

ANAL. Calcd for $C_{22}H_{22}N_2O_2Cl_2$: C, 63.31%; H, 5.27%; N, 6.70%; Cl, 16.99%. Found: C, 63.41%; H, 5.25%; N, 6.32%; Cl, 16.34%.

The polymer derived from piperazine (PIP) and XIV was white in color, yield 0.36 (92%), mp >330°C, $[\eta]$ = 0.39 (0.5%, TFE, 25.5°C), $[\alpha]_D^{20}$ = −6.7° (0.1, TFE).

ANAL. Calcd for $C_{20}H_{18}N_2O_2Cl_2$: C, 61.70%; H, 4.66%; N, 7.19%; Cl, 18.21%. Found: C, 61.53%; H, 4.74%; N, 7.09%; Cl, 18.06%.

The polymer derived from 1,2-pyrazolidine and XIV (PD) was white in color, yield 0.285 (94%), mp 280°C (dec.), $[\eta]$ = 0.10 (0.5%, TFE, 25.5°C), $[\alpha]_D^{20}$ = −6.7° (0.1, TFE).

ANAL. Calcd for $C_{27}H_{16}N_2Cl_2O_2$: C, 63.32%; H, 4.07%; N, 6.90%; Cl, 17.75%. Found: C, 63.10%; H, 4.11%; N, 6.60%; Cl, 17.34%.

The polymer derived from XI (0.825 g) and DMP (0.25 g) was white in color, yield 0.952 g (95%), mp >320°C (dec.), $[\eta]$ = 0.12 (0.5% TFE, 25°C); $[\alpha]_D^{20}$ = −28.00° (1, TFE).

ANAL. Calcd for $C_{22}H_{23}O_6N_4$: C, 60.24%; N, 12.78%; H, 5.02%. Found: C, 60.10%; H, 4.93%; N, 12.10%.

The polymer derived from XI (0.993 g) and PD (0.435 g) was white in color, yield 0.88 g (88%), mp >280°C (dec), $[\eta]$ = 0.09 (0.5% TFE, 25°C), $[\alpha]_D^{20}$ = +5.4° (1, TFE).

ANAL. Calcd for $C_{19}H_{16}N_4O_6$: C, 57.57%; H, 4.04%; N, 14.14%. Found: C, 57.59%; H, 4.23%; N, 13.87%.

Characterization

Polarimetry. The measurements were carried out with an ETL-NPL automatic polarimeter, Type 143A, using a 1 cm cell. The concentrations are given in units of g/100 ml.

Infrared Spectroscopy. Infrared spectra were measured as Nujol mulls by using a Perkin-Elmer grating infrared spectrophotometer Model 257.

Ultraviolet Spectroscopy. Ultraviolet spectra were obtained with a Perkin-Elmer spectrophotometer, Model 202, using 1 cm quartz cells.

Melting Points. Melting points below 250°C were obtained with a Thomas-Hoover Unimelt capillary melting point apparatus with a silicon oil bath. Melting points over 250°C were measured with a Fischer heating block.

Elemental Analyses. Analyses were carried out by Spang Laboratories, Ann Arbor, and Galbraith Laboratories, Knoxville, Tennessee.

Viscometry. Viscosities of the polymers were measured in an Ubbelohde viscometer, No. 200, which gave a flow time of 97 sec for concentrated sulfuric acid at 25.0 ± 0.1°C and 94 sec for trifluoroethanol at 25.5 ± 0.1°C.

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An Optically Active Vinyl Sulfoxide Copolymer and the Configuration of Sulfoxide Adjacent to Radical or Anionic Sites*

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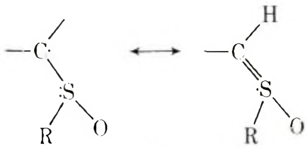
Synopsis

Optically active vinyl *p*-tolyl sulfoxide was synthesized and copolymerized with styrene to produce an optically active copolymer. The question of the configuration of sulfur in a sulfoxide when adjacent to a radical site is discussed. The configuration of sulfur in a sulfoxide is proven to be nonplanar when adjacent to an anionic site.

INTRODUCTION

It has long been known that sulfoxides are not planar and are capable of existing in stable, isolable enantiomeric forms. It seemed that an optically active vinyl sulfoxide would be an interesting comonomer with which to induce asymmetry into a polymeric chain backbone. Furthermore, although sulfoxides are known to be nonplanar, the situation when sulfoxide is adjacent to a radical site as in I is not known. If there is any double-bond character to the carbon–sulfur bond as indicated by the resonance structure on the right, this would involve the formation of a $(p\text{-}d)\ \pi$ bond, the geometrical requirements of which are not necessarily the same as those of a $(p\text{-}p)\ \pi$ bond. In this paper we discuss some aspects of the sulfur stereochemistry problem.



I

RESULTS AND DISCUSSION

R-(+)-Isopropenyl *p*-tolyl sulfoxide (II) was prepared by the general method of Andersen[1] as indicated in eq. (1).

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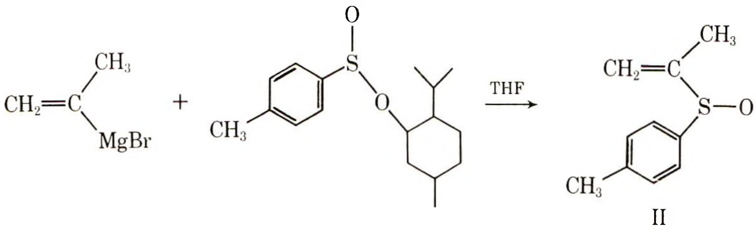
* In honor of C. S. Marvel on the occasion of his 75th birthday.



(1)

S-(−)-Menthyl (−)-*p*-toluenesulfinate was prepared from *p*-toluenesulfinyl chloride and (−)-menthol. Repeated fractional crystallization provided one of the diastereoisomers, the known *S*-(−)-menthyl (−)-*p*-toluenesulfinate. Sulfinate esters have been shown to react with Grignard reagents with 100% inversion of configuration at sulfur.[2–4] Treatment of *S*-(−)-menthyl (−)-*p*-toluenesulfinate with isopropenylmagnesium bromide provided *R*-(+)-isopropenyl *p*-tolyl sulfoxide in 65% yield, $[\alpha]_D^{25}$ 106.9 ± 0.6°. Unfortunately, this compound resisted all attempts at homopolymerization and copolymerization with the use of anionic and radical initiators. We therefore turned our attention to *R*-(+)-vinyl *p*-tolyl sulfoxide, $[\alpha]_D^{25}$ 390.4 ± 0.6°, prepared in the same manner as the isopropenyl compound. This compound did not homopolymerize when treated with initiators such as benzoyl peroxide, azobisisobutyronitrile, *n*-butyllithium, and boron trifluoride etherate.

