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CONTENTS

Vol. 5, Issue Nos. 1–12

Journal of Polymer Science
Part A-1: Polymer Chemistry

ISSUE NO. 1, JANUARY

Notes

Book Review

Issue No. 2, February

Notes

Book Review

ISSUE NO. 3, MARCH

Notes

Book Review

Issue No. 4, April

Notes

Book Review

ISSUE NO. 5, MAY

ISSUE NO. 6, JUNE

Notes

ISSUE NO. 7, JULY

Notes

Book Reviews

ISSUE NO. 8, AUGUST

Notes

ISSUE NO. 9, SEPTEMBER

Notes

Book Reviews

Issue No. 10, October

Notes

Book Review

ISSUE NO. 11, NOVEMBER

Notes

Book Reviews

ISSUE NO. 12, DECEMBER

Notes

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Crosslinking of Gelatin by Aqueous Peroxydisulfate

H. L. NEEDLES, *Western Regional Research Laboratory,*
Western Utilization Research and Development Division,
Agricultural Research Service, U.S. Department of Agriculture,
Albany, California 94710

Synopsis

Aqueous gelatin (5%) is crosslinked in the presence of 0.040–0.020*M* peroxydisulfate at 70°C., but in 0.40*M* peroxydisulfate, gelatin initially is crosslinked and then redissolves to give a solution of reduced viscosity. The rate of crosslinking depends on the concentration of peroxydisulfate, the nature of peroxydisulfate's cation, and the pH range of the solution during crosslinking. Addition of silver ion to gelatin–peroxydisulfate solutions increases the rate of crosslinking, whereas addition of hydroquinone inhibits crosslinking. Further, induced decomposition of peroxydisulfate is observed in the presence of gelatin. Acetylated and esterified gelatins are crosslinked by aqueous peroxydisulfate, but the ability of deaminated gelatin to crosslink is greatly reduced. Crosslinking is believed to proceed via sulfate and hydroxyl free-radical attack of gelatin, with *in situ* generation of reactive intermediates that crosslink with other reactive sites in gelatin. Possible sites of crosslinking in gelatin have been suggested in light of viscosity data, chemical and amino acid analyses, and peroxydisulfate's known mode of decomposition.

INTRODUCTION

In recent studies of wool keratin degradation by aqueous peroxydisulfate,[1,2] we found evidence for oxidative cleavage of the protein main chain, as well as other oxidative reactions of the side chains. In order to further characterize and follow this protein main chain cleavage in a homogeneous system, we determined viscosity change with time of 5% gelatin in aqueous peroxydisulfate at 70°C. The viscosity of these solutions, however, increased with time, the solutions finally setting to gels. If the concentration of peroxydisulfate was high, the solution gelled almost immediately and then eventually degraded to yield a solution of decreased viscosity.

This novel crosslinking of gelatin is of interest, because the crosslinking reaction involves *in situ* generation of reactive intermediates in gelatin, that are capable of crosslinking with other gelatin molecules. The usual methods of crosslinking gelatin solutions involve addition of a bifunctional agent to the solution[3,4] to effect crosslinking.

We have used viscosimetric and chemical methods to gain further insight into the nature of peroxydisulfate crosslinking of gelatin at 70°C. Crosslinking has been interpreted in light of peroxydisulfate's known mode of decomposition and physical and chemical changes in representative samples of the crosslinked gelatin.

EXPERIMENTAL

Gelatins and Reagents

A pure granular, acid-processed, U.S.P. grade gelatin was used. It had a Bloom rating of 175. A 5% aqueous solution of this gelatin at 70°C. has a pH of 5.3. *N*-Acetylation of gelatin was by the method of Kenchington[5] by use of acetic anhydride in aqueous sodium acetate. Free carboxyl groups were esterified by the method of Fraenkel-Conrat and Olcott,[6] with the use of 0.1*N* hydrochloric acid in absolute methanol. Gelatin

TABLE I
Chemical Analyses of Gelatins

Modification	Total N, %	Van Slyke N, %	Amide N, %	Methoxyl, %	η_{inh}, dl./g.[a]
None[b]	17.3	0.63	0.59	—	0.220
Acetylation	17.3	<0.01	0.34	—	0.236
Esterification	16.9	0.57	0.30	4.78	0.160
Deamination[b]	16.8	0.19	0.04	—	0.222

[a] Inherent viscosity of 5.0% gelatin in water at 70°C.
[b] See Table IV for amino acid analyses.

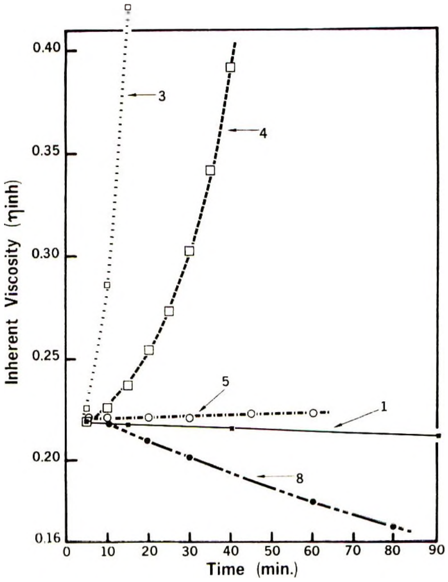


Fig. 1. Viscosity change of gelatin in the presence of ammonium peroxydisulfate at various concentrations.

(10.0 g. in 100 ml. of water) was deaminated by reaction with 10.0 g. sodium nitrate and 15 ml. acetic acid for 30 min. at 35°C. The solution was immediately dialyzed, and water was finally removed by rotary evaporation at reduced pressure. All gelatins were dried at 1 mm. pressure over sodium hydroxide before use or analysis. Analyses of these gelatins are found in Table I. All other reagents were Baker-Analyzed, with the exception of hydroquinone, which was Eastman White Label grade.

Viscosity Measurements

Compositions of the solutions used in the viscosity studies are listed in Table II. Peroxydisulfate and/or other additives were dissolved in 25 ml. of 5% aqueous gelatin. The resulting solution was placed in a Cannon-

TABLE II

Composition of Solutions for Viscosity Studies at 70°C.

Run no.	Gelatin modification	Peroxydisulfate		Additive		Time to reach $\eta_{inh} > 0.4$ or other change, min.
		Cation	Concn., M	Compound	M	
1	None	—	—	—	—	[a]
2	"	NH_4^+	0.40	—	—	<5[b]
3	"	"	0.040	—	—	15
4	"	"	0.020	—	—	41
5	"	"	0.0040	—	—	[c]
6	"	"	0.020	$AgNO_3$	0.0002	33
7	"	—	—	NH_4HSO_4	0.080	[a]
8	"	—	—	"	0.040	[a]
9	"	NH_4^+	0.040	K_2HPO_4	0.080	24
10	"	"	0.020	"	0.040	76
11	"	K^+	0.040	—	—	15
12	"	"	0.020	—	—	35
13	"	"	0.020	$AgNO_3$	0.0002	29
14	"	—	—	$KHSO_4$	0.080	[a]
15	"	K^+	0.040	K_2HPO_4	0.080	20
16	"	"	0.020	"	0.040	67
17	"	—	—	$KHSO_4$, K_2HPO_4	0.080	[a]
18	None	K^+	0.020	Hydroquinone	0.020	[a]
19	Acetylation	"	0.020	—	—	32
20	"	"	0.020	K_2HPO_4	0.040	38
21	Esterification	"	0.040	—	—	30
22	"	"	0.020	—	—	61
23	Deamination	"	0.020	—	—	[d]

[a] Viscosity decreases.

[b] At 35 min. gel degrades to solution of reduced viscosity.

[c] Viscosity slowly increases.

[d] Viscosity slowly increases to 3.43 at 75 min., then decreases.

Fenske viscometer (size 100) and rapidly equilibrated to 70.0 ± 0.1°C. in a constant temperature bath. The viscosity was followed until cross-linking occurred or until the trend of viscosity change was evident (Table II, Figs. 1–4).

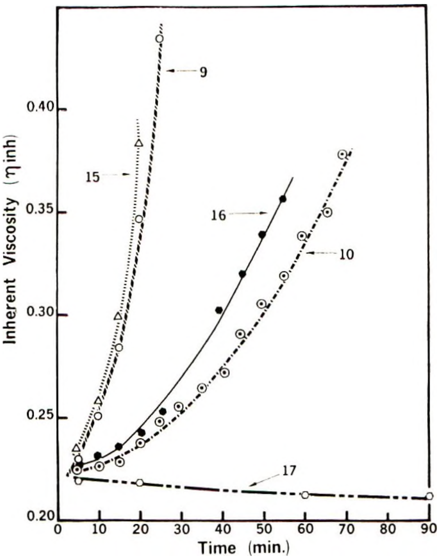


Fig. 2. Viscosity change of gelatin in the presence of peroxydisulfate–dipotassium hydrogen phosphate at various concentrations.

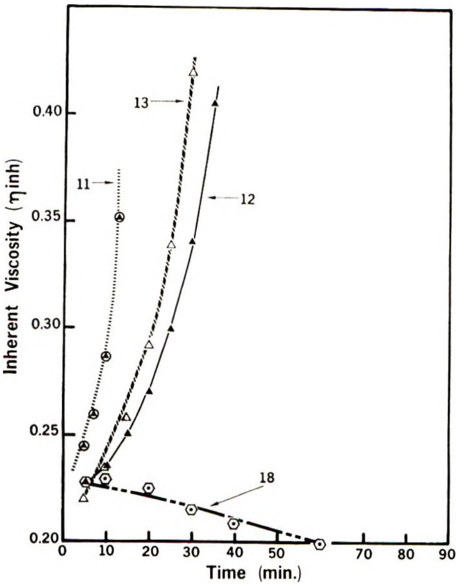


Fig. 3. Viscosity change of gelatin in the presence of potassium peroxydisulfate and other additives at various concentrations.

Preparation and Isolation of Crosslinked or Degraded Gelatins

Representative samples of crosslinked and degraded gelatins were prepared for analysis as follows. A 5% gelatin solution was made 0.40 or 0.040*M* in ammonium peroxydisulfate, rapidly brought to 70.0 ± 0.1°C., and maintained at this temperature for 1 or 2 hr. The resulting gel or solution was dialyzed for 3 days, and then water was removed at reduced pressure on a rotary evaporator to yield the modified gelatin. The gelatin was further dried over sodium hydroxide at 1 mm. before analysis (Tables III, IV).

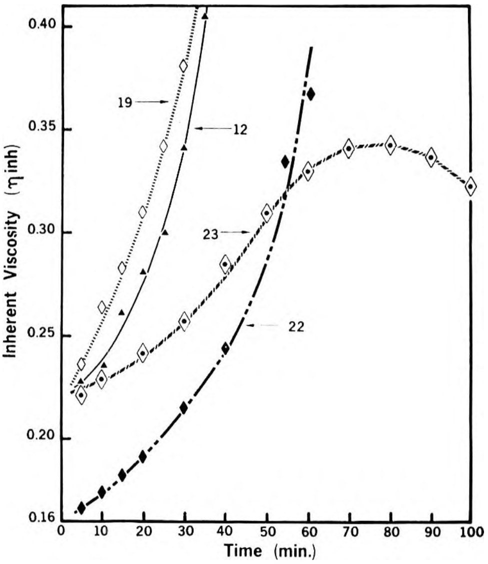


Fig. 4. Viscosity change of chemically modified gelatins in the presence of 0.020*M* potassium peroxydisulfate.

TABLE III
Reaction of Gelatin with Ammonium Peroxydisulfate at 70°C.

$(NH_4)_2S_2O_8$ concn., *M*	Reaction time, hr.	Total N, %	Van Slyke N, %	Amide N, %	Total S, %
Control	—	17.3	0.63	0.59	0.55
0.040	1	17.1	0.55	0.52	0.95
0.040	2	17.1	0.49	0.51	0.86
0.40	2	15.3	0.66	1.66	0.74

Analytical Methods

All chemical analyses were performed at this laboratory by standard techniques (Tables I and III). Dried gelatin samples weighing 40 mg. were prepared for amino acid analysis by heating for 22 hr. at 120°C. in 10 ml.

TABLE IV
Amino Acid Composition of Gelatins

Amino acid	Amino acid content, mole/10^5 g. protein			
		5% Gelatin, 2 hr. 70°C.		
	Control gelatin	0.040*M* $(NH_4)_2S_2O_8$	0.40*M* $(NH_4)_2S_2O_8$	Deaminated gelatin
Lysine	26.4	26.5	16.6	1.7
Histidine	4.2	3.2	0.8	5.3
Ammonia	58.3	59.1	145	55.5
Arginine	51.1	48.4	22.6	51.2
Aspartic acid	45.4	44.6	45.8	48.6
Threonine	16.6	16.6	10.7	17.6
Serine	31.8	32.2	23.1	34.2
Glutamic acid	72.1	76.1	103	81.1
Proline	117	109	3.7	127
Glycine	318	316	249	330
Alanine	110	111	96.7	114
Half cystine[a]	0.0	3.8	6.0	0.0
Valine	19.5	21.2	16.7	21.9
Methionine	3.6	1.8	0.3	5.4
Isoleucine	11.1	11.4	7.4	11.5
Leucine	25.0	25.5	13.8	26.5
Tyrosine	3.7	1.7	0.0	0.8
Phenylalanine	13.7	11.0	0.0	13.9
Hydroxyproline	78.5	78.5	87.8	69.0
Cysteic acid	0.3	0.6	0.6	0.0

[a] All samples gave a negative test for sulfhydryl with sodium nitroprusside.

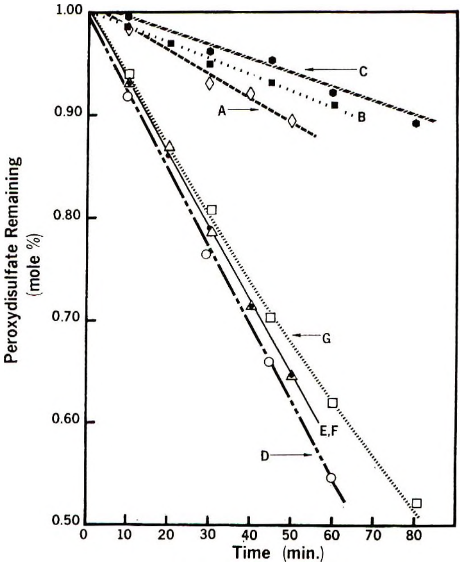


Fig. 5. Changes in the concentration of peroxydisulfate in the presence and absence of gelatin.

of 6*N* hydrochloric acid. After removal of hydrochloric acid by flash evaporation, the hydrolyzates were analyzed on a Beckman Spinco amino acid analyzer, Model 120 (Table IV).

In certain experiments, pH values were checked periodically on a Beckman pH meter, Model 76 (Table V).

Peroxydisulfate concentrations in representative experiments in the presence and absence of gelatin were determined iodometrically by the method of Bartlett and Cotman.[7] In the run made in the absence of oxygen, the solution was degassed with nitrogen prior to placement in the constant temperature bath. Solution compositions are found in Table VI, and peroxydisulfate concentration changes with time are found in Figure 5.

TABLE V
pH Change With Time of 5% Gelatin at 70°C.

Run no.	Additive(s)	Additive concn., *M*	pH at 0	30 min.	60 min.	80 min.
1	Control	—	5.3	5.3	5.3	5.3
4	$(NH_4)_2S_2O_8$	0.020	5.3	5.0	5.0	—
10	$(NH_4)_2S_2O_8$ K_2HPO_4	0.020 0.040	7.3	7.1	6.8	6.7
12	$K_2S_2O_8$	0.020	5.3	5.1	5.1	—
—	$KHSO_4$	0.040	3.4	3.2	3.2	—
16	$K_2S_2O_8$ K_2HPO_4	0.020 0.040	7.4	7.3	7.0	6.9
—	$KHSO_4$ K_2HPO_4	0.040 0.040	5.3	5.3	5.3	5.3

TABLE VI
Composition of Solutions Used in Peroxydisulfate Titrations

Run	Peroxydisulfate[a] cation	Dipotassium hydrogen phosphate concn., *M*	Gelatin present	Oxygen excluded
A	NH_4^+	—	No	No
B	K^+	—	"	"
C	"	0.040	"	"
D	NH_4^+	—	Yes	"
E	K^+	—	"	"
F	"	—	"	Yes
G	"	0.040	"	No

[a] Concn. 0.020*M* at $T = 0$.

RESULTS AND DISCUSSION

Mode of Decomposition of Peroxydisulfate

Peroxydisulfate is known to yield sulfate and hydroxyl free radicals on thermal decomposition in aqueous solutions.[8] In the presence of an oxidizable substrate, induced free-radical decomposition occurs.[8]

$$^{1}/_{2}S_2O_8^{=} \rightarrow SO_4^{-\cdot} \xrightarrow{H_2O} OH\cdot + HSO_4^{-}$$

$$X{-}H \xrightarrow[\text{or } OH\cdot]{SO_4^{-\cdot}} X\cdot + HSO_4^{-} \text{ or } H_2O \xrightarrow{S_2O_8^{=}} X{-}OSO_3^{-} + SO_4^{-\cdot} \rightarrow \text{etc.}$$

where X—H denotes oxidizable substrate. Peroxydisulfate attack on gelatin is thought to occur via such an induced free-radical decomposition forming reactive groups in gelatin that are capable of crosslinking or degradation.

Chemical Analyses of Gelatins

Chemical analyses of gelatin and modified gelatins are listed in Table I. Modification of gelatin lowers the amide nitrogen content in every case, probably through partial hydrolysis of free amide groups. *N*-Acetylation is virtually complete, as reflected by the decrease of Van Slyke nitrogen content from 0.63 to <0.01%. Methoxyl content of esterified gelatin is very nearly equal to the total free carboxyl groups found in gelatin.[5] Nitrous acid deamination is somewhat less effective than acetylation in decreasing the Van Slyke nitrogen content of gelatin, but amino acid analysis shows that nitrous acid does cause significant destruction of lysine, tyrosine, and possibly hydroxyproline (Table IV).

Viscosity Studies with Gelatin

Gelatin solutions 0.040 and 0.020*M* in peroxydisulfate (Table II, runs 3, 4, 11, and 12, Figs. 1 and 3) crosslink and set to stable gels in less than 1 hr., the rate of viscosity increase being more rapid with potassium than with ammonium peroxydisulfate. Although gelatin in 0.40*M* ammonium peroxydisulfate (run 2) immediately sets to a gel, the gel redissolves in about 35 min. to give a solution of lower viscosity.

These data suggest that two separate reactions are operating, one resulting in crosslinking and the other in degradation of the gelatin. With 0.40*M* peroxydisulfate, the peroxydisulfate probably initially reacts for the most part to generate reactive groups which crosslink the protein.[9] When these sites are exhausted, peroxydisulfate attacks the gelatin main chain eventually, causing resolubilization of the gelatin.

Gelatin in 0.0040*M* ammonium peroxydisulfate (run 5, Fig. 1) does not gel but does show a slow increase of viscosity with time, while control solutions (runs 1, 7, 8, 14, 17, Figs. 1 and 2) show decreases in viscosity. Addition of dipotassium hydrogen phosphate to gelatin–peroxydisulfate solutions (runs 9, 10, 15, 16, Fig. 2) nearly doubles the time necessary for crosslinking to take place.

Small amounts of silver nitrate, a known catalyst for peroxydisulfate decomposition,[8] added to gelatin–peroxydisulfate solutions (runs 6 and 13, Fig. 3) increase the rate of crosslinking. Also, hydroquinone, an antioxidant and free-radical scavenger, prevents crosslinking from taking place, presumably through preferential reaction with peroxydisulfate or reaction with radicals resulting from its decomposition (run 18, Fig. 3).

Acetylated and esterified gelatins (runs 19–22, Fig. 4) are effectively crosslinked by peroxydisulfate, at rates somewhat faster than control for acetylated gelatin and slower than control for esterified gelatin. Acetylated gelatin's faster rate of crosslinking is probably explained by its higher initial solution viscosity. Esterified gelatin's slower rate may be due to its lower initial viscosity caused by hydrolytic degradation of gelatin during esterification. Deaminated gelatin (run 23, Fig. 4) slowly begins to crosslink initially and then degrades with time. Acetylation and esterification of gelatin do not prevent crosslinking, whereas deamination greatly reduces gelatin's capacity to crosslink. These data suggest that modification of free amino and carboxyl groups in gelatin does not prevent crosslinking, but deamination, which destroys free amino groups and attacks other amino acid side chains, does greatly reduce the number of sites available for crosslinking.

pH Ranges and Rate of Decomposition of Peroxydisulfate Solutions

Control gelatin solution has a pH of 5.3 at 70°C. The pH ranges of selected gelatin–peroxydisulfate solutions are 5.3–5.0 during crosslinking (Table V). Further, gelatin solutions containing potassium bisulfate, the probable decomposition product of peroxydisulfate, have a pH range of 3.4–3.2. These data show that gelatin acts as its own buffer in these crosslinking experiments reacting with any bisulfate as it is formed from peroxydisulfate decomposition. Dipotassium hydrogen phosphate added to gelatin–peroxydisulfate solutions results in pH ranges of 7.4–6.7 during crosslinking (Table V).

Since the pH ranges (Table V) and the rates of peroxydisulfate decomposition (Table VI, Fig. 5) for ammonium and potassium peroxydisulfate crosslinking of gelatin are nearly the same, these factors apparently do not account for differences in crosslinking rates for ammonium and potassium peroxydisulfate. These differences in rate may be attributable to the different effects of ammonium and potassium ions on aggregation and conformation of gelatin molecules in solution,[10] thereby affecting the solution's viscosity. The decrease in crosslinking rate observed when dipotassium hydrogen phosphate is added to gelatin–peroxydisulfate solutions is only partially explained by the lower rate of peroxydisulfate decomposition at this higher pH range (Table VI, Fig. 5), since the difference in peroxydisulfate decomposition is very small, but the rate of crosslinking is almost twice as slow. Marked differences in aggregation, conformation, and charge distribution in gelatin at these two pH ranges may explain the observed difference in crosslinking rates.

Peroxydisulfate's rate of decomposition increases by a factor greater than three when gelatin is added to the solution (Table VI, Fig. 5). This observation is consistent with peroxydisulfate's known mode of induced homolytic decomposition.[8] Oxygen has little effect on the rate of peroxydisulfate decomposition. Apparently the high concentration of gelatin in solution masks any effect that dissolved oxygen might have on peroxydisulfate decomposition.

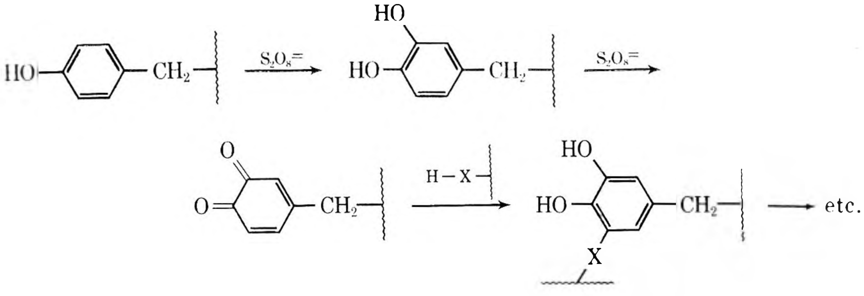
Analyses of Crosslinked Gelatin

Two samples of crosslinked gelatin were isolated and characterized by chemical and amino acid analyses to gain further insight into the nature of the crosslinking reaction. These data (Tables III and IV) suggest that crosslinking involves a number of complex reactions.

Chemical analyses of crosslinked gelatins from the action of $0.040M$ ammonium peroxydisulfate on 5% gelatin at 70°C. for 1 and 2 hr. are characterized by slightly lower total nitrogen, Van Slyke nitrogen, and amide nitrogen contents and increased total sulfur content as compared with control gelatin.

The small loss of total nitrogen in the crosslinked gelatins is probably due to the oxidative nature of peroxydisulfate attack. Small decreases in Van Slyke nitrogen suggest loss of free amino groups in gelatin through either crosslinking or oxidation of the group. As stated previously, *N*-acetylated gelatin crosslinks at a slightly more rapid rate than does control gelatin. *N*-Acetylation may not necessarily block crosslinking reactions, however, for Green[11] has found that *N*-acetylation of collagen does not prevent crosslinking of the protein by benzoquinone, which suggests that other amino acid sites (i.e., hydroxyl, guanidino, histidino, imino, free heterocyclic groups) may be involved. Slight decreases in amide nitrogen content in crosslinked gelatins probably result from partial hydrolysis of free amide groups within the gelatin. Increases in total sulfur found in crosslinked gelatins give further indication that induced decomposition of peroxydisulfate in aqueous gelatin solutions is occurring, since the expected result of such an induced decomposition would be grafting of sulfur (as sulfate) into the gelatin.

Amino acid analysis of one sample of crosslinked gelatin shows significant losses of histidine, methionine, tyrosine, phenylalanine, and possibly proline and increases of half cystine and cysteic acid in the protein. Histidine, tyrosine, and phenylalanine[12] are known to oxidize to quinone intermediates, and quinones are known[13] to bind to active sites in proteins. In gelatin, histidine, tyrosine, and phenylalanine are believed to be oxidized to quinone intermediates which can condense with reactive sites (amino, hydroxyl, guanidino, histidino, imino, etc.) to give crosslinks.



Decreased ability of deaminated gelatin (Table II, run 23) to crosslink in the presence of peroxydisulfates is thought to be due to its decreased free amino content as well as to loss of tyrosine during deamination.

Loss of methionine shows the ease with which radicals attack sulfur-containing side chains. Proline loss apparently occurs through free-radical attack on the proline ring to give hydroxyprolines and glutamic acid through oxidative ring opening, a result which is especially evident when excess peroxydisulfate is used.

The source of half cystine and cysteic acids in crosslinked gelatin is unknown. It is presumed that these amino acids result from complex oxidative attack of amino acids in gelatin by sulfate free radicals. Cystine formation would necessarily have to involve a complex redox reaction.

Analyses of Degraded Gelatin

Degraded gelatin from the reaction of gelatin with 0.40*M* ammonium peroxydisulfate for 2 hr. at 70°C. (Table III) is characterized by lower total nitrogen, essentially unchanged Van Slyke nitrogen, greatly increased amine nitrogen, and increased sulfur content. Large losses in total nitrogen content and large increases in amide nitrogen are indicative of the high degree of degradation that has taken place in this gelatin. The small increase in Van Slyke nitrogen suggests that some hydrolytic cleavage of the peptide chain has taken place, and increased sulfur content again indicates induced decomposition of peroxydisulfate. High amide nitrogen content suggests oxidative main chain cleavage, as has been proposed for peroxydisulfate oxidation of keratin.[1,2]

Amino acid analysis of degraded gelatin shows that its amino acid content is generally lower, but that histidine, arginine, proline, and methionine are destroyed to a greater degree, and that tyrosine and phenylalanine are completely destroyed. These amino acids are the same amino acids destroyed by peroxydisulfate oxidation of wool keratin.[1,2] A large increase in glutamic acid and a lesser increase in hydroxyproline is found, and, as stated before, these increases are thought to result from sulfate radical attack of proline. Half cystine and cysteic acid contents also increased, as in the case of crosslinked gelatin.

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Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

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Résumé

Une gélatine aqueuse (5%) est pontée en présence de 0.040–0.020*M* de peroxydisulfate à 70°C, mais dans le peroxydisulfate 0.40*M*, la gélatine est initialement pontée et puis redissoute pour former une solution de viscosité amoindrie. La vitesse de pontage dépend de la concentration en peroxydisulfate, de la nature du cation peroxydisulfaté et du domaine de pH de la solution en cours de pontage. L'addition d'ion argentique aux solutions de gélatine peroxydisulfatée accroît la vitesse de pontage, alors que l'addition d'hydroquinone inhibe ce même pontage. En outre, une décomposition induite du peroxydisulfate est observée en présence de gélatine. Les gélatines acétylées et estérifiées sont pontées au moyen de peroxydisulfate aqueux mais la capacité d'une gélatine déaminée au pontage est fortement diminuée. Semblablement ce pontage résulte d'une attaque de la gélatine par des radicaux libres, sulfates et hydroxylés, avec génération in situ de réactifs intermédiaires qui subissent le pontage entre eux avec d'autres sites réactifs dans la gélatine. Des sites possibles dans la gélatine ont été présentés sur la base des données viscosimétriques, des analyses chimiques et des aminoacides, et sur la base également du mode de décomposition bien connu des peroxydisulfates.

Zusammenfassung

Wässrige Gelatine (5%) wird in Gegenwart von 0,040–0,020*M* Peroxydisulfat bei 70°C vernetzt, in 0,40*M* Peroxydisulfat jedoch tritt zwar anfangs Vernetzung, dann aber Auflösung zu einer Lösung mit herabgesetzter Viskosität ein. Die Vernetzungsgeschwindigkeit hängt von der Peroxydisulfatkonzentration, vom Peroxydisulfatkation und vom pH-Bereich der Lösung während der Vernetzung ab. Zusatz von Silberion zu Gelatine-Peroxydisulfatlösungen erhöht die Vernetzungsgeschwindigkeit, während ein Hydrochinonzusatz die Vernetzung inhibiert. Ausserdem wird in Gegenwart von Gelatine eine induzierte Peroxydisulfatzersetzung beobachtet. Acetylierte und veresterte Gelatine werden durch wässriges Peroxydisulfat vernetzt, dagegen ist die Vernetzungsfähigkeit von desaminierter Gelatine stark herabgesetzt. Es wird angenommen, dass die Vernetzung über einen Angriff von freien Sulfat- und Hydroxylradikalen an Gelatine mit in situ Bildung reaktiver Zwischenprodukte, welche eine Vernetzung mit anderen reaktionsfähigen Zentren in der Gelatine liefern, verläuft. Mögliche Vernetzungszentren in Gelatine wurden im Lichte von Viskositätsdaten, chemischen und Aminosäureanalysen sowie des bekannten Zersetzungsverlaufes von Peroxydisulfat wahrscheinlich gemacht.

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Synthesis of Polyamides by the Polyaddition of Bissuccinimides with Diamines

TSUTOMU KAGIYA, MASATSUGU IZU,
TAKEHISA MATSUDA, and KENICHI FUKUI,
Faculty of Engineering, Kyoto University, Kyoto, Japan

Synopsis

Polyamides which contain succinamide units, $-NHCO-(CH_2)_2-CONH-$ were prepared by the ring-opening polyaddition of bissuccinimides with diamines at 200°C. in bulk. Nylon 24 and nylon 64 were prepared by the reaction of *N*,*N*′-ethylenedisuccinimide with ethylenediamine and of *N*,*N*′-hexamethylenedisuccinimide with hexamethylenediamine, respectively. It was suggested that the transamidation reaction by aminolysis influenced the detailed structures of the polymers prepared from *N*,*N*′-ethylenedisuccinimide and hexamethylenediamine and from *N*,*N*′-hexamethylenedisuccinimide and ethylenediamine. The detailed structures of the polymers are discussed on the basis of their melting points and x-ray diagrams. It is concluded that the polymers contain a crystalline portion of $\{NH-(CH_2)_2-NHCO-(CH_2)_2-CONH-(CH_2)_6-NHCO-(CH_2)_2-CO\}$ sequences.

Introduction

Since Carothers and his co-workers prepared high molecular weight polyamides by polycondensation, a number of preparative routes to polyamides have been reported. Little attention, however, has been paid to the method of preparation of polyamides with the use of imide compounds.[1,2]

The purpose of this paper is to report the synthesis of polyamides by polyaddition of bissuccinimides to diamines.

Experimental

N,*N*′-Ethylenedisuccinimide (ES) and *N*,*N*′-hexamethylenedisuccinimide (HS) were prepared according to the method reported by Mason.[3] Crude materials were further purified by recrystallization from water before use. Melting points were 251–253°C. (lit.: 250–251°C.) and 116–118°C. for the ethylenedisuccinimide and hexamethylenedisuccinimide, respectively.

ANAL. Calcd. for $C_{10}H_{12}N_2O_4$: C, 53.6%; N, 12.5%. Found: C, 53.6%; N, 12.5%. Calcd. for $C_{14}H_{20}N_2O_4$: C, 60.0%; N, 10.0%. Found: C, 60.2%; N, 10.1%.

Commercial hexamethylenediamine (HA) was purified by sublimation under vacuum. Ethylenediamine (EA) (G.R. grade) was used without purification.

Reactions were carried out in a glass ampule under a nitrogen atmosphere. Reaction products of *N*,*N*′-ethylenedisuccinimide with diamines were washed with water and chloroform, and those of *N*,*N*′-hexamethylenedisuccinimide were washed with water and acetone. The products were further washed with hot water under reflux for 1 hr. and dried at 60°C. under vacuum.

TABLE I
Experimental Results

	Polymer A	Polymer B	Polymer C	Polymer D	Polymer E
Reactants, mole × 10^{3} [a] Succinimide	ES, 4.46	HS, 17.0	ES, 4.32	HS, 7.25	ES, 11.1; HS, 11.1
Amine	EA, 4.46	HA, 17.0	HA, 4.32	EA, 7.25	EA, 11.1; HA, 11.1
Reaction conditions					
Time, hr.	8	6	5	8	6
Temp., °C.	200	200	200	200	200
Yield, wt.-%	63.3	78.4	38.2	85.5	70.8
η_{sp}/c dl./gr.	0.21	0.50	0.24	0.31	0.33
Melting point, °C. [b]	>305 [c]	277–278	286–287	275–278	256–258
Anal.					
Found					
C, %	49.9	61.4	56.4	56.4	56.7
N, %	20.1	14.1	16.5	16.3	16.4
H, %	7.3	9.3	8.4	8.6	8.4
Calcd.	$C_{12}H_{20}N_4O_4$	$C_{20}H_{36}N_4O_4$	$C_{16}H_{28}N_4O_4$	$C_{16}H_{28}N_4O_4$	$C_{16}H_{28}N_4O_4$ [d]
C, %	50.7	60.6	56.4	56.4	56.4
N, %	19.7	14.1	16.5	16.5	16.5
H, %	7.1	9.2	8.3	8.3	8.3

[a] ES = *N*,*N*′-ethylenedisuccinimide; HS = *N*,*N*′-hexamethylenedisuccinimide; EA = ethylenediamine; HA = hexamethylenediamine.

[b] The melting range determined was from the softening point to liquifaction.

[c] Decomposition of the polymer occurred at about 305°C.

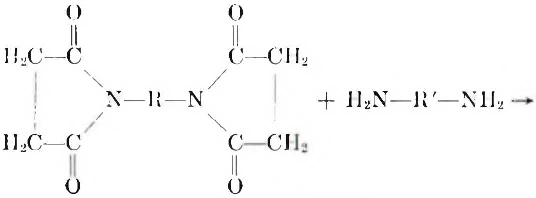
[d] Values calculated on the basis of equal rates for the four kinds of reactions.

The infrared spectra were determined with a Shimadzu infrared spectrophotometer, Model IR-27, on KBr pellets. The specific viscosity of a 0.25 g./100 cc. solution in formic acid was measured at 35°C. with an Ubbelohde-type viscometer. The melting points of the polymers were determined visually in a sealed capillary under a nitrogen atmosphere with the Yanagimoto melting point measuring apparatus, Model MP-S2, equipped with a microscope (×10). The x-ray diffraction diagrams were obtained with a powder camera in a Shimadzu x-ray diffraction apparatus, Model GX-3B.

Results and Discussion

As shown in Table I, solid products which were insoluble in boiling water were obtained by the reactions of *N,N'*-bissuccinimides with diamines. Figure 1 shows the infrared spectra of the polymers. The characteristic absorption peak of imide at 1700 cm.$^{-1}$ disappeared, while the spectra displayed the characteristic absorption peaks of secondary amide. The spectra were very similar to those of polyamides. These products were soluble in formic acid and insoluble in common organic solvents, and the reduced viscosities of formic acid solutions at 35°C., were 0.2–0.5.

It was reported that imide ring is readily opened by the reaction with amine, forming two amide groups.[4] It is suggested that a polyaddition reaction took place, and a polyamide was produced:



$$+NH-R'-NHCO-(CH_2)_2-CONH-R-NHCO-(CH_2)_2-CO+$$

In the case of R = R' = ethylene, $+CH_2+_2$, the polymer obtained (A) is nylon 24, and in the case of R = R' = hexamethylene, $-(CH_2)_6-$, the polymer obtained (B) is nylon 64.

On the other hand, polymers C and D will have four amide groups $+NH-(CH_2)_2-NHCO-(CH_2)_2-CONH-(CH_2)_6-NHCO-(CH_2)_2-CO+$ in a repeating unit if the rate of transamidation is negligible compared with that of polymerization. If complete transamidation were to take place, the structures of polymers C and D would approach that of the random polymer which contains 24 and 64 amide units at random. Regardless of occurrence of the transamidation, the structure of the polymer E produced from all four kinds of monomers is considered to have a structure similar to that of the random polymer, since in this polymerizing system four kinds of polyaddition reactions take place simultaneously. It is considered that the transamidation in this case is caused by reverse polyaddition and by aminolysis of polyamide with unreacted diamines and the amines of polymer chain ends. On the basis of this consideration, degradation and aminolysis of the polyamide were carried out.

A 0.78-g. portion of polyamide A and 1.8 g. of ethylenediamine were heated at 200°C. under a nitrogen atmosphere for 6 hr. The reaction mixture was completely soluble in water at room temperature. On the other hand, heating of polymer A at 200°C. for 6 hr. under a nitrogen atmosphere neither produced a detectable change in its infrared spectrum, nor gave a product soluble in boiling water. These results indicate that aminolysis which caused transamidation occurs to a considerable extent in this polymerizing system.

The aminolysis mentioned above was, however, carried out with a much higher amine concentration than the case of polyadditions. In order to determine to what extent the detailed structure of the polymer was really disturbed by the transamidation under the actual reaction condition of equimolar polyadditions, the difference in the melting points and x-ray diffraction diagrams of polymers, C, D, and E, were compared.

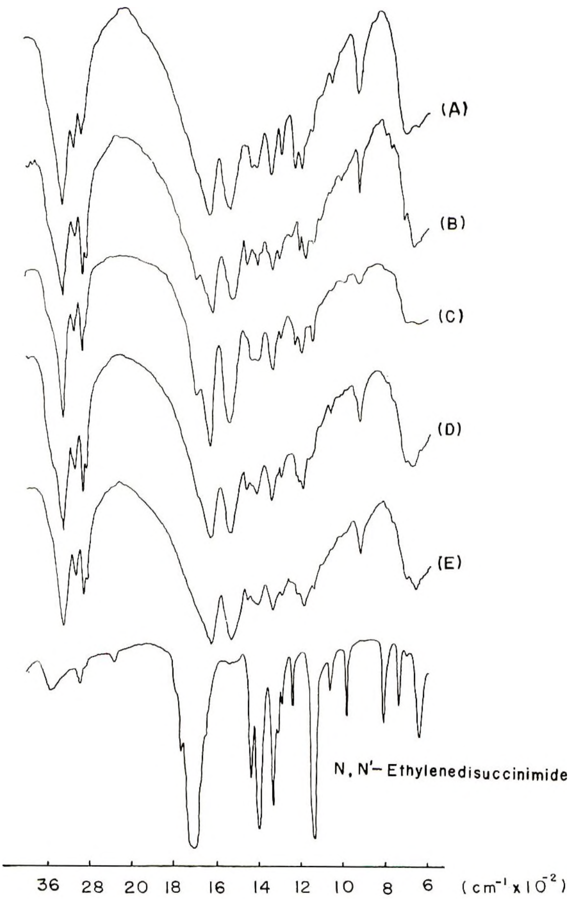


Fig. 1. Infrared spectra of polymers A–E.

Polymers C, D, and E which were confirmed to have almost same composition by elementary analysis have different melting points, as shown in Table I. The conspicuously low melting point of polymer E must be attributed to the irregularity of the sequences of amide units in that polymer. Polymers C and D must have a considerably more regular structure than polymer E. Therefore, at least some parts of the chain of polymers C and D are considered to retain ordered sequences of 24 and 64 amide groups, and the structure of polymer C was less disturbed by the transamidation than that of the polymer D.

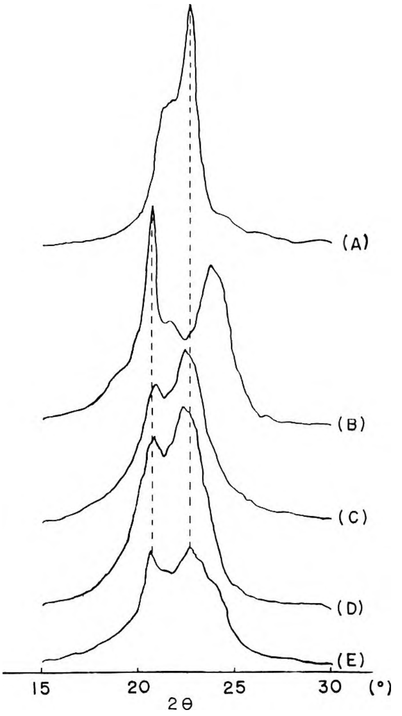


Fig. 2. X-ray diffraction diagrams of polymers A–E.

The x-ray diffraction diagrams of the polymers and the 2θ angles are shown in Figure 2 and Table II. The x-ray diffraction diagrams of polymers C, D, and E displayed two peaks. The peak of polymer E at the higher angle was at the same angle as the characteristic peak for polymer A, and another peak was at the same angle as the characteristic peak of polymer B. It follows that two peaks of polymer E indicate the presence of blocks of 2-4 sequences [—NH—$(CH_2)_2$—NHCO—$(CH_2)_2$—CO—], and 6-4 sequences [—NH—$(CH_2)_6$—NHCO—$(CH_2)_2$—CO—]. On the other hand, as shown in Table II, the 2θ angles of the two peaks of polymer C were equal to those of the polymer D, but different from those of polymer E.

TABLE II

Bragg Angles 2θ of the X-Ray Diffraction Diagrams of the Polymers

Polymer	Mean 2θ, degrees[a]
A	20.6 (shoulder), 22.69 ± 0.01
B	20.78 ± 0.03, 23.88 ± 0.02
C	20.89 ± 0.02, 22.49 ± 0.03
D	20.89 ± 0.02, 22.51 ± 0.02
E	20.73 ± 0.02, 22.69 ± 0.03

[a] The mean value of three measurements, ± the average deviation from the mean.

These results lead to the conclusion that polymers C and D have a crystalline portion with other than 2-4 and 6-4 sequences, and, considering the reaction mechanism, it is suggested that this crystalline part consists of 2-4-6-4 sequences:

$$—[NH—(CH_2)_2—NHCO—(CH_2)_2—CONH—(CH_2)_6—NHCO—(CH_2)_2—CO]_n—$$

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Résumé

Des polyamides qui contiennent des unités succinamides $\{NHCO—(CH_2)_2—CO-NH\}$ ont été préparés par polyaddition avec ouverture de cycle de bissuccinimides avec des diamines à 200°C en bloc. Les nylons 24 et nylons 64 ont été ainsi préparés par réaction du *N*,*N*'-éthylènedisuccinimide avec l'éthylènediamine, et par le *N*,*N*'-hexaméthylènedisuccinimide avec l'hexaméthylènediamine, respectivement. On admet que la réaction de transamidation par aminolyse influence les structures détaillées des polymères préparés au départ de N,N'-éthylènedisuccinimide et hexaméthylènediamine et au départ de *N*,*N*'-hexaméthylènedisuccinimide et l'éthylènediamine. Les structures détaillées des polymères ont été discutées sur la base de leur point de fusion et les diagrammes aux rayons-X, et on en conclut que les polymères ont une partie cristalline due à des séquences $\{NH—(CH_2)_2—NHCO—(CH_2)_2—CONH—(CH_2)_6—NHCO—(CH_2)_2—CO\}$.

Zusammenfassung

Polyamide mit Succinamidbausteinen $\{NHCO—(CH_2)_2—CONH\}$ wurden durch die Ringöffnungspolyaddition von Bissuccinimiden mit Diaminen bei 200°C in Substanz dargestellt. Nylon-24 und Nylon-64 wurden durch die Reaktion von *N*,*N*'-Äthylendisuccinimid mit Äthylenediamin, bzw. durch diejenige von *N*,*N*'-Hexamethylendisuccinimid mit Hexamethylendiamin erhalten. Es wird angenommen, dass die Struktureinzelheiten der aus *N*,*N*'-Äthylendiscuccinimid und Hexamethylendiamin sowie aus *N*,*N*'-Hexamethylendisuccinimid und Äthylendiamin dargestellten Polymeren durch die aminolytische Transamidierungsreaktion beeinflusst werden. Die Struktureinzelheiten der Polymeren wurden auf Grundlage ihrer Schmelzpunkte und Röntgendiagramme diskutiert; man kam zu dem Schluss, dass die Polymeren einen kristallinen Anteil mit $\{NH—(CH_2)_2—NHCO—(CH_2)_2—CONH—(CH_2)_6—NHCO—(CH_2)_2—CO\}$ Sequenzen besitzen.

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Boundary Effect on the Thermal Degradation of Copolymers

YOSHIO SHIBASAKI, *Polymer Research Division,*
Institute of Space and Aeronautical Science,
The University of Tokyo, Tokyo, Japan

Synopsis

The mechanism of thermal degradation of vinyl-type copolymers at high temperatures was investigated theoretically and experimentally. A parameter β was proposed to account for the boundary effect. Values of β for acrylonitrile–styrene and methyl methacrylate–styrene copolymers were determined experimentally. It was ascertained that the value of β was independent of the distribution of monomer sequence lengths in a copolymer, but dependent on the pyrolysis temperature and on the nature of the copolymer. The boundary effect is attributed to differences in the dissociation energies of C—C bonds connecting terminal monomer units to adjacent monomer units in copolymer chain radicals.

INTRODUCTION

The yields of monomers obtained from the thermal decomposition of copolymers generally differ from those obtained in homopolymer decompositions.[1-12] This phenomenon was ascribed by Wall[5,13,14] to a boundary effect, the yield of monomer obtained from a copolymer pyrolysis reaction being influenced by the sequence distribution of monomer units in the copolymer. Wall defined a parameter θ for the boundary effect as

$$\theta = 2\left(\frac{\text{internal monomer bonds broken}}{\text{internal monomer bonds in polymer}}\right)$$

and obtained values of the parameter for several copolymers.

The objectives of the present work are to propose another parameter which gives physical meaning to the boundary effect and to investigate the influence of side groups or the sequence distribution in a copolymer chain on its decomposition. As a result, it has been ascertained that the boundary effect is due mainly to the influence of penultimate units on the stability of depropagating copolymer chain radicals. A boundary-effect parameter β for acrylonitrile–styrene and methyl methacrylate–styrene copolymers was determined experimentally from the monomer yields obtained on pyrolysis.

