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Polymerization of Aromatic Nuclei. XII. Oligomerization of Halobenzenes by Aluminum Chloride–Cupric Chloride

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Synopsis

Polymerization of chloro- and fluorobenzene by aluminum chloride–cupric chloride produced highly colored oligomers. Chlorobenzene reacted under the standard conditions, i.e., 6/1/0.5 (molar ratio) of aromatic/catalyst/oxidant at 60°C. for 1 hr., to give a red solid in 14% yield. Evidence concerning the structure was obtained from elemental analyses, infrared and ultraviolet spectra, dechlorination, oxidation, solubility, molecular weight, and color. The data indicate that the backbone chain consists of an *o*-polyphenyl structure with chlorine atoms situated at the 4-positions. Polynuclear regions presumably comprise part of the structure. Molecular weight data pointed to an average of 10–12 units per chain. The coupled product from fluorobenzene was very similar to the chlorobenzene oligomer in most respects. In contrast to the chlorobenzene case, there was evidence of propagation occurring to some extent by attack *ortho* to the fluorine. Bromobenzene produced brominated *p*-polyphenyl apparently by disproportionation to benzene which then functioned as the monomer. An oxidative cationic mechanism (σ polymerization) is proposed for the nuclear coupling.

INTRODUCTION

Benzene has been polymerized to *p*-polyphenyl by various reagents, viz., aluminum chloride–cupric chloride,[1] ferric chloride,[2] and molybdenum pentachloride.[3] Excellent yields were obtained in the aluminum chloride–cupric chloride system.[4] In a similar fashion, other aromatic monomers have been studied in this laboratory: biphenyl,[5] *p*-terphenyl,[5] naphthalene,[6] mesitylene,[7] and *m*- and *p*-xylene.[8] Bilow and Miller[9] prepared fusible polyphenyls by the oxidative cationic polymerization (in the molten state) of *m*-terphenyl, *o*-terphenyl, 1,3,5-triphenylbenzene, or mixtures of the terphenyls with biphenyl and benzene. Naphthalene[10] has also been converted to a polychloronaphthyl, and triphenylene to chlorinated polytriphenylene[11] in a ferric chloride–sodium chloride–potassium chloride eutectic mixture. Benzene, anthracene, dibenzofuran,[10] and *p*-terphenyltriphenylene were also employed in this system, but the nature of the products was not disclosed.

The objective of our study was to extend the polymerization scheme to the halobenzenes and to study the derived products in order to establish their nature and elucidate the reaction pathway.

The previous literature on halogenated polyphenyls is comparatively scant. Lawlor and Miville[12] prepared a chlorinated polyphenyl of undefined structure by treating hexachlorocyclohexane with an aromatic compound in the presence of aluminum chloride. With trichlorobenzene, they obtained a black, friable, solid product composed of 45% chlorine. In an attempt to synthesize pure *p*-polyphenyl from *p*-dichlorobenzene by the Wurtz-Fittig method, Goldfinger isolated a polymer having an average degree of polymerization of 34 and analyzing for approximately 6 chlorine atoms per molecule.[13] Using a different approach, McCall and Hughes[14] produced chlorinated and brominated terphenyls by reacting a benzenesulfonyl halide with a halobenzene in the presence of a copper catalyst.

Fluorinated polyphenyls have also been synthesized. Hellmann and coworkers[15] condensed brominated or iodinated tetrafluorobenzene via the Ullmann reaction to an oligomer, the benzene-insoluble fraction of which had an average of 8–10 units. Wright and Fielding[16] treated dichlorotetrafluorobenzene with activated copper and obtained a solid which they believed to be $Cl(C_6F_4)_{16}Cl$.

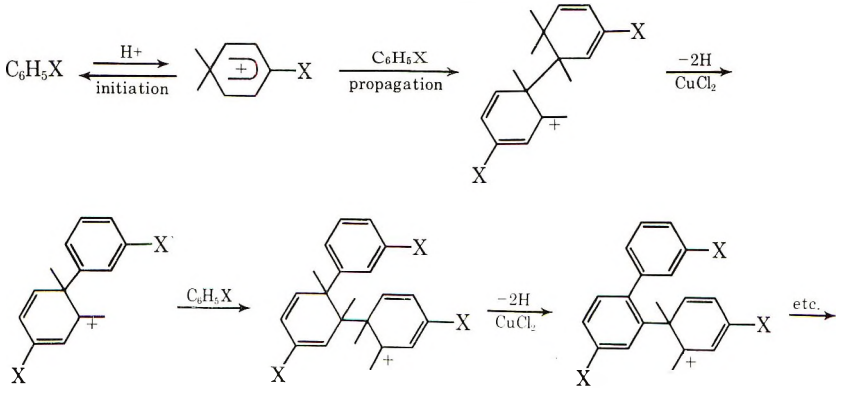
Halogenation of *p*-polyphenyl[17] by various reagents, e.g., antimony pentachloride, chlorine–aluminum chloride, or bromine–aluminum bromide has been effected. In addition, bromination of the lower members in the polyphenyl series has been studied.[18]

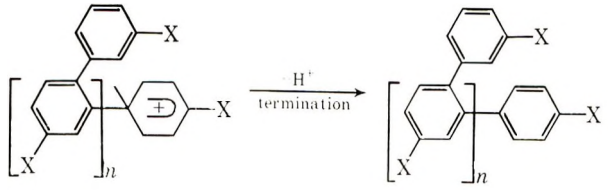
RESULTS AND DISCUSSION

Polymerization of the halobenzene monomers was performed with monomer/aluminum chloride/cupric chloride in 6/1/0.5 molar ratio at 60°C. for 1 hr. In all cases, highly colored material resulting from nuclear coupling was obtained. Various approaches were utilized in characterization of the products, including elemental analyses, molecular weight determination, infrared and ultraviolet spectroscopy, oxidative degradation, dehalogenation, solubility, and color.

By analogy to the oxidative cationic mechanism[1] (σ polymerization)[19] for formation of *p*-polyphenyl, the reaction pathway shown in eqs. (1)

$$H_2O + AlCl_3 \rightleftharpoons H_2O \cdots AlCl_3 \rightleftharpoons H^+AlCl_3(OH)^- \qquad (1)$$

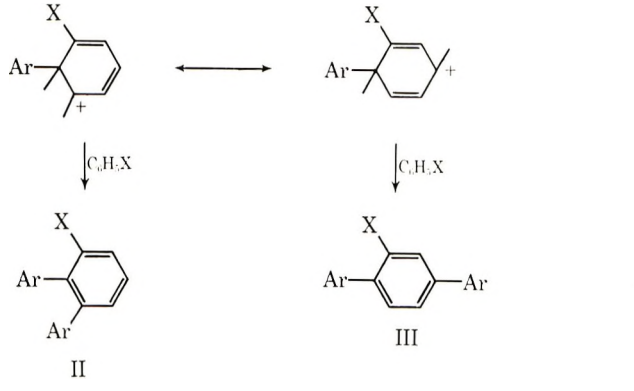




(2)

I

and (2) is postulated for halobenzene polymerization (X = F or Cl). In this scheme, the *para* position is employed for fixation of the electrophile in initiation and propagation. Since halobenzenes are susceptible to *ortho-para* attack, the alternative possibility of *ortho* participation should also be considered [eq. (3)]



(3)

II III

It should be made clear that, for polymerizations in this general category, little is known about the nature of the oxidation step and the stage at which it occurs.

Chlorobenzene

Reaction Variables. The effects of variation in time, temperature, and concentration on product yield and color were determined. Chlorobenzene polymerized in fairly low yield (Table I) to an orange-red solid on exposure to aluminum chloride–cupric chloride. A cationic mechanism is in keeping with the less favorable yield relative to benzene.[4] In the initial phases of the study, various conditions were utilized in an attempt to find a system which would provide the optimum yield and, at the same time, an oligomer with little or no color. We theorized that color reflects the occurrence of undesirable, accompanying transformations.

The following observations apply: (*1*) at a given temperature, a 2:1 ratio of catalyst:oxidant provided a better yield than did a 1:1 ratio (analogous to benzene polymerization)[4]; (*2*) higher yields were favored by an increase in temperature; (*3*) in all cases, the color varied from orange to a dark red. Previously with very mild conditions (30°C., 0.5 hr.) and monomer/catalyst/oxidant in 12/1/0.5 molar ratio, a yellow solid was obtained (3% yield).[20] On the basis of the data, the indicated standard conditions for polymerization were chosen: monomer/aluminum chloride/

cupric chloride = 6/1/0.5 (molar ratio) at 60°C. for 1 hr. Although optimum yields were realized at the higher temperatures, the more drastic conditions were avoided in order to minimize side reactions and thus provide a more homogeneous product.

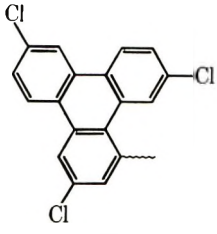
TABLE I
Oligomerization of Chlorobenzene

$C_6H_5Cl/AlCl_3/CuCl_2$, molar ratio	Temp., °C.	Time, hr.	Oligomer Yield, %	Oligomer Color
12/1/1.0	80	1	11.5	Orange-red
12/1/0.5	80	1	23.4	Dark orange
10/1/0.5	80	1	15.5	Orange-red
8/1/0.5	80	1	17.3	Orange-red
6/1/1.0	80	1	7.2	Dark red
6/1/0.5	80	0.5	23.2	Dark red
6/1/0.5	80	1	18	Orange-brown
6/1/0.5[a]	80	1	7	Orange-red
4/1/0.5	80	1	15.1	Orange-red
2/1/0.5	80	1	16	Dark brick red
20/1/0.5	60	1	14.5	Dark orange
12/1/0.5	60	1	11.3	Dark orange
6/1/0.5	60	2	14.2	Orange-red
6/1/0.5	60	1	13.9	Orange-red
6/1/0.5	50	2	11.8	Red
6/1/0.5	40	6	8.8	Orange-red
6/1/0.5	40	1	7.1	Orange-brown
12/1/0.5	30	12	6.7	Red-brown
6/1/0.5	30	12	5.6	Red-brown

[a] Pulverized cupric chloride.

Elemental Analyses and Color. The analytical results for the chlorobenzene oligomer are shown in Table II. The sum of carbon, hydrogen, and halogen fell in the range 94.8–98.2%. In all cases per cent chlorine did not differ appreciably from the theoretical value, suggesting that chlorination via the metal halide did not occur. This result is in contrast to the polymerization of other monomers in the same system, wherein small amounts of halogenation were shown to take place[1,4,6] (see also the results for fluorobenzene). Note that the C/Cl atomic ratio is near the theoretical value of 6 calculated for $(C_6H_3Cl)_n$.

Carbon analyses were somewhat at variance with the calculated figures, but the most significant discrepancy existed in the amount of hydrogen present, the values being 23–33% below theory. This is strikingly shown by the C/(H + Cl) atomic ratios, 1.8–2.0, which diverge considerably from theory (1.5). Hydrogen loss can most easily be explained on the basis of polynuclear formation.



IV

It is obvious that such a cyclization reaction can theoretically occur at any stage following trimerization, and to varying degrees. Ring closure is also possible when propagation takes place through a combination of *ortho* and *para* attack. This type of structure might also arise during termination. Another point in favor of the existence of polynuclear regions is provided by the color of the product. It is pertinent that the oligomer prepared under very mild conditions, i.e., 30°C. for 0.5 hr., possessed a yellow color in contrast with the darker hue characteristic of the 60°C. product. It may well be that cyclization diminishes with decrease in reaction temperature. It should be borne in mind that the polynuclear moiety is a much more potent chromophore than the analogous polyphenyl entity. Alternatively, *p*-quinoid units may be partially responsible for the observed color.[21] Since an increase in chlorine content is known to darken the color of *p*-polyphenyl,[21] perhaps halogen contributes to oligomer color in the present case.

Related dehydrogenation reactions can be found in the literature. For example, 1,1′-binaphthyl is converted to perylene in the presence of aluminum chloride (Scholl reaction).[22a] An even more striking citation to corroborate the working hypothesis is formation of triphenylene from *o*-terphenyl.[23] It seems apparent from the literature cases that either an oxidant or a strong catalyst is effective. Since our system possesses a dual character in this respect, it should be particularly amenable to cyclization.

Infrared Spectrum. Information concerning the structure of the oligomer was provided by the infrared spectrum. 1,2,4-Substitution was indicated by absorption maxima in the aromatic region at 865 cm.$^{-1}$ (lit.[24] 860–900 cm.$^{-1}$ for an isolated hydrogen) and at 820 cm.$^{-1}$ (lit.[24] 800–860 cm.$^{-1}$ for two adjacent hydrogens). Referring to the proposed structures, one can see that these results tie in nicely with units in I and III, but not II. A minor band at 750 cm.$^{-1}$ can be assigned to either three adjacent hydrogens at one end of the chain arising from initiation (see structure I; lit.:[24] 750–850 cm.$^{-1}$ for three adjacent hydrogens) or to four adjacent hydrogens arising from termination by attack *ortho* to halogen (lit.:[24] 735–770 cm.$^{-1}$ for four adjacent hydrogens).

The existence of polynuclear regions at various intervals along the chain cannot be verified or excluded by the infrared data. With structure IV in mind it can be seen that the spectrum of the polynuclear moiety in the aromatic region should be the result of two 1,2,4-substituted nuclei

TABLE II
Oligomerization of Halobenzenes[a]

Monomer	Temp., °C.	Time, hr.	Yield, %	Color	Oligomer							
					C, %		H, %		Hal, %		C/Hal, Atomic[c]	C/H + Hal), Atomic[d]
					Calcd.[b]	Found	Calcd.[b]	Found	Calcd.[b]	Found		
C_6H_5Cl	80	1	18	Red	65.16	63.54	2.74	2.10	32.09	31.57	5.94	1.77
C_6H_5Cl	60	1	13.9	Red	65.16	63.74	2.74	1.84	32.09	31.93	5.92	1.94
C_6H_5Cl	60	1	14	Red	65.16	63.93	2.74	2.06	32.09	32.17	5.86	1.80
C_6H_5Cl	30	12	5.6	Red	65.16	61.78	2.74	2.00	32.09	31.06	5.85	1.78
C_6H_5Cl[e]	80	1	16	Red	65.16	64.12	2.74	1.82	32.09	31.40	6.04	1.98
C_6H_5F	60	1	14.5	Brown	76.60	75.28	3.20	2.83	20.20	13.57[f]	8.83	1.72
C_6H_5F	60	1	14.5	Brown	76.60	75.26	3.20	2.85	20.20	13.75[g]	8.70	1.70
C_6H_5F	60	1	9.2	Brown	76.60	74.19	3.20	2.52	20.20	14.74[h]	7.92	1.81
C_6H_5Br	60	1	45.9[i]	Black	46.40	74.76	1.95	2.91	51.50	15.62	31.9	2.00

[a] Monomer/$AlCl_3$/$CuCl_2$ = 6/1/0.5 (molar ratio).
[b] Calcd. for $-(-C_6H_3X-)_n-$.
[c] C/Hal = 6 (atomic ratio), calcd. for $-(-C_6H_3X-)_n-$.
[d] C/(H + Hal) = 1.5, calcd. for $-(-C_6H_5X-)_n-$.
[e] 2/1/0.5 molar ratio.
[f] 4.50% Cl present.
[g] 4.02% Cl present.
[h] 4.43% Cl present.
[i] Calcd. for $-(-C_6H_4-)_n-$ containing 15.62% Br.

and a 1,2,3,5-substituted type. The characteristic absorption of 1,2,3,5-substitution is such (860–900 cm.$^{-1}$)[25a] that it could overlap with the 860–900 cm.$^{-1}$ band for the 1,2,4-system. Structure IV arises from cyclization of the first three units of the oligomer chain and the point at which the cyclization occurs is *para* to the chloro substituent of the first phenyl ring. Alternatively, ring closure might occur *ortho* to the substituent, giving rise to three adjacent hydrogens. Since the infrared spectrum shows no absorption characteristic of 1,2,3-substitution (lit.:[25a] 770–800 cm.$^{-1}$, 685–720 cm.$^{-1}$), few, if any, units of this nature would be expected. Also, the infrared spectrum would not provide any clues to exclude gross polynuclear formation.

Ultraviolet and Visible Spectra. The solution spectrum of the oligomer in the ultraviolet and visible regions was obtained in various solvents, namely, chloroform, dioxane, and cyclohexane. Although chloroform was quite suitable from a solubility standpoint, it is not transparent in the ultraviolet portion of the spectrum below 250–260 mμ. Dioxane and cyclohexane, though being poorer solvents, permitted extension of the spectrum, in the case of cyclohexane to about 195 mμ. In chloroform, absorptions were observed at 380 and 315 mμ, and with dioxane at 380, 318 and 250 mμ. Cyclohexane solutions revealed λ_{max} 205 and 255 mμ with small absorptions at 315 and 380 mμ. Fine structure was absent from the spectra in all cases.

It is instructive to compare the spectral data to those for *o*-terphenyl structures similar to I. In addition, let us consider the effect of electron-releasing substituents on the ultraviolet spectrum of the benzene nucleus. The literature[26] reveals, in general, a shift to longer wavelengths in the ultraviolet λ_{max} on introduction of groups of this type. A similar effect (bathochromic shift) is observed when *o*-terphenyl is substituted in the 4′ and 4″ positions with oxygen-bearing functionalities. Previous work[26] reveals that chloro and hydroxy substituents cause a shift of 10 and 16 mμ, respectively. By utilization of these data and those for the substituted *o*-terphenyls,[27] a value of 245 mμ is estimated for the λ_{max} of 4′, 4″-dichloro-*o*-terphenyl. This is in good agreement with the figure, 255 mμ, observed for the chlorobenzene oligomer, thus lending additional support to the existence of I.

Additional insight is gained by considering the spectral characteristics of chlorobenzene. The absorption maxima for the monomer and oligomer correspond quite nicely: monomer λ_{max} 210, 257 mμ;[25b] oligomer λ_{max} 205, 255 mμ. Jones has pointed out that when steric effects repress conjugation, the spectrum approximates that of the parent aromatic compound.[28] In our case, the *ortho* linkages permit little conjugative interaction because of a pronounced adverse steric factor. Woods[29] and coworkers have cautioned that other influences must also be taken into account in spectral interpretations, e.g., the energy difference between the ground state and first excited state.

The minor absorption observed at 315 and 380 mμ may be the result of

polynuclear structures. By analogy, auxochromically substituted triphenylenes, e.g., hydroxytriphenylene and 1,2-dihydroxytriphenylene,[30] have small absorption bands in the region of 310–360 mμ.

Oxidative Degradation. Oxidation of the oligomer in a chromic acid–acetic acid medium was performed in order to obtain further information concerning structural parameters. Esterification of the crude oxidation product was followed by gas–liquid chromatographic analysis. Two components were isolated and identified (infrared spectra) as methyl *p*-chlorobenzoate and dimethyl 4-chlorophthalate. Structure I then constitutes a coherent basis for rationalizing these findings. There was no evidence for the presence of the following acids: *o*-chlorobenzoic, *m*-chlorobenzoic (from I), 3-chlorophthalic (from II), and chloroterephthalic (from III). The results indicate specificity in orientation during propagation. This can be interpreted in part by a steric factor associated with the halogen substituent and the attacking electrophile. From a consideration of the data[31] for electrophilic attack on chlorobenzene by various species it is obvious that as the size of the attacking entity increases, the *ortho/para* ratio correspondingly decreases. On the basis of the appreciable bulk associated with the arenonium ion, a fairly low amount of *ortho* attack would be predicted.

One should also consider the recent report of Kovacic and Hiller[32] on alkylation of chlorobenzene. Isopropylation, for instance, gave a higher *ortho/para* ratio than chlorination or nitration, opposite to the expectation arising from steric arguments alone. To elucidate the unusual distribution in alkylation, the authors advanced a linear coordination hypothesis, i.e., coordination of certain electrophiles with a specific Lewis base substituent on the nucleus, followed by entrance into the ring so as to favor *ortho* attack. The linear coordination effect does not seem to play an important role during chlorobenzene oligomerization, presumably a reflection of the decreased activity (delocalization) of the σ-complex intermediate through resonance stabilization.

It is indeed interesting that no methyl *m*-chlorobenzoate was detected since, using I as a guide, one would certainly anticipate its presence. Reference to polynuclear formation can be used to explain the observed negative result. It would appear necessary to adopt the corollary that the nucleus generated during initiation is particularly suited for participation in ring closure (see IV). On the other hand, of necessity, some doubt is cast on the validity of the initiation postulate. There is the possibility that the isomeric *meta* acid was subsequently destroyed by oxidation after formation. However, when the reaction was performed under milder conditions, its existence was still not detected. Also, addition of *m*-chlorobenzoic acid to the reaction mixture of oligomer undergoing oxidation resulted in recovery of methyl *m*-chlorobenzoate upon work-up. Thus, *m*-chlorobenzoic acid is stable toward further degradation under our oxidizing conditions.

Dechlorination. Dechlorination of the oligomer under the agency of

sodium in mesitylene worked best on a small scale. Analysis of the product after a typical run showed less than 0.5% chlorine remaining. The infrared spectrum of the product revealed a drastic diminishing of absorption at 865 and 820 cm.$^{-1}$, indicative of 1,2,4-substitution, accompanied by a pronounced increase in the band at 740–750 cm.$^{-1}$, characteristic of *ortho* substitution. Unfortunately, the system had the drawback of unwanted participation by solvent to some extent. This was evidenced by an increase in product weight in some cases and by a band at 2850 cm.$^{-1}$, believed to reflect aliphatic carbon–hydrogen stretching.

Dechlorination was also effected on the soluble fraction of the oligomer (75–80% soluble in tetrahydrofuran when extracted for 24 hr.) via the Grignard reaction with ethylene bromide as an entrainment reagent. The dechlorinated product retained only a small amount of chlorine (1.6%) and the infrared spectrum revealed absorption in the 750 cm.$^{-1}$ region, characteristic of *ortho* substitution. However, a sizeable band at 800 cm.$^{-1}$ still remained, possibly indicative of *para* substitution along the chain or a result of a side reaction of oligomer with ethylene bromide.

The dechlorinated material was oxidized, and the resultant product was examined by gas–liquid chromatography after esterification. The presence of dimethyl phthalate was established by infrared spectral analysis. A second component was also isolated from the crude ester, which had an infrared spectrum essentially identical to that of authentic methyl benzoate (from terminal units of the oligomer).

Attempts were also made to dechlorinate the oligomer by other means. With lithium metal in various media, dechlorination appeared incomplete as evidenced by the infrared spectrum. Both lithium aluminum hydride and hydrazine hydrate also proved to be unsatisfactory.

The infrared spectrum of the dehalogenated substance, together with resulting oxidation data, verifies the existence of *ortho* junctions in the backbone chain. This observation provides additional conviction that I represents the predominant structure of the oligomer.

Interestingly, polyphenyls containing *ortho* linkages exclusively are not common. Those members of the series up to and including *o*-quaterphenyl have been characterized,[33a] in addition to *o*-sexiphenyl.[34] The syntheses of polyphenyls containing some *ortho* linkages have been reported by Woods and Scotti,[35] as well as Kern and co-workers.[36]

Solubility. Oligomer solubility was determined in various solvents (Table III). Chloroform was found to be an excellent solvent for the product prepared under standard conditions. Various other solvents, e.g., carbon tetrachloride and benzene, proved to be less effective. Exhaustive extraction of the oligomer with tetrahydrofuran revealed 75–90% solubility. The high solubility can be accounted for by a number of structural features: (*1*) *o*-polyphenyl units, (*2*) presence of halogen substituents, (*3*) irregularities in the chain, e.g., structures II, and III, polynuclear regions, and branching, and (*4*) the relatively low molecular weight. The *o*- and *m*-polyphenyls are known to possess greater solubility than the *para* counter-

TABLE III
Solubility of Chlorobenzene Oligomers

Oligomer (entry in Table I)	Solvent	Solubility, %[a]	
		25°C.	65–70°C.
14	Benzene	57.5	72
		57	72.5
7	Benzene	36	45
		34.5	47
19	Benzene	77	78
		80.5	77
14	Chloroform	88	88
		87	88
7	Chloroform	61.5	[b]
		59	—
19	Chloroform	81.5	[b]
		83	—
14	Carbon tetrachloride	59	77
		60	74
14	Cyclohexane	4	[b]
14	Dioxane	53	[b]
[c]	Cyclohexane	1.5	[b]
		2.3	[b]

[a] Measured with a sample (0.4–0.6 g.) in 15 ml. of solvent left standing overnight.
[b] Not determined.
[c] Fluorobenzene oligomer.

parts.[33b] Also, substituents have been shown to exert a favorable influence on dissolution.[37]

One should note the effect of polymerization temperature on solubility (Table III). Higher temperatures produced oligomers of lower solubility, due possibly to a higher average molecular weight or enhanced incorporation of polynuclear structures.

The solubility results are in marked contrast to those for *p*-polyphenyl prepared by the same method. In this case, less than 0.2% of soluble material was obtained by extraction with ether, chloroform, or *p*-xylene.[1] Factors making for high insolubility in this case are: (*1*) *para* configuration, (*2*) relatively high molecular weight, (*3*) minor number of substituents, and (*4*) structural regularity.

Molecular Weight. Since the chlorobenzene oligomer dissolved appreciably (88%) in chloroform, molecular weight determinations of the soluble fractions were feasible. The data are summarized in Table IV. The average molecular weight for various samples can be seen to vary slightly according to reaction conditions. However, the values all lie within the range, 1127–1340, corresponding to 10–12 units per chain. It is instructive to compare these results with those from other monomers. Although the molecular weight of *p*-polyphenyl has not been ascertained, Marvel and co-workers obtained a sulfonated derivative exhibiting solubility in ethanol–water.[38,39] Biphenyl and *p*-terphenyl gave primarily

TABLE IV
Molecular Weight Data for Halobenzene Oligomers

Reaction conditions[a]			Oligomer		
Monomer	Temp., °C.	Time, hr.	Solubility, %[b]	Average mol. wt.	Monomer units (avg.)
C_6H_5Cl	80	1	61.5	1319	12
C_6H_5Cl	80	1	59	1340	
C_6H_5Cl	60	1	87.5	1263	11
C_6H_5Cl	60	1	87	1244	
C_6H_5Cl	30	12	81.5	1137	10
C_6H_5Cl	30	12	83	1127	
C_6H_5F	60	1	36.4	1263	13
C_6H_5F	60	1	38	1117	
C_6H_5F	60	1	42.4	1205	12
C_6H_5F	60	1	43.6	1077	

[a] Monomer/$AlCl_3$/$CuCl_2$ (molar ratio) = 6/1/0.5.
[b] Measured with a 0.4–0.6 g. sample in 15 ml. of chloroform at room temperature.

p-sexiphenyl,[5] and naphthalene produced low molecular weight polynaphthyls[6] (approximately 3–6 units per chain).

Let us now attempt to correlate the degree of polymerization with monomer structure. Various factors should be taken into consideration, e.g., the relative susceptibility of the aromatic monomers to propagative attack, the nature of the growing carbonium ion, steric effects, polymer solubility, and diverse influences (dipole moment, polarity, solvating power, complexing ability, etc.) of solvent or excess aromatic. Furthermore, the apparent increasing ease of termination in the order, *p*-terphenyl, mesitylene, *m*- and *p*-xylene, biphenyl, naphthalene > chlorobenzene > benzene suggests that the relative stabilities of the postulated σ-complex intermediates may be an important factor. Based on a direct relationship between degree of resonance stabilization in the propagating end and susceptibility to termination, the predicted extent of polymerization would correlate quite closely with that observed.[5,6] Resonance stabilization of the growing cation by involvement of the substituent would be expected for the chlorobenzene reaction. Also, diminished activity could conceivably result from complexing of the carbonium ion with *n*- and π-electrons of excess aromatic in the halobenzene system.[40a] The formation of *n*-complexes might so deactivate the charged species that the rate of propagation decreases and termination by proton loss assumes a more favored status.[21]

Low Molecular Weight Products. Halobenzenes are known to undergo disproportionation in Friedel-Crafts systems.[40b] In order to determine whether such a process was occurring with chlorobenzene under our conditions, some exploratory studies were carried out (Table V). First it should be mentioned that there was no evidence for the presence of *p*-polyphenyl from chlorobenzene–aluminum chloride–cupric chloride. When the monomer was exposed to aluminum chloride–cupric bromide or aluminum

bromide–cupric bromide, essentially no polymer was formed. If benzene were generated in these systems, subsequent conversion to *p*-polyphenyl would be expected in comparison with the result from bromobenzene (discussed later). Therefore, the observed dihalobenzenes apparently originate by halogenation of the monomer with cupric halide–aluminum chloride. Presumably, monomer is favored over oligomer in chlorination during polymerization, as evidenced by the analytical data for the coupled product. Since chlorobenzene retained its structural integrity on treatment with aluminum chloride–hydrogen chloride under simulated reaction conditions, additional evidence is available against the involvement of disproportionation.*

TABLE V
Low Molecular Weight Products from Halobenzenes[a]

System[b]	Low mol. wt. product[c]	Oligomer yield %
C_6H_5Cl–$AlCl_3$[d]	C_6H_5Cl	none
C_6H_5Cl–$AlCl_3$–$CuCl_2$	*o*- and *p*-$C_6H_4Cl_2$	14
C_6H_5Cl–$AlCl_3$–$CuBr_2$	*o*- and *p*-$C_6H_4Cl_2$, *o*- and *p*-C_6H_4BrCl	<1
C_6H_5Cl–$AlBr_3$–$CuBr_2$	*o*-, *m*-, and *p*-C_6H_4BrCl	<1
C_6H_5Br–$AlCl_3$–$CuCl_2$	*o*-, *m*-, and *p*-$C_6H_4Br_2$, *p*-C_6H_4BrCl	45.9

[a] Obtained from the steam-volatile organic portion.

[b] Monomer/catalyst/oxidant = 6.0/1/0.5 (molar ratio); 60°C., 1 hr.

[c] Isolated by gas–liquid chromatography and identified by infrared spectrum and melting point when possible.

[d] No cupric chloride; hydrogen chloride was bubbled into the reaction mixture.

Fluorobenzene

Fluorobenzene oligomerized under the standard conditions adopted for chlorobenzene to afford a dark brown solid in 10–15% yield. No attempts were made to optimize conditions, since studies of this nature were carried out in the chlorobenzene system.

Elemental Analyses and Color. The analytical data are summarized in Table II. Fluorine analyses were quite low in comparison with theory for the structure $+C_6H_3F+_n$. One should note, however, that an appreciable quantity of chlorine (4–4.5%) was incorporated into the oligomer during reaction, thus complicating interpretation of the figures. Chlorination could well come about through the action of cupric chloride with alumi-

* In recent work, H. Kuwata, *Mem. Proc. Fac. Eng. Hiroshima Univ.*, **2**, No. 3, 55 (1965), converted chlorobenzene by treatment with cupric chloride–aluminum chloride to an oligomer which was assigned structure III (see above) in contrast with our conclusions. However, characterization was based solely on infrared spectroscopy and elemental analyses. He reported an average of 30 monomer units per chain, in comparison with our figure of 10–12, and the earlier one of 18 from scouting work.[20]

num chloride as promoter.[41] On the assumption that chlorine is introduced by replacement of hydrogen, the C/(H + Cl + F) ratio was found to be 1.72–1.81. However, caution should be exercised in interpretation of these figures, since the C/F ratio indicated loss of fluorine during oligomerization on the basis of observed values of 7.9–8.8 as compared to 6 for theory. One means of rationalizing the low fluorine content is by analogy to the finding of Olah and co-workers[42] that an aromatic fluoride can function as an arylating agent under Friedel-Crafts conditions. Although a much higher temperature was employed in the intermolecular reaction, the presumed intramolecular nature of the arylation in our case would be a favorable driving force necessitating less drastic conditions. The color of the oligomer also lends support to the hypothesis of polynuclear formation.

Infrared Spectrum. The infrared spectrum provided further insight concerning the nature of the product. The fluorobenzene material exhibited a broad band at 810–830 cm.$^{-1}$ with a shoulder at 855 cm.$^{-1}$. This can be interpreted on the basis of a 1,2,4-substitution pattern (see infrared spectral data of the chlorobenzene oligomer for literature values). Minor absorption in the 750–760 cm.$^{-1}$ region can be assigned to either three or four adjacent hydrogens on endgroups. Structures I and III correlate nicely with the infrared data. It is interesting to compare the spectral results to those obtained for the chlorobenzene oligomer. In both cases, 1,2,4-substitution is indicated, but somewhat more clearly for the chlorobenzene product.

Ultraviolet and Visible Spectra. The spectrum of the fluorobenzene oligomer in the ultraviolet and visible regions was similar to that of the chlorobenzene product, including the absence of fine structure. The λ_{max} values (cyclohexane) occurred at 195 and 247 mμ, compared to 205 and 255 mμ for the coupled material from chlorobenzene. Furthermore, there is fairly close correspondence of the absorption maxima with those (λ_{max} 204 and 254) reported for fluorobenzene.[43] The fluorobenzene product also exhibited small absorptions near 310 and 380 mμ, which may be a consequence of polynuclear structures in the oligomer. The reader should refer to the chlorobenzene section for a theoretical treatment and structure–spectral correlations.

Oxidation. Oxidation was performed on the fluorobenzene product as an aid in structural elucidation. Products were isolated by gas–liquid chromatography after esterification. One was found to be dimethyl 4-fluorophthalate. Identification of methyl *o*- and *p*-fluorobenzoate, both of which can be attributed to oxidation of end groups, was accomplished *via* the infrared spectra. It is pertinent to mention that the ratio, methyl *p*-fluorobenzoate to methyl *o*-fluorobenzoate, was found to be 3.

The fact that propagative attack occurs partly *ortho* to the fluoro substituent can superficially to rationalized by a decreased steric effect, i.e., the small fluorine atom does not hinder the electrophile as much as the large chlorine would. On the other hand, there is ample evidence to support the contention that steric factors do not play a predominant role in many

cases of electrophilic substitution in halobenzenes. Nitration can be cited as an example. Thus, in spite of the fact that the size of the substituent increases in the halobenzene series from fluorobenzene to iodobenzene, *ortho* nitration becomes increasingly more pronounced in descending the series.[40c] A similar situation has been observed in halogenation with metal halides.[44,45] The possibility of linear coordination must also be considered, for as Kovacic and Hiller[32] have emphasized, the nature of both the donor and acceptor plays an important role in determining whether or not complexing at the substituent, followed by intramolecular rearrangement will occur. With the realization that fluorine is generally a much better coordinating site than chlorine, this approach bears distinct merit.

No methyl *m*-fluorobenzoate was found from the oxidation products, a situation analogous to that observed with the chlorobenzene oligomer. The possible significance is treated in the chlorobenzene section. The presence of methyl *o*-fluorobenzoate and the absence of methyl *m*-fluorobenzoate lend support to the belief that the small band in the infrared spectrum at 750 cm.$^{-1}$ is due to an *o*-fluorophenyl endgroup arising from termination, rather than a *m*-fluorophenyl structure from initiation.

Solubility. Since chloroform proved to be an excellent solvent for the chlorobenzene oligomer, it was chosen for use with the fluorobenzene product. As the results of Tables III and IV indicate, the oligomer was about half as soluble as the coupled product from chlorobenzene. The lower solubility of the fluoro analog can be interpreted in terms of a higher average molecular weight, increased polycyclic character, or enhanced formation of structures such as III in the chain. If III contributes appreciably, then the oligomer would resemble the extremely insoluble *p*-polyphenyl at various intervals along the chain.

Molecular Weight. The molecular weight of the chloroform-soluble fraction (36–44%) of the oligomer (Table IV) was found to be similar to that of the analogous portion of the chlorobenzene product. The average molecular weight was in the range of 1077–1263, corresponding to 12–13 units per chain. The reader is referred to the chlorobenzene section for a discussion of factors influencing molecular weight.

Bromobenzene

Bromobenzene underwent polymerization under the standard conditions to produce a black solid in 46% yield. However, a different reaction course was followed with this monomer. On the basis of the available evidence, one can conclude that the product is a brominated *p*-polyphenyl. From the analytical results (Table II) it is clear that direct polymerization of the monomer did not take place. Carbon, hydrogen, and halogen analyses are all significantly different from the theoretical values for $+C_6H_3Br+_n$.

Evidence in support of a *p*-polyphenyl structure was provided by infrared studies. Instead of displaying a spectrum similar to that of the chlorobenzene or fluorobenzene oligomer, the polymer from bromobenzene possessed one very similar to that of *p*-polyphenyl. Bromination of *p*-

polyphenyl was performed and the spectra of the product and of the oligomer were compared. Although the bromine content differed significantly (47.1 and 15.6%, respectively), the absorption patterns in the region of interest (880–780 cm.$^{-1}$) were quite akin, indicating essentially the same type of backbone structure. The more pronounced absorption for the minor bands at 695 and 750 cm.$^{-1}$ in the bromobenzene product can be attributed to a greater prevalence of unsubstituted phenyl end-groups.

The observations can be nicely rationalized on the basis of monomer disproportionation followed by preferential polymerization of the benzene formed *in situ*. This hypothesis is quite reasonable since benzene would comprise the most reactive monomer in the system. A study of the non-polymeric products proved to be revealing. Indeed, *p*-dibromobenzene was found to be present, along with smaller amounts of the *ortho* and *meta* isomers (Table V). Also identified was *p*-bromochlorobenzene, presumably arising via chlorination of the monomer by cupric chloride–aluminum chloride. Examples of bromobenzene disproportionation under similar conditions can be found in the literature.[22b,40b] Apparently some of the bromine lost from the monomer effects halogenation of the benzene polymer.

EXPERIMENTAL

Materials

Chlorobenzene was distilled from calcium hydride prior to use. *p*-Polyphenyl was synthesized via the standard procedure.[4] Other substances were high-purity commercial materials which were used directly.

Analytical Procedures

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Clark Laboratories, Urbana, Illinois.

Infrared spectra were taken with a Beckman IR-8 spectrophotometer (potassium bromide pellet). A Cary model 15 spectrophotometer was used for the ultraviolet and visible spectra. The molecular weight of the chloroform soluble fraction of the polymer was determined in chloroform at room temperature with a Mechrolab 301A vapor pressure osmometer. Biphenyl served as the reference standard. Gas–liquid chromatographic analyses were carried out on a home-made unit with the indicated columns: (A) 20 ft. × 0.25 in., 0.5% Carbowax-PEG-6000 and 15% silicone grease on Chromosorb, column temperature, 180–210°C., 25–30 psi of He; (B) 6 ft. × 0.25 in., SF-96 on acid-washed Chromosorb P, 30–60 mesh, column temperature, 180–210°C., 6–10 psi of He.

Polymerization of Halobenzenes: General Procedure

Chlorobenzene (6 moles, 615 ml.) was placed in a 1-liter, three-necked flask (fitted with mechanical stirrer, condenser, thermometer, and gas inlet tube) and heated to 60°C. under a nitrogen atmosphere with stirring.

Aluminum chloride (1 mole, 133 g.) was then introduced, followed by portionwise addition of anhydrous cupric chloride (0.5 mole, 67 g.) during 5 min. The mixture was stirred for 1 hr. and then mixed with a slush of crushed ice and concentrated hydrochloric acid. The resulting dark brown mixture was agitated by means of a magnetic stirrer for at least 1 hr. and then steam-distilled.

The crude polymer was filtered from the aqueous layer, pulverized in a blender with some added water, and then triturated with 18% hydrochloric acid until the filtrate was colorless. Final washings were performed with boiling deionized water until the test (silver nitrate) for chloride ion was negative. The purified product, a red solid, was dried at room temperature overnight. Yield is based on cupric chloride.

In an investigation of the lower molecular weight products, the volatile organic material from steam distillation was separated from the aqueous layer, dried over anhydrous sodium sulfate, and distilled to remove excess monomer. The residue was then subjected to gas chromatography.

Oligomer Solubility

Room Temperature. A mixture of oligomer (approximately 0.5 g.) and solvent (15.0 ml.) was placed in a stoppered vial, occasionally shaken, and then allowed to stand overnight at room temperature. The mixture was filtered under nitrogen pressure with collection of the filtrate in a cooled receiver to minimize solvent loss. An aliquot (5 ml.) was placed in a weighed receiver, the solvent evaporated by placing the receiver on a radiator overnight, and then the residue weighed to determine the amount of soluble material.

At 65–70°C. The same size of oligomer sample as in the room temperature experiments was placed in a 50-ml. round-bottomed flask to which solvent (15 ml.) was added. The flask was quickly topped with a reflux condenser, shaken, and then kept at 65–70°C. overnight. The cooled mixture was worked-up as in the room temperature experiments.

Oxidation of Chloro- and Fluorobenzene Oligomers

The chromic acid method[1–3] was used (70–80°C. for 5–7 hr.) followed by esterification of the product acids in the reaction mixture without isolation. In the case of the fluorobenzene oligomer, five components were found to be present by gas–liquid chromatographic analysis (column A). Methyl *o*- and *p*-fluorobenzoate and dimethyl 4-fluorophthalate were identified by comparison of the infrared spectra with those of the authentic materials.

In the case of the chlorobenzene oligomer, gas chromatography on column A revealed two components. The major one was identified as methyl *p*-chlorobenzoate by retention time and infrared spectrum. The second was found to be dimethyl 4-chlorophthalate by comparison of its infrared spectrum to that of the authentic material. No methyl *m*-chlorobenzoate could be detected.

Dechlorination of Chlorobenzene Oligomer

With Sodium. In a three-necked 100-ml. flask equipped with a 20,000 rpm Labline Stir-O-Vac stirrer, thermometer, and reflux condenser topped with a calcium chloride drying tube, a mixture of oligomer (1 g.), sodium metal (3–5 g.) and solvent (70–80 ml. of mesitylene, Decalin, or mineral oil) was heated to 130–150°C. while stirring was gradually increased to half the rated speed. After 4–5 hr., the cooled mixture was treated with excess ethanol acidified with dilute hydrochloric acid, and steam-distilled. The product was filtered (in the case of mineral oil, nonvolatile solvent was separated at this stage), washed with boiling deionized water and dried.

In one case, with mesitylene as solvent, dechlorination was nearly complete; 0.583 of dark brown product resulted; found: Cl, 0.36%.

Attempts to duplicate the results on a larger scale were less successful as evidenced by the infrared spectrum and weight of the product.

With the Grignard Reagent. Magnesium turnings (1 mole, 24.3 g.) were placed in a 1 liter, three-necked flask equipped with a reflux condenser, Teflon stirrer paddle, and nitrogen gas inlet tube. The flask was gently heated, purged with a stream of nitrogen, and then cooled to room temperature under a nitrogen atmosphere. A solution of oligomer (6.05 g. of soluble fraction) in tetrahydrofuran (500 ml.) was quickly introduced and heated to gentle reflux with stirring. To this mixture was added a solution of ethylene bromide (0.1 mole, 8.7 ml.) in tetrahydrofuran (100 ml.) over a 10 min. period by means of a dropping funnel. Approximately 5 min. after the addition was complete, frothing was noted on the surface and the reaction had to be controlled by means of a water bath. After the exothermic reaction had subsided, the heating mantle was replaced and the mixture was heated at gentle reflux. Throughout the 144-hr. period, solvent loss was compensated for by the addition of tetrahydrofuran.

The black solution was poured onto a mixture of ice and hydrochloric acid, stirred well, and then steam distilled. Final washings were performed with hot deionized water; yield, 6 g. of black solid; found: Cl 1.60%; Br, 0.14%.

Oxidation of Dechlorinated Chlorobenzene Oligomer

To a mixture of dechlorinated oligomer (Grignard method) (5 g.) in glacial acetic acid (285 ml.) was added a solution of chromic anhydride (50 g.) in water (200 ml.). The solution was stirred at 65°C. for 7.5 hr., cooled in an ice bath, diluted with methanol, and filtered to remove unchanged oligomer (1.22 g.). Work-up of the dark green filtrate was then effected by the usual procedure.

Gas–liquid chromatography on column A revealed the presence of three components. The first was not identified. The second had a retention time and infrared spectrum essentially the same as those of authentic methyl benzoate. The third product possessed a retention time and infrared spectrum identical with those of authentic dimethyl phthalate. The

absence of methyl *o*-, *m*-, and *p*-chlorobenzoate, dimethyl isophthalate, and dimethyl terephthalate was shown by comparison of retention times in gas–liquid chromatography.

Preparation of Dimethyl 4-Chlorophthalate

The synthesis was performed essentially according to the method of Ayling.[46] The desired product melted at 35–36°C., lit.[46] m.p.: 37°C.

Preparation of Methyl *o*-, *m*-, and *p*-Chlorobenzoates and Methyl *o*-, *m*-, and *p*-Fluorobenzoates

The general method for synthesis from the corresponding acid was followed as outlined by Vogel[47] for methyl benzoate. Two modifications were used: (*1*) a solution of methanol saturated with hydrogen chloride and containing some sulfuric acid, and (*2*) a longer reaction period, usually overnight.

4-Fluorophthalic Anhydride

Dimethyl 4-aminophthalate was prepared from the nitro precursor by the procedure of Bogert and Renshaw.[48] Conversion of amino to fluoro was effected by a literature procedure.[49] The ester was characterized by conversion to the anhydride through hydrolysis and subsequent gas chromatography, m.p. 76–76.5°C.: lit.[49] m.p.: 76–78°C.

Bromination of *p*-Polyphenyl

In a 250-ml., three-necked flask equipped with a thermometer, reflux condenser, and Teflon paddle stirrer were placed *p*-polyphenyl (2.58 g.), aluminum bromide (6.5 g.), stannic chloride (50 ml.), and bromine (2.8 ml., 0.051 mole). After 2 hr. at 50–60°C., the cooled reaction mixture was slowly poured into concentrated hydrochloric acid. Trituration with acid was carried out in order to insure removal of inorganic material. Final washings were performed with boiling, deionized water; yield, 5.2 g. of brown polymer.

ANAL. Calcd. for $+C_6H_3Br+_n$: C, 46.6%; H, 1.9%; Br, 51.6%. Found: C, 45.69%; H, 1.88%; Br, 47.13%.

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Résumé

La polymérisation du chloro- et fluorobenzene par des chlorures d'aluminium, chlorures de cuivre permet l'obtention d'oligomères fortement colorés. Le chlorobenzène réagit dans des conditions standards, c'est-à-dire dans un rapport molaire 6/1/0.5 des composants aromatique/catalyseur/oxydant à 60°C durant 1 heure et fournit un solide rouge avec 40% de rendement. La structure a été élucidée au départ d'analyses élémentaires par analyse spectrale infra-rouge et ultraviolette, par déchloration, oxydation, mesures de solubilité et de poids moléculaire, et au départ de la couleur. Apparemment la chaîne principale consiste en des unités substituées 1,2,4 avec des atomes de chlore situés en position 4. Les régions polynucléaires sont apparemment comprises dans cette structure. Les données de poids moléculaires indiquent en moyene 10–12 unites par chaîne. Le produit de couplage au départ de fluorobenzène est très semblable aux oligomères chlorobenz'eniques, pour la plupart des aspects. Contrairement au cas du chlorobenzène, il n'y a pas de preuve de propagation résultant d'une attaque en position ortho par rapport à l'atome de fluor. Au départ de bromobenzène, on obtient un para-polyphényl bromé apparemment par disproportionnement en benzène qui alors agit comme monomère. Un mécanisme d' oxydation cationique est proposé pour ces polymérisations.

Zusammenfassung

Die Polymerisation von Chlor- und Fluorbenzol durch Aluminiumchlorid-Kupferchlorid führt zu stark gefärbten Oligomeren. Chlorobenzol reagierte unter den Standardbedingungen, nämlich Molverhältnis Aromat/Katalysator/Oxydationsmittel entsprechend 6/1/0,5 bei 60°C während 1 h unter Bildung eines roten Festkörpers mit 14% Ausbeute. Schlüsse auf die Struktur waren aus Elementaranalyses, Infrarot- und Ultraviolettspketrum, Entchlorierung, Oxydation, Löslichkeit, Molekulargewicht und Farbe möglich. Offenbar besteht die Hauptkette aus 1,2,4-substituierten Bausteinen mit dem Chloratom in 4-Stellung. Ein Teil der Struktur wird von polynuklearen Bereichen gebildet. Molekulargewichtsbestimmungen ergeben im Mittel 10 bis 12 Bausteine pro Kette. Das Kopplungsprodukt aus Fluorbenzol war dem Chlorbenzololigomeren in den meisten Beziehungen sehr ähnlich. Im Gegensatz zum Falle des Chlorbenzols scheint aber das Wachstum in gewissem Ausmass durch einen Angriff in ortho-Stellung zum Fluor stattzufinden. Brombenzol lieferte bromiertes p-Polyphenyl, offenbar durch Disproportionierung zu Benzol, welches dann als Monomeres wirkte. Ein oxydativer kationischer Polymerisationsmechanismus wird vorgeschlagen.

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Studies on Anionic Polymerization of Lactams. Part III. Copolymerization of Pyrrolidone and Caprolactam

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Synopsis

On reacting acetylcaprolactam (AcCL) and pyrrolidonate MgBr (Py^-) in tetrahydrofuran solution, transacetylation takes place, giving acetylpyrrolidone (AcPy) and caprolactamate MgBr (CL^-). The rate constants for the transacetylation reactions were measured at 25°C. Their values in units of liters/mole-second were:

$$AcCL + Py^- \rightarrow AcPy + CL^- \qquad k_{trans\,1} = 60 \times 10^{-2}$$

$$AcPy + CL^- \rightarrow AcCL + Py^- \qquad k_{trans\,2} = 20 \times 10^{-2}$$

The rate constants for the addition reactions measured were:

$$AcPy + Py^- \rightarrow AcPyPy^- \qquad k_{11} = 2.8 \times 10^{-2}$$

$$AcCL + CL^- \rightarrow AcCLCL^- \qquad k_{22} = 0.75 \times 10^{-2}$$

$$AcCL + Py^- \rightarrow AcCLPy^- \qquad k_{21} = 5 \times 10^{-2}$$

$$AcPy + CL^- \rightarrow AcPyCL^- \qquad k_{12} = 2 \times 10^{-2}$$

As the transacetylation is much faster than the addition reaction, the copolymer composition should be given by the equation:

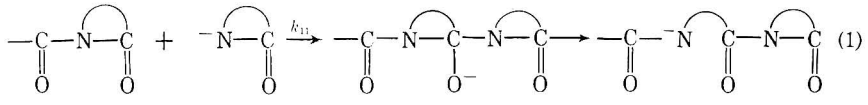
$$[PyH] \text{ in polymer}/[CLH] \text{ in polymer} = K_{trans}K_{acidity}[PyH] \text{ in monomer}/[CLH] \text{ in monomer}$$

where K_{trans}, the transacetylation equilibrium constant, equals 0.3 while $K_{acidity}$ reflects the relative acidities of the monomers and its value (from the literature) is about 0.4. Pyrrolidone is, therefore, more reactive than caprolactam in anionic copolymerization by a factor of about 8.

Introduction

In a previous publication[1] we have studied the addition reaction of pyrrolidonate anion to pyrrolidone and its derivatives, in homogeneous solution in tetrahydrofuran (THF). We have shown that by interacting pyrrolidonate MgBr (Py^-) with acetylpyrrolidone (AcPy) an addition product is formed, and the reaction follows second-order kinetics (Fig. 1). The rate constant determined at 25°C. was $k_{11} = 2.8 \times 10^{-2}$ l./mole-sec. This

value corresponds to the rate of propagation in an actual polymerization experiment, as it is now accepted[1] that the rate-determining step in the anionic polymerization of lactams is the addition reaction shown in eq. (1)



(1)

where $\overset{\frown}{H—N—C=O}$ is a general representation of a lactam. Thus taking acetylpyrrolidone as a model for the propagating chain enables us to study

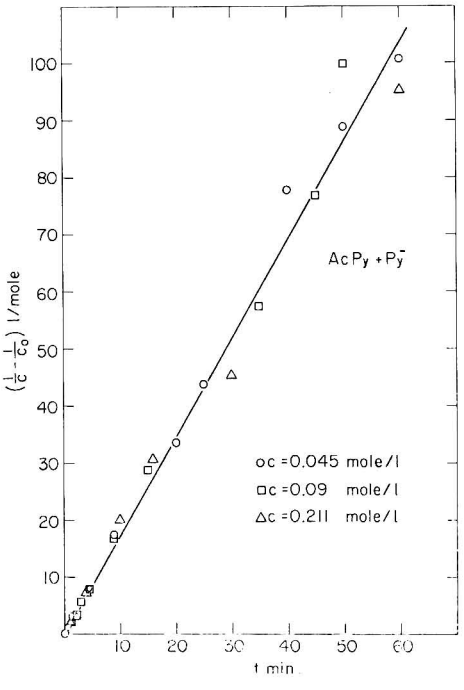


Fig. 1. Second-order plot for the reaction of addition of pyrrolidone MgBr to acetylpyrrolidone.

the addition reaction in the absence of monomer and avoid all the other reactions taking place in an actual polymerizing mixture.

In the present work we have studied the addition of caprolactamate MgBr (CL^-) to acetylcaprolactam (AcCL) as well as the coaddition of Py^- and AcCL. We have found in the latter reaction that instead of simple addition, a rapid transacetylation reaction takes place, yielding AcPy and CL^-. As will be shown later this reaction is rather important and may be the determining factor in the copolymerization of lactams.

Experimental

The experimental procedure was basically similar to that used in Part II.[1]

The solvent, THF, was dried by continuous reflux over Na benzophenone, followed by distillation.

Acetylpyrrolidone and acetylcaprolactam were prepared by prolonged reflux of the respective monomers with acetic anhydride. They were then purified by fractional distillation. The *N*-acetylpyrrolidone had a boiling point of 99°C./4 mm. Hg, while the *N*-acetylcaprolactam had a boiling point of 104°C./3 mm. Hg.

