Vol. 8, Part A-1, No. 11, November 1970

Journal of Polymer Science
Part A-1: Polymer Chemistry

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Published by INTERSCIENCE PUBLISHERS a division of John Wiley & Sons, Inc.

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The Journal of Polymer Science is published in four sections as follows: Part A-1, Polymer Chemistry, monthly; Part A-2, Polymer Physics, monthly; Part B, Polymer Letters, monthly; Part C, Polymer Symposia, irregular.

Published monthly by Interscience Publishers, a Division of John Wiley & Sons, Inc., covering one volume annually. Publication Office at 20th and Northampton Sts., Easton, Pa. 18042. Executive, Editorial, and Circulation Offices at 605 Third Avenue, New York, N. Y. 10016. Second-class postage paid at Easton, Pa. Subscription price, $325.00 per volume (including Parts A-2, B, and C). Foreign postage $15.00 per volume (including Parts A-2, B, and C).

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3045–3050 (1970)

Influence of Mass Transfer at the Monomer-Water Interface on Polymerization Emulsion

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Synopsis

A quasi-spontaneous process of mass transfer takes place at the interface of a monomer and water in the presence of surface-active substances soluble in both phases as a result of their diffusion through the interfacial boundary. This process is accompanied by the formation of a microemulsion whose particle size depends on the emulsifier concentration and its molecular structure. While investigating various nonionic surface-active substances as emulsifiers in the emulsion polymerization of vinyl acetate, it was established that polymerization occurs in droplets of the monomer microemulsion in water, which are formed as a result of mass transfer at the interface.

The mechanism of emulsion polymerization has been studied in the most detailed manner, especially the processes occurring in the presence of ionic emulsifiers. It is assumed[1–4] that in the case of ionic surface-active substances (SAS) polymerization takes place in the emulsifier micelles and in the case of water-soluble monomers it is observed in the aqueous solution of SAS.[4,5] Investigations of the regularities of styrene polymerization with nonionic SAS have shown[6,7] that the polymerization process develops in a volume of discrete particles with vast surfaces without increasing their size, and in large monomer droplets, there being no diffusion from them into small droplets. Neither the nature of such highly dispersed particles nor the mechanism of their formation has been clarified, however. On the other hand, a thorough study of the stabilization of concentrated emulsions by nonionic SAS has demonstrated[8–11] that the process is connected with the formation of a quasi-spontaneous microemulsion (ME) at the interface as a result of the redistribution of SAS among the phases. This process of mass transfer from one phase into another takes place with the interfacial tension vastly different from zero. One could presume that in emulsion polymerization due to the redistribution of SAS among the monomer and water, mass transfer might also influence the polymerization process substantially.

Materials and Methods

The monomer used was doubly distilled vinyl acetate, bp 72.5°C; d = 0.932 g/cc; n^{20} = 1.3958. Initiators were water-soluble potassium persulfate ($K_2S_2O_8$) and dinitrylazoisobutyric acid. Polymerization took place in the presence of nonionic emulsifiers: (a) poly(oxyethylene ethers) of octylphenol with 15 to 80 ethylene oxide groups or (b) Pluronics, i.e., block polymers of ethylene oxide and propylene oxide.

The polymerization of vinyl acetate was carried out in a nitrogen atmosphere in ampoules maintained in a water thermostat at 60°C ± 0.5°C, with vigorous stirring. The phase ratio (monomer: aqueous emulsifier solution) was 1:1 in all experiments.

Experimental Results and Discussion

The results obtained for emulsion polymerization of vinyl acetate in the presence of nonionic SAS and the distribution coefficient between the monomer and water are summarized in Table I.

TABLE I

SAS	$K = C_m/C_w$	Maximal degree of conversion, %
OP-15	0.212	7.5
OP-30	0.069	24.5
OP-45	0.040	63.3
OP-65	0.034	99.0
OP-80	0.031	99.8
Pluronic		
L-64	0.256	15.5
F-68	0.0033	99.8

The data obtained show that distribution greatly depends on the polarity of SAS, and with an increase of the hydrophilic properties of the emulsifier, i.e., with the lengthening of the polyoxyethylene chain, it is abruptly shifted in the direction of the aqueous phase. A layer of spontaneous microemulsion could be distinctly seen at the monomer–water macrointerface in the case of a static phase contact. It was established that if *K* values are small (0.03–0.04), microemulsion of oil-in-water type is formed only; if $K > 0.04$, not only a direct, but also an inverse emulsion appears, the latter growing in quantity as the SAS solubility in the monomer increases. Table I shows that complete conversion is attained only with those emulsifiers in whose presence the process of mass transfer mostly involves the formation of microemulsion of the oil-in-water type.[9] Thus, in the series of emulsifiers OP-65, OP-45, OP-30, and OP-15, with optimal values of the polymerization time and emulsifier concentration, the degree of conversion greatly diminishes. The same regularity is also observed for Pluronics.

Figure 1 shows the kinetics of the microemulsion layer thickness growth with time for the Pluronic F-68 and the OP-65 preparation when these are introduced into water and vinyl acetate. It is clear that for both SAS the mass-transfer intensity is considerably greater when SAS is introduced into the monomer. This difference in the mass transfer rate, it would

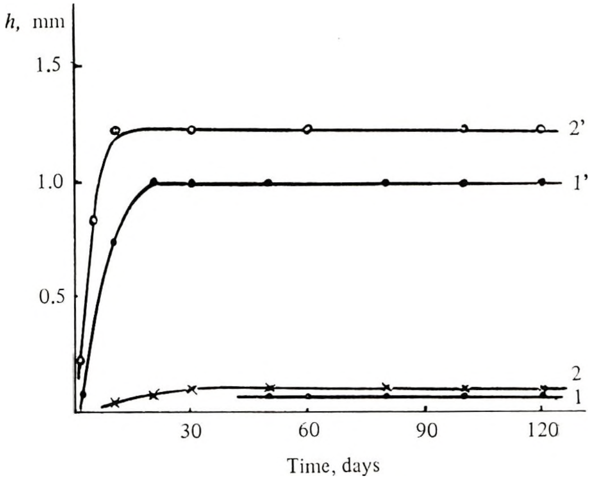


Fig. 1. Kinetics of the microemulsion layer thickness growth: (*1*),(*2*) OP-65 and Pluronic F-68 are introduced into water; (*1'*), (*2'*) OP-65 and Pluronic F-68 introduced into vinyl acetate.

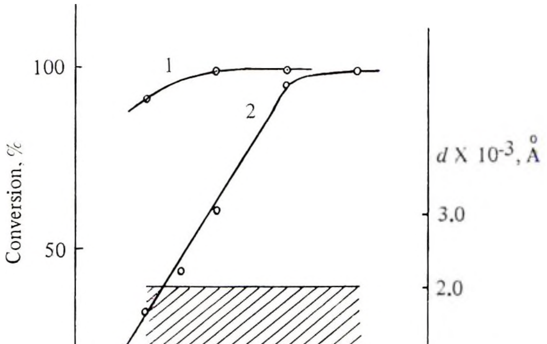


Fig. 2. Dependence of the vinyl acetate conversion on the conditions of introducing the emulsifier into one of the phases: (*1*) Pluronic F-68 introduced into vinyl acetate; (*2*) Pluronic F-68 introduced into water.

appear, can be accounted for by the presence of an interface barrier in the shape of an adsorption layer which hinders the diffusion of SAS from water into vinyl acetate. Indeed, if we break this film mechanically from time to time, the volume of microemulsion will increase sharply. When SAS is distributed from vinyl acetate into water, intensive surface turbulence can be observed. This probably makes the adsorption layer no longer whole and facilitates the diffusion of SAS through the interface.

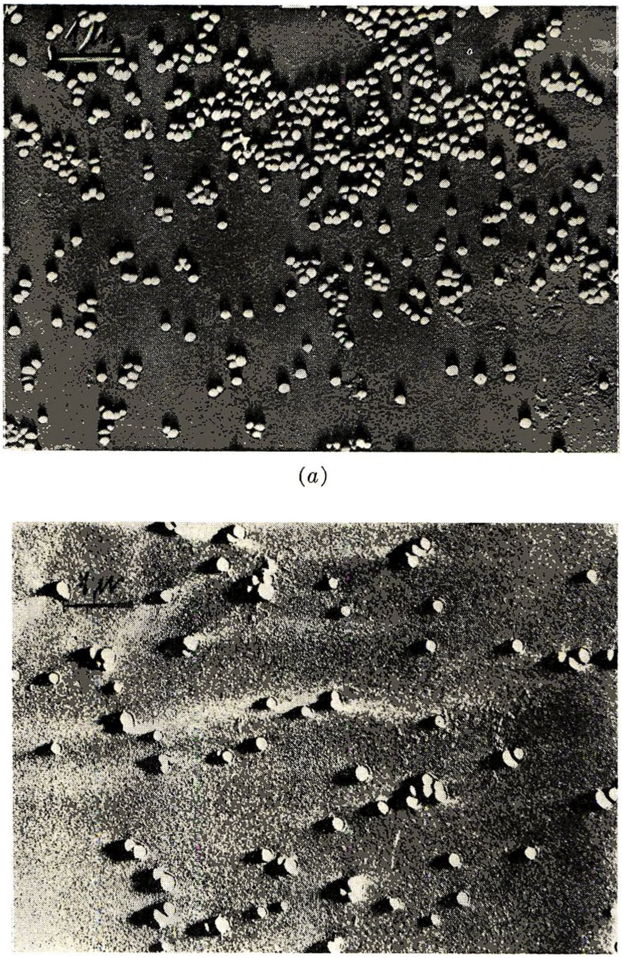
TABLE II

SAS	Number of ethylene oxide groups	Average diameter of latex particles, Å		Average diameter of ME particles, Å	
		Fraction I	Fraction II	Fraction I	Fraction II
OP-15	15	550	7000	500	8000
OP-30	30	300	3000	300	4250
OP-45	45	200	2000	200	2000
OP-65	65	150	1300	150	1300
Pluronics					
L-64	26–31	500	1500	500	1500
F-68	136–164	150	1600	150	1600

If the polymerization of vinyl acetate is carried out in these conditions, i.e., when Pluronic F-68 is introduced into vinyl acetate and not into water, the process is greatly accelerated. Figure 2 demonstrates that this process is practically completed in 30 min (curve *1*), whereas when the emulsifier is introduced into the aqueous phase the conversion reaches only 33% in the same time (curve *2*), the whole process taking 100–120 min for its completion. The data obtained allow us to assert that the process of emulsion polymerization is connected with quasi-spontaneous emulsification at the interface.

It is obvious that monomer polymerization in emulsifier micelles cannot be at work here, for it proceeds much more quickly under conditions less favorable for the solubilization process i.e., when SAS is introduced into vinyl acetate, than in the case of introducing SAS into water. Besides, the ultimate values of solubilization for the OP preparations of varying oxyethyl contents are similar to each other and equal 5–6 g/100 g of the aqueous solution However, the emulsion polymerization of vinyl acetate greatly depends on the degree of oxyethyl substitution of the emulsifier molecule.

The particle size of the poly(vinyl acetate) latex and microemulsion forming as a result of mass transfer was determined by means of electron microscopy.[10] The determination of latex dispersion was carried out at different polymerization times (every 30 min) and, consequently, at different degrees of monomer conversion. It was found that the diameter of the latex particles does not increase with an increase in the conversion volume (beginning with 12%) but remains constant. This dependence is represented in Figure 2 by the shaded areas. A comparison was made between the particle size of the latex and of the microemulsion monomer in water) forming quasi-spontaneously at the macrointerface of vinyl acetate and the aqueous solution of SAS. Vinyl acetate microemulsion was polymerized in the presence of both a water-soluble and an oil-soluble initiator, and nature of the initiator was found to have no influence on the size of microemulsion particles. The results of dispersion determination are given in Table II and in Figure 3.



(a)

(b)

Fig. 3. Electron microscope photos of (a) latex, and (b) microemulsion. 10,000×.

The data on dispersion of latex and ME show that the size of their particles is practically identical and it diminishes with increasing number of ethylene oxide groups in the emulsifier molecule. The second, more highly dispersed fraction of the latex and ME is readily discoverable if the magnification is great enough (>30,000). But the quantity of this fraction does not exceed 2.0–4.0% of the initial monomer volume, which corresponds to the quantity of monomer solubilized in emulsifier micelles.

The coincidence of the latex and microemulsion particle sizes corroborates the assumption that polymerization takes place in monomer droplets in water which are formed as a result of mass transfer. Only a small portion of the latex in the form of a highly dispersed fraction, no more than 4.0%, is formed as a result of monomer solubilization in emulsifier micelles.

Thus it has been established that the process of emulsion polymerization of vinyl acetate in the presence of non-ionic SAS distributed among the phases is determined by mass transfer (monomer–water).

The supposition that the polymerization of vinyl acetate can occur in an aqueous solution[5] has not been substantiated, for in this case, as we have shown, there is no change of the particle size with polymerization time.

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Received December 16, 1969

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3051-3059 (1970)

Production of Organometallic Polymers by the Interfacial Technique. X. Influence of the Nature of Base Employed on the Synthesis of Polysilylalkylene (arylene) diamines*

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Synopsis

The influence of base type on polymerization and on polymer properties in the synthesis of polysilylalkylene(arylene)diamines by a modified interfacial system was investigated. The modified system utilizes 2,5-hexanedione or acetonitrile in place of the usual aqueous solvent. Protonation of both diamine and amine groups in the polymer chain is important when NaOH or diamine itself is employed as the base. Protonation is unimportant when triethylamine is used. In triethylamine systems the highest yield is formed with the silane containing the most electron-deficient silicon, and the highest molecular weight products are formed with the least sterically hindered silane. When NaOH or diamine itself is employed there is no apparent correlation between silane and amine electronic or steric nature and any of the measured polymer properties. As diamine solubility decreases, polymer yield increases.

INTRODUCTION

Aylett[1] has recently reviewed the topic of silicon–nitrogen polymers. He notes that, in contrast to Si—O polymers, polymers with Si—N bonds in the main chain have received little attention mainly because of a lack of suitable preparative methods. The review includes a review of polymer types considered in this paper.

In the interfacial method, two fast-reacting monomers are dissolved in a pair of immiscible liquids, one of which is generally water. The water phase contains a monomer such as a diamine and any added alkali. The other phase consists of a monomer, such as a diacid halide, and an organic liquid. Polymerization occurs at or near the liquid interface. It is found in systems with the diamine in water and dichlorosilane in an organic solvent, that silane is preferentially hydrolyzed to give a product with a repeating backbone of —Si—O— and not the desired inclusion product with diamine. Thus nonwater systems were devised.

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* Presented in part to the Division of Polymer Chemistry, 159th National Meeting, American Chemical Society, Houston, Texas, February 1970.

The first interfacial synthesis of polyalkyloxysilanes by a modified interfacial system was recently reported by Carraher.[2-4] Since then this has been extended to include the synthesis of polyaryloxysilanes.[5]

Carraher[6] recently reported the first synthesis of polysilylalkylenediamines by a modified interfacial system where liquid diamine was used in place of the aqueous solvent. The diamine also acted as a reactant. The major disadvantage with this system is that it is limited to diamines which are liquid or which have low melting points so the temperature of the interfacial system can be raised above the melting point of the diamine. This excludes the synthesis of polysilylarylenediamines by this "modified" interfacial system.

Carraher and Green[7] recently reported a more general interfacial system capable of producing polysilylalkylene(arylene)diamines. It is found that 2,5-hexanedione and acetonitrile are immiscible with intermediate- to long-chain hydrocarbon liquids and that diamines are soluble in the dione. The new system employs 2,5-hexanedione or acetonitrile in place of the aqueous solvent.

The nature of the acid acceptor in interfacial polymerizations has been a subject of study.[8] The exact role of the base is still not well understood and probably varies in nature and extent from system to system; possibly even within a system several roles may be served simultaneously.

It is the purpose of this paper to compare results derived from studying the new interfacial system as a function of the nature of the base employed.

The polymerization is rapid, the reaction system heterogeneous (containing two immiscible phases), and the reaction parameters plentiful, so that a detailed kinetic study of the separate reactions is laborious. Instead, polymer yield and product limiting viscosity number are used as indices of conditions which favor the polymerization reaction. The dependence of these indices on reaction parameters can be informative.

Experimental

Polymerizations were carried out in a 1-pt Kimax emulsifying jar placed on a Waring Blendor (Model 1001 or 1043) unless otherwise noted. The jar was vented by placing a glass tube, inserted in a cork stopper, through a hole in the jar cap. A second hole in the jar cap contained a separatory funnel secured in a cork stopper. The insoluble base, hydrocarbon solvent, and silane were added to the reaction jar. (When a soluble base was employed, the base was added to the dione phase.) The lid was screwed on the jar. The 2,5-hexanedione (or acetonitrile) containing diamine was poured into the separatory funnel. The blender was turned on and after approximately $^1/_2$ min the stopcock of the funnel was opened, allowing all the dione phase to enter the jar. After a set time the blender was turned off. The dione (or acetonitrile) phase is highly colored, while the hydrocarbon phase is colorless. A 50-ml portion of carbon tetrachloride was added to the dione phase. The screw cap was screwed on and the blender turned on for 1 min. The cap was removed and the liquid in the jar filtered to remove insoluble salt and base; the polymer is soluble in dione and carbon tetrachloride. The liquid was then added to a separatory funnel to which 50 ml of hot water (60°C) was added. The mixture was shaken and allowed to sit for about 5 min and then the aqueous portion removed. Another 50 ml of hot water was added and the process repeated (the diamine and dione will go preferentially into the aqueous layer). The carbon tetrachloride layer containing polymer was evaporated to a solid.

Viscometry was performed in dimethyl sulfoxide at 30°C with the use of a Cannon-Ubbelohde viscometer. Limiting viscosity numbers (LVN, ml/g) were obtained by serial dilution of solutions of 1 g/100 ml and less.

Melting ranges (softening ranges) were determined on a Fisher-Johns melting point apparatus at an approximate heating rate of 2C°/min and were taken to be the temperature at which melting initially began to where melting was complete. Melting ranges obtained are given without claim to being a measure of the glass transition temperature or the crystalline melting point.

Infrared spectra were obtained with a Perkin-Elmer 237 instrument using potassium bromide pellets.

Discussion and Results

In all of the systems diamine probably acts as an acid acceptor. In the product from the condensation of *p*-phenylenediamine and diphenyldichlorosilane with either NaOH or diamine as the base, bands are observed at 2975 and 2927 cm^{-1}. These bands are small in the polymer produced with 15 sec stirring time and increase as stirring time increases. (The relative intensities of these lines are essentially the same for products produced from stirring times of 30 sec and greater.)

A polymer sample produced with 2 min stirring time was dissolved in acetone. To this was added several drops of 5*N* aqueous sodium hydroxide. The mixture was allowed to remain at room temperature for one day. The polymer was recovered, and its spectrum showed a decrease in the size of the 2975 and 2927 cm^{-1} bands. Rao[9] assigns the region from about 3000 to 2900 cm^{-1} as being characteristic of absorptions of the $=NH_2^{\oplus}$ group. It is believed that the bands at 2975 and 2927 cm^{-1} originate from the protonation of the silicon-nitrogens and/or endgroup amines by hydrogen chloride which is given off as the silane and diamine condense.

Protonation of the diamine and amine endgroups will compete with polymer formation, since $—NH_3^{\oplus}$ ions are not good nucleophiles and consequently do not react with silane.

When triethylamine is employed as the base, one band appears in the 3000–2900 cm^{-1} range. The infrared spectrum of triethylamine shows a band at 2940 cm^{-1}. It is believed that in such systems protonation is not important and that at least some of the polymer chains have triethylamine endgroups.

Triethylamine is employed as the soluble base since the amine nitrogen is sterically hindered, permitting reaction with hydrogen chloride but not favorable competition with the diamine for reaction with the silane. In addition it is volatile (b p = 90°C). In a run where silane is omitted (*p*-phenylenediamine and triethylamine added) and the normal recovery procedure followed, no residue is found where polymer is normally found.

Infrared spectra of the insoluble salts formed in "no-base" and NaOH systems show that at least part of the material consists of salt formed from the reaction between diamine and hydrogen chloride. (The infrared spectra of the insoluble salts formed when triethylamine was used show a large amount of triethylamine salt and a small amount of diamine salt.) It is believed that diamine and polymer amine protonation is important in no-base and NaOH systems but unimportant in triethylamine systems. This is substantiated by a lack of color changes in triethylamine systems which are present in no-base and NaOH systems.

When no added base was employed (the diamine itself acting as the base), polymer yields are lower than for analogous systems employing either insoluble or soluble bases (Tables I and II). This would be true if protonation (and consequently inactivation) of amine groups is more important in systems where no base is employed, since only the diamine is present as an acid acceptor.

The greater yields found for triethylamine systems than for NaOH systems may be a consequence of more effective acceptance of hydrogen chloride by the soluble triethylamine and/or may be due to a decreased solubility of the diamine (salting out) in the triethylamine system caused by the addition of the soluble base.

The solubility of diamine is a critical factor in such systems. As the concentration of reactants varies, other parameters are affected. As the amount of polymer produced increases, the viscosity of the reaction system increases, presumably resulting in a decrease in the stirring rate. In the present system polymer yield and molecular weight are constant as stirring rate is varied.[9]

It is known that polymerization rate is influenced by the addition of additives to one or both of the phases.[10] The polymer is soluble in the dione phase; thus it is possible that dissolution of increasing amounts of polymer in the dione phase decreases solubility of the diamine, and forces the diamine into the reaction zone. Similarly, with increased concentration of reactants and higher amounts of polymer produced, diamine solubility is decreased, possibly resulting in the observed trend of higher yield at higher reactant concentrations (Table III).

If the above is correct, then the addition of an additive to the dione phase which would cause a decrease in diamine solubility should result in an increase in polymer yield. Salts (such as sodium acetate, ammonium nitrate, and sodium chloride) are essentially insoluble in 2,5-hexanedione and acetonitrile, polymer was used as the additive. Polymer from the condensation of *p*-phenylenediamine with diphenyldichlorosilane, having an LVN value of 6, was added to the dione phase. Polymer yield was higher than that in analogous systems without added polymer (Table III). This is in agree-

TABLE I
Polymer Properties as a Function of Base

	Sodium hydroxide[a]			Triethylamine[b]			No base[c]		
Comers	Yield, %	LVN, ml/g	Melting range, °C	Yield, %	LVN, ml/g	Melting range, °C	Yield, %	LVN, ml/g	Melting range, °C
Diphenyldichlorosilane 4,4′-methylenedianiline	41	3	67–73	65	6	112–118	8	3	98–108
Methylphenyldichlorosilane 4,4′-methylenedianiline	71	4	40–43	60	9	106–112	11		
Dimethyldichlorosilane 4,4′-methylenedianiline	35	3	45–50	58	17	72–75	6	4	60–67
Diphenyldichlorosilane 4,4′-methylenebis(cyclohexylamine)	55	5	70–76	33	10	175–189			
Methylphenyldichlorosilane 4,4′-methylenebis(cyclohexylamine)	29	8	220–224	33	15	250–265			
Dimethyldichlorosilane 4,4′-methylenebis(cyclohexylamine)	13	6	60–64	21	36	245–258			
Diphenyldichlorosilane 1,3-propanediamine	99	5	67–73						
Methylphenyldichlorosilane 1,3-propanediamine	65	6	50–53	93	7	110–118			
Dimethyldichlorosilane 1,3-propanediamine	70	3	[d]	90		110–123			
Diphenyldichlorosilane 1,6-hexanediamine	21	15							
Diphenyldichlorosilane *p*-phenylenediamine	49[e]	6		53	9	103–108	17	5	78–84

[a] 0.0094 mole silane, 0.0104 mole diamine, 0.0188 mole sodium hydroxide, 15 ml 2,5-hexanedione, 15 ml *n*-heptane, 25°C, 2 min stirring at 17,500 rpm stirring rate (no load).

[b] 0.00237 mole diamine, 0.00237 mole silane, 0.00475 mole triethylamine.

[c] 0.00237 mole diamine, 0.00237 mole silane, no base.

[d] A viscous liquid at room temperature.

[e] With 0.0094 mole diamine.

TABLE II
Polymer Properties as a Function of Base[a]

Comers	No base			Sodium hydroxide			Triethylamine		
	Yield, %	LVN, ml/g	Melting range, °C	Yield, %	LVN, ml/g	Melting range, °C	Yield, %	LVN, ml/g	Melting range, °C
Diphenyldichlorosilane 4,4′-methylenedianiline	8	3	98–108	10	5	76–80	65	6	112–118
Methylphenyldichlorosilane 4,4′-methylenedianiline	11			13	6		60	9	106–112
Dimethyldichlorosilane 4,4′-methylenedianiline	6	4	60–67	9	4		58	17	72–75
Diphenyldichlorosilane *p*-phenylenediamine	17	5	78–84	36	8	160–170	53	9	103–108
Diphenyldichlorosilane *p*-phenylenediamine[b]							45	8	

[a] 0.00237 mole silane, 0.00237 mole diamine, 0.0047 mole base, 15 ml 2,5-hexanedione, 15 ml *n*-heptane, 25°C, 2 min stirring at 17,500 rpm stirring rate (no load).

[b] Same conditions except with 20 ml *n*-pentane and 20 ml acetonitrile.

TABLE III

Polymer Properties as a Function of Comer Concentration[a,b]

Diamine and silane, mole	Sodium hydroxide, mole	Yield, %
0.0190	0.0380	78
0.0141	0.0282	76
0.0094	0.0188	49
0.0047	0.0094	45
0.0024	0.0048	36
0.0012	0.0024	25
0.0012[c]	0.0024	92
0.0024[d]		65
0.0024[e]		70
0.0024[f]		75

[a] Equal molar amounts of diphenyldichlorosilane and *p*-phenylenediamine, 15 ml 2,5-hexanedione, 15 ml *n*-heptane, 25°C, 2 min stirring at 17,500 rpm (no load) stirring speed; reaction carried out in a 1-pt Kimax emulsifying jar.

[b] LVN was approximately constant for all systems and varied from 6 to 8 ml/g.

[c] A 1-g portion of polymer was initially dissolved in the dione phase along with the diamine.

[d] With 0.0047 mole of triethylamine.

[e] With 0.0047 mole of triethylamine and 0.03 g of polymer initially dissolved in the dione phase along with the diamine.

[f] With 0.0047 mole triethylamine and 0.18 g of polymer initially dissolved in the dione phase along with the diamine.

ment with the suggestion that diamine solubility is a critical factor in determining polymer yield and that polymer yield increases as diamine solubility decreases.

Polymer molecular weight remains essentially constant as comer concentration is varied (Table III). Thus diamine solubility is presumably important in determining polymer yield but does not greatly influence polymer molecular weight.

It may be argued that the endgroups of the added polymer offer additional reactive sites and that polymer yield would be expected to increase as additional polymer is added. If this were an important reaction, then polymer from such systems could be expected to exhibit higher LVN's than polymer synthesized from analogous systems containing no added polymer. This is not the case. There is little difference in the LVN's of such systems (Table III).

There is no apparent correlation between polymer yield and polymer molecular weight and either steric or electronic nature of the diamine regardless of base employed (Table I).

There is no apparent correlation between silane electronic or steric nature and any of the measured polymer properties in NaOH and systems without added base.

In the triethylamine systems, polymer yield varies (diphenylsilane > methylphenylsilane > dimethylsilane, Table I), the most electron-deficient silane giving the highest polymer yield. This suggests that steric considerations are minimal in determining polymer yield since the more electron-withdrawing phenyl group offers more bulk than does the methyl group.

It is generally not possible to compare viscosities of different polymers to determine molecular weight trends; however, it is probable that for similar polymers where there are major viscosity differences general molecular weight trends can be reliably described. Whereas electronic arguments were offered to account for the yield trend, just the opposite trend is observed for polymer molecular weight; the molecular weight trend is diphenylsilane < methylphenylsilane < dimethylsilane. It is suggested that steric considerations may be important in determining polymer molecular weight.

Thus the sterically more bulky, more electron-withdrawing phenyl group acts to increase polymer yield but to decrease polymer molecular weight. The less bulky, less electron-withdrawing methyl group acts to give the opposite trend. An explanation is that the greater steric hindrance of the phenyl group, while tending not to block the entrance of comers and oligomeric material, does tend to block the approach of larger molecules resulting in stepwise growth. The methyl group, by comparison, does not block the approach of larger molecules making it possible for larger molecules to add greatly increasing the molecular weight of the product.

The yield and molecular weight trends observed for the triethylamine systems are the same as those observed in analogous silane–diol systems employing NaOH.[7,9] Protonation is found to be unimportant in such silane–diol systems.

Protonation reactions may be responsible for obscuring the yield and molecular trends in the NaOH and diamine base systems. A further study of the importance of the nature of the base is underway. More study is needed to clarify the influence of steric and electronic effects on polymer yield and molecular weight.

Softening ranges vary as reaction conditions and employed bases vary (Tables I–III). No explanation can be given for these differences. Many of the products are of low molecular weight, and differences in endgroups, molecular weight, crystallinity, etc. may be responsible for these variations. (The products are found to be linear on the basis of methods presented in preceding papers.[6])

Evidence has been presented showing that protonation is important when diamine or NaOH is employed as the base but is (relatively) unimportant when triethylamine is used as the base.

This research was supported by an American Chemical Society Petroleum Research Grant No. 1338-G13.

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Received February 17, 1970
Revised March 13, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3061-3077 (1970)

Radiation-Induced Postpolymerization of Trioxane in the Solid State. II. Kinetic Study of Radiation-Induced Postpolymerization of Trioxane in Dry and High-Vacuum System*

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Synopsis

A kinetic study of the radiation-induced postpolymerization of trioxane in the solid state has been made. Trioxane was purified by sublimation through Ag_2O and Na-K alloy *in vacuo* and was both irradiated and polymerized in a super-dry system under high vacuum. In the present study it was found that the initial rate of polymerization is larger than that reported previously. It is reasonably suggested that the postpolymerization of trioxane consists of two stages, i.e., a very large rate at the first stage and a relatively small one at the second stage. By using the kinetic scheme proposed previously kinetic parameters at the second stage were determined. It was found that trioxane can be postpolymerized even at a temperature below 30°C with good reproducibility and that the overall activation energy of the polymerization was less than 15 kcal/mole. No chain-transfer reaction seems to occur except at low temperatures. These results have been discussed in comparison with data reported previously.

INTRODUCTION

The radiation-induced polymerization of trioxane has been studied by many workers[2-9] since Okamura and Hayashi found that trioxane can be polymerized in the solid phase by ionizing radiation at a temperature of from 20°C to its melting point[2] and give a well orientated polyoxymethylene crystal.[3] It is well known that this monomer can be polymerized not only by in-source polymerization but also by the post-polymerization. We have also reported a detailed kinetic study of postpolymerization in air.[1]

Hayashi et al.[6] found that when both preirradiation and polymerization were carried out *in vacuo*, the polymer yield fell to about half compared with that obtained by postpolymerization in air. On the other hand, Rao et al.[10] reported that little or no polymer was formed in the postpolymerization when samples were irradiated *in vacuo*. However, we found that trioxane can be postpolymerized *in vacuo* as well as in air, even if preirradiation was carried out *in vacuo*, when trioxane was carefully purified by sublimation.

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* For Part I, see Sakamoto et al.[1]

It is difficult to obtain the reproducible results in the polymerization of trioxane, especially *in vacuo*, unless purification of the monomer is carried out carefully. In other words, when trioxane containing a small amount of impurities is postpolymerized *in vacuo*, the rate of postpolymerization decreases markedly or fails to occur.

In 1922, Hammick et al.[11] found that polyoxymethylene was obtained by the repeated sublimations of dry trioxane at 46°C. Kohlschütter et al.[12] found that topochemical polymerization occurred spontaneously on the surface of a trioxane crystal without catalyst when trioxane was stored *in vacuo*.

Jaacks et al.[13] recently studied the polymerization of trioxane by sublimation in detail and considered that this polymerization was induced by formaldehyde present in the trioxane, since well purified trioxane can not be polymerized and in the catalytic polymerization of trioxane an induction period is necessary to form formaldehyde.[14]

On the other hand, Kamachi et al.[15] found that trioxane was polymerized by heating above 10°C after sublimation under high vacuum and crystallization on the surface of vessel kept at a low temperature. This polymerization differs from that found by Hammick et al.,[11] since, in this case, trioxane was polymerized by heating after sublimation and crystallization.

We found that when trioxane sublimed and crystallized in a super-dry, a high-vacuum system was used for the radiation-induced postpolymerization, no polymerization by heating after sublimation and crystallization occurred and reproducible results were easily obtained.

Kinetics of the radiation-induced postpolymerization of trioxane have been studied by Hayashi et al.[6] and Sakamoto et al.[1] Recently, Trofimova et al.[9] investigated the postpolymerization of trioxane in the solid phase and analyzed the results on the basis of the kinetic scheme of anisotropic solid-phase polymerization. They considered that the rate curves of the postpolymerization of trioxane above 45°C contained two sections with different rates, and that the rate of polymerization in the second stage fell to a smaller value than that in the first stage, because active centers are trapped in a defect in the crystal and then start polymerization up to the next defect after the annealing of the first defect. They assumed that the yield–polymerization-time curves at the second stages are straight lines over the entire range of preirradiation dosages and postpolymerization temperatures. However, the yield–polymerization-time curves obtained by us or other workers[1,6,7] cannot be adequately fitted to straight lines.

In the present study an investigation was made of the radiation-induced postpolymerization of trioxane which was purified in a super-dry, high-vacuum system. The results were analyzed kinetically and compared with those reported previously.

EXPERIMENTAL

Materials

Commercial trioxane was purified by distillation as described in detail in previous paper.[1] Barium oxide and silver oxide were obtained commercially and were used without purification. Sodium–potassium alloy was prepared in dry cyclohexane in a ratio of sodium to potassium of 1:2 (w/w).

Apparatus and Procedure

The apparatus for preparation of the samples is shown in Figure 1. Container 1 of Figure 1 held trioxane prepurified by distillation and barium oxide which had been baked under high vacuum for 10–15 hr. at 300–400°C and completely degassed. The mixture of trioxane and BaO was then heated at 90–100°C and trioxane was refluxed for 30 min. This treatment with BaO removed water and acids from the trioxane. The melt was rapidly solidified at a liquid nitrogen temperature. After complete degassing in vessel 1, the mixture was kept at a room temperature and the middle fraction of trioxane was sublimed and crystallized into vessel 2, which was kept at liquid nitrogen temperature.

Sodium–potassium alloy was poured into tube 4 and the organic materials contained in the alloy were eliminated by evacuation at 1×10^{-6} mm Hg for 15 hr. The wall of the vessel was then coated with a small amount of the alloy by heating. After the vacuum line had been baked out, the middle fraction of trioxane stored in ampoule 2 was sublimed through the U-tube (3) containing Ag_2O, the fresh alloy (4), the trap (5), and the U-tube containing glass wool (6), and was crystallized in the ampoules (7) kept at a liquid nitrogen temperature. Na-K alloy and Ag_2O were used to remove water, acids, and formaldehyde, respectively.[13] Trioxane in ampoule 7 was once again degassed under high vacuum for 30 min. at -78°C and the ampoule sealed off in a vacuum of less than 1×10^{-6} mm Hg.

Acids, water, and formaldehyde contained in the purified trioxane were analyzed by acid–base titration, Karl Fischer titration, and colorimetric determination with phenylhydrazine, respectively. No detectable amount of impurities (1 ppm) was present.

The ampoules containing 0.5–1 g of the purified trioxane were placed in a Dry Ice–methanol bath and subjected to γ-ray irradiation from a ^{60}Co source. The dose rate was determined by Fricke dosimetry. The irradiated samples were postpolymerized in a constant temperature bath.

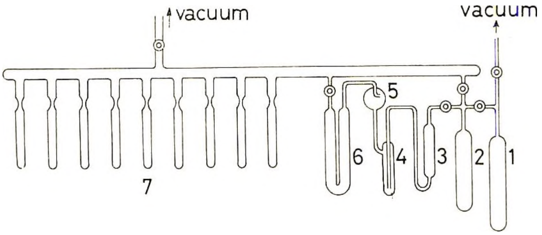


Fig. 1. Apparatus for purification of trioxane: (1) trioxane source (raw trioxane plus baked BaO); (2) trioxane source (trioxane purified by the first sublimation); (3) U-tube containing Ag_2O; (4) Na-K alloy; (5) trap; (6) U-tube containing glass wool; (7) ampoules.

The reaction mixture was washed with methanol or acetone to remove residual monomer, and the polymer yield was determined after drying *in vacuo*. The solution viscosities of the polymers were measured at 60°C in *p*-chlorophenol containing 2% α-pinene after the polymer samples had been dissolved at 115°C for 10–15 min.

The molecular weights of the samples were calculated by using the equation[16]

$$[\eta] = 5.43 \times 10^{-4} \bar{M}_n^{0.66}$$

RESULTS AND DISCUSSION

Polymerization Induced by Sublimation and Crystallization

A few preliminary experiments were carried out to determine whether sublimation and crystallization of trioxane *in vacuo* affect the radiation-induced postpolymerization.

The samples were polymerized by heating without addition of catalyst or γ-ray irradiation. The results are shown in Figure 2. We found that trioxane was not polymerized during the sublimation and crystallization process *in vacuo*, but polymerized on heating at a temperature above 0°C after the purification. No polymer was obtained if the trioxane was washed with acetone immediately after the sublimation and crystallization. It is reasonable to consider that trioxane is polymerized by some active species formed during sublimation and crystallization of trioxane under a high vacuum system. The polymerization of trioxane on heating after sublimation and crystallization was studied in detail by Kamachi et al.[15]

However, the reproducibility is so poor as to preclude any definitive statements regarding such a polymerization, since the polymerizability may be affected by, for example, the degree of vacuum, the temperature at which sublimed trioxane is crystallized, and the purity of the trioxane.

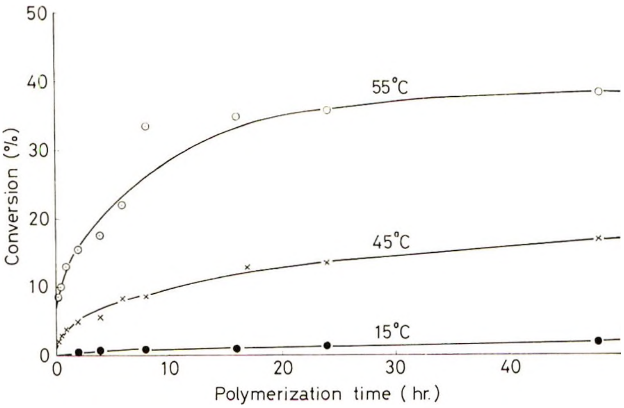


Fig. 2. Polymerization of trioxane by heating after sublimation and crystallization *in vacuo*

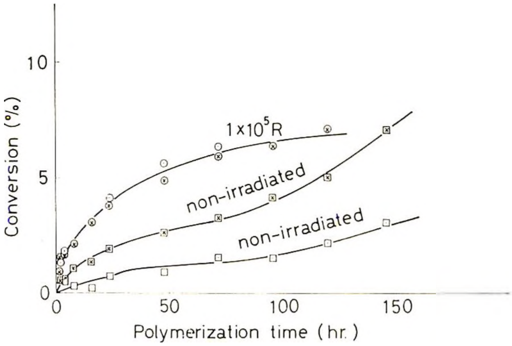


Fig. 3. Polymerization of trioxane *in vacuo:* polymerization temperature, 15°C; the same symbol represents the same purification batch.

As shown in Figure 2, the shape of the yield–polymerization time curves and the temperature dependence of the polymer yield were quite similar to that obtained by the radiation-induced postpolymerization.

A dozen samples could be prepared at the same time by using the apparatus for purification of monomer. Figure 3 shows the yield–polymerization time curves with or without the preirradiation for different batches of trioxane purification. It was found that for different batches of monomer, the form of the yield–time curve is satisfactorily reproducible but the absolute values of polymer yields vary from batch to batch for the samples without preirradiation. On the other hand, for the preirradiated samples, no such difference batch-to-batch was observed. We found that no polymer was obtained when trioxane, sublimed and crystallized *in vacuo,* was irradiated at 1.0×10^6 R at −78°C and heated for 240 hr at 25°C, a temperature at which one can obtain polymer at 20–30% yield when the trioxane is not irradiated. These results may indicate that whatever active species are formed by sublimation and crystallization of trioxane under high vacuum are deactivated by the ionizing radiation. Therefore, it seems to be reasonable that the polymerization ascribed to sublimation need not be taken into account when the results of the radiation-induced postpolymerization of trioxane thus purified are evaluated.

Radiation-Induced Postpolymerization

Polymer yield–polymerization time and molecular weight–polymerization time curves were obtained at various preirradiation doses and polymerization temperatures for the radiation-induced postpolymerization of trioxane in the super-dry and high-vacuum system.

The yield–polymerization time curves at various preirradiation doses and a constant temperature (45°C) are shown in Figure 4. The initial rate of polymerization increased with increasing preirradiation dose, and for a large preirradiation dose the yield–time curves became S-shaped. This relation is analogous to that found for postpolymerization in air. In this study, however, the lower limit of the dosage, where the curve becomes

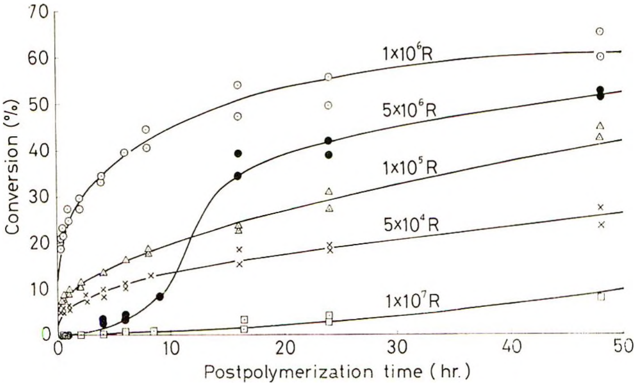


Fig. 4. Postpolymerization of trioxane *in vacuo:* postpolymerization temperature, 45°C.

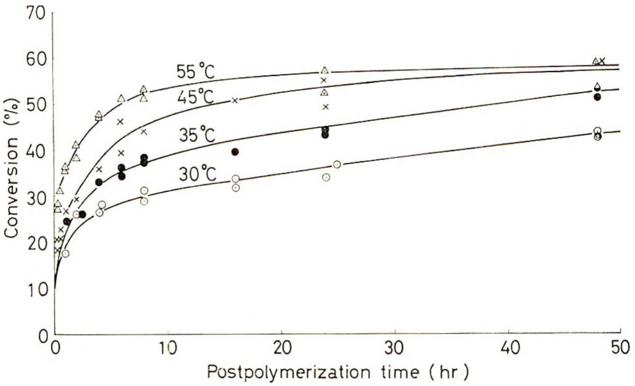


Fig. 5. Postpolymerization of trioxane *in vacuo:* pre-irradiation, 1.0 × 10^6 R at −78°C.

S-shaped, was 5 × 10^6 R; this value is larger than that previously reported.[1] In the region where the initial rate of polymerization increases with increase in dosage, i.e., 0.05–1.0 × 10^6 R, the yield–time curve could be approximated by an exponential curve.

Figures 5 and 6 show the relationships between the polymer yields and polymerization times for a constant dosage of 1.0 × 10^6 R. We found that the higher the polymerization temperature, the larger the initial rate of polymerization; all the curves were expressed by an exponential function over the entire temperature range of 30–50°C, while for the postpolymerization in air[1] the curves become S-shaped at a temperature below 45°C. As shown in Figure 6, when the irradiated trioxane was heated for a long time, the polymer yield reached about 60% (saturation yield) even at a low temperature such as 30°C, i.e., for a preirradiation dose of 1.0 × 10^6 R the saturation yields assume a constant value at various polymerization temperatures.

Figure 7 shows the plots of polymer yields versus polymerization times for preirradiation dose of 1.0 × 10^5 R. Although it has been reported that

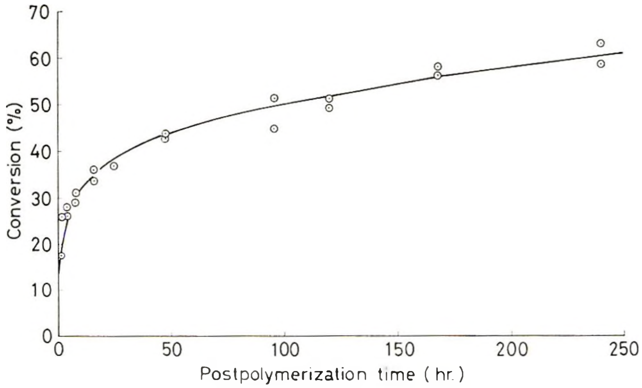


Fig. 6. Postpolymerization of trioxane *in vacuo:* pre-irradiation, 1.0 × 10^6 R at −78°C; postpolymerization at 30°C.

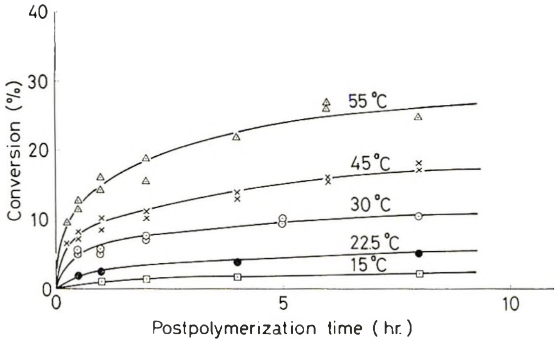


Fig. 7. Postpolymerization of trioxane *in vacuo:* pre-irradiation, 1.0 × 10^5 R at −78°C.

the radiation-induced postpolymerization of trioxane occurs in the range of temperature from 30°C to slightly below the melting point,[6,7] it was found that trioxane can be considerably postpolymerized, i.e., more than 10% conversion, at a temperature above 15°C with satisfactory reproducibility when it is purified by sublimation and crystallization under a super-dry, high-vacuum system.

The relationships between molecular weight of the polymer and polymerization time were also similar to the yield–polymerization time curve, as shown in Figure 8. In the early stage of polymerization, the higher the temperature, the larger the molecular weight of polymer. However, the molecular weight of polymer reached a constant value and its dependence on the polymerization temperature gradually disappeared as polymerization time increased. This suggests that, in this polymerization system, the increase of polymer yield results from an increase in the degree of polymerization rather than the number of polymer chains. As shown later, no chain-transfer reaction occurs in this system.

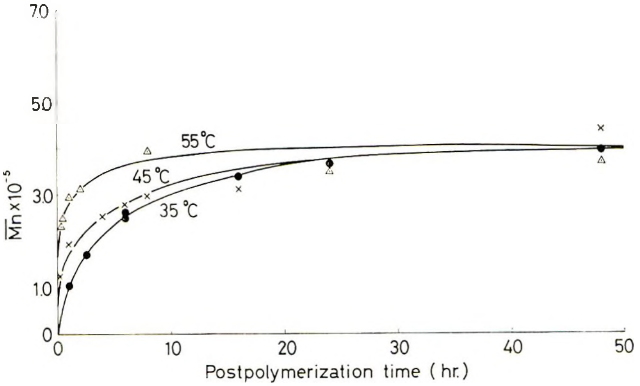


Fig. 8. Molecular weight of polyoxymethylene obtained by postpolymerization of trioxane *in vacuo:* pre-irradiation, 1.0 × 10^6 R at −78°C.

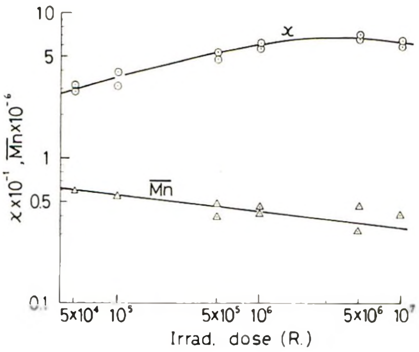


Fig. 9. Effects of preirradiation dose on yield x and molecular weight M_n of polyoxymethylene obtained by postpolymerization of trioxane *in vacuo:* pre-irradiation at −78°C; postpolymerization at 55°C for 48 hr.

Figure 9 shows the polymer yield and molecular weight of the polymer as functions of preirradiation dose. For the smaller dosage the polymer yield increased with the increase of preirradiation dose. The maximum polymer yield was obtained at preirradiation doses of 1.0 × 10^6 to 5.0 × 10^6 R, and the polymer yield fell slightly with further increases in dosage. This decrease in the polymer yield at larger dosage may be attributed to radiolysis of the monomer. It is also suggested that the rate of termination increases at larger dosage, since polymer of lower molecular weight was obtained. This suggestion was supported experimentally. Irradiated trioxane was degassed under high vacuum at various temperatures and then polymerized at 55°C. The results are summarized in Table I. Upon degassing of the irradiated trioxane, the higher the temperature at which the trioxane was kept, the larger the polymer yield and the molecular weight of the polymer. Thus the amount of radiolysis products formed at a large dosage such as 1.0 × 10^7 R seems enough to cause the appreciable decrease in molecular weight. However, the products could be eliminated by evacuation at a temperature above −78°C without decreasing the polymer yield.

TABLE I

Effect of Degassing after Pre-irradiation of Trioxane on Yield of Polyoxymethylene[a]

Experiment No.	Temperature, °C[b]	Degassing time, min	Polymer conversion, %	Intrinsic viscosity, dl/g
1	—[c]	—	9.98	1.2
2	−196	60	13.5	1.2
3	− 78	60	47.0	1.5
4	0	8	67.4	1.9

[a] Pre-irradiation, 1.0×10^7 R at −78°C; postpolymerization at 45°C for 48 hr.

[b] At temperature irradiated trioxane was kept during degassing.

[c] No degassing.

On the other hand, we have reported previously[17] that the polymer yields were little affected by degassing at low temperatures when the preirradiation dose was 1.0×10^6 R. These results suggest that the active species formed by irradiation may be held firmly in the crystal lattice of trioxane.

Kinetics

Previously we reported[1] a kinetic study on the radiation-induced postpolymerization of trioxane in air and proposed the reaction scheme summarized in eq. (1).

Reaction I

$$\begin{tikzcd} M \arrow[r, squiggly] & A^* \arrow[rr] \arrow[dr, "O_2"'] & & M^* \arrow[r] & M_n^* \arrow[r] & P \\ & & A^{**} \arrow[ur] & & & \end{tikzcd} \tag{1}$$

Reaction II

In this scheme the active species A* is formed by irradiation and is converted directly to M* via reaction I and, in the reaction II, A* reacts with oxygen to give A** which gradually generates M*. The polymer with active end M_n^* grows by adding monomer M and finally gives deactivated polymer P.

It was found that the experimental results can be explained kinetically by evaluating the rate constants of the elementary reactions for the given dosages and polymerization temperatures.

In the present study we exclude reaction II, since the postpolymerization was carried out *in vacuo*. Therefore, we consider the overall scheme of postpolymerization of trioxane *in vacuo* to be as shown in eq. (2):

$$M \overset{\phi_i}{\rightsquigarrow} A^* \xrightarrow{k_d} M^* \xrightarrow{k_p} M_n^* \xrightarrow{k_t} P \tag{2}$$

where ϕ_i, k_d, k_p, and k_t represent the G value of A* and the rate constants of the elementary reactions, respectively.

It is assumed that propagation and termination reactions are pseudo-unimolecular because the reaction is carried out in the solid state and the active ends must react only with the neighboring monomer molecule in one direction. It was observed that the radiation-induced polymerization of trioxane occurs predominantly along the c axis of the monomer crystal.[3,4,18,19] Therefore, the propagation reaction rate seems to be pseudo-unimolecular. Similarly, polymerization may be terminated when the growing chains encounter with either the lattice defects or impurities contained in monomer crystal.

From eq. (2), the expressions (3)–(5) can be set up for the rate of polymerization R_p, the polymer yield x, and the degree of polymerization $\overline{\mathrm{DP}}$.[20]

$$R_p = k_d k_p \phi_i D[\mathrm{M}_0]\,(\exp\{-k_d t\} - \exp\{-k_t t\})/(k_t - k_d) \tag{3}$$

$$x = (k_p \phi_i D/k_t)\,[(k_t - k_d) + k_d\exp\{-k_t t\} - k_t\exp\{-k_d t\}]/(k_t - k_d) \tag{4}$$

$$\begin{aligned}\overline{\mathrm{DP}} &= \textstyle\int R_p dt/\int R_i dt = (k_p/k_t)\,[(k_t - k_d) \\ &\quad + k_d\exp\{-k_t t\} - k_t\exp\{-k_d t\}]/(k_t - k_d)(1 - \exp\{-k_d t\})\end{aligned} \tag{5}$$

where D, t, and R_i represent preirradiation dose, polymerization time, and the rate of initiation reaction, respectively. If the rate constant of the formation of M* is much larger than that of the termination reaction, i.e., $k_d \gg k_t$, eqs. (3), (4) and (5) can be simplified to

$$R_p = k_p \phi_i D[\mathrm{M}_0]\exp\{-k_t\} \tag{6}$$

$$x = k_p \phi_i D(1 - \exp\{-k_t t\})/k_t \tag{7}$$

$$\overline{\mathrm{DP}} = k_p\,(1 - \exp\{-k_t t\})/k_t \tag{8}$$

Upon combination of eqs. (7) and (8) we find

$$(1/\overline{\mathrm{DP}}) = \phi_i D(1/x) \tag{9}$$

A plot of $1/\overline{\mathrm{DP}}$ against $1/x$ should give a straight line which intercepts at the origin and whose slope has the value $\phi_i D$. Experimentally, as seen in Figures 10 and 11, we obtained straight lines as expected for the most of experimental results.

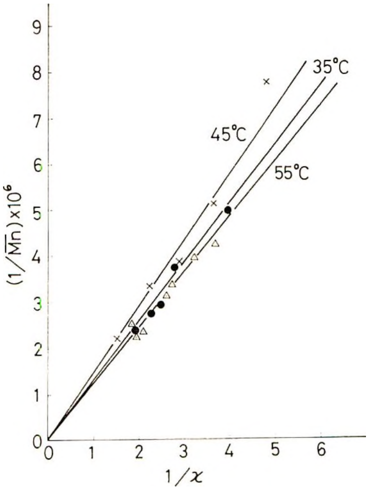


Fig. 10. Reciprocal of molecular weight vs. reciprocal of polymer yield in postpolymerization of trioxane *in vacuo:* pre-irradiation, 1.0×10^6 R at −78°C.

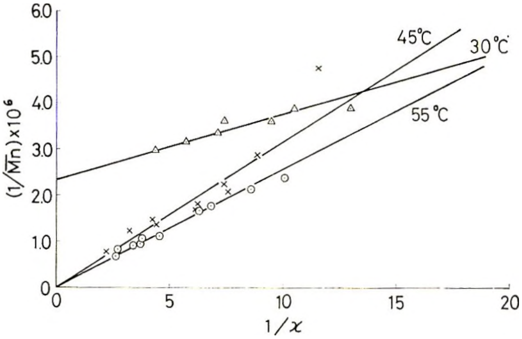


Fig. 11. Reciprocal of molecular weight vs. reciprocal of polymer yield in postpolymerization of trioxane *in vacuo:* pre-irradiation, 1.0×10^5 R at -78°C.

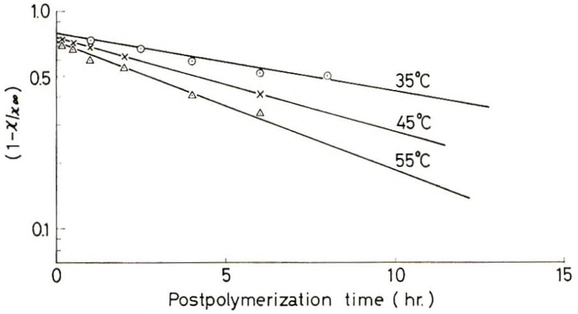


Fig. 12. Plots of $[1 - (x/x_\infty)]$ vs. postpolymerization time of trioxane; pre-irradiation, 1.0×10^6 at -78°C, *in vacuo.*

From these results we can conclude that the chain-transfer reaction does not occur in most cases of radiation-induced postpolymerization of trioxane *in vacuo.* An exception was observed when the preirradiation dosage is small and polymerization temperature is low.

From eqs. (7) and (8) the saturation yield at infinite polymerization time and the degree of polymerization at saturation are given by $k_p\phi_iD/k_t$ and k_p/k_t, respectively. Equation (7) can be written as

$$-k_t t = \ln[1 - (x/x_\infty)] \tag{10}$$

where x_∞ represents the saturation yield, $k_p\phi_iD/k_t$. A logarithmic plot of $[1 - (x/x_\infty)]$ against time t should give a straight line whose slope has the value $-k_t$. The value $[1 - (x/x_\infty)]$ should approach unity at $t = 0$. As shown in Figure 12, however, the plots of $[1 - (x/x_\infty)]$ deviate from unity at $t = 0$. This deviation is attributed to the fact that the initial rates of polymerization are extremely large. The larger the rate of polymerization, the larger the deviation in Figure 12.

It is reasonably assumed that the radiation-induced postpolymerization of trioxane consists of two stages, i.e., a very large rate at the first stage and a relatively small one at the second stage.

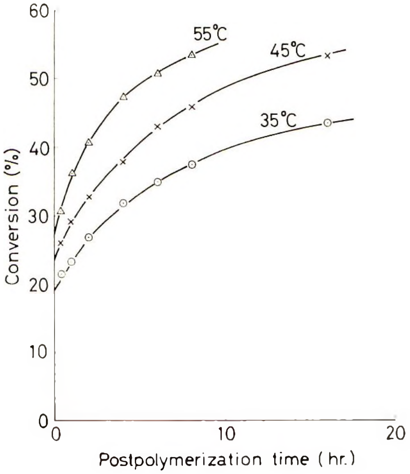


Fig. 13. Intercept polymer yield in postpolymerization of trioxane *in vacuo:* pre-irradiation, 1.0×10^6 R at −78°C.

The yield–polymerization time curve at the second stage did not extrapolate back to the origin, and the intercept at the ordinate ($t = 0$) is denoted the intercept yield. Experimental results are shown in Figure 13. It was found that the intercept yield agreed closely with the deviation obtained in Figure 12 and that the intercept yield increased with the increasing preirradiation dose and postpolymerization temperature.

However, the intercept yield was almost zero when the yield–polymerization time curve was S-shaped at large dosage and when the postpolymerization temperature is below 30°C. In the latter case, the logarithmic plots of $[1 - (x/x_\infty)]$ against t did not deviate from unity at $t = 0$. Therefore, under those polymerization conditions at which the intercept yield appears, the increase in polymer yield obtained at polymerization time more than 15 min is mainly due to the polymerization reaction at the second stage.

By subtracting the intercept yield from the total polymer yield, the plots of experimental results for eq. (10) can be drawn as shown in Figure 14. The value of k_t obtained from Figure 14 are tabulated in Table II.

On the other hand, by making use of expression (6), the initial rate of polymerization, R_{p0}, can be written as

$$R_{p0} = k_p \phi_i D[M_0] \tag{11}$$

The values of R_{p0} at the second stage were obtained from the extrapolated yield–polymerization time curves. Consequently, by putting the values of R_{p0} and ϕ_i into eq. (11), the rate constants of propagation k_p can be determined.

The values of kinetic parameters thus obtained are tabulated in Tables II and III. It was found that the values of ϕ_i are dependent on preirradiation dosage and decrease as the dosage increased. This indicates that active

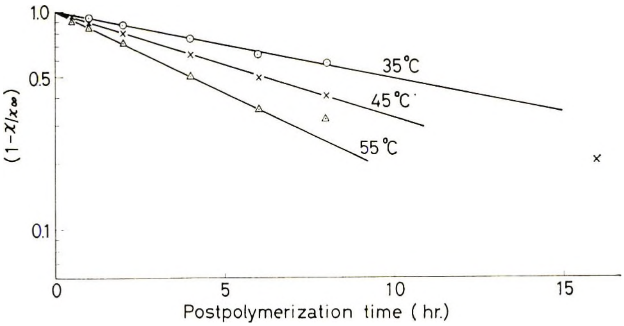


Fig. 14. Plots of $[1 - (x/x_\infty)]$ at the second stage vs. postpolymerization time of trioxane; pre-irradiation, 1.0×10^6 R at −78°C.

species may recombine together and/or may react with radiolysis products of trioxane when dosage is large. The rate constant of termination reaction increased with the increasing preirradiation dose and polymerization temperature. This indicates that the probability of the termination reaction becomes large for a large dosage. These tendencies are similar to those reported previously.[1]

While the rate constant of propagation reaction decreased slightly as the preirradiation dose increased, even at constant polymerization temperature, it was expected to be constant irrespective of the preirradiation dose. The possible reason for this finding is as follows. The polymerization results analyzed here kinetically are those obtained at the second stage. There-

TABLE II
Kinetic Parameters at the Second Stage in Radiation-Induced Postpolymerization of Trioxane *in Vacuo*[a]

Postpolymerization temperature, °C	x_0, %[b]	R_{p0}, %/hr	$\phi_i \times 10^2$, eV^{-1}	k_p, sec^{-1}	k_t, sec^{-1}
35	20	2.85	1.23	6.76×10^{-2}	2.10×10^{-5}
45	23	4.75	1.31	1.13×10^{-1}	3.22×10^{-5}
55	27	7.25	1.21	1.72×10^{-1}	4.90×10^{-5}

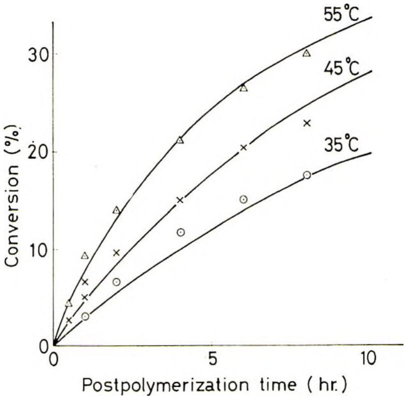
[a] Preirradiation, 1.0×10^6 R at −78°C.
[b] Intercept yield.

TABLE III
Kinetic Parameters at the Second Stage in Radiation-Induced Postpolymerization of Trioxane *in Vacuo* at 45°C

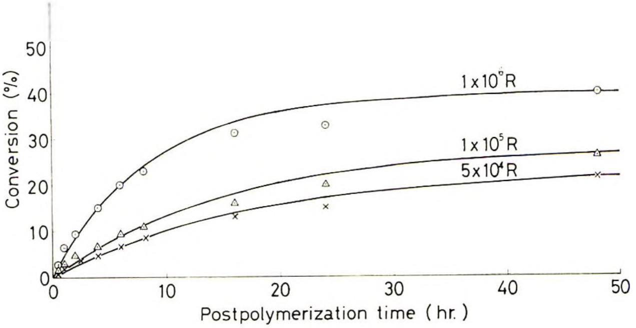
Preirradiation dose, R	x_0, %	R_{p0}, %/hr	$\phi_i \times 10^2$, eV^{-1}	k_p, sec^{-1}	k_t, sec^{-1}
5.0×10^4	4	1.50	4.75	1.88×10^{-1}	1.61×10^{-5}
1.0×10^5	7	1.65	3.00	1.67×10^{-1}	1.78×10^{-5}
1.0×10^6	23	4.75	1.31	1.13×10^{-1}	3.22×10^{-5}

fore, the propagation reaction is affected by polymer formed at the first stage, i.e., the crystal lattice of the remaining monomer is disordered by the polymer. Alternatively, it may be considered that k_p is affected by the defects resulting from preirradiation and radiolysis.[3,8] Actually, as shown in Table III, the larger the value of the intercept yield x_0, the smaller that of k_p. Strictly speaking, k_p and k_t may vary gradually in the course of polymerization. In the present study, however, for simplification we have assumed that the radiation-induced postpolymerization of trioxane consists of two stages and that k_p and k_t at the second stage are constant.

By putting the kinetic parameters obtained experimentally into eq. (7), the relationships between the polymer yield and the polymerization time shown in Fig. 15 are obtained.



(*a*)



(*b*)

Fig. 15. Kinetic curves for postpolymerization of trioxane at the second stage: (*a*) pre-irradiation, 1 × 10^6 R at −78°C; (*b*) postpolymerization temperature 45°C. Experimental points were obtained by subtracting intercept yields from total polymer yields; continuous curves were calculated from eq. (7).

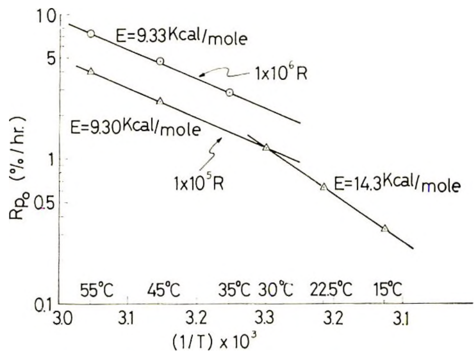


Fig. 16. Arrhenius plots of initial postpolymerization rate of trioxane *in vacuo:* experimental plots at postpolymerization temperatures higher than 30°C were obtained by extrapolating yield–time curves in the second stage of postpolymerization.

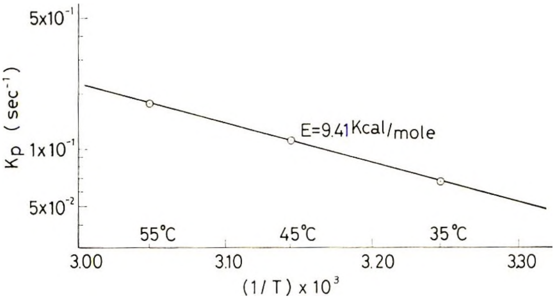


Fig. 17. Arrhenius plot of propagation rate constants: pre-irradiation, 1.0×10^6 R at −78°C.

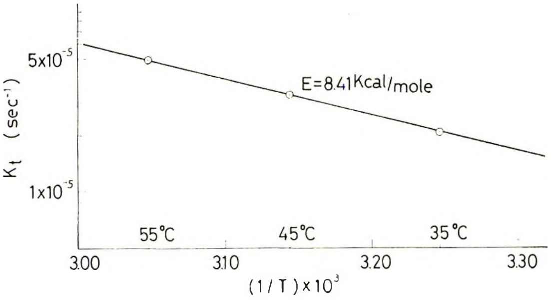


Fig. 18. Arrhenius plot of termination rate constants: pre-irradiation, 1.0×10^6 R at −78°C.

The calculated and the observed behavior is represented by the full lines and the points, respectively. The agreement between these values in Figure 15 supports the polymerization scheme represented by eq. (2).

Figures 16, 17, and 18 show Arrhenius plots of the initial rates of polymerization, the rate constants of the propagation reaction, and the rate constants of the termination reaction, respectively. From eq. (11), it is evident that the overall activation energy, E_{Rp0} should be equal to the activation energy of propagation reaction, E_{k_p}. The overall activation energy of 9.3 kcal/mole is very small in comparison with the values of 30–40 kcal/mole reported previously.[1,7,9] This difference may be attributable to the experimental conditions, such as a purity of monomer and atmosphere in which preirradiation and postpolymerization was carried out. In this case the purity of the monomer was extremely high, because trioxane was carefully purified by sublimation and crystallization in a super-dry, high-vacuum system. In the present study preirradiation and postpolymerization were both carried out *in vacuo* and with the use of highly purified trioxane, so the polymer yields were as almost high as those previously obtained in air.[1] In addition, the trioxane can be postpolymerized at a temperature below 30°C. These results are consistent with the difference of the overall activation energy.

In the postpolymerization of trioxane in air, the yield–polymerization time curve was S-shaped when preirradiation dose was small and polymerization temperature was low or when preirradiation dose was very large and polymerization temperature was relatively low. On the other hand, we found that an S-shaped curve is obtained only when the preirradiation dose is very large and polymerization temperature is relatively low (see Figs. 4 and 7). In this case, as mentioned above, k_t increases with increasing preirradiation dose. Therefore, the condition $k_p \doteqdot k_t$ can be assumed, and the yield–polymerization time curve is expressed by eq. (4).

As mentioned above, at below 30°C, the intercept yield did not appear. In this case, an overall activation energy of 14.3 kcal/mole was calculated from Arrhenius plots of the initial rate of polymerization (see Fig. 16). This value is different from that obtained above 30°C. It is not so unreasonable to consider that the former corresponds to the activation energy in the first stage and the latter to that in the second stage. However, the absolute value of the overall activation energy in the first stage was much smaller than that reported previously.[1,7,9]

As discussed above, in the radiation-induced postpolymerization of trioxane it is difficult to make a kinetic analysis over the entire range of various polymerization conditions. To elucidate the kinetics of postpolymerization of trioxane in the anisotropic solid phase it is necessary to study the initial stage of the postpolymerization, because the polymer yield is low so that the crystal lattice of the monomer is not disordered by the polymer formed. One may obtain the more accurate kinetics on the postpolymerization of trioxane when, the postpolymerization of trioxane purified *in vacuo* is carried out at a smaller dosage and a lower temperature.

To clarify the effect of oxygen on the postpolymerization of trioxane for comparison, it is necessary to study the postpolymerization in dry air with the use of highly purified trioxane. A detailed study on the postpolymerization of trioxane in dry air in comparison with the present paper will be presented in the near future.

The author would like to express cordial thanks to Prof. S. Okamura of Kyoto University for his encouragement of this work. We are grateful to Mr. M. Yoshida and Mr. N. Morishita for their assistance in carrying out the experiments.

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Received February 13, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3079–3088 (1970)

Studies on the Polymerization of Ethyl Acrylate. III. Effect of Temperature on the Solvent-Transfer Reaction

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Synopsis

The effect of temperature on transfer constants for different solvents in the polymerization of ethyl acrylate was observed. Activation energy differences ($E_{tr\mathrm{S}} - E_p$) and frequency factors were computed. It is observed that high frequency factors are associated with high activation energies. Values of $E_{tr\mathrm{S}}$ were calculated by an approximate method and were compared with the available data on methyl methacrylate, isobutyl methacrylate, and styrene.

In our earlier communication[1] we presented transfer constants for different solvents in the thermal polymerization of ethyl acrylate at 80°C. Since it is quite conceivable that the activity of a solvent in the transfer reaction can be best judged by the knowledge of the activation parameters for the transfer reaction, we have determined the values of transfer constants at four different temperatures. The results are utilized to compute the activation parameters, and the reactivities of different solvents in transfer reactions with ethyl acrylate radical are discussed.

EXPERIMENTAL

Monomer, Solvent, and Initiator

Monomer was purified as described in our earlier paper.[2] Solvents used are mostly of A.R. (B.D.H.) or G.R. (E. Merck) quality, further purified by the usual methods.[3] 2,2′-Azobisisobutyronitrile (AIBN) was used as initiator; it was thrice recrystallized from ethanol and had a melting point of 103–104°C.

Polymerization

Polymerization was carried out in sealed pyrex glass ampoules.[2] Initiator was not used in experiments at temperatures of 80°C and above. Since the thermal rate of polymerization was extremely low at temperatures below 80°C, initiator (AIBN) was used. The concentration of initiator was kept very low, even though the experiments were time-consuming. The molar ratio of initiator to monomer was kept constant; the value of [I]/[M] being 1.31×10^{-3} and 6.51×10^{-4} for experiments conducted at 40 and 60°C, respectively. Intrinsic viscosities of the polymer samples were determined in an Ubbelohde viscometer at 30°C in benzene solutions and the number-average degrees of polymerization were calculated from the equation, $\bar{P}_n = k[\eta]^{\alpha}$. The values of k and α used in the present work are 2.03×10^3 and 1.492, respectively.[4]

RESULTS AND DISCUSSION

It was observed that in AIBN-initiated polymerization the values of $\delta^2 R_p/[M]^2$ under our experimental conditions are very low, i.e., nearly one-twentieth of $1/\bar{P}_n$ and at higher temperatures, where polymerization has been effected thermally, the values of $\delta^2 R_p/[M]^2$ are almost negligible in comparison to $1/\bar{P}_n$. Hence the values of C_S was calculated by the conventional plot of $1/\bar{P}_n$ against [S]/[M]. The generalization that the plot of $1/\bar{P}_n$ against [S]/[M] at low conversions should converge to an intercept equal to C_M, which is a constant at a certain temperature irrespective of the solvent was not found valid in the case of ethyl acrylate polymeriza-

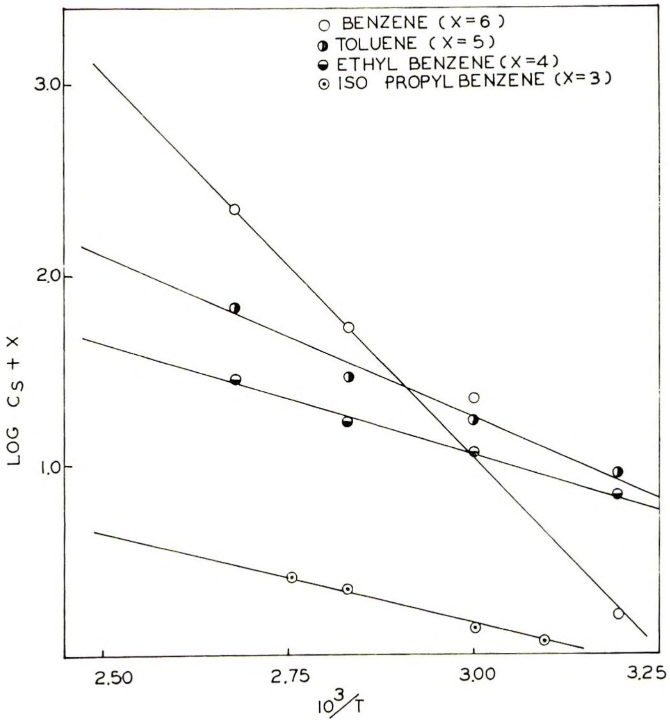

Fig. 1. Effect of temperature on the chain transfer of hydrocarbons in the polymerization of ethyl acrylate.

TABLE I

Transfer Constants for Various Solvents in the Polymerization of Ethyl Acrylate at Different Temperatures

Solvent	[S]/[M]	50°C		60°C		80°C		100°C		$E_{trS} - E_p$, kcal/mole	log (A_{trS}/A_p)
		$10^4/\bar{P}$	10^5C_S	$10^4/\bar{P}$	10^5C_S	$10^4/\bar{P}$	10^5C_S	$10^4/\bar{P}$	10^5C_S		
Benzene	1.22	0.24^{a}	0.16*	0.3	2.2	0.78	5.3	2.17	22	18.26	7.08
	2.03	—		0.46		1.32		—			
	2.85	0.27^{a}		0.64		1.69		6.17			
	4.88	0.30^{a}		0.95				11.10			
Toluene	1.01	1.05^{a}	8.8^{a}	2.80	17	2.56	29	10.63	68	7.69	1.29
	1.70	—		—		4.59		11.10			
	2.36	2.34^{a}		5.11		7.27		17.05			
	4.04	3.76^{a}		8.07		11.47		28.63			
Ethyl-benzene	0.88	6.03	6.88^{a}	14.42	116	14.40	168	22.50	287	5.40	0.60
	1.47	9.63^{a}		21.16		23.70		34.10			
	2.06	13.90^{a}		25.85		58.70		60.00			
	3.53	27.91^{a}		45.06		59.50		102.2			
Isopropyl-benzene	0.77	8.60	117	10.7	138	17.4	222	20.9^{b}	260^{b}	4.80	0.31
	1.29	—		16.5		24.2		32.6^{b}			
	1.80	21.0		24.7		39.6		46.2^{b}			
	3.09	37.5		—		69.2		—			
Cyclohexane	1.00	0.87	289	1.07	4.8	1.76	12.2	4.58	30.8	11.29	3.09
	1.67	1.07		1.43		2.58		6.50			
	2.34	1.29		1.70		3.34		—			
	2.68	—		—		—		9.81			
n-Hexane	0.83	1.34	5.24	1.48	5.93	2.10	9.7	4.45	14.6	5.06	0.87
	1.38	1.58		1.72		2.59		5.23			
	1.94	1.88		2.04		3.12		6.06			
Chloro-benzene	1.06	0.22^{a}	0.54^{a}	—	—	0.99	3.7	2.21	16.8	12.79	3.62
	1.77	0.26^{a}		—	—	1.18		2.93			
	2.48	—		—		1.90		4.53			
	4.26	0.40^{a}		—		2.15		7.72			

Continued

Table I (*continued*)

Solvent	[S]/[M]	50°C		60°C		80°C		100°C		$E_{tr\text{S}} - E_p$, kcal/mole	log $(A_{tr\text{S}}/A_p)$
		$10^4/\bar{P}$	10^5C_S	$10^4/\bar{P}$	10^5C_S	$10^4/\bar{P}$	10^5C_S	$10^4/\bar{P}$	10^5C_S		
Bromo-benzene	1.03	—		0.46	1.63	—	6.88	1.65	33.4	16.44	6.01
	1.71	—		0.57		1.23		2.64			
	2.41	—		0.69		1.51		4.71			
	4.12	—		—	—	3.08		9.20			
Chloroform	1.35	0.35^{a}	1.95^{a}	—		2.28	14.9	7.1	47.4	12.14	3.74
	2.25	0.53^{a}		—		3.66		11.39			
	3.15	0.72^{a}		—		5.69		17.71			
	5.40	1.14^{a}		—		19.32		26.46			
Carbon tetrachloride	1.12	0.81^{a}	3.32^{a}	—	9.0	2.30	15.5	3.95	28	8.09	1.20
	1.87	1.07^{a}		1.59		3.48		6.10			
	2.62	1.33^{a}		2.60		7.61		8.15			
	4.49	—		4.53		7.56		13.45			
n-Butyl alcohol	1.17	2.42^{a}	12.80^{a}	3.88	29.1	6.24	58.5	—	126	8.75	2.21
	1.95	3.44^{a}		6.18		11.61		20.10			
	2.73	3.09^{a}		6.88		16.00		34.00			
	4.68	6.89^{a}		14.08		—		60.00			
sec-Butyl alcohol	1.17	15.7^{c}	106^{c}	22.7^{d}	185^{d}	23.2	222	34.2	315	4.49	0.14
	1.95	19.3^{c}		34.4^{d}		42.4		69.2			
	2.74	29.5^{c}		50.9^{d}		55.3		87.9			
	4.69	49.4^{c}		87.1^{d}		104.0		148.4			
tert-Butyl alcohol	1.90	0.28^{a}	0.68^{a}	0.54	1.7	0.79	7.12	1.80	16.4	12.72	3.67
	2.66	0.34*		0.67		1.92		4.45			
	4.55	0.47*		0.80		3.41		7.74			

Isobutyl alcohol	1.16	2.46[c]	21[c]	4.00[d]	33.1[d]	6.87	46.5	18.40	80.6	5.66	0.20
	1.93	—		6.10[d]		8.93		24.50			
	2.71	5.69[c]		—		12.92		30.10			
	4.64	9.79[c]		15.76[d]		21.40		46.20			
Acetone	1.46	0.39[a]	2.07[a]		—	1.60	11	3.11	23	9.28	1.79
	2.44	0.61[a]				2.72		5.63			
	3.41	0.82[a]				3.75		7.95			
	5.85					—		13.65			
Methyl ethyl ketone	1.20	1.65	14.4	2.35	19.2	3.85	32.9	5.40	44.5[b]	5.48	0.12
	2.00	3.00		3.78		6.35		9.00[b]			
	2.80	4.15		5.44		9.36		12.70[b]			
	4.80	7.07		—		—		28.00[b]			
Acetic acid	1.88	0.33	1.76	—	—	1.16	5.37	1.89	10.5	8.54	1.02
	3.13	0.56		—	—	1.78		3.29			
	4.39	0.79		—	—	2.27		4.70			
Ethyl acetate	1.10	0.41	2.98	0.51	4.48	0.98	8.90	—	18.2	8.60	1.29
	1.83	0.61		0.81		1.54		3.30			
	2.56	0.83		1.16		2.08		4.75			
	4.39	—		2.07		—		7.95			
Acetonitrile	2.06	0.59	1.58	0.88	2.45	1.06	5.50	3.15	14.3	10.44	3.25
	3.44	0.83		1.19		1.75		4.78			
	4.81	1.04		1.54		2.56		6.87			

[a] At 40°C.
[b] At 90°C.
[c] At 45°C.
[d] At 63°C.

tion, and a similar phenomenon was observed in the polymerization of methyl methacrylate,[5,6] although in the case of styrene[7] the above generalization found viable. An explanation in the case of methyl methacrylate was offered by Basu et al.[5,6] in our earlier paper from this laboratory, and it was also observed that experiments at very near bulk concentration showed the plot of $1/\bar{P}_n$ against [S]/[M] taking a steep turn finally converging at C_M; the nature of the turn, either upwards or downwards, depended upon the solvent.[8]

It may be observed from Table I and Figure 1 that for a series of hydrocarbons the activation energy difference $(E_{tr\mathrm{S}} - E_p)$ is maximum for benzene and is minimum for isopropylbenzene, an observation expected from the substitution at the α-carbon atom. A similar trend of results consistent with the α-hydrogen concept is noticed in alcohols (Fig. 2), ketones, acids, and esters. Although the C_S value for ethyl acetate is slightly higher at elevated temperature in comparison to acetic acid, the activation parameters indicate that α-hydrogens are equally active in both cases and consistent with the results of Kharasch and Brown[9] and Price and Schwarz.[10]

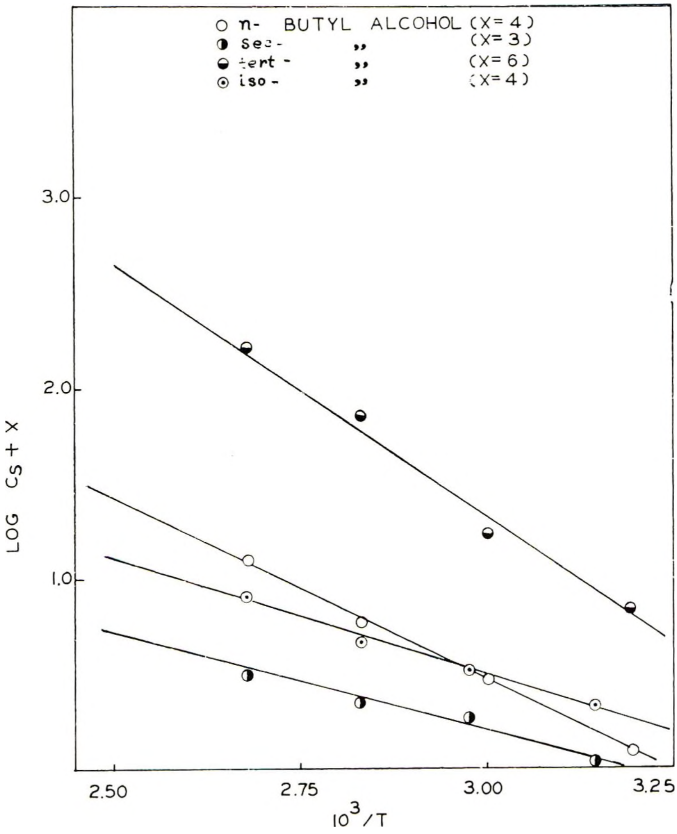

Fig. 2. Arrhenius plot for the chain transfer of alcohols in the polymerization of ethyl acrylate.

It appears that the activity of the halogen atom increases from chlorobenzene to bromobenzene, which is difficult to explain since the activation energy difference for chlorobenzene (12.79 kcal/mole) is lower than for bromobenzene (16.44 kcal/mole), and in view of observation made,[11] the actual transfer process is believed to be rather complex.[12]

It is seen from Table I that the transfer constants for carbon tetrachloride are higher than the values for chloroform below 80°C, but C_S for chloroform is evidently higher than that of carbon tetrachloride at 100°C. It is reported in the literature that C_S for carbon tetrachloride is higher than C_S for chloroform in the case of methyl methacrylate,[5] ethyl methacrylate,[13] styrene,[14] and vinyl acetate,[15] and the reverse is true for methyl acrylate[16] and acrylonitrile.[17]

Mayo[11] assumed that the transfer activity of chloro compounds increases with the increase in number of chlorine atoms in the molecule, provided all the chlorine atoms are attached to the same carbon atom and this was strikingly successful in majority of cases. It has been suggested by Price[18] that when carbon tetrachloride is replaced by chloroform, it is the paraffinic

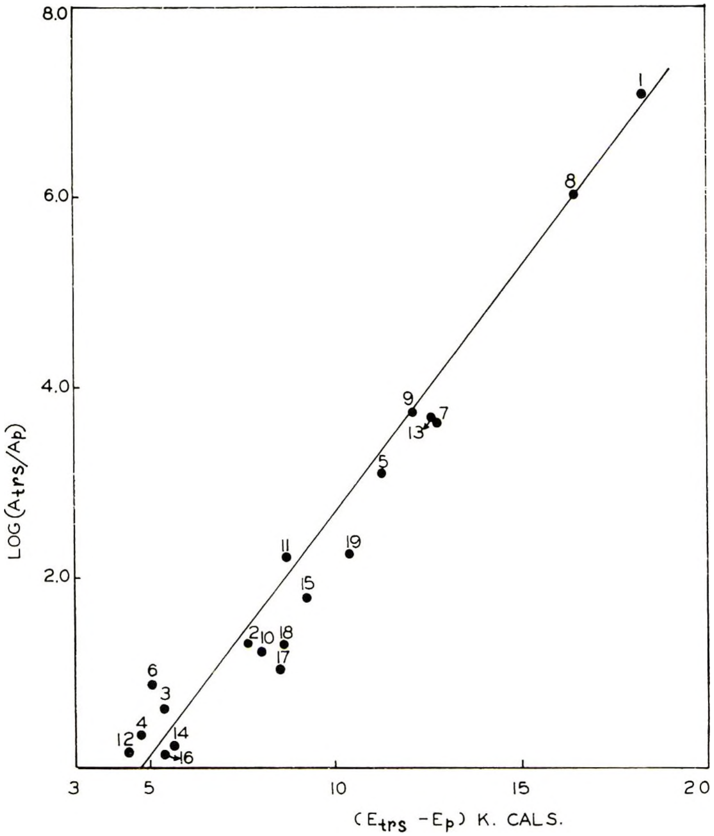

Fig. 3. Energy of activation and frequency factor in the chain-transfer step in ethyl acrylate polymerization.

TABLE II

Comparison of Activation Energies for Solvent Transfer Reaction in Different Monomers with Different Solvents

Solvent	$E_{tr\mathrm{S}}$, kcal/mole Ethyl acrylate	 Methyl methacrylate[a]	 Styrene[b]	 Isobutyl methacrylate[c]
Benzene	25.06	15.89	23.80	13.60
Toluene	14.49	13.90	19.10	12.60
Ethylbenzene	12.20	11.30	14.50	—
Isopropylbenzene	11.60	12.20	14.50	—
Cyclohexane	18.09	—	22.40	—
n-Hexane	11.86	—	—	—
Chlorobenzene	19.59	—	—	—
Bromobenzene	23.24	—	—	—
Chloroform	18.92	—	—	16.90
Carbon tetrachloride	14.89	—	13.80	15.40
Acetone	16.08	—	—	13.40
Methyl ethyl ketone	12.28	—	—	12.90
Acetic acid	15.34	—	—	19.80
Ethyl acetate	15.40	—	—	12.90
n-Butyl alcohol	15.55	—	—	17.80
sec-Butyl alcohol	11.29	—	—	—
tert-Butyl alcohol	19.52	—	—	—
Isobutyl alcohol	12.46	—	—	—
Acetonitrile	17.24	—	—	—

[a] Data of Sen et al.[26]

[b] Data at Gregg and Mayo.[7,14]

[c] Data of Khanna.[27]

hydrogen rather than the chlorine atom that participates in the transfer; this is also supported by the work of Basu et al.[5] Explaining higher C_S values for chloroform in methyl acrylate polymerization, Sen et al.[16] pointed out that abstraction of a hydrogen atom from chloroform is preferred by methyl acrylate and acrylonitrile radicals to removal of a chlorine atom from carbon tetrachloride. Their interpretation is based, more or less, on structural considerations.

In Table I are listed the values of $(E_{tr\mathrm{S}} - E_p)$ and $\log(A_{tr\mathrm{S}}/A_p)$ for a number of solvents studied in the present work. It is observed that higher activation energy differences accompany high frequency factors, which is in line with Gregg and Mayo's suggestion[7] that "for a series of related transfer agents with a particular polymer radical a reduction in activation energy for hydrogen abstraction is frequently accompanied by a reduction in frequency factor." Similar results have been found in other reactions, such as ionic[19] and oxidation[20] reactions. On plotting $\log(A_{tr\mathrm{S}} - A_p)$, against $(E_{tr\mathrm{S}} - E_p)$, the points are almost on straight line, as can be seen from Figure 3. Since E_p is a constant, it should be expected that the lowest reactivity goes with the highest activation energy. Temperature coefficients varied from 1.5 to 3.0, and the values are higher for less reactive solvents.