So far, nuclear magnetic resonance, infrared spectroscopy, and many other techniques have been used for the determination of sequence distribution in copolymers.[15] In this paper, it is proposed that rapid thermal degradation techniques may be useful for the determination of sequence distribution in copolymers whose boundary effects are relatively large.

THEORETICAL

Mechanism of Thermal Decomposition

At relatively high temperatures, the C—C chain bonds of vinyl polymers are generally ruptured at random by the thermal motions of the polymer chain. Unzipping of monomer units from the resulting free-radical chain ends then takes place. The zip length, i.e., the number of monomer units which split off from the free-radical chain end, generally increases as temperatures are increased up to 850°C., but pyrolysis of regenerated monomer results in decreased monomer yields at temperatures above 650°C.[1]

The activation energy for the decomposition of linear polymers is affected by side groups in the polymer chain, as previously discussed by Wall.[16] Since dissociation energies of the C—C bonds in organic compounds vary, the activation energies for the scission of C—C bonds at different sites in polymer chains differ from each other. The influence of side groups on the dissociation energy of C—C bonds may be attributed to resonance and steric and polar effects.

Let us consider the thermal decomposition of a typical vinyl-type copolymer: one with a predominantly head-to-tail structure and a molecular chain sufficiently long that end effects may be neglected. As a first approximation, a relatively short zip length will be assumed. The errors involved in making such an assumption will be dealt with later.

During the pyrolysis of an A–B copolymer, A type monomer units may split off from the free-radical chain ends as shown in

$$\cdot\mathrm{CHA{-}CH_2}\underset{\mathrm{I}}{\vdots}\mathrm{CHA{-}CH_2}\sim\sim \rightarrow \mathrm{CHA{=}CH_2} + \cdot\mathrm{CHA{-}CH_2}\sim\sim \qquad (1)$$

$$\cdot\mathrm{CHA{-}CH_2}\underset{\mathrm{II}}{\vdots}\mathrm{CHB{-}CH_2}\sim\sim \rightarrow \mathrm{CHA{=}CH_2} + \cdot\mathrm{CHB{-}CH_2}\sim\sim \qquad (2)$$

$$\cdot\mathrm{CH_2{-}CHA}\underset{\mathrm{III}}{\vdots}\mathrm{CH_2{-}CHA}\sim\sim \rightarrow \mathrm{CH_2{=}CHA} + \cdot\mathrm{CH_2{-}CHA}\sim\sim \qquad (3)$$

$$\cdot\mathrm{CH_2{-}CHA}\underset{\mathrm{IV}}{\vdots}\mathrm{CH_2{-}CHB}\sim\sim \rightarrow \mathrm{CH_2{=}CHA} + \cdot\mathrm{CH_2{-}CHB}\sim\sim \qquad (4)$$

Similar reactions may be written for the formation of B monomer units. All the A units formed during the decompositon process must result from the decomposition of radicals as shown in eqs. (1)–(4). If a bond other than those marked is ruptured, however, an A monomer unit will not be liberated. The C—C bond dissociation energies at the dashed points in eqs. (1)–(4) differ from each other. In particular, there is a significant difference between the dissociation energies for eqs. (1) and (2), since the resulting chain radicals will differ in stability. Therefore, the nature of the penultimate unit has a remarkable influence on the probability that a C—C bond will cleave at a dashed point and liberate a monomer unit.

The Parameter β_A of the Boundary Effect

If the unzipping reaction of a vinyl-type A–B copolymer occurs according to the eqs. (1) and (2), the probability that structure I ($\cdot AA\sim \rightarrow A + \cdot A\sim$) will yield a regenerated monomer unit [eq. (1)] may differ from the corresponding probability for eq. (2) ($\cdot AB\sim \rightarrow A + \cdot B\sim$). The ratio of these probabilities, designated the boundary effect parameter, β_A, may be adopted as a measure of the boundary effect.

The boundary effect parameter β_A is defined as follows:

$$\beta_A = P_{AB}/P_{AA} \tag{5}$$

where P_{AA} and P_{AB} are, respectively, the probabilities that A type monomer units will result from the decomposition of radicals in eqs. (1) and (2). In addition, if the depolymerization reaction of an A–B copolymer proceeds according to eqs. (3) and (4), another parameter, $\beta_A' = P_{AB}'/P_{AA}'$, may be defined, where P_{AA}' and P_{AB}' are the probabilities of reproducing A type monomers in eqs. (3) and (4), respectively. The parameters, β_A and β_A', should be constants which depend only on the pyrolysis temperature and on the nature of the copolymer studied. When β_A is less than unity, the probability of regenerating an A monomer unit is less for the copolymer than for the homopolymer. When β_A is larger than unity, the converse is true. If β_A is equal to unity, the yield of A obtained from the A–B copolymer is identical with that obtained from the homopolymer of A.

A parameter for characterizing the sequence distribution in copolymers, the run number R, was defined by Harwood.[17] This quantity is the average number of monomer sequences (runs) occurring in a copolymer per 100 monomer units. Similarly, we can define the run fraction R_f, which is the sum of the number fraction of A and B runs in a copolymer. Every A type monomer sequence (A run) in an A–B copolymer is followed by an A–B linkage and there are as many A runs as B runs in the copolymer. Then:

$$\text{number fraction of A–B linkages} = R_f/2$$

$$\text{number fraction of B–A linkages} = R_f/2$$

$$\text{number fraction of A–A linkages} = \Phi_A - R_f/2$$

$$\text{number fraction of B–B linkages} = \Phi_B - R_f/2$$

where Φ_A is the molar fraction of A monomer units in the copolymer.

The yield of A monomer units obtained in a pyrolysis experiment, $Y(\mathrm{A})$, as the molar fraction of all units initially present, may be written as follows.

$$Y(\mathrm{A}) = [\Phi_{\mathrm{A}} - (R_f/2)]P_{\mathrm{AA}} + (R_f/2)P_{\mathrm{AB}} \tag{6}$$

Using the definition of β_{A} given by eq. (5), we obtain:

$$Y(\mathrm{A}) = P_{\mathrm{AA}}[\Phi_{\mathrm{A}} - (R_f/2)(1 - \beta_{\mathrm{A}})] \tag{7}$$

P_{AA} can be shown to be equal to the fractional yield of monomer obtained from the homopolymer of A, $Y_0(\mathrm{A})$, since the run fraction R_f is zero and Φ_{A} is unity for the homopolymer of A. Hence:

$$P_{\mathrm{AA}} = Y_0(\mathrm{A}) \tag{8}$$

The run fraction of copolymer formed instantaneously from a given feed composition is predicted by eq. (9), where r_1 and r_2 are the reactivity ratios according to the terminal model, and where x is the molar ratio of monomers (A/B) in the feed.[16]

$$R_f = 2x/(r_1x^2 + 2x + r_2) \tag{9}$$

Then:

$$\beta_{\mathrm{A}} = 1 - \left[\Phi_{\mathrm{A}} - \frac{Y(\mathrm{A})}{Y_0(\mathrm{A})}\right]\left(\frac{r_1x^2 + 2x + r_2}{x}\right) \tag{10}$$

Therefore, if the values of r_1, r_2, x, Φ_{A}, and $Y_0(\mathrm{A})$ are known, the value of β_{A} can be determined from the measured value of $Y(\mathrm{A})$.

Relation Between the Parameter β_{A} and the Dissociation Energy

On the assumptions that all the pyrolysis products come from free-radical chain ends by unimolecular processes only and that regenerated monomer units do not decompose or recombine with radical chain ends, the probability P_{AB} of splitting off an A monomer unit from a free-radical chain end of type II can be expressed as follows:

$$\begin{aligned} P_{\mathrm{AB}} &= k_{\mathrm{MAB}}[F_{\mathrm{AB}}]/(k_{\mathrm{MAB}}[F_{\mathrm{AB}}] + k_{\mathrm{OAB}}[F_{\mathrm{AB}}]) \\ &= k_{\mathrm{MAB}}/(k_{\mathrm{MAB}} + k_{\mathrm{OAB}}) \end{aligned} \tag{11}$$

where $[F_{\mathrm{AB}}]$ is the concentration of appropriate free-radical chain ends, k_{MAB} is the velocity constant for monomer regeneration, and k_{OAB} is the sum of the velocity constants for processes leading to products other than monomer. The velocity constants of each reaction, however, are not known individually at present. The constant k_{MAB} can be expressed in terms of the Arrhenius equation:

$$k_{\mathrm{MAB}} = A_{\mathrm{MAB}} \exp\{-E_{\mathrm{MAB}}/RT\} \tag{12}$$

Concerning the probability, P_{AA}, similarly,

$$\begin{aligned} P_{AA} &= k_{MAA}[F_{AA}]/(k_{MAA}[F_{AA}] + k_{OAA}[F_{AA}]) \\ &= k_{MAA}/(k_{MAA} + k_{OAA}) \end{aligned} \tag{13}$$

and

$$k_{MAA} = A_{MAA} \exp\{-E_{MAA}/RT\} \tag{14}$$

Therefore, the boundary effect parameter β_A is given by eq. (15):

$$\begin{aligned} \beta_A &= P_{AB}/P_{AA} \\ &= [k_{MAB}/(k_{MAB} + k_{OAB})]/[k_{MAA}/(k_{MAA} + k_{OAA})] \end{aligned} \tag{15}$$

The constant k_{MAB} is not equal to k_{MAA}, because, as mentioned above, the activation energies for the monomer regeneration steps, i.e., E_{MAB} and E_{MAA}, are not equal to each other, due to radical stabilization effects. During rapid thermal degradation at high temperatures, however, the overall rate of decomposition of free-radical chain ends may be assumed to be a constant which depends only on pyrolysis temperature, regardless of the nature of the neighboring unit. The values of the velocity constants are of the same order, i.e., $k_{MAB} \geq k_{OAB}$ and $k_{MAA} \geq k_{OAA}$. The value of k_{MAB} increases when the value of k_{OAB} decreases and vice versa. It may be assumed, that the term $(k_{MAB} + k_{OAB})$ is nearly equal to the term $(k_{MAA} + k_{OAA})$. In situations where $k_{MAB} \gg k_{OAB}$ and $k_{MAA} \gg k_{OAA}$, as would be the case when zip lengths are very long, the probabilities P_{AB} and P_{AA} approach unity, and monomers are regenerated almost quantitatively. In this case, the parameter β_A becomes unity, and it is nonsense to consider the boundary effect. Therefore, we neglect this case in this investigation, and assume, as a first approximation, that β_A can be calculated by the expression:

$$\beta_A = k_{MAB}/k_{MAA} \tag{16}$$

From eqs. (12), (14), and (16), the parameter β_A can be derived as follows:

$$\beta_A = (k_{MAB}/k_{MAA}) \exp\{-(E_{MAB} - E_{MAA})/RT\} \tag{17}$$

In either case I or II, the activation energies for splitting off monomers, E_{MAB} and E_{MAA}, are not exactly equal to the dissociation energies Q_{AB} and Q_{AA}, respectively. However, it is not unreasonable to assume that the difference between E_{MAB} and E_{MAA} should be equal to the difference between Q_{AB} and Q_{AA}, since the activation energies of the back reactions (monomer addition) may be only a few kilocalories, and the difference between these activation energies is negligibly small compared to the difference between those for the forward reactions. Then, an approximate value of β_A is obtained by eq. (18):

$$\beta_A = (A_{MAB}/A_{MAA}) \exp\{-(Q_{AB} - Q_{AA})/RT\} \tag{18}$$

The magnitude of the pre-exponential factor for breakdown of the free radicals of almost all hydrocarbons is about 10^{13} sec.$^{-1}$.[17] Hence, it may be supposed that the ratio $A_{\mathrm{MAB}}/A_{\mathrm{MAA}}$ is nearly equal to unity, and β_A is mainly affected by the magnitude of the difference between the two dissociation energies. If the dissociation energies, Q_{AB} and Q_{AA}, can be estimated by a proper method, the magnitude of β_A can then be estimated.

Estimation of the Dissociation Energies of C—C Bonds

Simple equations for estimating the dissociation energies of C—C bonds have been proposed by Vedeneev[18] and by Errede.[19] In this work, the semiempirical method proposed by Vedeneev was used. The dissociation energy, Q_{R-X}, of a bond in a molecule, R—X, can be represented as follows:

$$Q_{R-X} = E_{R-X}' - (B_R + B_X) \tag{19}$$

where E_{R-X}' is the specific energy for a given type of bond, i.e., C—C, C—H, and C—Br, etc., and where B_R and B_X are the stabilization energies of the radicals R and X, respectively. In general, B_R and B_X can be calculated by relationships of the following type shown in eq. (20) where M_i

$$B_R = \sum_m M_i\alpha_i \exp\{-\omega m\} + aE_{\mathrm{conj}} \tag{20}$$

is the number of bonds of type i which are bonded with the mth carbon from the bond under consideration, where α_i is the specific value of the stabilization due to a given bond type, and where $\exp\{-\omega\}$ is a coefficient having the value 0.4. In this relationship, a is the number of conjugated groups adjacent to the bond under consideration and E_{conj} is the stabilization energy imparted to a free radical by a conjugated group. The general expression for Q_{R-X}, then, is that given by eq. (21):

$$Q_{R-X} = E_{R-X}' - (\sum_m M_i\alpha_i \exp\{-\omega m\} + aE_{\mathrm{conj}}) - (\sum_n N_i\alpha_i \exp\{-\omega n\} + bE_{\mathrm{conj}}) \tag{21}$$

It may be understood from eq. (21) that the bonds five or six atoms removed from the bond in question do not have much influence on the Q_{R-X} value. Values of the α, E_{R-X}', and E_{conj} parameters determined from experimental data on the dissociation energies of the bonds in simple hydrocarbons are shown in Table I.

In Table II, C—C bond dissociation energies calculated by Vedeneev's equation and several values observed for relatively complicated hydrocarbons are shown. The calculated values are in agreement with the observed ones within about 3 kcal./mole. Hence, it seems to be reasonable to apply Vedeneev's method to calculate the dissociation energies of C—C chain bonds in polymers.

TABLE I

The Values of the Constants in Vedeneev's Equation

Constant	Value
$\exp\{-\omega\}$	0.4
$\alpha_{\mathrm{C-H}}$	10 kcal./mole
α_{π}	11 kcal./mole
$B_{-\mathrm{C_6H_5}}$	26 kcal./mole
$B_{-\mathrm{C\equiv N}}$[a]	8.3 kcal./mole
$\alpha_{\mathrm{C-F}}$	8.2 kcal./mole
$E_{\mathrm{C-C}}'$[b]	143.3 kcal./mole
$E_{\mathrm{C-H}}'$	127.8 kcal./mole
$E_{\mathrm{C-Cl}}'$	109.3 kcal./mole
$E_{\mathrm{C-F}}'$	143.8 kcal./mole
$E_{\mathrm{C-I}}'$	79.0 kcal./mole
E_{conj}	19.4 kcal./mole

[a] By using the bond dissociation energy, $Q_{\mathrm{CH_3-CN}} = 105$ kcal./mole,[20] the $B_{\mathrm{C\equiv N}}$ value was determined as $B_{-\mathrm{C\equiv N}} = E_{\mathrm{C-C}}' - Q_{\mathrm{CH_3-CN}} - 3\alpha_{\mathrm{C-H}} = 143.3 - 105 - 30 = 8.3$ kcal./mole.

[b] The value of $E_{\mathrm{C-C}}'$ was determined from the reported data of bond dissociation energies for ten hydrocarbons.[20]

TABLE II

Dissociation Energies of the C—C Bonds of Hydrocarbons

Compound	$Q_{\mathrm{C-C}}$, kcal./mole Calc.[a]	Obs.[b]	Difference, kcal./mole
n-$\mathrm{C_3H_7}$—n-$\mathrm{C_3H_7}$	77.7	76	+1.1
n-$\mathrm{C_4H_9}$—n-$\mathrm{C_3H_7}$	77.4	75	+2.4
n-$\mathrm{C_4H_9}$—n-$\mathrm{C_4H_9}$	77.1	74	+3.1
$\mathrm{C_6H_5CH_2}$—n-$\mathrm{C_3H_7}$	60.7	59	+1.7
$\mathrm{C_6H_5CH_2}$—n-$\mathrm{C_3H_7}$	60.7	65.0[d]	−4.3
$\mathrm{C_6H_5CH_2}$—n-$\mathrm{C_4H_9}$	60.4	57.5	+2.9
$\mathrm{C_6H_5CH_2}$—$\mathrm{CH_2C_6H_5}$	43.7	47[c]	−3.3
$\mathrm{CH_2{=}CHCH_2}$—n-$\mathrm{C_3H_7}$	59.5	57.5	+2.0
$\mathrm{CH_2{=}CHCH_2}$—$\mathrm{CH_2CH{=}CH_2}$	41.4	38	+3.4
$\mathrm{CH_2{=}CHCH_2}$—n-$\mathrm{C_4H_9}$	59.2	56.5	−2.7

[a] Calculated by Vedeneev's equation.

[b] Data of Szwarc[20] unless otherwise noted.

[c] Data of Szwarc and Taylor.[21]

[d] Data of Leigh and Szwarc.[22]

Sequence Distribution in Copolymers

As mentioned above, we can define the sequence distribution parameter R_f for A type monomers in a given copolymer. If the boundary effect parameter, β_{A}, for an A–B type copolymer has been previously determined from thermal degradation studies, it is possible to compute the sequence distribution parameter R_f for a given A–B copolymer from eq. (22) which is derived from eqs. (7) and (8).

$$R_f = 2[\Phi_{\mathrm{A}} - Y(\mathrm{A})/Y_0(\mathrm{A})]/(1 - \beta_{\mathrm{A}}) \qquad (22)$$

For B monomer units, the boundary effect parameter β_B can be determined in a similar way:

$$\beta_B = 1 - [\Phi_B - Y(B)/Y_0(B)][(r_1x^2 + 2x + r_2)/x] \tag{23}$$

EXPERIMENTAL

Copolymers of styrene with acrylonitrile and methyl methacrylate having widely varied compositions were synthesized at low conversions (5–10%). These samples were pyrolyzed at temperatures of 400–700°C. in a stream of nitrogen gas by using the degradation apparatus shown in Figure 1. The thermal decomposition products were analyzed by means of a gas chromatograph. On turning the glass joint (c) a pellet of sample (15 mg.) was dropped from the tray (b) to the bottom of the quartz pyrolysis tube (d). The sample decomposed instantaneously at the desired temperature. The change in the temperature during pyrolysis of the sample was negligible, since the heat capacity of the sample was small compared to that of the pyrolysis tube. The diameter of the pyrolysis tube was 10 mm. and the depth (from b to d), was about 100 mm. The volatile pyrolysis products were directly swept into the column of the gas chromatograph with nitrogen gas for analysis before thermal decomposition of monomer or its repolymerization could occur.

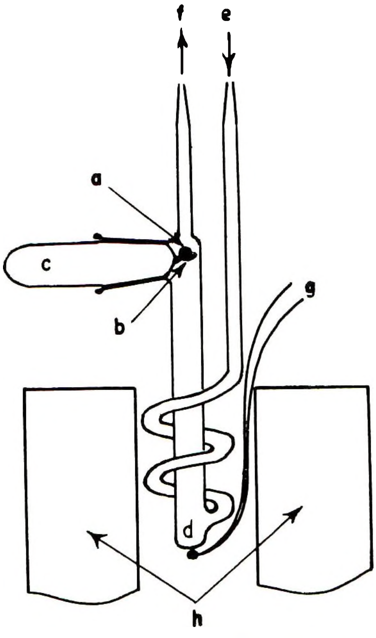


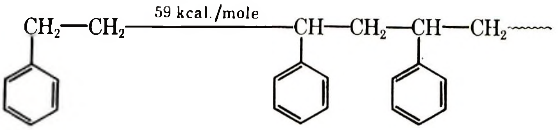
Fig. 1. Pyrolysis apparatus: (a) sample; (b) turning tray; (c) glass joint; (d) quartz pyrolysis tube; (e) carrier gas; (f) pyrolysis products and carrier gas; (g) thermocouple; (h) electric furnace.

RESULTS AND DISCUSSION

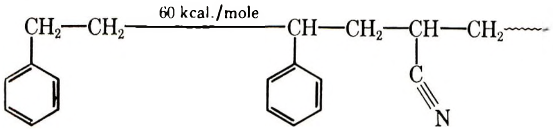
Acrylonitrile–Styrene Copolymer

In Figure 2, a typical gas chromatogram of the pyrolysis products obtained from an acrylonitrile–styrene copolymer is shown. In Figure 3, the values of β_{AN} and β_{St} are plotted against the copolymer compositions. The parameters β_{AN} and β_{St} were determined from eqs. (10) and (23), respectively. Although these plots were slightly dispersed, the values of β_{AN} and β_{St} might be regarded as constants, independent of the copolymer composition. As defined above, these parameters should be independent of copolymer composition and sequence distribution.

In the case of acrylonitrile–styrene copolymers, the influence of the side groups on the bond dissociation energies were estimated from eq. (21). As an example, calculated bond dissociation energies for several bonds [eqs. (24)–(28)] are shown,



(24)



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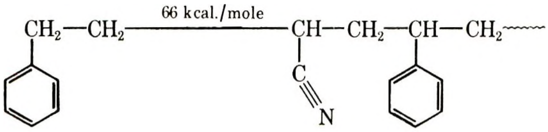
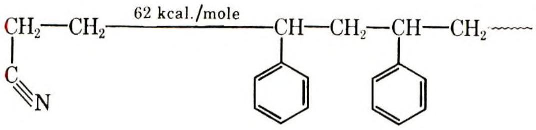
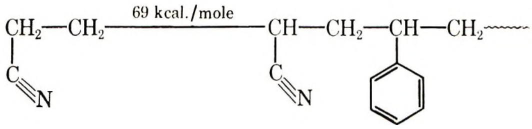


(26)



(27)



(28)

In these cases, the dissociation energies were computed for chains having saturated ends, since precise values of C—C bond dissociation energies are not available for cases where the chains have free-radical ends. For the regeneration of a vinyl-type monomer by the cleavage of a bond β to a carbon atom bearing a free radical, the dissociation energy of that bond is decreased about 50 kcal./mole since a π bond is established in the monomer during the cleavage step.[17] This effect might be about the same for both

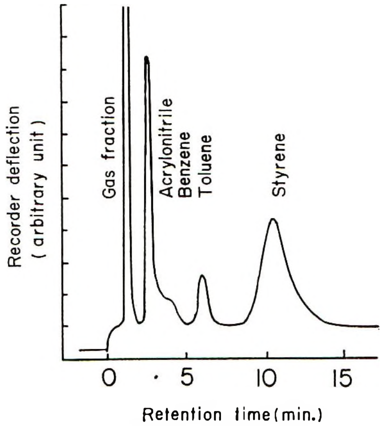


Fig. 2. Typical gas chromatogram of pyrolysis products of acrylonitrile–styrene copolymer (AN 38.3 mole-%). Pyrolysis temperature, 600°C.; sample size, 15 mg.; column, silicone DC-550 on Celite, 3 m., 160°C.; carrier gas N_2, 27 ml./min.

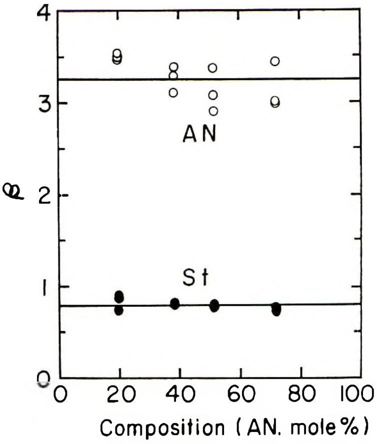
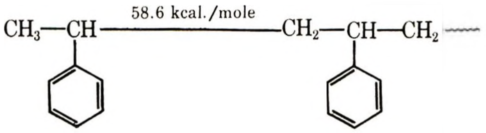


Fig. 3. Boundary effect parameters of acrylonitrile–styrene copolymers on pyrolysis at 600°C. in a stream of N_2.

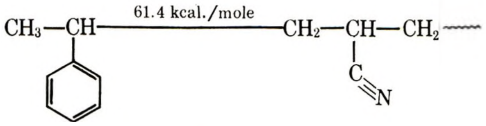
acrylonitrile and styrene units. Therefore, the difference between the calculated C—C bond dissociation energies should correspond with that of the dissociation energies of the corresponding bonds in the free-radical chains. Depending on the nature of the penultimate monomer unit, the dissociation energy of the C—C chain bond varies by 7 kcal./mole. In addition to this, the Q_{C-C} values varied about 1 kcal./mole by the nature of the penpenultimate monomer unit. Consequently, it is reasonable to consider that the dissociation energy of the C—C bond for splitting off a terminal monomer unit is determined mainly by the side groups or atoms of the penultimate monomer unit. Therefore, the previous assumption that the magnitude of the boundary effect depends mainly on the nature of the nearest neighboring monomer unit seems to be acceptable.

As shown from eqs. (24)–(28), the dissociation energy of the secondary C—C bond is increased due to the penultimate acrylonitrile unit, and hence the probability that a styrene radical end will become a styrene unit decreases with the acrylonitrile content in the copolymer. This prediction coincides well with the experimental results.[1]

If a terminal monomer unit splits off as shown in (29) and (30) the variation of the dissociation energy of the C—C bond ($Q_{SA} - Q_{SS}$) is smaller than the case shown in (24)–(28)



(29)



(30)

In Figure 4, the influence of the degradation temperature on values of β_{AN} and β_{St} is shown. These values were computed on the basis of monomer yields from the copolymer which was pyrolyzed at various temperatures for 1.5 min. in nitrogen. The boundary effect was greater at relatively lower temperatures and it became smaller at higher temperatures. Therefore, it is reasonable to assume that the sensitivity of the boundary effect to temperature is caused by the difference in the activation energies for radical decomposition.

From eq. (18),

$$\log \beta_A = \log (A_{MAB}/A_{MAA}) - [(Q_{AB} - Q_{AA})/2.303RT] \qquad (31)$$

In Figure 5, values of $\log \beta_A$ and $\log \beta_B$ which were determined experimentally from 430°C. to 640°C. are plotted against the reciprocal of absolute

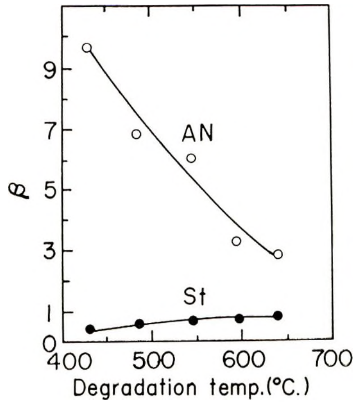


Fig. 4. Effect of the degradation temperature on the boundary effect parameters of acrylonitrile–styrene copolymers pyrolyzed for 1.5 min. in N_2.

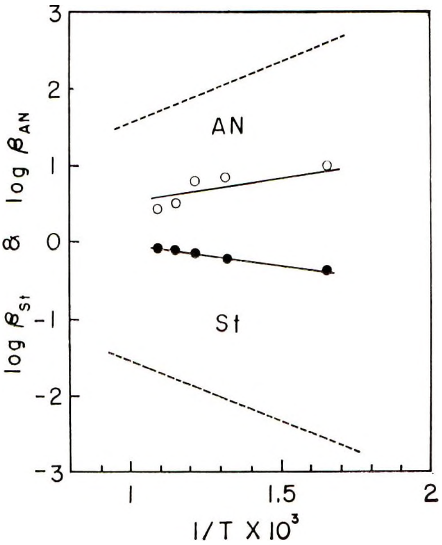


Fig. 5. Estimation of the values of ($Q_{AS} - Q_{AA}$) and ($Q_{SA} - Q_{SS}$).

temperature. Values of ($Q_{SA} - Q_{SS}$) and ($Q_{AS} - Q_{AA}$) were determined from the gradients of these lines; $Q_{SA} - Q_{SS} = 2.56$ kcal./mole, and $Q_{AS} - Q_{AA} = -2.56$ kcal./mole. Two dashed lines in Figure 5 show the values of log β_{St} and log β_{AN} calculated from eq. (31) by assuming that the values of (A_{MSA}/A_{MSS}) and (A_{MAS}/A_{MAA}) are unity. For reactions of the type shown in eqs. (24)–(28), the values of ($Q_{SA} - Q_{SS}$) and ($Q_{AS} - Q_{AA}$) are 7 kcal./mole and -7 kcal./mole, respectively. For the case of eqs. (29) and (30), $Q_{SA} - Q_{SS} = 2.8$ kcal./mole and $Q_{AS} - Q_{AA} = -2.8$ kcal./mole. The experimental data seem to correspond more closely to the latter type. In either case the observed values of ($Q_{AB} - Q_{AA}$) were less than the calculated values.

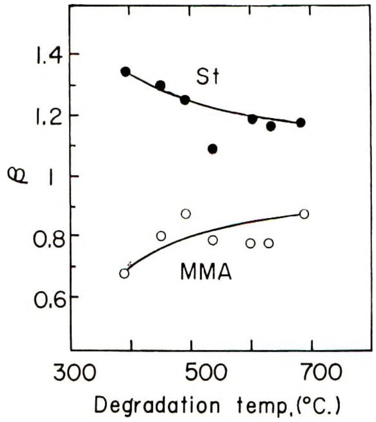


Fig. 6. Effect of degradation temperature on the boundary effect parameters of methyl methacrylate–styrene copolymer.

Methyl Methacrylate-Styrene Copolymers

The observed values of β_{MMA} and β_{St} were constant, independent of the copolymer composition at any temperature. The yield of styrene monomer obtained from the copolymer was greater than that from polystyrene, and β_{St} was therefore greater than unity. On the other hand, β_{MMA} was less than unity. In Figure 6, the influence of the degradation temperature on the boundary effects for methyl methacrylate–styrene copolymers is shown. The boundary effect of this copolymer became smaller at high temperatures also. In Figure 7, the values of $\log \beta_{St}$ and $\log \beta_{MMA}$ are plotted against the reciprocal of absolute temperature. From the gradients of these lines the values of $(Q_{SM} - Q_{SS})$ and $(Q_{MS} - Q_{MM})$ were determined to be −0.71 and 0.71 kcal./mole, respectively.

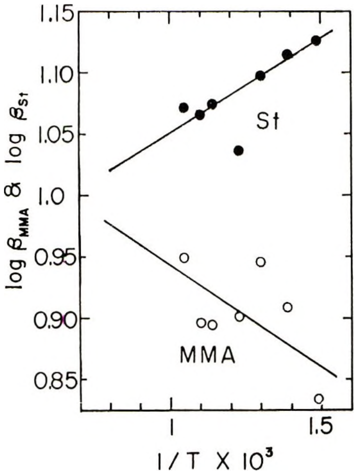


Fig. 7. Estimation of the values of $(Q_{MS} - Q_{MM})$ and $(Q_{SM} - Q_{SS})$.

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Résumé

Un mécanisme de dégradation thermique de copolymères de type vinylique à des températures élevées a été étudié théoriquement et expérimentalement. Un paramètre β a été proposé pour rendre compte des effets de frontière. Les valeurs de β pour les copolymères acrylonitrile–styrène et méthacrylate de méthyle-styrène ont été déterminées expérimentalement. On a prouvé que les valeurs de β étaient indépendantes de la distribution des longueurs des séquences d'un monomère au sein d'un copolymère, mais dépendante de la température de pyrolyse et de la nature du copolymère. Les effets de frontière étaient attribués à des différences des énergies de dissociation des liens C—C reliant le monomère terminal aux unités monomériques adjacentes au sein des radicaux des chaines copolymériques.

Zusammenfassung

Der Mechanismus der thermischen Abbaus von Copolymeren vom Vinyltyp bei hohen Temperaturen wurde theoretisch und experimentell untersucht. Ein Parameter β wurde zur Berücksichtigung des "Boundary Effect" eingeführt. β-Werte wurden für Acrylnitril–Styrol- und Methylmethacrylat–Styrolcopolymere experimentell bestimmt. Es wurde festgestellt, dass der β-Wert unabhängig von der Verteilung der Monomersequenzlängen in einem Copolymeren, aber abhängig von der Pyrolysetemperatur und von der Natur des Copolymeren ist. Der "Boundary Effect" wird auf Unterschiede in den Dissoziationsenergien der C—C-Bindungen zwischen dem endständigen Monomerbaustein und dem benachbarten Monomerbaustein in einem Copolymerkettenradikal zurückgeführt.

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Complex Formation between Catalysts, Alcohols, and Isocyanates in the Preparation of Urethanes

K. C. FRISCH, S. L. REEGEN, and W. V. FLOUTZ, *Wyandotte Chemicals Corporation, Wyandotte, Michigan 48192*, and J. P. OLIVER, *Chemistry Department, Wayne State University, Detroit, Michigan*

Synopsis

The mechanism of the catalyzed reaction between alcohols and isocyanates was investigated by means of NMR, infrared, and ultraviolet spectroscopy. The shift of the —OH proton resonance in the NMR spectra indicated the existence of a 1:1 complex in the system dibutyltin dilaurate (DBTDL)–1-methoxy-2-propanol. Complex formation was also observed when lead naphthenate or triethylamine (TEA) were substituted for the DBTDL. Mixtures of the DBTDL–TEA catalysts caused a shift of the —OH proton resonance greater than that observed for either catalyst alone. This correlates with the synergistic effect noted when preparing urethanes with a mixture of these catalysts. No direct evidence of alcohol–catalyst complex formation could be obtained by infrared spectroscopy. Efforts were also made to detect complex formation in mixtures of phenyl isocyanate and catalysts. These complexes could not be detected by NMR, infrared, or ultraviolet spectroscopy.

INTRODUCTION

It has been shown that the reaction rates of methoxypropanols with phenyl isocyanate are influenced by the proximity of the methoxy and methyl groups to hydroxyl as well as by the type and concentration of metal catalyst.[1,2] It was also shown that dibutyltin dilaurate catalysis resulted in significantly higher rates in reaction of 3-methoxy-1-propanol than were obtained by catalysis with lead naphthenate. Conversely, Pb catalysis resulted in higher rates for the reactions of 1-methoxy-2-propanol and 2-methoxy-1-propanol than were obtained by catalysis with Sn. These apparent variations in catalytic activity have led to further attempts to elucidate the mechanisms involved, including a search for evidence of complex formation (by the interaction of these catalysts with alcohol and isocyanate).

EXPERIMENTAL

NMR spectra were recorded on a Varian Model DP-60 and a Varian Model A-60 spectrometer at ambient temperatures. The former spectra were calibrated by using the audiofrequency sideband technique. The chemical shift was expressed in terms of the parameter δ (in ppm), tetramethylsilane (TMS) or cyclohexane being used as the internal reference. When cyclohexane was used as solvent and internal standard, chemical shift values were converted to correspond to a TMS reference (assuming 86 cps separation between TMS and cyclohexane at 60 Mc./sec.). Infrared spectra were recorded on a Perkin-Elmer Model 521 grating spectrophotometer. Ultraviolet spectra were recorded on a Perkin-Elmer Model 4000 Spectracord.

RESULTS AND DISCUSSION

Infrared Spectroscopy

Smith[3] has reported evidence, based on infrared spectra, for the presence of a ternary complex as the reactive intermediate in the alcohol–isocyanate reaction catalyzed by metal salts such as stannous 2-ethylhexoate. He attributed shifts in absorption bands to the formation of reactant–catalyst complexes. In the present study, mixtures of 10–20% dibutyltin dilaurate or stannous 2-ethylhexoate in 1-methoxy-2-propanol or phenyl isocyanate were examined. No significant evidence for band shifts or intensity changes could be observed. Mixtures of reactant and catalysts in 1:1 ratio gave evidence of a slight shift in the —OH band to a lower frequency. This can be attributed to a change in the hydrogen-bonding character of the system but does not provide proof for complex formation.

Pestemer and Lauerer[4] proposed that new absorption bands which appeared in their infrared spectra of catalyst–phenyl isocyanate mixtures were due to the formation of an addition complex; they did not show evidence for the band shifts reported by Smith. Using amine or organometallic catalysts, they observed decrease or disappearance of —NCO absorption in isocyanate–catalyst mixtures. Their procedures were followed closely in this study, but no evidence of complex formation was observed. Indications were obtained only of a reaction between trace moisture and phenyl isocyanate. No measurable decrease in —NCO absorption, in the presence of excess catalyst, could be detected. Recent work by Farkas and Strohm[5] was in agreement with these data; they could find no evidence of catalyst–isocyanate complexing using this approach.

The above results point out limitations in applying infrared spectroscopy to the detection of alcohol or isocyanate complexing with metallic catalysts. At normal catalyst levels, the concentration of any complex intermediate is below that required for detection by infrared. When the catalyst concentration is increased to a reactant level, spectral changes can occur that are unrelated to complex formation.

Hydroxyl–Catalyst Complex by NMR

Little work has been reported utilizing the NMR technique for the study of urethane reactions. Sumi et al.[6] reported the spectra of a series of urethanes and used them to identify the nitrogen-containing linkages, but the technique has not been adapted to the study of the mechanism of the reaction of alcohols and isocyanates, in the presence of catalyst, to form urethanes.

In this study an effort has been made to obtain confirmation of complex formation with the aid of NMR spectra. A study of the dibutyltin dilaurate–1-methoxy-2-propanol system was started by examination of the spectra of each of the two components in carbon tetrachloride solution. Due to the complexity of the spectrum, a complete assignment for the dibutyltin dilaurate peaks was not possible; they all occurred in a very narrow region. The assignments for the peaks in 1-methoxy-2-propanol are given in Table I as well as the effect of concentration on their positions. It is apparent that only the peak associated with the —OH proton exhibits significant downfield shifts with increasing alcohol concentration, indicative of increased hydrogen bonding.

TABLE I
Concentration Dependence of the NMR Spectrum of 1-Methoxy-2-propanol, $H_3C—CH(OH)CH_2—OCH_3$

Alcohol concn., mole/l.	NMR shift δ, ppm[a]				
	A	B	D	E	F
0.54	—	—	2.56	—	—
0.62	1.00 1.13	—	2.75	3.12 3.19 3.23 —	3.36
1.03	1.02 1.14	—	2.93	3.15 3.21 3.25 3.28	3.38
3.10	0.99 1.09	—	3.52	3.19 3.22 3.30 —	3.37

[a] Letters refer to protons in the structure: $A_3C—CB(OD)—CE_2—OCF_3$.

On mixing the two compounds it can be seen (Fig. 1) that the peak associated with the —OH group shifted downfield considerably with increasing concentration of Sn, which may be readily interpreted on the basis of complex formation between the catalyst and the alcohol, resulting in electron withdrawal from the hydroxyl group. The shifts measured were downfield from tetramethylsilane which was used as an internal standard. It is evident from Figure 1 that a 1 : 1 complex is formed; a sharp decrease in slope of the plot of chemical shift versus catalyst concentration is obtained beyond the addition of equimolar concentrations of Sn to the alcohol. The continued increase in chemical shift beyond that concentration may be due to a change in the viscosity of the solvent or to a change in the bulk magnetic susceptibility.

A study of the lead naphthenate–1-methoxy-2-propanol system in carbon tetrachloride and cyclohexane solution was also carried out. The data (Fig. 2) clearly show the formation of a stable complex; the peak associated with the —OH group shifted downfield with increasing concentration of Pb. The composition of the complex was not determined, although it can be seen that the ratio of Pb:alcohol was at least 1:1.

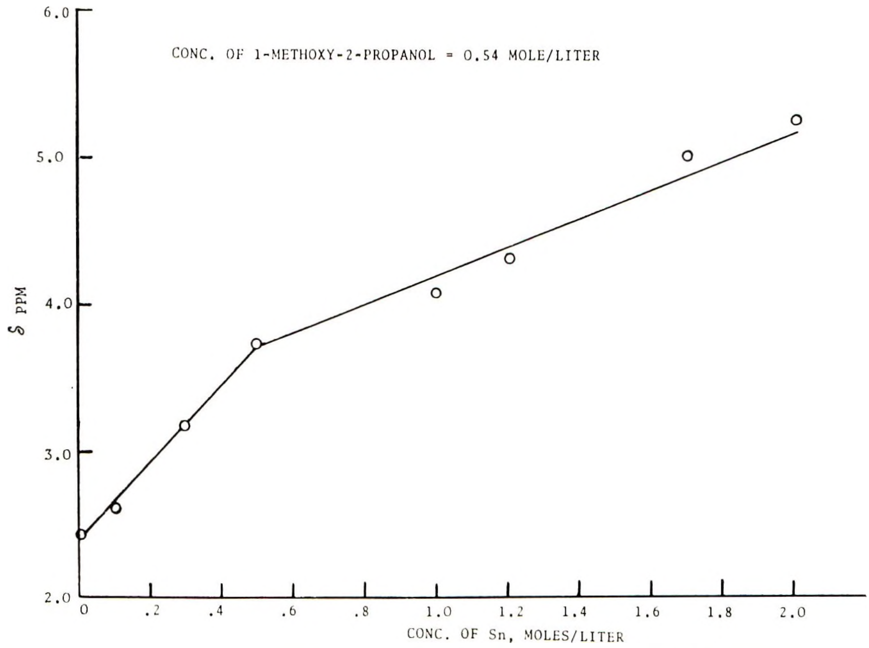

Fig. 1. Effect of Sn concentration on shift of —OH proton by NMR. 1-Methoxy-2-propanol concentration = 0.54 mole/l.

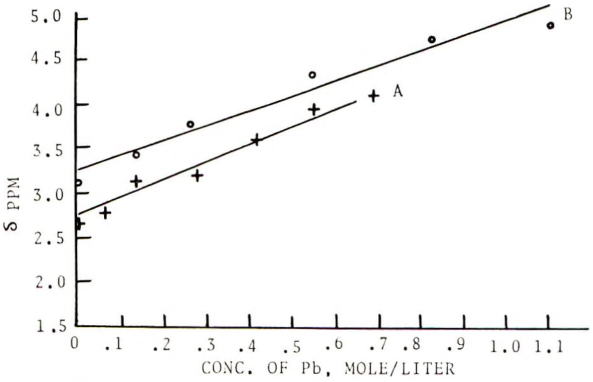

Fig. 2. Concentration dependence of the OH NMR resonance of 1-methoxy-2-propanol on lead naphthenate concentrations: (*A*) TMS used as internal standard, CCl_4 solution, concentration of ROH = 0.53 mole/l.; (*B*) cyclohexane used as solvent and internal standard corrected to TMS by the addition of 86 cps, concentration of ROH = 0.56 mole/l.

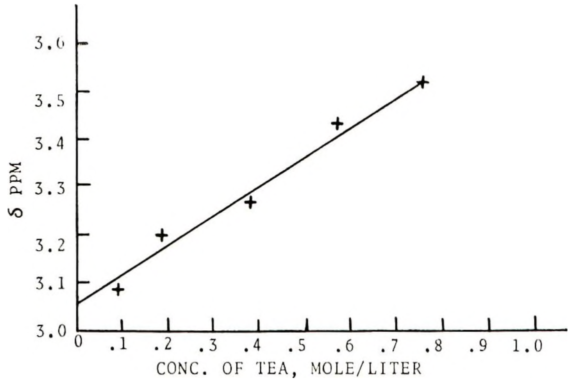

Fig. 3. Concentration dependence of the OH proton of 1-methoxy-2-propanol on triethylamine concentration. Cyclohexane was used as solvent and internal standard, corrected to TMS by the addition of 86 cps. Concentration of ROH = 0.50 mole/l.

The data resulting from the triethylamine–1-methoxy-2-propanol system in cyclohexane solution are shown in Figure 3. The downfield shift of the —OH resonance with increasing concentration of catalyst is evidence of association between the amine catalyst and alcohol. This shift is evidently significantly less than that caused by either of the two metal catalysts. It may be assumed that the hydrogen-bonding type of interaction resulting from the addition of amine to the alcohol is of a lower energy than the oxygen–metal bond in the complex resulting from the addition of either Sn or Pb to the alcohol.

The effect of catalyst combinations on complex formation was also investigated with the use of solvent-free mixtures of catalyst and alcohol. The shift of the —OH peak was determined on the addition of triethylamine, dibutyltin dilaurate, and mixtures of the two catalysts. The data in Table II show the shift to be greater for the mixture of the two catalysts than for either catalyst alone, indicating that both hydrogen bonds and oxygen–metal bonds are formed. The direction of the shifts was opposite to that expected from dilution of the —OH proton. The increased shift appears to correlate with the synergistic effect noted when preparing urethanes with a mixture of these two catalysts.[7]

TABLE II
Effect of Triethylamine–Dibutyltin Dilaurate Mixture on Chemical Shift of OH Proton in 1-Methoxy-2-propanol

Molar ratio alcohol/TEA/DBTDL	δ, ppm[a]
5/0/0	4.22
5/1/0	4.44
5/0/1	4.47
10/1/1	4.94

[a] Shift based on TMS.

Isocyanate–Catalyst Complexes by NMR

Efforts were also made to detect complex formation in mixtures of phenyl isocyanate and catalyst. Table III shows no significant shifts occurred by the interaction with triethylamine; this is true for protons on the phenyl group of the isocyanate (two prominent peaks were obtained in the phenyl region) or on the methyl and methylene groups of the amine. Table IV shows no shifts occurred (for protons on the phenyl group) on the addition of dibutyltin dilaurate to phenyl isocyanate. These data indicate there are no interactions between the isocyanate group and these catalysts that are measurable by NMR spectroscopy.

TABLE III
Effect of Mixtures of Triethylamine and Phenyl Isocyanate on NMR Spectra

$N(C_2H_5)_3$ concn., mole/l.[a]	NMR shift δ, ppm			
	CH_3[b]	CH_2	$Phenyl_1$	$Phenyl_2$
0	—	—	6.98	7.07
0.095	0.95	2.41	7.00	7.09
0.189	0.96	2.44	7.01	7.09
0.379	0.97	2.45	7.02	7.11
0.568	0.95	2.39	7.01	7.11
0.758	0.95	2.44	7.01	7.10

[a] Cyclohexane was used as solvent and internal standard, corrected to TMS by the addition of 86 cps (phenyl isocyanate = 0.54*M*).

[b] The CH_3 resonance is upfield from TMS; all other lines are downfield.

TABLE IV
Effect of Mixtures of Di-*n*-butyltin Dilaurate and Phenyl Isocyanate on NMR Spectra

Sn concn., mole/l.[a]	NMR shift δ, ppm[b]	
	$Phenyl_1$	$Phenyl_2$
0	7.16	7.23
0.057	7.17	7.27
0.285	7.18	7.25
0.570	7.12	7.19

[a] Solutions were in methylene chloride; the phenyl isocyanate was 0.557*M*.