The lactam salts were prepared by reacting the respective monomers with equivalent amounts of freshly prepared butyl MgBr in dry THF.

The reactions were carried out as follows. A measured volume of the acetyl derivative was injected into a small reaction flask kept under nitrogen. The required amount of the appropriate salt solution was then injected into the flask and the contents were mixed rapidly. After the specified period, the reaction was stopped by injecting glacial acetic acid to the mixture. The acid decomposed the Grignard salts and released the free lactams. The solution containing the free lactams and the acetyl derivatives were then analyzed by gas chromatography over a diethylene glycol polyester adipate column at 220°C.

Results and Discussion

The addition of CL^- to AcCL follows a second-order path as shown in Figure 2. The reaction was studied at initial concentrations of 0.165 and

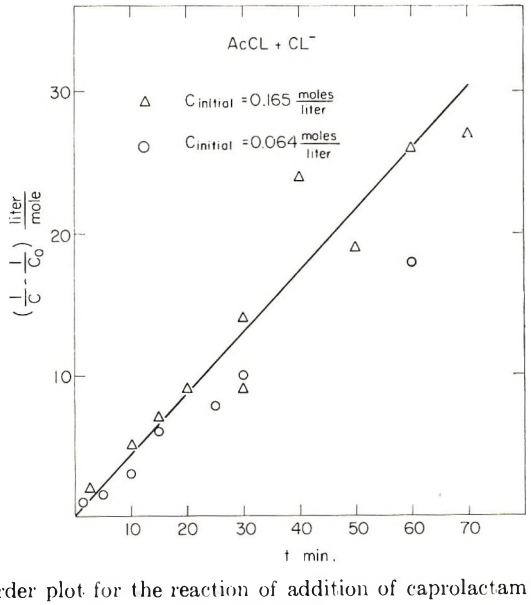
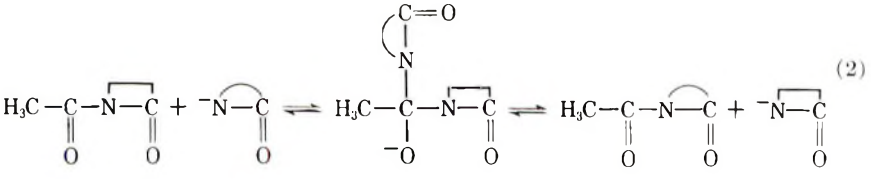


Fig. 2. Second-order plot for the reaction of addition of caprolactam MgBr to acetylpyrrolidone.

0.064 moles/l. The ratio of the two reactants was 1:1 and remained so throughout the reaction. The measured rate constant was $k_{22} = 0.75 \times 10^{-2}$ l./mole-sec. This is a value somehow lower than the corresponding rate constant for pyrrolidone and probably reflects the higher stability of the caprolactamate ring.

The reaction of AcCL + Py^- showed a completely different pattern (Fig. 3). The concentration of the reactants decreased very rapidly and two new products AcPy and CL^- appeared. The concentration of the latter products increased rapidly to a sharp maximum and then decreased at a slower rate. The fast reaction is transacetylation: the anion adds to the penultimate carbonyl group and the original C—N bond breaks, yielding AcPy and CL^- [eq. (2)],



(2)

where H—N—C denotes pyrrolidone and H—N—C denotes caprolactam.

This reaction is very fast, as evidenced by the fact that the maximum is reached in less than 2 min. In order to determine the rate constants for the transacetylation we have carried out a series of experiments at a lower initial concentration of the reactants, namely 0.09 mole/l. The initial parts of the curves are presented in Figure 4. From the initial slope of the curve describing the formation of AcPy and CL^- we can determine the rate constant for the transacetylation reaction, while the initial slope of the curve describing the disappearance of AcCL and Py^- gives the sum of the rate constants of transacetylation and addition of AcCL + Py^-.

TABLE I
Rate Constants for the Reactions of Addition and Transacetylation of Acetylpyrrolidone, Acetylcaprolactam with Pyrrolidone MgBr, and Caprolactam MgBr at 25°C.

Reaction	Rate constant, l./mole-sec.
Homoaddition	
AcPy + Py^- → AcPyPy$^-$	$k_{11} = 2.8 \times 10^{-2}$
AcCL + CL^- → AcCLCL$^-$	$k_{22} = 0.75 \times 10^{-2}$
Coaddition	
AcCL + Py^- → AcCLPy$^-$	$k_{21} = 5 \times 10^{-2}$
AcPy + CL^- → AcPyCL$^-$	$k_{12} = 2 \times 10^{-2}$
Transacetylation	
AcCL + Py^- → AcPy + CL^-	$k_{\text{trans }1} = 60 \times 10^{-2}$
AcPy + CL^- → AcCL + Py^-	$k_{\text{trans }2} = 20 \times 10^{-2}$

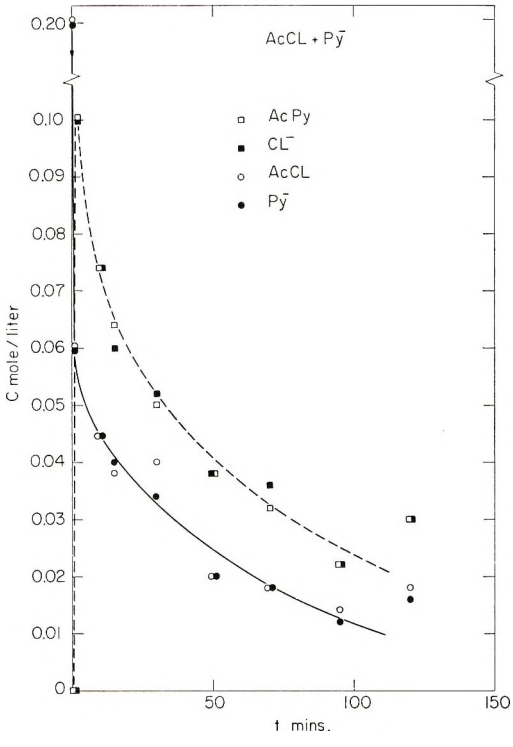


Fig. 3. Plot of the concentrations of the reactants, acetylcaprolactam and pyrrolidone MgBr, as well as the concentrations of the transacetylation products, acetylpyrrolidone and caprolactam MgBr, vs. time. Initial concentration of reactants 0.2 mole/l.

The reaction can also be started from the other direction, namely, interaction of AcPy and CL^-. This is presented in Figure 5 for an initial concentration of reactants, 0.2 mole/l. One should notice that, unlike Figure 3, the curves in this case do not cross. The reason is that the reverse transacetylation is faster. Here too, we have determined the rate constants from experiments carried out at lower initial concentration (0.09 mole/l.). The initial parts of these curves are presented in Figure 6 and the rate constants were determined, as in the previous case from the initial slopes.

Table I summarizes all the reactions and the values of the respective rate constants.

It should be noted that the values for the coaddition constants k_{12} and k_{21} were calculated by the subtraction of two large numbers obtained from initial slopes. Therefore, their accuracy is rather small. It is, however, quite well established that while all the addition rates are more or less of the same order of magnitude, the transacetylation rates are much higher and should be the factor determining the composition of the reaction mixture. One expects therefore, that after transacetylation equilibrium has been achieved, i.e., after reaching the maxima in the curves, the ratio of the components should be maintained constant. This can be verified by com-

paring Figures 3 and 5. It can be seen that the curves describing the concentration of AcCL (or Py^-) are identical in both cases, irrespective of the initial conditions. The same applies to the curves describing the concentration of AcPy (or CL^-). From the concentration of the components at every point one can calculate the transacetylation equilibrium constant:

$$AcPy + CL^- \underset{}{\overset{K_{trans}}{\rightleftharpoons}} AcCL + Py^-$$

$$K_{trans} = [AcCL][Py^-]/[AcPy][CL^-]$$

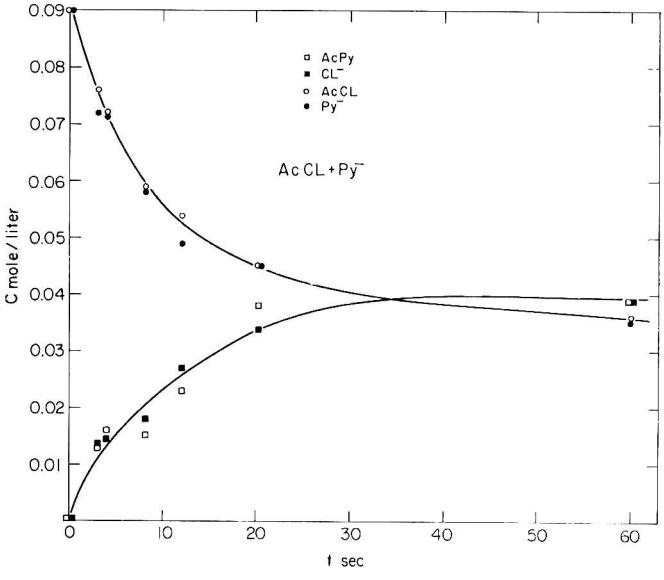


Fig. 4. Initial part of the plot of the concentrations of the reactants, acetylcaprolactam and pyrrolidone MgBr, as well as the concentrations of the transacetylation products, acetylpyrrolidone and caprolactam MgBr, vs. time. Initial concentration of reactants 0.09 mole/l.

The average value obtained from all the measurements is 0.38. The equilibrium constant can also be calculated from the rate constants measured from initial rates:

$$K_{trans} = k_{trans\ 2}/k_{trans\ 1} = 0.3$$

which is in good agreement with the above value.

Another point worth noticing is that all the rate constants of the reactions involving the pyrrolidonate anion are higher than those of the corresponding reactions involving the caprolactamate anion by a factor of about three. This is an indication that Py^- is more reactive than CL^-. However, further elaboration of this point should await more extensive and accurate experimental data.

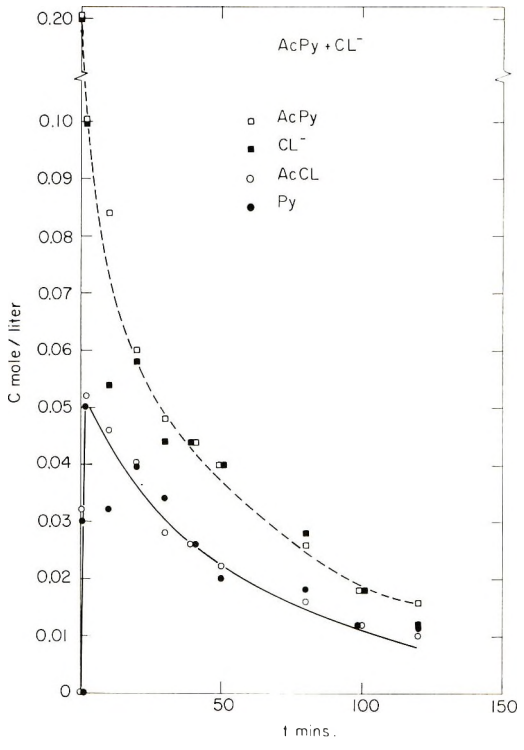


Fig. 5. Plot of the concentrations of the reactants, acetylpyrrolidone and caprolactam MgBr, as well as the concentrations of the transacetylation products, acetylcaprolactam and pyrrolidone MgBr, vs. time. Initial concentration of reactants 0.2 mole/l.

Application to Copolymerization Systems

The copolymerization of pyrrolidone and caprolactam was studied by Kobayashi and Matsuya.[2] The polymerizations were carried out in bulk with the sodium salts of the lactams as initiators and the acetyl derivatives as activators. They analyzed the copolymer composition and concluded that pyrrolidone polymerizes faster than caprolactam at the early stage of the reaction. They admit that the alkaline polymerization of lactams is not the same as addition polymerization and it is therefore improper to discuss the monomer reactivity ratios, but they nevertheless calculate "apparent" reactivity ratios from the results obtained at low conversions. Taking PyH = M_1 and CLH = M_2 they find $r_1 = 5.0$ and $r_2 = 0.75$ at 90°C.

From the results presented here it is our opinion that the monomer reactivity ratios will not have any pronounced effect on the copolymer composition but this will be determined by the transacetylation reaction and the relative acidity of the two monomers, as will be shown below.

Let us denote a growing polymer chain with a pyrrolidone ring at the end by PCH_2COPy. This should react in a way similar to acetylpyrrolidone,

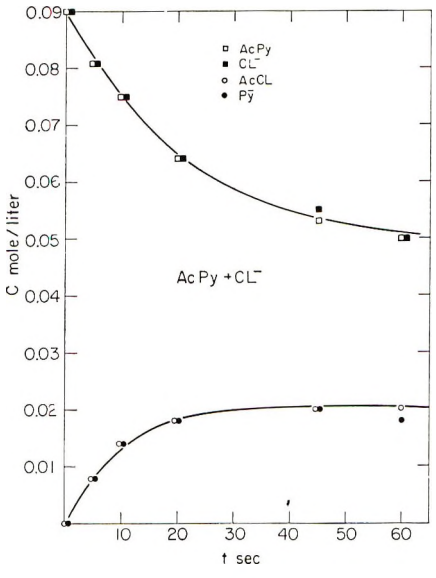


Fig. 6. Initial part of the plot of the concentrations of the reactants, acetylpyrrolidone and caprolactam MgBr, as well as the concentrations of the transacetylation products acetylcaprolactam and pyrrolidone MgBr, vs. time. Initial concentration of reactants 0.09 mole/l.

HCH_2COPy. Denoting a growing polymer chain with a caprolactam ring at the end by PCH_2COCL we can write down a reaction equivalent to transacetylation, namely,

$$PCH_2COPy + CL^- \overset{K_{trans}}{\rightleftharpoons} PCH_2COCL + Py^-$$

As the transacetylation is much faster than the addition reactions we have to conclude that the copolymer composition will be given by the equation

$$[PCH_2COCL]/[PCH_2COPy] = K_{trans}[CL^-]/[Py^-]$$

The ratio $[CL^-]/[Py^-]$ will be determined by the relative acidities of the two monomers

$$Py^- + CLH \overset{K_{acidity}}{\rightleftharpoons} PyH + CL^-$$

This is a proton transfer reaction, and we have shown previously that such reactions are very fast.[3] Kobayashi claims that pyrrolidone is more acidic than caprolactam as its rate of reaction with sodium is higher. However, he does not give any numerical value for the relative acidity. Huisgen[4] measured the pK_a's of various lactams by several methods. From his data we have chosen the values obtained by potentiometric measurements and calculated $K_{acidity} = 0.4$. We can therefore, predict the copolymer composition by the equation

$$[PCH_2COCL]/[PCH_2COPy] = K_{trans}K_{acidity}[CLH]/[PyH]$$
$$= 0.12[CLH]/[PyH]$$

i.e., under our experimental conditions pyrrolidone should be more reactive than caprolactam by a factor of 8. We do not have any copolymerization data from experiments carried out with the Grignard salts of lactams in THF solution at 25°C. in order to verify our prediction. Moreover, such experiments will be difficult to perform, as a precipitate results and the whole kinetic treatment becomes doubtful. We can, however, point out that our predictions are in general agreement with the copolymer composition data obtained by Kobayashi. We hope that extension of this work will bring additional evidence for the effect of transacetylation on the copolymer composition.

In conclusion one should note that the transacetylation reaction described here is only an example of a more general case, where a reversible reaction on a penultimate group can be more significant than the reactions on the endgroup.

This report is taken in part from the Ph.D. thesis of S. Bar-Zakay, submitted to the Graduate School of the Weizmann Institute of Science, 1966.

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2. F. Kobayashi and K. Matsuya, *J. Polymer Sci. A*, **1**, 111 (1963).
3. S. Bar-Zakay, M. Levy, and D. Vofsi, *J. Polymer Sci. B*, **3**, 601 (1965).
4. R. Huisgen and H. Brade, *Chem. Ber.*, **90**, 1437 (1957).

Résumé

En faisant réagir l'acétyl caprolactame (AcCL) et le pyrrolidonate MgBr (Py) en solution dans le tétrahydrofurane, il se fait une transacétylation, donnant l'acétyl pyrrolidone (AcPy) et la caprolactamate MgBr (CL). Les constantes de vitesse de transacétylation furent mesurées à 25°C. Leur valeur en l/mole sec sont: AcCL + Py $\rightarrow$ AcPy + CL, $k_{trans\,1} = 60 \times 10^{-2}$; AcPy + CL $\rightarrow$ AcCL + Py, $k_{trans\,2} = 20 \times 10^{-2}$; Les constantes de vitesse mesurées pour les réactions d'addition sont: AcPy + Py $\rightarrow$ AcPyPy, $k_{11} = 2.8 \times 10^{-2}$; AcCL + CL $\rightarrow$ AcCLCL, $k_{22} = 0.75 \times 10^{-2}$; AcCL + Py $\rightarrow$ AcCLPy, $k_{21} = 5 \times 10^{-2}$; AcPy + CL $\rightarrow$ AcPyCL, $k_{12} = 2 \times 10^{-2}$. Si la transacétylation est plus rapide que la réaction d'addition, la composition du copolymère sera donnée par l'équation: PyH dans le polymère/(CLH) dans le polymère = $K_{trans} \cdot K_{acidité}$ [(PyH) dans le monomère/(CLH) dans le monomère]. où K_{trans}, la constante d'équilibre de transacétylation vaut 0.3 tandis que $K_{acidité}$ donne l'acidité relative des monomères et sa valeur (tirée de la littérature) est environ 0.4. La pyrrolidone est, pour cela, plus réactionnelle que la caprolactame dans la copolymérisation anionique, et ce par un facteur de 8 environ.

Zusammenfassung

Bei der Reaktion von Acetylcaprolactam (AcCL) mit Pyrrolidonat -MgBr(Py^-) in Tetrahydrofuranlösung findet Transacetylierung unter Bildung von Acetylpyrrolidon (AcPy) und Caprolactamat-MgBr (CL^-) statt. Die Geschwindigkeitskonstanten der Transacetylierungsreaktionen wurden bei 25°C gemessen. Ihre Werte betragen in l/Mol sec: AcCL + Py^- $\rightarrow$ AcPy + CL, $k_{trans\,1} = 60 \times 10^{-2}$; AcPy + CL^- $\rightarrow$ AcCL

+ Py^-, $k_{trans\,2} = 20 \times 10^{-2}$; Die Geschwindigkeitskonstanten der gemessenen Additionsreaktionen waren: AcPy + Py^- → $AcPyPy^-$, $k_{11} = 2{,}8 \times 10^{-2}$; AcCL + CL^- → $AcCLCL^-$ $k_{22} = 0{,}75 \times 10^{-2}$; AcCL + Py^- → $AcCLPy^-$, $k_{21} = 5 \times 10^{-2}$; AcPy + CL^- → $AcPyCL^-$, $k_{12} = 2 \times 10^{-2}$. Da die Transacetylierung viel rascher verläuft als die Additionsreaktion sollte die Copolymerzusammensetzung durch die Gleichung ([PyH]/[CLH]) im Polymeren = $K_{trans} \cdot K_{Säurestärke}$([PyH]/[CLH]) im Monomeren gegeben sein, wo K_{trans}, die Transacetylierungsgleichgewichtskonstante, gleich 0,3 ist, während $K_{Säurestärke}$ die relative Säurestärke der Monomeren enthält und ihr Wert (nach der Literatur) etwa 0,4 beträgt. Pyrrolidon ist daher bei der anionischen Copolymerisation etwa um einen Faktor 8 reaktiver als Caprolactam.

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Poly(chloroaldehydes). IV. Copolymerization of Chloral and Dichloroacetaldehyde Catalyzed by Organometallic Compounds*

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Synopsis

The copolymerization of chloral and dichloroacetaldehyde (DCA) has been studied with the use of organometallic compounds as initiators. The alkylzincs were the most effective catalysts, giving good conversions to copolymers of apparently high molecular weight. The polymerizations were best carried out at temperatures below −40°C. at an initiator concentration of at least 0.4 mmole/mole of monomers. The copolymerization proceeds to high conversions in toluene as the solvent, but the presence of small amounts of either *n*-heptane or tetrahydrofuran greatly decreases the yield. This, coupled with the fact that little polymerization occurs at DCA concentrations above 70 mole-%, leads to the proposal of a propagation reaction mechanism involving the coordination of the monomeric aldehydes with a cyclic zinc alkoxide dimer. Monomer reactivity ratios with chloral as M_1 and DCA as M_2 were $r_1 = 1.50$ and $r_2 = 0.65$. The copolymer is stiff and inelastic with a tensile strength of ca. 6000 psi.

Previous reports[1–3] from this laboratory have described the homopolymerization of both chloral and dichloroacetaldehyde (DCA). Polychloral is very intractable and no solvent for it has been found. Polydichloroacetaldehyde, on the other hand, is much more manageable[3,4] and can be dissolved and molded. This paper deals with some of the factors surrounding the copolymerization of these two similar, yet dissimilar, aldehydes. Organometallic catalysts were chosen for the study because previous work[2,5] with chloral showed high molecular weight polymers to result when this type of initiator is used.

EXPERIMENTAL

Monomers and Solvents

The chloral and DCA were purified by distillation under high purity nitrogen as described previously.[2,3] The DCA was a commercial product

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(FMC Corp.) and contained, after purification, about 95% DCA and 5% chloral. The water content of the dried aldehydes, as determined by a colorimetric Karl Fisher technique, was generally less than 20 ppm.

The solvents employed were purified by distillation from sodium and were stored over sodium.

All reaction components were stored under nitrogen in specially equipped vessels which permitted transfers to be made with hypodermic syringes, following the technique described by Ford and Kiss.[6]

Polymerization

Two polymerization techniques (agitated and/or in-place) were employed, depending on the type of data desired.

In the agitated system, the reaction was carried out in a four-necked flask equipped with a stirrer, gas inlet, and a small auxiliary side-arm flask connected to the reactor by means of a combination of a 75° connecting tube and vacuum adapter. The fourth opening was closed with a serum cap. The apparatus was dried by baking at 130°C. and was assembled while hot in a stream of high-purity nitrogen. The system was made dry and oxygen-free by the usual technique of alternately evacuating it and bleeding it back to atmospheric pressure with nitrogen. The solvent and catalyst were introduced into the reactor with hypodermic syringes through the serum cap. The monomers were injected into the auxiliary flask through the side arm which was then closed with a stopcock.[6] After cooling all components to the desired temperature with Dry Ice–methanol baths, the monomers were added to the catalyst solution by inverting the small flask, i.e., by rotating the entire flask–75° connecting tube assembly 180° around the vacuum adapter connection. High viscosity generally made the agitation ineffective after about a 30% conversion.

Except where otherwise noted, polymerizations carried out by this method were at −78°C. with 0.25 mole of monomers in 18 ml. of toluene at a catalyst concentration of 1.6 mmole/mole of monomers. The agitated system was primarily employed to study polymerization variables.

In-place polymerization, the second polymerization technique, was used to provide samples for physical testing. This process, which was successful only when at least 15 mole-% DCA was present in the monomer mixture, involved conducting the reaction in a horizontal 12 × 12 × 0.5 in. stainless steel mold. The prechilled reactants were combined in a jacketed mixing vessel the bottom opening of which was attached to the mold through a large stopcock. Mixing time did not exceed 30 sec., and the transfer to the mold was as rapid as possible. The mold and mixer temperatures were kept at −70 to −75°C. by means of suitable Dry Ice–methanol baths, and both were freed of oxygen and moisture as described previously for the agitated system. After 20 hr. at −70°C., the polymerization was halted with a small amount of 0.3% ethanolic HCl. The slab of polymer, varying in thickness according to the quantity of monomers used, was soaked for 3–4 hr. in 0.5% methanolic HCl, followed by several

days' extraction with cold diethyl ether. It was then dried in a vacuum oven.

The uncapped polymers, pulverized when necessary, were purified for analysis by extracting for 8 hr. with chloroform in a Soxhlet extractor. The compositions were calculated from analyses for carbon and chlorine.

Capping

The capping procedure was much as described previously.[1] However, a modification was required for the slabs produced by the in-place technique. These sheets were soaked for 1 day in acetic anhydride at room temperature, after which the temperature was raised to 150°C. for 50 min. The treated polymer was extracted first with a 1:1 (volume) methanol–methyl ethyl ketone mixture for 2–3 hr., then with methanol, and finally was dried in a vacuum oven. The capping efficiency was determined in the same manner as in the previous work.[1]

RESULTS AND DISCUSSION

While success was achieved in copolymerizing chloral and DCA, no significant improvement in solubility over chloral homopolymer was found. Similarly, the copolymers are infusible, although something akin to cold flow occurs under heat and pressure. A number of interesting facets were uncovered however, and the in-place polymerization provided samples for studies of physical properties. These are discussed in the following sections.

Effect of Organometallic Compounds

Table I is a summary of the results obtained when several different organometallic compounds were used to initiate the copolymerization.

TABLE I
Copolymerization of Chloral and DCA with Various Organometallic Catalysts[a]

Catalyst	Catalyst concn., mmoles/mole monomers	Conversion, %	DCA in copolymer, mole-%
Et_2Zn	1.6	72	39
$Et_2Zn \cdot 2MeOH$	1.6	57	32
$Et_2Zn \cdot H_2O$	1.6	84	28
$EtZnCl$	1.6	25	49
$n\text{-}Bu_2Zn$	1.6	61	23
$n\text{-}Hex_2Zn$	1.6	38	30
$(C_6H_5)_2Zn$	1.6	0	—
Et_2Cd	2.8	36	37
Et_2Mg	1.6	1.4	—
$n\text{-}BuLi$	2.4	0.5	48

[a] Monomer mole charge ratio 70:30 (chloral/DCA).

These data show, in agreement with the work of Furukawa et al.[5] on polychloral, that the zinc alkyls are the most efficient initiators. The diethylzinc–water system however, is not as advantageous as these results imply, for reproducibility was at times difficult with this catalyst. It is suspected that this difficulty was due to sensitivity to minor amounts of impurities in the monomers or solvent. As will become evident later, the higher zinc alkyls have some practical advantages over diethylzinc. These advantages compensate for the somewhat reduced conversions.

Apparently, all of these initiators produced high molecular weight polymers, although insolubility prevented quantitative determinations by the usual techniques. All at least were of degrees of polymerization greater than 40, as estimated by the end-capping technique.[1]

Polymerization Temperature

Increasing the polymerization temperature severely decreases the conversion (Fig. 1). This effect is undoubtedly related to a greater opportunity at more elevated temperatures for the initiator and monomers to become involved in reactions other than polymerization. If the less reactive dihexylzinc is substituted for the diethylzinc–water initiator system used here, the slope of the line is lessened, as is predictable on the basis of decreased competition by interfering side reactions. If the chloral concentration is raised from 70 mole-% to 90 mole-%, a somewhat increased sensitivity to temperature has been found.

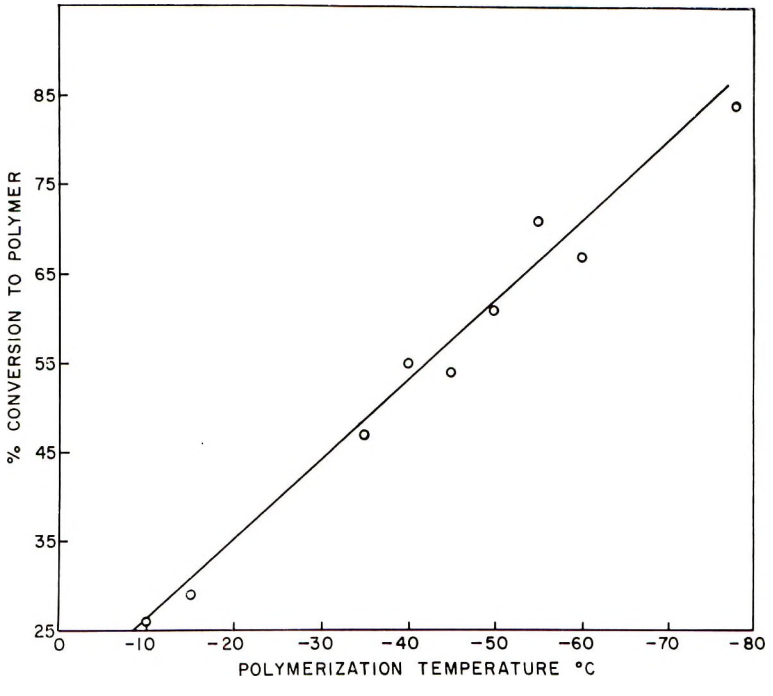


Fig. 1. Effect of polymerization temperature on conversion.

A corollary to the effect of temperature on conversion is the expected simultaneous decrease in degree of polymerization. This, however, must remain a qualitative observation based on the appearance and instability of copolymers prepared at higher temperatures, particularly when that temperature exceeds −25°C.

Effect of Solvent

An important component of this polymerization system is the solvent, and considerable specificity has been found in this respect (Table II).

TABLE II
Effect of Solvent on Chloral–DCA Copolymerization[a]

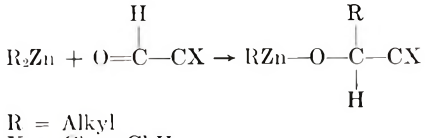
Secondary solvent[b]	Vol.-% secondary solvent in system	Conversion, %	DCA in copolymer, mole-%
None	0	84	28
THF[c]	3	18	83
n-Heptane	100	2	54
"	50	20	58
"	10	70	32

[a] Monomer mole charge ratio 70:30 (chloral/DCA); catalyst, $Et_2Zn \cdot H_2O$.
[b] Primary solvent was toluene.
[c] Catalyst concentration 4.6 mmole/mole monomers.

Toluene is clearly the best medium for the reaction. Both tetrahydrofuran and heptane drastically reduce the conversion, even when present in minor proportions. Tetrahydrofuran substantially increases the proportion of DCA incorporated, but at the expense of polymer yield. Heptane, predictably, does not have much effect on copolymer composition but it causes a striking and unexpected decrease in conversion. This behavior has not been found to occur with chloral alone, although some solvent effects in the cationic polymerization of DCA have been observed.[3]

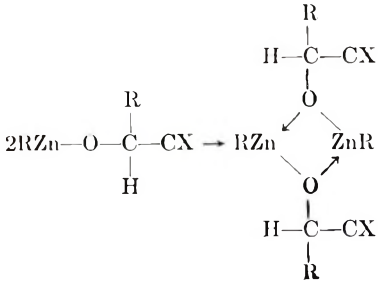
A suggested explanation for the effect of solvent on the copolymerization is that toluene promotes the coordination of the catalyst with one or both monomers so that copolymer propagation is facilitated. The work of Fujii et al.[7] on the mechanism of the aluminum alkyl-initiated stereoregular acetaldehyde polymerization lends some support to this concept. These workers found that the stereospecific initiating species appeared to be a cyclic complex involving two molecules each of acetaldehyde and triethylaluminum. The steric features of this complex are such that they encourage the propagation of a stereoregular polymer chain. A similar intermediate may be required for the chloral–DCA copolymerization (stereospecific or otherwise), and the series of reactions shown in eqs. (1)–(3) can be postulated.

Initiation



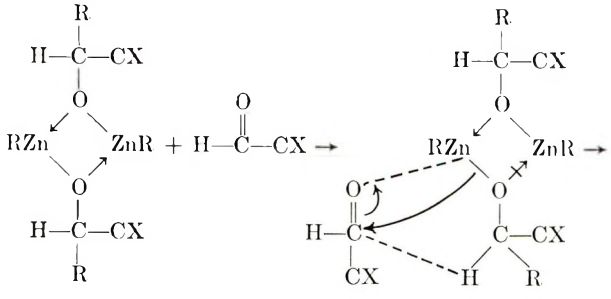
(1)

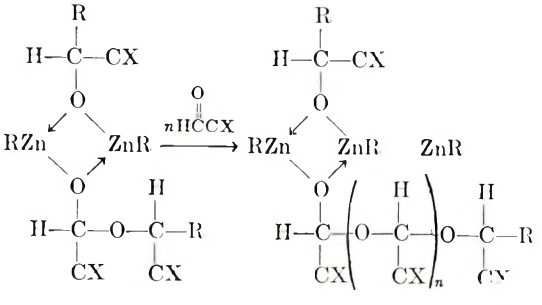
R = Alkyl
X = Cl_3 or Cl_2H



(2)

Propagation:





(3)

It is speculated that because of the combination of the bulk and polarity of the two monomers, the requirements for this complex are more stringent than those of more simple systems. Thus, the assistance of an aromatic solvent such as toluene is required to form the initiating complex.

Monomer Composition

Table III shows the effect upon conversion of increasing the proportion of DCA in the monomer mixture. The change from $Et_2Zn{\cdot}H_2O$ to Et_2Zn

as the catalyst at higher DCA concentrations was necessitated by the poor reproducibility which occurred with the water-modified system. As intimated previously, this probably is related to the difficulty found in purifying the DCA, which is somewhat more troublesome than chloral.

TABLE III
Effect of Chloral/DCA Ratio on the Copolymerization

DCA monomer, mole-%	Catalyst	Conversion, %	DCA in copolymer, mole-%
10	$Et_2Zn \cdot H_2O$	54	23
30	"	84	28
40	"	50	41
50	"	64	48
60	Et_2Zn	45	75
65	"	39	60
70	"	Trace	—

It is apparent that the copolymerization proceeds best when the system is rich in chloral. This effect is not unexpected, since earlier work[3] has shown that DCA homopolymerization does not proceed well under anionic or neutral conditions, but requires a Lewis acid catalyst.

If the mechanism proposed previously in this paper is valid, it must be assumed that DCA does not participate in the cyclic complex to any great extent when another molecule of DCA is already present. Thus, at least one of the two aldehyde molecules coordinated with the zinc alkoxide in the propagation step seems required to be chloral.

Catalyst Concentration

The conversion to copolymer was found to be relatively insensitive to catalyst concentration, as is illustrated by Table IV.

TABLE IV
Effect of Et_2Zn Concentration on the Chloral–DCA Copolymerization[a]

Et_2Zn concentration, mmole/mole monomers	Conversion, %	DCA in copolymer, mole-%
1.6	58	46
0.6	47	56
0.5	50	41
0.37	45	58

[a] Monomer mole charge ratio 70:30 (chloral/DCA).

At low initiator levels, monomer and solvent purity become exceedingly important if reliable results are to be obtained. For this reason, it is not generally practical to operate below the 1 mmole/mole concentration.

Monomer Reactivity Ratios

While monomer reactivity ratios obtained in ionic systems are of limited value, they do have some utility under specific conditions. The initiator used in this determination was dibutylzinc and the reaction was conducted

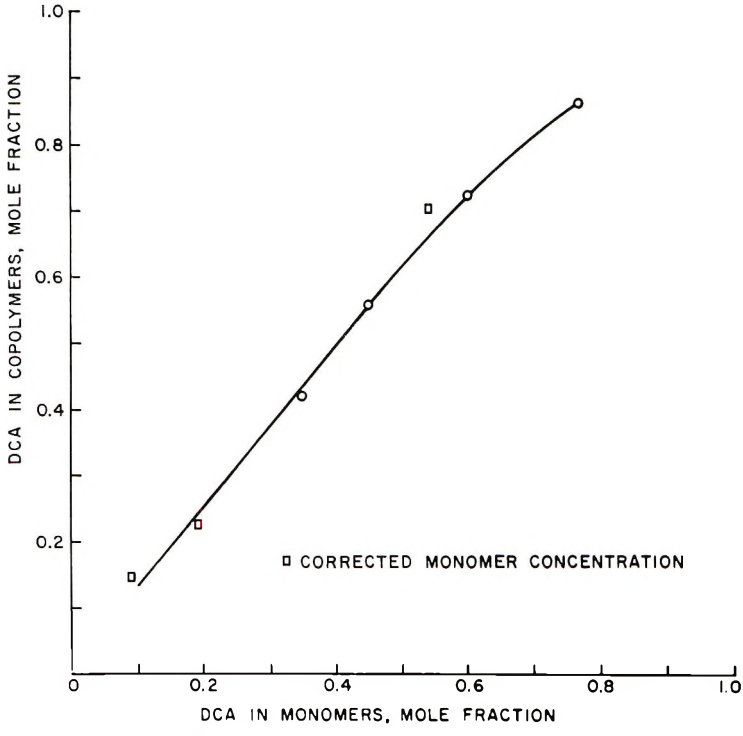


Fig. 2. Copolymer composition curve.

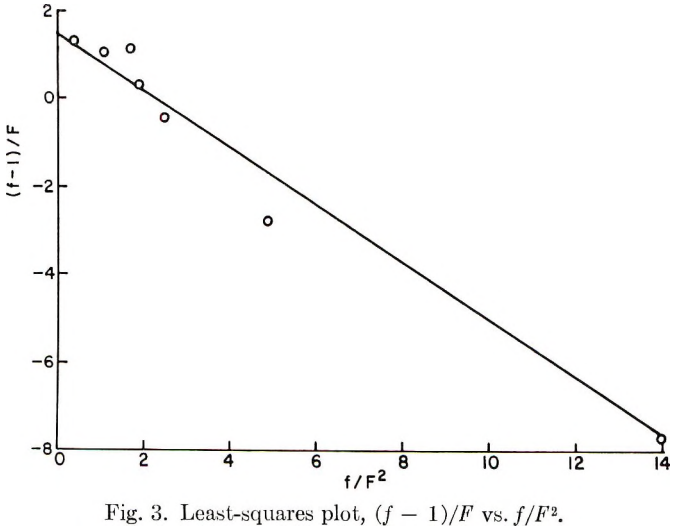


Fig. 3. Least-squares plot, $(f - 1)/F$ vs. f/F^2.

at −78°C. in toluene. In spite of all efforts to limit the conversion to 10%, the rapidity of the polymerization made this difficult. Thus, when 10, 20, and 55 mole-% DCA were present in the monomer mixture, polymer yields obtained were 14, 14, and 13%, respectively. These three monomer concentrations were converted to average values for use in the reactivity ratio calculations by employing the simple empirical relationship of Alfrey et al.:[8] $M(\text{av.}) = M + {}^1/_2(M\text{-}m)$ (% conversion), where M is the mole fraction DCA in the monomeric mixture and m is the mole fraction DCA in the copolymer.

Figure 2 presents the copolymer composition curve drawn with these values. From these data the reactivity ratios were computed by using the relationship of Fineman and Ross.[9] An IBM 1620 computer was used to perform the actual calculations, and the monomer reactivities were determined by the method of least squares as represented in Figure 3. With chloral as M_1 and DCA as M_2, $r_1 = 1.50$ and $r_2 = 0.65$. The fact that $r_1r_2 \approx 1$ is in agreement with the behavior often found in ionic vinyl copolymerizations, particularly when the monomers are similar in polarity.[10] This is attributed to entropy effects in the transition state.[11]

Physical Properties

As has already been mentioned, an in-place polymerization technique was developed to prepare samples suitable for physical testing. These copolymers were made at −78°C. with either dibutyl- or dihexylzinc as the catalyst. These higher zinc alkyls were found preferable to diethylzinc

TABLE V
Mechanical Properties of Chloral–DCA Copolymers

Conversion, %	DCA, mole-%	Tensile strength, psi	Tensile modulus, psi × 10^2	Elongation, %	Deflection temperature (264 psi), °C.
76[a]	28	6200	1450	16	127
74[b]	28	5700	1807	8	121
75[c]	44	6450	2450	12	138
78[c]	46	5650	1745	12	125

[a] Dihexylzinc catalyst, 1 mmole/mole of monomers.
[b] Dibutylzinc catalyst, 1 mmole/mole of monomers.
[c] Dibutylzinc catalyst, 1.6 mmole/mole of monomers.

because when the latter was employed, the sheets were filled with many tiny bubbles. Acting on the premise that these voids are due to ethane generated by side reactions of the initiator with the monomers and/or impurities, we substituted long-chain alkyl zincs for diethylzinc. This eliminated the problem.

The slabs of copolymer were prepared for testing by pressing at 8000 psi and 400°F. between polished plates. Under these conditions, sufficient

flow occurred to eliminate surface irregularities. In Table V are listed some of the results of this evaluation.

The copolymers can be described as moderately strong, stiff, and inelastic materials with good heat distortion properties. Their Shore D hardness was about 80, in the same range as polyoxymethylene and unplasticized poly(vinyl chloride). A limited number of determinations of impact strength indicated an Izod notched impact strength of about 1.3 ft.-lb./in. of notch. Interestingly, all properties measured were independent of the proportion of DCA present. This lack of sensitivity to

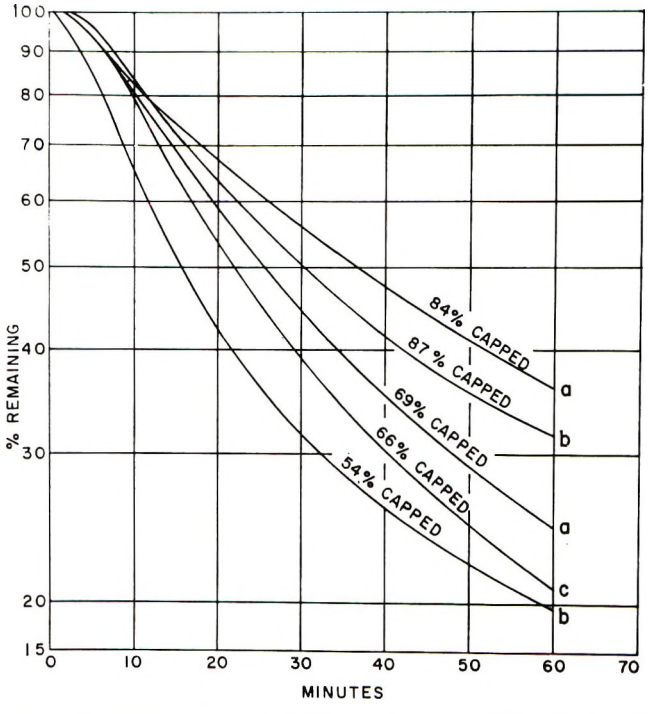


Fig. 4. Thermogravimetric analysis at 220°C. in nitrogen: (*a*) 70:30 Chloral:DCA molar ratio; (*b*) 85/15 Chloral:DCA; (*c*) 80/20 Chloral:DCA.

copolymer composition can be attributed to the isomorphism of polychloral and polydichloroacetaldehyde.[12] Catalyst concentration, in the range studied, also does not have much of an effect on mechanical properties.

The thermal stability of the copolymers is illustrated by the family of thermogravimetric analysis curves in Figure 4. These curves were obtained at 220°C. in a nitrogen atmosphere with a Stanton thermobalance. The percent capped refers to the proportion of treated copolymer surviving exposure to hot dimethylformamide.[1] The curves show that even when terminated by ester groups, the thermal stability of chloral–DCA copolymers is rather poor. In this respect, the capped copolymers are intermediate between similarly terminated homopolymers of DCA and chloral, i.e.,

they are more stable than the former and less stable than the latter.[1,3] The efficiency of the elimination of unstable endgroups, however, does have an appreciable effect upon the ultimate thermal properties of the copolymer just as has been found with other linear aldehyde polymers.

The authors wish to thank G. Enyedy and his co-workers for their aid in the determination of the monomer reactivity ratios. In addition, the technical assistance of Mr. A. Riihimaki and Mr. W. E. Marshall in the experimental work is gratefully acknowledged.

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Résumé

La copolymérisation du chloral et du dichloracétaldéhyde (DCA) a été étudiée en utilisant des composés organométalliques comme initiateurs. Les zincs alkoyls étaient les catalyseurs les plus efficaces donnant de bonnes conversions de copolymères de poids moléculaire apparemment élevé. Les polymérisations étaient le mieux effectuées à des températures inférieures à -40°C, avec concentration en initiateur d'au moins 0.4 mmole/mole de monomère. La copolymérisation atteint des degrés élevés de conversion dans le toluène comme solvant, mais la présence de faibles quantités soit de *n*-heptane ou de tétrahydrofurane décroit considérablement le rendement. Ceci, outre le fait que la polymérisation ne se passe que faiblement à des concentrations en DCA supérieures à 70% mole, amène à la supposition que le mécanisme de la réaction de propagation résulte de la coordination des aldéhydes monomériques avec le dimère cyclique du zinc dialkoxide. Les rapports de réactivité des monomères avec le chloral (M_1) et le DCA (M_2) sont $r_1 = 1.50$ et $r_2 = 0.65$. Le copolymère est rigide, il est non élastique avec une force de tension d'environ 6000 psi.

Zusammenfassung

Die Copolymerisation von Chloral und Dichloracetaldehyd (DCA) wurde mit metallorganischen Verbindungen als Starter untersucht. Die Zinkalkyle waren die wirksamsten Katalysatoren und lieferten offenbar hochmolekulare Copolymere in guter Ausbeute. Die Polymerisation wurde am besten bei Temperaturen unterhalb -40°C bei einer Starterkonzentration von mindestens 0,4 mMol pro Mol Monomeres ausgeführt. Die Copolymerisation verläuft in Toluollösung zu hohen Umsätzen, die Gegenwart kleiner Mengen von *n*-Heptan oder Tetrahydrofuran setzt aber die Ausbeute stark herab. Dieser Umstand führt gemeinsam mit der Tatsache, dass bei DCA-Konzentrationen oberhalb 70

Mol% nur geringe Polymerisation stattfindet, zur Annahme eines Wachstumsmechanismus mit Beteiligung einer Koordination der monomeren Aldehyde und einem cyclischen Zinkalkoxyddimeren. Die Monomer aktivitätsverhältnisse mit Chloral als M_1 und DCA als M_2 sind: $r_1 = 1{,}50$ und $r_2 = 0{,}65$. Das Copolymere ist steif und unelastisch, mit einer Zugfestigkeit von ca. 6000 psi.

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Effect of Temperature and Polymer Type on Gel Permeation Chromatography*

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Synopsis

A series of polyisobutene and polystyrene fractions was subjected to gel-permeation chromatography at 150°C. The two types resulted in distinctly different calibration curves in a plot of projected, extended chain length versus elution volume. The average end-to-end distances of the samples were determined by intrinsic viscosity measurements. It was found that these data plotted versus elution volume could be represented by a common curve for both polymer types. The elution volumes of the polyisobutene series were determined at three additional temperatures, 35, 70, and 110°C. It could be shown that elution volume is again determined by polymer coil size at the temperature of measurement.

Introduction

Gel permeation chromatography (GPC) is a convenient and rapid method for determining the molecular weight distribution of polymers.[1] Each particular set of gel columns has to be calibrated, usually by eluting a series of fractions of known molecular weight. A calibration curve may be obtained by plotting elution volumes versus projected, extended chain length of the corresponding polymers.[2,3] Present theory of GPC suggests that molecular coil size should be a more universal measure than extended chain length. Various papers in the literature report the use of molecular radii for establishing calibration curves, for instance, Ackers,[4] Smith and Kollmannsberger,[5] Meyerhoff,[6] and Hendrickson and Moore.[7] In the following, experiments are described to vary the coil size for given molecular weights by changing polymer type and GPC operating temperature. Attempts are made to correlate polymer size under these conditions and corresponding elution volumes.

Experimental

The chromatographic measurements were carried out on a commercial Waters GPC unit.[3] A combination of four columns containing crosslinked polystyrene gel with 10^3, 10^4, 10^5, and 10^6 A. nominal pore size were used. The solvent was 1,2,4-trichlorobenzene. Three sharp polyisobutene frac-

* Part X in a series of papers on column fractionation of polymers.

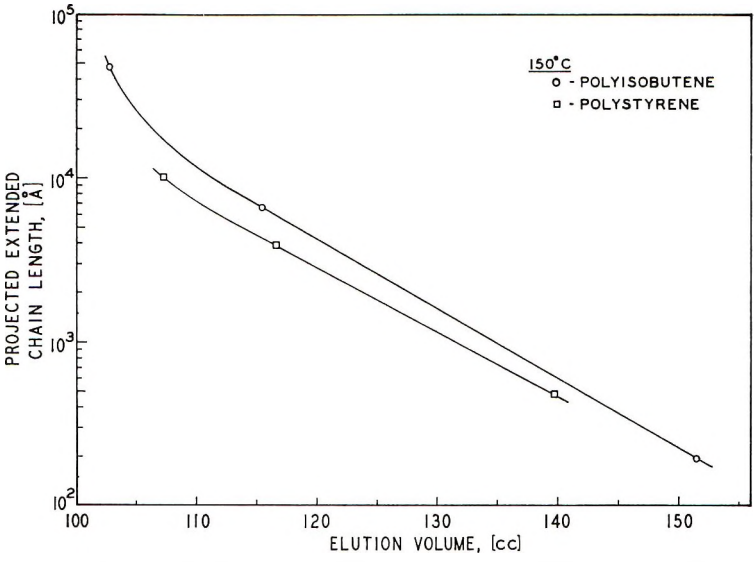

Fig. 1. Dependence of elution volume on extended chain length.

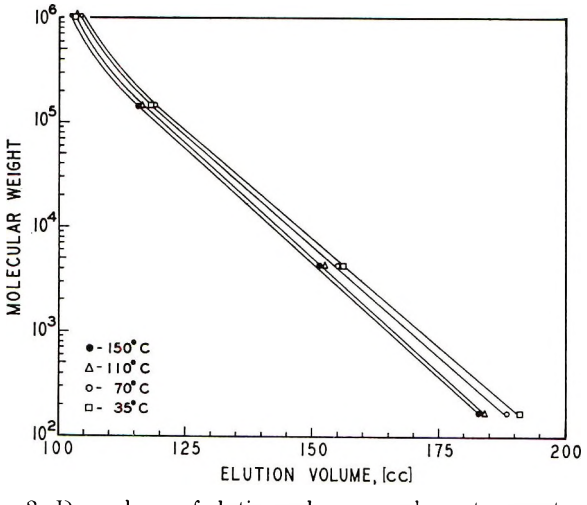

Fig. 2. Dependence of elution volume on column temperature.

tions, obtained by a Baker-Williams type column fractionation,[8] of viscosity-average molecular weights 1,050,000; 146,000; and 4,300; respectively, and three sharp polystyrene fractions (Pressure Chemical Company, Pittsburgh) of viscosity-average molecular weights 411,000; 160,000; and 19,800, respectively, were eluted at 150°C. The flow rate was 0.93 cc./min. The elution volumes are plotted in Figure 1 in the conventional way as functions of their projected, extended chain lengths. Two distinctly different calibration curves are obtained in this manner.

The same three polyisobutene fractions and triisobutylene were eluted at three additional temperatures, 110, 70, and 35°C., at flow rates of 1.05,

0.63, and 0.51 cc./min., respectively. Figure 2 shows the results, again plotted in the conventional manner. A pronounced shift with increasing temperature toward lower elution volumes is observed.

The Staudinger indices $[\eta]$ were determined for all six fractions in 1,2,4-trichlorobenzene at 35 and 150°C. The measurements were carried out at one low concentration only, and a Huggins constant of 0.3 was used to extrapolate to zero concentration. No kinetic energy corrections were applied. From the values of $[\eta]$ and the known molecular weights M, the end-to-end distances, h, of the fractions at the two temperatures were determined according to the method described by Ptitsyn and Eizner[9]

$$[\eta] = \Phi(\epsilon)(\bar{h^2})^{3/2}/M \tag{1}$$

with

$$\Phi(\epsilon) = 2.86 \times 10^{23}(1 - 2.63\epsilon + 2.86\epsilon^2) \tag{2}$$

The proper values of ϵ were obtained from the measured relations between $[\eta]$ and M.

Discussion

Figure 3 shows a plot of end-to-end distance versus elution volume for polystyrenes at 150°C. and polyisobutenes at 35 and 150°C. All points, with the possible exception of the highest elution volume, are well represented by a single curve. This indicates that the effective size of a molecule under experimental conditions largely determines its elution volume.

It might be well to consider what other variables would affect elution volume if the operating temperature of the GPC unit is raised:

The solvent flow rate can increase due to a decrease in viscosity. Meyerhoff[6] observed a minor shift toward lower elution volumes by a four- to

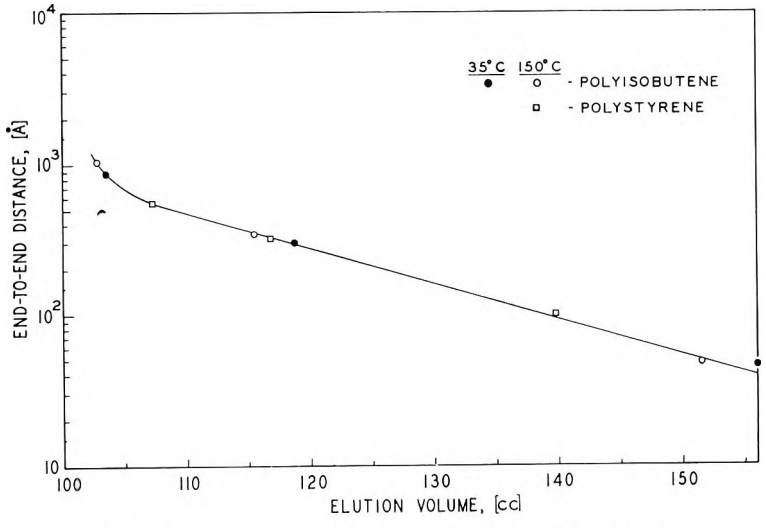

Fig. 3. Dependence of elution volume on polymer coil size.

eightfold increase in flow rate. Experimental conditions in this investigation make an effect of flow rate improbable.