It is suggested here that a comparison of the reactivities of different solvents towards poly(ethyl acrylate) radical could be made if k_p and E_p are known. Since E_p and k_p values in ethyl acrylate polymerization are unknown, we have made a rough calculation of the value of $E_{tr\mathrm{S}}$ from the present set of results. The energy of activation for δ, i.e., $(E_p - {}^1/_2E_t)$ has been found to be 6.8 kcal/mole for ethyl acrylate.[2] As it is commonly known that the energy of activation for the termination reaction for various monomers is either zero or very close to zero,[21–25] the addition of $(E_p - {}^1/_2E_t)$ to our value of $(E_{tr\mathrm{S}} - E_p)$ will give $(E_{tr\mathrm{S}} - {}^1/_2E_t)$ and in view of the very low value of ${}^{1/2}E_t$, this can be approximated to be equal to $E_{tr\mathrm{S}}$. In Table II, we have compiled the values $E_{tr\mathrm{S}}$ in ethyl acrylate polymerization along with similar data available for other monomers. It might be observed that the order of $E_{tr\mathrm{S}}$, more or less, is same for all the monomers. In case of benzene, $E_{tr\mathrm{S}}$ values are almost identical for ethyl acrylate and styrene. Excluding benzene, for the rest of the solvents listed in Table II the energies of activation for solvent transfer reaction are strikingly similar for ethyl acrylate and methacrylic esters. More so, the values of $E_{tr\mathrm{S}}$ in isobutyl methacrylate and ethyl acrylate are identical in some cases. The similarity in the energy values probably indicates that the mode of transfer as well as the focal point of attack by the polymer radical concerned are identical in all these monomers. A more constructive discussion would have been possible if the entropy and free energy factors were determined the rate constants for propagation must be known for such calculations.

The authors express their gratitude and indebtedness to Prof. S. R. Palit for helpful discussions and encouragement during the course of work. Thanks are due to Mr. C. H. Sastry for his help in getting the calculations done on IBM 1401 computer.

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Received May 13, 1969
Revised April 3, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3089-3111 (1970)

Structure-Property Relationships of Ring-Containing Nylon 66 Copolyamides

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Synopsis

Several series of nylon 66 copolyamides were prepared with up to 30 mole-% substitution of ringed comonomers of the type X-$(CH_2)_n$-R-$(CH_2)_n$-X, where $n = 0$, 1, or 2; X = $-NH_2$ or $-CO_2H$; and R = phenylene, cyclohexylene, or naphthylene. The ring structure was correlated with glass transition temperature and melting point. The important features of ring structure fall into the following categories: ring isomerism, aromaticity, diamine vs. diacid substitution, chain length, and ring substitution. Proper "fit" (isomorphism) of the comonomer into the nylon 66 chain appears to be the main criterion for ringed copolymers of high T_g and high melting point.

INTRODUCTION

Numerous copolymers have been described since the preparation of polyamides was first reported by Carothers. Structure-property relationships have been established among a wide variety of polyamides and copolyamides. The isomorphous replacement of the phenylene linkage for a methylene segment in polyamides was explored by Edgar and Hill,[1] Yu and Evans,[2,3] and Tranter.[4] These studies have examined the effect of copolymerization upon the crystalline region of the polymer, as measured by changes in melting point and crystallinity. The glass transition temperature, T_g, is a measure of the amorphous character of a polymer. However, changes in crystallinity do influence T_g.[5] Accordingly, the degree of isomorphism exhibited by a comonomer should produce changes in T_g. This paper describes the relationship between molecular "fit" and T_g, melting point, and boiling water shrinkage for a series of ring-containing nylon 66 copolyamides.

EXPERIMENTAL

Materials

All chemicals were obtained from commercial sources. The amine salts were generally prepared by a slow addition of a 75% aqueous solution of a pure diamine to a 50-75% aqueous solution, or slurry, of a pure diacid in

TABLE I

Diacids		Diamines	
Designation	Name	Designation	Name
TA	Terephthalic acid	t-CBMA	*trans*-1,4-Cyclohexanebis (methylamine)
IA	Isophthalic acid	PXD	*p*-Xylenediamine
TBIA	5-*tert*-Butylisophthalic acid	MXD	*m*-Xylylenediamine
HHTA	Hexahydroterephthalic acid	PBE	2,2′-*p*-Phenylenebis(ethylamine)
1,6-NDA	1,6-Naphthalenedicarboxylic acid	DBE	2,2′-*p*-Durylenebis(ethylamine)
2,6-NDA	2,6-Naphthalenedicarboxylic acid		
HHIA	Hexahydroisophthalic acid		
PPDAA	*p*-Phenylenediacetic acid		
MPDAA	*m*-Phenylenediacetic acid		
OPDAA	*o*-Phenylenediacetic acid		
DDAA	Durenediacetic acid		

a 1:1 molar ratio. The mixture was warmed until solution was attained, then it was treated with activated carbon, Celite filter aid, and filtered. An excess of ethanol was added, and the solution was cooled at 0-5°C. for 24 hours. The precipitated salt was filtered, washed with ethanol, and dried under vacuum at 65°C. Yields of 85–95% were generally obtained by this method.

The adipic acid salt of *trans*-1,4-cyclohexanebis(methylamine) was obtained by this procedure from a 60% *trans*–40% *cis* isomer mixture (ratio verified by VPC). The *trans* isomer precipitated, leaving in solution the *cis* form. One recrystallization from water–ethanol was sufficient to remove any trace quantities of *cis* isomer remaining in the salt.

The polymers are designated by the following code: the first number shows the number of carbon atoms in the diamine, while the second shows the number of carbon atoms in the diacid. The designations used for the ringed comonomers are listed in Table I. Therefore, 6-TA is the polyamide from hexamethylenediamine and terephthalic acid, and MXD-6 is the polyamide from *m*-xylylenediamine and adipic acid.

Methods

Polymerization. The copolyamides were prepared from combinations of the various amine salts. The mixed salts were combined with sufficient water to form a 75% aqueous slurry. This slurry was added to a stainless steel, high pressure autoclave which was purged of air by the use of purified nitrogen. The temperature and pressure were slowly raised to 220°C and 250 psig. Then the temperature was further increased to 243°, while the pressure was maintained at 250 psig, during which time there was the continuous removal of steam condensate. At this point the pressure was gradually reduced to atmospheric over a 25-min period. The polymer melt was allowed to equilibrate for 30 min at about 15°C above the melting point. This finished polymer was melt-spun directly from the autoclave through a single-hole spinneret into a quench water bath, and then taken up on a bobbin with a Universal Winder.

This fiber was drawn four to five times its original length over a 60–90°C hot pin.

In many of the copolymers, the melting points were sufficiently high that degradation occurred in the melt; therefore, comonomer substitution was limited to about 30 mole-%. The intrinsic viscosities in *m*-cresol ranged from 0.74 to 1.1 with no particular pattern discernible in regard to comonomer type. These data show that sufficiently high molecular weights were obtained for polymer-fiber formation.

Sonic Modulus. The dynamic tensile modulus (E_s), in grams per denier, was measured at 15,000 cps as a function of temperature over the range of 30–150°C at 0.03 g/den stress level at 0 and 30% RH. Drawn samples were preconditioned at constant length at 150°C in nitrogen for 15 min before measurements were made.

Glass Transition Temperature. The glass transition temperatures T_g were determined on the Vibron (Toyo Instrument Company), a direct-reading dynamic viscoelastometer. The glass transition temperature was taken as the maximum in the tan δ peak. The tan δ curve was obtained from the plot of the loss modulus E'' divided by the dynamic modulus E' as a function of temperature ($\tan \delta = E''/E'$). Measurements were made at 11 cps at 0.03 g/den load on drawn samples, at 0% R.H.

In general, discussions of T_g are confined to indirect measurements obtained from the plot of sonic modulus vs. temperature. This method was chosen for convenience, because direct measurements of the T_g of fibers are difficult and time-consuming. In addition, moisture greatly affects T_g in many polyamides,[6] which requires that great care be taken to control humidity during the course of the measurement. The physical state of the polymer also exerts an influence on T_g. Orientation and crystallinity produce changes in T_g, which means that all samples should be in the same state during measurement.

The sonic modulus–temperature curves for nylon 66 at 0 and 30% RH are illustrated in Figure 1.

An increase in T_g results in a shift of the curve along the axis to the right. Similarly, a decrease in T_g produces a shift to the left. For convenience, approximate differences in T_g can be expressed by the percent retention of modulus at a particular temperature, T. This value is obtained from the modulus at temperature T divided by the modulus at 30°C, multiplied by 100. If the retention of modulus of a polymer at a particular tempera-

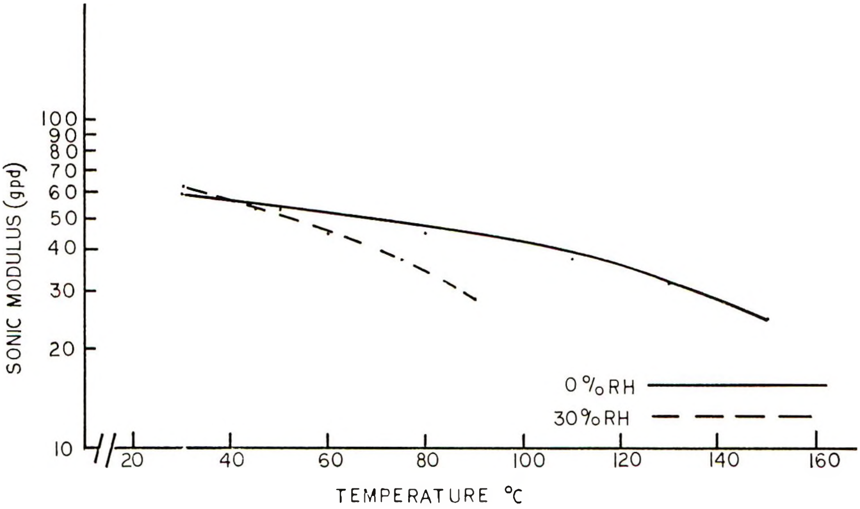


Fig. 1. The relationship of sonic modulus of nylon 66 to temperature and humidity.

ture is higher than that of the control sample at the same temperature, then the polymer is said to have a higher T_g than the control. Such a measurement is useful in establishing the relative differences in T_g among fibers. While the actual value of sonic modulus varies from sample to sample, such changes do not affect the T_g comparisons made in this paper.

Sonic modulus–temperature measurements were made at both 0 and 30% RH in order to determine differences in in the moisture sensitivity of T_g, as well as to establish relative differences in transition temperatures. The value of 90°C at 30% RH was selected because humidity control in the instrument is quite difficult above this temperature.

Actual measurements of T_g are given in only a few selected cases, and are intended only to orient the reader as to the significance of the modulus retention values.

However, both dynamic techniques sometimes show some variation in data due to sample-to-sample differences in crystallinity, orientation, and draw ratio. While these differences are small, they will cause some data scatter in fiber-fiber comparisons.

Polymer Melting Point. The melting point was determined by observing filaments of drawn fiber between crossed nicol polarizers on an electrically heated hot-stage microscope. The melting point T_m was taken as the temperature at which the last trace of birefringent crystallinity disappeared.

Boiling Water Shrinkage. The boiling water shrinkage was determined on fibers which had been drawn approximately five times. These fibers were immersed in boiling water for 5 min. A comparison of the original and final length gives the boiling water shrinkage, which is expressed as a percentage of original length.

RESULTS AND DISCUSSION

Background

Considerable information exists in the literature on the structure–property relationships of polymers, particularly the influence of structure upon the glass transition temperature, T_g. The most extensive data are concerned with trends observed in addition polymers. These data indicate that the most important factor influencing the value of T_g is polymer chain flexibility. Flexible chains such as those made up of linear alkylene groups have low glass transitions. Stiff polymer chains containing ring systems or bulky groups have high transition temperatures. Factors which are difficult to separate from chain flexibility in affecting T_g are steric hindrance and bulkiness of the side groups attached to the backbone chain. If either factor is present, the T_g is increased. However, if the flexibility of the side group is greatly increased, either by lengthening slightly the alkylene chains or by introducing flexibility with ether linkages, the T_g will decrease.

Symmetry may also affect T_g. An increase in symmetry will lower T_g in amorphous polymers, as seen from the examples of poly(vinyl chloride) (87°C) and poly(vinylidene chloride) (-17°C).[5] In this case, the increased number of side groups acting to increase T_g are offset by the increased symmetry. However, in crystalline polymers, the T_g is often increased where symmetrical rings are present.

Finally, an increase in polarity has a tendency to raise T_g, but this effect is believed small compared to other factors, within the polyamide family.

Investigations with condensation polymers such as polyamides, polycarbonates, and polyesters, have generally confirmed these trends in T_g with structure. However, only limited T_g data exist for random condensation copolyamides, particularly those of the economically important nylon 66.

This lack of data is somewhat surprising in view of the general information available from copolymerization studies, where extensive investigations have been made on isomorphic substitution of comonomers. Many of these polymer compositions differed in both the comonomer concentration and in the type of property which was measured. Therefore, valid comparisons among much of the copolymer data available are impossible. This study describes an attempt to correlate the effect of comonomer structure with the physical properties, especially the T_g, of nylon 66 copolyamides. Investigations were confined to the study of ringed comonomers in which the effects of ring isomerism, aromaticity, chain length, ring substitution, and diamine versus diacid substitution could be determined. It is conceivable that the general rules which apply to the effect of structure upon T_g in homopolymers may not apply to random copolymers. This study, unfortunately, is not comprehensive, for only several examples of each type of substitution were available. However, general conclusions may still be drawn from the data.

Influence of Ring Isomers

A series of ring containing random copolyamides was prepared to determine the influence of ring isomers upon physical properties. In three of the copolymer series, the effect of 1,4- and 1,3-substitution was determined. These copolymers included three basic types of cyclic monomers: aromatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and arylaliphatic diamines. A fourth series dealt with a comparison of 1,4-, 1,3-, and 1,2-substitution in arylaliphatic dicarboxylic acid copolymers. In addition, the 2,6- and 1,6-substitution of naphthalene dicarboxylic acid copolymers was compared. Within a series of copolymers, several concentrations of comonomers were examined as well, to obtain more precise comparisons among the various groupings.

The effects of ring substitution upon the glass transition temperature, T_g (as measured indirectly from the sonic modulus retention) of copolyamides appear in Table II.

The sonic modulus data in Table II clearly show that the symmetrical 1,4-substitution gives copolyamides of higher T_g than the unsymmetrical 1,3-substitution. This result appears in the comparison of aromatic dicarboxylic acids (TA vs. IA), cycloaliphatic dicarboxylic acids (HHTA vs. HHIA), arylaliphatic diamines (PXD vs. MXD), and arylaliphatic dicarboxylic acids (PPDAA vs MPDAA) at all concentration levels. Within a monomer type, acid or diamine, the differences in retention values begin to decrease as the functional groups are moved further out from the ring causing the polymer to achieve a more aliphatic character (TA vs. PPDAA). This result will be discussed in detail later.

The relationship between molecular structure and melting point closely parallels that observed with T_g. However, there are exceptions.

Copolymers of nylon 66 with symmetrically substituted rings (1,4-substitution) melt higher than those of unsymmetrical ring configuration, provided that the basic aromatic character is not obscured by an increase in the alkyl character of the ring (e.g., PPDAA), at which point the melting points are equivalent.

The melting point of a copolymer appears more dependent than T_g upon the degree of "fit" of the comonomer in the polymer chain. If the fit is good, then the stiffening effect produced by the ring is reflected by increased melting point. However, care must be taken with this interpretation, because a depressed melting point may be observed because of the presence of a melting point eutectic.[4] Such an occurrence does not imply that there is not isomorphism among monomers. From the knowledge of the melting characteristics of the homopolymer and relating this to that of the copolymers, a fairly accurate picture may be drawn of the degree of fit, at least as regards to those samples selected in this study.

The one example of 1,2-substitution in the OPDAA series (OPDAA = *o*-phenylene diacetic acid) shows that the T_g of 1,2- ring copolyamides resembles that of 1,3- ring copolyamides. These data are limited, because only two concentration levels in the *ortho* series could be obtained. Also, the copolymers begin to assume a more aliphatic character, which obscures the effects of the aromatic ring. The lack of symmetry in the 1,2 and 1,3 rings most likely produces similar disruption in the polymer chain.

The two naphthalene dicarboxylic acid copolymers do not differ greatly in T_g or melting point, although there is an indication that the more symmetrical 2,6 isomer has a somewhat higher T_g. Both the 1,6 and 2,6 isomers have increased glass transition temperatures over control nylon 66. The degree of response resembles that obtained with the unsymmetrical MXD-6 copolymers and with the arylaliphatic dicarboxylic acid copolymers of the phenylene diacetic acids. This result indicates that stiffening of the polymer chains occurs, but because of the poor molecular fit of the unsymmetrical naphthalene ring, a relatively small increase in T_g results, despite the presence of the bulky naphthalene ring. The T_g is somewhat improved over 66–6IA copolymers at equivalent concentrations, however.

Only two isomers of the naphthalene ring system, therefore, appear theoretically capable of producing larger changes in T_g than the 1,6- and 2,6-isomers. These acids would be the fairly symmetrical 2,7- and 1,4-isomers. Unfortunately, these acids were not available for confirmation studies.

Several interesting points may be made with regard to the data in Table II. Nielsen has stated that an increase in symmetry in certain amorphous polymers will reduce T_g.[5] However, he also points out that many other factors also affect T_g, such as side chain groups. If the other factors are ignored, one would predict that 1,2 and 1,3 ring substitution in copolyamides should result in higher values of T_g than 1,4 substitution, because of increased hindrance and lack of symmetry. As such is not the case, the other factors must over-ride these effects. One explanation for higher T_g values in 1,4 ring polymers is that a better molecular fit is achieved in the polymer backbone, resulting in better hydrogen bonding, which in turn, leads to better chain packing and improved orientation upon drawing. Such improvements would, therefore, restrict the movement of the polymer chains upon heating, thus producing increased T_g. Copolyamides containing 1,2 and 1,3-substituted rings cannot assume a favorable fit and thus obtain the benefits of improved chain packing and better orientation.

Some evidence of the lack of crystallinity of these 1,3 and 1,2 rings is suggested from the appearance of the fibers. In general, they become transparent with increased substitution.

From a structural standpoint, boiling water shrinkage appears the most affected by the ability of a comonomer to fit within the polymer chain. Hence, small, symmetrical, compact molecules incorporated into nylon 66 produce little change in boiling water shrinkage. Symmetrical, compact intermediates such as terephthalic acid, *p*-xylylenediamine and hexahydroterephthalic acid do not greatly affect shrinkage, although a slight increase (to about 14%) does occur with increased substitution of the comonomer. Copolymers of the phenylene diacetic acids produce a greater increase in

TABLE II
Influence of Isomers upon Copolyamide Properties

Substitution	Composition	Melting point, °C	Boiling water shrinkage, %	Sonic modulus, % retention from 30°C: 0% RH/150°C	Sonic modulus, % retention from 30°C: 30% RH/90°C
1,4 and 1,3 Ring substitution					
Aromatic dicarboxylic acids					
	66	262	10	33	48
	66–10 mole-% 6TA	264	10	45	55
	66–10 mole-% 6IA	255	8	35	54
	66–20 mole-% 6TA	268	10	47	62
	66–20 mole-% 6IA	238	21	33	58
	66–30 mole-% 6TA	278	13	56	63
	66–30 mole-% 6IA	226	24	35	45
Cycloaliphatic dicarboxylic acids					
	66–10 mole-% 6HHTA	276	8	49	55
	66–10 mole-% 6HHIA	259		35	51
Arylaliphatic diamines					
	66–10 mole-% PXD-6	261	11	49	53
	66–10 mole-% MXD-6	262	14	48	53

	66–20 mole-% PXD-6	258	13	63	62
	66–20 mole-% MXD-6	252	10	42	54
	66–30 mole-% PXD-6	270	14	71	68
	66–30 mole-% MXD-6	247	11	40	49
Arylaliphatic dicarboxylic acids					
	66–5 mole-% 6PPDAA	261	10	49	52
	66–5 mole-% 6MPDAA	263	12	43	48
	66–5 mole-% 6OPDAA	261	9	43	49
	66–10 mole-% 6PPDAA	255	13	39	53
	66–10 mole-% 6MPDAA	261	13	41	49
	66–10 mole-% 6OPDAA	257	10	40	43
	66–20 mole-% 6PPDAA	245	15	44	57
	66–20 mole-% 6MPDAA	244	17	42	47
	66–30 mole-% 6PPDAA	231	18	47	57
	66–30 mole-% 6MPDAA	233	23	36	48
Naphthalene dicarboxylic acids (2,6 and 1,6 substitution)					
	66–5 mole-% 6-(2,6-NDA)	259	10	41	54
	66–5 mole-% 6-(1,6-NDA)	263	11	42	51
	66–10 mole-% 6-(2,6-NDA)	258	7	44	55
	66–10 mole-% 6-(1,6-NDA)	260	3	40	51

shrinkage because of their lessened ability to fit within the polymer chain, while those of isophthalic acid produce yet higher shrinkages because of the inability of the ring to be accommodated in the chain.

Strangely, the unsymmetrical copolymers of *m*-xylylene diamine and the naphthalenedicarboxylic acids do not produce much change in shrinkage. However, Yu and Evans[3] attribute the crystallinity of MXD–6 to hydrogen bonds which bind the polymer chains into sheets as still being effective. The unsymmetrical ring interferes only with the polymeric sheet formation, but not in the stacking of sheets into crystallites. Apparently, this partial disruption allows enough packing of polymer chains that shrinkage is not affected. In the copolymers which had high shrinkage values, the disruption of hydrogen bonding (fit) is both within and among the polymeric sheets. The copolymers of naphthalene dicarboxylic acids are of too low a level of substitution for any definite conclusion to be drawn.

The two-thirds rule[5,7,8] also appears violated in random copolyamides. This general rule states that an approximation of T_g may be obtained by eqs. (1) and (2).

$$T_g = {}^2/_3\ T_m \text{ (for unsymmetrical polymers)} \tag{1}$$

$$T_g = {}^1/_2\ T_m \text{ (for symmetrical polymers)} \tag{2}$$

where T is expressed in degrees Kelvin and $T_m°$ denotes polymer melting point. The following example illustrates the above rule (nylon 66 is generally regarded[9] as being unsymmetrical.):

nylon 66–20 mole-% 6TA (unsymmetrical), mp = 264°C
nylon 66–20 mole-% 6IA (unsymmetrical), mp = 235°C
nylon 66 (unsymmetrical), mp = 262°C
nylon 6IA (unsymmetrical), mp = 220°C

Application of eq. (1) to the 66–20 mole-% 6TA copolymer predicts a T_g of 85°C, with a T_g of 66°C for 66–20 mole-% 6IA, 84°C for nylon 66, and 56°C for nylon 6IA. However, Beaman[7] has stated that copolymers do not follow the ²/₃ rule because the melting point of a copolymer is a depressed melting point for one ingredient rather than the actual copolymer melting point. It is interesting to note that the ²/₃ rule predicts that nylon 6IA has a lower T_g than nylon 66 (mp of 6IA = 220°C). Such has not been found to be the case.[10]

Furthermore, if 1,4 ring copolymers were considered symmetrical (in the sense of the T_g rules) and follow the ¹/₂ rule, the 1,2 and 1,3 ring copolymers which are unsymmetrical would have higher T_g's because of the ²/₃ rule. Again, this is unsupported by the data. One may, therefore, conclude that no rule of thumb exists for predicting the T_g values of copolyamides, other than they may be intermediate between values for the two homopolyamides. Further comments on this statement will be made during the discussion of diamine versus diacid substitution.

The data also indicate that these copolymers all appear to have similar lowering of T_g due to moisture. Differences between polymers at 0%

RH are also reflected at 30% RH. In other words, if A > B > C > D occurs at 0% RH, then A > C > C > D at 30% RH for these polyamides. However, small changes do occur in the degree in which the polymers differ from each other. There is no strong indication from sonic modulus T_g measurements of the reported moisture sensitivity of 6IA polyamides.[10,11] However, the sonic modulus measurement may not be sensitive enough to detect smaller differences (~10°C) between the polymers. One would conclude that polymers which are supposedly moisture sensitive for a particular end use are so mainly because their T_g's are simply not high enough to overcome the plasticizing action of water in use. More marked changes would be expected if moisture regain varied appreciably; however, the copolymers discussed in this paper do not vary significantly.

Influence of Aromaticity

The influence of ring character upon T_g is illustrated by two comparisons, simple aromatic versus alicyclic rings (TA vs. HHTA and IA vs. HHIA) and arylaliphatic vs. cycloalkylaliphatic structures (PXD vs. t-CBMA).

In the example of TA vs HHTA (Table III) the glass transition temperatures of the cycloaliphatic copolymers appear slightly higher than those of the corresponding aromatic copolymers. However, the cycloaliphatic copolymer appears more moisture-sensitive. This result indicates that the alicyclic ring contributes greater rigidity to the polymer backbone. This rigidity may be attributed to the effects produced by the chair conformation of the cyclohexane ring, which enables the polymer backbone to adopt a slightly contracted configuration. Contributions to structure by the boat form are negligible, because this form is unstable. As a consequence of this puckered structure, the repeat distance is shorter than the analogous TA copolymer. A comparison of the Dreiding models of TA and HHTA indicates that an approximate carboxyl separation of 6.1 Å occurs in TA, while distances of 4.8 Å (*trans*, axial–axial), 5.8 Å (*trans*, equatorial–equatorial), and 4.4 Å (*cis*, axial–equatorial) occur for the isomer mixture of HHTA. Thus, the ring system occurs more frequently per unit length of polymer chain in the alicyclic ring copolymer, resulting in increased rigidity.

However, Frunze and co-workers[12] have established that the *cis–trans* mixture of HHTA rearranges to the all-*trans* isomer in the polymer. Therefore a fairly close carboxyl separation between HHTA and TA exists (5.8 vs. 6.1 Å), which renders both materials roughly equivalent in T_g. However, the difference is sufficient to reflect the clearly higher melting points obtained with the HHTA copolyamides. This result also appears to indicate that HHTA is more easily accommodated into the polymer chain.

Only two copolymers were compared at 10M% substitution in the HHIA and IA series, which resulted in insufficient data for structure–property relationships to be noted.

The comparison of arylaliphatic and cycloalkylaliphatic copolymers of nylon 66 (PXD vs. t-CBMA) gives similar results to those of the TA and

TABLE III
Influence of Aromaticity upon Copolyamide Properties

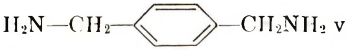
Ring types	Composition	Melting point, °C	Boiling water shrinkage, %	Sonic modulus, % retention from 30°C	
				0% RH/150°C	30% RH/90°C
Aromatic vs. cycloaliphatic TA vs. HHTA					
	66	262	10	33	48
	66–10 mole-% 6TA	264	10	45	55
	66–10 mole-% 6HHTA	276	8	49	55
	66–20 mole-% 6TA	268	10	47	62
	66–20 mole-% 6HHTA	299	5	57	57
	66–30 mole-% 6TA	278	13	56	63
	66–30 mole-% 6HHTA	321	8	64	60
IA vs. HHIA					
	66–10% 6IA	255	8	35	54
	66–10M% 6HHIA	259	—	35	51
Arylaliphatic vs. cycloalkyl-aliphatic (PXD vs. t-CBMA)					
	66–10 mole-% PXD-6	261	11	49	53
	66–10 mole-% t-CBMA-6	263	11	59	58
	66–20 mole-% PXD-6	258	13	63	62
	66–20 mole-% t-CBMA-6	275	10	66	66
	66–30 mole-% PXD-6	270	14	71	68
	66–30 mole-% t-CBMA-6	283	11	70	73

HHTA series. That is, the cycloalkylaliphatic copolymers have slightly increased glass transition temperatures over the arylaliphatic copolymers. In this case, these differences are seen more readily at 30% RH than at 0% RH. The mechanism for the increased T_g of the CBMA polymers may be partially attributed to the smaller repeat unit distance of CBMA-6 compared to that of PXD-6, which results in the ring system occurring more frequently in the polymer chain. Indeed, Bell, et al.[13] attribute the increased rigidity of CBMA polymer to this effect. Once again, the improved fit and shorter repeat unit of the cycloaliphatic ring is shown by increased melting points.

In summary, the effects of aromatic and cycloaliphatic rings upon the glass transition temperatures of copolyamides are quite similar. In all four cases where 1,4 rings were employed, the disruption to chain packing was slight. All fibers were opaque, which indicates fairly high crystallinity. Boiling water shrinkage was also near nylon 66 levels, although lower shrinkages, and hence less chain disruption, were obtained with the cycloaliphatic ring structures. However, the puckered configuration of the *trans*-cyclohexane ring does appear to produce slightly increased glass transition temperatures over similar aromatic polymers. The degree of difference is difficult to establish because small differences in crystallinity. Orientation, and test accuracy may influence the T_g measurements enough to account for such small changes. Although the theoretical explanations why the cycloaliphatic polymers possess slightly increased glass transition temperatures appear reasonable, more intensive investigations of molecular motion and the effects of ring substitution upon crystallinity must be made before firm conclusions can be drawn.

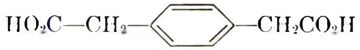
Diamine and Diacid Substitution in Nylon 66

The influence of diamine and diacid substitution in nylon 66 copolyamides was compared in two general cases. In one example, diacids were compared to diamines, each of which possessed the same number of atoms in their moiety. For example, PXD was compared to PPDAA and MXD to MPDAA.

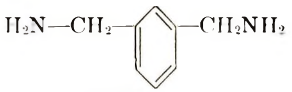


PXD

vs.

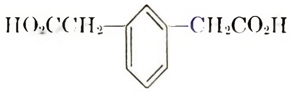


PPDAA



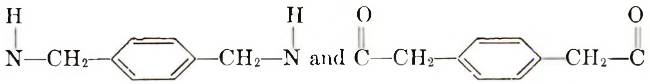
MXD

vs.



MPDAA

The moieties of the first case are:



Similar moieties exist for the other example. Both reactive endgroups are separated by the xylylene linkage.

The effect upon the T_g by these similar structures is not the same (Table IV). The diamine clearly contributes to higher glass transition temperatures and melting points than the similar diacid. In addition, lower shrinkages result with ringed diamine substitution.

The diamine response might be attributed to differences in moiety lengths. These differences result from a shortened C–N bond length (1.47 Å), compared to the C—C bond distance (1.54 Å). Such a difference might allow a better molecular fit in the polymer chain. In addition, the ring should occur more frequently per unit length of polymer.

However, such speculation appears premature. If the repeat unit of nylon 66 is examined, one observes that it consists of a six-carbon acid and a six-carbon diamine, which are not of the same moiety length. Accordingly, the study of the effect of equivalent moieties may not be valid.

Hence, if the ring is considered to be equivalent to roughly a four-carbon zigzag aliphatic chain in the *p*-isomer comparison, (PPDAA vs. PXD), the substitution of an "eight-carbon" diacid for adipic acid is not equivalent to the substitution of a "six-carbon" diamine for HMD. Ideally, such monomers would better be substituted in nylon 68, rather than 66. One would, therefore, predict that the ring diamines would be more effective in increasing T_g than the ring diacids, because the chain length of the diamine segment has been maintained, while that of the diacid has been increased. The initial comparison would be valid if equivalent moieties existed in 66.

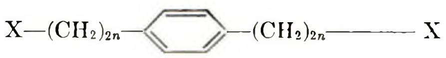
Similar reasoning may be applied in the comparison of the *meta* isomers, except the rings are considered to be equivalent to a three carbon atom chain. A more realistic comparison of diamines and diacids should consider that a six-atom acid is being replaced by a comonomer, while an eight-atom diamine is similarly replaced.

Therefore, the comonomers were adjusted for the unequal moieties of adipic acid and hexamethylene diamine by comparison of rings of equal linear carbon atom content (Table IV).

Such a study is certainly not without precedence. Hill and Walker[14] state that isomeric (same total number of chain atoms in repeating unit) linear polyamides possess roughly similar melting points, provided comparisons are segregated into systems of odd and even numbers of carbon atoms. For example, nylons 48, 2–10, and 66 should be equivalent. Similarly, nylons 47 and 74 would be alike. Saotome and Komoto[15] have extended this comparison to ring-containing polyamides. Their investigations indicate that polyamides such as 14-TA and 10-BDP (*p*-benzenedipropionic acid) are equivalent in melting points and densities. Again, care must be taken to compare even to even and odd to odd total carbon atom content in isomeric polyamides.

Yu and Evans[2] have stated a formula for copolymer isomorphism which gives further justification to the second approach. A copolymer is isomorphous where the comonomers have the same values of n and same groups represented by X:

$$X \text{———} (CH_2)_{4n+4} \text{———} X$$



where $n = 0$, 1, and 2 and $X = -NH_2$ or $-COOH$.

Hence, in nylon 66 if both comonomers (diacid and diamine) are isomorphous, they should be equivalent. Similarly, if the comonomers are not isomorphous, but are still equivalent, then similar effects should be achieved by both diacid and diamine. However, in the case of isomorphism, this formula applies only to polymers which have an even number of methylene groups between the benzene ring and the functional groups. Apparent support for this conclusion was furnished in the example of copolymers of suberic acid and *p*-benzenediacetic acid which fulfill the formula requirements for isomorphism, but which also contain an odd number of methylene groups. This system displays a melting point eutectic. Their conclusion is that these copolymers are nonisomorphous, and, therefore, the formula cannot be applied to *p*-phenylene polymers containing odd numbers of methylene groups.

However, the employment of melting point–composition curves as a criteria for isomorphism has been criticized by Tranter.[4] His investigations indicate that melting-point eutectics are not valid indications of isomorphism, but that other properties should be observed. In addition, Saotome and Komoto[16] and Cramer and Beaman[17] have shown isomorphism may also exist among monomers with odd numbers of methylene groups. Therefore, comparisons of monomer effects among *p*-phenylene groups containing odd numbers of methylene groups appears valid. However, in Table IV the comparison is made between odd and even *p*-phenylene groups, which the previous discussion showed to be incorrect. Unfortunately, no other comparison is possible for the copolymers if a proper moiety adjustment is to be made while remaining within the framework of a 66 copolyamide. How might this then be accomplished?

Beaman[18] believes that the T_g of homopolyamides is determined by the contribution of the component diacid and diamine. This may be expressed as:

$$T_g = 0.5\ (\text{diamine number} + \text{diacid number})$$

The numbers assigned to a particular component do not vary, and will remain the same regardless which complementary component is used.

Therefore, if the T_g's of 6TA and PXD-6 are known, then the effectiveness of PXD and TA in nylon 66 copolyamides can be estimated and checked with the experimental results in Table IV. Unfortunately, T_g data for the two homopolymers could not be found in the literature. However, the T_g's can be estimated from those of homologs. Investigations of a series of PXD polymers with long chain aliphatic diamines indicated that there is a linear relationship between T_g and methylene numbers in the repeating chain unit.[15] (Note that this statement is exclusive of the odd–even relationship, but merely dependent upon the ring and amide group concentration—further justification of Table IV. Extrapolation of these

TABLE IV
Influence of Diamine and Diacid Substitution upon Copolyamide Properties

Substitution	Composition	Melting point, °C	Boiling water shrinkage, %	Sonic modulus, % retention from 30°C	
				0% RH/150°C	30% RH/90°C
Equal number of atoms in in both diacid and diamine					
PXD vs. PPDAA					
	66–10 mole-% PXD-6	261	11	49	53
	66–10 mole-% 6PPDAA	255	13	39	53
	66–20 mole-% PXD-6	258	13	63	62
	66–20 mole-% 6PPDAA	245	15	44	57
	66–30 mole-% PXD-6	270	14	71	68
	66–30 mole-% 6PPDAA	231	18	47	57
MXD vs. MPDAA					
	66–10 mole-% MXD-6	262	14	48	53
	66–10 mole-% 6MPDAA	261	13	41	49
	66–20 mole-% MXD-6	252	10	42	54
	66–20 mole-% 6MPDAA	244	17	42	47
	66–30 mole-% MXD-6	247	11	40	49
	66–30 mole-% 6MPDAA	233	23	36	48
Equal number of carbon atoms in both diacid and diamine					
PXD vs. TA					
	66–10 mole-% PXD-6	261	11	49	53
	66–10 mole-% 6TA	264	10	45	55
	66–20 mole-% PXD-6	258	13	63	62

	66–20 mole-% 6TA	268	10	47	62
	66–30 mole-% PXD-6	270	14	71	68
	66–30 mole-% 6TA	278	13	56	63
MXD vs. IA					
	66–10 mole-% MXD-6	262	14	48	53
	66–10 mole-% 6IA	255	8	35	54
	66–20 mole-% MXD-6	252	10	42	54
	66–20 mole-% 6IA	238	21	33	58
	66–30 mole-% MXD-6	247	11	40	49
	66–30 mole-% 6IA	226	24	35	45
PBE vs. PPDAA					
	66–10 mole-% PBE-6	258	11	44	50
	66–10 mole-% 6PPDAA	255	13	39	53
	66–20 mole-% PBE-6	248	10	46	53
	66–20 mole-% 6PPDAA	245	15	44	57
	66–30 mole-% PBE-6	248	12	47	58
	66–30 mole-% 6PPDAA	231	18	47	57
DBE vs. DDAA					
	66–10 mole-% DBE-6	258	16	49	51
	66–10 mole-% 6DDAA	255	15	51	62
	66–20 mole-% DBE-6	248	20	51	58
	66–20 mole-% 6DDAA	257	19	46	62
t-CBMA vs. HHTA					
	66–10 mole-% t-CBMA-6	263	11	59	58
	66–10 mole-% 6HHTA	276	10	49	55
	66–20 mole-% t-CBMA-6	275	10	66	66
	66–20 mole-% 6HHTA	299	10	57	57
	66–30 mole% t-CBMA-6	283	11	70	73
	66–30 mole-% 6HHTA	321	8	64	60

data to the value of PXD-6 indicates a T_g of about 135°C. Assuming a similar relationship for polyamides of TA, and that the T_g of nylon 7TA is 123°C[17] and that of poly(2-methylhexamethylene terephthalamide) is 146°C,[10] the T_g of nylon 6TA may be estimated between 130 and 150°C. (Caution should be observed in comparison of T_g data from different sources, as considerable variation occurs because of differences in experimental techniques. For example, MXD-6 is reported to have a T_g of 115°C,[10] whereas Temin[19] obtained a T_g at 73°C. However, this value may be as high as 110°C[18].) Therefore, one must conclude that the T_g's of 6TA and PXD-6 are very close, and that only small differences would be observed in their copolymers.

The results obtained with 66–6TA and 66–PXD-6 show that PXD copolymers have higher glass transition temperatures than those of TA, although the diamine copolymers appear more moisture sensitive. Similar results were obtained with 66–6IA and 66–MXD-6 copolymers.

Data obtained for PXD homopolymers[20] and copolymers[2] indicate that *p*-xylylene-diamine does not form isomorphous copolyamides with adipic acid–hexamethylene-diamine, in contrast with the isomorphous 66–6TA system.[1] Therefore, disruption of chain orientation occurs. This disruption is not as severe as that obtained with the unsymmetrical rings where such interference prevents the expected increased T_g response. In this case, a small amount of disruption may actually contribute to T_g increase by reinforcing the interference among polymer chains.

An increase in the aliphatic character in the aromatic ring, however, obscures the differences between diacid and diamine substitution. At 0% RH, the copolymers of PPDAA and PBE and of DBE and DDAA are virtually equivalent in T_g. The increased moisture sensitivity of ringed-diamine-substituted copolyamides is again shown at 30% RH.

The superiority in T_g from a ringed diamine rather than a ringed diacid is shown with cycloaliphatic rings as well. Copolymers of t-CBMA have markedly higher T_g's and melting points than the corresponding HHTA copolyamides.

In the case of MXD and IA, the literature[3] states that the MXD-6 polymer possesses crystallinity because partial fit is obtained through the stacking of the polymeric sheets. In this case, increased fit allows higher glass transition temperatures than could be obtained with the amorphous 6IA polymer.

In general, melting points did not follow the same trends as did the glass transition temperatures. The melting behavior of the copolymers resembled that of the homopolymers made from the ringed intermediates. For example, 6TA melts higher than PXD-6, 6HHTA higher than t-CBMA-6, MXD-6 higher than 6IA, and PBE-6 higher than 6PPDAA. Similarly, copolymers of 6TA melt higher than those of PXD-6, those of MXD-6 higher than 6IA, those of PDE-6 higher than 6PPDAA, and in the cycloaliphatic rings, copolymers of 6HHTA melt above those of t-CBMA-6.

This behavior may be supported by the data of Saotome and Komoto,[15] who state "...the melting point of the polymer which has a methylene chain with even numbers of carbon atoms between the phenylene and the amide groups is generally higher than that of the corresponding one which has a methylene chain with an odd number of carbon atoms." This rule is well known among polyamides. As this effect was not observed upon T_g, different mechanisms must operate for T_g and melting point behavior. Most likely, molecular fit, hydrogen bonding, and chain orientation are far more important in their effect upon melting point than upon T_g. The chain stiffening by the ring perhaps produces a greater reduction in fit, hydrogen bonding, and orientation without affecting T_g, which is more dependent upon the ring-amide group concentration, whereas these properties do greatly affect melting behavior. The differences between the IA and MXD copolymers fit such a hypothesis. MXD copolymers possess the ability to maintain some hydrogen bonding and fit through the undisturbed stacking of polymeric sheets. Therefore, its copolymers with nylon 66 have increased melting points over the more amorphous IA copolymers.

Effects of Chain Length

Three sets of copolymers were compared to show the effects of increased monomer chain length upon T_g. These comparisons included PXD and PBE, TA and PPDAA, and IA and MPDAA. As expected, the shorter monomer chains lead to higher glass transition temperatures in their copolymers (Table V), although T_g sensitivity to moisture was greater. The longer, more hydrocarbonlike chain comonomers would be expected to be less affected by water. Once again, differences were more difficult to detect in unsymmetrical polymers because of their general lack of fit in the polymer chain. The copolymers of IA revealed T_g's over those of MPDAA only at 0% RH. In these cases, the T_g simply reflects the ring/amide group concentration in the polymer chain.

Melting-point behavior should, on the other hand, follow the odd–even rule. One would predict that the copolymers of PBE and TA would melt higher than those of PXD and PPDAA, respectively. However, the melting behavior resembles that noted for T_g. That is, the shorter segments (TA and PXD) have higher melting points than the longer ones. This is analogous to saying copolymers of nylon 66–67 melt higher than 66–68! The most probable explanation for this behavior is that at lower levels of substitution, the longer chain rings cannot easily be accommodated into the crystal lattice of nylon 66, and hence depress melting points more than do the shorter chain rings. The longer chain MPDAA copolymers melt higher than IA copolymers probably because of a similar mechanism to those of MXD. That is, MPDAA probably disrupts the molecular fit within polymeric sheets, but not among the stacked sheets.

Boiling water shrinkage follows the melting point relationships, and confirms the greater disruption in the polymer chains of the lower melting copolymers.

TABLE V
Effect of Comonomer Chain Length upon Copolyamide Properties

Composition		Melting point, °C	Boiling water shrinkage, %	Sonic modulus, % retention from 30° 0% RH/150°C	30% RH/90°C
PXD vs. PBE					
	66–10 mole-% PXD-6	261	11	49	53
	66–10 mole-% PBE-6	258	11	44	50
	66–20 mole-% PXD-6	258	13	63	62
	66–20 mole-% PBE-6	248	10	46	53
	66–30 mole-% PXD-6	270	14	71	68
	66–30 mole-% PBE-6	248	12	47	58
TA vs. PPDAA					
	66–10 mole-% 6TA	264	10	45	55
	66–10 mole-% 6PPDAA	255	13	39	53
	66–20 mole-% 6TA	268	10	47	62
	66–20 mole-% PPDAA	245	15	44	57
	66–30 mole-% 6TA	278	13	56	63
	66–30 mole-% 6PPDAA	231	18	47	57
IA vs. MPDAA					
	66–5 mole-% 6IA	256	8	40	58
	66–5 mole-% 6MPDAA	263	12	43	48
	66–10 mole-% 6IA	255	8	35	54
	66–10 mole-% 6MPDAA	261	13	41	49
	66–20 mole-% 6IA	238	21	33	58
	66–20 mole-% 6MPDAA	244	17	42	47
	66–30 mole-% 6IA	226	24	35	45
	66–30 mole-% 6MPDAA	233	23	36	48

Effects of Symmetrical Ring Substituents

The effects of ring substituents on the T_g are illustrated by the substitution of a single bulky group, 5-*tert*-butylisophthalic acid (TBIA), and by the addition of several smaller groups to the benzene ring, as in 2,2′-*p*-durylenebis(ethylamine) (DBE) and durene diacetic acid (DDAA). In all cases, a symmetrically substituted ring is employed. In many addition polymers, chain branching with small substituents increases T_g, while an increase in symmetry decreases T_g. Therefore, a study of symmetrical branching on the benzene ring should prove of interest.

The copolymers of TBIA exhibit higher glass transition temperatures than those obtained with only isophthalic acid substitution. These results occur at both 0 and 30% RH (Table VI). Such effects must be due to the bulky *tert*-butyl group.

In the other two examples, symmetrical substitution of small alkyl groups on the ring might be expected to perhaps show T_g reduction if trends observed with addition polymers hold true. If harmful effects due to symmetry do occur, the durene ring would be best suited as an example.

TABLE VI
Effect of Ring Substitution upon Copolyamide Properties

Composition	Melting point, °C	Boiling water shrinkage, %	Sonic modulus, % retention from 30°C: 0% RH/ 150°C	Sonic modulus, % retention from 30°C: 30% RH/ 90°C
IA vs. TBIA				
66-10 mole-% 6IA	255	8	35	54
66-10 mole-% 6TBIA	256	20	42	58
66-20 mole-% 6IA	238	21	33	58
66-20 mole-% 6TBIA	241	30	44	68
PBE vs. DBE				
66-10 mole-% PBE-6	258	11	44	50
66-10 mole-% DBE-6	258	16	49	51
66-20 mole-% PBE-6	248	10	46	53
66-20 mole-% DBE-6	248	20	51	58
66-30 mole-% PBE-6	248	12	47	58
66-30 mole-% DBE-6	243	40	52	61
PPDAA vs. DDAA				
66-10 mole-% 6PPDAA	255	13	39	53
66-10 mole-% 6DDAA	255	15	51	62
66-20 mole-% 6PPDAA	245	15	44	57
66-20 mole-% 6DDAA	257	19	46	62

However, in both cases T_g is increased by the substitution on the benzene ring over that obtained without alkyl substitution. Apparently, symmetrical substitution of aromatic rings acts to increase bulkiness, rather than reduce T_g through symmetry.

The influence of ring substitution upon melting point does not appear significant. Although the hydrocarbon content of the polymer has been increased, melting points do not decrease as expected. Apparently, the substitution upon the ring reinforces the chain stiffness, which cancels out the increased hydrocarbon character of the polymer (Table VI).

Polymer chain disruption does occur with the substituted ring-containing copolymers, however. Shrinkage is greatly increased, and the fibers tend to be transparent, which shows a loss of crystallinity.

These copolymers, therefore, achieve T_g increase through an increase in bulk and subsequent reduction in free volume, rather than improved molecular fit.

Relationship between Modulus Retention and T_g

As it was pointed out in this discussion, care must be taken in comparing T_g values from varied sources because of differences in experimental method and the state of the sample. The relationships among the copolymers described are meant to show relative differences only. Therefore, sonic modulus retention was selected because of the ease of measurement. However, modulus retention can be related to glass transition as seen in Table VII.

TABLE VII
Relationship between Sonic Modulus Retention and T_g at 0% RH

Polymer	Sonic modulus E_s, % of 30°C E_s retained at 150°C	T_g, °C
66	33	110
66–10 mole-% 6TBIA	42	120
66–30 mole-% 6TA	56	130
66–15 mole-% 6PIDA[a]	65	145
66–40 mole-% t-CBMA-6	71	155

[a] PIDA = 1,1,3-trimethyl-5-carboxy-3-*p*-carboxyphenyl indan. Data of Ridgway.[21]

Table VII shows that a difference of 10% in modulus retention corresponds roughly to a 10°C change in T_g. There will be some sample-to-sample variation in both tests due to differences in orientation, crystallinity, and molecular weight.

CONCLUSIONS

The isomorphous character of a ringed comonomer influences the T_g of the copolyamide. In general, higher glass transition temperatures and melting points are obtained through the use of fairly isomorphous, compact, symmetrical ringed structures. However, some increase in bulk through symmetrical ring substitution, while decreasing the molecular fit of the comonomer in the polymer chains, does increase T_g.

Melting points appear more sensitive to isomorphous substitution than do glass transition temperatures.

Higher glass transition temperatures and melting points are obtained in nylon 66 copolyamides from cycloaliphatic ring structures than the aromatic analogs, provided the cycloaliphatic ring is of the *trans* configuration.

The use of ringed diamines is more effective than ringed diacids in obtaining higher T_g in nylon 66, provided the separation of the functional group from the ring is no greater than one methylene segment. However, the T_g of such copolyamides appears more sensitive to plasticization.

The glass transition temperature is quite dependent upon the ring and amide group concentration in the polymer. The odd–even melting point rule governs melting behavior more so than T_g.

The boiling water shrinkage of a fiber reflects the isomorphous character of a comonomer in a polymer. Nonisomorphous copolyamides have greater fiber shrinkages than isomorphous copolyamides.

The author gratefully acknowledges the technical assistance of Mr. J. A. Shaver in the preparation of some of the polymers described in this paper. Assistance was also obtained from Mr. W. H. Howard and Mr. T. Murayama for the dynamic mechanical data. The author is also indebted to Mr. G. C. Stow for his interest and encouragement in this work. Acknowledgment is made to Drs. O. A. Pickett, Jr., and J. H. Saunders for their helpful suggestions and criticisms.

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Received December, 19, 1969

JOURNAL OF POLYMER SCIENCE: PART A-1   VOL. 8, 3113-3121 (1970)

Reactivity Ratios and Copolymerization Parameters for Copolymers Incorporating *n*-Octadecyl Acrylate and *N*-*n*-Octadecylacrylamide

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Synopsis

Monomer reactivity ratios and copolymerization parameters were determined for *n*-octadecyl acrylate and *N*-*n*-octadecylacrylamide with several monomers not previously reported. Values of Q and e for the long-chain acrylate now agreed more closely than before with the average of values for the lower acrylate homologs. The average polarity parameter for *N*-*n*-octadecylacrylamide still showed more electron withdrawal from the double bond ($e = 0.42$) than was expressed by the average literature value ($e = -0.10$) for *N*-*n*-octylacrylamide. Because penultimate effects were absent in this work, the reason for the discrepancy seems to reside in the copolymer analysis. Reactivity ratios for oleyl and octadecyl acrylate with methyl methacrylate were similar. Coefficients for the relation between overall rates of copolymerization and composition were obtained on some systems by curve fitting with a computer. They generally showed a slight minimum.

It is generally accepted that homologous series of vinyl monomers with linear side chains exhibit similar reactivity in copolymerization[1] and therefore have proximate Q and e parameters.[2] As published lists of Q and e values reveal,[3] similar reactivity is found for broad classes of vinyl monomers, including vinyl esters, ethers, 1-alkenes, *n*-alkyl acrylates, methacrylates, *N*-*n*-alkylacrylamides, and methacrylamides. Although especially refined techniques, involving use of labeled monomers, have demonstrated recently that small drifts in reactivity occur with side-chain length,[4] these techniques have not been widely applied so far. Apparent deviations for individual vinyl homologs exist, however, in the published compilations. Discrepancies were found, for example, in the values of Q and e for *n*-octadecyl acrylate and *N*-*n*-octadecylacrylamide which are monomers of concern to this laboratory. Values for *n*-octadecyl acrylate ($Q = 0.42$, $e = 1.12$),[3] compared with an average value for the shorter *n*-alkyl acrylates ($Q = 0.44 \pm 0.06$, $e = 0.67 \pm 0.32$)[3] showed a discrepancy in the polarity parameter e. Values found for *N*-*n*-octadecylacrylamide, reported from this laboratory,[5] ($Q = 0.66$, $e = 1.13$), conflict even more seriously with those reported[6] for *N*-*n*-octylacrylamide ($Q = 0.18$, $e = -0.10$). *N*-*n*-Octadecylacrylamide had been copolymerized under conditions causing copolymer precipitation, because acrylonitrile and vinylidene chloride were two of the three comonomers employed, and *tert*-butanol was the solvent medium. While heterogeneity caused by the reaction medium should not affect the results,[7a] a recent examination by light scattering[8] has revealed that examples of these two copolymer systems, polymerized to high conversion, showed marked compositional drift in the nitrile copolymer but the expected drift in the vinylidene chloride system. Although cognizance was taken of the special problems found in the copolymerization of acrylonitrile,[9] these results were still troubling. Accordingly, the present investigation of reactivity ratios was undertaken to obtain Q and e values that might more realistically apply to the long side-chain comonomers.

n-Octadecyl acrylate was copolymerized at 60°C with several comonomers not previously reported, both under heterogeneous conditions (styrene in *tert*-butanol, acrylonitrile in benzene) and homogeneously (the remainder). In addition, both the saturated C_{18} side-chain acrylate and oleyl acrylate were copolymerized with methyl methacrylate. Results, listed in Table I, show somewhat similar Q and e parameters for all, the average values now agreeing more closely with the average values for the shorter side-chain homologs. Within the deviations found in published values[3] these parameters were insensitive to the effect of heterophase copolymerization and the nature of the alkyl group.

N-*n*-Octadecylacrylamide was copolymerized with the same two comonomers used by Bork et al.[6] with *N*-*n*-octylacrylamide. Values of Q (Table I) were now similar to those found by Bork, but the value of e still indicated marked electron withdrawal from the double bond. Bork found specifically with methyl methacrylate $Q = 0.17$, $e = -0.17$, and with styrene $Q = 0.19$, $e = -0.02$.

These differences could conceivably be caused by penultimate amide groups[10] acting to retard amide addition, the effect being more apparent in the limits of a low M_1/M_2 ratio. The longer side chains in the C_{18} amide might exhibit this effect to a greater extent than the shorter-chain comonomers, although the available data[1,9] do not lend support to this idea. Nevertheless, the data for the two amide systems, as well as those for octadecyl and oleyl acrylate with methyl methacrylate and octadecyl acrylate with acrylonitrile, were tested for penultimate effects at both extremes of the feed ratios. Methods used were those of Barb[10] and Ham,[11] together with the more recent treatments of Hecht[12] and Guyot and Guillot.[13] The last method is convenient when both r_1 and r_2 are significantly large, as in the present cases. No evidence was found for a penultimate effect by any treatment. On the other hand, the copolymer composition–feed data were well fitted by the reactivity ratios of Table I, especially in those cases (Tables II, III) where many observations were made.

The disturbingly large and unlikely[14] r_1r_2 product ($r_1r_2 = 1.7$) found for the *N*-*n*-octadecylacrylamide–methyl methacrylate system was thought to

TABLE I

Monomer Reactivity Ratios and Copolymerization Parameters for *n*-Octadecyl Acrylate and *N*-*n*-Octadecylacrylamide with Various Monomers at 60°C

M_1	M_2	Solvent	r_1	r_2	Q_2	e_2
Styrene	*n*-Octadecyl acrylate	*tert*-Butanol	0.44 ± 0.07	0.18 ± 0.45	0.64	0.79
"	"	Benzene	0.79 ± 0.09	0.31 ± 0.31	0.49	0.39
"	"	None	0.75 ± 0.12	0.34 ± 0.06	0.52	0.37
Acrylonitrile	"	Benzene	1.61 ± 0.34	0.40 ± 0.12	0.17	0.54
Methyl methacrylate	"	"	2.36 ± 0.04	0.48 ± 0.12[b]	0.33	0.50
"	Oleyl acrylate	"	2.23 ± 0.01	0.30 ± 0.03	0.43	1.03
Vinylidene[a] chloride	*n*-Octadecyl acrylate	None	0.91 ± 0.05	1.01 ± 0.01	0.27	0.65
				Avg.	0.41 ± 0.13	0.61 ± 0.18
Methyl methacrylate	*N*-*n*-Octadecylacrylamide	Benzene	3.85 ± 0.17	0.44 ± 0.04[c]	0.26	0.50
Styrene[d]	"	"	1.41 ± 0.10	0.20 ± 0.05	0.29	0.33
				Avg.	0.28 ± 0.02	0.42 ± 0.09

[a] Data of Jordan et al.[1]

[b] For the Q_2, e_2 parameter calculation, r_2 was set equal to 0.42.

[c] For the Q_2, e_2 parameter calculation, r_1 and r_2 were fitted by an iterative procedure to the experimental copolymer composition feed curve by assuming $r_1r_2 = 0.99$. Reactivity ratios by this procedure were: $r_1 = 3.00$, $r_2 = 0.33$.

[d] At 80°C.

TABLE II

Copolymerization of *n*-Octadecyl (or Oleyl) Acrylate (M_2) and Various Monomers (M_1)

Monomer	Solvent	Conversion, %	Analysis			Rate of copolymerization[a] R_p, mole/kg-sec × 10^4	
			M_2	C, %	m_2	Found	Calcd
Styrene	*tert*-Butanol	0.48	0.1500	85.52	0.2169		
		10.11	0.1500	85.06	0.2392		
		2.39	0.3000	84.32	0.2783		
		5.77	0.5000	82.37	0.4054		
		2.59	0.7500	78.97	0.7727		
Styrene	Benzene	9.55	0.1500	86.90	0.1577		
		10.56	0.3000	83.66	0.3170		
		10.16	0.5000	83.35	0.3366		
		10.56	0.7500	79.92	0.6424		
Styrene	Bulk	13.76	0.0500	89.92	0.0579		
		14.10	0.1000	88.10	0.1138		
		12.74	0.1500	86.62	0.1689		
		13.52	0.2000	85.58	0.2141		
		9.81	0.3000	84.13	0.2891		
		10.36	0.4000	81.61	0.4674		
		6.18	0.5000	82.77	0.3759		
		3.75	0.7500	80.07	0.6243		
Acrylonitrile		4.87	0.1000	18.83[b]	0.0617		
		6.52	0.2000	14.77[b]	0.1141		
		9.00	0.3000	12.77[b]	0.1486		
		6.49	0.4000	8.70[b]	0.2496		
		7.14	0.6000	3.45[b]	0.5210		
		6.70	0.7500	2.82[b]	0.5775		

Methyl methacrylate	9.47	0.0514	61.22	0.0227	1.41	1.41
	9.93	0.1008	62.30	0.0444	0.93	1.28
	13.33	0.1008	62.40	0.0465	1.37	1.25
	8.13	0.1028	62.29	0.0441	1.46	1.25
	9.95	0.2003	64.37	0.0921	0.85	1.04
	11.87	0.1997	64.53	0.0962	1.02	1.04
	7.33	0.2021	65.18	0.1134	0.99	1.04
	4.05	0.3005	66.71	0.1587	0.34	—
	13.32	0.2975	66.32	0.1464	0.98	0.94
	7.12	0.3020	66.74	0.1596	0.93	0.93
	7.57	0.4021	68.79	0.2333	0.94	0.90
	5.84	0.5990	72.14	0.4020	0.84	0.95
	8.92	0.7005	73.75	0.5169	1.11	1.02
	9.02	0.8001	75.21	0.6518	1.20	—
Methyl methacrylate (oleyl acrylate)	7.64	0.0510	61.28	0.0233	1.06	1.08
	7.92	0.1004	62.48	0.0470	1.08	0.98
	7.19	0.2195	65.06	0.1072	0.71	0.78
	6.51	0.2993	66.67	0.1526	0.64	0.68
	6.33	0.4014	68.71	0.2221	0.59	0.59
	4.62	0.5990	72.20	0.3873	0.50	0.46
	4.71	0.7068	72.98	0.4360	0.44	0.42
	3.02	0.7985	75.30	0.6212	0.30	0.39
	4.69	0.8071	74.30	0.5327	0.36	0.39

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[a] Rates at 60°C calculated by using the coefficients of Table IV.

[b] Values for the acrylonitrile system are % nitrogen.

TABLE III
Copolymerization of N-n-Octadecylacrylamide (M_2) and Various Monomers (M_1)

Monomer (M_1)	Conversion, %	Analysis			Rate of copolymerization[a] R_p, mole/kg-sec × 10^4	
		M_2	C, %	m_2	Found	Calcd
Methyl methacrylate	6.25	0.0575	60.83	0.0151	0.21	0.28
	7.11	0.1085	61.46	0.0270	0.24	0.27
	6.23	0.1077	61.52	0.0282	0.21	0.27
	5.39	0.2089	63.42	0.0683	0.16	0.20
	4.82	0.2099	63.72	0.0752	0.15	0.20
	9.23	0.3078	65.27	0.1143	0.27	0.20
	7.08	0.3070	65.42	0.1184	0.21	0.20
	3.01	0.4069	66.45	0.1483	0.08	0.21
	7.57	0.4072	67.26	0.1740	0.21	0.21
	11.68	0.6059	70.84	0.3209	0.30	0.29
	11.46	0.6051	70.82	0.3199	0.29	0.29
	11.76	0.6890	72.74	0.4311	0.32	0.36
	15.67	0.6878	72.87	0.4398	—	—
	15.46	0.7020	73.10	0.4556	0.38	0.35
	12.45	0.7978	74.84	0.5965	—	—
Styrene	6.82	0.0513	90.85	0.0340	1.96	2.13
	7.38	0.0998	89.09	0.0839	2.03	1.95
	7.07	0.1611	89.16	0.0817	1.85	1.78
	7.30	0.3024	86.20	0.1912	1.63	1.54
	6.34	0.4018	84.69	0.2655	1.30	1.47
	6.91	0.5981	82.39	0.4171	1.36	1.47
	6.07	0.6979	80.99	0.5441	0.88	1.52
	8.72	0.7986	79.77	0.6884	1.63	1.59

[a] Calculated by using coefficients of Table IV for 60°C, except for styrene (80°C).

arise from perturbations in the Fineman and Ross variables caused by accumulated analytical errors. This effect was noticed before[1,5] with long side-chain comonomers as r_1r_2 approaches unity. Accordingly, plots of f_2 versus M_2 were fitted by an iterative method by setting $r_1r_2 = 0.99$. Values of $r_1 = 3.00$ and $r_2 = 0.33$ were found to give the best fit. These were used to calculate Q_2 and e_2 in Table I, as well as to calculate a set of per cent carbon values for the various copolymers prepared. The calculated values were within experimental error of the per cent carbon values listed in Table III.

The reasons for the differences in e_2 between this work and that of Bork et al. are still not known. They may reside in small copolymer composition differences resulting from the analytical method employed (analysis for carbon used in this work; analysis for nitrogen used by Bork et al.). The data of Bork, where r_1r_2 is 0.84 instead of unity as in this work, predicts greater alternation for amides with methyl methacrylate and less with styrene (r_1r_2 is 0.54 instead of 0.28 in this work). The difference in the r_1r_2 products between the two works is small however. The well known uncertainties[7b] in copolymer composition by the usual methods of analysis are probably responsible for the differences. It would seem that these sources of error can have an even greater effect on the isolation of penultimate group effects[15] and consequently may result in their presence being masked in this work.

Rates of Copolymerization

Copolymerization rate data are presented in Tables II and III. Correlation of $R_p/[M][I]^{1/2}$ against composition enabled the drift in rate with composition to be ascertained under conditions simulating identical monomer and initiator concentrations. This correlation assumes the constancy of the quantity $R_p/[M][I]^{1/2}$ as the comonomer concentrations are changed at constant feed composition. The assumed constancy of this quantity is compatible with the effects of cross-termination,[16] which affect rates as composition changes, because overall initiation equals overall termination under the steady-state conditions prevailing. Even if the ratio were not constant, the twofold change in concentration across the range of composition employed in this work would not introduce sufficient error to affect the desired correlation. However, the use of the rate data to estimate ϕ would be unwarranted in view of the uncertainties prevailing.[16]

Plots of $R_p/[M][I]^{1/2}$ against the mole fraction of long side-chain ester or amide (m_b) were curve-fitted by computer through a fifth-degree polynomial. A computed F test revealed that the second degree was the most significant. The coefficients and intercepts are given in Table IV. The magnitude and sign of these coefficients reveal that the rate data went through a minimum for all systems and that the extrapolated homopolymerization rate for the acrylamide and acrylate ester exceeded the rate for the other comonomers. An exception was oleyl acrylate, for which degradative allylic-type transfer presumably retarded rates at high fatty ester concentrations. The constants of Table IV were used to calculate the rates given in Tables II and III for the experimental concentrations. These may be considered smoothed data for the found values.

TABLE IV
Rate-Composition Coefficients for Selected Copolymers

M_1	M_2	$R_p/[M]$ $[I]^{1/2} \times 10^4$	$\alpha \times 10^4$	$\beta \times 10^4$
Methyl methacrylate	*n*-Octadecyl acrylate	2.738	−2.928	7.609
" "	Oleyl acrylate	2.051	−0.919	0.852
" "	*N*-*n*-Octadecyl-acrylamide	1.934	−4.409	9.192
Styrene	"	4.132	−1.891	7.781

Experimental

All reagents, including the long-chain amine and alcohol and the commercial monomers, were 99% pure, usually as determined by gas–liquid chromatography.

The preparation and purification of *N*-*n*-octadecylacrylamide has been described.[17] *n*-Octadecyl acrylate was prepared by the acylation of pure *n*-octadecanol by essentially the same procedure.[17] The crude ester was treated with Skellysolve B (2 ml/g) to remove salt, washed with two 10% solutions of sodium carbonate (1 ml/ml), freed of alkali, and crystallized at −20°C. Recrystallization from acetone at 0°C (3 ml/g) gave the pure ester (98.5% pure by gas–liquid chromatography) mp 31.5–32.5°C, in 45.8% yields with the correct elementary analysis.

A similar procedure was followed for the oleyl acrylate, except that the Skellysolve B was removed after alkali washing and the crude product was crystallized once from acetone (3 ml/g) at −62°C. Purity was 94% by gas-liquid chromatography, the yield was 66%, and the correct elementary analysis was obtained. However, infrared analysis revealed that the ester was the equilibrium *cis-trans* mixture.

The purity of the starting oleyl alcohol was about 95% by gas–liquid chromatography; oleyl alcohol was predominantly in the cis form, indicating that the synthesis caused rearrangement.

The monomers were charged with analytic precision into suitably sized vessels under nitrogen and sealed. Where rates were determined, the initiator was added to the thermally equilibrated comonomers by a technique previously described.[18] On an assumption of linearity of the conversion–time curve, the initial rate was estimated from the polymer weight. The monomer charge for the *n*-octadecyl acrylate copolymers with styrene and acrylonitrile was 30 g, the initiator was azobisisobutyronitrile (AIBN) (0.2 and 0.4 mole-%, respectively), and the solvent/monomer mole ratio was 4 except for the acrylonitrile, where the ratio was 3. *n*-Octadecyl acrylate was polymerized with methyl methacrylate, a charge of 15 g and a benzene/monomer mole ratio of one being used, while with oleyl acrylate, a 5-g charge was used at the same solvent/monomer ratio. A 5-g charge of long-chain amide and methyl methacrylate was utilized, and the benzene/monomer ratio was 3.91. In the amide–styrene system (15-g charge), benzene was used at a solvent/monomer ratio of 1. The initiator for these systems was AIBN (0.2%). Additional experimental data are given in Tables II and III. Analytical data were obtained at this laboratory and at a commercial laboratory and some samples were cross-checked.

The Fineman and Ross procedure[19] was used, and r_1 was obtained as both slope and intercept. The values of r_1 and r_2 having the least error were reported. All calculations were written as programs for an IBM 1130 computer. Regression analysis was performed by program designation VGM58, usually carried through a fifth degree polynomial and programmed to yield an *F* test at each polynomial degree. Error was expressed as the

95% confidence limit. Other calculations were written for insertion into a general calculation subroutine designated QREAD.

The authors thank Mrs. Ruth D. Zabarsky for the operation of the computer and Dr. Clyde L. Ogg, Miss Oksana Panasiuk, and Miss Marta T. Lukasewycz for some of the elementary analyses.

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Received April 14, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3123-3133 (1970)

Investigation of the Mechanism of Chlorination of Poly(vinyl Chloride) as Influenced by Chain Microstructure

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Synopsis

Samples of poly(vinyl chloride) polymerized at different temperatures (+30, 0, −30, and −78°C) and a commercial sample were chlorinated by a photoinitiated, free-radical method in *o*-dichlorobenzene at ambient temperature. The chlorine content was determined by difference by using a carbon-hydrogen analyzer. High-resolution infrared analysis revealed a selective attack on the methylene hydrogens along with a concomitant decrease in intensity of the isotactic methylene deformation band and the syndiotactic carbon-chlorine stretching band. Graphical representation of the relative intensities of the $\nu(CH)$, $\delta(CH_2)$, and $\nu(C—Cl)$ modes indicate that the chlorine radical preferentially attacks the middle carbon of the heterotactic *triad*. The increased "stiffness" of this unit causes the rotational energy of the system to be transferred to the syndiotactic portion of the chain. It is proposed that this additional energy causes the TTTT conformer of the syndiotactic unit to rotate into the less-preferred TTGG conformation, which would be more reactive. Facile chlorination of this latter conformer is predicted. This mechanism is in accord with the reported equilibrium composition of the different conformers.

INTRODUCTION

The relative rates of chlorination of samples of poly(vinyl chloride), PVC, differing widely in chain microstructure[1] were determined by direct measurement of the chlorine content. High-resolution infrared spectra of the chlorinated derivatives were obtained, and the observed changes, both in band intensity and in band frequency, in selected absorption modes were correlated with the chlorine content and sample microstructure. A mechanism of chlorination is proposed which is sensitive to the chain microstructure and which includes the equilibrium composition of the rotational conformers as the primary rate controlling factor.

The system of nomenclature of Huggins et al.[2] is based on three repeat units, or "triads," to describe the microstructure of vinyl-type polymers. A schematic diagram of this system of nomenclature showing the three configurational isomers for poly(vinyl chloride) with short vertical bars for the chloride substituent is given in Figure 1. The conformation of a macromolecule is characterized by a measure of the internal rotation angles

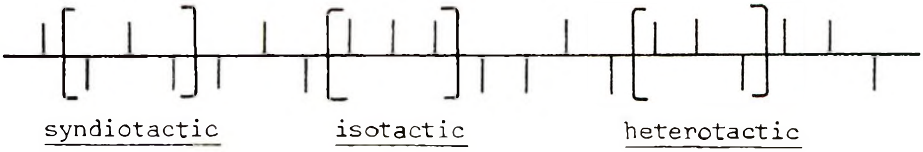

Fig. 1. Configurational isomers for poly(vinyl chloride).

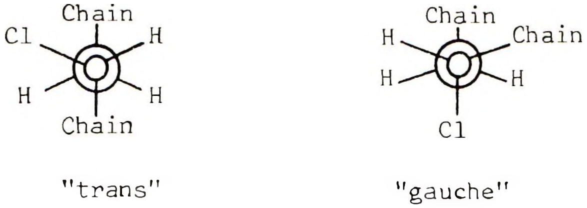

Fig. 2. Projection models for poly(vinyl chloride).

within the molecular framework. Thus, each configurational isomer can have different conformations due to rotation about the molecular axis. These conformations can be pictured for poly(vinyl chloride) from the projection models presented in Figure 2. The *trans* conformer has the two parts of the chain directly opposite, or rotated 180°, while the *gauche* conformer has the two parts of the chain rotated 60° from each other. Assignment of the carbon-chlorine stretching bands in the 600–700 cm^{-1} region of the infrared spectrum to conformational isomers of the syndiotactic and isotactic structures[3–5] illustrates the significance of these isomeric structures and suggests possible influence on the chemical reactivity.

Recently, Millan and Smets[6] examined the stability of PVC samples prepared by different methods. They reported a rapid dechlorination of samples containing a large fraction of isotactic placements with formation of cyclopropane units. For samples containing a higher percentage of syndiotactic units, however, the formation of double bonds was reported to be increasingly important as dechlorination progressed. These authors also reported a slower rate of dehydrochlorination for the sample richer in syndiotactic units.

Fukawa and co-workers,[7] along with Germar[8] and Fuchs and Lewis,[9] studied the infrared spectra of chlorinated PVC and reported that initially the chlorine attacks the methylene (CH_2) group as opposed to the chloromethylene unit, which was only attacked after considerable increase in the chlorine content. Fukawa also noted that the carbon-chlorine stretching band at 615 cm^{-1} disappeared as chlorination proceeded and concluded that the syndiotactic portion of the chain was attacked preferentially. The disappearance of the 615 cm^{-1} band was reported to be due to the replacement of a hydrogen atom in the syndiotactic portion of the chain causing a heavy atom to be trans to the C—Cl bond. On the other hand, Germar and Fuchs and Lewis reported the intensity of the isotactic 1434 cm^{-1} (H—C—H) bending mode decreased with chlorination. Germar attributed the decrease to the influence of the added chlorine as a neighboring group. Since it had been proposed[1] that a hydrogen atom in a heterotactic *triad* unit is more "exposed" to free-radical attack than in a syndiotactic unit, it seemed important to continue the investigation of the influence of the chain microstructure on the chemical reactivity of poly(vinyl chloride). To this end we have examined the kinetics of chlorination of PVC and the infrared spectra of the chlorinated products and have proposed a mechanism of chlorination based on the stereochemistry of the parent sample.

EXPERIMENTAL

Sample Preparation and Chlorination

Four of the five samples were prepared by Thompson[1] during the initial phase of this continuing investigation. The fifth sample was supplied generously by the Dow Chemical Company, Louisiana Division. Characterization parameters of these samples are given in Table I.

TABLE I
Physical Properties of Poly(vinyl Chloride) Samples

				Calculated syndiotacticity α	
Sample designation	Polymerization temp, °C	Yield, %	Molecular weight[a]	From absorbance[b]	From smoothed curve[c]
LFT-78	−78	4.6	7900	0.77	0.69
LFT-30	−30	11.0	11400	0.69	0.60
LFT 0	0	10.0	11300	0.58	0.57
LFT + 30	+30	8.6	6100	0.54	0.52
133-4	(+50)	—	(high)	0.53	0.50

[a] Calculated from dilute solution viscosity in cyclohexanone using the relation reported by Danusso.[10]

[b] Calculated by use of the A_{1434}/A_{1428} ratio as described by Germar et al.[8] and the values of the energy difference between the rotational isomers given by Nakajima et al.[11]

[c] Read from smoothed curve (their Fig. 2) of Talamini and Vidotto.[12]

The samples were chlorinated with the use of a filtered 100-W nonfrosted tungsten filament light as energy source for radical generation. A green plastic filter allowed only light of wavelength greater than 400 mμ, the minimum energy photons needed to form chlorine radicals, to enter the reaction flask. It was assumed that high-energy photons would generate radicals of higher kinetic energy and decrease the desired radical selectivity during attack on the hydrogen atom. Chlorination was accomplished by using a 0.8 wt-% solution of sample in prechlorinated *o*-dichlorobenzene at ambient temperature. Aliquots were taken and these purged with nitrogen to remove dissolved chlorine. The samples were recovered by precipitation from a methanol–water mixture, filtered, and vacuum-dried.

Sample Analysis

The chlorine content was measured by difference using a Coleman Model 33 carbon-hydrogen analyzer with silver vanadate as the chlorine absorbent.[12] This method required sample size of only 10 mg with 15 min per analysis routine. The accuracy was excellent and the precision quite good as shown by the results of ten analyses on the commercial (Dow) sample yielding 56.6 ± 0.64% (calculated Cl = 56.7%). The results reported are average values representing a minimum of two analyses.

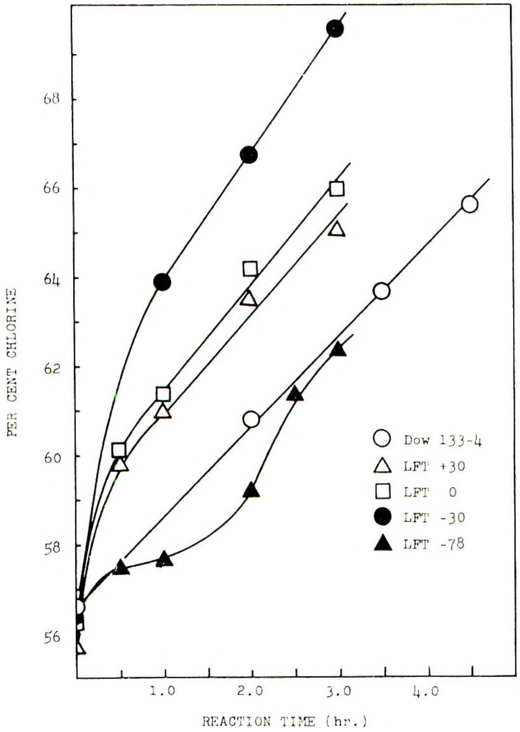

Fig. 3. Chlorine content as a function of time.

The infrared spectra of the parent and chlorinated samples were recorded using a Beckman IR-20 infrared spectrophotometer from KBr pellets containing 5% sample. The use of accurately prepared KBr disks allowed direct determination of relative absorbances. The selected absorption modes discussed in the next section were the doublet at 2970 and 2920 cm^{-1}, corresponding to the C—H and H—C—H stretching modes; the doublet at 1434 and 1428 cm^{-1}, assigned the isotactic and syndiotactic H—C—H bending modes; and the (low resolution) doublet at 690 and 630–610 cm^{-1}, the "isotactic" and "syndiotactic" C-Cl stretching modes, respectively.

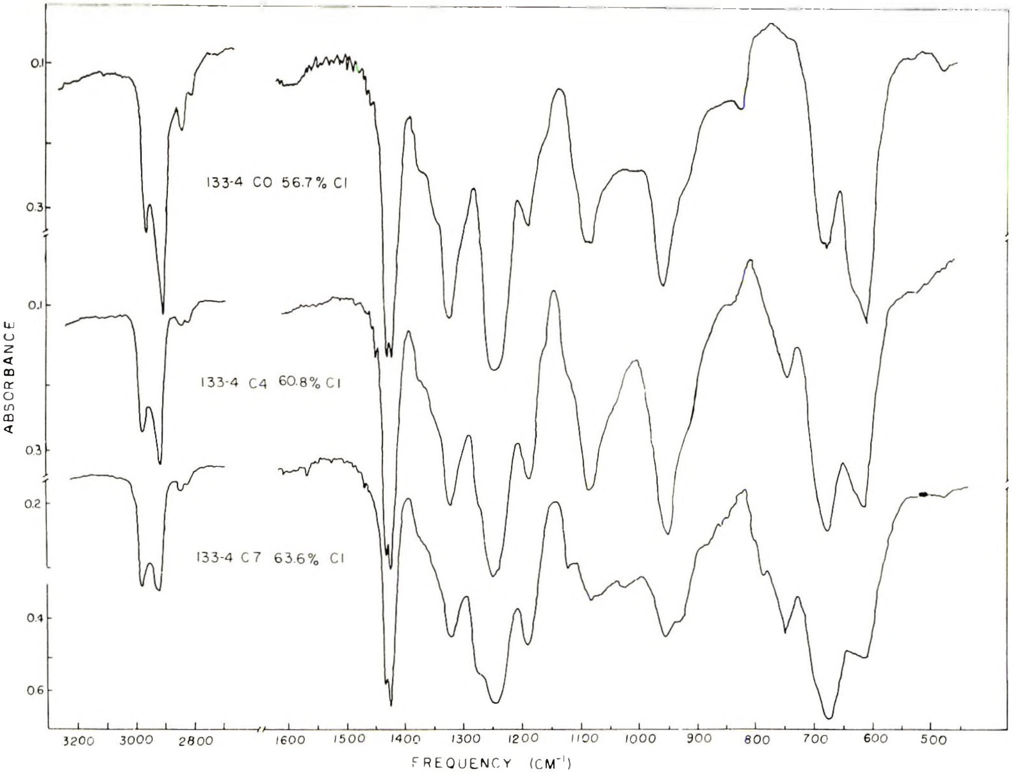

Fig. 4. High-resolution infrared spectra of conventional free-radical poly(vinyl chloride)-133-4 CO— and of chlorinated derivatives C4— and C7— with chlorine content indicated.

RESULTS

Four samples of PVC, which has been polymerized at +30, 0, −30, and −78°C, and a commercial sample were chlorinated in *o*-dichlorobenzene saturated with chlorine by exposing the system to low-energy green filtered light. The rates of chlorination of these samples are graphically presented showing percentage chlorine as a function of time in Figure 3.

The high-resolution infrared spectrum of the commercial sample and of two of its chlorinated derivatives are reproduced in Figure 4. Since it is apparent that chlorination causes major changes only in the carbon-hydrogen stretching and bending modes and in the carbon-chlorine stretching modes, these absorption bands are represented in detail for each sample in Figures 5–9. These bands were used to calculate the absorbance ratios plotted versus percentage chlorine in Figures 10–12.

DISCUSSION

Examination of the rates of reaction shown in Figure 3, except for samples designated LFT-78 and Dow 133-4, reveals an initial rapid chlorine uptake. The initial rapid reaction rate is attributed to the catalytic in-

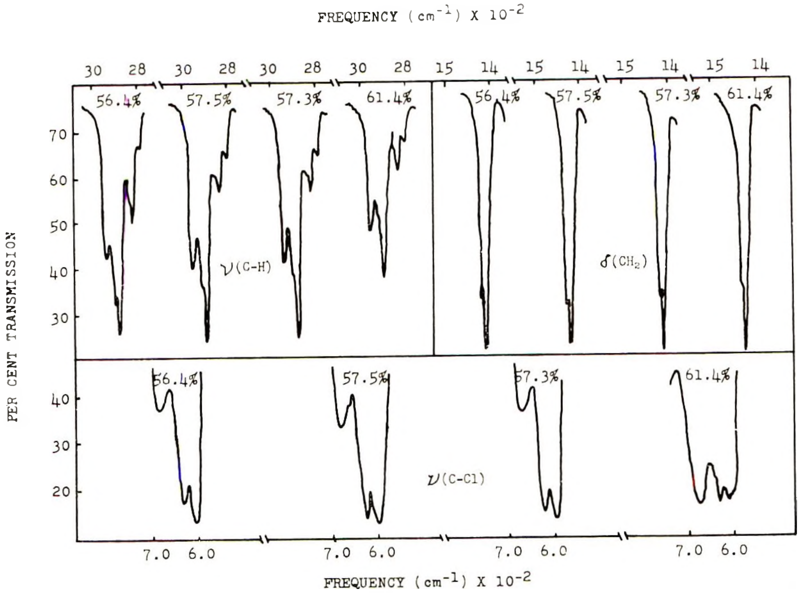

Fig. 5. Selected infrared bands of LFT – 78 and chlorinated adducts. Chlorine content as indicated.

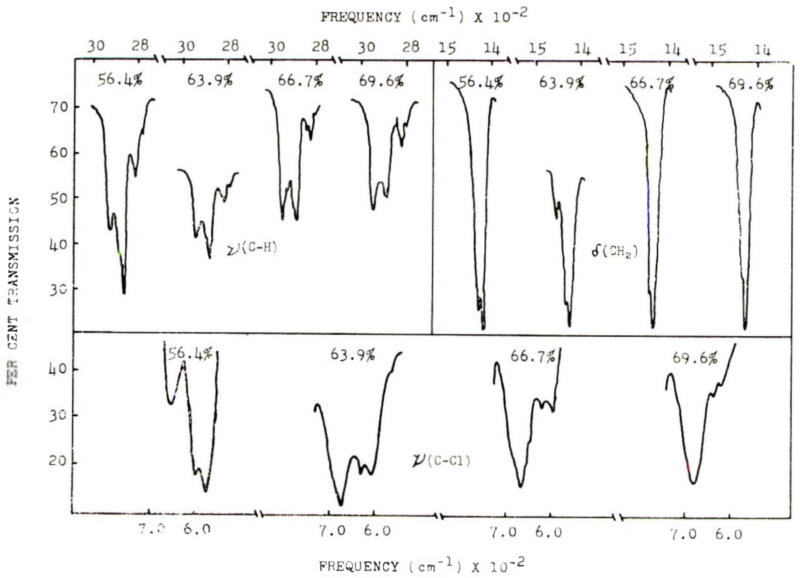

Fig. 6. Selected infrared bands of LFT – 30 and chlorinated adducts. Chlorine content as indicated.

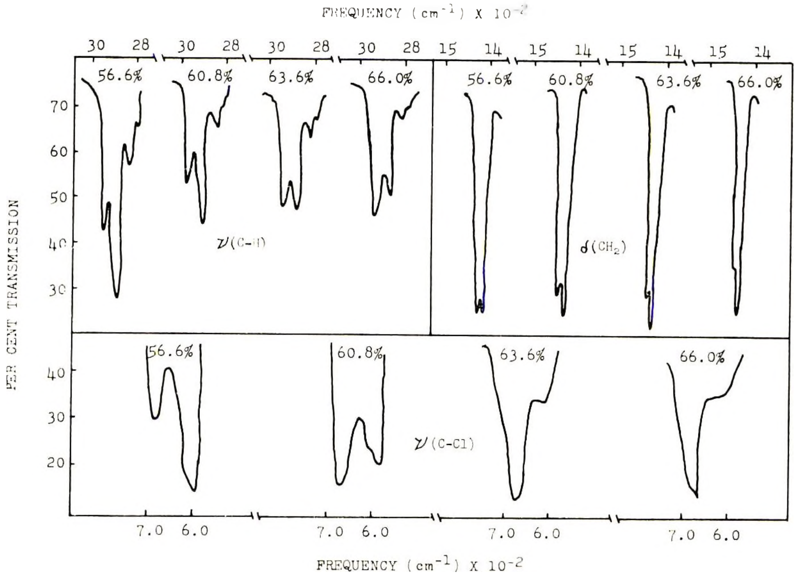

Fig. 7. Selected infrared bands of Dow 133-4 and chlorinated adducts. Chlorine content as indicated.

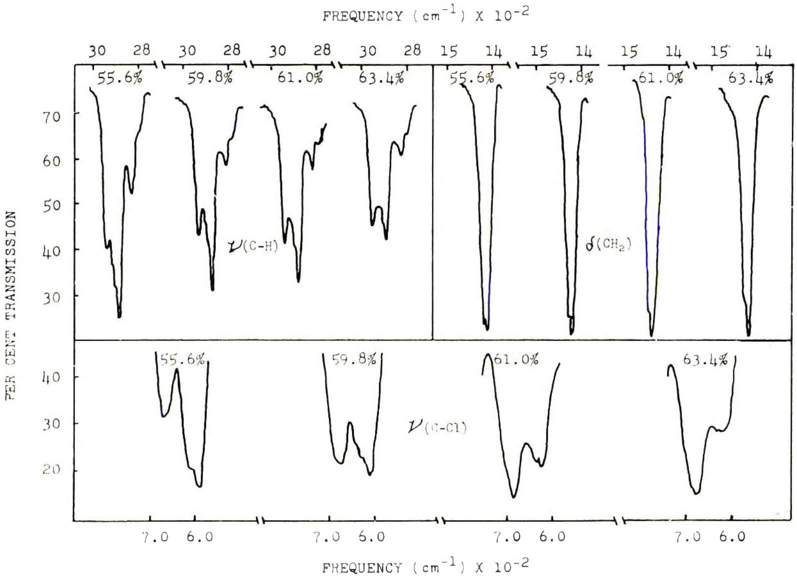

Fig. 8. Selected infrared bands of LFT +30 and chlorinated adducts. Chlorine content as indicated.

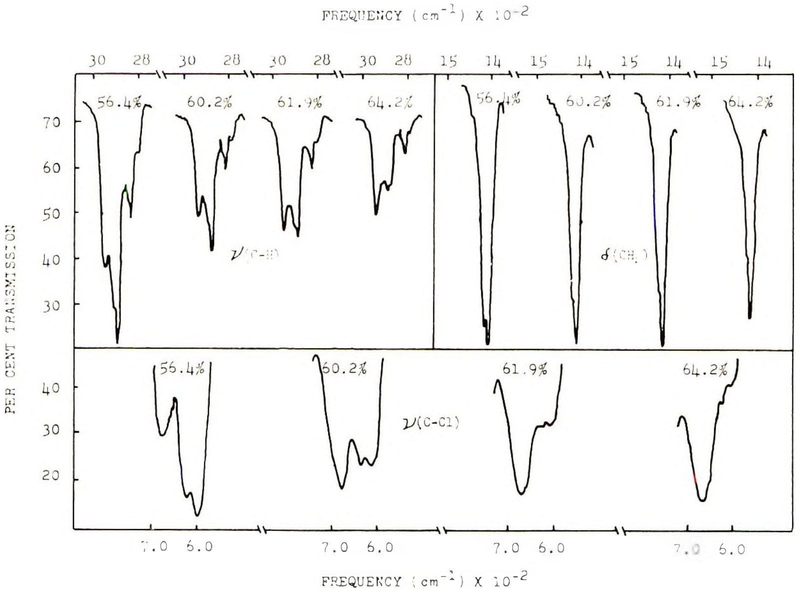

Fig. 9. Selected infrared bands of LFT 0 and chlorinated adducts. Chlorine content as indicated.