[b] Chemical shifts are relative to tetramethylsilane.

Isocyanate–Catalyst Complexes by Ultraviolet Spectroscopy

Examination of ultraviolet spectra for phenyl isocyanate and for mixtures of phenyl isocyanate with tertiary amines, tri-*n* propylamine, and triethylamine, in a manner similar to that reported by Pestemer and Lauerer,[4] and with organometallic catalysts (lead naphthenate and stannous octoate) showed no evidence of catalyst–isocyanate complexes. Absorption maxima for the benzenoid chromophore in the dry cyclohexane solution were unaffected by the presence of the catalyst compounds, even when approximately equivalent amounts of isocyanate and catalyst were mixed. Combinations of amine and organometallic catalysts also had no effect on the phenyl isocyanate absorption maximum. The ultraviolet spectrum for a nonaromatic isocyanate, hexamethylene diisocyanate, was also investigated, but exhibited no distinct absorption in the 220–375 mμ ultraviolet range for the —N=C=O chromophore.

The authors wish to express their appreciation to Dr. J. H. Y. Niu of this laboratory for the NMR data involving catalyst mixtures, and to Professor F. R. Eirich of the Polytechnic Institute of Brooklyn for some NMR measurements and their interpretation.

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Résumé

Le mécanisme de la réaction catalysée des alcools avec les isocyanates a été étudié au moyen de résonance nucléaire magnétique, la spectroscopie infrarouge et ultraviolette. Le glissement de la résonance du proton hydroxylé dans les spectres NMR indiquait l'existence d'un complexe 1/1 dans le système dilaurate de dibutylétain (DBTDL)-1-méthoxy-2-propanol. La formation du complexe était également observée lorsque le naphthénate de plomb ou la triéthylamine (TEA) était employée au lieu de DBTDL. Des mélanges de catalyseurs DBTDL–TEA causent un glissement de la résonance du proton hydroxylé plus important que celui observé pour un système catalytique isolé. Ceci est en accord avec l'effet synergique remarqué lorsque l'on prépare des uréthanes avec un mélange de ces catalyseurs. Il n'a pas été possible de démontrer par spectroscopie infrarouge la formation d'un complexe alcool catalyseur. Des efforts ont également été déployés pour détecter la formation d'un complexe dans un mélange d'isocyanate de phényle es des catalyseurs. Ces complexes n'ont pas pu être détectés par résonance nucléaire magnétique ou par spectroscopie infrarouge, ni ultraviolette.

Zusammenfassung

Der Mechanismus der katalysierten Reaktion zwischen Alkoholen und Isocyanaten wurde mittels NMR-, Infrarot- und Ultraviolett-spektroskopie untersucht. Die Verschiebung der OH-Protonenresonanz im NMR-Spektrum liess die Existenz eines 1:1-Komplexes im System Dibutylzinndilaurat-(DBTDL)-1-Methoxy-2-propanol erkennen. Auch beim Ersatz von DBTDL durch Bleinaphthenat oder Triäthylamin (TEA) wurde Komplexbildung beobachtet. Mischungen der DBTDL–TEA–Katalysatoren führten zu einer grösseren Verschiebung der OH-Protonenresonanz als sie für jeden

Katalysator allein beobachtet wurde. Das entspricht dem bei der Darstellung von Urethanen mit einer Katalysatormischung festgestellten synergistischen Effekt. Infrarotspektroskopisch konnte keine direkte Evidenz für Komplexbildung aus Alkohol und Katalysator erhalten werden. Schliesslich wurde versucht eine Komplexbildung in Phenylisocyanat-Katalysatormischungen aufzudecken; es konnten aber weder durch NMR-, noch durch Infrarot-, noch durch Ultraviolettspektroskopie Komplexe festgestellt werden.

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Block Copolymerization of Methyl Methacrylate with Poly(ethylene Oxide) Radicals Formed by High-Speed Stirring

YUJI MINOURA, TANEKAZU KASUYA,* SHINJI KAWAMURA,† and AKIHIKO NAKANO,‡ *Department of Chemistry, Osaka City University, Osaka, Japan*

Synopsis

A block copolymer of methyl methacrylate with poly(ethylene oxide) was synthesized by initiation with poly(ethylene oxide) radicals formed by high-speed stirring. The effects of the concentration of the monomer, the concentration of the polymer, the degree of polymerization, the rotation speed, and the solvent on the rate of copolymerization were studied. It was found that the rate of copolymerization was proportional to the concentration of the monomer and to the square root of the rate of scission of the polymer chain. The block copolymerization of methyl methacrylate monomer and styrene monomer (1:1 mole ratio) with poly(ethylene oxide) radicals was also carried out by the same method and it was found that the block copolymerization was a radical one.

INTRODUCTION

It is well known that a polymer chain in solution is broken down to polymer radicals by mechanical forces such as ultrasonic waves and high-speed stirring. Watson,[1] Ceresa,[2] and Berlin[3] have studied the chemical reactions of polymers obtained by the use of these mechanical forces. Goto[4] has studied the block copolymerization of vinyl acetate initiated by polymer radicals formed by high-speed stirring and found that the rate of polymerization of vinyl acetate with the polymer radical was proportional to the square root of the concentration of the polymer [poly(vinyl acetate)] in the solution.

In this paper, the block copolymerization of poly(ethylene oxide) (PEO) radicals with methyl methacryalte (MMA) and the copolymerization with styrene (ST) and MMA were studied. The PEO radicals were formed by the high-speed stirring (10,000-30,000 rpm) of the monomers with PEO in a nitrogen atmosphere. The effects of the monomer concentration,

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* Present address: Pioneering Research Laboratory, Asahi Chemical Industry Co., Ltd., Tokyo, Japan.

† Present address: Osaka Research Laboratory, Japan Gas-Chemical Co., Hyogoken, Japan.

‡ Present address: Research Laboratory, Wireless Division, Matsushita Electric Industry Co., Ltd., Osaka, Japan.

polymer concentration, degree of polymerization ($\overline{DP}$), rotating speed of the stirrer, and the nature of the solvent on the rate of polymerization were also investigated.

EXPERIMENTAL

Materials

The PEO used was the same as that described in a previous paper.[5] The MMA and ST used as monomers and the diethyl ether used as a precipitant were purified by the usual methods.

Method of Block Copolymerization

The required amount of PEO was dissolved in the monomer at 45°C. and the solution was transferred to a type M Homomixer, (a high-speed mixer made by Tokushu Kika Kogyo Co., Ltd.). About 200 ml. of the solution was stirred violently with the mixer in a nitrogen atmosphere, and then 10-ml. aliquots of the solution which contained the block copolymer, degraded PEO, and the unreacted monomer were removed the container at various time intervals.

The weighed reaction mixture was poured into diethyl ether to precipitate the polymer formed, and the precipitate was filtered, washed, dried under vacuum, and weighed. The amount of monomer polymerized was estimated from the difference between the weight of the polymer precipitated from the known weights of the solutions before stirring and that after stirring.

Block Copolymerization of MMA

The effect of the concentration of PEO on the copolymerization of MMA with PEO radicals was studied with concentrations of 2, 3, 4, and 5 g./100 ml. of MMA (0.454, 0.682, 0.909, and 1.136 mole/l.). PEO-5N (molecular weight 1×10^6, $\overline{DP}$ 22,700) was used as the polymer and the solution was stirred at a speed of 30,000 rpm.

The influence of the concentration of the monomer on the copolymerization was also studied by varying the concentration of the monomer (9.22, 7.50, 4.70, and 2.35 mole/l.). The concentration of the monomer was changed by diluting the monomer with benzene. The other conditions were the same as described previously.

In another series of experiments, three different types of PEO, Polyox-WSR 206 (molecular weight 1.7×10^6, $\overline{DP}$ 38,600), PEO-5N (molecular weight 1×10^6, $\overline{DP}$ 22,700) and Polyox-WSR 205 (molecular weight 4.17×10^5, $\overline{DP}$ 9,500) were dissolved in purified MMA to obtain solutions, of 4 g./100 ml. concentration, and these solutions were stirred at a speed of 30,000 rpm.

The changes in the $\overline{DP}$ of the PEO were investigated.

The relationship between the rotation speed of the mixer and the copolymerization was studied in the following manner. PEO-5N was dissolved in MMA to obtain a solution of 4 g./100 ml. concentration, and the solution was stirred at speeds of 10,000, 20,000, and 30,000 rpm. PEO-6N solutions (4 g./100 ml.) in benzene–MMA (50/50), ethyl acetate–MMA (50/50) and acetonitrile–MMA (50/50) were stirred in order to study the effect of solvents.

Copolymerization of MMA and ST

The required amount of PEO-6N (molecular weight 12×10^5, DP 27,300) was dissolved in an equimolar mixture of MMA and ST (concentration each comonomer: 4.5 mole/l.) at 45°C. to obtain a solution of 4 g./100 ml. concentration (concentration of PEO: 0.87 mole/l.). After degassing the solution, it was stirred at a speed of 30,000 rpm in an argon atmosphere. The stirred solution was treated in a similar manner to the previous method.

Analysis of Block Copolymer

The stirred polymer mixture containing PEO and the copolymer of MMA with PEO, was dissolved in benzene to obtain a solution of about 10% concentration. The solution was painted on a rock salt plate to obtain a film of the polymer for infrared spectroscopic analysis.

The infrared spectrum of the film after evaporation of the benzene was obtained with a Perkin-Elmer 337 grating infrared spectrophotometer. A turbidity test on the stirred polymer was also carried out by the usual method in chloroform and *n*-hexane solutions.

The stirred polymer mixture containing PEO and the copolymer of MMA and ST with PEO was fractionated in the following manner. The polymer mixture was dissolved with heating in a mixed solvent (benzene–methanol, 1:9) and then the solution was allowed to stand at 8°C. for a day. Most of the polymer precipitated and the clear fluid was poured into ether. The ether solution was filtered and concentrated. A pale orange polymer was obtained. The infrared spectra of the polymers thus fractionated were taken and elementary analyses were also carried out.

RESULTS AND DISCUSSION

Identification of the Block Copolymer of MMA with PEO

The infrared spectrum of the polymer mixture containing PEO and the copolymer with MMA is shown in Figure 1. The polymer showed an absorption band at 1750 cm.$^{-1}$, which was assigned to the carbonyl group PEO showed no band between 1800 and 1500 cm.$^{-1}$.

The intensity of the absorption increased with increasing in stirring time. It was thought, therefore, that the polymer contained MMA. Because the polymer mixture was completely soluble in hot methanol, it seemed that the homopolymer of MMA was not formed and that therefore the MMA was copolymerized with the PEO. The formation of block copolymer of MMA with PEO was also detected by a turbidity test (Fig. 2).

Because no polymerization of MMA occurred when MMA was stirred

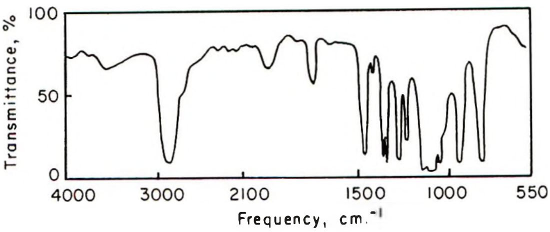

Fig. 1. Infrared absorption spectrum of the reaction mixture of PEO with MMA.

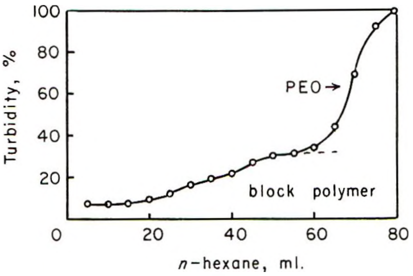

Fig. 2. Turbidity test of the polymer obtained. Precipitation with *n*-hexane from chloroform solution.

without PEO under the same conditions, the increase in the weight, described above, was considered to be the weight of the block-copolymerized MMA units.

Effect of the Concentration of PEO

PEO–MMA solutions of various polymer concentrations (0.454, 0.682, 0.909, and 1.136 mole/l.) were stirred by the mixer (30,000 rpm). The

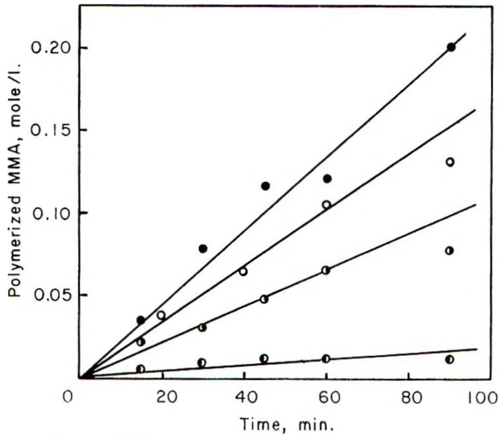

Fig. 3. Time–conversion curves for various PEO polymer concentrations: (●) 5 g./100 ml. (1.136 mole/l.); (○) 4 g./100 ml. (0.909 mole/l.); (◑) 3 g./100 ml. (0.682 mole/l.); (◐) 2 g./100 ml. (0.454 mole/l.). Polymer, PEO-5N; stirring speed 30,000 rpm.

relationships between the amount of MMA polymerized and the time were obtained. For the first hour the amount of MMA polymerized increased almost linearly for all concentrations of the polymer. The results are shown in Figure 3.

The relationship between the rate of polymerization at each concentration, calculated from Figure 3, and the square roots of the polymer concentration, is shown in Figure 4. A linear relationship was observed, and the straight line intersected the abscissa. These results are in agreement with the results obtained by Goto.[4]

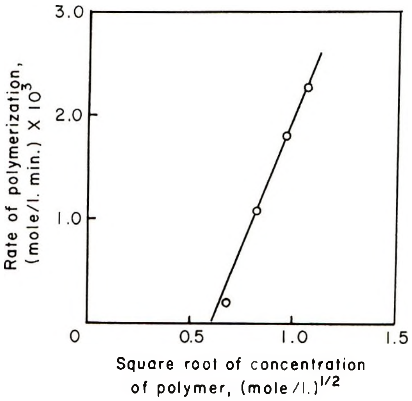

Fig. 4. Relationship between the rate of polymerization and the square root of PEO polymer concentration. Polymer, PEO-5N; monomer, MMA; stirring speed, 30,000 rpm.

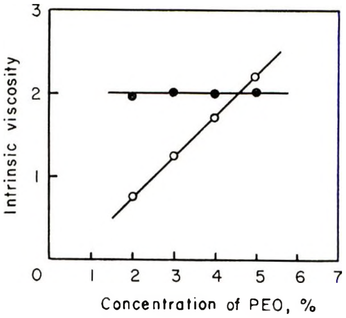

Fig. 5. Relationship between the intrinsic viscosity of the reaction mixture and the PEO concentration: (●) reaction mixture obtained after stirring in benzene for 1 hr.; (○) reaction mixture in MMA. Polymer, PEO-5N; stirring speed, 30,000 rpm.

The intrinsic viscosity of the PEO–MMA block copolymer mixture in the system decreased with stirring regardless of the concentration. The relationship between the intrinsic viscosity of the reaction mixture obtained after 1 hr. and the concentration of PEO is shown in Figure 5. The viscosity increased linearly with increasing concentration of PEO.

Effect of the Concentration of MMA

The amounts of polymerized MMA at various MMA monomer concentrations (2.35, 4.70, 7.05, and 9.22 mole/l.) at a stirring speed of 30,000 rpm were determined. The results obtained are shown in Figure 6.

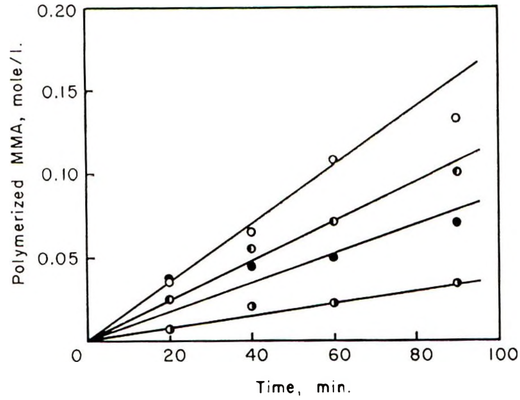

Fig. 6. Time–conversion curves for various MMA concentrations: (○) 9.22 mole/l.; (◐) 7.05 mole/l.; (●) 4.70 mole/l.; (◑) 2.35 mole/l. Polymer, PEO-5N; polymer concentration, 4 g./100 ml.; stirring speed, 30,000 rpm.

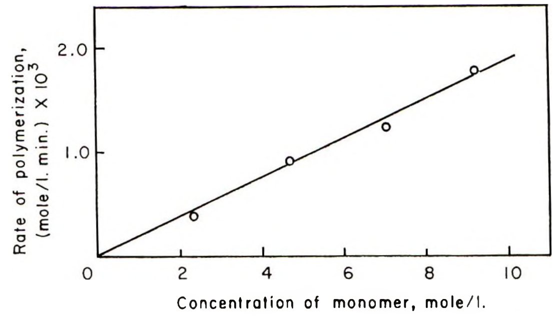

Fig. 7. Relationship between the rate of polymerization and MMA concentration. Polymer, PEO-5N; polymer concentration, 4 g./100 ml.; stirring speed, 30,000 rpm.

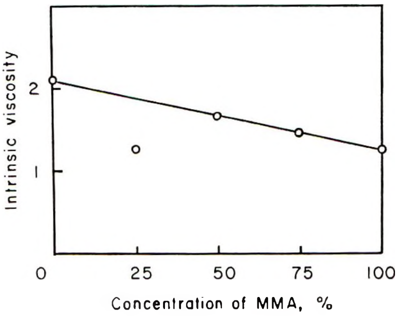

Fig. 8. Relationship between the intrinsic viscosity of the reaction mixture and the MMA concentration. Polymer, PEO-5N; polymer concentration 4 g./100 ml.; stirring speed, 30,000 rpm; solvent, benzene.

For the first hour, linear time–conversion relationship was obtained. The rates of polymerization were calculated from Figure 6 and plotted against the monomer concentration, as shown in Figure 7. The rate of polymerization was found to be proportional to the monomer concentration. With increasing monomer concentration, a change in the rate of scission due to the solvent was expected to occur. However, this was not observed because the rate of scission of PEO in MMA was not so different from that in benzene, and the rate of polymerization was a function of the square root of the rate of scission (radical formation) as will be described later. Hence, it was considered that the rate of polymerization was proportional to the monomer concentration.

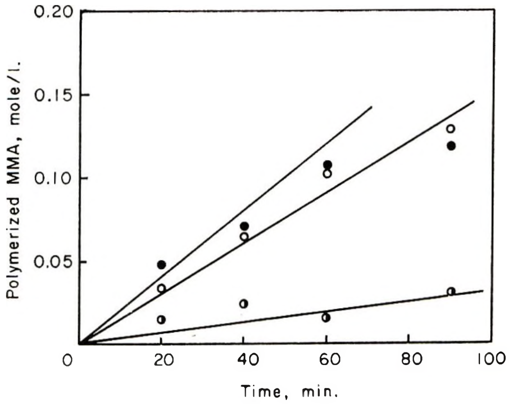

Fig. 9. Time–conversion curves for PEO of various initial $\overline{DP}$: (●) 38,600; (○) 22,700 (◐) 9,500. Polymer concentration, 4 g./100 ml.; stirring speed, 30,000 rpm.

The intrinsic viscosity of the PEO–MMA copolymer mixture obtained for a reaction system stirred for 1 hr. was found to decrease with increasing monomer concentration as shown in Figure 8. The reason for this is discussed later.

Effect of $\overline{DP}$ of PEO

The amount of polymerized MMA obtained with PEO of various $\overline{DP}$ (38,600, 22,700, and 9,500) after varying times at a stirring speed of 30,000 rpm was studied. The results obtained are shown in Figure 9. The higher the $\overline{DP}$ of the PEO, the larger the amount of polymerized MMA. The rates of polymerization in the early stage, calculated from Figure 9, are shown in Table I.

These rates of polymerization were plotted against the square roots of the initial shear rates of PEO in benzene, which were given in Figure 7 of a previous paper,[5] although the shear rate of PEO in MMA would be different from that in benzene. Figure 10 shows the relationship obtained. From this relationship it was concluded that the rate of polymerization is proportional to the square root of the shear rate of PEO molecules.

TABLE I

Effect of Initial $\overline{DP}$ of PEO on the Rate of Polymerization of MMA[a]

Initial $\overline{DP}$	Rate of polymerization of MMA × 10^3, mole/l.-min.	Initial shear rate of PEO in benzene × 10^2 l./min.-molecule
38,600	2.0	5.9
22,700	1.5	5.0
9,500	0.3	3.4

[a] PEO concentration, 4 g./100 ml., (0.909 mole/l.); rotation speed, 30,000 rpm.

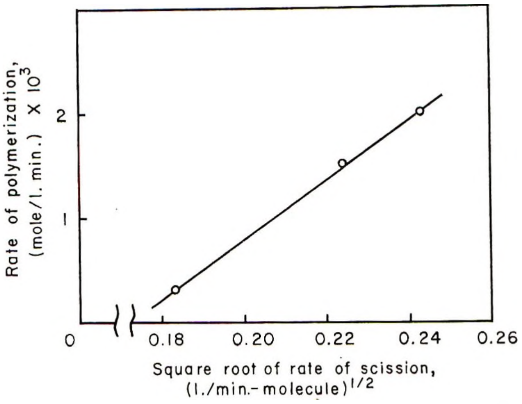

Fig. 10. Relationship between the rate of polymerization and the square root of the initial rate of scission of PEO in benzene, Initial $\overline{DP}$ of PEO, 38,600, 22,700, and 9,500; polymer concentration, 4 g./100 ml.; stirring speed, 30,000 rpm.

Effect of Stirring Speed

A PEO–MMA solution (polymer concentration: 1.136 mole/l.) was stirred at speeds of 10,000, 20,000, and 30,000 rpm. The results are shown in Figure 11. The higher the speed, the larger the amount of polymerized MMA. The rates of polymerization at each speed are shown in Table II.

Figure 12 shows the relationship between the rate of polymerization and the square root of the initial shear rates of PEO in benzene, which were given in Figure 10 of a previous paper.[5] It was concluded that the rate of polymerization is proportional to the square root of the shear rate of the PEO molecule.

TABLE II

Effect of Stirring Speed on the Rate of Polymerization of MMA[a]

Stirring speed, rpm	Rate of polymerization of MMA × 10^3, mole/l.-min.	Initial shear rate of PEO in benzene × 10^2, l./min.-molecule
30,000	2.44	4.06
20,000	1.25	3.00
10,000	0.09	1.92

[a] Polymer concentration, 4 g./100 ml.; polymer, PEO^5.

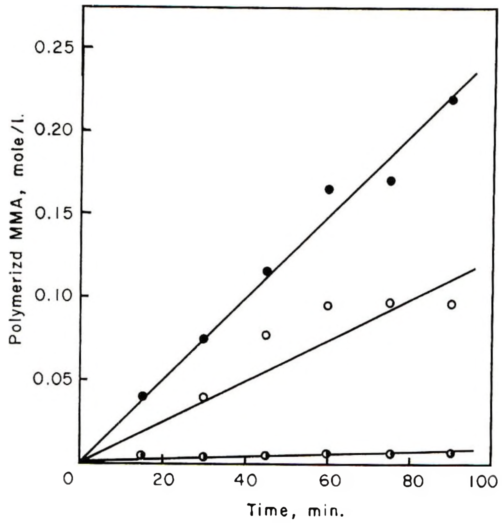

Fig. 11. Time-conversion curves for various stirring speeds: (●) 30,000 rpm; (○) 20,000 rpm; (◑) 10,000 rpm. Polymer, PEO-5N; polymer concentration, 4 g./100 ml.

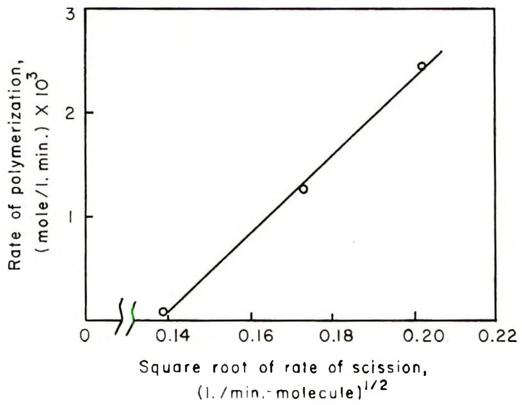

Fig. 12. Relationship between the rate of polymerization and the square root of the initial rate of scission of PEO in benzene. Polymer, PEO-5N; polymer concentration, 4 g./100 ml.; stirring speed, 10,000, 20,000, and 30,000 rpm.

The intrinsic viscosity of the resulting polymer decreased with time. The rate of decrease in viscosity in MMA was higher than that in benzene, as shown in Figure 13.

The fact that the rate of decrease of the viscosity of the stirred polymer, was higher in MMA than in benzene, in spite of the increasing amount of copolymerized MMA, seemed to be due to the higher rate of scission of PEO in MMA than in benzene.

In fact, the rate of scission of PEO-6N (DP 27,300) in MMA containing 0.5% phenyl-β-naphthylamine as an inhibitor when stirred at a speed of 30,000 rpm, was higher than that in benzene. (The rate constant k in Jellinek's equation[5] was 3.9×10^{-6}/min.-molecule, 2.7×10^{-6}/min.-

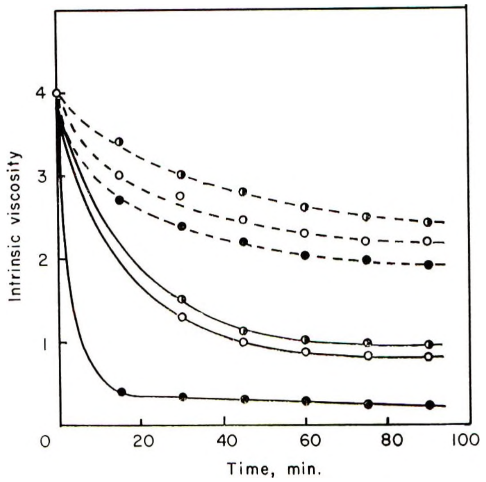

Fig. 13. Relationship between the intrinsic viscosity of the reaction mixture and the stirring time of polymer stirred (——) in MMA and (- -) in benzene at various stirring speeds: (◑) 10,000 rpm; (○) 20,000 rpm; (●) 30,000 rpm. Polymer, PEO-5N; polymer concentration, 4 g./100 ml.

molecule, respectively.[6]) Furthermore, the formation of the block copolymer may have contributed to the increase in the rate of scission. The decrease in the intrinsic viscosity of the PEO–MMA copolymer mixture with the increase in the monomer concentration, as shown in Figure 8, was attributed to the same reason as above.

Effect of Solvent

PEO–benzene–MMA (B), PEO–ethyl acetate–MMA (EA) and PEO–acetonitrile–MMA (AN) solutions (polymer concentration 0.909 mole/l.,

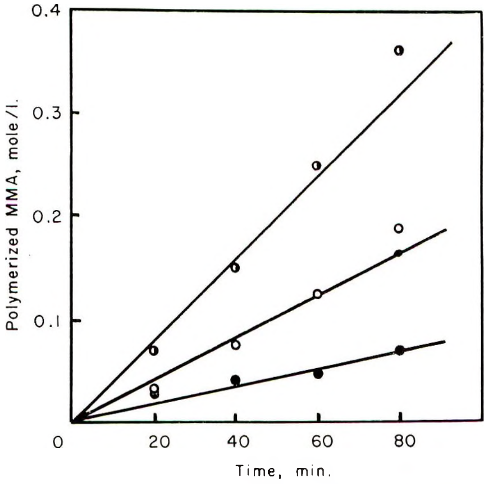

Fig. 14. Time-conversion curves in various systems: (◑) PEO–acetonitrile–MMA; (○) PEO–ethyl acetate–MMA; (●) PEO–benzene–MMA. Polymer, PEO–6N; polymer concentration, 4 g./100 ml.; stirring speed, 30,000 rpm.

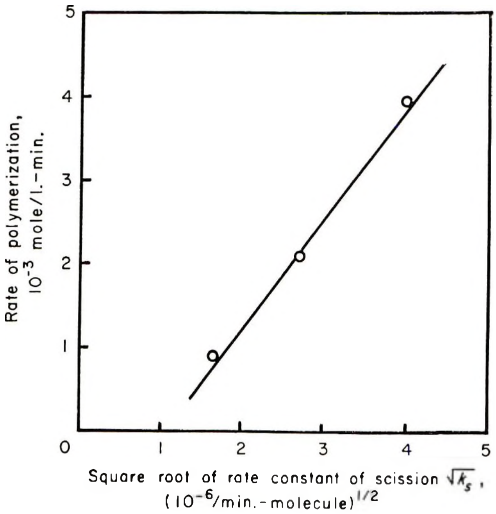

Fig. 15. Relationship between the square root of the rate constant for scission and the rate of polymerization of MMA.

monomer concentration 4.5 mole/l.) were stirred at a speed of 30,000 rpm. The results are shown in Figure 14. The rates of polymerization were 0.9×10^{-3}, 2.1×10^{-3}, and 4.0×10^{-3} mole/l.-min., respectively, in the three systems. It was observed that the rate of polymerization was faster in the systems containing solvents where PEO was degraded more rapidly. The rate constants, k_s, in Jellinek's equation,[6] were 2.7×10^{-6}/min. molecule in benzene,[6] 7.4×10^{-6} in ethyl acetate,[6] and 15.6×10^{-6} in acetonitrile.[6]

Although these rate constants may not represent the actual rate constants in the systems containing MMA, the relationship between $\sqrt{k_s}$ and R_p is shown in Figure 15. R_p seems to be proportional to the rate of scission.

Rate Equation for Polymerization of MMA

From the results described above, the rate equation for the polymerization of MMA initiated by PEO radicals formed by high-speed stirring may be expressed by eq. (1).

$$R_p = k([\mathrm{P}] - [\mathrm{P}_\alpha])^{1/2} [\mathrm{M}] [\Delta(B/n_0)/\Delta t]^{1/2} \qquad (1)$$

Here R_p is the rate of polymerization, k is the rate constant for the propagation reaction, $([\mathrm{P}] - [\mathrm{P}_\alpha])$ is the difference between the total concentration of PEO [P] and the concentration required for the initiation of polymerization $[\mathrm{P}_\alpha]$, [M] is the concentration of monomer, B is the total number of scissions, n_0 is the number of molecules in the system (and hence B/n_0 is the number of scissions per molecule), and t is the stirring time. $\Delta(B/n_0)/\Delta t$ is the rate of scission per molecule in a short time which depends upon $\overline{\mathrm{DP}}$ at the initial stage, the rotation speed, the solvent, the pressure and the temperature. Because $([\mathrm{P}] - [\mathrm{P}_\alpha])[\Delta(B/n_0)/\Delta t)]$ in eq. (1) is proportional to the rate of scission $(\Delta B/\Delta t)$, eq. (1) may be rewritten as follows:

$$R_p = k'\,[\mathrm{M}]\,(dB/dt)^{1/2} \tag{1'}$$

It was observed experimentally that rate of polymerization is proportional to the concentration of the monomer and the square root of the rate of scission.

The kinetics of the polymerization of the monomer initiated by the polymer radicals formed by high-speed stirring, is discussed as follows. At the steady state, the rate of initiation by the polymer radical R_i is expressed by eq. (2)

$$R_i = (d[\mathrm{P}\cdot]/dt)_i = 2fk_d[\mathrm{P}] \tag{2}$$

where $[\mathrm{P}\cdot]$ is the total concentration of polymer radicals, $(d[\mathrm{P}\cdot]/dt)_i$ is the rate of formation of polymer radicals, $[\mathrm{P}]$ is the concentration of the polymer dissolved in the monomer, k_d is the rate constant for the decomposition of the polymer to two polymer radicals, and f is the proportion of the radicals effective for initiating the propagation of the monomer. Since the polymer cannot be sheared until its concentration exceeds a certain concentration $[\mathrm{P}_\alpha]$, $([\mathrm{P}] - [\mathrm{P}_\alpha])$ may be used in eq. (2) instead of $[\mathrm{P}]$.

$$R_i = 2fk_d([\mathrm{P}] - [\mathrm{P}_\alpha]) \tag{2'}$$

The rate of termination R_t is shown by eq. (3):

$$R_t = -(d[\mathrm{P}\cdot]/dt)_t = 2k_t[\mathrm{P}\cdot]^2 \tag{3}$$

where k_t is the rate constant for the reaction in which two polymer radicals combine with each other for the termination. At the steady state, $R_t = R_i$, so the concentration of the polymer radicals at the steady state may be obtained from eq. (2′) and eq. (3) as shown by eq. (4).

$$[\mathrm{P}\cdot] = \{fk_d([\mathrm{P}] - [\mathrm{P}_\alpha])/k_t\}^{1/2} \tag{4}$$

On the other hand, the rate of propagation is expressed by eq. (5), and this may be rewritten as eq. (6) by substitution for $[\mathrm{P}\cdot]$.

$$R_p = k_p\,[\mathrm{M}]\,[\mathrm{P}\cdot] \tag{5}$$

$$R_p = k_p\,(fk_d/k_t)^{1/2}\,[\mathrm{M}]\,([\mathrm{P}] - [\mathrm{P}_\alpha])^{1/2} \tag{6}$$

Here $[\mathrm{M}]$ is the concentration of the monomer and k_p is the rate constant for the propagation reaction. The rate of propagation is regarded as the rate of polymerization. It can be seen in eq. (6) that the rate of polymerization is proportional to $[\mathrm{M}]$ and to $([\mathrm{P}] - [\mathrm{P}_\alpha])^{1/2}$. This equation is consistent with eq. (1′).

It was concluded that the rates of initiation, termination, and propagation can be expressed by eqs. (2′), (3), and (5), respectively, for the polymerization of MMA initiated by PEO radicals formed by high-speed stirring.

Infrared Spectrum of Block Copolymer of PEO–MMA–St

The infrared spectrum of the polymer obtained when a solution of PEO-6N in MMA and St was stirred with the high-speed mixer (30,000 rpm) in an argon atmosphere is shown in Figure 16. An absorption band which might be assigned to the carbonyl group appeared at 1750 cm.$^{-1}$ and a band assigned to the phenyl group was also observed at 1600 cm.$^{-1}$, while PEO itself had no band in the region 1800–1500 cm.$^{-1}$. Absorption bands which did not appear in PEO were observed at 3400, 2940, 2910, 750, and 700 cm.$^{-1}$ in the copolymer. Therefore, a PEO–MMA–St block copolymer seems to have been formed.

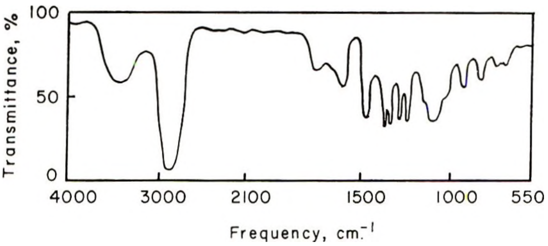

Fig. 16. Infrared absorption spectrum of the reaction mixture of PEO with MMA and St.

Amount of Polymerized MMA and St

The amounts of polymerized MMA and St increase almost linearly with time. The rate of polymerization R_p was about 0.6×10^{-3} mole/l.-min.

Composition of the PEO–MMA–St Block Copolymer

An elemental analysis of the fractionated block copolymer showed that the polymer contained about 76.4 wt.-% carbon, 7.9% hydrogen, and 15.7% oxygen (by difference). From these values, the proportion of each polymer in the copolymer was calculated as PEO, 11.7 mole-%; St, 47.3 mole-%; MMA, 40.9 mole-%. The ratio of St to MMA in the copolymer was 1.15, and therefore it appeared that St and MMA copolymerized almost alternately with PEO. This ratio is nearly equal to the value 1.05 calculated from r_1 and r_2 for the radical copolymerization,[7] and differed considerably from the value of 10.5 for the cationic copolymerization[8] and from the value of 0.15 for the anionic copolymerization.[9] Hence, the initiation and propagation in this work seemed to be in agreement with the radical mechanism. The low molar fraction of PEO in the copolymer might be due to the fractionating operation.

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Résumé

Un copolymère séquencé de méthacrylate de méthyle et d'oxyde de polyéthylène a été synthétisé par initiation au moyen de radicaux d'oxyde de polyéthylène formés par agitation à très grande vitesse. Les effets de la concentration de monomères, de la concentration en polymères, du degré de polymérisation, de la vitesse de rotation et du solvant sur la vitesse de copolymérisation, ont été étudiés. On a trouvé que la vitesse de copolymérisation était proportionnelle à la concentration en monomères et à la racine carrée de la vitesse de rupture de la chaîne polymérique. La copolymérisation séquencée du méthacrylate de méthyle monomérique et du styrène monomère (rapport molaire 1/1) avec les radicaux polyéthylèneoxyde a également été effectuée par la même methode et on a trouvé que la copolymérisation séquencée était de nature radicalaire.

Zusammenfassung

Ein Methylmethacrylat–Polyäthylenoxydblockcopolymeres wurde durch Start mit den durch Rühren mit hoher Geschwindigkeit gebildeten Polyäthylenoxydradikalen synthetisiert. Der Einfluss von Monomer- und Polymerkonzentration, von Polymerisationsgrad, Rotationsgeschwindigkeit und des verwendeten Lösungsmittels auf die Copolymerisationsgeschwindigkeit wurde untersucht. Die Copolymerisationsgeschwindigkeit war der Monomerkonzentration und der Quadratwurzel aus der Spaltungsgeschwindigkeit der Polymerkette proportional. Schliesslich wurde auch die Blockcopolymerisation von monomerem Methylmethacrylat und Styrol mit Polyäthylenoxydradikalen nach der gleichen Methode ausgeführt und gezeigt, dass die Blockcopolymerisation radikalisch verlief.

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α,ω-Disubstituted Polymethylpolyphosphonates and Polyphenylpolyphosphonates from Condensation Polymerization

DAVID GRANT,* JOHN R. VAN WAZER, and CLAUDE H. DUNGAN, *Central Research Department, Monsanto Company, St. Louis, Missouri*

Synopsis

Condensation polymerization of phosphonates through formation of P—O—P linkages has been achieved by (*1*) volatilization of methyl chloride from mixtures of $CH_3P(O)Cl_2$ with $CH_3P(O)(OCH_3)_2$; (*2*) volatilization or chemical removal of water from $CH_3P(O)(OH)_2$; and (*3*) volatilization of HCl from mixtures of $CH_3P(O)Cl_2$ with $CH_3P(O)(OH)_2$ or $C_6H_5P(O)Cl_2$ with $C_6H_5P(O)(OH)_2$. Depending on the proportions of the reagents, the polymerization products consist of various mixtures of chain molecules of the type $X—P(O)(R)\{O—P(O)(R)\}_nX$ for R = CH_3 and X = OCH_3, Cl, or OH, or for R = C_6H_5, X = Cl or OH. ^{31}P nuclear magnetic resonance (NMR) was used to investigate both the polymethylpolyphosphonates and the polyphenylpolyphosphonates; and ^1H NMR of the CH_3P and CH_3O moieties was also used to study the polymethylpolyphosphonates. In the methoxyl-terminated polymethylpolyphosphonates, which was the system studied most extensively, no detectable amounts of cyclic molecules were found at equilibrium, but a crystalline methylphosphonic anhydride, CH_3PO_2, exhibited some ring structures. The equilibrium size distributions gave evidence that the sorting of the mono- and difunctional phosphorus-based units making up the oligomeric chains is affected by neighboring units. Kinetic measurements demonstrated that the condensation polymerization is a complicated process involving considerable scrambling of terminal groups with bridging oxygen atoms.

Molecular structures (the polyphosphonates) based on repeating —(R)P(O)O— groupings are simultaneously phosphorus analogs of the siloxanes,[1] derivatives of the polyphosphorous acids[2] (of which only the pyro molecule is capable of straightforward preparation), and interesting relatives of the polyphosphoric acids and their organic and inorganic derivatives.[3] In addition to the original work of Michaelis[4] over a half century ago, several recent papers[5–7] have mentioned the polyphosphonates. However, no studies previous to this investigation have done more than touch briefly on the existence of these interesting molecules.

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* Visiting from Scotland, 1962–63.

EXPERIMENTAL

Reagents

Dimethyl methylphosphonate, $CH_3P(O)(OCH_3)_2$, was prepared[8] by isomerization of commercial trimethyl phosphite (samples from Eastman and Monsanto) and purified by distillation to give middle fractions having the physical properties reported for the pure compound. Hydrolysis[8] of some of the dimethyl methylphosphonate gave the respective acid which was purified by recrystallization from ethyl acetate. A portion of the acid was further converted to the chloride, $CH_3P(O)Cl_2$, by reaction with two moles of PCl_5.[8] Similar PCl_5 treatment of phenylphosphonic acid (obtained from Matheson and Coleman) gave its chloride, $C_6H_5P(O)Cl_2$. The compounds $CH_3P(O)(OH)(OCH_3)$ and $(HO)CH_3(O)P—O—P(O)(CH_3)OH$ were made according to the published procedure,[7] as was the crystalline compound,[4] $(C_6H_5PO_2)_n$. Crystalline methylphosphonic anhydride, $(CH_3PO_2)_n$, was also made according to the literature.[9] However, exactly the same material could be prepared more readily by adding one mole of water to one mole of $CH_3P(O)PCl_2$. The resulting $(CH_3PO_2)_n$ was purified by sublimation at ca. 150°C. in a vacuum (<1 mm. Hg). All of these reagents showed no more than 3% of the total H or P as hydrogen- or phosphorus-containing impurities by nuclear magnetic resonance (NMR).

Analysis

The ^1H NMR studies were carried out with a Varian A-60 spectrometer running at a frequency of 60.0 Mc./sec., as well as with a field-sweep HR-100 spectrometer running at 100.0 Mc./sec. Decoupling of the hydrogen from the phosphorus with the HR-100 unit was achieved by using a NMR Specialties SD-60 decoupler. Since the band width of the phosphorus-saturating frequency was not sufficiently strong over its full range to give decoupling at a single frequency setting, a different saturating frequency was used for the $CH_3P(O)$ moieties (*1*) bearing two methoxyl groups (40.495375 Mc./sec.), (*2*) having one methoxyl group and a bridging oxygen (40.495750 Mc./sec.), and (*3*) having two bridging oxygen atoms (40.496200 Mc./sec.). For the various monomeric and condensed methylphosphonates, the HCP coupling constant was in the range of 17–18 cps, with the exact value depending on the detailed structure. For the methoxyl-terminated species, the HCOP coupling constant was 11–12 cps. Phosphorus-free organic products could be readily identified by their smaller or zero coupling constants.

The ^{31}P NMR spectra were obtained at 24.3 and 40.5 Mc./sec. However, the spectra run at the higher frequency did not give any additional information over that of the 24.3 Mc./sec. spectra since the greater separation of the chemical shifts was still insufficient to separate the complicated multiplets due to HCP, HCOP, and POP spin–spin coupling. In both the ^1H and ^{31}P spectra, upfield shifts were considered to be positive. The various ^1H chemical shifts are reported in Figure 1.

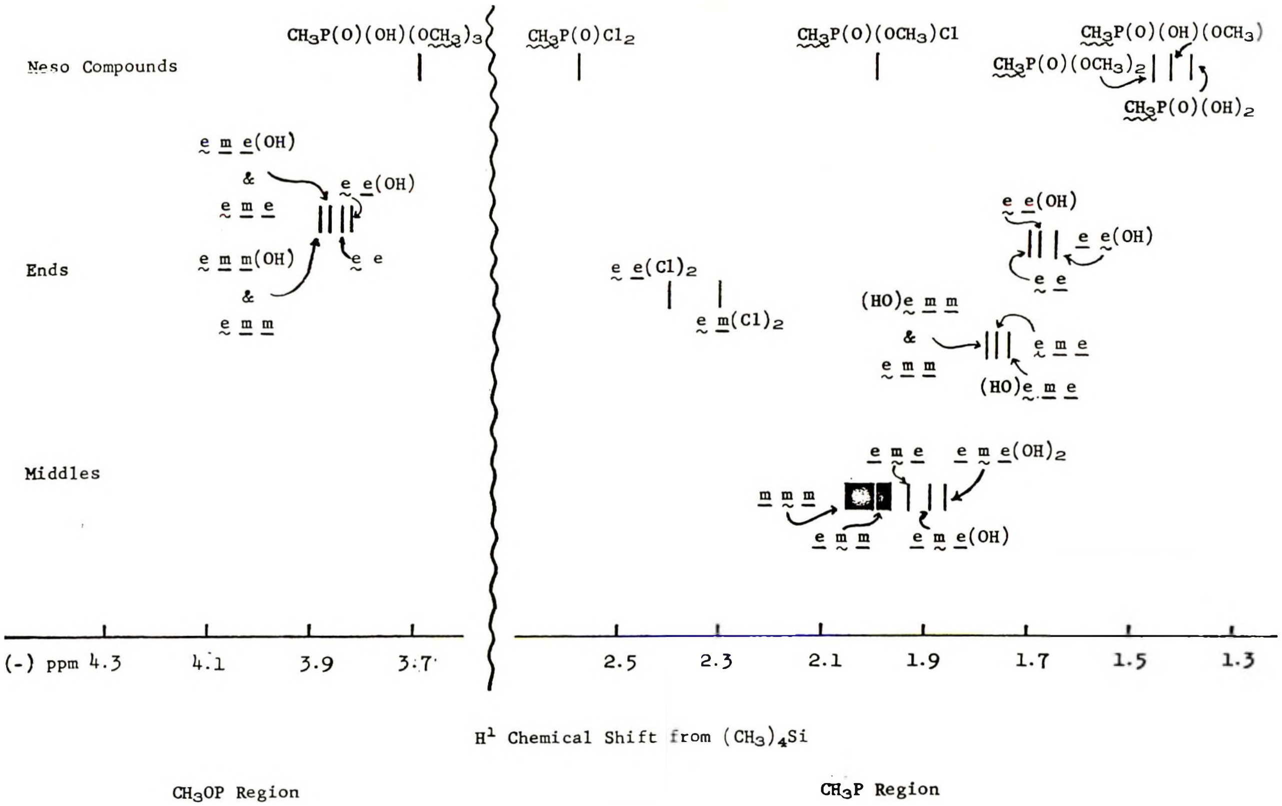


Fig. 1. Proton NMR chemical shifts for various arrangements of atoms about a given phosphorus atom in the methylphosphonic monomers and condensed species. *e* stands for a monofunctional unit and *m* for a difunctional unit. The unit in the molecule seen by NMR is indicated with a wavy underline and the neighboring units affecting its shift have a straight underline. Molecular species having substituents other than methoxyl groups are shown with the exchangeable ligand(s) in parentheses.