A temperature increase will tend to expand the gel in the columns and thus change the distribution of pore sizes. In the experimental part, the increase of size with temperature was determined for free polystyrene molecules. At a molecular weight of 100,000 and an increase in temperature of 115°C., the linear expansion coefficient of polystyrene was found to be 1.05 and that of polyisobutene 1.17. The expansion of the highly restricted polystyrene gel in the columns should be much less pronounced. Nevertheless, a limited increase in internal gel volume V_2 and a decrease in interstitial volume V_1 must be expected. A model calculation advanced by Vink[10] allows one to estimate the effect of this change upon the relative peak velocity ν, which is defined as the ratio between the absolute peak velocity and the velocity of the mobile phase. This quantity is given by

$$\nu = [1 + \gamma(V_2/V_1)]^{-1} \tag{3}$$

where γ is the partition coefficient. Equation (3) would predict an increase in elution volume with increasing temperature. The experimental results, therefore, exclude swelling of the gel as a significant factor in affecting elution volumes under the given conditions.

Adsorption of the polymer on the gel is assumed to play no part in an ideal GPC separation. In an actual experiment, however, adsorption will occur to a limited extent. For all practical purposes, it will be restricted under existing experimental conditions to the lower molecular weight polymers, since they have a much higher surface area in the gel at their disposal.[11,12] It is in this molecular weight region where a decrease of adsorption with increasing temperature could be expected. This might explain the rather large difference in elution volume with temperature at the low molecular weight end of Figure 3, where a change in coil size is not detectable by experiment.

Separation by GPC is largely determined by the pore volume accessible to each polymer species. If a variation in diffusion coefficient has any effect on the elution volume,[5,13] then this effect would again be more pronounced for lower molecular weights by a factor of $M^{-\delta}$. Here δ is the exponent in the equation relating molecular weight and coefficient of diffusion.

In summary, it was found that the effective hydrodynamic size of a polymer molecule is the quantity which largely determines the elution volume of that particular molecule in GPC under the experimental conditions employed in this investigation.

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Résumé

Une série de polyisobutène et de fractions de polystyrène ont été soumises à la chromatographie par permeation sur gel à 150°C. Les deux types résultaient en des courbes de calibrage différentes en ce qui concerne le diagramme de la longueur de chaine étendue projetée en fonction du volume d'élution. Les rayons hydrodynamiques moyens des échantillons ont été déterminés par mesure de la viscosité intrinsèque; on a trouvé que ces rayons portés en diagramme en fonction du volume d'élution pouvaient être représentés par une courbe commune pour les deux types de polymères. Les volumes d'élution des séries polyisobuteniques étaient déterminés à trois température additionnelles, 35, 70 et 110°C. On a pu montré que le volume d'élution étaient à nouveau déterminé par les dimensions de la pelote polymérique à la température de mesure.

Zusammenfassung

Eine Reihe von Polyisobuten- und Polystyrolfraktionen wurden der Gelpermeationschromatographie bei 150°C unterworfen. Die beiden Typen führten im Diagramm, Projektion der gestreckten Kettenlänge gegen Eluierungsvolumen, zu deutlich verschiedenen Kalibrierungskurven. Der mittlere Fadenendenabstand der Proben wurde durch Viskositätszahlmessungen bestimmt. Die Auftragung dieser Werte gegen das Eluierungsvolumen lieferte für beide Polymertypen eine gemeinsame Kurve. Das Eluierungsvolumen wurde in der Polyisobutenreihe bei drei weiteren Temperaturen, 35, 70, und 110°C, bestimmt. Auch in diesen Fällen ist das Eluierungsvolumen durch die Knäuelgrösse des Polymeren bei der Messtemperatur bestimmt.

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Electron-Transfer Polymers. XXVIII. Synthesis of Vinyl Hydroquinone Derivatives by Means of the Wittig Reaction

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Synopsis

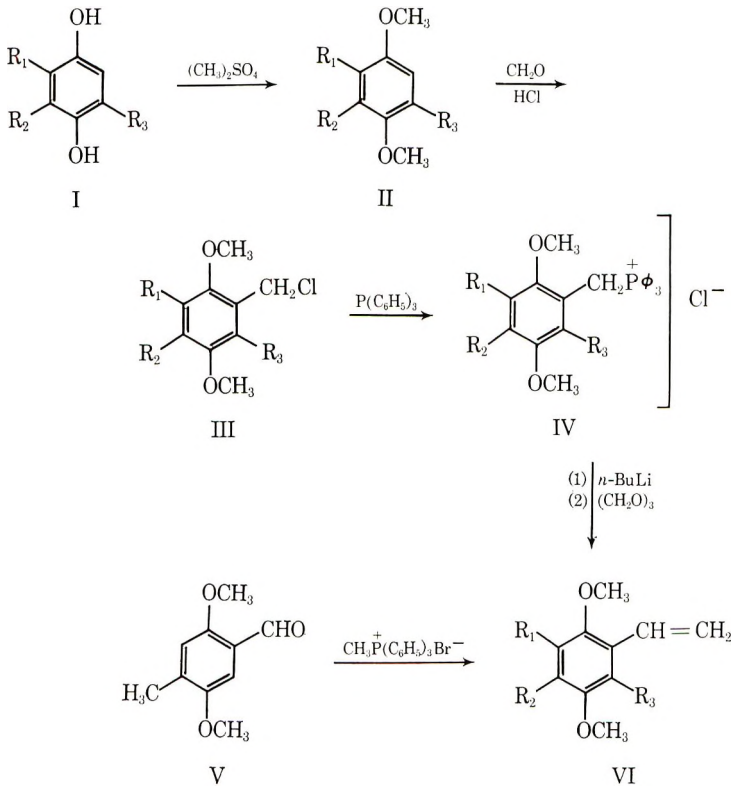
The Wittig reaction has been applied to unsubstituted, monomethyl-, 3,6-dimethyl-, and trimethyl-2,5-dimethoxybenzyl chlorides to produce in quantitative to good yields the corresponding vinyl monomers, unsubstituted, monomethyl-, 3,6-dimethyl-, and trimethyl-2,5-dimethoxystyrenes. The reaction is applicable also to 2,5-dimethoxy-4-methylbenzaldehyde, and to *O,O'*-bis-(methoxymethyl)resorcinol-4-aldehyde to yield the corresponding vinyl monomers. The reaction is particularly suitable with all these compounds because it is run at room temperature or below and gives good to quantitative yields.

Many synthetic methods for nonsubstituted or substituted vinylhydroquinones with protected hydroxyl groups have been published.[1] The best method that we have found[2] is excellent for the preparation of unsubstituted vinylhydroquinone monomer and the monomethyl-substituted monomer.[3] The yields are good, and the protecting groups (bisethoxyethyl) are readily removed after polymerization.

The method, however, is not applicable with profit to di- and trimethyl hydroquinones. It appears that the bulky acetal protecting groups, standing *ortho* to the β-hydroxyethyl that is to be the source of a vinyl group and *ortho* also to a methyl substituent on the other side, conspire to produce by-products in the high-temperature dehydration step.

We wished to prepare polyvinyltrimethylhydroquinone because of its low oxidation potential and its high stability over a wide range of pH. We therefore looked into other methods of preparing the requisite monomer and found that by use of the Wittig reaction the desired product (VId) could be made in nearly quantitative yield and in high purity. Because the reaction is carried out at room temperature, the formation of thermal by-products is minimized, and thermal polymerization is avoided.

The method is particularly suitable to making the trimethyl monomer VId, though the yields are good in preparing VIa, VIb, and VIc. In these, the yield of the step to the benzyl chloride, IIIa, b, c, is decreased due to formation of the bis-substituted product. The compounds IIIa and IIIb



a, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_3 = H$; $R_2 = CH_3$
c, $R_2 = H$; $R_1 = R_3 = CH_3$
d, $R_1 = R_2 = R_3 = CH_3$

are prepared by the method of Mndzhoyan and co-workers[4] and can be purified by vacuum distillation. However, IIIc decomposes under these conditions and must be fractionally crystallized.[4] Presence of starting material, difficult to remove in this case, seems to decrease the yield of phosphonium salt, IVc.

The Wittig reaction was found applicable to 2,5-dimethoxy-4-methylbenzaldehyde (V). Moreover, it was found that bismethoxymethyl protecting groups are able to resist Wittig conditions when used with 2,4-dihydroxybenzaldehyde, so that the vinyl monomer could be prepared from *O,O'*-bis(methoxymethyl)resorcinol-4-aldehyde (VII) in fair yield. However, all attempts to prepare 1,4-dihydroxybenzaldehydes protected with acetal groups have failed so far.

EXPERIMENTAL

2,5-Dimethoxystyrene (VIa)

2,5-Dimethoxybenzylchloride (IIIa) was prepared by the method of Mndzhoyan and co-workers.[4] A mixture of 9.5 g. (0.05 mole) of IIIa with

13 g. (0.05 mole) triphenylphosphine in 50 ml. toluene was refluxed for 1 hr. The oily product which first separated gradually solidified. At the end of the reflux period the mixture was cooled, and the solid product filtered off and washed first with toluene, then with ether. It was dried over phosphorus pentoxide. A quantitative yield of white triphenyl-2,5-dimethoxybenzylphosphonium chloride (IVa) was obtained.

Dried and finely powdered IVa (13 g., 0.03 mole) was suspended in 150 ml. dry ether under nitrogen. To the mixture, cooled in an ice-bath, was added 20 ml. (0.03 mole) of 15% *n*-butyllithium in hexane, whereupon the reaction mixture turned deep red indicating the formation of the corresponding phosphorane. After 10 min. a suspension of 2.5 g. trioxane in 50 ml. dry ether was added in one portion with stirring. At the end of 1 hr. at room temperature the mixture had become colorless. When diethyl ether is the solvent, triphenylphosphine oxide precipitates out as a crystalline adduct with one mole of lithium halide.[7] This material was removed by filtration, and the filtrate was washed with water and dried over anhydrous sodium sulfate. Upon evaporation of the solvent and extraction of the residue with petroleum ether an additional amount of crystalline by-product was left behind. The petroleum ether extract was evaporated to yield 2.5 g. (50%) of colorless oil, b.p. 82–85°C./1.5 mm. (lit.[8] b.p.: 78–80°C./0.01 mm.)

The NMR spectrum of this oil in carbon tetrachloride gave signals at $\tau = 6.36$ (singlet, intensity 6), $\tau = 2.99$ (quartet, intensity 1, $J = 11, 18$), $\tau = 4.83$ (quartet, intensity 1, $J = 2, 11$), $\tau = 4.36$ (quartet, intensity 1, $J = 2, 18$), $\tau = 3.05$ (singlet, intensity 1), $\tau = 3.36$ (singlet, intensity 1), $\tau = 3.40$ (singlet, intensity 1) here assigned to methyl hydrogen in two methoxy groups, vinyl hydrogen, vinyl hydrogen, vinyl hydrogen, aromatic hydrogen, aromatic hydrogen, and aromatic hydrogen, respectively. No signal which would correspond to another hydrogen was observed.

2,5-Dimethoxy-4-methylstyrene (VIb)

By a procedure similar to that just described, but starting with 2,5-dimethoxy-4-methylbenzylchloride (IIIb)[4] and preparing from it the corresponding phosphonium chloride (IVb), there was prepared in overall yield of 77%, 2,5-dimethoxy-4-methylstyrene (VIb) as a colorless oil, b.p. 91–92°C./2 mm. The NMR spectrum of this compound, in carbon tetrachloride, gave signals at $\tau = 7.85$ (singlet, intensity 3), $\tau = 6.38$ (singlet, intensity 3), $\tau = 6.34$ (singlet, intensity 3), $\tau = 3.05$ (quartet, intensity 1, $J = 11, 18$), $\tau = 4.91$ (quartet, intensity 1, $J = 2, 11$), $\tau = 4.44$ (quartet, intensity 1, $J = 2, 18$), $\tau = 3.23$ (singlet, intensity 1), $\tau = 3.51$ (singlet, intensity 1). These signals correspond to hydrogen in the methyl group adjacent to the aromatic nucleus, methyl hydrogen in methoxy group, methyl hydrogen in methoxy group, vinyl hydrogen, vinyl hydrogen, vinyl hydrogen, aromatic hydrogen, and aromatic hydrogen, respectively. No other signal was observed. (For C and H analysis see section on polymerization below.)

2,5-Dimethoxy-4-methylstyrene was obtained from 2,5-dimethoxy-4-methylbenzaldehyde[10] and triphenylmethylphosphonium bromide by the Wittig reaction in 55% yield based on aldehyde.

2,5-Dimethoxy-3,6-dimethylstyrene (VIc)

This colorless oil was obtained from 2,5-dimethoxy-3,6-dimethylbenzyl chloride[5] by the same procedure as in the case of VIa. The boiling point of the oil was 63.5–64°C./0.13 mm. (lit.[9] b.p.: 78–81 C./0.02 mm.). The overall yield was 46%. The NMR spectrum gave signals corresponding to hydrogen in the methyl groups adjacent to the aromatic nucleus at τ 7.87 (singlet, intensity 3) and 7.80 (singlet, intensity 3); signals corresponding to hydrogen in methoxy groups at τ = 6.94 and 6.32 (both singlet, intensity 3); signals corresponding to vinyl hydrogen at τ = 3.27 (quartet, intensity 1, J = 11, 18), τ = 4.56 (quartet, intensity 1, J = 2, 11), and τ = 4.48 (quartet, intensity 1, J = 2, 18); and a signal corresponding to aromatic hydrogen at τ = 3.57 (singlet, and intensity 1). No other signal was observed.

2,5-Dimethoxy-3,4,6-trimethylstyrene (VId)

The colorless oil was obtained from 2,5-dimethoxy-3,4,6-trimethylbenzyl chloride[6] by the same procedure described above. The overall yield was 90%. The boiling temperature of the oil was 79–81°C./0.4 mm. (lit.[9] b.p.: 78°C./0.1 mm.), m.p. 25°C. The NMR spectrum gave signals at τ = 7.87 (singlet, intensity 6) and τ = 7.80 (singlet, intensity 3) which correspond to hydrogen in the methyl groups adjacent to the benzene ring; signals at τ = 6.50 (singlet, intensity 3), and at τ = 6.45 (singlet, intensity 3) which correspond to hydrogen in the methoxy groups; signals at τ = 3.33 (quartet, intensity 1, J = 11, 18), τ = 4.62 (quartet, intensity 1), and τ = 4.50 (quartet, intensity 1, J = 2, 18), which correspond to vinyl hydrogen. No other signal was observed.

Vinyl-2,4-dihydroxyphenylbismethoxymethyl Ether (VIII)

In a sodium methoxide solution prepared by dissolving 5 g. metallic sodium in 200 ml. anhydrous methanol was dissolved 14 g. (0.1 mole) of 2,4-dihydroxybenzaldehyde. This was cooled in an ice bath, and 16 g. (0.2 mole) of chloromethyl methyl ether was added dropwise with stirring. After standing for 1 hr., the mixture was poured onto cracked ice and the product extracted with ether. The extract was dried, and the solvent was removed. Fractionation yielded 5 g. (25%) of colorless oil, b.p. 135–140°C./0.3 mm. This compound (VII) was then used in the following step.

To a suspension of 5 g. triphenylmethylphosphonium bromide in 50 ml. dry ether was added 10 ml. of 15% n-butyllithium in hexane, with cooling under a nitrogen atmosphere. After 10 min., 3 g. of VII in 15 ml. of dry ether was added in one portion and stirring was continued for 30 min.

The reaction mixture was poured onto ice and extracted with ether. This extract was dried and the solvent removed by evaporation. Distillation of the residue yielded 1 g. (32%) of colorless oil, b.p. 125–128°C./1.5 mm. The NMR spectrum gave signals at $\tau = 6.64$ (singlet, intensity 3) and $\tau = 6.61$ (singlet, intensity 3) which correspond to hydrogen in the methoxy groups; signals at $\tau = 4.96$ (singlet, intensity 2) and $\tau = 4.92$ (singlet, intensity 2) which correspond to hydrogen of the methylene group between two oxygens; signals at $\tau = 4.93$ (quartet, intensity 1, $J = 2, 11$) and $\tau = 4.46$ (quartet, intensity 1, $J = 2, 18$) which correspond to hydrogen of the terminal methylene of the vinyl group; a signal at $\tau = 3.05$ (quartet, $J = 11, 18$) which corresponds to vinyl hydrogen; signals at $\tau = 3.27$ (quartet, $J = 1, 2.5$), $\tau = 3.42$ (quartet, $J = 2.5, 8$), and $\tau = 2.74$ (quartet, $J = 1, 8$) which correspond to aromatic hydrogen. No other signals were observed.

Polymerization

With azobisisobutyronitrile as an initiator, polymerizations of vinyl monomers, VIa, VIb, VIc, VId, and VIII were carried out under a nitrogen atmosphere. Vinyl monomers, VIa, VIb, and VIII, gave their polymers easily. On the other hand, polymerizations of monomer VIc and VId were very difficult, and yielded only traces of their polymers. These polymers were purified by reprecipitation from benzene and methanol.

ANAL. Calcd. for $C_{10}H_{12}O_2$ (polymer from VIa): C, 73.14%; H, 7.36%. Found: C, 73.02%; H, 7.54%.

Calcd. for $C_{11}H_{14}O_2$ (polymer from VIb); C, 74.12%; H, 7.92%. Found: C, 74.08%; H, 7.88%.

Calcd. for $C_{12}H_{16}O_4$ (polymer from VIII): C, 64.28%; H, 7.19%. Found: C, 64.27%; H, 7.32%.

Calcd. for $C_{12}H_{16}O_2$ (polymer from VIc): C, 74.96%; H, 8.39%. Found: C, 74.76%; H, 8.84%.

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Résumé

La réaction de Wittig a été appliquée aux chlorures de 2,5-diméthoxybenzyl non-substitué, au monométhyle, 3,6-diméthyle et triméthyle en vue d'obtenir avec des rendements quantitatifs les monomères vinyliques correspondants à savoir le 2,5-diméthoxystyrène non-substitute, monométhylé, 3,6-diméthylé et triméthylé. La réaction est également appliquable au 4-méthyl-2,5-diméthoxybenzaldéhyde et au O,O′-bis-(méthoxyméthyl)-résorcinaldégyde-4 en vue de former les monomères vinyliques correspondants. La réaction est particulièrement adaptée à tous des composés parce qu'elle se passe à la température de chambre et fournit de bons rendements, voir quantitatifs.

Zusammenfassung

Die Wittig-Reaktion wurde auf unsubstituierte, monomethyliere, 3,6-dimethylierte, und trimethylierte 2,5-Di-methoxybenzylchloride angewendent und lieferte in quantitativer bis guter Ausgeute die entsprechenden Vinylmonomeren, nämlich unsubstituierte, mono-, 3,6-di- und trimethylierte 2,5-Dimethoxystyrole. Die Reaktion ist auch auf 2,5-Dimethoxy-4-methylbenzaldehyd und O,O′-Bis-(methoxymethyl)-resorcin-4-aldehyd anwendbar und ergibt die entsprechenden Vinylmonomeren. Die Reaktion ist für alle diese Verbindungen besonders geeignet, da sie bei Raumtemperatur oder darunter durchgeführt wird und gute bis quantitative Ausbeuten liefert.

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Linear Polymers of Some Vinyl Monomers Containing a Terminal Acetylenic Group

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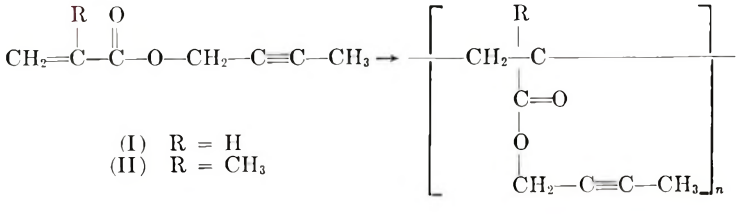
Synopsis

The synthesis and polymerization of representative acrylic-type esters containing a terminal acetylene group, $CH_2{=}C(R)COO(CHR')_m{-}C{\equiv}CH$, where R and R′ are H and CH_3 and $m = 1$ or 2, by anionic initiation to linear polymers are described. In contrast, crosslinked polymers were formed when radical and cationic initiators were used. Crosslinked polymers were also obtained with organolithium compounds but not with sodium naphthalene and sodium benzalaniline; this observation is discussed and compared to the behavior of the acetylenic acrylic esters which do not contain a terminal acetylenic hydrogen. The unpolymerized acetylenic bonds in the resulting linear polymers were shown to be present by infrared spectroscopic methods and by the following post-reactions of these bonds: (*1*) the heat- and radical-initiated crosslinking of the polymers through the acetylenic bonds; (*2*) the post-bromination of the acetylenic bonds; and (*3*) the reaction of decaborane with the acetylenic bonds. The anionic copolymerization of acrylonitrile and styrene with these acetylenic monomers were performed and compared to the copolymerizations with 1-acryloxy-2-butyne and 1-methacryloxy-2-butyne. Dibromination of the linear polymers affords self-extinguishing polymers, while decaboronation yields soluble polymers which do not soften up to 300°C. The linear polymers may be classified as "self-reactive" polymers which yield thermosetting polymers.

INTRODUCTION

Recently, we reported the anionic polymerization of 1-acryloxy-2-butyne (I) and 1-methacryloxy-2-butyne (II) to linear polymers containing unreacted acetylenic groups in the pendant side chain.[1] These polymeriza-



(I) R = H
(II) R = CH_3

tions were achieved by means of anionic initiators which were capable of initiating polymerization of the vinyl group but were unreactive towards the acetylenic group. At that time, monomers I and II were specifically

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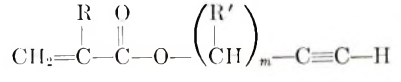
chosen because they did not contain a terminal acetylenic hydrogen. It was thought that the labile ≡C—H bond would be attacked by the anionic initiator. The acidic hydrogen of the terminal acetylenic group could conceivably be replaced by the counterion, M^+, of the anionic initiator and an alkali-metal acetylide, —C≡C$^-$---M$^+$, would be formed. Since the carbon–alkali metal bond, with the exception of lithium, is generally considered as ionic,[2] an acetylide anion would thus be present in the polymerziation system. This process could have two possible effects upon the polymerization: (*1*) the acetylide anion would be incapable of further reaction and the polymerization would be retarded due to loss of the initiator; or (*2*) the acetylide anion would be capable of initiation of the vinyl groups of the monomer and a highly branched or crosslinked polymer would result.

The purpose of this study was to evaluate the influence of the terminal acetylenic group in acrylic monomers on the preparation of linear polymers by appropriate initiators. This paper describes the synthesis and polymerization under the influence of various radical, cationic, and anionic initiators of propargyl acrylate (III), propargyl methacrylate (IV), 1-acryloxy-3-butyne (V), and 2-acryloxy-3-butyne (VI), all of which contain a terminal acetylenic group. The chemical and spectroscopic methods used in determining the structure of the resulting polymers are given. Also described are selected copolymerizations with other vinyl monomers.



(III) R = H, R′ = H, m = 1
(IV) R = CH_3, R′ = H, m = 1
(V) R = H, R′ = H, m = 2
(VI) R = H, R′ = CH_3, m = 1

EXPERIMENTAL

Materials

Reagent-grade tetrahydrofuran was purified[1] by refluxing over potassium hydroxide pellets for several hours, distilled, then redistilled from over lithium aluminum hydride into glass receivers which had been flamed prior to use and which contained calcium hydride, and then saturated with helium.

Commercial styrene, acrylonitrile, methyl acrylate, and methyl methacrylate were refluxed over and distilled off calcium hydride. They were stored over calcium hydride in glass receivers which had been flamed, then saturated with helium, and were generally used within 48 hr.

Initiators

n-Butyllithium, as a 20% hexane solution, was obtained from the Foote Mineral Company and diluted with purified tetrahydrofuran as required.

Only relatively fresh bottles were used. Sodium naphthalene in tetrahydrofuran was prepared by the method of Scott et al.[3] It was stored under helium in tightly sealed vials and in the absence of light. It was used as soon as possible after preparation. Sodium benzalaniline in tetrahydrofuran was prepared by the method of Ringsdorf[4] and stored in a similar manner and also used as soon as possible after preparation.

Monomers

1-Acryloxy-3-butyne and 2-acryloxy-3-butyne were prepared by azeotropic esterification methods from acrylic acid and the appropriate acetylenic alcohol. Yields of 64% and 51%, respectively, were obtained. The reaction conditions and work-up procedures were very similar to those described[1] previously for 1-acryloxy-2-butyne and 1-methacryloxy-2-butyne. The following analytical data and physical constants were recorded.

ANAL. Calcd. for 1-acryloxy-3-butyne, $C_7H_8O_2$: C, 67.74%; H, 6.45%. Found: C, 67.62%; H, 6.76%. B.p. 88°C./100 mm., $n_D^{20} = 1.4505$.

ANAL. Calcd. for 2-acryloxy-3-butyne, $C_7H_8O_2$: C, 67.74%; H, 6.45%. Found: C, 67.74%; H, 6.68%. B.p. 58°C./8 mm.; $n_D^{20} = 1.4391$.

Propargyl acrylate and propargyl methacrylate were also prepared by azeotropic esterification methods.[1] It was necessary to recycle the propargyl alcohol in order to obtain yields of 60% and 44%, respectively. The following analytical data and physical constants were recorded.

ANAL. Calcd. for propargyl acrylate, $C_6H_6O_2$: C, 65.46%; H, 5.45%. Found: C, 65.89%; H, 5.57%. B.p. 72°C./65 mm., $n_D^{20} = 1.4107$.

ANAL. Calcd. for propargyl methacrylate, $C_7H_8O_2$: C, 67.74%; H, 6.45%; Found: C, 67.78%; H, 6.52%. B.p. 83°C./65 mm., $n_D^{20} = 1.4075$.

The monomers, after synthesis, were refluxed over calcium hydride, redistilled, collected over calcium hydride, then saturated with helium and stored at 0°C.

Polymerizations

Radical and Cationic. These polymerizations were carried out in rubber-capped serum glass vials with 1.0 g. of the monomer and 0.001 g. benzoyl peroxide as the radical initiator and 0.001 g. aluminum chloride as the cationic initiator. A typical polymerization was as follows.[1] In a dry-box with a nitrogen atmosphere, into a thoroughly heat-dried 5-ml. serum vial was placed the monomer and the initiator. The contents of the vial were then flushed with dry deoxygenated nitrogen, sealed and placed in a 60°C. oven. At the end of 24 hr., the contents of the vials were tough, infusible masses insoluble in acetone, toluene, dimethylformamide, and dimethyl sulfoxide.

Anionic Homopolymerization. A typical anionic polymerization by a modification of previously described procedure[5] is given as follows. The reaction vessel, attached to a high-vacuum manifold, consisted of a five-necked glass flask fitted with an externally driven magnetic stirrer, a side-arm to which was attached a 50-ml. round-bottomed flask, a stopcock crowned with a serum cap, and a helium inlet tube.

The solution of 5.0 g. of monomer in 20 ml. of tetrahydrofuran, stored over calcium hydride in the round-bottomed flask for at least 8 hr., was degassed twice at 3×10^{-6} mm. Hg and distilled into the reaction vessel, which had been previously flamed in a stream of helium. The system was then pressured with helium to slightly above atmospheric pressure. The reaction vessel was then cooled to the desired temperature. Then initiator solution, in a mole ratio to monomer of 1:300, was injected volumetrically by means of a hypodermic syringe through the serum cap. The polymerization was terminated by injecting 3 ml. of methanol into the solution mixture.

Insoluble polymer, if present, was removed by filtration and the polymer in the tetrahydrofuran solution was isolated by filtration after pouring the polymer solution slowly into vigorously stirred hexane containing 0.2% 2,6-di-*tert*-butyl-*p*-cresol as an inhibitor. The isolated polymer was washed with hexane containing 0.2% inhibitor and dried to constant weight in a vacuum oven at 25°C. The filtrate was evaporated under reduced pressure to isolate hexane-soluble polymers. The infrared spectra of the monomers and polymers were recorded and the intrinsic viscosities of representative samples of linear polymers determined.

In addition, 1-acetoxy-2-butyne and propargyl acetate which had been purified and saturated with helium were also subjected to similar polymerization conditions with butyllithium; in all cases polymerization did not occur.

Copolymerization. The general procedure described above for the anionic polymerization was used to prepare the copolymers. The copolymerizations were carried out in a 50% solution of tetrahydrofuran at −40°C. with sodium naphthalene as the initiator. The initiator to comonomer mole ratio was 1:400. Copolymerizations were generally carried out to about 10% conversion. The copolymerizations were allowed to proceed until a noticeable increase in viscosity occurred before they were terminated. If the conversion was found to exceed 10% the polymerization was repeated and terminated at a shorter reaction time. The polymers were isolated by precipitation in nonsolvent, redissolved, and reprecipitated three times in a suitable solvent–nonsolvent system; the polymer solutions were filtered through sintered discs before reprecipitation. For the purification of the acrylonitrile copolymers, dimethylformamide was used as the solvent and methanol as the precipitant. In the remainder of the copolymerizations, benzene was used as the solvent and heptane as the precipitant. Solvents and precipitants contained 0.2% inhibitor. The isolated copolymers were dried to constant weight in a vacuum over at 25°C.

Post-Reactions

Bromination of the Linear Polymers. Into a 125-ml. glass-stoppered flask was placed approximately 0.6 g. of polymer dissolved in 3 ml. of carbon tetrachloride. To this was added twice the theoretical amount of bromine. The reaction mixture was mixed well, stoppered, and placed in the refrigerator at 0°C. for one week. Then, 15 ml. of heptane was added and the precipitated polymer was isolated by filtration, redissolved, and reprecipitated twice, carbon tetrachloride being used as the solvent and heptane as the precipitant.

ANAL. Calcd. for polymer III, $C_6H_6O_2Br_2$: Br, 59.26%. Found for sodium naphthalene polymer III: Br, 59.26%. Found for butyllithium (THF-soluble) polymer III: Br, 57.60%. Found for butyllithium (DMF-insoluble) polymer III: Br, 54.91%. Found for lithium naphthalene (DMF-insoluble) polymer III; Br, 56.73%.

ANAL. Calcd. for polymer IV, $C_7H_8O_2Br_2$: Br, 56.30%. Found: Br, 55.07%.

ANAL. Calcd. for polymer V, $C_7H_8O_2Br_2$: Br, 56.30%. Found: Br, 55.82%.

ANAL. Calcd. for polymer VI, $C_7H_8O_2Br_2$: Br, 56.30%. Found: Br, 55.64%

Thermal Crosslinking of Linear Polymers. A 10% solution of the polymers was prepared in dry benzene. The solutions of the polymers were then poured onto glass plates and the solvent allowed to evaporate at room temperature. After being placed in a 120°C. oven for 8 hr., films were formed which were insoluble in chloroform, carbon disulfide, acetone, and dimethylformamide.

Free-Radical Crosslinking of Linear Polymers. To a 10% solution of polymers in benzene was added benzoyl peroxide, 0.25 wt.-% on the polymer. After being thoroughly mixed, the solutions of the polymers were poured onto glass plates, the solvent allowed to evaporate, and the plates placed in a 100°C. oven for 1 hr. At that time, films formed which were insoluble in benzene, acetone, chloroform, and dimethylformamide.

Reaction of Decaborane with the Linear Polymer of III. Into a 500-ml. round-bottomed, three-necked flask fitted with a reflux condenser, a mechanical stirrer, and a nitrogen inlet was placed 1.43 g. (0.013 mole) of polymer, $[\eta] = 0.238$, and decaborane (5.0 g., 0.041 mole) so that the decaborane would be present in excess of the theoretical amount. To this was added acetonitrile (1.8 g., 0.0436 mole) dissolved in 200 ml. of dry toluene along with 0.1 g. of di-*tert*-butyl-*p*-cresol as an inhibitor. This reaction mixture was refluxed for 84 hr., at which time the clear solution was poured into 500 ml. of vigorously stirred heptane. The precipitated polymer was isolated by filtration and washed well with heptane to remove any unreacted decaborane. The product was insoluble in carbon tetrachloride, chloroform, and carbon disulfide but was soluble in toluene and acetone. A toluene solution of the polymer was poured into heptane and the precipitated polymer was isolated and then dried in a vacuum oven at room temperature. The pale yellow product when heated on a Fisher-

Johns melting point apparatus showed no appreciable softening up to 300°C.

ANAL. Calcd. for $C_6H_{16}B_{10}O_2$: C, 31.55%; H, 7.01%. Found: C, 30.88%; H, 7.09%.

Reaction of Decaborane with Linear Polymer of IV. Into a 250-ml. round-bottomed, three-necked flask fitted with a mechanical stirrer, a reflux condenser, and a nitrogen inlet were placed 1.6 g. (0.013 mole) of the polymer, $[\eta] = 0.317$, and decaborane (5.0 g., 0.041 mole) so that the decaborane would be in large excess of the theoretical amount. To this was added acetonitrile (0.61 g., 0.015 mole) dissolved in 150 ml. of dry toluene with 0.1 g. of di-*tert*-butyl-*p*-cresol as an inhibitor. The reaction mixture was refluxed for 140 hr., at which time it was poured into 250 ml. of vigorously stirred heptane and the precipitated polymer separated by filtration. The product was insoluble in chloroform, carbon tetrachloride, and carbon disulfide, but was soluble in acetone and toluene. After the polymer was dissolved in 50 ml. of toluene and reprecipitated in 150 ml. of heptane, it was isolated by filtration and dried in a vacuum oven at room temperature. The cream-colored product showed no softening up to 300°C. when heated on a Fisher-Johns melting point apparatus.

ANAL. Calcd. for $C_7H_{18}B_{10}O_2$: C, 34.64%; H, 7.43%. Found: C, 33.60%; H, 7.59%.

Viscosity Determinations

The intrinsic viscosities of the acrylic and methacrylic homopolymers prepared in this investigation were determined in benzene solution in semimicro Ubbelohde dilution viscometers. The bath temperature was maintained at 20 ± 0.2°C., and flow times were determined for at least three solution concentrations.

RESULTS AND DISCUSSIONS

Polymerization Reactions

It had been confirmed[1] previously that both the radical- and the cationic-initiated polymerization of acrylic esters having acetylenic structures I and II in the ester moiety led to crosslinked, insoluble polymers since both the vinyl and the acetylenic groups were susceptible to these types of initiators. This result has been confirmed when monomers III, IV, V, and VI were subjected to both radical and cationic polymerization reactions with benzoyl peroxide and aluminum chloride, respectively, as the initiators. In all cases an insoluble, crosslinked gel was formed, indicating that both potential reaction sites had participated in the polymerization.

It was also reported[1] that the anionic polymerization of I and II led to linear soluble polymers with pendant acetylenic groups. These linear polymers were the result of selective polymerization through the vinyl

groups of the respective monomers with the use of three different anionic initiators: *n*-butyllithium, sodium naphthalene, and sodium benzalaniline. The polymers formed in each case were soluble in a number of organic solvents and softened to viscous masses or liquids at higher temperatures. Monomers I and II were chosen originally because they did not contain a terminal acetylenic group which could possibly be attacked by the anionic initiator. To determine the influence of the acidic hydrogen of the terminal acetylenic group in anionic polymerizations, monomers III–VI were synthesized and subjected to anionic polymerizations. The experimental data are summarized in Table I.

TABLE I
Anionic Polymerization of Acetylenic Monomers

Monomer	Initiator[a]	Temp., °C.	Time, min.	Conversion, %			[η]
				Soluble	Cross-linked	Total	
III	SN	−78	120	81.1	0.0	81.1	0.428
III	BuLi	−78	120	47.5	28.7	76.2	0.361
III	BuLi	−40	120	45.0	24.6	69.6	0.232
III	LiN	−40	120	55.1	13.3	68.4	0.238
III	SN	−20	120	56.6	0.0	56.6	0.116
IV	SN	−78	90	86.1	0.0	86.1	0.511
IV	SBA	−78	90	88.7	0.0	88.7	0.507
IV	BuLi	−78	90	52.6	32.2	84.8	0.473
IV	LiN	−78	90	71.2	11.7	82.9	0.454
IV	SN	−40	90	77.2	0.0	77.2	0.317
IV	BuLi	−40	90	45.8	30.5	76.3	0.294
IV	LiN	−40	90	61.2	10.3	71.5	0.281
IV	SN	−20	90	62.6	0.0	62.6	0.117
IV	BuLi	−20	90	39.2	24.2	63.4	0.128
IV	LiN	−20	90	51.4	9.4	60.8	0.106
V	SN	−78	90	76.7	0.0	76.7	0.403
V	BuLi	−78	90	47.9	25.9	73.8	0.392
V	BuLi	−40	90	43.9	24.4	68.3	0.222
V	LiN	−40	90	51.5	12.6	64.1	0.207
VI	SN	−78	90	80.2	0.0	80.2	0.414
VI	BuLi	−78	90	49.3	25.1	74.4	0.393
VI	LiN	−78	90	57.8	14.3	72.1	0.337
VI	SN	−40	90	66.3	0.0	66.3	0.241

[a] SN = sodium naphthalene, 0.496*N* solution; SBA = sodium benzalaniline, 0.481*N* solution; BuLi = *n*-butyllithium, 1.601*N* solution; LiN = lithium naphthalene, 0.506*N* solution.

A comparison of the infrared spectrum of propargyl acrylate with that of the corresponding polymer disclosed the disappearance of the peak at 6.12 μ attributable[1] to the carbon–carbon double bond. However, the peaks at 4.73 μ, attributable to the carbon–carbon triple bond, and at 3.04 μ, attributable to the acetylenic carbon–hydrogen bond, were still present. Similar correlations in spectra were also noted in the polymeriza-

tion of monomers IV, V, and VI. This spectroscopic evidence and the physical character of the polymers formed indicates that polymerization occurred substantially through the double bond.

In the cases in which sodium naphthalene or sodium benzalaniline was used as the initiator, monomers III–VI yielded clear, linear, soluble polymers.

Since both sodium napthalene[6–9] and sodium benzalaniline[4] exist as radical-anions,[4,6–9] it was believed that these polymerizations would exhibit some radical character and thereby initiate some radical polymerization of the triple bond with subsequent crosslinking of the polymer. If such was the case, the degree of radical polymerization was sufficiently low that the polymers did not become insoluble. In this respect, these results agree with those obtained previously[1] with monomers I and II.

However, when *n*-butyllithium and lithium naphthalene were used as initiators, a portion of the polymer was infusible and insoluble in the reaction medium and in benzene. The benzene-insoluble polymer was also insoluble in dimethylformamide. The infrared spectra of the simultaneously formed soluble fractions were identical to those of the polymers obtained in the sodium naphthalene polymerizations.

The above observations would lead to the assumption that the organolithium compounds can cause polymerization through the acetylenic bond; this, however, may be questioned, since neither the lithium nor the sodium initiators was effective in polymerizing propargyl acetate or 1-acetoxy-2-butyne. Butane was formed in the reaction of propargyl acetate with butyllithium but not with 1-acetoxy-2-butyne. A visual reaction was not observed when either acetate was added to lithium or sodium naphthalene solutions. The formation of crosslinked polymers would indicate that some lithium acetylide was formed when *n*-butyllithium was used as an initiator. Since appreciable amounts of insoluble polymers were formed, it appears that the lithium acetylide was capable of initiating polymerization of the vinyl group of propargyl acrylate, thus resulting in a highly branched or crosslinked structure. Also, since the major portion of the polymer formed was soluble, it appears that a major amount of the polymerization occurred as an anionic polymerization through the acrylic double bond.

The formation of crosslinked polymers from these monomers containing a terminal acetylenic hydrogen is in marked contrast to the results previously obtained[1] with monomers I and II which have terminal methyl groups on the acetylene function. Bockmann and Schuerch have shown[9] that many disubstituted ethylenic monomers possessing electron-withdrawing structures adjacent to the double bond are not polymerized by butyllithium as well as by other anionic initiators. Beneš has shown that if the acetylenes contain electronegative substituents, such as in monocyanoacetylene[10] and in dicyanoacetylene,[10,11] they are readily polymerized by typical anionic initiators. Accordingly, one would not expect the nonactivated disubstituted acetylenic groups of monomers I and II or the nonactivated monosubstituted acetylenic groups of III–VI to participate in the polymerization.

In the case of III–VI, however, acetylide formation is possible and would be expected in the reactions with sodium naphthalene and sodium benzalaniline as well as with butyllithium. That some degree of reaction between the initiator and the terminal acetylenic group may have occurred is indicated by the retarded rates and lower conversions to polymers of monomers III–VI relative to I and II. The anion of sodium acetylide, if formed, does not seem to have been capable of initiation of the vinyl group since no insoluble polymer was isolated. Thus, these sodium acetylides, $-C\equiv C-Na$, differ from sodium diphenylacetylene, $C_6H_5-C=C-C_6H_5^- Na^+$ which polymerizes[12] α-methylstyrene readily, forming a chemical bond between sodium diphenylacetylene (SDPA) and the monomer with the incorporation of a stilbene residue in the polymer. The unpaired electron and the negative charge of the radical-anion of SDPA are not completely localized.

On the other hand, it is known that sodium naphthalene and sodium benzalaniline exist as radical-anions and initiate polymerization through an electron transfer mechanism[4,13,14] with the formation of dianions of the monomers. Apparently, in the acetylenic systems reported here, the dianions dominate the propagation, even if the assumption is made that the sodium counter ions exist to some extent as acetylides.

In contrast, the lithium–carbon bond is largely, but not exclusively, covalent.[2] Because of their different chemical natures, one might expect these two types of anionic initiators to react differently toward the $\equiv C-H$ bond. The butyllithium initiation can be considered as proceeding through a Michael-type addition to the monomer.[2,15] Since the major portion of the polymer was soluble, the polymerization by butyllithium was dominated by the reaction of the initiator with the acrylic double bond. When lithium naphthalene was used as the initiator, the amount of crosslinked polymer obtained was reduced, indicating that, though the electron-transfer mechanism dominated the polymerization through the acrylic bonds and some polymerization occurred by the lithium acetylide bond, lithium naphthalene differs from sodium naphthalene. Though both sodium and lithium naphthalene are radical-anion initiators, it has been shown that not all initiators of this type initiate by electron transfer to monomer.[12,16] It has been shown also that, if the radical anions are all formed at once, as occurs when lithium naphthalene is used as the initiator, the amount of radical growth is negligible.[17] In these polymerizations, the amount of insoluble polymers obtained with lithium naphthalene was less than the amount obtained with butyllithium and appeared to fall between the values found for butyllithium and sodium naphthalene.

Due to inherent differences between a radical-anionic and a strictly anionic initiator, other differences in the polymerizations certainly are expected to have occurred. However, the present investigation did not cover this aspect of the anionic polymerizations but was intended only to establish the validity of the concept that a monomer containing a terminal unactivated acetylenic moiety and a vinyl moiety flanked by an electron-

withdrawing group can be predominantly polymerized through the vinyl double bond by means of an appropriate anionic initiator. The difference in conversions of the methacrylic ester IV and of the acrylic esters III, V, and VI is similar to the difference found in the anionic polymerizations of the alkyl methacrylates and acrylates[18-20] and of allyl methacrylate and allyl acrylate[21] and of 1-methacryloxy-2-butyne and 1-acryloxy-2-butyne.[1] However, whereas the alkyl, allyl, and butynyl methacrylates can be polymerized readily and substantially quantitatively at −78°C., this was not true for those esters containing terminal acetylenic groups, at least under comparable conditions. This may indicate some degree of reaction between initiator and the terminal acetylenic group.

The conversions reported are based on the sum of the amounts of infusible polymer, if any, of polymer isolated on precipitation in hexane and of hexane-soluble lower molecular weight polymers recovered from the hexane solution. At a polymerization temperature of −78°C., the amount of low molecular weight polymers obtained averaged less than 1%, while at −40°C. this value averaged about 2.5%, and at −20°C. about 8.7%.

Appreciable amounts of hexane-soluble polymers were found[22] by Wiles and Bywater in their work on the anionic polymerization of methyl methacrylate, and they attributed this to side reactions involving attack of butyllithium on the carbonyl of the monomer. The attack was more evident at higher temperatures. The molecular weight distribution of poly(methyl methacrylate) prepared by anionic initiators has been shown to be broad,[8,18,22] and undoubtedly it is also broad in these acetylenic polyesters, as evidenced by the presence of some low molecular weight products.

The intrinsic viscosities given in Table I are those of the hexane-insoluble polymers, and some relative values of their molecular weights may be estimated from other viscosity–molecular weight relationships. Meyerhoff gives[23] the relationship $[\eta] = 7.5 \times 10^{-5}M^{0.75}$ for poly(butyl acrylate) in acetone, and Glusker[5] uses $[\eta] = 5.2 \times 10^{-5}M^{0.76}$ for poly(methyl methacrylate) in benzene. From these equations, it is estimated that the highest molecular weight for the methacrylic ester IV is about 125,000 and for the acrylic esters III, V, and VI it is about 100,000.

Kinetic measurements to determine the effects of solvent, monomer, and initiator concentrations on molecular weight, rate of polymerization, and microstructure are now under consideration.

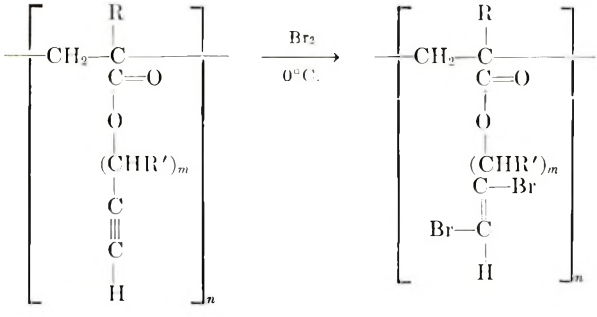
The linear polymers give some evidence of crosslinking, i.e., a continuous increase in viscosity on standing in air, and their stability appears to be intermediate between that of the corresponding allyl esters, which crosslink readily,[21] and that of the butynyl esters, which are relatively stable.[1]

Post-Reactions of the Linear Polymers

Several of the linear polymers prepared from monomers IV–VI were subjected to various post-reactions of the pendant acetylenic group. The primary purpose of these post-reactions was to lend support to the

proposed linear structures by characterizing the products formed from these reactions. Among the reactions employed were the bromination of the acetylenic group, the radical and thermal crosslinking of the polymers through the acetylenic group, and the reaction of the acetylenic group with decaborane to form linear polymers with carborane groups in the pendant side-chains.

Samples of the soluble linear polymers obtained by the anionic polymerization of IV–VI were subjected to bromination with bromine as the brominating agent. Prolonged reaction times were necessary in order to obtain a substantial degree of bromination. In all cases the bromine content is in fair or good agreement with the calculated values for the dibromide.

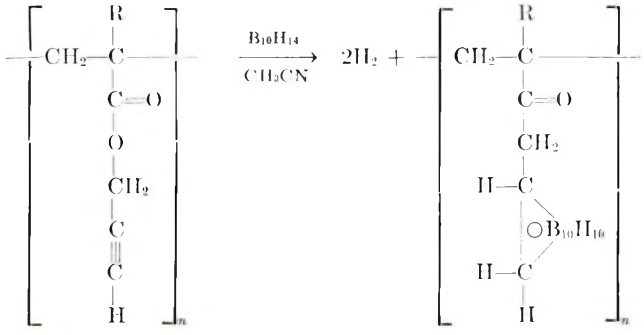


A comparison of the infrared spectrum of initial polymer III and that of the brominated product disclosed the disappearance of the acetylenic peak at 4.73 μ and the subsequent appearance of a peak at 6.03 μ attributable to a carbon–carbon double bond.[1,24] In the case of crosslinked polymers of III, the bromine contents are less than that calculated for the linear polymer; while a lower value would be expected, the low value may indicate that a number of acetylene groups are less available to bromine attack because of the crosslinked structure.

When ignited in the flame of a bunsen burner and withdrawn from the flame, all of the post-brominated polymers were found to be self-extinguishing. This post-bromination affords a convenient method of preparing self-extinguishing polymers and avoids the problems associated with polymerizing the equivalent monomers, CH_2—CR—$COO(CHR')_mCBr$=CHBr.

Further confirmation of the linear structure of these polymers and of the reactivity of the free acetylenic bond was obtained by both the heat- and the radical-induced crosslinking of the polymers through the triple bonds. The major portion of the radical-induced post-reactions consisted of casting films of the polymer from solutions containing benzoyl peroxide and then heating the solvent-free films at 100°C. to produce insoluble, crosslinked films. The thermally induced post-reactions were conducted in a similar manner except that benzoyl peroxide was not included in the polymer solutions and heating was carried out at 120°C.

The linear polymers from the anionic polymerizations of III and IV were both subjected to reactions with decaborane; acetonitrile was used as the catalyst.



The elemental analyses indicated that the reaction had been substantially complete. The infrared spectrum indicated a decrease in III of the acetylenic peak[24] at 4.73 μ and the presence of the B—H peak at 3.92 μ.[25,26] It was also observed that the reaction of these polymers containing the terminal acetylene group with decaborane appeared to be more facile than that of the related 2-butyn-1-ol esters containing a methyl group in place of hydrogen in the acetylenic structure.[1] This behavior appears to be in agreement with the known reactivity of decaborane with mono- and disubstituted acetylenes.[27] The decaboronated polymers did not melt when heated to 300°C. and gave no external evidence of decomposition at this temperature. This appears to be in accord with previous findings that the 1,2-dicarbaclovodecaborane-(12) nucleus exhibits a high degree of oxidative, hydrolytic, and thermal stability. That the decaboronated polymers were not crosslinked was shown by their solubility in benzene, toluene, and acetone.

The decaboronated polymers burned slowly with a greenish, smoky flame when ignited, but burned with an intense greenish-white flame when mixed in powdered form with ammonium perchlorate; hence they may be of interest as propellants.

Decaboronation of these polymers offers a convenient way of preparing soluble, tractable boron-containing polymers in relatively high yields. In contrast, the radical polymerization[1] of the corresponding decaboronated propargyl acrylate yields a mixture of soluble and insoluble polymers.

The reactivity of the acetylenic groups in the soluble polymers in the above post-reactions is additional evidence that the acetylenic group was unaffected in the original polymerization. Taken along with the physical character of the polymers and the spectroscopic evidence, these post-reactions conclusively prove that polymerization occurred substantially through the double bond without affecting the acetylenic bond.

Copolymerizations

The effect of the pendant acetylenic groups on the anionic copolymerization reactivities of monomers of structures represented by IV–VI was not known. Some change would be expected from the values of the acrylic and methacrylic esters of saturated alcohols. In order to gain some in-

TABLE II
Copolymerization of III and Acrylonitrile at −40°C.

III, mole-%	Acrylonitrile, mole-%	Conversion, %	Nitrogen %[a]	III in copolymer, mole-%	Acrylonitrile in copolymer, mole-%
9.67	90.33	6.3	23.34	8.39	91.61
65.54	34.46	5.7	12.57	37.32	62.68
71.91	28.09	7.8	8.98	50.68	49.32

[a] Corrected value.[1]

TABLE III
Copolymerization of IV and Acrylonitrile at −40°C.

III, mole-%	Acrylonitrile, mole-%	Conversion, %	Nitrogen, %[a]	III in copolymer, mole-%	Acrylonitrile in copolymer, mole-%
1.51	98.49	8.7	25.83	1.39	98.61
45.61	54.39	7.6	13.60	29.38	70.62
75.04	24.96	9.2	4.48	48.43	31.57

[a] Corrected value.[1]

TABLE IV
Copolymerization of III and Styrene

III, mole-%	Styrene, mole-%	Conversion, %	Carbon, %	Hydrogen, %	III in copolymer, mole-%
47.97	52.03	8.6	65.30	5.30	~100
31.34	68.66	9.1	65.23	5.37	~100
22.94	77.06	6.9	65.34	5.19	~100

TABLE V
Copolymerization of IV and Styrene

IV, mole-%	Styrene, mole-%	Conversion, %	Carbon, %[a]	Bromine, %[b]	IV in copolymer, mole-%	Styrene in copolymer, mole-%
9.10	90.90	9.1	87.21	21.39	18.6	81.4
55.56	44.44	7.8	76.84	44.76	58.7	41.3

[a] Before bromination.
[b] In brominated copolymer.

sight into the reactivity of these monomers, III and IV were subjected to anionic copolymerization reactions with styrene and acrylonitrile. Experimental data are shown in Tables II–V. The compositions of the copolymers were determined from their elemental analyses.

In both the III–acrylonitrile and IV–acrylonitrile copolymerizations, acrylonitrile is preferentially incorporated into the copolymer. These values are compatible with those obtained in other anionic copolymerizations involving acrylonitrile and acrylate or methacrylate esters[15,28] and with the values obtained[1] with 1-acryloxy-2-butyne and 1-methacryloxy-2-butyne.

The III–styrene copolymerization yielded the expected result. The copolymers consisted almost exclusively of III, despite the fact that large excesses of styrene were used in some of the copolymerizations. This copolymerization can be compared to the sodium naphthalene- and sodium benzalaniline-initiated copolymerization of styrene and methyl methacrylate. Other investigators have found that the resulting copolymers contained almost exclusively methyl methacrylate.[4,29] Though the results of the IV–styrene copolymerization are somewhat surprising, in that an appreciable amount of styrene appeared in the copolymers, they are compatible with similar results obtained[1] in the anionic copolymerization of styrene and 1-methyacryloxy-2-butyne.