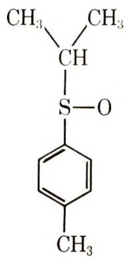
However, we did find that vinyl *p*-tolyl sulfoxide, $[\alpha]_D^{25}$ 390.4°, could be copolymerized with styrene in bulk using azobisisobutyronitrile initiator. The data are summarized in Table I. The copolymer 1, Table I (η_{inh} 0.10) had a specific rotation of −7.2 ± 0.4° in acetone and +4.0 ± 0.3° in benzene (Na D line). The starting material and other sulfoxides were shown to be configurationally stable under the conditions of the polymerization reaction.

If a homopolymer of the vinyl sulfoxide contained only sulfoxide units, of the same degree of optical purity as those in the copolymer, then one might assume that such a homopolymer would have a specific rotation in acetone of

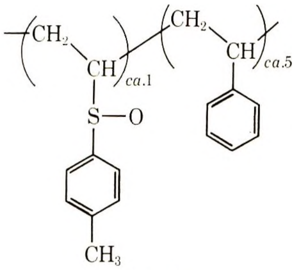
TABLE I
Copolymerization of Vinyl *p*-Tolyl Sulfoxide (M_1) and Styrene (M_2)

	M_1, mole	M_2, mole	Initiator (AIBN), mg	Temp, °C	Time, hr	Conversion, %	Sulfur in copolymer, %	M_1 in copolymer, mole-%
1	0.006	0.006	12-15	60	17.0	21.8	5.40	19.8
2	0.0010	0.0045	5.0	70	0.5	10.8	1.18	3.9
3	0.0010	0.0045	5.0	70	2.75	45.6	—	—
4	0.0015	0.0040	5.0	70	2.75	38.2	—	—
5	0.00275	0.00275	5.0	70	2.75	12.4	4.49	15.5
6	0.0035	0.0020	5.0	70	4.0	7.0	5.72	22.1
7	0.0040	0.0015	5.0	70	8.0	4.9	6.79	25.3
8	0.023	0.023	45	70	16.0	19.5	4.50	15.9

100/19.8 × 7.2 or approximately 36°. An attempt to determine the optical purity of the copolymer by examining the NMR spectrum in optically active 2,2,2-tri-fluorophenylethanol (see Discussion below) was unsuccessful because of the lack of resolution of the appropriate proton signal. However, we do know that *R*-(+)-isopropyl *p*-tolyl sulfoxide has a specific rotation (in acetone) of +176.5°.[3,4] If it is reasonable to assume that isopropyl



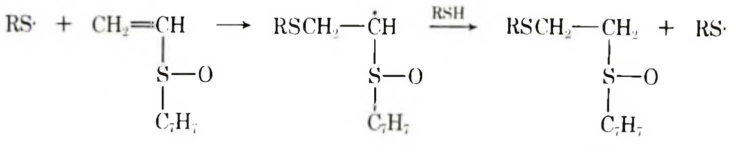
$[\alpha]^{25}_{D}$ 176.5



$[\alpha]^{25}_{D}$ -7.2

p-tolyl sulfoxide is a good model from which the rotation of the optically pure copolymer might be predicted, then considerable racemization of the sulfoxide has occurred during polymerization. The question is, of course, how good a model is the isopropyl compound for the polymer? We are only comparing rotations at the sodium D line and the benzene chromophore from the styrene units could effect the rotation of the copolymer. We are currently carrying out circular dichroism studies to clarify this point. At this moment we can say that the sulfoxide does not racemize completely when adjacent to a radical site, but whether partial racemization occurs is not yet known.

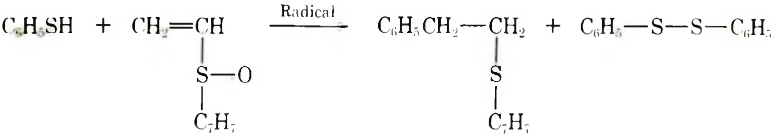
Of course it would have been desirable to carry out the radical addition of a small molecule, such as a mercaptan, to optically active vinyl-*p*-tolyl sulfoxide. This would result in the formation of III, and we know how to



$$RS\cdot + CH_2{=}CH{-}S{-}O{-}C_7H_7 \longrightarrow RSCH_2{-}\dot{C}H{-}S{-}O{-}C_7H_7 \xrightarrow{RSH} RSCH_2{-}CH_2{-}S{-}O{-}C_7H_7 + RS\cdot \qquad (2)$$

III

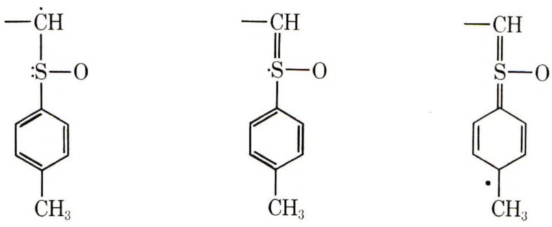
determine the optical purity of III (See below). Unfortunately, thiophenol and vinyl *p*-tolyl sulfoxide in the presence of benzoyl peroxide or azobisisobutyronitrile, do not yield the desired product, but rather the compounds shown in eq (3). A number of other small molecule radical additions were attempted with CCl_4, $CHCl_3$, $BrCCl_3$ and *n*-$C_6H_{13}CHO$. In no



$$C_6H_5SH + CH_2{=}CH{-}S{-}O{-}C_7H_7 \xrightarrow{\text{Radical}} C_6H_5CH_2{-}CH_2{-}S{-}C_7H_7 + C_6H_5{-}S{-}S{-}C_6H_5 \qquad (3)$$

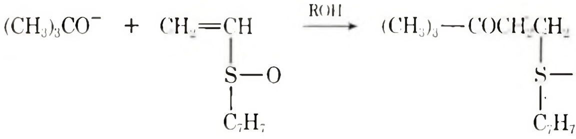
case did spectra of the crude products indicate that the desired product was present to a significant extent. The reaction products were oils from which we were not able to isolate pure compounds.