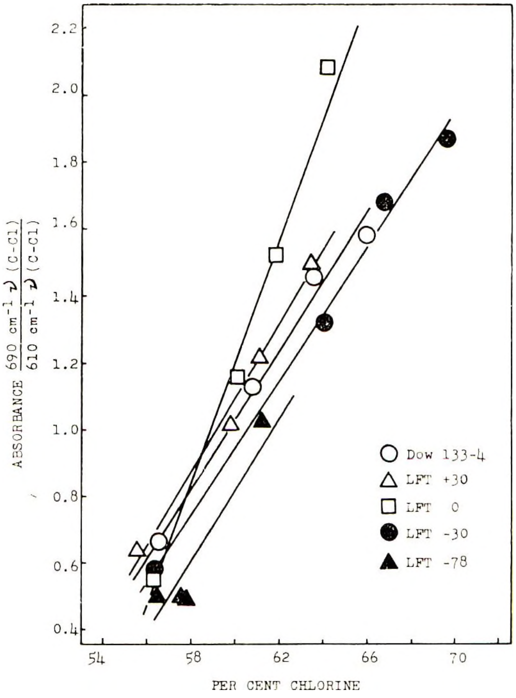

Fig. 10. Absorbance ratios of infrared carbon-chlorine stretching bands as a function of chlorine content.

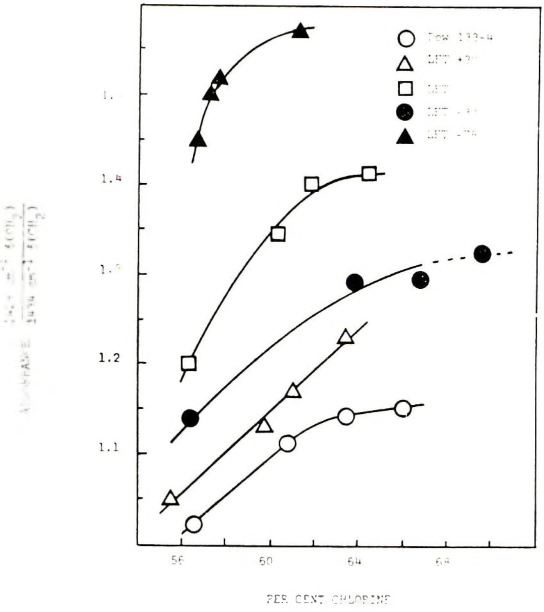

Fig. 11. Absorbance ratios of infrared methylene bending bands as a function of chlorine content.

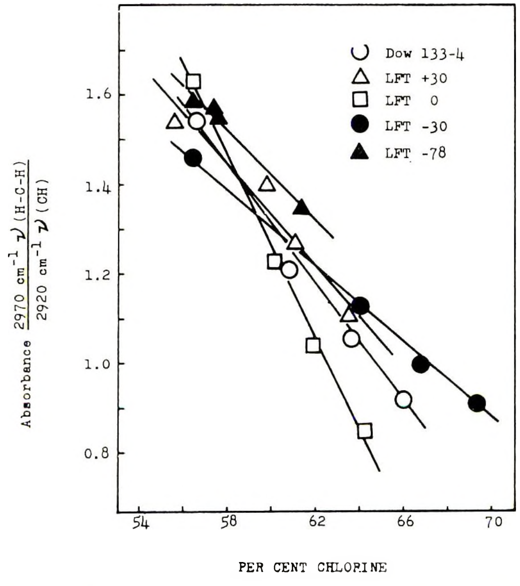

Fig. 12. Absorbance ratios of infrared carbon-hydrogen stretching bands as a function of chlorine content.

fluence of the chain end units, shown previously[1] to be the controlling factor in rates of bromination of these same samples of PVC. The absence of the initial rapid rise for the sample of high molecular weight (Dow 133-4) is consistent with this interpretation. The unusual behavior of the sample designated LFT-78, polymerized at −78°C and containing the highest fraction of syndiotactic units, is not explained. After the initial rapid rate of chlorination, the similarity in slopes of the linear regions suggests that the kinetics of the reaction are relatively insensitive to the microstructure of the sample, expecially when complicated by the presence of highly reactive chain ends.

Examination of the high-resolution infrared spectra of the chlorinated samples (Figs. 4–9) shows a decrease in the 630–610 cm^{-1} stretching band with a concomitant increase in the 690 cm^{-1} stretching mode with increasing percentage chlorine, as reported by Fukawa and co-workers.[7] Also, the 1434 cm^{-1} isotactic methylene bending mode clearly decreases with increasing chlorine content, as reported by Germar[8] and Fuchs and Lewis.[9] However, the independent explanations as to the causes of these changes are not in accord with the changes in relative absorbance of these bands as shown in Figures 10 and 11. The linear increase in the absorbance ratio of the 690 cm^{-1} to the 610 cm^{-1} bands up to 69% chlorine does not suggest selective attack at the syndiotactic placements, as proposed by Fukawa, but rather a smooth, continuous transition from the —CH_2—CHCl—CH_2—CHCl— vinyl structure to the —CHCl—CHCl—CHCl—CHCl— chloromethylene repeat structure. This is consistent with the observation by Fukawa that, "as chlorination progresses, a portion of the zigzag part of the chain is bent; then it becomes possible for the C—C combination in *trans* position against C—Cl." According to Krimm and Enomoto,[13] the rotation of an S_{HH} mode (611 cm^{-1}) of the syndiotactic planar zigzag chain segment to the bent form would yield a S_{HC} mode (690 cm^{-1}). This latter form is energetically less favored because of the proximity of the chlorine atoms. However, if chlorination of the neighboring unit forces the chain out of the planar zigzag form into the bent form, then the observed Figure 10 monotonic increase in the absorbance ratio is explained.

The initial linear increase in the absorbance ratio of the 1428 cm^{-1} syndiotactic to the 1434 cm^{-1} isotactic (H—C—H) bending modes may simply be due to the influence of the adjacent substituted chlorine groups, as suggested by Germar, or may be considered evidence for the selective attack on the exposed hydrogen atom in the isotactic part of a heterotactic triad unit, as proposed previously.[1] Indeed, the apparent leveling off of the ratio as the percentage chlorine is increased not only would be expected as the heterotactic units are used up but also the decrease in slope occurs at the lowest percentage chlorine in the sample polymerized at −78°C, which contains the lowest fraction of isotactic (or heterotactic) units.

As observed on examination of the carbon-chlorine stretching region, the absorbance ratio of the (H—C—H) stretching mode (2970 cm^{-1}) to the (C—H) stretching mode (2920 cm^{-1}) is a linear function of the percentage chlorine (Fig. 12). This is surprising in light of the high yield of —CCl_2— units reported by Germar and by Petersen and Rånby[14] as chlorination proceeds. This difference is probably due to the lower energy chlorine radicals used in this study, assumed incapable of attacking the sterically-blocked chloromethylene units.

The examination of scale models of PVC shows that the TTGT conformer of the heterotactic portion of the chain and the TTGG conformer of the syndiotactic portion each have a hydrogen atom that is surrounded by other hydrogen atoms and opposite three chlorine atoms. It is proposed that these sites are most susceptible to chlorine attack. Since there are only a few TTGG conformations present in the syndiotactic segments under ordinary conditions, 15% at 20°C. calculated by Doskocilova and co-workers,[3] it appears likely that the chlorine radicals initially attack the TTGT part of the heterotactic triads. The additional chlorine lowers the number of degrees of freedom in this unit causing the rotational energy to be transferred to the syndiotactic segments, causing these units to rotate into the less favored TTGG conformation, susceptible to radical attack.

The partial support by the National Science Foundation (GY-3902) is acknowledged. The authors wish to recognize the assistance of Dr. R. L. Sublett of this department in development of the analytical procedures.

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Received March 30, 1970
Revised April 30, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3135-3144 (1970)

Self-Regulating Polycondensations: Ordered Aromatic Polyamide-Esters*

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Synopsis

The polycondensation of aminophenols with diacid chlorides was examined to determine if the amide-ester polymers obtained are random or ordered. All of the evidence obtained points to the conclusion that ordered copolymers indeed are prepared and that a "self-regulating" polymerization process is operating by virtue of the considerably greater reactivity of aromatic amino groups relative to phenol groups. The first step of the reaction involves the *in situ* preparation of a diphenol-amide which undergoes further condensation. The diphenol-amide intermediate may be isolated or reacted *in situ*. In addition to the ordered polymer from a given aminophenol and a single diacid chloride, ordered copolymers from two different diacid chlorides were prepared in which the diacid moieties appear in an alternating fashion; the structure of such polymers depends on the order of addition of the diacid chlorides. Corresponding polymers also may be prepared from the preformed diphenol-amide monomers. The molecular weights of certain of the polymers were sufficient for the preparation of films which could be hot-stretched severalfold. Interfacial polycondensations gave polymers of higher inherent viscosities than did solution polymerizations when aminophenols or diphenol-amide monomers were condensed with diacid chlorides.

INTRODUCTION

Polyamide-esters from aminophenols and diacid chlorides *via* interfacial polycondensation have been reported earlier by Panaiotov.[1] However, as Morgan[2a] has pointed out, these polymers probably are not of the random alternating type because of the differences in the relative reactivity of the amine groups versus the phenol groups and because of the polymerization conditions. In the present work it is shown that Morgan's assumption regarding the inherent differences in reactivity between amino and phenol groups is indeed correct—the more reactive amine groups react first to produce preformed intermediates which may be isolated or reacted *in situ*. The reaction may be illustrated by eq. (1).

The preparation of these ordered polyamide-esters is not unlike the formation of certain polypiperazineamides which are ordered because steric

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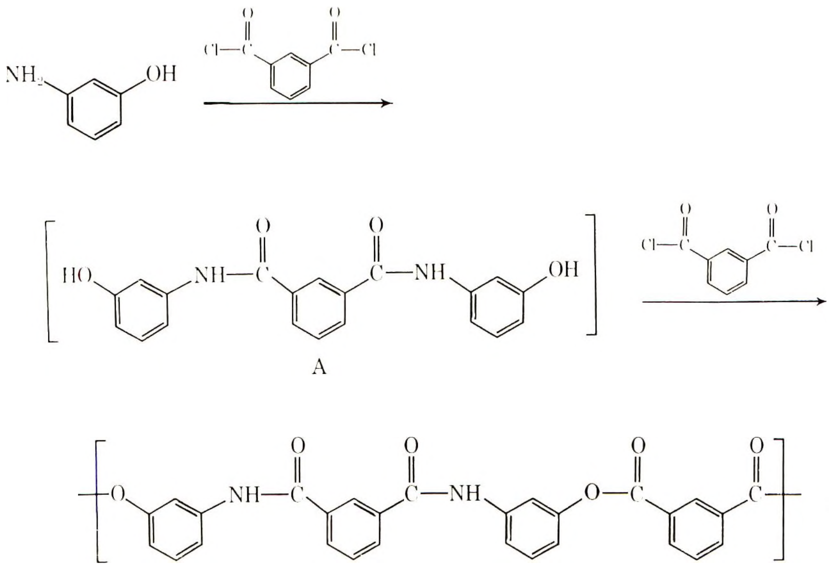
* Presented at the IUPAC Symposium on Macromolecular Chemistry, Budapest, Hungary, August 25–30, 1969.



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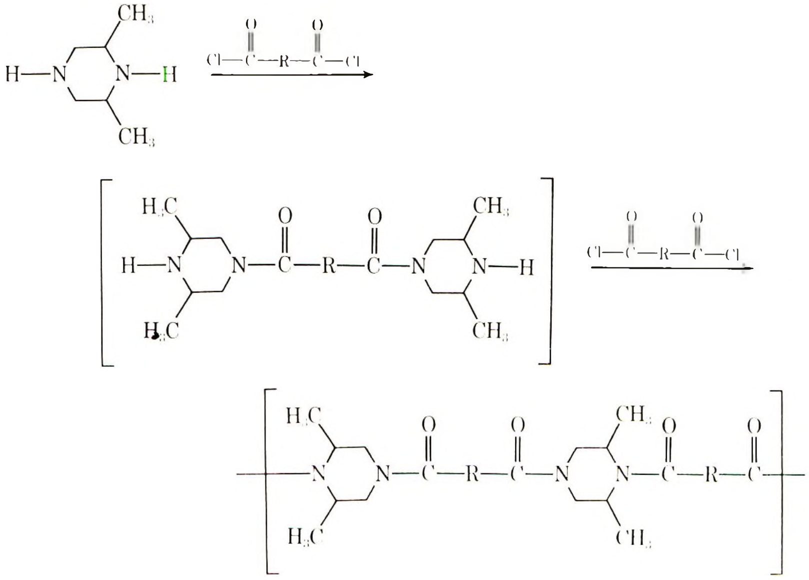
(1)

hinderance in the piperazine monomer leads to a preferential reaction[3] resulting in the formation of a symmetrical intermediate.*



(2)

Lyman and Jung showed that differences in reactivity between certain acid chlorides could be used preferentially to prepare amides and inferred that ordered copolymers could be prepared by such a route.[4]

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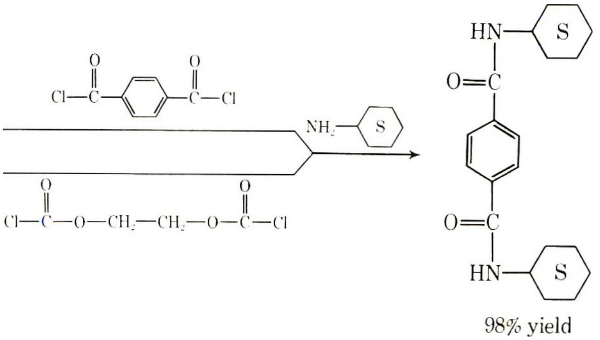
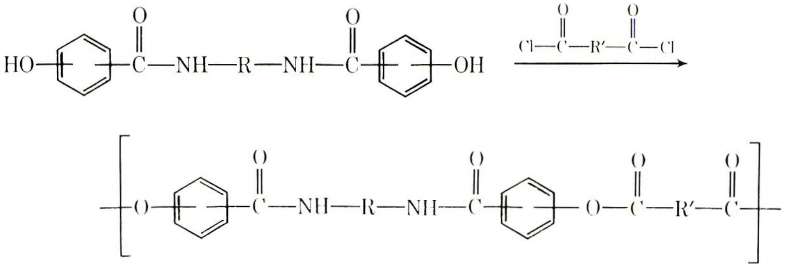
*However, rapid local polymerization makes the direct synthesis difficult even in dilute solutions with rapid stirring.[2b]



(3)

Another series of ordered polyamide-esters (including polyamide-carbonates from phosgene) from preformed diphenol-amides have previously been reported.[5] In these polymers the positions of the amide groups are reversed relative to the polyamide-esters discussed in the present work because *m*- or *p*-hydroxybenzoic acid moieties are employed instead of *m*- or *p*-aminophenol ones in the diphenol-amide monomers.



(4)

Ordered polyamide-esters of this class from the constituent monomers *via* a self-regulating process would appear to be exceedingly difficult because no *in situ* preparation for the intermediates required for the synthesis of such polymers is known nor is readily apparent.

Polyamide-esters from the polycondensation of diacid chlorides with mixtures of diphenols and diamines or diphenols and aminophenols also have been described;[6,7] such mixtures would, of course, naturally lead to polymers of a random type. The preparation of aromatic amide-esters in a melt has been described;[8] such conditions for polycondensation presumably would yield random polymers.

Polyamide-esters* have been obtained from the reaction of dicarboxylic acids with aminoalcohols, with diamines and glycols, with aminoalcohols and diamines, or with aminoalcohols and glycols.[1] Also, polyamide-esters obtained *via* ester interchange between glycols and diester-amides have been reported.[9] Because the ester linkages are not of the arylate type, no further discussion will be given to this class of polymer.

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* It is interesting to note that Panaiotov[1] considered that the arrangement of ester and amide groups in his polymers was the same as in the polyamide-esters obtained through the polycondensation of dicarboxylic acids with aminoalcohols.

TABLE I
Diphenol-Amides

No.	Compound	Mp, °C
A	*N*,*N*′-Bis(*m*-hydroxyphenyl)isophthalamide	260–261
B	*N*,*N*′-Bis(*m*-hydroxyphenyl)terephthalamide	344–346
C	*N*,*N*′-Bis(*m*-hydroxyphenyl)adipamide	238–240
D	*N*,*N*′-Bis(*p*-hydroxyphenyl)isophthalamide	dec.
E	*N*,*N*′-Bis(*p*-hydroxyphenyl)terephthalamide	dec.
F	*N*,*N*′-Bis(*p*-hydroxyphenyl)adipamide	258–260

RESULTS AND DISCUSSION

It is readily seen from the evidence presented here that the polymers prepared interfacially by Panaiotov from aminophenols and diacid chlorides were probably ordered amide-ester copolymers. Polymers of unequivocally determined structure are readily prepared by interfacial or solution polycondensation with diacid chlorides from the preformed intermediates of the type given in Table I.

The fact that symmetrical intermediates are formed and can be isolated in excellent yield supports the conclusion that ordered polyamide-esters are produced *in situ* when aminophenols are reacted with diacid chlorides. Also, the physical properties of the corresponding polymers produced from either the simple monomers or diphenol-amides are identical, in so far as can be determined.

Preparation of Diphenol-Amides

The diphenol-amides (Table I) are readily prepared in high yields by interfacial or solution techniques. In general, the intermediates are more easily isolated when formed by the interfacial method. When the acid acceptor is a weak base, e.g., sodium bicarbonate, only the diphenol-amide is formed, even when stoichiometric amounts of reactants for the polymer may be present. Unlike the reaction illustrated in eq. (2), local polymerization (owing to high local concentrations of diacid chloride) with attendant random polycondensation is blocked until the phenol group is converted to the reactive phenoxide ion.

Interfacial Method. The acid chloride, either solid or in a solution of chloroform or tetrahydrofuran, is added to an aqueous solution of the aminophenol containing sodium bicarbonate equivalent to the by-product hydrogen chloride produced in the reaction. The product is isolated, dried, and recrystallized prior to use.

Solution Method. For the reaction in amide type solvents, no acid acceptor is required because the solvent also serves as acid acceptor. Solid acid chloride is added to a stirred solution of the aminophenol at 0°C. The product is isolated by pouring the reaction mixture into water and collecting the precipitate, which is subsequently dried and recrystallized.

TABLE II
Ordered Polyamide-Esters

Polymer	Diphenol-amide	Diacid chloride	η_{inh}[a]	Polymerization method[b]	PMT,[c] °C
I	A	Isophthaloyl		I	225
			0.25	S	227–230
II	A	Terephthaloyl	0.58	I	265–270
III	B	Isophthaloyl		I	370
			0.18	S	345–350
IV	B	Terephthaloyl		I	375–380
			0.25	S	
V	C	Isophthaloyl		I	240
VI	D	Isophthaloyl		I	d
VII	D	Terephthaloyl		S	
VIII	E	Isophthaloyl		S	
IX	E	Terephthaloyl		I	d
			0.13	S	
X	F	Isophthaloyl		I	320–322
XI	F	Terephthaloyl		I	

[a] Determined at 30°C for a solution of 0.5 g/100 ml of solvent (dimethylacetamide containing 5% dissolved lithium chloride).

[b] I = interfacial polymerization; S = solution polymerization.

[c] Polymer melt temperature; PMT observed by means of a hot-stage microscope.

[d] No PMT observed to 500°C.

Polycondensation

The polyester-amides were prepared *via* interfacial or solution methods by polycondensation of the *in situ* or isolated diphenol-amide intermediates. Polymers of higher inherent viscosity (Table II) were obtained by means of the interfacial polymerization technique, presumably because the phenoxide species required for formation of the ester linkage is more readily formed with strong aqueous base, e.g., sodium carbonate or sodium hydroxide.

Strong bases, such as triethylamine, may be used to accelerate the reaction of the diacid chlorides with the diphenolamides, presumably through formation of the phenoxide ion in solution,[2c] but any phenoxide ion species present must compete with the amide type solvent for reaction with the acid chloride. The latter side reaction[10] presumably is the cause of the relatively low molecular weights observed for the polyamide-esters formed in solution.

Structural Variations

Polymerization of the diphenol-amides of Table I with diacid chlorides of the type used to prepare the diphenol-amide intermediates leads to polymers of the type reported earlier by Panaiotov[1] (e.g., Table II, polymers I, III, VI, IX). Polymerization of the diphenol-amides of Table I with a diacid chloride which is different from that used to prepare the di-

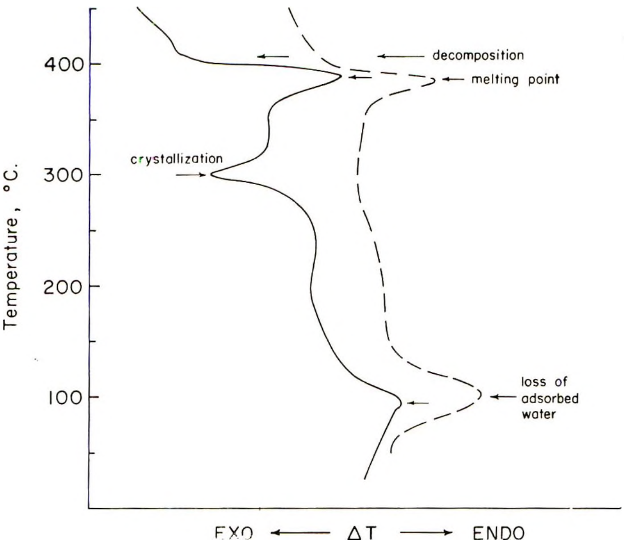

Fig. 1. Programmed DTA of polymer IV in nitrogen: (---) polymer prepared from an authentic sample of diphenol-amide B; (——) polymer prepared by *in situ* formation of diphenol-amide B. Heating rate, 20°C/min.

phenol amide leads to the new polymers, II, IV, V, VII, VIII, X; the reaction is illustrated in eq. (5). The diphenol-amides may be isolated prior to their polymerization or they may be formed and reacted *in situ*.

In addition to the amide-arylate esters described in this work, it should be possible to prepare amide-carbonate polymers by substituting phosgene for the dicarboxylic acid chlorides in the condensation step involving ester formation.*

Melting Points

The melting points of the various polymers (Table II) were observed by means of a hot-stage microscope. For certain selected polymers, melting points could be determined by means of programmed differential therma-analysis (DTA). Such a determination requires that the polymers as prepared possess a certain degree of crystallinity or that the polymers undergo thermal crystallization during the analysis. Figure 1 shows that the *in situ* prepared polymer IV crystallizes during the DTA determination of

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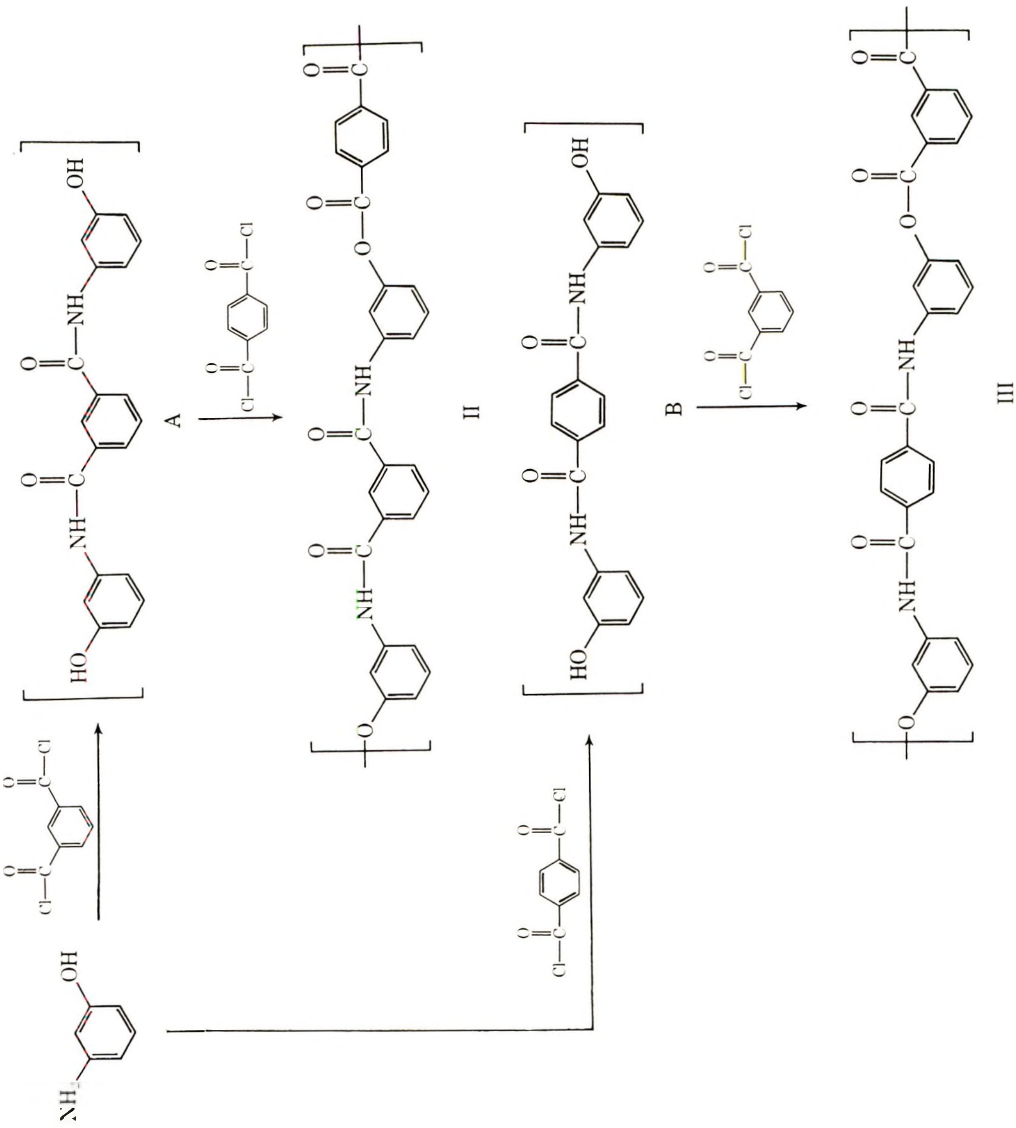
* Polyurea-carbonates from the condensation of aminophenols and phosgene were reported very recently by Giori;[11] the urea-diphenol intermediate was reported to be formed *in situ* followed by polycondensation with phosgene.

A Russian patent has described the preparation of *bis*(4-aminophenyl) carbonate which is treated with diacid chlorides, diisocyanates, or dianhydrides to yield ordered copolymers containing the carbonate linkage alternating with another linkage formed by a polycondensation reaction.[12] It should be obvious that the same combination of amide and carbonate linkages could be obtained by use of the diphenol-amide intermediates of this report and phosgene.



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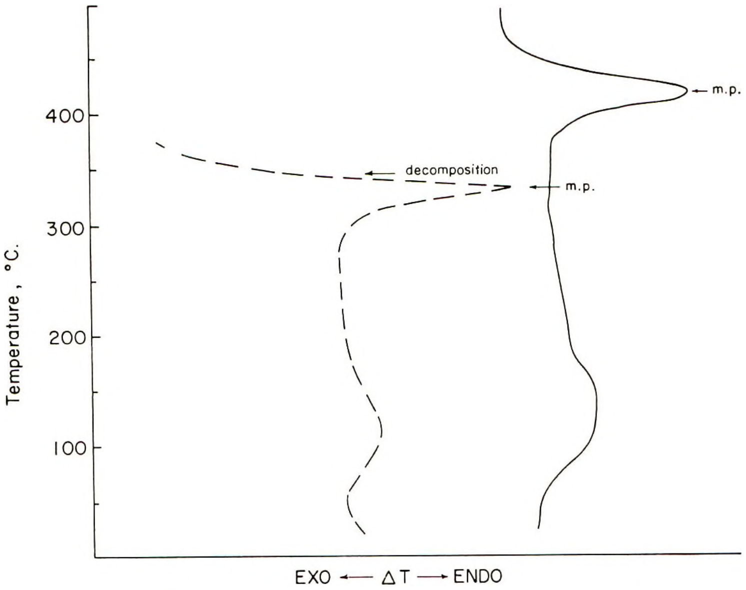


Fig. 2. Programmed DTA of polymer X (---) and XI (—) polymer in nitrogen. Heating rate, 20°C.

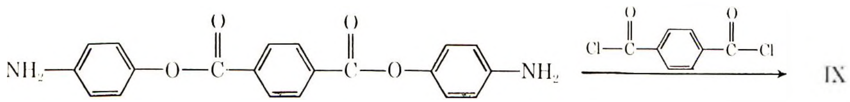
the melting point, while polymer IV prepared from the diphenol-amide, B, is crystalline as prepared; both polymers show the same melting point, ~385°C.

Electron-diffraction patterns were obtained for polymer IV (both the *in situ* prepared polymer and that prepared from B); these indicated that IV was crystalline or could be readily crystallized upon heating. The electron diffraction patterns for I (prepared by the two routes) showed these polymers to be amorphous.

The terephthalate amide-esters consistently were, predictably, of higher melting point thatn the isophthalate amide-esters. Figure 2 illustrates this point for the polymers X and XI derived from diphenol-amide F.

Polymers I–V apparently were too amorphous as prepared to show a DTA melting point; however, the DTA curves for the polymers prepared *in situ* and from the diphenol-amides were superimposable.

Polymer IX was prepared in solution (4) from bis(*p*-aminophenyl) terephthalate (G, mp 250°C). The properties determined for this polymer were identical to those for IX prepared from F (both the authentic and *in situ* intermediate).



G

(6)

Films

Films were cast from solutions of the various polymers in dimethylacetamide or dimethylacetamide containing dissolved lithium chloride (~5%). Polymers prepared in solution were frequently cast from the solution in which they were prepared. Solvent was removed from the films in an oven at 110°C; dissolved salts were leached from the films and the films were redried.

Strips of film could be drawn several times their original length by drawing them across a heated surface.

EXPERIMENTAL

Acid chlorides were distilled under reduced pressure; aminophenols were recrystallized first from water and then from toluene.

In a typical preparation, the diphenol-amide C was obtained by reacting 5.5 g (0.03 mole) of adipoyl chloride in 40 mls. of chloroform with 6.5 g (0.06 mole) *m*-aminophenol in 300 ml water containing .06 moles sodium bicarbonate. The mixture was agitated rapidly in a Waring Blendor jar for about 5 min and then the organic phase was removed under reduced pressure. A quantitative yield of product, mp 236–240°C (238°–240°C from ethanol–water), was obtained.

A typical polymerization was performed as follows: 10.4 g (0.03 mole) of diphenol-amide F was dissolved in 30 ml of 1*N* sodium hydroxide and the resulting solution diluted with 250 ml of water. A solution of 6.09 g (0.03 mole) of isophthaloyl chloride in 40 ml of chloroform was added to the aqueous solution of diphenol-amide and the mixture was stirred rapidly in a Waring Blendor jar for about 10 min. The contents of the Blendor jar were poured into acetone (alternatively, the chloroform was removed under reduced pressure) to precipitate the polymer, X; yield 13 g. A similar procedure was used to prepare polyamide-esters from *m*- and *p*-aminophenol and diacid chlorides.

The author wishes to thank Dr. V. F. Holland for obtaining the electron diffraction patterns. The excellent technical assistance of Mrs. N. J. Wildman and Mr. W. L. Hofferbert, Jr., is gratefully acknowledged.

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Received March 31, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1   VOL. 8, 3145–3153 (1970)

Phenylated Imide–Quinoxaline Copolymers

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Synopsis

Phenylated, ordered imide–quinoxaline copolymers of high oxidative-thermal stability were prepared by one-step solution condensation of aromatic tetraamines with *N*,*N'*-bis(4-benzilyl)pyromellitimide. Polymerization in *m*-cresol leads to high molecular weight polymers that remain soluble. Thermal gravimetric analysis and isothermal decomposition at 400°C shows that these polymers are as stable as polyimides or polyquinoxalines. The polymer decomposition temperatures range between 495 and 550°C, depending upon structure. Also, the rate of isothermal decomposition at 400°C in air showed a strong dependency of weight loss on structure. Tough films were cast from solution.

INTRODUCTION

In previous publications[1,2], we have reported the one-step syntheses of a number of ordered imide–amide copolymers by condensing diacid chlorides containing a preformed imide ring with aromatic diamines. This method led to high molecular weight, soluble imide–amide copolymers. At temperatures above 400°C in air these polymers are, however, not quite as stable as pure aromatic polyimides (such as H-film), due to their thermally less stable amide linkages.

In other studies[3–5] we reported the syntheses of phenylated polyquinoxalines. These polymers showed better solubility properties than their nonphenylated analogues, and they were also thermal-oxidatively more stable.

The object here was to improve the solubility properties of aromatic polyimides without reducing their thermal stability. This was accomplished by introducing an ordered sequence of phenylated quinoxaline moieties into the polymer chain. Again, we used a monomer with a preformed imide ring to circumvent the amic acid route for the imide synthesis and, consequently to reduce the chances for chain branching or crosslinking. Unlike the reported imide–amide copolymers, the imide–quinoxalines have no amide linkages and are, therefore, thermally more stable. The polymerization was carried out in *m*-cresol. The final polymers were of high molecular weight and remained soluble.

EXPERIMENTAL

Monomer Synthesis

4′-Aminodeoxybenzoin. A mixture of 64.0 g of 4′-nitrodeoxybenzoin, 40.0 g of iron powder, 3.5 ml of concentrated hydrochloric acid, 500 ml of ethanol, and 250 ml of water was refluxed for 1 hr. The hot solution was filtered and the filtrate was poured into 1.5 liters of water, giving a slight yellow precipitate. The yield was 48.4 g (86%), mp 95–97°C (lit.[6] mp 95–96°C).

4′-Acetamidodeoxybenzoin. A mixture of 20.0 g of 4′-aminodeoxybenzoin, 50 ml of glacial acetic acid, and 50 ml of acetic anhydride was heated at reflux for 2 hr. The solution was then poured into one liter of water, giving a white solid which was recrystallized from a mixture of ethanol–water (1:1). The yield was 21.0 g (88%), mp 158–60°C.

4-Acetamidobenzil. A mixture of 18.0 g of 4′-acetamidodeoxybenzoin, 8.5 g of selenium dioxide, and 200 ml of glacial acetic acid was heated at reflux for 2 hr. Then the mixture was poured into one liter of water. The yield of 4-acetamidobenzil monohydrate was 20.0 g (98%), mp 105–108°C.

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 68.60%; H, 5.23%; N, 4.93%. Found: C, 68.06%; H, 5.29%; N, 4.88%.

After two recrystallizations from benzene, the solid was dehydrated, mp 136–138°C (lit.[7] mp 140°C). The solid was used without further purification for the next step.

4-Aminobenzil. A mixture of 15.0 g of 4-acetamidobenzil and 150 ml of concentrated hydrochloric acid was refluxed for 4 hr. The solid was filtered and made basic with sodium hydroxide to obtain the free base. The precipitated solid was recrystallized from ethanol–water (1:1) to give 12.1 g (95%) of a pale yellow solid, mp 127–129°C (lit.[7] mp 130°C). The solid was used without further purification for the next step.

N,N′-Bis(4-benzilyl)pyromellitimide (**I**). A mixture of 5.8 g of 4-aminobenzil, 2.81 g of pyromellitic dianhydride, and 50 ml of dimethylacetamide was stirred at room temperature for 3.5 hr, while nitrogen was slowly passed through the reaction flask. Then 8 ml of acetic anhydride and 2 ml of pyridine were added. The solution was refluxed for 8 hr. A tan solid precipitated, which was filtered and washed with acetone. The yield was 5.9 g (74%), mp 365–367°C. (The microanalysis is given on Table I.) The solid was recrystallized from *m*-cresol. No change in the infrared spectra was observed upon refluxing the compound for 3 hr in *m*-cresol.

Aromatic Tetraamines. The following tetraamines are commercially available: 3,3′-diaminobenzidine (DAB), 4,4′,3,3′-tetraaminodiphenylether (TADE), and 4,4′,3,3′-tetraaminobenzophenone (TABP). These amines were purified by recrystallization from water with charcoal and a trace of sodium sulfide. The synthesis of tetraaminodiphenylsulfone

(TADS) was a modified preparation of Stille[8] which we will report elsewhere.

Model Compounds

7-Bis[2-(4′-acetamidophenyl)-3-phenyl]quinoxaline (VII). A stirred mixture of 1.07 g (0.005 mole) of 3,3′-diaminobenzidine, 2.85 g (0.01 mole) of 4-acetamidobenzil monohydrate, and 10 ml of *m*-cresol was heated slowly to 180°C. The solution was kept at this temperature for one hour. A yellow solid precipitated, which was filtered and washed several times with acetone. The yield was 2.2 g (73%), mp 380°C. The microanalysis is given in Table I.

TABLE I
Characterization of Monomers and Model Compounds

			Elemental analyses					
			Calculated			Found		
Compound	Mp, °C	Formula	C, %	H, %	N, %	C, %	H, %	N, %
I	365–367	$C_{38}H_{20}N_2O_8$	72.16	3.19	4.43	72.29	3.17	4.43
VII	380	$C_{44}H_{32}N_6O_2$	78.09	4.77	12.42	78.22	4.93	12.19
VIII	460	$C_{50}H_{28}N_6O_4$	77.31	3.63	10.82	76.78	3.68	10.60

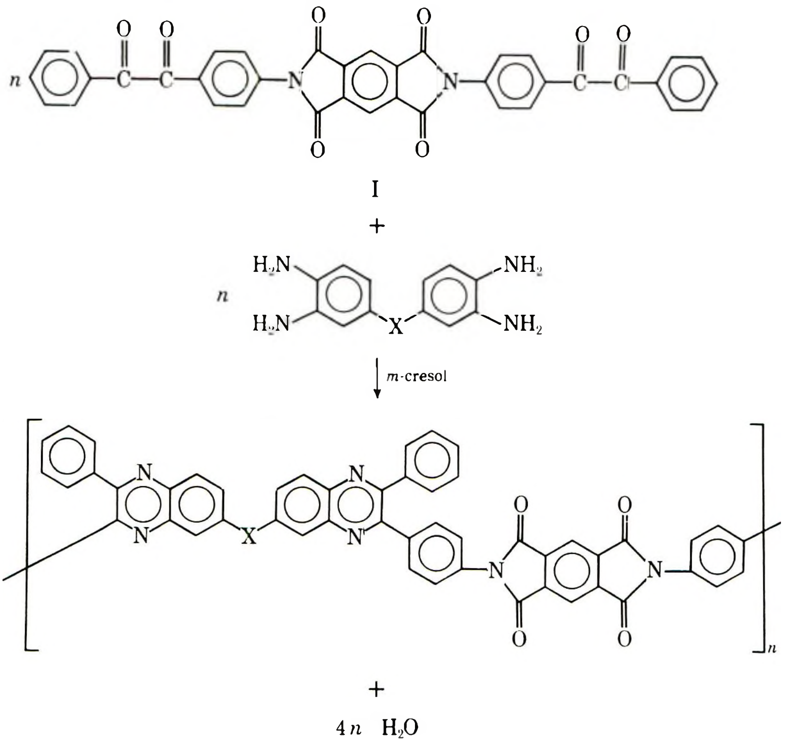
N,N′ - Bis{1,4 - [2 - (3 - phenylquinoxalinyl)]phenylene}pyromellitimide (VIII). A mixture of 0.316 g (0.005 mole) of *N,N′*-bis(4-benzilyl)pyromellitimide, 0.108 g (0.001 mole) of *o*-phenylenediamine, and 8 ml of *m*-cresol was refluxed for 3 hr. The precipitated slightly pale yellow solid was filtered and washed several times with acetone. The yield was 0.35 g (45%), mp 436°C. The elemental analysis is given in Table I.

Polymer Synthesis

The polymers II to V were synthesized under similar reaction conditions. The concentrations, temperatures and reaction times are listed in Table II. The reaction mixture of the monomers and *m*-cresol was stirred under nitrogen at elevated temperature and finally, for a short period, at reflux temperature. The characterization of the polymers is given in Table III.

RESULTS AND DISCUSSION

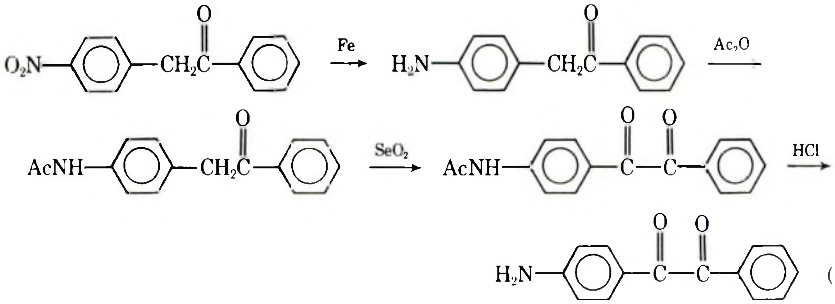
Four new ordered imide–quinoxaline copolymers were prepared by one-step solution condensation of aromatic bis(*o*-diamines) with *N,N′*-bis(benzilyl)pyromellitimide [eq. (1)].



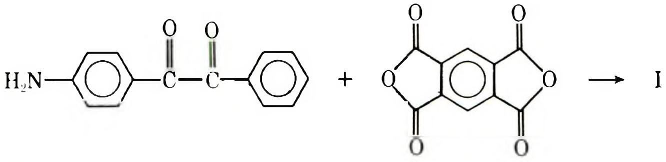
(1)

X = nil (II)
X = O (III)
X = CO (IV)
X = SO_2 (V)

The *N*,*N′*-bis(4-benzilyl)pyromellitimide (I) was obtained by the route shown in eqs. (2) and (3).



(2)



(3)

The polymerization was carried out at moderately elevated temperatures (70–100°C). In all cases, high molecular weight polymers were

TABLE II
Syntheses of Polymers

Polymer	Tetraamine		Glyoxal, [*N*,*N*′-bis(4-benzilyl)-pyromellitimide], mole	Concentration (in *m*-cresol), %	Pot temperature and reaction time
	Type[a]	Amt, mole			
II	DAB	0.001	0.001	15 (after 16 hr at room temp diluted to 3%)	16 hr room temp; then diluted to 3% and heated 15 min at reflux
III	TADE	0.001	0.001	5	1 hr at 120°C; then 20 min reflux
IV	TABP	0.001	0.001	4.3	30 min room temp; then 60 min 80°C plus 1 hr 110°C, plus 10 min reflux
V	TADS	0.001	0.001	5	2 hr at 120°C; then 20 min at reflux

[a] DAB = 3,3′-diaminobenzidine, TADE = 4,4′,3,3′-tetraaminodiphenyl ether, TABP = 4,4′,3,3′-tetraaminobenzophenone, TADS = 4,4′,3,3′-tetraaminodiphenyl sulfone.

TABLE III
Characterization of Phenylated Imide-Quinoxaline Copolymers

Polymer	Inherent viscosity, dl/g	Glass transition temperature, °C[a]	Polymer decomposition temperature, °C[b]	Isothermal weight loss at 400°C in air after 100 hr, %[c]	Elemental analyses[d]		
					C, %	H, %	N, %
II	1.80[e]	217	550	97.1	77.45	3.37	10.27
					(77.51)	(3.38)	(10.85)
III	2.07[f]	274	535	93.0	74.96	3.05	10.39
					(75.94)	(3.31)	(10.63)
IV	1.06[f]	240	530	56.0	75.36	3.31	10.11
					(76.30)	(3.26)	(10.47)
V	1.13[f]	186	495	65.5	70.64	2.99	9.82
					(71.59)	(3.12)	(10.02)

[a] Measured by dielectric loss as a function of temperature at a heating rate of 5°C/min.

[b] Obtained from TGA data in vacuum at a heating rate of 5°C/min.

[c] Poly[*N*,*N*′-(4,4′-oxydiphenyl)pyromellitimide] was included for comparison; its weight loss was 80.5%, indicating a thermal-oxidative stability between those of polymers III and V.

[d] The calculated values are shown in parentheses.

[e] Determined in 98% sulfuric acid (0.5 g in 100 ml, at 30°C).

[f] Determined in *m*-cresol (0.5 g in 100 ml, at 30°C).

obtained which remained soluble in *m*-cresol. Dimethylacetamide, which is frequently used as a solvent for polyimide synthesis, could not be used in this case since the final polymers were insoluble in this solvent. The use of *m*-cresol as solvent does not affect the imide ring. No solvolysis was observed even at reflux temperature for many hours. Polymers III–V give highly viscous solutions in *m*-cresol, and films could be readily cast. Polymer II gives a gelatinous solution at room temperature (even in a concentration of only 3%). This gel is, however, easily liquified at elevated temperature (>150°C), and films were cast from a hot solution on preheated glass plates. The reason why polymers III–V do not gel at room temperature is probably due to the chain-flexibilizing influence of the ether, carbonyl, or sulfone linkages. The course of the reaction was followed by the disappearance of one of the three carbonyl bands in the infrared spectra. (The band at 1660 cm^{-1} corresponding to the glyoxal part of the imide monomer decreases during the polymerization. The two imide bands at 1720 cm^{-1} and 1700 cm^{-1} remain unchanged. Likewise, the strong NH bands of the aromatic tetraamines decrease during the polymerization.) Details of synthesis and characterization of the polymers are given in Tables II and III.

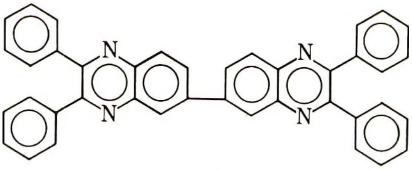
Unlike our previously reported phenylated polyquinoxalines, the imide–quinoxalines are not soluble in chloroform, nitrobenzene, or dichlorobenzene. They are, however, soluble in phenolic solvents such as *m*-cresol or *m*-methoxyphenol, in hexafluoroacetone, hexafluoroisopropanol, and are moderately soluble in tetrachloroethane. Table IV shows qualitatively the solubility of the polymers in a number of solvents.

TABLE IV
Solubilities of Imide–Quinoxaline Copolymers[a]

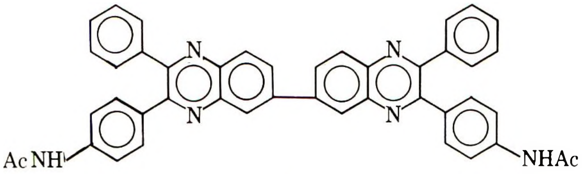
Solvent	Solubility			
	Polymer II	Polymer III	Polymer IV	Polymer V
m-Cresol	+	+	+	+
m-Methoxyphenol	+	+	+	+
Tetrachloroethane	−	+	+	+
Hexafluoroacetone	+	+	+	+
Hexafluoroisopropanol	+	+	+	+
N-Methylpyrrolidone	−	+	−	+
Sulfuric acid	+	+	+	+

[a] The solubilities were determined qualitatively by letting the polymers dissolve at room temperature without continued mechanical agitation: + means soluble, − means insoluble.

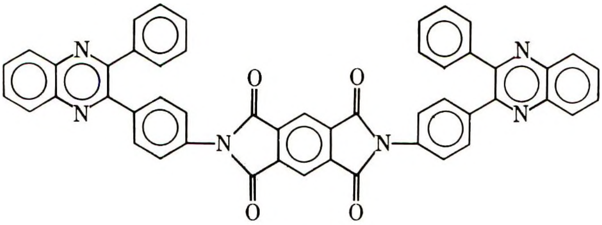
The three models VI–VIII served as a further proof of structure. The synthesis of compound VI was reported elsewhere;[4] VII and VIII were prepared by reacting diaminobenzidine with acetamidobenzil and by condensation of *o*-phenylenediamine with *N*,*N*′-bis(4-benzilyl)pyromellitimide, respectively. The reactions were carried out under similar conditions as used for the polymerization. All bands found in the infrared spectra of polymer II could be accounted for from the spectra of the models.



VI



VII



VIII

Thermal Properties

Thermogravimetric analysis (TGA) was performed on powdered samples of polymers. The decomposition was carried out under vacuum of about 30 μ at a heating rate of 5°C/min. Under these conditions the temperature of initial weight loss, arbitrarily defined as polymer decomposition temperature (PDT), varied between 495 and 550°C (see Table III).

A relative scale of the oxidative-thermal stability of the polymers was obtained by measurements of isothermal weight loss on powdered samples at 400 ± 7°C in static air. To reduce errors caused by temperature variations, all samples were placed simultaneously into a muffle oven lined with aluminum foil. To compare the stabilities of the polyimide–quinoxalines with pure aromatic polyimides, H-film [poly-*N*,*N*′-(4,4′-oxidiphenyl)pyromellitimide] was included in this experiment. As in our previous studies,[1–5] we found again that the nature of the flexibilizing links in the polymer chain determines the oxidative-thermal stability. The order of decreasing stability is: carbonyl > sulfone > ether, which is in agreement with the earlier observations on imide-amide copolymers and polyquinoxalines. The oxidative stability of oxydiphenylpyromellitimide is somewhere between polymers III and V. Presently, we have no explanation why polymer II is less stable than all the others. One may argue that the highly rigid structure of the polymer chain facilitates its thermal-oxidative breakdown. Such a conjecture is, however, highly speculative.

Apparent glass transition temperatures T_g of the polymers are shown in Table III. They were obtained from dielectric loss measurements on polymer films, in vacuum at a heating rate of 5°C/min. The T_g ranged between 186 and 274°C. As expected, the copolymer effect lowers the T_g values considerably as compared to those of straight polyimides such as H-film, which under the same conditions shows a T_g of 365°C.

The author wishes to express his appreciation to Mr. Leon Wish for running the TGA and dielectric measurements.

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Received May 11, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3155-3162 (1970)

Effects of Substituents on the Anionic Copolymerization of Ring-Substituted Cinnamonitriles

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Synopsis

trans-Cinnamonitrile (M_1) was copolymerized with several of its ring-substituted derivatives (M_2) in toluene at 25°C, calcium zinc tetraethyl being used as catalyst. The ring substituents investigated include H, *p*-CH_3O, *m*-CH_3O, *p*-CH_3, *m*-CH_3, *p*-Cl, and *m*-Cl. It was found that the values of log ($1/r_1$) are linearly correlated with Hammett's σ constants with the reaction constant $\rho = 0.7$. The effects of coordination between monomer and catalyst sites upon the Hammett relation are discussed.

INTRODUCTION

A study of substituent effects on the copolymerizability of substituted styrenes in Ziegler-Natta systems has demonstrated the importance of the coordination character of the monomer.[1] The negative ρ-value of a Hammett plot indicated that coordination between monomer and the electron-deficient part of the reactive center was actually the rate-determining step, in contrast with the ordinary anionic polymerization.

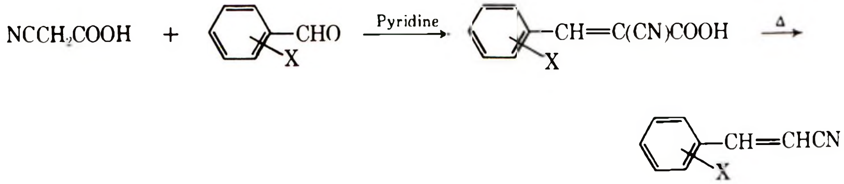
Our previous studies of the relative reactivities of *cis* and *trans* isomers of crotonic ester, crotononitrile, and cinnamonitrile in anionic polymerization have also suggested the importance of the coordination of polymer end and/or monomer to stereospecific polymerization catalysts, such as calcium zinc tetraethyl.[2,3] Thus, anionic copolymerization of cinnamonitrile with its ring-substituted derivatives have been carried out with use of calcium zinc tetraethyl as catalyst, in order to determine the effect of coordination on the Hammett relation.

The results have been compared with those observed in the copolymerization of ring-substituted styrenes.

EXPERIMENTAL

Materials

Cinnamonitrile (CNN) and its *p*-CH_3O, *m*-CH_3O, *p*-CH_3, *m*-CH_3, *p*-Cl, *m*-Cl, *m*-NO_2, and *p*-$(CH_3)_2N$ derivatives were prepared from cyanoacetic acid and appropriate substituted benzaldehydes according to the method of Ghosez.[4]



The cinnamonitrile derivatives thus were subjected to fractional distillation through a Taika Kogyo TS-SB_1 spinning-band column. The *cis* and *trans* isomers were separately collected, stored in the dark under nitrogen atmosphere, and redistilled immediately before use.

Gas chromatography of the nitriles prepared as above indicated that they were over 99.0% pure. Their boiling or melting points are summarized in Table I. All boiling points are uncorrected.

TABLE I
Boiling Points or Melting Points of the Substituted *cis*- and *trans*-Cinnamonitriles[a]

	cis		*trans*	
Substituent	Observed	Literature value	Observed	Literature value
H	115°/12 mm	115°/12 mm[1]	129°/12 mm	129°/12 mm[4]
p-CH_3O	98°/0.3 mm	—	(64°)	(64°)[6]
m-CH_3O	115°/2 mm	—	112°/0.5 mm	—
p-CH_3	99–100°/14 mm	—	(74–75°)	(70–71°)[6]
m-CH_3	130°/14 mm	—	45°/14 mm	—
p-Cl	(64–65°)	—	(88–89°)	(84–85°)[6]
m-Cl	(26–28°)	—	(56°)	—
m-NO_2	—	—	(159–161°)	(159°)[6]
p-$(CH_3)_2N$	—	—	(171–172°)	(168–169°)[7]

[a] The figures in parentheses are melting points.

Toluene was distilled in the presence of sodium benzophenone ketyl under nitrogen atmosphere. Calcium zinc tetraethyl was obtained according to the method of Gilman.[5]

Polymerization Procedure

Polymerization was carried out under dry nitrogen in a flask equipped with a stirrer and a filling tube having a side arm for nitrogen inlet. Toluene, cinnamonitrile, and a substituted cinnamonitrile were introduced into the flask immersed in a bath thermostatted at 25.0°C. The total volume of the solution was 12 ml, and the total monomer concentration was 0.5 mole/l. A catalyst suspension in toluene (1.0 mole-% with respect to the monomer mixture) was then added to the monomer solution by use of a syringe under stirring, and the reaction started. After a specified interval of reaction time, methanolic hydrochloric acid was added to stop the reaction. It took 5 to 60 min to obtain conversions below 10%. The precipitated polymer was collected on a sintered glass-filter, washed several times with methanol, and dried *in vacuo* at room temperature.

Copolymer Characterization

The compositions of monomers in the copolymer obtained as above were determined by infrared spectrophotometry. A Nihon Bunko spectrometer model 402G was used. The polymer sample to be analyzed was dispersed in a KBr pellet. Table II shows the absorption maxima of unsubstituted and substituted polycinnamonitriles used for the determination of the copolymer compositions.

TABLE II
Absorption Maxima Characteristic of Substituted and Unsubstituted Cinnamonitriles Used for the Determination of the Copolymer Compositions

	Frequency, cm^{-1}	
Substituent	Un-substituted	Substituted
p-CH_3O	3034, 3063	2837
m-CH_3O	3034, 3063	2837, 3009
p-CH_3	1500	1517
m-CH_3	3063, 3089	2850, 2920
p-Cl	1456	1416
m-Cl	1456, 1500	1435, 1480

A system of cinnamonitrile (CNN) and p-CH_3-CNN is shown in Figure 1 as an example.

The copolymer compositions were evaluated from the ratios of the heights of the characteristic absorption peaks corresponding to the substituted and unsubstituted nitriles. The calibration curves were drawn for the homopolymer blends of known compositions. As an example, such a calibration curve for the system of p-CH_3-CNN and CNN is shown in Figure 2.

RESULTS

Copolymerization was carried out in toluene at 25.0°C by using calcium zinc tetraethyl as catalyst. Each *trans* isomer of the substituted cinnamonitriles (M_2) was copolymerized with the unsubstituted compound (M_1).

Copolymerization data are given in Table III for the system CNN–p-CH_3-CNN as an example. Monomer reactivity ratios, r_1 and r_2, were evaluated by the least-squares treatment of the Fineman-Ross plots.

Monomer reactivity ratios obtained for the various substituted CNN(M_2) and CNN(M_1) pairs are summarized in Table IV, along with related

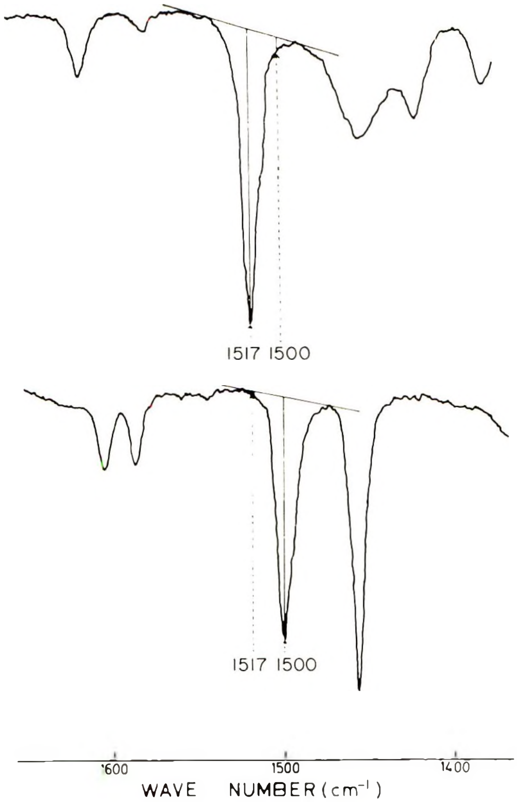


Fig. 1. Characteristic absorption peaks of homopolymers corresponding to *p*-methylcinnamonitrile and cinnamonitrile.

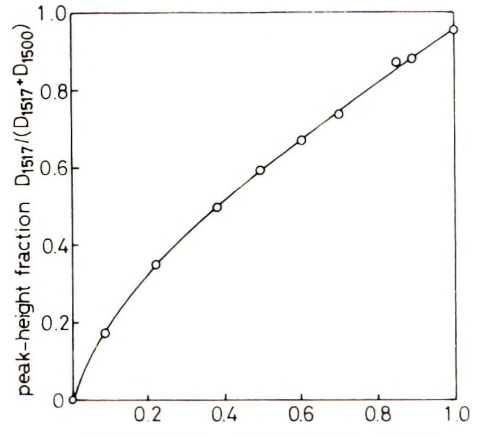


Fig. 2. Calibration curve for the determination of copolymer compositions of the system *p*-methylcinnamonitrile–cinnamonitrile.

TABLE III
Copolymerization Data for the System,
Cinnamonitrile (M_1)–*p*-Methylcinnamonitrile (M_2)[a]

No.	M_1 in monomer feed $[M_1°/(M_1° + M_2°)]$	M_1 in copolymer $[M_1/(M_1 + M_2)]$	Polymerization time, min	Polymer yield, %
1	0.10	0.13	47	4.9
2	0.20	0.22	6	4.0
3	0.30	0.37	43	3.6
4	0.40	0.44	35	4.6
5	0.50	0.53	57	8.3
6	0.60	0.64	17	3.5
7	0.70	0.76	19	1.7
8	0.80	0.82	54	7.9
9	0.90	0.92	21	2.7

[a] The total initial concentration of the monomers, $[M_1°] + [M_2°] = 0.50$ mole/l. Concentration of catalyst was 5 mmole/l. Solvent, toluene; temperature, 25.0°C.

TABLE IV
Monomer Reactivity Ratios for the Anionic Copolymerizations
of Cinnamonitrile (M_1) with its Ring-Substituted Derivatives (M_2)

Substituent	σ	r_1	r_2	$1/r_1$	r_1r_2
p-CH_3O	−0.268	1.56 ± 0.09	0.71 ± 0.04	0.64	1.11
m-CH_3O	0.115	0.78 ± 0.14	1.09 ± 0.03	1.28	0.85
p-CH_3	−0.170	1.19 ± 0.04	0.85 ± 0.02	0.84	1.02
m-CH_3	−0.069	1.25 ± 0.15	0.78 ± 0.10	0.80	0.98
p-Cl	0.227	0.56 ± 0.05	0.87 ± 0.01	1.79	0.49
m-Cl	0.373	0.62 ± 0.08	1.03 ± 0.01	1.62	0.64

quantities. Inspection of the data given in Table IV shows that polymerizabilities of substituted CNN are greater, the more electron-withdrawing the substituents.

In other experiments, we attempted to copolymerize the *p*-$(CH_3)_2N$- and *m*-NO_2-cinnamonitriles. However, neither of these cases was successful; the former tended to form a quarternary ammonium salt with hydrochloric acid added to stop the reaction and the latter showed very low solubility in the solvent used.

DISCUSSION

In the preceding report,[3] it was demonstrated that *cis*-cinnamonitrile undergoes geometrical isomerization at a rate not negligibly small as compared with that of its anionic polymerization, but that the *trans* isomer is far less subject to isomerization and is more polymerizable than the corresponding *cis* isomer. This latter finding ensures the validity of the determinations of the monomer reactivity ratios for copolymerization between

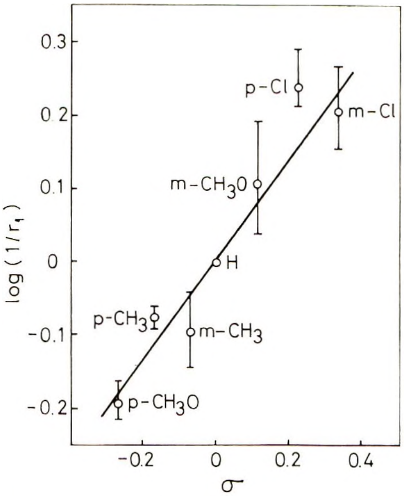


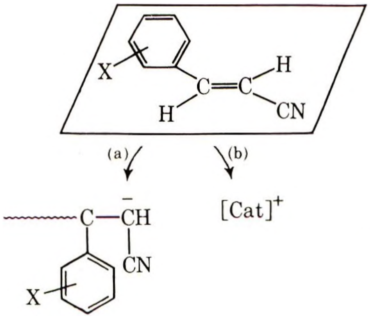
Fig. 3. Plots of $\log(1/r_1)$ vs. Hammett σ.

trans-cinnamonitrile and its ring-substituted derivatives from the analysis of the copolymer composition, provided that the copolymerizations are terminated at low conversions.

The monomer reactivity of a given substituted cinnamonitrile (M_2) relative to the unsubstituted monomer (M_1) may best be represented by the value $1/r_1$. In Figure 3, the values of $\log(1/r_1)$ for the various substituted *trans*-cinnamonitriles are plotted against the Hammett σ constants of the substituents.

It may be said that the relation between $\log(1/r_1)$ and σ values is satisfactorily linear in view of experimental errors inherently involved in studies of the anionic polymerizations effected by complex catalysts. The reaction constant ρ is evaluated to be 0.7.

The positive, but small ρ value characterizing the anionic copolymerization of ring-substituted cinnamonitriles should be compared with $\rho = +5.0$ and $\rho = -0.95$ found for the intrinsically anionic polymerization[8] and the coordinated anionic polymerization[1] of ring-substituted styrenes, respectively. The positive ρ value seems to be unfavorable for the proposed coordination of polar olefins to catalyst sites.



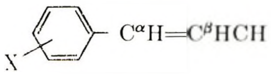
In view of the fact that cinnamonitrile is far more reactive toward nucleophilic reagents than styrene, the interaction between monomer and polymer end anion, path (a), could not be neglected compared with that between monomer and catalyst sites, path (b).

The above two interactions might eventually compete with each other in the rate-determining step. This concept seems to rationalize the small ρ value observed in the present Hammett plots.

However, there seems to be another possibility that could account for the small ρ value. In view of the results of molecular orbital calculations of superdelocalizabilities for the various substituted cinnamonitriles (Table V), the α-carbon with respect to the phenyl ring is considered to be more subject to the attack of nucleophiles than the β-carbon. A small ρ value is supposed to be characteristic of this type of ionic addition reactions of styrene derivatives.

TABLE V

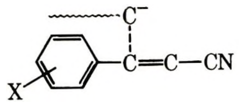
Superdelocalizabilities of Substituted Cinnamonitriles[a]



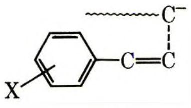
Substituent	$S_{\beta}^{-}(-\gamma^2/\beta)$	$S_{\alpha}^{-}(-\gamma^2/\beta)$
p-CH_3O	1.1519	1.6996
p-CH_3	1.1538	1.7216
m-CH_3	1.1624	1.7282
H	1.1963	1.7537
m-CH_3O	1.2132	1.7673
p-Cl	1.3049	1.8154
m-Cl	1.3125	1.8370

[a] The coulomb and resonance integrals of substituents were adopted from Fueno et al.[9]

In order to clarify these situations, the delocalization energies, ΔE_{α}, for α-addition of substituted cinnamonitriles and those, ΔE_{β}, for the β-addition of styrenes were calculated. The results are tabulated in Table VI.



ΔE_{α}



ΔE_{β}

Inspection of the data given in Table VI shows that the $\delta\Delta E_{\alpha}$'s of substituted cinnamonitriles are smaller than $\delta\Delta E_{\beta}$'s of styrene derivatives by a factor of 2.

Although the attack of polymer end toward the α-carbon is certainly important, the possibility of the coordination of the catalyst to the mono-

TABLE VI
Delocalization Energies of Ring-Substituted Cinnamonitriles and Styrenes

	Delocalization energy[a] $(-\gamma^2/\beta)$			
	Cinnamonitrile[b]		Styrene[b]	
Substituent	ΔE_α	$\delta\Delta E_\alpha$	ΔE_β	$\delta\Delta E_\beta$
p-CH_3O	0.3536	−0.0046	0.3693	−0.0049
p-CH_3	0.3564	−0.0020	0.3680	−0.0062
m-CH_3	0.3568	−0.0016	0.3692	−0.0050
H	0.3584	0.0000	0.3742	0.0000
m-CH_3O	0.3592	0.0008	0.3765	0.0023
p-Cl	0.3607	0.0023	0.3898	0.0156
m-Cl	0.3629	0.0045	0.3902	0.0160

[a] The integral parameters for substituents are adopted from Fueno et al.[9]

[b] To a first approximation, the integral parameter k_{C-} was assumed to be zero.

mer cannot wholly be negated.[2,10–14] Probably, competitive interactions of monomer with polymer end and with catalyst are involved in the rate-determining step.

In the copolymerization of substituted CNN with CNN, some of the products r_1r_2 are not equal to unity. This observation implies that the propagating polymer end units derived from substituted and unsubstituted monomers are different in reactivity. The results are against the expectation, in view of the lack of the conjugation between polymer end units and substituted phenyl group. This might be suggestive of some specific interaction of the catalyst with substituted phenyl ring, which might lead to intermolecular complexation, influencing the monomer selection.

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Received May 22, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3163-3175 (1970)

Photo-Oxidation of Polymers without Light: Oxidation of Polybutadiene and an ABS Polyblend with Singlet Oxygen

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Synopsis

In recent years much evidence has been accumulated to implicate electronically excited oxygen ($^1\Delta_g$) molecules as the agent responsible in photosensitized oxidations for the formation of allylic hydroperoxides from olefins and of endoperoxides from 1,3-dienes. Little regarding the mechanistic aspects of the photo-oxidative degradation of polybutadiene (PBD) is known, however. To determine if electronically excited oxygen ($^1\Delta_g$) molecules can oxidize PBD, the ABS polyblend and standard samples of PBD's containing high *trans*, high *cis*, and high vinyl content were treated in homogeneous solution at low temperature with chemically produced singlet oxygen *in situ*. The source of the singlet oxygen was the triphenylphosphite-ozone adduct. Studies by spectroscopy, elemental analysis, viscosity determinations, and gel measurements showed only the *cis*- and the *trans*-PBD were susceptible to oxidation; no chain scission was involved in the attack of *cis*- and *trans*-PBD by singlet oxygen; the oxidation of the cis PBD involved the initial formation of hydroperoxides which on thermal decomposition yielded gel. The *trans*-PBD was found to oxidize but apparently by a mechanism different from that of *cis*-PBD. Initial singlet oxygen attack of ABS proceeds by oxidation of the PBD portion of the polyblend. It was also observed that when only a small amount of the double bonds in the *cis*-PBD polymer had been oxidized to hydroperoxides, subsequent thermal treatment of this sample resulted in gross structural changes in the whole polymer.

INTRODUCTION

The past decade has seen a burgeoning of support for the hypothesis originally propounded by Kautsky[1,2] that electronically excited molecules of oxygen in their singlet state ($^1\Delta_g$) are the reactive intermediates responsible for the dye-sensitized photo-oxidation of olefins and dienes. The work of Foote et al.[3-5] has demonstrated that products derived from the oxidation of certain olefins and dienes with the hydrogen peroxide-hypochlorite reagent were precisely the same as those resulting from the photo-oxidation of the same compounds. This information, taken together with the assignments of the emission bands from the gas produced by the hydrogen peroxide-hypochlorite reaction[6,7] as being due to singlet oxygen, have given greater weight to Kautsky's theory.

Subsequently, other methods of preparing and using singlet oxygen for organic syntheses were discovered. The microwave discharge of ground state [$^3\Sigma_g$] oxygen was used by Corey and Taylor[8] to generate singlet oxygen externally and to perform a series of peroxidation reactions; however, reaction times were prohibitive. For preparative purposes, the *in situ* production of singlet oxygen is more attractive and can be accomplished by a number of procedures[9–12] in addition to Foote's method.

To our knowledge there have been only two suggestions that singlet oxygen is implicated in the oxidation of polymers.* One such hypothesis is that singlet oxygen may be involved in the photodegradation of polyethylene.[13] In another case, the photochemical degradation of elastomers accompanied by incorporation of oxygen has also been postulated to proceed by a singlet-oxygen mechanism.[14] In neither situation is direct evidence available to show that singlet oxygen reacts with these polymers.

Unfortunately, the state of our present knowledge of the mechanism involved in polydiene oxidation is inadequate to explain many of the observed experimental results.[15] The ready availability of some acrylonitrile–butadiene–styrene (ABS) resins and quantitative knowledge of their composition[16] along with easy access to standard samples of the polydiene components[17] makes this polyblend an excellent subject for a detailed study of its susceptibility to photo-oxidation by a nonradiative method. In order to approach this problem in a manner which might yield more fundamental information, we have endeavored to separate from the total oxidation picture only those effects due to the photo-oxidation of the polymer. This can be done by performing these oxidations with singlet oxygen prepared from the triphenyl phosphite–ozone adduct of Murray and Kaplan.[12] Since no light is used, this technique eliminates complications due to light-induced *cis-trans* isomerization[18] and photodegradation reactions.[19] Also, thermal oxidation effects are minimized[20–22] since the reaction is conducted at low temperature.

EXPERIMENTAL

Polymers

The following polymers were studied: *cis*-polybutadiene (PBD) containing 95.3% *cis*, 1.4% *trans*, and 3.3% vinyl unsaturation and having a viscosity-average molecular weight $\bar{M}_v$ of 563,000 (determined by intrinsic viscosity measurement in benzene solution at 30°C and by use of the constants of Fujita et al.[23]); vinyl PBD containing 91.5% vinyl, 7.0% *cis*, and 1.5% *trans* unsaturation; *trans*-PBD containing 88.5% *trans*, 8.9% *cis*, and 2.6% vinyl unsaturation and having $\bar{M}_v$ of 97,500 (determined by

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* Since this paper was submitted, two additional references have come to our attention, viz., T. Mill, K. C. Irwin, and F. R. Mayo, *Rubber Chem. and Tech.*, **41**, 296 (1968); G. Meyer, *Bull. Soc. Chim. Fr.*, **2**, 702, (1970).

TABLE I
Composition of Various Polymers

Polymer	Styrene, %	Acrylonitrile, %	Butadiene, %	Butadiene unsaturation		
				% *cis*	% *trans*	% vinyl
ABS[a]	55	23	18	21[b]	59[b]	20[b]
High-*cis* PBD[c]	—	—	100	95.3	1.4	3.3
High-*trans* PBD[c]	—	—	100	8.9	88.5	2.6
High-vinyl PBD[c]	—	—	100	7.0	1.5	91.5

[a] Data of Gesner.[16]

[b] Typical values for PBD synthesized by emulsion polymerization at 50°C.[26]

[c] Manufacturer's data.[17]

intrinsic viscosity measurement in toluene at 30°C and by use of the constants of Takeda and Endo[24]). The polybutadiene reference samples were obtained from Phillips Petroleum Company and contained 0.5% Cyanox SS antioxidant.

The styrene-acrylonitrile copolymer (SAN) used was a commercial grade containing a 73:27 ratio of styrene to acrylonitrile. The $\bar{M}_v$ was 184,000 (determined by intrinsic viscosity measurements in butanone at 30°C and by use of the constants of Shimura et al.[25]).

Also used was a commercial grade of acrylonitrile-butadiene-styrene resin (ABS) shown by previous analysis[16] to contain 18% butadiene, 55% styrene, 23% acrylonitrile, and 4% additives.

Polymers were dissolved in methylene chloride in an argon atmosphere, except for *trans*-PBD, which was dissolved in warm toluene. The polymers were precipitated with methanol, dried, and stored at 25°C/0.01 mm Hg until used. Compositions are shown in Table I.

Oxidation of Polymers in Solution with Singlet Oxygen

Triphenyl phosphite (3.10 g, 0.01 mole, Eastman Kodak) was dissolved in 200 ml methylene chloride and cooled to −78°C. The solution was ozonized to the blue color of excess ozone, then purged with dry nitrogen well beyond the time required to remove the ozone color. A solution of the polymer (0.25 g/100 ml methylene chloride) at −78°C was added to the phosphite-ozone adduct. Mixing was accomplished with the nitrogen stream. The reaction mixture was permitted to warm to 25°C.

In the ordinary reactions about twice the amount of singlet oxygen to react with every double bond was produced. The reaction mixture was concentrated on a rotary evaporator, without heating the solution, and methanol was added to precipitate the polymer. After two subsequent reprecipitations the polymer was dried *in vacuo* and used for the various analytical procedures.

In one experiment, 0.25 g 2,2′-methylene bis(4-methyl-6-*tert*-butyl phenol) was added to the solution of *cis*-PBD which was then treated with singlet oxygen. In a separate experiment, the hindered phenol was added to the solution after reaction with singlet oxygen. In another experiment, 0.310 g (0.001 mole) triphenyl phosphite was reacted with ozone as above. This adduct was used to oxidize *cis*-PBD.

Treatment of Polymers in Solution with Ground-State Oxygen

Triphenyl phosphate (mp 49–50°C, 3.26 g, 0.01 mole) was dissolved in 300 ml methylene chloride along with 0.25 g polymer and cooled to −78°C. Oxygen was bubbled into the solution until it warmed to 25°C.

After treatment with ground-state oxygen, the polymers were precipitated at least twice with methanol to remove triphenyl phosphate, dried, and stored at 25°C/0.01 mm Hg.

TABLE II

Intrinsic Viscosity [η] and Viscosity-Average Molecular Weights ($\bar{M}_v$) of Various Polymers Determined at 30°C

Polymer	Solvent	State	[η]	$\bar{M}_v \times 10^{-5}$
ABS	$CHCl_3$	Unoxidized	0.484	
		Control, oxidized with ground-state O_2	0.510	
		Oxidized with singlet oxygen	0.516	
SAN	Butanone	Unoxidized	0.661	1.84
		Control, oxidized with ground-state O_2	0.654	1.81
		Oxidized with singlet oxygen	0.659	1.83
trans-PBD	Toluene	Unoxidized	1.67	0.975
		Control oxidized with ground-state O_2	1.64	0.945
		Oxidized with singlet oxygen	1.61[a]	0.922[a]
cis-PBD	Benzene	Unoxidized	2.60	5.63
		Control, oxidized with ground-state O_2	2.48	5.30
		Oxidized with singlet oxygen	Gel	
		Oxidized with $^1\Delta O_2$ in the presence of oxidation inhibitor	2.83	6.28
		Oxidized with $^1/_5$ theoretical amount of $^1\Delta O_2$	Gel	
Vinyl PBD	Benzene	Unoxidized	0.822	
		Control, oxidized with ground-state O_2	0.834	
		Oxidized with singlet oxygen	0.915	

[a] Polymer added when complex reached −20°C.

Analytical Methods

Solutions for intrinsic viscosity measurements were made as follows. The *cis*-polybutadiene and vinyl polybutadiene were dissolved in benzene; *trans*-polybutadiene in toluene; styrene acrylonitrile in butanone; ABS in chloroform. Concentration of the solution before dilution was 0.1 g/10 ml. Solutions were stored at 5°C until used. Solutions were filtered through 0.45 μ Flotronic silver membrane filters immediately before use. Although we have referred to "solutions" of ABS previously, we are aware that ABS, because of the cross-linked rubber, does not completely dissolve and that even after filtration through 0.45 μ filters solutions containing ABS still appear cloudy. Viscosities determined with such solutions are not as meaningful as those measurements made with truly homogeneous solutions. Viscosities were measured with a Cannon-Ubbelohde viscometer at 30 ± 0.05°C. Least-squares calculations of intrinsic viscosities were made for each polymer solution. Where possible, viscosity-average molecular weights were determined by using the Mark-Houwink equation[27,28] (Table II).

Infrared spectra in the 2–15 μ range were taken with a Perkin-Elmer Model 21 spectrophotometer. A Cary model 15 spectrophotometer was used for spectra from 2300–5000 Å. Films were cast from solutions described above; SAN and ABS were cast in Al dishes; PBD samples were cast on NaCl disks. The ultraviolet spectra of the polymers before and after oxidation were identical, therefore, investigations with this technique were abandoned.

Gel was measured by extracting 0.1-g samples with chloroform for 48 hr under N_2 in a Soxhlet apparatus. Polymer samples were contained in coarse (RA98) Alundum thimbles which are reported to retain particles greater than 20 μ (Table III).

TABLE III
Gel Determinations by Chloroform
Extractions of the Various Polymers

	Gel, %		
	Unoxidized	Treated with ground-state O_2	Treated with singlet oxygen
ABS	17.5[a]		40.6
SAN	1.3	3.6	0.2
cis-PBD	1.8[a]	1.5	97.8
			1.6[b]
			1.7[c]
trans-PBD	0.95[a]	0.4	33.9[d]
Vinyl PBD	0.1	0.1	15.2

[a] Average values for duplicate runs.
[b] With antioxidant present.
[c] With less than theoretical amount of singlet oxygen available (1/5).
[d] Polymer added to phosphite–ozone adduct at −20°C.

TABLE IV
Oxygen Analyses of PBD Samples

	O, %	
	Unoxidized	Treated with singlet oxygen
cis-PBD	0	2.40[a] 0.40[b] 0.86[c]
trans-PBD	0	1.88[d]

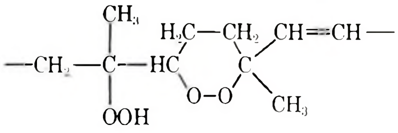
[a] Duplicate average.
[b] With antioxidant present.
[c] With $^1/_3$ theoretical amount of $^1\Delta$ oxygen available.
[d] Polymer added to phosphite–ozone adduct at −20°C.

Elemental analyses were performed by Midwest Microanalytical Laboratory. Oxygen analyses appear in Table IV.

RESULTS AND DISCUSSION

During the course of this work, it became obvious that we would have to know, in the case of difficultly oxidized polymers, whether their solubilities were playing a role in their resistance to oxidation. Solubility was determined by filtering polymer solutions in methylene chloride through membrane filters with pore sizes of 0.45 μ. Both the polymer solution and filtration apparatus were cooled to −78°C. Only the high-*trans* content PBD was retained by the filter, whereas at higher temperature it was not. To effect solubility of the *trans*-PBD during the oxidation reaction, the phosphite–ozone adduct solution was allowed to reach −20°C before the addition of the polymer solution. The *trans*-PBD reacted above −20°C but not when the polymer was added to the adduct at −78°C as was done with all the other polymer solutions.

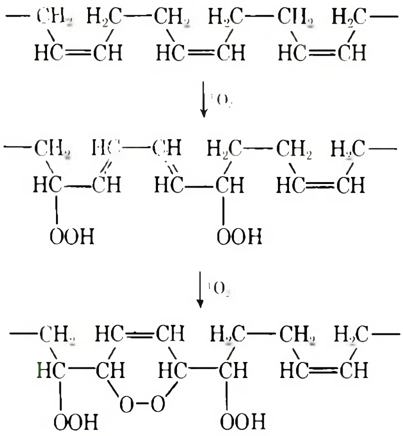
ABS polyblends are manufactured by polymerization of styrene and acrylonitrile in the presence of polybutadiene.[29] Under these circumstances the resulting polyblend has enhanced physical properties due to grafting of the PBD to the SAN copolymer as well as some crosslinking of the PBD component. The incorporation of the polybutadiene poses a problem in relation to polymer aging, since the double bonds present are now prime sites for oxidative attack.[20] In large measure, the information now available to explain polydiene oxidation is derived from the pioneering work of Bolland and Hughes[30] on the thermal oxidation of squalene (a model for polyisoprene). The subsequent modifications (I) of Bolland and Hughes' proposed structure by Bevilacqua[31] helped to account for some of the products isolated. The adequacy of this formulation is open to question, since all products from the thermal oxidation of rubber cannot be accounted for and the cyclic peroxide structure is not known to result from the autoxidation of any other 1,5-dienes.



I

Although cyclic peroxide structures are not known to arise from thermal oxidation except for Bolland and Hughes' work,[30] their existence can be explained if one invokes the singlet oxygen mechanism in a photosensitized reaction. In order to permit formation of cyclic peroxides by the attack of singlet oxygen, the initially unconjugated double bond system must become conjugated.

It is significant that autoxidation of 1,4-polyenes has been found to result in increasing double-bond conjugation during the course of the reaction.[32] A conjugated double-bond system formed in this manner can then, by a photosensitized oxidation (i.e., singlet oxygen), be converted to a cyclic peroxide.[33] A plausible series of events that could lead to a cyclic peroxide structure in 1,5-polybutadienes without involving a thermal autoxidation step requires the addition of singlet oxygen to two nearest-neighbor double bonds with the formation of two allylic hydroperoxides followed by addition of singlet oxygen across the resulting conjugated system. This scheme is pictured in eqs. (1).



(1)

It is clear from our infrared results that singlet oxygen treatment of *cis*-PBD does indeed result in hydroperoxide formation, and it is not unreasonable to assume that the double-bond shift which occurs in this reaction would lead to some conjugated systems. In photo-oxidations the formation of allylic hydroperoxides from olefins and of cyclic peroxides from 1,3-dienes are characteristic of singlet oxygen.[33]

Infrared spectra were taken of thin films (~0.5 mil) of the various polymers both before and after solution oxidation. Films of ABS and SAN were cast from chloroform and butanone, respectively. Films of the polybutadienes were formed on salt plates. Upon treatment with ground-state oxygen in solution in the control experiments it was found that the infrared spectra of these polymers did not appear different from those of the unoxidized polymers. Treatment with singlet oxygen, did, however, cause changes in the spectra of *cis*- and *trans*-PBD and of ABS. The oxidized ABS and *trans*-PBD films indicated the appearance of a band at 3 μ although both were much smaller than that in the *cis*-PBD. In addition, the ABS showed minor changes at 5 and 8.5 μ. The trans PBD showed weak new bands appearing at 6.7, 8.4, 8.6, 9.8, 13.3, and 14.6 μ.

The broad -OH band at 3 μ was the only observable change in the infrared spectrum of the $^1\Delta O_2$-treated *cis*-PBD. That this band was due to hydroperoxide was qualitatively tested for by treating a portion of the oxidized polymer with KI in acetone. The characteristic yellow color of iodine was liberated immediately. When a film was made of the oxidized *cis*-PBD soon after the reaction was complete and it was permitted to stand at room temperature for 6 hr, no further changes were found in the infrared spectrum. By permitting the oxidized polymer solution to stand at room temperature for any significant length of time (>1 hr), however, the isolated polymer was completely gelled. It is evident then that very few of the initially formed hydroperoxides must decompose in order for the polymer to gel. The crosslinking reaction can occur through formation of a peroxide bridge, an ether bridge, or a carbon-carbon bond, depending on the mode of hydroperoxide decomposition. More will be said later about the probable nature of the crosslink.

When the film of the singlet oxygen-treated *cis*-PBD had been allowed to stand at room temperature for 6 hr and was heated for 15 min at 140°C in air, the thermal decomposition of the hydroperoxides led to dramatic changes in the polymer spectrum with concomitant appearance of carbonyl groups (Fig. 1). When unoxidized *cis*-PBD was heated in the same manner, the infrared spectrum remained essentially unchanged. The hydroperoxides formed via our singlet oxygen reaction account for oxidation of ~7% of the double bonds in the polymer. It is highly significant that massive changes in the infrared spectrum of the polymer (Fig. 1) occur upon thermal decomposition of these hydroperoxides.

From the viscosity data which we have measured (Table II) it is apparent that the treatment of these polymers with singlet oxygen does not lead to chain scission.

As shown by previous work[16,29] and summarized in Table I, ABS resins are heterogeneous dispersions of emulsion-polymerized PBD particles with grafted SAN surfaces in a matrix of SAN copolymer. Since autoxidation of such a polyblend can produce chain scission, crosslinking, or both, we have measured the intrinsic viscosities and gel fractions to determine whether photosensitized oxidation (i.e., singlet oxygen) causes these reactions to occur. The large increase in gel (Table III) in the case of ABS must be caused by oxidation of the PBD portion of the polyblend, as found previously in aging studies,[20] since SAN exhibits no significant changes on treatment with excited oxygen.

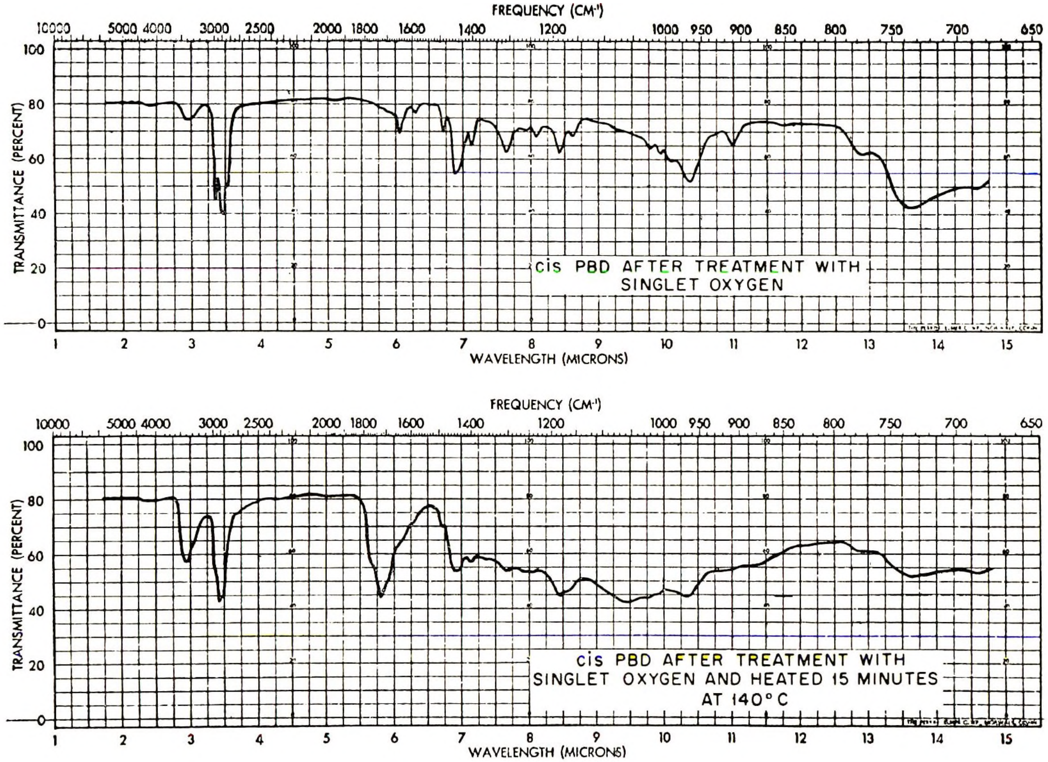


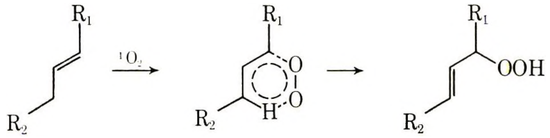
Fig. 1. Infrared spectra of *cis*-PBD: (top) after treatment with singlet oxygen and (bottom) after treatment with singlet oxygen and subsequent heating in air at 140°C.

The *trans*-PBD, on treatment with singlet oxygen, does not change in intrinsic viscosity. Other measurements, e.g., the infrared spectrum, gel fraction and oxygen analysis (Table IV) prove that reaction has taken place.

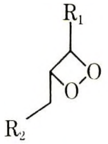
It was impossible to obtain viscosity measurements on the oxidized *cis*-PBD due to its complete conversion to gel when the usual oxidation procedure was used (i.e., two-fold $^1\Delta O_2$ excess).