The pH titrations used in hydrolysis and analysis[11] were carried out with the Titrigraph manufactured by Radiometer of Copenhagen and fitted with a pH-stat attachment. An Aminco Thermo-Grav thermobalance was used for the thermogravimetric studies. Estimates of viscosity were made with a Gardner bubble viscometer, and molecular weights were obtained in benzene with a Mechrolab vapor-pressure osmometer.

KINETIC AND STRUCTURE STUDIES

Condensation Polymerization

Preliminary thermobalance studies in nitrogen at atmospheric pressure indicated that methylphosphonic acid does not undergo appreciable loss of weight until melting and that complete elimination of water cannot be achieved without a small amount of carbon loss. As shown by the thermobalance, there are no separable intermediate stages in the dehydration of this acid, and the volatilization of carbon-containing compounds at the higher temperatures does not show up as a separate step. Neither thermal dehydration nor chemical elimination of water (using dicyclohexylcarbodiimide acetic anhydride or in aqueous media) from $CH_3P(O)(OH)_2$ gave as clean a preparation of methylphosphonic anhydride—the material having the exact CH_3PO_2 stoichiometry—as does elimination of HCl from equimolar amounts of $CH_3P(O)Cl_2$ and $CH_3P(O)(OH)_2$ or the controlled hydrolysis of $CH_3P(O)Cl_2$. Under conditions where all of the H_2O was removed thermally from methylphosphonic acid, there were always some reaction products attributable to scission of P—C and/or H—C bonds, while chemical dehydration (including the paraformaldehyde reaction[5]) gave short-chain structures terminating with OH groups.

In the majority of studies reported here, carefully proportioned mixtures of the following monomers were heated together in 5-mm. thin-walled NMR tubes under controlled conditions without solvent to achieve condensation polymerization of $CH_3P(O)Cl_2$ with $CH_3P(O)(OCH_3)_2$, of $CH_3P(O)Cl_2$ with $CH_3P(O)(OH)_2$, and of $C_6H_5P(O)Cl_2$ with $C_6H_5P(O)(OH)_2$. In the first of these systems, methyl chloride was the desired coproduct of the condensation reaction and, in the latter two, hydrogen chloride. Production of the maximum possible amount of the coproduct from equimolar mixtures of the two monomers should give a pure phosphonic anhydride, RPO_2, as a product. However, such thorough elimination from the equimolar mixture is difficult to achieve because, with the extended heating needed for diffusion of final traces of the volatile out of this highly viscous or solid product, some of the R groups may be lost,[4] thereby leading to a small amount of cross-linking and/or hydroxyl terminating groups. For other products, the kind and amount of endgroups present after complete condensation are controlled by the excess of one or the other of the two monomers over equimolar proportions in the starting mixture and the major problem in the synthesis is to avoid inadvertent hydrolysis of nonhydroxylic endgroups.

Following the notation used in previous papers from this laboratory,[14,15] $CH_3P(O)(OCH_3)_2$ is the neso molecule, *n*; $CH_3P(O)(OCH_3)O_{1/2}$—, where $O_{1/2}$ stands for half of a bridging oxygen atom is the end unit, *e*; and $CH_3P(O)(O_{1/2}—)_2$ is the middle unit, *m*. When the NMR peak corresponds to a methyl group directly bonded to a given phosphorus, the unit based on this phosphorus is shown in bold-faced type and the neighboring units affecting its chemical shifts are shown in italics; e.g., *e***m***m*. When the chemical shift of the methoxyl group is measured, this is indicated by a dagger behind the given unit designated in bold-faced type, e.g., **e**†*m*. The overall composition in this system after complete condensation has been effected (so that all the possible CH_3Cl has been formed) is given by the parameter $R \equiv CH_3O/P = (2n + e)/(n + e + m)$.

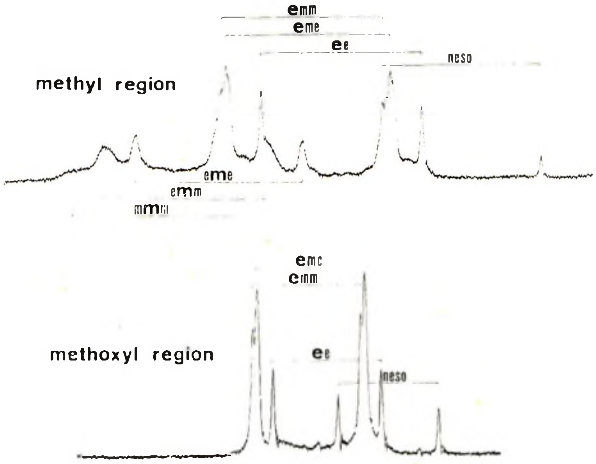


Fig. 2. 60 Mc./sec. undecoupled ¹H NMR spectra of a mixture of polymethylpolyphosphonates equilibrated at 85°C. which has an R value of 0.539 where $R = (CH_3O + OH)/P$. All molecular species are doublets due to $POCH_3$ and PCH_3 spin–spin coupling.

Most of the work reported herein was carried out on the methoxyl-terminated methyl polyphosphonates from mixtures of $CH_3P(O)(OCH_3)_2$ with $CH_3(O)Cl_2$, using an excess of the $CH_3P(O)(OCH_3)_2$ because, as illustrated by Figure 1, the ¹H NMR spectra gives more information than for the other systems investigated and side reactions could be avoided. As seen in Figure 2, the ¹H chemical shift of a given $CH_3P(O)\langle$ grouping, having two bridging oxygens on each of the bonds, is affected by whether or not the nearest-neighbor groupings to which it is linked by the bridging oxygen exhibits either a bridging oxygen or a methoxyl group on their other bonds. In the case of a terminal $(CH_3O)(CH_3)P(O)(O_{1/2})$ unit, the chemical shift of the CH_3P is affected by whether or not the next-nearest-neighbor unit exhibits a bridging oxygen or methoxyl group. Similarly, the chemical shift of the protons of the methoxyl group of such a unit is affected by whether the bridging oxygen or methoxyl group is bonded to the nearest-neighbor $CH_3P(O)\langle$ grouping.

Kinetics of Condensation Polymerization

A typical kinetic run carried out at 35°C. with a starting mixture of dimethyl methylphosphonate and methylphosphonyl chloride in a 25 vol.-% solution in chloroform is shown in Figure 3, in which the time in hours is presented on a logarithmic time scale. This time scale is employed for convenience and has no theoretical significance. It should be noted from this figure that condensation is complete in 8 hr., as evidenced by the methyl chloride formation, but that the exchange of methoxyl groups with bridging oxygen atoms on a given $CH_3P(O)\langle$ grouping continues for about 50 hr. more.

The first process occurring in Figure 3, and under all conditions where it could be observed because the condensation was kept sufficiently slow by use of lower temperatures and/or high dilutions, is the scrambling reaction [eq. (1)].

$$CH_3P(O)(OCH_3)_2 + CH_3P(O)Cl_2 \rightarrow 2CH_3P(O)(OCH_3)Cl \qquad (1)$$

Under the conditions of Figure 3, the product of eq. (1) is seen to increase for the first 2 hr. and then decrease because it is used up in some of the polymerization reactions.

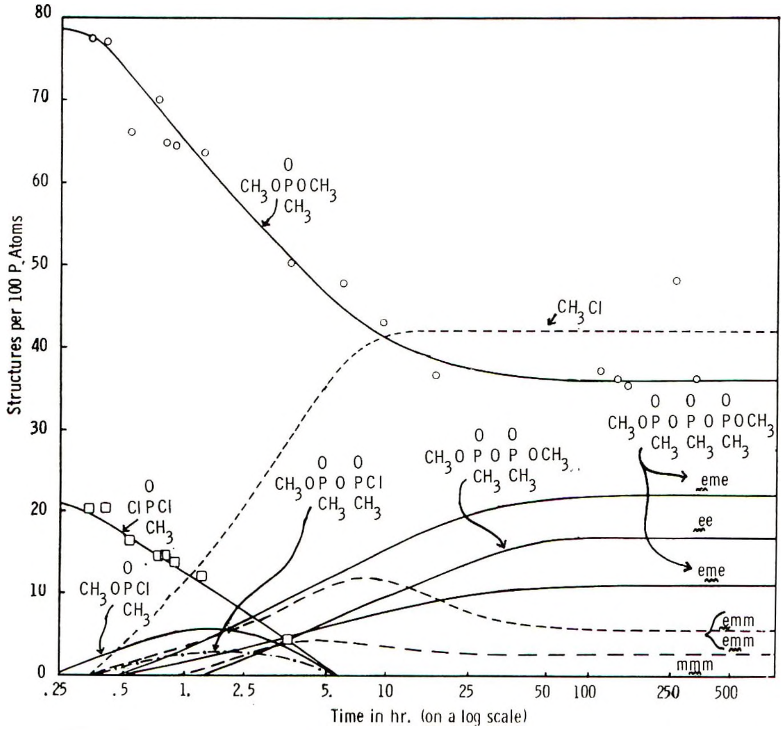
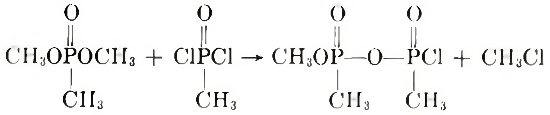


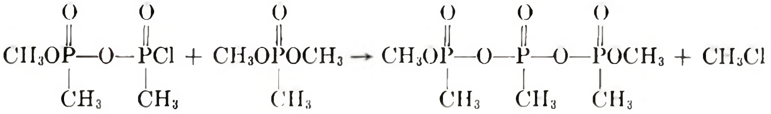
Fig. 3. Variation with time of the relative amounts (normalized over the $CH_3P(O)$ groupings) of the various structures observed by ^1H NMR when a mixture of dimethyl methylphosphonate and methylphosphoryl dichloride is reacted at 35°C. as a 25 wt.-% solution in chloroform. For clarity, data points are shown for only two of the ten curves.

The first step in polymerization is the expected one:



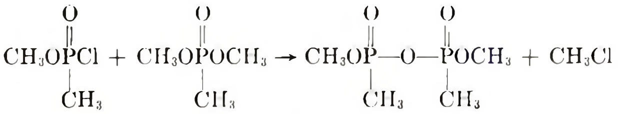
$$\mathrm{CH_3O\overset{O}{\underset{CH_3}{P}}OCH_3 + Cl\overset{O}{\underset{CH_3}{P}}Cl \rightarrow CH_3O\overset{O}{\underset{CH_3}{P}}{-}O{-}\overset{O}{\underset{CH_3}{P}}Cl + CH_3Cl} \tag{2}$$

The product of eq. (2) also has a transitory existence and is present in maximum amount at about 2.5 hr. under the conditions of Figure 3. The early appearance of the **e***me* and *e***m***e* resonances (which must, of course, always appear in a 2:1 ratio) is commensurate with the reaction:



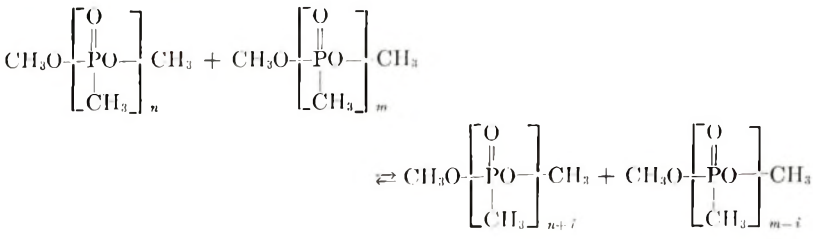
$$\mathrm{CH_3O\overset{O}{\underset{CH_3}{P}}{-}O{-}\overset{O}{\underset{CH_3}{P}}Cl + CH_3O\overset{O}{\underset{CH_3}{P}}OCH_3 \rightarrow CH_3O\overset{O}{\underset{CH_3}{P}}{-}O{-}\overset{O}{\underset{CH_3}{P}}{-}O{-}\overset{O}{\underset{CH_3}{P}}OCH_3 + CH_3Cl} \tag{3}$$

It is interesting to note that the compounds based on two phosphorus atoms having a methoxyl group at both ends, which is a major species when equilibrium is reached in Figure 3, does not begin to show up until the mixed monomer is present at maximum amount. It is probably first formed from reaction of the mixed monomer with the dimethyl methylphosphonate [eq. (4)].



$$\mathrm{CH_3O\overset{O}{\underset{CH_3}{P}}Cl + CH_3O\overset{O}{\underset{CH_3}{P}}OCH_3 \rightarrow CH_3O\overset{O}{\underset{CH_3}{P}}{-}O{-}\overset{O}{\underset{CH_3}{P}}OCH_3 + CH_3Cl} \tag{4}$$

The two resonances **e***mm* and **em***m* (which must always be equal in area since they represent the same arrangement of atoms) go through a maximum in Figure 3, while the **e***e* and the **e***me* and *e***m***e* pair of resonances continue to increase after methyl chloride evolution has ceased. This means that the initial condensation gives longer-chain species than correspond to the equilibrium molecular-size distribution. This effect was seen in all compositions studied (various R values). The final reactions in the kinetic runs—reactions which continue after a condition of dynamic equilibrium is achieved involves the interchange of parts between the various chain molecules including the neso.



$$\mathrm{CH_3O{-}\left[\overset{O}{\underset{CH_3}{P}}O{-}\right]_{n}CH_3 + CH_3O{-}\left[\overset{O}{\underset{CH_3}{P}}O{-}\right]_{m}CH_3 \rightleftarrows CH_3O{-}\left[\overset{O}{\underset{CH_3}{P}}O{-}\right]_{n+i}CH_3 + CH_3O{-}\left[\overset{O}{\underset{CH_3}{P}}O{-}\right]_{m-i}CH_3} \tag{5}$$

here n and i may independently have any integer value equal to or greater than unity and m is an integer greater than one and larger than i.

When the monomers were heated in nearly completely filled sealed tubes, it was found that the condensation also proceeds to completion but at a considerably slower rate than when the methyl chloride is vented. Thus, when an equimolar mixture of the monomers is heated in a sealed tube at 60°C., an essentially stoichiometric yield of methyl chloride is obtained after 9 days as compared with the period of less than 1 hr. for complete elimination of the methyl chloride in an open-top tube at the same temperature. At 23°C., the initial rate for the formation of methyl chloride was found to be practically identical to that observed at 60°C. However, after ca. 50–55% of the total methyl chloride was produced, the rate in the sealed tube became considerably slower, taking 17 days to go from 55 to 65% elimination of the methyl chloride as compared to 45% in the first day. When about three-fourths of the stoichiometric amount of methyl chloride is produced in an equimolar mixture of monomers under sealed-tube conditions, it forms a separate phase which is pure by NMR analysis (> ca. 98% of the total H as CH_3Cl). However, even in sealed tubes, the generation of the methyl chloride goes to completion.

In summary, the kinetic measurements show that the fastest process is exchange of chlorine atoms with methoxyl groups; and the next fastest is condensation to give more long-chain polymers than correspond to equilibrium conditions. A considerably slower process, when the methyl chloride is vented off, is the reshuffling of terminal methoxyl groups between the variously sized chains to give the equilibrium mixture. As discussed in the following section, considerable effort was spent on looking for cyclic molecules. There is no evidence from the NMR data of a buildup of appreciable concentrations of ring compounds during the condensation or subsequent reshuffling of terminal methoxyl groups.

Cyclic Molecules

Both methylphosphonic anhydride[9] and phenylphosphonic anhydride[4] (generic formula: RPO_2) have been prepared in crystalline form, but their structure is uncertain. The study of these compounds reported below was aimed towards establishing their molecular constitution in solution.

Crystalline methylphosphonic anhydride is obtained in the form of white needles exhibiting a melting point range of 90–150°. Sublimation and/or recrystallization was not found to narrow the melting point appreciably. This material is only slightly soluble in any nondestructive solvent, e.g., ca. 3% in chloroform at 150°C., and is readily sublimed at 150°C. and a pressure of 1 mm. Hg to give crystalline masses on the surface and edges of which well-formed needles are observed. Ebullioscopic molecular-weight measurements in chloroform correspond to ca. 34 CH_3PO_2 units per molecule.

The ^{31}P NMR spectrum taken at 150°C. on either the molten material or a 3% solution in chloroform showed a broad middle-group resonance, with some evidence of a small endgroup resonance. Under the same conditions, the proton spectra of the methyl groups directly bonded to the phosphorus showed two broad middle-group humps, with one or two superimposed sharp peaks. These broad resonances correspond to the *m***m***m* and

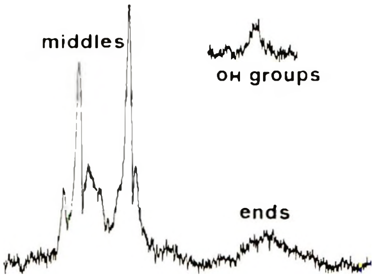


Fig. 4. Spin-decoupled, 100 Mc./sec. ^{1}H NMR spectra of methylphosphonic anhydride in chloroform. Decoupling of the hydrogen from the phosphorus in the endgroup and middle-group regions was achieved by using phosphorus-saturating frequencies of 40.497100 and 40.496200 Mc./sec., respectively.

em*m* arrangements, and the superimposed sharp peaks were attributed to cyclic molecules. In addition, various proportions of endgroups were found to show up as a broad resonance in the various samples studied.

The most pronounced sharp resonances superimposed on the middle-group humps were observed in purified chloroform solutions made from well-formed, needlelike crystals collected from the sublimation apparatus, when all operations were carried out in a dry nitrogen atmosphere (handling in a dry bag). A typical spectrum of this well-crystallized methylphosphonic anhydride is shown in Figure 4. As illustrated by Figure 2, rather sharp, outstanding middle-group resonances were never observed in equilibrated mixtures of oligomers in the family of methoxyl-terminated polyphosphonates nor were they seen in the related kinetic runs. The broadened middle-group resonances seen in the amorphous samples are typical of long-chain molecules where the broadening is attributable to the poorly resolved effects of distant atoms on the chemical shift (e.g., "seeing in depth"[10]) as well as to overall or localized high viscosity in the large molecules. Small-ring structures should give rather sharp peaks, as found for resonances corresponding to other small molecules, e.g., **n**, **e***e*, **e***me*, and **e***mme*.

The NMR spectrum of Figure 4 shows that in solution, well-crystallized methyl phosphonic anhydride consists of at least two cyclic molecules (or, less probably, two conformations of a given cyclic molecule) plus some long-chain species, chain termination being primarily effected by hydroxyl groups. It should be noted that the area of the endgroup peak in Figure 4 is somewhat greater than three times that of the hydroxyl groups. If all chains were hydroxyl-terminated, this area ratio should be exactly 3.

Crystalline phenylphosphonic anhydride is also an unusual compound. Such behavior as incomplete dissolution in any nonreactive solvent and conversion to a rubbery material instead of a powder upon grinding seems to indicate that the ring-chain equilibrium is easily displaced by physical treatment of this compound. As in the case of the methylphosphonic anhydride, the ^{31}P NMR spectrum shows a broad middle-group peak with indications of the presence of endgroups. Spin–spin coupling with the hydrogens of the phenyl group, however, is less than with the methyl hydrogens so that line broadening due to this source is somewhat lessened. The hydrogen spectra of the phenyl groups is too complicated for straightforward interpretation.

Hydrolysis of a reasonably well-powdered sample of this rubbery material at pH 9.6 and 30°C. showed two readily separable, accurately first-order rate processes, which were followed by automatic pH titration after complete dissolution. The half-lives for these two processes are 5.28 min. and 16 hr. In accord with the interpretation of the methanolysis of hydroxyl-terminated polymethylpolyphosphonates (see below), the first of these rate processes has been ascribed to the conversion of middle groups to endgroups, giving the essentially pure diphenyldiphosphonic acid, the hydrolysis of which corresponds to the 16-hr. half-life.

Methanolysis of Hydroxyl-Terminated Polymethylpolyphosphonates

The hydroxyl-terminated polymethylpolyphosphonates (or, alternatively, the polymethylpolyphosphonic acids) exhibit a much higher viscosity than the equivalent chloro- or methoxyl-terminated compositions. Presumably this high viscosity is due to hydrogen bonding between the terminal OH groups and the phosphonyl oxygens and is in accord with the fact that the dihydroxyl monomer has a melting point considerably higher than any of the other methylphosphonic monomers. No nonreactive solvents could be found which could be used over a wide range of compositions for these compounds. The $CH_3P(O)(OH)_2$ monomer is readily soluble in hydroxylated solvents (water and alcohol) which, however, cause solvolytic cleavage of the P—O—P linkages of its condensation products. The moderately sized oligomers could be dissolved in dimethylformamide, which is a poor solvent for the monomer and for the long-chain condensation products.

Kinetic studies indicated that the rate of hydrolysis of the P—O—P linkages in the polymethylpolyphosphonic acids is too fast to measure adequately, except for the dichain molecule (dimethyldiphosphonic acid). The hydrolysis of this acid in moderately dilute aqueous solution at 25°C. and pH 2 corresponded to a half-life of 0.9 hr. This should be compared with the half-life of 2×10^3 hr. for diphosphoric acid[12] under the same conditions.

The rates of methanolysis of all of the mixtures of polymethylpolyphosphonic acids are sufficiently slow so that they can readily be studied at room temperature. As is the usual case with solvolytic degradation[12,13] of P—O—P linkages, the dichain is found to undergo degradation much more slowly than the other species. In the methanolysis of equilibrium mixtures of the condensed acids, it was found that the endgroups in all but the dichains are essentially completely degraded to the monomers is about 20 min. at 23°C.; whereas, it takes about 40 hr. for the dichain to disappear at the same temperature. Although long-chain polyphosphate anions are believed[13] to undergo hydrolytic scission primarily at the ends, the data on the methanolysis of the hydroxyl-terminated polymethylphosphonates indicates that scission in these structures is least rapid at the ends for those compositions in which middle groups predominated (hence relatively long chains). Thus, the middle groups were solvolytically converted to endgroups within a period of 5 min., whereas, scission at the chain ends so as to convert endgroups to monomers was about fourfold slower. The overall solvolysis process appears to be one in which scission of the P—O—P linkages joining middle groups occurs the most rapidly, with the slowest rate of scission corresponding to solvolysis of the dimethyldiphosphonic acid (the *ee* molecule).

SIZE DISTRIBUTIONS AT EQUILIBRIUM

Methoxyl-Terminated Polymethylphosphonates

A series of equilibrium compositions in the family of α,ω-dimethoxyl polymethylphosphonates was prepared by heating the desired proportions of dimethyl methylphosphonate with methylphosphonyl chloride for 900 hr. at 35 and 85°C., with occasional opening of the tubes to vent the methyl chloride. This period of heating is about nine times longer than the time needed to reach equilibrium at 35°C. The experimental data are reported in Tables I and II. The assignments of the various observed NMR peaks to the molecules or molecular segments as given in these tables were based on the usual criteria[14] which include material balances, variation of peak intensity with overall composition, and the fixed-ratio relations between certain of the peaks. An example of the latter criterion is found in the 1,3-dimethoxyl trimethyltriphosphonate. For this compound, the **e***me* and *e***m***e* resonances due to the CH_3P group and the respective part of the **e**†*m* resonance due to the CH_3O group must exhibit relative areas of 2:1:2.

To a first approximation,[15] the equilibria leading to the distribution of molecules corresponding to the NMR resonances of Table I can be explained in terms of an equilibrium constant relating the exchange of methoxyl groups with bridging oxygen atoms on the $CH_3P(O)\langle$ grouping:

$$K_1 = [n][m]/[e]^2 \qquad (6)$$

where n, e, and m correspond respectively to $CH_3P(O)(OCH_3)_2$, $CH_3P(O)(OCH_3)O_{1/2}—$, and $CH_3P(O)(O_{1/2}—)_2$.

The values of this constant obtained for the various overall compositions (R values) are given in the first column for each temperature in Table III. The weighted-mean average[16] of these constants is 0.04 and 0.08 at 35 and 85°C. with standard deviations of 0.06 and 0.07, respectively. The values shown in parentheses in Tables I and II for the various NMR peak areas are calculated on the assumption that the sorting of the end and middle units into chain molecules is a statistically random process. The poor fit between the experimental and theoretical values indicates that this assumption is incorrect or that some of the middle groups are present in cyclic molecules, the NMR resonances of which are buried in the resonances for chain middle groups. However, if the poor fit between experiment and first-approximation theory were due solely to the presence of undetected

TABLE I. Equilibrium Data on the α,ω-Dimethoxyl Polymethylpolyphosphonates at 35°C.

$R = \left(\frac{CH_3O + OH}{P}\right)$	Percentage of total hydrogen[a] as										
		CH_3O			CH_3P						
	OH	**e**†*m*	**e**†*e*	**n**†	*m***m***m*	*e***m***m*	*e***m***e*	**e***mm*	**e***me*	**e***e*	**n**
0.42[b] [0.49][c] (0.52)[d]	0.1	29.7 (21.4)[e]	3.0 (10.4)	0.0 (2.4)	6.5 (14.9)	19.4 (14.4)	6.4 (3.5)	19.4 (14.4)	12.8 (7.0)	2.7 (10.4)	0.0 (1.2)
0.54 [0.65] (0.58)	0.2	32.8 (21.1)	6.0 (12.4)	0.0 (3.1)	3.9 (11.2)	14.6 (13.3)	7.4 (3.9)	14.6 (13.3)	14.9 (7.8)	5.6 (12.4)	0.0 (1.5)
0.74 [0.61] (0.69)	0.1	22.4 (19.3)	8.8 (16.7)	6.6 (4.9)	2.4 (5.9)	13.2 (10.4)	6.8 (4.4)	1.32 (10.4)	13.5 (8.9)	10.0 (16.7)	3.0 (2.4)
1.01 [1.28] (1.15)	1.2	15.2 (6.2)	8.3 (26.0)	30.4 (21.2)	0.7 (0.1)	3.1 (1.2)	4.9 (2.5)	3.1 (1.2)	9.9 (5.0)	7.9 (26.0)	15.3 (10.6)
1.24 [1.41] (1.38)	1.0	8.1 (2.3)	5.4 (21.4)	43.1 (34.2)	0.4 (0.0)	2.7 (0.2)	3.0 (1.1)	2.7 (0.2)	6.0 (2.1)	5.5 (21.4)	22.1 (17.1)
1.48 [1.64] (1.55)	0.4	7.2 (0.5)	3.1 (15.5)	51.1 (44.6)	0.0 (0.0)	3.1 (0.0)	1.3 (0.5)	3.1 (0.1)	2.6 (0.9)	2.5 (15.5)	25.6 (22.3)
1.76 [1.92] (1.87)	0.3	2.2 (0.1)	1.6 (4.5)	61.4 (60.6)	0.0 (0.0)	0.4 (0.0)	0.7 (0.0)	0.1 (0.0)	1.3 (0.1)	1.0 (4.5)	31.0 (30.0)

[a] Three doublets, totaling no more than 3% of the total hydrogen were omitted in this table. The doublets are due to unreactive impurities originally present in the reagents and hence played no role in this study.

[b] Calculated from the weighted proportions of the reagents.

[c] Calculated from the ratio of the hydroxyl plus methoxyl resonances to the methylphosphorus resonance.

[d] Calculated from the methylphosphorus resonances, i.e., $R = (2n + e)/(n + e + m)$.

[e] Values in parentheses calculated from first-order theory for $K_1 = 0.039$.

TABLE II. Equilibrium Data on the α,ω-Dimethoxyl Polymethylpolyphosphonates at 85°C.

$R = \left(\frac{CH_3O + OH}{P}\right)$		Percentage of total hydrogen[a] as									
		CH_3O			CH_3P						
	OH	e†*m*	e†*e*	n†	*mmm*	*emm*	*eme*	*emm*	*eme*	*ee*	n
0.42[b] [0.49][c] (0.49)[d]	1.2	25.2 (20.7)[e]	3.3 (8.2)	1.6 (3.9)	13.5 (18.7)	15.5 (14.8)	6.8 (2.9)	15.5 (14.8)	13.5 (5.9)	3.2 (8.2)	0.7 (1.9)
0.54 [0.54] (0.55)	1.2	24.7 (20.6)	4.5 (10.0)	2.9 (5.0)	7.8 (14.2)	17.4 (13.8)	5.8 (3.4)	17.4 (13.8)	11.7 (6.7)	5.4 (10.0)	1.2 (2.5)
0.74 [0.67] (0.71)	0.2	22.5 (18.7)	9.6 (14.2)	7.5 (8.4)	2.5 (7.0)	13.2 (10.6)	6.1 (4.0)	13.2 (10.6)	12.2 (8.1)	8.9 (14.2)	4.1 (4.2)
1.01 [0.98] (1.03)	0.7	15.1 (10.9)	10.5 (20.3)	22.4 (19.5)	0.6 (1.0)	4.8 (3.8)	5.6 (3.5)	4.8 (3.8)	11.2 (7.1)	11.8 (20.3)	12.5 (9.8)
1.24 [1.42] (1.35)	0.5	9.6 (4.1)	8.6 (18.7)	39.6 (34.6)	0.4 (0.1)	1.6 (0.7)	3.6 (1.7)	1.6 (0.7)	7.1 (3.4)	7.4 (18.7)	20.0 (17.3)
1.48 [1.57] (1.54)	1.7	4.8 (1.7)	5.3 (14.3)	48.0 (44.6)	0.0 (0.0)	1.0 (0.2)	2.6 (0.8)	1.0 (0.2)	5.3 (1.6)	4.9 (14.3)	25.4 (22.3)
1.76 [1.56] (1.86)	0.6	1.2 (0.1)	1.8 (4.7)	56.9 (60.2)	0.0 (0.0)	0.0 (0.0)	0.9 (0.1)	0.0 (0.0)	1.8 (0.2)	2.0 (4.7)	34.8 (30.1)

[a] Three doublets, totaling no more than 3% of the total hydrogen were omitted in this table. The doublets are due to unreactive impurities originally present in the reagents and hence played no role in this study.

[b] Calculated from the weighted proportions of the reagents.

[c] Calculated from the ratio of the hydroxyl plus methoxyl resonances to the methylphosphorus resonance.

[d] Calculated from the methylphosphorus resonances, i.e., $R = (2n + e)/(n + e + m)$.

[e] Values in parentheses calculated from first-order theory for $K_1 = 0.084$.

TABLE III

Values of the Equilibrium Constants for Individual Experiments

At 35°C.				At 85°C.			
R =	K_1			R =	K_1		
CH_3O/P	$\rho = 1$	$\rho = 2$	$\rho = 3$	CH_3O/P	$\rho = 1$	$\rho = 2$	$\rho = 3$
0.52	—	0.02	0.11	0.49	0.01	0.04	0.38
0.58	—	0.04	0.14	0.55	0.02	0.05	0.15
0.69	0.03	0.06	0.09	0.71	0.04	0.06	0.09
1.15	0.15	0.05	0.36	1.03	0.09	0.07	0.15
1.38	0.25	0.04	0.02	1.35	0.22	0.06	0.58
1.55	0.84	0.06	—	1.54	0.37	0.03	—
1.87	2.14	0.03	—	1.86	1.08	—	—

cyclic molecules, the calculated amount of **e***e* or **e**†*e* should be less than the observed amount since the incorporation of middle groups in unobserved ring molecules would effectively leave an excess of endgroups. The observed situation is exactly the opposite with, for example, the observed amounts of the *ee* molecule being consistently less than the calculated amounts.

Such a deviation between first-order theory and the experimental data may be due to either or both of two cases: (*1*) solution nonideality, demanding the use of activity coefficients in the equilibrium constants for exchange of parts between molecules and hence in the equilibrium of eq. (6), or (*2*) the effect[15,17] of the rearrangement of neighboring groups on the thermodynamic properties of a given $RP(O)\langle$ grouping. This latter effect has been called higher-order nonrandomness and the term[15] reorganization heat order ρ has been used to describe the longest sequence of groupings over which such a thermodynamic effect is operable. In view of the fact that the related P—O—P linked polymers, the alkyl polyphosphates[18] exhibit higher-order nonrandomness with $\rho = 2$ and the alkali metal polyphosphates[15] are even more nonrandom with $\rho = 3$–5, it seems reasonable to ascribe the deviation from first-order theory in the case of α,ω-dimethyl polymethylpolyphosphonates to higher-order nonrandomness.

Unfortunately, the NMR chemical shifts of the α,ω-dimethyl polymethylpolyphosphonates are at best sensitive only to the next nearest neighbor, $CH_3PO\langle$ grouping so that ρ and the respective higher-order equilibrium constants cannot be precisely evaluated; nor, indeed, can solution nonideality be ruled out. However, computer evaluation of the data of Tables I and II has given the higher-order equilibrium constants ($\rho \geq 2$) of Table III. From these calculated constants, we conclude that $\rho \approx 2$ and that the system is adequately described in terms of an equilibrium constant of the form of eq. (6) and another in the form of eq. (7):

$$^2K_1 = [ee][mm]/[em]^2 \qquad (7)$$

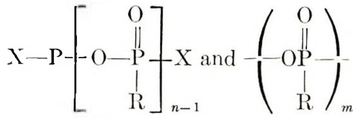
The best values for K_1 and $^2K_1$ appear, respectively, to be 0.055 and 0.042 at 35°C. and 0.053 and 0.055 at 85°C.

Higher-order equilibria involving longer sequences of $CH_3P(O)<$ groupings will all be random if $\rho = 2$. Thus, for $n > 2$

$$^{n}K_1 = [em_{n-2}e][m_n]/[em_{n-1}]^2 = {}^1/_4 \tag{8}$$

α,ω-Disubstituted Polyphenylpolyphosphonates

In the chain and ring polyphosphonates



$$X{-}P{-}\left[O{-}\overset{\overset{O}{\|}}{\underset{\underset{R}{|}}{P}}\right]_{n-1}{-}X \text{ and } \left({-}\overset{\overset{O}{\|}}{\underset{\underset{R}{|}}{OP}}{-}\right)_m$$

where R stands for a phenyl group, the NMR data are obtained from the ^{31}P spectra in which only the total amounts of neso, ends, and middle groups may be seen. Therefore, it is impossible to arrive at any conclusions concerning deviations from randomness in the sorting of building units into molecules or the possible presence of cyclic molecules. This means that the only equilibrium data which can be obtained must correspond to the first-approximation theory as presented in eq. (6).

Two polyphenylpolyphosphonate systems were studied. These corre-

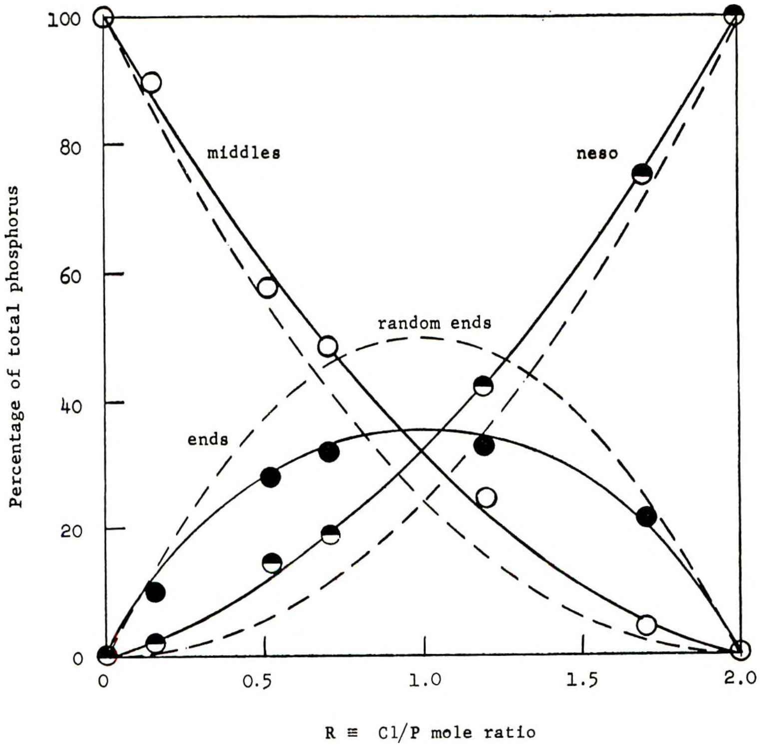


Fig. 5. Equilibrium between the various building units in the condensed polyphenylpolyphosphonates terminated with chlorine atoms. The dotted lines illustrate random sorting of chlorine atoms with bridging oxygens.

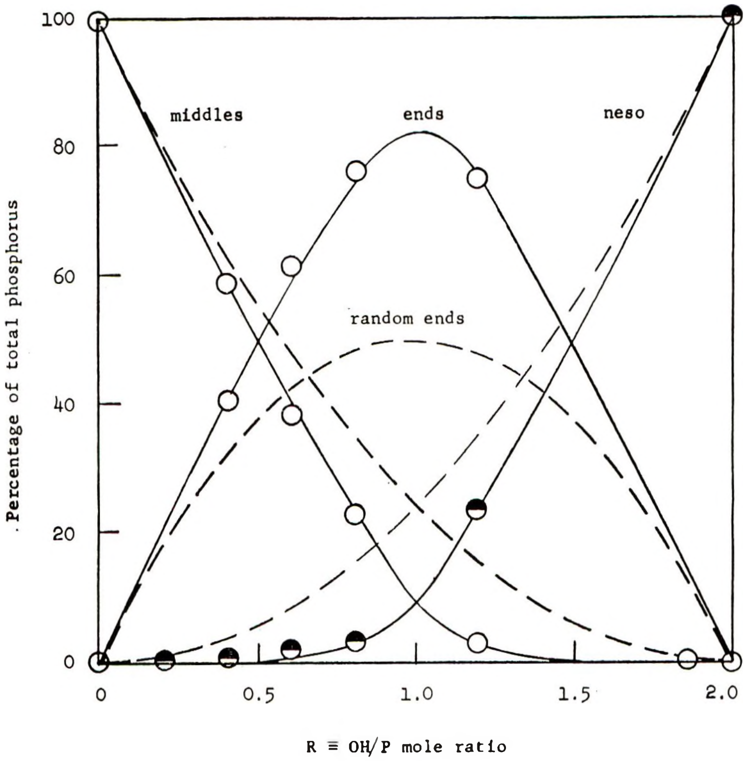


Fig. 6. Equilibrium between the various building units in the condensed polyphenylpolyphosphonates terminated with hydroxyl groups, i.e., the polyphenylpolyphosphonic acids. The dotted lines illustrate random sorting of hydroxyl groups with bridging oxygens.

spond to X = Cl and X = OH. For X = Cl, equimolar amounts or less of solid $C_6H_5P(O)(OH)_2$ were dissolved in liquid $C_6H_5P(O)Cl_2$, whereas when X = OH, equimolar or larger quantities were employed. At 65°C., dissolution was completed in a few minutes with nearly all of the HCl being evolved during that time and the ^{31}P spectra showed no change after several hours. The equilibrium values reported in Figures 5 and 6 were not obtained until after 48 hr. at temperature.

Upon rapid cooling to room temperature, the equilibrated systems in which X = Cl always gave single-phase liquids, from the NMR analysis of which it was found that $K_1 = 0.8$, with a standard deviation of 0.2. The experimental data are shown in Figure 5 and the lines in this figure were calculated[16] from $K_1 = 0.8$. As can be seen from this figure, the agreement between the first-order theory and the available experimental data is good. The amount of endgroups in the system is less than would be expected if the chlorine and bridging oxygen atoms were randomly sorted on the C_6H_5-$P(O)\langle$ groupings.

Upon rapid cooling of the equilibrated hydroxyl-terminated polyphenylpolyphosphate (i.e., polyphenylpolyphosphonic acid) mixtures from 65°C.

to room temperature, some solid was always seen to be formed in the composition range corresponding to $0.3 < R \equiv OH/P < 1.9$. The data shown in Figure 6 correspond to replicate runs on a number of different compositions which could be completely dissolved in benzene at room temperature for ^{31}P NMR measurements. For $R >$ ca. 1.3, suitable solutions could not be made, since $C_6H_5P(O)(OH)_2$ is insoluble in all of the solvents which were found not to react with the larger molecules in the system so as to cause P—O—P scission. From the data of Figure 6, the equilibrium constant of the form of eq. (6) was found to equal 0.012, with a standard deviation of 0.004. The curves shown in this figure were calculated from this constant; and it can be seen that the agreement between the available experimental data and the equilibrium constants is good. In this system, the sorting of hydroxyl groups with bridging oxygen atoms is also nonrandom, with the endgroups being present in larger amounts than expected for random sorting, as compared to the reverse situation for the chloro-terminated compounds.

All of the various mixtures made by dissolving $C_6H_5P(O)(OH)_2$ in C_6H_5-$P(O)Cl_2$ were liquids at the temperature of dissolution, 65°C.; but, in the composition range corresponding to the hydroxyl-terminated chains, the viscosity was many times greater than that corresponding to the chloro-terminated chains. Another obviously noticeable feature of these melts was that the viscosity increased with time during and after the period in which the phenylphosphonic acid underwent dissolution. A series of quantitative viscosity measurements carried out on the compositions after rapid cooling to room temperature showed that in the first 30 hr. of heating at 65°C., the viscosity for $R = 0$ (i.e., essentially no chloro or hydroxyl groups) reached 10^2 poises and was still increasing fairly rapidly with longer heating, presumably due to diffusion-controlled condensation involving the elimination of the last traces of HCl. The presence of hydroxyl endgroups led to a viscosity even greater than that observed for the essentially endgroup-free composition, $R = 0$. As expected, the liquids in which the chains were terminated with chlorine atoms were very fluid. It is interesting to note that molecular weights (taken on the samples used for viscosity measurements) showed an increase of only a few per cent under conditions where the viscosity increased by several hundred per cent. This results from the fact that the viscosity of such mixtures is primarily effected by the high molecular weight species, whereas, the number-average molecular weight is heavily weighted by the smaller molecules.

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Résumé

La polycondensation de phosphonates par formation de liens P—O—P a été effectuée par (*1*) la volatilisation du chlorure de méthyle au départ de mélanges de $CH_3P(O)Cl_2$. avec $CH_3P(O)(OCH_3)_2$; (*2*) la volatilisation ou élimination chimique de l'eau au départ de $CH_3P(O)(OH)_2$; (*3*) la volatilisation de l'acide chlorhydrique au départ de mélanges de $CH_3P(O)Cl_2$ avec $CH_3P(O)(OH)_2$ ou $C_6H_5P(O)Cl_2$ avec $C_6H_5(O)(OH)_2$. Suivant les proportions des réactifs, les produits de polymérisation étaient formés de mélanges variés de molécules en chaînes du type $X—P(O)(R)\!+\!O—P(O)(R)\!+_nX$ où $R = CH_3$ et $X = OCH_3$, Cl, ou OH, ou où $R = C_6H_5$, $X =$ Cl ou OH. On a utilisé la résonance nucléaire magnétique du phosphore^{31} pour étudier les polyphosphonates de méthyle et les polyphosphonates de phényle; de même on a utilisé la résonance de l'hydrogène^1 pour les parties CH_3P et CH_3O des polyméthylpolyphosphonates. Dans les polymethylpolyphosphonates terminés par des groupes méthoxylés, le système qui a été étudié le plus intensivement, on n'a pas trouvé de quantité appréciable de molécules cycliques à l'équilibre; on a par contre trouvé un anhydride méthylphosphonique cristallin CH_3-PO_2, qui manifestait certaines structures cycliques. Les distributions des dimensions moléculaires à l'équilibre montraient que l'assortement des unités phosphorés mono- et difonctionnelles qui forment les chaînes oligomériques est affecté par les unités directement voisines. Des mesures cinétiques ont montré que la polycondensation est un processus compliqué comprenant un échange de groupes terminaux avec des atomes d'oxygènes liant les atomes de phosphore.

Zusammenfassung

Die Kondensationspolymerisation von Phosphonaten durch Bildung von P—O—P-Bindungen wurde erreicht durch (*1*) Verflüchtigung von Methylchlorid aus Mischungen von $CH_3P(O)Cl_2$ mit $CH_3P(O)(OCH_3)_2$; (*2*) Verflüchtigung oder chemische Entfernung von Wasser aus $CH_3P(O)(OH)_2$; und (*3*) Verflüchtigung von HCl aus Mischungen von $CH_3P(O)Cl_2$ mit $CH_3P(O)(OH)_2$ oder von $C_6H_5P(O)Cl_2$ mit $C_6H_5P(O)(OH)_2$. In Abhängigkeit vom Mischungsverhältnis der Reagenzien bestehen die Polymerisationsprodukte aus verschiedenen Mischungen von Kettenmolekülen vom Typ $X—P(O)(R)\!+\!O—P(O)(R)\!+_nX$ mit $R = CH_3$ und $X = OCH_3$, Cl, oder OH, oder mit $R = C_6H_5$, $X =$ Cl oder OH. P^{31}-kernmagnetische Resonanz (NMR) wurde zur Untersuchung der Polymethylpolyphosphonate sowie der Polyphenylpolyphosphonate verwendet und

ebenso H^1-NMR der CH_3P- und CH_3O-Gruppen zur Untersuchung der Polymethylphosphonate. Bei den Polymethylphosphonaten mit Methoxylendgruppen, die am eingehendsten untersucht wurden, konnten im Gleichgewicht keine nachweisbaren Mengen cyclischer Moleküle festgestellt werden, ein kristallines Methylphosphonsäureanhydrid, CH_3PO_2 zeigte aber Ringstruktur. Die Gleichgewichtsgrössenverteilung lies erkennen, dass die Einordnung der Bausteine auf der Basis des mono- und difunktionellen Phosphors in den Ketten der Oligomeren durch Nachbareinheiten beeinflusst wird. Kinetische Messungen zeigten, dass die Kondensationspolymerisation ein komplizierter Prozess mit beträchtlicher Störung der Endgruppen mit Brückensauerstoffatomen ist.