The question here is whether or not there is any $p\pi$–$d\pi$ overlap, indicated in valence bond terms in resonance form I, and if so, what are the geometrical requirements of such a system. There has been some discussion in the literature of $p\pi$–$d\pi$ bonding in systems similar to ours. For example, Price and Gilbert[5] report a much larger value of Q for vinyl methyl sulfide (0.34) than for vinyl methyl ether (0.015) and attribute this to expansion of the sulfur octet. Vinyl methyl sulfoxide, however, has a considerably smaller Q value (0.10) than vinyl methyl sulfide. This would indicate that $p\pi$–$d\pi$ overlap is considerably less important in the case of vinyl methyl sulfoxide than in the case of vinyl methyl sulfide. Vinyl methyl sulfoxide, however, is not necessarily a good model from which to draw conclusions concerning the monomer used in this work; vinyl p-tolyl sulfoxide. In the latter case radical delocalization may extend through sulfur into the benzene ring.



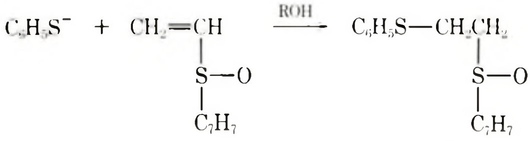
In fact this kind of delocalization through sulfur has been offered as an explanation for the greatly enhanced radical reactivity of divinyl sulfide relative to vinyl methyl sulfide.[6] In order to learn about the effect of the phenyl group, reactivity ratios were determined for vinyl p-tolyl sulfoxide and styrene. The copolymerization data used were runs 2, 5, 6, and 7 (see Table I). An averaging correction was necessary because of the relatively high conversions involved.[7] A plot of r_1 versus r_2 gives r_1 (vinyl p-tolyl sulfoxide) 0.10 ± 0.07, r_2 (styrene) 5.77 ± 0.10. The values for vinyl methyl sulfoxide (M_1) and styrene (M_2) are: r_1 0.01; r_2 4.2. These data support extended delocalization of the odd electron as indicated in the valence bond pictures.

Although short-lived carbanions adjacent to sulfoxide are reported to cause no stereomutation at sulfur,[8a] a long lived carbanion can cause such a change.[8b] In view of our observation with regard to a radical site adjacent to sulfur, it was desirable to confirm this observation in our system. Recently Abbott and Stirling[9] reported the nucleophilic addition of methoxide and piperidine to a racemic vinyl sulfoxide. In agreement we found that potassium *tert*-butoxide, piperidine, and sodium thiophenoxide readily added to vinyl p-tolyl sulfoxide as shown in eqs. (4)–(6).



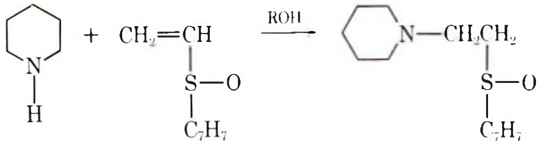
$$(CH_3)_3CO^- + CH_2{=}\underset{\substack{|\\ S-O\\ |\\ C_7H_7}}{CH} \xrightarrow{ROH} (CH_3)_3-COCH_2\underset{\substack{|\\ S-O\\ |\\ C_7H_7}}{CH_2} \qquad (4)$$

IV



$$C_6H_5S^- + CH_2{=}\underset{\substack{|\\ S-O\\ |\\ C_7H_7}}{CH} \xrightarrow{ROH} C_6H_5S-CH_2\underset{\substack{|\\ S-O\\ |\\ C_7H_7}}{CH_2} \qquad (5)$$

III



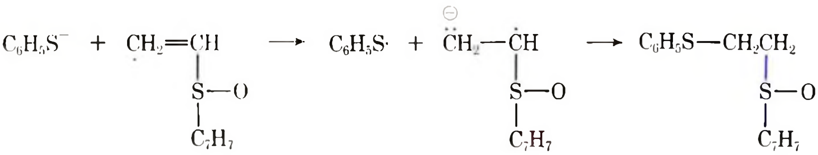
(6)

V

β-Phenylmercaptoethyl *p*-tolyl sulfoxide (III) was prepared by the addition of optically active vinyl *p*-tolyl sulfoxide to an equivalent of sodium thiophenoxide in water. The crude product (84.5%) had mp 76–79°C, $[\alpha]_D^{26}$ 145.4 ± 0.3° (*c* 1.44, acetone).

Recrystallization from methylene chloride–hexane yielded white needles with mp 83.5–84.0°C and $[\alpha]_D^{26}$ 162.1° (*c* 0.4, acetone) as well as elongated plates with mp 68.0–69.0°C and $[\alpha]_D^{26}$ 90 ± 1°. Comparison of these two crystalline forms in the infrared (CCl_4 solution) showed that they were identical. This is also indicated by their mixed melting point, mp 78.5–80.0°C, which lies between the two as expected. The racemic compound has mp 72–73°C (see below).

A number of apparently nucleophilic reactions have recently been shown to proceed by an electron transfer process involving radical intermediates.[10] A number of attempts to detect radical intermediates by electron spin resonance measurements of the reaction mixture were unsuccessful.



$$C_6H_5S^- + CH_2{=}\underset{\substack{|\\ S-O\\ |\\ C_7H_7}}{CH} \longrightarrow C_6H_5S\cdot + \overset{\ominus}{\ddot{C}H_2}-\underset{\substack{|\\ S-O\\ |\\ C_7H_7}}{\dot{C}H} \longrightarrow C_6H_5S-CH_2\underset{\substack{|\\ S-O\\ |\\ C_7H_7}}{CH_2} \qquad (7)$$

Graff et al.[11] were the first to describe an isotopic dilution technique for the determination of both L- and D-amino acids in biological material. Bersen and Ben-Efraim[12] developed this technique into a method for determining optical purities, and this subject has recently been reviewed.[13]

The method involves the addition of labeled racemate to unlabeled optically active compound and reisolating the racemate, generally by fractional crystallization. By measuring the label content and the rotation of the reisolated material, one can determine the rotation of optically pure enantiomer.[13]

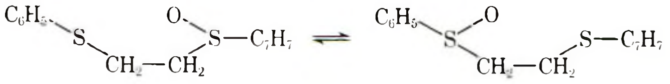
Deuterated, racemic β-phenylmercaptoethyl *p*-tolyl sulfoxide (mp 72–73°C) was prepared by the treatment of vinyl *p*-tolyl sulfoxide with sodium thiophenoxide in deuterium oxide or in a mixture of deuterium oxide and methanol-O,*d*. The product contained 0.86 deuterium atom per molecule.