Further efforts were made to oxidize the *cis*-PBD while suppressing gelation by addition of an equal weight of a thermal oxidation inhibitor to the polymer solution before treatment with singlet oxygen. The amount of gel decreased to almost zero (Table III). The viscosity did show a slight increase and the amount of oxygen found in the polymer was 0.4%. These results may be accounted for if the inhibitor was itself oxidized by the singlet oxygen. Similar types of substituted phenols are known to give good yields of oxidation products when treated with the triphenyl phosphite–ozone adduct.[34] By decreasing the amount of available oxygen to one-fifth based on the number of double bonds in *cis*-PBD (instead of the usual twofold excess) it was hoped that an oxidized polymer would result which would be sufficiently soluble to permit further studies. From the viscosity-average molecular weight of *cis*-PBD (560,000) we can estimate that there are about 10,000 repeating units per molecule and that approximately 7% or 700 are oxidized when twice the theoretical amount of $^1\Delta O_2$ is used. When 1/5 of the theoretical amount of oxygen was used only about 240 double bonds were attacked. What occurred in the latter, however, was a complete gelation as in the case of the usual oxidation. When this gel was subjected to the chloroform extraction procedure to get quantitative data, surprisingly, essentially all of the gel became soluble. The oxygen analysis of this oxidized polymer showed 0.86% oxygen. This behavior suggests that the crosslinking process, when only hydroperoxides are present initially, could take place by formation of a peroxide bridge. The thermal decomposition of peroxides is known to proceed by homolytic cleavage of the —O—O— bond, giving two alkoxy radicals which may then abstract hydrogens or go on to further decomposition.

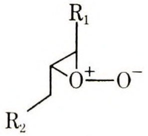
The reactions of the *cis*- and *trans*-PBD polymers seem to be different, both according to the spectroscopic changes observed and the amount of gel formed. The reasons for such differences may be rationalized in several ways. The geometry of the methylene units about the double bond may determine the reactivity of the bond toward electronically excited oxygen. Also, the ease with which this metastable oxygen species can penetrate into the polymer chain will be partly determined by the type of polymer molecule which exists in solution, i.e., whether a coil, sphere, or extended chain. Some question also arises concerning the actual reaction itself. The characterization of the reaction in which olefins form allylic hydroperoxides has usually been written as occurring via a concerted "ene" mechanism:[35]



This mechanism requires that the bonds formed (C—O) and broken (C—H) to *cis* to each other. In recent work, Kearns et al.[36,37] questioned the validity of the "ene" mechanism and proposed that initial attack of singlet oxygen resulted in either a deoxetane (II) or a perepoxide (III) intermediate which could then undergo transformation to products.



II



III

If indeed the concerted "ene" reaction is to be discarded, then it can be postulated that different intermediates may be involved in the oxidation of the *cis*- and *trans*-PBD which may lead to different products.

It should be noted that the intrinsic viscosity of vinyl PBD increases slightly on oxidation. This increase, we feel, is due to oxidation of the *cis*- and *trans*-PBD (Table I) which is found as an 8.5% impurity in the vinyl. The very slow reactivity of 1-olefins toward photosensitized oxidation (i.e., singlet oxygen) has been observed previously.[38]

One other factor which may be of importance in the oxidation scheme of polydienes is the possible production of singlet oxygen from the decomposition of the polymer hydroperoxides themselves. The self-reaction of sec-peroxy radicals has been shown to occur[10] and to lead to singlet oxygen. In the case of the polymers studied here, such internally produced singlet O_2 would then be available to undergo further reactions at appropriate sites.

Singlet oxygen is known to arise photochemically in polluted air. A comprehensive review of this subject by Pitts et al.[39] forcefully advances the view that electronically excited molecular oxygen in the atmosphere may indeed be an important agent responsible for certain pathological conditions in living tissues and for the oxidative degradation of various other substances. The results presented herein are evidence that the latter is almost certainly true for some polymeric materials.

CONCLUSION

Photosensitized oxidations of olefins and dienes are now generally accepted as occurring by a singlet oxygen mechanism. Through the use of chemically produced singlet oxygen in homogeneous solution, it is now possible to study the photosensitized oxidation of polymers without the use of light. By using $^1\Delta$ oxygen produced by the decomposition of the triphenyl phosphite-ozone adduct, we have demonstrated that *cis*- and *trans*-PBD and an ABS resin are easily oxidized. It appears that the oxidations of *cis*- and *trans*-PBD occur by different processes. Vinyl PBD and SAN are not oxidized. Our results indicate that the PBD portion of the ABS polyblend would be the primary point of attack in photooxidation.

We have shown that in *cis*-PBD the only products which result from singlet oxygen treatment are hydroperoxides. A small amount of hydroperoxides, when subsequently decomposed thermally in air, cause massive structural changes in the *cis* polymer. It has also been found that upon treatment with singlet oxygen, gelation occurs in solution. A peroxide bridge structure is apparently responsible for this crosslinking.

The authors thank Drs. G. N. Taylor and A. M. Trozzolo for helpful discussions and Dr. B. D. Gesner for constructive criticism of the manuscript.

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Received May 19, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3177-3187 (1970)

Polymers Containing Anthraquinone Units: Polymers from 1,2,5,6-Tetraaminoanthraquinone

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Synopsis

A preparation for 1,2,5,6-tetraaminoanthraquinone was worked out. The reactivity of this compound in nucleophilic substitutions and nucleophilic additions was studied. Polymers were made by condensation with pyromellitic anhydride, terephthaloyl chloride, and isophthaloyl chloride. The synthesis and properties of the corresponding model compounds are also reported. After reduction with sodium dithionite, the polymers are soluble in dimethylformamide-water mixtures.

INTRODUCTION

Many polymers with good thermal stability have been prepared in this laboratory. Most of these materials are poorly soluble in most solvents. The purpose of this work is to apply earlier described polymerization reactions to tetrafunctional anthraquinone compounds. The reduction of the quinone groups is expected to give polymers soluble in strongly basic media. This technique is common for vat dyes, and has been applied to poly-2-vinylanthraquinone and polyindigo.[1,2]

RESULTS AND DISCUSSION

Preparation of 1,2,5,6-Tetraaminoanthraquinone

1,2,5,6-Tetraaminoanthraquinone (TAA) was made before by rearrangement of 2,6-dinitraminoanthraquinone and subsequent reduction[3] and by reduction of 1,5-dinitro 2,6-diazidoanthraquinone.[4]

We prepared TAA using 2,6-diaminoanthraquinone as a starting material. This product was acetylated, nitrated, hydrolyzed, and finally reduced with sodium sulfide.

The formation of imidazole and imidazole derivatives from TAA proves that the new substituents are adjacent to the 2,6 substituents. In the NMR spectrum, the aromatic protons are split by each other, which proves the 1,2,5,6 substitution.

General properties of TAA Model Compounds.

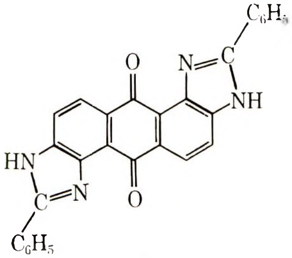
Basicity

Diluted solutions of TAA in water do not exhibit any spectral changes down to pH 1. At pH 0, the initially red solution turns yellow. This indicates that pK_b of the strongest basic function is about 13.5.

Quantitative treatment is complicated because of high insolubility and polyfunctionality of TAA. The pK_b value we proposed indicates a very low basicity, which is reflected in a decreased nucleophilic reactivity.

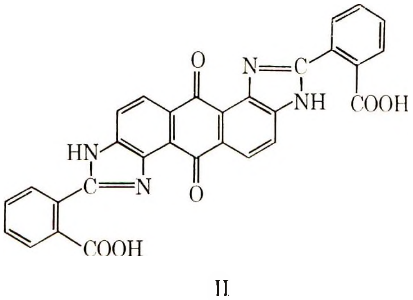
Nucleophilic Substitutions

TAA does not react (or reacts very slowly) with benzoic acid or phenyl benzoate at their boiling points. Bisimidazo[1,2,5,6]anthraquinone-2,8 diphenyl (I) can be prepared by treating TAA with excess benzoyl chloride in boiling acetophenone.

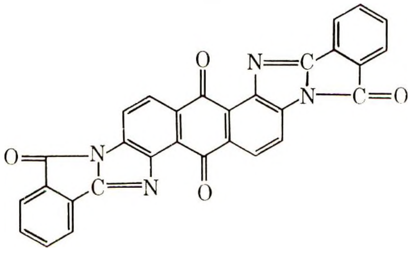


I

TAA reacts easily with phthalic anhydride to give mainly 2,8 di-*o*-carboxyphenyl-bisimidazo[1,2,5,6]anthraquinone (II). Analysis, however, indicates that some further ring closure to the pyrrolone derivative (III) has occurred.



II

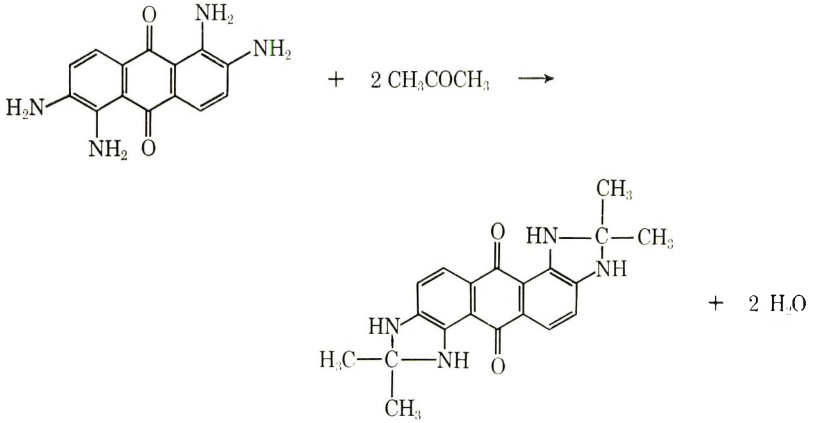


III

If II is heated at high temperatures, complete ring closure can be effected. Excess benzoyl chloride in dimethylacetamide at room temperature reacts with TAA to give 1,2,5,6-tetrabenzoylaminoanthraquinone.

Nucleophilic Additions

Reactions with Ketones. We found that TAA reacts very rapidly with most ketones according to eq. (1).

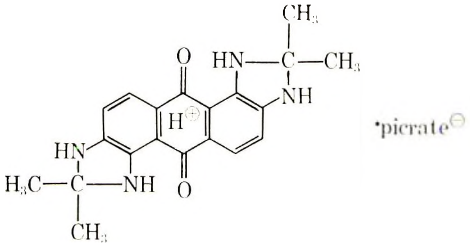


IV

(1)

The reaction product can be hydrolyzed with diluted sulfuric acid and yields the starting TAA. This proves that no carbon-carbon bonds are involved in this reaction.

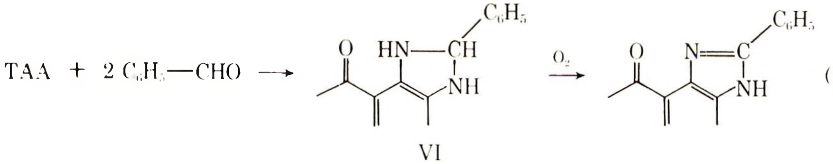
The product (IV) crystallizes with one mole of picric acid. Since anthraquinone compounds (and other conjugated systems) are often described as bases, we are inclined to think the proton of our complex is interacting with the π-electron system of the anthraquinone nucleus (V). If the free electron pairs of the nitrogens were to be considered as basic centers, we would expect more than one mole of picric acid in the molecule.



V

By using this reaction, ketones may be detected in low concentrations (less than 0.1% in acetic acid).

Reactions with Aldehydes. Upon heating in acetic acid, benzaldehyde and TAA give 2,8-diphenyl bisimidazo[1,2,5,6]anthraquinone in very good yield. We think an intermediate imidazoline product (VI) is likely (benzoic acid does not react with TAA).



VI

(2)

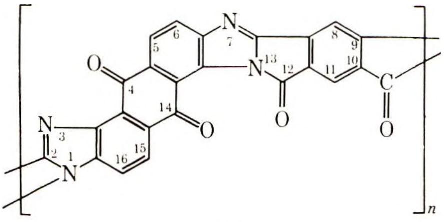
Polymerization

TAA with Pyromellitic Anhydride (PMA). The polycondensation of TAA and PMA was effected in dimethylacetamide as a solvent. After a while the polymer precipitates. The complete system is evaporated to remove the solvent and heated gradually to 400°C. A considerable increase in viscosity of the polymer during this dry heating is noticed (Table I).

TABLE I

	Heating		
Time, hr.	Pressure, mm Hg	Temperature, °C	η_{inh} (30°C, H_2SO_4)
20	0.5	150	0.16
20	0.5	250	0.2
4	0.5	310	
3	0.5	350	0.4
2	0.5	400	Insoluble

Analyses, after heating, indicate a complete ring closure to the pyrrolone structure (VII).



VII

The polymer with η_{inh} = 0.4 is soluble in a mixture of dimethylformamide $-H_2O-Na_2S_2O_4-KOH$ in concentrations up to 10%.

The TGA curve (Fig. 1) shows little weight loss below 500°C.

TAA and Phthaloyl Chlorides. When TAA is treated with acid chlorides in solvents more basic than TAA, a very slow reaction occurs. In acidic solvents, reaction occurs more easily. If TAA and isophthaloyl chloride are mixed in boiling nitrobenzene, a highly insoluble product separates. If a solution of acid chloride is dropped into a boiling solution of TAA

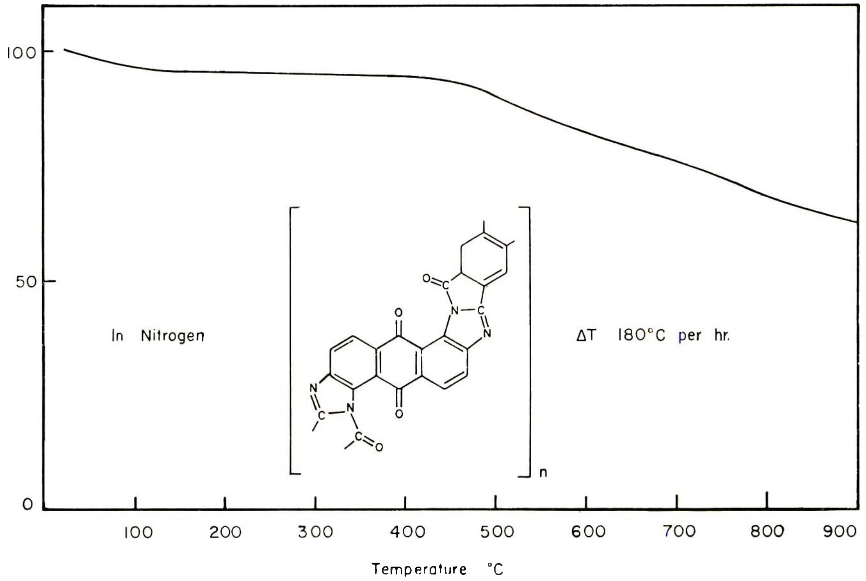
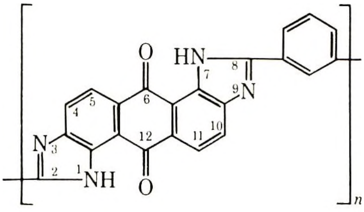


Fig. 1. TGA curve for pyrrolone from 1,2,5,6-tetraaminoanthraquinone and pyromellitic anhydride.

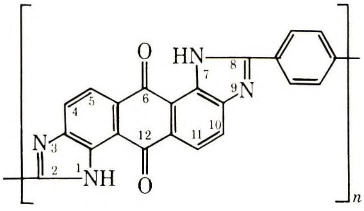
(nitrobenzene as a solvent), a soluble product separates (VIII) which has $\eta_{inh} = 0.19$ (30°C, H_2SO_4).



VIII

and shows λ_{max} at 5375, 5150, and 3875 Å. Absorptions at 5375 and 5150 Å indicate, most probably, free amine groups. This may be caused by incomplete ring closure (although the polymer has been heated to 350°C) or by substitution on two adjacent amine groups. Elemental analysis supports the same view. Figure 2 shows the TGA curve for VIII.

The polymer from terephthaloyl chloride and TAA (IX) has approximately the same properties ($\eta_{inh} = 0.22$) as the *m*-isomer. The TGA curve is given in Figure 3.



IX

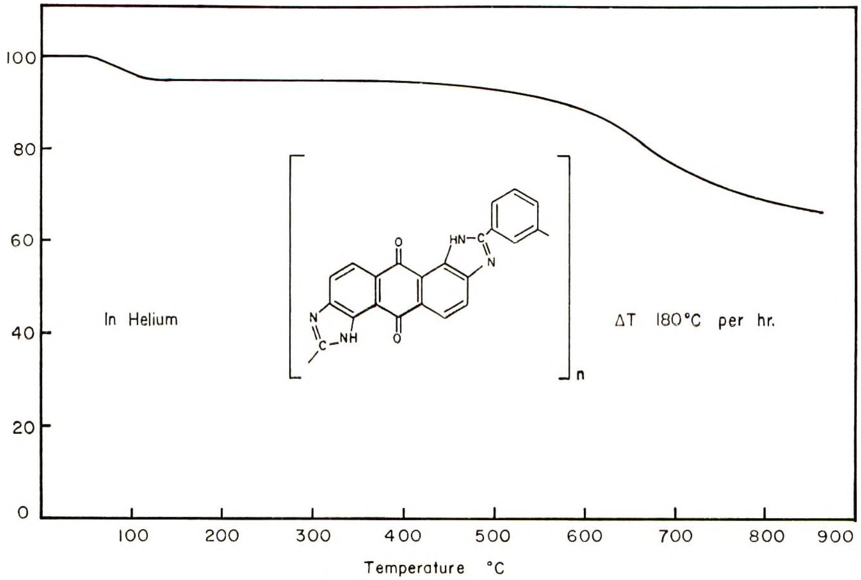


Fig. 2. TGA curve for polybenzimidazole from isophthaloyl chloride and 1,2,5,6-tetraaminoanthraquinone.

Both polymers dissolve in 60% dimethylformamide on reduction with sodium dithionite.

EXPERIMENTAL

Monomers and Model Compounds

1,2,5,6-Tetraaminoanthraquinone

2,6-Diacetaminoanthraquinone. In a 500-ml three-necked flask equipped with a heating jacket, a mechanical stirrer, and a reflux condenser were placed 100 ml of glacial acetic acid, 100 ml of acetic anhydride, 50 g of 2,6-diaminoanthraquinone, (K and K Laboratories) and 10 drops of concentrated sulfuric acid. The reaction mixture was heated to boiling and refluxed (while stirring) for 2 hr. The diaminoanthraquinone did not dissolve but changed color during its transformation. Afterwards, the mixture was cooled, filtered and washed with some glacial acetic acid. The diacetamino compound was dried in a vacuum oven. Diacetaminoanthraquinone melts higher than 360°C. The yield of brown product was 100% (67 g).

The product recrystallized from HOAc, nitrobenzene, and (more easily) dimethylformamide.

ANAL. Calcd for $C_{18}H_{12}N_4O_8$: C, 67.80%; H, 4.35%; N, 8.70%. Found: C, 66.50%; H, 4.33%; N, 8.66%.

2,6-Diaminoanthraquinone has the following absorption characteristics: λ_{max}, 3950 and 3440 Å; E, 17.564 and 32,368 l./mole-cm.

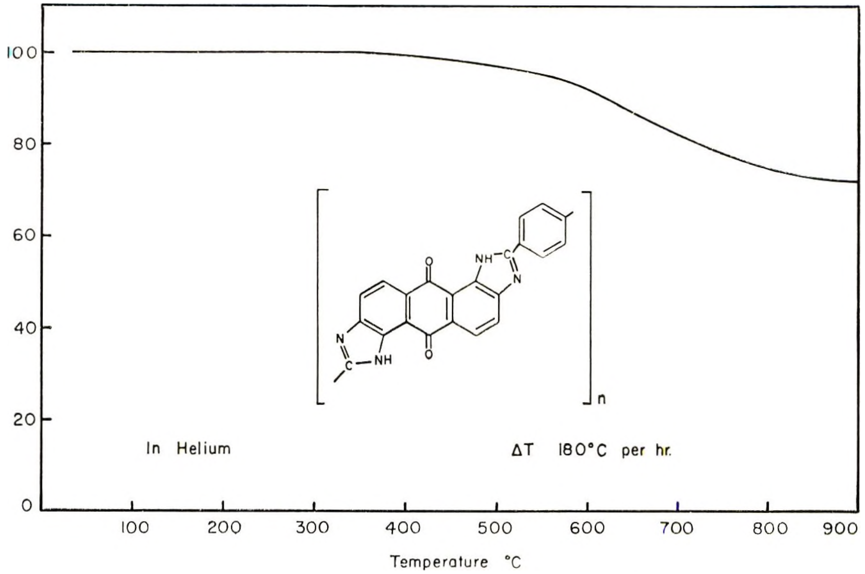


Fig. 3. TGA curve for polybenzimidazole from terephthaloyl chloride and 1,2,5,6-tetraaminoanthraquinone.

2,6-Diacetaminoanthraquinone has the following absorption characteristics: λ_{max}, 3580 and 3120 Å; *E*, 12,236 and 30,268 l./mole-cm.

1,5-Dinitro-2,6-diacetaminoanthraquinone. In a 500-ml three-necked flask, equipped with a mechanical stirrer and a thermometer, were placed 400 g of concentrated sulfuric acid and 50 g of potassium nitrate. The mixture was cooled in an ice bath. Then 25 g of finely divided diacetaminoanthraquinone was added to the vigorously stirred mixture. The temperature was not allowed to exceed 5°C. The diacetamino compound was dissolved within thirty minutes. The nitration was continued for 4 hr 0–5°C. During nitration some dinitro compound separated. The product was poured onto much ice. The mixture was filtered and washed throughly until the filtrate was acid-free. The dinitro compound remained as a yellow cake. It was dried in a vacuum oven at 60°C. The product can be recrystallized from dimethyl sulfoxide, mp >360°C. The yield, after precipitation, was quantitative. After recrystallization, the yield was 60–70%.

ANAL. Calcd for $C_{18}H_{12}N_4O_8$: C, 52.43%; H, 2.91%; N, 13.59%. Found: C, 52.70%; H, 3.34%; N, 13.97%. λ_{max}, 3450 and 2830 Å; *E*, 7,725 and 28,428 l./mole-cm.

1,5-Dinitro-2,6-diaminoanthraquinone. In a two-necked, 1-liter flask equipped with a mechanical stirrer, 400 ml of sulfuric acid was mixed with 200 ml of water (giving 80% sulfuric acid). The mixture was cooled, and 40 g of dinitrodiacetamino compound was added. The flask was heated to 95°C and held at this temperature for 90 min. After this time hydrolysis was complete. The mixture was poured on 1.5 kg of ice and filtered. The cake was washed until acid-free. A dark brown product resulted, mp >360°C.

ANAL. Calcd for $C_{14}H_8N_4O_6$: C, 51.22%; H, 2.44%; N, 17.07%. Found: C, 51,75%; H, 2.46%; N, 16.65%. λ_{max}, 3950 and 3420 Å; *E*, 11,676 and 19,680 l./mole-cm.

1,2,5,6-Tetraaminoanthraquinone. The wet cake obtained in the previous step was transferred to a two-necked, 1-liter flask, equipped with a mechanical stirrer. Additional water was added in such a quantity as to put the total weight of the cake plus the water at 400 g. Then $Na_2S \cdot 9H_2O$ (90 g) was added. The mixture was stirred and heated on a steam bath for 1 hr. The reduction proceeded in solid phase and the mixture turned violet. After 1 hr the flask was cooled and the contents filtered. The tetraamino compound was washed several times with distilled water until the filtrate was neutral.

The black product was dried *in vacuo* at 50°C. A 25-g portion of dinitrodiacetaminoanthraquinone yielded 15 g tetraaminoanthraquinone. A 100-ml portion of boiling acetophenone dissolved 1 g of tetraaminoanthraquinone and yielded upon cooling 0.4–0.5 g of pure compound, mp >360°C.

ANAL. Calcd for $C_{14}H_{12}N_4O_2$: C, 62.68%; H, 4.51%; N, 20.88%. Found: C, 63.26%; H, 4.69%; N, 20.39%. λ_{max}, 5600, 5300, and 3060 Å; *E*, 16780, 18626 and 15276 l./mole-cm.

The NMR resonance (DMSO-d_6) showed NH_2 singlets at 2.72 and 4.42 τ and aromatic doublets at 2.88 and 3.55 τ; $J = 8$ cps.

1-Nitro-2,6-diacetaminoanthraquinone. A 20-g portion of 2,6-diacetaminoanthraquinone was dissolved in 100 ml of nitric acid (90%). The product dissolved in 10 min, and the nitration was continued for 1 hr at 0–5°C. The mixture was precipitated in ice, filtered, and washed. The product was mainly a mononitro compound. It was easily recrystallized from formic acid, mp 300°C (dec).

ANAL. Calcd for $C_{18}N_{13}N_3O_6$: C, 58.86%; H, 3.54%; N, 11.44%. Found: C, 58.37%; H, 4.71%; N, 11.89%. λ_{max}, 3555 and 3090 Å; *E*, 8881 and 23671 l./mole-cm.

2,8-Diphenyl-bisimidazo[1,2,5,6]anthraquinone

A mixture of 0.75 g of TAA, 5 ml of benzoyl chloride, and 75 ml of acetophenone, was refluxed for 1 hr. After cooling, 100 mg of product separated. This compound was dried for 4 hr at 250°C/0.5 mm Hg and finally recrystallized from acetophenone; mp >360°C.

ANAL. Calcd for $C_{28}H_{16}N_4O_2$: C, 76.35%; H, 3.66%; N, 12.72%. Found: C, 76.48%; H, 3.94%; N, 12.73%. λ_{max}, 4125 and 3400 Å (DMF); 4075 Å (H_2SO_4).

Infrared analysis (in KBr) showed –NH– absorption at 3400 cm^{-1}.

*2,8-Di-*o*-carboxyphenyl-bisimidazo[1,2,5,6,]anthraquinone*

A 0.75-g portion of TAA and 20 g of phthalic anhydride were melted together and kept at 250°C for 1 hr. The mixture was cooled and treated with acetone. The imidazole was filtered and dried at 250°C/0.5 mm Hg for 5 hr.

For purification the product was dissolved in dilute sodium hydroxide, filtered, and precipitated by acidification. The precipitated compound was extracted with water for 24 hr. The imidazole compound was dried under vacuum at 110°C; mp >360°C.

Anal. Calcd for $C_{30}H_{16}N_4O_6$: C, 68.16%; H, 3.03%; N, 10.61%. Found: C, 69.24%; H, 3.25%; N, 10.90%.

Analysis indicated ring closure to a slight extent. Infrared analysis (in KBr) showed –NH– absorption at 3360 cm^{-1}.

Complete ring closure to a pyrrolone structure was effected by heating the product for 2 hr at 380°C/0.4 mm Hg.

Anal. Calcd for $C_{30}N_{12}N_4O_4$: C, 73.17%; H, 2.46%; N, 11.38%. Found: C, 73.19%; H, 2.64%; N, 11.61%. λ_{max}, 4025 Å (in H_2SO_4).

Infrared analysis (in KBr) indicated disappearance of the –NH– absorption.

1,2,5,6-Tetrabenzoylaminoanthraquinone

To a solution of 535 mg of TAA in 30 ml of dimethylacetamide, 5 ml of benzoyl chloride was added. After 3 hr at room temperature, 1.2 g of tetrabenzoyl derivative separated. The product was crystallized from nitrobenzene. It decomposed at 350°C.

Anal. Calcd. for $C_{43}H_{28}N_4O_6$: C, 74.13%; H, 4.04%; N, 8.04%. Found: C, 73.32%; H, 4.08%; N, 8.80%. λ_{max}, 3900 Å.

2,2,8,8-Tetramethyl-bis-dihydroimidazo[1,2,5,6]anthraquinone

To a mixture of 0.5 g of TAA and 30 ml of acetic acid, 1 ml of acetone was added. After 10 min at 80°C, the reaction was complete and the solution was cooled. Some of the addition product separated (150 mg) but most of it remained in solution. The product was recrystallized from HOAc–toluene; mp 340° (dec).

Anal. Calcd for $C_{20}H_{20}N_4O_2$: C, 68.95%; H, 5.79%; N, 16.08%. Found: C, 68.47%; H, 5.88%; N, 16.17%. λ_{max}, 6040 and 5500 Å (in HOAc).

The product is red in acetone, dimethylformamide, and pyridine and blue in formic acid, acetic acid, and water. In many solvents, the color depends upon the temperature: in toluene at −70°C it is blue; at 110°C it is red.

To prepare the picrate, the reaction was conducted in the same way as before. An additional gram of picric acid was added. The salt was less soluble than the free base: 600 mg separated. The product was purified by crystallization from acetic acid; mp >360°C.

Anal. Calcd for $C_{26}H_{23}N_7O_9$: C, 54.07%; H, 4.01%; N, 16.98%. Found: C, 54.40%; H, 4.44%; N, 16.52%. λ_{max}, 6060 and 5600 Å (in HOAc).

Hydrolysis of the imidazoline compound was carried out as follows: 100 mg of imidazoline product was dissolved in 3 ml of 80% sulfuric acid. The mixture was heated for 15 min at 80°C, cooled, and poured on ice. Ammonium carbonate was added until neutral. The TAA was filtered and identified by comparison of its infrared spectrum with that of an original sample.

2,8-Diphenyl-bisimidazo[1,2,5,6]anthraquinone from TAA and Benzaldehyde

To a mixture of 0.1 g of TAA and 50 ml of HOAc, 1 ml of benzaldehyde was added. The mixture was boiled for 15 min. After cooling, 75 mg of imidazole separated. The product was identical (infrared analysis) with a sample previously described in this paper.

Polymers

Condensation of TAA and PMA (Polymer VII)

A solution of 1073.1 mg of TAA and 872.4 mg of pyromellitic anhydride (recrystallized from toluene) in 15 ml of dimethylacetamide (distilled over CaH_2) was heated for 4 hr at 150°C. During this time, the prepolymer precipitated. The mixture was dried at 150°C/0.4 mm for 24 hr; η_{inh} = 0.2 (in H_2SO_4, 30°C). Subsequently, the product was heated 4 hr at 300°C/0.5 mm Hg and 3 hr at 350°C/0.5 mm Hg; = 0.4 (in H_2SO_4, 30°C). The polymer was still soluble in H_2SO_4.

ANAL. Calcd. for $(C_{24}H_6N_4O_4)_n$ (closed structure): C, 69.57%; H, 1.45%; N, 13.53%. Found: C, 67.97%; H, 3.04%; N, 13.64%. λ_{max}, 3810 Å (in H_2SO_4).

The presence of open rings in this compound is obvious. The ring closure was finally completed by heating the polymer for 2 hr at 400°C/0.5 mmHg.

ANAL. Found: C, 69.39%; H, 2.56%; N, 14.10%.

After the final ring closure, the polymer was highly insoluble (sulfuric acid or NaOH + $Na_2S_2O_4$). A 65 mg portion of the polymer with η_{inh} = 0.4 was soluble in a mixture of 0.75 ml of 60% DMF, 150 mg of $Na_2S_2O_4$, and 100 mg of KOH. The reaction was conducted at room temperature and under nitrogen. The reduction was complete in 1 hr.

The polymer name is: poly[(4,14-dihydro-4,12,14-trioxoisoindolo[2,1-a]-anthra[2,1-*d*:5,6-*d'*]diimidazole-1,2,9,10(12*H*)-tetrayl)-10-carbonyl].

Condensation of TAA and Phthaloyl Chlorides

The following procedure was used: 536.5 mg of TAA was dissolved in 200 ml boiling, dry nitrobenzene. A solution of 406 mg of isophthaloyl chloride in 50 ml nitrobenzene was dropped into the boiling TAA solution during 15 min. The mixture was boiled for an additional 2 hr and cooled. The polymer was filtered and dried for 15 hr at 250°C. The product (polymer VIII) dissolved completely in sulfuric acid within 24 hr. It had $\eta_{inh} = 0.19$ (30°C, H_2SO_4).

ANAL. Calcd for $(C_{22}H_{10}N_4O_2)_n$: C, 72.92%; H, 2.78%; N, 15.46%. Found: C, 69.69%; H, 3.24%; N, 14.89%.

A similar reaction was carried out with terephthaloyl chloride. The product, Polymer IX, had $\eta_{inh} = 0.22$ (30°C, H_2SO_4).

ANAL. Found: C, 68.92%; H, 3.26%; N, 14.46%; Cl 1.07%.

Both polymers were further heated at 350°C/0.5 mm Hg for 3 hr prior to TGA.

These imidazole polymers are soluble in a mixture of DMF, H_2O, $Na_2S_2O_4$, and KOH.

The polymers are named poly[1,6,7,12-tetrahydro-6,12-dioxoanthra-[1,2-*d*:5,6-*d'*]diimidazole-2,8-diyl)-*m*-phenylene] and poly[(1,6,7,12-tetrahydro-6,12-dioxoanthra[1,2-*d*:5,6-*d'*]diimidazole-2,8diyl)-*p*-phenylene].

Characterization

Viscosities were measured at 30°C with 0.5 g/100 ml H_2SO_4 solutions. The absorption maxima were measured on dimethylformamide solutions unless otherwise stated. Only the range from 6500 A to 3,000 Å was scanned.

We are indebted to Dr. G. Ehlers, Air Force Materials Laboratory, Wright Patterson Air Force Base, for the thermogravimetric curves and to Dr. K. Loening, Chemical Abstracts Service, for help in naming the new polymers.

This work was supported by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

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Received April 24, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3189–3198 (1970)

Polymers Containing Anthraquinone Units: Polyimidazoles and Polypyrrolones from 1,2,5,6-Tetraaminoanthraquinone

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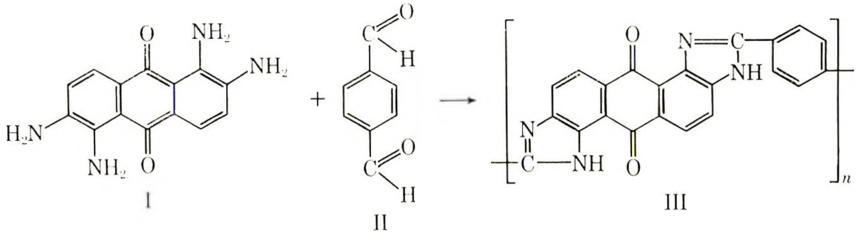
Synopsis

1,2,5,6-Tetraaminoanthraquinone has been condensed with isophthalaldehyde and terephthalaldehyde and their bisulfite addition compounds to yield new heat-stable polymers. It has also been condensed with pyromellitic anhydride to give the pyrrolone. The highest viscosities were obtained in polymers prepared with acid catalysts. The polymers were nearly all soluble in concentrated sulfuric acid but not in organic solvents. Those soluble in sulfuric acid could also be solubilized by reduction with sodium dithionite and potassium hydroxide in aqueous organic solutions. A few polymers were apparently crosslinked, since they would not dissolve in either sulfuric acid or in base on reduction. Weak fibers were obtained by spinning the reduced alkaline solutions of the polymers into aqueous acid.

Polymers with anthraquinone recurring units have been studied because they should be capable of solution in basic media on reduction with sodium hydrosulfite and therefore could be more easily fabricated than most of the thermally stable polymers. Some previous work in this laboratory[1] has indicated this possibility. However, it was found that 1,2,5,6-tetraaminoanthraquinone (TAA) reacted very poorly with aromatic dibasic acid chlorides or diphenyl esters so that imidazoles could only be obtained with low molecular weights. Likewise the condensation of TAA with pyromellitic anhydride gave only a low molecular weight pyrrolone under the conditions examined.

RESULTS AND DISCUSSION

It has now been found that the reaction of 1,2,5,6-tetraaminoanthraquinone (I) with isophthalaldehyde and terephthalaldehyde (II) will produce the desired imidazoles (III) in fair yields and with good viscosities.



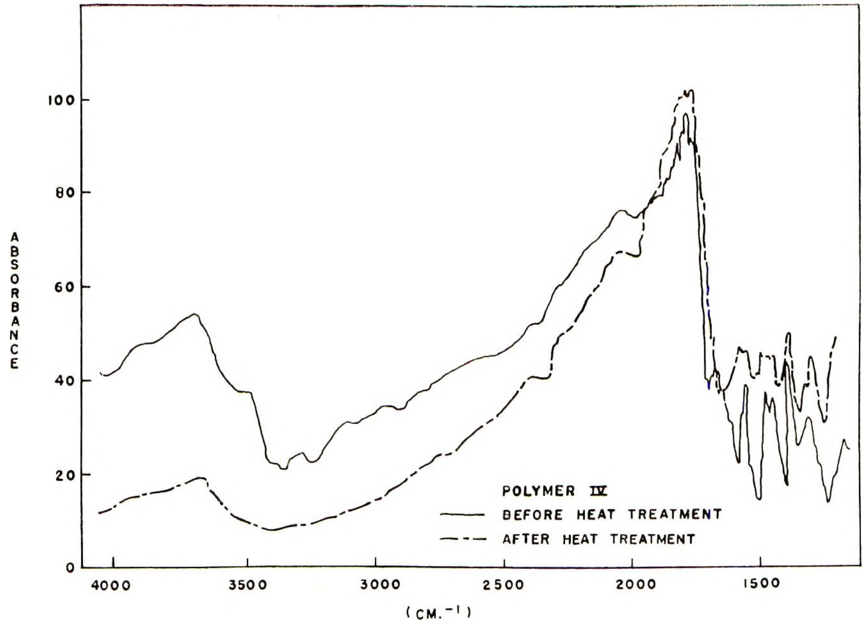


Fig. 1. TGA curve for anthraquinone benzimidazole polymer.

The use of a free aldehyde in the reaction, however, leads to the formation of some so-called aldehydines[2] and crosslinking results. When the dialdehyde dibisulfite adduct was used in place of the free aldehyde,[3] the reaction gave good yields of low molecular weight imidazole derivatives which were completely soluble.

It was found that polymer formation occurred best when the reagents were mixed in solution and heated rather slowly up to 90°C. This avoided early decomposition of the bisulfite adducts. After about 1 hr at 90°C the temperature was raised to 160°C for 2 hr to complete the reaction.

The polymers were all insoluble in organic solvents but were somewhat soluble in concentrated sulfuric acid. The portion soluble in sulfuric acid could also be dissolved in a mixture containing 65% aqueous dimethylformamide by reducing them with sodium dithionite and potassium hydroxide under a nitrogen atmosphere. One polymer from the tetraamine and terephthalaldehyde (expt. 6, Table I) was dissolved in concentrated sulfuric acid to give a 10% solution, and this was injected from a hypodermic needle into water. A weak fiber was produced. When the polymer was dissolved in 65% aqueous DMF by reduction it was only possible to get a very dilute solution. The use of 90% aqueous dimethyl sulfoxide and subsequent reduction gave an 8% solution of polymer. When 10% of polymer was added, the solution turned to a thick paste. By spinning the 8% solution in aqueous acid a self-supporting fiber was obtained.

A TGA curve (Fig. 1) taken on polymer 6, Table I, in nitrogen showed a weight loss of 2% at 100°C, indicating absorbed moisture. Above 100°C there was a slight weight loss up to 500°C and then up to 20% weight loss

TABLE I

Polybenzimidazoles from TAA with Terephthalaldehyde or Its Bisulfite Adduct

Expt.	Reactants	Amount, g	Solvent		Conditions	Yield, %	η_{inh} (H_2SO_4)	Solubility in H_2SO_4, %	Further treatment	η_{inh} (H_2SO_4)	Solubility in H_2SO_4, %
			Type[a]	ml							
1	TAA	0.8590	DMAc	80	7 hr, reflux (N_2);	70	0.26	70	7 hr, 250°C;		
	TPA	0.4427			2 hr, reflux (air)				3 hr, 300°C	0.3	70
2	TAA	0.8590	DMAc	80	2 hr, reflux (N_2);	93	0.54	64	7 hr, 250°C	0.79	38
	TPA	0.4427	HAc	8	2 hr, reflux (air)				3 hr, 300°C	0.80[b]	35
3	TAA	0.8448	HAc	150	1 hr, 140°C (N_2)	92	0.17	100			
	TPA	0.4204									
4	TAA	0.8448	DMAc	73	2 hr, 160°C (N_2);	83	0.3	100	6½ hr, 350°C	0.4	98
	TPA	0.4204		7	1 hr, 160°C (air)						
5	TAA	0.8590	DMAc	88	1 hr at 25°C (N_2);	89	0.17	100			
	Dibisulfite				1 hr at 90°C;						
	adduct TPA	1.1295			2 hr at 160°C (N_2);						
					2 hr at 160°C (air)						
6	TAA	0.8590	DMAc	80	As above	89	0.85	100	7 hr, 250°C	0.81[c]	100
	dibisulfite										
	adduct TPA	1.1295	HAc	8							
7	TAA	0.8590	$C_6H_5NO_2$	80	As above	93	0.97	100			
	Dibisulfite										
	adduct TPA	1.1295	HAc	8							
8	TAA	0.8590	DMAc	80	As above	86	0.48	100			
	Dibisulfite										
	adduct TPA	1.1295	TFAc	8							

[a] Solvents: dimethylacetamide (DMAc), glacial acetic acid (HAc), trifluoracetic acid (TFAc).

[b] ANAL. Calcd for $C_{22}H_{10}N_4O_2$: C, 72,92%; H, 2.78%; N, 15.46%. Found: C, 71.50%; H, 3.45%; N, 14.3%; Res. 1.19%.

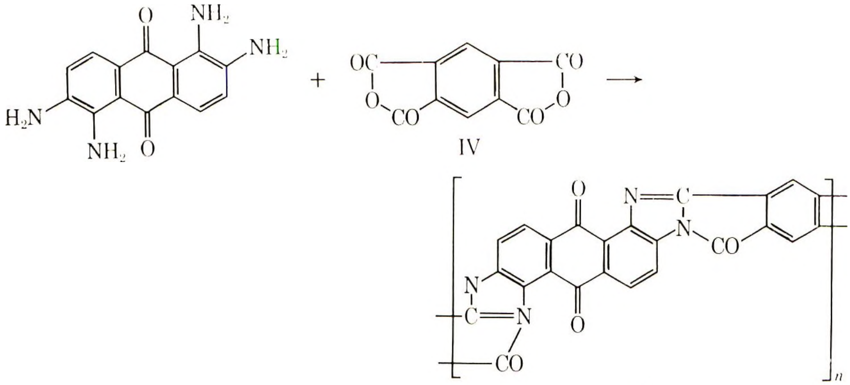
[c] ANAL. Found: C, 71.04%; H, 3.53%; N, 15.12%.

between 500 and 900°C. This is very much like other aromatic polybenzimidazoles performances in the same test.[4]

Some of the experiments with terephthalaldehyde (TPA) and 1,2,5,6-tetraaminoanthraquinone (TAA) are summarized in Table I.

1,2,5,6-Tetraaminoanthraquinone and the dibisulfite adduct of isophthalaldehyde also react better than do the amine and the free aldehyde. The free aldehyde gives an 86% yield of polymer which is only 73% soluble in sulfuric acid, whereas the dibisulfite gives essentially the same yield of a completely soluble polymer. Table II contains the details of some experiments. Again it will be noted that heating the low molecular weight polymer first obtained, raises the inherent viscosity of the product. It was not possible to get a polymer from isophthalaldehyde which had an inherent viscosity of more than 0.5 (H_2SO_4).

The condensation of pyromellitic anhydride (PMDA) (IV) and 1,2,5,6-tetraaminoanthraquinone was carried out under a variety of conditions as noted in Table III.



IV

V

When dimethylacetamide or dimethyl sulfoxide were used as solvents, only rather low inherent viscosities were observed for the polymers. When *p*-nitrophenol or dimethylacetamide containing acetic acid or trifluoroacetic acid as catalysts was used as a solvent, the polymers had higher inherent viscosities, and these could be increased by heating the polymer after the isolation from solution. Sulfuric acid did not seem to be a satisfactory acid to add as a catalyst.

The pyrrolone (V) obtained in experiment 19, Table III, could be dissolved in 90% aqueous dimethyl sulfoxide on reduction with sodium hydrosulfite to yield a 10% polymer solution. However, after heating this polymer to 350°C, no solution could be obtained in the above aqueous DMSO reduction system. However, a 20% solution could be obtained in 65% aqueous DMSO on reduction. Alkaline reduction seemed to open the imide ring to give a nonladder structure.

The TGA curve for this polymer (Fig. 2) in nitrogen shows very little loss of weight below 500°C.

TABLE II

Polybenzimidazoles from TAA and Isophthalaldehyde (IPA) or Its Bisulfite Adduct

			Solvent								
Expt.	Reactants	Amount, g	Type	Amount, ml	Conditions	Yield, %	η_{inh} (H_2SO_4)	Solubility in H_2SO_3, %	Further treatment	η_{inh} (H_2SO_4)	Solubility in H_2SO_4, %
9	TAA	0.8590	DMAc	80	2 hr reflux (N_2);	86	0.27	73			
	IPA	0.4427	HAc	8	3 hr reflux (air)						
10	TAA + dibisulfite adduct of IPA	0.8590	DMAc	80	1 hr, 25°C (N_2); 1 hr, 90°C (N_2); 1 hr, 160°C (N_2); 1 hr, 160°C (air)						
	IPA	1.1295	HAC	8		85	0.19	100	7 hr, 250°C	0.29	87
11	TAA + dibisulfite adduct of	0.8590	$C_6H_5NO_2$	80	As above	84	0.23	100	7 hr, 250°C	0.41	100
	IPA	1.8295	HAc	8					3 hr, 310°C	0.52	100

TABLE III
Polypyrrolones from TAA and PMDA

Expt.	Reactants	Amount, g	Solvent Type	Solvent Amount, ml	Conditions	Yield, %	η_{inh} (H_2SO_4)	Solubility in H_2SO_4, %	Further Treatment	η_{inh} (H_2SO_4)	Solubility in H_2SO_4, %
12	TAA	0.8590	DMAc	30	1 hr, 25°C (N_2);	94	0.08	100	7 hr, 250°C	0.1	100
	PMDA	0.7198			4½ hr, 160°C (N_2)				3 hr, 310°C	0.15	100
									3 hr, 350°C	0.2	100
									3 hr, 400°C	0.22	100
									3 hr, 450°C		Mostly insoluble
13	TAA	0.2812	DMSO	15	1 hr, 25°C (N_2);				7 hr, 250°C;		
	PMDA	0.2399			5 hr, 110°C (N_2)	91	0.08	100	3 hr, 320°C	0.1	5
14	TAA	0.2812	DMAc	27	1 hr, 25°C (N_2);						
					1 hr, 130°C (N_2);				7 hr, 250°C	0.23	100
	PMDA	0.2399	HAc	3	1 hr, 180°C (N_2)	97	0.15	100	3 hr, 310°C	0.25	86
15	TAA	0.4295	*p*-Nitrophenol 15 g		4 hr, 145°C (N_2)	96	0.16	98	5 hr, 250°C	0.2	90
	PMDA	0.3599							3 hr, 310°C	0.3	97
16	TAA	0.4295	DMAc	40	4 hr, 150°C (N_2)	76			7 hr, 250°C	0.53	100
									3 hr, 300°C	0.53	100
	PMDA	0.3599	TFAc	4					3 hr, 350°C	—	Insoluble
17	TAA	0.4295	DMAc	40	4 hr, 150°C (N_2)	55	0.15	100			
	PMDA	0.3599	H_2SO_4	7 drops							
18	TAA	0.8048	DMAc	30	3 hr, 120°C (N_2)	85			1 hr, 300°C	0.23	95
	PMDA	0.6544									
19	TAA	0.4295	DMAc	40	4 hr, 150°C (N_2)	76		100	7 hr, 250°C;		
	PMDA	0.3599	TFAc	4					5 hr, 300°C;		
									4 hr, 350°C	0.48[a]	10

[a] ANAL. Calcd for $C_{24}H_6N_4O_4$: C, 69.57%; H, 1.45%; N, 13.53%. Found: C, 68.81%; H, 2.21%; N, 12.98%.

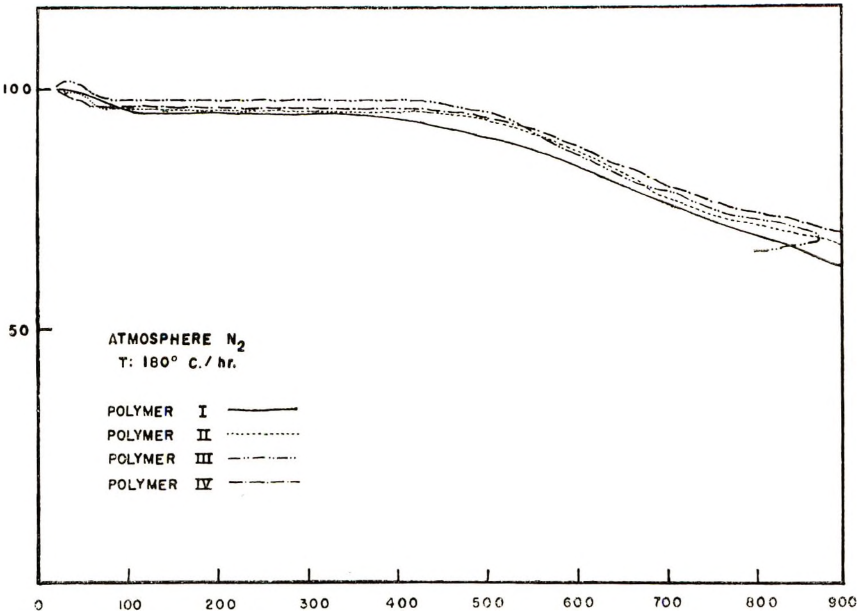


Fig. 2. TGA curve for anthraquinone pyrrolone polymer.

EXPERIMENTAL

Model Compounds

2,8-Diphenylbisimidazo[1,2,5,6]anthraquinone from TAA and Benzaldehyde in Acid DMAc. A solution of 0.39 g (0.0015 mole) of TAA and 0.35 g (0.0033 mole) of benzaldehyde in 36 ml DMAC and 4 ml glacial acetic acid was heated under nitrogen to 165°C for 2 hr and then for 1 hr in air. Most of the solvent was evaporated under vacuum and the residue precipitated in water. The yield was 0.68 g (100%). After recrystallization from acetophenone and evaporating the mother liquor to 5 ml, 45% of a yellow model compound was obtained, mp >360°C. By pouring the solution into ether–hexane (1:1), 27% of dark brown product was obtained. It had a melting point of 280°C after recrystallization from chlorobenzene. The infrared spectra of both products were identical but the ultraviolet absorption in H_2SO_4 had $\lambda_{max} = 4090$ Å for the model compound and $\lambda_{max} =$ 4000 and 2300 Å for the meltable product.

ANAL. Calcd for $C_{28}H_{16}N_4O_2$: C, 76.35%; H, 3.66%; N, 12.72%. Found: C, 75.78%; H, 3.80%; N, 12.19%; residue, 1.00%.

ANAL. Calcd for unknown sideproduct $C_{35}H_{20}N_4O_2$: C, 79.50%; H, 3.85%; N, 10.60%. Found: C, 76.74%; H, 4.14%; N, 10.84%; residue, 1.44%.

Model Compound from TAA and the Bisulfite Adduct of Benzaldehyde in Acidic Nitrobenzene. A solution of 0.39 g (0.0015 mole) of TAA and 0.65 g (0.0031 mole) of the bisulfite adduct of benzaldehyde in 72 ml of nitrobenzene and 8 ml of glacial acetic acid was stirred under nitrogen for 1 hr at room temperature and then heated 1 hr at 90°C, 1 hr at 160°C, and another 2 hr at 160°C under air. A yield of 0.53 g (80%) of the model compound was obtained.

Polymers

Polyimidazoles from TAA + Terephthalaldehyde. **(Expt. 1, Table 1).** In a three-necked 100 ml flask fitted with a stirrer, gas inlet tube, and a reflux condenser capped with a $CaCl_2$ tube, a mixture of 0.8590 g (0.0033 mole) of TAA and 0.4427 g (0.0033 mole) of terephthalaldehyde in 80 ml of dry DMAc was refluxed under nitrogen. After 4 hr the solution began to turn red; after heating 7 hr under nitrogen and 2 hr in air, the reaction mixture was poured into 800 ml of ligroin and filtered. The yield was 0.91 g (70%) of a polymer with an inherent viscosity of 0.26 (soluble to the extent of 70% in H_2SO_4). The inherent viscosity was measured on a solution prepared by dissolving 0.5–0.7 g in 100 ml concentrated H_2SO_4 at 40°C, sometimes with heating to 120°C. The solution was filtered through a M-size glass filter. After heating the dry polymer 7 hr to 250°C and 3 hr to 300°C *in vacuo*, the viscosity of the soluble portion was 0.23 (soluble to the extent of 60% in H_2SO_4).

The other experiments reported in Table I were performed in a similar manner, but occurred much more quickly under acid conditions.

Dibisulfite Adduct of Terephthalaldehyde. In 75 ml of H_2O, 7.86 g (0.075 mole) of $NaHSO_3$ was dissolved and the solution diluted to 500 ml with methanol. Then 5 g (0.037 mole) of terephthalaldehyde was added. After 60 hr stirring at room temperature and filtration, the precipitate was carefully washed with methanol and then ether. The adduct was dried at room temperature at 0.1 mm Hg to yield 12.8 g (about 100%) of a white crystalline product without a melting point up to 300°C.

ANAL. Calcd for $C_8H_8O_8S_2Na_2$: C, 28.1%; 2.34%; S, 18.7%. Found: C, 26.45%; H, 3.09%; S, 17.28%.

Stability of the Adduct under Acid Conditions. A mixture of 0.5648 g (0.00165 mole) of the dibisulfite adduct of terephthalaldehyde in 40 ml of DMAc and 4 ml of glacial acetic acid was stirred under nitrogen 1 hr at room temperature and heated 1 hr at 90°C. After pouring into 400 ml of benzene 0.35 g (63%) of the starting material was obtained as indicated by the infrared spectra. The same reaction was carried out with heating for 1 hr at 25°C, 1 hr at 90°C, and 1 hr at 160°C under nitrogen and 1 hr at 160°C in air. The adduct went completely into solution above 90°C, and over 0.12 g (70%) of $NaHSO_3$ separated.

Dibisulfite Adduct of Isophthalaldehyde. The dibisulfite adduct of isophthalaldehyde was prepared as described above for the terephthalaldehyde to yield 7.2 g (57%) of a white crystalline product without a melting point up so 300°C.

ANAL. Calcd for $C_8H_8O_8S_2Na_2$: C, 28.1%; H, 2.34%; S, 18.7%. Found: C, 25.91%; H, 2.70%; S, 17.29%.

Stability of the Adduct under Acid Conditions. A mixture of 0.5648 g (0.00165 mole) of the dibisulfite adduct of the isophthalaldehyde was stirred under nitrogen at room temperature for 1 hr and heated 1 hr at 90°C. The adduct went into solution and was precipitated in 100 ml of ether to yield 0.44 g (78%) of the starting material as shown by infrared spectra. The same reaction was carried out with 1 hr at 25°C, 1 hr at 90°C, and then 1 hr at 160°C under nitrogen and 1 hr at 160°C in air. The adduct dissolved completely at 90°C but after heating to 160°C, 0.11 g (65%) of $NaHSO_3$ precipitated.

Reduction of the Polymer. Polymer 2 (Table I) (12 mg) was stirred at room temperature and under nitrogen in 4 ml of 65% aqueous DMF solution containing 0.6 g of $Na_2S_2O_4$ and 0.6 g of KOH. Only 3 mg (20–25%) went into solution.

In concentrated H_2SO_4 the polymer was divided into a soluble (38%) and an insoluble (62%) part. The soluble part of the polymer could be completely solubilized in the same reaction mixture as above. A 1% solution was pressed through a syringe into acid to form a very brittle fiber. The insoluble part of the polymer could not be dissolved on reduction under the same conditions.

A mixture of 0.11 g (8%) of the polymer from Exp. No. 6; 0.5 g KOH, 0.5 g $Na_2S_2O_4$ and 1.4 ml of 90% aqueous solution of DMSO were stirred under nitrogen. The viscosity of the solution increased during the first 2 hr. After another hr. the viscous solution was pressed through a syringe into 1 N HCl to form a weak fiber.

A 10% solution (0.14 g) of polymer 6 formed a paste that could not be pressed through a syringe.

A 8% solution (0.11 g) of polymer 6 in a 90% aqueous solution of DMF also formed a paste.

Polybenzimidazoles from TAA and Isophthalaldehyde or Derivatives (Expt. 9, Table II). Analogous to the polymer preparation with terephthalaldehyde, the reaction of TAA and isophthalaldehyde was carried out in 80 ml of DMAc and 8 ml oi glacial acetic acid. After refluxing 2 hr under nitrogen and 3 hr in air, the reaction mixture was filtered to yield 1.12 g (86%) of a polymer with an inherent viscosity of 0.27 and a residue of 27% insoluble in sulfuric acid. The other experiments reported in Table II were similar.

Polypyrrolones from TAA and PMDA (Expt. 12, Table III). A mixture of 0.8590 g (0.0033 mole) of TAA and 0.7198 g (0.0033 mole) of PMDA in 30 ml of DMAc was stirred under nitrogen for 1 hr at 25°C; the temperature was then raised to 160°C for $4^1/_2$ hr. The reaction mixture was poured into 500 ml of ligroin and then filtered to collect the product. The yield was 1.5 g (84%) of a polymer with an inherent viscosity of 0.08. After heating for 7 hr at 250°C the product had $\eta_{inh} = 0.1$ and after a further 3 hr at 310°C $\eta_{inh} = 0.15$. After 3 hr at 350°C the product had $\eta_{inh} = 0.2$ and after 3 hr at 400°C, $\eta_{inh} = 0.22$. When the polymer was heated for another 3 hr to 450° C it became mostly insoluble in concentrated H_2SO_4.

The other experiments reported in Table III were similar.

We are indebted to Dr. G. F. L. Ehlers of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, for the thermogravimetric curves.

This work was supported by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

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Received April 24, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3199–3209 (1970)

Polymers Containing Anthraquinone Units: Benzimidazole and Benzothiazole Polymers

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Synopsis

In an attempt to synthesize soluble polymers, diphenyl 1,5-anthraquinonedicarboxylate was treated with 3,3′-dimercaptobenzidine and 3,3′-diaminobenzidine under various conditions. Although the ester reacted readily, side reactions prevented the formation of high molecular weight compounds. It was thought that at the elevated temperatures required for reaction, the quinone group was involved in a type of Schiff's base formation. The thermal stability of the polymers was evaluated. Model compounds were prepared and their absorption spectra were compared with those of the polymers. It was observed that 1,5-anthraquinonebibenzimidazole-2 formed a stable product with acetic acid. Some of the polymers could be solubilized by reduction with sodium dithionite in alkali, but no useful fibers were produced from these solutions.

INTRODUCTION

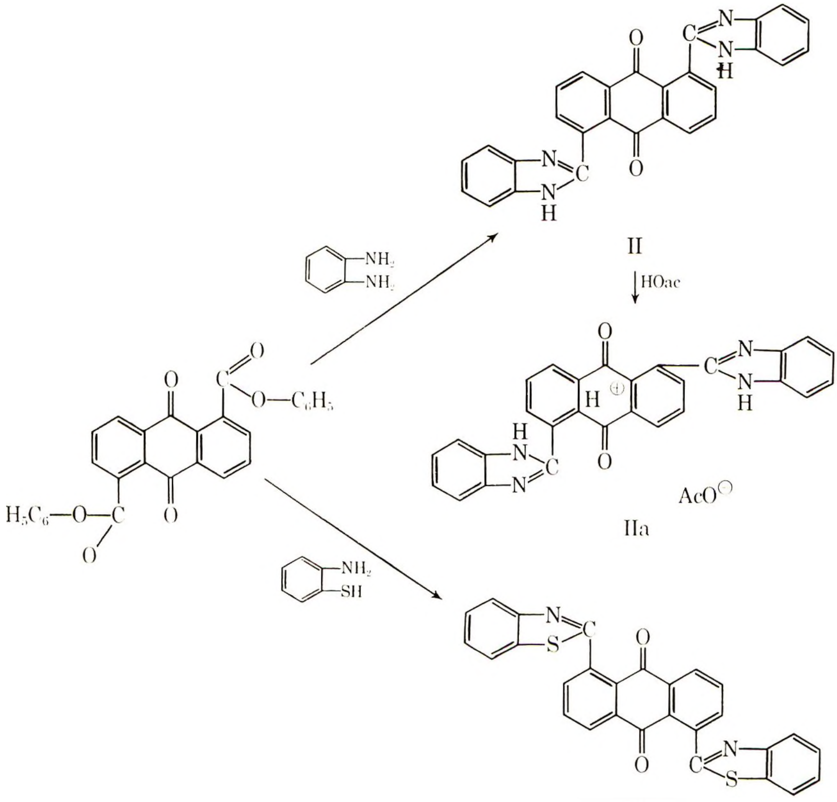
For several years, the thermal and oxidative stability of aromatic structures, linked by heterocyclic nuclei, has been recognized and a variety of this kind of polymers has been synthesized.[1,2] Benzimidazoles and benzothiazoles have been prepared from carboxylic acid derivatives and *o*-diamino- or *o*-aminothiol aromatic compounds. Brinker and Robinson[3] and Vogel and Marvel[4] prepared benzimidazoles, while Hergenrother et al.[5] synthesized benzothiazoles. However, most of these compounds had very high melting points and were usually insoluble in the common solvents. This problem would be overcome by having solubilizing groups in the polymer. One of the possibilities, it seemed to us, was the implantation of an anthraquinone unit in the chain. It has been known for a long time to vat dye chemists that such compounds can be transformed by reduction into an alkali soluble leucoform, which in turn by oxidation regenerated the water-insoluble starting material.[6]

RESULTS AND DISCUSSION

Model Compounds

The dicarboxylic acid derivative, best suited for synthesis of benzimidazoles or benzothiazoles of high molecular weight has been reported to be the diphenyl ester.[4] The diphenyl 1,5-anthraquinonedicarboxylate (DPAC) was expected to be more reactive due to the decreased electron withdrawing effect of the quinone carbonyl groups. The ease with which the condensation reactions occurred in the latter case proved this assumption to be correct. Reaction of *o*-aminothiophenol with diphenyl 1,5-anthraquinonedicarboxylate in veratrole resulted in 1,5-anthraquinonebibenzothiazole-2′(I).

The reaction of the same ester with *o*-phenylenediamine in veratrole or diphenyl ether did not occur, but with diethylaniline (DEA) as a solvent, 1,5-anthraquinonebibenzimidazole-2′ (II) was obtained. Compound (II) was soluble in acetic acid after prolonged boiling and crystallized then with one mole of acid. If salt formation occurred on the free electron pairs of the nitrogen, we would expect more than one mole of acid on the molecule. Since anthraquinone compounds (like other conjugated systems) are capable of forming a sigma complex [7] the proton could interact with the π-electrons of the anthraquinone unit (IIa). Bracke[8] reported an analogous behavior for other anthraquinone derivatives.



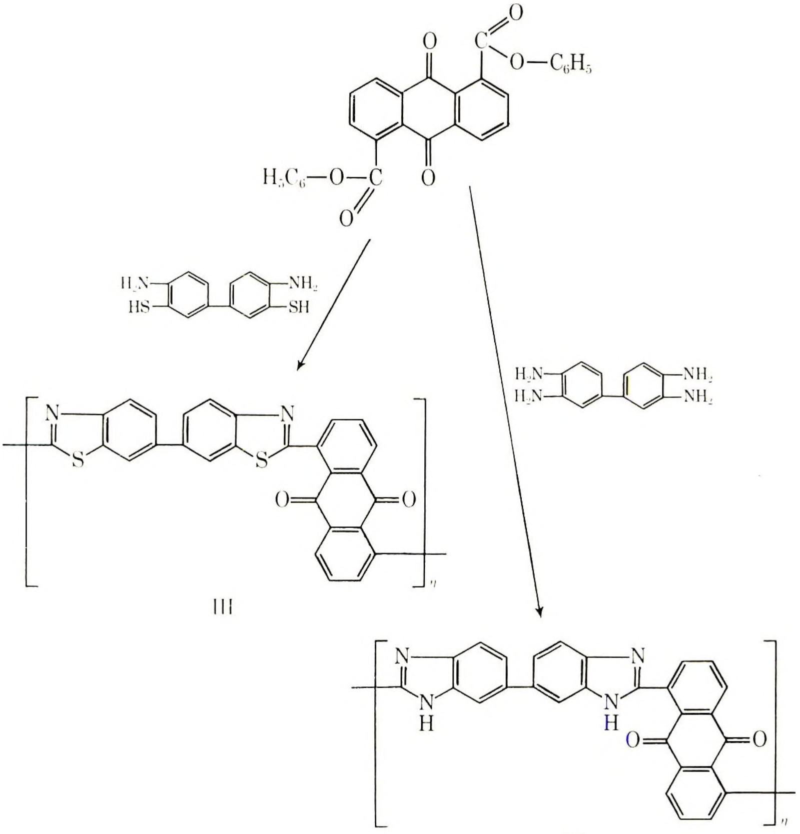
II

IIa

I

Polymers

The preparation of poly[(6,6′bibenzothiazole)-2,2′-diyl-1,5-anthraquinonylene] (III) and poly[(5,5′-bibenzimidazole)-2,2′-diyl-1,5-anthraquinonylene] (IV) was attempted in different solvents and in the melt.

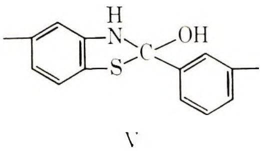


III

IV

Although polyphosphoric acid (PPA) has been used as a solvent in the synthesis of a variety of bisbenzothiazoles,[9] polybenzothiazoles,[5,10] and polybenzimidazoles[11] of high molecular weight, no experiments were done in this medium because reactions between anthraquinone and aniline were reported to be catalyzed by acids.[12] Bracke[8] described the self-condensation of 2,6-diaminoanthraquinone in PPA to a black insoluble product.

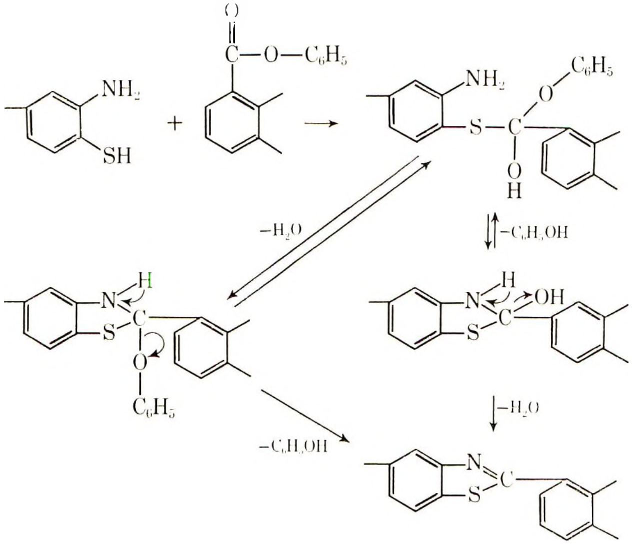
Reaction of diphenyl 1,5-anthraquinonedicarboxylate with 3,3′-dimercaptobenzidine (DMB) in veratrole yielded a low molecular weight compound (III). Analysis showed an incomplete loss of water, presumably due to the presence of some hydroxybenzothiazole structures (V). The same feature had been observed for polybenzimidazoles.[13]



V

Reactions of dimercaptobenzidine dihydrochloride and aromatic carboxylic and dicarboxylic derivatives in *N,N*-dimethylaniline[14] or *N,N*-diethylaniline[5] (DEA) have been reported. In DEA, diphenyl 1,5-anthraquinonedicarboxylate reacted with DMB to produce polybenzothiazoles with fairly high molecular weight. The heating time did not influence the molecular weight, due to the insolubility of the polymer. When the polymer was prepared in the melt, crosslinking started around 300°C, limiting the attainable molecular weight.

Our analytical results suggested that phenol is lost first, a slight modification of the mechanism, proposed by other authors.[5]



Diphenyl 1,5-anthraquinonedicarboxylate and 3,3′-diaminobenzidine (DAB) in hexamethylphosphoramide yielded an insoluble product. The high ratio of nitrogen to carbon suggested transamidation by the solvent. In tetrahydrothiophene-1,1′-dioxide, a polymer with a satisfactory analysis was obtained. However, this product proved to be insoluble.

A polybenzimidazole of fairly high molecular weight was obtained by melting the two monomers at elevated temperatures. Here too, as for the polybenzothiazoles, the polymer crosslinked at around 300°C. This was a quite general observation for all reactions involving anthraquinones and amino containing compounds at high temperatures. It was thought that the quinone group formed Schiff's bases. The phenol, liberated in the polymerization, could act as a weak acid to catalyze this condensation. Table I summarizes some of the results.

Ultraviolet spectra (Table II) of the benzothiazole compounds showed absorption at around 286 mμ and a second peak at 266 mμ. The first one, also found for the diphenyl ester derivative, was thought to be caused by the anthraquinone moiety; the absorption coefficient did not change very much for the model bibenzothiazole and the polymers. The peak at 266 mμ, believed to be due to the benzothiazole part, was characterized by a

TABLE I
Data on Preparation and Inherent Viscosity of Polyanthraquinones

Starting materials	Experimental conditions	Inherent viscosity[a]	Reduction[b]
DPAC + DMB	Boiling veratrole (207°C) for 12 hr	0.05	
DPAC + DMB·2HCl	Boiling DEA (215°C)		
	for 20 min	0.29	+
	for 2 hr	0.28	+
DPAC + DMB	Melt 3 hr at 240°C (N_2); 12 hr at 300°C (vacuum)	0.29	+
	Melt 3 hr at 240°C (N_2); 5 hr at 350°C (vacuum)	Insoluble	−
DPAC + DAB	Hexamethylphosphoramide 240°C for 1 hr	Insoluble	
DPAC + DAB	Tetrahydrothiophene-1,1′-dioxide 240° for 1 hr	Insoluble	
DPAC + DAB	Melt 12 hr at 220°C (N_2), 1 hr at 300°C (vacuum)	0.14	
	3 hr at 260°C (N_2) 10 hr at 300°C (vacuum)	0.33	+

[a] Inherent viscosity of an 0.1–0.2% solution in sulfuric acid at 30.2°C.

[b] (+) Soluble in alkali after reduction; (−) insoluble in alkali after reduction.

marked hypochromism. This had been observed for other polymers too and could be attributed to intramolecular effects.

All polymers which were soluble in sulfuric acid could be dissolved in alkali after reduction to the dihydroanthraquinone. They precipitated in an acid solution. Only in one case, poly[(6,6′-bibenzothiazole)-2,2′-diyl-1,5-anthraquinonylene], prepared in diethylaniline, could we spin a fiber which was still very brittle.

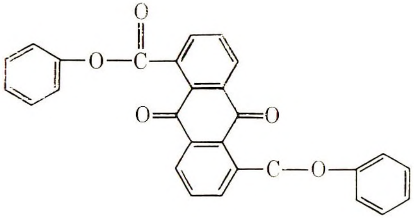
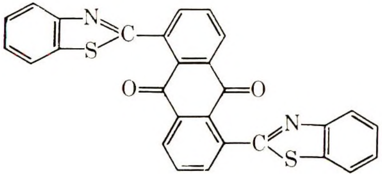
EXPERIMENTAL

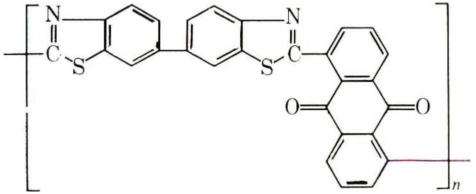
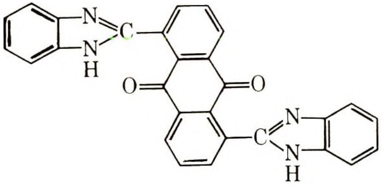
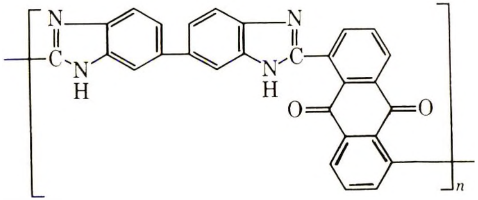
Monomers

1,5-Anthraquinonedicarboxylic Acid Dichloride. The free acid was prepared according to Scholl[15] (diazotation of 1,5-diaminoanthraquinone, a Sandmeyer reaction with cuprous cyanide, and alkaline hydrolysis of the obtained 1,5-dinitriloanthraquinone) or Coulson[16] (substitution by cuprous cyanide on 1,5-dichloroanthraquinone, followed by sulfuric acid treatment). The diacid dichloride was prepared by the action of phosphorus pentachloride in phosphorus oxychloride on the acid. It was obtained as yellow crystals, mp 260–263°C (lit.[15] mp 263°C).

Diphenyl 1,5-Anthraquinonedicarboxylate. 1,5-Anthraquinonedicarboxylic acid dichloride (10 g) and phenol (15 g) were boiled in 300 ml of pyri-

TABLE II
Ultraviolet Absorption of Some Anthraquinone Derivatives

Substance	Analysis		UV spectra	
	Calcd, %	Found, %	λ_{max}, mμ	$E^{1\%}_{1\ cm}$ cm × 10^{-3}
	C, 75.00	C, 74.83	235	0.64
	H, 3.59	H, 3.64	286	0.85
	O, 21.41	O, 21.38		
	C, 70.86	C, 70.86	264	1.08
	H, 2.97	H, 3.15		
	N, 5.90	N, 6.03	286	0.82
	S, 13.51	S, 13.38		

	C, 71.1 H, 2.52 N, 5.93 S, 13.55	C, 70.62 H, 3.02 N, 6.38 S, 12.83 Res., 1.98	266 287	0.63 0.6
	C, 76.31 H, 3.65 N, 12.71	C, 75.49 H, 4.13 N, 12.73	263 279	1.17 0.95
	C, 76.7 H, 3.21 N, 12.77	C, 77.08 H, 3.83 N, 14.09	250 280	0.89 0.69

dine for 2 hr. The mixture was cooled and the precipitate filtered off. This was recrystallized from DMF and for a second time from veratrole. A yellow-white product was obtained, mp 325–326°C (dec).

Anal. Calcd: C, 75.00%; H, 3.59%; O, 21.41%. Found: C, 74.83%; H, 3.64%; O, 21.38%.

3,3′-Dimercaptobenzidine. This compound was prepared according to the known procedure.[17] The free base was obtained by dissolving the dipotassium salt of 3,3′-dimercaptobenzidine (4 g) in water (60 ml) and filtering to remove the insoluble material. The filtrate was then poured into a solution of glacial acetic acid (2 ml) in water (2 ml) and cooled to 0°C. The white solid was filtered, washed with water, and dried. All the operations were done under nitrogen.

Anal. Calcd for $C_{12}H_{12}N_2S_2 \cdot 2HCl$: C, 44.86%; H, 4.39%; N, 8.72%; S, 19.96%. Found: C, 44.44%; H, 4.07%; N, 9.08%; S, 19.75%.

3,3′-Diaminobenzidine. This monomer was obtained from Celanese Corporation of America. It could be purified by sublimation at 175–178°C/0.04–0.05 mm Hg.

Model Compounds and Polymers

General Procedure. All the reactions were done under a nitrogen atmosphere. Therefore, the apparatus was carefully purged with pure nitrogen by repeated evacuation and refilling. For reactions in solution, the capacity of the vessel was about twice the volume of the solvent used, for reactions in the melt ten times the volume of the reactants. It is to be noted that, in reactions in the melt, the anthraquinone compound did not really melt, but around 220°C there was a darkening of the reaction mixture and evolution of water and phenol.

If not noted otherwise, the inherent viscosities were measured at 30.2°C in sulfuric acid solution and ultraviolet absorption spectra were taken on solutions at an $1.5 \times 10^{-3}\%$ concentration in sulfuric acid.

1,5-Anthraquinonebibenzothiazole-2′. Diphenyl 1,5-anthraquinonedicarboxylate (1 g) and *o*-aminothiophenol (750 mg) were boiled in 100 ml of veratrole for 1 hr. The red solution was cooled, the precipitate filtered, washed with alcohol and recrystallized from DMF. The yield of yellow-green crystals was 650 mg; mp > 350°C.

Anal. Calcd: C, 70.68%; H, 2.97%; N, 5.90; S, 13.51%. Found: C, 70.68%; H, 3.15%; N, 6.03%; S, 13.38%.

1,5-Anthraquinonebibenzimidazole-2′. Diphenyl 2,5-anthraquinonedicarboxylate (1.1 g) and *o*-phenylenediamine (800 mg) were boiled in 150 ml of diethylaniline. After 15 min a brown product began to precipitate. Boiling was continued for 45 min, the reaction mixture was then cooled, the crystals separated, washed with alcohol and dried. The yield of golden-brown product was 950 mg; mp > 350°C.

ANAL. Calcd: C, 76.31%; H, 3.65%; N, 12.71%. Found: C, 75.49%; H, 4.13%; N, 12.73%.

This product, insoluble in most organic solvents (alcohol, xylene, DMF) could be recrystallized from acetic acid.

ANAL. Calc. for $C_{28}H_{16}N_4O_2 \cdot CH_3COOH$: C, 72.0 %; H, 4.03%; N, 11.2%. Found: C, 72.59%; H, 4.13%; N, 11.14% After this compound was dried at 250°C/0.1 mm Hg, we found: C, 74.39%; H, 3.43%; N, 10.66%. After washing with diluted ammonia, we found: C, 72.23%; H, 3.59%; N, 11.20%.

Poly[(6,6′-bibenzothiazole)-2,2′-diyl-1,5-anthraquinonylene]. A solution of diphenyl 1,5-anthraquinonedicarboxylate (1.495 g) and 3,3′-dimercaptobenzidine (0.828 g) in 150 ml of veratrole was heated under nitrogen for 12 hr at 210°C. Precipitation began after a short time. The mixture was cooled and the brown-red precipitate filtered off and washed with hot DMF and methanol. The yield, after drying, was 1.319 g.

ANAL. Calcd: C, 71.1%; H, 2.52%; N, 5.93%; S, 13.55%. Calcd for an open structure $C_{28}H_{16}N_2O_4S_2$: C, 66.1%; H, 3.16%; N, 5.51%; S, 12.62%. Found: C, 65.9%; H, 3.09%; N, 6.00%; S, 12.77%.

The inherent viscosity, measured at 0.2% concentration in sulfuric acid, was 0.05.

Diphenyl 1,5-anthraquinonedicarboxylate (1.495 g) and 3,3′-dimercaptobenzidine dihydrochloride (1.071 g) were dissolved in diethylaniline and the solution warmed to boiling. After a few minutes, precipitation of a red product started. Refluxing was continued for an additional 2 hr. The mixture was then cooled, poured out into methanol, and the solid filtered off. The yield after drying was 956 mg.

ANAL. Calcd for $C_{28}H_{12}N_2O_2S_2 \cdot C_6H_5OH$: C, 72.06%; H, 3.21%; N, 4.95%; S, 11.31%. Found: C, 68.30%; H, 3.60%; N, 5.42%; S, 11.72%; residue, 1.01%.

The inherent viscosity, measured at 0.2% concentration in sulfuric acid was 0.28.

Equivalent amounts of diphenyl 1,5-anthraquinonedicarboxylate and 3,3′-dimercaptobenzidine were ground together and warmed under nitrogen for 3 hr at 240°C. The reaction flask was then cooled, vacuum was applied, and the mixture brought to 300°C and allowed to stay at that temperature for 12 hr. After cooling, the polymer was washed with hot DMF and alcohol. The yield, after drying was 97%.

ANAL. Found: C, 71.9%; H, 3.40%; N, 3.33%; S, 9.95%.

The inherent viscosity, measured at 0.12% concentration in sulfuric acid (product was soluble to the extent of 59%) was 0.29.

The same procedure was followed but this time the prepolymer was heated at 350°C for 5 hr/0.1 mm Hg pressure.

ANAL. Found: C, 70.62%; H, 3.02%; N, 6.38%; S, 12.83%; residue, 1.98%.

This product was insoluble in all solvents, even sulfuric acid.

Poly[(5,5′-bibenzimidazole)-2,2′-diyl-1,5-anthraquinonylene]. Diphenyl 1,5-anthraquinonedicarboxylate (1.495 g) and 3,3′-diaminobenzidine (714 mg) were dissolved in 100 ml of hexamethylphosphoramide and the solution heated at 240°C for 1 hr. After cooling, the reaction mixture was poured into methanol (800 ml) and the solid filtered off and dried. The yield was 744 mg.

Anal. Calcd: C, 76.7%; H, 3.21%; N, 12.77%. Found: C, 63.88%; H, 4.58%; N, 13.63%; residue, 4.38%.

This product was insoluble in sulfuric acid.

The same reaction procedure was followed, but with tetrahydrothiophene-1,1′-dioxide as solvent.

Anal. Found: C, 74.2%; H, 3.45%; N, 13.01%; residue, 1.07%.

This product, too, was almost completely insoluble in sulfuric acid.

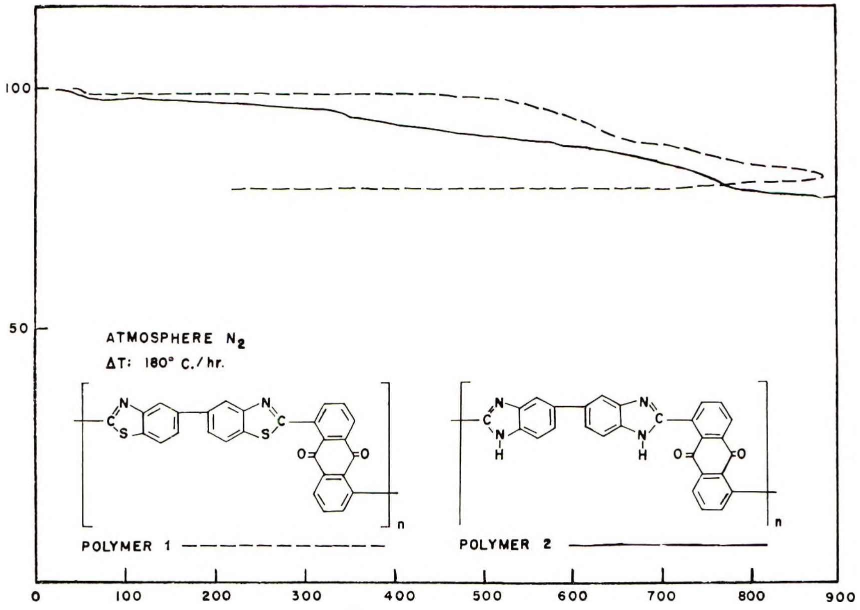


Fig. 1. TGA curves of (--) benzothiazole and (——) benzimidazole anthraquinone polymers.

Equivalent amounts of diphenyl 1,5-anthraquinonedicarboxylate and 3,3′-diaminobenzidine were melted together under nitrogen and kept for 12 hr at 220°C. Vacuum was then applied, while the temperature was raised to 300°C in 4 hr. The mixture was cooled, ground, washed with DMF and methanol. The yield, after drying, was 1.41 g.

Anal. Found: C, 77.08%; H, 3.83%; N, 14.09%; residue, 0.62%.

The inherent viscosity, measured at 0.2% concentration in sulfuric acid was 0.14.

The previous procedure was followed, but the monomers were heated for 3 hr at 260°C under nitrogen, and for 10 hr at 300°C/0.2 mm Hg.

ANAL. Found: C, 73.8%; H, 3.79%; N, 12.46%; residue, 2.44%.

The inherent viscosity, measured at 0.18% concentration in sulfuric acid (the product was soluble to the extent of 90%) was 0.33.

Reduction and Solubility in Base. Sodium dithionite (100 mg), potassium hydroxide (100 mg), and the polymer (100 mg) were mixed in 2 ml of a solution of water and DMF (1:1) under nitrogen. This solution was put into a syringe and discharged into an acid aqueous solution. The hydroanthraquinone polymer precipitated with a violet appearance, which gradually turned to brown due to oxidation. The fiber which precipitated was very brittle.

We are indebted to Dr. Kurt L. Loening, Chemical Abstracts Service for the names of our polymers. We are indebted to Dr. G. F. L. Ehlers, Air Force Materials Laboratory, Wright-Patterson Air Force Base, for thermogravimetric curves.

This work was supported by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

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Received April 28, 1970.

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3211–3224 (1970)

Polymers Containing Anthraquinone Units: Polycondensations 1,2,5,6-Tetraaminoanthraquinone with Some Tetrachloroquinoxaline Compounds

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Synopsis

New ladder and partial ladder aromatic heteropolymers have been synthesized from 1,2,5,6-tetraaminoanthraquinone, 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene, 2,2′-3,3′-tetrachloro-6,6′-diquinoxaline, 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl ether and 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl sulfone. The polycondensations were carried out in solution and in melt. The inherent viscosities of polymers were in the range of 0.1–0.44. These polymers were highly colored, showed good thermal stability and were soluble in concentrated sulfuric acid and methanesulfonic acid. The structures of the polymers were established by comparison with model compounds.

INTRODUCTION

In earlier publications,[1-5] it was demonstrated that polymers containing quinoxaline recurring units of high molecular weight could be prepared by the condensation of suitable aromatic tetraamines with tetrasubstituted quinoxaline derivatives. It was also shown that these polymers have remarkable thermal stability. In a continuation of this work, some new polymers and model compounds have been synthesized. This report describes the preparation of thermally stable ladder or partial ladder polymers from tetraaminoanthraquinone by the condensation with 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene, 2,2′,3,3′-tetrachloro-6,6′-diquinoxaline, 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl ether and 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl sulfone.

The melt condensation of 2,3-dichloroquinoxaline with *o*-aminophenol or *o*-aminothiophenol to give quinoxalinebenzooxazine[6] or quinoxalinebenzothiazine,[7] has been reported. It has also been reported that the model reaction of an *o*-diamine with 2,3-dihydroxy-,[8] 2,3-dichloro-,[9] or 2,3-diphenoxyquinoxaline[1] occurs. Similar model compounds were made to show that polymers with recurring unit from tetraaminoanthraquinone and tetrachloro compounds could be obtained with the closed ring structure (I).

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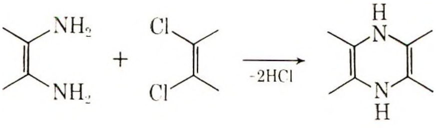
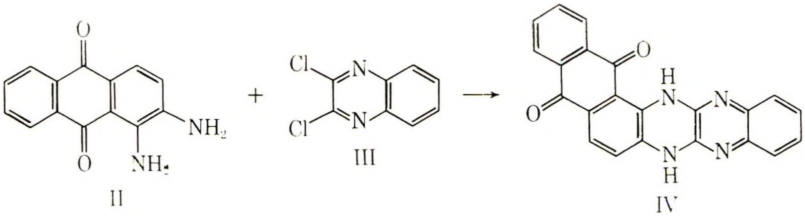


I

Model reactions for this type of polymerization have been studied in several solvents, such as pyridine, *N*,*N*-diethylaniline, *N*,*N*-dimethylacetamide, tetramethylene sulfone, and hexamethylphosphoramide to find conditions suitable for corresponding polymerization procedures.

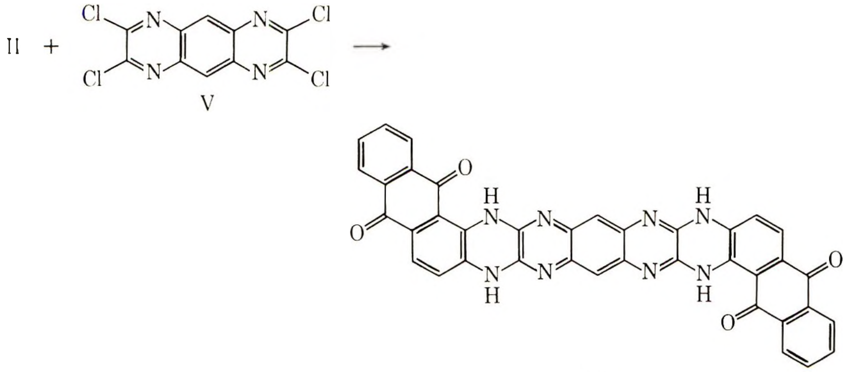
RESULTS AND DISCUSSION

Condensation of 1,2-diaminoanthraquinone (II) with 2,3-dichloroquinoxaline[10] (III) in tetramethylene sulfone yielded product IV in nearly quantitative yields.



II III IV

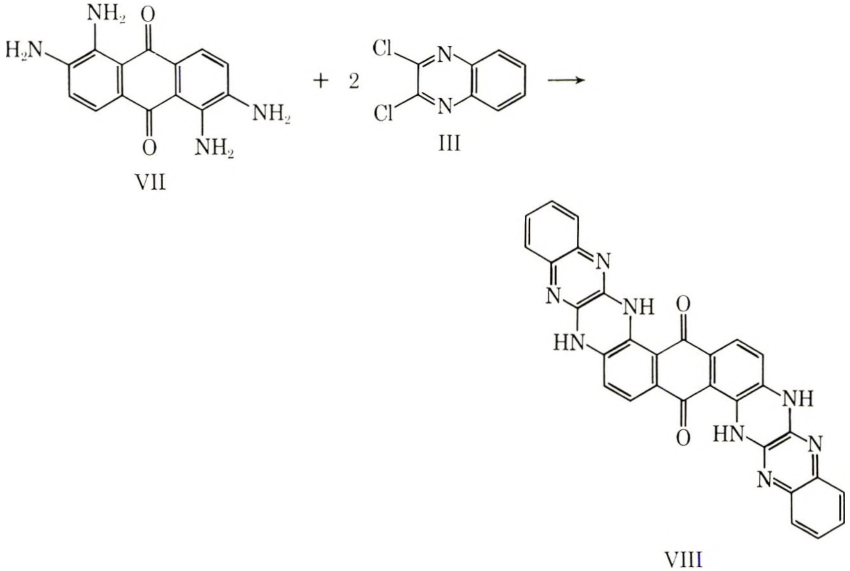
Model compound VI was prepared by condensation of 1,2-diaminoanthraquinone (II) and 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene[1] (V) in different solvents such as pyridine, *N*,*N*-diethylaniline, a 4:1 mixture of *N*,*N*-dimethylacetamide and *N*,*N*-diethylaniline at the boiling temperature, and tetramethylene sulfone at 220°C or 320°C. for 4 hr. The products thus obtained were finally heated at 350°C to produce completely closed ring structures.