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Résumé

La synthèse et la polymérisation d'esters du type acrylique contenant un groupe terminal acétylénique, $CH_2{=}C(R)COO(CHR')_m{-}C{\equiv}CH$, ou R et R' sont H et CH_3 et m est égal à un ou deux, par initiation anionique en vue d'obtenir des polymères linéaires ont été décrites. Par contre des polymères pontés ont été formés lorsqu'on utilise des initiateurs radicalaires et cationiques. Les polymères pontés étaient également obtenus avec des composés organolithiens non pas avec le sodium naphthalène et le sodium benzalaniline; cette observation est discutée et comparée au comportement d'esters acryliques acétyléniques qui ne contiennent pas d'hydrogène acétylénique terminal. La présence de liens acéthyléniques non polymérisés au sein de polymères linéaires résultants est prouvée par des méthodes spectroscopiques infrarouges et par les réactions ultérieures suivantes aux dépends de ces liens: (*1*) le pontage thermique et radicalaire des polymères au moyen de ces liens acétyléniques, (*2*) la bromuration ultérieure des liens acétyléniques et (*3*) la réaction du décaborane avec ces liens acétyléniques. La copolymérisation anionique de l'acrylonitrile et du styrène avec les monomères acétyléniques a été effectuée et comparée aux copolymérisations avec le 1-acryloxy-2-butène et le 1-méthacryloxy-2-butyne. La dibromuration des polymères linéaires produit des polymères non combustibles, dont la décoloration fournit des polymères solubles qui ne se ramolissent pas avant 300°C. Les polymères linéaires peuvent être classifiés comme des polymères réactionnels qui fournissent des polymères thermodurcissables.

Zusammenfassung

Die Synthese und Polymerisation repräsentativer Ester vom Acryltyp mit einer endständigen Acetylgruppe, $CH_2{=}C(R)COO(CHE')_m{-}C{\equiv}CH$, wo R und R' H und CH_3 sind und m gleich eins und zwei ist, mit anionischem Start zu linearen Polymeren werden beschrieben. Im Gegensatz dazu wurden mit radikalischen und kationischen Startern vernetzte Polymere gebildet. Vernetzte Polymere wurden auch mit lithiumorganischen Verbindungen, aber nicht mit Naphthalinnatrium und Benzolanilinnatrium erhalten; diese Beobachtung wird diskutiert und dem Verhalten von acetylenischen Acrylestern ohne endsändigen Acetylenwasserstoff gegenüber gestellt. Die Anwesenheit der unpoly-

merisierten Acetylenbindungen in den gebildeten linearen Polymeren wurde durch Infrarotspektroskopie und durch folgende Reaktionen dieser Bindungen nachgewiesen: (*1*) thermisch und radikalisch gestartete Vernetzung der Polymeren über die Acetylenbindungen; (*2*) Nachbromierung der Acetylenbindungen; und (*3*) Reaktion von Dekaboran mit den Acetylenbindungen. Die anionische Copolymerisation von Acrylnitril und Styrol mit diesen acetylenische Monomeren wurde durchgeführt und mit der Copolymerisation mit 1-Acryloxy-2-butin und 1-Methacrylox-2-butin verglichen. Dibromierung der linearen Polymeren liefert selbslöschende Polymere, während Dekaboranierung lösliche, bis 300°C nicht erweichende Polymere ergibt. Die linearen Polymeren können als "selbst-reaktive" Polymere bezeichnet werden, welche wärmehärtende Polymere liefern.

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Solid-State Polymerization of 1,2,3,4-Diepoxybutane Initiated by Cobalt-60 γ-Radiation

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Synopsis

The solid-state polymerization of 1,2,3,4-diepoxybutane appears to proceed "in-source" by an ionic mechanism and has an overall activation energy of 0.4 kcal./mole with an intensity dependency of 0.99. There is a rapid increase in the rate of polymerization just prior to the melting point and a very low rate for the liquid-phase reaction. Limiting conversions of 5% polymer are observed at −196°C. for irradiation *in vacuo*. No limiting conversion was observed when the monomer was polymerized in the presence of air or *in vacuo* at −78°C. Under all polymerization conditions the reactions were characterized by the absence of an induction period.

Introduction

Solid-state polymerizations initiated by γ-radiation have been reported for both vinyl and cyclic monomers.[1,2] Most investigations of cyclic monomers have centered around trioxane and substituted oxetanes, and little attention has been given to the polymerization of oxiranes. It has been reported that epoxyethylbenzene[3] and *o*-diepoxyethylbenzene[4] polymerize in the solid state when initiated by γ-radiation. 1,2,3,4-Diepoxybutane has been reported to polymerize with catalytic amounts of aluminum chloride[5]; however, this system has not been investigated in the solid state.

One of the major problems in solid-state polymerization studies is that of determining the influence of the crystal structure of the monomer on the mechanism of the reaction. The rates of the reactions and conformation of the polymer chains appear to be influenced by the crystal structure of the monomer for the polymerization of acrylic and methacrylic acid salts.[6] These reactions were studied well below the melting point of the monomer in order to minimize effects from localized melting caused by the heat of polymerization. Another phenomenon observed in solid-state polymerization reactions is a limiting conversion of the monomer into polymer. It is currently believed that the limiting conversion is the result of two factors: (*1*) the trapping of the reactive site of the growing chain in a region void of

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monomer and (*2*) the disruption of the crystal lattice caused by the volume changes due to the conversion of monomer to polymer.

Experimental

The 1,2,3,4-diepoxybutane used in these studies was a commercial grade supplied by Koppers Company, Inc.* Samples for irradiation were prepared by placing approximately 30 g. of monomer in an ampule, connecting the ampule to a high-vacuum system, then degassing the monomer by a freeze–thaw process, and distilling it into smaller ampules. These small ampules each contained approximately 5 g. of monomer and were degassed again and sealed *in vacuo* at pressures of 10^{-5} and 10^{-6} torr. The monomer was melted and then cooled by immersing it in a Dry Ice bath at −78°C. to produce small uniform crystals. In the cases where air was added to the samples, the ampules were removed from the vacuum line after distillation and sealed at atmospheric pressure. The monomer was then crystallized in the same manner as the ampules sealed *in vacuo*.

Samples were irradiated in a nominally 28,000-curie ^{60}Co "cave type" γ-radiation facility, and the dose rate was determined by the Fricke dosimeter (G = 15.5).

There is a major problem in determining the yield in solid-state polymerization reactions where the system shows a rapid increase in the rate of post-polymerization just prior to the melting point of the monomer. Care must be exercised to prevent polymerization during polymer isolation. Several methods, both instrumental and gravimetric, have been used to circumvent this problem. The most effective gravimetric technique has been the rapid melting of the monomer–polymer samples in a hot solvent which contains an inhibitor. A modification of this technique has been used in this study. After irradiation the ampules were removed from the source and while still in the frozen state immediately opened. Approximately 5 ml. of dimethylformamide, which contained 0.1% hydroquinone, was added to the contents of each ampule to quench any liquid-phase polymerization, and then the monomer was rapidly melted. The monomer and dimethylformamide were separated from the polymer by distillation, and the yield was determined in terms of the total solids.

Results

In Figure 1 the polymerization of 1,2,3,4-diepoxybutane at −78 and −196°C. is shown in plots of per cent conversion versus time in hours. At an intensity of 103 krad/hr. the initial rate of polymerization at −78°C. is 0.23%/hr. and at −196°C. it is 0.13%/hr.; there is no induction period at either temperature. A limiting yield at 5% conversion is found at −196°C.; however, no limiting conversion is observed at −78°C *in vacuo* or air (Figs. 1 and 2).

The initial rate of polymerization in the presence of air is comparable to the rate *in vacuo* at −78°C. for an intensity of 103 krad/hr.

* It is realized that this monomer is probably a mixture of all possible stereoisomers.

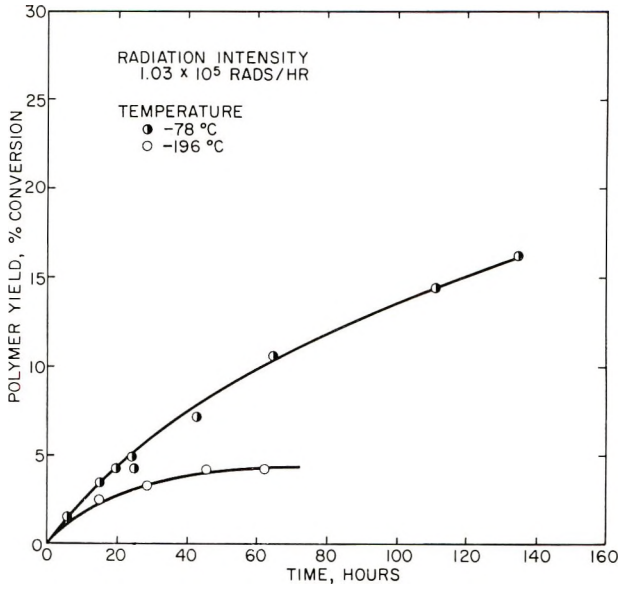

Fig. 1. Polymerization of 1,2,3,4-diepoxybutane *in vacuo* initiated by ^{60}Co γ-radiation. Polymer yield vs. irradiation time.

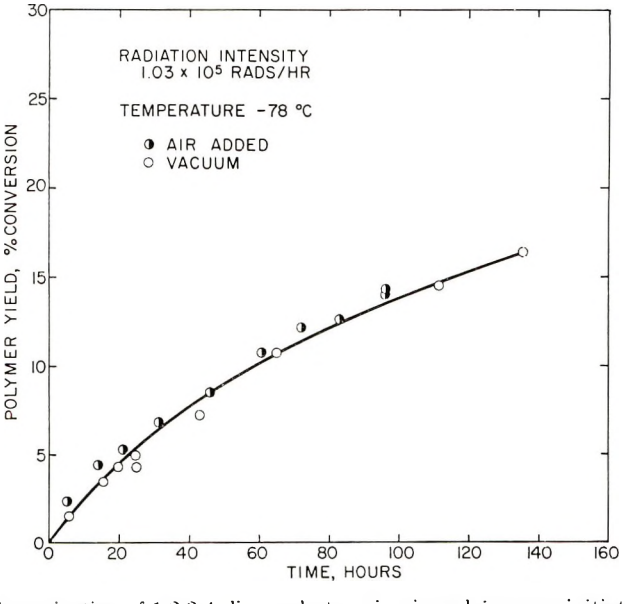

Fig. 2. Polymerization of 1,2,3,4-diepoxybutane in air and *in vacuo* initiated by ^{60}Co γ-radiation. Polymer yield vs. irradiation time.

In Figure 3, the temperature profile of the reaction for the range −196 to 30°C. is given. Here the per cent conversion is plotted against temperature for samples which have received a total dose of 1.56 Mrad at an intensity of 103 krad/hr. Under these conditions the rate of polymerization

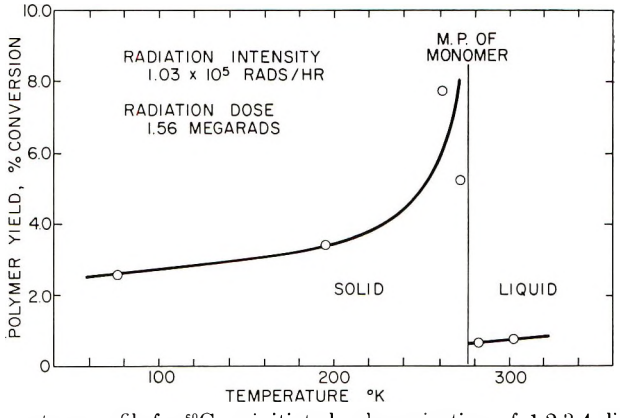

Fig. 3. Temperature profile for ^{60}Co γ-initiated polymerization of 1,2,3,4-diepoxybutane *in vacuo*. Polymer yield vs. temperature.

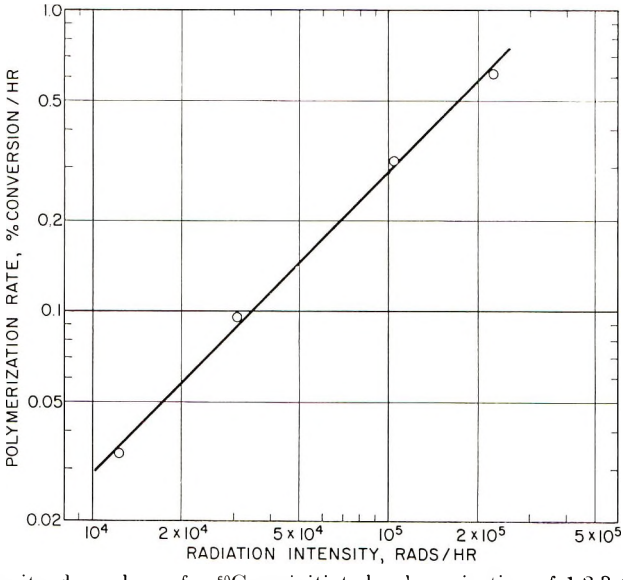

Fig. 4. Intensity dependence for ^{60}Co γ-initiated polymerization of 1,2,3,4-diepoxybutane *in vacuo*. Initial rate of polymerization vs. radiation intensity.

approaches a maximum just below the point of fusion. If a first-order reaction with respect to monomer concentration is assumed, then the overall Arrhenius activation energy for the temperature range −196 to −78°C. is 0.4 kcal./mole.

The intensity dependency for the range 12–226 krad/hr. is 0.99 for the initial rates of polymerization at −78°C. (see Fig. 4).

1,2,3,4-Diepoxybutane shows no evidence of post-polymerization for the temperature range from −78 to −27°C. The polymer produced in this study is completely amorphous and rubbery in nature, but has the exterior appearance of the monomer crystals when produced at low degrees of conversion. The polymer is very insoluble and is probably highly crosslinked.

Discussion

Trioxane, diketene, 3,3′-bis(chloromethyl)oxetane, and β-propiolactone may be polymerized in solution only with ionic catalysts. This, in conjunction with the low activation energies observed for radiation-induced solid-state polymerization, has been used to postulate an ionic mechanism for the solid-phase reaction.[6,7] In fact, trioxane has been successfully polymerized in the solid phase with BF_3, $BF_3 \cdot O(C_2H_5)_2$, $SnCl_4$, and $TiCl_4$.[7] These oxygen heterocyclic systems all exhibited a saturation in polymer yield for "in-source" polymerization and a rapid increase in the rate of polymerization just prior to the monomer melting point and showed no appreciable polymerization in the liquid phase.[6] It has been reported that epoxyethylbenzene[3] and *o*-diepoxyethylbenzene[4] polymerize in the solid state with γ-irradiation. Epoxyethylbenzene has an activation energy for the solid-state polymerization of from 0.5 to −0.2 kcal./mole, and an ionic mechanism is indicated.

The same reaction characteristics, such as maximum rate just prior to melting point and almost zero rate in the liquid phase, are observed for the radiation-induced polymerization of 1,2,3,4-diepoxybutane. The calculated activation energy for the temperature range −78 to −196°C. is 0.4 kcal./mole. This is in the range expected for an ionic reaction, and, in addition, there is no indication of an induction period for the samples irradiated in air. Also, an explosive polymerization has been reported when catalytic amounts of $AlCl_3$ are added to the liquid monomer.[5] When all of these factors are considered, there is a strong indication that butadiene diepoxide polymerizes in the solid phase by an ionic mechanism.

Currently there are two accepted explanations for the limiting conversions observed in solid-state polymerization reactions. One is that the polymer produced during the polymerization reaction disrupts the crystal lattice of the monomer and inhibits the propagation step. The other applies to the post-polymerization studies, and here the polymer chain traps the active site from the monomer. In this system, where there is no applicable post-polymerization, the limiting conversion is observed only at −196°C. At higher temperature the reaction appears to proceed in the absence of a limiting conversion. This could be due to an increased mobility of the monomer at the higher temperature, thus minimizing the effects of polymer produced in the crystal.

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Résumé

La polymérisation à l'état solide du 1,2,3,4-diépoxybutane résulte primairement d'un mécanisme ionique et présente une énergie d'activation globale de 0.4 Kcal/mole avec une dépendance de l'intensité de 0.99. Il y a une augmentation rapide de vitesse de polymérisation juste avant le point de fusion et une très petite vitesse pour la réaction en phase liquide. Les conversions limites de 5% en polymère ont été observées à −196°C lorsqu'on irradie sous vide. Il n'y a pas de conversion limite lorsque le monomère polymérisait en présence d'air ou sous vide à −78°C. Dans toutes ces conditions de polymérisation, les réactions sont caractérisées par l'absence d'une période d'induction.

Zusammenfassung

Die Polymerisation von 1,2,3,4-Diepoxybutan in fester Phase unter Bestrahlungsheint einem ionischen Mechanismus zu folgen und besitzt eine Bruttoaktivierungsenergie von 0,4 Kcal/Mol und einen Intensitätsexponenten 0,99. Knapp unter dem Schmelzpunkt nimmt die Polymerisationsgeschwindigkeit rasch zu; die Geschwindigkeit der Reaktion in flüssiger Phase ist sehr niedrig. Bei Bestrahlung im Vakuum bei −78°C trat kein Grenzumsatz auf. Unter allen Reaktionsbedingungen war die Reaktion durch das Fehlen einer Induktionsperiode charakterisiert.

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Studies of the Micro-Brownian Motion of a Polymer Chain by the Fluorescence Polarization Method. III. Fluorescent Conjugates of Polyethyleneimine

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Synopsis

Fluorescent conjugates of polyethyleneimine (PEI) were prepared by conjugation of fluorescent dyes, fluorescein isocyanate (FIC), and 1-dimethylaminonaphthalene-5-sulfonyl chloride (DNS), to PEI. The degree of polarization of the fluorescence was measured as a function of temperature and solvent viscosity on aqueous solutions of the conjugates and the data thus obtained were analyzed in terms of an equation of the Perrin type to calculate the mean relaxation time of the conjugate. The mean relaxation times obtained for the two types of the conjugates, which differ in the excited lifetime by a factor of about three, practically agree with one another and are about 2.5×10^{-8} sec. The relaxation time of the DNS conjugate increases with increasing molecular weight of the conjugate from 2×10^{-8} to 4×10^{-8} sec. These values are much larger than those of the PAA conjugates reported in Part I of this series. The relaxation time of this order may correspond to that for the cooperative rotary motion of about ten monomeric residues on the PEI chain, that is, for the motion of an intermediate segment of the PEI molecule in solution. Finally, relaxation time–molecular weight relationships for various types of fluorescent conjugates are compared. It is suggested that these data may serve as a basis for elucidating the mode of motion of a given molecule in solution from the polarization data.

INTRODUCTION

The fluorescence polarization method has recently been used successfully in the study of the Brownian motion of a macromolecule in solution.[1–4] Wahl[5] was the first to apply this method to flexible polymers. Since then, several studies on fluorescent conjugates of flexible polymers have been reported.[3,4,6–9] The theoretical basis of the fluorescence method has already been established for rigid macromolecules,[10] whereas it has not been well developed for flexible polymers. Wahl[11] and Gottlieb and Wahl[8] treated this problem by using simplified molecular models. However there are so many factors affecting the motion of the polymer molecule in solution in addition to the complexity inherent in this method that further studies

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are needed for satisfactory understanding of the problem. (To use the fluorescence polarization method effectively, it is necessary to know the absolute value for the excited lifetime of fluorescence in various solvent media and in a wide temperature range. This is, however, a rather difficult problem.) In this connection, we reported the studies on the micro-Brownian motion of the terminal segment in the previous publications.[6,12,13] The micro-Brownian motion of an intermediate segment was the next problem of interest. We prepared fluorescent conjugates of polyethyleneimine of various molecular weights and carried out fluorescence measurements on them. The results are reported in this paper. Polyethyleneimine was chosen as parent polymer because it was easy to bind fluorescent dyes to the polymer molecule[5] and also because the polymer was a polyelectrolyte soluble in water, in which the fluorescent characteristics of fluorescent dyes such as uranine or 1-aminonaphthalene-5-sulfonic acid derivatives have been well clarified. Effects on the polarization of fluorescence of various factors such as molecular weight of the conjugate, lifetime of fluorescence, and addition of extraneous salts were examined.

EXPERIMENTAL

Fluorescent Dyes

Fluorescein isocyanate (FIC) and 1-dimethylaminonaphthalene-5-sulfonyl chloride (DNS) were used as fluorescent dye. According to Fussganger[14] 1-dimethylaminonaphthalene-5-sulfonic acid (I) was synthesized by methylation of 1-aminonaphthalene-5-sulfonic acid with methyl iodide. The chloride (DNS) was then synthesized from the sulfonic acid (I) according to Weber.[15] Fluorescein isocyanate was a commercial product.

Preparation of Fluorescent Conjugates of Polyethyleneimine

Purification and fractionation of polyethyleneimine (PEI) were made as follows. About 30 g. of PEI (commercial product) was dissolved in 600 ml. of methanol. Then the solution was poured dropwise into an excess of vigorously stirred benzene, and the resulting precipitate was separated and dried. The polymer thus obtained was designated as PEI-U. A 10-g. portion of PEI-U dissolved in 400 ml. of methanol was separated into 14 fractions by successive addition of benzene as precipitant. The gels so separated were dried and then lyophilized. They were all soluble in water except for the first fraction.

Dye conjugation was performed by means of similar methods used for protein conjugates.[2,15,16] A typical procedure for a DNS conjugate is shown below for example. A 1-g. portion of PEI-U was dissolved in 100 ml. of 0.2*M* $NaHCO_3$. A 15-mg. portion of DNS dispersed in 10 ml. of water was added to the PEI solution. The solution, which looked turbid at the beginning of the reaction due to the dispersed DNS precipitate, became clear and showed weak fluorescence. The reaction was allowed

to continue for 2 days at room temperature with stirring. Then the reaction mixture was centrifuged off at 15,000 rpm for 1 hr. to remove gels and unreacted DNS. The supernatant solution was dialyzed against distilled water in a cellophane tubing for 10 days until no fluorescence was detected in the outer solution. Finally the dialyzed solution was passed successively through the columns of ion-exchange resins, IR-120 and IRA-400. Since the pH value for the resulting solution was about 11, the purified PEI conjugate (PEI-UN) was considered to exist as a free base in water.

Conjugation with fluorescein isocyanate was made in a manner similar to that used for protein conjugates by Coons and Kaplan.[16] Purification of the FIC conjugate so prepared, PEI-UF, was made in the same manner as PEI-UN. For both types of conjugate, the reagents appear to react equally probably with all imino residues on the chain of PEI[17] and to be bound to the chain by a primary bond. In addition to PEI-U, six PEI fractions were selected for conjugation with DNS. The number of dye residues bound per monomeric residue was estimated to be less than 0.005 for each conjugate.

Characterization of Polyethyleneimine Conjugates

Absorption spectra of the fluorescent dyes and the respective conjugates are compared in Figure 1. Figure 1*a* shows the absorption spectra of DNS and FIC in borate buffer containing 10% acetone (pH = 9.8), and Figure 1*b* shows those of PEI-UN and PEI-UF in water. It was found that the absorption spectrum of PEI-UF was actually the same as that of uranine in aqueous PEI and very similar to that of FIC. It should be noted that the addition of PEI to an aqueous uranine solution reduces the fluorescence intensity of the solution, suggesting that the lifetime of the fluorescence may be decreased.

The absorption spectrum of PEI-UN is similar to that of DNS. A literature survey indicates that the excited lifetime of fluorescence for various DNS conjugates may not differ appreciably for different conjugates. In fact, the values for the lifetimes of various protein conjugates in aqueous media[18] and of polystyrene conjugates in chlorobenzene–pyralene mixtures[7] are in the range from 1.0×10^{-8} to 1.3×10^{-8} sec. We therefore suppose that the excited lifetime of our DNS conjugates may be also in this range.

Titration of PEI with 0.1*N* HCl showed that PEI is a weak basic polyelectrolyte. The viscosity behavior of PEI in aqueous NaCl solutions was also characteristic of polyelectrolytes. In view of these observations, fractions of PEI conjugate were characterized by the limiting viscosity number of the sample in 0.2*M* NaCl at 30°C. The limiting viscosity number of PEI-U in 0.1*M* NaCl was measured as a function of temperature. It was found that the limiting viscosity number increased only slightly with increasing temperature in the range where the fluorescent measurements were performed. In conclusion, the molecular extension of PEI in salt solutions may be practically independent of salt concentration and of temperature.

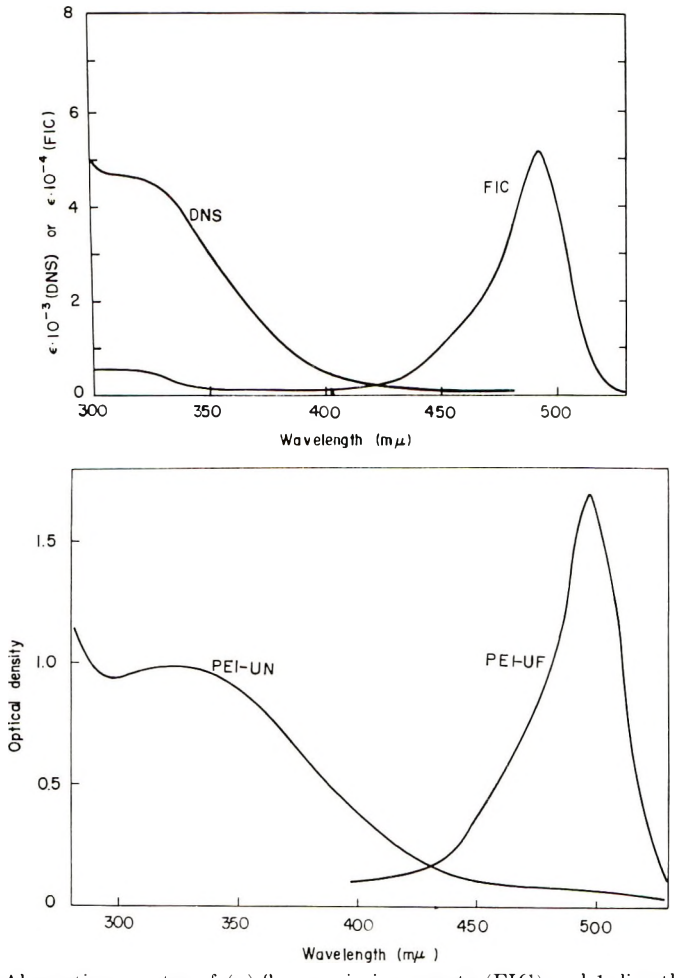

Fig. 1. Absorption spectra of (*a*) fluorescein isocyanate (FIC) and 1-dimethylamino-naphthalene-5-sulfonyl chloride (DNS) in borate buffer containing 10% acetone (pH = 9.8) and (*b*) fluorescent conjugates of polyethyleneimine, PEI-UF and PEI-UN in water.

Fluorescence Measurements

The apparatus used for fluorescence measurements was previously described.[3,4,12] For excitation of fluorescence, natural light of 436 mμ wavelength was used with DNS conjugates, whereas linearly polarized light of the same wavelength was used with FIC conjugates. Degrees of polarization of fluorescence are denoted by p_n for the natural light and by p for the polarized light.

RESULTS AND DISCUSSION

Linear Dependence of $1/p_n$ on T/η_0 and Mean Rotational Relaxation Time of Polyethyleneimine Conjugate

The degree of polarization of fluorescence was measured on solutions of PEI conjugates as a function of the viscosity of the solvent, η_0, in the range of

10–40°C. All the measurements were made at PEI concentrations lower than 0.5%. Thus the polarization data presented below may be regarded as all referring to infinite dilution. Figure 2 plots $1/p_n$ against T/η_0 for PEI-UN in water, where the viscosity of water was taken from the literature and T is the absolute temperature. It is seen that $1/p_n$ varies linearly with T/η_0 in the range of T/η_0 examined. Thus the polarization data for PEI-UN may be represented by an equation of the Perrin type,[10] and therefore the mean rotational relaxation time of the conjugate $\langle\rho\rangle$, may be estimated, as in the case of polyacrylamide conjugates,[12] by the equation:

$$1/p_n + {}^1/_3 = (1/p_{n_0} + {}^1/_3)(1 + \beta T/\eta_0)$$
$$= (1/p_{n_0} + {}^1/_3)(1 + 3\tau/\langle\rho\rangle) \quad (1)$$

where

$$\langle\rho\rangle = 3\tau\eta_0/\beta T \quad (2)$$

In these equations, β is a constant independent of T/η_0, and p_{n_0} is the limiting polarization.

The motion of the fluorescent residue may be mainly restricted by the segment, to which the residue is bound, and in addition may be affected by the interaction with neighboring segments. It should be noted that polyethyleneimine is a cationic polyelectrolyte and the fluorescent residues used here have ionizable groups. Effects of the electrostatic interaction between such ionizable groups should carefully be taken into consideration in the analysis of polarization data.

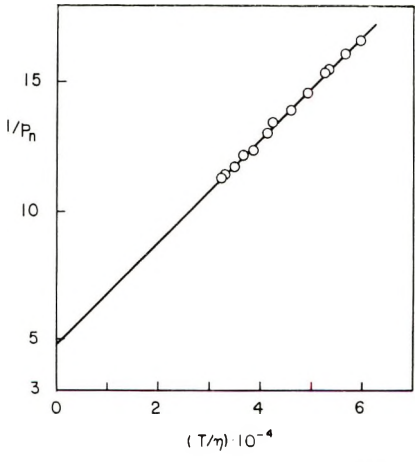

Fig. 2. Plot of $1/p_n$ against T/η_0 for PEI-UN in water.

Effect of Excited Lifetime on the Mean Rotational Relaxation Time of the Conjugate

When the reciprocal of degree of polarization is a linear function of T/η_0, the factors which determine the value for (p or p_n) are the excited lifetime τ

TABLE I
Mean Relaxation Times of PEI-UN in Aqueous NaCl Solutions at 20°C.

NaCl concn., M	$1/P_{n0}$	$\langle\rho\rangle \times 10^8$, sec.
0	4.49	3.02
0.1	4.20	2.90
0.2	4.61	3.05
0.5	4.68	3.10
Average	4.48	3.02

and the relaxation time $\langle\rho\rangle$. If $\langle\rho\rangle$ is truly a quantity characteristic of the segmental motion, it should be independent of τ, provided the range of τ is not too wide. To test this prediction, we carried out polarization measurements on two fluorescent conjugates, PEI-UN and PEI-UF, which had lifetimes differing by a factor of about three.

PEI-UN. Fluorescence measurements were made on PEI-UN in aqueous sodium chloride solutions having concentrations C_s of 0, 0.1, 0.2, and 0.5M. It was found that the degree of polarization as well as the

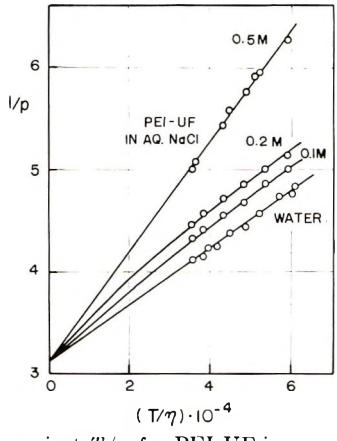

Fig. 3. Plots of $1/p$ against T/η_0 for PEI-UF in aqueous NaCl solutions.

fluorescent intensity was almost independent of salt concentration. All the data were analyzed in terms of eq. (1) to calculate $\langle\rho\rangle$, the excited lifetime of fluorescence for PEI-UN being assumed to be 1.2×10^{-8} sec. This value for τ is the average for various protein conjugates deduced from the data of Steiner and McAlister.[18] The results are summarized in Table I. The mean relaxation time $\langle\rho\rangle$ is independent of salt concentration, and the average value $3.0_2 \times 10^{-8}$ sec. is much larger than those of PAA conjugates.[12]

PEI-UF. In the case of PEI-UF, the degree of polarization p decreased with increasing salt concentration at a given temperature, whereas the fluorescent intensity increased. Figure 3 shows plots for $1/p$ versus T/η_0 for PEI-UF in aqueous NaCl solutions. All of these plots are approximately linear and have a common ordinate intercept of about 3.12, whereas

the slope of each straight line depends on salt concentration. This phenomenon suggests that either the excited lifetime or the mean relaxation time, or both of them depends on salt concentration. This is expected from the fact that PEI is a cationic polyelectrolyte whereas fluorescein residue is a divalent anion, because electrostatic interactions between these opposite ions may decrease the fluorescent intensity, and at the same time, restrict the motion of the fluorescent residue. First we assumed the excited lifetime τ of the conjugate to be 4.8×10^{-9} sec.* and evaluated the apparent relaxation time defined by the following equation as a function of salt concentration:

$$1/p - {}^1/_3 = (1/p_0 - {}^1/_3)(1 + \beta_a T/\eta_0)$$
$$= (1/p_0 - {}^1/_3)(1 + 3\tau/\langle\rho\rangle_a) \quad (3)$$

where

$$\langle\rho\rangle_a = 3\tau/\beta_a(T/\eta_0) \quad (4)$$

In these equations β_a is a parameter which depends on salt concentration.

Fluorescence measurements on aqueous uranine solutions containing PEI showed that the fluorescence was quenched by the presence of PEI, i.e., the fluorescence intensity was decreased, and, on the other hand, the degree of polarization was increased. Upon addition of extraneous salts such as sodium chloride or sodium sulfate to the uranine solution containing PEI, however, both the fluorescence intensity and the degree of polarization recovered their original values for free uranine in pure water. These observations suggest that the free fluorescein ion may be absorbed onto a PEI molecule due to the electrostatic interaction between them, and as a result, its fluorescence intensity and mobility may be reduced. This situation may be the same for PEI-UF in aqueous salt solutions, in which the interaction of a chemically bound fluorescein ion with the polymer chain plays a role similar to that of the interaction of a free fluorescein ion with the added polymer molecules plays in the former case. Therefore it is expected that by plotting $\langle\rho\rangle_a$ against $1/C_s$ and extrapolating to $1/C_s = 0$, one can obtain the limiting value for $\langle\rho\rangle_a$, which is considered to be free from any disturbing effects discussed above and to be compared with that of PEI-UN. Figure 4 plots $\langle\rho\rangle_a$ versus $1/C_s$, yielding 2.2×10^{-8} sec. for the limiting relaxation time for PEI-UF. In spite of as large a difference as a factor of 2.6 in the excited lifetime of fluorescence, the mean relaxation times for the two types of conjugates, PEI-UN and PEI-UF, do not differ appreciably from one another (by a factor of 1.4). The mean relaxation times of this order thus obtained may be associated with the rotational motion of an intermediate segment of polymer chain in dilute solutions.

* This value is the average of τ for various fluorescein conjugates of proteins deduced from the data of Steiner and McAlister.[18]

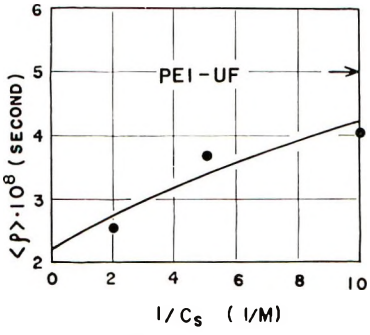

Fig. 4. Apparent relaxation time for PEI-UF plotted against reciprocal of salt concentration $1/C_s$.

Molecular Weight Dependence of Mean Rotational Relaxation Time

In order to examine the molecular weight dependence of the mean relaxation time for PEI-conjugate, fluorescence measurements were made on six fractions of DNS conjugate in 0.2M NaCl at temperatures from 15 to 40°C. Linear relations between $1/p_n$ and T/η_0 were found to hold for all the samples studied, and all the data were analyzed according to eq. (1). The results are summarized in Table II. The limiting viscosity number $[\eta]$

TABLE II
Mean Relaxation Times of PEI–DNS Conjugates in 0.2M NaCl at 20°C.

Sample code	$[\eta]$, dl./g.[a]	$1/p_{n0}$	$\langle\rho\rangle \times 10^8$, sec.
PEI-F2	0.452	4.53	3.30
F4	0.222	4.30	3.15
F6	0.206	3.88	3.10
F8	0.16	3.92	2.61
F12	0.112	3.94	2.50
F14	0.057	4.08	2.25
UN	0.296	4.48	3.02

[a] Limiting viscosity numbers in 0.2M NaCl at 30°C.

of each fraction in 0.2M NaCl at 30°C. is listed in the second column of Table II. Figure 5 shows the plot for $\langle\rho\rangle$ versus $[\eta]$. The data for whole polymer PEI-UN, which is represented by a filled circle, also falls on the same curve as that for the fractions. It is seen that $\langle\rho\rangle$ increases gradually from 2×10^{-8} up to 4×10^{-8} sec. with increasing limiting viscosity number. Since $[\eta]$ varies parallel with molecular weight, the plot for $\langle\rho\rangle$ versus $[\eta]$ shown in Figure 5 may be regarded as representing the molecular weight dependence of $\langle\rho\rangle$. Features of this plot are similar to those found previously for the PAA conjugates.[12] This indicates that $\langle\rho\rangle$ may be related not to the motion of the polymer molecule as a whole but to the local motion of the polymer segment. However, it is not clear to us why $\langle\rho\rangle$ depends appreciably on molecular weight at relatively high molecular

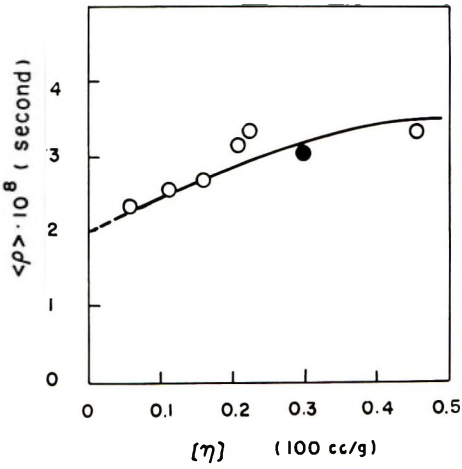

Fig. 5. Mean relaxation time at 20°C. plotted against limiting viscosity number in 0.2*M* NaCl at 30°C. for PEI-DNS; (●) data for the conjugate of whole polymer, PEI-UN.

weights. In any event, we are inclined to consider that $\langle\rho\rangle$ may be the mean rotational relaxation time of the intermediate segment of the PEI chain. The radius of the equivalent sphere corresponding to this value of $\langle\rho\rangle$ (the average value of 3×10^{-8} sec.) is estimated to be about 20 A. This is likely to be a reasonable value as compared with 10 A. for the PAA conjugate,[12] because in the case of the PEI conjugate the rotational motion of the fluorescent residue may be restricted by the two polymer chains which are connected on both its sides, whereas for the PAA conjugate the restriction of the motion of the fluorescent residue comes from one polymer chain only.

Although the plot for $1/p_n$ versus T/η_0 appears to be linear in the temperature range examined, it will curve downward at low values of T/η_0, because the value for p_0 obtained by graphical extrapolation is appreciably smaller than the true one.* This indicates that the PEI conjugate cannot be characterized by a single relaxation time. This similar phenomenon was found for other fluorescent conjugates of linear polymers.[7,8,11] For a quantitative analysis, detailed features of the plot for $1/p$ versus T/η_0 is necessary. We did not succeed in the analysis with PEI conjugates, because the plots for PEI conjugates in water and those in aqueous glycerol solution (50% by weight) were straight lines with different initial slopes and intercepts on the ordinate.

Finally we shall compare data for relaxation times of various fluorescent conjugates. Fluorescent conjugates considered here may be classified as follows: flexible polymers with a fluorescent residue at the chain end, flexible polymers with fluorescent residues on the chain, conjugates of rigid macromolecules (including fluorescent dyes). Typical results which

* The true values for the limiting degree of polarization are 0.44 for FIC Conjugates[12] and 0.253 for DNS conjugates.[15]

TABLE III
Comparison of the Mean Relaxation Times of Various Fluorescent Conjugates in Water at 20°C.

Conjugate	Molecular weight	ρ_h or $\langle\rho\rangle \times 10^8$, sec.[a]
Rigid molecules		
Uranine	376.2	0.068
Lysozyme[b]	15,000	2.8
Ovalbumin[b]	35,000	8.4
Bovine serum albumin[b]	65,000	14.6
Flexible polymers		
PEI[c]	—	5.41
PEI	$[\eta] \to 0$	2.0
PEI	$[\eta] \to \infty$	4.0
PAA[d]	$M \to 0$	0.31
PAA[d]	$M \to \infty$	0.72 ± 0.02
Polystyrene[e]	18,700–150,000	0.28–0.78

[a] ρ_h is the harmonic mean of the principal relaxation times.
[b] Data of Steiner and McAlister.[18]
[c] Data of Wahl.[5]
[d] Data of Nishijima et al.[12]
[e] Frey et al.[7] made fluorescent measurements on polystyrene–DNS conjugates in chlorobenzene–pyralene mixtures. The values for relaxation times cited above have been converted from the effective volumes determined in the mixtures to the present condition, i.e., in water at 20°C.

have appeared in the literature are summarized in Table III. It is seen that the absolute values for the relaxation times also follow the above classification. In Figure 6 the relaxation times for various conjugates in water at 20°C. are plotted against molecular weight, where filled circles

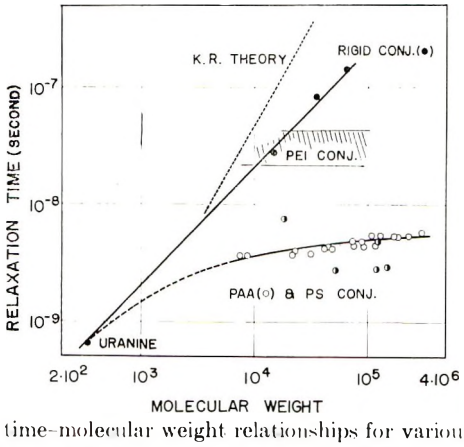

Fig. 6. Relaxation time–molecular weight relationships for various fluorescent conjugates in water at 20°C.: (●) rigid molecules; uranine,[12] lysozyme-conjugate,[18] ovalbumin conjugate,[18] and bovine serum albumin conjugate;[18] (○) PAA conjugates;[12] (◑) data of Frey et al.[7] for polystyrene conjugates; (- - -) theoretical value for the average relaxation time of the whole molecule calculated for PAA conjugates according to the Kirkwood-Riseman theory.[12,19]

indicate the data for rigid molecules, open circles those for the PAA conjugates,[12] and half-filled circles those for the polystyrene conjugates, which have been converted from the effective volumes of the respective conjugate in chlorobenzene–pyralene mixtures to the same condition, i.e., in water at 20°C. The data for the rigid molecules follow approximately a straight line of unit slope, whereas those for other conjugates do not. The data for fluorescein isothiocyanate conjugates of crosslinked polypeptides,[9] which are not shown in the figure, fall in the region between PEI conjugates and PAA conjugates. These results suggest that the mode of motion of a molecule, more precisely speaking, the segment to which the fluorescent residue is attached, and hence the internal structure of the molecule,[9] may be elucidated from the relaxation time–molecular weight relationships thus obtained.

The authors wish to thank Professor Masao Horio of this department for his continued interest and encouragement throughout the course of this study. They express their thanks to Professor Hiroshi Fujita, Department of Polymer Science, Osaka University, for his valuable discussion.

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Résumé

Des produits de condensation fluorescents de polyéthylèneimine (PEI) ont été préparés par condensation de colorants fluorescents tel que l'isocyanate de fluorescine (FIC) et le chlorure de 1-diméthylaminonaphtalène-5-sulfonyle (DNS) avec PEI. Le degré de polarisation de la fluorescence a été mesuré en fonction de la température et de la viscosité du solvant sur les solutions aqueuses de ces polycondensats et les valeurs ainsi obtenues ont été analysées sur la base d'équations du type de celles de Perrin pour calculer le temps moyen des relaxations du système conjugé. Les temps de relaxation moyens obtenus pour les deux types de produits qui diffèrent dans la durée de vie de l'état excité

par un facteur d'au moins 3, sont en accord pratiquement l'un avec l'autre et sont environ de 2.5×10^{-8} sec. Le temps de relaxation du produit à base de DNS croît avec une augmentation du poids moléculaire du produit de condensation de 2×10^{-8} à 4×10^{-8} sec. Ces valeurs sont beaucoup plus grandes que celles de condensats PAA rapportées dans la partie I de ces séries. Le temps de relaxation de cet ordre peut être considéré comme correspondant au mouvement rotatoire coopératif dans environ dix résidus monomériques le long de la chaîne PEI c'est-à-dire pour un mouvement d'un segment intermédiaire de la molécule PEI en solution. Finalement les rapports temps de relaxation poids moléculaire pour les différents types de systèmes fluorescents ont été comparés. On suggère que ces résultats peuvent servir comme base de mode de mouvement d'une molécule déterminée en solution au départ de données de polarisation.

Zusammenfassung

Fluoreszierende Polyäthylenimin-(PEI)-konjugate wurden durch Konjugation fluoreszierender Farbstoffe, Fluoresceinisocyanat (FIC) und 1-Dimethylaminonaphthalin-5-sulfonylchlorid (DNS), mit PEI dargestellt. Der Polarisationsgrad des Fluoreszenzlichtes wurde in Abhängigkeit von Temperatur und Lösungsmittelviskosität an wässrigen Lösungen der Konjugate gemessen und die so erhaltenen Daten mit einer Gleichung vom Perrin-Typ zur Gewinnung der mittleren Relaxationszeit des Konjugates ausgewertet. Die für die beiden, in ihrer Anregungslebensdauer etwa um einen Faktor drei verschiedenen Konjugattypen erhaltenen Relaxationszeiten stimmen praktisch miteinander überein und betragen etwa $2{,}5 \cdot 10^{-8}$ sek. Die Relaxationszeit des DNS-Konjugates nimmt mir steigendem Molekulargewicht des Konjugates von $2 \cdot 10^{-8}$ auf $4 \cdot 10^{-8}$ sek zu. Diese Werte liegen bedeutend höher als die in Teil I dieser Reihe für PAA-Konjugate mitgeteilten. Eine Relaxationszeit von dieser Grössenordnung kann einer kooperativen Rotationsbewegung von etwa zehn Monomerresten in der PEI-Kette entsprechen, d.h. der Bewegung eines mittleren Segmentes des PEI-Moleküls in Lösung. Schliesslich werden die Relaxationszeit–Molekulargewichtsbeziehungen für verschiedene Typen fluoreszierender Konjugate verglichen. Diese Ergebnisse könnten als Grundlage zur Aufklärung des Bewegungszustandes eines gegebenen Moleküls in Lösung aus den Polarisationsdaten dienen.

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Copolymerization of Styrene. II. Emulsion Copolymerization with Styrene Derivatives Containing Nitrile Groups in the Side Chain

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Synopsis

Copolymers of styrene with cinnamonitrile, ethyl benzylidenecyanoacetate, and benzylidenemalononitrile were prepared in emulsion with the use of the redox system potassium persulfate–sodium bisulfite. The kinetics of copolymerization as a function of the composition of monomers, of the concentration of emulsifier and initiators, and of temperature was studied. Copolymers of high molecular weight were obtained in good yields.

INTRODUCTION

In Part I,[1] the bulk polymerization of styrene with four styrene derivatives having a nitrile group in the vinylic side chain was studied and the parameters of copolymerization calculated.

Whereas the copolymers of styrene with atroponitrile had a very low molecular weight and decomposed on heating at about 140°C., the copolymers of styrene with cinnamonitrile (I), ethyl benzylidenecyanoacetate (II), and benzylidenemalononitrile (III) had high molecular weights and showed softening ranges distinctly higher than those of polystyrene.

A thorough investigation in the various methods of preparation of these copolymers and consequently a wider study of their properties was therefore considered warranted.

The present paper deals with the copolymerization of styrene with I, II, and III in emulsion. In the first study of these copolymerizations[1] azeotropic conditions for the copolymers of styrene with II and III at 0.3 and 0.35 mole fraction, respectively, were found. Therefore the greater part of this work was carried out at the azeotropic conditions of these two monomer pairs.

EXPERIMENTAL

Preparation of Monomers and Materials

Styrene was a commercial I.C.I. product, purified as described in Part I.[1]

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Cinnamonitrile, ethyl benzylidenecyanoacetate, and benzylidenemalononitrile were prepared as described in Part I.[1]

Water was demineralized and distilled.

Sodium lauryl sulfate (Dupanol C, du Pont) was used without further purification as emulsifier.

Polymerizations were initiated by the redox system potassium persulfate (Baker C.P.) and sodium bisulfite (Merck C.P.).[2]

Copolymerization in Emulsion

Polymerizations were carried out in a three-necked flask (500 ml.), fitted with stirrer, thermometer, and reflux condenser. The reaction flask was immersed in a water bath with temperature control (±0.5°C.). The type of stirrer and speed of stirring were identical for all reactions. All polymerizations were carried out in nitrogen atmosphere.

Sodium lauryl sulfate was dissolved in water in the reaction flask at the fixed temperature of polymerization. Nitrogen was passed through and the monomer mixture added. After stirring for 20 min., the aqueous solution of sodium bisulfite and afterwards the aqueous solution of potassium persulfate were added.

At the end of the reaction, the copolymers were precipitated by adding a saturated aqueous solution of sodium chloride. After filtration and washing of the polymers, first with water and then with methanol, the polymers were further purified by treating them twice in boiling methanol for 1 hr. each time.

After filtration and drying in the air, the products were dried finally for 15–20 hr. at about 100°C. under reduced pressure.

Characterization

The molecular weights of the polymers were determined by the solution viscosity method with an Ubbelohde viscometer. The polymers were purified by precipitating them twice with methanol from toluene solutions. The viscosity measurements were carried out in toluene solutions at 25 ± 0.05°C.

In order to calculate the average composition of the polymers, the nitrogen content of the polymers was determined by the Kjeldahl method.

Kinetics of Polymerization

In order to follow the rate of reaction, samples (about 2 g.) were taken during the polymerization. To the weighed sample, a 0.04% aqueous solution of hydroquinone (about 5 ml.) was added in order to stop further polymerization. The samples were dried first at 80–90°C. and then kept for 24 hr. at 120°C. under reduced pressure.

RESULTS AND DISCUSSION

In Tables I–III details of the copolymerization of styrene with each of the comonomers (I, II, and III) in emulsion are summarized. The poly-

TABLE I
Copolymerization of Styrene (M_1) with Cinnamonitrile (M_2) in Emulsion

No. of experiment	Monomer mixture, g.	M_2 in monomer mixture, mole-%	Water, ml.	Sodium lauryl sulfate, g.	Sodium bisulfite, g.	Potassium persulfate, g.	Temp., °C.	m_2 in copolymer, mole-%	$[\eta]$, dl./g. polymer
EC-1	60	0	180	1.0	0.6	0.6	50	0	—
EC-2	60	10.0	"	"	"	"	"	7.7	0.83
EC-3	60	20.0	"	"	"	"	"	14.4	0.80
EC-4	60	30.0	"	"	"	"	"	19.9	0.62
EC-5	60	40.0	"	"	"	"	"	25.9	0.44
EC-6	40	30.0	120	1.74	0.4	0.4	"	—	—
EC-7	40	30.0	"	0.67	"	"	"	—	—
EC-8	40	30.0	"	0.26	"	"	"	—	—
EC-9	40	30.0	"	0.10	"	"	"	—	—

TABLE II

Copolymerization of Styrene (M_1) with Ethyl Benzylidenecyanoacetate (M_2) in Emulsion

No. of experiment	Monomer mixture, g.	M_2 in monomer mixture, mole-%	Water, ml.	Sodium lauryl sulfate, g.	Sodium bisulfite, g.	Potassium persulfate, g.	Temp., °C.	m_2 in copolymer, mole-%	$[\eta]$, dl./g. polymer
EE-10	60	0	180	2.0	0.2	0.2	50	0	4.32
EE-11	"	10.0	"	"	"	"	"	11.1	6.40
EE-12	"	20.0	"	"	"	"	"	20.5	5.53
EE-13	"	30.0	"	"	"	"	"	29.0	5.42
EE-14	"	40.0	"	"	"	"	"	35.0	5.84
EE-15	"	50.0	"	"	"	"	"	40.3	6.20
EE-16	"	65.0	"	"	"	"	"	42.8	5.20
EE-17	30	30.0	90	0.1	0.1	0.1	50	—	—
EE-18	"	"	"	0.3	"	"	"	—	—
EE-19	"	"	"	0.9	"	"	"	—	—
EE-20	"	"	"	2.7	"	"	"	—	—
EE-21	30	30.0	90	1.0	0.1	0.1	27	—	—
EE-22	"	"	"	"	"	"	40	—	—
EE-23	"	"	"	"	"	"	50	—	—
EE-24	"	"	"	"	"	"	60	—	—
EE-25	30	30.0	90	1.0	0.033	0.033	35	—	—
EE-26	"	"	"	"	0.1	0.1	"	—	—
EE-27	"	"	"	"	0.3	0.3	"	—	—
EE-28	"	"	"	"	0.9	0.9	"	—	—

TABLE III
Copolymerization of Styrene (M_1) with Benzylidenemalononitrile (M_2) in Emulsion

No. of experiment	Monomer mixture, g.	M_2 in monomer mixture, mole-%	Water, ml.	Sodium lauryl sulfate, g.	Sodium bisulfite, g.	Potassium persulfate, g.	Temp., °C.	m_2 in copolymer, mole-%	[η], dl./g. polymer
EB-29	80	0	200	2.0	0.8	0.8	60	0	1.20
EB-30	"	10.0	"	"	"	"	"	9.7	0.84
EB-31	"	22.5	"	"	"	"	"	22.5	0.56
EB-32	"	35.0	"	"	"	"	"	31.6	0.60
EB-33	"	45.0	"	"	"	"	"	43.0	0.48
EB-34	32	35.0	80	0.8	0.32	0.32	"	—	—
EB-35	"	"	"	"	0.16	0.16	"	—	—
EB-36	"	"	"	"	0.08	0.08	"	—	—
EB-37	"	"	"	"	0.04	0.04	"	—	—
EB-38	"	"	"	"	0.16	0.16	50	—	—
EB-39	"	"	"	"	"	"	70	—	—
EB-40	20	0	100	0.5	0.20	0.20	50	—	—
EB-41	"	10.0	"	"	"	"	"	—	—
EB-42	"	22.5	"	"	"	"	"	—	—
EB-43	"	35.0	"	"	"	"	"	—	—
EB-44	20	35.0	100	0.5	0.20	0.20	50	—	—
EB-45	"	"	"	"	"	"	60	—	—
EB-46	"	"	"	"	"	"	70	—	—

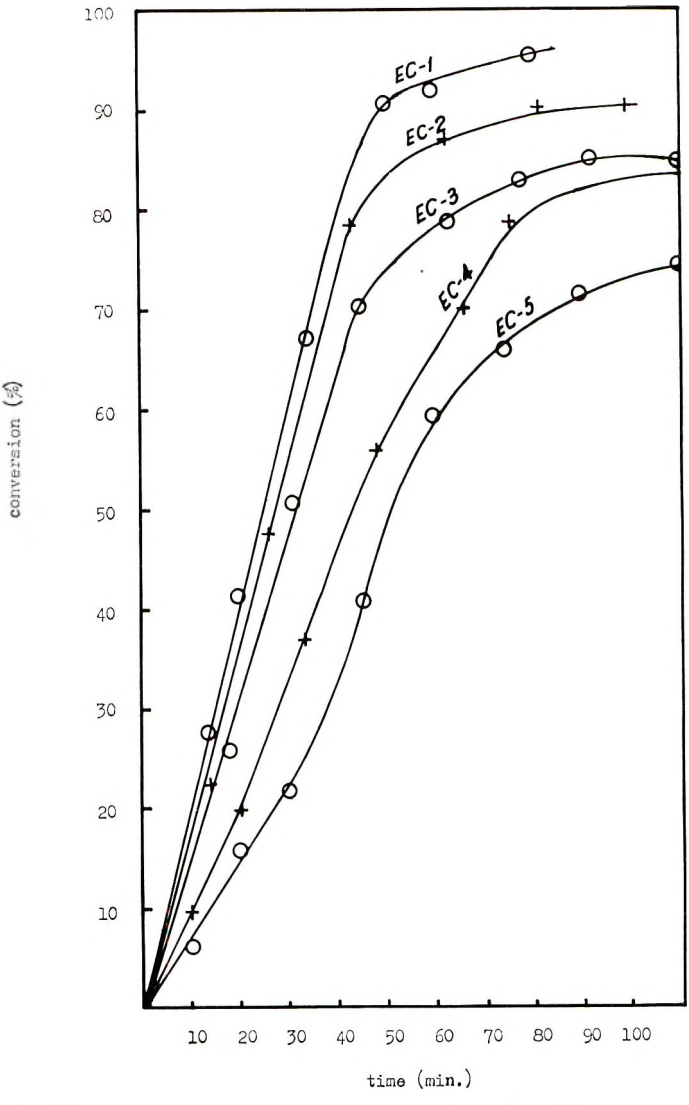

Fig. 1. Copolymerization of styrene with cinnamonitrile. Dependence on composition of initial monomer mixture.

mers are characterized by their intrinsic viscosity and their average composition as calculated from their nitrogen content.