Deuterated racemic sulfoxide was added to optically active sulfoxide $[\alpha]_D^{25}$ 162°, and the mixture was recrystallized until the rotation was 47°. The deuterium content of this material was determined and the absolute rotation of β-phenylmercaptoethyl *p*-tolyl sulfoxide was found[13] to be 176.9 ± 2.4°.

The crude product from the addition of sodium thiophenoxide to optically active vinyl *p*-tolyl sulfoxide had a specific rotation of 145.4 ± 0.3. It was necessary to determine if this value was enhanced by the presence of unreacted optically active vinyl *p*-tolyl sulfoxide $[\alpha]_D^{25}$ 390°. For one thing the NMR spectrum of the crude product showed no vinyl hydrogen. An examination of the ultraviolet spectra was also helpful. Pure β-phenylmercaptoethyl *p*-tolyl sulfoxide, mp 83.5–84.0°C, in 95% ethanol had λ_{max} 248 mμ(ϵ10,800), whereas the crude product had λ_{max} 248 mμ(ϵ 10,700). At 229 mμ pure vinyl *p*-tolyl sulfoxide has a maximum with ϵ 12,100. At 229 mμ the crude addition product has ϵ 9,500, whereas the pure compound has ϵ 9,300. The difference between 9,300 and 9,500 shows that the maximum amount of unreacted starting material would be approximately 2%. Assuming a linear relationship between composition and rotation, unreacted starting material could have increased the rotation by 6°. We may say then that the initially formed product had a rotation between 139° and 145°.

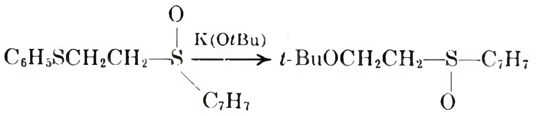
The optical purity of the crude β-phenylmercaptoethyl *p*-tolyl sulfoxide would then be 79–82%.

The vinyl *p*-tolyl sulfoxide and β-phenylmercaptoethyl *p*-tolyl sulfoxide were both found to be optically stable under the reaction conditions. However, one might argue that a facile equilibrium occurred, causing racemization as in eq. (8).



(8)

Treatment of crude β-phenylmercaptoethyl *p*-tolyl sulfoxide with potassium *tert*-butoxide in *tert*-butyl alcohol resulted in an elimination–addition reaction to yield β *tert*-butoxyethyl *p*-tolyl sulfoxide. Thus the equilibrium



$$C_6H_5SCH_2CH_2\overset{O}{\underset{C_7H_7}{S}} \xrightarrow{K(OtBu)} t\text{-}BuOCH_2CH_2\underset{O}{S}—C_7H_7$$

in eq. (8) does not take place under the reaction conditions. Furthermore the rotation remains constant with time and if the equilibrium above is occurring, then not only would both isomers have to have the same rotation, but, in addition, every oxygen transfer would have to occur with 100% retention of configuration, a highly unlikely prospect.

Because the Andersen method for the preparation of opically active sulfoxides is known to proceed with 100% inversion[2–4] and because our vinyl *p*-tolyl sulfoxide was prepared from diastereomerically pure menthyl sulfinate ester, we originally believed that the vinyl compound was optically pure and that the addition reaction proceeded with some racemization (ca. 20%). However, we determined that the vinyl compound was not optically pure using an NMR method described by Pirkle and Beare.[14] The 100 MHz NMR spectrum of vinyl *p*-tolyl sulfoxide ($[\alpha]_D^{25}$ 390.4°) was examined by using a sample composed of a 2:1:3 mole ratio of *R*-(−)-2,2,2-trifluorophenylethanol, sulfoxide, and carbon tetrachloride, respectively.

In the vinyl proton region, optically active vinyl *p*-tolyl sulfoxide shows a well defined ABX pattern in CCl_4. However, in optically active trifluorophenylethanol each ABX signal is accompanied by a new signal about 0.02 ppm removed at 1000 Hz sweep width. By integration the vinyl *p*-tolyl sulfoxide was determined to have an optical purity of 80–81%. The racemization of this sulfoxide probably resulted during the isolation and purification procedure which required distillation at elevated temperatures for considerable periods of time. Sulfoxides are known to racemize thermally.

The optical purity of the starting material and the product are the same. Comparison of the ORD and CD spectra of the starting material and product (Fig. 1 and Fig. 2) indicates that addition occurs with retention of configuration about sulfur and that the sulfoxide does not lose its configuration when adjacent to a carbanion.[8] *

In further confirmation, ethyl *p*-tolyl sulfoxide was observed to maintain configuration during hydrogen-tritium exchange. (See Khim, *et al.*[8a]) A $0.17M$ $t\text{-}C_4H_9OT$ solution of ethyl *p*-tolyl sulfoxide was observed to undergo approximately 33% exchange in the presence of $0.78M$ $t\text{-}C_4H_9OK$ at 60.4 ± 0.1°C over 17 hr. The rotations were followed in less concentrated solutions to approximately 12% exchange with no observable change. This observation is complicated, however, by the fact that exchange may have occurred at the *p*-tolyl group.

β-tert-Butoxyethyl *p*-tolyl sulfoxide (IV) was prepared in approximately 76% yield by treating 80–81% optically pure vinyl *p*-tolyl sulfoxide with *tert*-butoxide in *tert*-butyl alcohol. The NMR determination of optical purity of this sulfoxide in *R*-(−)-2,2,2-trifluorophenylethanol indicated it was approximately 77 ± 1% optically pure. Thus, the original conclusion is borne out again.

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* Since the completion of this work, Hutchinson et al.[16] have shown that base-catalyzed H–D exchange of the α-sulfinyl protons in conformationally rigid *cis* and *trans*-4-phenyltetrahydrothiopyron 1-oxides occurs without loss of configuration at sulfur.