VI

Another model reaction for the polymerization was studied by using 1,2,-5,6-tetraaminoanthraquinone[10] (VII) and 2,3-dichloroquinoxaline [11,12]

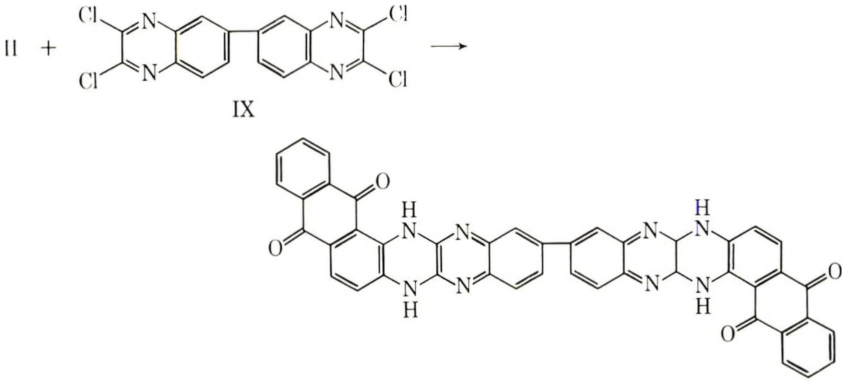
(III) in pyridine or tetramethylene sulfone. Elemental analysis showed that the two compounds did not react to give a completely ring closed structure until heated at 350°C under reduced pressure.



VII III

VIII

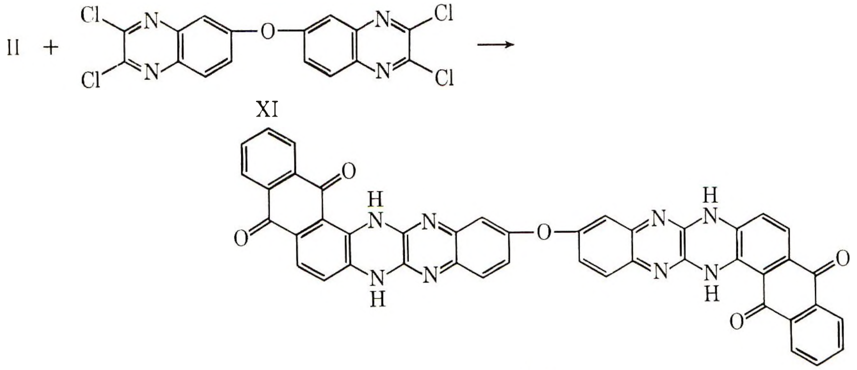
Model compound X was prepared from 1,2-diaminoanthraquinone (II) and 2,2′,3,3′-tetrachloro-6,6′-diquinoxaline[1] (IX) in pyridine solution with final heating at 350°C for 6 hr under vacuum. Structure X was confirmed by elemental analysis.



IX

X

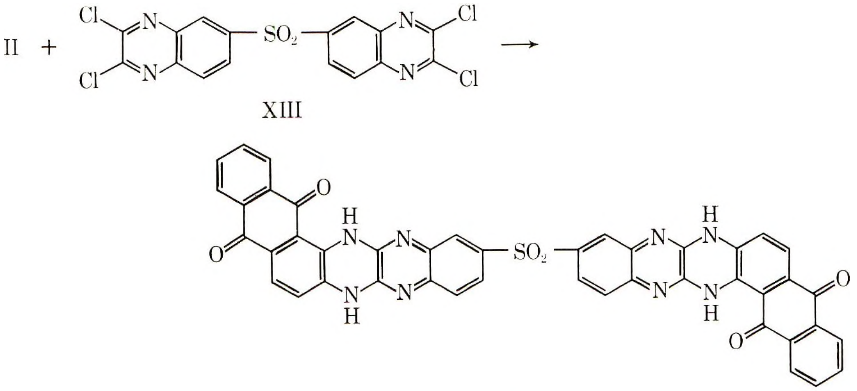
Condensation of 1,2-diaminoanthraquinone (II) with 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl ether[2] (XI) in pyridine or a 4:1 mixture of *N*,*N*-dimethylacetamide and *N*,*N*-diethylaniline yielded the expected model compound (XII). It was separated during the reaction and then heated at 350°C for 6 hr under reduced pressure.



XI

XII

The last model compound (XIV) was prepared by condensation of 1,2-diaminoanthraquinone (II) and 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl sulfone (XIII).



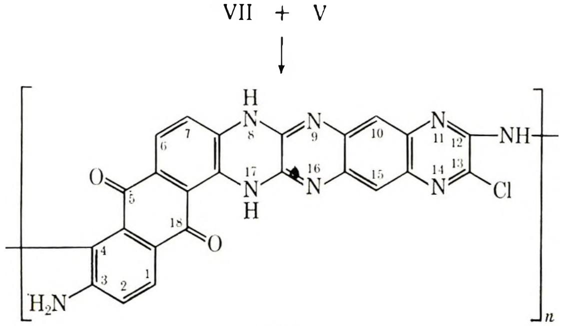
XIII

XIV

Pyridine was a good solvent for all of the described condensations. *N*,*N*-Dimethylacetamide, *N*,*N*-dimethylaniline, tetramethylene sulfone, and hexamethylphosphoramide are also satisfactory solvents for the reactions. The chlorine content in the products of the first step prepared in these solvents was lower than when the condensations were carried out in pyridine, but the yields were not as high as they were in pyridine solution. The first step of the condensation in the solvent was done under nitrogen atmosphere and the second step was done under reduced pressure. The result will be seen in the experimental part.

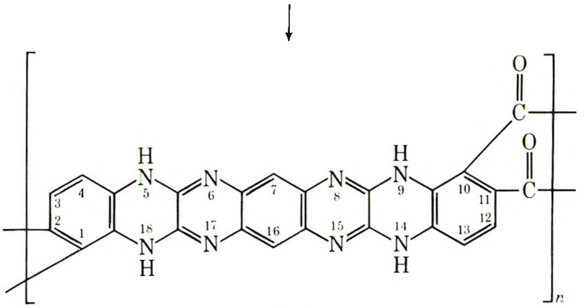
Polymerization was generally carried out by mixing equimolecular amounts of 1,2,5,6-tetraaminoanthraquinone and the respective tetrachloro compound in pyridine, tetramethylene sulfone, or mixture of *N*,*N*-dimethylacetamide and *N*,*N*-diethylaniline at room temperature. After stirring for 1 or 2 hr the reaction mixture was heated for 20–24 hr. During heating, a polymeric material precipitated out of the solution. It was separated from the reaction mixture by filtration or by treating with some solvent and subsequently extracting in a Soxhlet extractor. Since the polymers thus obtained seemed to have unclosed ring units to some extent and also to retain the solvent used in the polymerization, they were heated at 330–350°C for several hours under reduced pressure.

Polymer XVI was obtained by condensing compound VII with V in pyridine or tetramethylene sulfone. In the case of tetramethylene sulfone as solvent, the polymer with 50% ring closure (XV) was isolated. It was completely soluble in concentrated sulfuric acid; however, the polymer XVI had a very low solubility but the molecular weight increased from polymer XV to XVI.



XV

Poly[(3-amino-13-chloro-5,8,17,18-tetrahydro-5,18-dioxonaphtho[2,3-*f*]pyrazino[2,3-*b*:5,6-*g*′]diquinoxaline-4,12-diyl)imino]



XVI

Poly[(5,9,14,18-tetrahydrobenzo[1″,2″:5,6:4″,5″;5′,6′]dipyrazino[2,3-*b*:2′,3′-*b*′]diquinoxaline-1,2:10,11-tetrayl)-10,11-dicarbonyl]

The inherent viscosity of polymer XV was 0.17 and polymer XVI was 0.44 for the part soluble in concentrated sulfuric acid. Thermogravimetric analysis of this polymer (Fig. 1) showed that it gradually lost 4% of its weight up to 500°C and then lost about 36.7% of its weight up to 900°C.

When 1,2,5,6-tetraaminoanthraquinone[10] (VII) was condensed with 2,2′,3,3′-tetrachloro-6,6′-diquinoxaline[1] (IX) in pyridine, a black polymer was obtained. Analysis agreed with the expected formula (XVIII).

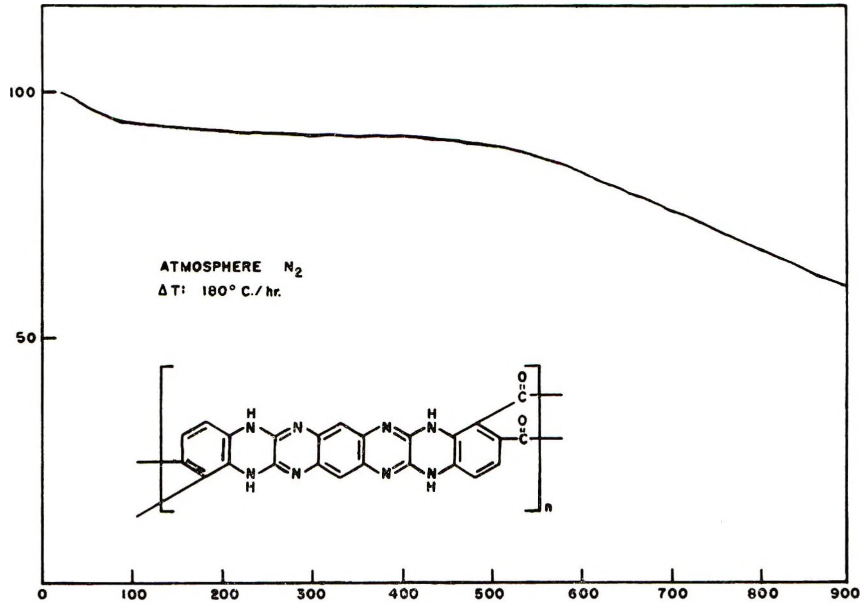
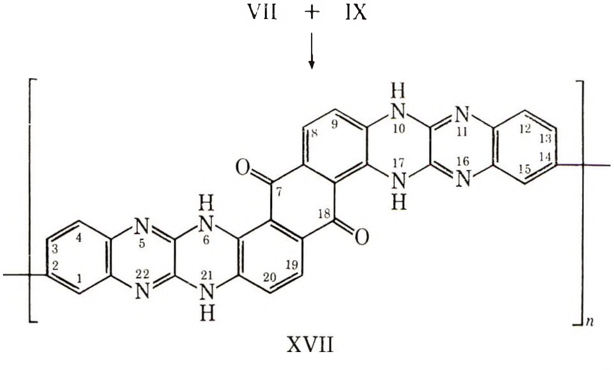


Fig. 1. TGA curve for polymer XVI.

This polymer was soluble in methanesulfonic acid and concentrated sulfuric acid and had an inherent viscosity of 0.1. The thermogravimetric analysis (Fig. 2) showed that it gradually lost 20% of its weight up to 900°C.

The polymer XVIII was prepared by the reaction of VII with XI.



XVII

Poly(6,7,10,17,18,21-hexahydro-7,18-dioxodiquinoxalino[2,3-*b*:2′,3′-*b*′]-benzo[1,2-*f*:4,5-*f*′]diquinoxaline-2,14-diyl)

The TGA curve (Fig. 3) showed little weight loss below 400°C in nitrogen and then gradual loss of about 20% of the weight up to 900°C.

Polymer (XIX) was obtained by the general method from TAA (VII) and 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl sulfone (XIII).

All of these polymers are highly colored, powdery materials and insoluble in common organic solvents. They are also very difficult to dissolve in

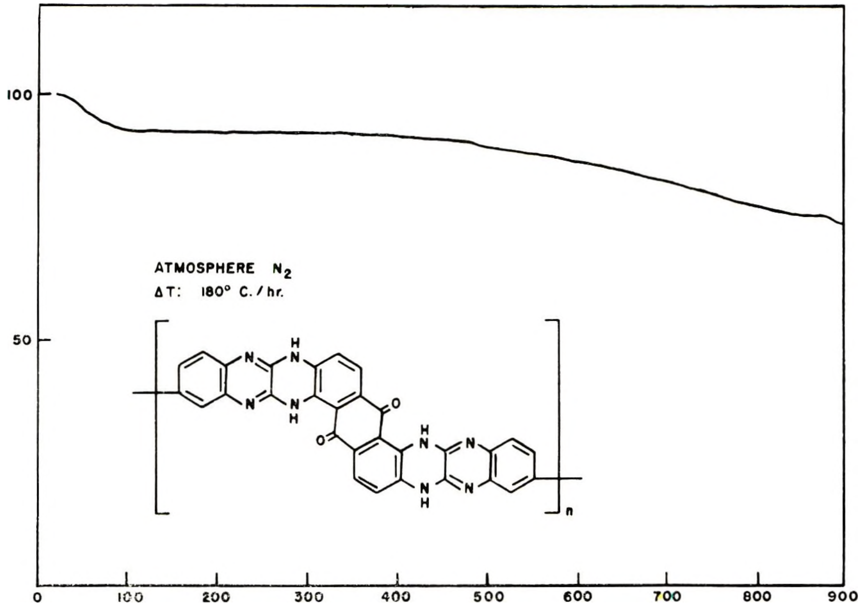
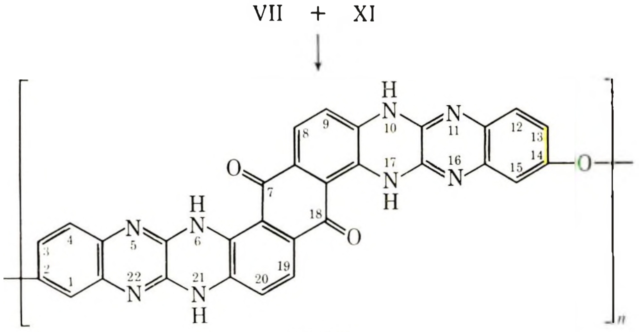


Fig. 2. TGA curve for polymer XVII.

such solvents as hexamethylphosphoramide *N*,*N*-dimethylacetamide, tetramethylene sulfone, and dimethyl sulfoxide but are slightly soluble in concentrated sulfuric acid and methanesulfonic acid.

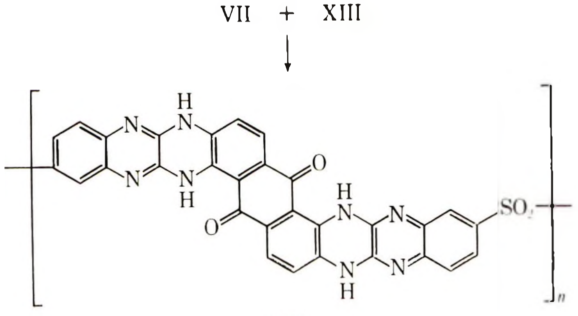


XVIII

Poly[(6,7,10,17,18,21-hexahydro-7,18-dioxodiquinoxalino[2,3-*b*:2′,3′-*b*′]benzo-[1,2-*f*:4,5-*f*′]diquinoxaline-2,14-diyl)oxy]

The TGA curve (Fig. 4) showed 5% weight loss at 400°C and 28% weight loss at 900°C.

None of these anthraquinone polymers were solubilized by alkaline hydrosulfite reduction.



XIX

Poly[(6,7,10,17,18,21-hexahydro-7,18-dioxodiquinoxalino[2,3-*b*:2′,3′-*b*′]benzo[1,2-*f*:4,5-*f*′]diquinoxaline-2,14-diyl)sulfone]

EXPERIMENTAL

Model Compounds

Condensation of 1,2-Diaminoanthraquinone and 1,2-Dichloroquinoxaline. To a solution of 0.19 g (0.005 mole) of 1,2-diaminoanthraquinone in 50 ml of tetramethylene sulfone was added 1 g (0.005 mole) of 1,2-dichloroquinoxaline.[10] The mixture was heated in an oil bath to 180°C and stirred at this temperature for 3 hr under nitrogen atmosphere. After cooling, the reaction mixture was poured into 250 ml of distilled water. The dark product was collected on the funnel and washed well with water. The

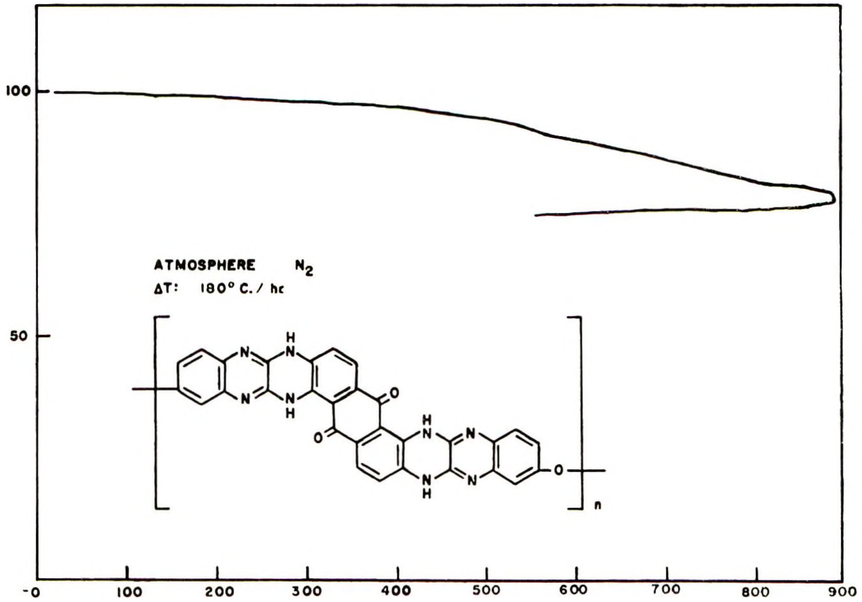


Fig. 3. TGA curve for polymer XVIII.

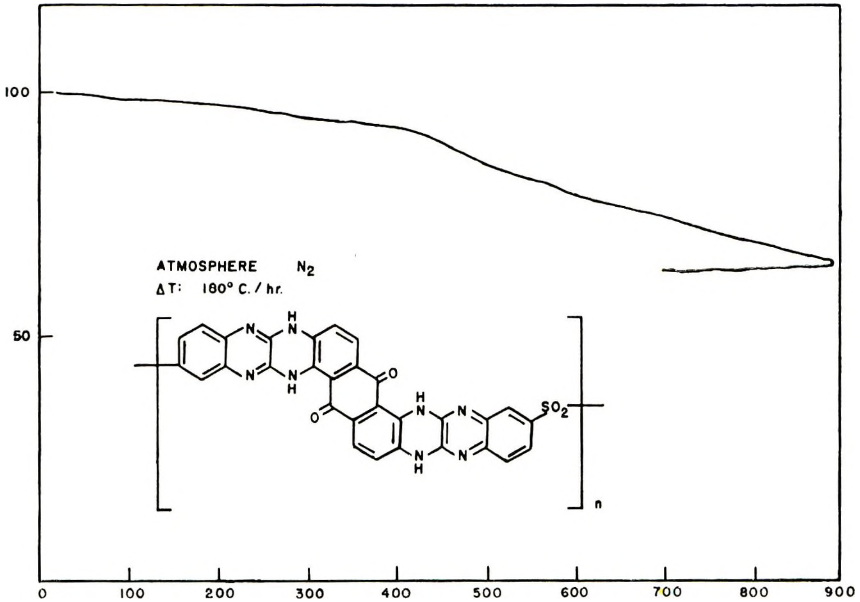


Fig. 4. TGA curve for polymer XIX.

product weighed 1.82 g (100%). It was recrystallized from nitrobenzene. It did not melt below 360°C.

ANAL. Calcd for $C_{22}H_{12}N_4O_2$: C, 72.52%; H, 3.32%; N, 15.37%. Found: C, 71.54%; H, 3.64%; N, 15.66%; Cl, 0.85%.

Condensation of 1,2-Diaminoanthraquinone and 2,3,7,8-Tetrachloro-1,4,6,9-tetraazaanthracene. To a solution of 2.38 g (0.01 mole) of 1,2-diaminoanthraquinone in 45 ml of tetramethylene sulfone was added with stirring 1.6 g (0.005 mole) of 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene[11,12] at room temperature. The reaction mixture was slowly raised to 220 or 320°C under nitrogen atmosphere and held there for 4 hr. The red-brown reaction mixture was cooled down and poured into 400 ml of distilled water. The precipitate was filtered and washed with water. The dry product weighed 2.3 g and contained 12.74% chlorine. It was extracted with alcohol for one day and residue was heated 6 hr at 260°C and another 6 hr at 350°C under vacuum. The solid was then extracted with ethanol for 3 days and dried under reduced pressure. The yield was 2.1 g (64.5%) and it did not melt under 360°C.

ANAL. Calcd for $C_{38}H_{18}N_8O_4$: C, 70.15%; H, 2.79%; N, 17.22%. Found (after heating at 260°C): C, 67.98%; H, 3.00%; N, 17.83%; Cl, 1.64%; residue 0.73%. Found (after heating at 350°C): C, 68.53%; H, 2.94%; N, 17.68%; Cl, 0.94%.

A solution of 0.8 g (0.0025) of 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene in 90 ml of dimethylaniline was added to a solution of 1.2 g (0.005) of 1,2-diaminoanthraquinone in 20 ml of the same solvent at room temperature.

The resulting red-brown solution was refluxed for 6 hr under nitrogen atmosphere. After cooling to room temperature, the reaction mixture was poured into 400 ml of ethyl alcohol. The dark brown precipitate was dried under reduced pressure, extracted with alcohol for 2 days and subsequently heated at 350°C for 6 hr under vacuum. It contained 3.46% chlorine before heating. The yield was 59%.

Anal. Found: C, 68.96%; H, 3.18%; N, 17.63%.

The best result was obtained by the use of a mixture of dimethylaniline and dimethylacetamide (10/40 ml) as solvent and the product precipitated into distilled water. The analysis shown below is for the product before heating at 300°C under vacuum. The yield was 60%.

Anal. Found: C, 70.00%; H, 4.83%; N, 16.86%; Cl, 0.61%.

Condensation of 1,2,5,6-Tetraaminoanthraquinone and 2,3-Dichloroquinoxaline. To a mixture of 0.67 g (0.0025 mole) of 1,2,5,6-tetraaminoanthraquinone in 50 ml of fresh distilled dry pyridine, was added with stirring, 1.0 g (0.005 mole) of 2,3-dichloroquinoxaline. The mixture was refluxed for 2 hr under nitrogen atmosphere. The dark product precipitated during the reaction. It was filtered, washed several times with pyridine and ether, extracted with alcohol for 2 days, and dried at 50°C under reduced pressure. This product contained 8.63% chlorine. It was heated at 350°C for 6 hr. The yield of the black solid was 0.96 g (74%); mp >360°C.

Anal. Calcd for $C_{30}H_{16}N_8O_2$: C, 69.23%; H, 3.08%; N, 21.54%. Found: C, 69.97%; H, 3.41%; N, 19.19%.

The same reaction was repeated with tetramethylene sulfone as a solvent; the yield was 73% at 300°C.

Anal. Found: C, 67.65%; H, 3.19%; N, 21.72%; Cl, 1.44%. Found (after heating at 350°C): C, 68.00%; H, 3.15%; N, 21.54%; Cl, 0.85%.

Condensation of 1,2-Diaminoanthraquinone and 2,2′,3,3′-Tetrachloro-6,6′-bisquinoxaline. A solution of 1.19 g (0.005 mole) of 1,2-diaminoanthraquinone and 0.995 g (0.0025 mole) of 2,2′,3,3′-tetrachloro-6,6′-diquinoxaline[11,12] in 40 ml of pyridine was refluxed for 20 hr. under stirring and in a nitrogen atmosphere. The resulting black reaction mixture was cooled, filtered, and washed with water and ether several times. It was extracted with ethanol and the residue was heated at 350°C for 6 hr under vacuum (0.05 mm Hg). After cooling to room temperature, it was extracted with alcohol for 3 days and also with benzene for 3 days. A black powder product was obtained in the yield of 1.2 g (66%).

Anal. Calcd for $C_{44}H_{22}N_8O_4$: C, 72.72%; H, 3.05%; N, 15.42%. Found: C, 69.61%; H, 2.89%; N, 15.78%; Cl, 0.52%.

Condensation of 1,2-Diaminoanthraquinone with 2,2′,3,3′-Tetrachloro-6,6′-diquinoxalyl Ether. 1,2-Diaminoanthraquinone (1.19 g, 0.005 mole) and 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl ether[13] (1.03 g, 0.0025 mole) were heated in 50 ml of freshly distilled pyridine for 20 hr under stirring and in a nitrogen atmosphere. After cooling, the mixture was filtered and washed with pyridine and ethanol. It was extracted with ethanol for one day and the residue was heated at 350°C for 6 hr. For purification, it was extracted again with ethanol and benzene for one day. The yield was 2.19 g (100%). It did not melt below 360°C.

ANAL. Calcd for $C_{44}H_{22}N_8O_5$: C, 71.15%; H, 2.99%; N, 15.09%. Found: C, 71.83%; H, 3.65%; N, 18.77%; Cl, 0.35%; residue, 0.43%.

The same reaction was carried out in a mixture of *N*,*N*-dimethylacetamide and *N*,*N*-diethylaniline as a solvent and precipitated in water after refluxing.

ANAL. Found: C, 70.00%; H, 4.83%; N, 16.83%; Cl, 0.61%.

Condensation of 1,2-Diaminoanthraquinone with 2,2′,3,3′-Tetrachloro-6,6′-diquinoxalyl Sulfone. A mixture of 1,2-diaminoanthraquinone (1.19 g, 0.005 mole), 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl sulfone[8] (1.15 g, 0.0025 mole), *N*,*N*-dimethylacetamide (40 ml), and *N*,*N*-dimethylaniline (10 ml) was heated at refluxing temperature for 16 hr under nitrogen atmosphere. After cooling, it was added to 350 ml of distilled water, filtered, washed well with water and ethanol several times, and dried. The powder was again heated at 350°C for 6 hr under vacuum and subsequently extracted with ethanol and benzene successively in a Soxhlet extractor. The yield of the black powder was 3.5 g (87%); mp >360°C.

ANAL. Calcd for $C_{44}H_{22}N_8O_6S$: C, 66.83%; H, 2.80%; N, 14.17%. Found: C, 67.63%; H, 3.82%; N, 13.26%.

Condensation of 1,2,5,6-Tetraaminoanthraquinone and 2,3,7,8-Tetrachloro-1,4,6,9-tetraazaanthracene. Into a 200-ml round-bottomed flask was placed 2.1 g (0.0065 mole) of 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene in 55 ml of freshly distilled dry pyridine. Then 1.73 g (0.0065 mole) of 1,2,5,6-tetraaminoanthraquinone was added. The mixture was refluxed and stirred for 2 hr. The flask was kept under a nitrogen atmosphere. A black solid separated which was filtered off, washed with pyridine and ether, and dried at 50°C under reduced pressure. This product contained 6.04% chlorine. It was heated at 350°C for 6 hr under vacuum. The final product after extracting with ethanol and benzene successively yielded 100%; mp >360°C, $\eta_{\text{inh}} = 0.44$ (0.1% concentrated H_2SO_4, 30°C); λ_{max}; 231 mμ (H_2SO_4).

ANAL. Calcd for $C_{24}H_{10}N_8O_2$: C, 65.15%; H, 2.28%; N, 25.33%. Found: C, 67.38%; H, 2.79%; N, 24.67%; residue, 0.58%.

A solution of 2,3,7,8-tetrachloro-1,4,6,9-tetraazaanthracene (0.8 g, 0.0025 mole) in tetramethylene sulfone (60 ml) was placed a 100-ml round-bottomed flask and 1,2,5,6-tetraaminoanthraquinone (0.67 g, 0.0025 mole) was added in small portions to the solution. The mixture was heated to 220°C and stirred for 17 hr under nitrogen atmosphere. A black solid separated which was filtered, washed with hot DMAc, then alcohol and dried at 50°C under reduced pressure. The product weighed 1.19 g (100%) mp >360°C.; $\eta_{\text{inh}} = 0.17$ (0.42%, completely soluble in concentrated sulfuric acid, 30°C.); $\lambda_{\max} = 253, 285$ mμ (H_2SO_4).

ANAL. Calcd. for $C_{24}H_{11}N_8O_2Cl$: C, 60.20%; H, 2.31%; N, 23.39%. Found: C, 59.74%; H, 2.75%; N, 22.28%; Cl, 7.29%; residue, 0.41%.

This product was heated at 300°C for 6 hr under vacuum.

ANAL. Found: C, 60.77%; H, 2.62%; N, 21.83%; Cl, 1.70%; residue 1.80%.

Condensation of 1,2,5,6-Tetraaminoanthraquinone and 2,2′,3,3′-Tetrachloro-6,6′-diquinoxaline. To a solution of 1,2,5,6-tetraaminoanthraquinone (0.67 g, 0.0025 mole) in pyridine (40 ml) was added 2,2′,3,3′-tetrachloro-6,6′-diquinoxaline (0.995 g, 0.0025 mole) at room temperature. After stirring for 2 hr, the reaction mixture was refluxed for 20 hr under a nitrogen stream. The cooled reaction mixture was filtered and washed with pyridine and ether. The resulting black prepolymer was heated at 320°C for 6 hr under vacuum (0.05 mm Hg). The black solid was extracted with ethyl alcohol for 5 days and benzene for 3 days. The black powder residue weighed 1.3 g (100%) after drying at 60°C under reduced pressure. The inherent viscosity was 0.1 (0.42% in concentrated sulfuric acid, 30°C); $\lambda_{\max} = 268, 400$, and 448 mμ ($H_2SO_4$).

ANAL. Calcd for $C_{30}H_{14}N_8O_2$: C, 69.74%; H, 2.72%; N, 21.61%. Found: C, 72.22%; H, 3.98%; N, 19.52%; Cl, 0.78%; residue, 1.00%.

Condensation of 1,2,5,6-Tetraaminoanthraquinone and 2,2′,3,3′-Tetrachloro-6,6′-diquinoxalyl Ether. A mixture of 1,2,5,6-tetraaminoanthraquinone (0.67 g, 0.0025 mole), 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl ether (1.03 g, 0.0025 mole) and freshly distilled pyridine (50 ml) was refluxed for 20 hr under a nitrogen atmosphere. After cooling, it was filtered, washed with pyridine and ethanol several times and extracted with ethanol and benzene for one day. The black residue was heated at 350°C for 6 hr under vacuum and subsequently extracted again with ethanol and benzene in a Soxhlet extractor. The yield of black powder was 1.15 g (86%); $\eta_{\text{inh}} = 0.16$ (0.2% in concentrated sulfuric acid, 30°C).

ANAL. Calcd for $C_{30}H_{14}N_8O_3$: C, 67.41%; H, 2.64%; N, 20.97%. Found: C, 67.92%; H, 2.90%; N, 18.46%; Cl, 1.73%.

The same reaction was repeated with a mixture of *N,N*-dimethylacetamide and *N,N*-diethylaniline as solvent and the product was precipitated in water after refluxing. This product had $\eta_{\text{inh}} = 0.13$ (0.22% in concentrated sulfuric acid at 30°C); $\lambda_{\max} = 248, 292$, and 413 mμ. ($H_2SO_4$).

ANAL. Found: C, 67.73%; H, 3.93%; N, 17.23%; Cl, <0.2%, residue 1.91%.

Condensation of 1,2,5,6-Tetraaminoanthraquinone and 2,2′,3,3′-Tetrachloro-6,6′-diquinoxalyl Sulfone. A mixture of 1,2,5,6-tetraaminoanthraquinone (0.67 g, 0.0025 mole), 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl sulfone (1.15 g, 0.0025 mole), *N*,*N*-dimethylacetamide (40 ml), and *N*,*N*-dimethylaniline (10 ml) was refluxed for 16 hr under nitrogen atmosphere and stirring. Water (300 ml) was added to the reaction mixture after cooling to room temperature. The resulting black solid was separated, washed with water and alcohol several times and dried. The black prepolymer was heated slowly at 350°C for 6 hr under vacuum and subsequently extracted with ethanol and benzene for 3 days. The yield of the polymer was 1.35 g (93%); $\eta_{inh} = 0.23$ (0.12% in concentrated sulfuric acid, 30°C); $\lambda_{max} =$ 223 and 302 mμ (H_2SO_4).

ANAL. Calcd for $C_{30}H_{14}N_8O_4S$: C, 61.85%; H, 2.42%; N, 19.24%. Found: C, 63.24%; H, 3.19%; N, 16.31%.

Preparation of 2,2′,3,3′-Tetrahydroxy-6,6′-diquinoxalyl Sulfone.[6] 3,3′,4,4′-Tetraaminodiphenyl sulfone (3.0 g, 0.011 mole) and oxalic acid (1.85 g) were dissolved in 75 ml of 4*N* hydrochloric acid, and the solution was heated to reflux for 5 hr. A light gray solid precipitated out of the solution during heating. After cooling, it was collected on a filter, washed with dilute hydrochloric acid and then with water until free of acid, and dried under reduced pressure. The yield was 3.91 g (94%); mp >360°C.

ANAL. Calcd for $C_{16}H_{10}N_4O_6S$: C, 49.74%; H, 2.61%; N, 14.5%. Found: C, 48.36%; H, 3.40%; N, 14.49%.

Preparation of 2,2′,3,3′-tetrachloro-6,6′-diquinoxalyl Sulfone.[6] A mixture of 2,2′,3,3′-tetrahydroxy-6,6′-diquinoxalyl sulfone (3 g), *N*,*N*′-dimethylaniline (16 ml), and phosphorus oxychloride (16 ml) was heated to reflux for 5 hr. The resulting black viscous reaction mixture was poured into a mixture of crushed ice and concentrated hydrochloric acid to give a precipitate which was collected and washed with dilute hydrochloric acid and then with water until free of acid. The product was extracted with absolute ethanol and the extract, after being concentrated to 50 ml, was allowed to stand in a freezer overnight to give light crystals. The yield was 1.2 g.

ANAL. Calcd for $C_{16}H_6N_4O_2S$: C, 41.76%; H, 1.31%; N, 12.18%. Found: C, 41.20%; H, 2.1%; N, 11.86%.

We are indebted to Dr. Kurt L. Loening of Chemical Abstracts Service for the names of the polymers. We are indebted to Dr. G. F. L. Ehlers, Air Force Materials Laboratory, Wright-Patterson Air Force Base, for thermogravimetric curves.

This work was supported by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

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Received April 28, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3225-3234 (1970)

Polymers Containing Anthraquinone and Quinoxaline Units: Polypyrrolones

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Synopsis

Four ladder or partial ladder polypyrrolones containing anthraquinone recurring units have been synthesized by condensing the dianhydride of 1,2,5,6-bis(α,β-dicarboxylpyrazino)anthraquinone with four different tetraamines, 1,2,4,5-tetraaminobenzene tetrahydrochloride, 3,3′,4,4′-tetraaminodiphenyl, 3,3′,4,4′-tetraaminodiphenyl ether, and 1,2,5,6-tetraaminoanthraquinone in dimethylacetamide and tetramethylene sulfone as reaction media. A prepolymer with an open structure was first formed which on further heating gave a closed-ring structure. These polymers which were highly colored, powdery materials, were insoluble in common organic solvents and slightly soluble only in concentrated H_2SO_4. They could, however, be solubilized in alkali by reduction with sodium dithionite. These polymers with an inherent viscosity in the range of 0.2–0.5, showed good thermal stability.

INTRODUCTION

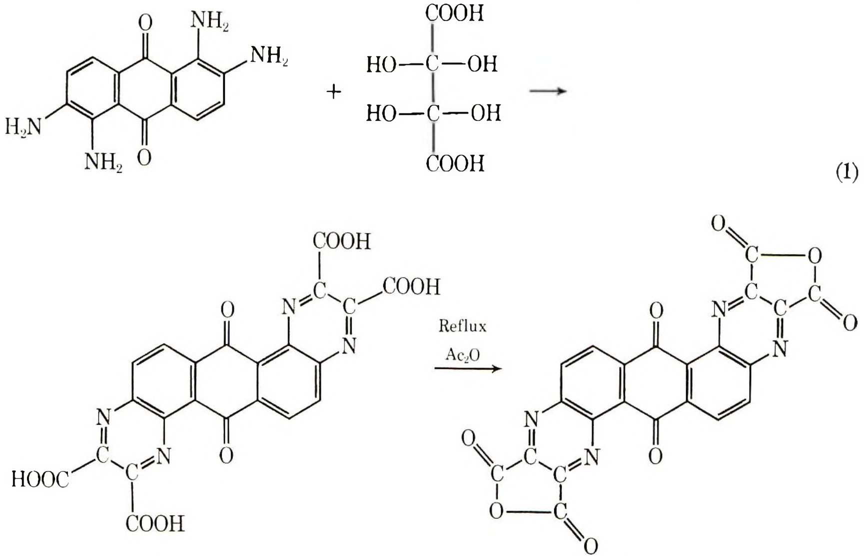
Research in the field of thermally stable polymers reveals that most of the presently known ladder or partial ladder polyaromatic heterocycles exhibit good thermal stability but are usually insoluble in all reagents except perhaps methanesulfonic acid and concentrated sulfuric acid, and as a result present enormous fabrication difficulties. As a possible solution to this solubility problem, anthraquinone recurring groups have been introduced into the polymer chain by using 1,2,5,6-tetraaminoanthraquinone as a component in polycondensation reactions.[1] As in the case of anthraquinone vat dyes, such polymers are solubilized by reduction in alkali with sodium hydrosulfite ($Na_2S_2O_4$) and can be wet-spun into fibers which on exposure to air and acidic conditions become oxidized to the original insoluble anthraquinone derivatives.

The present paper is concerned with the preparation and properties of four different polypyrrolones containing anthraquinone recurring units obtained by the condensation of dianhydride of 1,2,5,6-bis(α,β-dicarboxylpyrazino)anthraquinone with four different tetraamines, 1,2,4,5-tetraaminobenzene tetrahydrochloride, 3,3′,4,4′-tetraaminodiphenyl, 3,3′,4,4′-tetraaminodiphenyl ether, and 1,2,5,6-tetraaminoanthraquinone.

DISCUSSION AND RESULTS

The synthesis[1] of 1,2,5,6-tetraaminoanthraquinone (TAA) has opened up a field for a new group of polymers containing anthraquinone units by using the tetraamine or its derivatives as one of the intermediates in the polycondensation reactions.

The reaction of *o*-phenylenediamine with dihydroxytartaric acid to form quinoxaline-2,3-dicarboxylic acid has been reported.[2] TAA condensed easily with dihydroxytartaric acid to give 1,2,5,6-bis(α,β-dicarboxylpyrazino)anthraquinone, which could be easily converted to the corresponding dianhydride by refluxing it with acetic anhydride [eq. (1)].



(1)

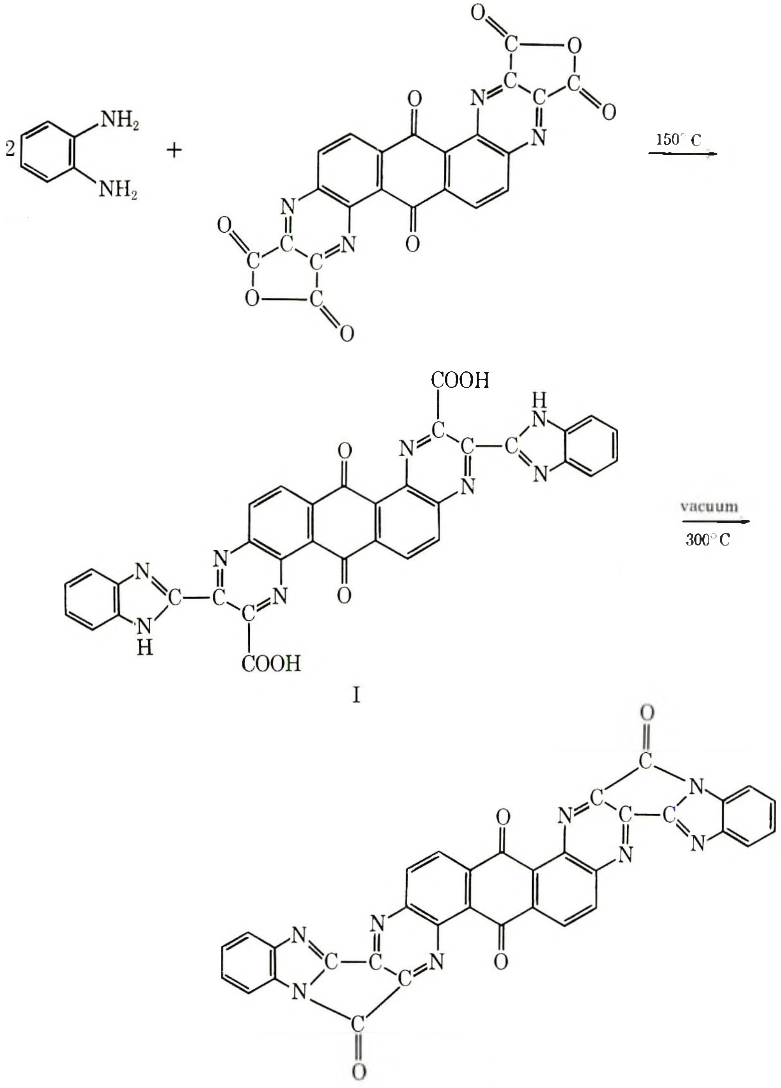
Model Reaction:

The dianhydride of 1,2,5,6-bis(α,β-dicarboxyl pyrazino)anthraquinone obtained in reaction (1) reacted easily with *o*-phenylenediamine in dimethylacetamide solvent [eq. (2)].

If I is heated under vacuum, complete ring closure can be effected. The model reaction was extended to the cyclopolycondensation reaction of four different tetraamines with the dianhydride, and the solution polymerization technique was employed for the polymerization of the stoichiometric amounts of the monomers.

Polycondensation Reaction

All of the polycondensations were carried out in dimethylacetamide (DMAc) and tetramethylene sulfone as solvents. In all cases, a prepolymer precipitated. The prepolymers were isolated, dried, and then gradually heated to 300–350°C to give a closed or almost closed-ring structure. An increase in viscosity during heating was noticed from about 0.15 to 0.55 on the average. Tetramethylene sulfone appeared to be a better reaction



I

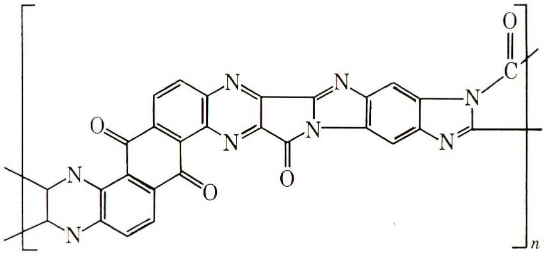
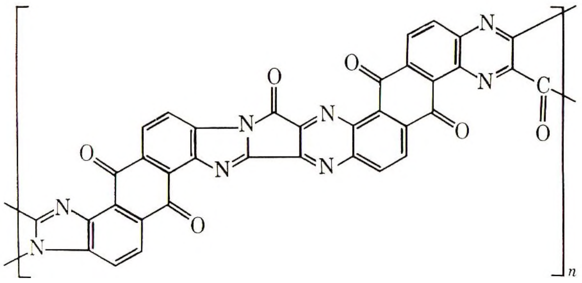
II

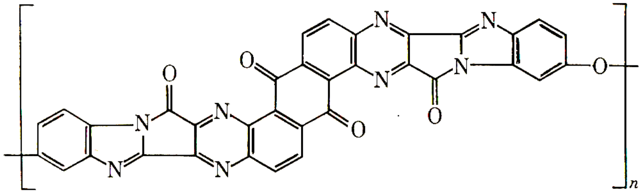
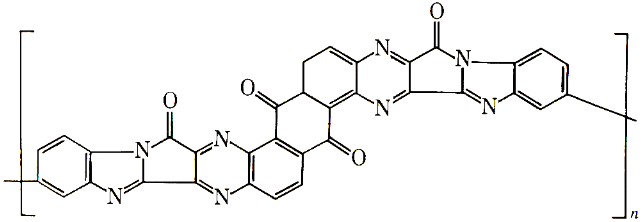
(2)

medium than dimethylacetamide, since higher molecular weight polymers were obtained in the former medium. The results are summarized in Table I.

All of those polymers when heated up to only 250°C were soluble in concentrated sulfuric acid, but the elemental analysis and infrared spectra (Fig. 1) showed a predominantly open structure. However, when the polymers were heated at 300–350°C for 3–4 hr, they became almost insoluble in concentrated sulfuric acid; the elemental analysis and the disappearance of -NH absorption in the infrared spectra (Fig. 1) indicated a closed or almost closed structure. The insolubility might be attributed to some intermolecular condensation at high temperatures. These polymers, how-

TABLE I
Data on Preparation, Structure, and Inherent Viscosity of Polypyrrolones

Monomers	Experimental Conditions	Further treatment	Structure of recurring unit	η_{inh} (conc. H_2SO_4, 30°C)
1,2,4,5-Tetra-aminobenzene tetrahydrochloride	DMAc, 150°C, N_2	20 hr, 150°C; 10 hr, 250°C; 4 hr, 300°C	 Polymer I	0.2
1,2,5,6-Bis(α,β-dicarboxylpyrazino)-anthraquinone dianhydride	Tetramethylene sulfone, 150°C, N_2	20 hr, 150°C; 10 hr, 250°C; 4 hr, 300°C		0.45
1,2,5,6-Tetraamino-anthraquinone	DMAc, 150°C, N_2	20 hr, 150°C; 10 hr, 250°C; 4 hr, 300°C	 Polymer II	0.18
1,2,5,6-Bis(α,β-dicarboxylpyrazino)-anthraquinone dianhydride	Tetramethylene sulfone, 150°C, N_2	20 hr, 150°C; 10 hr, 250°C; 4 hr, 300°C		0.32

3,3′,4,4′-Tetra-aminodiphenyl ether	DMAc, 150°C, N_2	20 hr, 150°C; 10 hr, 250°C; 4 hr, 300°C	 Polymer III	0.2
1,2,5,6-Bis(α,β-dicarboxylpyrazino)-anthraquinone dianhydride	Tetramethylene sulfone, 150°C, N_2	20 hr, 150°C; 10 hr, 250°C; 4 hr, 300°C		0.48
3,3′,4,4′-Tetra-aminodiphenyl	DMAc, 150°C, N_2	20 hr, 150°C; 10 hr, 250°C; 4 hr, 300°C	 Polymer IV	0.17
1,2,5,6-Bis(α,β-dicarboxylpyrazino) anthraquinone dianhydride	Tetramethylene sulfone, 150°C, N_2	20 hr, 150°C; 10 hr, 250°C; 4 hr, 300°C		0.53

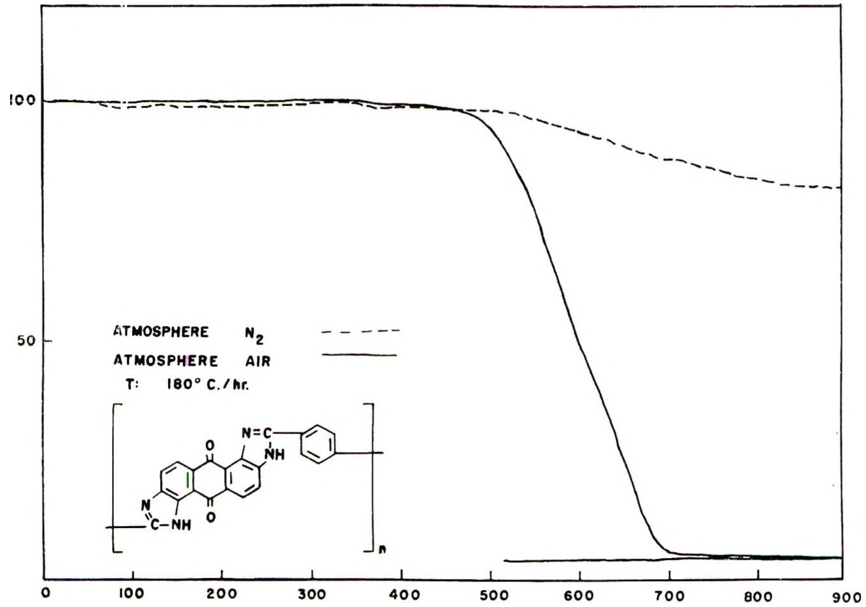


Fig. 1. Infrared spectrum of polymer IV.

ever, could be solubilized by reduction with $Na_2S_2O_4$ in alkali in a mixture of dimethylacetamide or dimethyl sulfoxide and water under nitrogen atmosphere and could be reoxidized to the insoluble anthraquinone derivative by exposure to air and acidic conditions.

The TGA curves of the polymers looked remarkably alike. The polymers seemed to lose about 10% of their weight at 600°C when heated at the rate of 3°C/min under nitrogen (Fig. 2).

EXPERIMENTAL

Dianhydride of 1,2,5,6-Bis(α,β-dicarboxylpyrazino)anthraquinone

Monomers

Condensation of TAA and Dihydroxytartaric Acid. To a solution of 1 g of TAA in 25 ml of dimethylacetamide, 2.5 g of dihydroxytartaric acid was added. The solution was kept at room temperature for 2 hr, when about 700 mg of the product separated. The product was filtered, washed with acetic acid, and dried at 80°C for 3 hr; mp >360°C.

ANAL. Calcd for $C_{22}H_8N_4O_{10}$: C, 54.11%; H, 1.56%; N, 11.47%. Found: C, 53.75%; H, 2.1%; N, 11.31%.

Conversion of 1,2,5,6-Bis(α,β-dicarboxylpyrazino)anthraquinone to Corresponding Dianhydride. A 1-g portion of the tetracarboxyl compound was refluxed with 25 ml of acetic anhydride for 2 hr. The product was

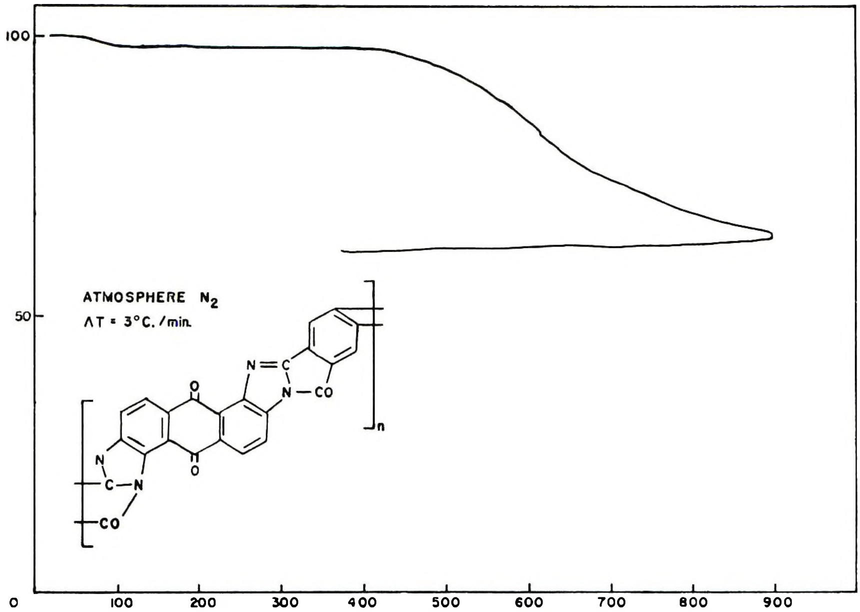


Fig. 2. TGA curves for ladder polymers with anthraquinone units.

filtered, washed with a little acetic acid, and dried under vacuum; mp >360°C.

Anal. Calcd for $C_{22}H_4N_4O_8$: C, 58.4%; H, 1 %; N, 12.40%. Found: C, 58.1%; H, 2.2%; N, 12.96%. C, 57.78%; H, 1.91%; N, 12.20%.

o-Phenylenediamine

The *o*-phenylenediamine (Eastman Organic Chemicals) was recrystallized several times from an ethyl alcohol–water mixture in the presence of activated charcoal; mp 102°C.

1,2,4,5-Tetraaminobenzene Tetrahydrochloride

The 1,2,4,5-tetraaminobenzene tetrahydrochloride (Burdick and Jackson Laboratories, Inc.) was used without further purification.

3,3′,4,4′-Tetraaminodiphenyl Ether

The 3,3′,4,4′-tetraaminodiphenyl ether was also purchased from Burdick and Jackson Laboratories, Inc., and used as received; mp 150–151°C.

3,3′,4,4′-Tetraaminodiphenyl

The 3,3′,4,4′-tetraaminodiphenyl was provided also by Burdick and Jackson Laboratories, Inc. It was recrystallized from boiling methanol, mp 179–180°C.

1,2,5,6-Tetraaminoanthraquinone

This was synthesized from 2,6-diaminoanthraquinone as previously described;[1] mp >360°C.

Model Compound

Condensation of *o*-phenylenediamine and dianhydride of 1,2,5,6-bis-(α,β-dicarboxylpyrazino)anthraquinone: The dianhydride (0.45 g) and 0.22 g of *o*-phenylenediamine were dissolved in 10 ml of dimethylacetamide. The solution was heated at 150°C under N_2 atmosphere for 3 hr. The product was poured into petroleum ether, filtered, and dried under vacuum at 50°C. The product was again heated under vacuum at 300°C for 4 hr to produce the closed ring structure.

ANAL. Calcd for $C_{34}H_{12}O_4N_8$: C, 68.4%; H, 2.0%; N, 18.6%. Found (before heating): C, 66.1%; H, 3.9%; N, 16.6%. Found (after heating): C, 68.33%; H, 3.1%; N, 17.8%.

Polycondensation Reactions

General Procedure

The polymers were synthesized according to the experimental procedure previously described.[3] The flask, fitted with a mechanical stirrer, containing the monomer components and solvent under a nitrogen stream was placed in oil bath and the bath was gradually heated to 150°C. Generally, a prepolymer separated while the temperature was kept at 150°C for about 4 hr. The product was filtered and dried at 150°C for 20 hr under vacuum. The polymers were further heated under vacuum at 250°C for 10 hr, followed by 4 hr at 300°C.

Condensation of 1,2,4,5-Tetraaminobenzene Tetrahydrochloride and Dianhydride of 1,2,5,6-Bis(α,β-dicarboxylpyrazino)anthraquinone

This yielded polymer I; poly [(16,18-dihydro-5,16,18-trioxoimidazo-[4″,5″:5′,6′]benzimidazo[1′,2′:1,2]pyrrolo[3,4-*b*]benzo[1,2-*f*:4,5-*f*′]diquinoxaline-2,3:11,12(5*H*)-tetrayl)-11-carbonyl].

In Dimethylacetamide. Dianhydride (0.9 g) and 0.6 g of tetraaminobenzene tetrahydrochloride are mixed with 25 ml of dimethylacetamide. The mixture was heated in a three-necked flask provided with a mechanical stirrer at 150°C under nitrogen atmosphere for 4 hr. A prepolymer separated after a while. The product was poured into petroleum ether, filtered, and dried at 120°C under vacuum for 24 hr followed by another 24 hr at 250°C. Subsequently the polymer was heated at 300°C for 4 hr/0.5 mm Hg; $\eta_{\text{inh}} = 0.2$ (0.25% concentration in concentrated sulfuric acid, 30°C).

ANAL. Calcd for $C_{28}H_6N_8O_4$ (closed structure): C, 64.86%; H, 1.17%; N, 21.62%. Found: C, 64.32%; H, 2.87%; N, 21.41%; residue, 0.8%.

In Tetramethylene Sulfone. The polymerization was carried out in the same way and the prepolymer was further heated similarly. The product had η_{inh} 0.45 (0.25% concentration in concentrated H_2SO_4 at 30°C).

ANAL. Calcd for $C_{28}H_6N_8O_4$ (closed structure): C, 64.86%; H, 1.17%; N, 21.62%. Found: C, 64.61%; H, 2.19%; N, 21.12%.

The analysis indicated almost completely closed structure.

Condensation of 1,2,5,6-Tetraaminoanthraquinone and dianhydride of 1,2,5,6-Bis(α,β-dicarboxylpyrazino)anthraquinone

This yielded polymer II, poly[(8,10,17,22-tetrahydro-4,8,10,17,22-pentaoxoimidazo[4‴,5‴:5″,6″]anthra[1″,2″:4′,5′]imidazo[1″,2″:1,2]-pyrrolo[3,4-*b*]benzo[1,2-*f*:4,5-*f*′]diquinoxaline-1,2(4*H*):14,15-tetrayl)-15-carbonyl].

In dimethylacetamide. TAA (0.536 g) and 0.904 g of dianhydride were condensed in dimethylacetamide in the same way as before and finally heated at 300°–350°C to get to closed ring structure, $\eta_{\text{inh}} = 0.18$ (0.25% concentration in concentrated sulfuric acid, 30°C).

ANAL. Calcd for $C_{36}H_8N_8O_6$ (closed structure): C, 66.7%; H, 1.4%; N, 17.2%. Found: C, 66.9%; H, 2.4%; N, 17.1%.

In Tetramethylene Sulfone. The viscosity of the polymer thus prepared was found to be 0.32 (H_2SO_4, 30°C).

ANAL. Calcd for $C_{36}H_8N_8O_6$ (closed structure): C, 66.7%, H, 1.4%; N, 17.2%. Found: C, 66.5%; H, 2.1%; N, 16.9%.

The analysis indicated almost completely closed structure.

Condensation of 3,3′,4,4′-Tetraaminodiphenyl Ether and Dianhydride of 1,2,5,6-Bis(α,β-dicarbonylpyrazino)anthraquinone

This yielded polymer III, poly[(6,8,18,20-tetrahydro-6,8,18,20-tetraoxobisbenzimidazo[1′,2′:1,2]pyrrolo[3,4-*b*:3′,4′-*b*′]benzo[1,2-*f*:4,5-*f*′]diquinoxaline-2,15-diyl)oxy].

In Dimethylacetamide. Tetraamine (0.456 g) and 0.904 g dianhydride were condensed in the same way. The product had $\eta_{\text{inh}} = 0.2$ (0.25% concentration in concentrated sulfuric acid, 30°C).

ANAL. Calcd for $C_{34}H_{10}N_8O_5$ (closed structure): C, 66.78%; H, 1.64%; N, 19.36%. Found: C, 66.89%; H, 2.96%; N, 19.44%.

In Tetramethylene Sulfone. The polymer had $\eta_{\text{inh}} = 0.48$ (0.25% concentration in concentrated sulfuric acid, 30°C).

ANAL. Calcd for $C_{34}H_{10}N_8O_5$ (closed structure): C, 66.78%; H, 1.64%; N, 19.36%. Found: C, 66.4%; H, 2.2%; N, 19.2%.

Here also the analysis indicated almost completely closed ring structure.

Condensation of 3,3′,4,4′-Tetraaminodiphenyl and dianhydride of 1,2,5,6-Bis-(α,β-dicarboxylpyrazino)anthraquinone

This yielded polymer IV, poly(17,19-dihydro-5,15,17,19-tetraoxo-5*H*,-15*H*,bisbenzimidazol[1′,2′:1,2]pyrrolo[3,4-*b*:3′,4′-*b*′]benzo[1,2-*f*:5,4-*f*′]diquinoxaline-11,22-diyl).

In Dimethylacetamide. Tetraaminodiphenyl (0.43 g) and 0.90 g of dianhydride were condensed in dimethylacetamide in the same way; the product had $\eta_{\text{inh}} = 0.17$ (0.25% concentration in concentrated sulfuric acid, 30°C).

ANAL. Calcd for $C_{34}H_{10}N_8O_4$ (closed structure): C, 68.91%; H, 1.68%; N, 18.89%, Found: C, 68.73%; H, 3.16%; N, 19.88%; residue, 0.79%.

In Tetramethylene Sulfone. The viscosity of this polymer was the highest, 0.53 in concentrated H_2SO_4 (0.25% concentration, 30°C).

ANAL. Calcd for $C_{34}H_{10}H_8O_4$ (for closed structure): C, 68.91%; H, 1.68%; N, 18.89%. Found: C, 68.6%; H, 1.98%; N, 18.71%.

The infrared spectra of this polymer indicated disappearance of -NH-group after the final heat treatment.

Reduction and Solubilization of Polymer

Reduction and solubilization experiments were carried out with the polymer prepared from 3,3′-4,4′-tetraaminodiphenyl and the dianhydride in tetramethylene sulfone solvent. This polymer ($\eta_{\text{inh}} = 0.53$, H_2SO_4, 30°C) was soluble in a mixture of 80% dimethyl sulfoxide in water containing 10% $Na_2S_2O_4$ and 10% KOH under N_2 atmosphere. A 10% solution of the polymer was prepared and extruded from a syringe into a dilute hydrochloric acid solution when the hydroanthraquinone fiberlike polymer precipitates and eventually was reoxidized to the original anthraquinone derivatives. The fiber was, however, very brittle.

We are indebted to Dr. Kurt L. Loening, Chemical Abstracts Service, for the names of our polymers. We are indebted to Dr. G. F. L. Ehlers, Air Force Materials Laboratory, Wright-Patterson Air Force Base, for the thermogravimetric curves.

This work was supported by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

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Received April 28, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3235-3249 (1970)

Benzimidazole, Benzothiazole, and Benzoxazole Polymers with Anthracene Recurring Units

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Synopsis

In an attempt to prepare polymers which might be oxidized to compounds soluble in alkali diphenyl 1,5-anthracenedicarboxylate was reacted with diaminobenzidine, dimercaptobenzidine, and diaminobiphenol in the melt and with dimercaptobenzidine dihydrochloride in polyphosphoric acid. Compounds of high molecular weight were obtained and their thermal and oxidative stability evaluated. Model compounds were prepared and their ultraviolet spectra compared with those of the polymers. Oxidation with nitric acid or chromium trioxide yielded some anthraquinone derivatives, but side reactions prevented the formation of useful products.

INTRODUCTION

Polymers, consisting solely of aromatic and heterocyclic nuclei (i.e., benzimidazoles,[1,2] benzothiazoles,[3] and benzoxazoles[4]) have been synthesized and have shown very remarkable thermal and oxidative stability.[1-6] However, they have high melting points and are usually insoluble in most organic solvents. Introduction of anthraquinone units in the polymer (which should be soluble in alkali after reduction)[7] has in some cases overcome that problem. But some attempts to prepare high molecular weight polymers with these moieties in the backbone have resulted in insoluble and intractable compounds.[8] This was probably due to side reactions involving the quinone group. Since anthracene and its derivatives were known to be easily oxidized to the analogous anthraquinones,[9] it was hoped that polycondensates with recurring anthracene units could be converted to anthraquinone derivatives, which in turn should be soluble in an alkaline medium after reduction.

RESULTS AND DISCUSSION

Model Compounds

Diphenyl 1,5-anthracenedicarboxylate (DPAC) proved to be less reactive than the antraquinone derivative in condensation with amines. Reaction conditions which were sufficient for the latter did not yield the expected products for the former ester. The lower reactivity of the carbonyl group on anthracene, compared with that on anthraquinone, may be explained by the absence of the quinone structure.

Attempts to prepare 1,5-anthracene-dibenzimidazole-2 (I) by treating the starting ester with *o*-phenylenediamine in boiling diethylaniline (DEA) failed (compare with the corresponding anthraquinone derivative[8]). The imidazole was synthesized by reacting the ester and the diamine in the melt at 250°C. The elemental analysis of this product, low in nitrogen, could be explained by assuming only partial loss of phenol. However, higher temperatures and longer reaction times did not seem to improve the analytical results. An infrared spectrum confirmed the presence of the benzimidazole structure.

1,5-Anthracene-dibenzothiazole-2 (II) could not be prepared by using boiling veratrole, boiling diphenyl ether, or boiling DEA as reaction media for the two reagents, diphenyl 1,5-anthracenedicarboxylate and *o*-aminothiophenol.

Use of *o*-aminothiophenol as its hydrochloride[3] in DEA did not initiate the reaction. This compound was finally made by melt condensation. Here too, the elemental analysis was not extremely good and indicated incomplete exchange of the phenol group against *o*-aminothiophenol. Attempts to further the reaction by use of higher temperatures or longer heating times did not improve the purity of the reaction product.

1,5-Anthracene-dibenzoxazole-2 (III) was prepared by mixing equivalent amounts of diphenyl 1,5-anthracenedicarboxylate and *o*-aminophenol and heating them at elevated temperatures. Again the elemental analysis of this compound showed some unreacted ester (low in nitrogen). It was supposed that the higher temperatures required for reaction by the lower reactivity of the diphenyl 1,5-anthracenedicarboxylate caused the loss of some amino compound by volatilization. Crystallization from most solvents caused only an incomplete separation of the reaction products, but from acetophenone, a pure compound was obtained although in a low yield.

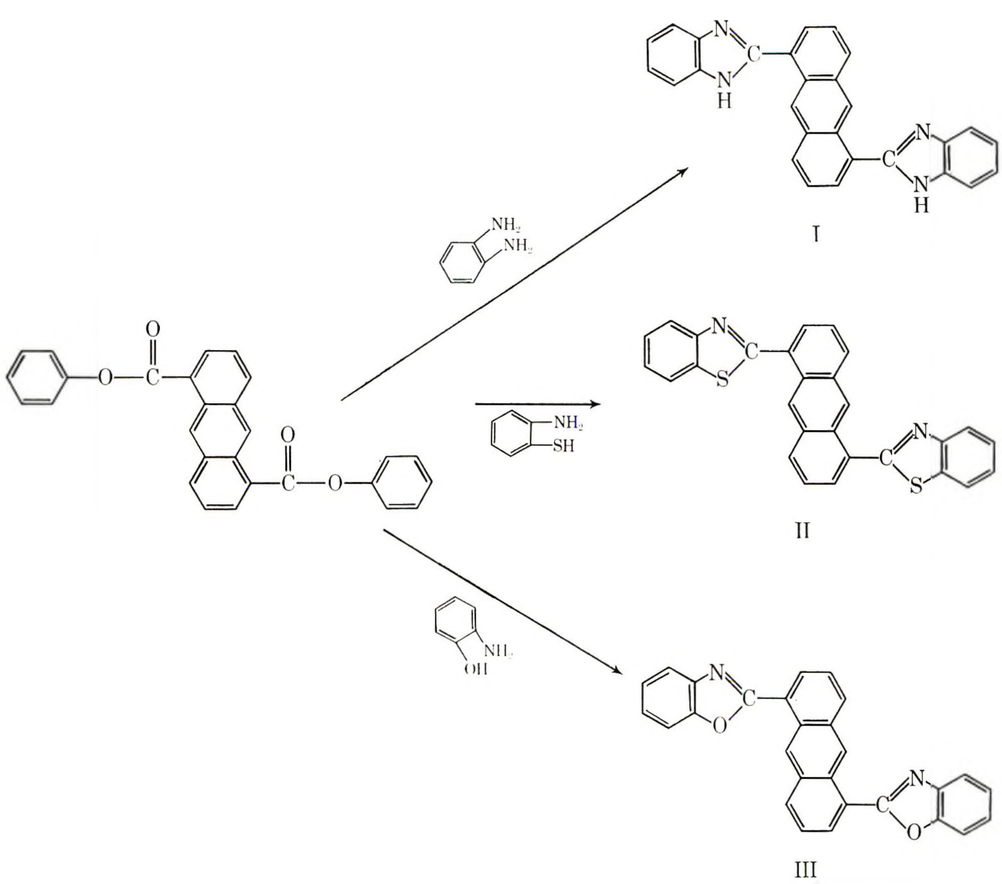
Polymers

The corresponding polymers were obtained as pure compounds by melt condensation.

Poly[(5,5′-bibenzimidazole)-2,2′-diyl-1,5-anthrylene] (IV) was obtained as a yellow-brown granular solid. The inherent viscosities ranged from 0.6 to 0.8. Higher viscosities (and also better analyses) were obtained with higher temperatures and longer heating times (Table I). This polymer, completely soluble in sulfuric acid, was also 2% soluble in hot formic acid.

Poly[(5,5′-bibenzoxazole)-2,2′-diyl-1,5-anthrylene] (V) was soluble in sulfuric acid to the extent of 77%.

Poly[(6,6′-bibenzothiazole)-2,2′-diyl-1,5-anthrylene] (VI) was obtained as a black product, 33% soluble in sulfuric acid. This last polymer was also prepared in solution. Because no reaction was observed between diphenyl 1,5-anthracenedicarboxylate and *o*-aminothiophenol hydrochloride in DEA,



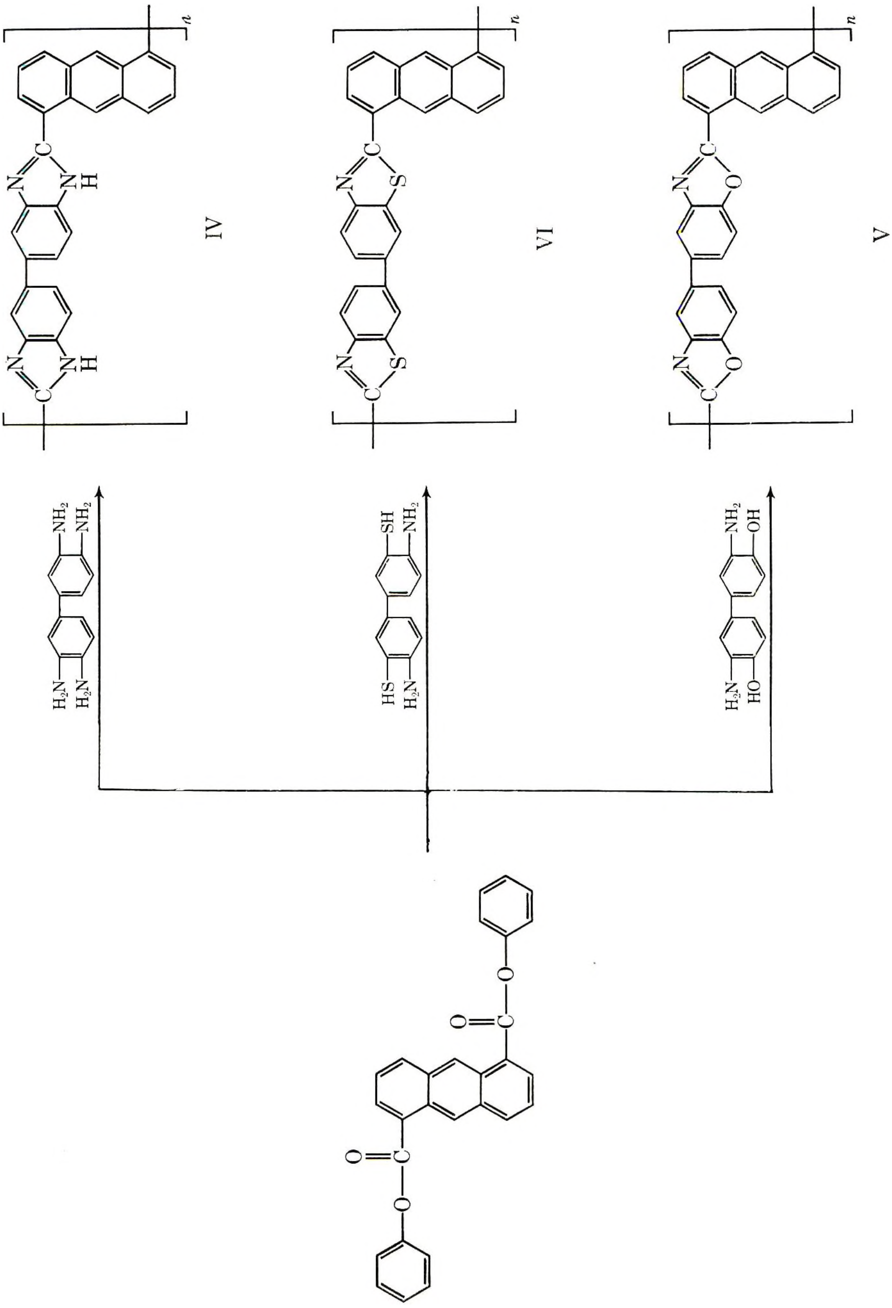
no attempts were undertaken to prepare a polymer in this solvent. Use of polyphosphoric acid as a solvent yielded a polymer that has a better solubility but a lower inherent viscosity than one in melt polymerization.

Oxidation of the model compounds and polymers was tried with nitric acid[10] and chromium trioxide[11] as oxidizing agents. 1,5-Anthracene-dibenzimidazole-2 in nitric acid gave an anthraquinone derivative, as proven by appearance of a band at 1675 cm^{-1} in the infrared spectrum. However, the elemental analysis suggested that there was some nitro moiety in the molecule. A salt formation was ruled out by experimental data. Nitration was suspected. These observations hold for the polymer too: elemental analysis and too much weight increase indicated nitration of the substance.

Chromium trioxide in boiling acetic acid converted 1,5-anthracene-dibenzimidazole-2, insoluble in this solvent, to a soluble product, presumably 1,5-anthraquinone-dibenzimidazole-2. By starting from the benzothiazole compound, 1,5-anthraquinone-dibenzothiazole-2 could be prepared. On the polymer the oxidation seemed coupled with a loss of a nitrogen-containing molecule (i.e., NO). This oxidation reaction caused also a

TABLE I
Polymers from 3,3′-Diaminobenzidine (DAB) and Diphenyl 1,5-Anthracenedicarboxylate (DPAC)

Reaction conditions		Analysis						η_{inh} (0.2% solution in H_2SO_4)
		Calcd			Found			
Under N_2	Vacuum	C, %	H, %	N, %	C, %	H, %	N, %	
18 hr at 260°C	5 hr at 290°C	82.35	3.94	13.71	79.86	4.07	13.09	0.59
18 hr at 260°C	5 hr at 250–350°C				81.23	4.12	13.83	0.65
15 hr at 280°C	5 hr at 320°C				81.79	4.12	13.89	0.76
15 hr at 280°C	5 hr at 300–350°C				82.08	4.13	13.71	0.79



IV

VI

V

decrease in inherent viscosity from 0.65 to 0.59 what could be explained by opening of the thiazole nucleus.

Although anthracene can be oxidized to anthraquinone in air[12] this feature did not show up in the TGA curves (Figs. 1–3) for these three polymers. (This should be accompanied by an increase in weight.)

Ultraviolet spectra for the different model compounds and polymers (Table II) were obtained using (for solubility reasons) sulfuric acid as solvent. A change of the absorption spectrum in the time was observed for the model compounds. The structure of poly[(5,5′-bibenzimidazole)-2,2′-diyl-1,5-anthrylene] did not change even after keeping its sulfuric acid solution for 2 days at 50°C or 1 day at 100°C. Poly[(5,5′-bibenzoxazole)-2,2′-diyl-1,5-anthrylene], however, showed a difference after 1 day at 100°C. This should be due to oxidation by the solvent. Indeed, spectra, similar to these of the anthraquinone derivatives were replacing the original ones.[8]

Each compound showed a peak between 233 and 245 mμ and a second one between 268 and 274 mμ (the benzimidazole model compound being the only exception, absorbing at 259 mμ) (Table II). These absorptions were thought to be related to the anthracene moiety. A third absorption, in a broad range around 300 mμ, seemed to be due to the heterocyclic nucleus. In this peak, the polymers showed a marked bathochromism over the model compounds (10 mμ).

In accord with observations by Iwakura[13] on similar compounds, the oxidative stability of the polybenzimidazole, polybenzothiazole, and polybenzoxazole derivatives of anthracene towards air is practically identical:

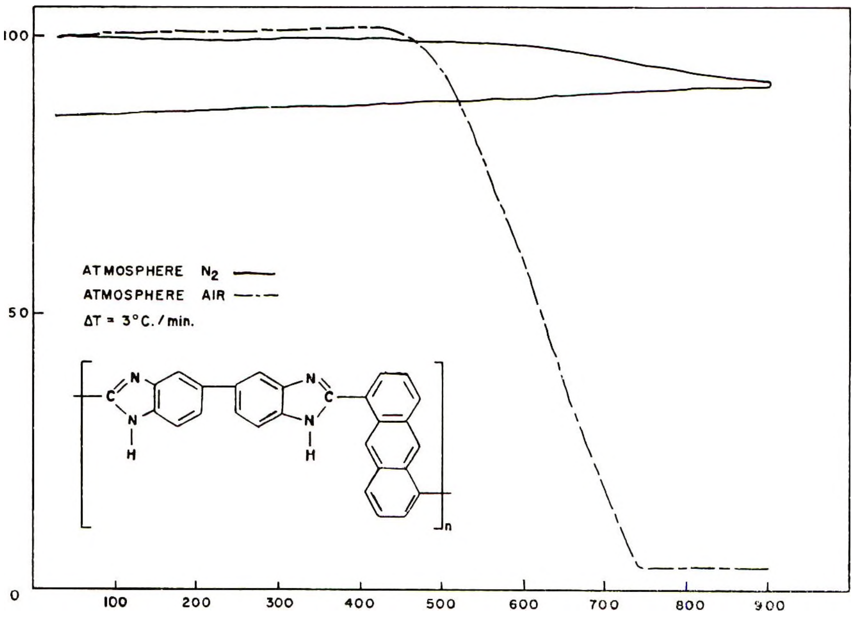


Fig. 1. TGA curve for polybenzimidazole from anthracene.

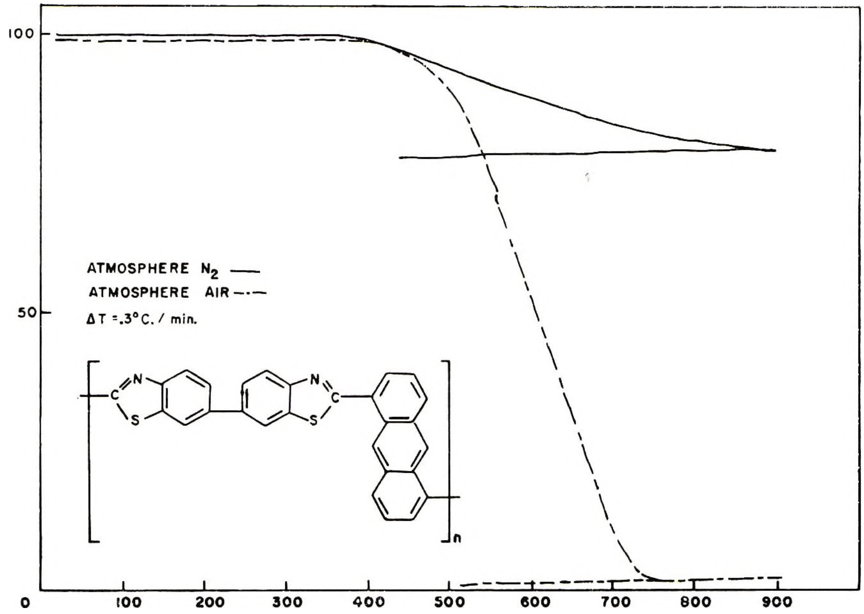


Fig. 2. TGA curve for polybenzothiazole from anthracene.

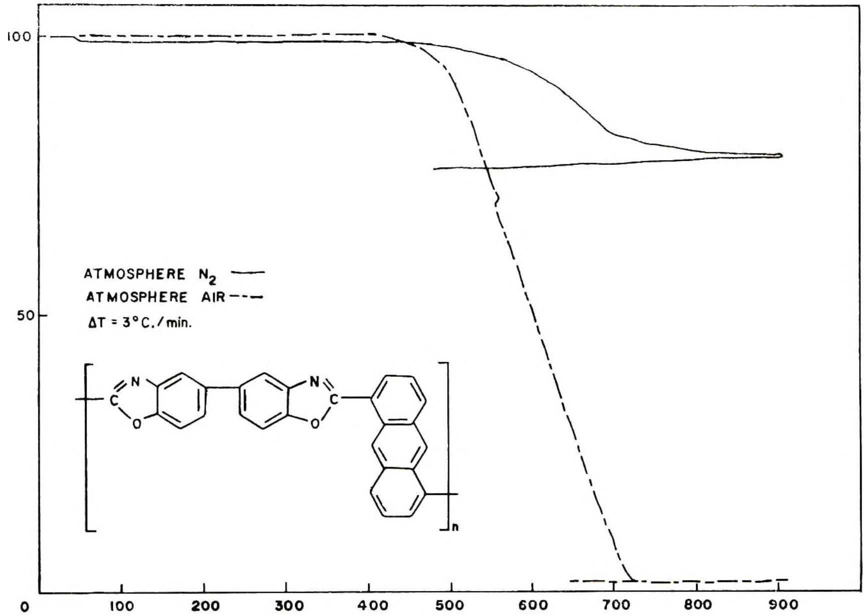
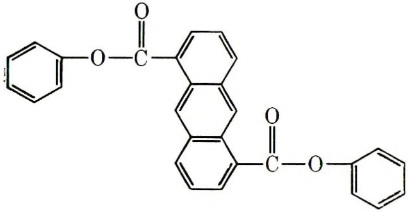
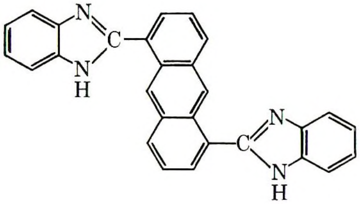
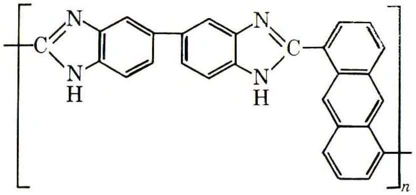
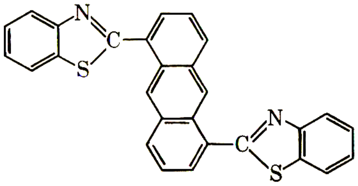
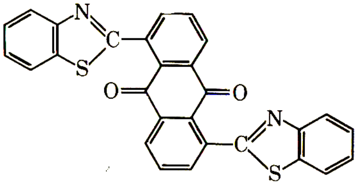
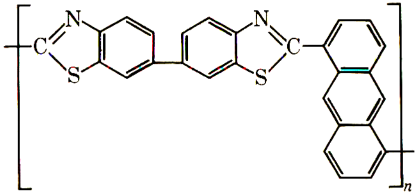


Fig. 3. TGA curve for polybenzoxazole from anthracene.

the breakdown started at around 500°C, and the combustion was complete at 750°C. The thermal stability (see Figs. 1–3), very high for the polybenzimidazole compound, was relatively low for the polybenzothiazole derivative. This feature could be explained by the impure state (i.e., thiol bridges) of the sample.

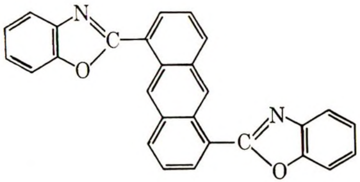
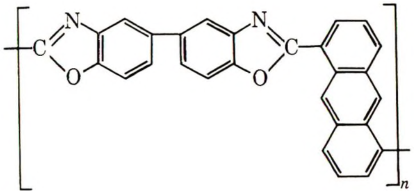
TABLE II
Analysis and Spectral Data on Model Compounds and Polymers

Compound	Analysis		Experimental conditions	UV spectra	
	Calcd, %	Found, %		λ_{max}, mμ	$E^{1\%}_{1cm} \times 10^{-3}$
	C, 80.36 H, 4.34 O, 15.30	C, 80.57 H, 4.37 O, 15.32	Cold, dissolved (12 mg/l.) after 1 hr	233	1.24
	C, 81.95 H, 4.42 N, 13.63	C, 82.03 H, 4.23 N, 13.37	Cold, dissolved (7.2 mg/l.) after 2 hr	234 259 299	0.93 1.91 0.78
Same	Same		Cold, dissolved (14.4 mg/l.) after 2 hr	234 259 299	0.96 1.93 0.80
Same	Same		Cold, dissolved (7.2 mg/l.) after 72 hr	264 289	1.45 0.77
	C, 82.35 H, 3.94 N, 13.71	C, 82.08 H, 4.13 N, 13.71	Cold, dissolved (8.6 mg/l.) after 16 hr	236 269 306	1.28 2.15 0.70

Same	Same		Dissolved and kept at 100°C 24 hr (15 mg/l.)	236 269 306	1.23 2.16 0.69
	C, 75.66 H, 3.62 N, 6.30 S, 14.42	C, 75.90 H, 3.69 N, 6.37 S, 14.20	Cold, dissolved (9.6 mg/l.) after 2 hr	245 274 292 (sh.)	0.97 0.69 0.45
Same		C, 75.13 H, 3.54 N, 6.10 S, 13.51	Cold dissolved (7 mg/l.) after 72 hr	247 266 272 (sh.)	0.74 0.69 0.68
	C, 70.86 H, 2.97 N, 5.90 S, 13.51	C, 70.01 H, 3.13 N, 6.25 S, 13.08	Cold, dissolved (13.2 mg/l.) after 4 hr	249 (sh.) 264 283	0.63 0.79 0.62
	C, 76.00 H, 3.19 N, 6.33 S, 14.48	C, 77.03 H, 3.35 N, 6.08 S, 11.36	Cold, dissolved (6.8 mg/l.) after 24 hr	239 274	1.36 0.90

continued

TABLE II (*continued*)
Analysis and Spectral Data on Model Compounds and Polymers

Compound	Analysis		Experimental conditions	UV spectra	
	Calcd, %	Found, %		λ_{max}, mμ	$E^{1\%}_{1cm} \times 10^{-3}$
Same	Same	C, 76.15 H, 3.43 N, 5.64 S, 11.74	Cold, dissolved (12.3 mg/l.) after 24 hr	245 273	1.01 0.75
	C, 81.55 H, 4.10 N, 6.78 O, 7.76	C, 81.58 H, 4.10 N, 6.13 O, 7.92	Cold, dissolved (13 mg/l.) after 2 hr	235 268 301 310	1.01 1.27 0.80 0.79
	C, 81.95 H, 3.43 N, 6.82	C, 81.78 H, 3.62 N, 6.47	Cold, dissolved (10 mg/l.) after 16 hr	235 270 323	1.24 1.24 0.64
Same	Same		Dissolved and kept at 100°C 24 hr (16.8 mg/l.)	273 3.18 3.42	1.69 0.61 0.55

EXPERIMENTAL

Monomers

Diphenyl 1,5-Anthracenedicarboxylate.[14,15] A mixture of 1,5-anthraquinone-dicarboxylic acid (20 g) and zinc dust (40 g) in 600 ml of 20% ammonium hydroxide was boiled until the initial carmine red coloration was completely discharged (about 4 hr). The hot solution was filtered and acidified with acetic acid to precipitate a yellow solid (when hydrochloric acid is used, the filtration of this product became time-consuming). The crystals were collected, washed with water and dried. The yield was 17 g.

The dried anthracenedicarboxylic acid (10 g) was boiled with thionyl chloride (20 g) in chlorobenzene (200 ml) until all was dissolved. Heating was continued for $^1/_2$ hr. By cooling, green-yellow needles (9 g) were obtained, which could be recrystallized from xylene.

Phenol (30 g) and anthracenedicarboxylic chloride (20 g) were boiled for 3 hr in pyridine. The solution was cooled, diluted with methanol, the precipitate filtered off and washed with methanol. Recrystallization from xylene (two times) yielded 16 g of pure compound.

ANAL. Calcd: C, 80.36%; H, 4.34%; O, 15.30%. Found: C, 80.31%; H, 4.31%; O, 15.17%.

3,3′-Dimercaptobenzidine. The free base was obtained according to the previously described procedure.[16] The dihydrochloride was prepared by dissolving dipotassium benzidine 3,3′-dimercaptide (4 g) in 60 ml of water, filtering off the insoluble material, and pouring this solution in 8 ml of hydrochloric acid solution (28%).

3,3′-Diaminobenzidine. This monomer, obtained from Celanese Corporation of America, could be purified by sublimation at 175–178°C/0.05 mm Hg pressure.

3,3′-Diaminobiphenol. The crude product[17] (20 g) was dissolved in 600 ml of 1% hydrochloric acid at 80–90°C, activated charcoal added, and the mixture kept at this temperature for 30 min. It was filtered while hot, and, after adding sodium acetate (20 g) to the filtrate, cooled under nitrogen. The precipitate was filtered off, washed with water and dried under vacuum.

Model Compounds

1,5-Anthracene-dibenzimidazole-2. Diphenyl 1,5-anthracenedicarboxylate (0.01 mole) and *o*-phenylenediamine (0.02 mole) were dissolved in boiling DEA and heated for 8 hr. After cooling, methanol was added and the yellow precipitate filtered off, washed with alcohol and dried. An infrared analysis showed this product to be identical with the starting ester.