Following up the rate of copolymerization of the three monomer pairs, the results can be summarized as follows.

Styrene–Cinnamonitrile

The rate of copolymerization and also the percentage of ultimate conversion decrease with increasing comonomer content (Fig. 1).

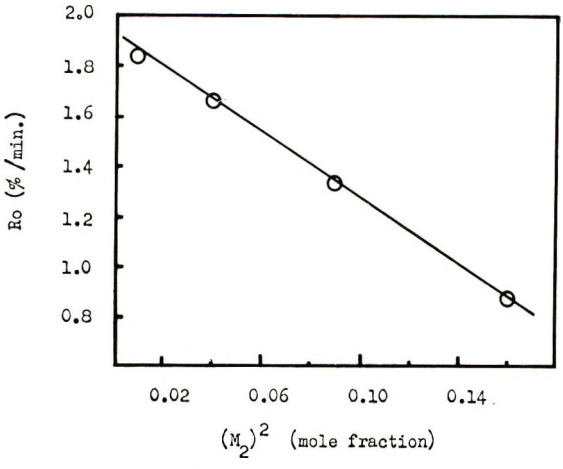

Fig. 2. Copolymerization of styrene with cinnamonitrile. R_0 against M_2^2.

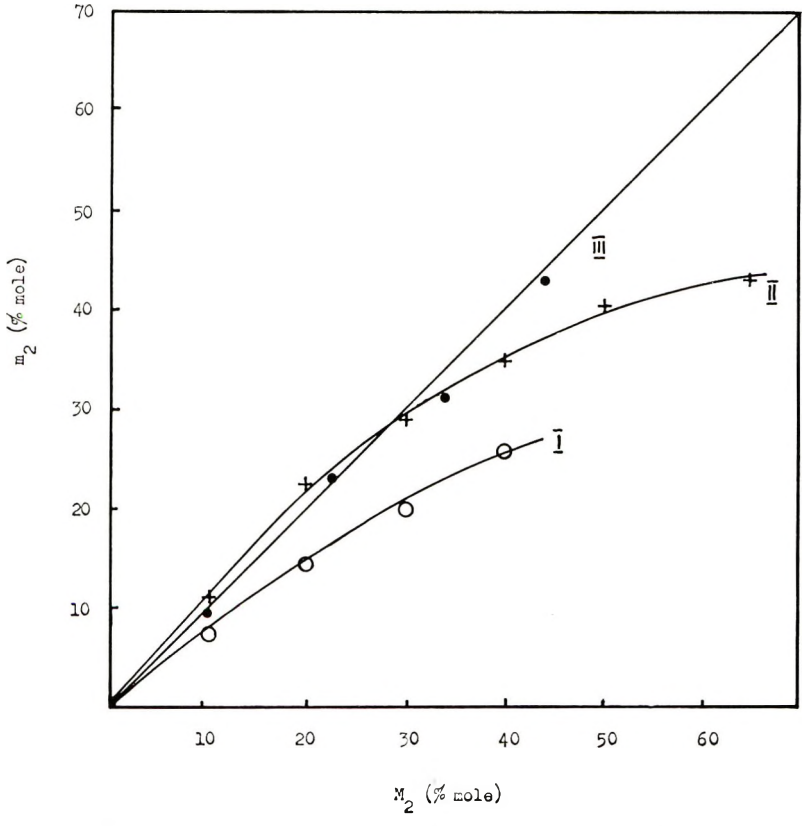

Fig. 3. Copolymerization of styrene with comonomers I, II, and III. m_2 at maximal conversion against M_2.

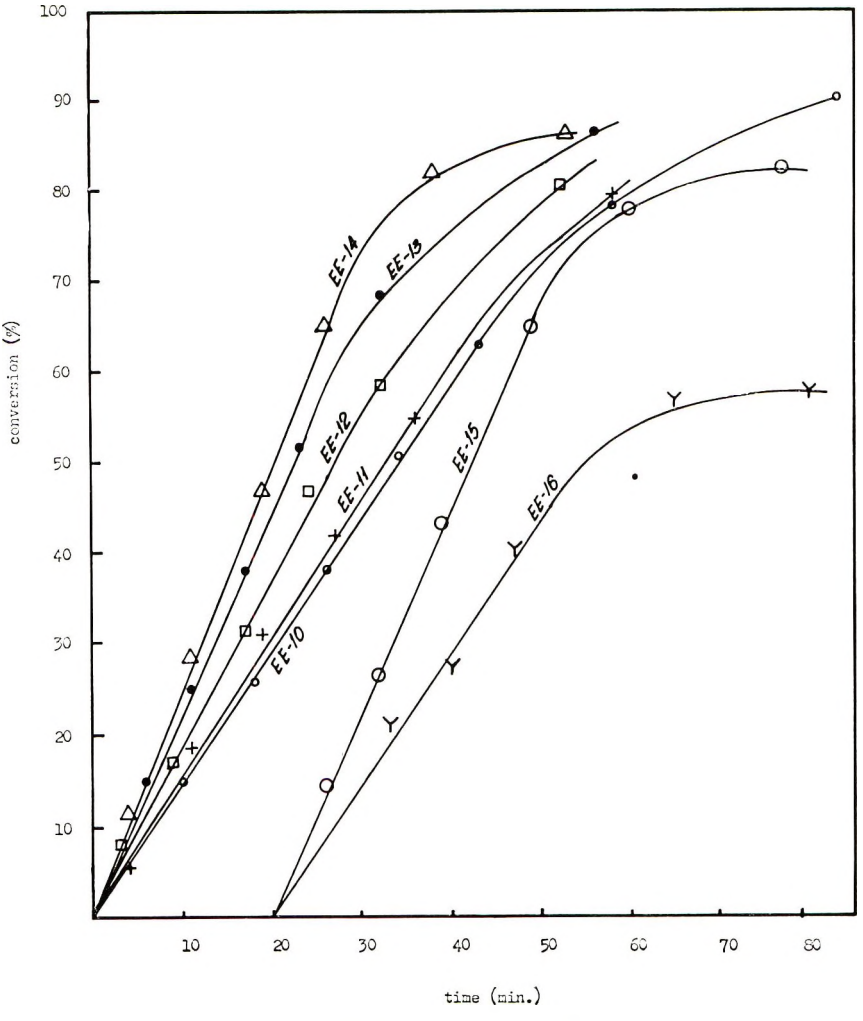

Fig. 4. Copolymerization of styrene with ethyl benzylidenecyanoacetate. Dependence on composition of initial monomer mixture. (EE-15 and EE-16 are shifted by 20 min.)

On plotting the initial rate of copolymerization R_0 (per cent conversion per minute) against the mole fraction of cinnamonitrile in the monomer mixture M_2 a parabolic curve is obtained (Fig. 2).

$$R_0 = -6.7\ M_2^2 + 1.94 \qquad \text{(i)}$$

Due to the fact that styrene enters quicker into the copolymer than I, the concentration of I in the monomer mixture increases steadily during polymerization. Comparing the copolymerization in emulsion (Fig. 3) to that in bulk[1] one finds therefore, that for a given initial concentration of I, the content of I in the copolymer is higher when prepared in emulsion at maximal conversion, than when prepared in bulk at low conversion.

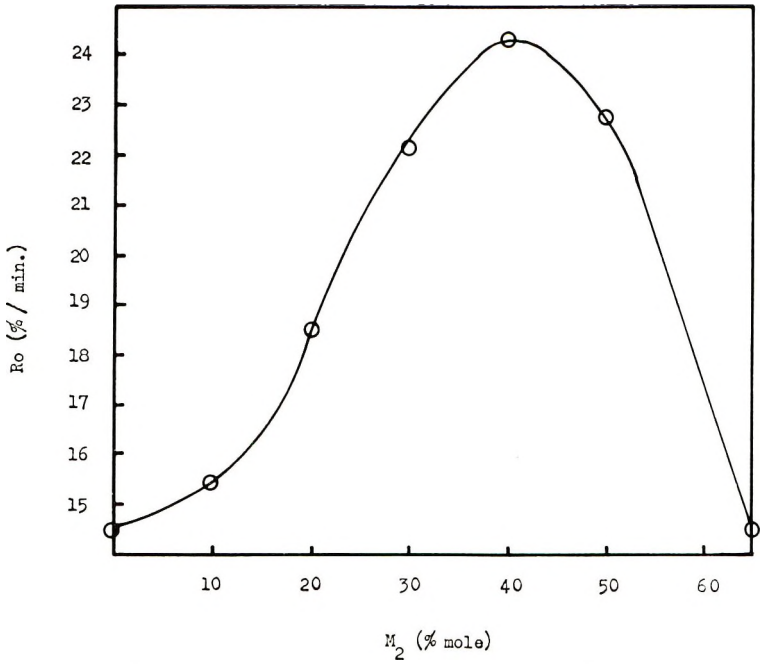

Fig. 5. Copolymerization of styrene with ethyl benzylidenecyanoacetate. R_0 against M_2.

Styrene–Ethyl Benzylidenecyanoacetate

Ethyl benzylidenecyanoacetate increases the rate of copolymerization with increasing concentration up to a maximum at a mole fraction of 0.4 (Fig. 4).

Plotting R_0 against the mole fraction of II in the monomer mixture yields a curve in the form of a bell (Fig. 5) which can not be expressed by a parabolic equation. A similar case is reported by Livingston et al.[3] for the copolymerization of styrene with α, β, β'-trifluorostyrene.

Comonomer II enters more quickly into the copolymer than styrene, whose concentration increases in the monomer mixture during polymerization. Consequently, for a given initial concentration of II, the content of II in the emulsion copolymer at maximal conversion is lower (Fig. 3) than for that prepared in bulk at low conversion.[1]

Styrene–Benzylidenemalononitrile

The concentration of this comonomer up to 35 mole-% has no marked influence on the rate of copolymerization when examined at 50°C. (Fig. 6) and up to 45 mole-% when polymerized at 60°C. (Fig. 7). The ultimate conversion is not influenced by the concentration of the comonomer III in the range examined.

The plot of M_2 in copolymer (m_2) against M_2 in the monomer mixture (M_2) for the pair styrene–III at maximal conversion (Fig. 3) shows that the

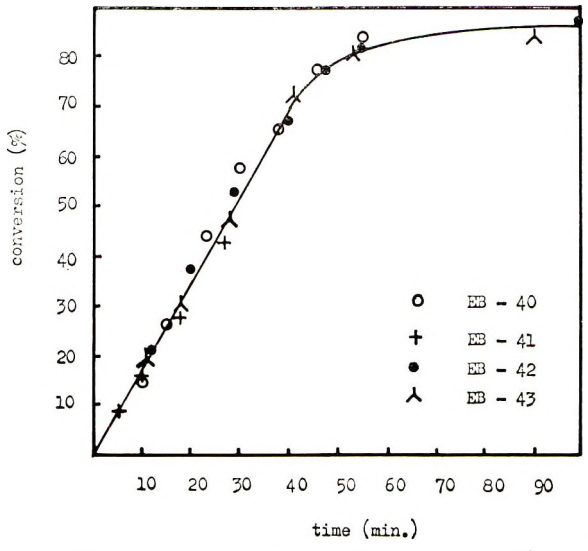

Fig. 6. Copolymerization of styrene with benzylidenemalononitrile. Dependence on composition of initial monomer mixture at 50°C.

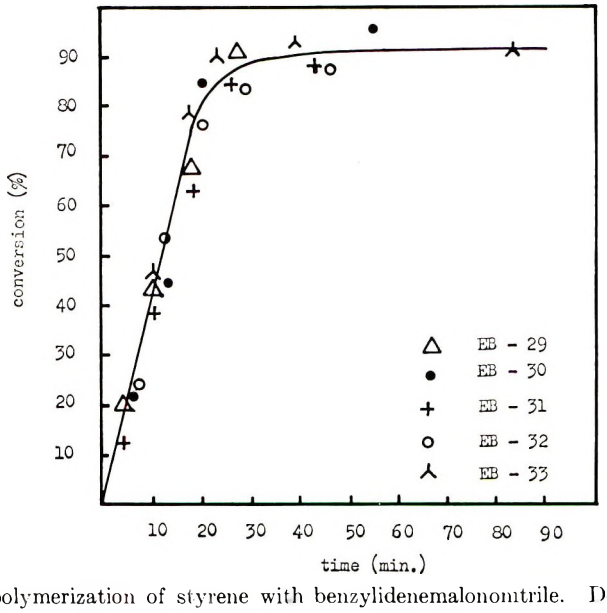

Fig. 7. Copolymerization of styrene with benzylidenemalononitrile. Dependence on composition of initial monomer mixture at 60°C.

copolymer composition is actually equal to the original monomer mixture up to 45 mole-% of III.

Effect of Emulsifier Concentration

The influence of the concentration of the emulsifying agent can be summarized as follows.

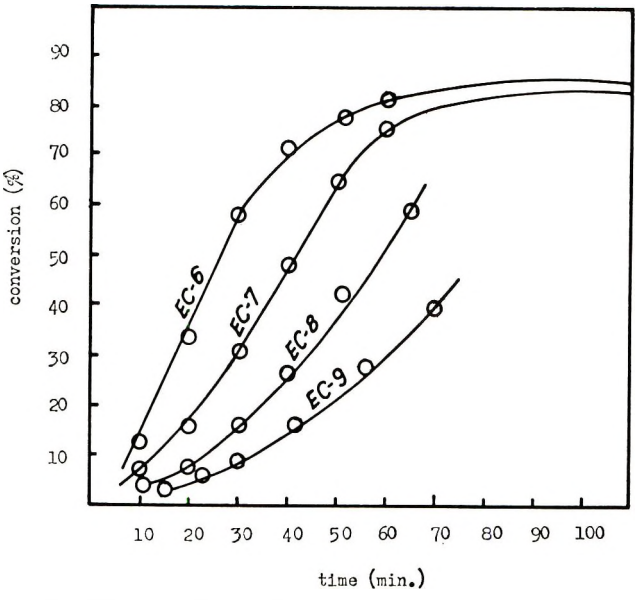

Fig. 8. Copolymerization of styrene with cinnamonitrile (M_2 = 30% mole). Dependence on concentration of emulsifier.

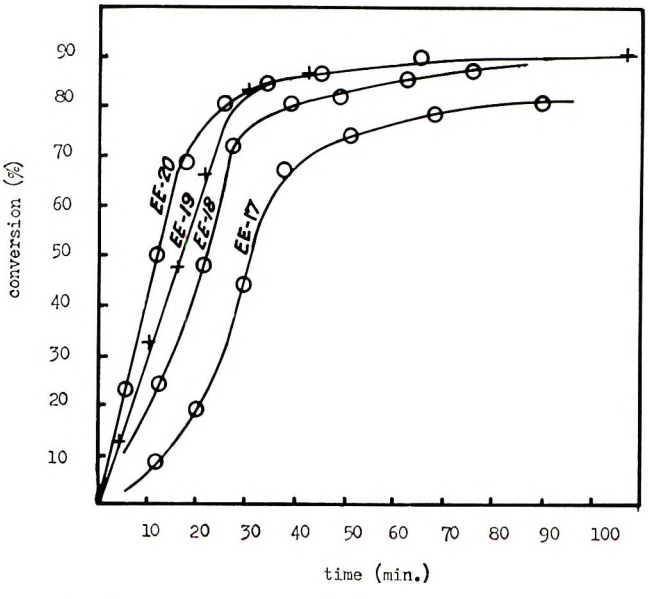

Fig. 9. Copolymerization of styrene with ethyl benzylidenecyanoacetate at azeotropic composition. Dependence on concentration of emulsifier.

Styrene–Cinnamonitrile. At a mole fraction of 0.3 of the comonomer, conversion drops sharply by decreasing concentration of the emulsifier (Fig. 8).

However, at a more advanced stage of copolymerization, the rate seems to

be much less dependent on the concentration of the emulsifier. Similar behavior has also been reported for vinylidene chloride.[4]

Styrene–Ethyl Benzylidenecyanoacetate. For this pair at azeotropic proportions, changes in the concentration of the emulsifier are not so critical, and a definite decrease of conversion is found at very low concentrations only (Fig. 9). After about 25% conversion, rates of reaction are approximately equal.

Styrene–Benzylidenemalononitrile. Increase of the emulsifier—examined at two different concentrations—resulted in higher rate of reaction.

Potassium Persulfate–Sodium Bisulfite Initiation

The system potassium persulfate–sodium bisulfite, whose mode of action was studied by Tsuda[2] and others, proved to be very effective for initiation of these copolymerizations.

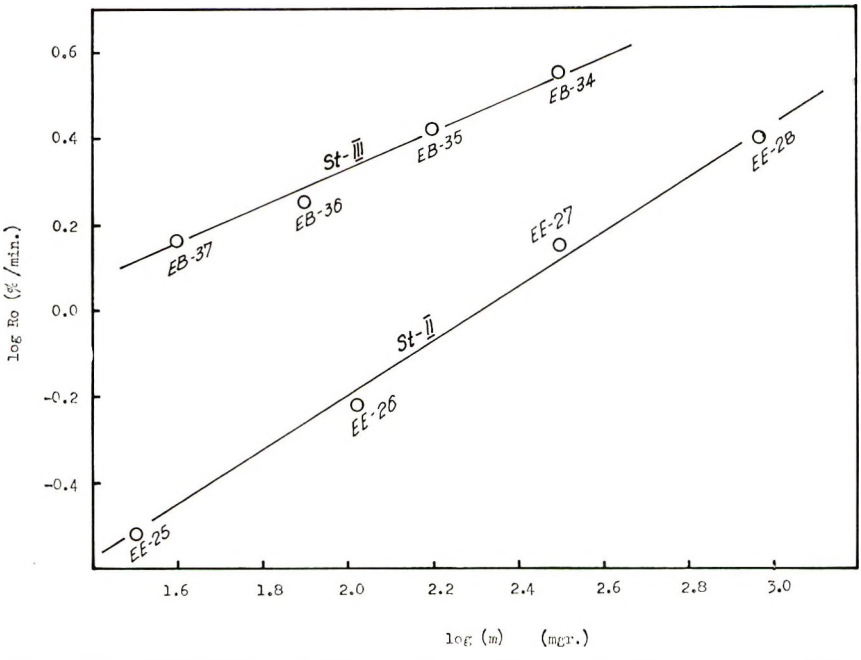

Fig. 10. Copolymerization of styrene with II and III at azeotropic compositions. R_0 against initiator (weight of potassium persulfate).

The influence of the concentration of this initiator system on the rate of copolymerization of styrene with II and III at azeotropic compositions was found to be as follows.

For the pair styrene–ethyl benzylidenecyanoacetate, the rate is proportional to the concentration to a power of 0.65 (Fig. 10). This value seems comparatively high. This could be due to the fact that at the temperature of polymerization (35°C.), the solubilities of the copolymer and even of the comonomer are too low.

A similar value of 0.6 for the dependence of initial rate on catalyst concentration has been reported by Hay and co-workers for vinylidene chloride.[4]

The pair styrene–benzylidenemalononitrile was examined at 60°C., and the relationship was found to be of the power of 0.43 (Fig. 10). This value is very near the theoretical value of 0.4 calculated by Smith and Ewart.[5]

Effect of Temperature

The rates of copolymerization as a function of temperature were examined for the azeotropic monomer mixtures of styrene with comonomers II and III only.

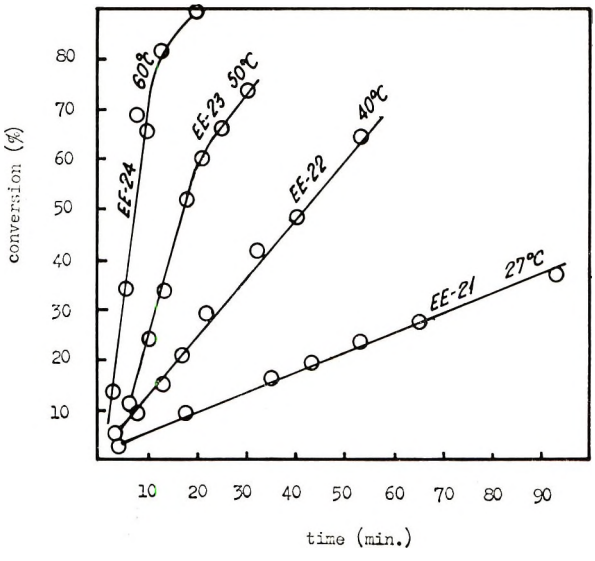

Fig. 11. Copolymerization of styrene with ethyl benzylidenecyanoacetate at azeotropic composition. Dependence on temperature.

Figure 11 shows the dependence of the rate on the reaction temperature for the pair styrene–II. On plotting the log of the calculated rates against $1/T$ (Fig. 12), the eq. (2) is obtained:

$$R_0 = 2.1 \times 10^{11} \exp \{-16/RT\} \tag{2}$$

The activation energy is 16 kcal./mole.

For the copolymerization of styrene with III, the relationship is

$$R_0 = 1.32 \times 10^{9} \exp \{-13.2/RT\} \tag{3}$$

which shows an activation energy of 13.2 kcal./mole (Fig. 12).

These values are of the same magnitude as for the pair styrene–butadiene in the production of GR-S, i.e., 14.4 kcal./mole.[6]

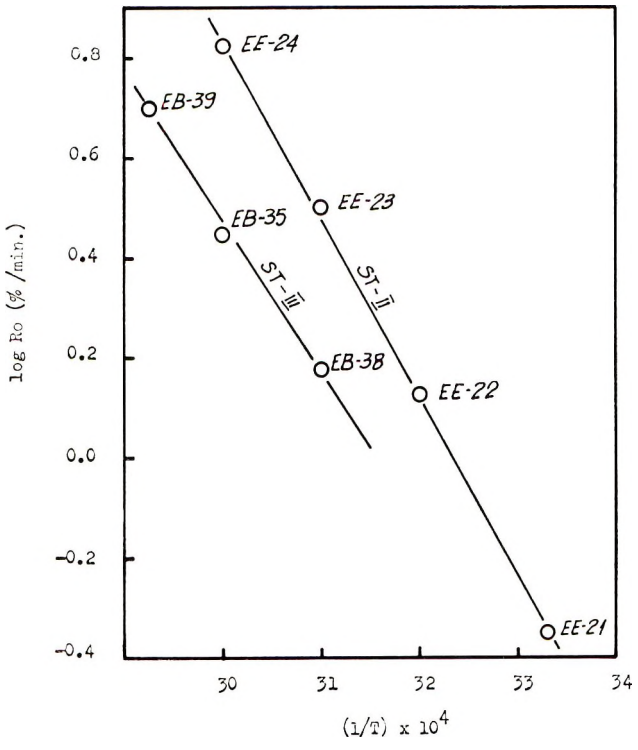

Fig. 12. Copolymerization of styrene with II and III at azeotropic compositions. R_0 against temperature.

Intrinsic Viscosity

The intrinsic viscosity of the copolymers styrene–I and styrene–III decreases with increasing contents of comonomers I and III, respectively (Tables I and III), as was already found for polymerization in bulk (1).

For the pair styrene–II there is a marked increase of the intrinsic viscosity already at a content of 10 mole-% of the comonomer, against polystyrene. Further increase of the comonomer II content up to 65 mole-% (Table II) has no marked influence on the intrinsic viscosity, whereas on polymerization in bulk an additional sharp increase occurred at 60 and 70 mole-% of comonomer II.[1]

Although the monomers I, II, and III do not homopolymerize, their copolymers with styrene were obtained by the conventional emulsion polymerization method in high yields and of high molecular weight. The basic mechanical properties of these copolymers were examined and are reported in the following paper.[7]

This paper is taken in part from a thesis submitted by Moshe Narkis to the Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa, in partial fulfillment of the degree of M.Sc.

The authors wish to thank the Scientific Department, Israel Ministry of Defense, for the permission given to M. N. to carry out this work in their laboratories.

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Résumé

Des copolymères du styrène et du cinnamonitrile, éthyl benzylidènecyanoacétate et benzylidènemalonitrile ont été préparés en émulsion utilisant un système oxydo-réducteur à base de persulfate de potassium et de bisulfite de sodium. Les cinétiques de copolymérisation en fonction de la composition en monomères et de la concentration en émulsifiants et initiateurs, de même qu'en fonction de la température ont été étudiées. Des copolymères de poids moléculaires élevés ont été obtenus avec de bons rendements.

Zusammenfassung

Copolymere von Styrol und Zimtsäurenitril, Äthylbenzylidencyanacetat sowie Benzylidenmalonsäurenitril wurden in Emulsion mit dem Redoxsystem Kaliumpersulfat–Natriumbisulfit dargestellt. Die Kinetik der Copolymerisation wurde in Abhängigkeit von Monomerzusammensetzung, Emulgator- und Starterkonzentration und Temperatur untersucht. Hochmolekulare Copolymere wurden in guter Ausbeute erhalten.

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Copolymerization of Styrene. III. Physical and Mechanical Properties of Copolymers with Styrene Derivatives Containing Nitrile Groups in the Side Chain

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Synopsis

Copolymers of styrene with cinnamonitrile (I), ethyl benzylidenecyanoacetate (II), and benzylidenemalononitrile (III) were prepared in bulk, in suspension, and in emulsion up to high conversion. Their softening points, flexural properties, impact resistance, hardness, and volumetric shrinkage due to polymerization were studied. All three copolymers show improved thermal resistance in comparison to polystyrene, but whereas copolymers styrene–I and styrene–III are inferior to polystyrene in flexural strength and the impact resistance, the copolymer styrene–II is about equal to polystyrene in its flexural properties and impact resistance.

INTRODUCTION

In the preceding paper[1] a detailed investigation on the copolymerization of styrene with cinnamonitrile (I), ethyl benzylidenecyanoacetate (II), and benzylidenemalononitrile (III) in emulsion was reported.

The present paper deals in its first part with the preparation of these copolymers in bulk and in suspension. The physical and mechanical properties of these copolymers and also of copolymers prepared in emulsion are discussed.

EXPERIMENTAL

Preparation of Copolymers

Bulk Polymerization. Monomer mixtures of different composition were polymerized in glass tubes (6.6–6.7 mm. inside diameter) previously covered with a release agent. In order to obtain high molecular weight polymers without bubbles, the polymerization was carried out over a period of 12 days with a gradual increase in temperature from 50 to 140°C. Benzoyl peroxide (0.2%) was used as initiator.

Suspension Polymerization. The various copolymers were prepared according to known practice with either poly(vinyl alcohol)[2] or calcium phos-

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TABLE I

Copolymerization of Styrene (M_1) with Comonomers I, II, and III (M_2) in Suspension[a]

No. of experiment	Comonomer	Monomer mixture, g.	M_2 in monomer mixture, mole-%	Water, ml.	Poly(vinyl alcohol), g.	Benzoyl-peroxide, g.	Yield, %	m_2 in copolymer, mole-%	[η], dl./g. polymer	VSP, °C.
SE-1	II	40	20	300	0.5	0.4	—	—	0.43	—
SE-2	"	150	30	900	1.5	0.15	80	31.5	1.58	135.5
SE-3	"	150	30	450	0.75	0.15	90	31.5	1.63	133.5
SE-4	"	150	30	900	1.5	0.75	74	29.2	0.72	136.5
SE-5	"	150	30	900	1.5	0.03	75	30.0	2.83	136.2
SE-6	"	100	30	600	1.0	0.20	80	32.0	1.22	134.5
SE-7	"	100	30	600	1.0	0.20	76	31.8	—	136.5
SE-15	II	50	30	200	[b]	0.50	89	—	—	132.5
SE-16	"	50	30	200	[b]	0.50[c]	85	—	—	135.0
SC-8	I	40	10	300	0.5	0.40	—	—	0.30	72.0
SC-9	"	100	20	600	1.0	1.00	96	15.5	0.31	91.5
SC-10	"	100	30	600	1.0	1.00	96	25.5	0.30	79.0
SC-11	"	75	30	450	0.75	0.20	67	28.2	—	64.2
SB-12	III	90	35	540	0.9	0.45	82	32.2	0.43	131.0
SB-13	"	90	35	540	0.9	0.09	80	34.3	0.60	123.5
SS-14	◓	50	0	300	0.5	0.50	—	0	0.35	—

[a] Conditions: 85°C. for 5 hr., 95°C. for 3 hr.

[b] Tricalcium phosphate instead of PVA.

[c] 2,2′-Azobisisobutyronitrile as initiator.

phate[3] as suspending agent. Details of monomer ratios, conditions of polymerization, and the copolymers obtained, are given in Table I.

Emulsion Polymerization. Details of the preparation of these copolymers in emulsion and their purification were reported in the preceding paper.[1]

Physical and Mechanical Tests

Preparation of Specimens. Type I specimens as obtained by bulk polymerization were used directly for determination of the density and impact resistance. Type II specimens, disks having a diameter of 32 mm. and a thickness of 3–4 mm., were molded by compression (at about 300 atm.) from copolymers prepared in suspension and in emulsion and were used for the Vicat test. Type III specimens having dimensions of 45 × 6 × 4 mm., prepared by injection molding, were used for determination of flexural properties and the Martens softening point.

The optimal temperatures for either compression or injection molding were experimentally determined for each copolymer.

Softening Point. The softening point of the copolymers was determined by the Vicat method 4 with the use of a needle with a circular cross-section of 1 mm.[2] and a load of 1 kg. Oil was used as heat transfer liquid. The temperature was raised at a uniform rate of 50°C./hour. The temperature at which the needle penetrated the specimen to a depth of 1 mm. was recorded as the Vicat softening point (VSP). The softening point was also determined by the method of Martens[5] on the type III specimens. The test was carried out in the standard air oven at a uniform heating rate of 50°C./hr.

Flexural Strength. The flexural strength and consequently the modulus of elasticity were calculated according to eqs. (1) and (2):

$$S = 3PL/2bh^2 \tag{1}$$

and

$$E = PL^3/4bh^3d \tag{2}$$

Specimens of type III were flexured at the center at a rate of 2 mm./min.

Impact Strength. Unnotched cylindrical specimens of type I were tested on a Charpy apparatus (Tensometer Ltd., Croydon, England) using a pendulum of $^1/_2$ lb.

Hardness. Hardness was tested by the Brinell method, by applying during 60 sec. a weight (P = 25 kg.) on a steel ball (diameter D = 5.0 mm.), which was placed on the specimen. After measuring the depth of penetration h, the hardness H was calculated according to eq. (3):

$$H = P/\pi Dh \tag{3}$$

Volumetric Shrinkage. In order to calculate the volumetric shrinkage, the densities of monomer mixtures and of copolymers having the same average composition were determined.

RESULTS AND DISCUSSION*

Softening Point

In order to get a significant value of the softening point—the limiting softening point (LSP)—which enables a comparison with other polymers, the following conditions must be fulfilled: (*a*) the polymer should not contain any residual monomer or low molecular weight polymers; (*b*) the polymer should possess at least such an average molecular weight, so that its softening point is independent of it; (*c*) the specimens should be either without internal stresses or a testing method independent of any residual stresses should be used.

There are several existing methods for determining the softening temperature, which give different results for the same polymer, although the above conditions are fulfilled. Barb[6] correlated the values of the softening points of polystyrene determined by different methods. A further correlation for the Vicat and the ASTM test has been reported.[7]

The sensitivity of the Vicat temperature against any residual monomers or low molecular weight polymers was stressed by Dixon and Saunders,[8] who reported that each per cent of residual monomer or low molecular weight polymer depresses the softening point by about 5°C.

TABLE II
Comparison of Purifying Methods for Copolymer EC-7
Tested by Vicat Method

Vicat softening point (VSP), °C.		
Precipitation and drying at 100°C. under reduced pressure	Precipitation, extraction with boiling methanol for 30 min. and drying at 100°C. under reduced pressure	Steam distillation, precipitation, and drying at 100°C. under reduced pressure
83.0	101.2	87.2
83.4	103.0	88.2
84.0	104.0	87.5
After additional extraction with boiling methanol		
131.0	135.8	134.2
131.5	135.5	134.0

Treatment of copolymer EC-7 with steam resulted in a rise of the VSP by a few degrees only. Extraction with boiling methanol for 30 min. gave an increase of about 20°C., but when the extraction was carried out over 2 hr., an increase of about 50°C. was reached (Table II).

It is obvious that extraction of the crude copolymer from residual monomers and low molecular weight fractions by boiling methanol is applicable

* The first letter of the codes of the experiments indicates: E, polymerization in emulsion;[1] S, polymerization in suspension (this paper).

for emulsion polymers only. However, this method is not efficient for polymers prepared in bulk or in suspension and thus will not influence their VSP.

Therefore, the VSP values for methanol-treated emulsion copolymers are much higher than those of bulk or suspension copolymers having the same average composition. Thus the VSP of the azeotropic styrene–II copolymer prepared in suspension is in the range of 133–137°C. (Table I), whereas the VSP of the corresponding emulsion copolymer is 185°C. (Fig. 1). This difference of about 50°C. corresponds to a content of about 10% of low molecular weight fractions.[8]

Similar results were obtained for the styrene–III copolymer.

The influence of heat treatment (annealing) on the molded specimens, determined by keeping the specimens first at 100°C. and then at 130°C. for 24 hr. each time, is actually negligible for the VSP test,[7] as shown in Table III.

TABLE III
Influence of Heat Treatment on the VSP

Treatment	VSP of copolymers, °C.			
	EB-31	SE-3	SE-5	SE-15
Untreated	171	134	138	136
After 24 hr. at 100°C.	169	136	140	134
After further 24 hr. at 130°C.	170	143	144	136

Contrary to the Vicat method, the influence of residual stresses in the specimen on the heat distortion temperature according to Martens is very strong, as shown in Table IV.

TABLE IV
Heat Distortion Temperature by Martens Method

Treatment	Heat distortion temperature of copolymers, °C.									
	SE-2	SE-3	SE-4	SE-5	SB-13	EC-1	EC-2	EC-3	EC-4	EE-12
Untreated	67	67	75	68.5	—	73.5	74	68	75.5	—
Annealed at 90°C. for 60 hr.	—	109	—	110	109.5	99.5	107	—	110.5	113

Under the conditions for determination of the limiting softening point as mentioned before, the Vicat method applied to methanol-extracted copolymers prepared in emulsion should thus actually depend on the copolymer composition only. This dependence of VSP on the comonomer content of the three types of copolymers is given in Figure 1.

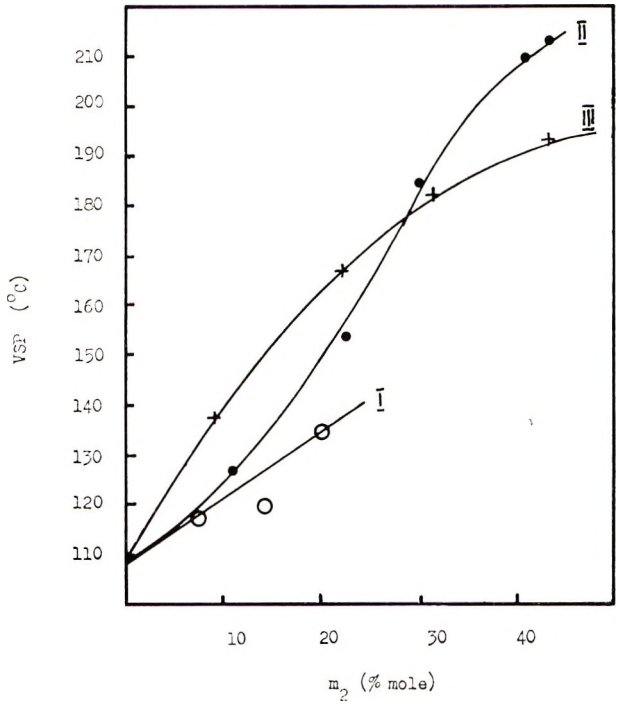

Fig. 1. Copolymerization of styrene with I, II, and III in emulsion. Dependence of VSP on m_2.

The VSP of the copolymers was compared with the value for polystyrene (108°C.); the increase of the VSP due to the presence of one of the three comonomers is given in Table V.

TABLE V
Temperature Increase Due to Comonomer

	Temperature increase due to comonomers, °C.		
m_2, mole-%	I	II	III
10	14	17	30
20	27	41	55

Thus even at comparatively low comonomer content, a considerable increase of VSP is obtained. This increase seems to be due to polarity of the comonomers and is especially striking for III.

Whereas the flexural strength of the styrene–I and styrene–III copolymers is considerably lower than for polystyrene (EC-1) and also below the lower limit for commercial polystyrene, the styrene–II copolymer gave values almost equal to the upper limit of the flexural strength of commercial polystyrene.[9] Regarding the modulus of elasticity, nearly all values are in the range of commercial polystyrene (Table VI).

TABLE VI
Flexural Properties of Copolymers

Copolymer	Flexural strength, kg./cm.^{2}	Modulus of elasticity, kg./cm.^{2}
EC-1 (polystyrene)	740	38,000
EC-2	365	30,000
EC-3	130	—
EC-5	172	—
EB-30	285	—
SB-13	285	22,000
SE-2	880	27,500
SE-3	840	33,000
SE-4	615	29,000
SE-5	1030	31,000

Like the flexural strength, the impact resistance of copolymers containing cinnamonitrile is very low in comparison with polystyrene. Also, a copolymer containing 15 mole-% of III gave a value of about $^1/_6$ that for polystyrene. Contrary to these two very brittle copolymers, the values for copolymers containing II are lower than that of polystyrene by 30–40% (examined up to 45 mole-% of II) (Table VII).

TABLE VII
Impact Resistance of Styrene–II Copolymers

II in copolymer (m_2), mole-%	Impact resistance, g.-cm.[a]
0	3050 ± 625
7.5	2010 ± 190
15	1800 ± 210
30	1730 ± 210
45	1730 ± 280

[a] Six specimens tested for each composition.

Whereas the influence of the comonomers on the flexural properties and on the impact strength is quite considerable, the Brinell hardness for all copolymers tested and also of polystyrene is in the range of 800–1250 kg./cm^2.

The densities of styrene–II and styrene–III copolymers increase with increasing comonomer content, and this can be expressed by the linear equation

$$\text{Density} = am_2 + b \tag{4}$$

where m_2 is the proportion of the comonomer and values of a and b are as given in Table VIII.

This relationship could be applied to determine the average composition of these two copolymers.

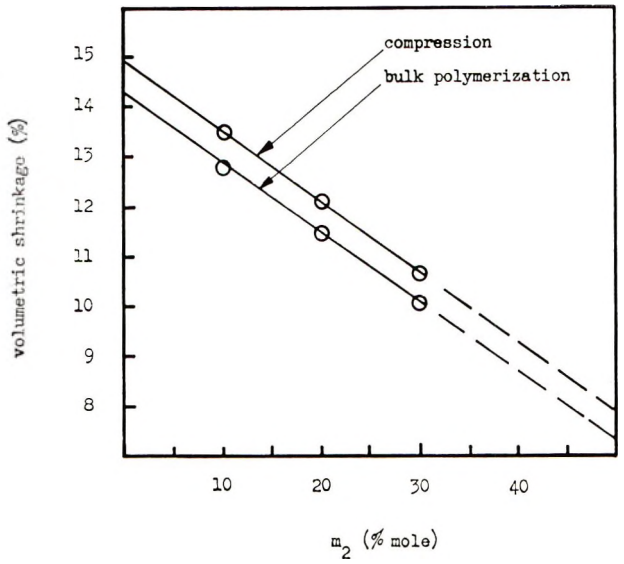

Fig. 2. Copolymerization of styrene with II and III. Dependence of volumetric shrinkage on m_2.

As can be seen from Table VIII, specimens prepared by compression molding had a higher density than those prepared in bulk.

No clear relationship was found for the pair styrene–I.

The volumetric shrinkage due to polymerization is almost equal for the two copolymers styrene–II and styrene–III at the same molar composition (Fig. 2).

TABLE VIII
Values for a and b

	Styrene–II		Styrene–III	
	Bulk	Compression-molded	Bulk	Compression-molded
a	2.05×10^{-3}	2.08×10^{-3}	1.55×10^{-3}	1.61×10^{-3}
b	1.05	1.057	1.05	1.057

Comparison of the properties of the three types of copolymers shows that copolymerization of styrene with ethyl benzylidenecyanoacetate gives an improved polymer regarding its thermal resistance, without significant change of its flexural properties and impact resistance, in comparison with polystyrene.

This paper is taken in part from a thesis submitted by Moshe Narkis to the Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa, in partial fulfillment of the degree of M.Sc.

The authors wish to thank the Scientific Department, Israel Ministry of Defense, for the permission given to M. N. to carry out this work in their laboratories.

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Résumé

Des copolymères du styrène avec le cinnamonitrile (I), l'éthylbenzylidènecyanoacétate (II) et le nitrile benzylidènemalonique (III) ont été préparés en bloc, en suspension, en émulsion jusqu'à conversion élevée. Leurs point de ramolissement, propriétés de flexion, résistance à l'impact, dureté et rétrécissement volumique dûs à la polymérisation ont été étudiés. Tous ces trois copolymères montrent une résistance thermique améliorée comparée au polystyrène, mais alors que la force à la flexion et la résistance à l'impact des copolymères de styrène–I et de styrène–III sont inférieures à celles du polystyrène, le copolymère de styrène–II est environ égal à ce dernier en ce qui concerne les propriétés de flexion et de résistance à l'impact.

Zusammenfassung

Copolymere von Styrol und Zimtsäurenitril (I), Äthylbenzylidencyanacetat (II) sowie Benzylidenmalonsäurenitril (III) wurden in Substanz, in Suspension und in Emulsion bis zu hohen Umsätzen dargestellt. Erweichungspunkt, Biegeeigenschaften, Stossfestigkeit und Härte der Copolymeren sowie die Volumsabnahme bei der Polymerisation wurden untersucht. All edrei Copolymere zeigen eine gegenüber Polystyrol verbesserte thermische Beständigkeit. Während Biege- und Stossfestigkeit der Styrol–I- und Styrol–III-copolymeren denjenigen von Styrol unterlegen sind, ist das Styrol–II-copolymer letzt eremin Bezug auf Biegeeigenschaften und Stossfestigkeit etwa gleichwertig.

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Studies on Tacticity of Polyacrylonitrile. I. High-Resolution Nuclear Magnetic Resonance Spectra of Polyacrylonitrile

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Synopsis

The nuclear magnetic resonance spectra of polyacrylonitriles prepared under various polymerization conditions were measured in NaCNS–D_2O solution. The methylenic proton resonance could be separated into two triplets: one is due to the protons of the syndiotactic methylene groups and the other is due to the isotactic ones. The tacticity of polyacrylonitrile could be determined by the ratio of the integrated intensities of the two triplets. Polyacrylonitriles prepared with radical catalysts are approximately 75% syndiotactic, and polyacrylonitriles prepared by the anionic polymerization at low temperature, γ-irradiation in the solid state, Mg molecular beam, and γ-irradiation on the urea canal complex are more isotactic but have no remarkable stereoregularity.

Introduction

The tactic structure of PAN has not yet been determined definitely, although there have been several studies on the estimation of the tactic structure of polyacrylonitrile (PAN), through x-ray diffraction,[1] infrared absorption,[2,3] electron diffraction,[4] and other methods. Yamadera et al.[3] have suggested from the infrared spectra and calculation of normal vibration of PAN and deuterated PAN's, that PAN has a structure close to the syndiotactic planar zigzag in an oriented specimen. However, they discussed the necessity of examining the high-resolution nuclear magnetic resonance (NMR) spectra of PAN in addition to the infrared and x-ray investigations, in order to discuss the tacticity of PAN in more detail.

Recently, Chiang[5] has measured the dissolution and crystallization behavior of PAN prepared under various conditions, and he reported that the dissolution and crystallization temperature measurement could be used for determining the tacticity.

For the determination of tacticity of high polymers, it is obvious that studies of the high-resolution NMR are also quite important. The tacticities of high polymers, such as poly(methyl methacrylate), poly(vinyl chloride), poly(vinyl alcohol) and others, have been elucidated by the NMR studies. The authors reported in the previous paper[6] that the NMR spectra of PAN and poly-α-deuteroacrylonitrile (PAN-αd_1) could be measured in NaCNS–D_2O solution at 100°C. and concluded that the syndiotactic con-

TABLE I
Polymerization of Acrylonitrile and α-Deuteroacrylonitrile

Polymer	Monomer	Polymerization	Catalyst	Solvent	Temperature, °C.	Reference	Figure
A_1[a]	AN	Radical	$NaHSO_3 + K_2S_2O_8$	H_2O	60		1,3,12,16
A_2	AN	Radical	$NaHSO_3 + K_2S_2O_8$	H_2O	60		5
B	AN	Radical	Azoisobutyronitrile	DMF	65		
C	AN-αd_1	Radical	Azoisobutyronitrile	Benzene	65		2,4,13
D	AN	Anionic	Li naphthalene	DMF	20		
E	AN	Anionic	NaCN	DMF	20		6
F	AN	Anionic	$LiAlH_4$	Diethyl ether	20		7
G	AN	Anionic	Na naphthalene	*n*-Hexane	0		
H	AN	Anionic	Li naphthalene	Diethyl ether	−78		
I	AN	Anionic	Na naphthalene	DMF	−78		
J	AN	Anionic	*n*-ButylLi	DMF	−78		8
K	AN	Anionic	Mg	—	—	17	9
L	AN	Irradiation in solid state	γ-ray	Bulk	−198	16	10
M	AN-αd_1	Irradiation in solid state	γ-ray	Bulk	−198		
N	AN	Irradiation on urea canal complex	γ-ray	—	−78	18	11
O	AN-αd_1	Irradiation on urea canal complex	γ-ray	—	−78		
P	AN	Irradiation on urea canal complex	γ-ray	—	−198		

[a] Molecular weight of A_1 is lower than that of A_2.

figuration is predominant in PAN polymerized with a redox catalyst, based upon the separation of methylenic proton resonance into two triplets.

Quite recently, Matsuzaki et al.[7] reported the NMR spectra of PAN in hexadeuterodimethyl sulfoxide, $(CD_3)_2SO$. They observed a triplet due to methylene protons of PAN and a singlet due to those of PAN-αd_1, but they could not arrive at any conclusion about the tactic structure of PAN from the NMR spectrum measured in $(CD_3)_2SO$ solution.

In the present paper, the NMR spectra of PAN prepared under various polymerization conditions were measured in NaCNS–D_2O solution at 60 and 100 Mc./sec., and the approximate tacticities of these PAN's are discussed from the methylenic proton resonance of the obtained spectra.

Experimental

The polymerization conditions of acrylonitrile (AN) and α-deutero-acrylonitrile (AN-αd_1) are shown in Table I.

Deuterium oxide solution of sodium thiocyanate (50% by weight) was used as a solvent for PAN to measure the NMR spectra. The NMR spectra of the PAN solutions at the concentration of 5% (by weight) were measured on a Varian A-60 NMR spectrometer at 120°C.

The NMR spectra of polymers A_1 and C were measured at 160°C. with $(CD_3)_2SO$ as a solvent.

The NMR spectra at 100 Mc./sec. were also taken for polymers A_1 and C in NaCNS–D_2O on a JNM-4H-100 NMR spectrometer.

The methylenic proton resonance spectrum decoupled from the methinic proton was taken for polymer A_1 at 100 Mc./sec. by the side-band method.

Results and Discussion

The NMR spectrum of PAN measured in $(CD_3)_2SO$ shows a triplet at around $\tau = 8.1$ ppm which is due to methylenic protons and a quintet at about $\tau = 7.0$ ppm due to the methinic proton, as shown in Figure 1. Figure 2 shows the spectrum of polymer C in $(CD_3)_2SO$, which consists of a singlet due to methylenic protons. A small peak at 7.7 ppm is due to protons remaining in the solvent.

The methylenic proton resonance in these spectra has no recognizable splitting into two parts as reported by Matsuzaki et al.[7] On the contrary, fine structure, which seems to consist of two triplets, can be observed in the methylenic proton resonance spectrum of PAN, and two singlets are found in that of PAN-αd_1 measured in NaCNS–D_2O solution as shown in Figures 3 and 4, respectively.

The effects of the solvent will be explained in the next paper,[8] which deals with the analysis on the NMR spectra of the model compounds of PAN, *meso* and racemic 2,4-dicyanopentane, in these solutions.

The present discussions are limited to the NMR spectra in NaCNS–D_2O solution.

The NMR spectra of the PAN samples in NaCNS–D_2O solution, as shown in Figures 3–11, consist of two parts: a multiplet due to methylenic protons at around 7.5 ppm and a multiplet due to methinic proton at around 6.5 ppm. If one can consider that PAN has two kinds of monomer

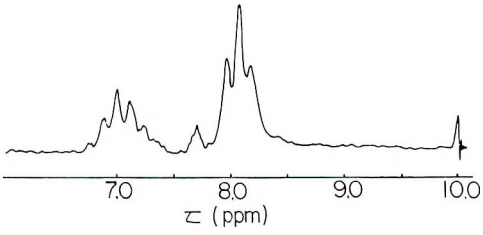

Fig. 1. NMR spectrum of PAN prepared with redox catalyst (polymer A_1) in $(CD_3)_2SO$ at 60 Mc./sec.

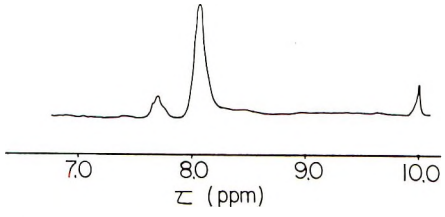

Fig. 2. NMR spectrum of PAN-αd_1 prepared with radical catalyst (polymer C) in $(CD_3)_2SO$ at 60 Mc./sec.

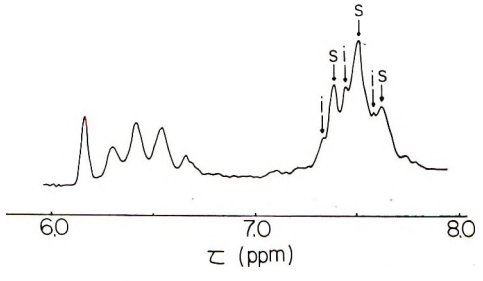

Fig. 3. NMR spectrum of PAN prepared with redox catalyst (polymer A_1) in NaCNS–D_2O at 60 Mc./sec.

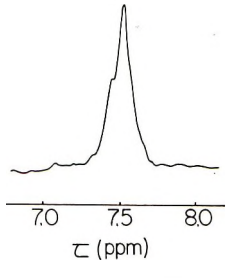

Fig. 4. Methylenic proton resonance spectrum of PAN-αd_1 prepared with radical catalyst (polymer C) at 60 Mc./sec.

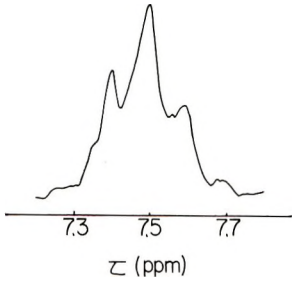

Fig. 5. Methylenic proton resonance spectrum of PAN prepared with redox catalyst (polymer A_2) at 60 Mc./sec.

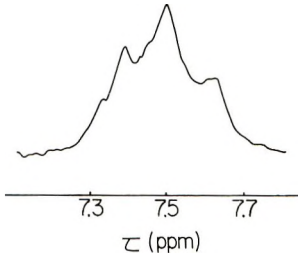

Fig. 6. Methylenic proton resonance spectrum of PAN prepared with anionic catalyst (polymer E) at 60 Mc./sec.