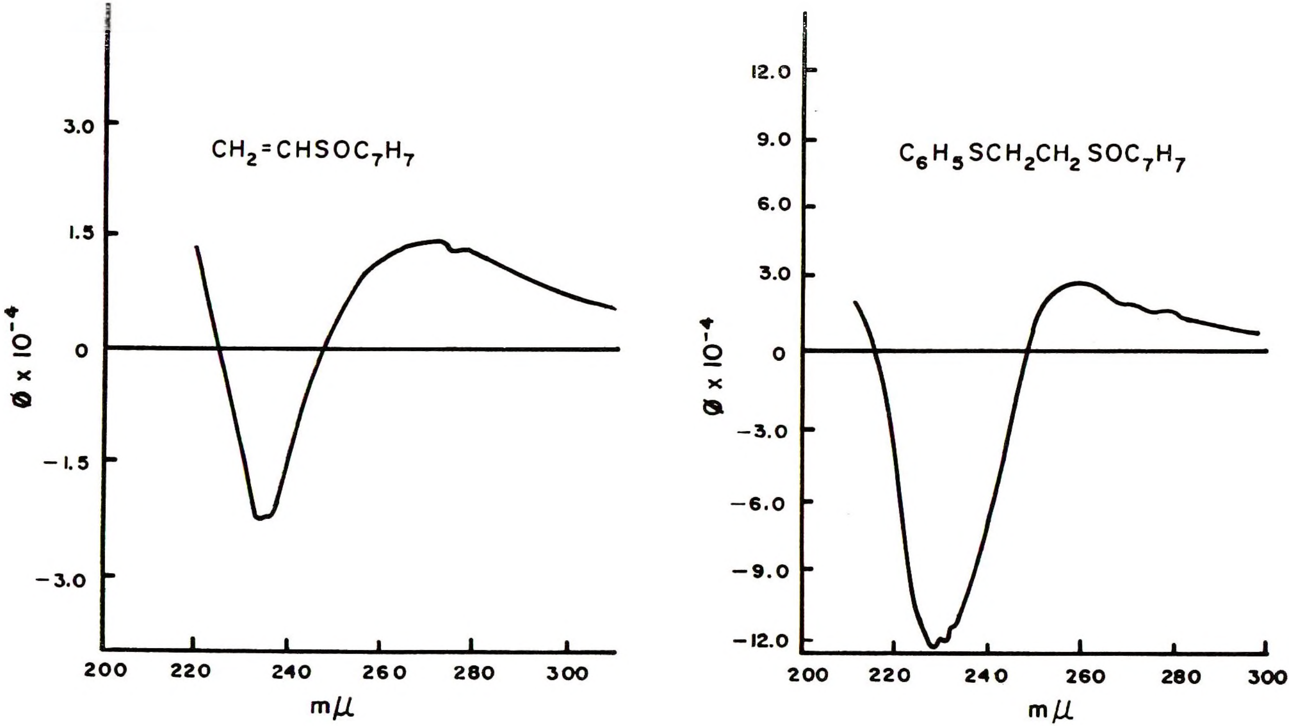

Fig. 1. Optical rotatory dispersion curves of vinyl *p*-tolyl sulfoxide and β-phenylmercaptoethyl *p*-tolyl sulfoxide.

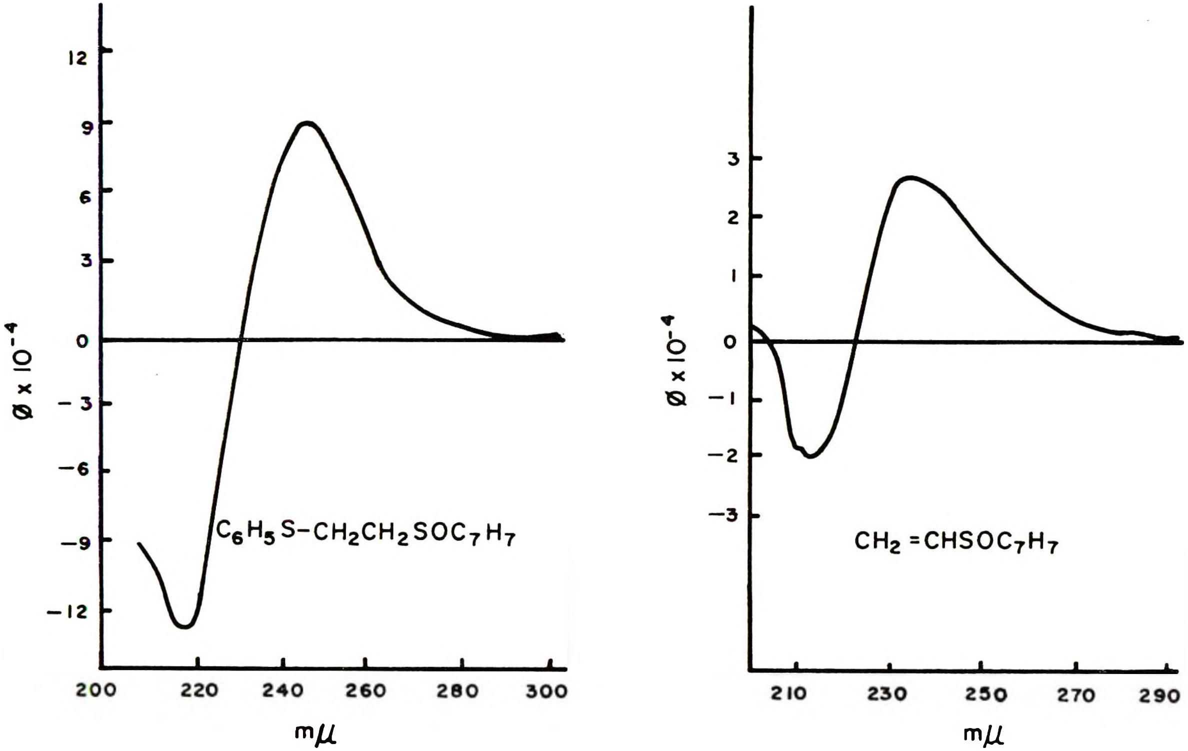

Fig. 2. Circular dichroism curves for vinyl *p*-tolyl sulfoxide and β-phenylmercaptoethyl *p*-tolyl sulfoxide.

β-*N*-Piperidinyl *p*-tolyl sulfoxide (V) was prepared by the reaction of vinyl *p*-tolyl sulfoxide and piperidine in methanol in approximately 60% yield. The NMR determination of its optical purity was unsuccessful. Nonequivalence was not observed.