Diphenyl 1,5-anthracenedicarboxylate (0.005 mole) and a slight excess of *o*-phenylenediamine (0.011 mole) were melted under nitrogen for 1 hr at

240°C. Vacuum was then applied for 15 min. The reaction mixture was cooled, the solid cake ground and washed with alcohol. Insoluble in most organic solvents (xylene, veratrole, acetophenone, DMF, acetic acid), 1,5-anthracene-dibenzimidazole-2 was crystallized from the mixture of formic acid and acetic acid (1:1).

ANAL. Calcd: C, 81.95%; H, 4.42%; N, 13.63%. Found: C, 80.79%; H, 4.42%; N, 12.60%.

The same two compounds in equivalent amounts were heated under nitrogen at 240°C, and the temperature raised in 3 hr to 300°C. Vacuum was then applied for 2 hr and the product worked up like the previous one.

ANAL. Found: C, 81.78%; H, 4.27%; N, 11.13%.

An excess of 10% of *o*-phenylenediamine was used, and the temperature raised from 220°C to 280°C in 1 hr. while vacuum was applied for 2 hr.

ANAL. Found: C, 81.79%, H, 4.51%; N, 12.49%.

Again an excess of 10% of *o*-phenylenediamine was used, and the temperature kept for 2 hr at 240°C, while vacuum was applied for 2 hr at 260°C.

ANAL. Found: C, 81.07%; H, 4.33%; N, 12.94%.

When the crude benzimidazole was treated with boiling acetophenone, we obtained a pure compound (see Table II).

1,5-Anthracene-dibenzothiazole-2. In boiling veratrole, diphenyl 1,5-anthracenedicarboxylate and o-aminothiophenol (equivalent amounts) were dissolved and heated for 17 hr. The solution was cooled, diluted with ligroin and the obtained yellow crystals filtered off. The precipitate was washed with alcohol and dried. By means of infrared spectroscopy, this product was identified as the starting ester. With diphenyl ether or DEA as solvent, also no reaction was observed.

Diphenyl 1,5-anthracenedicarboxylate (0.01 mole) and *o*-aminothiophenol (0.022 mole) were melted under nitrogen, while the temperature was raised in 3 hr from 220°C to 280°C. The reaction vessel was cooled; the green-black solid was ground, washed with hot alcohol and hot acetic acid, and finally dried.

ANAL. Calcd: C, 75.66%; H, 3.62%; N, 6.30%; S, 14.42%. Found: C, 75.13%; H, 3.54%; N, 6.10%; S, 13.51%; residue, 1.30%.

The same reaction procedure was used, but this time, the reaction mixture was kept under nitrogen for 3 hr at 280°C, and vacuum was applied at 300°C for 1 hr.

ANAL. Found: C, 75.80%; H, 3.52%; N, 5.93%; S, 13.41%.

The crude product was finally recrystallized from acetophenone, and pure 1,5-anthracene-dibenzothiazole-2 was obtained (See Table II).

1,5-Anthracene-dibenzoxazole-2. Diphenyl 1,5-anthracenedicarboxylate (0.01 mole) and *o*-aminophenol (0.022 mole) were kept under nitrogen for 16 hr at 270°C. The reaction mixture was cooled; the solid was ground, washed with alcohol, and recrystallized from xylene.

ANAL. Calcd: C, 81.55%; H, 3.91%; N, 6.78%. Found: C, 81.79%; H, 4.04%; N, 5.82%.

The mother liquor was concentrated, diluted with alcohol and cooled. A second crop of yellow crystals were obtained. These were recrystallized from acetic acid.

ANAL. Found: C, 79.43%; H, 4.28%; N, 1.43%.

Here too, a pure compound was obtained by recrystallization from acetophenone (see Table II).

Polymers

Polymerization in the Melt

Diphenyl 1,5-anthracenedicarboxylate (0.01 mole) and diaminobenzidine, diaminobiphenol, dimercaptobenzidine (0.01 mole) were heated under nitrogen at elevated temperatures. The resulting foamy mass was cooled, ground, washed with alcohol and dried. Reheating of these prepolymers under vacuum yielded the final products.

Poly[(5,5′-bibenzimidazole)-2,2′-diyl-1,5-anthrylene]. See Table I.

Poly[(5,5′-bibenzoxazole)-2,2′-diyl-1,5-anthrylene] was prepared by melting the monomers for 16 hr at 290°C, and applying vacuum at 340°C for 15 hr.

ANAL. Calcd: C, 81.95%; H, 3.43%; N, 6.82%. Found: C, 81.78%; H, 3.62%; N, 6.47%.

The inherent viscosity at 30.2°C for a 0.2% solution in sulfuric acid was 0.45.

Poly[(6,6′-bibenzothiazole)-2,2′-diyl-1,5-anthrylene]. The monomers were heated under nitrogen for 15 hr while the temperature was gradually raised from 220°C to 280°C. The obtained prepolymer was heated under vacuum for 5 hr at 300°C. The inherent viscosity at 30.2°C for a 0.065% solution in sulfuric acid was 0.51.

ANAL. Calcd: C, 76.00%; H, 3.19%; N, 6.33%; S, 14.48%. Found: C, 77.03%; H, 3.35%; N, 6.08%; S, 11.36%.

Polymerization in Polyphosphoric Acid

Poly[(6,6′-bibenzothiazole)-2,2′-diyl-1,5-anthrylene]. In freshly prepared polyphosphoric acid (from phosphorus pentoxide A.R. and deionized water) dimercaptobenzidine dihydrochloride (1.607 g) was dissolved at 150°C. When the evolution of hydrogen chloride had ended, diphenyl 1,5-anthracene-dicarboxylate (2.093 g) was added, and the temperature slowly raised to 250°C. The solution became more viscous, and the color changed to dark green. It was held at 250°C for 6 hr. The resulting mixture was cooled to 150°C and poured into a 10% solution of ammonium hydroxide (800 ml). The solid was filtered off, extracted with water for 2 days, for 1 day with ethanol and finally dried. The inherent viscosity at 30.2°C for 0.3% solution in sulfuric acid was 0.21.

ANAL. Found: C, 76.15%; H, 3.43%; N, 5.75%; S, 11.74%.

Oxidation Experiments

With Nitric Acid. 1,5-Anthracene-dibenzimidazole-2 (1 g) was boiled in 100 ml of nitric acid (50%) for 2 hr. After cooling, the yellow crystals were washed with water and methanol and extremely well dried (4 hr at 250°C/0.2 mm Hg pressure).

ANAL. Calcd: C, 76.31%; H, 3.65%; N, 12.71%. Found: C, 73.05%; H, 3.23%; N, 12.96%.

This product was washed with diluted ammonium hydroxide, water, and methanol and subsequently dried.

ANAL. Calcd for $C_{28}H_{16}N_4O_2 \cdot {}^1/_3\ HNO_3$: C, 73.0%; N, 13.2%. Found: C, 72.76%; H, 3.44%; N, 13.18%.

Polybenzimidazole (1 g), treated in the same way, yielded yellow-brown crystals which upon heating or washing with ammonium hydroxide turned into a dark brown product (1.1 g).

ANAL. Calcd: C, 76.7%; H, 3.21%; N, 12.77%. Found: C, 68.48%; H, 2.65%; N, 14.49%. Calcd for $(C_{28}H_{13}N_5O_4)_n$: C, 69.3%; H, 2.71%; N, 14.5%.

With Chromium Trioxide. 1,5-Anthracene-dibenzimidazole-2 (1 g) was treated with chromium trioxide (0.5 g) in boiling acetic acid. While the solution turned from brown-red to green, the product dissolved gradually. By cooling, no precipitation occurred.

1,5-Anthracene-dibenzothiazole-2 (1 g) was dissolved in acetic acid (100 ml) and chromium trioxide (700 mg) added. After boiling for 2 hr, the mixture was diluted with water, cooled, and the brown precipitate washed with alcohol and recrystallized from DMF. The yield of light tan product was 400 mg.

ANAL. Calcd: C, 70.68%; H, 2.97%; N, 5.90%; S, 13.51%. Found: C, 70.01%; H, 3.13%; N, 6.25%, S, 13.08%.

An infrared spectrum showed an intense peak at 1670 cm^{-1}, characteristic for anthraquinone derivatives.

Poly[(5,5′-bibenzimidazole)-2,2′-diyl-1,5-anthrylene] (0.5 g, $\eta_{inh.} = 0.65$) and chromium trioxide (0.3 g) were boiled in acetic acid (50 ml) for 3 hr. The reaction mixture was cooled, the solid product filtered off, washed with diluted ammonium hydroxide and water, and finally dried. The yield of brown product was 490 mg.

ANAL. Calcd: C, 76.79%; H, 3.21%; N, 12.77%. Found: C, 77.36%; H, 4.01%; N, 12.14%; residue, 2.24%.

If an excess of chromium trioxide (0.6 g) was used, we obtained a yield of 496 mg.

ANAL. Found: C, 76.56%; H, 3.72%; N, 9.29%.

The inherent viscosity at 30.2°C for a 0.16% solution in sulfuric acid was 0.59. The product was soluble to the extent of 85%.

Ultraviolet Spectra

For all compounds, sulfuric acid was used as solvent and two different concentrations of each compound were run. Because in some cases the spectra were time- or temperature-dependent, solutions with different history were used to check the compounds on their oxidative behavior in sulfuric acid.

We are indebted to Dr. G. F. L. Ehlers, Air Force Materials Laboratory, Wright-Patterson Air Force Base, for thermogravimetric curves.

This work was supported by the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

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Received April 28, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3251-3258 (1970)

Copolymerization of Aryldiazomethanes

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Synopsis

Several aryldiazoalkanes (M_2) have been copolymerized with phenyldiazomethane (M_1) in toluene–methanol solution at 40°C, namely, the *p*-chloro-, *p*-methoxy-, *p*-mesyl-*o* and -*p*-methyl-, 2,4- and 3,4-dichlorophenyldiazoalkanes, and the α- and β- naphthyldiazoalkanes. The copolymerization parameters r_1 and r_2 have been evaluated. By plotting $1/r_1$ against the Hammett σ values a negative ρ value was found equal to -0.88. From cationic copolymerizations carried out at -78°C in the presence of boron trifluoride–diethyl ether as catalyst a similar plot of $1/r_1$ against σ gives a value of ρ equal to -0.82. The negative sign and the agreement between these ρ values demonstrates the cationic mechanism of the methanol polymerization and copolymerization of aryldiazoalkanes.

The polymerization of diazoalkanes can be carried out in the presence of boron fluoride catalysts[1-4]; its cationic mechanism has been elucidated by Bawn, Ledwith, and co-workers[5-8] and discussed by several authors.[9-15] Diazoalkanes have also been polymerized in the presence of metallic salts and finely divided metals such as gold, silver, and copper, as shown by Nasini, Saini, Trossarelli, et al.[16-23] More recently Hermans[24] and Smets et al.[25] synthesized several polyarylidenes either by alkaline decomposition of tosylhydrazones and the resulting aryldiazomethanes in a benzene–methanol–water mixture or by thermal decomposition of aryldiazomethanes in benzene–alcohol solution. The kinetic scheme proposed for these reactions postulated a carbonium ion-pair propagation, although not clearly demonstrated.

The aim of the present study was to determine the copolymerization parameters of different aryldiazoalkanes and to compare these values with those of the corresponding styrenes during their radical and cationic copolymerizations. It is indeed well known that the r_1 and r_2 values are very sensitive to the nature of the propagating species and may therefore facilitate the elucidation of the cationic or radical polymerization mechanism.

EXPERIMENTAL

Phenyldiazomethane and *p*-chlorophenyldiazomethane were prepared by mercuric oxide oxidation of their corresponding hydrazones following the method of Staudinger.[26,27] The other aryldiazomethanes were obtained by alkaline decomposition of the corresponding tosylhydrazones[28] in a water–toluene (or benzene) medium. The diazoalkane contents of their toluene or benzene solutions were determined by addition of excess of benzoic acid and back-titration in the presence of phenolphthaleine.

Alcohol-Catalyzed Copolymerization

The phenyldiazomethane–*p*-chlorophenyldiazomethane copolymerizations were carried out at 67°C in benzene–methanol solutions. All the other copolymerizations were carried out at 40°C in toluene (benzene) solution containing 20% methanol by volume. The M_1/M_2 ratios were varied by mixing previously titrated diazoalkane solutions in different ratios. The reactions were carried out under nitrogen atmosphere in

TABLE I
Copolymerization of Phenyldiazomethane (M_1) with Substituted Aryldiazomethane (M_2) in Homogeneous Toluene–Methanol Systems

M_2 aryl substituent	M_1/M_2	Degree of conversion %	Molar fraction of comonomer in the copolymer f_2	Analysis
p-Chlorophenyl	3	2.8	0.205	7.47% Cl
	1	3.6	0.364	12.60% Cl
	1/3	5.2	0.593	19.03% Cl
p-Methoxyphenyl	3	2.1	0.314	Infrared, *p*-methoxy band at 1250 cm^{-1}
	1	1	0.59	
	1/3	1.66	0.79	
3,4-Dichlorophenyl	3/1	6.7	0.102	7.47% Cl
	1	10.35	0.23	15.41% Cl
	1/3	13.1	0.423	25.2% Cl
2,4-Dichlorophenyl	3/1	7.94	0.127	9.15% Cl
	1	9.37	0.278	18.05% Cl
	1/3	5.35	0.491	28.15% Cl
4-Mesylphenyl	3/1	8.17	0.033	1.15% S
	1	7.1	0.089	2.95% S
	1/3	11.16	0.219	6.55% S
p-Methylphenyl	3/1	5.6	0.35	Infrared, polybenzylidene at 705 cm^{-1}
	1	8.74	0.66	
	1/3	8.61	0.85	
o-Methylphenyl	3/1	9.44	0.333	"
	1/1	5.29	0.595	
	1/3	1.91	0.80	
α-Naphthyl	3/1	9.45	0.51	"
	1/1	3.37	0.711	
	1/3	3.24	0.87	
β-Naphthyl	3/1	15.14	0.545	"
	1/1	14.58	0.792	
	1/3	13.7	0.91	

closed polymerization tubes. The progress of the reaction was followed colorimetrically; when the solution was 10% decolored the reaction was stopped by adding benzoic acid and product precipitated in an excess of methanol. The copolymer was purified by solution in hot benzene and reprecipitation in methanol.

The copolymer compositions were determined by infrared spectrometry and by elemental analysis. The results of the copolymerization experiments are summarized in Table I.

All copolymerization experiments with *p*- and *m*-nitrophenyldiazomethane were unsuccessful.

Cationic Copolymerization ($BF_3 \cdot OEt_2$)

The diazoalkanes were dried on calcium hydride and the polymerizations were carried out at −80°C following the method of Bawn, Ledwith, et al.[5–8] The reactions were stopped by adding methanol. The main difficulty of these experiments consists in stopping the reaction at degrees of conversion inferior to 10% because the lack of reproducibility that must be attributed to impurities present in the monomer, as well as traces of moisture in the solvent. The degree of purity of aryldiazoalkanes seldom exceeds 85%, contamination by azine being most prominent besides some stilbenes.

Table II summarizes only the experiments at relatively low degree of conversion which have been used for the evaluation of the cationic copolymerization parameters.

TABLE II

Cationic Copolymerization at −78°C of Phenyldiazomethane (M_1) with Substituted Aryldiazomethanes (M_2) with $BF_3 \cdot OEt_2$ Catalyst

M_2 aryl substituent	M_1/M_2	Degree of conversion, %	Molar fraction of comonomer in the copolymer f_2	Analysis
2,4-Dichlorophenyl	3	7.5	0.016	1.24% Cl
	1	5.27	0.045	3.4% Cl
	1/3	4.78	0.204	13.90% Cl
3,4-Dichlorophenyl	4	3.07	0.082	3.66% Cl
	3	17.93	0.262	11.71% Cl
	1	13.75	0.283	12.62% Cl
	1/3	5.43	0.735	32.83% Cl
p-Chlorophenyl	3	2.09	0.162	6.02% Cl
	1	8.78	0.441	14.87% Cl
	1/3	5.58	0.539	17.61% Cl
p-Methylphenyl	3	12.53	0.322	Infrared, polybenzylidene absorption at 705 cm^{-1}
	1	2.78	0.638	
	1/3	3.22	0.858	

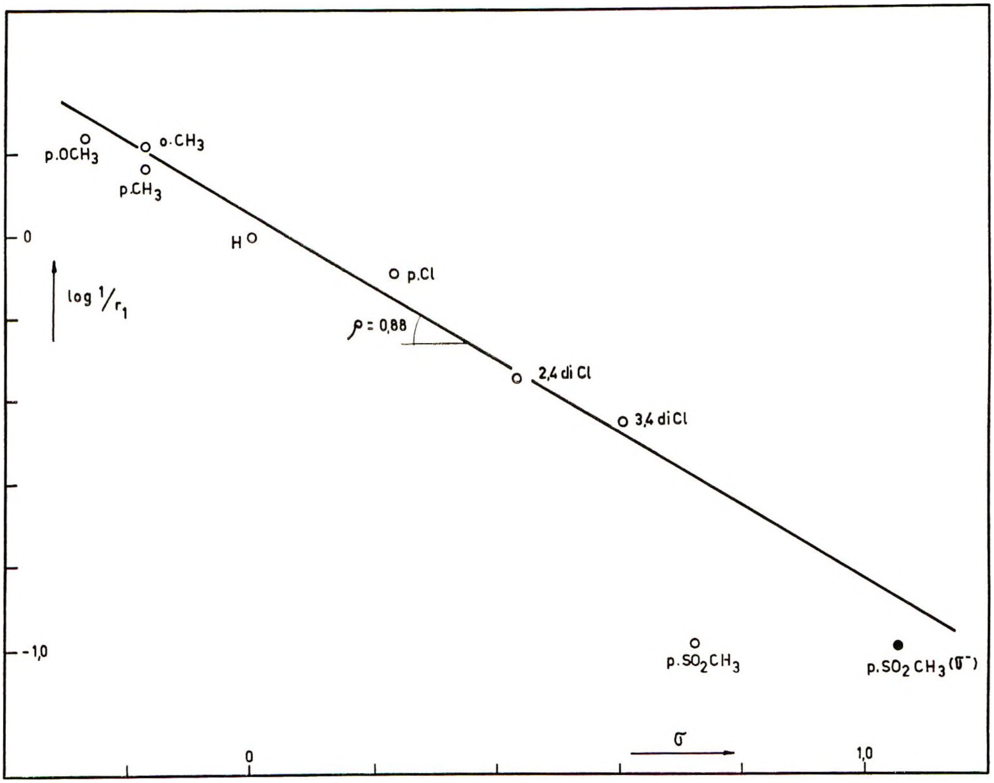

Fig. 1. Relative reactivities of substituted aryldiazomethanes as a function of Hammett σ values. Copolymerizations in toluene–methanol.

DISCUSSION

The parameters r_1 and r_2 of phenyldiazomethane (M_1) and substituted aryldiazomethanes (M_2) have been evaluated for their copolymerization in toluene–methanol medium; these values are summarized in Table III, where these are also compared with the r_1 and r_2 parameters for the $BF_3 \cdot OEt_2$ copolymerization.

The values of $1/r_1 = k_{12}/k_{11}$ have been considered a measure of the relative reactivity of different aryldiazoalkanes with respect to the same ion (or radical), the reactivity of phenyldiazoalkanes towards its own ion (or radical) being taken as unity. These values are plotted against the corresponding Hammett σ value in Figure 1.

This method was applied previously to the radical polymerization of styrene-substituted styrenes ($\rho = +0.51$)[29] as well as to the cationic copolymerization of styrene, *p*-chlorostyrene, and α-methylstyrene with *m*- and *p*-substituted styrenes in the presence of stannic chloride as catalyst. The ρ value was found equal to -1.7, except for *m*- and *p*-methoxy- and *p*-dimethylaminostyrene.[30] This discrepancy was resolved by Brown and

TABLE III

Copolymerization Parameters and Relative Reactivities of Phenyldiazomethane (M_1) with Substituted Aryldiazomethanes (M_2). Copolymerization in Benzene-Methanol Medium

Substituent	r_1	r_2	r_1r_2	log ($1/r_1$) (relative reactivity)	Hammett σ
p-OCH$_3$	0.62 ± 0.1	1.20 ± 0.1	0.80 ± 0.25	0.208	−0.268
p-CH$_3$	0.65 ± 0.15	2.3 ± 0.2	1.50 ± 0.4	0.187	−0.170
	0.88 ± 0.05[a]	2.3 ± 0.1[a]	2.0 ± 0.2[a]	0.0554[a]	
OCH$_3$	0.60 ± 0.07	1.3 ± 0.1	0.78 ± 0.14	0.221	−0.170
p-Cl	1.2 ± 0.1	0.30 ± 0.05	0.36 ± 0.1	−0.079	0.227
	1.54[a]	0.255[a]	0.39[a]	−0.1878[a]	
2,4-di Cl	2.13 ± 0.05	0.21 ± 0.02	0.45 ± 0.05	−0.329	0.427
	24 ± 2[a]	0.05 ± 0.02[a]	1.2 ± 0.4[a]		
3,4-di Cl	2.75 ± 0.07	0.12 ± 0.02	0.33 ± 0.06	−0.439	0.600
	3.6[a]	0.2[a]	0.72[a]	−0.5575[a]	
p-SO$_2$CH$_3$	9.7 ± 0.1	0.055 ± 0.015	0.55 ± 0.15	0.987	0.72 (σ^- 1.049)
α-naphthyl	0.22 ± 0.03	2.0 ± 0.05	0.44 ± 0.07	0.658	—
β-naphthyl	0.20 ± 0.1	3.55 ± 0.3	0.70 ± 0.4	0.699	—

[a] Cationic copolymerizations in toluene in the presence of $BF_3 \cdot OEt_2$.

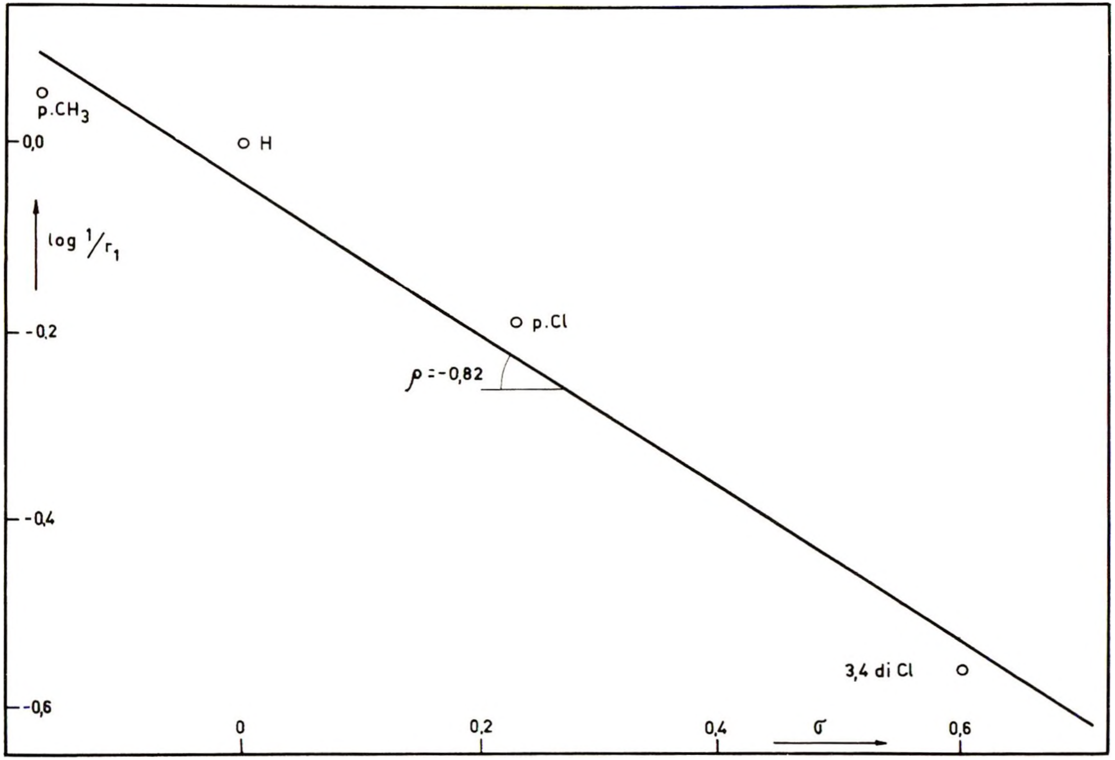

Fig. 2. Relative reactivities of substituted aryldiazomethanes as a function of Hammett σ values. Cationic copolymerizations in toluene with $BF_3 \cdot OEt_2$.

Okamoto[31,32] by the use of Brown's σ^+ value, the value of ρ becoming -2.34.

There is, however, a striking difference between the radical and the different ionic copolymerizations, namely the sign of the corresponding ρ values, being always negative for the cationic processes. In the case of the toluene–methanol copolymerizations of aryldiazoalkanes, a plot of $1/r_1$ versus Hammett σ values also gives a straight line with $\rho = -0.88$, suggesting a cationic polymerization mechanism.

For the *p*-mesyl compound the Taft σ value ($+1.049$) instead of the Hammett σ ($+0.72$) has been used,[3] assuming a delocalization of the negative charge of the diazoalkane carbon atom onto the sulfenyl oxygen atom (Table II).

Moreover, in the case of the boron trifluoride–diethyl ether copolymerizations, a plot of $1/r_1$ against Hammett σ values (Fig. 2) presents again a linear relationship with $\rho = -0.82$. This value is practically equivalent to that of the toluene–methanol copolymerization.

Consequently, the negative ρ values of the relative reactivities of the aryldiazoalkanes in the copolymerization in toluene–methanol as well as its equivalent value -0.88 as compared to -0.82 for the copolymerization with boron trifluoride, demonstrate the cationic mechanism of the methanol polymerization of aryldiazoalkanes postulated previously. Protonation of the aryldiazoalkane by methanol therefore probably involves formation of an ion-pair [$\mathrm{Ar\text{-}CH_2N_2^{+-}OCH_3}$] or solvated diazonium cation [$\mathrm{ArCH_2N_2^{+}\text{-}HO\text{-}CH_3}$], which on addition of diazoalkane propagates with nitrogen evolution. The much slower rate of polymerization compared to cationic polymerization with boron fluoride–diethyl ether must be related to differences in structure of the propagating species.

The authors acknowledge gratefully the financial support and equipment given by the Ministry of National Education (F.K.F.O.). One of them (A.B.) is indebted to the I.R.S.I.A., Belgium, for a fellowship.

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Received April 6, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3259–3264 (1970)

Depolymerization of Polysulfide Polymers by Dithionite Ions

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Synopsis

The action of sodium dithionite, $Na_2S_2O_4$ on desulfurized tetrasulfide polymers leads to their depolymerization. Our studies showed that successful depolymerization can be initiated only in an alkali medium when 1.9–3.2 mole of sodium hydroxide per mole of dithionite is used, and that this leads to the cleavage of disulfide bonds and the formation of polymers of lower molecular weight with —SH end groups. Liquid polymers of 1000–5000 molecular weight are obtained when 0.388–0.155 mole sodium dithionite per segment of polymer is used for depolymerization in the presence of the above-mentioned quantity of sodium hydroxide per mole of dithionite. The depolymerization of polysulfide polymers with sodium dithionite in the presence of sodium hydroxide was followed by determination of the molecular weight and sulfur content of the polymer and analysis of the mother liquid.

INTRODUCTION

According to the literature,[1] the depolymerization of polysulfide polymers can be carried out by means of one of the following procedures: by treating the polymers with an amalgam of sodium in the presence of an alkaline sulfide; by the action of ammonium hydrogen sulfide in the presence of sodium sulfide or polysulfide; by the action of ammonium hydrogen sulfide; or by reaction with sodium hydrogen sulfide in the presence of sodium sulfite.

Of these methods, the only one of practical significance is depolymerization with sodium hydrogen sulfide in the presence of sodium sulfite.[2–5]

A study of the depolymerization of polysulfide polymers led naturally to the question whether polysulfide polymers could also be successfully depolymerized by some other nucleophilic substances. For this we selected sodium dithionite, $Na_2S_2O_4$, expecting it to possess good nucleophilic properties.

EXPERIMENTAL

The tetrasulfide polymer was synthesized as follows. A 900-ml portion of freshly prepared $2M$ solution of sodium tetrasulfide was poured into a round-bottomed flask and to this was added 8 drops of sulfonated ricinoleic acid and 4.8 g of sodium hydroxide. A solution containing 12.18 g of magnesium chloride ($MgCl_2 \cdot 6H_2O$) was dropped and mixed into this solution. The flask was heated to 75°C, and a mixture composed of 254.4 g of bis-2-chloroethyl formal and 4.41 g of 1,2,3-trichloropropane was gently added through a dropping funnel. When addition was complete, the reaction system was maintained at 98–100°C with vigorous stirring for another hour. During this time, polysulfide polymer of very high molecular weight formed as a fine dispersion by polycondensation reaction. When this reaction was complete, the dispersion settled and was thoroughly washed in warm water to eliminate inorganic salts. A 150-g portion of a 50% solution of carbonate-free sodium hydroxide is then added to the washed polymer dispersion at 75°C. The reaction system was kept at 90–95°C with vigorous stirring, during which the "labile" sulfur is eliminated from the polymer. The thoroughly washed polymer dispersion was then depolymerized by treating the polymer at the selected temperature with a suspension of sodium dithionite in a solution of sodium hydroxide, the whole being vigorously stirred. The polymer dispersion was subsequently coagulated by gradually adding a 20% solution of sulfuric acid to a pH of about 4, after which the polymer was washed and dried under vacuum (20–30 mm Hg, 80°C).

RESULTS

In our investigation we proceeded from the fact that sodium dithionite behaves as a strong reducing substance; we therefore tried to conduct the depolymerization reaction through the action of sodium dithionite on the disulfide polymer dispersion. First attempts yielded no results, since the sodium dithionite reacts with water and leads to a disproportionation of sulfur, as a result of which sodium dithionite in an aqueous solution produces an acid reaction by sulfur dioxide separation. This leads to coagulation of the disulfide polymer dispersion and not to depolymerization, so that we used these experimental trials as a basis to attempt depolymerization in an alkali solution. Our studies showed that a fixed amount of sodium dithionite in the presence of a fixed amount of sodium hydroxide can be used to obtain liquid sulfide polymers of fixed molecular weight between 1000 and 5000. Such polymers have properties similar to those of polymers depolymerized by a mixture of sodium hydrogen sulfide and sodium sulfite.

Effect of Temperature

In determining the optimum temperature for this reaction, it was shown that no reaction occurs at room temperature, as shown in Table I. With a rise in temperature depolymerization occurs, and liquid polymers are obtained. If depolymerization is carried out at the boiling point of the reaction system (102°C), the degree of depolymerization is somewhat lower.

TABLE I
Effect of Temperature on Depolymerization Efficiency

	Amt. $Na_2S_2O_4$		Amt. NaOH				
No.	Mole/segment polymer	Mole	g	Mole/mole $Na_2S_2O_4$	Time hr	Temp, °C	Molecular weight of product
1	0.310	0.0766	6.0	1.94	1	25	Rubber
2	"	"	"	"	"	50–60	1185
3	"	"	"	"	"	80–85	1101
4	"	"	"	"	"	102	1403

Effect of Time

Reaction between a disulfide polymer and a dithionite ion is relatively fast. Within 5 min of heating to 80–85°C a liquid polymer is obtained. As shown in Table II, prolonged heating leads to further relatively small decreases in average molecular weight.

TABLE II
Effect of Time on Depolymerization Efficiency

	Amt. $Na_2S_2O_4$		Amt. NaOH				
No.	Mole/segment polymer	Mole	g	Mole/mole $Na_2S_2O_4$	Time, min.	Temp, °C	Molecular weight of product
1	0.310	0.0766	6.0	1.94	5	80–85	1672
2	"	"	"	"	20	"	1319
3	"	"	"	"	60	"	1101

Effect of Sodium Dithionite

The amount of sodium dithionite used in the reaction has a great influence on the degree of depolymerization of disulfide polymer by dithionite. From Table III it will be seen that a liquid polymer of average molecular weight around 5000 forms by the action of 0.155 moles of sodium dithionite per segment of polymer and 2.6 moles of sodium hydroxide per mole of sodium dithionite used. By increasing the mole ratio of sodium dithionite per segment of polymer, the value of the average molecular weight of the polymer is lowered, so that with 0.310 moles of dithionite per segment of polymer a polymer of average molecular weight of around 1000 is obtained.

Effect of Sodium Hydroxide

From the results given in Table IV on the effect of sodium hyd oxide, it follows that depolymerization can occur only if 1.9–3.2 mole sodium hydroxide per mole of dithionite is used. If less than 1.8 mole of sodium hydroxide per mole dithionite is employed no reaction whatsoever is obtained, and with 3.9 mole sodium hydroxide per mole of dithionite, rubbers are formed. If the proportion of sodium hydroxide is kept between 1.9 and 2.6 mole/mole dithionite, polymers are obtained whose molecular weights can be reproduced with a variation of up to ±10%. This variation is a consequence of the presence of trifunctional alkyl halide, which, after depolymerization, forms a certain number of polymers possessing a partly branched structure. The deviation in value of average molecular weight of depolymerized linear polymers is therefore much smaller and chiefly the consequence of a statistical distribution of polymer molecular weights and the result of experimental errors in determining average molecular weight.

TABLE III

Effect of Sodium Dithionite on Depolymerization Efficiency at 80–85°C for 1 hr

No.	Amt. $Na_2S_2O_4$		Amt. NaOH		Molecular weight of product
	Mole/segment polymer	Mole	g	Mole/mole $Na_2S_2O_4$	
1	0.155	0.0383	4.0	2.6	4910
2	0.194	0.0479	5.0	2.6	2334
3	0.233	0.0574	6.0	2.6	1437
4	0.310	0.0766	8.1	2.6	978
5	1.388	0.0957	10.0	2.6	1016

TABLE IV

Effect of Sodium Hydroxide on Depolymerization Efficiency with Sodium Dithionite at 80–85°C for 1 hr

No.	Amt. $Na_2S_2O_4$		Amt. NaOH		Molecular weight of product
	Mole/segment polymer	Mole	g	Mole/mole $Na_2S_2O_4$	
1	0.310	0.0766	6.0	1.94	1101
2	"	"	8.0	2.60	978
3	"	"	10.0	3.26	1349
4	"	"	12.0	3.91	Rubber
5	"	"	14.0	4.56	Rubber

DISCUSSION

In the study of the depolymerization of polysulfide polymers by dithionite ions, the sulfur content, average molecular weight of the polymer, and the composition of the solution after depolymerization were determined.

The sulfur content was determined by Wurzschmitt's semimicro method with sodium peroxide in a Parr bomb and then determination as barium sulfate. Analysis showed that the sulfur content corresponds to the theoretical sulfur content expected for linear polymers of corresponding molecular weight having the formula $HS{-}\!(CH_2CH_2OCH_2OCH_2CH_2S_2)_n\!{-}SH$). For example, a polymer with a molecular weight of 1394, consists of 8 segments ($—CH_2CH_2OCH_2OCH_2CH_2S_2—$) and two terminal —SH groups and contains 41.32% sulfur. It was found by experiment that a polymer with an average molecular weight of 1437 contains 41.40% sulfur, and it may be concluded that after depolymerization the polymers have a largely linear structure.

The molecular weights of polymers were determined by iodimetric titration of the terminal thiol groups.[6]

The composition of the solution remaining after depolymerization was determined by four iodimetric titrations.[7] Sulfide, dithionite, sulfite, and thiosulfate were determined by adding a solution of iodine of known normality to an aliquot of the tested solution and then titrating the remainder of the iodine with a solution of thiosulfate. Dithionite, thiosulfate, and sulfite were determined in the same way from an aliquot of the solution from which the sulfide ions and dithiols dissolved in water were eliminated by zinc carbonate. Dithionite and thiosulfate were determined by iodimetric titration of an aliquot of the solution from which the sulfide ions and dithiol dissolved in water are eliminated and the sulfite ions linked by formaldehyde. Finally thiosulfate was determined as the tetrathionate which forms on iodine oxidation.

Determination of the composition of the solution remaining after depolymerization ought to yield data which would establish the equation according to which depolymerization takes place. We assumed that the reaction would come about in such a manner that one mole of sodium dithionite and two moles of sodium hydroxide would be used per segment of disulfide polymer:

$$—RSSR— + Na_2S_2O_4 + 2NaOH \rightarrow 2\,—RSH + 2Na_2SO_3 \qquad (1)$$

As can be seen from the equation, only the lower polymers and sodium sulfite form as products of the reaction. The polymers of very low molecular weights (dithiols) which are water-soluble remain in the mother liquid and are titrated with the sulfide ions, which may remain after the desulfurization reaction if the polymer is not well washed. Analyses of the mother liquid showed that in the solution, besides sulfite, unreacted dithionite, sulfide, and polysulfide polymers dissolved in water (dithiols), there is always a certain quantity of thiosulfate not taken up into the reaction system as an ingredient of dithionite. This indicates that the depolymerization reaction does not proceed simply according to eq. (1). Further studies in this direction are proceeding.

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Received April 14, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3265-3283 (1970)

Polyamides: Decarboxylation and Desamination in Nylon 6 Equilibrium Polymer

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Synopsis

Rate and extent of both decarboxylation and desamination in the temperature range of 250–290°C were studied on equilibrium polymers obtained by the hydrolytic polymerization of ε-caprolactam. Mechanisms have been proposed that are characterized by the participation of the equilibrium monomer in the considered decomposition reactions. The mechanisms suggested accommodate both the experimental results of this study and findings of previous investigations as reported in the literature.

INTRODUCTION

The effect of heat on polyamides has been of considerable interest and has therefore been the subject of numerous studies. The corresponding investigations have been concerned with isolation and identification of products obtained by pyrolysis of polyamide samples, attempts to explain the phenomenon known as "gelling," and to suggest mechanisms for the respective reactions.[1–3] Most of the work reported on the decomposition of polyamides has been characterized by the use of rather severe conditions with respect to temperature, exposure time, and reaction medium. Furthermore, the samples employed were usually commercial materials that had been produced by conventional processes which, for nylon 6, generally involved the following steps: polymerization at temperatures of about 260°C, extrusion into ribbon or sheet, cutting into chip, extraction with hot water, drying to extremely low moisture content, and re-extrusion into filament or film. Extrusion temperatures are usually between 260 and 280°C; quenching and drying operations are usually carried out without exclusion of oxygen, and drying temperatures of about 100°C are common. The polyamide produced in this manner therefore experienced exposure to oxygen under conditions which may lead to the formation of oxidation products such as hydroperoxides.[4,5] For this reason, the effects resulting from the use of such materials in studies on thermal decomposition may, at least in part, be the result of oxidation. If exposure of the polymer to oxygen can be avoided at any time, certain of the observed side reactions may not occur, and the temperature effect on decomposition may be better assessed.

The present studies were therefore conducted directly on equilibrium polymers as they were obtained by hydrolytic polymerization of caprolactam in an essentially absolute oxygen-free atmosphere. Eliminating any operation concerned with the isolation of the polyamide from the original equilibrium composition was expected to provide information suitable to correlate the extent of certain side reactions with parameters such as initial composition of the reaction mixture, polymerization conditions, and reactor design (residence time distribution). It has been realized that the changes in the chemical composition resulting from prolonged heating of polyamides at temperatures such as usually employed in polymerization and extrusion may not be very apparent but may significantly affect further processing. Information in the literature indicates that the major gaseous by-products of the thermal decomposition are carbon dioxide and ammonia.[2] The work reported in this paper has therefore been mainly concerned with both rate and extent of formation of the two by-products in order to formulate corresponding reaction mechanisms.

EXPERIMENTAL

Materials

Pure caprolactam was redistilled under nitrogen at 1 mm Hg. ε-Amino caproic acid was obtained from Eastern Chemical Corp., Pequannock, N.J., and purified by two recrystallizations from ethanol–water, mp 202–203°C.

Polymerization

Into a 250 ml, three-necked flask, fitted with a nitrogen inlet, thermometer, serum cap, and containing a Teflon-encapsulated bar magnet, was introduced 3.86 g of ε-amino caproic acid. After sweeping the system for 10 min with dry nitrogen, 200 ml of molten ε-caprolactam at a temperature of 106°C was added by means of a heated hypodermic syringe. The mixture was heated rapidly to 150°C with stirring until a clear, colorless solution was obtained. This solution was then cooled to 106°C. Under an inert atmosphere, 30 ml was added to the polymerization tube, which is part (6) of the system shown in Figure 1. Four additional polymerization tubes were also charged with 30-ml aliquots, connected to a separate stream of helium, and placed together with the first tube into the heating block [Fig. 1 (7)]. All polymerization tubes were maintained under identical thermal conditions and helium flow during the experiment. The first tube, connected to the system in Figure 1, was used for both the carbon dioxide determination and analysis of the final polymer. Three tubes were used for the analysis of the polymer at the initial stage and two different intermediate stages, whereas the last tube was used to study the evaluation of ammonia. To effect polymerization, the tubes were heated to 250°C maintaining a helium flow of 20 ml/min. When this temperature had been

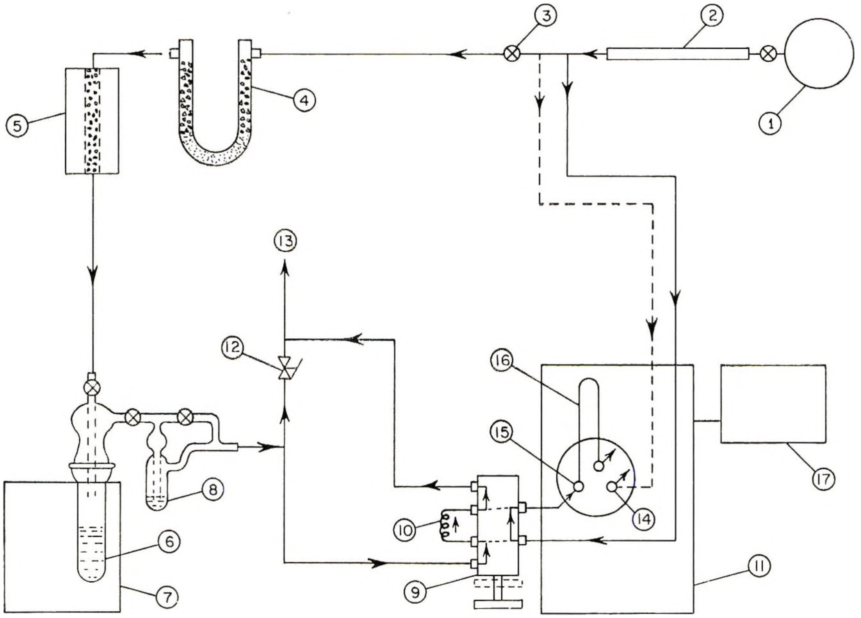


Fig. 1. Equipment flowsheet of the system used for polymerization and carbon dioxide measurements.

reached the tubes were sealed and held at this temperature for 22 hr. At the end of this period the CO_2 concentration in the gas phase of the first tube was measured, the temperature was increased to the desired level, and the first polymer sample removed for analysis. A constant stream of helium at a rate of 20 ml/min was then passed through the gas phase of the remaining tubes. This helium flow was maintained for several hours during each day, whereas the tubes were sealed overnight. The carbon dioxide that had accumulated was measured each morning. The withdrawn polymer samples were extracted and analyzed with respect to molecular weight (viscosity) and endgroup concentrations.

Carbon Dioxide Measurements

The liberated carbon dioxide was measured under both static and flow conditions by using a Perkin-Elmer Vapor Fractometer that had been calibrated with synthetically prepared CO_2–helium mixtures. The process is shown in the scheme in Figure 1.

Adjusted to a flow rate of 20 ml/min by the needle valve (3), helium gas was taken from the cylinder (1) and purified of trace amounts of H_2O, CO_2, and O_2 by passing it successively through a column of 13X molecular sieves (2), a Drierite–Indicarb tube (4), and a 700°C zirconium catalyst furnace (5). The helium stream was then passed through the gas phase of the polymerization tube (6) and then through polyphosphoric acid in (8) where all of the volatile basic decomposition products and traces of caprolactam and water were absorbed. From there the stream enters the sample injector (9) and the sample loop (10), either to be injected into the column (16) for analysis or fed into a $0.01N$ aqueous sodium hydroxide solution (13). During the actual gas analysis the stream is diverted directly to the sodium hydroxide solution by opening the by-pass valve (12).

For flow CO_2 measurements, the helium stream from the polymerization tube, which normally passed through the sample injector and sample loop, was shunted to the sample column by pushing the injector plunger in. The gas contained in the sample loop was swept through the column and analyzed.

For static CO_2 measurements, conducted once each day just as the polymerization tube was opened in order to determine the CO_2 accumulated in the tube while sealed overnight, a different technique was used. That part of the reaction tube on both sides of the PPA trap, as well as the lines leading to and including the sample injector and sample loop were evacuated and filled with helium gas several times (the lines used to accomplish this are not shown in Figure 1). A final evacuation was made, the vacuum source was shut off, and the gas phase above the polymer melt was drawn through the PPA trap and into the sample loop. The sample was thus injected into the fractometer for analysis. Since these CO_2 concentrations were always quite high, appropriate corrections had to be made for that portion of the gas phase actually lost to the instrument. Following this, flow CO_2 measurements were conducted throughout the remainder of the day, at regular time intervals, as previously described. At the beginning of each day, the helium stream was analyzed for impurities prior to entering the polymerization tube.

Ammonia Measurements

The apparatus used for measuring the NH_3 evolution from a nylon 6 sample is shown in Figure 2. Purified helium was passed through the polymerization tube, above the melt, at a flow of 20 ml/min. It then passed into a $0.01N$ sulfuric trap for absorption of NH_3 and then through two $0.01N$ sodium hydroxide traps before exiting out through the oil bubbler. The polymer was maintained at the desired degradation temperature and the polymerization tube was sealed overnight and swept with helium at a rate of 20 cc/min during the day.

The evolved ammonia was determined by titration of the sulfuric acid trap with $0.01N$ NaOH, with the use of a pH meter to determine the endpoint. The CO_2 evolved in this sample was determined by titration of the sodium hydroxide solution with $0.01N$ H_2SO_4.

Polymer Analysis

Degree of Polymerization. Reduced viscosities of the polymer solution were measured at 250 ± 0.05°C in a Ubbelohde viscometer employing concentrations of 0.52 g of polymer/100 ml of *m*-cresol. The viscometer

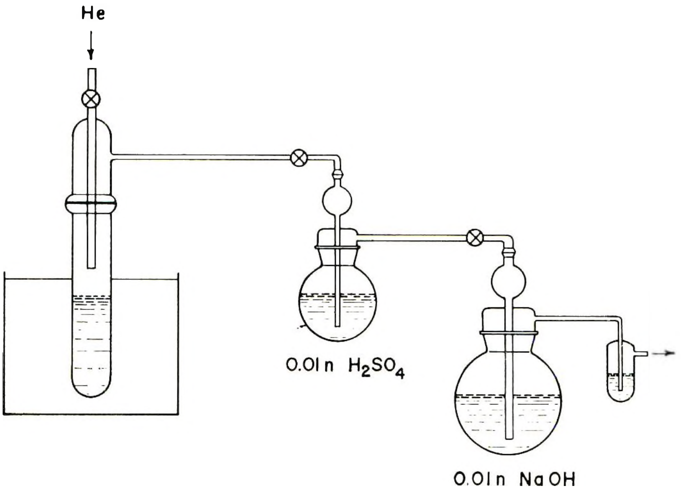


Fig. 2. Apparatus for determination of volatile bases and acids.

used had a flow time of more than 100 sec for the pure solvent. From the solution viscosities, number-average degrees of polymerization were calculated according to:

$$\log P_n = 2.003 + 1.274 \log \eta$$

The concentration of amide groups (milliequivalents per gram of polymer) was calculated by using the relation:

$$[\mathrm{NHCO}] = (P_n - 1) \times 10^3/113.16P_n$$

Concentrations of End Groups. The concentration of end-groups was determined by conventional endgroup titrations. The carboxyl groups were titrated with 0.01N KOH in 2% benzyl alcohol solutions. The basic functions were titrated with 0.01N p-toluenesulfonic acid in trifluoroethanol solutions.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental data are summarized in Table I. The times listed are the ones at which polymer samples were withdrawn, and the time intervals during which the rate of CO_2 formation was measured. The observed increase in viscosity at 250°C has been attributed to continued endgroup condensation, the extent of which obviously exceeds the loss of endgroups by both decarboxylation and desamination. The constancy of the viscosity at 260°C indicates that the effects of the two competitive processes are of about equal magnitude. At higher temperatures the reaction resulting in a decrease in the viscosity seemed to be the dominating one. Since the viscosity decrease was paralleled by an increase of both rate and extent of decarboxylation, the corresponding reactions appeared

TABLE I
Measured Quantities

Temp, °C	Sample time, hr	He flow interval ($t_1 \rightarrow t_2$), hr	$\frac{\eta_{sp}}{c}$	$[NH_2]$, meq/g	[COOH] meq/g	$[NH_3]$, mmole/g $\times 10^3$	$[CO_2]$, mmole/g $\times 10^3$	$d(CO_2)/dt$, mmole/g/hr $\times 10^5$
250	0		2.25	0.037	0.033	0	0	
		0–3.00						2.44
	24.00		2.41	0.036	0.028	0.24	0.67	
		20.10–27.08						2.44
	48.17		2.68	0.035	0.023	0.48	1.41	
		43.75–51.00						2.44
	73.50		3.01	0.030	0.018	0.74	2.21	
		72.22–73.50						2.44
260	0		2.24	0.0379	0.0325	0	0	
		0–0.50						3.99
	21.97		2.64	0.0336	0.0263	0.29	0.76	
		21.50–24.55						3.99
	43.17		2.67	0.0337	0.0237	0.59	1.72	
		43.00–48.50						3.99
	71.75		2.64	0.0379	0.0218	0.94	3.29	
		65.08–71.75						3.99

270	0		2.24	0.037	0.037	0	0	
		0–2.68						6.70
	23.18		2.47	0.036	0.026	0.39	2.46	
		19.22–26.52						6.85
	46.68		2.26	0.041	0.022	0.78	5.81	
		45.60–50.55						6.95
	70.00		2.08	0.047	0.020	1.26	10.53	
		67.60–70.00						7.07
280	0		2.30	0.0384	0.0339	0	0	
		0–2.60						10.07
	18.58		2.15	0.0467	0.0248	0.59	3.58	
		21.38–26.30						13.73
	42.58		1.89	0.0559	0.0178	1.46	10.18	
		45.20–51.02						17.55
	69.90		1.51	0.0713	0.0152	2.96	19.36	
		68.15–70.72						20.81
290	0		2.25	0.036	0.035	0	0	
		0–1.83						23.50
	22.50		1.70	0.061	0.025	1.03	11.02	
		18.50–25.80						50.50
	46.33		1.25	0.089	0.020	3.10	34.53	
		42.85–49.67						72.56
	69.17		0.90	0.141	0.012	7.12	59.51	
		66.38–69.17						97.40

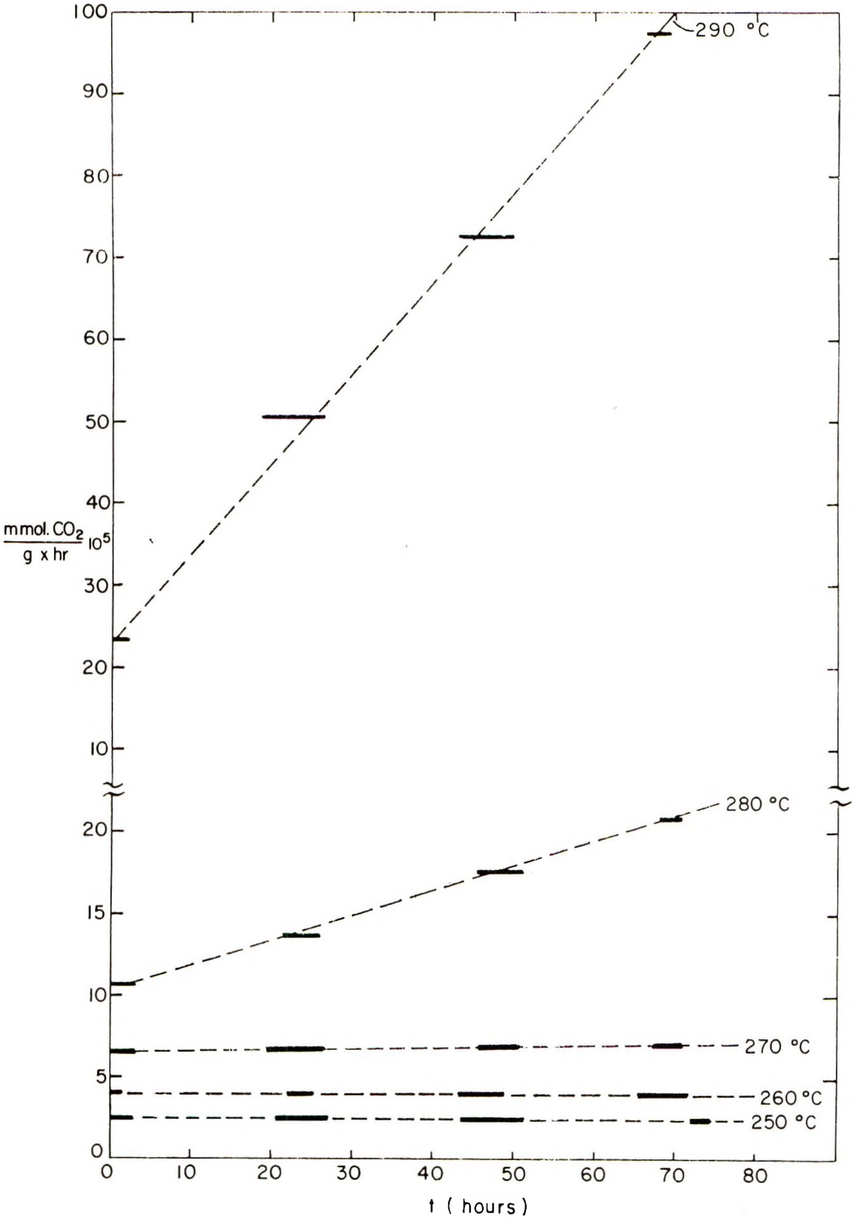


Fig. 3. Rate of carbon dioxide formation as a function of time and temperature.

to be coupled. Whereas an expected decrease of the concentration of acid endgroups was found at all temperatures, an unexpected and rather appreciable increase in the basic functions was observed at temperatures exceeding 270°C.

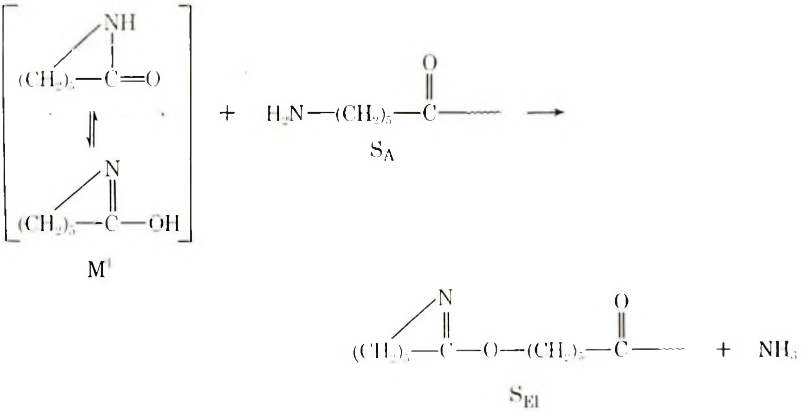
For this temperature range the effect of sealing the polymerization apparatus overnight became very apparent. Water had been identified as a product of the thermal decomposition. In an open system at least a part of this water will be carried off. In a closed system, however, if its concentration exceeds the equilibrium value, it will react with the amide groups cleaving the polymer molecule and forming additional amino and acid groups. The thereby resulting increase in the concentration of COOH groups may then lead to an increased rate of decarboxylation. This situation seems to prevail at higher temperatures as shown in Figure 3, where the distances on the time scale between the solid lines represent the periods during which the system was closed. The amount of carbon dioxide produced during these periods is then of course different from that to be expected according to the rates measured for the open system.

Mechanisms of Decomposition

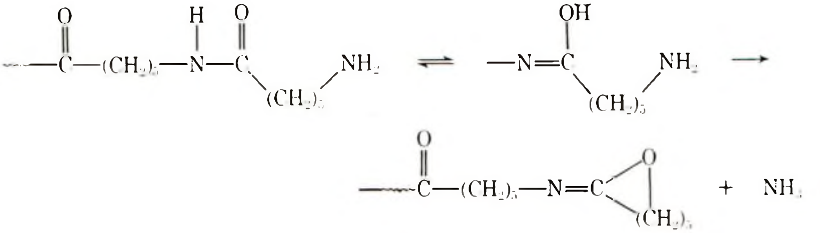
The formation of ammonia has been explained by a reaction between two primary amino endgroups resulting in a secondary amino group:

$$\sim\sim\text{—NH}_2 + \text{H}_2\text{N—}\sim\sim \rightarrow \sim\sim\text{—NH—}\sim\sim + \text{NH}_3 \qquad (1)$$

Kamerbeek et al.[2] concluded that this reaction must have occurred, at least to some extent, when nylon 6 was heated for 12 days at 281°C, since after hydrolysis of the resulting gelled polymer some di(ω-carboxypentyl)-amine was found. The amount of this amine was much smaller than the total amount of ammonia that was liberated. Additional reactions must therefore account for the formation of NH_3, and any corresponding mechanism should accommodate the observed increase of the basic functions upon prolonged heating. Since this increase has been indicated by titration, the corresponding basic functions may not necessarily be amino groups. For instance, Schlack has suggested that upon heat treatment of nylon 6 fibers, cyclic amidine endgroups may be formed.[6] Since amidine formation does not involve liberation of ammonia, we assume that it is either paralleled or preceded by the formation of an imino ether type endgroup according to either or both of the reactions (2) and (3).

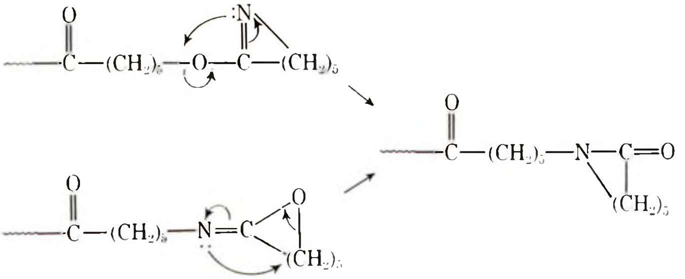


(2)



(3)

In these cases, the endgroups formed would be titrated as amino functions, and therefore the loss of an amino end-group could not be detected by titration. The presence of di(ω-carboxypentyl)amine in the hydrolysis product as observed by Kamerbeek et al. does not constitute proof that reaction (1) actually occurs. In the considered temperature range, some of the imino ether endgroups formed according to eqs. (2) or (3) may undergo a Chapman rearrangement[7] to a lactam moiety according to the



(4)

scheme of eq. (4). It is obvious that hydrolysis of a polymer containing such groups will produce di(ω-carboxypentyl) amine.

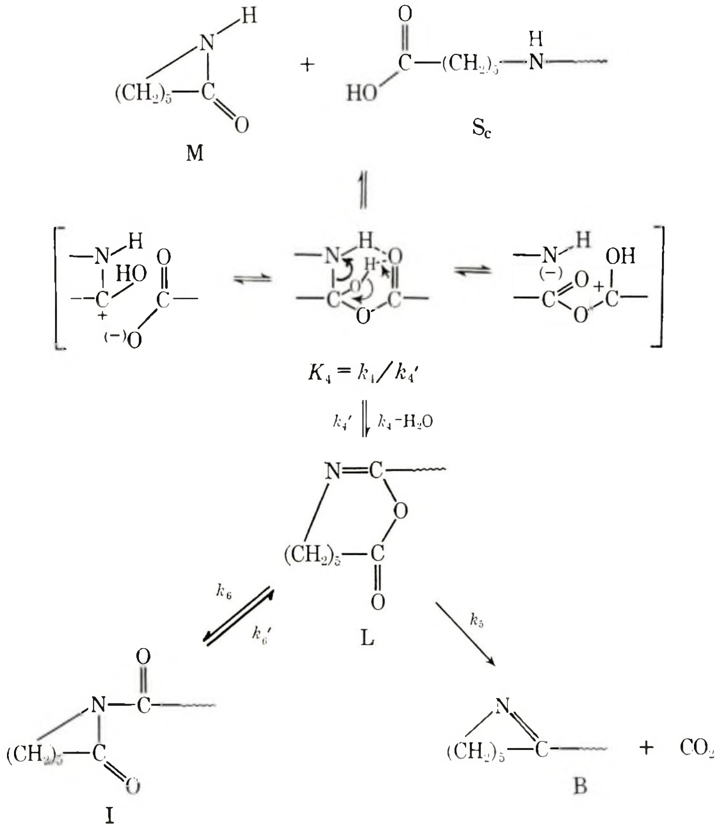
Although the loss of one amino group may be compensated by the generation of another titratable basic function, the considered mechanism does not explain the observed increase in the concentration of the basic functions. This phenomenon must therefore be related to other decomposition processes. In addition to water, carbon dioxide has been identified as the other major reaction product, even when the thermal decomposition of nylon 6 had been conducted under relatively mild conditions. It has been suggested that carbon dioxide is produced mainly by reaction between the carboxyl endgroups of two polymer molecules according to:

$$\begin{aligned} &R{-}CONH(CH_2)_5{-}COOH + HOOC(CH_2)_5NHCOR' \rightarrow \\ &\qquad RCONH(CH_2)_5{-}CO(CH_2)_5NHCOR' + CO_2 + H_2O \qquad (5) \end{aligned}$$

Kamerbeek et al.[2] isolated 1,11-diamino-6-oxo-undecane from the hydrolysis product of a gelled nylon 6 and concluded therefore that a reaction of the considered type must indeed take place. They found support for this conclusion when they observed that this compound caused gelling when added to a polymer melt. It is conceivable, however, that the observed phenomena may be explained by an alternate mechanism.

It was reported that water was immediately formed when extracted and dried nylon 6 was heated at temperatures above its melting point. The formation of both carbon dioxide and ammonia, on the other hand, showed a pronounced induction period.[2] In our studies on nylon 6 equilibrium polymers we did not measure the rate at which water was formed, but we followed the formation of carbon dioxide closely. We found that carbon dioxide was produced at a rather constant rate without any indication of a induction period. It is obvious that the initial presence of the equilibrium monomer constituted the main difference between our system and the one employed in the studies reported previously. It is therefore conceivable that decarboxylation is favored if appreciable quantities of caprolactam are present. Recent studies in this laboratory have been concerned with the polymerization of lactams containing carboxylic functions. The formation of novel polymers containing ring structures has been explained by a mechanism that involved protonation of the lactam moiety.[8] Similar interactions between lactam and carboxyl groups may be envisaged in a system consisting of caprolactam and the corresponding linear polyamide.

Since caprolactam is converted to polyamide predominantly by addition to the amino groups of the linear polymer molecules, the considered interaction with acid end-groups may be especially pronounced at the conversion equilibrium. The formation of CO_2 suggests that this is an essentially irreversible reaction the extent of which may therefore be considerable at prolonged periods of heating. In analogy with our previous consideration, the mechanism of decarboxylation may be represented by reaction (6).



(6)

$$-\text{CONH}- \;+\; \text{H}_2\text{O} \;\underset{k_2}{\overset{k_2'}{\rightleftharpoons}}\; \underset{\text{S}_c}{-\text{COOH}} \;+\; \text{H}_2\text{N}- \qquad (7)$$

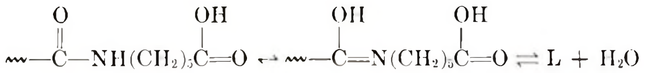
According to this mechanism the reaction of caprolactam with an acid endgroup results in the liberation of one mole of water and the formation of the intermediate L. The latter may then either isomerize to the imide I or decarboxylate and thereby form the cyclic Schiff base B.

The water formed in this reaction may either leave the system or react with an amide linkage. In the latter case additional amino and acid endgroups are formed which may continue to undergo all of the reactions discussed thus far. At a given temperature there will, of course, always be a constant concentration of caprolactam in the system because of the polymer-monomer equilibrium.

The Schiff base B constitutes a basic function that is titratable as an amino group. Its formation from a nonbasic function may explain the observed increase in the concentration of basic functions upon prolonged heating of nylon 6.

The mechanism for the decarboxylation reaction has been formulated as presented because of the different initial behavior of extracted and unextracted polyamide.

The postulated intermediate L, however, could also be formed without participation of caprolactam if reaction between the terminal carboxyl group and the adjacent amide group is assumed according to eq. (8)



$$\sim\!-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{NH}(\text{CH}_2)_5\overset{\overset{\text{OH}}{|}}{\text{C}}=\text{O} \leftrightarrow \sim\!-\overset{\overset{\text{OH}}{|}}{\text{C}}=\text{N}(\text{CH}_2)_5\overset{\overset{\text{OH}}{|}}{\text{C}}=\text{O} \rightleftharpoons \text{L} + \text{H}_2\text{O} \qquad (8)$$

Branched structures would result if this reaction occurred between an acid endgroup and any amide linkage of a second polymer molecule.

In any of the considered cases the hydrolysis product of the formed Schiff base structure would be the 1,11-diamino-6-oxo-undecane, the same compound that Kamerbeek et al isolated from hydrolyzed gelled nylon 6. If this occurs, gellation may be considered a secondary reaction involving the Schiff base structure. This structure may also be responsible for the formation of structures yielding a positive reaction with Ehrlich's reagent as reported recently by Schlack.[9]

EVALUATION OF EXPERIMENTAL DATA

Desamination

For the purpose of deriving kinetic expressions, the three reactions according to which ammonia could be formed may be written as follows:

$$\text{S}_\text{A} + \text{S}_\text{A} \xrightarrow{^1k_\text{A}} \text{S}_\text{SA} + \text{NH}_3 \qquad (9)$$

$$\text{M}^1 + \text{S}_\text{A} \xrightarrow{^2k_\text{A}} \text{S}_\text{E1} + \text{NH}_3 \qquad (10)$$

$$S_A \underset{{}^3k_{A1}{}^1}{\overset{{}^3k_{A1}{}^1}{\rightleftharpoons}} S\ddagger \xrightarrow{{}^3k_{A2}} S_{E2} + NH_3 \tag{11}$$

The first reaction is of second order and the corresponding rate equation is

$$d[NH_3]/dt = {}^1k_A[S_A]^2 \tag{12}$$

In this case the concentration of amino end groups $[S_A]$ is given by the relation

$$[S_A] = [S_A]_0^* - 2(NH_3)$$

where $[S_A]_0^* = [S_A]_0 + \Delta[Z]$, and $[S_A]_0$ is the initial concentration of amino endgroups, and $\Delta[Z] = [NHCO]_0 - [NHCO]$ is the change of the concentration of endgroups due to either condensation or cleavage of amide linkages.

Substitution and integration result in the expression

$$([NH_2]_0^* - 2[NH_3])^{-1} - ([NH_2]_0^*)^{-1} = 2{}^1k_At \tag{13}$$

A corresponding plot gave curved lines rather than straight lines, which indicated that this reaction may not play a significant part in the formation of ammonia.

Using steady-state approximations for the enol type tautomers in reactions (10) and (11), and employing the relation $[S_A] = [S_A]_0^* - [NH_3]$, simple kinetic equations are easily obtained. It follows for the reaction (10):

$$\ln\frac{[NH_2]_0^*}{[NH_2]_0^* - [NH_3]} = 2k_AK_t[M]t \tag{14}$$

where K_t is a constant of the lactam-lactim equilibrium and $[M]$ is equilibrium monomer concentration, and for the reaction (11):

$$\ln\frac{[NH_2]_0^*}{[NH_2]_0^* - [NH_3]} = \left(\frac{{}^3k_{A1}{}^3K_{A2}}{{}^3k_{A1}{}^1 + {}^3k_{A2}}\right)t \tag{15}$$

Figure 4 shows a plot involving the principal variables of both eqs. (14) and (15). The slopes of the straight lines were used to construct the Arrhenius plot in Figures 5.

The fairly linear relationships shown in Figures 5 could indicate that the ammonia is predominantly formed by reaction (10). However, without knowledge of the values of the individual rate constants, eq. (11) can not be excluded from consideration.

Decarboxylation

The mechanism proposed for the decarboxylation as shown in eqs. (6) and (7) may be represented by the simplified eqs. (16)–(18):

$$M + S_C \underset{k_4{}^1}{\overset{k_4}{\rightleftharpoons}} L + H_2O \tag{16}$$

$$L \xrightarrow{k_5} B + CO_2 \tag{17}$$

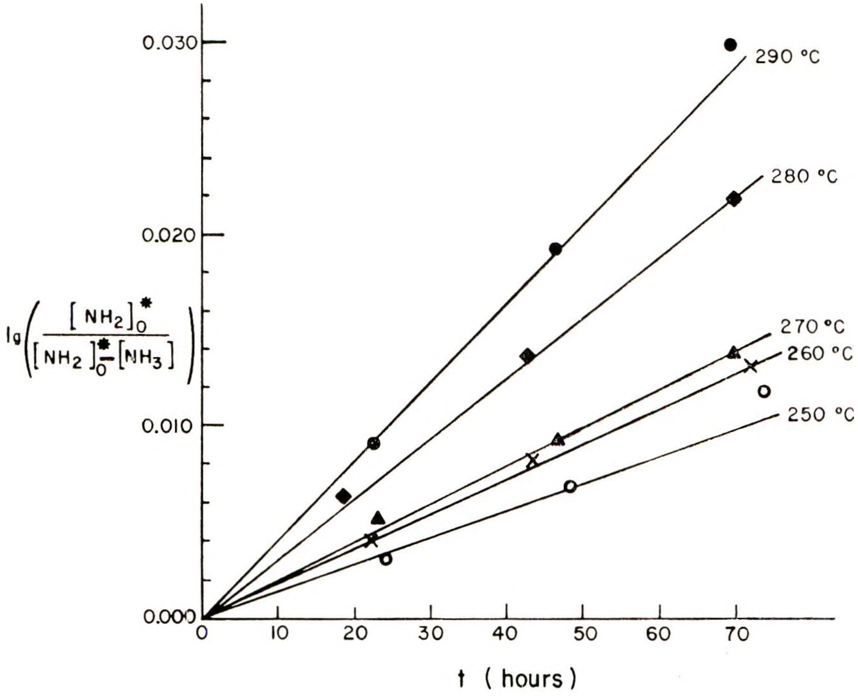


Fig. 4. First-order plot for ammonia formation.

$$L \underset{k_6^1}{\overset{k_6}{\rightleftharpoons}} I \tag{18}$$

Using a steady-state approximation for the intermediates:

$$\frac{d[CO_2]}{dt} = \frac{k_4[M][S_C] + k_6^1[I]}{(k_4^1/k_5)[H_2O] + (1 + k_6/k_5)} \tag{19}$$

and making the following substitutions

$$\Delta[H_2O] = [L] + [B] + [I] - \Delta[Z] = \Delta[S_C]$$

$$k_4 = a$$

$$k_4^1/k_5 = b$$

$$(1 + k_6/k_5) = c$$

and assuming that $[H_2O]_0 \approx 0$ therefore $[H_2O] = -\Delta[S_C]$ results in eq. (20):

$$\frac{d[CO_2]/dt}{[M][S_C]} = \frac{a + k_6^1[I]/[M][S_C]}{c - b\Delta[S_C]} \tag{20}$$

If we denote

$$\frac{d[CO_2]/dt}{[M][S_C]} = r$$

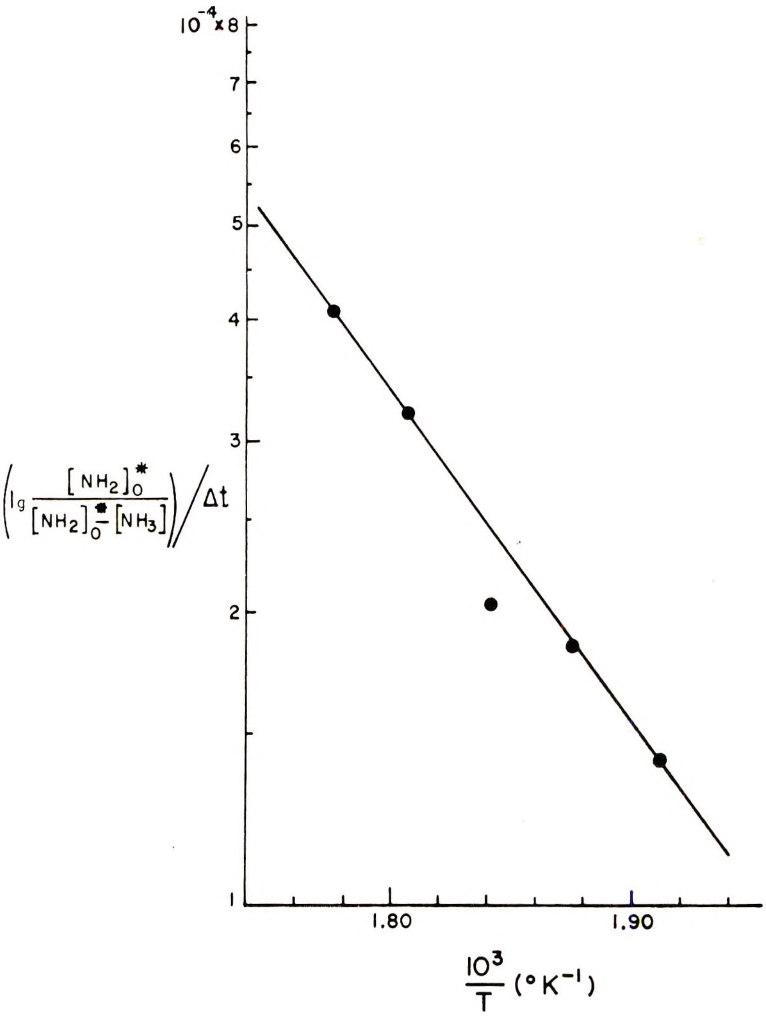


Fig. 5. Arrhenius plot related to ammonia formation.

and invoke the assumption

$$k_6{}^1[\mathrm{I}]/[\mathrm{M}][\mathrm{S_C}] \ll a$$

we obtain the linear equation, eq. (21)

$$\frac{1}{r} = \left(\frac{c}{a}\right) - \left(\frac{b}{a}\right) \Delta[\mathrm{S_C}] \tag{21}$$

The corresponding plot is shown in Figure 6. It can be seen that the expected linear relationships are obtained for the temperatures up to 280°C. The deviation from linearity at 290°C may be indicative of the occurrence of additional decomposition reactions probably of the types discussed by Kamerbeek et al.

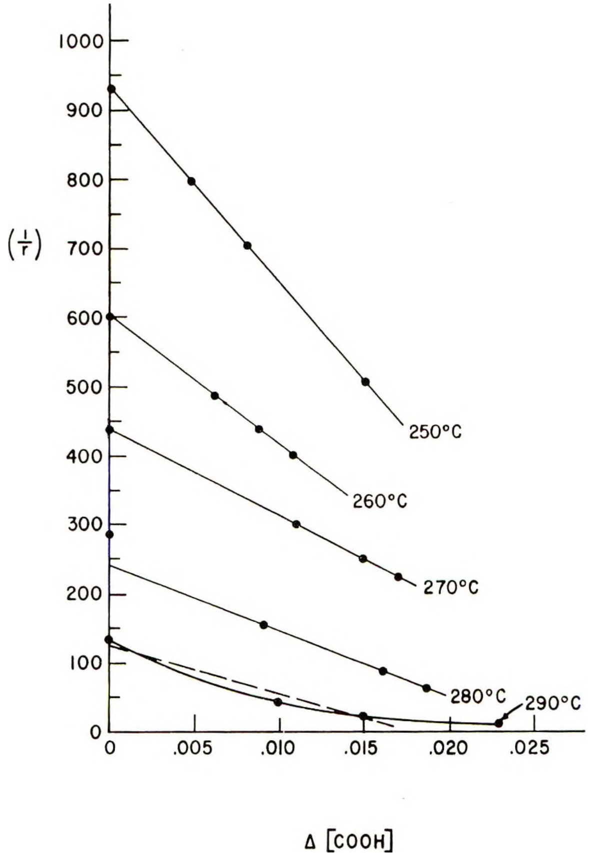


Fig. 6. Relationship between rate of decarboxylation and concentration of carboxy groups.

Values of the slopes and intercepts of the straight lines in Figure 6 have been summarized in Table II.

TABLE II
Slopes and Intercepts of the Plots of $1/r$ vs. ΔS_c

Temperature, °C	b/a	c/a
250	28.15×10^3	929.0
260	18.49×10^3	600.8
270	12.53×10^3	436.6
280	9.50×10^3	239.5
290	6.98×10^3	123.7

If all of the considered rate constants obey the Arrhenius relation, then a linear Arrhenius plot should result for the quotient a/b. This plot is shown in Figure 7. No corresponding linear relationship was found for the quotient a/c which contains the term $c = 1 + k_6/k_5$.

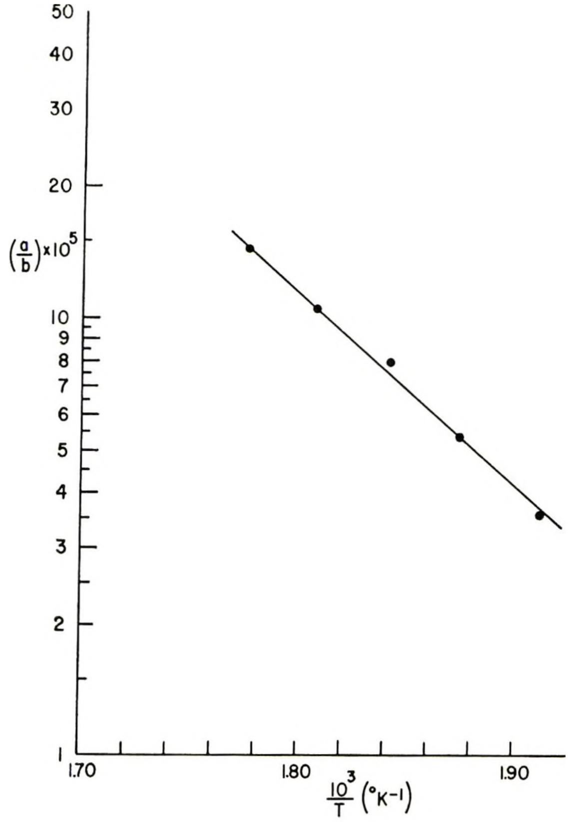


Fig. 7. Arrhenius plot for a/b.

According to the proposed mechanism, one equivalent of a basic function is formed as a consequence of the individual loss of an amino end-group or a molecule of carbon dioxide, the total concentration of basic equivalents—titratable as amino endgroups—may be calculated according to the stoichiometric relation (22):

$$[NH_2] + [B] = [NH_2]_0 + \Delta[NHCO] + [CO_2] \quad (22)$$

where $[NH_2]_0$ denotes the initial concentration of amino groups and $\Delta[NHCO] = [NHCO]_0 - [NHCO]$ denotes the change in the concentration of amide linkages.

In Table III are summarized the values calculated for the sum ($[NH_2] + [B]$) according to eq. (22) and the corresponding experimental data as obtained by titration. The rather good agreement between the calculated and experimental data indicates that the considered reactions may be explained by the proposed mechanisms. The following stoichiometric relation derives from the proposed mechanism for the decarboxylation [eqs. (6) and (7)]: $[COOH]_0 - [COOH] + [NHCO]_0 - [NHCO] = [L] + [I] + [CO_2]$, or

TABLE III
Measured and Calculated Data for the Concentration of Basic Functions

Temperature, °C	Time, hr	$[NH_2] + [B]$, meq/g Found	$[NH_2] + [B]$, meq/g Calcd
250	0	0.037	—
	24.00	0.036	0.035
	48.17	0.035	0.032
	73.50	0.030	0.029
260	0	0.0379	—
	21.97	0.0336	0.032
	43.17	0.0337	0.033
	71.75	0.0379	0.035
270	0	0.037	—
	23.18	0.036	0.036
	46.68	0.041	0.043
	70.00	0.047	0.051
280	0	0.0384	—
	18.58	0.0467	0.045
	42.58	0.0559	0.057
	69.90	0.0713	0.079
290	0	0.036	—
	22.50	0.061	0.061
	46.33	0.089	0.106
	69.17	0.141	0.166

TABLE IV
Temperature Dependence of the Quotient $\Delta[COOH] + \Delta([NHCO])/[CO_2]$

Temperature, °C	Time, hr	$\frac{\Delta[COOH] + \Delta[NHCO]}{[CO_2]}$
250	0	—
	24.00	3.492
	48.17	2.702
	73.50	2.348
260	0	—
	21.97	0.00
	43.17	1.337
	71.75	1.368
270	0	—
	23.18	2.967
	46.68	2.530
	70.00	1.909
280	0	—
	18.58	3.296
	42.58	2.446
	69.90	2.087
290	0	—
	22.50	2.151
	46.33	1.462
	69.17	1.576

$$\frac{\Delta[\mathrm{COOH}] + \Delta[\mathrm{NHCO}]}{[\mathrm{CO_2}]} = \frac{[\mathrm{L}] + [\mathrm{I}]}{[\mathrm{CO_2}]} + 1 \tag{23}$$

Values for $\{([\mathrm{L}] + [\mathrm{I}])/[\mathrm{CO_2}]\} + 1$ were calculated according to this relation and have been summarized in Table IV.

The values in Table IV indicate that the considered quantity does not depend significantly upon the temperature, although it appears that the value of the term $([\mathrm{L}] + [\mathrm{I}])$ has a minimum at 260°C. This could indicate that at this temperature the concentration of L is very small and the decarboxylation is the predominant reaction. One may speculate that at $T <$ 260°C there is a larger concentration of L, whereas, at 260°C $< T <$ 280°C the extent of the rearrangement of L to I is appreciable. Since in all probability at $T >$ 280°C additional reactions occur, corresponding data can not be explained exclusively by the considered mechanism.

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Received March 2, 1970
Revised April 3, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3285–3294 (1970)

Synthesis of Homologous Monomers and Polymers of Carbazole, Phenothiazine and Dibenzazepine

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Synopsis

Monomers and polymers of 3-vinyl-*N*-ethylcarbazole, 3-vinyl-*N*-methylphenothiazine, 3,7-divinyl-*N*-methylphenothiazine, *N*-acrylylcarbazole, *N*-acrylylphenothiazine, and *N*-acrylyl- and *N*-methacrylyldibenzazepine have been synthesized. The synthetic procedures for preparing the monomers and polymers are described.

INTRODUCTION

The synthesis and polymerization of compounds containing the heterocyclic aromatic nucleus has been the motivation for previous investigations reported from this laboratory.[1,2] Our continued interest in this class of compounds led us to investigate other derivatives containing the carbazole, phenothiazine and dibenzazepine nucleus; in particular, the *N*-alkyl-C-vinyl and *N*-acrylyl derivatives.

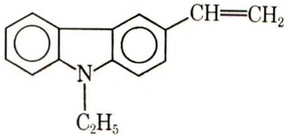
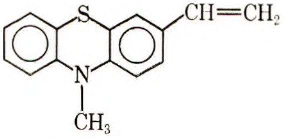
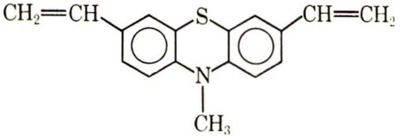
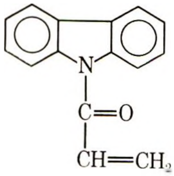
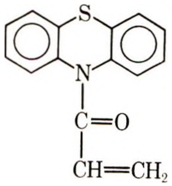
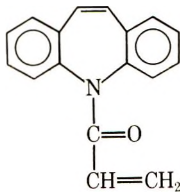
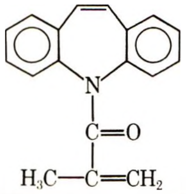
Literature reports of the synthesis and polymerization of these particular carbazole, phenothiazine and dibenzazepine monomers have been confined to only 3-vinyl-*N*-alkylcarbazoles[3] and phenothiazine[4] and to *N*-acrylylcarbazole.[5] 3-Vinyl-*N*-alkylcarbazoles have been polymerized to colorless polymers with radical initiators.[3] The reported synthesis of 3-vinyl-*N*-methylphenothiazine[4] has failed to give the monomer but had given instead a brown polymer in low yield. The polymerization of *N*-acrylylcarbazole with *n*-butyllithium was reported to give high-melting, insoluble polymers.[5]

In this investigation we report the synthesis of 3-vinyl-*N*-ethylcarbazole, 3-vinyl-*N*-methylphenothiazine, 3,7-divinyl-*N*-methylphenothiazine, *N*-acrylylcarbazole, *N*-acrylylphenothiazine, *N*-acrylyldibenzazepine and *N*-methacrylyldibenzazepine monomers. These structures are given in Table I. The polymerization of these monomers, with the exception of *N*-methacrylyldibenzazepine, was successfully carried out.

The synthesis of 3-vinyl-*N*-ethylcarbazole was previously reported.[6,7] The literature preparation of this compound was repeated and the vinyl compound was obtained in good yield.

The pure monomer could be homopolymerized by either free-radical or cationic initiators to high molecular weight poly-3-vinyl-*N*-ethylcarbazole in good conversion.

TABLE I
Monomer Synthesis

Monomer	Structure
3-Vinyl-*N*-ethylcarbazole	
3-Vinyl-*N*-methylphenothiazine	
3,7-Divinyl-*N*-methylcarbazole	
N-Acrylylcarbazole	
N-Acrylylphenothiazine	
N-Acrylyldibenzazepine	
N-Methylacrylyldibenzazepine	

N-Methylphenothiazine with acetic anhydride and $AlCl_3$ was found to give 3,7-diacetyl-*N*-methylphenothiazine and not the 3-substituted monoacetyl derivative as earlier reported.[8] Proof of structure was given by Cauquil and Casadevall[9] who reduced the diacetyl derivative to the 3,7-

diethyl derivative and by two consecutive Vilsmeier reactions obtained the dialdehyde, the substitution para to nitrogen in these reactions being well established.[10]

A Meerwein-Ponndorf-Verley reduction of the diacetyl derivative by aluminum isopropoxide in xylene gave 3,7-divinyl-*N*-methylphenothiazine and polymer. The homopolymerization of this monomer was not investigated.

3-Vinyl-*N*-methylphenothiazine monomer was obtained in high purity by a Wittig reaction between triphenylmethylphosphonium bromide and 3-formyl-10-methylphenothiazine. Polymer was also produced in this reaction. The monomer could be homopolymerized by thermal and by free radical initiator to high molecular weight poly-3-vinyl-10-methylphenothiazine.

Several attempts to prepare *N*-vinyldibenzazepine proved unsuccessful. The base-catalyzed condensation of dibenzazepine with 2-chloroethyltosylate resulted only in recovery of unreacted dibenzazepine. Direct vinylation of dibenzazepine with acetylene at 200 psig in toluene or in dimethyl sulfoxide solvents failed to give the *N*-vinyl derivative and unchanged starting material was recovered.

A direct synthesis of *N*-acrylylcarbazole, *N*-acrylylphenothiazine, *N*-acrylyldibenzazepine, and *N*-methacrylyldibenzazepine by reaction of acrylyl chloride or methacrylyl chloride with the corresponding amine or its salt[12] was not successful. However, a route involving the condensation of the amine with a β-halopropionylhalide followed by dehydrohalogenation of the condensation product as previously reported[5] was successful:

Dehydrohalogenation of the condensation products with sodium iodide and sodium acetate in absolute ethanol[5] gave only the acrylylcarbazole derivative in good yield. A satisfactory dehydrohalogenation of the phenothiazine and dibenzazepine derivatives was ultimately achieved by the use of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) as the dehydrohalogenating agent in dimethyl sulfoxide solvent.[13,14]

Thermal and free-radical-initiated polymerization of the acrylyl monomers with benzoyl peroxide or azobisisobutyronitrile catalysts gave high molecular weight polymers as determined by vapor-phase osmometry and confirmed by gel-permeation chromatography. These polymers were high melting and were soluble in the common organic solvents except for the thermally initiated polymer of acrylyldibenzazepine which was insoluble in all solvents. All attempts to homopolymerize *N*-methacrylyldibenzazepine with free-radical, cationic, and anionic initiators were unsuccessful; this must be attributed to steric interference by the bulky dibenzazepine ring system. The results of all polymerizations carried out are presented in Table II.