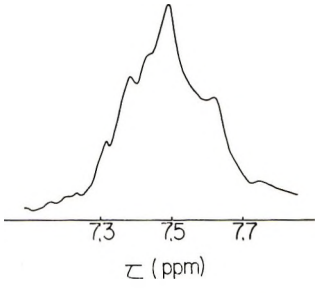

Fig. 7. Methylenic proton resonance spectrum of PAN prepared with anionic catalyst (polymer F) at 60 Mc./sec.

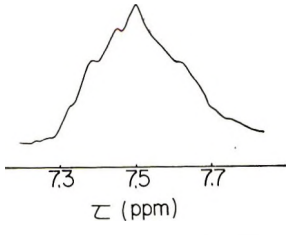

Fig. 8. Methylenic proton resonance spectrum of PAN prepared with anionic catalyst (polymer J) at 60 Mc./sec.

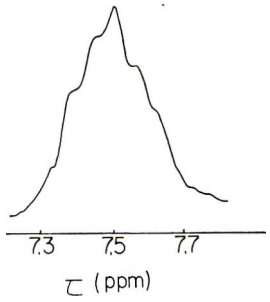

Fig. 9. Methylenic proton resonance spectrum of PAN prepared by Mg molecular beam method (polymer K) at 60 Mc./sec.

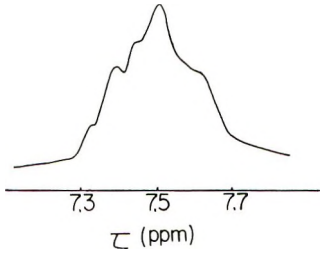

Fig. 10. Methylenic proton resonance spectrum of PAN prepared by γ-irradiation in the solid state (polymer L) at 60 Mc./sec.

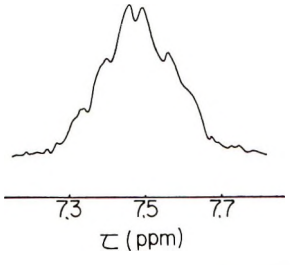

Fig. 11. Methylenic proton resonance spectrum of PAN prepared by γ-irradiation of urea–AN canal complex (polymer N) at 60 Mc./sec.

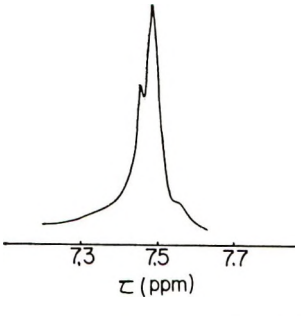

Fig. 12. Methylenic proton resonance spectrum of PAN (polymer A_1) decoupled from methine proton at 100 Mc./sec. (w = 98 cps).

linkage, syndiotactic and isotactic, in the polymer chain and the amount of head-to-head linkage is negligibly small, the methylenic proton resonance spectrum can be regarded as a superposition of the syndiotactic and isotactic methylene resonances.

Of these two kinds of methylenic proton resonance, syndiotactic methylene resonance consists of a triplet based upon an A_2B_2 spin system, because of the two magnetically equivalent protons.

On the other hand, the two protons of isotactic methylene are not equivalent in principle and should show a complicated spectrum of an ABC_2 spin system.

In this respect, there has been much discussion of the NMR studies of poly(vinyl chloride) (PVC). Johnsen[9] has interpreted the spectrum of PVC by the equivalent protons in isotactic CH_2, but Tincher[10] has considered the

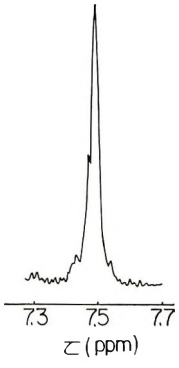

Fig. 13. Methylenic proton resonance spectrum of PAN-αd_1 prepared with radical catalyst (polymer C) at 100 Mc./sec.

protons as nonequivalent. On the examination of the model compounds, whereas the spectrum of the two-unit model (*meso*-2,4-dichloropentane) could be explained on the basis of the nonequivalent protons,[11,12] three unit models (2,4,6-trichloroheptane) showed methylenic proton resonance which could be analyzed on the basis of equivalent protons of isotactic CH_2.[13]

Furthermore, the methylenic proton resonance spectrum of PVC decoupled from methinic proton has indicated that the two protons of isotactic CH_2 could be treated as equivalent.[14] Recently, the NMR spectra of PVC and poly(vinyl alcohol) have been elucidated by Tincher[15] on the basis of equivalent protons in isotactic CH_2.

Six peaks are observed on the methylenic proton resonance of PAN in NaCNS–D_2O solution as described above, and the methylenic proton resonance decoupled from methine proton consists of two peaks as shown in Figure 12. The NMR spectrum of PAN-αd_1 has two peaks at 60 Mc./sec. (Fig. 4) and also at 100 Mc./sec. (Fig. 13). From these facts, the two protons of isotactic CH_2 can be seen to be approximately equivalent in PAN as in the case of PVC.

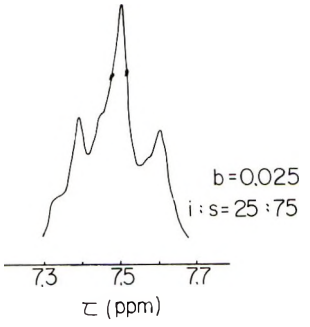

Fig. 14. Calculated methylenic proton resonance spectrum of PAN at 60 Mc./sec. assuming 75% syndiotactic and 25% isotactic diads (b = 0.025 ppm).

Consequently, the methylenic proton resonance of PAN is considered to be a superposition of two triplets: one is centered at 7.5 ppm and the other at 7.45 ppm. Based upon the results from the analysis of NMR spectra of the two-unit models of PAN (*meso*- and racemic 2,4-dicyanopentane), the triplet at higher magnetic field can be assigned to the syndiotactic CH_2 and the other to the isotactic CH_2.[8] This relation is analogous to that for other high polymers and then the approximate tacticity of PAN can be obtained from the ratio of integrated intensities of the two triplets.

If the six peaks follow a Lorentzian curve which has a given half-width value $2b$, one can obtain the triplets with syndiotactic CH_2 and isotactic CH_2, respectively, assuming the coupling constants between the α-proton and β-protons in both configurations. The observed spectrum should fall closely on the superposition of these two triplets, one of which for syndiotactic CH_2 is centered at 7.5 ppm and the other for isotactic CH_2 at 7.45 ppm.

When the six peaks are numbered 1 to 6 from the low magnetic field and represented by i, the hypothetical curve follows the equation

$$D(\tau) = \sum_{i=1}^{6} \frac{b^2 Dm_i}{b^2 + (\tau_0 - \tau_{0i})^2} \tag{1}$$

where $D(\tau)$ is the intensity at chemical shift τ, $2b$ the half-width value, τ_0 the chemical shift at each peak, and Dm the intensity of one peak at chemical shift τ_0.

In the eq. (1), the following conditions have to be satisfied, $Dm_1 : Dm_3 : Dm_5 = 1:2:1$ (triplet due to isotactic CH_2) $Dm_2 : Dm_4 : Dm_6 = 1:2:1$ (triplet due to syndiotactic CH_2), $\tau_{0_3} - \tau_{0_1} = \tau_{0_5} - \tau_{0_3}$ (coupling constant for isotactic CH_2), $\tau_{0_4} - \tau_{0_2} = \tau_{0_6} - \tau_{0_4}$ (coupling constant for syndiotactic CH_2). In order to obtain a hypothetical curve close to the observed methylenic proton resonance as shown in Figure 3, b, τ_{0i}, and $Dm_{2n+1} : Dm_{2n+2}$ (n = 0, 1, 2) were examined in some ranges. A fairly good agreement with Figure 3 could be obtained in Figure 14 assuming the values b = 0.025

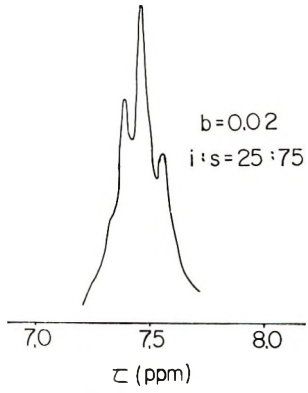

Fig. 15. Calculated methylenic proton resonance spectrum of PAN at 100 Mc./sec. assuming 75% syndiotactic and 25% isotactic diads (b = 0.02 ppm).

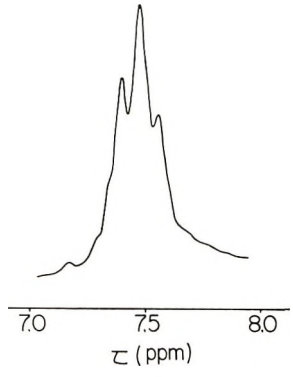

Fig. 16. Methylenic proton resonance spectrum of PAN prepared with redox catalyst (polymer A_1) at 100 Mc./sec.

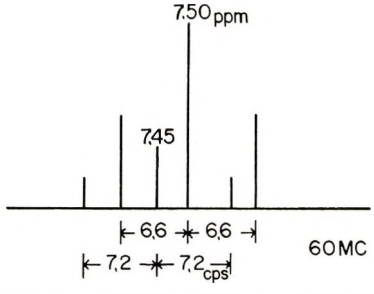

Fig. 17. Coupling constants and chemical shifts of methylenic protons of PAN at 60 Mc./sec.

ppm, τ_{0_1} = 7.33 ppm, τ_{0_2} = 7.39 ppm, τ_{0_3} = 7.45 ppm, τ_{0_4} = 7.50 ppm, τ_{0_5} = 7.57 ppm, τ_{0_6} = 7.61 ppm, $Dm_{2n+1}:Dm_{2n+2}$ = 25:75. Then the coupling constants are estimated as follows:

$$J_{\mathrm{CH-CH_2}} = 7.2 \text{ cps for isotactic } CH_2$$

$$J_{\mathrm{CH-CH_2}} = 6.6 \text{ cps for syndiotactic } CH_2$$

These values were examined for the spectrum at 100 Mc./sec. Figure 15, which was drawn by the use of the values obtained above except for b = 0.02 ppm, is very close to the observed spectrum of Figure 16. Then the coupling constants may be reasonable. The schematic diagrams of methylenic proton resonance at 60 and 100 Mc./sec. are shown in Figures 17 and 18, respectively.

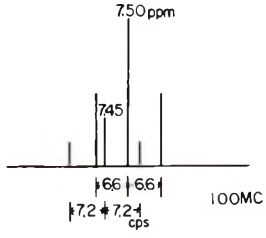

Fig. 18. Coupling constants and chemical shifts of methylenic protons of PAN at 100 Mc./sec.

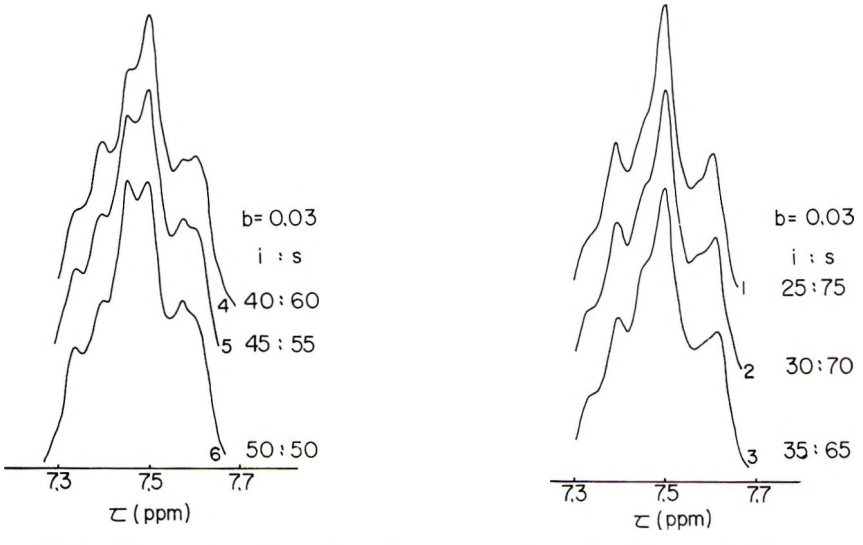

Fig. 19. Calculated methylenic proton resonance spectra of PAN at 60 Mc./sec. (b = 0.03 ppm) assuming: (*1*) 75% syndiotactic and 25% isotactic diads; (*2*) 70% syndiotactic and 30% isotactic diads; (*3*) 65% syndiotactic and 35% isotactic diads; (*4*) 60% syndiotactic and 40% isotactic diads; (*5*) 55% syndiotactic and 45% isotactic diads; (*6*) 50% syndiotactic and 50% isotactic diads.

The methylenic proton resonance spectrum of polymer A_2 agrees approximately with a curve obtained from the same coupling constants and the ratio of syndiotactic : isotactic CH_2 of 75 : 25, as shown in Figure 19, curve *1*. In this case, b is assumed to be 0.03 ppm, because its molecular weight is higher than that of polymer A_1.

Fairly good agreement can be seen between the observed spectra of the other PAN samples and the spectra calculated by assuming isotactic

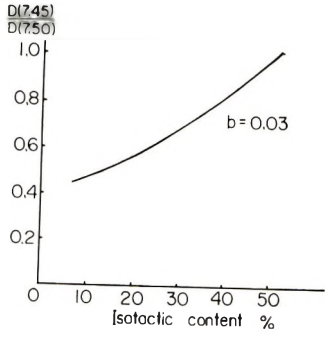

Fig. 20. Relationship between isotactic content and intensity ratio at 7.45–7.50 ppm.

CH_2 contents of 25–50% and b = 0.03 ppm. The calculated spectra are shown in Figure 19. From these spectra, a relationship between isotactic CH_2 content and the ratio of intensity at 7.45 ppm to that at 7.50 ppm is obtained, as shown in Figure 20.

Based on this relationship, the approximate tacticity can be given by the intensity ratio $D_{7.45}/D_{7.50}$ in an observed spectrum. The results obtained for 16 samples of PAN prepared under various polymerization conditions are shown in Table II.

TABLE II
Tacticity of PAN Approximately Estimated from Methylenic Resonance

Polymer		Polymerization	Syndiotactic	Isotactic
A_1	PAN	Radical (redox)	75	25
A_2	PAN	Radical (redox)	75	25
B	PAN	Radical	75	25
C	PAN-αd_1	Radical	75	25
D	PAN	Anionic	75	25
E	PAN	Anionic	75	25
F	PAN	Anionic	65	35
G	PAN	Anionic	60	40
H	PAN	Anionic	60	40
I	PAN	Anionic	55	45
J	PAN	Anionic	55	45
K	PAN	Molecular beam	60	40
L	PAN	Irradiation in solid state	65	35
M	PAN-αd_1	Irradiation in solid state	65	35
N	PAN	Irradiation on urea canal	50	50
O	PAN-αd_1	Irradiation on urea canal	50	50
P	PAN	Irradiation on urea canal	55	45

These estimations are based on an approximate analysis of methylenic proton resonance only, and it may be necessary to examine the methinic proton resonance in order to discuss the problem in more detail, but some new data on the tacticity of PAN could be obtained. Almost all PAN samples are predominantly syndiotactic, although the isotactic part in-

creases slightly in PAN polymerized with γ-rays and with anionic catalyst at low temperature. No remarkable stereoregularity was found for PAN prepared with γ-irradiation in the solid state,[16] with Mg molecular beam,[17] and with γ-irradiation on an AN–urea canal complex,[18] in spite of the several reports on the stereoregular PAN prepared by these methods.

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Résumé

Les spectres de résonance nucléaire magnétique de polyacrylonitriles préparés sous diverses conditions de polymérisation ont été mesurés dans une solution de NaCNS–D_2O. La résonance protométhylénique peut être séparée en deux triplets: un dû au proton des groupes méthylènes syndiotactiques et un autre du aux unités isotactiques. La tacticité du polyacrylonitrile peut être déterminée par le rapport des intensités intégrées de ces deux triplets. Les échantillons de polyacrylonitrile préparés avec des catalyseurs radicalaires présentent un pourcentage d'unités syndiotactiques d'environ 75%, tandis que les polyacrylonitriles préparés par polymérisation anionique à basse température, ceux préparés par irradiation aux rayons-γ, ou par un jet moléculaire de magnésium ou par irradiation-γ sous forme de complexe à base d'urée sont plus fortement isotactiques mais ils n'ont de stéréospécificité remarquable.

Zusammenfassung

Die kernmagnetischen Resonanzspektren von unter verschiedenartigen Polymerisationsbedingungen hergestellten Polyacrylnitrilen wurden in NaCNS–D_2O-Lösung gemessen. Die Methylenprotonenresonanz konnte in zwei Triplets getrennt werden: eines stammt von den Protonen der syndiotaktischen Methylengruppen und das andere von denjenigen der isotaktischen. Die Taktizität von Polyacrylnitril konnte aus dem Verhältnis der integrierten Intensität der beiden Triplets bestimmt werden. Mit radi-

kalischen Startern hergestellte Polyacrylnitrilproben besitzen etwa 75% syndiotaktischen Anteil, und durch anionische Polymerisation bei tiefer Temperatur, γ-Bestrahlung im festen Zustand, Mg-Molekular-strahl sowie γ-Bestrahlung im Harnstoffkanalkomplex dargestellte Polyacrylnitrile sind stärker isotaktisch, haben aber keine bemerkenswerte Stereospezifität.

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Mechanism of Initiation in the γ-Radiation-Induced Polymerization of Ethylene

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Synopsis

The relation between the gaseous products and the reaction conditions such as pressure, temperature, and dose rate in the γ-radiation-induced polymerization of ethylene was studied. The main gaseous products were hydrogen and acetylene, and the amounts of these products increased linearly with reaction time, monomer density, and dose rate, while they were independent of reaction temperature. The ratio of rate of formation of hydrogen to acetylene was about one-half. Further, it was found that the number of moles of polymer chain formed was almost equal to that of acetylene at room temperature. An initiation mechanism in which both hydrogen and acetylene are formed is proposed. The equation which is derived on the basis of the initiation mechanism is shown to be in good accordance with the experimental results.

INTRODUCTION

A number of papers have been published with reference to the radiolysis of ethylene under extremely low pressure.[1–9] It has been found that hydrogen, acetylene, and many other hydrocarbons are formed in this process. Little information has, however, been reported on the gaseous products in the γ-radiation-induced polymerization of ethylene under high pressure.

On the basis of the overall polymerization kinetics at room temperature, Machi et al.[10–12] have indicated that initiation and propagation are the main elementary reactions, and that the rate of initiation is proportional to the ethylene density and radiation intensity.

In this paper, the gaseous products formed by the γ-irradiation of ethylene are studied under high pressure from 150 to 400 kg./cm.^{2}. The mechanism of initiation for the polymerization is discussed on the basis of the relation between the amount of these products and polymer chain.

EXPERIMENTAL

The experiments were carried out in a stainless steel cylindrical vessel of 100 ml. capacity. After the vessel was repeatedly evacuated and filled with ethylene to about 20 kg./cm.^{2}, the vessel was charged with ethylene to the operation pressure by an oilless type compressor at the reaction

TABLE I
Impurities in Feed and Residual Monomer with Reaction at 30 and 45°C.[a]

	30°C.				45°C.			
	Feed		Residual		Feed		Residual	
	ppm	$\times 10^5$ mole/l.	ppm	$\times 10^5$ mole/l.	ppm	$\times 10^5$ mole/l.	ppm	$\times 10^5$ mole/l.
O_2	12	20	12	19	12	19	15	23
N_2	46	76	46	72	46	73	50	76
H_2	0	0	8	13	0	0	8	12
CH_4	74	122	74	116	74	117	74	112
C_2H_6	22	36	23	36	22	35	23	35
C_2H_2	3	5	17	27	3	5	20	30

[a] Reaction conditions: pressure, 400 kg./cm.^{2}; time, 1 hr.; dose rate, 2.9×10^5 rad/hr.; reactor volume, 100 ml.

temperature. During the irradiation period, the temperature was maintained constant within ±1°C. by using an automatic controller, and the pressure was held constant by means of a pressure regulator attached to the delivery tube of the compressor.

The γ-radiation was from a 10,000-curie ^{60}Co source. The dose rate in the reaction vessel was measured by means of a nitrogen-saturated ferrous dosimeter.

Commercially available ethylene (99.9% pure, free of CO and H_2S) containing impurities as shown in Table I was used. Hydrogen, methane, and ethane were determined at 50°C. by using a Shimadzu GC-1B gas chromatograph provided with a 3-m. column packed with activated alumina. Molecular sieves (5A) in a 2-m. column were used for oxygen and nitrogen. A Hitachi KGL-2A gas chromatograph provided with a 4-m. squalane (20%) column and/or with an 90-m. squalane capillary column (Hitachi Golay Column U-90) connected to a hydrogen flame ionization detector (Hitachi FID-2) was used at 40°C. for the detection of hydrocarbons higher than C_3. The amount of acetylene was measured by means of titration with 0.05*N* aqueous NaOH of free nitric acid which is formed by the reaction between acetylene and a propyl alcohol solution of silver nitrate. The gases produced were estimated from the difference in their contents determined before and after the irradiation.

The solid polymer was weighed, and the molecular weight was determined from the intrinsic viscosity in tetralin solution at 130°C. by using the Tung's equation.[13]

RESULTS AND DISCUSSION

Gaseous Products Formed in γ-Irradiation of Ethylene Under High Pressure

In the batch-type process under constant pressure, since the additional monomer is fed to the vessel continuously, the moles of various impurities in total feed monomer and those in residual monomer per liter reaction volume are calculated by eqs. (1) and (2), respectively.

For feed monomer:

$$C_F\rho_M[1 + M_w(v_M - v_P)\ M_p] \times 10^{-6} \tag{1}$$

For residual monomer:

$$C_R\rho_M(1 - M_w v_P M_p) \times 10^{-6} \tag{2}$$

Where M_w is the molecular weight of the monomer, v_M and v_P are the specific volume of monomer and polymer, respectively (in liters/gram), M_p is the amount of polymerized monomer (in moles/liter) at time t, ρ_M is the monomer density (in moles/liter), and C_F and C_R are concentrations (in parts per million) of various impurities in the feed and residual monomer, respectively.

Table I shows the content of various impurities in feed and residual monomer per liter calculated by above procedures. It is shown that the

amounts of oxygen, nitrogen, methane, and ethane are not changed, while hydrogen and acetylene are markedly increased by the irradiation.

In the polymerization under pressure of 400 kg./cm.^{2}, gaseous and solid products were obtained, and hydrocarbons higher than C_3 could not be detected in gaseous products. In the case of polymerization at lower pressure (5 kg./cm.^{2}), gaseous and liquid products were obtained, and C_4, C_6, and higher hydrocarbons were found in them.

This fact that no liquid products were obtained under higher pressure suggests that the chain propagation increases rapidly with increasing ethylene pressure.

Effect of Reaction Conditions on the Formation of Hydrogen and Acetylene

Table II shows the mole ratios of hydrogen and acetylene formed from the feed monomer are independent of temperature. The result indicates that the rates of formation of these compounds are not affected by the reaction temperature.

TABLE II
Effect of Reaction Temperature on the Mole Ratio X of Hydrogen and Acetylene Formed to Feed Monomer[a]

Reaction temperature, °C.	$X_{H_2} \times 10^6$ [b]	$X_{C_2H_4} \times 10^6$ [b]
30	7.7	15.2
45	7.7	16.1
60	5.9	16.3
70	7.2	17.4
80	6.9	15.3
90	9.8	14.6
100	6.8	17.1
Mean value	7.4 ± 1.1	16.0 ± 1.0

[a] Reaction conditions: pressure, 400 kg./cm.^{2}; time, 1 hr.; dose rate 2.9 × 10^5 rad/hr.; reactor volume, 100 ml.

[b] X_{H_2}, $X_{C_2H_2}$ denote mole ratio of H_2 and C_2H_2 to feed monomer, respectively.

TABLE III
Effect of Reaction Time on the Mole Ratio X of Hydrogen and Acetylene Formed to Feed Monomer[a]

Reaction time, hr.	$X_{H_2} \times 10^6$ [b]	$X_{C_2H_2} \times 10^6$ [b]
0.5	3.0 ± 0.0	6.4 ± 1.8
1.0	7.4 ± 1.1	16.0 ± 1.0
2.0	13.7 ± 2.2	27.8 ± 5.2
3.0	19.3	45.0

[a] Reaction conditions: pressure, 400 kg./cm.^{2}; temperature range, 30–100°C.; dose rate, 2.9 × 10^5 rad/hr.; reactor volume, 100 ml.

[b] X_{H_2}, $X_{C_2H_2}$ denote mole ratio of H_2 and C_2H_2 to feed monomer, respectively.

As is shown in Table III and Figure 1, the amounts of hydrogen and acetylene formed increase proportionally with reaction time. The slopes of the lines show that the rate of formation of hydrogen is about one-half of that of acetylene. Table IV and Figure 2 show that the rates of forma-

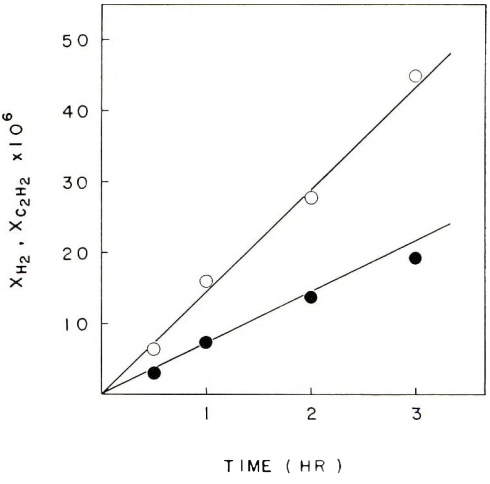

Fig. 1. Effect of reaction time on the mole ratio of hydrogen and acetylene formed to feed monomer: (●) hydrogen; (○) acetylene. Each point represents the mean values of the data in Table III. Reaction pressure, 400 kg./cm.^{2}; reaction temperature, 30–100°C.; dose rate, 2.9 × 10^5 rad/hr.

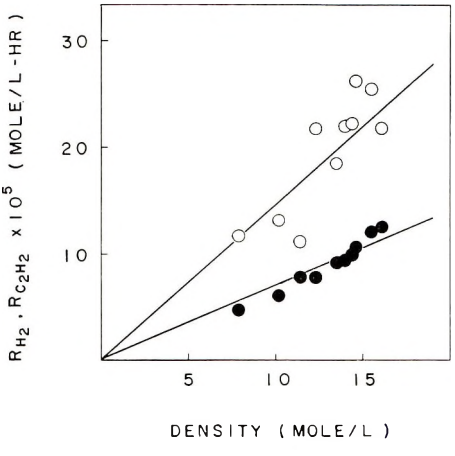

Fig. 2. Effect of monomer density on the rates of formation of hydrogen and acetylene: (●) hydrogen; (○) acetylene. Dose rate, 2.9 × 10^5 rad/hr.; reaction temperature, 30–100°C.

tion of hydrogen and acetylene increase proportionally with monomer density. Furthermore, it is shown in Table V and Figure 3 that the rates of formation of hydrogen and acetylene per unit monomer density increase linearly with dose rate.

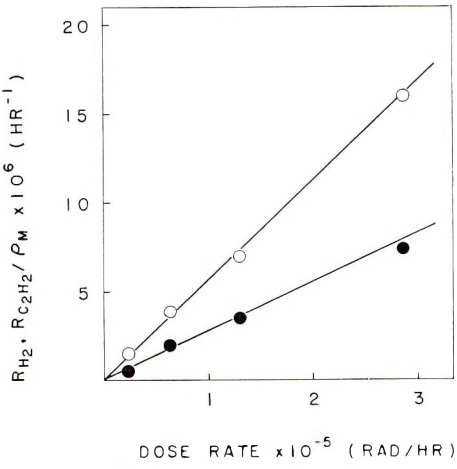

Fig. 3. Effect of dose rate on the rates of formation of hydrogen and acetylene formed per unit monomer density: (●) hydrogen; (○) acetylene. Reaction pressure, 400 kg./cm.^{2}; reaction temperature, 30–100°C.

TABLE IV
Effect of Monomer Density on the Rates of Formation of Hydrogen and Acetylene[a]

Reaction temperature, °C.	Reaction pressure, kg./cm.^{2}	Monomer density, mole/l.	$R_{H_2} \times 10^5$, mole/l.-hr.[b]	$R_{C_2H_2} \times 10^6$, mole/l.-hr.[b]
30	400	16.1	12.6	21.8
45	150	11.4	7.9	11.3
45	400	15.5	12.1	25.5
70	400	14.6	10.7	26.3
80	400	14.4	10.0	22.3
90	150	7.9	4.7	11.7
90	200	10.2	6.1	13.2
90	300	12.3	7.9	21.8
90	400	14.0	9.4	22.0
100	400	13.5	9.3	18.5

[a] Reaction conditions: dose rate, 2.9×10^5 rad/hr.; reactor volume, 100 ml.
[b] R_{H_2}, $R_{C_2H_2}$ denote rates of formation of H_2 and C_2H_2, respectively.

TABLE V
Effect of Dose Rate on the Rates of Formation of Hydrogen and Acetylene[a]

Dose rate $\times 10^{-5}$, rad/hr.	R_{H_2}/monomer density $\times 10^6$, hr.$^{-1}$ [b]	$R_{C_2H_2}$/monomer density $\times 10^6$, hr.$^{-1}$ [b]
0.2	0.5	1.5
0.6	2.0	3.9
1.3	3.5 ± 1.0	7.0 ± 1.4
2.9	7.4 ± 1.1	16.0 ± 1.0

[a] Reaction conditions: pressure, 400 kg./cm.^{2}; temperature range, 30–100°C.; reactor volume, 100 ml.
[b] R_{H_2}, $R_{C_2H_2}$ denote rates of formation of H_2 and C_2H_2, respectively.

From the above results, the rates of formation of hydrogen and acetylene, R_{H_2} and $R_{C_2H_2}$ (in mole/liter/hour), are given as follows by eqs. (3) and (4):

$$R_{H_2} = d[H_2]/dt = (2.5 \pm 0.3) \times 10^{-11}\rho_M I \quad (3)$$

$$R_{C_2H_2} = d[C_2H_2]/dt = (5.0 \pm 0.8) \times 10^{-11}\rho_M I \quad (4)$$

where I represents dose rate (in rad/hour). Thus, $R_{C_2H_2}$ is twice R_{H_2}.

Relation Between the Amounts of Acetylene and Polymer Chain

The ratio of the moles of polymerized monomer to the number-average degree of polymerization ($M_P/\bar{P}_n$) equals the number of moles of polymer

TABLE VI
Relation Between the Amounts of Acetylene and Polymer Chain[a]

Reaction temperature, °C.	Reaction time, hr.	Acetylene ($N_{C_2H_2}$) × 10^5, mole/l.	Polymer chain (N_P) × 10^5, mole/l.	$N_P/N_{C_2H_2}$
30	0.5	8.0	9.6	1.2
30	1.0	19.4	18.1	0.9
30	2.0	36.5	36.8	1.0
100	1.0	23.3	45.4	1.9
100	2.0	36.9	84.2	2.3

[a] Reaction conditions: pressure, 400 kg./cm.^{2}; dose rate, 2.9 × 10^5 rad/hr.; reactor volume, 100 ml.

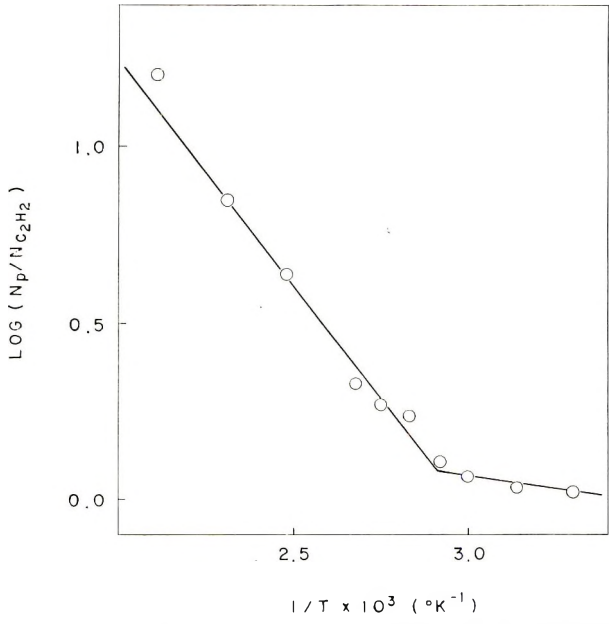

Fig. 4. Arrhenius plot for the mole ratio of polymer chain to acetylene. Reaction pressure, 400 kg./cm.^{2}; reaction time 0.5–4 hr.; dose rate, 2 × 10^4–3 × 10^5 rad/hr.

chain (N_P). It has been reported[11] that the chain termination and transfer reaction are almost absent at room temperature. Therefore, the number of moles of polymer chain represents the number of moles of initiating radical at room temperature.

Table VI shows the relation between the amounts of acetylene and polymer chains formed at 30 and 100°C. Since the ratio of the amount of polymer chain to acetylene formed is about unity at 30°C., the rate of formation of polymer molecule is equal to that of acetylene.

On the other hand, the ratio is about two at 100°C. Figure 4 shows an Arrhenius plot for the mole ratio of polymer chain to acetylene formed. It is shown that the difference between activation energy of the polymer formation and that of acetylene formation is about zero at 30–70°C. and about 6 kcal./mole at 70–200°C. These results will be discussed in detail in a future paper.

Mechanism of Initiation Reaction

As described above, in the γ-radiation-induced polymerization of ethylene under high pressure, the main gaseous products are hydrogen and acetylene, and gaseous hydrocarbons higher than C_3 are not formed. The amounts of hydrogen and acetylene formed increase with reaction time, monomer density, and dose rate, while they are independent of reaction temperature. The rate ratio of formation of hydrogen to acetylene is about one-half. Further, the number of moles of polymer chain is almost equal to that of acetylene formed at room temperature.

In addition, it has been reported[14] that radiation-polymerized polyethylene lacks both terminal vinyl and *trans*-vinylene types, and has only a small amount of vinylidene unsaturation. This result may indicate that a saturated hydrocarbon radical acts as an initiating species.

On the other hand, in the gas-phase radiolysis of a C_2H_4–C_2D_4 mixture under the pressure of 15–1,000 mm. Hg, Sauer and Dorfman[7] found that H_2, D_2, and a small amount of HD are produced, and that the yields in the pressure above 150 mm. Hg are $G(H_2) = 1.2$ and $G(C_2H_2) = 2.4$ molecules/100 e.v.

On the basis of these results at both high pressure and low pressure, the elementary reactions of the initiation reaction of the polymerization shown in eqs. (5)–(9) are proposed.

$$C_2H_4 \rightsquigarrow C_2H_4^* \tag{5}$$

$$C_2H_4^* \rightarrow C_2H_3\cdot^* + H\cdot \tag{6}$$

$$C_2H_3\cdot^* \rightarrow C_2H_2 + H\cdot \tag{7}$$

$$H\cdot + H\cdot \rightarrow H_2 \tag{8}$$

$$H\cdot + C_2H_4 \rightarrow C_2H_5\cdot \tag{9}$$

It is well known that under γ-radiation ethylene forms excited ethylene, and that the excited ethylene dissociates to radicals [reactions (5) and (6)].

On the basis of the fact that acetylene and hydrogen were formed in this study, reactions (7) and (8) were proposed. The excited vinyl radical ($C_2H_3\cdot$*) formed by reaction (6) is so unstable that it easily decomposes to produce C_2H_2 and H· [reaction (7)]. Sauer and Dorfman's results[7] indicate that hydrogen molecule is formed by the recombination of the hydrogen radicals released from same excited ethylene [reaction (8)].

Since ethane, hydrocarbons higher than C_3, and liquid products were not observed under high pressure in this work, it is considered that the ethyl radicals produced by the reaction (9) do not react with themselves by recombination and disproportionation to form butane, ethane, and ethylene, or with hydrogen radicals to form ethane. Therefore, it seems reasonable to consider that the addition of monomer to the ethyl radical, that is, the chain propagation reaction, proceeds predominantly under high pressure. This means that the ethyl radical is the initiating radical of the polymerization.

Assuming that the rate ratio of reactions (7), (8), and (9) is 2:1:2 from the experimental results, and that a steady state with respect to the concentrations of C_2H_4*, $C_2H_3\cdot$*, and H· is realized, the rates of formation of hydrogen, acetylene, and initiating radical are given by eqs. (10), (11), and (12), respectively.

$$R_{H_2} = d[H_2]/dt = (1/2)k_1\rho_M I \tag{10}$$

$$R_{C_2H_2} = d[C_2H_2]/dt = k_1\rho_M I \tag{11}$$

$$R_{C_2H_5\cdot} = d[C_2H_5\cdot]/dt = k_1\rho_M I \tag{12}$$

where k_1 represents the rate constant of reaction (5).

It is shown that eqs. (10) and (11) coincide with the experimental eqs. (3) and (4) with respect to the ethylene density, dose rate, and the ratio of hydrogen and acetylene formed. As described before, the number of polymer chains is equal to the acetylene formed at a normal temperature. The relation between eqs. (11) and (12) is in good accordance with this result. From eqs. (3), (4), (10), and (11), k_1 is obtained as 5.0×10^{-11} rad^{-1}.

In addition, eq. (12) is close to the rate expression[12] for initiation in this polymerization at a normal temperature,

$$R_i = k_i\rho_M I^{0.9}$$

where k_1 represents the overall rate constant of initiation reaction.

These results lead to the conclusion that initiation of the γ-radiation-induced polymerization of ethylene at room temperature follows a mechanism in which hydrogen and acetylene are formed.

Thanks are given to Mr. C. Hinaji and his group, especially Mr. F. Hosoi, for their assistance in the experimental work.

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Résumé

On a étudié la relation existant enete les produits gazeux et les conditions de réaction telles que la pression, la température et la vitesse de dose dans le cas de la polymérisation de l'éthylène induite par radiation-γ. Les produits gazeux principaux étaient l'hydrogène, et l'acétylène et les quantités de ces produits croissaient linéairement avec le temps de réaction, la densité en monomères et la vitesse de dose alors qu'elles étaient indépendantes de la température de réaction. Le rapport de vitesse de formation d'hydrogène à celle de l'acétylène était d'environ un demi. En outre, on a trouvé que les moles de chaînes polymériques étaient pratiquement égales à celles des molécules d'acétylène formés à la température normale. Un mécanisme d'initiation ou à la fois l'hydrogène et l'acétylène sont formés a été proposé. L'équation qui est dérivée sur la base d'un mécanisme d'initiation est en bon accord avec les résultats expérimentaux.

Zusammenfassung

Die gasförmigen Produkte bei der γ-strahlen-induzierten Polymerisation von äthylen wurden in Abhängigkeit von den Reaktionsbedingungen, wie Druck, Temperatur und Dosisleistung untersucht. Gasförmige Hauptprodukte waren Wassenstoff und Acetylen und die Menge dieser Produkte nahm linear mit Reaktionsdauer, Monomerdichte und Dosisleistung zu, war aber von der Reaktionstemperatur unabhängig. Das Geschwindigkeitsverhältnis für die Bildung von Wasserstoff und Acetylen betrug etwa ein halb. Weiters wurde gefunden, dass die Zahl der Mole Polymerketten derjenigen des bei normaler Temperatur gebildeten Acetylens fast gleich war. Es wurde ein Startmechanismus vorgeschlagen, bei dem sowohl Wasserstoff als auch Acetylen gebildet werden. Die auf Grund des Startmechanismus abgeleitete Geschwindigkeitsgleichung stimmt mit den Versuchsergebnissen gut überein.

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Effects of Metal Salts on Polymerization. Part III. Radical Polymerizabilities and Infrared Spectra of Vinylpyridines Complexed with Zinc and Cadmium Salts

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Synopsis

Radical polymerization of 4-vinylpyridine (4-VP), 2-vinylpyridine (2-VP), and 2-methyl-5-vinylpyridine (MVP) was studied in concentrated DMF solutions of $ZnCl_2$, $ZnBr_2$, ZnI_2, $Zn(CH_3COO)_2$, and $Cd(CH_2COO)_2$ at 50°C. Polymerization of 4-VP and MVP was accelerated by the addition of the metal salts, while the polymerization of 2-VP was greatly retarded. The sequence of the accelerating effect of metal salts for 4-VP was in the following order: $Cd(CH_3COO)_2 > ZnCl_2 > Zn(CH_3COO)_2 > ZnBr_2 > ZnI_2$. This sequence is almost the same as that reported in a previous report for MVP. However, the order was reversed for the retarding effect on the polymerization of 2-VP. At the intermediate concentration of metal salts, polymerization of 4-VP proceeded heterogeneously, which was explained by considering crosslinking of poly-4-VP by the metal ion. Since a linear correlation between the rate R_p and the degree of polymerization was observed for the 4-VP–$Zn(CH_3COO)_2$ system, the accelerating effect was postulated to be due to the enhancement in k_p. Results of copolymerization of VP with styrene as M_2 in a concentrated solution of $Zn(CH_3COO)_2$ indicated the strong activation of 4-VP by complex formation ($r_1 = 2.7 \pm 0.5$, $r_2 = 0.08 \pm 0.03$), whereas the change in the monomer reactivity of MVP is smaller ($r_1 = 2.0 \pm 0.2$, $r_2 = 0.35 \pm 0.05$). The behavior of 2-VP was abnormal ($r_1 = 3.35 \pm 0.3$, $r_2 = 0.55 \pm 0.15$, then $r_1 r_2 > 1$), which was attributed to the steric effect by complex formation. Solid complexes formed between pyridine, 4-VP, 2-VP, or MVP and zinc salts were prepared as samples for infrared spectroscopy. The shifts in infrared absorption bands of these amines were studied by comparing the infrared spectra of the amines before and after the complex formation, and the results were interpreted in terms of electronic as well as steric interactions of metal salts with ligands. Conjugation of the metal salt with the ligand π-orbitals was necessary to explain both infrared spectra and polymerization results.

INTRODUCTION

It was reported in the previous paper[1] that the polymerization of vinylpyridines is influenced when the monomers are complexed with group IIb metal salts. The influence depends on the structures of the vinylpyridine isomers. Polymerization of 4-vinylpyridine (4-VP) and 2-methyl-5-vinylpyridine (MVP) has been found to be accelerated by complexing the monomers with zinc thiocyanate, whereas polymerization of 2-vinylpyridine (2-VP) was retarded by the same metal salt. The results have

been interpretated by assuming electronic interactions between monomers and metal salts. However, the discussion was largely confined to the behaviors of the MVP complexes.

We have developed the study along the line of elucidating the polymerizability of metal complexed vinylpyridines and obtained more definitive evidence that the transmission of electronic effects through the coordination bond is an important factor deciding the reactivities of complexed monomers. Steric factors must also be considered in the case of 2-VP, since the coordinated metal salt would interact with the vinyl group. These electronic as well as steric effects are reflected in the infrared spectra of metal-complexed vinylpyridines.

EXPERIMENTAL

Materials

4-VP and 2-VP (Yuki Gosei Kogyo Co.) and MVP (Tokyo Kasei Kogyo Co.) were refluxed over potassium hydroxide and distilled in a stream of dry nitrogen under reduced pressure (5–10 mm. Hg). The monomers were stored at Dry Ice temperature and redistilled before use.

Styrene as a comonomer for copolymerization and *N*,*N*-dimethylformamide (DMF) as solvent for polymerization were purified by accepted procedures.

The metal salts used for complexing the vinylpyridines were G.R. grade reagents and used without further purification. Azobisisobutyronitrile (AIBN) as a radical initiator was recrystallized twice from methanol.

Infrared Spectroscopy

Infrared spectra of free monomers and their complexes as liquid films and KBr disks, respectively, were measured with a DS-402G spectrometer. The complexes were prepared by the same procedure reported previously.[1] The analytical data for the newly prepared complexes are shown in Table I. The solid complex of zinc acetate could not be isolated by the present procedure because of the high solubility of the complex.

TABLE I
Analytical Data for Vinylpyridine-Zn(II) Complexes

Complex	Metal content, %		Melting point, °C.
	Calcd.	Found	
$(4\text{-VP})_2\text{-}ZnCl_2$	18.87	18.8	124–128
$(4\text{-VP})_2\text{-}ZnBr_2$	15.01	15.1	134–137
$(4\text{-VP})_2\text{-}ZnI_2$	12.35	12.4	152–158
$(2\text{-VP})_2\text{-}ZnCl_2$	18.87	18.9	118–119
$(2\text{-VP})_2\text{-}ZnBr_2$	15.01	14.8	148–155
$(2\text{-VP})_2\text{-}ZnI_2$	12.35	12.4	153–163

The wavelength was calibrated against polystyrene film as standard reference. The position of absorption were determined with a precision of ± 1 cm.$^{-1}$.

Polymerization and Copolymerization

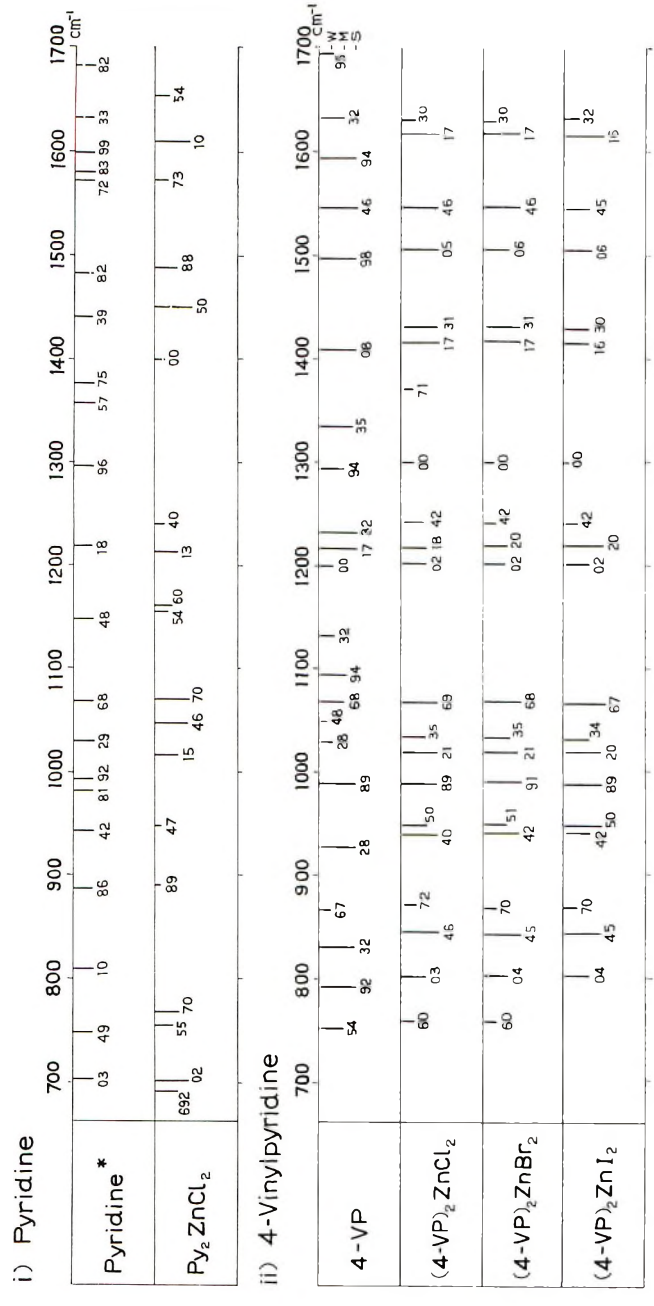
Polymerization and copolymerization were conducted *in vacuo*. The rate of polymerization for the MVP–$Zn(CH_3COO)_2$ and 4-VP–$Zn(CH_3COO)_2$ systems were measured dilatometrically and final conversions were checked by weighing polymer to insure the validity of the reported shrinkage factors[2] in the concentrated salt solutions. When the polymerization of 4-VP was conducted in the presence of $ZnCl_2$, $ZnBr_2$, ZnI_2, or $Cd(CH_3COO)_2$, the polymer complex of the salt precipitated. Consequently, dilatometric measurements could not be applied to these systems. The 4-VP–$Zn(CH_3COO)_2$ system was also heterogeneous at intermediate concentrations of zinc acetate. However, since the polymer complex of zinc acetate seemed to be more soluble than those of zinc halides or cadmium acetate, the dilatometric determination of the rate of polymerization R_p was possible unless the polymerization proceeded to too high conversion. The polymerization of 2-VP was greatly retarded by the metal salts, and much longer polymerization times were required to determine the rate. The slow hydrolysis of DMF or some other reactions between DMF and the metal salts affecting the volume of reaction system induced uncertainties in the dilatometric determination of R_p. The polymer yields of the 2-VP system were therefore determined by gravimetry, although the polymerization proceeded homogeneously.

After quenching the polymerization by cooling the reaction tube to Dry Ice–methanol temperature, the polymerization mixture was poured into a large excess of 5% ammonia containing 10 g./500 ml. of ammonium chloride as mentioned before.[1] Since the concentration of metal salts was very much higher than in the previous experiments, the polymer was reprecipitated once from 20% acetic acid solution with the same precipitant. The complete elimination of metal salts from the polymer was insured by the chelate titration of zinc which remained in the ash after decomposing the polymer above 1000°C. Not even traces of zinc ion could be detected. Poly-4-VP forms the most stable and insoluble complexes among VP polymers, and consequently other VP polymer complexes are thought to be decomposed completely by the same purification procedure.

Samples from copolymerizations were similarly purified, and the copolymer composition was determined by nitrogen analysis by a modified Kjeldahl method.[3] The reactivity ratios were determined by the Fineman-Ross plots. When the conversion exceeded 10%, the integrated equation was used.

The molecular weight of poly-4-VP was determined by the following equation derived for ethanol solution:[4]

$$[\eta] = 2.5 \times 10^{-4} M^{0.68}$$


i) Pyridine
Pyridine*
Py2ZnCl2
ii) 4-Vinylpyridine
4-VP
(4-VP)2ZnCl2
(4-VP)2ZnBr2
(4-VP)2ZnI2
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
cm-1
S - M - W

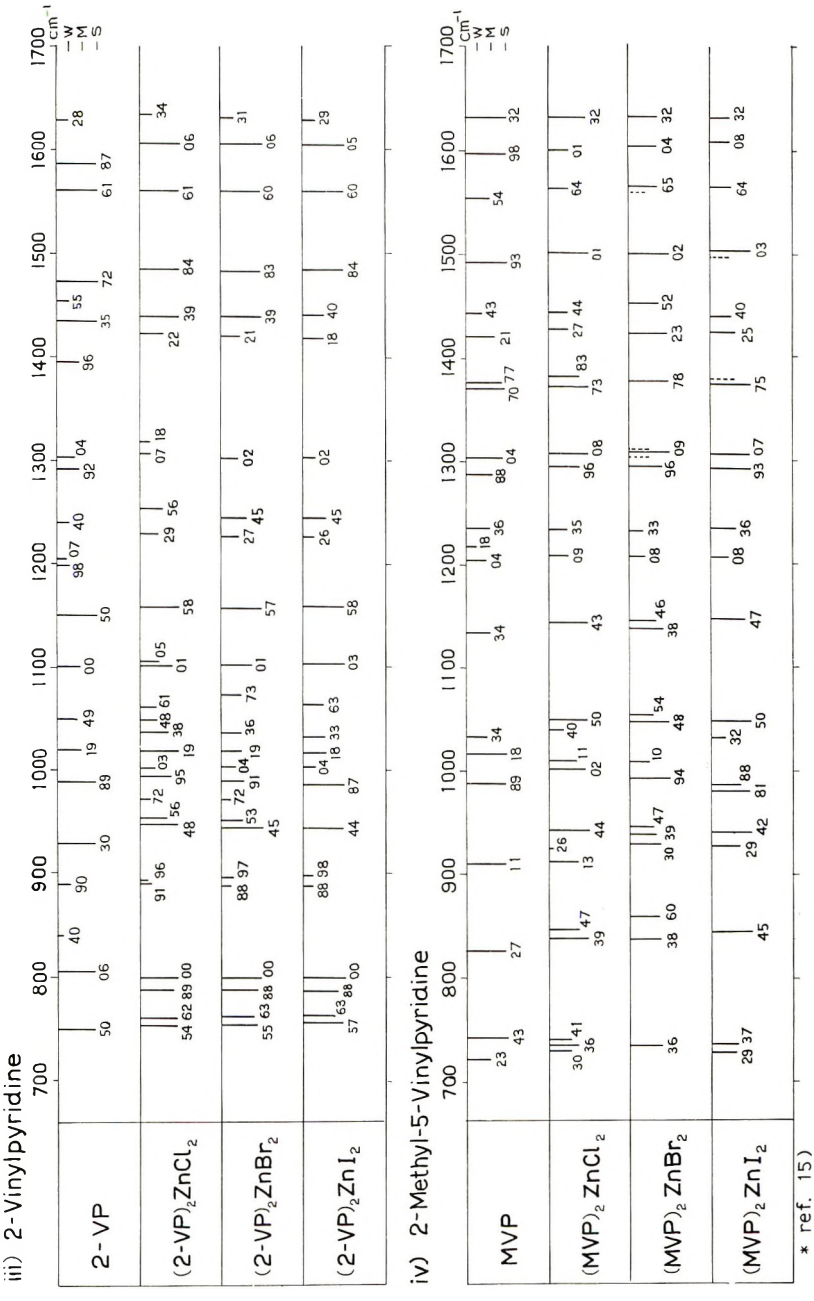


Fig. 1. Infrared spectra of vinylpyridines and their zinc complexes.