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Copolymerization Parameters of Acrolein and Acidic Vinyl Monomers

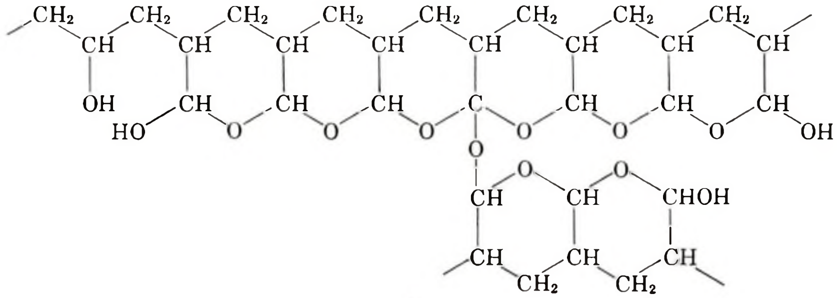
G. F. D'ALELIO and T. F. HUEMMER, *University of Notre Dame, Notre Dame, Indiana 46556*

Synopsis

Acrolein was copolymerized by radical initiation in aqueous solutions with sodium *p*-styrenesulfonate and acrylic acid, respectively, in the pH range of 3-7. The reactivities were shown to be pH-dependent. For the acrolein (M_1)-sodium *p*-styrenesulfonate (M_2) pair, $r_1 = 0.33 \pm 0.15$ and $r_2 = 0.32 \pm 0.05$ at pH 3; $r_1 = 0.23 \pm 0.12$ and $r_2 = 0.05 \pm 0.03$ at pH 5; $r_1 = 0.26 \pm 0.03$ and $r_2 = 0.025 \pm 0.025$ at pH 7. For the acrolein (M_1)-acrylic acid (M_2) pair, $r_1 = 0.50 \pm 0.30$ and $r_2 = 1.15 \pm 0.2$ at pH 3; $r_1 = 2.40 \pm 0.50$ and $r_2 = 0.05 \pm 0.05$ at pH 5; $r_1 = 6.70 \pm 3.00$ and $r_2 = 0.00$ at pH 7. For acrolein, the new values of $Q = 1.6$ and $e = 1.2$ have been calculated. For sodium *p*-styrenesulfonate, the values $Q = 0.76$ and $e = -0.26$ at pH 3, $Q = 0.51$ and $e = -0.87$ at pH 5, $Q = 0.39$ and $e = -1.00$ at pH 7 were obtained; and for acrylic acid, the values $Q = 1.27$ and $e = 0.50$ at pH 3, $Q = 0.11$ and $e = -0.22$ at pH 5 were derived. The changes in reactivity are explained on the basis of inductive and resonance effects.

INTRODUCTION

Although the first homopolymers of acrolein were reported by Redtenbacher[1] in 1843, only a limited amount of research was done in the field of acrolein polymers until the past twenty-five years. The development of acrolein polymers was discouraged for a variety of reasons. First, the polymers were found to be crosslinked and insoluble in many common organic solvents. Secondly, the occurrence of groups other than the free aldehyde in the polymer structure complicated the utilization of the polymer. Thirdly, the formation of the insoluble polymer, called disacryl, was discouraging to the early investigators. Disacryl is the white powder formed in acrolein monomer by the catalytic action of light and oxygen; it darkens but does not melt at high temperature, and is insoluble in common organic solvents. Polymers of acrolein are intriguing because, other than the polyacroleins, there are only a few high polymers containing aldehyde groups.[2,3] In the last decade, important advances have been made in the controlled polymerization and copolymerization of acrolein by Schulz. In a series of papers he elucidated the structure of disacryl and of acrolein polymers prepared under a variety of conditions. Schulz showed[4] that the free carbonyl is not preserved in the 1,2 radical polymerization of acrolein and a crosslinked structure is obtained; he proposed the structure I.



I

Later, he published a review article[5] in which he summarized much of his work.

In his early work,[6] Schulz was the first to make the significant discovery that certain crosslinks in polyacrolein can be reversed by reaction with carbonyl reagents. He found[7] that the radical-initiated polymers containing only about 6% free carbonyl would react with specific aldehyde reagents containing hydroxyl functions, such as alcohols and carboxylic acids, to give about 60–70% of the theoretical aldehyde value.[8] These reagents yield polymeric derivatives soluble in organic solvents, thus removing one of the major obstacles encountered in the earlier researches with acrolein polymers.

Schulz also demonstrated[9] that acrolein reacted with poly(vinyl alcohol) to produce crosslinked water-insoluble films. The reaction of cellulose with the water-soluble sulfurous acid adduct of polyacrolein was reported[10] by Schulz, and the application of this reaction product to impart wet-strength to paper was later patented.[11]

The recent development[12–14] of effective catalysts for the gas-phase oxidation of propylene with air or oxygen has made acrolein available commercially from relatively inexpensive materials and has stimulated intensive investigations on uses for this chemical. Among these patented uses, major attention has been given to the application of the polyacroleins to improve the wet-strength of paper. New methods of improving or modifying the properties of cellulose through crosslinking reactions are desirable for many reasons including compelling economic factors, among which are processing costs. To date, most crosslinking modifications of cellulose are accomplished by means of *N*-methylol derivatives of urea or of melamine. Preferably, any new crosslinking agent for cellulose should be soluble in water. For this reason, the reaction of cellulose with sulfurous acid adduct of polyacrolein as a wet-end additive to produce wet-strength paper has been extensively studied.[15] Water-soluble polyacroleins would also have value as crosslinking agents for proteins,[10,16,17] hides,[10,16,17] gelatin,[10,16,17] poly(vinyl alcohol),[9,18] cellulose,[15,16,19] as selective absorbants and exchangers,[20] and for the formation of complexes with metal salts.[21,22]

The copolymerization of acrolein with other monomers including water-soluble monomers has been studied also. Copolymerizations offer the possibility of producing soluble polymers and a number of copolymers of acrolein with vinyl monomers have been reported. Schulz reported[23] the copolymerizations of acrolein with acrylonitrile, acrylamide, vinyl acetate, and methyl acrylate in water and in dimethylformamide media. When water was used as the medium, all the copolymers precipitated when formed. He found[18] that the copolymerizations in dimethylformamide of acrolein with acrylonitrile or acrylamide were homogeneous if the conversions were 20% or less. The copolymerizations of acrolein with vinyl monomers such as acrylic acid,[24–26] methyl acrylate,[26] methacrylic acid,[24–26] acrylonitrile,[24,27,28] and acrylamide[26] have been mentioned or described in several patents. Copolymers soluble in the reaction medium were claimed if the copolymerizations were performed in aqueous media in the presence of another miscible organic solvent containing hydroxyl functions.[25–28] Acrylic acid–acrolein copolymers should be soluble in aqueous bases and precipitated by acids.

Although the copolymerization of acrolein with acidic-type acrylic monomers has been reported,[24–26] there has been no mention regarding their copolymerization parameters. The copolymerization parameters, r_1 and r_2, are especially important in those cases involving media in which the acidic vinyl monomer can ionize.

Earlier, Alfrey et al.[29] recognized that copolymerizations of ionizable monomers in ionizing media can lead to significant changes in the copolymerization parameters and that the values obtained depend markedly upon the pH of the reaction media. In the case of a monomer in which the acidic group is conjugated with a double bond, this variation in parameters was attributed principally to the difference in reactivities between the associated and unassociated acid. It might be expected that the reactivities of these two structures should differ appreciably since the anion might be considered to be an electron-donating substituent attached to the double bond, whereas the associated acid might be considered as an electron-withdrawing substituent. Thus, the charge on the double bond can change appreciably depending on the degree of ionization, or pH, and this in turn can alter the copolymer structure significantly. This was confirmed in another system by Ito, who showed[30] that the reactivity ratios of acrylonitrile and acrylic acid are pH-dependent; these results were correlated with the general Q and e copolymerization scheme.[31] In a similar study on the copolymerization of acrylonitrile and sodium *p*-styrenesulfonate by Izumi, it was shown[32] also that there is a considerable variation in the kinetic behavior of this strongly electrolytic-type monomer between pH 3 and 7. The reactivity ratios, r_1 and r_2, were shown to change in this pH range, and an attempt was made to correlate the effect of pH on the Q and e values.

This paper reports the studies on the copolymerization in homogeneous aqueous solutions at various pH values of acrolein and two ionizable vinyl monomers, namely, acrylic acid which is a weak acid, and sodium *p*-styrenesulfonate, which is derived from a strong acid.

RESULTS AND DISCUSSION

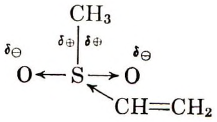
The r_1 and r_2 Parameters

The data obtained from the copolymerizations of acrolein and sodium *p*-styrenesulfonate at pH 3, 5, and 7 are shown in Tables I, II, and III, respectively. The corresponding data for the copolymerizations of acrolein with acrylic acid are shown in Tables IV, V, and VI, respectively. The copolymerization parameters, r_1 for acrolein and r_2 for the comonomers were obtained by the method of Mayo and Lewis[33] according to the equation, $r_1 = (dM_1/dM_2)r_2 + (dM_1/dM_2 - 1)M_2/M_1$. At least four lines from four different sets of data were used for each determination and the errors involved in the determinations defined. The r_1 and r_2 values for acrolein with sodium *p*-styrenesulfonate are given in Table VII and those for acrolein with acrylic acid are given in Table VIII.

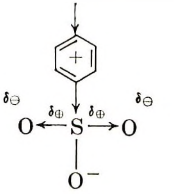
For the sodium *p*-styrenesulfonate copolymer the data of Table VII show that at a pH of 3, the r_1 and r_2 values are approximately equal and that the acrolein radical has about the same preference for the sodium *p*-styrenesulfonate monomer as the sodium *p*-styrenesulfonate radical has for the acrolein monomer. However, at a pH of 5 and 7 there is a preference for acrolein to be incorporated in the polymer and this incorporation is increased as the pH is raised from 3 to 7.

It will be noted in Table VII that the effect of pH on the r_2 values is considerably greater than the effect on r_1. Thus, the reactivity of the chains ending in a sodium *p*-styrenesulfonate radical is influenced markedly by the pH of the reaction media. This might be expected since sodium *p*-styrenesulfonate is the ionized species and the effect is in accordance with that observed by other investigators[29,30,32] for ionizable monomers.

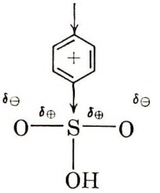
The change in reactivity of the sodium *p*-styrenesulfonate anion brought about by changes in pH might be explained by the combination of inductive and resonance effects on the labile π electrons of the vinyl double bond. It has been shown by Price and Zomlefer[34] that the overall effect is principally inductive when a sulfone is attached directly to the vinyl group. Thus, the formula for methyl vinyl sulfone or like groups may be represented as II



II



III



IV

In sodium *p*-styrenesulfonate a benzene ring is inserted between the vinyl group and the sulfone, and the inductive effect for the anion might be represented as III. The inductomeric effect thus draws the labile π elec-

TABLE I

Copolymerization at 52°C. of Acrolein (M_1) and Sodium *p*-Styrenesulfonate (M_2) at pH 3[a]

M_1, mole	M_2, mole	$\frac{M_1}{M_1 + M_2}$	Time, min.	Polymer, g.	Conversion, %	S, %	dM_1, mole[b]	dM_2, mole[c]	$\frac{dM_1}{dM_1 + dM_2}$
0.0084	0.0285	0.229	15	0.015	0.24	13.53	0.229	0.422	0.352
0.0160	0.0266	0.376	20	0.400	6.40	12.90	0.304	0.403	0.430
0.0215	0.0241	0.471	10	0.045	0.72	12.20	0.382	0.382	0.500
0.0261	0.0241	0.521	17	0.472	7.55	11.85	0.423	0.371	0.533
0.0448	0.0185	0.710	16	0.388	6.12	10.59	0.568	0.331	0.633
0.0571	0.0145	0.798	16	0.316	5.16	10.74	0.550	0.336	0.621

[a] Monomer concentration of 25% in water, with 2,2′-azobis-2-methyl-propionitrile, 0.25% on monomer weights, as initiator.
[b] dM_1 = moles of acrolein in copolymer.
[c] dM_2 = moles of sodium *p*-styrenesulfonate in copolymer.

TABLE II

Copolymerization at 54°C. of Acrolein (M_1) and Sodium *p*-Styrenesulfonate (M_2) at pH 5[a]

M_1, mole	M_2, mole	$\frac{M_1}{M_1 + M_2}$	Time, min.	Polymer, g.	Conversion, %	S, %	dM_1, mole[b]	dM_2, mole[c]	$\frac{dM_1}{dM_1 + dM_2}$
0.0082	0.0285	0.223	12	0.1273	2.04	12.27	0.383	0.377	0.496
0.0130	0.0272	0.324	12	0.1703	2.73	12.10	0.378	0.394	0.510
0.0225	0.0241	0.483	12	0.2660	4.20	11.47	0.359	0.465	0.565
0.0368	0.0205	0.642	12	0.2570	4.10	11.72	0.367	0.437	0.543
0.0555	0.0150	0.787	12	0.1690	2.70	11.17	0.350	0.499	0.588

[a] Monomer concentration of 25% in water, with 2,2′-azobis-2-methyl-propionitrile, 0.25% on monomer weights, as initiator.
[b] dM_1 = moles of acrolein in copolymer.
[c] dM_2 = moles of sodium *p*-styrenesulfonate in copolymer.

TABLE III

Copolymerization at 54°C. of Acrolein (M_1) and Sodium *p*-Styrenesulfonate (M_2) at pH 7[a]

M_1, mole	M_2, mole	$\frac{M_1}{M_1 + M_2}$	Time, min.	Polymer, g.	Conversion, %	S, %	dM_1, mole[b]	dM_2, mole[c]	$\frac{dM_1}{dM_1 + dM_2}$
0.0097	0.0285	0.254	7	0.269	4.35	12.82	0.401	0.312	0.438
0.0140	0.0268	0.343	7	0.285	4.55	11.72	0.367	0.438	0.545
0.0221	0.0241	0.478	8	0.307	4.90	11.69	0.365	0.441	0.547
0.0358	0.0205	0.636	8	0.315	5.05	11.07	0.346	0.515	0.598
0.0590	0.0150	0.797	10	0.114	1.80	10.26	0.321	0.605	0.656

[a] Monomer concentration of 25% in water, with 2,2′-azobis-2-methyl-propionitrile, 0.25% on monomer weights, as initiator.
[b] dM_1 = moles of acrolein in copolymer.
[c] dM_2 = moles of sodium *p*-styrenesulfonate in copolymer.

TABLE IV

Copolymerization at 54°C. of Acrolein (M_1) and Acrylic Acid (M_2) at pH 3[a]

M_1, mole	M_2, mole	$\frac{M_1}{M_1 + M_2}$	Time, min.	Polymer, g.	Conversion, %	C, %	dM_1, mole[b]	dM_2, mole[c]	$\frac{dM_1}{dM_1 + dM_2}$
0.0183	0.0747	0.197	90	0.1975	3.16	36.66	0.223	1.320	0.155
0.0307	0.0646	0.322	90	0.2505	4.00	38.00	0.303	1.150	0.208
0.0386	0.0583	0.398	90	0.3202	5.13	41.80	0.518	0.985	0.345
0.0476	0.0495	0.490	90	0.3003	4.80	46.70	0.795	0.771	0.508
0.0592	0.0395	0.598	90	0.2525	4.03	48.64	0.867	0.715	0.548
0.0706	0.0335	0.677	90	0.2722	4.35	47.26	0.830	0.743	0.527
0.0883	0.0231	0.795	90	0.2360	3.94	51.31	1.050	0.569	0.649

[a] Monomer concentration of 25% in water, with 2,2′-azobis-2-methyl-propionitrile, 0.25% on monomer weights, as initiator.
[b] dM_1 = moles of acrolein in copolymer.
[c] dM_2 = moles of acrylic acid in copolymer.

TABLE V

Copolymerization at 75°C. of Acrolein (M_1) and Acrylic Acid (M_2) at pH 5[a]

M_1, mole	M_2, mole	$\frac{M_1}{M_1 + M_2}$	Time, min.	Polymer, g.[b]	Conversion, %	C, %	dM_1, mole[c]	dM_2, mole[d]	$\frac{dM_1}{dM_1 + dM_2}$
0.0366	0.1480	0.198	90	0.1102	0.88	43.73	0.625	0.592	0.512
0.0560	0.1330	0.296	90	0.1200	0.95	35.85	0.179	0.817	0.180
0.0792	0.1140	0.410	90	0.0538	0.43	41.48	0.500	0.654	0.433
0.1020	0.0977	0.510	90	0.0811	0.64	58.53	1.460	0.164	0.900
0.1230	0.0807	0.605	90	0.0447	0.36	55.57	1.300	0.250	0.837
0.1450	0.0633	0.695	90	0.0767	0.60	57.41	1.400	0.195	0.877
0.1690	0.0422	0.797	90	0.1453	1.15	58.61	1.470	0.164	0.900

[a] Monomer concentration at 25% in water, with 2,2′-azobis-2-methyl-propionitrile, 0.50% on monomer weights, as initiator; [b] in all cases the copolymer precipitated during reaction; [c] dM_1 = moles of acrolein in copolymer; [d] dM_2 = moles of acrylic acid in copolymer.

TABLE VI

Copolymerization at 80°C. of Acrolein (M_1) and Acrylic Acid (M_2) at pH 7[a]

M_1, mole	M_2, mole	$\frac{M_1}{M_1 + M_2}$	Time, min.	Polymer, g.[b]	Conversion, %	C, %	dM_1 mole[c]	dM_2, mole[d]	$\frac{dM_1}{dM_1 + dM_2}$
0.0353	0.1450	0.195	90	0.0038	0.031	58.57	1.465	0.1635	0.900
0.0573	0.1300	0.305	90	0.0070	0.056	60.07	1.540	0.1250	0.925
0.0793	0.1160	0.405	90	0.0231	0.182	59.99	1.535	0.1265	0.923
0.1030	0.0983	0.513	90	0.0436	0.340	59.08	1.570	0.1430	0.912
0.1250	0.0790	0.613	90	0.0611	0.481	59.57	1.525	0.1320	0.921
0.1460	0.0627	0.700	90	0.0927	0.722	60.32	1.570	0.1110	0.935
0.1820	0.0449	0.801	90	0.0953	0.712	60.29	1.565	0.1120	0.933

[a] Monomer concentration of 25% in water, using 2,2′-azobis-2-methyl-propionitrile, 0.50% on monomer weights, as initiator; [b] in all cases the copolymer precipitated during reaction; [c] dM_1 = moles of acrolein in copolymer; [d] dM_2 = moles of acrylic acid in copolymer.

TABLE VII
Monomer Reactivity Ratios of Acrolein (M_1) and Sodium *p*-Styrenesulfonate (M_2) at Different pH Values

pH	Acrolein r_1	Sodium *p*-styrenesulfonate r_2	r_1r_2
3	0.33 ± 0.15	0.32 ± 0.05	0.106
5	0.23 ± 0.12	0.05 ± 0.03	0.012
7	0.26 ± 0.03	0.025 ± 0.025	0.0065

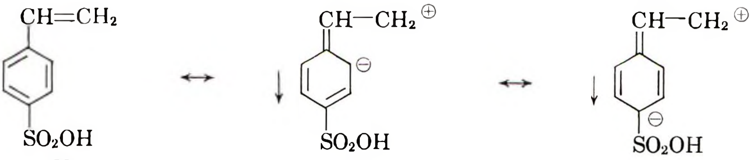
TABLE VIII
Monomer Reactivity Ratios of Acrolein (M_1) and Acrylic Acid (M_2) at Different pH Values

pH	Acrolein r_1	Acrylic acid r_2	r_1r_2
3	0.50 ± 0.30	1.15 ± 0.20	0.575
5	2.40 ± 0.50	0.05 ± 0.05	0.120
7	6.70 ± 3.00	0.00	0.00

trons from the double bond through the ring toward the sulfonyl group When the sulfonyl is protonated, III might be represented as IV.

Again, the inductive effect draws the labile π electrons through the ring toward the site of the sulfonic acid moiety. Since the net charge of the $SO_3^{\ominus}$ moiety in III is negative, whereas the net charge of the SO_3H moiety in IV is zero, it follows that the SO_3H group has the greater affinity for electrons. Therefore, the electron withdrawal from the double bond will be greater for the sulfonic acid molecule than for the sulfonate anion.

In addition to the inductomeric effect, the resonance effect should also be considered. While the sulfone group does not enter into direct resonance interaction with the rest of the molecule, it may contribute to the stability of the resonance hybrids by means of charge stabilization, as in V–VII



V VI VII

This effect would be greatest in resonance form VII, where the negative charge is in a position *para* to the vinyl group. Again, one should find that the sulfonic acid group contributes more to this stability than does the sulfonate anion.

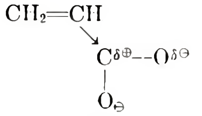
In the case of the acrolein–acrylic acid copolymer, the data of Table VIII show that acrylic acid is preferentially incorporated in the copolymer at a pH of 3 but, as the pH is raised to 7, the acrolein is preferentially incorporated almost exclusively; this preference increases with an increase in pH. The copolymers prepared at pH 5 and 7 have only small amounts of the solubilizing acrylic comonomer in their compositions. Since polyacrolein is insoluble in the reaction media, this would account for the precipitation of the copolymers at pH 5 and 7. Although the copolymers precipitated at pH 5 and 7, the reactivity ratios follow the same general trend as those reported by Ito and Suzuki[30] for acrylonitrile and acrylic acid, as shown in Table IX.

TABLE IX

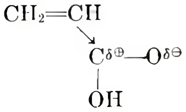
Comparison of the Reactivity Ratios of Acrolein (M_1) and Acrylic Acid (M_2) with Acrylonitrile (M_1) and Acrylic Acid (M_2)

	Acrolein			Acrylonitrile		
pH	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
3	0.5	1.15	0.575	0.35	1.15	0.403
5	2.4	0.05	0.120	—	—	—
7	6.7	0.00	0.000	0.77	0.21	0.162

The change in the reactivity of acrylic acid anion with the change in pH might be interpreted as the result of the changes in the inductive and the resonance effects brought about by the protonization of the carboxyl group conjugated with the vinyl double bond. For example, the inductive effects may be represented by structures VIII and IX.

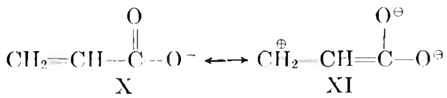


Anion
VIII



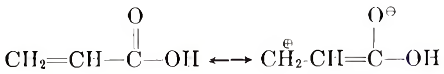
Associated acid
IX

The resonance effect for the anion may be shown by structures X and XI, and compared to XII and XIII for the associated acid.



$CH_2{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O^- \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}\overset{\displaystyle O^\ominus}{\overset{|}{C}}{-}O^\ominus$

X XI



$CH_2{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH \longleftrightarrow \overset{\oplus}{C}H_2{-}CH{=}\overset{\displaystyle O^\ominus}{\overset{|}{C}}{-}OH$

XII XIII

It is apparent from these resonance forms that the positive charge on the β carbon atom is more stabilized when the acid is protonated because of the unfavorable resonance form, XI, of the anion. Further, the CO_2H moiety is a stronger electron-withdrawing group than the CO_2^- moiety due to the difference in charge. Thus, the vinyl group of acrylic acid has a greater positive charge than the vinyl group of the acrylate anion.

The copolymers prepared at pH 5 and 7 were synthesized with a higher initiator concentration and at a higher temperature than those made at pH 3. These conditions were necessary because of the retarded polymerizations at pH values above 3; a similar retardation was reported by Ito and Suzuki[30] in the copolymerization of acrylonitrile and acrylic acid at pH values above 3.

In both the acrolein–sodium-*p*-styrenesulfonate and the acrolein–acrylic acid systems, the copolymers change from alternating copolymers to more random copolymers as the pH is increased from 3 to 7; the randomness is more pronounced in the case of the acrylic acid copolymer. Also, when r_1 is large and r_2 is very small, retardation is evident in most copolymerizations. It will be noted that as the pH is increased from 3 to 7, the ratio of r_1 to r_2 values in both copolymers increases, but the increase is much greater in the case of the acrylic copolymer, which is in agreement with the observed greater retardation.

The *Q* and *e* Parameters

The *Q* and *e* scheme developed[31] by Alfrey and Price associates two constants with an individual monomer to account for its behavior in copolymerizations. A variety of *Q* and *e* values have been reported for acrolein, and some of the more recent assignments are presented in Table X.

TABLE X
Literature *Q* and *e* Values for Acrolein

Q	*e*	Year	Reference
0.85	0.73	1964	35
0.67	0.69	1964	35
0.64	0.56	1964	35
0.99	0.05	1964	35
0.47	0.69	1964	35
0.20	0.69	1964	35
1.08	0.89	1961	36
0.55	0.88	1958	37

Rather wide variations are observed in the values shown in Table X and some of the variations have been attributed to the insolubility of the acrolein copolymers in the specific media used in the synthesis leading to questionable r_1 and r_2 values from which the *Q* and *e* were calculated.

It was a secondary objective of this study to derive a *Q* and *e* value for acrolein polymerized in aqueous systems homogeneously without copolymer precipitation. Accordingly, *Q* and *e* values were calculated by the method of Alfrey and Price[31] from our experimentally derived reactivity ratios of acrolein–sodium-*p*-styrenesulfonate found at pH 3 by using as the reference the *Q* and *e* values for sodium *p*-styrenesulfonate of 0.76 and −0.26 respectively, which values were based on copolymerizations at pH of 3 with acrylonitrile, a monomer whose Q and e values have been well established. The new calculated values for acrolein were found to be $Q = 1.6$ and $e = 1.2$.

Since it has been shown that in ionizing media the relative reactivities depend upon the degree of ionization of the ionizing species, the behavior of the ionizing monomer cannot be characterized by a single set of Q and e parameters. In order to demonstrate the pH effects on the ionizing monomer, the Q (1.6) and e (1.2) values, calculated for acrolein, were used to calculate the respective Q and e values for sodium *p*-styrenesulfonate and acrylic acid as a function of pH. These calculated values are shown in Table XI.

TABLE XI
Calculated Q and e Values for Sodium *p*-Styrenesulfonate and Acrylic Acid as a Function of pH

	Sodium *p*-styrenesulfonate		Acrylic acid	
pH	Q	e	Q	e
3	0.76	−0.26	1.27	0.50
5	0.51	−0.87	0.11	−0.22
7	0.39	−1.00	—	—

An analysis of the Q and e values presented for sodium *p*-styrenesulfonate in Table XI reveals that the e values are markedly effected by pH, while the effect on Q is not so large. It follows, then, that the overall effect of protonization is to lessen the push of electrons by the anion into the double bond. An analysis of the Q and e values for acrylic acid given in Table XI reveals that not only does protonization lessen the push of electrons into the double bond, but the double bond changes from a plus to a minus character depending on the pH. Moreover, a pronounced effect is also observed on the Q value for acrylic acid, which drops to a significantly low value of 0.11. This value is comparable to that of vinyl acetate which is known[38] to be difficult to initiate. It then follows that this low Q value may contribute to the retardation effects observed in the copolymerization of acrylic acid with acrolein as well as acrylic acid with acrylonitrile at pH values between 5 and 7. The retardation effect in the copolymerization observed for the acrylic acid anion was not observed for the sodium *p*-styrenesulfonate anion, probably because the Q value of the latter was influenced less than the former by changes in the system.

In comparing the copolymerization of acrolein and sodium *p*-styrenesulfonate, a comonomer derived from a strong acid, with the copolymerization of acrolein and acrylic acid, a weak acidic-type comonomer, it becomes apparent that the pH effects are more pronounced in the acrylic acid copolymerizations than in the sodium *p*-styrenesulfonate system, probably because the weaker acrylic acid is considerably more protonated at a given pH. The pK_a of *p*-styrenesulfonic acid[39] is similar to that of toluenesulfonic acid, −1.3, and compares to that of acrylic acid[40] with a pK_a of 4.25. Copolymer composition plots (Figs. 1 and 2) demonstrate effectively the difference in these two acidic vinyl monomers. The difference in the copolymer composition curves for sodium *p*-styrenesulfonate and acrolein at pH 5 and 7 is minor; this is probably due to the insignificant difference in protonization of this strong acid at these two pH levels. In contrast, the difference between the curves shown at pH 5 and 7 for acrylic acid and acrolein is significant; this is probably due to the greater protonization of this weaker acid at the higher pH. The shift occurring in the curves for the copolymerization of sodium *p*-styrenesulfonate and acrolein between pH 3 and 5 is appreciable, and the shift in the curves for the copolymerization of acrylic acid and acrolein between pH 3 and 5 is even more pronounced. One would expect this sharper change for acrylic acid, since the pK_a of the monomer lies in this region and a greater variation could be expected in the region in which protonization changes most rapidly. For sodium *p*-styrenesulfonate, which is the salt of a strong acid, this effect occurs in a pH region lower than that studied here.

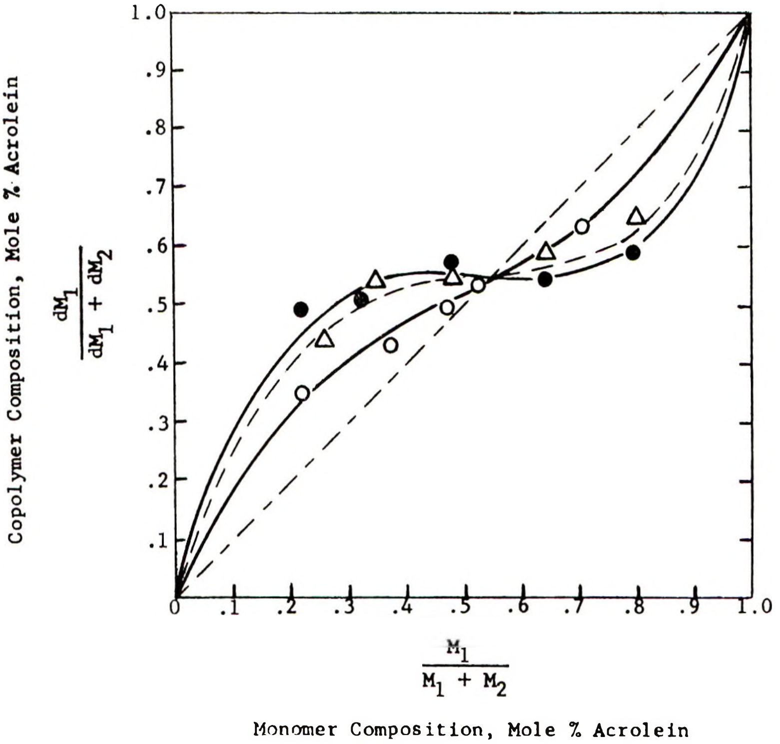


Fig. 1. Copolymer composition plots as a function of solution pH for the copolymerization of acrolein and sodium *p*-styrenesulfonate in aqueous solution: (○) pH 3; (●) pH 5; (△) pH 7.

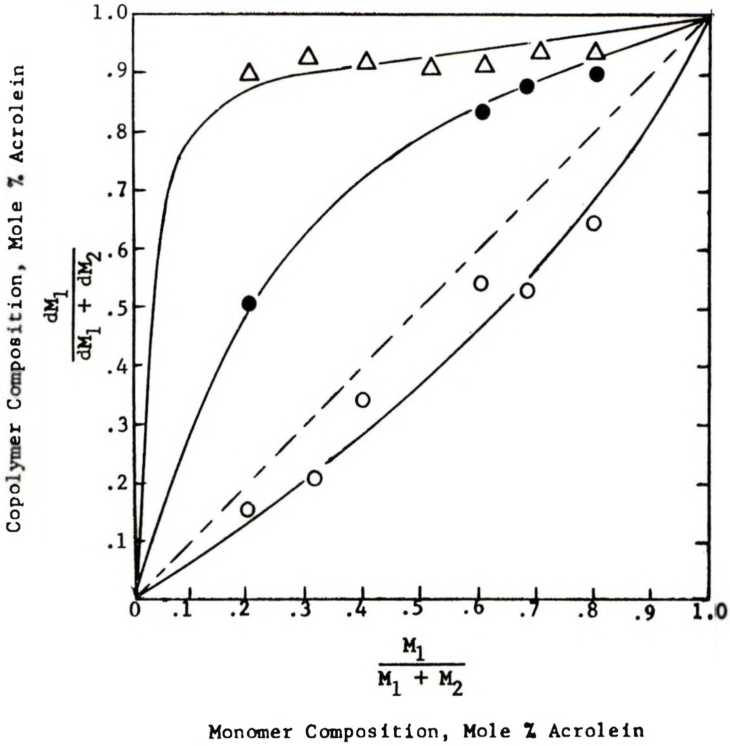


Fig. 2. Copolymer composition plots as a function of solution pH for the copolymerization of acrolein and acrylic acid in aqueous solution: (○) pH 3; (●) pH 5; (△) pH 7.

EXPERIMENTAL

Materials

Commercial acrolein was distilled under a nitrogen atmosphere in a $^3/_4$-in. diameter 18-in. long column packed with Berles saddles at a reflux ratio of 6:1. The fraction boiling at 47–48°C./600 mm. (lit.:[41] 46°C./603 mm.) was collected, blanketed with dry deoxygenated nitrogen, and stored in a glass container at 0°C. until ready for use.

Glacial acrylic acid was distilled under nitrogen in the column described above at a 6:1 reflux ratio. The fraction boiling at 65°C./33 mm. (Lit.:[42] 63°C./35 mm.) was collected, blanketed with dry deoxygenated nitrogen, and stored frozen until ready for use.

Sodium *p*-styrenesulfonate was dried to constant weight in a vacuum oven at room temperature and stored in vacuum in a desiccator over anhydrous calcium chloride until ready for use. Fresh azobisisobutyronitrile was kept at 0°C. and used without further purification.

Deionized distilled water was used in all experiments.

Copolymerizations

All copolymerizations were performed in aqueous solutions. The quantity of each monomer required to form a 25% solution by weight of total monomer was calculated at mole fractions of 0.2, 0.3, 0.5, 0.6, 0.7, and 0.8. The volume of acrolein corresponding to the acrolein weights was calculated from the density of acrolein (lit.:[43] 0.84 g./ml. at 20°C.). A typical copolymerization procedure was as follows.

All chargings were performed under a nitrogen atmosphere in a drybox. The desired amount of sodium *p*-styrenesulfonate was weighed into a 100-ml. glass-stoppered flask. Then 25 ml. of distilled deionized water was added to the flask and after the monomers dissolved, the pH of each solution was adjusted to 3.0, 5.0, or 7.0 ± 0.05 with 0.1*N* sodium hydroxide solution, a Beckman Model 76 Zeromatic expanded-scale pH meter being used for pH measurement. Then, the initiator, 2,2′-azobis-2-methylpropionitrile (0.156 g., 0.25% of monomer weight) was weighed into a 35-ml. serum vial which was then evacuated to 0.1 mm. Hg pressure with a vacuum pump through an attached three-way stopcock. The vials were then brought to atmospheric pressure by bleeding nitrogen gas into the vials. This procedure was repeated three times. Then the vials were transferred to the inert atmosphere of the drybox where the stopcocks were removed and the vials were sealed with sleeve-type rubber serum stoppers. After weighing the vials, the required volume of acrolein was injected into each vial with a 5-ml. hypodermic syringe. The vials were weighed again, and the difference in weight taken as that for the acrolein feed.

After the initiator had dissolved in the acrolein, the aqueous solutions of sodium *p*-styrenesulfonate were injected into the vial with a 5-ml. hypodermic syringe. The vials were then shaken to effect a homogeneous solution and placed in an oil bath controlled thermostatically to 52°C. The vials remained in the oil bath for the time periods indicated in Tables I–III. The copolymers were precipitated by mixing rapidly with stirring the contents of the vials with 100 ml. of alkaline ethanol (2.5% NaOH).

The precipitated polymers were isolated by filtration and dissolved immediately in 10 ml. of distilled water. Then 30 ml. of absolute ethanol were added to the aqueous solutions causing the copolymers to precipitate, after which it was isolated by filtration and dried in a vacuum oven at room temperature to constant weight. The polymer sample was purified further for microanalysis by dissolving approximately 0.1 g. of the polymer in 10 ml. of distilled water followed by precipitation with 30 ml. of absolute ethanol. This procedure was repeated three times. Finally, the samples were dried in an Abderhalden drying pistol for 48 hr. at 56°C./1 mm. Hg pressure. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside, New York, and the per cent sulfur used to calculate the reactivities.

The procedure used for the copolymerization of acrolein and sodium *p*-styrenesulfonate was repeated for the acrolein and acrylic acid copolymerizations except that the solutions of acrylic acid in the water solvent were adjusted to a pH of 3.0 ± 0.05 with 1*N* KOH, to a pH of 5 with 10*N* KOH, and to a pH 7 with 15*N* KOH. The polymerization time was 90 min., and the polymerization temperatures are as shown in Tables IV–VI.

The copolymers prepared at pH 3 were soluble in the reaction solvent. In order to achieve a large difference in the copolymers between the carbon contribution of acrolein which contains 64.3% carbon and of acrylic acid which contains 50% carbon, the copolymers were isolated as the potassium salts of acrylic acid, the per cent carbon in potassium acrylate being fixed as 32.7%. The copolymers were precipitated by mixing rapidly with stirring the contents of the vials with 100 ml. of acetone containing 10 ml. of 1.0*N* potassium hydroxide. The precipitated copolymers were recovered by filtration, dissolved in 3 ml. of 0.1*N* aqueous potassium hydroxide and reprecipitated by the addition of 15 ml. of acetone, refiltered, repeatedly washed with excess acetone, and dried in a vacuum oven at room temperature for 15 hr.

The polymer samples were purified further for microanalysis by washing approximately 0.1 g. repeatedly with distilled water until the pH of the washings tested neutral to Hydrion paper. The polymers were then dispersed in fresh distilled deionized water, and after 20 hr., the solution pH was checked with a pH meter and measured 7.0 ± 0.10. Finally, the polymers were isolated by filtration and washed repeatedly with excess acetone and dried in an Abderhalden drying pistol for 50 hr. at 56°C. at 3 mm. Hg pressure. The copolymers prepared at pH 5 and pH 7 precipitated during preparation; they were recovered by dilution with water followed by filtration and purified in the same manner as those prepared at pH 3. Elemental analyses were performed on the dried purified polymers and the per cent carbon used to calculate the reactivities, which data agreed well with the potassium content.

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Résumé

L'acroléine a été copolymérisée par initiation radicalaire en solutions aqueuses avec le parastyrénesulfonate de sodium et l'acide acrylique respectivement, dans le domaine de pH de 3 à 7. Cette réactivité était dépendante du pH. Pour l'acroléine (M_1), et le *p*-styrénesulfonate de sodium (M_2) on trouve: $r_1 = 0.33 \pm 0.15$ et $r_2 = 0.32 \pm 0.05$ à pH 3; $r_1 = 0.23 \pm 0.12$ et $r_2 = 0.05 \pm 0.03$ à pH 5; $r_1 = 0.26 \pm 0.03$ et $r_2 = 0.025 \pm 0.025$ à pH 7. Pour l'acroléine M_1 et l'acide acrylique M_2: $r_1 = 0.50 \pm 0.30$ et $r_2 = 1.15 \pm 0.2$ à pH 3; $r_1 = 2.40 \pm 0.50$ et $r_2 = 0.05 \pm 0.05$ à pH 5; $r_1 = 6.70 \pm 3.00$ et $r_2 = 0.00$ à pH 7. Pour l'acroléine, les nouvelles valeurs de $Q = 1.6$ et $e = 1.2$ ont été calculées. Pour le *p*-styrènesulfonate de sodium les valeurs $Q = 0.76$ et $e = -0.26$ à pH 3, $Q = 0.51$ et $e = -0.87$ à pH 5, $Q = 0.39$ et $e = -1.00$ à pH 7 et pour l'acide acrylique, les valeurs de $Q = 1.27$ et $e = 0.50$ à pH 3 et $Q = 0.11$ et $e = -0.22$ à pH 5 ont été trouvées. Les variations de réactivités sont expliquées sur lar base d'effets inductifs et de résonance.

Zusammenfassung

Acrolein wurde bei Radikalstart in wässriger Lösung mit Natrium-*p*-styrolsulfonat bzw. Acrylsäure im pH-Bereich von 3 bis 7 copolymerisiert. Für das Paar Acrolein

(M_1)-Natrium-*p*-styrolsulfonat (M_2) gilt: $r_1 = 0{,}33 \pm 0{,}15$ und $r_2 = 0{,}32 \pm 0{,}05$ bei pH 3; $r_1 = 0{,}23 \pm 0{,}12$ und $r_2 = 0{,}05 \pm 0{,}03$ bei pH 5; $r_1 = 0{,}26 \pm 0{,}03$ und $r_2 = 0{,}025 \pm 0{,}025$ bei pH 7. Für das Paar Acrolein (M_1)-Acrylsäure (M_2): $r_1 = 0{,}50 \pm 0{,}30$ und $r_2 = 1{,}15 \pm 0{,}2$ bei pH 3; $r_1 = 2{,}40 \pm 0{,}50$ und $r_2 = 0{,}05 \pm 0{,}05$ bei pH 5; $r_1 = 6.70 \pm 3{,}00$ und $r_2 = 0.00$ bei pH 7. Für Acrolein wurden die neuen Werte von $Q = 1{,}6$ und $e = 1{,}2$ berechnet. Für Natrium-*p*-styrolsulfonat wurden die Werte $Q = 0{,}76$ und $e = -0{,}26$ bei pH 3; $Q = 0{,}51$ und $e = -0{,}87$ bei pH 5; $Q = 0{,}39$ und $e = -1{,}00$ bei pH 7 und für Acrylsäure $Q = 1{,}27$ und $e = 0{,}50$ bei pH 3; $Q = 0{,}11$ und $e = -0{,}22$ bei pH 5 abgeleitet. Die Reaktivitätsänderungen können durch induktive und Resonanzeffekte erklärt werden.

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Rates of Polymer Formation and Monomer Consumption in the Solution Polymerization of Trioxane Catalyzed by $BF_3 \cdot O(C_2H_5)_2$

T. MIKI, T. HIGASHIMURA, and S. OKAMURA, *Department of Polymer Chemistry, Kyoto University, Kyoto, Japan*

Synopsis

In the solution polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ at 30°C. the amount of the methanol-insoluble polyoxymethylene is less than the amount of monomer consumed. This difference was much larger than the amount of formaldehyde determined in the polymerized system and could not also be explained in terms of the amount of the methanol-soluble oligomer. Tetraoxane was detected in large quantities by gas chromatography in the polymerized solution of trioxane. Therefore, the difference between the amounts of the methanol-insoluble polymer and the monomer consumed was ascribed partly to the formation of tetraoxane. In spite of the fact that tetraoxane was polymerized more easily than trioxane by $BF_3 \cdot O(C_2H_5)_2$, an almost constant amount of tetraoxane was produced, independent of the kind of solvent and the polymer yield. This suggests the existence of an equilibrium concentration of tetraoxane. On the other hand, the formation of trioxane was observed in the solution polymerization of tetraoxane by $BF_3 \cdot O(C_2H_5)_2$. This suggests that the formation of tetraoxane during the trioxane polymerization is due to a back-biting reaction in which the growing chain end of trioxane attacks the oxygen atom in its own chain with depolymerization of tetraoxane.

INTRODUCTION

Recently many papers on the polymerization of trioxane have been published. Kern[1] and Kučera[2] have carried out extensive kinetic studies of the trioxane polymerization. We have also investigated the solution polymerization of trioxane catalyzed by boron trifluoride diethyl etherate.[3-5] However, these kinetic investigations, not only ours but those of other researchers, are based on the measurement of the polymer formation rate, either by a gravimetric or by a dilatometric method. To elucidate the mechanism of trioxane polymerization, it is necessary to know the change in monomer as well as polymer formation.

We have now studied the solution polymerization of trioxane on the basis of the measurement of the monomer consumption rate, which was followed by gas chromatography, in addition to the measurement of the polymer formation rate (or the polymer yield) by a gravimetric method. It was observed that the rate of the polymer formation did not coincide with the rate of monomer consumption and that the former rate is smaller than the latter in each solvent. This difference was considered to be caused not by the existence of the low polymer (or oligomer) which is soluble in the precipitant but by the formation of certain materials other than the polymer, which are soluble in the precipitant. One such material detected was tetraoxane; that is, in the polymerization of trioxane, tetraoxane was produced. On the other hand, in the polymerization of tetraoxane, whose polymerization mechanism is considered to be the same as that of trioxane, the formation of trioxane was observed.

In this paper the difference between the monomer consumption rate and the polymer yield in various solvents, the amount of tetraoxane formed in the solution polymerization of trioxane in various solvents, and the polymerization mechanism will be discussed.

EXPERIMENTAL

The procedures of the polymerization, the purification method of trioxane, solvents, and boron trifluoride diethyl etherate, $BF_3 \cdot O(C_2H_5)_2$, were the same as described in the previous paper.[3]

The polymer yield was determined in the following way. The polymerization was stopped in a given period of time by adding methanol containing a small amount of ammonia; the polymer formed was filtered, washed with methanol, dried in vacuum at the room temperature, and weighed. The amount of monomer (trioxane) consumed was determined by measuring the amount of the residual monomer by gas chromatography. In this case the internal standard method was adopted, and the calibration curve was prepared beforehand for the same compositions as in the polymerization without the addition of the catalyst. The peak area was

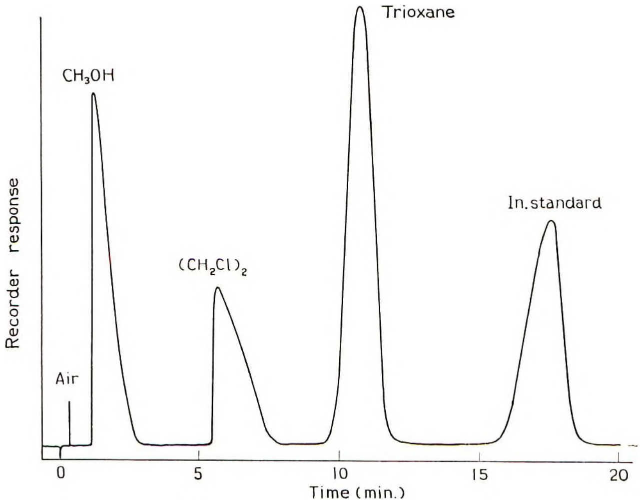


Fig. 1. Gas chromatogram of trioxane solution in ethylene dichloride containing methanol and the internal standard. Column temperature 95°C., carrier gas H_2 (60 ml./min.), chart speed 10 mm./min.

measured by using a planimeter in the chart analysis. A typical diagram is shown in Figure 1.

The amount of trioxane produced during the polymerization of tetraoxane, which was carried out in the same way as that of trioxane, was also measured by gas chromatography according to the same method. Tetraoxane, which was supplied by Toyo Koatsu Company, Ltd., was used without further purification. (m.p. 112.7°C., lit. m.p.[6] 112°C.).