TABLE II

Polymerization of Carbazole, Phenothiazine, and Dibenzazepine Monomers

Monomer	Wt monomer, g	Solvent	Temp, °C	Initiator		Time, hr	Yield, %	Softening point range, °C	Intrinsic viscosity[a]	$\bar{A}_w/\bar{A}_n$
				Type	wt, g					
3-Vinyl-*N*-ethylcarbazole	14.6	CH_2Cl_2	−78	$BF_3\cdot(C_2H_5)_2O$	6.7×10^{-2}	4	78	250–265	0.66	6.00
3-Vinyl-*N*-ethylcarbazole	2.0	None	80	AIBN	1.48×10^{-2}	5	99	>300	Insoluble[b]	—
3-Vinyl-*N*-methylphenothiazine	1.5	Benzene	80	Benzoyl peroxide	4×10^{-2}	24	87	212–222	0.28	2.34
N-Acrylylcarbazole	2.2	None	125	Benzoyl peroxide	9.7×10^{-3}	48	93	235–247	0.51	2.22
N-Acrylylphenothiazine	2.5	None	125	Benzoyl peroxide	9.7×10^{-3}	48	99	255–262	0.32	5.88
N-Acrylylphenothiazine	7.9	Benzene	80	AIBN	2.5×10^{-2}	24	52	242–251	0.21	2.36
N-Acrylyldibenzazepine	1.5	None	125	Benzoyl peroxide	6.1×10^{-3}	48	95	296–308	Insoluble[b]	—
N-Acrylyldibenzazepine	2.5	Benzene	80	AIBN	8.3×10^{-3}	24	40	302–310	0.48	2.69

[a] Determined in benzene at 37°C.

[b] Insoluble in the common organic solvents and in DMF, hexamethylphosphoramide, hexafluoroacetone, and H_2SO_4.

EXPERIMENTAL

Analysis

Melting points of the monomers are uncorrected and were taken on a Hoover Unimelt apparatus. Polymer softening temperatures were recorded as the range in which the polymers turned to a clear melt. NMR spectra were taken with a Varian AR-100 spectrometer with tetramethylsilane as an internal standard. Infrared spectra were obtained with a Perkin-Elmer 521 grating spectrophotometer. Gel-permeation chromatographic analyses were carried out in tetrahydrofuran, at ambient temperature with 10^4, 10^3, 250, and 60-Å polystyrene columns and with 1500, 1000, 500 and 200-Å Bioglass-packed columns. $\bar{A}_w$ and $\bar{A}_n$ values corresponding to extended chain molecular sizes were determined by a computer programmed analysis of the chromatograms. Viscosities were determined at 37°C with the use of Cannon-Fenske viscometers. Elemental analyses were performed by the Berkeley Analytical Laboratory of Berkeley, California.

Materials

N-Ethylcarbazole (Reilly Chemical) was recrystallized twice from ethanol, mp 71–71.5°C (lit.[15] mp 68°C). All other commercial reagents and solvents were treated as described in our previous paper.[2]

3-Acetyl-*N*-ethylcarbazole. This was prepared by the method of Lopatinskii and Sirotkina.[6] Recrystallization from methyl alcohol yielded 137.5 g (58.7%) pure product, mp 114–15°C (lit.[6] mp 114–115°C).

3-Vinyl-*N*-ethylcarbazole. A mixture of 3-acetyl-*N*-ethylcarbazole, 71.1 g (0.30 mole), 61.2 g (0.30 mole) aluminum isopropoxide, and 300 ml *m*-xylene was heated for 2.5 hr at 130–140°C. During this period, acetone was continuously distilled from the reaction mixture. The mixture was cooled, washed with 200 ml cold 20% NaOH, the organic layer separated and dried over Na_2SO_4. The organic layer was concentrated under vacuum to give a yellow oil. The oil was precipitated as a solid by the addition of water and vigorous stirring. The crude solid when recrystallized from hot alkaline ethanol did not completely dissolve. This residue amounted to 5.5 g of low molecular weight polymer. From the cooled filtrate was obtained 38.5 g (58%) of white crystals, mp 64–66 (lit.[7] mp 66–67°C). The infrared spectrum showed strong vinyl absorption peaks at 900 and 910 cm^{-1}.

ANAL. Calcd for $C_{16}H_{15}N$: C, 86.84%; H, 6.83%; N, 6.33%. Found: C, 86.87%; H, 6.51%; N, 6.76%.

***N*-Methylphenothiazine.** This was prepared by the method of Burger and Schmalz.[8] Two recrystallizations from ethanol yielded 179 g(74.3%) of colorless needles, mp 101–102°C (lit.[8] mp 99–100°C).

3,7-Diacetyl-*N*-methylphenothiazine. The Friedel-Crafts reaction of N-methylphenothiazine with acetyl chloride was reported by Burger and Schmalz to give the hemihydrate of 3-acetyl-*N*-methylphenothiazine.[8]

When this procedure was followed starting with 63.9 g (0.3 mole) *N*-methylphenothiazine, 24 g (0.3 mole) acetyl chloride, and 120 g (0.9 mole) $AlCl_3$ in 1000 ml CS_2, 60 g of crude solid was obtained, mp 164–174°C. A 20-g portion of this solid was recrystallized twice from ethanol/glacial acetic acid to give 8.5 g fine yellow needles, mp 205–206°C (lit.[8] mp 205–206°C). The elemental analysis was in agreement for the diacetyl derivative only.

ANAL. Calcd for $C_{17}H_{15}NO_2S$: C, 68.69%; H, 5.05%; N, 4.71%; S, 10.78%. Found: C, 68.95%; H, 5.08%; N, 4.73%; S, 10.90%.

3,7-Divinyl-*N*-methylphenothiazine. A mixture of 5 g (0.016 mole) 3,7-diacetyl-*N*-methylphenothiazine, 6.3 g (0.032 mole) aluminum isopropoxide, and 150 ml *m*-xylene was treated as previously described. Workup of the reaction products gave 1.5 g polymer and 0.5 g (8.4%) 3,7-divinyl-*N*-methylphenothiazine as fine yellow needles from ethanol, mp 107–108°C. The infrared spectrum showed strong vinyl bands at 990 and 910 cm^{-1}. This spectrum was different from that of the 3-vinyl derivative which contained a band at 750 cm^{-1}, indicative of four adjacent out-of-plane hydrogen atoms. This band was not present in the divinyl compound. Other absorption bands at 860–800 cm^{-1} and 900–860 cm^{-1} observed in both the mono and divinyl derivatives, indicative of one and two adjacent free hydrogens on an aromatic ring, were greatly enhanced in the divinyl compound.

ANAL. Calcd for $C_{17}H_{15}NS$: C, 76.98%; H, 5.68%; N, 5.28%; S, 12.08%. Found: C, 76.85%; H, 5.68%; N, 5.44%; S, 11.91%.

3-Formyl-*N*-methylphenothiazine. This was prepared by the method of Buu-Hoi and Hoan.[11] Recrystallization from ethanol yielded 40.5 g (36.4%) yellow crystals, mp 86.0–86.5°C (lit.[11] mp 89°C).

3-Vinyl-*N*-methylphenothiazine. To 44.6 g (0.125 mole) triphenylmethylphosphonium bromide in 250 ml anhydrous ether under a nitrogen atmosphere was added 12 ml (0.13 mole) of 1.6*M* *N*-butyllithium in hexane. After stirring at room temperature for 24 hr, 24.1 g (0.10 mole) 3-formyl-*N*-methylphenothiazine in 100 ml THF was added dropwise during a period of 1 hr. After 2 hr the ether was distilled from the reaction mixture and replaced by 150 ml THF. The solution was refluxed 24 hr, cooled, and then the THF was removed under vacuum. The residue which remained was extracted with benzene, the extract was washed to neutrality with 30% aqueous $NaHSO_3$ and water and then dried over Na_2SO_4. The benzene extract was passed through a 50 × 600 mm chromatographic column containing Alcoa F-20 chromatographic alumina to separate the products. 3-Vinyl-*N*-methylphenothiazine showing a slight yellow fluorescence was eluted first (benzene solvent). The benzene was removed under vacuum and the residue obtained was treated with hot ethanol. A large quantity of the residue was insoluble in ethanol and was filtered off. The filtrate was cooled to give 4.5 g (19%) yellow crystals after drying 24 hr in vacuum, mp 93.5–95.5°C. The NMR spectrum (benzene D_6) showed peaks at $\delta 2.7$ (singlet) assigned to the *N*-methyl group, $\delta 5.02$ and $\delta 5.48$ (two quartets) assigned to the β-protons on the vinyl group and δ6.24, δ7.2 (two quartets) assigned to the α-protons on the vinyl group.

ANAL. Calcd for $C_{15}H_{13}NS$: C, 75.31%; H, 5.44%; N, 5.86%; S, 13.39%. Found: C, 75.06%; H, 5.56%; N, 6.02%; S, 13.18%.

The ethanol-insoluble residue was found to be polymeric. The residue was dissolved in THF, filtered, and precipitated in methanol to give 8.0 g (33%) of polymer, mp range 243–253°C.

ANAL. Calcd for $C_{15}H_{13}NS_x$: Found: C, 75.01%; H, 5.37%; N, 5.79%; S, 13.43%.

***N*-(β-Chloropropionyl)carbazole.** The procedure of Heller and Kingsley[5] was used to prepare 56.1 g (72.5%) of this derivative, mp 123.5–124.5°C (lit.[5] mp 123.5–124.0°C). (The analogous phenothiazine and dibenzazepine derivatives were also prepared by this method.)

***N*-Acrylylcarbazole.** This compound was prepared by the method of Heller and Kingsley.[5] Several recrystallizations from a 50/50 benzene–pentane solvent mixture yielded 11.0 g (37%) of pure product, mp 50.0–51.5°C (lit.[5] 50–52°C).

***N*-(β-Chloropropionyl)phenothiazine.** A yield of 110 g (77%) of pure product was obtained after recrystallization from benzene–petroleum ether (30–60°C), mp 143.5–144° (lit.[16] mp 140–143°). The NMR spectrum ($CDCl_3$) showed two symmetrical triplets at δ 2.90 and δ 3.78 assigned to the chloroethyl group and a multiplet from δ7.12 to δ7.57 assigned to the phenyl ring protons.

ANAL. Calcd for $C_{15}H_{12}ClNOS$: C, 62.17%; H, 4.17%; N, 4.83%; S, 11.06%; Cl, 12.24%. Found: C, 62.24%; H, 4.14%; N, 4.93%; S, 11.03%; Cl, 12.15%.

***N*-Acrylylphenothiazine.** A stirred mixture of 29.0 g (0.10 mole) of *N*-(β-chloropropionyl)phenothiazine and 15.2 g (0.1 mole) 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in 150 ml DMSO was heated for 2 hr at 80–90°C. The mixture was allowed to cool and was then poured into 500 ml of ice water precipitating a white solid. After two recrystallizations from hexane, 9.2 g (36.4%) of pure product was recovered, mp 110–111°C. The NMR spectrum ($CDCl_3$) consisted of an unsymmetrical multiplet from δ5.62 to δ5.76 assigned to the α- and β-vinyl protons, a quartet at δ6.45 assigned to the β-vinyl protons and a multiplet from δ7.12 to δ7.64 assigned to the phenyl ring protons.

ANAL. Calcd for $C_{17}H_{11}NOS$: C, 71.09%; H, 4.38%; N, 5.53%; S, 12.65%. Found: C, 71.05%; H, 4.25%; N, 5.45%; S, 12.66%.

***N*-(β-Chloropropionyl)dibenzazepine.** A yield of 10 g (35%) of a white crystalline solid was obtained after recrystallization from benzene–petroleum ether (30–60°C), mp 126.5–127.5°C. The NMR spectrum* ($CDCl_3$)

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* The spectrum was different from that expected. One would normally expect to see two symmetrical triplets for the chloroethyl group. The observed spectrum is explained in terms of hindered rotation about the C-N and C-C bonds at room temperature. Upon heating to 110°C the multiplets collapsed to the expected triplets shown in Figure 1. This work will be published in the near future.

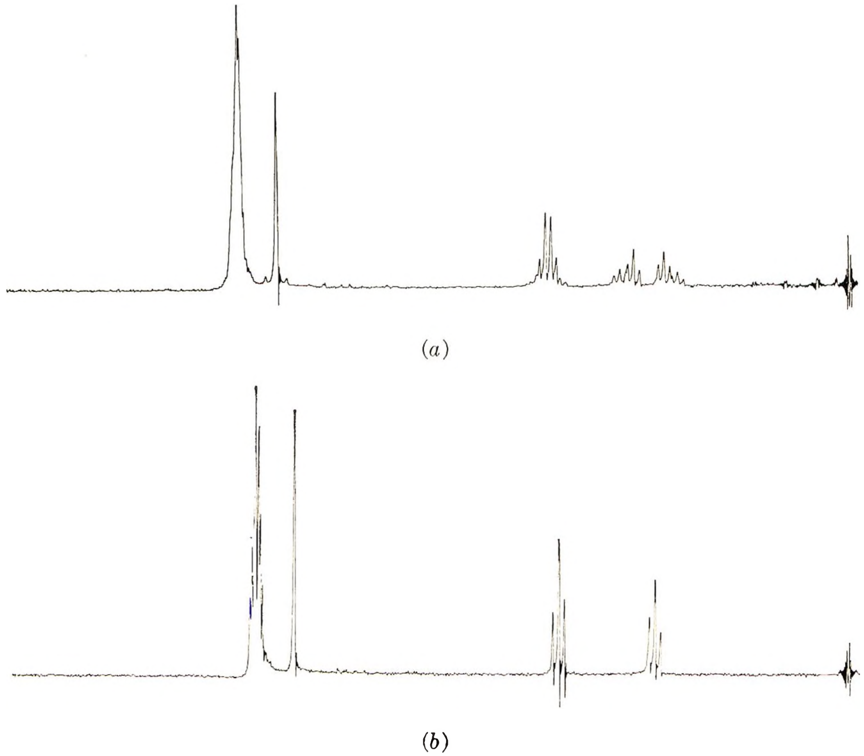

Fig. 1. NMR spectra of *N*-(β-chloropropionyl)dibenzazepine in $CDCl_3$ at (*a*) 25°C and (*b*) 110°C.

consisted of two multiplets from δ1.96 to δ2.27 and from δ2.49 to δ2.79 assigned to the chloroethyl group, a multiplet from δ3.36 to δ3.78 assigned to the methylene protons, a doublet at δ6.76 assigned to the ethylenic protons of the azepine ring and a multiplet from δ7.25 to δ7.38 assigned to the phenyl ring protons.

ANAL. Calcd for $C_{17}H_{14}ClNO$: C, 71.95%; H, 4.97%; N, 4.94%; Cl, 12.50%. Found: C, 72.09%; H, 4.99%; N, 4.91%; Cl, 12.42%.

***N*-Acrylyldibenzazepine.** A mixture of *N*-(β-chloropropionyl)dibenzazepine, 5 g (0.018 mole), 2.7 g (0.018 mole) DBU, and 150 ml DMSO was heated for 2 hr at 80–90°C. After recrystallization of the crude product from benzene–petroleum ether (60–90°C), 2.9 g (65.2%) of white platelets, mp 122.5–123.5°C, were obtained. The NMR spectrum (CCl_4) consisted of two unsymmetrical multiplets from δ5.36 to δ5.49 and from δ5.73 to δ6.00 assigned to the α- and β-vinyl protons, a quartet at δ6.32 assigned to the β-vinyl protons, a doublet at δ6.80 assigned to the ethylenic protons of the azepine ring, and a multiplet from δ7.08 to δ7.30 assigned to the phenyl ring protons.

ANAL. Calcd for $C_{17}H_{13}NO$: C, 82.57%; H, 5.30%; N, 5.66%. Found: C, 82.07%; H, 5.31%; N, 5.91%.

N-(α-Bromoisobutyryl)dibenzazepine. From 19.3 g (0.10 mole) dibenzazepine and 45 g (0.20 mole) α-bromoisobutyryl bromide refluxed 18 hr in 600 ml toluene was obtained a viscous orange oil. The oil solidified to a crystalline white solid after repeated recrystallizations from a benzene-heptane solvent mixture and Norit. Final recrystallization from heptane gave 19.2 g (56.1%) of white needles, mp 94–95°C. The NMR spectrum ($CDCl_3$) consisted of a singlet at δ 1.58 assigned to the methyl protons (on cooling to −40°C, the singlet split into a well-defined doublet), a doublet at δ6.95 assigned to the ethylenic protons of the azepine ring and a multiplet from δ7.17 to δ7.69 assigned to the phenyl ring protons.

ANAL. Calcd for $C_{18}H_{16}BrNO$: C, 63.17%; H, 4.71%; N, 4.09%; Br, 23.25%. Found: C, 63.31%; H, 4.78%; N, 4.05%; Br, 23.42%.

N-Methacrylyldibenzazepine. A mixture of 17.1 g (0.05 mole) N-(α-bromoisobutyryl)dibenzazepine, 7.6 g (0.05 mole) DBU, and 135 ml DMSO was heated for 2 hr at 80–90°C. Recrystallization of the crude product from benzene–petroleum ether (30–60°C) yielded 9.1 g (69.5%) of white crystals, mp 141°C. The NMR spectrum ($CDCl_3$) consisted of a poorly resolved quartet at δ1.76 assigned to the α-methyl protons with very small allylic coupling, a multiplet of poor definition at δ2.98 assigned to the β-vinyl protons with very small allylic coupling, a doublet at δ6.96 assigned to the ethylenic protons of the azepine ring, and a multiplet from δ7.24 to δ7.42 assigned to the phenyl ring protons.

ANAL. Calcd for $C_{18}H_{15}NO$: C, 82.73%; H, 5.79%; N, 5.36%. Found: C, 82.44%; H, 5.69%; N, 5.38%.

Polymerizations of Vinyl and Acrylyl Monomers

Bulk polymerizations were carried out in heavy-walled glass polymerization tubes. Monomer samples were degassed through three freeze-thaw cycles after addition of the initiator in the free radical polymerizations and the tubes were sealed at 10^{-5}–10^{-6} mm pressure. Solution polymerizations were carried out in 100 and 200 ml three-necked flasks equipped with stirrer, reflux condenser, thermometer, and gas-inlet. Moisture was rigorously excluded by flaming the entire apparatus prior to introduction of solvent and monomer. Oxygen was excluded by maintaining a blanket of purified argon over the solution. The catalyst was then added to the stirred mixture. At the termination of the polymerization the entire reaction mixture was added to a large excess of methanol. The polymer was filtered, washed with methanol, and purified by repeated precipitation from benzene or THF with methanol. After repeated washing with fresh methanol the polymer was vacuum dried at 40–50°C for 24–48 hr. The analytical data are presented for those polymers prepared in Table II.

ANAL. Calcd for $(C_{16}H_{15}N)_n$: C, 86.84%; H, 6.83%; N, 6.33%. Found for poly-3-vinyl-*N*-ethylcarbazole: C, 86.58%; H, 6.52%; N, 6.50%.

Calcd for $(C_{15}H_{13}NS)_n$: C, 75.31%; H, 5.44%; N, 5.86%; S, 13.39%. Found for poly-3-vinyl-*n*-methylphenothiazine: C, 75.02%; H, 5.37%; N, 5.79%; S, 13.43%.

Calcd for $(C_{15}H_{11}NO)_n$: C, 81.42%; H, 5.01%; N, 6.32%. Found for poly-*N*-acrylylcarbazole: C, 81.08%; H, 4.97%; N, 6.32%.

Calcd for $(C_{15}H_{11}NOS)_n$: C, 71.09%; H, 4.38%; N, 5.53%; S, 12.65%. Found for poly-*N*-acrylylphenothiazine: C, 71.11%; H, 4.39%; N, 5.45%; S, 12.59%.

Calcd for $(C_{17}H_{13}NO)_n$: C, 82.57%; H, 5.30%; N, 5.66%. Found for poly-*N*-acrylyldibenzazepine: C, 82.31%; H, 5.74%; N, 5.51%.

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Received February 10, 1970
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JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3295-3302 (1970)

Importance of the Singlet–Triplet Transition of Ethylene in its Photopolymerization in the Presence of Oxygen

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Synopsis

The rate of the photopolymerization of ethylene initiated by a mercury arc lamp was investigated under a pressure of 400 kg/cm² at 30 ± 5°C by varying the wavelength of incident light. Ethylene was found to polymerize by ultraviolet light below about 3500 Å. The yield decreased gradually as the wavelength became longer, and no polymer was obtained at wavelength greater than 3900 Å. The addition of a small amounr (<100 ppm) of oxygen promoted the polymerization. Ultraviolet absorption spectat measured for the mixture of ethylene and a small amount of oxygen displayed several absorption peaks in the region 2700–3500 Å. The absorption began at about 3680 Å and became stronger with the concentration of oxygen. The average separation between the peaks was about 1000 cm^{-1}. The spectra were also measured for oxygen containing a small amount of ethylene. Similar absorption peaks with those described above were observed. On the basis of these results, it was pointed out that an excited triplet ethylene is formed under the irradiation of light due to a perturbing effect of oxygen contained in ethylene monomer and the reaction between the excited ethylene and oxygen is important in initiating the polymerization.

INTRODUCTION

We recently reported some results of a study on the photopolymerization of ethylene in a gas phase under high pressure.[1] It was noted in the previous report that ethylene reacts without any catalysts to produce polyethylene of high molecular weight under the irradiation of ultraviolet light emitted from a super high-pressure mercury arc lamp. The importance of oxygen in initiating the polymerization has also been suggested.

In the present work the polymerization rate was investigated by varying the wavelength of the light used, and the ultraviolet absorption spectrum of ethylene was measured under high pressure. The excitation of ethylene and the role of oxygen in the polymerization are discussed.

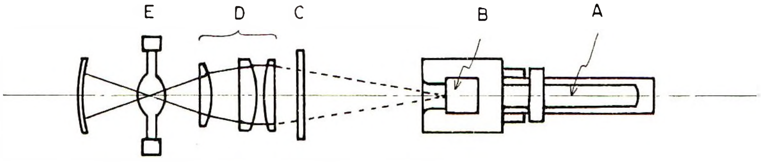


Fig. 1. Diagram of apparatus: (A) reactor, (B) quartz window, (C) glass filter, (D) lenses, (E) super high-pressure mercury arc lamp.

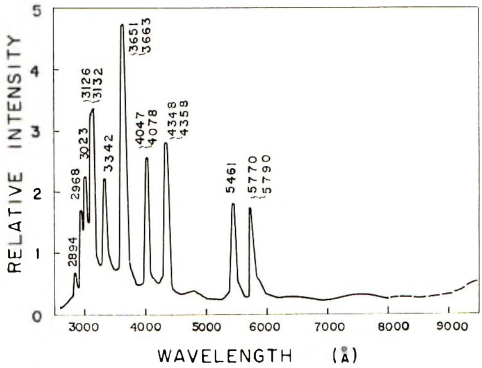


Fig. 2. Energy distribution curve of the mercury arc lamp.

EXPERIMENTAL

Polymerization

The experimental arrangement is shown schematically in Figure 1. Ethylene was polymerized under a pressure of 400 kg/cm^2 at 30 ± 5°C in a specially designed stainless steel autoclave with 23 ml capacity. Before the vessel was filled with high pressure ethylene, it was evacuated and swept five times with ethylene. The ethylene used was polymerization-grade material from the Nisseki Kagaku Company, listed as 99.9% pure (free of CO and H_2S) with a typical analysis of 5 ppm of oxygen. The source of ultraviolet light was a super high-pressure mercury arc lamp of 250 W from Ushio Electric Works, Model USH-250 which emits a spectrum ranging from 2700 to 6000 Å. The spectrum–energy distribution curve of the lamp is given in Figure 2. The light was condensed on the window of the reaction vessel through a glass filter by using three pieces of quartz lens. The distance from the lamp to the window was 300 mm.

Ultraviolet Absorption Spectrum

Measurements were made on a recording spectrophotometer (Perkin-Elmer Spectrocord 450) with a high-pressure cell (Fig. 3). After the cell was cleaned with methanol and evacuated by rotary vacuum pump, the needle valve of the cell was connected to a compressor, and ethylene was fed in. The cell, now containing a known pressure of the gas, was disconnected and the spectrum recorded. A desired amount of oxygen was

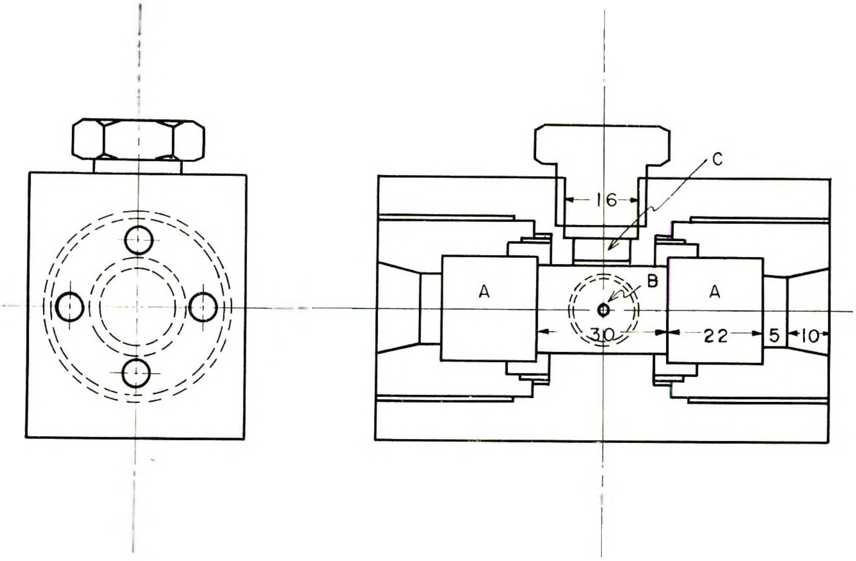


Fig. 3. High-pressure cell for an ultraviolet absorption spectrum measurement: (A) quartz window, (B) gas inlet valve, (C) stainless steel plug; units, millimeters.

introduced prior to the feed of ethylene when the spectrum was measured in the presence of a small amount of oxygen, and the procedure was reversed when the measurement was made for ethylene contained in a large amount of oxygen.

RESULTS AND DISCUSSION

Photopolymerization

Table I shows the variation of the polymer yield with the wavelength of the light used. Ethylene was found to polymerize under the irradiation of ultraviolet light in the region below about 3500 Å. The yield decreased gradually as the wavelength became longer, and no polymer was obtained over 3900 Å though ethylene was exposed for a sufficiently long time. It

TABLE I

Photopolymerization of Ethylene under High Pressure[a]

Wavelength λ, Å	Polymer yield, mg
>2700	7.2
>2900	5.9
>3100	2.3
>3500	Trace
>3900	No polymer[b]

[a] Reaction conditions: pressure, 400 kg/cm^2; temperature, 30 ± 5°C; reaction time, 2.0 hr reactor volume, 23 ml.

[b] After 20.0 hr.

TABLE II
Effect of Oxygen on the Polymer Yield[a]

Oxygen concentration, ppm	Polymer yield, mg
5	23
50	43
100	60
200	12
1000	Trace[b]

[a] Reaction conditions: pressure, 400 kg/cm^2; temperature, 30 ± 5°C; reaction time, 6.5 hr; wavelength, >2700 Å; reactor volume, 23 ml.

[b] Polymerization was first inhibited for about 6.0 hr.

was pointed out in the previous paper[1] that the photopolymerization is strongly promoted by the presence of 100 ppm of oxygen. The characteristic effects of oxygen on the rate of polymerization is shown in Table II. The rate first increased with the addition of oxygen. It passed through a maximum at about 100 ppm, and thereafter decreased with increasing concentration of oxygen. At the maximum, the polymerization took place about three times faster than in the case of ethylene containing 5 ppm of oxygen. The inhibiting effect of a large amount of oxygen may indicate that the polymerization proceeds by a free-radical chain process.

Ultraviolet Absorption Spectrum of a Mixture of Ethylene and Oxygen under High Pressure

Figure 4 shows the ultraviolet absorption spectra measured for the gaseous mixture of ethylene and oxygen under a pressure of 400 kg/cm^2 at 20°C. When ethylene contained only 5 ppm of oxygen, the absorption was too weak to be observed in the region effective for polymerization. However, ethylene containing a larger amount of oxygen displayed several absorption peaks in the 2700–3500 Å region. The absorption began at about 3680 Å and became stronger with increasing concentration of oxygen. The average separation between peaks was about 1000 cm^{-1}.

The spectra given in Figure 5 were also obtained for ethylene–oxygen mixtures. In this case, however, the spectra were measured for high-pressure oxygen containing small amounts of ethylene. Similar absorption peaks were observed though most were shifted to lower wavelength by ~5–16 Å than those in Figure 4. The two extra peaks at 3787 Å and 3594 Å were observed only when the mixture was pressurized by a large amount of oxygen. Since their absorbance did not depend on the concentration of ethylene, these two peaks can be ascribed to the absorption by high pressure oxygen. This concept is supported by comparing the spectra in Figure 5 with that in Figure 6 (Fig. 6*B*). The latter was obtained for pure oxygen.

From the results in Figures 4 and 5, the absorbance of every peak is expected to increase proportionally with the concentration of each constituent of the mixture. For example, the absorbance was plotted in Figure 7 for

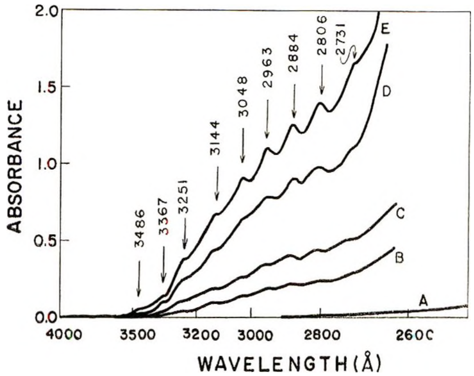


Fig. 4. Ultraviolet absorption spectra of ethylene containing a small amount of oxygen: (*A*) 5×10^{-4} mole-% O_2; (*B*) 0.23 mole-%; (*C*) 0.50 mole-%; (*D*) 1.48 mole-%; (*E*) 1.94 mole-%. Pressure, 400 kg/cm²; temperature, 20°C.

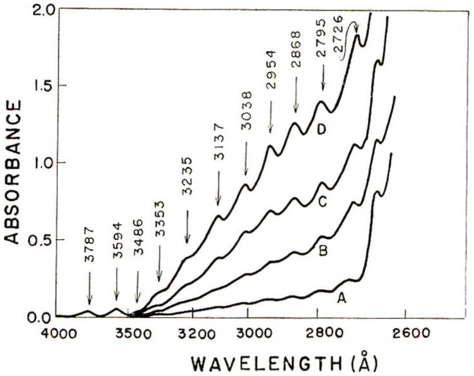


Fig. 5. Ultraviolet absorption spectra of oxygen containing a small amount of ethylene: (*A*) 0.86 mole-% ethylene; (*B*) 1.41 mole-%; (*C*) 1.96 mole-%; (*D*) 2.50 mole-%; (*E*) 3.04 mole-%. Pressure, 400 kg/cm²; temperature, 20°C.

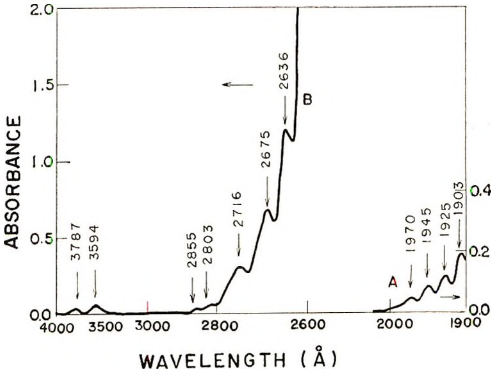


Fig. 6. Ultraviolet absorption spectra of pure oxygen at 20°C: (*A*) 10 kg/cm²; (*B*) 400 kg/cm².

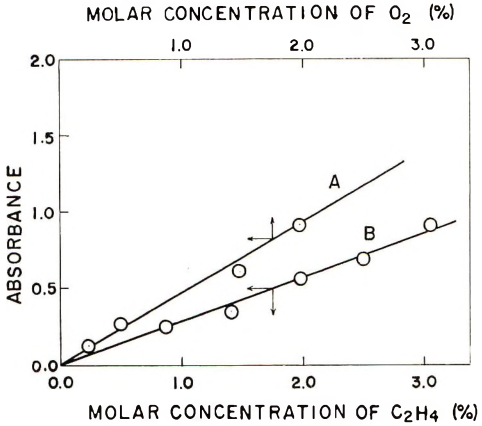


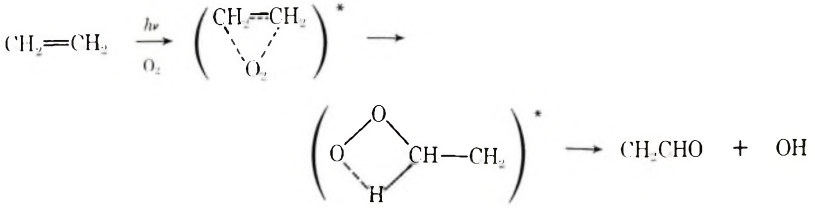
Fig. 7. Variation of the absorbance of the peaks around 3038–3048 Å with the concentration of ethylene or oxygen. (*A*) 3048 Å in Fig. 4, (*B*) 3038 Å in Fig. 5.

the peaks at 3048 Å in Figure 4 and at 3038 Å in Figure 5 against the concentration of ethylene and oxygen, respectively. Straight lines through origin were obtained. Therefore, it can be said that the absorption may take place in a state of one-to-one interaction between ethylene and oxygen.

Formation of Triplet Excited Ethylene and Role of Oxygen in the Initiation Reaction

The ultraviolet absorption spectrum of ethylene in the region reported above was first observed by Reid[2] (2600–3400 Å) for long path length of liquid ethylene, and then by Evans[3] (2700–3500 Å) for the case in the presence of a large amount of oxygen. In his detailed discussion, Evans ascribed the absorption to a singlet–triplet transition of ethylene, T ← N ($^3B_{1u} \leftarrow {}^1A_{1g}$), induced by a magnetic perturbation due to oxygen. This concept is of considerable interest in connection with the present results of the polymerization and the ultraviolet absorption spectrum measurement. As reported above, the polymerization takes place under the irradiation of light below about 3500 Å and not over 3900 Å, and it is strongly promoted by trace amounts of oxygen. On the other hand, the absorption of light is observed below 3680 Å and becomes stronger with the addition of oxygen. Thus, in view of these facts, it can be said that an excitation of ethylene into its triplet state is indispensable to initiating the polymerization, and that the first increase in the rate of polymerization with the addition of oxygen may be brought about by the increase in the rate of initiation. Further, the latter may be caused by the promoting effect of oxygen on the excitation of ethylene.

In the previous paper,[1] the existence of the carbonyl group in the polymers formed was confirmed by measuring their infrared absorption spectra. Therefore, on the basis of these results, a bimolecular reaction between excited ethylene and oxygen may be considered as a possible source of radicals which initiate the polymerization. Since the excited ethylene is a biradical, it may readily react with oxygen to form peroxide. However, owing to an excess energy of excitation, it may decompose by scission at the O—O bond to radicals in such a way as to form a carbonyl group. A possible route leading to radicals may be as shown in eq. (1).



(1)

Although it is not clear which is predominant, another process of initiation might be direct addition of excited ethylene to monomer [eq. (2)].

$$CH_2{=}CH_2 \xrightarrow[O_2]{h\nu} (CH_2{=}CH_2)^* \xrightarrow{CH_2=CH_2} \dot{C}H_2(CH_2)_2\dot{C}H_2 \qquad (2)$$

In this case, propagation proceeds by a biradical mechanism. Oxygen may first serve to promote the singlet–triplet transition in ethylene and become incorporated into polymers through termination.

In contrast with the case of ultraviolet light, a small amount of oxygen retards the polymerization when ethylene is exposed to γ-rays.[4,5] For the initiation step of the γ-ray-induced polymerization, the decomposition of excited ethylene to yield hydrogen atom has been proposed.[6] The decomposition may be:

$$CH_2{=}CH_2 \rightarrow 2H + CH{\equiv}CH \qquad (3)$$

$$CH_2{=}CH_2 \rightarrow H + CH_2{=}CH \qquad (4)$$

where ΔH for eqs. (3) and (4) is 146 and 104 kcal/mole, respectively. The high endothermicity of these process makes it very unlikely that reactions (3) and (4) take part in the above photopolymerization.

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Received December 15, 1969
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JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3303-3310 (1970)

Participation of an Excited Monomer in the Propagation Reaction of the γ-Ray Induced Polymerization of Ethylene

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Synopsis

In the polymerization of ethylene, the reactivity of the growing radical produced by γ-radiation was compared with that of the radical from 2,2′-azobisisobutyronitrile. The radicals produced in the polymerization at around room temperature were long-lived irrespective of the method of initiation. However, it was found that the radical produced by γ-radiation became unreactive to ethylene when the reaction system was not exposed to γ-rays. Irradiation with γ-rays or ultraviolet light in a region below about 3900 Å was required for its chain growth. On the other hand, the radical from AIBN was always reactive, and the reactivity was little changed by γ-radiation or by the presence of a trace amount of radiolysis products of ethylene. In explaining of these characteristic differences between the nature of these radicals produced by two different methods of initiation, some other information on their reactivity was reviewed, and the participation of an excited ethylene in a dimer form was proposed, as for the propagation reaction of the γ-ray-induced polymerization.

INTRODUCTION

In the preceding reports on the polymerization of ethylene initiated by γ-rays[1,2] or by 2,2′-azobisisobutyronitrile (AIBN)[3,4] at around room temperature, the existence of long-lived growing chain radicals was described from the point of kinetics. Our studies on reactivities showed that the radicals produced by γ-radiation were quite abnormal, in that they became unreactive to ethylene when the reaction system was not exposed to radiation. In explaining this characteristic nature of the radicals in the radiation polymerization, we must consider the effects of radiolysis products of ethylene such as C_2H_2 and H_2 which are very reactive to radical species.

In the present paper, the behavior of the growing radicals produced by two different methods are compared under the same reaction conditions, and the effect of ultraviolet light is investigated as for the radicals formed by γ-ray irradiation. As a result of these studies, the role of an excited monomer in the radiation polymerization is considered in relation to the unusual nature of the radicals.

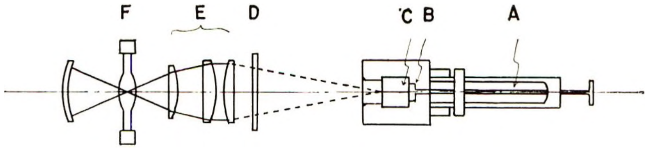


Fig. 1. Schematic diagram of equipment for ultraviolet light irradiation: (A) reaction vessel, (B) wiper, (C) quartz window, (D) glass filter, (E) quartz lenses, (F) super high-pressure mercury arc lamp.

EXPERIMENTAL

The polymerization was carried out in a specially designed stainless-steel autoclave illustrated elsewhere.[5,6] It consisted of a main reactor chamber with a capacity of 75 ml and a small container of 2 ml capacity for AIBN. The latter was attached to the inside surface of a top cover of the autoclave, and it could be sealed off from the main reactor chamber when lifted to the cover by a handle outside. Another autoclave was designed for the investigation of the effect of ultraviolet light on the reactivity of growing radicals produced by γ-radiation. As shown in Figure 1, the vessel had a quartz window 24 mm thick and a device for removing polymers which deposited on the inside surface of the window.

Ethylene used was a commercially available material containing less than 5 ppm of O_2. The γ-radiation was from a 5000-Ci ^{60}Co source. Guaranteed grade AIBN was twice recrystallized from diethyl ether before use. The source of ultraviolet light was a super high-pressure mercury arc lamp (250 W) from Ushio Electric Works, Model USH-250 which emitted a spectrum ranging from about 2700 to 6000 Å. The number-average molecular weight of obtained polymers was determined by solution viscosity measurements with the use of Tung's formula.[7]

RESULTS AND DISCUSSION

Difference Reactivity of Growing Radicals Produced by γ-Rays and AIBN

Figure 2 shows the plots of the polymer yield versus reaction time of the polymerization runs carried out in two stages. In the γ-ray-induced two-stage polymerization, ethylene was first irradiated at a dose rate of 25,000 rad/hr, and this was followed by irradiation at a lower dose rate of 500 rad/hr. The increase in amount of polymer in the latter stage [Fig. 2*a* (line *A*)], where additional polymer chain formation was negligibly small, was unexpectedly large compared with that in the polymerization at 500 rad/hr from the beginning [Fig. 2*a* (line *B*)]. The increase in the number-average molecular weight of the polymer was also remarkable as shown by Figure 3. As reported previously,[8,9] it was concluded from the same results that the radicals introduced in the first stage were long-lived and that their chain growth took place in the second stage with no transfer and

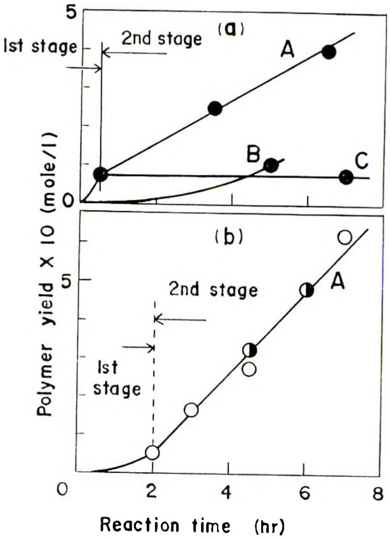


Fig. 2. Polymer yield vs. reaction time. (*a*) γ-Radiation-induced polymerization: (*A*) first stage, 400 kg/cm^2, 40°C, 2.5 × 10^4 rad/hr; second stage, 400 kg/cm^2, 40°C, 500 rad/hr, (*B*) 400 kg/cm^2, 40°C, 500 rad/hr; (*C*) first stage, 400 kg/cm^2, 40°C, 2.5 × 10^4 rad/hr; second stage, 400 kg/cm^2, 40°C, 0 rad/hr. (*b*) AIBN-initiated polymerization: (*A*) first stage, 400 kg/cm^2, 40°C, AIBN 1.22 mmole; second stage, 400 kg/cm^2, 40°C, (○) 0 rad/hr, (●) 500 rad/hr.

termination. It was also described that the γ-irradiation was required for the chain growth, since the polymer yield did not increase when the reaction system was not exposed to radiation [Fig. 2*a* (line *C*)].[8]

In the polymerization initiated by AIBN, the initiator container was opened to the main reactor for 2.0 hr in the first stage, and the system was then kept at a constant pressure and temperature after the initiator container was closed. As shown in Figures 2*b* and 3, both the polymer yield and the polymer molecular weight increased markedly in the second stage [Fig. 2*b* (line *A*); Fig. 3*B*]. However, in contrast to the results of the radiation polymerization, the magnitude of the increase in the molecular weight became less pronounced as the reaction proceeded. This may indicate that the chain transfer as well as the chain growth occurred in the polymerization by AIBN. The points given as half closed circles in Figures 2*b* and 3 were obtained by runs in which the system was exposed to γ-radiation at a dose rate of 500 rad/hr in the second stage. Since all points for the yield and the molecular weight fell on the same lines which were obtained without the exposure to radiation, it can be said that the γ-irradiation has no effect on the rate of propagation and transfer reactions as for the radicals from AIBN. The results given above also show that the grafting of ethylene onto the polymers formed in the first stage is not important under irradiation at such low dose rates in the second stage.

These differences in the nature of the chain radicals are more clearly shown in Figure 4. The polymerization was run in three stages. The

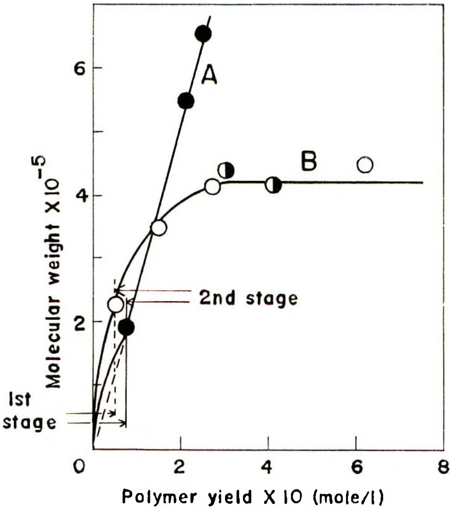


Fig. 3. Number-average molecular weight vs. polymer yield: (*A*) reaction conditions same as in Fig. 2*a*, line *A*; (*B*) reaction conditions same as in Fig. 2*b*, line *A*.

first and the second stages were carried out in two ways, following procedures a and b. In procedure a, ethylene was first irradiated at 25,000 rad/hr for 0.5 hr, and then the AIBN container was opened for 2.0 hr in the absence of γ-radiation. This was reversed in procedure b; thus, the container was opened for 2.0 hr, and the γ-irradiation was carried out next. For either procedure, a straight line *A* was obtained in the third stage under the γ-irradiation at 500 rad/hr and with no irradiation (line *B*). It is clear that the rate of polymer increase with irradiation is almost equal to the sum of those given in lines *A* in Figures 2*a* and 2*b*, while, without irradiation, the rate is only comparable to that in Figure 2*b*.

From these results, it can be said that the propagation reaction of the two types of radicals produced in the stages a and b took place at the usual rate under γ-irradiation (case A); however, the radicals produced by γ-rays did not react with ethylene in the absence of radiation (case B). Thus, the reactivity of the radicals from AIBN is not changed by the presence of γ-rays or a trace amount of radiolysis products of ethylene. On the other hand, although they exist under the same circumstances as those from AIBN, the radicals produced by γ-radiation remain unreactive if they are not exposed to radiation. Excitation by radiation might be necessary for their chain growth.

Ultraviolet Light Irradiation

Table I shows the effect of ultraviolet light on the chain growth of the radicals produced by γ-ray. It can be seen that ethylene was polymerized by light in the region 2700–3900 Å (runs 2 and 3). In our detailed investigation[10] reported previously it was shown that the photopolymerization was initiated by light of wavelength <3500 Å. The polymer yield de-

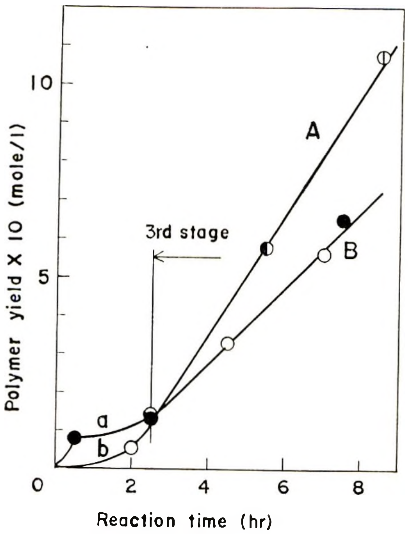


Fig. 4. Polymer yield vs. reaction time: (◐) procedure a, *A*; (⊖) procedure b, *A*; (●) procedure a, *B*; (○) procedure b, *B*. Procedure a: first stage, 400 kg/cm^2, 40°C, 2.5×10^4 rad/hr; second stage, 400 kg/cm^2, 40°C, AIBN 1.22 mmole. Procedure b: first stage, 400 kg/cm^2, 40°C, AIBN 1.22 mmole; second stage, 400 kg/cm^2, 40°C, 2.5×10^4 rad/hr. Third stage: (*A*) 400 kg/cm^2, 40°C, 500 rad/hr; (*B*) 400 kg/cm^2, 40°C, 0 rad/hr.

creased gradually as the wavelength became longer, and no polymer was obtained at wavelengths >3900 Å. Further, it was pointed out that ethylene was excited in the photopolymerization into its triplet state by absorbing light in the 2700–3480 Å range due to a perturbing effect of oxygen contained as an impurity in the monomer.

In run 4 and 5, the polymerization was divided into two stages. Ethylene was irradiated by γ-rays for 1.0 hr in the first stage and by light for 10 hr in the second stage. Thus, run 4 was a combination of runs 1 and 2, and run 5 was a combination of runs 1 and 3. The total yield of polymer of run 4 was 156.7 mg, which was larger by 50.9 mg than the sum of those of runs 1 and 3. Further, the polymer molecular weight became higher by 57,000 than in the case of run 1. On the other hand, run 5 gave almost the same results as run 1. In run 6, the radicals produced in the first stage were allowed to stand in contact with oxygen for 10.0 hr before entering into the second stage. The yield and the molecular weight were 107.3 mg and 260,000, respectively. The former is almost the same as the sum of runs 1 and 2, and the latter is the same as that for run 1.

The observed increase in the polymer yield and the polymer molecular weight in the second stage of run 4 can be ascribed to the chain growth of the radicals produced in the first stage, and the promotion by light may occur in just the same way as in the case of γ-rays at a low dose rate. The results of run 6 indicate that the final deactivation of radicals is brought about by the reaction with oxygen. Further, the fact that the chain growth

TABLE I

Photoinduced Chain Growth of Radicals Produced in the Polymerization of Ethylene by ^{60}Co γ-Radiation

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6[a]
γ-Irradiation						
Dose rate, rad/hr	25,000			25,000	25,000	25,000
Pressure, kg/cm^2	400			400	400	400
Temperature, °C	25			25	25	25
Reaction time, hr	1.0			1.0	1.0	1.0
Light						
Wavelength λ, Å		>2700	>3900	>2700	>3900	>2700
Pressure, kg/cm^2		400	400	400	400	400
Temperature, °C		30	30	30	30	30
Reaction time, hr		10.0	10.0	10.0	10.0	10.0
Polymer yield, mg	95.5	10.3	0	156.7	98.2	107.3
Molecular weight	260,000			317,000	262,000	260,000

[a] Unreacted ethylene monomer was once purged after the γ-irradiation in the first stage, and oxygen was fed to atmospheric pressure at 30°C. The system was then allowed to stand in the dark for 20.0 hr. Fresh ethylene monomer was next charged after purging oxygen under 10^{-3} mm Hg.

occurs only when the system is irradiated by light below about 3900 Å, which has an energy enough to excite ethylene into its triplet state, may suggest that the less reactive radicals produced by γ-rays can be activated by the interaction with excited monomer.

In the previous papers, the rate of propagation reaction was shown to be proportional to the second power of ethylene fugacity, and the activation energy of the reaction was found to be -9.0 kcal/mole. The high fugacity exponent and the negative activation energy have led us to suggest that ethylene may react with the growing radicals in dimer form.

In view of these considerations, the sequence of reactions (1)–(3) could be proposed as for the propagation of the radiation polymerization.

Monomer excitation:

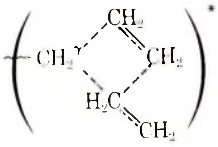
$$CH_2{=}CH_2 \rightleftharpoons CH_2{=}CH_2^* \qquad (1)$$

Excited dimer formation:

$$CH_2{=}CH_2 + CH_2{=}CH_2^* \rightleftharpoons (CH_2{=}CH_2)_2^* \qquad (2)$$

Addition to chain radical:

$$\sim CH_2^{\gamma} + (CH_2{=}CH_2)_2^* \longrightarrow$$



$$\longrightarrow \sim CH_2CH_2\dot{C}H_2^{\gamma} + CH_2{=}CH_2^* \qquad (3)$$

Here $\sim\dot{C}H_2^{\gamma}$ means that the growing radicals produced by γ-radiation differ in their reactivity from the radicals produced by AIBN.

An excited ethylene may first undergo a reaction with another monomer of ground state to form an excited dimer, which then reacts with a growing radical by passing through a transition state arising from a sort of conjugation. Less reactive radicals may be activated by receiving excess energy of the dimer, and no chain transfer in the radiation polymerization may be caused by the specific monomer configuration in the radical activation, in which addition of radical to olefinic bond is predominant. The negative activation energy of the propagation may be ascribed to the temperature dependence of equilibrium constant of reaction (2), since dimer formation is considered to be exothermic. Reproduction of an excited monomer in reaction (3) is assumed by considering the experimental facts the radical is always unreactive when the system is placed out of the radiation field and that an extremely large amount of ethylene can polymerize at the expense of small amount of radiation energy. Thus, the G value (number of ethylene molecules reacted per 100 eV of absorbed energy) can reach 10^5–10^6 in the second stage.

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Received February 16, 1970
Revised April 20, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3311–3328 (1970)

Stereospecific Polymerization of Isobutyl Vinyl Ether by AlR_3–$VCl_3 \cdot LiCl$ Catalyst. II. Effects of Polymerization Conditions on Polymerization*

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Synopsis

The effect of polymerization conditions such as aging time of the catalyst, polymerization temperature, polymerization time, monomer concentration, and catalyst concentration on the polymerization of isobutyl vinyl ether was intensively studied by using the $VCl_3 \cdot LiCl$–$Al(i\text{-}Bu)_3$ system at an $Al(i\text{-}Bu)/VCl_3 \cdot LiCl$ ratio of 6 at which the cationic polymerization by $VCl_3 \cdot LiCl$ is sufficiently depressed. About 10 min aging of the catalyst in the presence of monomer yields a fairly stable catalytic system. The optimum polymerization temperature is around 30°C. The conversion increased with increasing monomer concentration, whereas the stereospecificity of polymerization decreased. Unexpectedly, the conversion decreased as total catalyst concentration increased. This phenomenon is explained by considering the deactivation of catalytic sites by the excess of $Al(i\text{-}Bu)_3$. A reasonable mechanism from kinetic considerations is that two molecules of $Al(i\text{-}Bu)_3$ deactivate the catalytic site in an equilibrium reaction. This deactivation is understandable by considering that the coordination of two molecules of $Al(i\text{-}Bu)_3$ will occupy all the coordination positions of vanadium, so that there is no room for coordination of monomer coming to the catalytic site.

INTRODUCTION

In the previous paper,[1] we reported that $VCl_3 \cdot LiCl$ and $VCl_2 \cdot 2LiCl$ which are prepared by the reduction of VCl_4 with BuLi in stoichiometric proportions are effective catalysts in the polymerization of isobutyl vinyl ether. When $VCl_3 \cdot LiCl$ was combined with large excess of $Al(i\text{-}Bu)_3$ (over 6 mole equivalents to $VCl_3 \cdot LiCl$), a new catalytic system was formed, and a crystalline poly(isobutyl vinyl ether) can be obtained by this catalyst[1] even at room temperatures.

In the present paper, the influence of polymerization conditions[2] such as aging time of the catalyst, polymerization temperature, polymerization time, monomer concentration, and catalyst concentration upon the

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* Presented at the Annual Meeting of the Society of Polymer Science, held in Osaka, Japan, 1962.

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polymerization of isobutyl vinyl ether by $VCl_3 \cdot LiCl$–Al(*i*-Bu)$_3$ catalyst is described. The optimum polymerization temperature is around 30°C. Unexpectedly, total conversion decreased with increasing total catalyst concentration. A kinetic consideration is made assuming that the decrease in total conversion is due to a deactivation of the catalyst by an excess of Al(*i*-Bu)$_3$, and a reasonable mechanism in which two molecules of Al(*i*-Bu)$_3$ deactivate the catalytic site is proposed.

EXPERIMENTAL

Materials

Isobutyl vinyl ether, *n*-heptane, vanadium tetrachloride (VCl_4), and triisobutyl aluminum [Al(*i*-Bu)$_3$] were the same as described in the previous paper.[1] An *n*-heptane solution of *n*-butyllithium (*n*-BuLi) was obtained from Foote Mineral Co. *n*-BuLi was analyzed in the same manner[3] as described in the previous paper.

Preparation of $VCl_3 \cdot LiCl$

A given amount of VCl_4 was dissolved in *n*-heptane under a nitrogen atmosphere, and to this an equimolar amount of *n*-BuLi was added dropwise under vigorous stirring. A purple dispersion of $VCl_3 \cdot LiCl$ was formed, and the brown color of VCl_4 in the solution disappeared when the addition of *n*-BuLi was complete. The reaction mixture was boiled to complete the reaction and then allowed to cool at room temperature. A suspension of this reaction mixture in the solution was used as a catalyst component. Acid titration of the supernatant liquid showed that there was no butyl lithium in the solution.

In order to examine the presence of a soluble vanadium compound in the solution, 1 ml of the supernatant liquid was withdrawn and placed in a test tube, then a 3-ml portion of 4*N* HCl methanol solution was introduced. Subsequent addition of 1 ml of 3% H_2O_2 solution shows no color reaction,[4] indicating there is no appreciable vanadium component in the supernatant solution.

The $VCl_3 \cdot LiCl$ precipitated was not analyzed.

Polymerization

The polymerizations were carried out in a Schlenk-type reactor with the use of *n*-heptane as solvent. All procedures were carried out under a nitrogen atmosphere.

First, Al(*i*-Bu)$_3$ was mixed in *n*-heptane in the polymerization reactor followed by an equimolar amount of isobutyl vinyl ether. To this, $VCl_3 \cdot LiCl$ suspension was added. After the mixture had been aged for a given time (10 min unless otherwise noted), the polymerization was started by introducing an additional monomer so that the sum of the monomer should be a prescribed amount. The ratio of Al(*i*-Bu)$_3$ to $VCl_3 \cdot LiCl$ in the catalytic system was kept at 6 in all cases. As reported in the previous paper,[1] partial addition of the monomer to $Al(i\text{-}Bu)_3$ plays an important role in depressing the reducing power of $Al(i\text{-}Bu)_3$.

After a given polymerization time, the mixture was poured into acidic methanol containing a small amount of phenyl-β-naphthylamine and allowed to stand overnight to decompose the catalyst. The white polymer mass obtained was immersed in ethanol to remove the decomposed catalyst and dried *in vacuo*. The conversion was calculated on the basis of the total monomer used.

Gas-Chromatographic Analysis of the Residual Monomer

A typical polymerization mixture was poured into methanol and the residual monomer was analyzed by vapor-phase chromatography on a TCP column. The estimate of residual monomer thus obtained was in agreement with the difference between the total monomer used and the polymer formed.

Solubility Index

The polymer obtained was extracted in boiling acetone for 4 hr using 100 ml of acetone per gram of the polymer. The solubility index represents the percentage of insoluble fractions; this figure was used as a measure of the stereospecificity of the polymerization.

Viscosity Measurement

Intrinsic viscosity $[\eta]$ and η_{sp}/c $(c = 1.0)$ of the acetone-insoluble fractions were measured at 30°C in benzene with the use of Ostwald and Ubbelohde viscometers.

Molecular Weight

The molecular weight of the polymer was calculated by using Imanishi's relationship:[5]

$$[\eta] = 7.55 \times 10^{-5} M^{0.75}$$

RESULTS

As reported in the previous paper,[1] vanadium compounds are easily reduced to lower valence states in the presence of AlR_3; therefore, the effect of aging time of the catalyst on the polymerization was studied. The catalyst was prepared by adding $VCl_3 \cdot LiCl$ to an equimolar $Al(i\text{-}Bu)_3$–monomer mixture in heptane so that the molar ratio of $Al(i\text{-}Bu)_3$ to $VCl_3 \cdot LiCl$ was 6. After aging the above mixture for a given time, the polymerization was started by introducing an additional monomer.

The results are shown in Figure 1. During the initial 10 min of aging, the total conversion (based on total monomer) and the acetone-insoluble

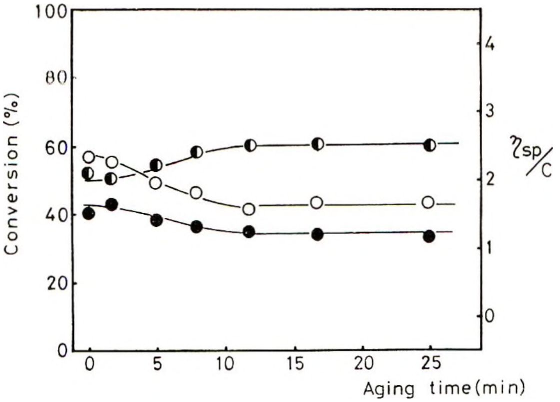

Fig. 1. Influence of the aging time of catalyst: (○) total conversion; (●) acetone-insoluble fraction; (◐) η_{sp}/c (c = 1.0) of the acetone-insoluble portion measured at 30°C in benzene. Polymerization conditions: n-heptane, 20 ml; monomer, 3 g; $VCl_3 \cdot LiCl$, 0.0005 mole; $Al(i\text{-}Bu)_3$, 0.0030 mole; polymerization temperature, 30°C; polymerization time, 3 hr.

fraction decreased with aging, while the viscosity of the polymer increased in the same period. However, after 10 mins, these became constant and did not change on further aging.

Influence of the Polymerization Temperature

The influence of temperature on the polymerization was studied in the range of −78°C to 60°C. The results are summarized in Table I. With this catalytic system the polymerization proceeded rather slowly, and at a low temperature like −78°C only very little polymer was obtained. The catalytic activity showed a maximum at around 30°C and the viscosity of the acetone-insoluble fraction was highest when the polymerization was performed at 0°C.

From the Arrhenius plot of the initial rates of polymerization in the range of 0–30°C at which the polymerization proceeds most smoothly, the apparent activation energy was estimated at 8.6 kcal/mole.

Influence of Polymerization Time

The influence of reaction time on the polymerization at 30°C was examined. The results are shown in Figures 2 and 3. The total conversion, the acetone-insoluble fraction, and also the acetone-soluble fraction increased with increasing polymerization time. The viscosity of the acetone-insoluble fractions also increased slightly with increasing conversion.

Influence of Monomer Concentration

The influence of monomer concentration on the polymerization was studied at 30°C. The results are shown in Figures 4 and 5.

TABLE I
Effect of Temperature on the Polymerization of Isobutyl Vinyl Ether by the $Al(i\text{-}Bu)_3$–VCl_3 System[a]

Experiment No.	Polymerization temperature, °C	Polymerization time, hr	Conversion, %	Solubility index, %[b]	η_{sp}/c, dl/g[c]
1[d]	−78	5.0	3.2	57.3	1.52
2[d]	−78[e]	9.0	12.0	41.0	1.60
3[d]	−20	5.0	4.3	60.2	2.02
4[d]	0	4.0	38.4	76.3	2.48
5[d]	30	4.0	57.9	75.9	2.31
6[d]	30[e]	1.0	50.3	89.6[f]	1.98
7[g]	30[e]	1.0	77.7	85.6[f]	1.30
8[h]	30[e]	1.0	80.3	80.7[f]	1.24
9[d]	50	5.0	32.3	74.7	2.14
10[h]	60[e]	3.0	69.3	68.8	0.83
11[g]	60[e]	3.0	69.8	48.3	0.68

[a] Polymerization conditions: n-heptane, 30 ml; isobutyl vinyl ether, 3 g; $VCl_3 \cdot LiCl$, 0.0005 mole, $Al(i\text{-}Bu)_3$, 0.0030 mole. Order of addition: $Al(i\text{-}Bu)_3$, VCl_3, monomer unless otherwise noted.

[b] Acetone-insoluble part/total polymer, at 100 cc of acetone/g of polymer.

[c] Measured in benzene solution at the concentration of $c = 1$ at 30°C.

[d] $VCl_3 \cdot LiCl$ was prepared by the reaction between VCl_4 and BuLi.

[e] Order of addition: monomer, $Al(i\text{-}Bu)_3$, VCl_3.

[f] 50 cc of acetone used/g of polymer.

[g] VCl_3 was prepared by the reaction between $AlEt_3$ and VCl_4 at Al/V ratio of 0.5 in heptane at room temperature and used without washing.

[h] VCl_3 was prepared in heptane by the reaction between $AlEt_3$ and VCl_4 at the Al/V ratio of 0.5. Reaction product was boiled for 2 hr, then washed with heptane.

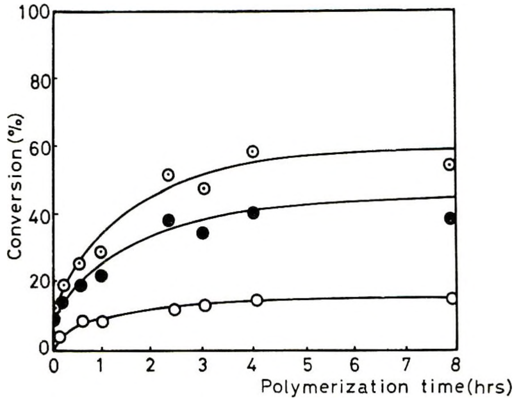

Fig. 2. Influence of polymerization time on the polymerization: (⊙) total conversion; (●) acetone-insoluble fraction; (○) acetone-soluble, fraction. Polymerization conditions: n-heptane, 30 ml, monomer, 3 g; $VCl_3 \cdot LiCl$, 0.0005 mole; Al $(i\text{-}Bu)_3$, 0.0030 mole; polymerization temperature, 30°C.

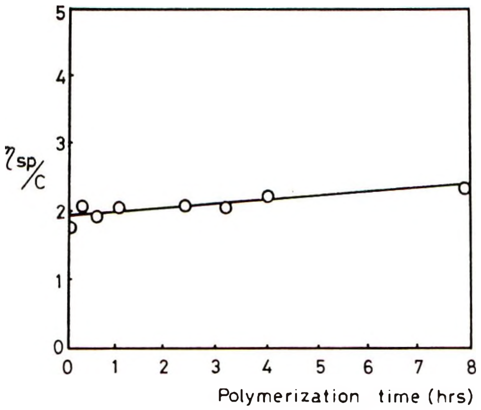

Fig. 3. Influence of polymerization time on the reduced viscosity of the resulting polymer. The reduced viscosity was measured for the acetone-insoluble fractions at 30°C in benzene at $c = 1.0$. Polymerization conditions are those given in Fig. 2.

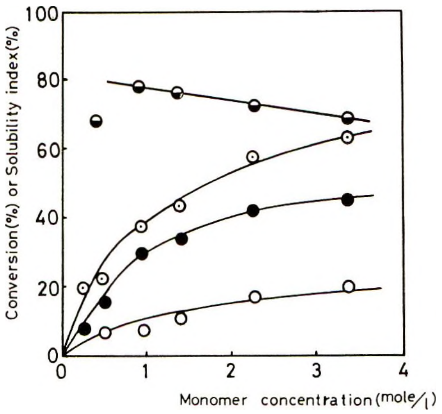

Fig. 4. Influence of monomer concentration on the polymerization: (◒) solubility index; (⊙) total conversion; (●) acetone-insoluble fraction; (○) acetone-soluble fraction. Polymerization conditions; $VCl_3 \cdot LiCl$, 0.0005 mole; $Al(i\text{-}Bu)_3$, 0.0030 mole; *n*-heptane, 30 ml; polymerization temperature, 30°C; polymerization time, 3 hr.

The total conversion, the acetone-insoluble fraction and the acetone-soluble fraction increased as monomer concentration increased, whereas the solubility index of the polymer decreased with increasing monomer concentration.

The viscosity of the acetone-insoluble fraction was approximately constant, regardless of monomer concentration.

Effect of the Amount of Solvent

The influence of the amount of solvent (*n*-heptane) used on the polymerization was examined at 30°C, the other polymerization conditions remaining unchanged. As shown in Figure 6, the total conversion, the

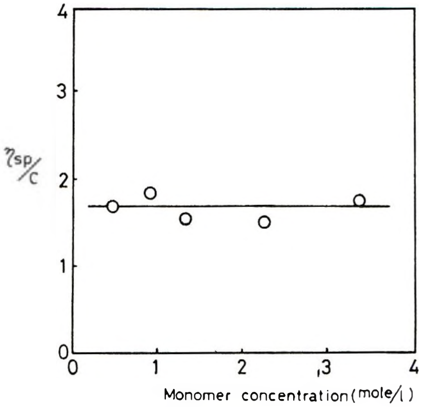

Fig. 5. Influence of monomer concentration on the reduced viscosity of the polymer. The reduced viscosity was measured for the acetone-insoluble fractions at 30°C in benzene at $c = 1.0$. The polymerization conditions are those given in Fig. 4.

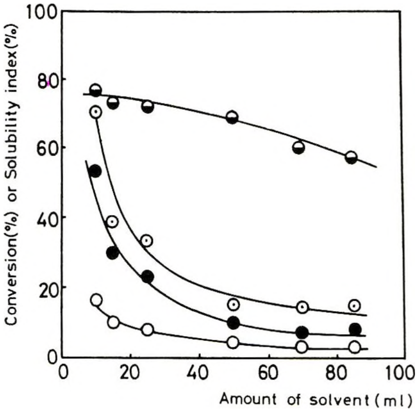

Fig. 6. Influence of amount of solvent (n-heptane) on the polymerization: (◒) solubility index of the polymer; (⊙) total conversion; (●) acetone-insoluble fraction; (○) acetone-soluble fraction. Polymerization conditions: $VCl_3 \cdot LiCl$, 0.0005 mole; Al-(i-Bu)$_3$, 0.0030 mole; monomer, 3 g; polymerization temperature, 30°C; polymerization time, 1 hr.

acetone-insoluble fraction, and the acetone-soluble fraction decreased as volume of solvent increased. The solubility index of the polymer also decreased as the amount of solvent used increased. Figure 7 shows that the viscosity of the acetone-insoluble fraction decreased as the solvent increased.

Influence of Total Catalyst Concentration

The polymerizations were carried out with the catalyst of various concentrations in which the molar ratio $Al(i\text{-}Bu)_3/VCl_3 \cdot LiCl$ was fixed at 6. The results are summarized in Figure 8.

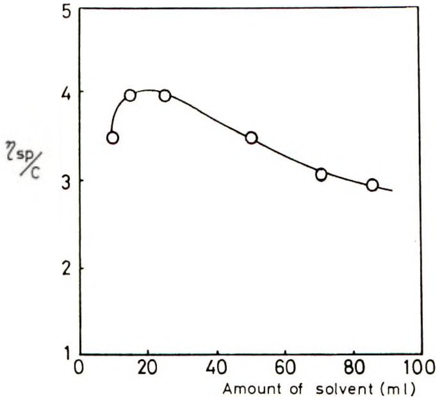

Fig. 7. Influence of amount of the solvent (*n*-heptane) on the reduced viscosity of the polymer. The reduced viscosity was measured at 30°C in benzene at $c = 1.0$. The polymerization conditions are those given in Fig. 6.

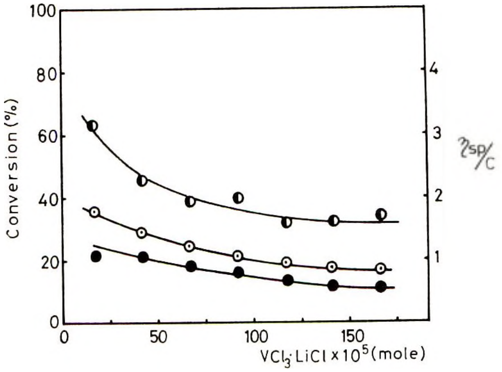

Fig. 8. Influence of total catalyst concentration on the polymerization (I): (⊙) total conversion; (●) acetone-insoluble fraction; (◐) η_{sp}/c of the acetone-insoluble fraction. Polymerization conditions: *n*-heptane, 30 ml; monomer, 3 g; $Al(i\text{-}Bu)_3/VCl_3 \cdot LiCl = 6$; polymerization temperature, 30°C; polymerization time, 90 min. The reduced viscosity was measured at 30°C in benzene at $C = 1.0$.

Generally, the number of active sites in the catalyst increases in proportion to catalyst concentration; therefore, the conversion after a given period of time usually increases with increasing amount of catalyst used.

In the polymerization of isobutyl vinyl ether by the $Al(i\text{-}Bu)_3$–$VCl_3 \cdot LiCl$ system, however, the total conversion as well as the acetone-insoluble fraction decreased with increasing total catalyst concentration. Here, the total conversion is based on the total monomer which includes the monomer coordinated to $Al(i\text{-}Bu)_3$ before mixing $Al(i\text{-}Bu)_3$ with $VCl_3 \cdot LiCl$ as described in the experimental section.

Figure 9 shows plots of the amount of polymer formed per mole of $VCl_3 \cdot LiCl$ against concentration of $VCl_3 \cdot LiCl$. A decrease of the polymer yield per $VCl_3 \cdot LiCl$ is clearly observed with increasing total catalyst concentration.

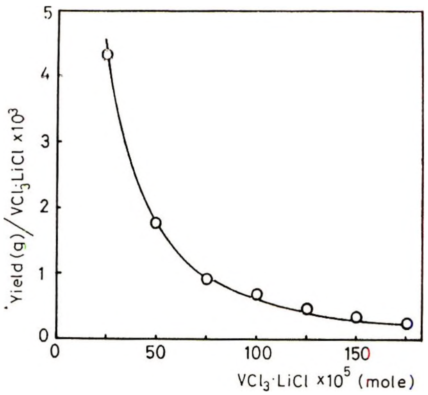

Fig. 9. Influence of total catalyst concentration (II). Amount of the polymer formed per mole of $VCl_3 \cdot LiCl$. Polymerization conditions are those given in Fig. 8.

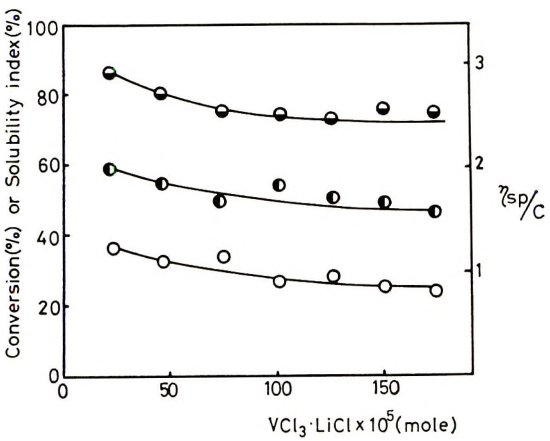

Fig. 10. Influence of total catalyst concentration on the polymerization (III): (◓) solubility index of the polymer; (○) total conversion (calculated based on 5 g of the monomer, assuming the complexed monomer does not participate in the polymerization); (◐) η_{sp}/C for the acetone-insoluble fraction. Polymerization conditions: *n*-heptane, 30 ml; monomer, 5 g, in addition to monomer complexed to $Al(i\text{-}Bu)_3$. Polymerization temperature, 30°C, polymerization time, 90 min.

Figure 10 shows that even when a constant amount of monomer (5 g) besides that complexed to $Al(i\text{-}Bu)_3$ was polymerized by changing the total catalyst concentration, the conversion decreased similarly with increasing total catalyst concentration.

Noticeably, when $VCl_3 \cdot LiCl$ was introduced to an equimolar monomer–$Al(i\text{-}Bu)_3$ mixture and was allowed to react for 90 min at 30°C without further addition of monomer, an almost quantitative yield of polymer was obtained.

Kinetic Consideration on the Deactivation of the Catalyst by Al(i-Bu)$_3$

The active center on the surface of $VCl_3 \cdot LiCl$ particles in the Al(i-Bu)$_3$–$VCl_3 \cdot LiCl$ catalyst system (Al/V $\geqq$ 6) is expressed by V*. We assume that Al(i-Bu)$_3$ (hereafter expressed as Al) and V* form an active center C* in the following equilibrium:

$$V^* + Al \overset{K_1}{\rightleftarrows} V^*Al \equiv C^* \text{ (active)} \tag{1}$$

We assume also that the deactivation of C* is caused by two molecules of Al(i-Bu)$_3$ as shown by the following equilibrium:

$$C^* + 2Al \overset{K_2}{\rightleftarrows} C \text{ (inactive)} \tag{2}$$

Here, K_1 and K_2 are equilibrium constants. We denote the initial concentration of V* by $[V^*]_0$; thus we have,

$$[V^*] + [V^* \cdot Al] = [V^*]_0$$

thus,

$$K_1 = \frac{[V^* \cdot Al]}{([V^*]_0 - [V^* \cdot Al])[Al]} \tag{3}$$

Therefore,

$$[C^*]_0 = [V^* \cdot Al] = \frac{K_1[Al][V^*]_0}{1 + K_1[Al]} \tag{4}$$

On the other hand, eq. (5) can be derived from eq. (2):

$$K_2 = [C]/[C^*][Al]^2 \tag{5}$$

Expressing the initial concentration of the active centers C* by $[C^*]_0$, we have

$$[C^*]_0 = [C] + [C^*] \tag{6}$$

Therefore,

$$K_2 = ([C^*]_0 - [C^*])/[C^*]\,[Al]^2 \tag{7}$$

Thus we have,

$$[C^*] = \frac{[C^*]_0}{1 + K_2[Al]^2} = \frac{K_1[Al][V^*]_0}{(1 + K_2[Al]^2)(1 + K_1[Al])} \tag{8}$$

Under the conditions of Al/V $\geqq$ 6, almost all the V* should be in the form of V*Al.[1] In such a case, the following relation (9) can be derived from eq. (3).

$$K_1[Al] = \frac{[V^* \cdot Al]}{[V^*]_0 - [V^* \cdot Al]} \gg 1 \tag{9}$$

Consequently, eq. (8) can be simplified as follows

$$[C^*] = [V^*]_0/(1 + K_2[Al]^2) \tag{10}$$

As $VCl_3 \cdot LiCl$ is prepared under the same conditions, the particle size of the $VCl_3 \cdot LiCl$ can be considered nearly equal. Thus we have the relation

$$[V^*]_0 = a[VCl_3] \tag{11}$$

where $[VCl_3]$ represents the total concentration of $VCl_3 \cdot LiCl$ in the catalyst. Therefore,

$$[C^*] = a[VCl_3]/(1 + K_2[Al]^2) \tag{12}$$

The results of actual polymerization were analyzed as follows.

Case 1. Concentration of Al(*i*-Bu)$_3$ Varied and $VCl_3 \cdot LiCl$ Kept Constant. The reaction rate R_p of the polymerization by the Al(i-Bu)$_3$–$VCl_3 \cdot LiCl$ catalyst at the molar ratio of $Al/V \geq 6$ can be expressed by eq. (13).

$$R_p = k_p[C^*][M] = k_p \frac{[M]a[VCl_3]}{1 + K_2[Al]^2} \tag{13}$$

where k_p is the rate constant of the propagation reaction and $[M]$ is monomer concentration.

On denoting the initial concentration of monomer by $[M]_0$, the initial reaction rate of polymerization is given by eq. (14):

$$R_p = A/(1 + K_2[Al]^2) \tag{14}$$

where $A = K_p a[M]_0[VCl_3]$, which is constant when $[M]_0$ and $[VCl_3]$ are fixed.

From the eq. (14), we have

$$\frac{1}{R_p} = \frac{1}{A} + \frac{K_2}{A}[Al]^2 \tag{15}$$

Figure 11 shows a plot of the rate of polymerization against concentration of Al(i-Bu)$_3$ at a fixed concentration of $VCl_3 \cdot LiCl$ (reproduced from Figure 8 of Part I[1]) at Al/V ratios higher than 6. From these data, $1/R_p$ was plotted against $[Al]^2$, and we have a linear relationship as given in Figure 12. From the intercept and the slope in Figure 12, we can calculate $A = 3.33 \times 10^{-4}$ (l.·sec/mole), $K_2 = 9.67 \times 10^2$ (l.^{2}/mole^2).

Case 2. Total Catalyst Concentration Varied. The rate of polymerization R_p at Al(i-Bu)$_3$/$VCl_3 \cdot LiCl = 6$ is represented by eq. (16):

$$R_p = \frac{k_p a[M][VCl_3]}{1 + 36K_2[VCl_3]^2} \tag{16}$$

This equation shows that, if the concentration of monomer is kept constant, R_p should decrease with increasing total concentration of the catalyst. From eq. (16) we have

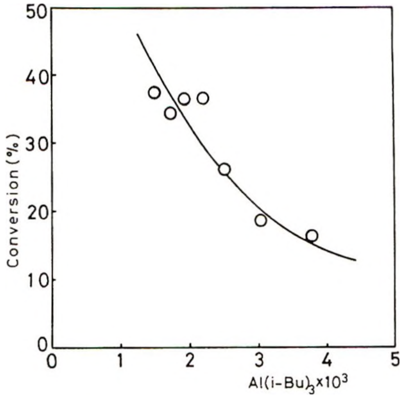

Fig. 11. A decrease of polymerization rate with increasing Al(i-Bu)$_3$ at fixed VCl$_3$·LiCl concentration [Al(i-Bu)$_3$/VCl$_3$·LiCl = 6]. Polymerization conditions: VCl$_3$·LiCl, 0.00025 mole; n-heptane, 30 ml; monomer, 3 g; polymerization temperature, 30°C; polymerization time, 1 hr.

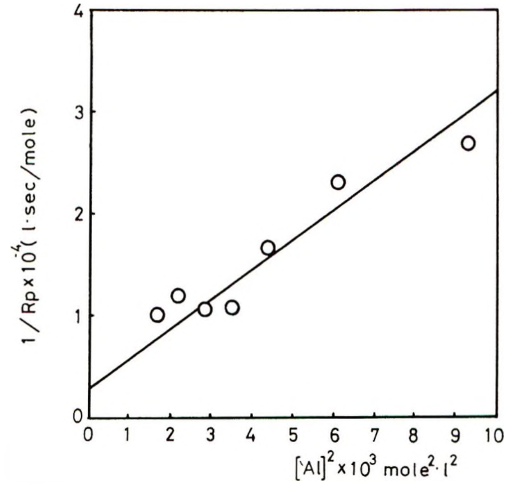

Fig. 12. Plot of $1/R_p$ vs. $[Al]^2$ at fixed VCl$_3$·LiCl concentration. Al(i-Bu)$_3$/VCl$_3$·LiC ≧ 6.

$$\frac{[\mathrm{VCl_3}]}{R_p} = \frac{1}{B} + \frac{36K_2}{B}[\mathrm{VCl_3}]^2 \qquad (17)$$

where

$$B = k_p a[\mathrm{M}]$$

From Figure 8 in this paper R_p for the various total catalyst concentrations were calculated, and $[\mathrm{VCl_3}]/R_p$ was plotted against $[\mathrm{VCl_3}]^2$. Thus we have a linear relationship as given in Figure 13. From the slope and the intercept in Figure 13, we can calculate B and K_2 as 3.33×10^2 sec^{-1} and 9.65×10^2 l.^{2}/mole^2, respectively; the latter is in good agreement with the estimate from eq. (15).

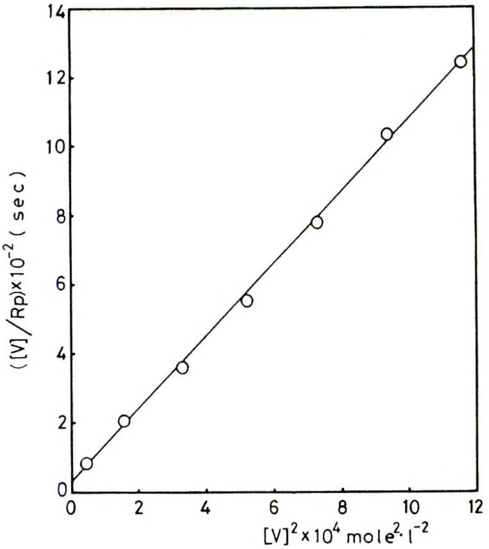

Fig. 13. Plot of [V]/R_p vs. $[V]^2$ at Al(i-Bu)$_3$/VCl$_3$·LiCl = 6.

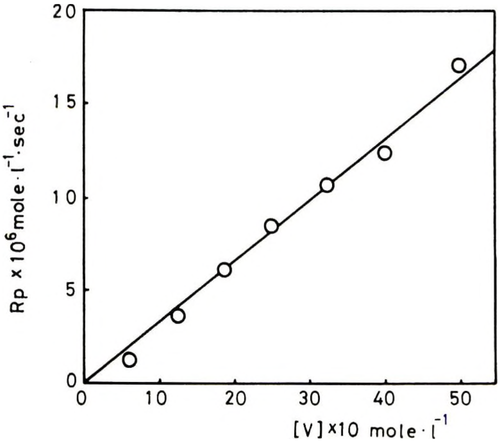

Fig. 14. Plot of R_p vs. [V] at fixed Al(i-Bu)$_3$ concentration. Al(i-Bu)$_3$/VCl$_3$·LiCl ≧ 6.

Case 3. Concentration of Al(i-Bu)$_3$ Fixed and Concentration of VCl$_3$·LiCl Varied. When the concentration of VCl$_3$·LiCl was varied, and other variables were kept constant under the conditions of Al/V ≧ 6, the total conversion for a given time of the polymerization increased in proportion to [VCl$_3$], as shown in Figure 14.

The rate of polymerization R_p is expressed as follows:

$$R_p = k_p[C^*][M] = k_p a[M]\frac{[VCl_3]}{1 + K_2[Al]^2} \qquad (18)$$

where [M] and [Al] are constant; thus R_p is proportional to [VCl$_3$].

As discussed above, the decrease of polymerization rate with increasing catalyst concentration in the Al(i-Bu)$_3$–VCl$_3$·LiCl system in the range of Al/V ≧ 6 is considered to be due to the deactivation of the catalyst by the interaction of two molecules of Al(i-Bu)$_3$ with an active center on the surface of VCl$_3$·LiCl particles. For a Ziegler-type catalyst, similar results that the catalytic activity decreases in the presence of an excess of AlR$_3$ have been reported, but the mechanism has not been clarified as yet. The kinetic consideration shows that the deactivation might be due to the complex formation between the active center and two molecules of Al(i-Bu)$_3$ in an equilibrium reaction.

DISCUSSION

In the previous paper[1] we pointed out that the vanadium compound in the catalyst can be easily reduced. However, in the presence of isobutyl vinyl ether the vanadium component in the Al(i-Bu)$_3$–VCl$_3$·LiCl system was fairly stable, and almost no change in the catalytic activity was observed, even after aging for 2 hrs as shown in Figure 1. This observation indicates, as described in the previous paper,[1] that the vanadium component is not appreciably reduced during the polymerization and acts in a trivalent state. The decrease of conversion together with the increase of molecular weight of the polymer during the initial 10 min of aging time suggests that it takes about 10 min to form a stable complex catalyst.

In this catalytic system, the coexistence of LiCl in VCl$_3$ seems very important, since, as reported in the previous paper, when thermally decomposed VCl$_3$ from VCl$_4$ was used instead of VCl$_3$·LiCl, the resulting polymer is mostly soluble in acetone, indicating low stereospecificity. Table II shows that a simple mixture of a commercial VCl$_3$ and LiCl does not show the same stereospecific activity as VCl$_3$·LiCl in combination with Al(i-Bu)$_3$; therefore, LiCl in VCl$_3$·LiCl may be present as a solid solution in the crystalline lattice, which seems very important for the stereospecific polymerization.

The asymptotic increase in the time–conversion curve before reaching 100% in Figure 2 is explained in terms of a hard penetration of monomer to the heterogeneous catalytic sites. This phenomenon is usually observed in the polymerization by heterogeneous catalysts.

The polymerization of isobutyl vinyl ether by the Al(i-Bu)$_3$–VCl$_3$·LiCl catalyst system is different from that by conventional cationic polymerization catalysts and hardly proceeds at low temperatures. The polymerization activity increases with increasing polymerization temperature until it reaches a maximum at 30°C and then decreases again with further rise in temperature.

The decrease of conversion at higher temperature is probably due to unfavorable side reactions together with the deactivation of active centers on VCl$_3$·LiCl particles by Al(i-Bu)$_3$. A similar phenomenon is observed with most of the Ziegler-type catalysts.[6–10]

TABLE II
Polymerization of Isobutyl Vinyl Ether with $Al(i\text{-}Bu)_3$ and Various VCl_3 Preparations[a]

Catalyst		Conversion (%)	Solubility index
V	Al		
VCl_3[b]	$Al(i\text{-}Bu)_3$	72.3	32.5
VCl_3[c]	$Al(i\text{-}Bu)_3$	65.4	34.2
VCl_3[c] + LiCl[d]	$Al(i\text{-}Bu)_3$	63.0	30.6
$VCl_3 \cdot LiCl$[e]	$Al(i\text{-}Bu)_3$	70.6	87.9

[a] Polymerization conditions: *n*-heptane, 30 ml; monomer, 3 g; $Al(i\text{-}Bu)_3$, 0.0015 mole, polymerization temperature, 30°C; polymerization time, 1 hr. $Al(i\text{-}Bu)_3/VCl_3 = 6$ in all cases.

[b] Prepared by thermal decomposition of VCl_4 in heptane solution.

[c] Commercial product from Mitsuwa Chem. Co.

[d] Commercial, special grade from Wako Drug Co.

[e] Prepared by the reaction between VCl_4 and BuLi in stoichiometric proportion.

Generally, in the polymerization of isobutyl vinyl ether by heterogeneous catalyst,[11–15] for example, a metal sulfate–sulfuric acid complex, the polymerization behavior is different from that in the usual cationic polymerizations. For example, the higher the polymerization temperature, the higher the degree of polymerization and also the higher the crystallinity of the resulting polymer. This is probably due to the fact that the activity of heterogeneous catalyst is relatively small and that the polymerization proceeds without unfavorable side reactions which are usually induced at higher temperatures in the conventional cationic polymerization.

In the polymerization by $Al(i\text{-}Bu)_3$–$VCl_3 \cdot LiCl$, the stereospecificity (solubility index) of the polymerization decreased with increasing monomer concentration, although the total conversion, the acetone-insoluble fraction increased. This phenomenon is explained in terms of the changes of dielectric constant in the polymerization medium caused by the polarity of monomer. This is generally observed in the stereospecific polymerization of vinyl-ethers.[16,17]

In the stereospecific polymerization of isobutyl vinyl ether by $VCl_3 \cdot LiCl$–$Al(i\text{-}Bu)_3$ catalyst system, the increase of total catalyst concentration causes an unexpected decrease of the rate of polymerization. There are three possible reasons for such a decrease.