The above reactions represent conditions under which the anions adjacent to sulfur are only transient species. For this reason *n*-butyl-lithium was added to vinyl *p*-tolyl sulfoxide in the hope of forming "long-lived" carbanions. Also, the desired product, *n*-hexyl *p*-tolyl sulfoxide, could be conveniently synthesized by Andersen's method. Organolithium compounds are known to undergo complex reactions with sulfoxides, yielding products of reduction, disproportionation, etc. However, we had hoped that the use of *N*,*N*,*N'*,*N'*-tetramethylethylenediamine and low temperatures would lead to a clean addition reaction. This proved not to be the case. Treatment of vinyl *p*-tolyl sulfoxide with *n*-butyllithium gave a complex mixture; spectroscopic evidence indicated the presence of *n*-hexyl *p*-tolyl sulfide and *n*-butyl *p*-tolyl sulfide.

The fact that a sulfoxide adjacent to a carbanion retains its configuration makes it appear likely that the low rotation of the styrene vinyl *p*-tolyl sulfoxide copolymer, prepared by radical initiation, is not due to extensive racemization at the sulfoxide. Further work on this problem is underway.

EXPERIMENTAL

Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Nuclear magnetic resonance (NMR) spectra were determined on either a Varian Model A-60 spectrometer at 60 MHz or a Varian Model HA-100 spectrometer at 100 MHz with the use of tetramethylsilane as an external or internal standard. NMR spectra are presented in tau (τ) units, with peak description and integration in parentheses, followed by assignment. The solvent used is also presented in parentheses preceding the tau values. Viscosities were determined at 25°C in Cannon-Fenske viscometers. Optical rotations were determined on a Cary 60 recording spectropolarimeter, and concentrations (*c*) are given in grams per 100 ml of solvent.

Microanalyses were performed by either the Micro-Tech Laboratories, Skokie, Illinois, or by the Huffman Laboratories, Wheatridge, Colorado. Deuterium analyses and molecular weight determinations were determined on a Hitachi Perkin Elmer RHU-6E mass spectrometer.

Mallinckrodt reagent-grade styrene was purified by stirring with 5% potassium hydroxide, washing with distilled water, drying over magnesium sulfate and distilling over calcium hydride at reduced pressure.

Thionyl chloride (500 ml) was purified by rapid distillation from 25 ml of dipentene. Eastman practical grade piperidine was purified by 24 hr reflux over potassium hydroxide prior to final distillation.

p-Toluenesulfinyl Chloride

This compound was prepared by the method of Phillips.[17] The *p*-toluenesulfinyl chloride was obtained as a pale yellow oil in 98% yield.

S-(−)-Menthyl (−)-*p*-Toluenesulfinate

This compound was prepared essentially according to the published procedure of Phillips[17] with slight modification of Herbrandson.[18] A solution of (−)-menthol (156 g, 1.0 mole) in pyridine (100 g) was cooled to −10°C, and *p*-toluenesulfinyl chloride (174 g, 1.0 mole) was added in small quantities. The reaction mixture was maintained at −18°C for 24 hr. At the end of this time, water was added, and the liberated oil was extracted with three 500-ml portions of diethyl ether, washed with water, and dried over anhydrous magnesium sulfate. After removal of diethyl ether, the oil deposited crystals on cooling which were separated by filtration and recrystallized from petroleum ether to give a mixture of diastereoisomers of menthyl *p*-toluenesulfinate (79 g, 27%), mp 101–103°C. The remaining oil from the above was treated with hydrogen chloride for a few minutes and placed in the refrigerator at 2°C. After several hours, crystals deposited which were collected on a filter and recrystallized from petroleum ether to give 160 g (55%) of a mixture of diastereoisomers of menthyl *p*-toluenesulfinate. The combined solids were recrystallized 8 to 12 times from a 3:17 water-acetone mixture to give pure *S*-(−)-menthyl (−)-*p*-toluenesulfinate, mp 106–106.5°C, $[\alpha]_D^{25}$ −200° (*c* 2, acetone), lit.[2] 106–107°C, $[\alpha]_D^{25}$ −199° (*c* 2, acetone). The ester was stored in the dark over phosphorus pentoxide in a desiccator.

Isopropenyl- and Vinylmagnesium Bromide

The above Grignard reagents were prepared according to the method of Normant.[19]

Isopropenyl *p*-Tolyl Sulfoxide

The procedure was similar to that of Andersen[1] for the synthesis of other optically active sulfoxides. *S*-(−)-Menthyl (−)-*p*-toluenesulfinate (294 g, 1.0 mol) and anhydrous diethyl ether (250–300 ml) were placed in a flask protected by a drying tube under nitrogen. A solution of isopropenylmagnesium bromide (1.50 mole) in 750 ml of tetrahydrofuran was added dropwise over 0.5 hr with stirring at room temperature. After stirring overnight and an additional 3 hr under reflux, saturated aqueous ammonium chloride was added until the inorganic salts precipitated, leaving a clear pale green ethereal solution. The solvent was decanted, and the inorganic residue was extracted by stirring with diethyl ether. The combined ether solutions were dried over anhydrous magnesium sulfate and concentrated leaving a red wine colored liquid. The sulfoxide was distilled through a spinning band column to yield 117 g (65%) of the sulfoxide, bp 85.5–86.5°C (0.2 torr), n_D^{23} 1.5691, $[\alpha]_D^{25}$ 106.9 ± 0.6° (*c* 1.55, acetone). The NMR spectrum (CCl_4) showed peaks at 2.60 τ (quartet, 4H) assigned to the aromatic protons; 4.05 τ (doublet, 1H), 4.48 τ (multiplet, 1H) assigned to the vinyl protons; 7.63 τ (singlet, 3H) assigned to the *p*-methyl group; and 8.34 τ (doublet, 3H) assigned to the α-methyl group. The infrared spectrum (neat) showed a strong absorption at 1055 cm^{-1} assigned to the sulfoxide S-O stretch.

ANAL. Calcd for $C_{10}H_{12}OS$: C, 66.62%; H, 6.70%; S, 17.78%. Found: C, 66.55%; H, 6.76%; S, 17.70%.