RESULTS

Difference between Monomer Consumption Rate and Polymer Yield in Various Solvents

The time–conversion curves in the polymerization of trioxane were obtained in benzene as a nonpolar solvent, ethylene dichloride as a polar solvent, and nitrobenzene as a highly polar solvent. The results at the similar monomer concentration are shown in Figures 2, 3, and 4, respectively. Three runs of the trioxane polymerization were carried out in order to examine the reproducibility in the determination of conversion by the gas chromatographic method (Fig. 3). In each solvent the conversion was determined by the gravimetric and gas chromatographic methods. The gravimetric method (giving the polymer yield) yields $[P]_t/[TO]_0$ and the gas chromatographic method (giving the monomer consumption rate) yields $([TO]_0 - [TO]_t)/[TO]_0$, where $[TO]_0$ denotes the initial amount of trioxane, $[P]_t$ denotes the amount of the polymer precipitated from methanol at time t, and $[TO]_t$ denotes that of unreacted trioxane at time t, which was measured by gas chromatography.

It is clear from these figures that the time–conversion curves determined by the two methods did not coincide in all solvents. Although an induction period was observed for the polymer yield, none was observed for the monomer consumption. The amount of the polymer obtained is less than that of

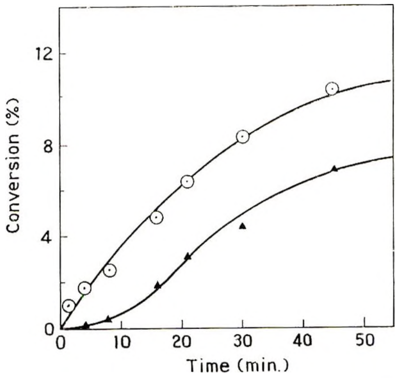


Fig. 2. Dependence of conversion on the reaction time in the polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in benzene at 30°C.: (○) gas chromatographic method; (▲) gravimetric method. $[M]_0 = 3.22$ mole/l.; $[BF_3 \cdot O(C_2H_5)_2]_0 = 10$ mmole/l.; $[H_2O]_0 = 0.9$ mmole/l.

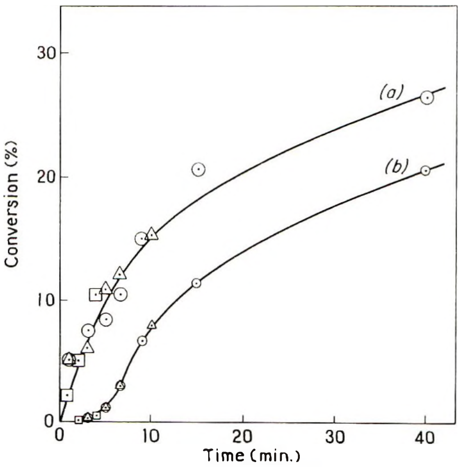


Fig. 3. Dependence of conversion on the reaction time in the polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in ethylene dichloride at 30°C.: (*a*) gas chromatographic method; (*b*) gravimetric method. $[M]_0 = 3.30$ mole/l.; $[BF_3 \cdot O(C_2H_5)_2]_0 =$ 10 mmole/l.

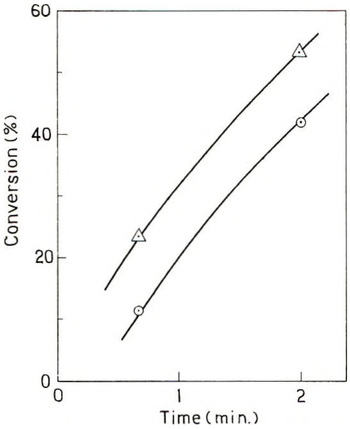


Fig. 4. Dependence of conversion on the reaction time in the polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in nitrobenzene at 30°C.: (△) gas chromatographic method; (○) gravimetric method. $[M]_0 = 3.30$ mole/l.; $[BF_3 \cdot O(C_2H_5)_2]_0 = 1.0$ mmole/l.; $[H_2O]_0 = 0.9$ mmole/l.

the monomer consumed in all conditions. The amount of consumed trioxane which was not weighed as the polymer is 2–4% of the initial amount of charged trioxane in benzene, 7–10% in ethylene dichloride, and 10–13% in nitrobenzene. Thus this amount increases with increasing the polarity of solvent.

It is necessary to elucidate the cause of this difference. It may be taken as one of the probable causes that a large amount of low polymer (oligomer) which is soluble in methanol was produced and not determined by the gravimetric method. If this is true, that difference in conversion

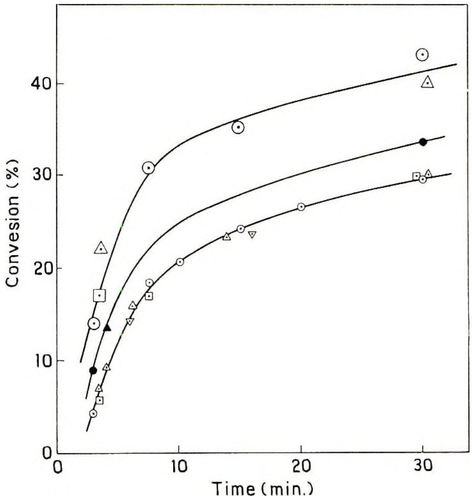


Fig. 5. Effect of the nature of the precipitant on the amount of polymer obtained and the amount of tetraoxane produced in the polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in ethylene dichloride at 30°C. with various precipitants: (○) methanol; (□) petroleum ether; (△) acetone; (▽) *n*-hexane. Results were obtained by (large symbols ○, △, □) the gas chromatographic method, (small symbols ○, ▽, □, △) by the gravimetric method, and the sum (●, ▲) of the amount of methanol-insoluble polymer and tetraoxane produced was also plotted.

will be affected by the nature of the precipitant and become smaller on using a more effective precipitant which would dissolve a smaller amount of oligomer. However, as is shown in Figure 5, the time–conversion curve (determined by the gravimetric method) in the polymerization of trioxane was unaffected by the nature of the precipitant. Therefore the difference in conversion between the two methods does not seem to be due primarily to formation of oligomer which is soluble in the precipitant.

Another cause must be taken into account, namely, that trioxane was converted into materials other than a polymer and oligomer. One such material may be formaldehyde. Indeed, the formation of formaldehyde has been observed in the polymerization of trioxane,[1,4,7,8] but the amount formed was so small that formaldehyde was not detected in the polymerizing solution by infrared spectroscopy.[9] Therefore, a material other than formaldehyde ought to be produced during the polymerization of trioxane.

Production of Tetraoxane in Polymerization of Trioxane

As is shown in Figure 6, a substance other than methanol, the solvent, trioxane and the internal standard was observed in the gas chromatogram of the polymerized system. This new substance was not detected in gas chromatograms of the unpolymerized system which contained only trioxane and solvent. This substance was not the unconsumed catalyst, $BF_3 \cdot O(C_2H_5)_2$. This means that a new compound was produced either during the polymerization of trioxane or on addition of methanol which stops the poly-

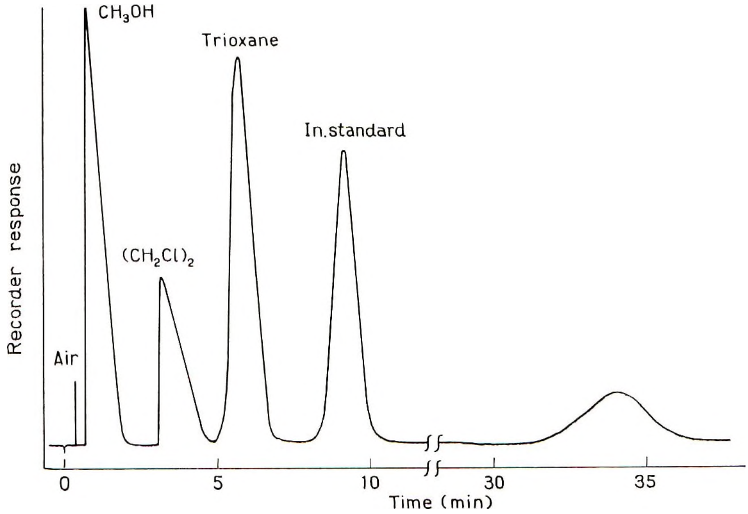


Fig. 6. Gas chromatogram of the polymerized trioxane system. Column temperature 110°C.; carrier gas H$_2$ (60 ml./min.), chart speed 10 mm./min.

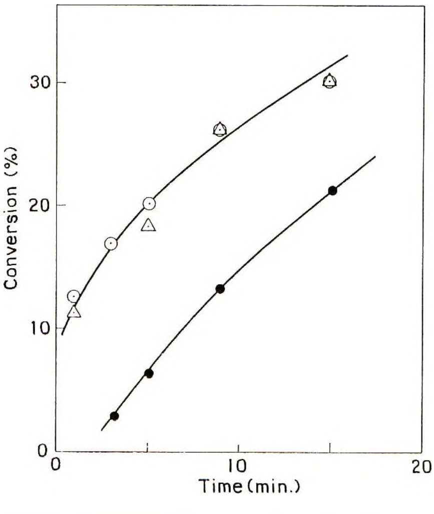


Fig. 7. Amount of tetraoxane produced in polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in nitrobenzene at 30°C.: (●) gravimetric method; (○) gas chromatographic method; (△) sum of amounts of methanol-insoluble polymer and tetraoxane. $[M]_0 = 1.10$ mole/l.; $[BF_3 \cdot O(C_2H_5)_2]_0 = 10$ mmole/l.; $[H_2O]_0 = 2.0$ mmole/l.

merization. Even in using acetone as the precipitant, this new substance appeared, and its retention time was the same as that of the product found with methanol as precipitant. Therefore, this compound must be produced during the polymerization.

The retention time of this compound was found to be the same as that of tetraoxane. Moreover, when the unknown compound was isolated through gas chromatography by a fraction collector, the melting point of the

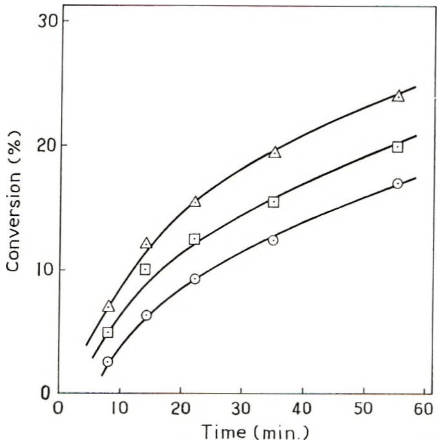


Fig. 8. Amount of tetraoxane produced in the polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in benzene at 30°C.; (○) gravimetric method; (△) gas chromatographic method; (□) sum of amounts of methanol-insoluble polymer and tetraoxane. $[M]_0 = 3.30$ mole/l.; $[BF_3 \cdot O(C_2H_5)_2]_0 = 20$ mmole/l.; $[H_2O]_0 = 2.4$ mmole/l.

fraction coincided with that of tetraoxane; m.p. of the fraction collected 112°C.; m.p. of tetraoxane supplied by Toyo Koatsu Co. 112.7°C. (lit.[6] 112°C.). Therefore, this compound is identified as tetraoxane.

The amount of tetraoxane produced during the polymerization of trioxane in various solvents was determined by gas chromatography according to the internal standard method. These results are shown in Figures 5, 7, and 8. In each figure, the time–conversion curves are expressed in the three ways: that is, the amount of trioxane consumed, the amount of polymer obtained, and the sum of the amounts of polymer and tetraoxane obtained. As is clear from these figures, a large amount of tetraoxane was produced during the trioxane polymerization and its amount was almost equal in each solvent, that is, 200–250 mg. of tetraoxane was produced in 20 ml. of polymerization solution containing 2 g. of trioxane in nitrobenzene and in that containing 6 g. of trioxane in benzene and ethylene dichloride. The amount of tetraoxane produced is no less than 10% of the amount of charged trioxane in nitrobenzene. Moreover, in nitrobenzene the amount of tetraoxane produced corresponds to that of the methanol-soluble substances, while in benzene and ethylene dichloride it is a part of the methanol-soluble substances.

Production of Trioxane in the Polymerization of Tetraoxane

The polymerization of tetraoxane was carried out in ethylene dichloride by $BF_3 \cdot O(C_2H_5)_2$. As is shown in Figure 9, the rate of polymerization of tetraoxane was much larger than that of trioxane, in spite of the fact the catalyst concentration in the polymerization of tetraoxane was twenty times smaller than that in the polymerization of trioxane. In Figure 9, the conversion was determined by the gravimetric

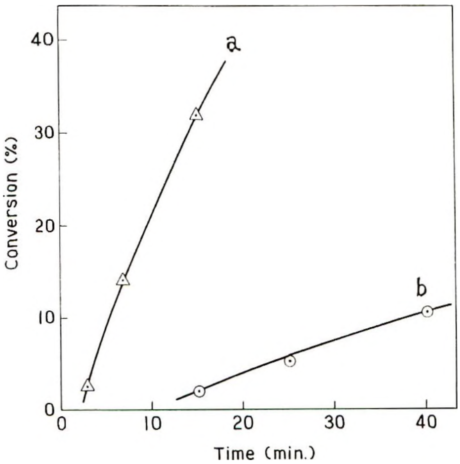


Fig. 9. Comparison of the polymerization rate of tetraoxane with that of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in ethylene dichloride at 30°C.: (*a*) tetraoxane, [Cat] = 0.9 mmole/l.; (*b*) trioxane, [Cat] = 18 mmole/l. $[M]_0$ = 1.5 mole/l.

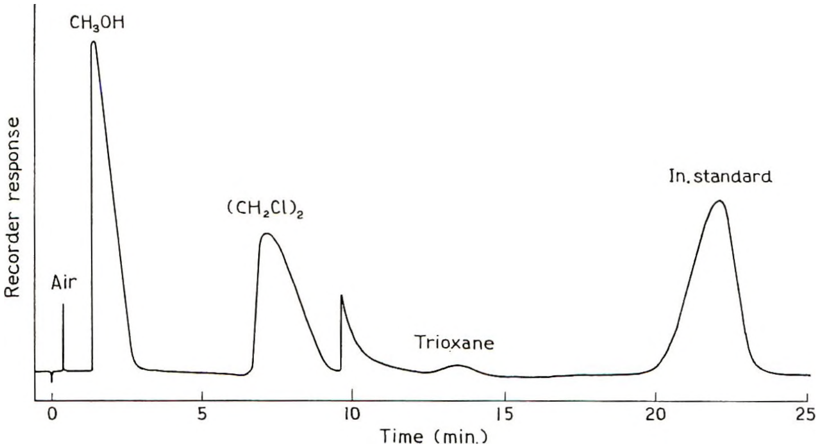


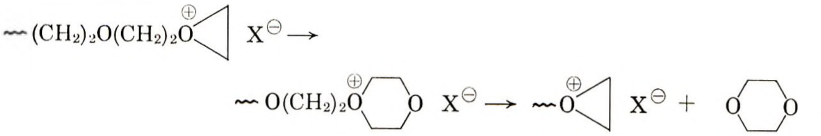
Fig. 10. Gas chromatogram of the polymerized tetraoxane system. Column temperature 85°C., carrier gas H_2 (60 ml./min.), chart speed 10 mm./min.

method. In the gas chromatogram of the polymerized system of tetraoxane, as is shown in Figure 10, in which the peak corresponding to tetraoxane was excluded, trioxane was detected. However, the amount of trioxane produced during the polymerization of tetraoxane was small in comparison with the amount of tetraoxane produced during the polymerization of trioxane.

DISCUSSION

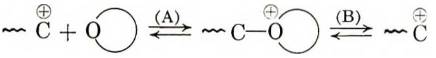
It is very interesting that tetraoxane can be produced during the polymerization of trioxane. It has been reported that, in the polymerization of

α-oxides such as ethylene oxide, dioxane or substituted dioxane in addition to the polymer is produced as shown in eq. (1).[10–12]

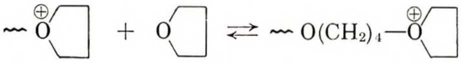

(1)

Therefore, it seems to be a general phenomenon in the ring-opening polymerization through the cationic mechanism that a cyclic oligomer is produced during the polymerization. In the case of α-oxides, dioxane, which cannot be polymerized by the usual cationic catalyst, may exist in the polymerization system. Tetraoxane, however, can be polymerized by $BF_3 \cdot O(C_2H_5)_2$ more easily than trioxane under the similar condition, as is shown in Figure 9. We try to make it clear how tetraoxane is produced and exists in the polymerization system in spite of such a fact.

Kučera et al. have supposed from the kinetic study that the polymerizations of trioxane and dioxolane are equilibrium reactions expressed schematically as follows:[13,14]


(2)

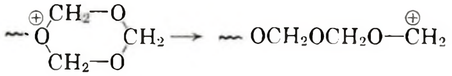
where the cyclic compound may be either trioxane or dioxolane. The polymerization of tetrahydrofuran is also considered to be an equilibrium reaction expressed as follows:[15–17]


(3)

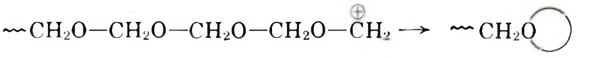
In these reaction schemes, the reverse reactions should be particularly noticed. The occurrence of these reactions is supposed only on the basis of the kinetic investigation and has not yet been proved by a chemical method, because the monomer which is split off in the reverse reaction could not be distinguished from the charged monomer.

The reverse reaction of stage A in eq. (2) and that of eq. (3) means the depolymerization. However, the back-biting reaction of stage B in eq. (2) is very remarkable for usual cationic polymerization, except the polymerizations of α-oxides, as mentioned above.

Our result proves chemically the occurrence of a reaction in which the carbonium ion gives rise to an oxonium ion by cyclization. It has already been reported that the chain carrier of the trioxane polymerization may be the oxonium ion rather than the carbonium ion. This oxonium ion, through opening the ring, leads to the carbonium ion as shown in eq. (4).

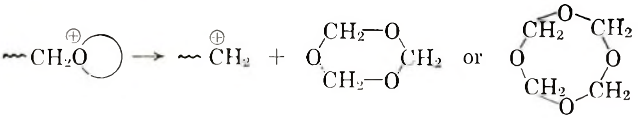

I II
(4)

Although the carbonium ion (II) is stabilized by resonance, II is considered to be more unstable than the oxonium ion (I). Therefore, the carbonium ion II must be stabilized by another molecule. When II is stabilized by the trioxane molecule, leading to the formation of the ion I, the polymerization proceeds. On the other hand, the carbonium ion II may be also stabilized by cyclization in which the carbonium ion II attacks the oxygen atom in its own chain, forming the oxonium ion I′ as shown in eq. (5).


(5)

II I′

In this case, if the carbon atom at the end of the carbonium ion II attacks the third oxygen atom from the end, a six-membered oxonium ion is formed, and if it attacks the fourth, an eight-membered ring is formed. Therefore, the oxonium ion I′ in eq. (5) stands for either the six-membered or eight-membered ring. Then the oxonium ion (I′) may depolymerize, splitting off tetraoxane or trioxane as follows:


(6)

I′ II

The tetraoxane so formed could be detected experimentally by gas chromatography, while the trioxane cannot be distinguished from the charged trioxane.

According to this, it may be expected that trioxane is detected during the polymerization of tetraoxane, since the polymerization intermediate of tetraoxane is considered to be similar to that of trioxane. In fact, trioxane was detected, by gas chromatography in the tetraoxane–$(CH_2Cl)_2$–$BF_3 \cdot O(C_2H_5)_2$ system though the amount of trioxane was small. This fact suggests that the production of tetraoxane during the polymerization of trioxane is not due to the reaction of trioxane with formaldehyde which is split from a growing chain end and that the flexibility of the growing chain endgroup plays an important role in the back-biting reaction. The latter suggestion was also supported by the fact that a very small amount of tetraoxane was produced in the solid-state polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$, in which the growing chain end has limited freedom, unlike the solution polymerization.[9]

It is concluded that the polymerization of trioxane takes place according to eq. (2), and that the back-biting reaction of stage B in eq. (2) (cyclization) exists, in which not only the six-membered but also eight-membered ring is formed. It may be generally supposed that this above-reaction mechanism can be applied to the polymerization of monomers containing an oxygen atom, i.e., cyclic ether or cyclic formal, leading to the formation of a linear polymer containing the oxygen atom. Larger membered rings than the six- and eight-membered ones may be formed through the back-biting reaction, e.g., the ten- or twelve-membered rings. In fact, it has been reported that a sixteen-membered cyclic compound was produced in the polymerization of oxetane.[18] However, the other than six- and eight-membered cyclic compounds were not studied in this investigation.

It is interesting that tetraoxane is more easily obtained during the polymerization of trioxane than trioxane is produced during the polymerization of tetraoxane, in spite of the fact that tetraoxane is more easily polymerized than trioxane. As is shown above, the amount of tetraoxane produced in the trioxane polymerization seems to be independent of the kind of solvent and the polymer yield. This suggests that tetraoxane may exist at an equilibrium monomer concentration.

The difference between the amount of consumed trioxane and the polymer yield in the trioxane polymerization seems to depend on the nature of the solvent and increases with increasing the polarity of solvent. The value of this difference, however, does not always coincide with the amount of tetraoxane produced during the trioxane polymerization, so the relation between this difference and the nature of solvent can not be discussed in detail here. This point must be clarified in the future.

The kinetics of the trioxane polymerization which has already reported must be re-examined, since these results were based only on the yield of the methanol-insoluble polymer. These results will be the subject of a future paper.

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Résumé

On a trouvé que dans la polymérisation en solution du trioxane catalysé par $BF_3 \cdot O(C_2H_5)_2$ à 30°C, la quantité de polyoxyméthylène insoluble dans le méthanol est inférieure à celle du monomère consommé. Cette différence était beaucoup plus importante que la quantité de formaldéhyde trouvé dans le système polymérisé et ne peut pas être expliquée par l'existence de d'oligomère soluble dans le méthanol. On a pu détecter par chromatographie gazeuse du tétraoxane en grande quantité dans la solution de trioxane en cours de polymérisation. C'est ainsi que la différence entre les quantités de polymère insoluble dans le méthanol et le monomère consommé doit être, du moins partiellement, attribué à la formation de tétraoxane. Bien que le tétraoxane soit polymérisé plus facilement que le trioxane par le $BF_3 \cdot O(C_2H_5)_2$, la quantité de tétraoxane était pratiquemnt constante, indépendamment de la nature du solvant et du rendement en polymère. Ceci suggère l'existence de concentration de tétraoxane à l'équilibre. Par ailleurs la formation de trioxane a été observée au cours de la polymérisation en solution de tétraoxane par $BF_3 \cdot O(C_2H_5)_2$. Ceci suggère que la formation de tétraoxane en cours de polymérisation du trioxane est due à une réaction inverse au cours de laquelle la chaleur en croissance du trioxane attaque l'atome d'oxygène dans sa propre chaîne avec dépolymérisation et formation de tétraoxane.

Zusammenfassung

Bei der durch $BF_3 \cdot O(C_2H_5)_2$ bei 30°C katalysierten Lösungspolymerisation von Trioxan ist die Menge des methanol-unlöslichen Polyoxymethylens geringer als diejenige des verbrauchten Monomeren. Der Unterschied war viel grösser als die im auspolymerisierten System noch vorhandene Formaldehydmenge und konnte auch durch die Menge des methanollöslichen Oligomeren nicht gedeckt werden. Gaschromatographisch wurden grosse Mengen Tetraoxan in der polymerisierten Trioxanlösung festgestellt. Der Unterschied zwischen der Menge des methanol-unlöslichen Polymeren und der des verbrauchten Trioxans wurde daher zum Teil der Bildung von Tetraoxan zugeschrieben. Ungeachtet der Tatsache, dass Tetraoxan durch $BF_3 \cdot O(C_2H_5)_2$ leichter polymerisiert wurde als Trioxan, wurde doch Tetraoxan in einer fast konstanten, von der Art des Lösungsmittels und von der Polymerausbeute unabhängigen Menge erzeugt. Das spricht für das Bestehen einer Gleichgewichtskonzentration an Tetraoxan. Andrerseits wurde bei der Lösungspolymerisation von Tetraoxan durch $BF_3 \cdot O(C_2H_5)_2$ die Bildung von Trioxan beobachtet. Das weist darauf hin, dass die Bildung von Tetraoxan bei der Trioxanpolymerisation durch eine Rückwärtsreaktion verursacht wird, bei welcher das wachsende Kettenende von Trioxan das Sauerstoffatom in der eigenen Kette angreift und dass Tetraoxan wieder depolymerisiert.

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N-Alkyl-Substituted Polyamides and Copolyamides Having Long Methylene Chain Units

KAZUO SAOTOME and HIROSHI KOMOTO,
Technical Research Laboratory, Asahi Chemical Industry Company, Itabashi, Tokyo, Japan

Synopsis

N-Alkyl-substituted polyamides and copolyamides have been prepared from *N,N'*-dialkyl *p*-xylenediamine and *N,N'*-dialkyl hexamethylenediamine with long-chain aliphatic dicarboxylic acids. Crystalline *N*-alkyl polyamides were obtained by the use of dicarboxylic acids higher than C_{16}. The melting point versus composition curves for the crystalline *N*-alkyl copolyamides which were prepared from a mixture of diamine and the corresponding *N*-alkyl diamine with α,ω-octadecanedioic acid showed convex type plots. X-ray examination of *N*-alkyl copolyamides revealed that all the systems behaved in the same basic manner, the second component was always present without dissolving in the lattice of the first. Dilatometric curves showed two inflection points, corresponding to the melting points of the *N*-alkyl and unsubstituted polyamides respectively. From these results, a block copolymer structure was suggested for the *N*-alkyl copolyamides. The mechanisms for the formation of the block structure were also discussed.

INTRODUCTION

According to the literature,[1,2] *N*-alkyl-substituted polyamides are low melting and amorphous, and some of these have good elastic properties. The effect of *N*-methylation on the structure and properties of polydecamethylene sebacamide was reported by Baker and Fuller.[3] Biggs et al.[4] investigated the melting points of several aliphatic polyamides in which the amide hydrogen atoms were progressively replaced with alkyl substituents. The preparation of *N*-alkyl polyamides was also reported.[5,6]

In our preceding paper,[7] polyamides from *p*-xylylenediamine or aliphatic diamines with higher aliphatic dicarboxylic acids were reported. These polymers are highly crystalline, and typical isomorphous relationships were observed in the copolyamides containing the corresponding oxa- and thiaalkylene linkages. These results suggest that *N*-alkyl polyamides with very long polymethylene linkages may become crystalline even in the absence of the intermolecular hydrogen bonds. Copolyamides which had been prepared from a mixture of diamine and the corresponding *N*-alkyldiamine with octadecanedioic acid were found to be crystalline over the whole range of compositions. The structure of copolymers was investigated by x-ray and dilatometric examinations.

EXPERIMENTAL

Materials

The diamines and the dicarboxylic acids were described in the preceding paper.[7] *N,N'*-Dialkyl hexamethylenediamine was prepared by the reaction of hexamethylene dichloride with a large excess of the corresponding alkyl amine. *N,N'*-Dimethyl hexamethylenediamine had b.p. 78°C./3 mm. Hg, HCl salt m.p. 243–244°C. (lit.:[8] 210°C.); N 12.85% (calcd. 12.90%). *N,N'*-Diethyl hexamethylenediamine had b.p. 79°C./2 mm. Hg, HCl salt m.p. 285°C. (lit.:[8] 278°C.); N 11.40% (calcd. 11.42%). The reaction of *p*-xylylene dichloride with alkyl amine was reported to produce only resinous product.[9] However, *N,N'*-dialkyl *p*-xylylenediamine was obtained in good yields by carrying out the reaction in a dilute alcoholic solution in an autoclave; the product had b.p. 85°C./2 mm. Hg, picrate m.p. 225–226°C. (lit.:[9] 216°C.); HCl salt N 11.52% (calcd. 11.81%). *N,N'*-Diethyl *p*-xylylenediamine had b.p 105°C./2 mm. Hg, picrate m.p. 198–199°C.; HCl salt N 10.52% (calcd. 10.56%).

Methods

Polymer Melting Points. The melting points were measured by observing particles of the polymer between crossed Nicol polarizers under an electrically heated hot-stage microscope. The melting point was determined as the temperature at which the last trace of birefringent crystallinity disappeared.

Reduced Viscosities. The polymer was dissolved in *m*-cresol at temperatures of 50–70°C. with a magnetic stirrer. The viscosity was measured for the solution of 0.5% concentration at 25°C.

Preparation of *N,N'*-Dialkyl Polyamides. An equimolar mixture of the *N,N'*-dialkyl diamine and the dicarboxylic acid was dissolved in ethanol by heating the solution to reflux. Crystals of the nylon salt were precipitated from the solution after being stored overnight in a refrigerator. In some cases when using *N,N'*-dialkyl hexamethylenediamine, the nylon salts were separated by adding ether to the alcoholic solutions. The nylon salts were recrystallized from ethanol or ethanol–ether. The polycondensations of nylon salts were carried out through the following three steps; heating at 220°C. for 5 hr. in a sealed ampule, heating at 250°C. for 3 hr. in atmospheric nitrogen, and then heating for 2 hr. under reduced pressure at 1 mm. Hg. The polymers produced were treated in boiling water for 1 hr. to induce crystallization.

Preparation of Copolyamides. The copolyamides were prepared by treating the nylon salt mixtures as above. The materials extracted during the crystallization process were low molecular weight polymers, amounting to about 1% by weight.

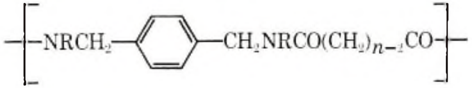
RESULTS AND DISCUSSION

N,N'-Dialkyl Polyamides

The polyamides of *N,N'*-dialkyl *p*-xylylenediamine (RPXD-n) and *N,N'*-dialkyl hexamethylenediamine (R6-n) are shown in Tables I and II.

TABLE I

N,N'-Dialkyl Polyamides (RRXD-n)



Polymer			*N*-salt m.p., °C.	Polymer m.p., °C.[a]	η_{sp}/c	Form	Solubility	
$n-2$	R	Code					MeOH	CHCl$_3$
4	Me	MPXD-6	188	45–47	0.73	Amorph.	Sol.	Sol.
6	"	MPXD-8	152	52–154	0.68	"	"	"
8	"	MPXD-10	149	54–56	0.75	"	"	"
10	"	MPXD-12	113	55–58	0.73	"	"	"
12	Me	MPXD-14	111	60–62	0.69	"	"	"
14	"	MPXD-16	110	85	0.73	Cryst.	"	"
16	"	MPXD-18	108	80	0.72	"	"	"
4	Et	EPXD-6	171	25–30	0.73	Amorph.	Insol.	"
6	"	EPXD-8	160	28–31	0.82	"	Sol.	"
8	"	EPXD-10	136	38–41	0.85	"	"	"
10	"	EPXD-12	125	39–42	0.90	"	"	"
12	"	EPXD-14	114	43–45	0.65	"	"	"
14	"	EPXD-16	107	45–48	0.63	"	"	"
16	"	EPXD-18	105	50	0.82	Cryst.	"	"

[a] The melting points of amorphous polymers denote the softening points.

TABLE II

N,N'-Dialkyl Polyamides (R6-n)

$-\!\!\left[\!-NR(CH_2)_6NRCO(CH_2)_{n-2}CO-\!\right]\!\!-$

Polymer							Solubility	
$n-2$	R	Code	N-salt, m.p., °C.	Polymer m.p., °C.	η_{sp}/c	Form	Form	CHCl$_3$
10	Me	M6-12	103	38–41	0.59	Amorph.	Sol.	Sol.
12	"	M6-14	101	40–43	0.53	"	"	"
14	"	M6-16	99	43–46	0.76	"	"	"
16	"	M6-18	96	52	0.61	Cryst.	"	"
10	Et	E6-12	114	35–8	0.58	Amorph.	"	"
16	"	E6-18	96	38–40	0.57	"	"	"

The polymers of the MPXD-n series are crystallized when *n* becomes as large as 16, while the corresponding ethyl derivatives become crystalline at $n = 18$. In the *N,N'*-dialkyl hexamethylenediamine analogs, however, M6-n can not be crystallized until *n* becomes as large as 18, and the corresponding ethyl derivative remains amorphous. It is of interest to find the different effects on the crystallinity of polymer between *p*-xylylene and hexamethylene groups. There is no large difference in the chain length between the two groups, and the isomorphous replacement in the copolyamides of hexamethylenediamine and *p*-xylylenediamine was reported by Yu and Evans.[10] It is not easy to compare the effects on the polymer crystallinity between *p*-xylylene and hexamethylene linkages in the main chains. The greater tendency toward crystallization in the polyamides of *N,N'*-dialkyl *p*-xylylenediamine may be attributed to the rigid and symmetrical structure of the *p*-phenylene linkage.

N-Alkyl Copolyamides

Since it was found that *N,N'*-dialkyl polyamides of very long methylene chains are crystalline, the effect of *N*-alkyl substituents in the copolyamides which have the repeating unit of equal length was investigated. The following copolyamides of different compositions were prepared: PXD-18/MPXD-18, PXD-18/EPXD-18, 6-18/M6-18, and PXD12/MPXD-18. The last series contains two different acid residues in a molecule. The formation of copolyamides (not being simple mixtures of two homo-

TABLE III
Copolyamides of PXDA/*N,N'*-Dialkyl PXDA and HMDA/*N,N'*-Dialkyl HMDA

Polymer	Composition, mole-%	M.p., °C.	η_{sp}/c	Form
PXD-18/MPXD-18	100/0	242	1.42	Cryst.
"	75/25	220	0.93	"
"	50/50	200	0.82	"
"	25/75	168	0.73	"
"	0/100	80	0.72	"
PXD-18/EPXD-18	75/25	220	1.03	Cryst.
"	50/50	200	0.85	"
"	25/75	155	0.76	"
"	0/100	50	0.82	"
6-18/M6-18	100/0	192	1.50	Cryst.
"	75/25	170	1.05	"
"	50/50	145	0.89	"
"	25/75	126	0.85	"
"	0/100	52	0.61	"
PXD-12/MPXD-18	100/0	270	1.48	Cryst.
"	75/25	250	1.13	"
"	50/50	171	0.79	"
"	25/75	75	0.83	Amorph.
"	0/100	80	0.72	Cryst.

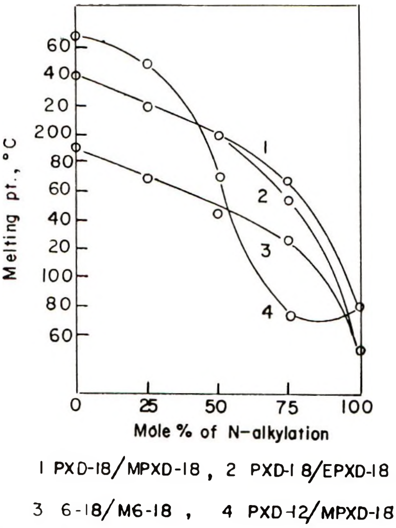


Fig. 1. Melting points of N-alkyl copolyamides: (*1*) PXD-18; (*2*) PXD-18/EPXD-18; (*3*) 6-18/M6-18; (*4*) PXD-12/MPXD-18.

polymers) was ascertained by fractionation with solvent. The results are summarized in Table III.

The melting points are plotted against the polymer composition in Figure 1.

Biggs and co-workers[4] showed that the melting point curves for N-alkyl-substituted polyamides such as polydecamethylene sebacamide derivatives were not concave upward as shown in a usual copolymer system and explained that the repeating units themselves were not disturbed by the N-alkylation. It is not clear in the previous discussion of the melting point whether the polymer is crystalline or not.[4] The shapes of the melting point curves for the present three crystalline copolyamide systems are all convex upward, but the melting point curve for PXD-12-MPXD-18 has a minimum point at which the polymer was observed to be amorphous. In this case, the polymers have two different acid residues in the main chain and are considered to have a random copolymer structure in the usual sense. The convex shapes of the melting point curves can hardly be explained by the assumption that the repeating units in the crystal lattice are not disturbed by N-alkylation. The small depression of the melting points in the composition range up to 75% N-alkylation may be considered to suggest that the polymers have a block copolymer structure rather than one with random sequences of repeating units.

Preparation of Block Copolyamide

Since the assumption that the N-alkyl copolyamides have a block-type structure has been presented, the preparation of the block copolyamide with the same components by another method was attempted. Two different polyamides of relatively lower molecular weight of which terminal groups are amino and carboxyl groups, respectively, were polycondensed into a block copolymer. The details of this method will be reported elsewhere. Thus, an endgroup equivalent mixture of amino-ended PXD-18 (DP = 48) and carboxyl-ended EPXD-18 (DP = 53) was finely powdered in a mortar and was heated at 250°C. for 1 hr. under reduced pressure (1 mm. Hg). The resulting polymer had a reduced viscosity of 0.85. The structure and properties of this polymer are compared with those of the corresponding copolyamide below.

X-Ray Examination

The x-ray diffraction patterns were obtained with the use of nickel-filtered copper Kα radiation. The lattice spacings were calculated from the diameters of the Debye-Scherrer rings. The change in lattice spacings of the copolyamides of different compositions are shown in Figure 2.

It is known that polyamides give the two characteristic reflections which are much stronger than others, one at about 3.7 A. corresponding to the separation of the hydrogen-bonded planes and the other at about 4.4 A.[11] Another set of planes parallel to the chain direction also contributes to the 3.7 A. reflection.[12] The crystal structure of PXD-10 was analyzed by Vogelsong,[13] and its diffraction pattern indicates a strong reflection at 4.4 A. due to both 100 and 010 planes. It was also found that the polyamides quenched into Dry Ice–acetone from the melt show a new reflection at 4.1–4.2 A. suggestive of hydrocarbon chain packing. Baker and Fuller[3] observed the same reflection at 4.2 A. in *N*-methyl-substituted polyamides. The methyl side groups do not appear to disturb directly the lateral separation of the chains, since there is evidently enough space for the methyl group between the main chain axes which can not approach much closer

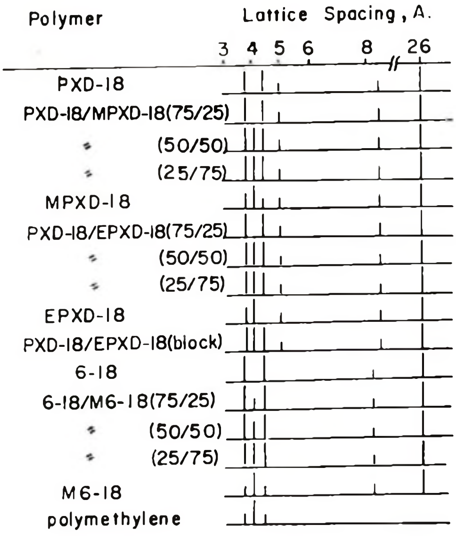


Fig. 2. Lattice spacings of *N*-alkyl copolyamides.

than 4.7 A. from each other. The characteristic feature in the diffraction patterns of these *N*-alkyl copolyamides is represented by the appearance of the lattice spacing at 4.1 A. This clear reflection which agrees with that of polymethylene indicates the interplanar spacing of the hydrogen bond-free long methylene chains. Besides, the characteristic polyamide spacings of 3.8 A. (3.7 A. for the aliphatic copolyamides) and 4.4 A. are still observed in the copolyamide patterns. No differences are observed in the diffraction patterns between *N*-methyl- and *N*-ethyl-substituted polymers. Also, the lattice spacings of PXD-18/EPXD-18 (block) agree well with those of PXD-18/EPXD-18(50/50). The results of the x-ray examination suggest that these crystalline *N*-alkyl copolyamide molecules contain both structures of *N*-alkyl and unsubstituted polyamide long-chain sequences which are individually crystallizable.

Dilatometric Examination

In order to obtain further evidence for the block structure in these *N*-alkyl copolyamides, a dilatometric examination was carried out. Two different melting points should be expected if the polymer has two different kinds of fairly long chain sequences in its molecule. A representative dilatometric curve is shown in Figure 3. The temperature was raised at the rate of 1°C./min., and the increase in specific volume was followed.

The two different melting points of the copolyamides obtained by dilatometry and the melting points of the corresponding homopolymers are tabulated in Table IV.

The two break points (T_{m1} and T_{m2}) which were observed on a dilatometric curve correspond to the melting points of *N*-alkyl and unsubstituted polyamides, respectively. While the lower melting points agree with those of the corresponding *N*-alkyl polyamides, the higher melting points are somewhat lower than those of the corresponding polyamides, especially

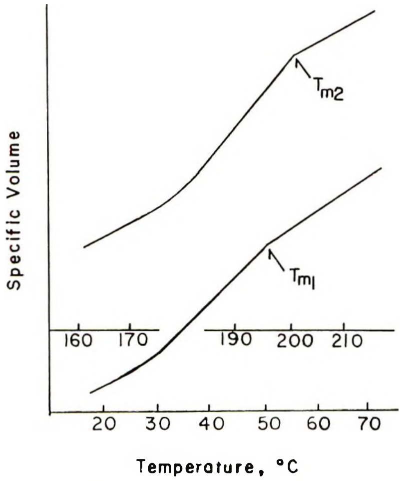


Fig. 3. Dilatometric curve of *N*-alkyl copolyamide (50:50 PXS-18/EPXD-18).

TABLE IV
Comparison of the Melting Points of *N*-Alkyl Copolyamides

Polymer	M.p. of copolymer by dilatometry, °C.		M.p. of homopolymer, °C.	
	T_{m1}	T_{m2}	*N*-alkyl	unsubstituted
PXD-18/MPXD-18 (50/50)	75	200	80	242
PXD-18/EPXD-18 (50/50)	50	200	50	242
PXD-18/EPXD-18 (25/75)	46	155	50	242
PXD-18/EPXD-18 (block)	60	230	50	242

in the case of highly *N*-alkylated copolyamide. The larger depression in T_{m2} can be explained by the effect of the presence of lower-melting ingredients. In the crystal lattice of either polyamide chain sequences, the isomorphous replacement or the interchange of the other repeating unit can occur, since there is no large difference in the chain length between the two repeating units. It is interesting to compare the melting points of PXD-18/EPXD-18(block) and PXD-18/EPXD-18(50/50). Though the analytical compositions of the two polymers are nearly equal, relatively large differences in both T_{m1} and T_{m2} are found dilatometrically. Moreover, T_{m1} of the former is 10°C. higher than the melting point of the corresponding *N*-alkyl homopolymer. The block copolyamide has still a segmented structure in the polymer chain, though amide exchange reactions leading to random copolymer may occur to some extent. In the regular block copolyamide, the thermal movement of the lower melting segments of *N*-alkyl polyamide may be prohibited to some degree by the presence of higher-melting rigid crystallites of the unsubstituted chains. At any rate, the coexistence of the two different melting points gives a strong evidence that these *N*-alkyl copolyamides are of a block-type structure.

Mechanisms for the Formation of Block Copolyamides

It has been reported that, when a mixture of two polyamides is heated at temperatures of 280–300°C. for several hours, a copolyamide with random chain sequences is produced through the amide interchange reaction.[14,15] Beste and Houtz[16] made a kinetic study of amide interchange reactions and concluded that the reaction rate was evidently decreased by *N*-alkylation.

In the formation of the *N*-alkyl copolyamides, the reaction shown in eqs. (1)–(5) are important in governing the polymer structure:

$$\text{—NH}_2 + \text{HOOC—} \rightarrow \text{—NHCO—} + \text{H}_2\text{O} \quad (1)$$

$$\text{—NRH} + \text{HOOC—} \rightarrow \text{—NRCO—} + \text{H}_2\text{O} \quad (2)$$

$$\text{P}_1\text{—NHCO—P}_2 + \text{HOOC—P}_3 \rightarrow \text{P}_1\text{—NHCO—P}_3 + \text{HOOC—P}_2 \quad (3)$$

$$P_1\text{—NHCO—}P_2 + H_2N\text{—}P_3 \rightarrow P_1\text{—NH}_2 + P_3\text{—NHCO—}P_2 \quad (4)$$

$$P_1\text{—NHCO—}P_2 + P_3\text{—NRCO—}P_4 \rightarrow P_1\text{—NHCO—}P_4 + P_2\text{—CONR—}P_3 \quad (5)$$

Since the condensation rate of a primary amine [eq. (1)] is much larger than that of a secondary amine [eq. (2)], the primary diamine is consumed in the initial stage of the reaction, producing long chains of unsubstituted polyamide, and the reaction is completed by the post-stage polycondensation of the remaining *N*-alkyl diamine. This tendency was actually ascertained by the extraction of monomers from the reaction intermediate with ethanol. In another study of the preparation of block copolyamides, the occurrence of amide interchange, even between unsubstituted polyamides, was found to be slow at temperatures below 250°C. The interchange reaction between the primary and the secondary amide linkages [eq. (5)] is much slower than the others. The most probable reactions which interrupt the regular chain sequences are considered to occur between the amide linkages and the terminal reactive groups, especially carboxyl groups [eq. (3)]. The unsubstituted polyamide chains which were initially produced will be attacked by the terminal carboxyl groups of newly formed *N*-alkyl polamide chains so that the block chains are shortened. The attack of the terminal amino groups [eq. (4)], on the other hand, will disturb the block regularity less because their attack on the primary amide linkage scarcely changes the structure.

The regularity of the block structure in these *N*-alkyl copolyamides should depend on the conditions (temperature and duration) of polycondensation. Naturally, there are many chances for the block sequences of repeating units to be interrupted by the copolycondensation of primary and secondary amines and by the amide interchange reaction. The differences between the block copolyamide and the corresponding *N*-alkyl copolyamide are already proven by the dilatometric examination.

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Résumé

Les polyamides *N*-alcoyl-substitué et copolyamides ont été préparés au départ de *N*,*N'*-dialcoyl-*p*-xylylènediamine et *N*,*N'*-dialcoyl-hexaméthylènediamine avec des acides dicarboxyliques aliphatiques à longue chaîne. Les polyamides *N*-alcoylés cristallins ont été obtenus en utilisant des acides dicarboxyliques supérieurs à C_{16}. Les courbes de point de fusion en fonction de la composition pour les copolyamides cristallins *N*-alcoylés qui ont été préparés au départ de mélange de diamine et de diamine *N*-alcoylée correspondante avec l'acide α,ω octa-décanedioique montraient des diagrammes convexes. L'examen aux rayons-X des copolyamides *N*-alcoylés révélaient que tous les systèmes se comportaient de facon globale semblable à savoir que le second composant était toujours présent sans se dissoudre dans la matrice du premier. La courbe dilatométrique montrait deux cassures correspondant au point de fusion du polyamide *N*-alcoylé et non-substitué respectivement. Au départ de ces résultats les copolyamides N-alcoylés sont supposés avoir une structure de copolymère séquencé. Le mécanisme de formation de structures séquencées est soumis également à discussion.