RESULTS AND DISCUSSION

Infrared Spectra of Vinylpyridines and Their Complexes

All complexes listed in Table I contain two vinylpyridine molecules and two anions and are thought to take the tetrahedral configuration as has been mentioned for pyridine–zinc complexes.[5,6]

When a molecule is complexed with a metal salt, electronic interactions as well as steric effects affect the infrared spectra of the ligand. Various reports have been published on the infrared spectra of pyridine complexes.[7–14] Since complex formation accompanies the change of state from liquid pyridine to solid complex, the change of infrared spectra might in part be due to the change in state.[7] The correlations of infrared spectra of substituted benzenes and pyridines with the nature of substituents have been discussed for many instances in connection with the electron density of phenyl or pyridine rings.[15] Coordination of a metal ion to the nitrogen of pyridine would be expected to act in a similar manner as organic substituents through formation of σ and π coordination bonds. In fact, most absorptions of VP are affected by complexing, as shown in Figure 1. Some of them, however, could not be assigned satisfactorily, and, since splitting of absorption is often observed when vinylpyridines are complexed, the correspondences of absorptions for free and complexed monomers are not clear in some occasions. The C—H deformation vibration of the pyridine ring, the skeletal vibration of the pyridine ring and the C=C stretching vibration of vinyl group were chosen for discussion. These absorption bands permit fairly clear comparison before and after complexing the monomers. Results are summarized in Table II.

C—H Out-of-Plane Deformation Vibration of Pyridine Ring. In general, the C—H out-of-plane deformation vibrations of pyridine derivatives appear in a higher frequency region than those of the corresponding substituted benzene, since the electron density of the pyridine ring is lower than that of benzene due to the electron-withdrawing properties of nitrogen. The higher π-electron density would reduce the energy needed for the deformation vibration which requires a sp^2 hybrid structure. The coordination of the lone electron pair of nitrogen to a metal salt would increase the electron-withdrawing power of nitrogen. This electronic effect would indeed be comparable to the substituent effect in aromatic systems. The positive shift of the C—H deformation vibration of aromatic systems has been found to be linearly correlated with the increase in the Hammett σ values of substituents.[16] The blue shift of the deformation vibration by complexing is clearly observed for pyridine, 4-VP, and MVP complexes, indicating electron withdrawal by the metal ion. Splittings of the absorption are often observed, and the $\Delta\nu$ values in Table II were calculated as averaged values. Results for 2-VP are more complicated. There is an absorption at 750 cm.$^{-1}$ for 2-VP which might be assigned to the C—H deformation, since the C—H deformation vibration of 2-substituted pyridine has been reported[15] to appear in the region 740–810 cm.$^{-1}$. However, in

TABLE II
Changes in Infrared Spectra of Vinylpyridines by Complex Formation

Sample	CH deformation vibration of pyridine ring, cm.$^{-1}$	$\Delta\nu$, cm.$^{-1}$ [b]	Skeletal vibration of pyridine ring, cm.$^{-1}$	$\Delta\nu_{total}$, cm.$^{-1}$ [c]	C=C stretching vibration, cm.$^{-1}$	$\Delta\nu$, cm.$^{-1}$
Pyridine[a]	749		1482, 1572, 1583, 1599	?	—	—
Py_2ZnCl_2	755, 770	+13	1488, 1573, 1610		—	—
4-VP	832		1498, 1546, 1594		1632	
$(4\text{-VP})_2$–$ZnCl_2$	846	+14	1505, 1546, 1617	+30	1630	−2
$(4\text{-VP})_2$–$ZnBr_2$	845	+13	1506, 1546, 1617	+31	1630	−2
$(4\text{-VP})_2$–ZnI_2	845	+13	1506, 1545, 1616	+28	6132	0
2-VP	806		1472, 1561, 1587		1628	
$(2\text{-VP})_2$–$ZnCl_2$	789, 800	−11	1484, 1561, 1606	+31	1634	+6
$(2\text{-VP})_2$–$ZnBr_2$	788, 800	−12	1483, 1560, 1606	+29	1631	+3
$(2\text{-VP})_2$–ZnI_2	788, 800	−12	1484, 1560, 1605	+29	1629	+1
MVP	827		1493, 1554, 1598		1632	
$(MVP)_2$–$ZnCl_2$	839, 847	+16	1501, 1564, 1601	+21	1632	0
$(MVP)_2$–$ZnBr_2$	838, 860	+22	1502, 1565, 1604	+26	1632	0
$(MVP)_2$ ZnI	845	+18	1499, 1565, 1605	+24	1632	0

[a] Data of Shindo.[15]

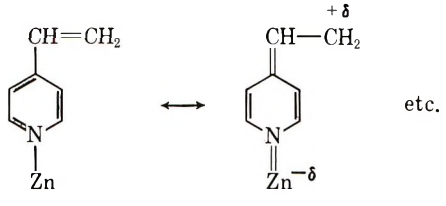
[b] When splitting of absorption was observed, the average value was taken.

[c] Sum of shift for corresponding absorptions.

comparison with pyridine, which shows the C—H deformation vibration at 749 cm.$^{-1}$, the absorption at 806 cm.$^{-1}$ is more likely to be the C—H deformation vibration, since this absorption shifts towards higher frequency with increasing number of substituents. The presence of a steric effect in the complex formation of 2-substituted pyridines was discussed on the basis of thermodynamic measurements of complex formation.[17] Any steric interactions of coordinated metal salt with vinyl group would reduce the conjugation between vinyl and pyridyl groups and consequently reduce the substituent effect of vinyl group on the infrared spectrum while the electron-withdrawing effect of metal salts in the 2-VP complexes would also be smaller than in the MVP or 4-VP complexes. The red shift of the C—H deformation vibration as observed for 2-VP complexes would therefore be expected from the discussion above.

C=C and C=N Skeltal Vibrations of Pyridine Ring. By analogy to three absorptions at 1583, 1572, and 1482 cm.$^{-1}$ assigned to C=C and C=N vibrations of pyridine, the three absorptions which appear between 1470 and 1600 cm.$^{-1}$ were attributed to the skeltal vibrations of vinylpyridines. However, there are some ambiguities that the overtone absorption of pyridine at 1599 cm.$^{-1}$ disappears in vinylpyridines and that one of the absorptions assumed as the skeltal vibration may in fact be the overtone absorption.

The total sums of shifts ($\Delta\nu$) are shown in Table II. The magnitude of positive shifts are in the order, 4-VP$\simeq$ 2-VP > MVP. This order indicates that the shifts might be related to the mesomeric effect of the coordinated metal ion. Strong evidence[2,18,19] in support of conjugation between metal salt and coordinated pyridine ring have already been obtained from the thermodynamic and also from the kinetic studies on the complex formation on the reactivities of the complexes.



These mesomeric structures would increase the bond order of the C=C or C=N bonds of the pyridine ring and consequently would cause blue shifts of these absorptions. This interpretation implies that the effect of coordination should affect the infrared absorption of the C=C stretching vibration of the vinyl group as well.

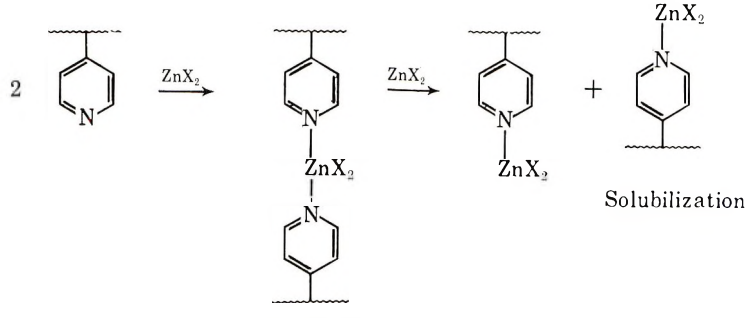
C=C Stretching Vibration of the Vinyl Group. Although the shifts are very small, the tendency for a red shift of the C=C stretching vibration is observed for the 4-VP complexes, whereas the position of the corresponding absorption for the MVP complexes is the same as for free MVP. These observations are in accord with the discussions presented above. On the contrary, the 2-VP complexes showed blue shifts of the C=C stretching

vibration. Provided that the conjugation of the vinyl group of 2-VP complexes with the pyridyl group is somewhat reduced by steric effects as mentioned above, the position of the C=C stretching absorption would shift towards the region for the nonconjugated vinyl group.

It seems necessary to consider both steric and electronic effects to understand the results of infrared spectroscopy. Differences of infrared spectra among complexes consisting of the same amine and different anions were quite small. No general correspondence between the spectra and the properties of the anion could be found.

Polymerization of 4-VP

The dependence of polymer yield on metal salt concentration is shown in Figures 2 and 3. For the system with zinc acetate, the rate of polymerization by dilatometry was converted to polymer yield after polymerization for 2 hr. in order to permit comparison with other systems. The general trend is to have the maximum polymer yield at the intermediate metal salt concentration. The heterogeneity of the polymerization system, particularly at intermediate metal salt concentrations, differs from the polymerization systems of MVP and 2-VP. The ease of crosslinking of poly-4-VP by metal ions in comparison to the sterically hindered poly-MVP or poly-2-VP would account for the insolubility of the polymer complexes. It is interesting to note that the insoluble polymer complexes are solubilized again at higher concentrations of zinc salts. Conversion of 2/1 complex to 1/1 complex would take place.



The formation constants of zinc–pyridine complexes in aqueous media have been reported to be 0.95 for the first step and 0.5 for the second step.[20] Assuming that the values could be applied to the poly-4-VP–zinc complexes in DMF, the 1/1 complex is predominantly formed when [poly-4-VP] $\ll$ [Zn(II)].

Among those metal salts used in the present experiment, zinc acetate forms the most soluble complexes with poly-4-VP. Although the polymerization system becomes heterogeneous, it is still possible to determine the rate of polymerization by an ordinary dilatometer. When the polymerization was carried out in a medium 0.557*M* in zinc acetate, precipita-

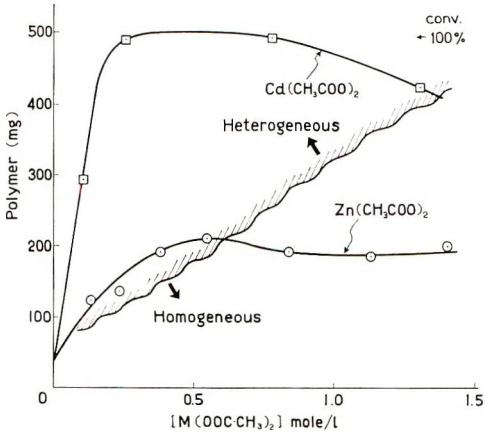


Fig. 2. Dependence of polymer yield on the concentration of zinc and cadmium acetate. Polymerization conditions: 0.5 ml. 4-VP, 20 mg. AIBN; DMF solution of metal salt, 10 ml.; sealed *in vacuo;* polymerization at 50°C. for 2 hr.

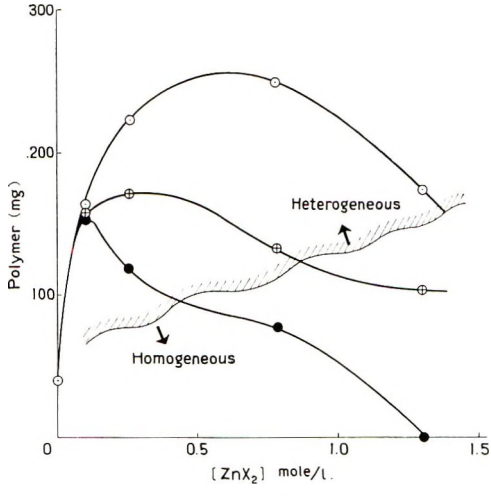


Fig. 3. Dependence of yield of poly-4-VP on the concentration of zinc halides. Polymerization conditions: 0.5 ml. 4-VP; 20 mg. AIBN; 10 ml. DMF; polymerization at 50°C. for 2 hr.

tion of polymer complex started at approximately 22% conversion to polymer. The rate of polymerization was unchanged before and after the transition from a homogeneous to heterogeneous system. The peak of polymer yield shown in Figure 2 is broad and small for the zinc acetate system, indicating the acceleration of polymerization due to suppression of the bimolecular termination reaction in the heterogeneous system is not important. The approximately linear correlation between R_p and degree of polymerization as measured at different zinc acetate concentrations would imply that the main effect of complex formation is to enhance

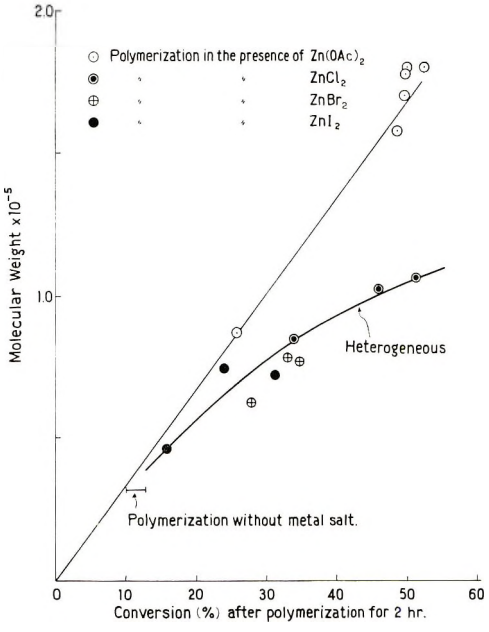


Fig. 4. Plots of polymer yield vs. molecular weight of poly-4-VP.

the rate of propagation. The enhancement of k_p seems to be a common feature of acceleration of radical polymerization by neutral metal salts. It has been discussed in the previous paper[1] that the effect of zinc halides on radical polymerization of MVP is predominantly to enhance the rate of propagation, and also the determination of absolute rate constants in somewhat different polymerization systems indicates that k_p increases exclusively by the addition of lithium chloride to acrylonitrile[21] or zinc chloride to methyl methacrylate.[22]

The linear relationship as shown in Figure 4 does not hold for the 4-VP systems with zinc halides, however. The increase in R_p approximated by polymer yield after polymerization for 2 hr. exceeds the increase in molecular weight of polymer in these systems. This indicates that the bimolecular termination is probably suppressed due to heterogeneity of the systems, whereas the molecular weight of polymer is determined by chain transfer to solvent.

The accelerating effect of metal salt is very much affected by the anion. The order of accelerating effect is $Cd(CH_3COO)_2 > ZnCl_2 > Zn(CH_3COO)_2 > ZnBr_2 > ZnI_2$. This order is almost the same as that obtained for MVP.[1] Since physical as well as chemical effects are included in the sequence of acceleration, further discussion is not warranted.

Polymerization of 2-VP

Unlike the polymerization of 4-VP, with 2-VP strong retarding effects are observed for all metal salts (Fig. 5). The retardant effectiveness

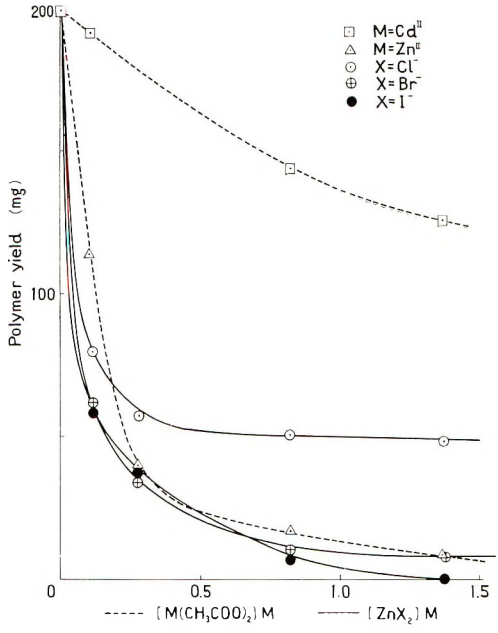


Fig. 5. Dependence of the yield of poly-2-VP on the concentration of metal salts: (--) $M(CH_3COO)_2$ where M = Zn(II) or Cd(II); (——) (ZnX_2) where X = halogen. Polymerization conditions: 1 ml. 2-VP; 10 ml. DMF; 40 mg. AIBN; polymerization at 50°C. for 8 hr. in DMF.

determined at the highest concentration of metal salt employed follows the order: $ZnI_2 > ZnBr_2 > Zn(CH_3COO)_2 > ZnCl_2 > Cd(CH_3COO)_2$. Comparing this sequence with the results mentioned in the previous section the accelerating effect for polymerization of 4-VP and the retarding effect for polymerization of 2-VP are in the reversed order. The most effective accelerator for 4-VP, $Cd(CH_3COO)_2$, is the weakest retarder for 2-VP. For the 2-VP complexes, steric as well as electronic effects have to be considered. As discussed in the section on infrared spectroscopy, there is

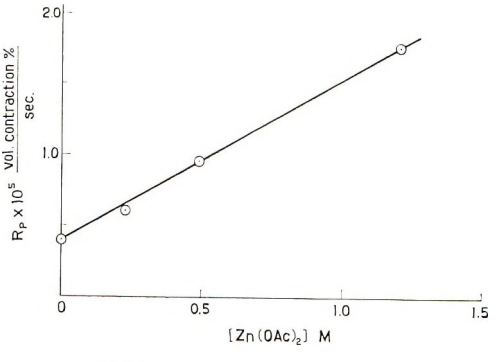


Fig. 6. Dependence of R_p for MVP on the concentration of zinc acetate at 50°C. in DMF. Polymerization conditions: 0.5 ml. MVP; 10 ml. DMF; 20 mg. AIBN.

evidence for steric interaction between the metal salt and the vinyl group. It is, however, not clear as to whether the steric effect is to reduce the reactivity of monomer in a manner similar to steric hindrance or whether it increases the rate of reaction by increasing the local concentration of vinyl groups, since the tetrahedral coordination by zinc or cadmium would bring one vinyl group to the periphery of another. The fact that the bulkier cadmium salts shows a smaller influence than zinc salts would suggest that the retarding effect is not due to steric hindrance.

Polymerization of MVP

Polymerization of MVP in the presence of various concentrations of zinc thiocyanate, zinc chloride, zinc bromide, and zinc iodide has already been reported.[1]

When zinc acetate is added to the polymerization system, the rate of polymerization increases linearly with the metal salt concentration, as shown in Figure 6. Saturation of the rate of polymerization is not observed even at the highest concentration of zinc acetate.

Copolymerization with Styrene

Results of copolymerization of VP with styrene in the presence of zinc acetate are shown in Figure 7, and the monomer reactivity ratios are tabulated in Table III. All copolymerizations proceeded in homogeneous

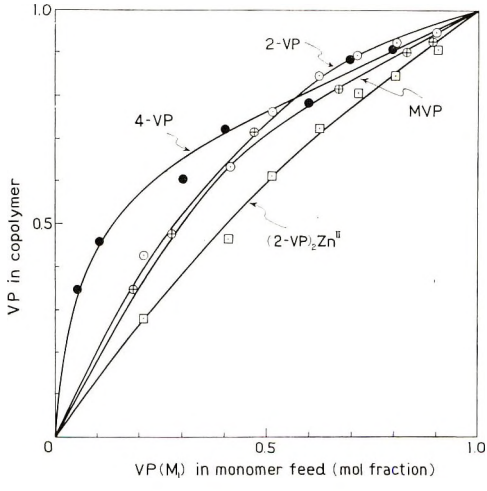


Fig. 7. Copolymerization of 4-VP, 2-VP, and MVP with styrene in the presence of zinc acetate in DMF at 50°C.: (●) M_1 = 4-VP, $M_1 + M_2$ = 0.5 ml., 10 ml. of DMF solution containing 11.0 g. of $Zn(OAc)_2$ and 20 mg. of AIBN per 50 ml.; (○) M_1 = 2-VP, $M_1 + M_2$ = 3.0 ml.; [Zn]/[2-VP] was kept constant at 1.75 by adding different amounts of DMF solution containing 32.0 g. of $Zn(OAc)_2$ and 300 mg. of AIBN per 100 ml.; (⊡) $(2\text{-VP})_2Zn$ was assumed as a bifunctional monomer; (⊕) M_1 = MVP, $M_1 + M_2$ = 0.715 ml., total volume 15 ml., $Zn(OAc)_2$ = 3.05 g./15 ml., AIBN = 14.3 mg./15 ml.

systems. There is some discrepancy between the results of the previous report and the present result for the copolymerization of MVP. Direct comparison with the former report is, however, not possible, since the previous results were obtained for a system in which $[Zn(CH_3COO)_2]/[MVP] = 1/2$ and, in fact, this was the copolymerization of a ternary system consisting of styrene, MVP, and MVP complex, whereas the present system was studied at much higher ratio of zinc to MVP.

A marked increase in monomer reactivity was observed for 4-VP on addition of zinc acetate, while the monomer reactivity of MVP was not changed greatly. It is very likely that the $d\pi$ or $p\pi$ orbitals of zinc salt could interact with the π orbital of pyridine. Now, a question arises as to whether Zn(II) having the $3d^{10}$ ground state could effectively induce $d\pi$–$P\pi$ or $p\pi$–$p\pi$ overlaps. So far as the $3d^{10}$ state is considered, the double-bond nature of the coordination bond is difficult to assume. However,

TABLE III
Copolymerization of VP with Styrene in the Concentrated Solution of Zinc Acetate at 50°C. (M_1 = VP, M_2 = Styrene)

M_1	r_1	r_2	Q_1	e_1
4-VP[a]	0.52–0.7	0.54–0.62	0.82	−0.20
4-VP–Zn(II)	2.7 ± 0.5	0.08 ± 0.03	4.7	+0.44
2-VP[a]	0.9–1.81	0.55	1.30	−0.50
2-VP–Zn(II)	3.35 ± 0.3	0.55 ± 0.15	r_1r_2 = 1.84	
MVP[a]	0.68–1.19	0.6–0.88	0.99	−0.58
MVP–Zn(II)	2.0 ± 0.2	0.35 ± 0.05	1.75	−0.26

[a] Data of copolymerization were taken from Ham.[24]

if a d^9sp state could be taken as a result of donation of an electron from the σ lone pair of nitrogen or possibly from the anions attached to the central metal ion, the $p\pi$–$p\pi$ interaction would seem to be energetically possible. A detailed discussion will be published elsewhere in connection with the molecular orbital consideration of these complexed monomers.[23]

The conjugation effect would be expected to enhance the reactivity of 4-VP rather than MVP. The fact that the positive shift of the e value is larger for 4-VP than for MVP might be another indication that the electronic effects are transfered through π conjugation to vinyl group. The reactivities of complexed 4-VP may be compared with those of styrene derivatives[24] having an electron-withdrawing substituent at the *para* position. On comparing styrene with *p*-nitrostyrene (Q = 1.63, e = +0.39), *p*-cyanostyrene (Q = 1.86, e = −0.21), *p*-chlorostyrene Q = 1.03, e = −0.33), and *p*-bromostyrene (Q = 1.04, e = −0.32), the same trend of shift in e value as for 4-VP relative to complexed 4-VP is noticed. The Q value of styrene is enhanced by introducing a nitro or cyano group

which would have mesomeric interaction to the *para* position, as is the Q value of 4-VP by complexing the monomer.

The reactivity of 2-VP is abnormal. The product of r_1 and r_2 exceeds unity, indicating the block nature of the copolymer. When two monomers are connected by coordination to zinc ion, the two monomers might act as a bifunctional monomer to yield cyclic polymerization. Consequently, 2-VP content in the copolymer may be much higher than it should be in the absence of the steric effect. Assuming $(2\text{-VP})_2\text{Zn}$ to be the bifunctional monomer involved in cyclic polymerization, the monomer reactivity ratios were calculated to be $r_1 = 1.1 \pm 0.15$, $r_2 = 0.6 \pm 0.15$.

CONCLUSION

The coordination bond formed between vinylpyridines and metal salts brings about both chemical and physical modification of the polymerization systems. The polymerization behavior of 4-VP and MVP complexes was interpreted by considering electronic effects transmitted to the monomers through both σ- and π-type interactions. In a way, the effects of complex formation are quite similar to the substituent effects in organic chemistry. For the 2-VP system, steric factors have to be considered also.

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Résumé

La polymérisation radicalaire de 4-vinylpyridine (4-VP), 2-vinylpyridine (2-VP), et 2-méthyl-5-vinylpyridine (MVP) a été étudiée en solution concentrée dans le DMF de $ZnCl_2$, $ZnBr_2$, ZnT_2, $Zn(CH_3COO)_2$ et $Cd(CH_3COO)_2$ à 50°C. La polymérisation 4-VP et MVP était accélérée par addition de sels métalliques alors que la polymérisation de DVP était fortement retardée. La séquence de l'effet accélérateur des sels métalliques pour la 4-VP était dans l'ordre suivant: $Cd(CH_3COO)_2 > ZnCl_2 > Zn(CH_3COO)_2 > ZnBr_2 > ZnI_2$. Cette séquence est pratiquement la même que celle rapportée dans une communication antérieure concernant la MVP. Toutefois, l'ordre était renversé pour l'effet retardateut en ce qui concerne la polymérisation de la 2-VP. A une concentration intermédiaire de sels métalliques, la polymérisation de la 4-VP se passe de façon hétérogène qui est expliquée en considérant le pontage de la poly-4-VP par l'ion métallique. Comme la corrélation linéaire entre R_p et DP était observée pour 4-VP–$Zn(CH_3COO)_2$, l'effet accélérant était postulé être attribué à une augmentation de k_p. Les résultats de copolymérisation de VP avec le styrène en solution concentrée de $Zn(CH_3COO)_2$ indiquait une forte activation de la 4-VP par formation de complexes ($R_1 = 2.7 \pm 0.5$, $R_2 = 0.08 \pm 0.03$) tandis que la variation de réactivité du monomère de MVP est plus faible ($r_1 = 2.0 \pm 0.2$, $r_2 = 0.35 \pm 0.05$). Le comportement de 2-VP était anormal ($r_1 = 3.35 \pm 0.3$, $r_2 = 0.55 \pm 0.15$) c'est-à-dire $r_1r_2 > 1$, ce qui est attribué à un effect stérique par formation de complexes. Les complexes solides formés entre la pyridine et 4-VP, 2-VP et MVP et les sels de zine, ont été préparés comme échantillons pour la spectroscopie infrarouge. Les glissements des bandes d'absorption des spectres infrarouge de ces amines ont été étudiés en comparant les spectres infrarouge des amines avant et après formation des complexes, et les résultats ont été interprétés sur la base de données électroniques aussi bien que d'interactions stériques de sels métalliques avec les ligants. La considération de la conjugaison du sel métallique avec les orbitales-π-de ligant était nécèssaire pour expliquer les spectres infrarouges et les résultats de polymérisation.

Zusammenfassung

Die radikalische Polymerisation von 4-Vinylpyridin (4-VP), 2-Vinylpyridin (2-VP) und 2-Methyl-5-vinylpyridin (MVP) wurde in konzentrierten DMF-Lösungen von $ZnCl_2$, $ZnBr_2$, ZnJ_2, $Zn(CH_3COO)_2$ und $Cd(CH_3COO)_2$ bei 50°C untersucht. Die Polymerisation von 4-VP und MVP wurde durch Zusatz dieser Metallsalze beschleunigt, während die Polymerisation von 2-VP stark verzögert wurde. Für 4-VP bestand folgende Reihenfolge für die Beschleunigung durch Metallsalze: $Cd(CH_3COO)_2 > ZnCl_2 > Zn(CH_3COO)_2 > ZnBr_2 > ZnJ_2$. Diese Reinhenfolge stimmt fast vollständig mit der früher für MVP mitgeteilten überein. Bei der Verzögerung der 2-VP:Polymerisation wurde jedoch die Reihenfolge umgekehrt. Bei einer intermediären Metllsalzkonzentration verlief die Polymerisation von 4-VP heterogen, was mit einer Vernetzung von Poly-4-VP durch das Metallion erklärt wird. Da im 4-VP–$Zn(CH_3COO)_2$-System eine lineare Korrelation zwischen R_p und DP besteht, wird der Beshleunigungseffekt einer Erhöhung von k_p zugeschrieben. Ergebnisse bei der Copolymerisation von VP mit Styrol als M_2 in konzentrierter $Zn(CH_3COO)_2$-Lösung lassen die starke Aktivierung von 4-VP durch Komplexbildung ($r_1 = 2{,}7 \pm 0{,}5$, $r_2 = 0{,}08 \pm 0{,}03$) erkennen, während die Veranderung der Monomerreativitäten von MVP kleiner ist ($r_1 = 2{,}0 \pm 0{,}2$, $r_2 = 0{,}35 \pm 0{,}5$). 2-VP zeigte ein abnormales Verhalten ($r_1 = 3{,}35 \pm 0{,}3$, $r_2 = 0{,}55 \pm 0{,}15$ und damit $r_1r_2 > 1$), was auf sterische Effekte bei der Komplexbildung zurückgeführt wird. Feste Komplexe zwischen Zinksalzen und Pyridin, 4-VP, 2-VP oder MVP wurden als Proben für die IR-spektroskopische Untersuchung dargestellt. Die Verschiebungen in den Absorptionsbanden der IR-Spektren dieser Amine wurden durch Vergleich der IR-Spektren der Amine

vor und nach der Komplexbildung festgestellt und die Ergebnisse durch die Annahme elektronischer und sterischer Wechselwirkungen zwischen den Metallsalzen und den Liganden interpretiert. Zur Erklärung sowohl der IR-Spektren als auch des Polymerisationsverhaltens war es notwendig, eine Konjugation des Metallsalzes mit den π-Orbitalen des Liganden in Betracht zu ziehen.

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Applications of Limiting Conversion Free-Radical Polymerizations. I. *tert*-Butyl Hydroperoxide-Initiated Polymerization of Styrene in Benzene

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Synopsis

Data for the *tert*-butyl hydroperoxide-initiated polymerization of styrene in dilute benzene solution at 126°C. are presented. These data are discussed in terms of Tobolsky's limiting conversion kinetics. Several rate laws are considered. Simple unimolecular decomposition of the peroxide appears to be unimportant under these conditions, as does solvent interaction.

Introduction

By following initiated free-radical polymerizations to infinite time, limiting conversions of monomer to polymer may be obtained. The relationship

$$-\ln ([M_\infty]/[M_0]) = 2K[P_0]^{1/2}/k \quad (1)$$

has been derived[1–4] and verified[1–3] for the azobisisobutyronitrile-initiated polymerization of styrene and the azobisisobutyronitrile- and benzoyl peroxide-initiated polymerization of isoprene. In eq. (1) $[M_\infty]$, $[M_0]$ are monomer concentration at infinite and zero times, respectively; $[P_0]$ is initiator concentration at zero time; K is the overall rate constant for polymerization from eq. (2):

$$-d[M]/dt = K[M][P]^{1/2} \quad (2)$$

and k is the rate constant for initiator decomposition from eq. (3):

$$-d[P]/dt = k[P] \quad (3)$$

Two more free-radical-initiated polymerization systems have been examined in an effort to extend the general applicability of limiting conversion kinetics. These two systems are the *tert*-butyl hydroperoxide-initiated polymerization of styrene (Part I) and the azobisisobutyronitrile-initiated polymerization of methyl methacrylate (Part II).[5]

In order to avoid complications of diffusion-controlled termination, known as the Trommsdorff-Norrish[6,7] effect, which has demonstrably limited this technique,[2] polymerizations were carried out in dilute benzene

solution. Styrene conversions were measured spectrophotometrically. Methyl methacrylate conversions were measured by gas chromatography.

EXPERIMENTAL

Chemicals

Styrene (Eastman Organic Chemicals), pure grade, was fractionally distilled at reduced pressure prior to use. *tert*-Butyl hydroperoxide (Lucidol Div., Wallace and Tiernan Corp.) was purified by the method of Walling and Zavitsas[8] to > 95% purity as determined by iodometric assay. Thiophene-free benzene was used as a solvent in polymerization studies. Azobisisobutyronitrile (Eastman white label) was purified by recrystallization from diethyl ether, m.p. 104°C.

Styrene Polymerization

Measured amounts of styrene, thiophene-free benzene, and *tert*-butyl hydroperoxide were degassed, evacuated, sealed in new Carius tubes, and thermostated at 126 ± 0.1°C. The tubes were removed periodically and analyzed for remaining styrene spectrophotometrically in the range 2835–2925 A.[9] It was experimentally determined that for the system styrene–benzene–*tert*-butyl hydroperoxide–polystyrene only styrene absorbs in this region. The tabulated data were obtained at 2925 A. Absorptions of aliquots of the polymerized mixtures were determined in CCl_4 on a Cary 14 spectrophotometer. A set of azobisisobutyronitrile-initiated bulk polymerizations of styrene at 102 ± 0.2°C. gave excellent agreement with the gravimetrically determined conversions of Tobolsky et al.[2] A blank tube (containing no initiator) was always run with a tube containing initiator. The amount of thermal polymerization was subtracted from the initiated polymerization. Since polymerizations were carried out in dilute solution, the small correction[2] from volume contraction was considered negligible. Thermal polymerization data are presented in Table I.

RESULTS AND DISCUSSION

tert-Butyl Hydroperoxide-Initiated Styrene Polymerization

Table I sets forth the results of dilute solution polymerizations of styrene with *tert*-butyl hydroperoxide in benzene at 126°C. It is clear from these results that a limiting conversion was reached. Several series at lower temperatures and higher initial monomer concentrations failed to give a limiting conversion because of appreciable thermal polymerization.

Considerable effort has been spent elucidating the complexities of hydroperoxide-initiated polymerizations.[10–14] Each new study uncovers additional complicating features. Attempts to fit the data of Table I to several of the kinetic equations that have been proposed leads to the conclusion that at 126°C. the most important mode of *tert*-butyl hydroperoxide dissappearance is first-order.

TABLE I
Fractional Conversions of Styrene Polymerized with *tert*-Butyl Hydroperoxide (TBHP) in Benzene at 126°C. *in vacuo*

[Styrene], mole/l.	Time, sec. $\times 10^{-4}$	Fractional conversion			
		[TBHP] = 0 mole/l.	[TBHP] = 0.0025 mole/l.	[TBHP] = 0.0050 mole/l.	[TBHP] = 0.0100 mole/l.
0.5	1.80	0.0225			0.217
	3.96	0.0676			0.408
	10.08	0.127			0.572
	12.96	0.146			0.600
	14.76	0.194	0.501		0.580
	19.80	0.211			0.639
	22.68	0.234	0.486		0.600
	26.28	0.268	0.491		0.592
	26.64	0.270	0.506		0.620
	27.72	0.276			0.624
	x_∞		0.496 ± 0.008		0.614 ± 0.013
1.0	0.72	0.015		0.127	0.142
	1.44	0.028		0.266	0.315
	3.60	0.100		0.342	0.441
	5.76	0.130		0.391	
	6.84	0.150			0.506
	7.92	0.206		0.431	0.539
	9.36	0.283			0.524
	12.60	0.265		0.456	0.544
	14.76	0.313			0.527
	16.56	0.342	0.384	0.471	0.533
	18.36	0.356		0.472	
	21.24	0.369		0.472	0.522
	22.68	0.406	0.403		0.523
	24.48	0.437		0.468	
	26.28	0.441	0.411		
	26.64	0.416	0.408		
	35.28	0.483			
	42.84	0.695			
	x_∞		0.402 ± 0.008	0.456 ± 0.020	0.526 ± 0.010
2.0	14.76	0.569	0.200	0.261	0.323
	22.68	0.605	0.229	0.283	0.329
	26.28	0.647	0.187	0.256	0.301
	26.64	0.647	0.206	0.266	0.302
	x_∞		0.205 ± 0.012	0.266 ±0.008	0.314 ± 0.011

If eq. (3) is generalized to

$$-d[\mathrm{P}]/dt = k[\mathrm{P}]^a \tag{4}$$

it may be combined with eq. (2) and integrated:

$$\ln(-\ln[1 - x_\infty]) = b + [(3 - 2a)/2] \ln[\mathrm{P}_0] \tag{5}$$

where

$$x_\infty = ([M_0] - [M_\infty])/[M_0]$$

$$b = \ln [(K/k)(3 - 2a)/2]$$

Plots of $\ln (-\ln [1 - x_\infty])$ versus $\ln [P_0]$ give good straight lines from which a, the molecularity of peroxide disappearance, is calculated (Table II). Clearly despite the linearity of the plots neither a nor b is constant

TABLE II
Kinetic Constants

[Styrene], mole/l.	Eq. (5)		Eq. (11), $[P_0]^{1/2}/([M_0]^{1/2} - [M_\infty]^{1/2})$
	a	b	
2.0	1.15	0.666	0.39 ± 0.03
1.0	1.27	0.714	0.27 ± 0.04
0.5	1.37	1.03	0.30 ± 0.06

and eq. (4) is an inadequate description of the system. Altering eq. (2) to

$$-d[M]/dt = K[M][P]^{a/2} \tag{6}$$

combining with eq. (4) and integrating gives an equation similar to eq. (5). A plot of $\ln (-\ln [1 - x_\infty])$ vs. $\ln [P_0]$ is linear; the spread in values of a and b is greater than that reported in Table II.

It is also possible to examine the system in terms of the more complex equations proposed by Tobolsky and Matlack[12] and expanded by Walling and Heaton[13]

$$-d[P]/dt = k_1[P] + k_2[P][M] + k_3[P][M][S] = R_i \tag{7}$$

where [S] = solvent.

$$-d[M]/dt = K[M]R_i^{1/2} \tag{8}$$

$$d[M]/d[P] = K[M](k_1 + k_2[M] + k_3[M][S])^{-1/2}[P]^{-1/2} \tag{9}$$

Integration of eq. (9) gives

$$2(A^{1/2} - B^{1/2}) + k_1^{1/2} \ln \frac{(A^{1/2} - k_1^{1/2})(B^{1/2} + k_1^{1/2})}{(A^{1/2} + k_1^{1/2})(B^{1/2} - k_1^{1/2})} = 2K[P_0]^{1/2} \tag{10}$$

$$A = k_1 + (k_2 + k_3[S])[M_\infty]$$

$$B = k_1 + (k_2 + k_3[S])[M_0]$$

By obtaining values of $[M_\infty]$ over a wide range of conditions it is possible to verify relationships (7)–(10) and to evaluate k_1, k_2, and k_3. If k_1 is small,

$$(k_2 + k_3[S])^{1/2}/K \approx [P_0]^{1/2}/([M_0]^{1/2} - [M_\infty]^{1/2}) \tag{11}$$

Table II lists values of $[P_0]^{1/2}/([M_0]^{1/2} - [M_\infty]^{1/2})$ for the range of conditions studied. The reasonable constancy of the values speaks for the validity of eqs. (7)–(10) and indicates that solvent dependence in benzene is slight.

The experimental examination of these kinetic laws in terms of limiting monomer conversion is simpler than methods whereby initiator decomposition studies are required to parallel polymerization rate studies, for no rate measurements are required if limiting conversion is verified.

A serious difficulty in the *tert*-butyl hydroperoxide–styrene system is the appreciable amount of thermal polymerization which occurs at elevated temperatures. Despite the reproducibility of our thermal runs and their close correspondence with literature values,[15–18] there is no firm basis for assuming that thermal and initiated styrene polymerization in the case of *tert*-butyl hydroperoxide are independent. The case of simpler systems has been considered by Tobolsky.[19] Examination of *tert*-butyl hydroperoxide-initiated polymerization under limiting conversion conditions for methyl methacrylate, a monomer whose thermal polymerization rate is very low, is under way.

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Résumé

On présente les résultats pour la polymérisation du styrène en solution benzénique diluée à 126°C initiée initiée au moyen de l'hydroperoxyde de *tert*-butyle. Ces résultats sont discutés sur la base de la cinétique de conversion limite de Tobolsky. De nombreuses lois de vitesse sont considérées. Une décomposition unimoléculaire simple du peroxyde semble être sans importance dans ces conditions où l'interaction des solvants intervient.

Zusammenfassung

Ergebnisse bei der *t*-Butylhydroperoxyd-initiierten Polymerisation von Styrol in verdünnter Lösung in Benzol bei 126°C werden vorgelegt. Die Daten werden nach der von Tobolsky entwickelten Kinetik mit Umsatzgrenze behandelt. Verschiedene Geschwindigkeitsgesetze werden in Betracht gezogen. Einfache unimolekulare Zersetzung des Peroxyds und Lösungsmittelwechselwirkung scheinen unter diesen Bedingungen keine Bedeutung zu besitzen.

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Applications of Limiting Conversion Free-Radical Polymerizations. II. Azobisisobutyronitrile-Initiated Polymerization of Methyl Methacrylate in Benzene

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Synopsis

Data for the azobisisobutyronitrile-initiated polymerization of methyl methacrylate in dilute benzene solution is presented at 80, 100, and 126°C. in terms of Tobolsky's limiting conversion kinetics. Number-average molecular weights were obtained viscometrically. Attempts to evaluate the relative amounts of combination and disproportionation in the chain-terminating reaction were foiled by the discovery that under the conditions reported the initiator efficiency is temperature-dependent decreasing markedly with increasing temperature.

INTRODUCTION

As in Part I[1] it has been attempted to extend the general applicability of limiting conversion kinetics. By following azobisisobutyronitrile polymerizations of methyl methacrylate to limiting conversions, a simple method of determining the mode of chain termination may be studied. A marked lowering in initiator efficiency is noted with rising temperature. Polymerizations were performed in benzene solution, as in Part I,[1] to avoid the difficulties of diffusion-controlled termination. Methyl methacrylate conversions were measured by gas chromatography.

EXPERIMENTAL

Chemicals

Methyl methacrylate, pure grade, (Matheson Co.) was fractionally distilled at reduced pressure prior to use. Thiophene-free benzene (Fisher Chemicals) was used as a solvent in polymerization studies and in molecular weight determinations. Azobisisobutyronitrile, m. p. 104°C. (Eastman Organic Chemicals), was purified by recrystallization from diethyl ether.

Methyl Methacrylate Polymerization

Measured amounts of methyl methacrylate, thiophene-free benzene, and azobisisobutyronitrile were degassed, evacuated, sealed in new Carius

TABLE I
Limiting Conversion Data for Azobisisobutyronitrile-Initiated Polymerizations of Methyl Methacrylate in Benzene

Temperature, °C.	[Methyl methacrylate]$_0$, mole/l.	[Azobisisobutyronitrile]$_0$, mole/l.	x_∞	$[\eta]$	$\bar{P}_n$	α
80	2.66	0.0045	0.817	0.283	612	1.54
	2.13	0.0091	0.917	0.148	304	1.54
	2.13	0.0018	0.723	0.448	1062	1.51
	2.13	0.00091	0.552	0.711	1789	1.67
	1.59	0.0018	0.677	0.392	912	1.85
	1.59	0.00091	0.632	0.627	1550	1.68
100	3.16	0.0045	0.207	0.358	824	5.12
	3.16	0.0018	0.123	0.464	1105	4.61
	2.80	0.00090	0.342	0.315	714	5.35
	2.62	0.0045	0.185	0.335	765	6.37
	2.10	0.0090	0.411	0.262	579	5.42
	2.10	0.0045	0.273	0.320	726	5.13
	2.10	0.0018	0.135	0.380	881	5.08
	1.57	0.0045	0.337	0.548	1332	4.83
	1.57	0.0018	0.253	0.396	923	3.75
	1.57	0.00090	0.166	0.283	632	4.13
126	3.06	0.0044	0.170	0.341	780	7.87
	2.54	0.00087	0.029	0.333	760	10.8
	2.04	0.0087	0.183	0.168	350	9.83
	1.53	0.0087	0.557	0.251	552	6.79
	1.53	0.0044	0.515	0.442	1062	7.07
	1.53	0.0017	0.370	0.666	1662	6.16

tubes, and thermostated at 80, 100, and 126 ± 0.1°C. Tubes were removed after 16 hr. at 80°C., 900 sec. at 100°C., and 515 sec. at 126°C. Data obtained at 100°C. correspond to ~2 half lives of azobisisobutyronitrile.[2] Data of Table I take this into account. The remaining monomer was analyzed by gas chromatography on a Perkin-Elmer Model 154D instrument equipped with a disk integrator. A Perkin-Elmer A column containing diisodecyl phthalate on Celite at 75°C. helium gas flow 20 psi, gave convenient retention times for benzene (5.9 min.) and methyl methacrylate (8.3 min.). Poly(methyl methacrylate), azobisisobutyronitrile, or its decomposition products did not interfere with the analysis. Volume contraction from polymerization was considered negligible. Volumes were assumed to be additive. Molarities were corrected from literature values of density.[3,4] Thermal polymerization was found to be erratic but usually close to zero under conditions described. Data of Table I assume negligible thermal polymerization.

Molecular Weight Determinations

Polymerized methyl methacrylate samples were poured into methanol, and polymer was collected on a sintered glass filter and dried at 50–80°C.

in a vacuum oven overnight. Intrinsic viscosity measurements were made in modified Ubbelohde dilution viscometers (Ace Glass Inc.) at 20 ± 0.01°C. with thiophene-free benzene as diluent. Flow times for benzene were >100 sec. Number-average molecular weights were calculated from the relationship of Tobolsky and Baysal.[5]

$$\log P_n = 3.420 + 1.13 \log [\eta]$$

Although the molecular weight relationship was not verified by measuring osmotic molecular weights, it is believed that the number-average molecular weight distributions were not unusually broad because initial monomer concentrations were low.

RESULTS AND DISCUSSION

One of the problems in methyl methacrylate polymerization which has received considerable attention is the chain-termination reaction.[6] It is generally agreed that both combination and disproportionation occur in the termination step and that more disproportionation occurs at elevated temperatures owing to a higher activation energy for that process. Most attempts to elucidate this problem quantitatively have utilized radioactive tracer methods to count polymer chain ends.[6-10] By using radioactive initiators and obtaining number-average molecular weights of polymers produced from them it is possible to calculate the number of initiator fragments per polymer chain.

The use of limiting conversion conditions for the solution of this problem seems particularly appropriate since the method for counting initiator fragments is quite direct. Let us define

$$\alpha = \frac{\text{No. of initiator fragments in polymer}}{\text{No. of polymer chains}} = \frac{(f)\ (\beta)\ (\text{No. of initiator molecules})}{\text{No. of polymer chains}} \tag{1}$$

where f initiator efficiency and β is maximum possible of initiator fragments from each initiator molecule.

The limiting cases of exclusive disproportionation and exclusive combination correspond to values of 1 and 2 for α. The relative probability of combination to disproportionation is related to α by[6]

$$k_{tc}/k_{td} = 2(\alpha - 1)/(2 - \alpha) \tag{2}$$

Since the initiator molecules are completely consumed, the number of initiator molecules in the polymer produced is simply the fraction of initiator fragments that actually initiate polymerization. Under a fairly broad range of conditions, the number of fragments β and the efficiency f for

azobisisobutyronitrile have been established[6,7,11] (2 and 0.6, respectively). The number of polymer chains can be obtained from the relationship

$$\text{No. of polymer chains} = \frac{\text{No. of monomer units polymerized}}{\text{No. of monomer units/polymer chain}} \qquad (3)$$

The numerator is obtained by measuring remaining monomer and the denominator is essentially the number-average molecular weight.

Table I shows results obtained in dilute benzene solution at 80, 100, and 126°C. Data were obtained after more than 10 half-lives of azobisisobutyronitrile based on the temperature dependence of Van Hook and Tobolsky[12] for azobisisobutyronitrile decomposition.

At 80°C. the values of α correspond to about three times as much combination as disproportionation. [It may be noted from eq. (2) that k_{tc}/k_{td} is extremely sensitive to small variations in α for values of $\alpha > 1.3$; an error in α of $\sim 6\%$ when $\alpha \sim 1.6$ corresponds to an error in k_{tc}/k_{td} of $\sim 40\%$.] Literature values[6,8-10] show great variation among different workers arising from different methods of molecular weight determination. The literature values of α (none of which depend on a knowledge of the initiator efficiency) all imply lower values than here measured. The values of α at 100 and 126°C. fall outside the maximum permissible values of eq. (2). Extrapolation of the literature values to 100 or 126°C. indicate that at these temperatures only a vanishingly small amount of chain termination by coupling would take place. Hence real values of α should approach unity as the temperature increases.

Two possible explanations for high values of α are a temperature dependence of efficiency and depolymerization.

The first of these possibilities requires that azobisisobutyronitrile efficiency is reduced by at least five- to tenfold in going from 60 to 126°C. The mechanistic implication of this requirement in terms of the solvent cage picture of inefficiency[3-5] is that the

$$\text{caged } [2(CH_3)_2\dot{C}CN] \begin{cases} \xrightarrow{k_1} 2(CH_3)_2\dot{C}CN \\ \xrightarrow{k_2} (CH_3)_2CCNCCN(CH_3)_2 \\ \xrightarrow{k_3} CH_2{=}C(CH_3)CN + (CH_3)_2CHCN \end{cases}$$

activation energy for $(k_2 + k_3)$ is greater than for k_1, escape from the cage, a completely reasonable possibility in light of the best estimates of an activation energy of ~ 5 kcal./mole for the disproportionation of the polymeric radical of methyl methacrylate.[3,4]

The possibility of depolymerization was investigated by allowing poly(methyl methacrylate) to react in benzene alone, with azobisisobutyronitrile, and with decomposed benzene solutions of azobisisobutyronitrile at 126°C. Reaction tubes were examined for the presence of methyl methacrylate monomer and for reduction in polymer molecular weight. Neither depolymerization nor chain rupture was found to be significant during the reaction times investigated. It is therefore concluded that the efficiency of

azobisisobutyronitrile in benzene solutions of methyl methacrylate is temperature-dependent and is apparently lower than 0.6 at 80°C. A systematic error which may have been introduced into the results of Table I by a molecular weight–intrinsic viscosity relationship that did not account for possibly broader molecular weight ranges than were used to obtain the relationship does not alter the conclusion. The relationship between the number-average molecular weights and the weight-average molecular weights[11] of the polymers produced will be investigated.

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Résumé

La polymérisation du polyméthacrylate de méthyle en solution benzénique diluée est présentée à 80, 100 et 126°C sur la base des cinétiques de conversion limite de Tobolsky; ces polymérisations ont été initiées au moyen d'asobisisobutyronitrile. Les poids moléculaires moyens en nombre ont été obtenus viscosimétriquement. Des essais pour évaluer l'importance relative de la réaction de terminaison par combinaison disproportionnée ont été sans succès parce qu'on a découvert que dans les conditions rapportées l'efficacité de l'initiateur dépend de la température, décroissant remarquablement avec une température croissante.

Zusammenfassung

Ergebnisse bei der Azobisisobutyronitril-initiierten Polymerisation von Methylmethacrylat in verdünnter Lösung in Benzol bei 80, 100 und 126°C werden nach der von Tobolsky angegebenen Kinetik für begrenzten Umsatz ausgewertet. Die Zahlenmittelmolekulargewichte wurden viskosimetrisch erhalten. Versuche, den relativen Beitrag von Kombination und Disproportionierung zum Kettenabbruch zu ermitteln, scheiterten, da gefunden wurde, dass unter den angewendeten Bedingungen die Initiatorausbeute temperaturabhängig ist; sie nimmt mit steigender Temperatur deutlich ab.

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Polybenzimidazoles. VI. Polybenzimidazoles Containing Aryl Sulfone Linkages*

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Synopsis

Four new polybenzimidazoles with aryl sulfone linkages between the recurring units have been prepared in order to study their thermal stability and solubility properties. The polymers prepared were high molecular weight materials with good thermal stability.

Introduction

In previous publications[2–4] it has been shown that polymers containing benzimidazole nuclei could be prepared by melt condensation of suitable tetramines and the phenyl esters of aromatic dicarboxylic acids. Introduction of oxygen between the benzimidazole units has been shown[5] to increase the solubility of the polymer over that of polybenzimidazoles containing no such linkages, but without loss in thermal stability. More recently,[6] a polymer with a diphenyl sulfone link in the main chain has been prepared and was found to lose 19% of its weight in air when heated 500°C., but with limited solubility in solvents like dimethylacetamide, formic acid, and sulfuric acid. It has also been reported[7] that sulfide or sulfone groups between the aromatic and quinoxaline segments enhanced the solubility of polyquinoxalines without any sacrifice in thermal stability.

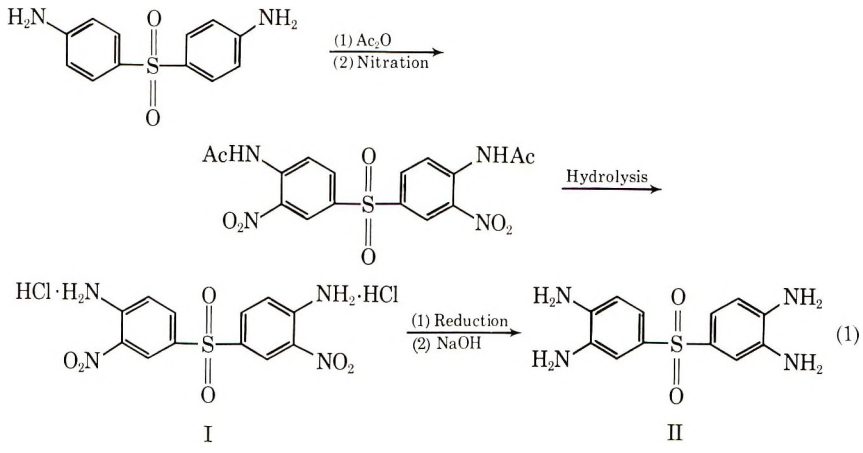
This paper describes some new polybenzimidazoles containing aryl sulfone linkages which were prepared to study their properties.

Synthesis of Monomers

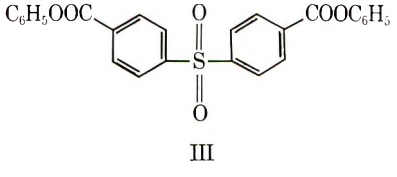
3,3′4,4′-Tetraminodiphenyl sulfone (II) was prepared as shown, starting with 4,4′-diaminodiphenyl sulfone following a known procedure.[7] Some modifications have been made in the preparation of 3,3′-dinitro-4,4′-diaminodiphenyl sulfone hydrochloride (I) and 3,3′,4,4′-tetraminodiphenyl sulfone (II). These are given in some detail in the experimental section.