Vinyl *p*-Tolyl Sulfoxide

Vinyl *p*-tolyl sulfoxide was prepared by the above procedure with the exception that the best yields (45%) were obtained by using a 1:1 molar ratio of the vinylmagnesium bromide to *S*-(−)-menthyl (−)-*p*-toluenesulfinate, and a large excess of diethyl ether (800 ml). An analytical sample distilled from calcium hydride had bp 79–80°C (0.04 torr), $n_D^{24.4}$ 1.5766, $[\alpha]_D^{25}$ 390.4 ± 0.6° (*c* 1.2, acetone). The NMR spectrum (CCl_4) showed peaks at 2.71 τ (quartet, 4.2H) assigned to the aromatic protons; 3.40 τ (quartet, 1H), 4.03 τ (doublet, 1H), 4.28 τ (doublet, 1H) assigned to the three vinyl protons; and 7.68 τ (singlet, 3H) assigned to the *p*-methyl group. The infrared spectrum (neat) showed a strong absorption at 1050 cm^{-1} assigned to the sulfoxide S—O stretch.

ANAL. Calcd for $C_9H_{10}OS$: C, 65.05%; H, 6.01%; S, 19.30%. Found: C, 65.10%; H, 6.30%; S, 19.29%.

Ethyl *p*-Tolyl Sulfoxide

This compound was prepared by the method of Andersen[1] with slight modification. To a solution of 47 g (0.16 mole) of *S*-(−)-menthyl (−)-*p*-toluenesulfinate in 900 ml of anhydrous diethyl ether was added approximately 50% excess of ethylmagnesium bromide prepared by the reaction of 27.3 g (0.25 mole) of ethyl bromide and 6.0 g (0.25 g-atom) of magnesium in 350 ml of anhydrous diethyl ether. The addition was completed within 0.5 hr and the reaction mixture was then washed with 10% hydrochloric acid, 10% sodium carbonate and water. The ethereal layer was dried over anhydrous magnesium sulfate and concentrated. The residue was distilled to give 10.1 g (35.8%) of product, bp 97–98° (0.3 torr), $[\alpha]_D^{25}$ 189.5 ± 1° (*c* 1.37, acetone); lit.[3,4,20] bp 94°C (0.4 torr), $[\alpha]_D$ 187.5° (acetone); $[\alpha]_D^{25}$ 203.2° (*c* 0.6, acetone).

β-Phenylmercaptoethyl *p*-Tolyl Sulfoxide

To a solution of 1.6 g (0.012 mole) of sodium thiophenoxide (prepared by reaction of equimolar quantities of thiophenol and finely cut sodium in anhydrous diethyl ether) in 50 ml of water was added 2.0 g (0.012 mole) of vinyl *p*-tolyl sulfoxide. The heterogeneous mixture was stirred at 30–32°C for 1 hr and then extracted with diethyl ether. The ethereal solution was washed with water and then dried over magnesium sulfate and concentrated, yielding 2.8 g (84.5%) of the crude product, mp 76–79°, $[\alpha]_D^{26}$ 145.4 ± 0.3 (c 1.44, acetone). The NMR spectrum (CCl_4) showed peaks centered at 2.75 τ (multiplet, 8.7H) assigned to the aromatic protons; 7.05 τ (multiplet, 4H) assigned to the two methylene groups; and 7.69 τ (singlet, 2.9H) assigned to the p-methyl groups. The infrared spectrum showed a strong absorption at 1050 cm^{-1} assigned to the sulfur–oxygen stretching vibration.

ANAL. Calcd for $C_{15}H_{16}OS_2$: C, 65.24%; H, 5.79%; S, 23.19%; MW, 276. Found: C, 64.71%; H, 5.91%; S, 23.10%; MW, 276 (mass spectrometer).

β-Phenylmercaptoethyl p-tolyl sulfoxide was also prepared in 80–83% crude yield by the homogeneous reaction of sodium thiophenoxide and vinyl p-tolyl sulfoxide in aqueous methanol at 30–32°C $[\alpha]_D^{25}$ 135.9 ± 0.01 (c 0.74, acetone), and in 20–60% crude yield by the reaction of vinyl p-tolyl sulfoxide, thiophenol, and sodium methoxide at 70–75°C.

β-*t*-Butoxyethyl *p*-Tolyl Sulfoxide

To a solution of 0.67 g (0.006 mole) of potassium *tert*-butoxide in 25 ml of *tert*-butyl alcohol was added 1.0 g (0.006 mol) of vinyl p-tolyl sulfoxide. The reaction mixture was stirred at room temperature for 4–7 hr and then extracted with diethyl ether. The ether layer was dried over anhydrous magnesium sulfate, and concentrated under vacuum yielding 1.1 g (76.4%) of product. This material was distilled by using a Hickman still (0.001 torr, 90–100°) to give 950 mg of product, $[\alpha]_D^{25}$ 149.4 ± 0.3 (c 0.79, acetone). The NMR spectrum (CCl_4) showed peaks at 2.78 τ (quartet, 4H) assigned to the aromatic protons; 6.52 τ (multiplet, 1.9H) assigned to the CH_2—O protons; 7.36 τ (multiplet, 2.1H) assigned to the CH_2—S protons; 7.79 τ (singlet, 3.2H) assigned to the p-methyl group; and 8.97 τ (singlet, 10H) assigned to the *tert*-butyl group. The infrared spectrum showed a strong S—O stretching band at 1045 cm^{-1}.

ANAL. Calcd for $C_{13}H_{20}O_2S$: C, 65.00%; H, 8.33%; S, 13.33%. Found: C, 64.77%; H, 8.43%; S, 13.61%.

β-*N*-Piperidinyl *p*-Tolyl Sulfoxide

To a solution of 1.02 g (0.012 mole) of piperidine in 5 ml of methanol was added 2.0 g (0.012 mole) of vinyl p-tolyl sulfoxide. The reaction mixture was stirred for 24 hr at room temperature and then extracted with diethyl ether. The ethereal layer was dried over magnesium sulfate and concentrated to give 1.8 g (59.7%) of crude product. Distillation through a Hickman still (0.001 torr, 90–100°) yielded 1.4 g of product, $[\alpha]_D^{25}$ 122.0 ± 0.3 (c 0.58, acetone). The infrared spectrum showed a strong S—O stretching band at 1040 cm^{-1}.

ANAL. Calcd for $C_{14}H_{21}NOS$: C, 66.93%; H, 8.36%; S, 12.74%; N, 5.57%. Found: C, 64.08%; H, 8.37%; S, 12.68%; N, 5.21%.