Zusammenfassung

N-Alkylsubstituierte Polyamide und Copolyamide wurden aus *N*,*N'*-Dialkyl-*p*-xylylendiamin und *N*,*N'*-Dialkylhexamethylendiamin mit langkettigeu aliphasischen Dikarbonsäuren dargestellt. Kristalline *N*-Alkylpolyamide wurden mit Dikarbonsäuren höher als C_{16} erhalten. Die Abhängigkeit des Schmelzpunktes von der Zusammensetzung lieferte für die kristallinen, aus einer Mischung von Diamin und dem entsprechenden *N*-Alkyldiamin mit α,ω-Octadekandikarbonsäure dargestellten Copolyamide Kurven vom konvexen Typ. Die Röntgenuntersuchung der *N*-Alkylcopolyamide zeigte, dass alle Systeme sich grundsätzlich gleichartig verhielten, so dass die zweite Komponente immer auftrat, ohne sich im Gitter der ersten zu lösen. Die Dilatometerkurve zeigte zwei Knickpunkte, entsprechend den Schmelzpunkten des *N*-Alkylpolyamides und dem des unsubstituierten Polyamides. Die Ergebnisse führen zu der Annahme, dass die *N*-Alkylcopolyamide die Struktur eines Blockocpolymeren besitzen. Der Mechanismus der Bildung der Blockstruktur wird diskutiert.

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Polyurethanes and Polyureas Having Long Methylene Chain Units

KAZUO SAOTOME and HIROSHI KOMOTO, *Technical Research Laboratory, Asahi Chemical Industry Company, Itabashi, Tokyo, Japan*

Synopsis

Polyurethanes and polyureas containing long methylene chain units have been prepared from the following six series of monomer combinations; aliphatic diisocyanates with aliphatic glycols or diamines, methylene bis(4-phenyl isocyanate) with aliphatic glycols or diamines, and *p*-xylylene diisocyanate with aliphatic glycols or diamines. A good linear relationship was noted between the polymer melting points of each series against the concentration of functional groups. Both polyurethanes and polyureas from *p*-xylylene diisocyanate showed higher melting points than those from methylene bis(4-phenyl isocyanate) with corresponding aliphatic monomers. The relations between the melting points of these polymers with long methylene chains, including polyamides which were previously reported, and the chain components were discussed. The higher melting points of polymers containing *p*-xylylene group are attributed to the high rigidity of this group.

INTRODUCTION

In our preceding papers,[1,2] the synthesis of α,ω-disubstituted higher alkanes and the preparation of polyamides containing long methylene chain units were reported. The present work deals with the preparation of polyurethanes and polyureas having long methylene chain units up to C_{18} and the comparison of their thermal properties with those of the corresponding polyamides. The relations between the melting points and the structures in aliphatic linear polymers (polyesters, polyamides, polyurethanes, and polyureas) containing polymethylene linkages less than C_{10} were discussed by Hill and Walker.[3] Various polyurethanes from aromatic diisocyanates with ethylene glycol were reported by Lyman.[4] Polyurethanes from symmetric diisocyanates such as *p*-phenylene diisocyanate and biphenylene diisocyanate do not melt below their decomposition temperatures. The structures of polyurethanes based on methylene bis(4-phenyl isocyanate) analogs and ethylene glycol were recently investigated, and the effects of aromatic rings were discussed.[5]

In this work, many polyurethanes and polyureas of aromatic series have also been prepared from *p*-xylylene diisocyanate and methylene bis(4-phenyl isocyanate) with aliphatic glycols or diamines of long alkylene linkages. The effects of methylene chain length on the melting points and the glass transition temperatures of these polymers of both aliphatic and aromatic series have been investigated.

EXPERIMENTAL

Materials

The preparation and the characteristics of aliphatic glycols and diamines were described in preceding paper.[1] Hexamethylene diisocyanate and methylene bis(4-phenyl isocyanate) were obtained commercially. Decamethylene diisocyanate and *p*-xylylene diisocyanate were prepared from the corresponding diamines with phosgene.

Methods

Polymer Melting Points. The melting point was determined by observing solid particles of the polymer between crossed Nicol polarizers on an electrically heated hot-stage microscope. The melting point was taken as the temperature at which the last trace of birefringent crystallinity disappeared. This is the crystalline melting point of the polymer.

Glass Transition Temperatures. The glass transition temperature T_g was determined by dilatometry. The temperature was raised at the rate of 1°C./min., and the increase in specific volume was observed.

Reduced Viscosities. The polymer was dissolved in *m*-cresol at temperatures of 50–70°C. with the use of a magnetic stirrer. The viscosity was measured for the solution of 0.5% concentration at 25°C. Since the polyureas of methylene bis(4-phenyl isocyanate) were insoluble in *m*-cresol, 98% sulfuric acid was used as the solvent.

Preparation of Polyurethanes. The polyaddition reactions were carried out according to the method described in the literature.[4] Into a solution of diisocyanate in dimethyl sulfoxide heated at temperatures of 120–130°C., an equimolar glycol dissolved in the same solvent was gradually added over 30 min. with vigorous stirring. The reaction mixture was kept at that temperature for another hour. The viscous solution was poured into water, and the precipitated polymer was washed with acetone and dried under reduced pressure.

Preparation of Polyureas. The reactions were carried out according to Kwolek's method.[6] To a dilute solution of diisocyanate kept at temperatures of 40–60°C., a dilute equimolar solution of diamine was mixed all at once and stirred for 15 min. Chloroform and tetramethylene sulfone were used as solvents. The precipitation of polymer occurred immediately after mixing in the case of chloroform, but precipitation was gradual when tetramethylene sulfone was used. The separation and the purification of polymers were carried out as above.

RESULTS AND DISCUSSION

The polymers are classified according to their structures into six series as shown in Table I.

TABLE I

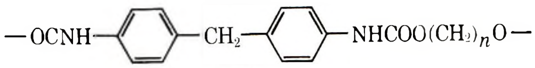
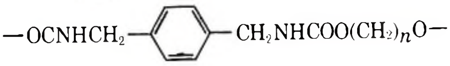
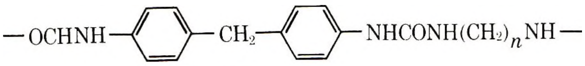
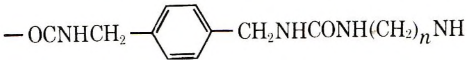
Polymer type	Repeating unit	Polymer code
Polyurethanes	$—OCNH(CH_2)_mNHCOO(CH_2)_nO—$	UT-*mn*
		UT-MD*n*
		UT-PXD*n*
Polyureas	$—OCNH(CH_2)_mNHCONH(CH_2)_nNH—$	UA-*mn*
		UA-MD*n*
		UA-PXD*n*

TABLE II
Polyurethanes

Polymer	Yield, %	M.p., °C. (lit.)	T_g, °C.	η_{sp}/c	Analysis N, % Calcd.	Analysis N, % Found
UT-66	59	164 (163)[7]		0.38	9.78	9.51
UT-68	60	152 (155–157)[7]		0.38	8.91	8.71
UT-610	58	148 (151–154)[8]		0.39	8.18	7.98
UT-612	60	139	36	0.41	7.56	7.50
UT-616	61	134	39	0.41	6.56	6.38
UT-106	62	144		0.40	8.18	7.95
UT-108	60	137		0.43	7.56	7.41
UT-1010	61	142 (138–145)[3]		0.38	7.03	6.81
UT-1012	60	133	34	0.37	6.56	6.32
UT-1016	63	128	34	0.41	5.86	5.63
UT-MD4	94	194		0.50	8.02	7.81
UT-MD6	93	179	51	0.52	7.43	7.57
UT-MD8	92	172		0.51	6.91	6.98
UT-MD10	93	166	48	0.50	6.46	6.20
UT-MD12	94	164	43	0.49	6.07	6.12
UT-MD16	94	152	40	0.40	5.41	5.70
UT-PXD4	60	227		0.38	10.07	10.30
UT-PXD6	59	209	56	0.41	9.14	9.35
UT-PXD8	60	196		0.42	8.38	8.01
UT-PXD10	62	184	49	0.40	7.73	7.79
UT-PXD12	65	178	45	0.43	7.17	6.93
UT-PXD16	68	168	47	0.41	6.27	6.43

TABLE III
Polyureas

Polymer	Yield, %	M.p., °C. (lit.)	T_g, °C.	η_{sp}/c	Analysis N, % Calcd.	Analysis N, % Found
UA-66	85	268 (270)[9]		0.61	19.70	19.53
UA-68	83	239		0.58	17.93	17.77
UA-610	81	216 (216–218)[10]		0.52	16.45	16.65
UA-612	83	205	49	0.61	15.20	15.10
UA-614	69	198	47	0.53 (1.28)[a]	14.12	14.00
UA-618	63	192		0.52	12.38	12.06
UA-106	68	212		0.63	16.45	16.41
UA-108	75	201		0.58	15.20	15.33
UA-1010	80	197 (210)[3]		0.59	14.12	13.91
UA-1012	85	190		0.56 (1.50)[a]	13.19	13.23
UA-1014	75	180	40	0.63	12.38	12.59
UA-1018	71	172		0.62	11.01	10.85
UA-MD6	97	274	55	0.79 (1.44)[a]	15.29	15.43
UA-MD8	96	263	50	0.68	14.20	13.98
UA-MD10	85	246	46	0.53	13.26	13.50
UA-MD12	96	240	51	0.69	12.43	12.21
UA-MD14	89	229		0.61	11.71	11.68
UA-MD18	75	225	48	0.71	10.48	10.22
UA-PXD6	58	306	72	0.53	18.41	18.53
UA-PXD8	75	278	68	0.48	16.85	16.57
UA-PXD10	75	260	55	0.39 (1.36)[a]	15.54	15.48
UA-PXD12	79	258		0.51	14.42	14.14
UA-PXD14	63	248	54	0.67	13.45	13.60
UA-PXD18	62	226	52	0.65	11.85	11.97

[a] The reaction was carried out in tetramethylene sulfone.

All polymers obtained in this study were crystalline and indicated distinct melting points. The results are summarized in Tables II and III.

In the preparation of polyurethanes, side reactions such as the ring formation of dimeric and trimeric diisocyanates and branching and cross-linking due to the formation of allophanate linkages are known to occur. However, the polyurethanes of the present investigation were of relatively high viscosity and easily soluble in *m*-cresol. The analytical results were in good agreement with the calculated values. Therefore, the melting points in Table II could be considered to denote the correct values of the polymer melting points of the described structures. The same evaluation applies to the polyureas of the present study. Polyureas of much higher molecular weights (reduced viscosities) were obtained when tetramethylene sulfone was used as the solvent. The effect of solvent on the molecular weight of the produced polymer, as already pointed out by Kwolek,[6] can be related to the dissolving (or welling) power of the solvent.

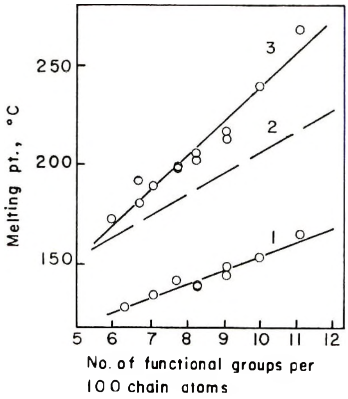


Fig. 1. Melting points of aliphatic polymers vs. concentration of functional groups: (*1*) UT-*mn*; (*2*) polyamide; (*3*) UA-mn.

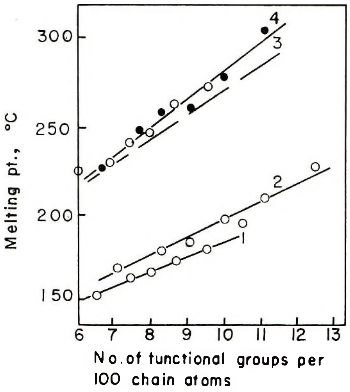


Fig. 2. Melting points of aromatic polymers vs. concentration of functional groups: (*1*) UT-MD*n*; (*2*) UT-PXD*n*; (*3*) polyamide (PXD-even); (*4*) (○) UA-MD*n* and (●) UA-PXD*n*.

The relations between the melting points and the concentration of functional groups are plotted in Figures 1 and 2. The phenylene group was calculated as a linkage of four chain atoms. The plots of polyamide series were cited from the preceding paper[2] for comparison with the other polymers.

The melting points of each polymer series give linear plots. In these polymers, there are four linkages which contribute to increase of the polymer melting point, i.e., amide, urethane, urea, and phenylene linkages. The comparison between the first three functional groups is represented in Figure 1. The main factors which are known to influence the melting point are the intermolecular cohesion energy, the chain shape, and the chain flexibility.[11] The higher melting points of polyureas are attributed chiefly to the large cohesion energy of the urea linkage, while the relatively lower melting points of polyurethanes are considered due to the introduction of ether linkage which cause easy rotation of chain molecules around the oxygen atom. It is probable that in the series of closely related polymers the chain shape and the chain flexibility are of major importance in governing the melting point.

Those polymers containing phenylene groups have melting points considerably higher than those of the corresponding aliphatic series. The effect of the phenylene group on the melting point is somewhat complicated, however, and depends on the type of linkage. Lyman et al.[5] recently investigated the crystalline structures of polyurethanes from methylene bis(4-phenyl isocyanate) analogs with ethylene glycol by x-ray diffraction. The diffraction pattern of the polyurethane of MDI–ethylene glycol is different from that of other linear polymers which have been reported to have a helical structure. The polymer chain has twisted chain conformation. Accordingly, the chain shape of UT-MD*n* polymers is considered to be more complicated than that of the corresponding UT-PXD*n* series so as to enlarge the entropy of fusion in $T_m = \Delta H/\Delta S$. From another viewpoint, the chain flexibility of the diphenylmethane group is greater than that of the *p*-xylylene group, and the ease of rotation around the oxygen atom in the urethane linkage may be decreased by the introduction of the neighboring rigid *p*-xylylene group to a greater extent so that this tendency predominates the effect of larger concentration of phenylene group in UT-MD*n*. The fact that UT-MD*n* polymers have lower melting points than the corresponding UT-PXD*n* polymers in spite of their larger cohesion energy densities could be explained by the above consideration.

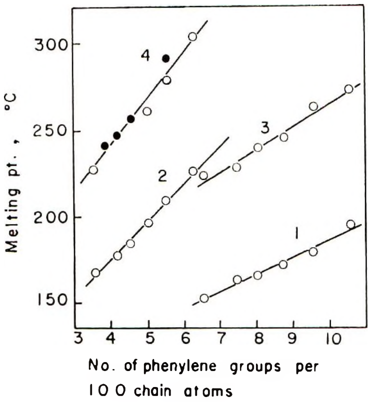


Fig. 3. Melting points of aromatic polymers vs. concentration of phenylene groups: (*1*) UT-MD*n*; (*2*) UT-PXD*n*; (*3*) UA-MD*n*; (*4*) (○) UA-PXD*n* and (●) polyamide (PXD-even).

While the melting points of aliphatic polyureas are considerably higher than those of the corresponding polyamides, the differences in the melting points in the aromatic series become much smaller. It is interesting that plots of the melting points of both UA-MDn and UA-PXDn lie on a line. Though the chain configurations in UA-MDn are not yet elucidated, the larger cohesion energy densities of the molecules may be compensated for by chain shape and chain flexibility for the contribution to the melting point.

The different contributions to the melting point between the phenylene groups in the two diisocyanates are shown by plotting the melting points against the concentration of phenylene groups (Fig. 3). The melting point lines of the PXDn series lie much above those of the corresponding MDn series for both the polyurethanes and polyureas. On the other hand, no practical differences in the melting points are found between the corresponding polyureas and polyamides.

The glass transition temperatures of the aromatic series were observed to be higher than those of the aliphatic series. The decreasing tendency in T_g is observed in every aromatic series as the chain length of the aliphatic components increases. It is to be noted that the glass transition temperatures of PXDn polyureas are relatively lower than those of the corresponding polyamides obtained in the previous paper[2] irrespective of the correspondence in the melting points between these two polymers.

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Résumé

Les polyuréthanes et urées contenant des unités caténaires méthylèniques longues ont été préparées au départ de six séries de combinaisons de monomères à savoir les diisocyanates aliphatiques avec des glycols ou diamines aliphatiques, le méthylène-bis-(4-phényl isocyanate) avec les glycols ou diamines aliphatiques, et les diisocyanates de p-xylylène avec les glycols ou diamines aliphatiques. Une relation linéaire satisfaisante a été obtenue entre les points de fusion des polymères de chaque série et la concentration en groupe fonctionnel. Aussi bien les polyuréthanes que les polyurées obtenues au départ de diisocyanate de p-xylylène montraient des points de fusion plus élevés que ceux du méthylène-bis-(4-phényl isocyanate) avec le monomère aliphatique correspondant. Les relations entre les points de fusion de ces polymères avec des chaînes méthylèniques longues y compris les polyamides qui ont été rapportés précédemment et les composants de la chaîne sont soumis à discussion. Les points de fusion plus élevés des polymères contenant des groupes p-xylylènes sont attribués à la rigidité élevée de e groupe.

Zusammenfassung

Polyurethane und Polyharnstoffe mit langen Methylenkettenbausteinen wurden aus folgenden sechs Reihen von Monomerkombinationen dargestellt: aliphatische Diisocyanate mit aliphatischen Glykolen oder Diaminen, Methylen-bis-(4-phenylisocyanat) mit aliphatischen Glykolen oder Diaminen und *p*-Xylylendiisocyanat mit aliphatischen Glykolen oder Diaminen. Eine gute lineare Beziehung zwischen den Schmelzpunkten der Polymeren einer jeden Reihe und der Konzentration an funktionellen Gruppen wurde festgestellt. Polyurethane und Polyharnstoffe aus *p*-Xylylendiisocyanat besassen höhere Schmelzpunkte als diejenigen aus Methylen-bis-(4-phenylisocyanat) mit den entsprechenden aliphatischen Momomeren. Die Beziehungen zwischen den Schmelzpunkten dieser Polymeren mit langen Methylenketten, einschliesslich der früher beschriebenen Polyamide und den Kettenkomponenten wurden diskutiert. Die höheren Schmelzpunkte der Polymeren mit der *p*-Xylylengruppe werden auf die grössere Starrheit dieser Gruppe zurückgeführt.

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Copolymerization of the Cyclic Monomer, 5,5-Dichloro-4-hydroxy-2,4-pentadienoic Acid Lactone*

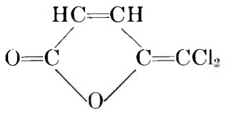
ANTHONY WINSTON and GEORGE T. C. LI, *Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506*

Synopsis

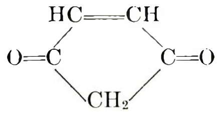
The copolymerization of 5,5-dichloro-4-hydroxy-2,4-pentadienoic acid lactone with methyl methacrylate, methyl acrylate, vinyl acetate, and vinylidene chloride to give yellow to red copolymers is described. Infrared, nuclear magnetic resonance, and ultraviolet spectroscopy indicate that the polymerization of the lactone proceeds by a 1,4-addition mechanism, followed by hydrogen chloride elimination, to give a highly conjugated structural unit closely related to the structure of the original monomer. The intense colors of the copolymers may arise from conjugated sequences of lactone units or through further eliminations along comonomer sequences.

INTRODUCTION

The recent availability in this laboratory of the cyclic monomer, 5,5-dichloro-4-hydroxy-2,4-pentadienoic acid lactone (I), has made possible the extension of our copolymerization studies of cyclic monomers to a ring system containing external olefinic unsaturation in conjugation with the ring double bond. Our earlier work[1,2] in this area involved the copolymerization of 4-cyclopentene-1,3-dione (II), a monomer, which like maleic anhydride,[3] maleimide,[4] and *N*-butylmaleimide,[5] copolymerizes through the ring double bond to give either (with styrene) highly alternating copolymers or (with methyl methacrylate or acrylonitrile) copolymers rich in the other monomer. Since the cyclic monomers of this series are electronically and sterically similar, it is not surprising to find similar copolymerization behavior.



I



II

The lactone I, although closely related to maleic anhydride, presents quite a different steric and electronic picture. On steric grounds the greater

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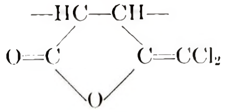
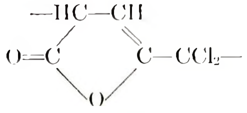
bulk of the dichloromethylene group in comparison with the carbonyl of maleic anhydride would surppress the formation of structure III by the usual 1,2-addition to the ring double bond. On the other hand, the copolymerization might proceed by a 1,4-addition mechanism through the conjugated diene system to give structure IV. This path, being much more favorable from both steric and electronic considerations, would result in a greater reactivity of the lactone monomer in comparison with other cyclic monomers polymerizing by the 1,2-addition mechanism.



III



IV

The purpose of this paper is to report the copolymerization of lactone I with methyl methacrylate, methyl acrylate, vinyl acetate, and vinylidene chloride, and through infrared, nuclear magnetic resonance, and ultraviolet spectroscopy to establish the structure of the lactone I residue in the copolymers.

EXPERIMENTAL

Materials

The monomer, 5,5-dichloro-4-hydroxy-2,4-pentadienoic acid lactone (I), was prepared through the reaction of sodium trichloroacetate with succinic anhydride according to the method of Winston and Sharp.[6] The white crystalline compound was purified by sublimation at 95°C./1.0 mm., m.p. 97.5°C.

Methyl methacrylate and methyl acrylate were washed with aqueous sodium hydroxide, dried, and distilled twice under reduced pressure. Vinyl acetate and vinylidene chloride were distilled twice under reduced pressure and middle fractions were collected for use. Azobisisobutyronitrile was recrystallized from ether and dried.

Copolymerization

Homogeneous benzene solutions of lactone I, the comonomer, and 1 mole-% azobisisobutyronitrile were charged into thick-walled tubes. The samples were degassed, sealed under 1.0 mm. of nitrogen, and shaken in a constant temperature bath at 65°C. During the polymerizations the solutions developed yellow-orange colors and some colored material precipitated. When the ampules were opened, a slight odor of hydrogen chloride was detected. Dilution of the reaction mixture with ligroin precipitated the copolymers, which were then collected, washed with ligroin, and dried under reduced pressure. The copolymers of methyl methacrylate, methyl acrylate, and vinyl acetate were analyzed for chlorine by Crobaugh Laboratories, Charleston, West Virginia. The reaction conditions and results are summarized in Table I.

TABLE I
Feed–Copolymer Composition Data for the Copolymerization of Lactone I

No.	Comonomer	Mole fraction lactone I in feed	Time, hr.	Conversion, %	Cl, %
1	Methyl methacrylate	0.2	6	12.1	4.55
2	Methyl methacrylate	0.5	21	43.4	11.64
3	Methyl methacrylate	0.4	21	58.6	9.99
4	Methyl acrylate	0.5	9	12.6	13.45
5	Methyl acrylate	0.4	21	32.0	12.61
6	Vinyl acetate	0.5	21	6.0	20.58
7	Vinyl acetate	0.4	21	6.0	20.47
8	Vinylidene chloride	0.5	21	15.5	—
9	Vinylidene chloride	0.4	21	24.4	—

Although both lactone I and the vinyl monomers are colorless, the copolymers of lactone I with methyl methacrylate, methyl acrylate, vinyl acetate, and vinylidene chloride were colored yellow, orange, orange and red, respectively. The copolymers were soluble in dioxane, dimethyl sulfoxide, acetone, methyl ethyl ketone, chloroform, nitrobenzene, dimethylformamide, and cyclohexanone. They were partially soluble in methanol and carbon tetrachloride and were insoluble in ligroin.

SPECTRAL RESULTS

Infrared

Infrared spectra of the four copolymers dispersed in KBr disks, were recorded on the Perkin-Elmer Model 137-G grating instrument. The C—H stretching absorption centered about 3000 cm.$^{-1}$ is shown in Figure 1. The alkene proton absorption frequencies, and the lactone and ester carbonyl frequencies are reported in Table II. All of the copolymers exhibit a weak peak for an alkene proton and a band in the region of a γ-lactone. The acrylate copolymers both show characteristic strong bands for the ester.

TABLE II
Infrared Absorption Bands for Copolymers of Lactone I (KBr)

Comonomer	Absorption, cm.$^{-1}$		
	C—H (Alkene)	C═O (Lactone)	C═O (Ester)
Methyl methacrylate	3100	1790	1740
Methyl acrylate	3090	1790	1750
Vinyl acetate	3100	1790	[a]
Vinylidene chloride	3100	1790	—
Lactone I[b]	3020, 3060, 3090	1770	—

[a] A very weak shoulder on the lactone peak appeared at 1750 cm.$^{-1}$.

[b] Pure monomer (KBr), see ref. 6.

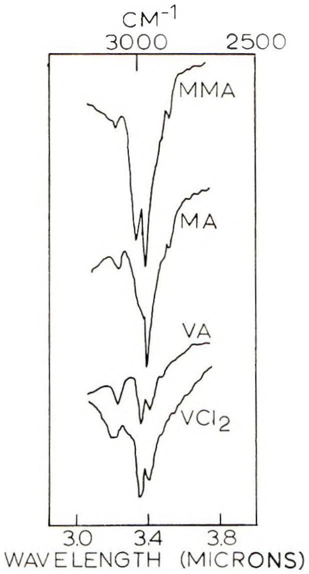


Fig. 1. Infrared spectra of the lactone I copolymers in the C—H stretching region (KBr)

The vinyl acetate copolymer fails to show the ester peak clearly, but a weak shoulder in the proper location for this function is present.

Nuclear Magnetic Resonance

The nuclear magnetic resonance spectra of the copolymers were recorded on a Varian HA-60 instrument at sample temperatures of 100°C. Dioxane was the choice of the solvents because of the temperature desired and the insolubility of the copolymers in carbon tetrachloride. Deuterochloroform was unsatisfactory because of the chloroform impurity line at τ 2.83, which is in the same region as the expected alkene proton lines.

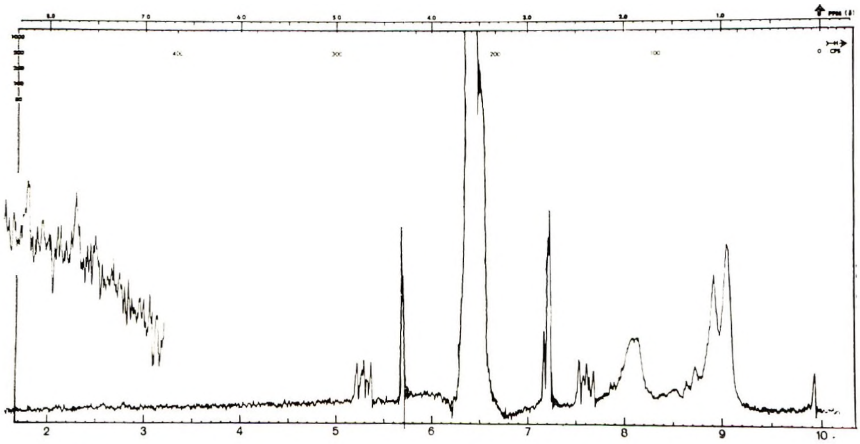


Fig. 2. NMR spectrum of lactone I–methyl methacrylate copolymer 1 (dioxane, 100°C.)

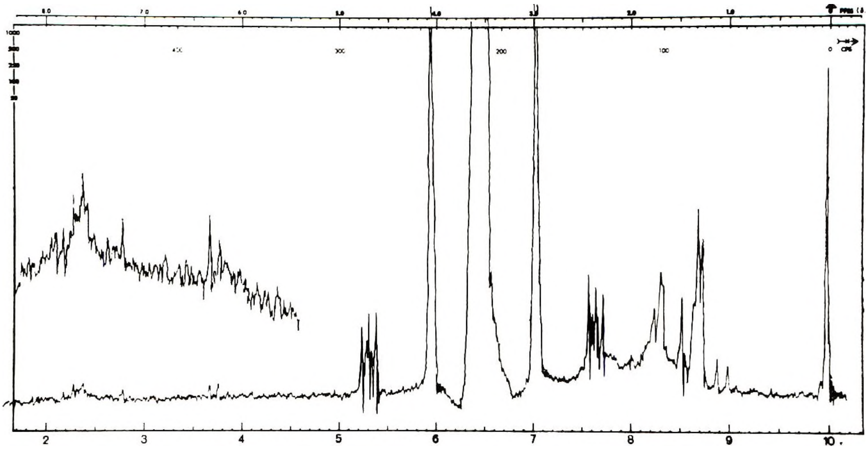


Fig. 3. NMR spectrum of lactone I–methyl acrylate copolymer 4 (dioxane, 100°C.).

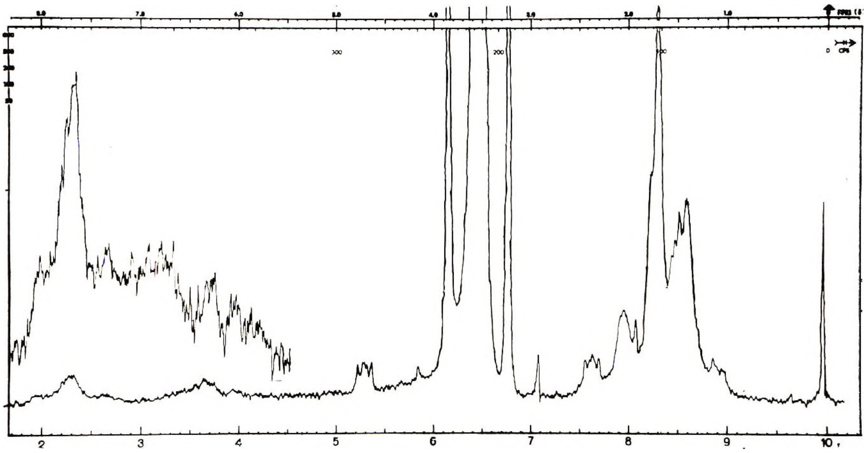


Fig. 4. NMR spectrum of lactone I–vinyl acetate copolymer 6 (dioxane, 100°C.).

The NMR spectra of the methyl methacrylate, methyl acrylate, and vinyl acetate copolymers (1, 4, and 6, Table I) are shown in Figures 2, 3, and 4. The lines between $\tau = 5.0$ and 7.8 arise from the dioxane solvent. The lines between $\tau = 7.8$ and 9.5 (Figs. 1 and 3), agree with those reported for poly(methyl methacrylate)[7] and poly(vinyl acetate).[8] In the case of the methyl acrylate copolymers (Fig. 3), the line at $\tau = 2.8$ is due to a trace of benzene impurity, while the two doublets at $\tau = 2.15$ and 3.55 ($J = 9$ cps) may be attributed to a trace of lactone I monomer.[6] For each of the copolymers weak lines at $\tau = 2.0$–2.5 are in the proper position for alkene protons.

Ultraviolet

The ultraviolet spectra of the copolymers in dioxane solution (Table III) were recorded on a Beckman DU spectrophotometer powered by a Beckman

DU power supply. The extinction coefficients, evaluated by a least-squares treatment of values measured over a 10-fold concentration range, were calculated for the molar concentration of lactone I residue, as determined from the chlorine analyses of the copolymers and assuming two chlorine atoms per lactone structural unit.

Each of the copolymers exhibited an intense ultraviolet absorption peak about 300 mμ, an indication of the presence of a highly conjugated chromophore.

TABLE III
Ultraviolet Absorption of Copolymers in Dioxane Solution

Comonomer	Concn., g./l.[a]	Absorbance[a]	λ_{max}, mμ	ϵ_{max}
Methyl methacrylate (no. 2)	0.0400	0.840	295	13,140[b]
Methyl acrylate (no. 4)	0.0486	0.723	295	8,400[b]
Vinyl acetate (no. 6)	0.0227	0.825	295	12,500[b]
Vinylidene chloride (no. 8)	0.0432	0.540	300	—
Lactone I[c]	—	—	297	21,000

[a] A typical determination.

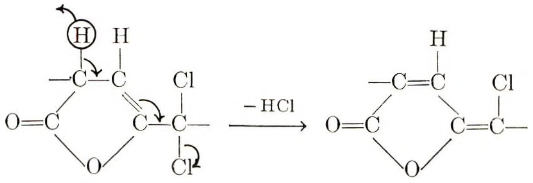
[b] Least-squares value from a 10-fold concentration range. Based upon the molar concentration of lactone I residue as calculated from the chlorine analyses.

[c] Pure monomer in ethanol, see ref. 6.

DISCUSSION

In considering the possible structure of the lactone residue in the copolymer, neither the 1,2-addition product III nor the 1,4-addition product IV is completely consistent with the spectroscopic data. Structure III does not possess an alkene proton and would not be expected to absorb above 3000 cm.$^{-1}$ in the infrared or to exhibit NMR lines in the alkene proton region. Structure IV, as well as structure III, since their double bond systems are nonconjugated, would not be expected to absorb above 220 mμ in the ultraviolet and thus both fail to account for the intense absorption at 300 mμ.

A structure for the lactone residue in the copolymer, accounting remarkably well for the spectroscopic data, is structure V, readily obtained by elimination of hydrogen chloride from the 1,4-addition product IV. Support for this polymerization scheme is provided by the following evidence. Hydrogen chloride was detected on opening the reaction vessels. The infrared peak at 3100 cm.$^{-1}$ and the NMR lines between τ = 2.0 and 2.5 are consistent with the alkene proton of structure V. The highly conjugated



IV V

double bond system of V accounts well for the intense ultraviolet absorption at 300 mμ.

A spontaneous elimination would be extremely favorable, as the hydrogen and chlorine involved are both allylic, and a more stable conjugated system is formed. A similar mechanism was proposed in 1951 by Kooyman[9] to explain the spontaneous elimination of hydrogen chloride from the polymer of 1,1-dichlorobutadiene to give a red polymer having a highly conjugated structure.

Since the lactone monomer itself is colorless, the colors of the copolymers are undoubtedly due to extended conjugated chromophores. Several processes may be responsible for further conjugation leading to color formation. Two lactone units in sequence give rise to a five double-bond system. Each additional lactone in sequence would produce two additional double bonds together with a conjugated carbonyl branch. These species would certainly cause absorption in the visible. The vinyl acetate copolymer appears to be the best case to support lactone sequences since the mole fraction of lactone may be greater than 0.5. The lack of a clearly resolved acetyl carbonyl peak in the infrared may also indicate a low concentration of vinyl acetate in the copolymer. A low vinyl acetate content would not be surprising in view of the effect of benzene solvent in suppressing vinyl acetate polymerizations. Also, since the polymerization proceeds by a 1,4-addition mechanism, the lactone may be much more reactive than other cyclic monomers which polymerize by 1,2-addition. Possibly, the low-reactive monomer vinyl acetate, a benzene solvent, and a fairly reactive lactone combine to produce a high concentration of lactone in the copolymer.

A second process by which the conjugation can be extended is through subsequent eliminations involving the comonomer residues. The dark red color of the vinylidene chloride copolymers may arise through further eliminations of hydrogen chloride, since a vinylidene chloride unit next to a lactone would possess either an allylic hydrogen or an allylic chlorine, depending upon on which side the lactone was situated. In either case, a stepwise elimination along a vinylidene chloride sequence beginning at a lactone would cause considerable extension of the conjugated system and would account for the intense red color. In the case of vinyl acetate copolymers, elimination of acetic acid by a similar mechanism would again provide further unsaturation and could also account for the lack of an ester carbonyl band in the infrared.

Further work in this area is now in progress, particularly with respect to determining quantitatively the extent of elimination of hydrogen chloride. This will lead to the determination of the reactivity ratios from which the general reactivity of the lactone monomer can be evaluated.

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This paper is taken in part from the Ph.D. dissertation of G. T. C. Li, West Virginia University, 1966.

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Résumé

La copolymérisation de la lactone de l'acide 5,5-dichloro-4-hydroxy-2,4-pentadiènoique avec le méthacrylate de méthyle, l'acrylate de méthyle, l'acétate de vinyle et le chlorure de vinylidène fournit des copolymères jaunes à rouges. L'analyse spectra le infrarouge, par résonance magnétique nucléaire, et ultraviolette, indique que la polymérisation de la lactone résulte d'un mécanisme d'addition 1,4 suivi d'une élimination d'acide chlorhydrique en fournissant une unité structurale fortement conjuguée, étroitement reliée à la structure du monomère de départ. La couleur intense des copolymères peut résulter de séquences de double soudure conjuguée des unités lactoniques ou résulter d'éliminations ultérieures le long des séquences de comonomères.

Zusammenfassung

Die Copolymerisation von 5,5-Dichlor-4-hydroxy-2,4-pentadiensäurelacton mit Methylmethacrylat, Methylacrylat, Vinylacetat und Vinylidenchlorid unter Bildung gelber bis roter Copolymerer wird beschrieben. Infrarot-, kernmagnetische Resonanz- und Ultraviolettspektroskopie zeigen, dass die Polymerisation des Lactons über einen 1,4-Additionsmechanismus mit darauffolgender Chlorwasserstoffeliminierung unter Bildung eines hochgradig konjugierten, mit der Struktur des ursprünglichen Monomeren eng verwandten Strukturelementes verläuft. Die intensive Farbe des Copolymeren kann durch konjugierte Folgen von Lactonbausteinen oder durch weitere Eliminierung längs der Comonomersequenzen bedingt sein.

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Redox-Initiated Vinyl Polymerization with Thiourea as the Reductant

ASISH R. MUKHERJEE, RUNU PAL (MITRA), AMARENDRA, M. BISWAS, and SUKUMAR MAITI, *Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, India*

Synopsis

A few redox systems containing thiourea as reductant have been found to be quite effective in initiating vinyl polymerization in aqueous media and polymers obtained in the process have all been found to contain amino endgroups to various extents by the application of dye techniques. Quite a few oxidants have so far been utilized for this purpose; among them are ferric chloride (Fe^{3+}), ethylene dibiguanide complex salts of tripositive silver (Ag^{3+}), hydrogen peroxide (H_2O_2), persulfate ($S_2O_8^{2-}$), bromate (BrO_3^-) + hydrochloric acid (HCl). In case of oxidants Fe^{3+} and Ag^{3+}, amino endgroups are mainly incorporated in polymers; but in case of oxidants H_2O_2 and $S_2O_8^{2-}$, fragments of oxidants are also incorporated as hydroxyl and sulfate endgroups. BrO_3^-, however, forms a very efficient redox-initiating system with thiourea, as is evidenced by its capability of polymerizing even hydroquinone-stabilized water-soluble vinyl monomers at very low temperature (~0°C.) and at a quite rapid rate. Besides amino endgroups, sulfonate endgroups have also been detected in polymers in this case, and the relative extents of these two types of endgroups depend generally on the acid concentration of the system. Evidences so far collected indicate the generation of $S—C(=NH)NH_2$ radicals in the system by oxidation of isothiourea, $HS—C(=NH)NH_2$, and these are incorporated in polymers as endgroups. Sulfonate endgroups may be generated by oxidation of these amino-bearing endgroups. Suitable initiation mechanisms have been suggested in each case.

Use of thiourea and *N*-substituted thioureas as redox components for initiation of aqueous vinyl polymerization is rather recent. Two groups of workers[1,2] have used these reducing agents with hydrogen peroxide as the oxidant for initiation of aqueous polymerization of acrylonitrile and have suggested a tentative initiation mechanism on the basis of their kinetic results. In case of dye (eosin)-sensitized aqueous photopolymerization of acrylamide in oxygen atmosphere, Delzenne et al.[3] also used thiourea as the reductant and concluded that the initiating redox system actually consists of thiourea and hydrogen peroxide.

Palit has developed very sensitive dye techniques, namely dye interaction[4] and dye partition[5] techniques for detection and estimation of several endgroups in polymers; recently the partition technique has been successfully extended to the case of amino-bearing endgroups.[6,7] This has induced us to use thiourea as a redox initiator component, as the incorporation of amino-bearing endgroups (as initiator fragments) in the resultant polymers is a distinct possibility in such cases. Methyl methacrylate (MMA) has generally been used as the monomer, since the resulting polymer facilitates thorough endgroup analysis, and for its aqueous initiation at room temperature (25–30°C.) or at any other specified temperature, a large number of oxidants have been tried along with thiourea as the reductant. Many of the oxidants have been found to form initiating redox pairs with thiourea, with varying efficiencies, and special mention may be made of the redox pairs formed by thiourea with the following oxidants: ferric chloride (Fe^{3+}); ethylene dibiguanide complex salts of tripositive silver (Ag^{3+}); hydrogen peroxide (H_2O_2); persulfate ($S_2O_8^{2-}$); and potassium bromate + hydrochloric acid ($BrO_3^- + HCl$). Among these oxidants $FeCl_3$, H_2O_2, and $BrO_3^- + HCl$ have no initiating capacity by themselves at room temperature, but the other two do, though only after a prolonged induction period. In principle, possibility of formation of such redox pairs, with thiourea as reductant, is of indefinite extension. Results of endgroup analysis of polymers produced by the above-mentioned five redox pairs indicate that while polymers produced by the first four redox systems, always contain amino endgroups in varying proportions [almost exclusively in case of Fe^{3+} and Ag^{3+}], polymers produced by $BrO_3^- + HCl$ contain either sulfonate or amino endgroups or a mixture of amino and sulfonate endgroups, depending on the concentration of acid and bromate in the medium. Results of our endgroup analysis have been found to provide conclusive evidence in favor of the initiation mechanism suggested by Sugimura et al.,[2] and suitable initiation mechanisms have been suggested in other cases also. Detailed kinetic study of a few systems is in progress.

EXPERIMENTAL

Materials

Monomers were purified by the usual procedures and were stored in a refrigerator. Dye samples used were obtained in purified form and were used without further purification. All other reagents used were either B.D.H. or E. Merck analytical grade reagents. Ethylene dibiguanide complexes of silver(III) were prepared in the laboratory, following standard procedures.[8]

Preparation of Polymers

Aqueous polymerization of freshly distilled methyl methacrylate was carried out in stoppered Pyrex flasks either under an atmosphere of purified nitrogen or in air-flushed systems at specified temperatures (generally at room temperature).[9] The induction period was generally 0–15 min. in the case of thiourea with Fe^{3+}, Ag^{3+}, H_2O_2, and $S_2O_8^{2-}$ in nitrogen atmosphere. But in the presence of oxygen, the induction period was rather prolonged. In the case of Fe^{3+}, a relatively high concentration of Fe^{3+} and thiourea was needed to initiate polymerization; but at very high Fe^{3+} concentration, the induction period was quite prolonged and the rate of polymerization was very slow, probably due to inhibiting action of Fe^{3+} ion. In the case of H_2O_2 polymerization did not start at all unless a certain minimal concentration of H_2O_2 ($\sim 0.005M$) was present in the system. The rate of polymerization was quite fast in all these cases and the total yield was also quite high except in the case of Ag^{3+} where color of the Ag(III) complex was discharged on addition of thiourea and polymerization stopped after some time (maximum yield, about 70%). In the case of BrO_3^-, the induction period varied between 0 and 60 min., depending on the concentration of ingredients in the system.

MMA was photopolymerized in air-flushed aqueous systems containing eosin and thiourea. Flasks containing all the ingredients were placed in front of a 200-w. bulb for a few hours and the temperature of the system increased to about 50–55°C. during this period. The induction period was quite prolonged. To maintain the pH of the medium at 9.2 and 8.0, borax and phosphate buffers were used.

The polymers formed were washed repeatedly with slightly warm distilled water and dried in an air oven at 45–50°C. These polymers were then subjected to rigorous purification by repeated precipitation following the standard procedure[10] to make these polymers suitable for endgroup estimation by the application of dye techniques.

Endgroup Analysis by Dye Techniques

The dye-partition technique using methylene blue dye for estimation of sulfoxy endgroups[11] and the dye-interaction technique using rhodamine 6GX dye for estimation of hydroxyl[12] have been discussed in detail in our previous communications.[11,12] Another dye-partition technique using methylene blue for estimation of hydroxyl endgroups[13] (after chlorosulfonic acid treatment) has been reported recently, but this method is perhaps not so satisfactory in the presence of amino endgroups, as amino groups themselves may react with chlorosulfonic acid.

The dye-partition technique with the use of disulfine blue VN 150 dye reagent for the detection and estimation of amino-bearing endgroups in polymers is similar to the method with methylene blue dye reagent[11] as regards operation and has been described elsewhere.[6,7] In actual practice, 10 ml. of dye solution prepared by dissolving 80 mg. dye in 1 liter $0.01N$ HCl is mixed with 10 ml. of chloroform solution of the polymer of desired concentration in a centrifuge tube; the usual procedure is then followed,[11] and the optical density of the color developed in the chloroform layer is measured at 630 mμ. The method is sensitive even for micronormal amine concentrations, but it is yet to be calibrated for quantitative estimation of amino endgroups; only a relative picture of amino endgroup content has now been obtained by this dye partition technique by using a calibration curve based on pure n-dodecyl amine.

TABLE I
Aqueous Polymerization of Methyl Methacrylate Initiated by Redox Systems Containing Thiourea as the Reductant at Room Temperature (25–30°C.)[a]

Oxidant	[Oxidant], mole/l.	Polymerization rate	Inhibition period (I.P.), min.	$[\eta]$	Endgroup expected	Endgroup found by dye techniques	Remarks
Acidified Potassium bromate	10^{-2}	Very fast	12	0.90	Amino	Amino, sulfonate	Initiation with neutral bromate occurs with long I.P. (3–4 days). Oxidation of amino-bearing endgroup to sulfoxy is possible
Potassium permanganate (acidic and neutral)	10^{-2}	Moderate	20	0.30	Amino	Amino (trace) and sulfonate	MnO_2 separates out immediately. Oxidation of amino-bearing endgroup to sulfoxy is possible
Potassium persulfate	10^{-2}	Fast	12	0.94	Amino and/or sulfate	Amino, sulfate and hydroxyl	Amino predominates
Benzoyl peroxide[b]	10^{-3}	Very slow	20	—	—	—	Little polymerization; propagation stops after some time
m-Nitrobenzoyl peroxide[b]	10^{-3}	Very slow	25	—	—	—	

Potassium dichromate	10^{-3}	—	—	—	—	—	No initiation even with acid dichromate
Potassium perchlorate	10^{-3}	—	—	—	—	—	No initiation
Potassium chlorate with/without acid	10^{-2}	—	—	—	—	—	
Hydrogen peroxide	10^{-2}	Very fast	10	0.10	Amino and/or hydroxyl	Amino and hydroxyl	Very low DP; hydroxyl predominant
Ferric chloride	10^{-3}	Fast	25	0.94	Amino and/or chlorine	Amino	
Bromine	10^{-4}	Moderate	45	0.50	Amino and/or bromine	Amino	Bromine endgroup also may be present
Ammoniacal silver nitrate	10^{-3}	—	—	—	—	—	Reduction to metallic silver takes place immediately
Fehling's solution	10^{-2}	—	—	—	—	—	Slow reduction to cuprous state
Erythrosin J[c]	10^{-5}	Moderate	30	0.42	Amino	Amino	
Methylene blue[c]	10^{-4}	Slow	160	0.82	Amino	Amino	Inhibition period very long

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[a] [MMA] = 0.094 mole/l.; [thiourea] = 10^{-2} mole/l.; N_2 atmosphere.