* For Part V in this series, see Mitsuhashi and Marvel.[1]

† Postdoctoral Research Associate supported by the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, 1965–66.



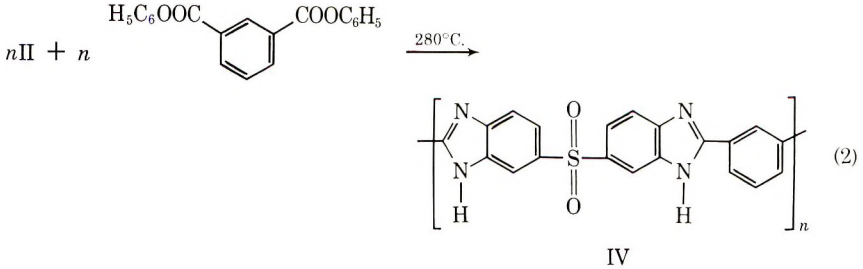
The synthesis of diphenyl 4,4′-sulfonyldibenzoate (II) was carried out starting with *p*-tolyl sulfoxide.



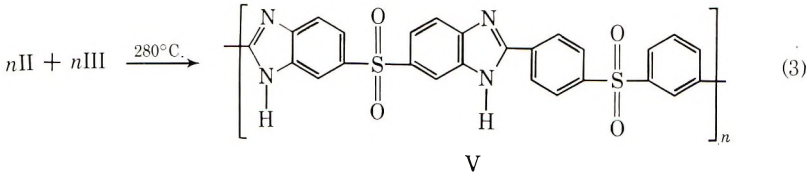
III

Polymerization

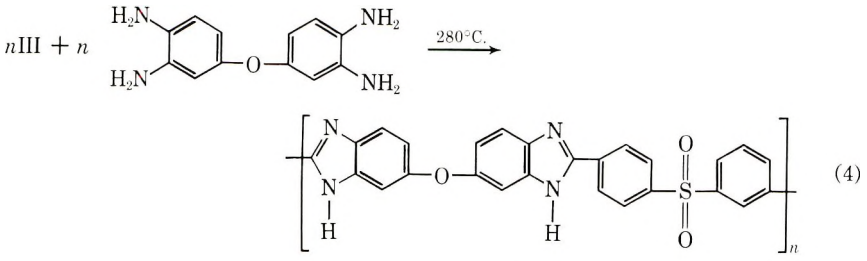
Poly[2,2′-(1,3-phenylene) sulfonyldiphenylene-5,5′-bibenzimidazole] (IV), poly[2,2′-(4,4′-sulfonyldiphenylene) sulfonyl-5,5′-bibenzimidazole] (V), poly[2,2′-sulfonyldiphenylene) oxy-5,5′-bibenzimidazole] (VI) and poly[2,6-(4,4′-sulfonyldiphenylene) diimidazobenzene] (VII) were prepared by the reactions shown in eqs. (2)–(5).



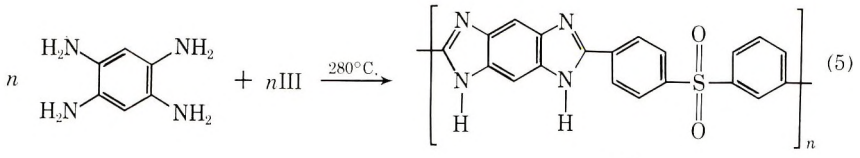
IV



V



VI



VII

Polymers IV, V, and VI were 100% soluble in dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMP) and formic acid. Thermal gravimetric analyses of polymers IV, V, and VI were performed by heating in nitrogen with the temperature increase of 150°C. each 1 hr. Polymer IV lost quickly 10% of its weight below 440°C. and then gradually lost about 40% of its weight up to 900°C. Polymer V lost about 4% of its weight below 450°C. and then quickly lost about 40% of its weight up to 700°C. Polymer VI lost about 12.5% of its weight below 450°C. and then about 45% of its weight up to 700°C. Unlike polymers IV, V, and VI, polybenzimidazole VII had limited solubility in DMAC, DMSO and HMP. The poor carbon analyses of polymers IV, V, VI, and VII may be ascribed to difficulties encountered in burning them.

Experimental

4,4′-Diacetamidodiphenyl Sulfone. This compound was prepared according to Stille and Arnold[7] by acetylation of 4,4′-diaminodiphenyl sulfone followed by nitration, m.p. 245–247°C. (lit.:[7] 247–248°C.).

3,3′-Dinitro-4,4′-diaminodiphenyl Sulfone Hydrochloride (I). To a warm solution containing 44 g. (0.104 mole) of 3,3′-dinitro-4,4′-diacetamidodiphenyl sulfone in 250 ml. of absolute ethanol was added dropwise 150 ml. of concentrated hydrochloric acid. The mixture was refluxed for 4 hr. and allowed to cool to room temperature. The light orange precipitate was collected by filtration, washed with a small amount of water and dried at 40°C. under reduced pressure. The yield was 25.0 g. (60.9%), m.p. 286°C. (dec.) (lit.:[7] 307–308°C.).

3,3′,4,4′-Tetraminodiphenyl Sulfone (II). To a stirred solution of 150 g. of stannous chloride dihydrate in 500 ml. of concentrated hydrochloric acid was added 20.0 g. (0.048 mole) of 3,3′-dinitro-4,4′-diaminodiphenyl sulfone hydrochloride in small portions. After the addition was complete the reaction mixture was heated to the reflux temperature under a nitrogen

atmosphere for 2 hr., and the solution became homogeneous. On cooling to room temperature 23.0 g. (94%) of 3,3′,4,4′-tetraminodiphenyl sulfone hydrochloride precipitate. The tetrahydrochloride was dried at 40°C. in a vacuum oven for 4 hr. A 10-g. portion of the hydrochloride was dissolved in 100 ml. of water, filtered, and the water solution added dropwise to a vigorously stirred solution of 50 g. of sodium hydroxide in 250 ml. of water cooled in an ice bath. The white precipitate (3.3 g., 56%) was collected, washed with water, then a small amount of methanol and dried in a vacuum oven overnight. The tetramine was recrystallized from obsolute ethanol in an atmosphere of nitrogen, m.p. 175°C. (lit.:[7] 174–174.5°C.).

ANAL. Calcd. for $C_{12}H_{14}N_4O_2S$: C, 51.80%; H, 5.04%; N, 19.40%. Found: C, 51.67%; H, 5.30%; N, 19.54%.

***p*-Tolyl Sulfone.** This compound was prepared by the oxidation of *p*-tolyl sulfoxide with hydrogen peroxide in acetic acid, m.p. 160°C. (lit.:[8] 159°C.).

4,4′-Sulfonyldibenzoic Acid. A modified procedure of Adámek and Novák was followed. *p*-Tolyl sulfone was oxidized with excess potassium permanganate in pyridine–water mixture. The authors have reported a yield of 27%. The yield in this preparation was 92%, m.p. 372–373°C. (lit.:[9] 355–360°C.; lit.:[10] 370–371°C.).

4,4′-Sulfonyldibenzoyl Chloride. The diacid chloride was prepared according to the method described by Stephens.[11]

Diphenyl 4,4′-Sulfonyldibenzoate (III). A 3-g. portion (0.0087 mole) of 4,4′-sulfonyldibenzoyl chloride was heated on a steam bath with 5 g. (0.0426 mole) of phenol for 4 hr. The solution became homogeneous after a few minutes and solidified. After cooling to room temperature, 200 ml. of methanol was added, the solid was filtered, washed with methanol, and dried. It was recrystallized from acetic acid to yield 2.7 g. (60.6%) of the diester, m.p. 223–224°C. (lit.:[6] 222–223°C.).

ANAL. Calcd. for $C_{26}H_{18}O_6S$: C, 68.13%; H, 3.93%; S, 6.99%. Found: C, 67.50%; H, 4.06%; S, 6.98%.

Poly[2,2′-(1,3-phenylene)sulfonyl-5,5′-bibenzimidazole] (IV). A mixture of 0.5184 g. (0.0019 mole) of 3,3′,4,4′-tetraaminodiphenyl sulfone and 0.5929 g. (0.0018 mole) of diphenyl isophthalate were placed in a 50-ml. round-bottomed flask. The flask was heated in a nitrogen atmosphere at 280°C. A dark brown melt first formed solidified after 30 min., during which time phenol and water had been distilling. After 1/2 hr., vacuum was applied for 1 hr. The material was then powdered and reheated to 400°C. employing high vacuum for 5 hr. The polymer was purified by dissolving it in DMSO and precipitating in benzene. The yield of nearly black polymer was 0.4314 g. (59.9%) (η_{inh} = 0.14 in DMSO at 30°C., 0.24% solution; η_{inh} = 0.38 in formic acid at 30°C., 0.13% solution). The polymer was 100% soluble in DMSO and DMAC at room temperature.

ANAL. Calcd. for $(C_{20}H_{12}N_4SO_2)_n$: C, 64.52%; H, 3.23%; N, 15.05%; S, 8.60%. Found: C, 66.36%; H, 3.63%; N, 14.36%; S, 8.10%.

Poly[2,2′-(4,4′-sulfonyldiphenyl) sulfonyl-5,5′-bibenzimidazole] (V). A mixture of 0.4765 g. (0.0017 mole) of 3,3′,4,4′-tetraaminodiphenylsulfone and 0.7862 g. (0.0017 mole) of diphenyl 4,4′-sulfonyldibenzoate was placed in a 50 ml. flask which was then evacuated and filled with nitrogen repeatedly. The mixture was then heated at 280°C. for $^1/_2$ hr. The material was then powdered and reheated at 400°C. in a Morton flask employing high vacuum for 5 hr. The polymer was purified by dissolving it in DMAC and precipitating in benzene. The yield of the purified polymer was 0.30 g. (34.2%). η_{inh} = 0.99 in formic acid (0.26% solution) at 30°C. The polymer was soluble in DMSO, DMAC, HMP, and formic acid.

ANAL. Calcd. for $(C_{26}H_{16}N_4S_2O_4)_n$: C, 60.94%; H, 3.13%; N, 10.93%; S, 12.50%. Found: C, 58.56%; H, 3.88%; N, 10.06%; S, 12.00%.

Poly[2,2′-(4,4′-sulfonyldiphenylene)oxy-5,5′-bibenzimidazole] (VI). A mixture of 2.00 g. (0.0087 mole) of 3,3′,4,4′-tetraaminodiphenyl ether and 3.9130 g. (0.0086 mole) of diphenyl 4,4′-sulfonyldibenzoate was placed in a 100 ml. flask which was then evacuated and filled with nitrogen repeatedly. The mixture was then heated at 280°C. for $^1/_2$ hr. Water and phenol were liberated during this period. The system was slowly evacuated to 0.1 mm. and heated at 280°C. for another $^1/_2$ hr. The brown solid formed was powdered and reheated in a Morton flask at 400°C. for 5 hr. The polymer was purified by dissolving it in DMAC and precipitating in benzene. The yield of the purified polymer was 1.3 g. (33%); η_{inh} = 0.2078 in DMSO (0.24% solution) at 30°C. The polymer was soluble in DMSO, DMAC, HMP, and formic acid.

ANAL. Calcd. for $(C_{26}H_{16}SO_3N_4)_n$: C, 67.25%; H, 3.45%; N, 12.07%; S, 6.89%. Found: C, 63.41%; H, 4.30%; N, 11.18%; S, 6.36%.

Poly[2,6-(4,4′-sulfonyldiphenylene)diimidazobenzene] (VII). A mixture of 1.000 g. (0.0072 mole) of 1,2,4,5-tetraaminobenzene and 3.3188 g. (0.0072 mole) of diphenyl 4,4′-sulfonyldibenzoate was polymerized and worked out as indicated in the procedure for the preparation of VI. The polymer was purified by dissolving it in DMAC and precipitating in benzene; η_{inh} = 0.17 in formic acid (0.24% solution) at 30°C. The yield of the purified polymer was 1.15 g. (44%).

ANAL. Calcd. for $(C_{20}H_{12}N_4SO_2)_n$: C, 64.52%; H, 3.23%; N, 15.05%; S, 8.60%. Found: C, 59.73%; H, 3.86%; N, 13.33%; S, 7.68%.

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Résumé

Quatre nouveaux polybenzylimidazoles avec des liens aryles sulfoniques entre des unités périodiques ont été préparés en vue d'étudier la stabilité thermique et leurs propriétés de solubilité. Les polymères préparés sont de poids moléculaire très élevés avec une bonne stabilité thermique.

Zusammenfassung

Vier neue Polybenzimidazole mit Arylsulfonbindungen zwischen den Kettenbausteinen wurden zur Untersuchung ihrer thermischen Stabilität und Lösungseigenschaften dargestellt. Die dargestellten Polymeren waren hochmolekulare Stoffe mit guter thermischer Stabilität.

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Homopolymerization of Ethylene and Copolymerization with 1-Butene in the Presence of Bis(cyclopentadienyl)titanium Dichloride and Diisobutylaluminum Chloride

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Synopsis

Ethylene was homopolymerized and copolymerized with 1-butene in benzene at 30°C. with the use of bis(cyclopentadienyl)titanium dichloride and diisobutylaluminum chloride as catalyst. Both freshly prepared catalyst and catalyst which had been aged up to 114 hr. were used. When the catalyst was aged prior to adding the monomer, the yields were lower and the products had higher molecular weights. In the case of copolymers, aging of the catalyst also affected the relative concentrations of the comonomers in the products. 1-Butene was an effective chain transfer agent under all reaction conditions. The data were found to be consistent with the previously suggested mechanism according to which different species initiate polymerizations with freshly mixed and aged catalysts.

INTRODUCTION

Ethylene polymerizations with soluble initiators consisting of bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) and aluminum alkyls have been studied extensively over a number of years.[1–10] It was shown recently that those initiators may also be used to polymerize deuteroethylene;[11] attempts to homopolymerize higher α-olefins have, so far, been unsuccessful.[8,12] A previous report from our laboratory described the copolymerization of ethylene and 1-butene catalyzed by mixtures of Cp_2TiCl_2 and diethylaluminum chloride,[12] either *in situ* prepared or aged. In all cases the copolymers contained less than 10 wt.-% of butene. The reaction rates and the composition and molecular weights of the products were found to depend upon the method of catalyst preparation. Copolymers made with aged catalysts had higher molecular weights than similar materials prepared with fresh catalyst; they also contained less comonomer. The reaction rates decreased with catalyst aging. These observations could be explained satisfactorily by postulating that the copolymerizations could be initiated by at least two types of active species. A tentative polymerization mechanism based on the concept of two active initiators was suggested.

This work has now been extended to ethylene homopolymerizations and ethylene–1-butene copolymerizations initiated by Cp_2TiCl_2 and diisobutyl-

aluminum chloride. Two problems are considered: (*1*) the applicability of the postulated reaction scheme to alkylaluminum derivatives other than diethylaluminum chloride, and (*2*) a determination of the effect of prolonged initiator aging on ethylene homopolymerizations.

EXPERIMENTAL PROCEDURE

The experimental procedures involved in preparing and isolating the products were identical to those described previously.[12] All the starting materials were scrupulously dried and purified in the previously described manner, and the polymerization tubes were filled on the specially designed high vacuum equipment. The polymerizations were run in 40 cc. benzene at 30°C.; the concentration of Cp_2TiCl_2 was 1.60×10^{-6} mole/g. of benzene and that of $Al(i\text{-}C_4H_9)_2Cl$ either 3.50×10^{-5} or 1.75×10^{-5} mole/g. of benzene. The amount of ethylene was always 0.94 g., while that of 1-butene ranged from zero to 0.92 g. 1-Butene alone did not polymerize. To age the catalysts, they were stored with occasional shaking at 30°C. for either 0.42, 19, or 114 hr.

Ostwald-Fenske viscometers were used for viscosity measurements in decalin at 130°C.; the solutions were inhibited with 0.1% of 2,6-di-*tert*-butyl-4-methylphenol. No kinetic energy corrections were deemed necessary, since the efflux time of the solvent exceeded 150 sec. Intrinsic viscosities $[\eta]$ were obtained from extrapolations to zero concentration of four viscosity measurements at concentrations ranging between 0.01 and 0.5 g./dl. The viscosity data on the high molecular weight samples ($[\eta] > 5$–6) were rather scattered, and the $[\eta]$ values for these polymers are believed, therefore, to be considerably less reliable than those for the lower molecular weight materials. No definite reason for this behavior can be offered at present; insolubility of the polymers may have been a contributing factor.

Since all of the copolymers were synthesized with 1-butene-1-^{14}C their composition was determined by combusting the samples, collecting the CO_2 in an organic base, and analyzing the resulting solutions using standard scintillation counter techniques. Two 1-butene batches were used in these runs; their specific activities were, respectively, 1.88×10^{-4} and 0.558×10^{-4} mc./mg.

RESULTS AND DISCUSSION

Polymerization

Figures 1 and 2 and Table I show the effect of initiator aging and starting mixture composition on the homopolymer and copolymer yields. The data in all of the figures shown were obtained at an Al:Ti ratio of 21.8:1, 0.94 g. ethylene and, in the case of copolymerizations, 0.92 g. 1-butene being used. As may be seen, the rates of both homopolymerizations and copolymerizations decreased gradually with increasing catalyst aging times. With the *in situ* mixed catalyst, essentially all the ethylene was poly-

TABLE I

Effect of Starting Composition on Copolymerization Behavior; Catalyst Aged 19 Hr.

Wt. ethylene, g.	Wt. 1-butene, g.	$Cp_2TiCl_2 \times 10^6$, mole/g. benzene	$Al(i\text{-}C_4H_9)_2Cl \times 10^5$, mole/g. benzene	Polymerization time, min.	Yield, g.	1-Butene in polymer, wt.-%	$[\eta]$, dl./g.
0.94	0.62	1.60	3.50	5.5	0.09	3.7	—
0.94	0.62	1.60	3.50	7.5	0.18	3.0	—
0.94	0.62	1.60	3.50	12.5	0.30	3.1	—
0.94	0.62	1.60	3.50	18.0	0.36	3.5	3.6
0.94	0.62	1.60	3.50	26.5	0.46	2.3	3.1
0.94	0.62	1.60	3.50	60.0	0.65	3.5	3.2
0.94	0.92	1.60	3.50	3.0	0.03	7.4	—
0.94	0.92	1.60	3.50	6.0	0.06	3.9	—
0.94	0.92	1.60	3.50	9.0	0.27	3.9	—
0.94	0.92	1.60	3.50	14.0	0.43	3.8	2.1
0.94	0.92	1.60	3.50	22.0	0.56	3.6	1.8
0.94	0.92	1.60	3.50	29.0	0.68	4.2	1.9
0.94	0.92	1.60	1.75	3.0	0.04	6.9	—
0.94	0.92	1.60	1.75	6.0	0.10	3.9	—
0.94	0.92	1.60	1.75	9.0	0.21	4.0	3.1
0.94	0.92	1.60	1.75	14.0	0.32	3.5	3.0
0.94	0.92	1.60	1.75	22.0	0.47	3.5	2.5
0.94	0.92	1.60	1.75	29.0	0.55	3.8	2.2

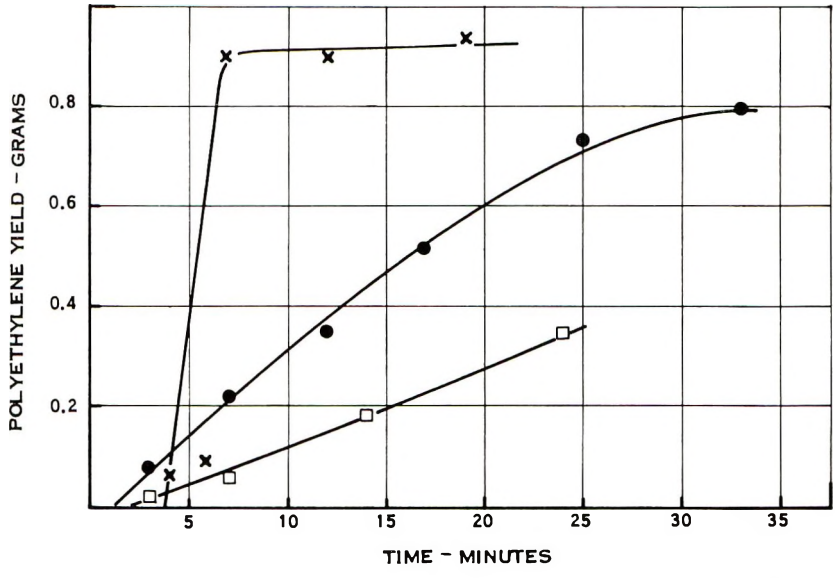

Fig. 1. Effect of catalyst aging on ethylene homopolymerization: (×) catalyst mixed *in situ;* (●) catalyst aged 19 hr.; (□) catalyst aged 114 hr.

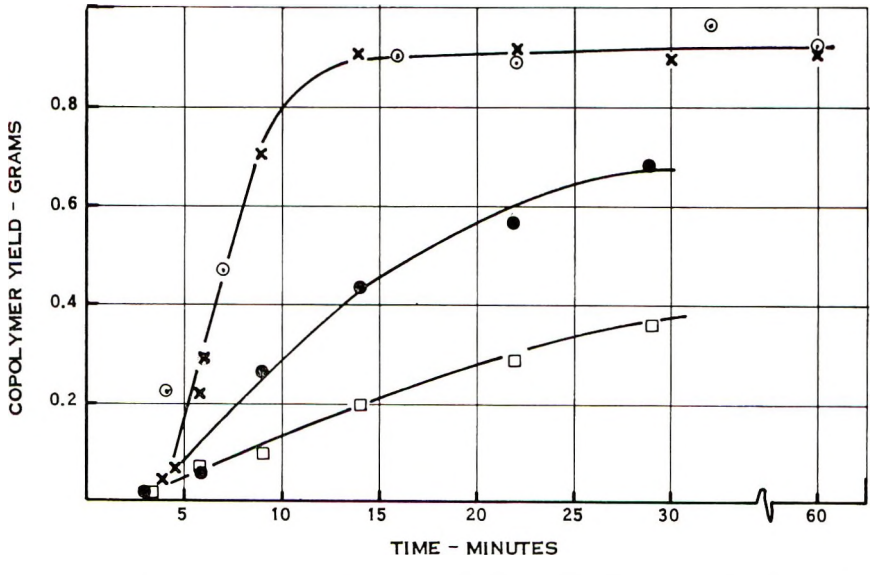

Fig. 2. Effect of catalyst aging on copolymerization: (×) catalyst mixed *in situ;* (⊙) catalyst aged 0.42 hr.; (●) catalyst aged 19 hr.; (□) catalyst aged 114 hr.

merized in about 10–15 min.; when initiator aged for either 19 or 114 hr. was used, only about 20–50% of the ethylene was polymerized after 15 min. The presence of 1-butene in the reaction mixture seemed to have only a minor effect on the overall rate of polymer formation (Figs. 1 and 2). With both freshly mixed and aged catalysts the initial copolymerization

rates were either equal to or only slightly lower than the rates of homopolymer formation. At longer reaction times when aged catalyst was used, the rates of copolymer formation decreased more rapidly than the homopolymerization rates.

The copolymerization runs followed the trend established previously for similar reactions initiated by Cp_2TiCl_2 and $Al(C_2H_5)_2Cl$;[12] no homopolymerizations had been carried out with the aged Cp_2TiCl_2–$Al(C_2H_5)_2Cl$ system, and, therefore, no comparison can be made.

In an attempt to assess the influence of the initiator on the reaction, the concentration of the aluminum-containing cocatalyst was reduced by half in one of the copolymerization series carried out with catalyst aged for 19 hr. The yields in these runs were slightly lower than those realized when the Al:Ti ratio was 21.8:1.

Generally, polymerizations initiated by Ziegler-Natta type catalysts proceed fastest at lower Al:Ti ratios than those employed in this work. It was expected, therefore, that a reduction in the Al:Ti ratio would result in an increase in the polymerization rate and not a decrease. It is conceivable, however, that, since the reactions described in this paper were carried out with extremely low catalyst concentrations, the rates might have been affected adversely by side reactions of the catalyst components. Such side reactions involving $Al(i\text{-}C_4H_9)_2Cl$ could reduce the amount of this component available for interaction with Cp_2TiCl_2 below that necessary for optimum polymer yields. This would result in a decreased number of active species capable of initiating the polymerization. The presence of a smaller number of initiating species should affect the molecular weights but not the compositions. Table I shows that this is indeed what has been found.

Copolymer Composition

The effect of catalyst aging on copolymer composition is shown in Figure 3. The results with freshly mixed catalyst and catalyst which had been aged for 25 min. are similar to those reported previously for Cp_2TiCl_2 and $Al(C_2H_5)_2Cl$. In all cases the percentage of 1-butene incorporation increased gradually with conversion to a limiting value of about 7.0–7.5 wt.-%. With Cp_2TiCl_2–$Al(i\text{-}C_4H_9)_2Cl$ mixtures aged for either 19 or 114 hr., the concentration of the comonomer in the products decreased rapidly with time in the initial stages of the copolymerization. Thus, after 3 min. the products contained 7–9% of butene, and after 7 min. only about 3–4%. As the reaction times were lengthened, the copolymer composition became essentially independent of time. Similar results were obtained whether the Al:Ti ratio was 21.8:1 or 11.9:1 (Table I). It would have obviously been of interest to determine the copolymer composition at extremely short reaction times; however, the low rates with aged catalysts made this unfeasible with the use of the specially designed small scale equipment in which these polymerizations were carried out. In contrast to these results with $Al(i\text{-}C_4H_9)_2Cl$, when $Al(C_2H_5)_2Cl$ was used under similar

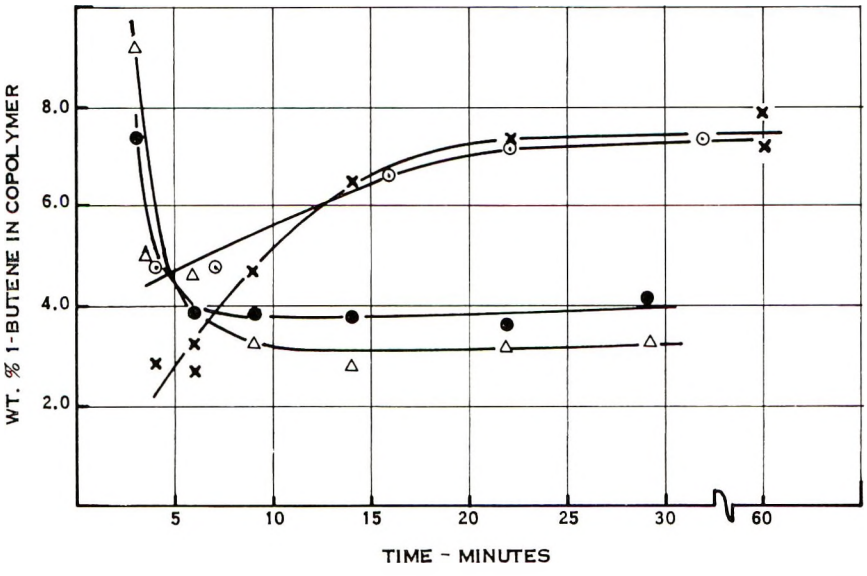

Fig. 3. Change of copolymer composition with time: (×) catalyst mixed *in situ;* (⊙) catalyst aged 0.42 hr.; (●) catalyst aged 19 hr.; (△) catalyst aged 114 hr.

conditions, the product composition was essentially constant throughout the duration of the reaction.

Intrinsic Viscosities

The intrinsic viscosities of the homopolymers and copolymers obtained in this work were investigated as a function of catalyst aging times and polymer yields. The data are summarized in Figure 4 and Table I. The molecular weights of the products prepared with aged catalysts were always considerably higher than those of similar materials made with *in situ* mixed catalysts. Thus, for instance, when the initiator was aged for 19 and 114 hr., the $[\eta]$ values for the copolymers ranged from 1.8 to 2.1 and 2.7 to 2.9 dl./g., respectively, while freshly prepared initiator solutions yielded copolymers having $[\eta]$ values of only 0.5–0.7 dl./g. In the case of homopolymers, the molecular weights likewise increased upon catalyst aging; aging for 19 hr., however, resulted in materials with higher $[\eta]$ values than aging for 114 hr. Why this should have occurred is not clear.

The intrinsic viscosities of both types of materials were either independent of polymerization time or decreased as the reaction time was lengthened. Since at any given catalyst aging time the copolymers were found to have considerably lower molecular weights than the polyethylene, it is apparent that 1-butene acts as an efficient chain transfer agent. The relatively high intrinsic viscosity values of some of the copolymers provide ample evidence that not all of the 1-butene units constitute chain ends, but that some of them are incorporated within the chains. If, for instance, a copolymer containing 4 wt.-% 1-butene were to incorporate but one

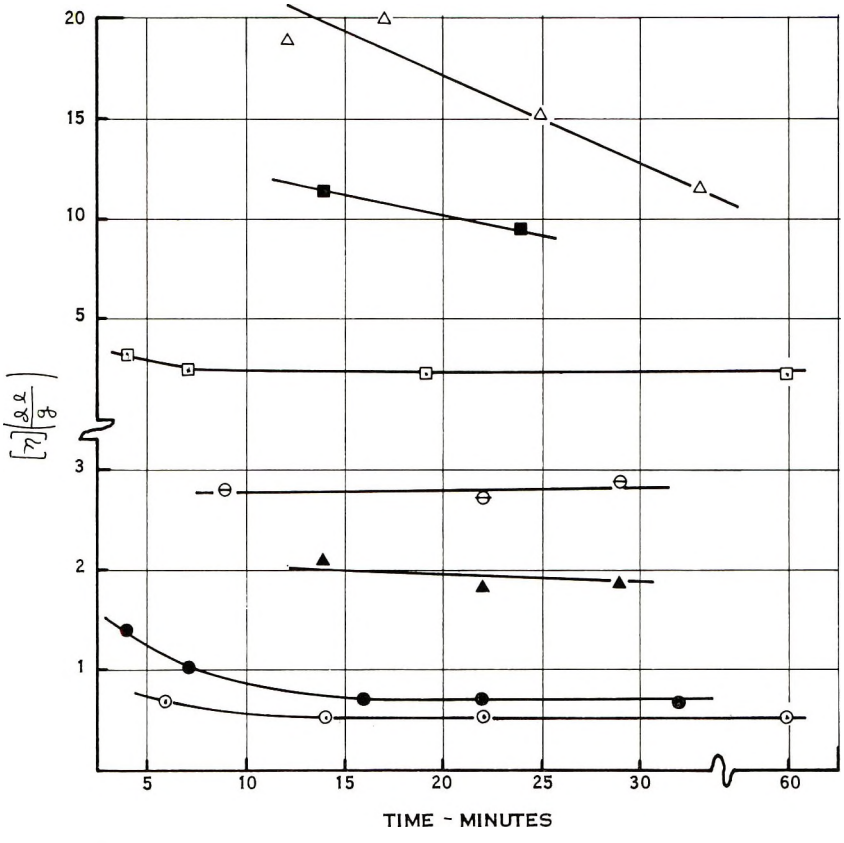

Fig. 4. Molecular weight dependence of homopolymers and copolymers on polymerization conditions: (⊡) homopolymer, catalyst mixed *in situ;* (△) homopolymer, catalyst aged 19 hr.; (■) homopolymer, catalyst aged 114 hr.; (⊙) copolymer, catalyst mixed *in situ;* (●) copolymer, catalyst aged 0.42 hr.; (▲) copolymer, catalyst aged 19 hr.; (⊖) copolymer, catalyst aged 114 hr.

comonomer unit per chain, its number-average molecular weight would be below 1.5×10^3. It is hard to visualize how copolymers with such low DP values could have intrinsic viscosities in the neighborhood of 2–3 dl./g.

General Comments

The copolymerization data with $Al(i\text{-}C_4H_9)_2Cl$ discussed in the preceding sections are in agreement with the general conclusions drawn from the previous work in which $Al(C_2H_5)_2Cl$ has been used. The postulated mechanism accounts satisfactorily for the data obtained now. According to this mechanism, the details of which have already been described,[12] mixing of the two cocatalyst components results in the rapid formation of an active species; on standing, this complex is slowly transformed into a different and possibly less active form. If this suggestion is correct, different catalytic species would be responsible for initiation in freshly prepared and aged

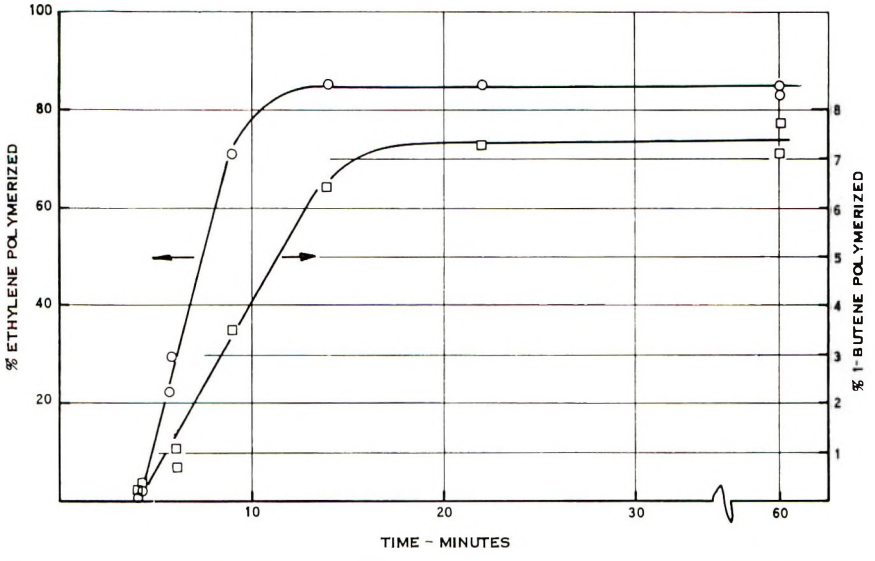

Fig. 5. Rates of (○) ethylene and (□) 1-butene incorporation in copolymer; catalyst mixed *in situ*.

solutions. These differences in the initiator should be reflected in the copolymer viscosity and composition as well as in the polymerization behavior itself. As indicated before, the homopolymerization and copolymerization rates decreased on aging the catalyst while the intrinsic viscosities increased. Also, significant differences were observed in the composition of the copolymers prepared with the two types of catalysts. It would be difficult, if not impossible, to account for the observed results by attributing them entirely to a gradual decay of the active species on aging. Similar difficulties would be encountered if the data were ascribed to side reactions of one of the initiator components. Reactions resulting in a decrease in catalytic species would be expected to give the type of results obtained when the Al:Ti ratio was reduced by one-half, i.e., an increase in intrinsic viscosity, a possible decrease in product yield and essentially no change in copolymer composition.

It might be useful at this point to consider briefly the reason for the failure of 1-butene to homopolymerize and for the low incorporation of this monomer in the copolymers. Since ethylene is incorporated into the product at a much faster rate than butene, toward the end of the polymerization the reaction mixture will contain predominantly 1-butene, most of the ethylene having been converted to polymer. One might expect, therefore, an increase in butene incorporation in the product at long polymerization times. This, however, is not what has been observed; after the initial reaction stage the percentage of butene in the copolymer does not change appreciably. Furthermore, when freshly mixed catalyst is used, the rate of butene incorporation in the product decreases abruptly to either zero or an extremely low value at about the time corresponding

to essentially complete disappearance of ethylene from the mixture (Fig. 5). This means that a macromolecule with a 1-butene unit at the growing end is either incapable of propagating chain growth by adding more 1-butene or capable of propagating only extremely slowly. Addition of butene to such a chain, if possible at all, leads most likely to transfer reactions. The failure of 1-butene to homopolymerize with soluble Cp_2TiCl_2–alkylaluminum initiators under conditions used for copolymerizing it may be ascribed at least partially to the reluctance of this monomer to add to chains with butene units in the terminal position. The fact that the amount of butene in the copolymers does not increase with time when catalysts aged for either 19 or 114 hr. are used seems to indicate that these copolymerizations follow a similar pattern.

Valvassori et al.,[13] who studied the copolymerization of ethylene and propylene initiated by VCl_4 and $Al(C_6H_{13})_3$, found that this catalyst, while effective for the copolymerizations, could not be used to initiate the homopolymerization of propylene. They postulated that the homopolymerization did not proceed because the catalyst failed to initiate it; it was assumed that once chain growth was started the monomer could add to the active end regardless of its structure. Shilov et al.[8] disclosed that the reaction of Cp_2TiCl_2–$Al(C_2H_5)_2Cl$ with α-olefins resulted in alkylation and not polymerization. Our results now show that the failure of 1-butene, and presumably also other α-olefins, to polymerize with Cp_2TiCl_2 and alkylaluminum halides is due not only to the inability of the system to initiate polymerization but also to the failure of the monomer to extend the growing chain at a measurable rate.

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Résumé

L'éthylène a été homopolymérisé et copolymérisé avec le 1-butène dans le benzène à 30°C utilisant le bis-cyclopentadiènyl-titane et le chlorure de diisobutylaluminum. Les

deux produits avaient été fraîchement préparés et le catalyseur vieilli jusque 114 heures. Lorsque le catalyseur était vieilli avant son addition au monomère, les rendements étaient plus faibles et les produits avaient des poids moléculaires plus élevés. Dans le cas des copolymères, le vieillis sement des catalyseurs affectent également les concentrations relatives des comonomères dans le produit. 1-butène était un agent de transfert de chaine effectif dans toutes les conditions de réaction. Les données ont été trouvées être en rapport avec le mécanisme suggéré préalablement suivant lequel différentes espèces initient la polymérisation dans le cas des catalyseurs fraîchement préparés ou au préalable vieillis.

Zusammenfassung

Äthylen wurde in Benzol bei 30°C mit Bis(cyclopentadienyl)-titandichlorid und Diisobutylaluminiumchlorid homopolymerisiert und mit Buten-1 copolymerisiert. Es wurde frisch dargestellter Katalysator und ein bis zu 114 h gealterter Katalysator verwendet. Bei Alterung des Katalysators vor dem Monomerzusatz waren die Ausbeuten niedriger und die Produkte besassen höhere Molekulargewichte. Im Falle der Copolymeren beeinflusst die Katalysatoralterung auch die Zusammensetzung der Produkte aus den Monomeren. Buten-1 war bei allen Reaktionsbedingungen ein wirksamer Kettenüberträger. Die Ergebnisse waren mit dem früher vorgeschlagenen Mechanismus konsistent, nach welchem in frisch gemischten und gealterten Katalysatoren verschiedene Spezies den Polymerisationsstart bewirken.

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Synthesis of Polyamides by the Polyaddition of Bisimidazoline with Dicarboxylic Acids

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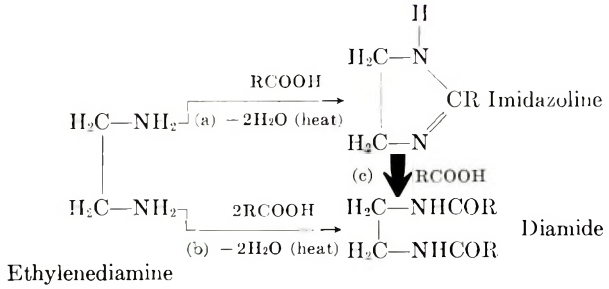
Synopsis

N,N'-Dipropionylethylenediamine was synthesized by the ring-opening addition reaction of 2-ethyl-2-imidazoline with propionic acid at 220°C. By applying this reaction to polymerization, polyamides were synthesized by the ring-opening polyaddition reaction at 220°C. of 1,4-bis(imidazoline-2-yl)butane with adipic acid, succinic acid, sebacic acid, and terephthalic acid. The reaction product of 1,4-bis(imidazoline-2-yl)butane with adipic acid, which was proposed to be nylon 26, was compared with an authentic sample of nylon 26 and shown to possess a very similar infrared spectrum and melting point.

INTRODUCTION

Since Carothers and his co-workers prepared high molecular weight polyamides by polycondensation reactions, a number of preparative routes to polyamides have been reported. In our laboratory, various novel synthetic methods of preparing polyamides by polyaddition have been studied.[1–5]

It is well known that ethylenediamine undergoes condensation with equimolar quantities of carboxylic acid to give imidazoline[6,7] [eq. (1a)]. On the other hand, one mole of ethylenediamine condenses with two moles of carboxylic acid to give diamide [eq. (1b)]. From these, we expected that the addition reaction of imidazoline with an equimolar amount of carboxylic acid would give diamide [eq. (1c)]. On the basis of this consideration, we have succeeded in the synthesis of polyamides by the polyaddition of bisimidazoline with dicarboxylic acid.



(1)

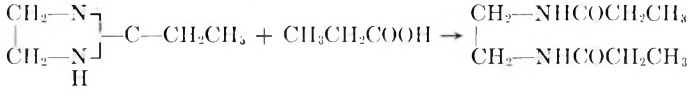
We report here the synthesis of polyamides by the polyaddition of bisimidazoline to dicarboxylic acids. The bisimidazoline used in this paper was 1,4-bis(imidazoline-2-yl)butane, and the dicarboxylic acids used were succinic acid, adipic acid, sebacic acid, and terephthalic acid.

RESULTS AND DISCUSSION

Ring Opening of Imidazoline by the Addition Reaction with Carboxylic Acid

The reaction of 2-ethyl-2-imidazoline with propionic acid at 220°C. gave a white solid product in good yield. The infrared spectrum of the product displayed the characteristic peaks of secondary amide at 1640 and 1550 cm.$^{-1}$ The disappearance of the characteristic adsorption peaks of imidazoline ring at 1620 and 985 cm.$^{-1}$ indicated the ring opening of imidazoline by the reaction. The result of the elementary analysis was nearly equal to the values calculated for *N,N'*-dipropionyl ethylenediamine. The melting point was identical with that of *N,N'*-dipropionylethylenediamine (lit.:[8] 191–192°C.).

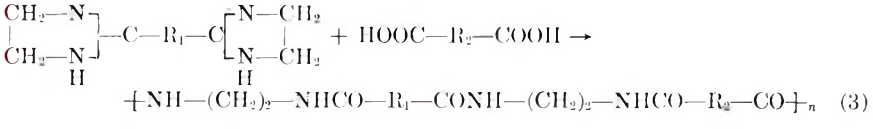
These results lead to the conclusion that imidazoline ring was cleaved by carboxylic acid quantitatively to form diamide [eq. (2)].



(2)

Polyaddition of Bisimidazoline with Dicarboxylic Acid

From the above results, it was suggested that polyamides would be obtained by the ring-opening polyaddition of bisimidazolines with equimolar dicarboxylic acids as shown in eq. (3).



(3)

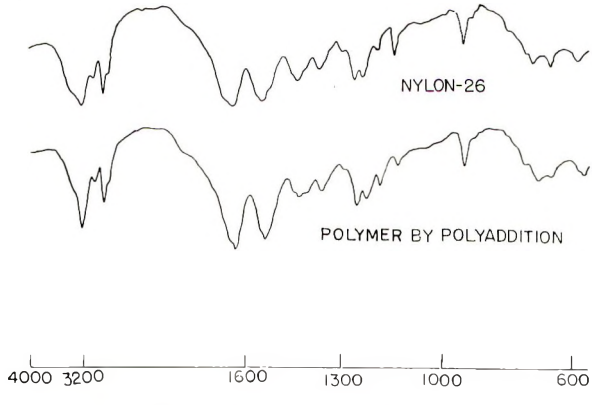


Fig. 1. Infrared spectra of nylon 26 and the polymer obtained by reaction of 1,4-bis(imidazoline-2-yl)butane with adipic acid.

The reaction of 1,4-bis(imidazoline-2-yl)butane with adipic acid was, therefore, proposed to give nylon 26. The white solid product obtained by this reaction at 220°C. was compared with nylon 26 prepared by the interfacial polycondensation of ethylenediamine with adipyl chloride.

The infrared spectrum (Fig. 1) and melting point of the polymer obtained by the reaction of 1,4-bis(imidazoline-2-yl)butane with adipic acid were very similar to those of nylon 26 prepared by the interfacial polycondensation. Elementary analysis of the former polymer was also very close to the calculated values for nylon 26.

From these results, we concluded that the ring-opening polyaddition of the bisimidazoline with the carboxylic acid occurred according to eq. (3).

Various Polyamides Obtained by Polyaddition

The experimental results (Table I) show that white solid products, which had proper values of elementary analysis, were obtained in good yield by the reaction of bisimidazoline with dicarboxylic acids.

The products were found to have the following characteristics of polyamide. (*1*) The infrared spectra of products did not show the characteristic peaks of the monomers, but did show those of secondary amide (Fig. 2). (*2*) The products were soluble in formic acid and insoluble in common organic solvents. (*3*) The reduced viscosities of 0.25 g./100 ml. formic acid solution at 35°C. were about 0.2–0.5.

It is believed that, in the preparation of some kinds of polyamides (nylon 24, for example) by polycondensation of the nylon salt, the formation of low molecular weight substances prevents the preparation of high molecular weight polymer. We also have observed, in the course of

TABLE I
Various Polyamides Obtained by Polyaddition[a]

	A	B	C
Reactants, 10^{-3} mole			
1,4-Bis(imidazoline-2-yl)butane	2.07	1.78	1.74
Succinic acid	2.07	—	—
Sebacic acid	—	1.78	—
Terephthalic acid	—	—	1.74
Yield, wt.-%	90	86	89
Melting point, °C.	293 ⌣ 294	233 ⌣ 234	>315
η_{sp}/c, dl./g.	0.48	0.24	0.16
Anal.			
Found			
C, %	53.76	60.75	60.14
H, %	8.03	9.32	6.99
N, %	17.88	13.84	15.76
Calculated for	$C_{10}H_{24}N_4O_4$	$C_{20}H_{36}N_4O_4$	$C_{18}H_{24}N_4O_4$
C, %	53.83	60.58	59.98
H, %	7.74	9.15	6.71
N, %	17.94	14.13	15.55

[a] Reaction temperature: 220°C.; reaction time: 7 hr.

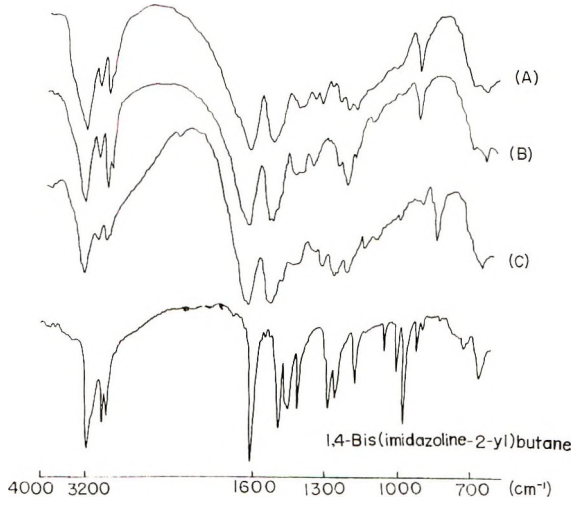


Fig. 2. Infrared spectra of various polymers. Code refers to polymers described in Table I.

preparation of the random copolymer of nylons 24 and 26, by polycondensation (the composition of the copolymer would be equal to that of the polymer A in Table I), that heating of equimolar 24 and 26 nylon salts at 200°C. under vacuum for 5 hr. after heating at 200°C. for 2 hr. in a closed autoclave gave a product in low yield (4 wt.-%) insoluble in hot water. This distinct difference of the polymer yield between the two preparative methods might imply that the polyaddition reaction avoided the formation of low molecular weight substances which prevented the production of high molecular weight polymer in the case of polycondensation.

The structure of polyamide obtained by the polyaddition of 1,4-bis-(imidazoline-2-yl)butane with adipic acid is not influenced by the transamidation. However, the detailed structures of the other polyamides obtained would be influenced by the transamidation. The studies on the structures of these polyamides and on transamidation are now being carried out, and will be reported in the near future.

EXPERIMENTAL

Materials

Imidazolines. 2-Ethyl-2-imidazoline and 1,4-bis(imidazoline-2-yl)butane were prepared according to the method reported in a patent.[9] 2-Ethyl 2-imidazoline was prepared by the reaction of ethylenediamine and propionitrile catalyzed by sulfur at 100°C., yield: 88%; b.p. 92–95°C./13 mm. (lit.:[9] 109–110°C./15 mm.).

1,4-Bis(imidazoline-2-yl)butane was prepared by the reaction of ethylenediamine and adiponitrile catalyzed by sulfur at 100°C., yield: 50%; m.p. 218–219°C. (lit.:[9] 215–216°C.).

ANAL. Calcd. for $C_{10}H_{18}N_4$: C, 61.82%; H, 9.34%; N, 28.84%; Found: C, 61.92%; H, 9.33%; N, 29.02%.

Dicarboxylic Acids. Commercial (G.R. Grade) propionic acid, succinic acid, adipic acid, sebacic acid, and terephthalic acid were used without purification.

Nylon 26. Nylon 26 was prepared by the interfacial polycondensation of ethylenediamine and adipyl chloride;[10] m.p. 315–316°C.; η_{sp}/c, 0.98 at 35°C. in a 0.25 g./100 ml. solution of formic acid.

ANAL. Calcd. for $C_{16}H_{18}N_4O_4$: C, 56.45%; H, 8.29%; N, 16.46%. Found: C, 56.01%; H, 8.37%; N, 16.05%.

Reaction of 2-Ethyl-2-imidazoline with Propionic Acid

Equimolar amounts of 2-ethyl-2-imidazoline (3.05 g.) and propionic acid (2.30 g.) were placed into a test tube having a capacity of about 10 ml. The test tube was sealed under nitrogen atmosphere, and heated at 220°C. for 5.5 hr. The reaction mixture was dried at 80°C. for 5 hr. under vacuum. The yield of yellow crystalline crude product was 92.6% (4.95 g.), m.p. 184–185°C. Recrystallization from ethanol (about 20 ml.) gave white crystals of *N,N'*-dipropionylethylenediamine (3.66 g.), m.p. 191–192°C. (lit.: 191–192°C.). White crystals of *N,N'*-dipropionylethylenediamine (0.79 g.) were recovered on cooling of filtrate in a Dry Ice–methanol bath, m.p. 190–191°C.

ANAL. Calcd. for $C_8H_{16}N_2O_2$: C, 55.79%; H, 9.36%; N, 16.2%. Found: C, 55.86%; H, 9.38%; N, 16.14%.

Polyaddition of 1,4-Bis(imidazoline-2-yl)butane with Adipic Acid

1,4-Bis(imidazoline-2-yl)butane (0.372 g.) and adipic acid (0.279 g.) were placed into a test tube. The glass tube was sealed under nitrogen atmosphere, and placed in an autoclave. The autoclave was heated at 220°C. for 7 hr. The reaction product was pulverized and washed with hot water under reflux for 1 hr. Solid products were dried for 6 hr. at 60°C. *in vacuo*, and weighed (conversion: 95 wt.-%). The reduced viscosity of the 0.25 g./100 ml. solution of formic acid at 35°C. was 0.26, m.p. 314–315°C.

ANAL. Calcd. for $C_{16}H_{18}N_4O_4$: C, 56.33%; H, 8.98%; N, 16.68%; Found: C, 56.45%; H, 8.29%; N, 16.46%.

Other Polyadditions

The experimental conditions and results are listed in Table I. The procedures were same as that in the case of the polyaddition of 1,4-bis-(imidazoline-2-yl)butane with adipic acid except the washing procedure. The reaction product of 1,4-bis(imidazoline-2-yl)butane with succinic

acid was washed with hot water under reflux for 1 hr. Reaction products in the other cases were washed with hot ethanol under reflux for 1 hr.

Characterization of the Polymers

The infrared spectrum was determined with a Shimadzu Infracord, Model IR-27, on KBr pellets. The reduced viscosity of a 0.25 g./100 ml. solution of formic acid was measured at 35°C. with an Ubbelohde-type viscometer. The melting point of the polymer was determined visually from the sintering point to the meniscus point in a sealed capillary under nitrogen with the Yanagimoto melting point measuring apparatus, Model MP-52, equipped with a microscope (×10).

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Résumé

La *N,N'*-dipropionyl éthylènediamine a été synthétisée par réaction d'addition par ouverture de cycle de 2-éthyl-2-imidazoline avec l'acide propionique a 220°C. En appliquant cette réaction à la polymérisation, des polyamides ont été synthétisés par réaction d'addition par ouverture de cycle à 220° de 1,4-bis(imidazoline-2-yl)butane avec l'acide adipique, l'acide succinique, l'acide sébacique, et l'acide téréphtalique. Le produit de réaction du 1,4-bis(imidazoline-2-yl) butane avec l'acide adipique, qui est proposé comme nylon 2,6 était comparé avec un échantilon identique de nylon 2,6; son spectre infrarouge est très semblable et le point de fusion également.

Zusammenfassung

N,N'-Dipropionyläthylendiamin wurde durch die Ringöffnungsreaktion zwischen 2-Äthyl-2-imidazolin und Propionsäure bei 220°C synthetisiert. Mit Anwendung dieser Reaktion auf die Polymerisation wurden durch Ringöffnungspolyaddition von 1,4-Bis (imidazolin-2-yl)butan mit Adipinsäure, Bernsteinsäure, Sebazinsäure und Terephthal-

säure bei 220°C Polyamide synthetisiert. Das Reaktionsprodukt aus 1,4-Bis(imidazolin-2-yl)butan und Adipinsiure, das als Nylon-2,6 angesehen wurde, wurde mit einer authentischen Nylon-2,6-Probe verglichen und stimmte mit dieser im Infrarotspektrum und Schmelzpunkt nahe überein.

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