(1) The monomer which is coordinated to $Al(i\text{-}Bu)_3$ in the catalyst does not participate in the polymerization, and the proportion of such a monomer increases with increasing total catalyst concentration. As a result, the amount of actually polymerizable monomer decreases, and therefore, the apparent rate of the polymerization decreases.

(2) As total concentration of the catalyst increases, $VCl_3 \cdot LiCl$ might be dissolved in the reaction medium by the presence of high concentration of $Al(i\text{-}Bu)_3$. In such a case, polymerization might occur in the solution to form a polymer of extremely low molecular weight, soluble in methanol.

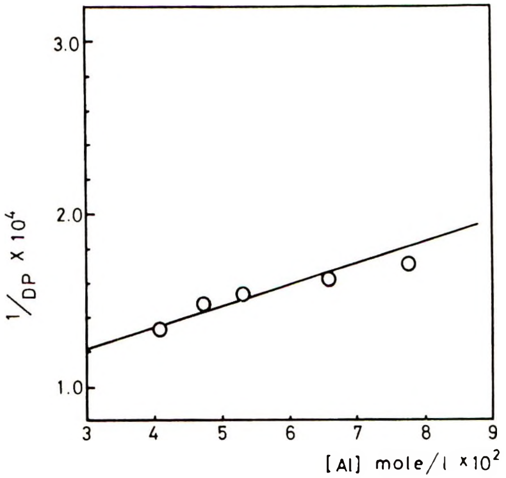

Fig. 15. Plot of 1/DP versus [Al] at fixed $VCl_3 \cdot LiCl$ concentration. $Al(i\text{-}Bu)_3/VCl_3 \cdot LiCl \geqq 6$.

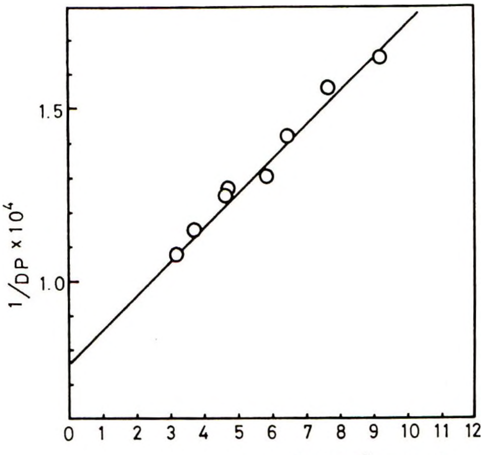

Fig. 16. Plot of 1/DP vs. [V] at fixed $Al(i\text{-}Bu)_3$ concentration. $Al(i\text{-}Bu)_3/VCl_3 \cdot LiCl \geqq 6$.

Thus the estimate of apparent rate of polymerization is lower because of the loss of the soluble polymer.

(3) An increase of concentration of $Al(i\text{-}Bu)_3$ with increase of total catalyst concentration brings the deactivation of active centers on the surface of $VCl_3 \cdot LiCl$. Consequently, the rate of polymerization becomes smaller due to deactivation of effective catalytic sites.

Among these three possibilities, (1) can be ruled out by the following reason, that is, the conversion calculated by subtracting the monomer coordinated to $Al(i\text{-}Bu)_3$ from the total monomer still decreases with increasing total catalyst concentration. The results in Figure 10 also show that reason (1) is not acceptable. Furthermore, a mixture of $Al(i\text{-}Bu)_3$, the complexed monomer, and $VCl_3 \cdot LiCl$ in the molar ratio of 6:6:1 in the catalyst preparation yields a polymer almost quantitatively.

This presents convincing evidence that the coordinated monomer do polymerize. Reason (2) can also be ruled out because vanadium was not detected in the supernatant liquid of the catalyst suspension and the gas-chromatographic examination of the residual monomer after polymerization shows that amount of the residual monomer just agrees with the difference between the total monomer used and the polymer obtained. This indicates that there is no oligomer soluble in methanol.

On the other hand, as shown in Figure 9, the amount of polymer formed per mole of $VCl_3 \cdot LiCl$ apparently decreased with increasing $VCl_3 \cdot LiCl$ concentration. This strongly suggests that the decrease of conversion with increasing total catalyst concentration is due to deactivation of active centers in the catalyst.

In conclusion, (3) seems to be the most probable explanation for the polymerization behavior as carefully discussed by kinetic consideration.

It is very interesting to know whether this deactivation reaction by Al-$(i\text{-Bu})_3$ participates in chain scission or not.

The relations between $1/\overline{DP}$ and $[Al(i\text{-Bu})_3]$ and between $1/\overline{DP}$ and $[VCl_3 \cdot LiCl]$ are given in Figures 15 and 16. There are linear relations in both cases.

These facts can be reasonably explained by considering the following equations*:

$$\overline{DP} = \frac{k_p[PM^-][M]}{k_{trm}[PM^-][M] + k_t[PM^-] + k_{tal}[PM^-][Al] + k_{tv}[PM^-][V]} \qquad (19)$$

$$\frac{1}{\overline{DP}} = \frac{k_{trm}}{k_p} + \frac{k_t}{k_p}\,\frac{1}{[M]} + \frac{k_{tal}}{k_p}\,\frac{[Al]}{[M]} + \frac{k_{tv}}{k_p}\,\frac{[V]}{[M]} \qquad (20)$$

where, $[PM^-]$,* $[M]$, $[Al]$, and $[V]$ denote concentrations of active polymer chain, monomer, $Al(i\text{-Bu})_3$, and active catalyst, V,* respectively, and k_p is a rate constant for propagation; k_{trm}, k_{tal}, k_{tv} are chain transfer constants to monomer, $Al(i\text{-Bu})_3$, and to $VCl_3 \cdot LiCl(AlR_3)$, respectively, and k_t is a rate constant of monomolecular termination in a spontaneous disproportionation.[18,19] Equation (20) agrees with the fact that when $Al(i\text{-Bu})_3$ concentration is varied and other variables are fixed, $1/\overline{DP}$ is proportional to $[Al(i\text{-Bu})_3]$, and when VCl_3LiCl is varied and other variables are fixed, $1/\overline{DP}$ is proportional to $[VCl_3 \cdot LiCl]$.

If the deactivation reaction by two molecules of $Al(i\text{-Bu})_3$ participates in chain breaking reaction of the propagating chain, the relation of $1/\overline{DP}$ and $[Al]$ must not be a linear, but should give a parabola because in such a case an $[Al]^2$ term should be involved in eq. (20).

The above consideration led us to conclude that two molecules of Al-$(i\text{-Bu})_3$ deactivate the catalytic centers, but does not participate in termination reaction, although $Al(i\text{-Bu})_3$ acts as a chain-transfer agent.[18,19]

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* A coordinated anionic mechanism is proposed in the previous paper.[1]

It can be reasonably understood that the coordination of two molecules of Al(i-Bu)$_3$ to the active catalytic site in an equilibrium reaction will occupy all the coordination positions of vanadium, so that there is no room for coordination of monomer to the catalytic site. The kinetic consideration proposed here is the most probable explanation of this polymerization behavior.

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Received April 28, 1970
Revised April 28, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3329–3337 (1970)

Effect of Swelling on Radiation-Induced Grafting of Styrene to Polyethylene

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Synopsis

The radiation-induced grafting of low-density polyethylene in contact with styrene solution was studied. The effect of the degree of swelling of the polymer on the rate of grafting was investigated by diluting the styrene with methanol and with *n*-octane. For styrene–methanol solution, the rate of grafting was found to increase with degree of swelling, passing through a maximum when the sorbed solvent reaches 6.2 wt-% (70 vol-% methanol in the outside solution) and decreasing thereafter. The methanol fraction of the sorbed liquid is far too small to cause precipitation of the grafted chains and inhibition of their termination rate. The dilution of styrene by octane has no effect on the swelling of polyethylene, but it decreases the grafting rate over the entire concentration range. The results are explained in terms of the concentration of sorbed monomer and the viscosity of the amorphous region of the polyethylene swollen by nonpolar liquids. Supporting evidence for the mechanism is presented in the form of grafting kinetic data as a function of dose rate (2.8×10^2–9.5×10^4 rad/hr), and post-irradiation grafting measurements for polyethylene in methanol–styrene (70/30, v/v). The data indicate that at the maximum grafting rate an optimum is achieved between a high concentration of sorbed monomer and a low viscosity for the poorly swelled polymer matrix.

Introduction

It has been reported by Matsuda,[1] Chen,[2] and this laboratory[3] that the rate of radiation-induced grafting of styrene to polyethylene is markedly affected by the degree of crystallinity of the polymer. Less crystalline polyethylene which swells more in styrene gives a lower grafting rate than more crystalline polyethylene. Ethylene–propylene copolymer, which is completely amorphous and swells to a great extent, was found to exhibit a very low rate of grafting.[3] An explanation has been offered in terms of the viscosity of the intercrystalline zone in the polyolefin.[3] Since the viscosity of a well swelled amorphous polymer matrix is lower, the termination of growing radicals is not as hindered as in a poorly swelled highly crystal-

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line polymer. In the latter case, the termination rate is small because of the high viscosity of the matrix and the small mobility of the growing radicals; this leads to a larger grafting rate.

This paper is concerned with the study of the effect of swelling on the grafting where the swelling is controlled by dilution of the monomer by methanol, which does not swell the polymer. An explanation for the effect of the alcohol is presented that differs from those advanced in earlier works.[4–6]

Experimental

Strips of additive-free duPont low-density polyethylene film (8 × 60 × 0.063 mm) were used. Commercial grade styrene was first washed with an aqueous solution of sodium hydroxide and then with water, dried over calcium chloride and then over calcium hydride, and then vacuum-distilled over calcium hydride. Spectrograde methanol and Baker grade *n*-octane were used without further purification.

The strips of polyethylene film were immersed in styrene–methanol mixtures in a glass tube. Each mixture was degassed by four cycles of freezing and thawing under vacuum and then sealed off at 10^{-4} Torr. The sample was kept at room temperature overnight and irradiated in the University of Maryland ^{60}Co source. Each tube was opened within 5 min after its removal from the source. Post-grafting in this time interval is negligible. This was shown by investigations on the post-effect in which samples were stored at 27°C for various intervals following irradiation before opening them. The grafted polyethylene was removed from the styrene-methanol mixture and soaked in benzene for 3 days. It was then dried under vacuum. The weight difference before and after treatment was determined. Even though the weight gain determined under these conditions includes occluded homopolymer along with true graft,[7] it will be referred to as the amount of graft in this paper. Previous work indicates that the net weight gain or apparent graft is about twice the true or the covalent graft.[2,3]

Swelling measurements were performed in the following manner. Strips of polyethylene sheet, 0.85 mm thick, were immersed in various styrene–methanol mixtures and styrene–octane mixtures at 25°C. Enough solution was used so that the concentration changes in the liquid phase arising from sorption of solution by the polyethylene were negligible. After selected intervals the strips were removed from the solution and rapidly wiped dry. The samples were then hung vertically on a balance arm and the weight change was measured as a function of time. Extrapolation of these values to zero time gave the degree of swelling. The equilibrium swelling was measured after 45 hr soaking which is much greater than required for attainment of the equilibrium (see below, Fig. 2). The composition of the liquid absorbed in the polyethylene samples was determined in the following manner. Several strips of 0.85 mm thick polyethylene totaling 3–7 g in weight were equilibrated in various methanol–

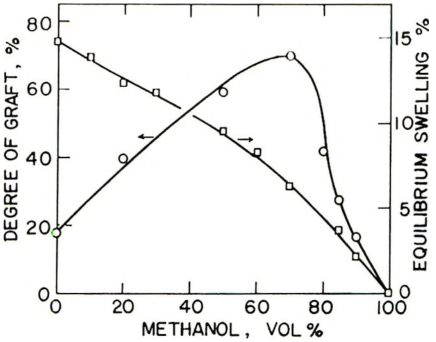

Fig. 1. Plots of (○) amount of graft for 3 hr and (□) equilibrium swelling of polyethylene vs. methanol concentration in outside solution. Grafting, 20°C, 9.5×10^4 rad/hr; swelling, 25°C.

styrene mixtures at 25°C for 45 hr. Soon after being wiped dry, the samples were placed in a tube fitted with a stopcock connected to a trap cooled by liquid nitrogen. The tube was then evacuated by a rotary pump for 18 hr. By this process the liquid absorbed in the polyethylene was transferred to the cold trap. The trapped liquid was examined for methanol content by an F & M 720 gas chromatograph fitted with an 8-ft column packed with 10% Carbowax 20 M on Chromosorb G(AW).

Results and Discussion

As shown in Table I and Figure 1, the grafting rate of styrene to polyethylene is increased as the styrene is diluted with methanol up to 70 vol-% methanol. Further dilution decreases the grafting rate. As reported here, the results are higher and the methanol effect is more pronounced than reported by Odian.[5] Some of this discrepancy arises from the more effective removal of oxygen by the freeze-thaw method than by the method of nitrogen bubbling used by Odian. Both results are, however, essentially consistent as far as the effect of methanol is concerned.

TABLE I
Effect of Methanol on the Grafting of Styrene to Polyethylene[a]

Methanol in outside solution, vol-%	Degree of graft for 3 hr, %
0	17.5
20	39.7
50	59.3
70	69.7
80	42.0
85	27.6
90	16.3

[a] Dose rate, 9.5×10^4 rad/hr; temperature, 20°C; irradiation time, 3 hr.

TABLE II
Swelling of Polyethylene by Methanol–Styrene Solution at 25°C

Methanol content of outside solution, vol-%	Swelling at equilibrium, wt-%	Methanol content of sorbed solution, vol-%	
		This work	Odian et al.[5]
0	14.8		
10	13.9		1.9
20	12.3	0.9	
30	11.8	0.9	1.6
50	9.5	1.9	2.2
60	8.2		
70	6.2	2.5	4.0
85	3.7	3.4	
90	2.2	3.8	7.5

The degree of swelling of 0.85 mm thick polyethylene strips in pure styrene and mixtures of styrene and methanol is shown in Figure 2. The time required to attain equilibrium increases with decreasing styrene fraction in the mixture. Equilibrium was attained in 10 hr in all cases. This indicates that in the case of 0.065 mm thick samples actually used for grafting, equilibrium was attained in a few minutes.

The equilibrium swelling of polyethylene, shown in Figure 1 and Table II, decreases with increasing methanol fraction. No swelling is observed in pure methanol. The composition of sorbed solution in the polymer as determined by gas chromatography is shown in Table II for various compositions of the outside solution. The methanol fraction of the sorbed liquid increases with the methanol fraction of the outside solution; but the methanol fraction in the film is very small regardless of the composition of the outside solution. The swelling is due almost entirely to styrene. The same conclusion can be reached from similar results reported by Odian and included in Table II. His procedure involved polymerization of the sorbed material at Dry Ice temperature followed by a weighing of the nonvolatile fraction.

In Figure 3 the rate of grafting is plotted against the degree of swelling of polyethylene. The rate of grafting increases with degree of swelling, passes through a maximum at 6.2 wt-%, and decreases continuously thereafter.

The accelerating effect on the grafting rate has been explained in terms of the following causes: (1) a radiation protection effect exerted by the styrene which decreases the formation of grafted chains; (2) a precipitation of the growing grafted chains by the alcohol. Dobo[6] proposed the first mechanism for the accelerating effect of 2-propanol on styrene grafting. According to him, acceleration by an alcohol precipitation effect on the growing chain is not important since the termination step is already severely hindered in polyethylene swelled with pure styrene. We find that this explanation cannot account for the observation of Odian[5] that the grafting

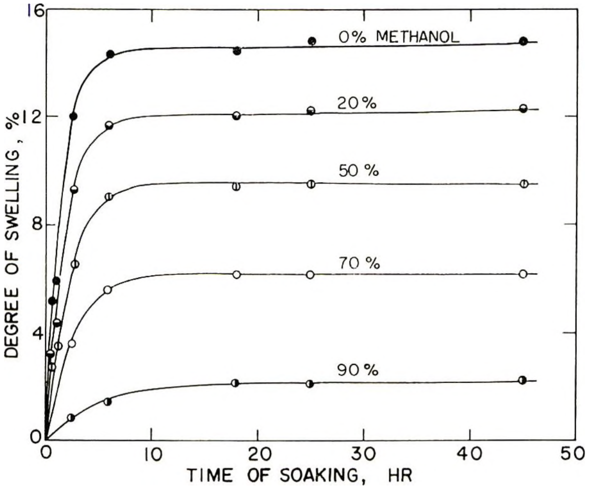

Fig. 2. Effect of methanol on swelling of polyethylene in styrene and styrene–methanol mixtures at 25°C.

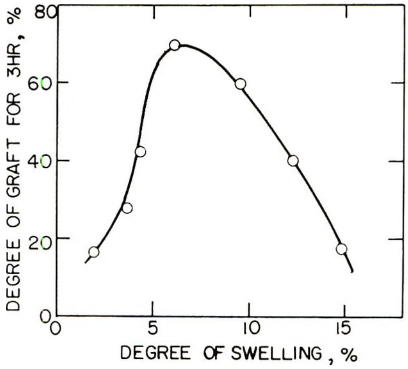

Fig. 3. Effect of swelling of polyethylene on rate of grafting at 20°C, 9.5 × 10^4 rad/hr.

rate decreases monotonically with the concentration of *n*-octane in a styrene–octane mixture. Dobo's protection mechanism implies that the accelerating effects of the alcohol and the alkane are similar.

Odian[5] offers the second explanation. He suggests that the polystyrene radical chains precipitate and curl up in methanol–styrene solutions so that the termination is sharply reduced. This effect has been observed in the homopolymerization of styrene in methanol–styrene solutions.[8,9] At a methanol content of 87 vol-%, a very sharp increase in the homopolymerization rate occurs. We suggest, however, that the methanol concentration in polyethylene, which is less than 5% of the sorbed solvent, is far too small to cause the precipitation effects that supposedly occur.

We propose a mechanism that is based on two factors: the concentration of the monomer in the polyethylene and the viscosity of the amorphous

TABLE III

Swelling of Polyethylene by *n*-Octane–Styrene Solution at 25°C

n-Octane content of outside solution, vol-%	Swelling at equilibrium, wt-%
0	14.8
20	16.5
50	16.9
80	14.7
100	12.7

region of the polyethylene swollen by the monomer. By this mechanism, the methanol, being almost completely insoluble in polyethylene, has no direct effect on its viscosity; its sole function is to reduce the concentration of the styrene in the polyethylene. It produces an indirect viscosity effect, since polyethylene swelled with a lower concentration of monomer is a medium of higher viscosity.[3]

Consider the grafting reaction in terms of monomer concentration and its attendant viscosity effects. At low monomer concentration, the rates of propagation and chain initiation increase with increasing monomer concentration. The termination rate is small because the viscosity of the reaction medium is extremely high and the mobility of the polymer radical is very small. High monomer concentrations tend to increase the rate of the propagation reaction, but this effect is overcome by the greatly increased termination rate of the more mobile chains in the swollen matrix. Thus there is a monomer concentration below the maximum value at which the grafting rate is a maximum.

Our data on the gas phase grafting of styrene to polyethylene are in accord with this mechanism.[10] Variation in the preirradiation exposure of the film to the gaseous monomer is another means of modifying monomer concentration in the film. Results so obtained show that the grafting rate goes through a maximum at about the same monomer concentration in the film as is produced by equilibration with a 70 vol-% solution of methanol in styrene.

Another interesting implication of this mechanism concerns the effect of *n*-octane. Octane as a diluent decreases the monomer concentration in the film but, as shown in Table III, it also swells polyethylene about as effectively as styrene itself. Since the viscosity of a polyethylene matrix swelled by an octane–styrene solution is essentially the same, the only significant effect of octane dilution should be reduction of the grafting rate caused by a lower propagation rate. The results obtained by Odian[5] are consistent with this picture.

The grafting rate data obtained in this work can be interpreted in terms of this mechanism. Figures 4 and 5 show the per cent weight gain as a function of time in 70 vol-% methanol where the maximum rate is obtained. Note that the weight increases with the 1.43 power of time (Fig. 5). If the radical chains do not terminate during the experiment, a square dependence

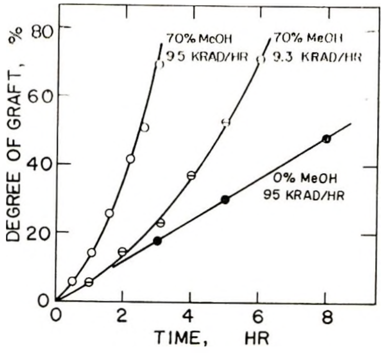

Fig. 4. Degree of grafting vs. irradiation time at 20°C: (○) 30% styrene–70% methanol–PE system, 9.5×10^4 rad/hr; (⊖) 30% styrene–70% methanol–PE system, 9.3×10^3 rad/hr; (●) 100% styrene–PE system, 9.5×10^3 rad/hr.

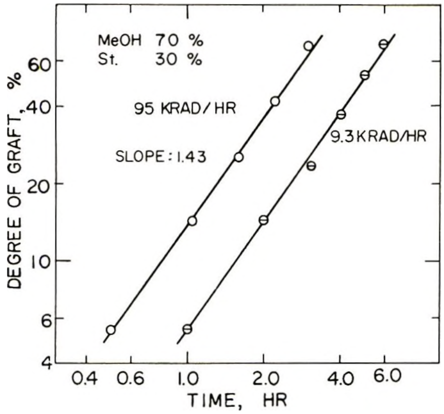

Fig. 5. Time exponents of degree of grafting.

on time is expected, and the rate constant is proportional to the weight gain divided by the square of time. If steady-state radical concentration is achieved very rapidly, a first-order time dependence is expected, and the rate constant is proportional to the weight gain divided by time. These data indicate that both mechanisms are in simultaneous operation, and that a specific rate of grafting can be determined by dividing per cent graft by the 1.43 power of irradiation time. Table IV and curve *A* in Figure 6 show the specific rate of grafting for the methanol-styrene system as a function of dose rate. At low dose rates, the specific rate varies with the 0.9 power; at the higher dose rates the dependence is 0.4. Even at the highest dose rate, a superlinear increase in weight gain with time is observed. The evidence is consistent with the view that the grafted radical chains are long-lived. The decrease of the dose rate exponent at higher dose rates is ascribed to the increase of primary radical disappearance prior to initiation of the grafting reaction.[3]

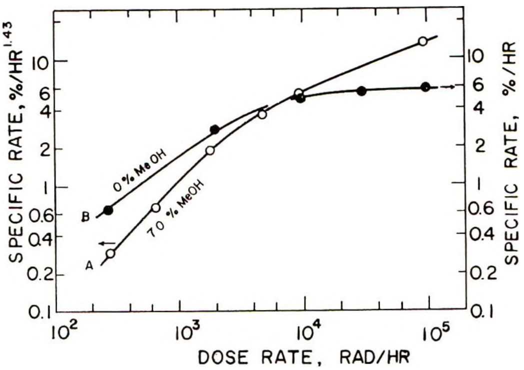

Fig. 6. Specific rate of grafting vs. dose rate at 20°C: (*A*) 30% styrene–70% methanol–PE system; (*B*) 100% styrene–PE system.

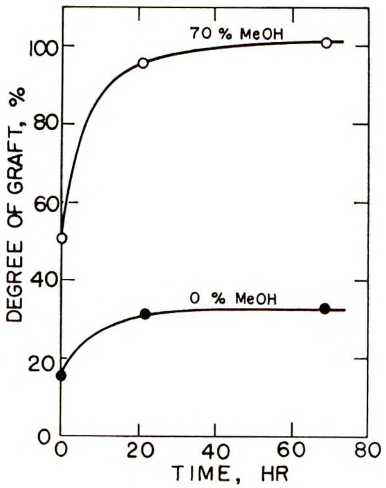

Fig. 7. After-effect of styrene graft in styrene–methanol–PE system and styrene–PE system. Irradiation dose: 9.5×10^4 rad/hr for 2.5 hr; irradiation at 20°C, post-grafting at 27°C.

Curve *B* in Figure 6 gives the rate of weight gain versus dose rate for the styrene–polyethylene system obtained in this laboratory.[3] Here the weight gain is proportional to time over the entire dose rate range, indicating rapid achievement of the stationary state. The half-order dependence on low dose rates is attributed to conventional bimolecular chain recombination kinetics. The dependence on dose rate approaches zero at the higher dose rates where primary radical recombination dominates the initiation step.

The post-irradiation grafting effect was also investigated to confirm the existence of long-lived radicals. It can be seen in Figure 7 that the after-effect is much greater in the styrene–methanol–PE system than in the styrene–PE system treated with the same dose. This indicates that a

TABLE IV
Effect of Dose Rate on the Grafting of Styrene to Polyethylene in the Presence of Methanol[a]

Dose rate, krad/hr	Irradiation time, hr	Degree of graft, %	Specific rate of grafting, $\%/\mathrm{hr}^{1.43}$
0.28	24.8	22.5	0.29
0.65	19.2	44.2	0.15
1.8	8.6	41.0	1.9
4.8	4.1	26.2	3.6
9.3	2.0	14.4	6.0
95.0	2.2	41.7	13.5

[a] Methanol concentration, 70 vol-%; temperature, 20°C.

larger population of radicals accumulates in the styrene–methanol–PE system because of lower termination rate in highly viscous polyethylene–styrene matrix.

We have not chosen to derive rate constants for these systems since the data are complicated by homopolymer occlusion. Nevertheless, the results offer adequate support to the qualitative features of the mechanism we propose.

We are pleased to acknowledge useful discussions with Professor A. Charlesby and Mr. I. Block, as well as the generous support of the Division of Research, U. S. Atomic Energy Commission.

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Received March 19, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3339-3348 (1970)

Electroinitiated Cationic Polymerization of Styrene

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Synopsis

A constant controlled current was passed through a solution of styrene in methylene chloride containing a tetraalkylammonium salt as supporting electrolyte. Reproducible rates of polymerization were initiated by the electrochemical techniques employed and the kinetics of the reaction were investigated. Sigmoidal curves of conversion versus time were observed. A kinetic relationship of the form $\ln([M_0]/[M]) = {}^1/_2 Kt^2$ was derived on the basis of simple assumptions regarding the mechanism and fitted the data accurately. The rate constants obtained were compared to others reported, and the influences of ion association on the values of the rate constants obtained are discussed. The reactions were decreased in rate by a reversal of polarity of the electrodes. However, the stoichiometry of the production of active centers and of their destruction was not ideal, in that each electron did not result in the initiation of a polymer chain.

INTRODUCTION

Breitenbach in 1962 reported the first definitive evidence of an electrochemically initiated polymerization proceeding by a cationic mechanism.[1] In a copolymerization study of a system containing acrylonitrile and styrene, almost pure polystyrene was obtained in the anode compartment of a divided cell. Breitenbach also found that polystyrene was formed at the anode on electrolysis of a nitrobenzene solution of styrene containing $(C_4H_9)_4NBF_4$ as supporting electrolyte.

He also reported that silver perchlorate was sufficiently soluble in pure monomers to allow the passage of current without the presence of solvent. Polymers of styrene, isobutyl vinyl ether, and vinylcarbazole were formed readily by this technique which was characterized by two important features: (1) a very high current efficiency and (2) an "after effect" in which the solution maintained its reactivity after the current was switched off. Except for recent electrochemical studies on the polymerization of tetrahydrofuran,[2-4] no other reports of cationic polymerization have appeared in the literature.

Breitenbach's pioneering studies were limited to a "broad brush" approach to the subject. No kinetic curves were obtained and there was no investigation of the degree of control over the rate of reaction or of the

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kinetics of the reaction which could be achieved by varying the current. Furthermore, it is known that the silver perchlorate system can initiate polymerization of vinyl monomers in the absence of any current passage[5] if the system is not rigorously dry. Although work by Burton and Praill[6] demonstrated that pure extremely dry silver perchlorate would not function as a catalyst, there is insufficient experimental detail in Breitenbach's work to show that the salt used in his electrolytic studies was sufficiently dry.

A similar type of criticism could apply to the tetraethylammonium perchlorate and tetrafluoroborate salts. However, even in the absence of a blank (that is the absence of polymer formed without current), the passage of current could have served to remove an impurity in the solution which prevented the initiation of polymerization by the salt itself.

These and other considerations led us to attempt a detailed kinetic study of an electrochemically initiated polymerization proceeding by a cationic mechanism.

EXPERIMENTAL

It is well known that it is difficult to obtain reproducible kinetic results in cationic polymerizations due to the very great sensitivity of cationic reactions to trace impurities. Our initial attempts were thwarted by irreproducibility, which was later traced to impurities in the solvent. However, rigorous attention to purification techniques and the use of vacuum line transfers and thorough de-gassing and drying led to highly reproducible results in the systems reported upon in this paper.

The reaction cell is shown in Figure 1. It is similar to types employed by us previously[7,8] but contains some modifications which were designed for this work. The platinum electrodes, a and b, were attached to demountable conical joints to enable thorough and easy cleaning. The application of nitrogen pressure through stopcock 1 resulted in a small sample of anolyte solution being forced into the capillary above the stopcock. Therefore, a gas chromatographic sample could be removed from the capillary without the syringe needle touching the reaction solution. For each sample taken in this manner, it was necessary to flush all the liquid from the previous sample remaining in the capillary tube and stopcock. For this reason, a total of 0.5 ml was removed for each sample taken as described.

In a typical experiment, 157 ml of solution was placed into the anode compartment and 41 ml into the cathode compartment. The anode and cathode consisted of circular sheets of platinum, 1 cm in diameter and 6.5 cm apart. A 3-in. diameter sintered glass disk of fine porosity was used as a separating membrane.

Samples were analyzed for monomer content by gas chromatography. For the analysis of styrene reaction solutions, a column of $^1/_4$ in. copper tubing, 4 ft long, filled with 25% Apiezon L on Chromosorb G DMCS was used with a flow rate of 85 ml He/min and a column temperature of 88°C.

A solvent peak was used as an internal standard and an overall reproducibility of about ±1.0% was obtained.

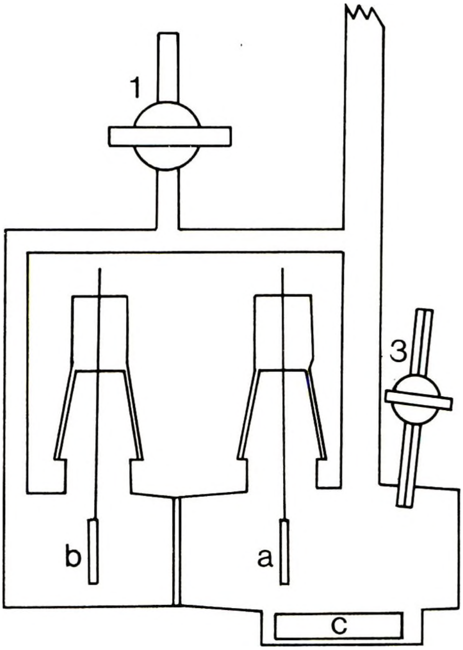


Fig. 1. Electrolysis cell.

In the experiments conducted in this investigation, a constant current was employed. This was obtained from a commercial Wenking potentiostat employed in the constant current mode.

Materials

Methylene chloride (Fisher Certified) was washed with concentrated sulfuric acid, five or six times, or until the acid layer remained colorless. This was followed by six or seven washings with distilled water and then drying over calcium chloride. The liquid was then stirred over calcium hydride for several days and fractionally distilled, discarding the initial and final 20% by volume. The resulting liquid was passed through a column of activated alumina onto fresh calcium hydride and alumina, then degassed and stored on a vacuum line with constant stirring by a Teflon-coated magnetic stirring bar. Immediately before use, the methylene chloride was distilled under high vacuum into a measured cylinder from whence a measured quantity was distilled into the reaction vessel.

Salts

$(C_4H_9)_4NBF_4$ was prepared by adding a filtered aqueous solution of NH_4BF_4 (Alpha Inorganics) dropwise to a solution of $(C_4H_9)_4NBr$ (Eastman) in a large volume of water. The required salt precipitated and was filtered on a Büchner funnel. It was then dissolved in a small quantity of acetone and filtered dropwise into a fairly large quantity of water to pro-

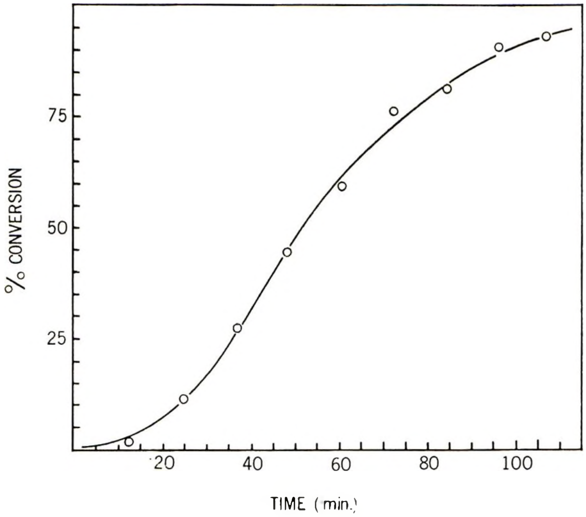


Fig. 2. Polymerization of styrene in methylene chloride at 25°C. Electrolyte, 15.0 meq/l. tetrabutylammonium perchlorate; magnitude of current, 0.987 mA; initial monomer concentration, 0.739 mole/l.

duce a precipitate. The latter step was repeated once, and as a result a considerable amount of salt was lost as the tetrabutylammonium tetrafluoroborate is not completely insoluble in water. However, this step served to eliminate tetrabutylammonium bromide and/or ammonium tetrafluoroborate (which are both water-soluble) from the required salt. The remaining salt was reprecipitated several times from freshly distilled ethyl acetate.

RESULTS

When a current was passed through a solution of the perchlorate salt in styrene in methylene chloride, polymer was formed only in the anode compartment. A green color formed across the inner face of the anode during the passage of current. However, no insoluble polymeric film formed on the anode. Instead, a very thin brown coating was formed which did not resemble a film. The reaction appeared to begin as soon as the current was passed, no significant induction current being involved.

Reaction curves at three different currents and three different monomer concentrations at 25°C are shown in Figures 2 and 3. Sigmoidal curves were invariably found for these reactions. Such behavior is characteristic of polymerizations in which steady-state concentrations of active polymerization centers were not attained because the production of active centers occurred throughout the reaction, while termination was either absent or much slower than initiation. By using the above observations and by analogy with conventional polymerization of styrene by perchloric acid as described by Pepper,[9] the derivation of the kinetic relation to fit this system

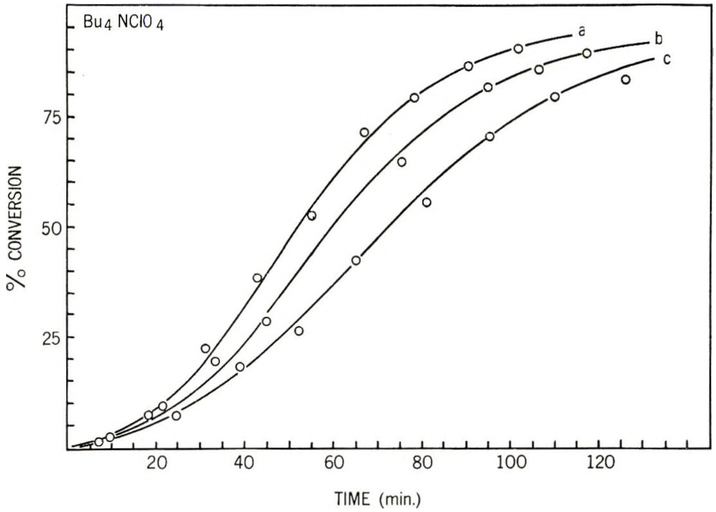


Fig. 3. Polymerization of styrene in methylene chloride at 25°C. Electrolyte, 15.0 meq/l. tetrabutylammonium perchlorate, magnitude of current and initial monomer concentrations: (*a*) 1.454 mA, $[M]_0 = 0.388$ mole/l.; (*b*) 0.987 mA, $[M]_0 = 0.449$ mole/l.; (*c*) 0.658 mA, $[M]_0 = 0.449$ mole/l.

was carried out under the following assumptions: (a) at any time t the reaction rate was directly proportional to the first power of the initiator and monomer concentrations existing at that time; (b) the total number of active centers present at any time t was directly proportional to the total amount of current passed to that time; (c) no termination occurred in the polymerization; (d) there was no induction period.

Algebraically, this is stated as follows:

$$-(dM/dt) = k_p[C^*][M] \tag{1}$$

$$[C^*] = \frac{1}{96{,}493}\int_0^t i\,dt = it/96{,}493 \tag{2}$$

where $[C^*]$ is in moles if i is in amperes.

$$\text{Then } -\left(\frac{dM}{dt}\right) = k_p\,[M][C^*] = \frac{k_p i}{96{,}493}\,[M]t \tag{3}$$

Writing

$$K = \frac{k_p i}{96{,}493} \tag{4}$$

$$-\int_{[M]_0}^{[M]} d[M]/[M] = K\int_0^t t\,dt \tag{5}$$

$$\ln\,[M]_0/[M] = {}^1/_2\,Kt^2 \tag{6}$$

Thus a plot of $\ln\,([M]_0/[M])$ against t^2 should give a straight line on a slope equal to $^1/_2\,K$ from which the rate constant k_p could be obtained.

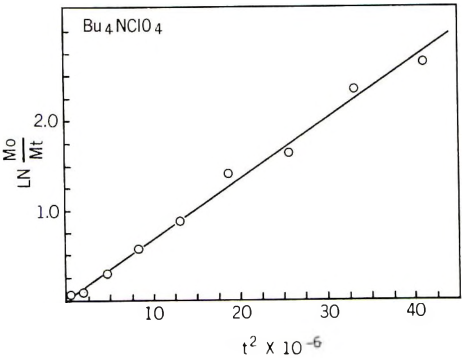


Fig. 4. Test of eq. 6 for data of Fig. 2.

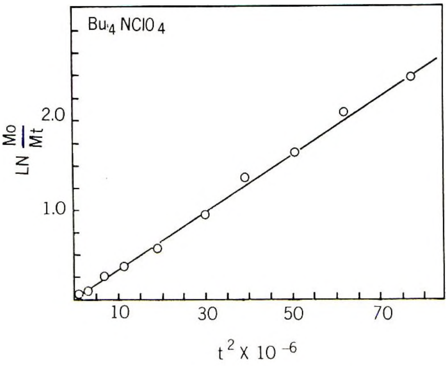


Fig. 5. Test of eq. 6 for data of Fig. 3.

Straight lines were obtained at all currents and for all monomer concentrations used. The plots for reactions at 25°C are shown in Figures 4 and 5. The slopes for the curves were found by linear regressional analysis and the corresponding rate constants were calculated. The results are summarized in Table I. Similar experiments were performed at 0 and 40°C, and the corresponding plots were also linear. The variation of the rate constant with temperature led to an activation energy derived from the linear Arrhenius plot shown in Figure 6.

TABLE I

Rate Constants for the Polymerization of Styrene with Bu_4NClO_4

Approximate potential across electrodes, V	Current, mA	Temperature, °C	Monomer concentration mole/l.	Slope × 10^8	constant, l./mole-sec
13.8	0.987	25	0.449	4.91	1.51
15.2	1.454	24	0.388	7.81	1.50
11.1	0.658	25	0.449	3.60	1.65
15.0	0.987	25	0.739	5.13	1.57
24.0	1.974	0	0.588	3.24	0.50
10.2	0.658	40	0.494	6.70	3.05

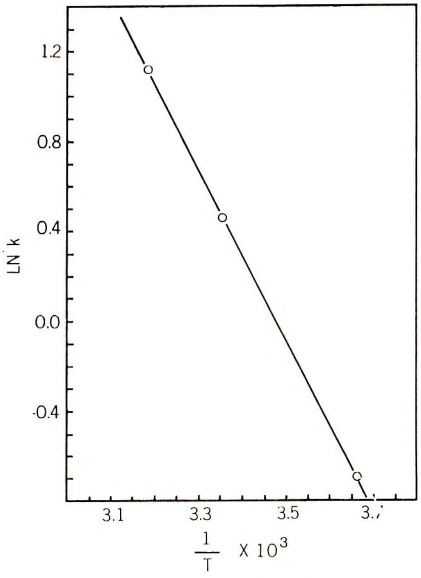


Fig. 6. Variation of rate constant with temperature.

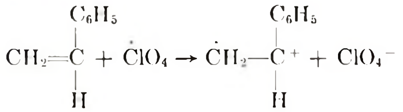
Some results were obtained using other supporting electrolytes. The data with tetrabutylammonium hexafluorophosphate showed the same sigmoidal character as the results already described. However, the log plot extrapolated to an intercept other than zero, and the system was not investigated in detail. The polymer isolated from this particular experiment had an intrinsic viscosity of 0.081 dl/g in benzene at 25°C, corresponding to a number-average molecular weight of 2700.

Results with tetrabutylammonium tetrafluoroborate were also similar to those described here.

Some experiments were conducted with reversal of the current. In all instances a reduction in the rate of reaction was obtained when the current was reversed. In general, the efficiency of the terminating reaction induced by the reversal of the current was greater than that of the initiating reaction, and a smaller number of coulombs was required to stop the reaction than required to bring it to a given rate. Some more detailed studies of pulsed reactions will be described separately.

DISCUSSION

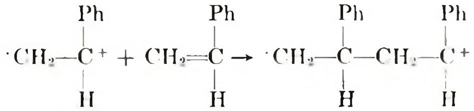
The electroinitiated character of this polymerization is beyond question. First, there is the absence of a significant amount of polymer in blank experiments which demonstrated that polymer formation did not occur before current had passed. Secondly, there is the precise control of the current over the course of polymerization. This showed that the reaction did not occur from initiation by some component in the solution after any impurities had been removed by the passage of current. Although the electric field was applied across the solution between the electrodes during their entire polymerization process, an accelerating effect of the electric field such as that claimed by Ise[10,11] could not have accounted for the increase in the rate of reaction. It is, in fact, unlikely that the electric field could have affected the rate of propagation at all, as the proportion of the total anolyte volumne between the electrodes is very small and the maximum electric field applied to any one of these experiments was 4 V/cm. This is much weaker than the field employed by Tanaka et al.[12] The mechanism of the primary electrode reaction at the anode was not determined clearly from the experimental techniques employed in our work. We consider it likely that it involves the oxidation of a perchlorate ion to a perchlorate radical or, alternatively, the direct oxidation of styrene monomer to a propagating radical cation. If it is the former, then an electrolytically formed perchlorate radical could either abstract a hydrogen atom to form perchloric acid as initiator or oxidize the monomer to form a radical cation.



$$\mathrm{CH_2{=}\underset{H}{\overset{C_6H_5}{C}} + \dot{C}lO_4 \rightarrow \dot{C}H_2{-}\underset{H}{\overset{C_6H_5}{C}}{}^{+} + ClO_4^{-}} \qquad (7)$$

The possibility of the formation of radical cations in the electrolysis was again supported by the observation of a green color similar to that of conventionally produced radical cations. This color was observed across the inner face of the anode. Furthermore, the absence of an insoluble anodic coating may be considered as an indication that crosslinking or degrading hydrogen atom abstractions did not occur in the initiation process.

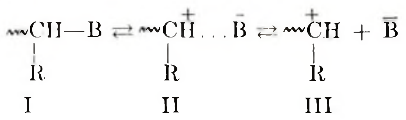
If radical cations were formed at the anodes, they may have dimerized to form difunctional propagating species or they may have added monomer to form separated free-radical and cationic or styrene perchlorate ester ends.



$$\mathrm{\cdot CH_2{-}\underset{H}{\overset{Ph}{C}}{}^{+} + CH_2{=}\underset{H}{\overset{Ph}{C}} \rightarrow \cdot CH_2{-}\underset{H}{\overset{Ph}{C}}{-}CH_2{-}\underset{H}{\overset{Ph}{C}}{}^{+}} \qquad (8)$$

Unlike isobutyl vinyl ether, styrene can also polymerize by free-radical mechanisms. However, the evidence on electrical efficiency and the kinetic analysis all indicate that the free-radical contribution would be minimal or nonexistent.

The net result of the various reaction mechanism considered here would be the formation of polystyryl carbonium ions with perchlorate counter ions or propagating perchlorate esters of polystyryl carbonium ions. In view of the work reported by Bywater and Worsfold,[13] it is unlikely that a valid mechanism can be proposed which is based upon the existence of a long lived carbonium ion concentration in the systems under study. Instead, one must consider a very close association of the anion with the growing carbonium ion, yielding a very low instantaneous concentration of the free cabonium ions.[14] The association in our system must be considered to be higher, because of the high salt concentration, than that found by Gandini and Plesch.[15,16] Their rate constant at 0°C was 2.65 l./mole-sec at 0°C and an activation energy of 11.6 ± 0.2 kcal/mole was found. However, Higashimura has commented on this recently and noted that even in the same polymerizing system the derived values of k_p may show an apparent variation which is very large.[17] This can be understood if one assumes that the various active species proposed may be in equilibrium with one another, as in eq. (9).



$$\underset{\mathrm{I}}{\underset{\mathrm{R}}{\sim\mathrm{CH}}}-\mathrm{B} \rightleftarrows \underset{\mathrm{II}}{\underset{\mathrm{R}}{\sim\overset{+}{\mathrm{C}}\mathrm{H}}}\ldots\bar{\mathrm{B}} \rightleftarrows \underset{\mathrm{III}}{\underset{\mathrm{R}}{\sim\overset{+}{\mathrm{C}}\mathrm{H}}} + \bar{\mathrm{B}} \qquad (9)$$

In case I, B is bound by a covalent bond, whereas in III it is a free ion. Higashimura succinctly points out that the case where only I exists and the concentration of II and III are zero corresponds to the pseudocationic theory. Bywater's treatment is considered as the free-ion case III.[18] An intermediate case, probably applicable to our results, is to consider that the carbonium ion concentration is influenced by equilibria between the last two structures.

The high salt concentrations, of necessity employed in the electrolytic polymerizations, would favor the shift of the equilibrium to the left in eq. (9).

The kinetic evidence and the supporting subsidiary observations are in keeping with a propagation step based on growth of radical cations. This, together with the dominant role of chain transfer reactions at temperatures above 0°C, presents a reasonable model for the data. Direct confirmatory physical measurements of radical cation or carbonium ion concentrations were not obtained.

Our data do not permit us to obtain a quantitative assessment of the position of the equilibria of the various species, nor does the analysis permit an estimation of the change in activation energy which would be assoicated with any particular equilibrium distribution. However, such a quantitative knowledge of the fine structure of the reaction has not been forthcoming in cationic polymerizations carried through without electrochemical initiation.

The application of techniques of cyclic voltammetry was not fruitful in this work, as quite featureless scans were obtained with the systems employed. This is one of the main reasons why a detailed interpretation of the primary electrode reactions is not possible from the work described here. Nevertheless, the simple kinetics observed, the reproducibility obtained, and the degree of control over the course of reaction which has been demonstrated in the polymerization of styrene by cationic electrochemical techniques are noteworthy.

The authors are indebted to the National Research Council for grant-in-aid in support of this work.

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Received April 14, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8, 3349-3357 (1970)

Mechanism of Charge-Transfer Polymerization. II. Propagation Mechanism of the Polymerization of *N*-Vinylcarbazole with Organic Electron Acceptors

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Synopsis

Copolymerizations of *N*-vinylcarbazole with both isobutyl vinyl ether and *N*-vinylpyrrolidone initiated by some organic electron acceptors have been investigated for the purpose of elucidating the propagation mechanism in the charge-transfer polymerization. Copolymerizations of the same system catalyzed by authentic cationic catalysts have also been made for comparison. The results indicate that the propagation mechanism of the charge-transfer polymerization studied is cationic.

INTRODUCTION

Polymerization of monomers having electron-donating properties by electron-accepting compounds, the so-called charge-transfer polymerization, has been the subject of current interest and has been investigated rather extensively, especially with regard to *N*-vinylcarbazole.[1] However, the polymerization mechanism—initiation, propagation, as well as termination mechanism—is still controversial, and definite conclusions have not yet been drawn.

Various organic electron acceptors were reported by Scott et al.[2] and Ellinger[3] to polymerize *N*-vinylcarbazole(VCZ). Concerning the propagation mechanism, recent studies on several systems, e.g., VCZ–*p*-chloranil (p-CA),[4] VCZ–tetracyanoethylene (TCNE),[5] VCZ–maleic anhydride (MAnh),[6] and VCZ–tetranitromethane,[7] have concluded that the propagation is cationic in all the above-mentioned cases, the propagating chain end being a carbonium cation. The method of investigating the effect of additives which are known to retard or inhibit the radical or cationic propagation and/or the copolymerization method, in which the compositions of copolymers are compared among different polymerization methods, are used to elucidate the nature of the active species of chain propagation. Kinetic examination is sometimes also used.

In charge-transfer polymerizations, however, the study of the effect of additives on the polymerization sometimes does not lead to conclusive criteria, because in some cases undesired chemical side reactions occur between the added compound, especially cation inhibitors, and the electron-accepting initiator of the polymerization. Therefore, the copolymerization experiment, although classical, seems to be preferable, especially in studying the charge-transfer polymerization.

With this method, Pepper and his co-workers[8] have recently investigated the VCZ–TCNE system with *p*-methoxy-styrene as a comonomer in ethylene dichloride, confirming cationic propagation. The system VCZ–*p*-CA has also been examined by Hatano et al. with 3,6-dibromo-*N*-vinylcarbazole as a comonomer.[9] We also studied the copolymerization of this system with isobutyl vinyl ether (IBVE) as a comonomer.[10]

With the latter system, however, we recently found, in the course of our study of the polymerization of VCZ with *p*-CA and a series of related quinoid compounds in a nonpolar solvent, that the hitherto reported rapid charge-transfer polymerization of VCZ ostensibly initiated by *p*-CA was actually mainly a conventional cationic one initiated by a trace of 3,5,6-trichloro-2-hydroxy-*p*-benzoquinone which was retained tenaciously in *p*-CA purified by repeated recrystallizations or simple sublimations.[11,12] We have stressed in the preceding paper[13] that the reagent must be purified with utmost care, if true charge-transfer polymerization is to be investigated. When *p*-CA was specially purified with a chromatographic technique, only very slow polymerization of VCZ was observed; we concluded that this slow polymerization was the "true" charge-transfer polymerization which must be reinvestigated anew in detail.

In the present study we attempted to clarify the nature of the growing end in the propagation of the "true" charge-transfer polymerization of VCZ initiated by strictly purified *p*-CA and *p*-bromanil(*p*-BA) by examining the copolymerization with isobutyl vinyl ether (IBVE) and *N*-vinylpyrrolidone (VPD) both in benzene and in nitrobenzene.

In this study we have also carried out the copolymerization of VCZ with IBVE initiated by MAnh in nitrobenzene. Although this system* has already been reported to be a cationic propagation in various solvents from the effect of additives on the rate of polymerization, no investigation with the use of the copolymerization method has been made. In addition, the copolymerization of the VCZ–TCNE system with IBVE as a comonomer has also been examined here in nitrobenzene. At the same time, cationic copolymerizations between VCZ and IBVE or VPD have been examined both in benzene and in nitrobenzene solutions with the use of authentic cationic catalysts such as titanium tetrachloride ($TiCl_4$), stannic tetrachloride ($SnCl_4$), or chloranilic acid (CAA) in order to compare these typical cationic copolymerizations with the charge-transfer-initiated copolymerizations.

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* In this case also, attention must be paid to the purity of MAnh. We have observed that the polymerization rate of VCZ differs appreciably when MAnh was purified only by recrystallizations and purified by recrystallizations followed by vacuum sublimation.

EXPERIMENTAL

Reagents

N-Vinylcarbazole (K & K Lab., Inc., U.S.A.) was purified as reported in the preceding paper.[13]

Isobutyl vinyl ether (IBVE) was washed by shaking with aqueous potassium hydroxide several times, allowed to stand overnight over solid potassium hydroxide, refluxed over sodium metal for 8 hr, and distilled in a stream of dry nitrogen (bp 83.0°C).

N-Vinylpyrrolidone (VPD) was purified by vacuum distillation.

Purifications of *p*-chloranil (p-CA) and *p*-bromanil (p-BA) were performed as reported in the previous communications.[11,12] Commercial, extra-pure material was recrystallized twice from purified benzene followed by two fractional sublimations *in vacuo*. Materials purified through calcium carbonate chromatography, which were absolutely free from any acidic impurity, were also used. Provided that the fractional sublimation was performed very carefully, almost no difference in purity exists between these two kinds of p-CA.

Tetracyanoethylene (TCNE) was synthesized from malononitrile, and the crude product was recrystallized from chlorobenzene, sublimed twice, again recrystallized and sublimated.

Maleic anhydride (MAnh) was prepared from commercial material by recrystallizations from purified benzene and subsequent sublimations. As maleic anhydride is very sensitive to moisture, sublimations and rapid handling in air are very important to obtain MAnh free from maleic acid.

Titanium tetrachloride ($TiCl_4$) was purified by refluxing commercial material with Cu powder for 5 hr followed by distillation (bp 136°C). Stannic tetrachloride ($SnCl_4$) was purified by distillation in an atmosphere of dry nitrogen (bp 114°C).

Chloranilic acid (CAA), 2,5-dihydroxy-3,6-dichloro-*p*-benzoquinone, was prepared from commercial material by sublimation *in vacuo*.

Nitrobenzene was purified by shaking with dilute sodium hydroxide solution several times, vacuum-distilled through a column of synthetic zeolite A-4 (Wako Pure Chemical Ind. Ltd., Japan) in powder form (<200 mesh) or granules (<50 mesh) to remove water and distilled immediately before use. Benzene was purified as usual.

Polymerization Procedure

Polymerization was carried out in a glass tube connected to a vacuum line. The catalyst and IBVE or VPD were mixed with the solvent in this tube, and the solution was degassed twice by freezing and thawing at 10^{-4} mm Hg. Nitrogen gas, dried with sulfuric acid and passed through a Nujol suspension of triethylaluminum, was introduced, and under the nitrogen stream a solution of VCZ was introduced, degassed again by freezing and thawing, and the tube was sealed.

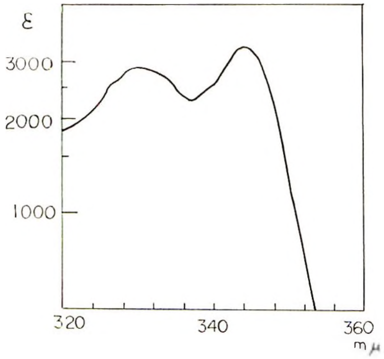

Fig. 1. Absorption spectrum of polyvinylcarbazole (PVCZ) in benzene.

After an appropriate time, the reaction mixture was poured into an excess of methanol; the precipitated polymer was filtered, dissolved in benzene, reprecipitated with methanol, dried, and weighed.

Analyses

The content of the carbazyl groups in the copolymers of VCZ and IBVE was determined from Kjeldahl nitrogen analysis. In this method, the copolymer (100 mg) was decomposed with sulfuric acid (20 ml) containing potassium persulfate and copper sulfate (2–3 spoons of each on a small spatula) for about 4–5 hr till the color of the solution turned to faint blue. Determination of NH_3 in this solution was performed as usual.

In determining the content of the carbazyl groups, a spectroscopic method was used for copolymers of VCZ and IBVE or VPD. As polyvinylcarbazole (PVCZ) in benzene has an absorption peak at 344 mμ (Fig. 1) and neither poly(isobutyl vinyl ether) nor polyvinylpyrrolidone has absorption at this region, the content of carbazyl groups was determined by using the molar extinction coefficient of 3.326×10^3 at this wavelength. Values obtained by this method agreed well with those of the Kjeldahl method.

The absence of homopolymers of IBVE in copolymers of IBVE and VCZ was confirmed by extraction of the copolymer with boiling *n*-hexane, the amount of the extract being almost none.

RESULTS AND DISCUSSION

Copolymerizations of VCZ and IBVE

In a preliminary experiment, it was observed that the copolymer yield was very low in a nonpolar solvent such as benzene, but that in nitrobenzene the copolymer yield was high enough to permit detailed examination of the copolymers for different monomer feed ratios. Accordingly, nitrobenzene was mainly used in the present investigation.

The p-CA used in the present study appears to be absolutely free from any acidic impurities, and the results obtained here refer to true charge-

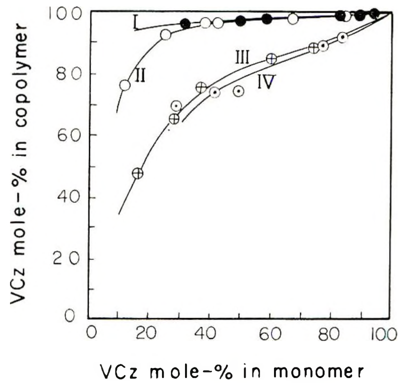

Fig. 2. Copolymer composition vs. monomer feed ratio for copolymerizations of *N*-vinylcarbazole (VCZ) and isobutyl vinyl ether (IBVE) in benzene: (I) p-CA, [C] = 1.34×10^{-2} mole/l., 80° C; (II) CAA, [C] = 5.0×10^{-3} mole/l., 80°C; (III) $SnCl_4$, [C] = 1.55×10^{-3} mole/l., 30°C; (IV) $TiCl_4$, [C] = 4.8×10^{-3} mole/l., 30°C. Total monomer concentration [M] = 0.5 mole/l.

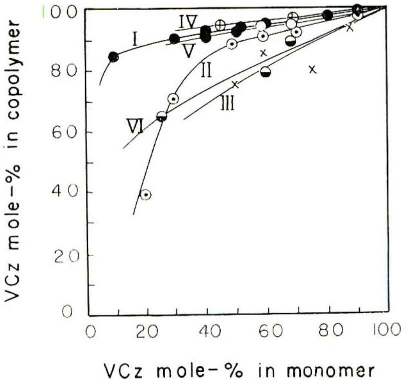

Fig. 3. Copolymer composition vs. monomer feed ratio for copolymerizations of *N*-vinylcarbazole (VCZ) and isobutyl vinyl ether (IBVE) in nitrobenzene: (I) (●) p-CA, [C] = 1.42×10^{-2} mole/l., 30°C; (II) (⊙) CAA, [C] = 5.0×10^{-3} mole/l., 30°C; (III) (×) TCNE, [C] = 2.35×10^{-2} mole/l., 30, 60°C; (IV) (⊗) MAnh, [C] = 2.0×10^{-2} mole/l., 80°C; (V) (○) p-BA, [C] = 2.0×10^{-2} mole/l., 80°C; (VI) (◒) $TiCl_4$, [C] = 4.8×10^{-3} mole/l., 30°C. Total monomer concentration [M] = 0.5 mole/l.

transfer polymerization. With this p-CA, copolymerization of VCZ with IBVE took place both in benzene and in nitrobenzene, although the polymerization rate was much faster in nitrobenzene.† The copolymer compositions were found to be similar in both solvents, VCZ being heavily predominant. The copolymer compositions corresponding to various monomer feed ratios are shown in Figures 2 (curve I) and 3 (curve I). Typical cationic copolymerizations initiated by $SnCl_4$ and $TiCl_4$ are also demon-

† Detailed results of the charge-transfer polymerization of VCZ with a series of related quinoid compounds in nitrobenzene will be reported in a later paper.[14]

strated in Figure 2 (curves III and IV) and in Figure 3 (curve VI), the proportions of the IBVE being larger than those obtained by using initiation by p-CA. Radical copolymerization initiated by azobisisobutylonitrile (AIBN) did not occur in either solvent. Although copolymer compositions differ considerably between in the charge-transfer polymerization initiated by p-CA and in authentic cationic polymerizations, the fact that IBVE was incorporated into a polymer suggests that the propagation of the polymerization with p-CA is not radical but cationic. Concurrent free-radical polymerization to give homopolymers of VCZ does not seem to proceed in the present charge-transfer polymerization, in view of the fact that the polymerization took place in the presence p-CA or nitrobenzene which acts as a radical trap and that the polymerization was not retarded by DPPH.[13]

Very recently Ellinger has reported[15] that IBVE is copolymerized with VCZ following lithium halide initiation and that this polymerization is neither radical nor cationic since the polymerization is insensitive to oxygen or hydroquinone and the copolymer composition is different from those following boron trifluoride etherate initiation, the initiation being ascribed to increased mesomeric polarization. However, we think that the incorporation of IBVE into the polymer in the present charge-transfer polymerization is suggestive of cationic propagation, regardless of the initiation modes, in view of the fact that the comonomer IBVE did not polymerize alone with the electron acceptors described here. The difference in copolymer compositions, therefore, seems attibutable to another factor, such as the property of comonomers or the differences in the gegenions in cationic polymerizations with Friedel-Crafts type catalysts from those in the charge-transfer polymerization with p-CA.

That the polymerization by p-CA is cationic in character may also be indicated by the results of copolymerization with initiation by chloranilic acid (CAA). CAA is a protonic acid, dissociating in water to form a deep red-purple solution exhibiting $\lambda_{\max}$ at 332 mμ (log ϵ 3.97) and at 535 mμ (log ϵ 2.14), which proved to be a powerful initiator for the polymerization of VCZ.[11] Chloranilic acid may act as an weak electron acceptor toward VCZ, but it may be difficult to interpret the rapid polymerization with this even in benzene in terms of the charge-transfer-initiated polymerization in the light of the features of slow charge-transfer polymerizations of VCZ initiated by p-CA and related quinoid compounds in benzene.[13] The polymerization initiated by CAA may be reasonably regarded as a cationic one initiated by the addition of a proton to VCZ. The composition curves of the copolymer initiated by CAA coincided with that obtained with p-CA as an initiator in benzene (curve II in Fig. 2), and they were very similar to each other in nitrobenzene (curve II in Fig. 3). These results appear to indicate that the propagation is cationic in the present system.

Copolymerization was likewise observed in every case where p-BA, MAnh, and TCNE were used as electron acceptors in nitrobenzene. Figure 3 illustrates these results. Thus the present copolymerization experiments confirm the cationic propagation mechanism in all above systems studied.

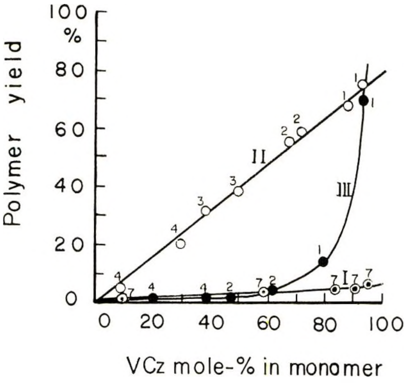

Fig. 4. Copolymer yield vs. monomer feed ratio for copolymerizations of *N*-vinylcarbazole (VCZ) and isobutyl vinyl ether (IBVE): (I) p-CA, [C] = 1.34 × 10^{-2} mole/l., 80°C, in benzene; (II) p-CA, [C] = 1.42 × 10^{-2} mole/l., 30°C, in nitrobenzene: (III) TCNE, [C] = 1.17 × 10^{-2} mole/l., 30°C, in nitrobenzene. [M] = 0.5 mole/l. Numbers in the figure in small letters for each plot are polymerization time in hours.

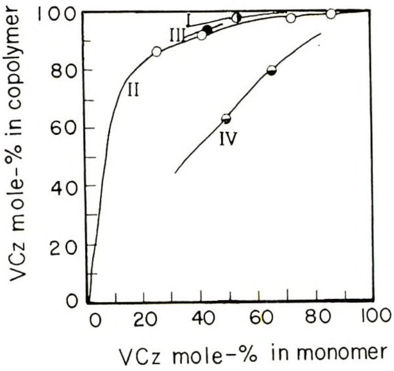

Fig. 5. Copolymer composition vs. monomer feed ratio for copolymerizations of *N*-vinylcarbazole (VCZ) and *N*-vinylpyrrolidone (VPD): (I) (◑) p-CA, [C] = 1.22 × 10^{-2} mole/l., 80°C, in benzene; (II) (○) p-CA, [C] = 1.22 × 10^{-2} mole/l., 80°C, in nitro, benzene; (III) (●) $SnCl_4$, [C] = 1.55 × 10^{-3} mole/l., 80°C, in benzene; (IV) (◒) AIBN-[C] = 6.0 × 10^{-3} mole/l., 80°C, in benzene. [M] = 0.5 mole/l.

A marked decrease in polymer yield was observed in the copolymerization of VCZ with IBVE with increasing feed ratios of IBVE as shown in Figure 4. Curves I and II demonstrate this behavior observed with p-CA as the initiator in benzene and in nitrobenzene, respectively; the decrease appears to be much larger in nitrobenzene. The decrease of the polymerization rate with increasing feed ratios of IBVE in these systems may, in part, arise from the retardation of the initiation reaction. Retarding and inhibiting effects of ethers or thioethers are known in some cationic polymerization systems.[16] In particular, the rate of copolymerization by TCNE in nitrobenzene decreased strikingly with increasing amounts of IBVE as revealed by curve III of Figure 4. In this case, the consumption of TCNE by such a reaction as the formation of cycloadduct[17] between TCNE and IBVE may perhaps be responsible for the decrease in the copolymer yield.

Moreover, lowering of the molecular weight of the copolymers was especially apparent in benzene at high IBVE feed ratios. Occurrence of frequent terminations by IBVE may be conceivable in benzene rather than in nitrobenzene. This difference in the termination reaction in benzene and in nitrobenzene might be interpreted in terms of the variation of the environment of the propagating site because of the difference in solvent polarity.

Copolymerizations of VCZ and VPD

Copolymerizations occurred also in this comonomer pair with p-CA and with the other electron acceptors cited in this report. *N*-Vinylpyrrolidone is known to polymerize both by a cationic and a radical process. Cationic copolymerization initiated by $SnCl_4$ and radical copolymerization initiated by AIBN were examined and compared with the charge-transfer-initiated copolymerization. The data obtained are shown in Figure 5. Copolymerizations with p-CA as an initiator in benzene and in nitrobenzene (curves I and II, respectively) were similar to the cationic copolymerization initiated by $SnCl_4$ in the copolymer compositions, and quite different from the radical copolymerization by AIBN (curve III).

These results, together with the results of the copolymerization with IBVE, lead to the conclusion that the propagation mechanism in the presently studied charge-transfer polymerization is cationic.

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Received February 16, 1970
Revised April 8, 1970

JOURNAL OF POLYMER SCIENCE: PART A-1 VOL. 8 (1970)

NOTES

Polyethylene Formation in Ziegler-Natta Polymerization of 3-Methylbutene-1

INTRODUCTION

It has been reported by Ketley et al.[1] that poly-3-methylbutene-1 obtained by $TiCl_3$–$(C_2H_5)_3Al$ catalyst was sometimes contaminated with polyethylene. They further found that polyethylene formation was considerable at low monomer concentration or at polymerization temperatures in excess of 80°C, and the source of ethylene was ascribed to triethylaluminum used. On the other hand, in the polymerization of propylene by the same catalyst, ethylene has been said to be incorporated into the polymer, yielding a decrease in the apparent isotacticity.[2,3] In this case, ethylene seems to copolymerize rather randomly with propylene.

The aim of the present study was to investigate the behavior of the ethylene derived from triethylaluminum in Ziegler-Natta polymerization of olefins under different polymerization conditions.

EXPERIMENTAL

Polymerization

3-Methylbutene-1 was obtained from Phillips Petroleum Co. (polymerization grade). The purity was +99 mole-% by vapor-pressure chromatography (VPC). *n*-Heptane (E. P. grade) was shaken with sulfuric acid, washed with water, dried by refluxing over sodium, and then distilled under nitrogen atmosphere. Triisobutylaluminum and triethylaluminum were obtained from Texas Alkyl Co. They were distilled under a nitrogen atmosphere *in vacuo* before use. Trimethylaluminum was prepared by Pitzer's method[4] and purified by refluxing over sodium followed by distillation under nitrogen. Titanium (III) chloride (AA grade) was obtained from Stauffer Chemical Co. Products of two different lot numbers were used. As they were slightly different in polymerization activity, they were designated A and B to distinguish them.

Polymerization was carried out as follows. Heptane, titanium (III) chloride, alkylaluminum compound, and monomer were introduced in that order into a 120-cc pressure bottle under a nitrogen atmosphere. The bottle was then stoppered with a rubber-lined crown cap and shaken in a thermostatted bath maintained at the polymerization temperature. After polymerization, the reaction mixture was poured into methanol–isopropanol (1:1) mixture to deactivate the catalyst and kept overnight. Polymer was separated by filtration, refluxed with methanol for several hours, separated again by filtration, and finally dried at 50°C for 24 hr *in vacuo*. In the polymerization at different polymerization temperatures, a 200 cc autoclave with magnetic stirring device was used instead of a pressure bottle. The polymerization procedure was the same as the above except that magnetic stirring was used.

Polyethylene Determination by Infrared Spectra

The amount of polyethylene in the sample was determined from the absorbance ratio of 720 cm^{-1} for polyethylene to 870 cm^{-1} for poly-3-methylbutene-1. The calibration curve was prepared by plotting the ratio of absorbance (A_{720}/A_{860}) against the weight

TABLE I

Polymerization of Different Catalyst Concentrations[a]

		Molar ratio,			Extraction			
Expt. no.	$TiCl_3$ (A), mmole	$\frac{(C_2H_5)_3Al}{TiCl_3}$	Yield of polymer, g	Density at 25°C, g/cc	Ether-soluble, %	n-Heptane-soluble, %	Residue, %	Melting point, °C
84	0.5	1.5	1.36					
85	1.0	1.5	4.65		2.4	4.7	92.9	305.5
86	2.0	1.5	6.95		5.2	3.3	91.5	298
87	4.0	1.5	9.05		7.1	7.9	85.0	289.5
88	8.0	1.5	10.04		10.2	7.4	82.5	281.5
89	0.5	3.0	1.99					306.5
90	1.0	3.0	3.07	0.9080	6.5	6.5	87.0	297.5
91	2.0	3.0	4.92	0.9069	9.0	6.1	84.9	289.3
92	4.0	3.0	6.92	0.9051	10.3	7.8	81.9	277.5
93	8.0	3.0	8.04	0.9045	13.1	8.8	78.1	261.5

[a] Conditions: *n*-heptane, 60 cc; monomer, 12.96 g; temperature, 60°C; time, 5 hr.

ratio (W_{PE}/W_{3MBI}). Standard samples were poly-3-methylbutene-1 prepared by $TiCl_3$–(i-C_4H_9)$_3$Al catalyst and commercial high-density polyethylene. Polymer samples were run as melt-compressed films in all cases.

Properties of the Polymers

About 1 g of the polymer powder was extracted at the boiling point of solvent for 24 hr with a Kumagawa extractor.

Polymer powder was melted at 310–330°C in a small test tube under vacuum (5mm Hg-N_2) and compressed to form a block, which was then heat-treated at 200°C for 0.5 hr under nitrogen. Small pieces cut from the block were used for melting point and density measurements. The melting point was determined with a modified penetrometer at a heating rate of 1°C/min. Density was determined by flotation method with an Ostwald pycnometer at 25°C. An ethanol–water mixture was used as flotation liquid.

RESULTS

3-Methylbutene-1 was polymerized with triethylaluminum–titanium (III) chloride catalyst at 60°C. The results of polymerization with different concentrations of catalyst are shown in Table I. Among the effects of catalyst concentration on the properties of polymer, the effect on melting point is especially remarkable. The melting point of the polymer decreases with increasing catalyst concentration. Such a marked melting point depression has never been reported in the polymerization of olefins. In parallel to this, the density of polymer decreases and solubility increases with increasing catalyst concentration. These effects seem to indicate that the crystallinity of the polymer decreases with increasing catalyst concentration. The presence of ethylene which might come from triethylaluminum can be considered as one of the reasons for the melting point depression. If ethylene is incorporated into the product as homopolymer or block copolymer with 3-methylbutene-1, however, such a remarkable melting point depression would not be observed. As a matter of fact, no polyethylene segment could be found in these polymers, on the basis of the infrared spectra. On the other hand, if ethylene is incorporated into the product as random copolymer, the melting point will decrease as the amount of triethylaluminum used increases.

To confirm the above hypothesis, trimethylaluminum or triisobutylaluminum was used instead of triethylaluminum as the aluminum component. The results are shown in Table II. Figure 1 is a plot of melting point of the polymer versus the catalyst concentration.

It is evident that the melting point of the polymer does not depend on the catalyst concentration when trimethylaluminum or triisobutylaluminum is used. This result supports the hypothesis that the ethylene evolved from triethylaluminum decreases the melting point of polymer. When triisobutylaluminum is used, isobutene may evolve during polymerization. Isobutene, however, does not polymerize under these reaction conditions. At a low catalyst concentration, below 1 mmole of $TiCl_3$/l., for example, the melting point of the polymer obtained with $TiCl_3$–$(CH_3)_3Al$ catalyst is lower by a few degrees than that of the polymer with $TiCl_3$–$(C_2H_5)_3Al$ catalyst. The reason for this difference is not clear.

At polymerization temperatures higher than 60°C, polyethylene was found in the polymers. Kelley et al.[1] reported that polyethylene formation occurred on polymerization at above 80°C or at low monomer concentration. In the present study, the effect of polymerization temperature on the polyethylene formation was investigated over the temperature range 45–135°C. Results are summarized in Table III. The infrared spectra of polymers shown in Figure 2 indicate that the polymer obtained at high temperature has strong absorption peaks at 720 and 730 cm^{-1}. The doublet, 720 and 730 cm^{-1}, indicates that the polyethylene in the sample exists in a crystalline state. However, it is not clear whether polyethylene segments exist as homopolymer or block copolymer with 3-methylene-1. Of course, when triisobutylaluminum or trimethylalu-

TABLE II
Polymerization with the Catalyst System Containing Trimethylaluminium or Triisobutylaluminium[a]

Expt. no.	Alkylaluminum compound	$TiCl_3$ (A), mmole	Molar ratio, Al/Ti	Yield of solid polymer, g	Extraction		Melting point, °C
					n-Heptane-soluble, %	Residue, %	
B7	$(CH_3)_3Al$	0.5	1.5	1.74			300.5
B8		1.0	1.5	2.92			302.7
B9		2.0	1.5	5.32			300.3
B10		4.0	1.5	7.52	7.4	92.6	298.7
B11		8.0	1.5	9.54			298·7
B12	$(i\text{-}C_4H_9)_3Al$	0.5	3.0	2.66			301.4
B13		1.0	3.0	3.27			299.1
B14		2.0	3.0	6.94	7.1	92.9	300.1
B15		4.0	3.0	9.32			
B16		8.0	3.0	9.85			297.6

[a] Conditions: *n*-heptane, 60 cc; monomer, 12.96 g; temperature, 60°C; time, 5 hr.

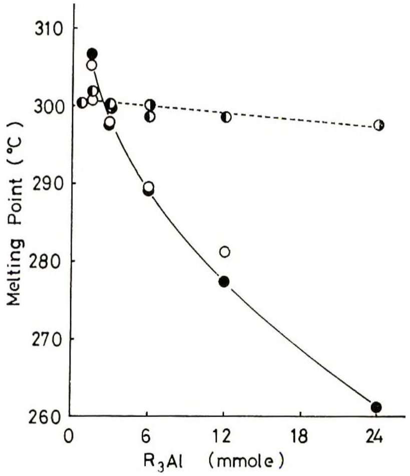

Fig. 1. Variation of melting point with the concentration of catalyst: (◐) $TiCl_3$–$(CH_3)_3Al$, molar ratio 1.5; (○) $TiCl_3$–$(C_2H_5)_3Al$, molar ratio 1.5; (●) $TiCl_3$–$(C_2H_5)_3Al$, molar ratio 3.0; (◑) $TiCl_3$–$(i\text{-}C_4H_9)_3Al$, molar ratio 3.0.

minum was used instead of triethylaluminum, no polyethylene segment could be found at all, even at a polymerization temperature of 135°C. The weight of polyethylene in the polymer was calculated from the values of Table III and plotted against polymerization temperature in Figure 3. From Figure 3, it is obvious that polyethylene formation occurs only at above 60°C, becomes more marked at higher temperatures, and does not depend on the amount of solvent under these experimental conditions.

DISCUSSION

From the above results, it is very probable that the ethylene came from triethylaluminum and is responsible for the formation of polyethylene. The ethylene polymerizes

TABLE III

Polymerization at Different Temperatures[a]

Expt. no.	*n*-Heptane, cc	Temperature, °C	Yield of polymer, g[b]	Polyethylene %[c]	Polyethylene mg
212	60	45	6.83	0	0
213	60	60	6.17	0	0
214	60	75	5.14	1.38	71
215	60	90	4.26	2.53	108
216	60	105	3.44	3.57	122
217	60	120	2.97	4.94	147
218	60	135	2.23	7.83	174
219	120	60	4.05	0.47	19
220	120	75	3.72	1.97	73
221	120	90	3.23	3.15	102
222	120	105	2.44	5.66	138
223	120	120	1.93	9.42	182
224	120	135	1.47	11.35	167

[a] Conditions: $TiCl_3$(B), 2.07 mmole; $(C_2H_5)_3Al$, 6.21 mmole; time, 6 hr.

[b] Contains polyethylene.

[c] Determined from infrared spectra.

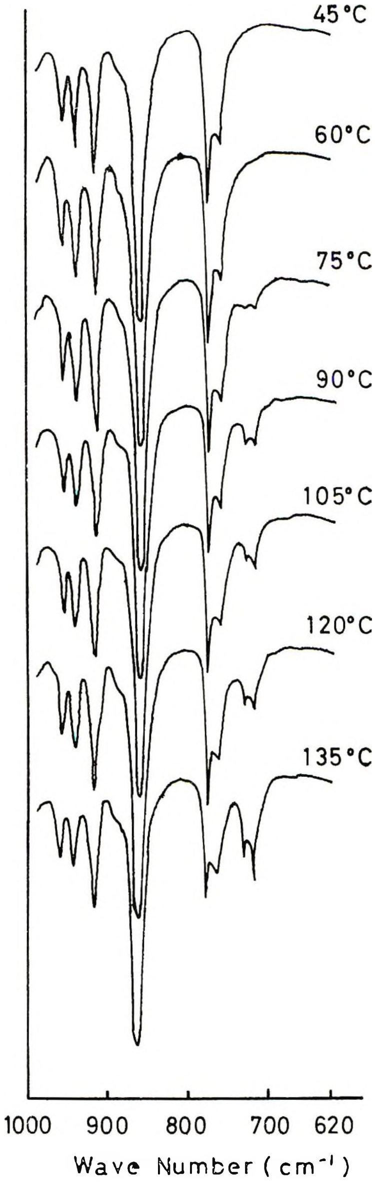

Fig. 2. Infrared spectra of the polymers obtained at different polymerization temperatures.

mainly to form polyethylene when polymerization is carried out at above 60°C, but copolymerizes with 3-methylbutene-1 at lower temperatures. The amount of polyethylene formed increases with increasing polymerization temperature and does not depend on the amount of solvent. The crystallinity of the polyethylene is very high.

From these, two ways for the mechanism of polyethylene formation can be considered.

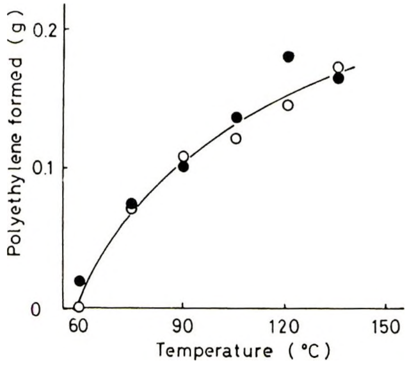

Fig. 3. Effect of polymerization temperature on the formation of polyethylene: (○) 60 cc solvent; (●) 120 cc solvent.

(A) If there exists one kind of active site for olefin polymerization, ethylene and 3-methylbutene-1 must polymerize at different stages of polymerization to form block copolymer or mixture of homopolymers.

(B) The high crystallinity of polyethylene would indicate that ethylene, at least some part of it, must be polymerized to form pure polyethylene segments without comonomer. Thus, two kinds of active sites, one of which polymerizes only ethylene but not 3-methylbutene-1, and another one which polymerizes both monomers, can be considered. If the activity of the former is more temperature-dependent than that of the latter, the experimental results can be explained qualitatively. In our experiment, it is not clear which one of the two mechanisms is in effect.

The mechanism of ethylene formation will be as follows.

(A) Through alkylation of $TiCl_3$:

$$TiCl_3 + (C_2H_5)_3Al \rightarrow (C_2H_5)_2AlCl \tag{1}$$

$$C_2H_5TiCl_2 \rightarrow TiCl_2 + C_2H_5\bullet \tag{2}$$

$$2C_2H_5\bullet \rightarrow C_2H_4 + C_2H_6 \tag{3}$$

(B) Olefin exchange reaction in alkylaluminum compounds:

$$(C_2H_5)_3Al \rightarrow (C_2H_5)_2AlH + C_2H_4 \tag{4}$$

$$(C_2H_5)_2AlH + H_2C{=}CH{-}CH(CH_3)_2 \rightarrow (C_2H_5)_2AlC_5H_{11} \tag{5}$$

or

$$(C_2H_5)_3Al + H_2C{=}CH{-}CH(CH_3)_2 \rightarrow (C_2H_5)_2AlC_5H_{11} + C_2H_4 \tag{6}$$

Concerning mechanism A, Kern et al.[5] have reported on the formation of ethylene in the $TiCl_4$–$(C_2H_5)_3Al$ system. Though titanium (III) chloride is less readily reducible by triethylaluminum than titanium (IV) chloride, similar reactions, eqs. (1)–(3), can take place at high temperatures. It has been found[6] that titanium (III) chloride (AA) is more easily alkylated by triethylaluminum than other types of titanium (III) chloride. By these reactions, however, titanium (III) chloride can be reduced to give only 0.5 equivalent at the most, as shown in eqs. (1)–(3). On the other hand, as shown in Figure 3, the amount of ethylene should be much more than expected from eqs. (1)–(3). Thus, route A, if it exists, is not important, and route B should be the main route for ethylene formation.

According to Ziegler,[7] there exists an equilibrium between alkylaluminum compounds and olefins.

$$\text{al} - \text{R(I)} + \text{Olefin (II)} \rightleftharpoons \text{Olefin (I)} + \text{al} - \text{H} + \text{Olefin (II)} \rightleftharpoons \text{Olefin (I)} + \text{Al} + \text{R}'\text{(II)} \quad (7)$$

where (al = $^1/_3$ Al).

Affinity of olefins to an aluminum-hydrogen bond decreases in the order, $H_2C{=}CH_2 > RCH{=}CH_2 > RR'C{=}CH_2$ (R, R'=alkyl group). Thus, assuming that olefin (I) and olefin (II) are ethylene and 3-methylbutene-1, respectively, the equilibrium in eq. (7) must lie towards the left. However, as ethylene is much more active to polymerize, free ethylene in the reaction system will be nearly completely consumed in polymerization as it forms. Therefore, reactions (4) or (6) will be the rate-determining steps for the polymerization of ethylene. If the activation energy of reactions (4) or (6) is larger than that of the polymerization of 3-methylbutene-1, a high polymerization temperature will be favorable for formation of polyethylene.

If eq. (4) or (6) proceeds completely to the right, 3 moles of ethylene will be produced from 1 mole of triethylaluminum. This is in agreement with the fact that the amount of polyethylene does not depend on the amount of solvent, as shown in Figure 3.

The author wishes to thank Dr. H. Kobayashi and Dr. O. Fukumoto for their encouragement during the work. The technical assistance of Messrs. T. Nakae and I. Sakayama is also acknowledged with thanks.

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Received April 1, 1970

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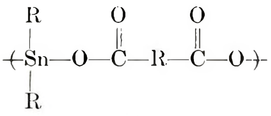
Production of Organometallic Polymers by the Interfacial Technique. XII. Importance of Hydrolysis in the Interfacial Synthesis of Poly(tin Esters)

We have been interested in the interfacial production of organometallic polymers and in the description of the polymerizing systems.[1-5]

Frankel and co-workers[6-9] and Carraher and Dammeier[10] recently reported the interfacial synthesis of products of the form I.

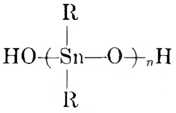


$$-\!\!\left(\underset{R}{\overset{R}{\mathrm{Sn}}}-O-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O\right)\!\!-$$

I

The products are of low molecular weight and exhibit water repellency, antifungal and antibacterial activity, form fibers,[6] and possess moderate thermal stability.[11] Carraher and Dammeier[10] recently reported on the effect of some associated reaction variables on polymer properties in an attempt to increase molecular weight. Molecular weight was independent of such reaction variables as organic solvent nature and stirring rate but increased as stirring time increased.

Hydrolysis may be an important reaction competing with the diacid salt for the tin chloride. II is rapidly formed in reactions carried out in a manner analogous to the normal polymerization procedure, except that the diacid salt is omitted.



$$\mathrm{HO}\!\left(\underset{R}{\overset{R}{\mathrm{Sn}}}-O\right)_{\!n}\mathrm{H}$$

II

Hydrolysis can occur as described in eq. (1). The reactivity and/or

$$\equiv\mathrm{Sn{-}Cl} + \mathrm{H_2O} \xrightarrow{-\mathrm{HCl}} \underset{\mathrm{III}}{\equiv\mathrm{Sn{-}OH}} \xrightarrow[-\mathrm{HCl}]{\equiv\mathrm{Sn-Cl}} \underset{\mathrm{IV}}{\equiv\mathrm{Sn{-}O{-}Sn}\equiv} \tag{1}$$

abundance of III and IV under reaction conditions is not known. III competes with the diacid salt for the tin chloride. The present paper reports on the importance of such hydrolysis in the interfacial production of poly(tin esters).

Organotin dichlorides (0.01 mole) were added to water (10 ml) and shaken to form a white solid of form II. Infrared spectra were taken of II, the parent organotin dichloride, adipic acid, and poly(tin esters) by using the Perkin-Elmer 237B and Beckman IR 12 instruments (KBr pellets). On comparing the spectra and using assignments reported previously for organotin products the Sn-O-Sn band is assigned the region of 580–590 cm^{-1}. The Sn-OH characteristic absorption occurs as a broad band between 3400 and 3500 cm^{-1}.* The Sn-Cl stretching frequency is assigned the region of 620–

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* In certain cases, such as with diphenyltin hydroxide (II where R is C_6H_5–) the band between 3400 and 3500 cm^{-1} is weak and is of limited use in determining the relative amount of such a group present in the corresponding poly(tin ester).

TABLE I
Polymer Properties as a Function of Aqueous Volume[a]

Water, ml	Yield, %	LVN, ml/g[b]
100.	79	3.0
50.	74	
7.0	78	2.7[c]
5.0	74	2.3
3.5[d]	70	2.4

[a] Reaction conditions: 0.01 mole of the disodium salt of adipic acid, 0.01 mole of dibutyltin dichloride in 50 ml of carbon tetrachloride at 25°C; 17,500 rpm stirring rate; 0.50 min stirring time.
[b] Viscosity run in 2-chloroethanol.
[c] Corresponds to a number-average molecular weight of 2200 by the Rast method.
[d] Represents a saturated salt solution.

650 cm^{-1}, with aromatic organotin halides absorbing in the upper region (635–650 cm^{-1}) and aliphatic organotin halides absorbing in the lower region (620–635 cm^{-1}). This is in agreement with Sn-Cl assignments reported by others.[15,16]

Polymer formation and isolation procedures are described elsewhere.[10] In general, diacid salts in water are added to stirred solutions of organotin dichlorides in an organic solvent. The polymer is precipitated by addition of the organic phase to water. Spectra of poly(tin esters) produced as described above show no band between 570 and 600 cm^{-1}, indicating the absence of detectable amounts of Sn-O-Sn bonds. The absence of detectable amounts of III is proof that II is relatively less reactive than the salt towards the tin chloride. The spectra do generally show small broad bands between 3400–3500 cm^{-1} indicating the presence of at least some chains with Sn-OH endgroups. The products show no infrared detectable Sn-Cl endgroups.

Since hydrolysis does occur, the amount of water in the aqueous phase may be important in determining polymer molecular weight and yield. Table I shows polymer results as a function of the aqueous solvent volume. Spectra of the products produced with varying amounts of water generally show little change in the absorption band in the 3400–3500 cm^{-1} region, indicating little change in the relative amount of Sn-OH endgroups. Polymer yield and molecular weight remain approximately constant as volume of water increases. This indicates that, though hydrolysis does occur, it is not the predominating factor in determining polymer molecular weight or yield.

The above is unexpected. Poly(tin ester) synthesis by the interfacial technique has been conducted with the use of saturated or nearly saturated aqueous phases to minimize hydrolysis. This now appears unnecessary. While hydrolysis does occur, the fact that even oligomeric poly(tin esters) are formed attests to the greater nucleophilicity of the diacid salt. (The acetate ion has a Swain-Scott nucleophilic constant of 2.72.[17])

This work was supported in part by an American Chemical Society Petroleum Research Fund Grant, 1338-G13. Portions were taken from the thesis of Roger Dammeier.

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Received April 8, 1970

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ERRATUM

Substituent Effects in Free Radical Copolymerization of Substituted Styrenes with Acrylates and Methacrylates

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[article in *J. Polym. Sci. A-1,* **8,** 1777 (1970)]

In Table VII, on p. 1783, the second substituent should be *meta* methyl (instead of para), the ninth substituent should be *meta* chloro (instead of para), and in the thirteenth substituent there is a bond missing in the cyano group.

Contents (continued)

NOTES

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