The picrate of β-N-piperidinylethyl *p*-tolyl sulfoxide was prepared according to the procedure of Shriner et al.[21] After recrystallization from ethanol the product had mp 128.5–130.5°C.

ANAL. Calcd for $C_{20}H_{24}N_4O_8S$: C, 50.00%; H, 5.00%; N, 11.66%; S, 6.66%. Found: C, 49.94%; H, 5.18%; N, 11.58%; S, 6.88%.

Poly(vinyl *p*-Tolyl Sulfoxide-co-Styrene)

In a typical experiment a mixture of 1.0 g (0.006 mole) of vinyl *p*-tolyl sulfoxide, 0.63 g (0.006 mole) of styrene, and 12–15 mg of azobisisobutyronitrile was degassed by the freeze–thaw method, flushed with nitrogen, and heated at 60°C for 17 hr. The copolymer was dissolved in benzene and precipitated from methanol in a high-speed mixer. The copolymer was again dissolved in benzene and precipitated from methanol. The solid was then dissolved in benzene, filtered, and freeze-dried to give 350 mg (21.8% conversion) of a fine white powder (see Table I). This material contained 5.40% sulfur, indicating the incorporation of 19.8 mole-% vinyl *p*-tolyl sulfoxide into the copolymer; η_{inh} 0.10 (0.59 g in 100 ml benzene), $[\alpha]_D^{25} -7.2 \pm 0.4°$ (*c* 0.52, acetone), $[\alpha]_D^{25} +4.0 \pm 0.3°$ (*c* 0.50, benzene).

β-Phenylmercaptoethyl *p*-Tolyl Sulfide

In attempting to add thiophenol to vinyl *p*-tolyl sulfoxide by a free-radical reaction, β phenylmercaptoethyl *p*-tolyl sulfide was formed in 10–30% yield. In a typical experiment 7.8 g (0.07 mole) of thiophenol was added to a mixture of 8.0 g (0.046 mole) of vinyl *p*-tolyl sulfoxide and 100 mg of azobisisobutyronitrile. The mixture was purged with nitrogen and then heated at 72–75°C for 5–6 hr. Distillation of the reaction mixture at reduced pressure yielded, in addition to recovered thiophenol, 3.8 g (47%) of vinyl *p*-tolyl sulfoxide and 3.6 g of a high-boiling fraction (130–150°C, 0.05 torr) which solidified on cooling. This material was recrystallized from aqueous methanol to give 1.2 g (10%) of β-phenylmercaptoethyl *p*-tolyl sulfide, mp 47–48°C.

ANAL. Calcd for $C_{15}H_{16}S_2$: C, 69.40%; H, 6.16%; S, 24.60%. Found: C, 69.21%; H, 6.08%; S, 24.63%.

The NMR and infrared spectra were consistent with the structure of the isolated product, and a mixed melting point with an authentic sample (prepared in 60% yield by the reaction of equimolar quantities of β-chloroethyl *p*-tolyl sulfide, thiophenol, and sodium methoxide at room temperature) showed no depression.

Determination of the Absolute Rotation of β-Phenylmercaptoethyl *p*-Tolyl Sulfoxide via the Isotopic Dilution Technique

β-Phenylmercaptoethyl *p*-tolyl sulfoxide was found to have an absolute rotation of 176.9 ± 2.4° by the method of Bersen and Ben-Efraim.[12] In a typical experiment, 0.23953 g of the test sample ($[\alpha]_D^{25}$ 162.1°, mp 83.5–84.0°C) was added to 0.29163 g of the deuterated racemate, β-phenylmercaptoethyl *p*-tolyl sulfoxide (mp 72–73°C), shown to have 0.861 deuterium atom per molecule. Recrystallization from methylene chloride-hexane gave material having 0.507 deuterium atom per molecule and $[\alpha]_D^{25}$ 47.1. Calculation of the absolute rotation (see Discussion) gave a value of 174.6°; a second determination gave a value of 179.3°.

Hydrogen–Tritium Exchange of *R*-(+)-Ethyl *p*-Tolyl Sulfoxide

The procedure of Cram and Pine[8] for hydrogen–deuterium exchange of sulfoxides was employed for the hydrogen-tritium exchange of *R*-(+)-ethyl *p*-tolyl sulfoxide, $[\alpha]_D^{25}$ 189.5 ± 1°. The exchange reaction was carried out at 60.4 ± 0.1°C on a 0.17*M* solution of the substrate in 0.78*M* solution of potassium *tert*-butoxide in *tert*-BuOT. The tritiated alcohol was prepared by treating potassium *tert*-butoxide with HTO followed by distillation over calcium hydride. After 17 hr, the reaction was terminated by addition of water and extracted with diethyl ether. The ether layer was washed with water, dried over magnesium sulfate and concentrated under vacuum for 36 hr. The recovered sulfoxide had 5.05×10^9 disintegration/min-mole compared to 15.3×10^9 disintegration/min-mole for the alcohol, corresponding to approximately 33% exchange.

The optical rotation of a 0.04*M* solution of sulfoxide (0.16*M* *t*-BuOK) in *tert*-butyl alcohol at 60.4 ± 0.1°C was followed to an estimated 12% exchange (7 days) with no observed change in rotation.

β-Chloroethyl *p*-Tolyl Sulfide

This compound was prepared according to the procedure of Angeletti et al.[22] in 85% yield, $n_D^{24.5}$ 1.5685, lit.[21] n_D^{20} 1.5728. This compound was identified by its nmr and ir spectra.

R-(—)-2,2,2-Trifluorophenylethanol

Trifluoroacetophenone was prepared in 72% yield by the method of Levine and Dishard.[23] *dl*-2,2,2-Trifluorophenylethanol was obtained in approximately 80% yield by treating trifluoroacetophenone with methanolic sodium borohydride.

Partial resolution was accomplished by the procedure of Pirkle et al.[24] to yield approximately 75% of the alcohol, $[\alpha]_D^{25}$ −10.5° (neat, lit.[24] $[\alpha]_D^{25}$ −40° (neat, identified by its infrared and NMR spectra.

Vinyl *p*-Tolyl Sulfide and Vinyl Phenyl Sulfide

These compounds were prepared by the method of Bohome and Bentler[25] in 20–30% yield, and identified by their NMR and infrared spectra.

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We wish to thank Dr. W. H. Pirkle for obtaining the NMR spectrum of one of our compounds in optically active *α*-phenyltrifluoroethanol.

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Contents (continued)

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