[b] Monomer solution of oxidant was used (oxidant being insoluble in water).

[c] Exposed to 200-w. bulb.

Since amino endgroups also respond to rhodamine reagent, the estimation of hydroxyl (transformed to carboxyl) endgroups by the dye-interaction method becomes difficult in the presence of amines, especially when the response is very intense. But when the amino endgroup content is low (i.e., the response to disulfine blue is weak), the dye-interaction technique may be safely utilized for estimation of hydroxyl endgroup content.

Determination of Molecular Weight

The number-average molecular weights $\bar{M}_n$ of poly(methyl methacrylate) samples were calculated from the intrinsic viscosity $[\eta]$ values obtained by the usual method of extrapolation. Viscosity measurements were carried out in an Ostwald-type viscometer at 30 ± 0.1°C. with benzene solutions of the polymers. $\bar{M}_n$ values were obtained with the help of the equation[14]

$$\bar{M}_n = 2.81 \times 10^5 [\eta]^{1.32}$$

The osmometric molecular weights of a few of the purified samples (determined in a Pinner-Stabin osmometer) were found to be quite close ($\pm 10\%$) to the $\bar{M}_n$ values obtained by employing the above equation; therefore the endgroups calculated by utilizing these $\bar{M}_n$ values have been reported as endgroups/polymer chain.

RESULTS AND DISCUSSION

Altogether fifteen reagents have been tested as oxidants in conjunction with thiourea as reductant and quite a few of them have been found to form redox initiation pairs. The polymers produced have been found to contain amino endgroups almost in all cases; results of these experiments are summarized in Table I.

Endgroup Analysis

The results of endgroup analysis of poly(methyl methacrylate) samples, initiated by redox pairs formed by thiourea and Fe^{3+}, Ag^{3+}, H_2O_2, and $S_2O_8^{2-}$ are presented in Table II. These results indicate that in case of Fe^{3+} and Ag^{3+} oxidants, endgroups incorporated in polymers are mainly amino, with little or no hydroxyl, and it appears that amino-bearing radicals derived from thiourea are mainly responsible for both initiation and termination in these cases. In case of H_2O_2, besides amino endgroups, hydroxyl endgroups are also found to be incorporated in the polymers, to a relatively much greater extent than the amino endgroups. These hydroxyl radicals are inevitably derived from hydrogen peroxide, as also suggested by other workers.[1,2] In case of $S_2O_8^{2-}$, polymers are found to contain amino, sulfate, and occasionally hydroxyl endgroups to various extents. It appears that amino-bearing radicals are generated from thiourea and sulfate and hydroxyl radicals are formed from persulfate.

TABLE II
Endgroup Analysis of Poly(methyl Methacrylate) Obtained by Aqueous Initiation with Redox Systems Containing Thiourea as the Reductant[a]

[Thiourea], mole/l. × 10^2	Oxidant	[Oxidant], mole/l. × 10^2	[η]	Average number of endgroups per polymer chain[b]		
				NH_2	OH	SO_4
1.0	$FeCl_3 \cdot 6H_2O$	0.1	1.61	1.68	0.79	—
2.5		0.1	0.80	2.10	0.28	—
5.0		0.1	0.56	1.80	0.26	—
10.0		0.1	0.46	1.85	—	—
2.5		0.05	1.12	1.65	0.16	—
2.5		0.2	0.70	3.0	0.23	—
5.0		0.88	0.31	2.99	—	—
20.0		4.8	0.46	3.70	—	—
5.0[c]		0.1	0.87	1.79	—	—
2.5[d]		0.1	1.08	1.45	—	—
0.02	$[Ag \cdot C_2H_4\text{-}(C_2H_6N_5)_2]^{3+} ClO_4^-$	0.04	0.55	1.51	—	—
0.04		0.04	0.46	1.45	—	—
0.08		0.04	0.47	2.27	—	—
0.16		0.04	0.51	3.20	—	—
0.08		0.08	0.34	2.17	—	—
0.04[c]		0.04	0.66	1.80	—	—
0.1	H_2O_2	1.0	0.78	0.11	0.93	—
0.5		1.0	0.36	0.24	0.99	—
1.0		1.0	0.27	0.35	1.02	—
0.5		5.0	0.28	0.13	1.55	—
5.0		2.0	0.33	0.18	0.74	—
5.0[c,e]		2.0	0.32	0.86	—	—
1.0[c]		2.0	0.23	0.31	—	—
0.5	$K_2S_2O_8$	0.5	1.35	0.38	1.80	0.65
5.0		0.5	1.22	2.10	0.90	0.22
10.0		0.5	1.24	3.00	—	0.24
1.0		0.1	1.44	0.81	—	—
1.0		0.5	1.14	1.00	—	0.47
1.0		1.0	1.07	0.52	0.36	0.62

[a] [MMA] = 0.094 mole/l.; temperature 25–30°C.; N_2 atmosphere (unless otherwise noted).

[b] Endgroup analysis with the help of dye techniques.[6,7,11,12]

[c] O_2 atmosphere.

[d] 50°C.

[e] Carried out in the presence of light.

Among all the redox systems containing thiourea, acidified bromate–thiourea system merits special investigation due to the following features: (*1*) the initiating efficiency is very high, probably the highest of all the redox systems containing thiourea, and the inhibition period is practically undetectable in some cases; (*2*) most of the water-soluble vinyl monomers can

TABLE III

Aqueous Polymerization of Methyl Methacrylate by Thiourea–Acidified Bromate Redox System at Room Temperature (25–30°C.)[a]

[Thiourea], mole/l. × 10^2	[KBrO$_3$], mole/l. × 10^2	[HCl], mole/l. × 10^2	Inhibition period (I.P.), min.	[η]	Dye-partition technique for endgroup analysis			
					Sulfonate endgroups[b]		Amino endgroups[c]	
					O.D. of 0.1% polymer solution at 660 mμ	Sulfonate endgroups per chain	O.D. of 0.1% polymer solution at 630 mμ	Amino endgroups per chain
1.0	1.0	10.0	Nil	0.34	1.55	1.22	—	—
1.0	1.0	1.0	12	0.90	0.11	0.34	0.67	1.83
1.0	1.0	0.1	40	1.05	—	—	0.70	2.34
1.0	1.0	0.01	60	1.41	0.11	0.61	0.44	2.20
1.0	0.1	1.0	15	1.88	—	—	0.35	2.55
1.0	0.01	1.0	60	Very little polymerization	—	—	—	—
0.1	1.0	1.0	15	0.39	0.48	0.47	—	—
0.01	1.0	1.0	17	1.07	0.20	0.71	—	—

[a] [MMA] = 0.094 mole/l.; N_2 atmosphere.

[b] Method with methylene blue.[11]

[c] Method with disulfine blue.[6,7]

TABLE IV
Effect of Acid Concentration on the Aqueous Polymerization of Methyl Methacrylate by Thiourea-Acidified Bromate Redox System at Room Temperature (25–30°C.)[a]

			Dye partition techniques for endgroup analysis			
			Sulfoxy endgroups[b]		Amino endgroups[c]	
[HCl], mole/l. × 10^2	Inhibition period (I.P.), min.	$[\eta]$	O.D. of 0.1% polymer solution at 660 mμ	Sulfoxy endgroups (nonhydrolyzable) per chain	O.D. of 0.1% polymer solution at 630 mμ	Amino endgroups per chain
10.0	Nil	0.34	1.55	1.22	—	—
7.0	1–2	0.25	1.54	0.83	—	—
5.0	2	0.37	0.67	0.61	—	—
4.0	5	0.38	0.86	0.78	—	—
2.0	10	0.68	0.16	0.34	—	—
1.0	12	0.90	0.11	0.34	0.67	1.83
0.1	40	1.05	—	—	0.70	2.34

[a] [Thiourea] = $[KBrO_3]$ = 10^{-2} mole/l.; [MMA] = 0.094 mole/l.; N_2 atmosphere.

[b] Method with methylene blue.[11]

[c] Method with disulfine blue.[6,7]

be polymerized with it, with little or no induction period, even when they are stabilized with hydroquinone; (*3*) initiation does take place even at as low a temperature as 0°C., and in the range of 5–10°C. the rate is fairly high, and (*4*) the acidity of the polymerization medium governs the endgroup profile of the resultant polymers; initiating ability and rate of polymerization are also directly linked with it. The initiating power of the system becomes almost latent in the complete absence of acid and the duration of the inhibition period, which is a measure of the initiating power, becomes shorter and shorter until it vanishes as the acid concentration is increased from $10^{-4}N$ to $0.1N$ (Table III).

When the acidity of the system is high ([acid] > $10^{-2}N$), amino endgroups are not detected in polymers. On the contrary, sulfonate (nonhydrolyzable) endgroups are found to be incorporated in polymers, indicating that an acidic sulfur atom is directly linked to the carbon atom of the polymer chain. In highly acidic media, polymers are found to contain almost one sulfonate endgroup per chain. Sulfonate endgroup content gradually decreases, however, with reduction of the acidity of the medium, and below $10^{-2}N$ acid concentration, amino and/or sulfonate endgroups are detected in polymers (Table IV).

Nature of Primary Radicals

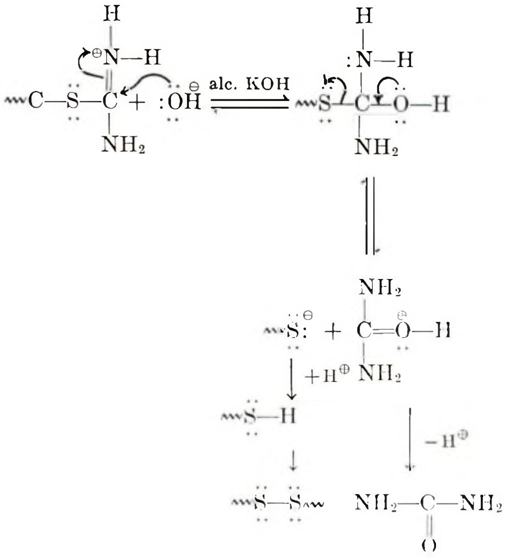
Sugimura et al.[2] found that both urea and guanidine are incapable of forming redox pairs with H_2O_2 and concluded that nitrogen-bearing groups in thiourea do not take any part in radical generation. They also studied the initiating efficiencies of thiourea and a number of *N*-substituted thioureas in presence of H_2O_2 and suggested that isothiourea, HS—C(=NH)-NH_2, a thiol, which exists in tautomeric equilibrium with thiourea in aqueous solution, is the reductant. When it takes part in reduction, the reactive hydrogen atom attached to sulfur may be removed, and a primary isothiocarbamido radical, $\dot{S}$—C(=NH)NH_2, may be generated.

Oxidation of thiourea with acid permanganate is known to generate formamidine disulfide,[15] NH_2C(=NH)SSC(=NH)NH_2, and the initiating capability of this redox pair suggests that intermediate isothiocarbamido radicals might be formed during this redox reaction. If this isothiocarbamido radical initiates polymerization, the resultant amino-bearing polymeric endgroup should be represented as ⁓C—S—C(=NH)NH_2.

Our dye-partition technique with disulfine blue dye reagent also indicates the presence of such an endgroup, though it is very difficult to predict at this stage whether both NH and NH_2 groups would respond to our dye-partition technique. If the radical end was on the nitrogen and not on the sulfur, then the endgroup should have been ⁓NHC(=S)NH_2, which is very similar to the ⁓NHC(=O)NH_2 endgroup present in polyacrylamide; but the latter is found to be insensitive to disulfine blue dye reagent.

We have failed to detect the presence of amino groups in such polymers by the infrared technique, evidently due to their very low concentration.

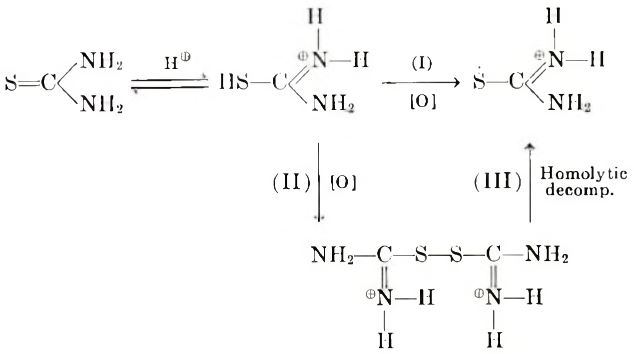
Mandal et al.[16] in our laboratory have shown that on treating benzene or acetone solution of such polymers with alcoholic KOH under very mild conditions, the response to disulfine blue dye reagent disappears. In most cases the molecular weight of the treated polymers increases considerably. A polymer of the same starting molecular weight and having carboxyl endgroups, on similar treatment, does not show any significant change in molecular weight. This indicates a hydrolytic cleavage of the terminal



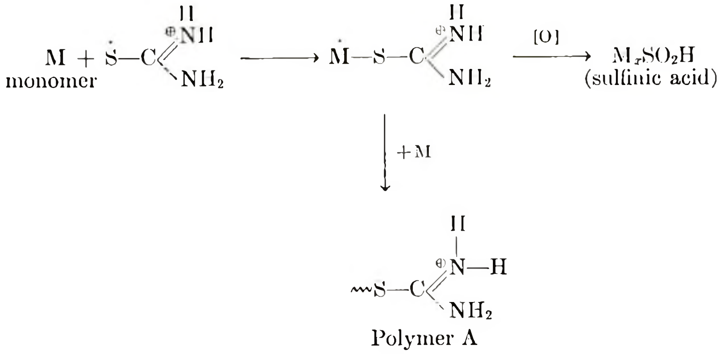
(1)

~~~S—C bond during this treatment with subsequent removal of the amino group-bearing part from the polymer chain.[17] The increase in molecular weight may be due to disulfide formation, as indicated eq. (1).

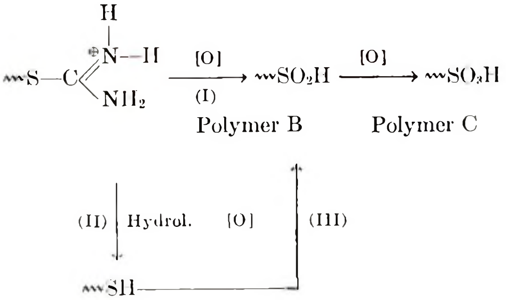
The general features of the acidic thiourea–bromate redox-initiation system and endgroup analysis of resultant polymers indicate a complex and quite different initiation mechanism. It has been reported earlier that sulfonic acids[18–21] are produced by disproportionation of sulfinic acids, and the latter are excellent low-temperature catalysts for vinyl polymerization.[22,23] The initiating efficiency of sulfonic acids is rather controversial. Since notable features of acidic thiourea–bromate initiation (as mentioned before) show close resemblance to sulfinic acid initiation, a tentative reaction mechanism has been elicitated for this system which is shown in eqs. (2)–(4).



(2)



(3)



(4)
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Polymer A would give a response for amino endgroups and polymer C for nonhydrolyzable sulfonate endgroups. Polymer B, which is a sulfinic acid, may be responsible for initiation as well. Formation of formamidine sulfinic and sulfonic acids during oxidation of thiourea has been reported by earlier workers also.[24,25] The variation of average sulfonate endgroup content of polymers (Table IV) may be explained in terms of either incomplete oxidation of amino-bearing endgroups [eq. (4) or participation of both isothiocarbamido radical and sulfinic acid in initiation [eqs. (2) and (3)]. However, this system requires more detailed experimental investigation to formulate any definite mechanism.

Effect of Oxygen

All these redox systems can also initiate polymerization in oxygen-flushed closed systems with a prolonged induction period. If oxygen is slowly bubbled into any of these systems, however, polymerization does not start. This indicates that oxygen is an inhibitor for these systems, as for many other typical free-radical-initiated systems. When O_2 is present in limited quantity, however, it is rather quickly consumed, giving products which probably do not inhibit the process. The endgroup picture does not suffer any significant change in the presence of oxygen (Table II). In the case of the photosensitized eosin–thiourea system, however, oxygen has been claimed to be a necessary constituent of the redox-initiating system.[3]

Effect of pH of the Medium

Normally, with thiourea as a reductant, polymerization either proceeds very slowly or does not proceed at all in an alkaline medium. In case of H_2O_2–thiourea redox, polymerization does not occur in alkaline medium at room temperature. Bonvicini et al.,[1] however, have reported some results of experiments carried out in an alkaline medium at 60°C.; the possibility of decomposition of H_2O_2 at such a high temperature cannot be ruled out in those systems. They have also polymerized acrylonitrile in both acid and alkaline medium with Fe^{3+}–H_2O_2–thiourea at 60°C.; in that case also, an independent redox reaction between H_2O_2 and Fe^{3+} is a distinct possibility. Thiourea probably loses its reducing property to a great extent in alkaline media, as is evidenced by the fact that while it can reduce selenium dioxide to metallic selenium almost quantitatively in an acid medium, it practically fails to do so in an alkaline medium. MMA could, however, be polymerized in air-flushed closed systems with prolonged induction period at pH 8 and 9.2 with the photosensitized eosin–thiourea redox system[3] as initiator; but very little or no amino endgroups were found to be incorporated in the resultant relatively high molecular weight polymers. Similar experiments, when carried out in acid or neutral medium, produced polymers of relatively low molecular weight and of very high amino endgroup content (Table V). The reason for incorporation of quite a large number of amino endgroups in that case is still obscure. The presence of any hydroxyl endgroup in both these types of polymers could not be established

TABLE V
Endgroup Analysis of Poly(methyl Methacrylate) Obtained by Aqueous Photoinitiation with Eosin and Thiourea[a]

[Thiourea], mole/l. × 10^2	[Eosin], mole/l. × 10^4	pH of the medium	[η]	O.D. of 0.01% polymer soln. with disulfine blue at 630 mμ	Amino endgroups/chain[b]
1	1.0	5–6	0.44	0.54	6.0
5	1.0	"	0.40	0.50	4.70
10	1.0	"	0.43	0.40	4.05
5	0.5	"	0.33	0.68	4.87
5	0.2	"	0.37	0.43	3.65
5	1.0	9.2	0.80	0.01	0.25
1	1.0	9.2	0.73	0.04	0.92
5	1.0	8.0	0.65	0.01	0.19
1	1.0	8.0	1.40	0.01	0.48

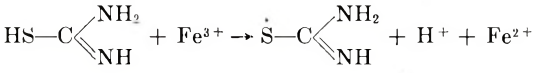
[a] [MMA] = 0.094 mole/l.; O_2 atmosphere; Samples were placed in front of a 200-w. lamp for a few hours; temperature increased to about 55°C. during polymerization.

[b] We failed to detect any hydroxyl endgroup in these polymers by our dye technique.

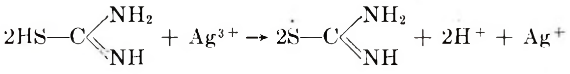
by the application of dye techniques.[12,13] (The applicability of pyridine–phthalic anhydride technique[12] in these cases is, however, rather limited due to the presence of large number of rhodamine-responsive groups in the original polymers.) Thus the comparison of results presented in Tables II and V together with the fact that in the thiourea–H_2O_2 redox initiation system a minimal concentration ($\sim$0.005M) of H_2O_2 is essential, indicate that the thiourea–eosin system in no way resembles the thiourea–H_2O_2 system and thus the participation of H_2O_2 in the initiation mechanism of the thiourea–eosin system[3] could not be established by our work.

Mechanism

In conformity with the results of endgroup analysis, the redox reaction for Fe^{3+} and Ag^{3+} may be represented as

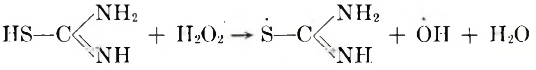


$$HS{-}C\begin{smallmatrix}\nearrow NH_2\\ \searrow NH\end{smallmatrix} + Fe^{3+} \rightarrow \dot{S}{-}C\begin{smallmatrix}\nearrow NH_2\\ \searrow NH\end{smallmatrix} + H^+ + Fe^{2+} \qquad (5)$$

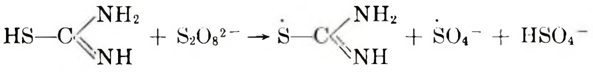


$$2HS{-}C\begin{smallmatrix}\nearrow NH_2\\ \searrow NH\end{smallmatrix} + Ag^{3+} \rightarrow 2\dot{S}{-}C\begin{smallmatrix}\nearrow NH_2\\ \searrow NH\end{smallmatrix} + 2H^+ + Ag^+ \qquad (6)$$

In the cases of H_2O_2 and $S_2O_8^{2-}$, the corresponding redox reactions may be represented as



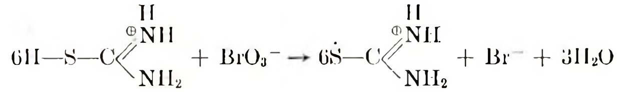
$$HS{-}C\begin{smallmatrix}\nearrow NH_2\\ \searrow NH\end{smallmatrix} + H_2O_2 \rightarrow \dot{S}{-}C\begin{smallmatrix}\nearrow NH_2\\ \searrow NH\end{smallmatrix} + \dot{O}H + H_2O \qquad (7)$$



$$HS{-}C\begin{smallmatrix}\nearrow NH_2\\ \searrow NH\end{smallmatrix} + S_2O_8^{2-} \rightarrow \dot{S}{-}C\begin{smallmatrix}\nearrow NH_2\\ \searrow NH\end{smallmatrix} + \dot{S}O_4^- + HSO_4^- \qquad (8)$$

$$\dot{S}O_4^- + H_2O \rightarrow HSO_4^- + \dot{O}H \qquad (9)$$

The proposed tentative initiation mechanism for the acidic bromate–thiourea redox system has already been discussed, and the initial radical generation reaction may be represented as



$$6H{-}S{-}C\left\langle{}^{\overset{\textstyle H}{\oplus NH}}_{NH_2}\right. + BrO_3^- \rightarrow 6\dot{S}{-}C\left\langle{}^{\overset{\textstyle H}{\oplus NH}}_{NH_2}\right. + Br^- + 3H_2O \qquad (10)$$

It may be seen that isothiourea, which exists only in aqueous solution, takes part in all these redox reactions. So, it is apparent that the reducing property of thiourea should operate only in systems containing water.

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Résumé

Quelques systèmes oxydo-réducteurs, contenant de la thiourée (TU) comme réducteur, ont été trouvés vraiment efficaces pour l'initiation de la polymérisation vinylique en milieu aqueux et les polymères obtenus dans ce processus contiennent tous des groupes aminés terminaux dans une certaine mesure ainsi que cela a été démontré par la méthode aux colorants. Quelques oxydants ont jusqu'ici été utilisés dans ce but et parmi eux principalement le chlorure ferrique (Fe^{3+}), les sels complexes d'éthylène-dibiguanides d'argent trois fois positifs (Ag^{3+}), le peroxyde d'hydrogène (H_2O_2), le persulphate ($S_2O_8^{2-}$), les bromates (BrO_3^-)+ l'acide chlorhydrique (HCl). Dans le cas des oxydants Fe^{3+} et Ag^{3+} les groupes aminés terminaux sont surtout incorporés dans les polymères, mais dans le cas des oxydants H_2O_2 et $S_2O_8^{2-}$ les fragments des oxydants sont également incorporés sous la forme de groupes terminaux hydroxyles et sulphates. L'oxydant BrO_3^-, toutefois forme un système initiateur oxydo-réducteur très efficace avec la T.U. ainsi que cela a été démontré par sa capacité de polymériser des monomères vinyliques solubles dans l'eau mêmes lorsqu'ils sont stabilisés à l'hydroquinone et à basse température environ à 0°C et avec des vitesses vraiment élevées. À côté des groupes aminés terminaux, les groupes sulphonés terminaux ont également été détectés dans les polymères dans ce cas, et l'importance relative de ces deux groupes terminaux dépend généralement de la concentration en acides de ces systèmes. On admet la formation de radicaux $\dot{S}—C(=NH)NH_2$ dans ce système par oxydation d'isothiourée $HS—C(=NH)$-NH_2 et ces radicaux sont incorporés dans les polymères commes groupes terminaux. Les groupes terminaux sulphonates peuvent être engendrés par oxydation de ces groupes terminaux aminés. Des mécanismes d'initiation correspondants ont été suggérés dans chacuns des cas.

Zusammenfassung

Einige Redoxsysteme mit Thioharnstoff als Reduktionsmittel erwiesen sich beim Start der Vinylpolymerisation in wässrigen Medien als recht wirksam und an allen dabei erhaltenen Polymeren konnten mittels des Anfärbeverfahrens in verschiedenem Ausmass Aminoendgruppen gefunden werden. Es wurden bei diesen Systemen schon eine Reihe von Oxydationsmitteln verwendet, unter welchen besonders Ferrichlorid (Fe^{3+}); Athylenbiguanidinkomplexsalz von dreiwertigem Silber (Ag^{3+}), Wasserstoffperoxyd (H_2O_2), Persulfat ($S_2O_8^{2-}$) und Bromat (BrO_3^-) + Chlorwasserstoffsäure (HCl) bemerkenswert sind. Im Falle der Oxydationsmittel Fe^{3+} und Ag^{3+} werden hauptsächlich Aminoendgruppen in das Polymere eingebaut; bei H_2O_2 und $S_2O_8^{2-}$ werden jedoch auch Bruchstücke des Oxydationsmittels nämlich Hydroxyl- und Sulfatendgruppen eingebaut. Oxydationsmittel BrO_3^- bildet ein sehr wirksames Redoxstartsystem mit Thioharnstoff, wie seine Fähigkeit, sogar Hydrochinonstabilisierte wasserlösliche Vinylmonomere bei sehr niedriger Temperatur (~0°C) und mit recht grosser Geschwindigkeit zur Polymerisation zu bringen, zeigt. Neben Aminoendgruppen wurden in diesem Falle in den Polymeren auch Sulfonatendgruppen gefunden und das relative Ausmass dieser beiden Endgruppentypen hängt im allgemeinen von der Säurekonzentration im System ab. Die bischerigen Befunde sprechen für eine Bildung von $\dot{S}—C(=NH)NH_2$-Radikalen im System durch Oxydation von Isothioharnstoff $HS—C$-$(=NH)NH_2$ und diese Radikale werden in das Polymere als Endgruppen eingebaut. Sulfonatendgruppen können durch Oxydation dieser aminohältigen Endgruppen gebildet werden. In jedem Falle wurden geeignete Startmechanismen vorgeschlagen.

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Detection and Incorporation of Amino Endgroups in Free-Radical Polymerization of Methyl Methacrylate

SUKUMAR MAITI and MIHIR K. SAHA,* *Department of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, India*

Synopsis

Amino endgroups have been incorporated in poly(methyl methacrylate) by two methods: (*a*) initiation with systems producing amine radicals and (*b*) chain transfer with amines. A new dye-partition technique with the use of disulfine blue was developed for qualitative and in some cases quantitative estimation of amino endgroups in the polymer.

INTRODUCTION

In radical polymerization a monomer molecule receives the stimulus of becoming larger and larger from the initiator radical fragment which is attached to one of its ends till its stimulus is lost either by transfer to other molecules (monomer, solvent, or polymer molecules) or by the collision between two growing radicals. Thus, initiating radical fragments are the "birth-marks" of the polymers and the study of their detection might throw some light on the initiation step in the mechanism of the polymerization process. The detection of initiating radical fragments in polymers is one of the most formidable tasks in polymer chemistry. Although carboxyl, sulfoxyl, sulfate, halogen, and hydroxyl endgroups in polymers have been very successfully detected by the ultra-sensitive dye technique first proposed by and developed by Palit and co-workers,[1-5] unfortunately amino end fragments in polymers evade detection by almost all such dye techniques.

The present communication reports some of the possibilities of incorporation of amino endgroups in poly(methyl methacrylate) and a new dye-partition technique for the detection of amino endgroups in polymers.

Amino groups may be introduced in a polymer chain by the following general methods; (*1*) initiation with systems producing amino radicals, (*2*) chain transfer with amines, (*3*) copolymerization with a monomer containing amino groups, and (*4*) chemical transformation of an existing group in the polymer. Only the first two methods have been attempted and some of the results are described herein.

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* Present address: Department of Chemistry, University of Notre Dame, Notre Dame, Indiana, U. S. A.

EXPERIMENTAL

Materials

Methyl methacrylate monomer (MMA) was purified by the usual method and the distilled monomer was kept in a refrigerator (5–10°C.). All the amines used were of very pure quality and their purity, checked by acidimetry, was of the order of 98%. Disulfine blue VN (I.C.I.), Eosin Saure L neu and Erythrosin J (Badische Anilin & Soda-Fabrik), and methylene blue (E. Merck) were used as received. Azobisisobutyronitrile was purified and recrystallized according to a standard method.[6] Water was obtained by redistilling distilled water with alkaline permanganate in an all-Pyrex glass apparatus. Dry, completely oxygen-free nitrogen was prepared by the usual method.[7] All other chemicals used were of analytical reagent grade and supplied by either BDH or E. Merck.

Aqueous Polymerization

Aqueous polymerization of methyl methacrylate was carried out in 100-ml. Pyrex Erlenmeyer flasks in an atmosphere of nitrogen at room temperature (25–30°C.). Polymerization with methylene blue–EDTA was carried out in the light from a 500-w. tungsten filament bulb (without any optical filter) at a constant voltage of 220 v. All other aqueous polymerization experiments were, however, carried out in the dark. After completion of polymerization (18–20 hr.), the polymers were filtered, washed scrupulously with warm water to remove all soluble impurities and unreacted monomer, and then dried in an air oven at 45°C. They were then finally purified by the usual method of repeated precipitation from benzene solution, a mixture of alcohol and petroleum ether being used as the nonsolvent.[4]

Nonaqueous and Bulk Polymerization

Nonaqueous polymerization of methyl methacrylate was carried out in sealed ampules under vacuum at 60 ± 0.1°C. in the dark. The bulk polymerization, i.e., dye-sensitized photopolymerization, of methyl methacrylate was also carried out in ampules sealed under vacuum with the use of filtered[8] light (490–530 mμ, i.e., in the absorption maximum range of eosin) at 40 ± 0.1°C. The polymers obtained were purified by repeated precipitation.

Detection of Amino Endgroups

Amino endgroups in polymers have been detected by an extension of the dye-partition technique.[1,9] In the dye-partition test the reagent used was an aqueous solution of disulfine blue VN 150 (80 mg./l.) in 0.01*M* HCl. A known amount of purified polymer was dissolved in 10 ml. chloroform in a 25-ml. well-stoppered Pyrex centrifuge tube. The concentration of the polymer solution was ca. 0.1–0.2%. A 10-ml. portion of aqueous

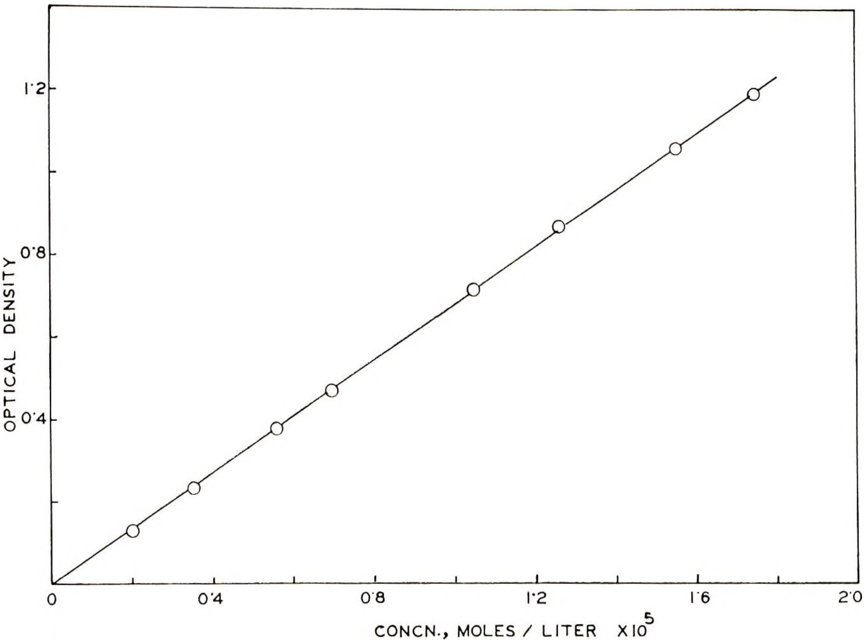

Fig. 1. Plot of optical density against molar concentration of *n*-dodecylamine (reference standard curve for estimation of amino endgroup incorporation in polymers).

disulfine blue reagent was added to it, and the mixture was thoroughly shaken and kept for at least 2 hr. so as to allow complete partition. Blue coloration of the chloroform layer indicates the presence of amino endgroups in the polymer. The chloroform layer was separated and centrifuged, if necessary, to obtain a clear solution, and the optical density (O.D.) of the colored chloroform was then measured in a 1-cm. quartz cell in a Hilger spectrophotometer at 630 mμ (the absorption maximum of disulfine blue VN 150). A blank was always run concurrently, the chloroform layer in the blank being colorless. The dye-partition test with disulfine blue reagent has been found to obey Beer's law in chloroform, benzene, and carbon tetrachloride, and the partition test has been successfully applied for the micronormal estimation of long-chain aliphatic amines.[9] A rough estimate of the amino endgroup content of the polymers was obtained by comparing the experimental optical density values with a calibration curve (Fig. 1) for *n*-dodecylamine, obtained by following a similar procedure.

The distribution of the amino–dye complex between the chloroform and aqueous phase was also examined by separating the colored chloroform layer (color developed by both short chain and long chain amines) from the aqueous dye solution and subsequent shaking of the chloroform layer with an equal volume of water or with $0.01M$ HCl solution in a centrifuge tube for 2–3 hr. The optical densities of both the chloroform layer and the aqueous layer at 630 mμ were then compared to the distribution of the dyes in the two phases. It was observed, however, that in case of both water and 0.01M HCl solution the original optical density of the chloroform layer decreased to some extent with simultaneous development of some color in the aqueous phase, indicating some loss of dyes due to distribution.

Determination of Molecular Weight

Viscosity measurements were performed in 0.2% benzene solution of polymer at 30 ± 0.1°C. by use of an Ostwald viscometer. The intrinsic viscosity $[\eta]$ was calculated by the usual method of extrapolation. The number-average molecular weight $\bar{M}_n$ for unfractionated poly(methyl methacrylate) samples was obtained by using the equation[10]

$$[\eta] = 8.69 \times 10^{-5}\bar{M}_n^{0.76}$$

for benzene solutions at 30°C.

RESULTS AND DISCUSSION

Very few amino endgroups are incorporated in polymers by the amine–azobisisobutyronitrile system (Table I), quite in conformity with the low

TABLE I
Nonaqueous Polymerization of Methyl Methacrylate by the Azobisisobutyronitrile–Amine System[a]

Expt. no.	Amine	Amine concn., mole/l.	Solvent	Solvent concn., mole/l.	$[\eta]$	O.D. of 0.2% polymer solution at 630 mμ	Amine endgroups/chain
1	n-Butylamine	0.62	Toluene	3.30	0.70	0.013	0.01
2	Methyl butylamine	0.64	Toluene	3.30	0.71	0.085	0.08
3	Tri-n-butylamine	0.63	Toluene	3.30	0.72	0.162	0.15
4	n-Hexylamine	0.66	Toluene	3.30	0.72	0.168	0.17
5	n-Dodecylamine	0.65	Toluene	3.30	0.75	0.205	0.23
6	Dodecyl dimethylamine	0.48	Toluene	3.30	0.78	0.226	0.26
7	N,N'-Diethyldodecylamine	0.47	Toluene	3.30	0.76	0.220	0.25
8	Cetyl dimethylamine	0.45	Toluene	3.30	1.58	0.208	0.62

[a] At 60 ± 0.1°C.; under vacuum, [AIBN] = 0.27×10^{-2} mole/l.; [MMA] = 4.70 moles/l.

TABLE II
Photopolymerization of Methyl Methacrylate in Bulk at 40 ± 0.1°C. under Vacuum

Expt. no.	Photo-sensitizer	Photo-sensitizer concn., mole/l. $\times 10^5$	Activator	Activator concn., mole/l.	$[\eta]$	Polymer solution concn., %	O.D. at 630 mμ	Amino endgroups/chain
1	Eosin Saure L neu	6.0	Dodecyl dimethylamine + light[a]	0.12	0.72	0.1	0.940	1.98
2	Eosin Saure L neu	6.0	Cetyl dimethylamine + light[a]	0.05	0.50	0.1	1.890	2.46
3	Eosin Saure L neu	6.0	Octadecyl dimethylamine + light[a]	0.15	0.90	0.1	1.102	3.12

[a] The light from the tungsten filament lamp is filtered through a dye-solution filter[8] to obtain the light at 490–530 mμ.

TABLE III

Aqueous Photopolymerization of Methyl Methacrylate at Room Temperature (25–30°C.), under N_2, [MMA] = 0.094 mole/l.

Photo-sensitizer	Photosensitizer concn., mole/l.	Activator	Activator concn., mole/l.	Polymerization rate	Induction period, min.	$[\eta]$	Polymer solution concn., %	O.D. at 630 mμ	Amino endgroups /chain
Erythrosin J	10^{-5}	Triethanol amine + light[a]	10^{-2}	Very fast	10	1.11	0.1	0.462	1.72
Erythrosin J	10^{-5}	EDTA + light[a]	10^{-2}	Moderate	45	0.94	0.1	0.410	1.23
Erythrosin J	10^{-5}	Phenyl hydrazine hydrochloride + light[a]	10^{-2}	Moderate	15	0.76	0.2	—	—
Erythrosin J	10^{-5}	Hydrazine hydrate + light[a]	10^{-2}	Slow	40	0.61	0.2	—	—
Methylene blue	1.2×10^{-4}	EDTA + light[a]	10^{-2}	Moderate	45	0.87	0.2	0.235	0.32
Chlorine[b]	10^{-2}	Triethanolamine	8×10^{-2}	Moderate	25	0.96	0.2	1.140	1.76

[a] Light from 500-w. tungsten filament lamp at a constant voltage of 220 v. without any optical filter was used.

[b] Other members of halogen family, viz., bromine, also form redox-initiating systems with hydroxy aliphatic amines[13] in the dark.

transfer constant of amines. However, the extent of incorporation follows the order primary < secondary < tertiary amine. The enhanced activity of tertiary amine with respect to amino endgroup incorporation is probably due to the formation of unstable quaternary compound[11] with the initiating radical. The magnitude of incorporation, however, is greater with long-chain aliphatic amines.

In the bulk photopolymerization of methyl methacrylate by use of eosin–aliphatic long-chain amines (Table II), the amino endgroup content of the polymers is fairly high. This definitely proves that the amino radicals, formed *in situ* by the interaction of amines with the photoexcited dye molecules, play an important role in the initiation of polymerization. The extent of incorporation of amino group in polymer increases with increasing chain length of the amine used. This may be due to the ease of formation as well as the stability of long-chain amino radicals generated by the photoreduction of the dye molecule, to the increased solubility of amines in nonaqueous media with the increase of their chain length, or both. However, our system needs further study to settle the dispute, and the kinetic aspect of this system is under investigation.

TABLE IV

Incorporation of Amino Groups in Poly(methyl Methacrylate) by Titanous(III) Chloride and Hydroxylamine Hydrochloride in Acidic Media[a]

[$TiCl_3$], mole/l.	[HCl], mole/l.	[$NH_2OH \cdot HCl$], mole/l.	[η]	Polymer solution, %	O.D. at 630 mμ	Amino endgroups/chain
10^{-3}	2×10^{-2}	10^{-3}	0.26	0.05	1.100	1.24
10^{-3}	2×10^{-2}	5×10^{-4}	0.24	0.03	0.660	1.10
10^{-3}	2×10^{-2}	10^{-4}	0.96	0.10	0.390	1.20
5×10^{-4}	2×10^{-2}	10^{-3}	0.43	0.03	0.408	1.47
10^{-4}	2×10^{-2}	10^{-3}	1.13	0.10	0.498	1.90
10^{-3}	5×10^{-2}	2×10^{-2}	0.43	0.03	0.400	1.44
10^{-4}	0.1	10^{-4}	0.82	0.10	0.450	1.12
5×10^{-4}	1.0	5×10^{-4}	0.32	0.03	0.525	1.29
5×10^{-4}	2.0	10^{-4}	0.51	0.05	0.494	1.30

[a] The aqueous polymerization was carried out under nitrogen with methyl methacrylate 0.094 mole/l. at room temperature (~30°C.). The rate of polymerization was very fast with little or no inhibition period.

In the aqueous photopolymerization, hydroxy aliphatic amines are suitable as activators due to their high solubility in water. Long-chain aliphatic amines which are efficient activators for the nonaqueous system are found to be unsuitable for aqueous polymerization due to their insolubility.[12,13] However, lower aliphatic amines are miscible with water, but their efficiency is not as high as that of hydroxy aliphatic amines. Peculiarly enough, while EDTA is effective in introducing amino groups in polymer chains, hydrazines are incapable of effecting such incorporation (Table III).

The validity of our method of amino endgroup detection has been further verified by the incorporation of amino endgroup in poly(methyl methacrylate) by the redox initiation with the Ti(III)–hydroxylamine system in an acidic medium and their subsequent detection by the dye-partition test. From the endgroup results (Table IV) it is demonstrated that NH_2 radicals formed in the intermediate stages of the reaction are the main initiating species, which corroborates the findings of Davis et al.[15]

In aqueous polymerization of methyl methacrylate and other water-soluble monomers with various redox systems containing thiourea, amino endgroups have been detected in the polymer backbone.[14] Thus thiourea has been found to be a suitable initiating system for the incorporation of amino endgroups in polymers.

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Résumé

Des groupes aminés terminaux ont été incorporés dans le polyméthacrylate de méthyle, par deux moyens, à savoir, (*a*) l'initiation avec des systèmes produisant des radicaux aminés, et (*b*) par transfert de chaînes avec des amines. Un nouveau test de partimon aux colorants utilisant une solution aqueuse de bleu disulfine a été développé pour la détection qualitative et dans certains cas pour l'estimation quantitative de ces groupes aminés terminaux au sein des polymères.

Zusammenfassung

Aminoendgruppen wurden in Polymethylmethacrylat auf zwei Wegen eigenführt, nämlich (*a*) durch Start mit Systemen, welche Aminoradikale bilden und (*b*) durch Übertragung mit Aminen. Zur qualitativen, und in manchen Fällen quantitativen, Bestimmung der Aminoendgruppen in Polymeren wurde ein neuer Farbstoff-Verteilungstest mit wässrigem Disulfinblaureagens entwickelt.

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High-Pressure Reactions. III. Hydrolysis of Polyacrylonitrile

M. PRINCE and J. HORNYAK, *Chemical Engineering Research Division, New York University, Bronx, New York*

Synopsis

Polyacrylonitrile prepared from γ-irradiated monomer was found to react readily with water over a pressure range of 5,130–34,200 atm. to yield polyacrylamide, while polymer prepared by conventional free-radical catalysts will not hydrolyze under the same conditions. Reaction rates at 85°C. were measured; hydrolysis was extremely rapid at higher temperatures. Results are presented to indicate the radical nature of the reaction. Addition of a free-radical source increases the amount of hydrolysis. Pressure has an effect on the properties of the resulting polyacrylamide.

INTRODUCTION

The most important property of acrylonitrile is its ability to undergo addition polymerization to form high molecular weight products. Rapid polymerization takes place in the presence of substances capable of producing free radicals.[1,2] Radiation (γ-rays) has been employed successfully to bring about acrylonitrile polymerization.[3-10] Radiolysis of acrylonitrile in aqueous solutions yields polyacrylonitrile.[5,11]

When acrylonitrile is polymerized in bulk by radiation, the resulting polymer precipitates in the reacting medium and separates as a fine powder.[4] This behavior is due to the insolubility of the polyacrylonitrile in its own monomer. Some crosslinking may occur during polymerization. Peebles[12] postulated such reactions as taking place through the nitrile groups. One nitrile group in 700 reacted would be sufficient to form a gel in a highly polar solvent such as dimethylformamide.

The importance of this paper is shown in the production of polyacrylamide, at about 100% conversion, from γ-irradiated polyacrylonitrile under high pressure. The hydrolysis of polyacrylonitrile is difficult to stop at the amide but rather goes to completion producing the poly(acrylic acid). Polyacrylamide is less stable than poly(acrylic acid) towards hydrolysis and evidences two distinct steps in its hydrolysis.[13] Polymers and copolymers of acrylonitrile can be hydrolyzed by aqueous alkali to give water-soluble materials containing carboxylate groupings.[14-18] On heating above 80°C. with concentrated alkali, the product is chiefly the salt of poly(acrylic acid).[15] Polyacrylonitrile fibers may be surface-hydrolyzed by dilute caustic to give a material readily amenable to sulfonate dyes.[19] Partial hydrolysis of polyacrylonitrile with concentrated sulfuric acid has been reported to give a solution from which fibers may be spun.[20] Acrylonitrile is hydrated rapidly at 100°C. by 84.5% sulfuric acid to produce acrylamide sulfate, which upon neutralization yields free acrylamide.[21–23]

This study has shown that polyacrylonitrile prepared by γ-irradiation may be hydrolyzed to polyacrylamide with water under neutral conditions by the application of high pressure. It was found that polymer prepared by conventional free-radical techniques did not undergo this hydrolysis. Addition of a free-radical source increased polymer conversion in the first case and caused the hydrolysis reaction to occur to a limited extent in the latter case.

EXPERIMENTAL

Acrylonitrile

Acrylonitrile was obtained from the Fisher Scientific Company. It was distilled through a 2-ft. spinning band column (Nester and Faust) to give material with a boiling point of 78–79°C.

Preparation and Irradiation of Samples

Freshly distilled acrylonitrile was sealed in Pyrex ampules under dry nitrogen. These samples were irradiated with a high-intensity ^{60}Co source at the Brookhaven National Laboratory. Details of this unit have been described elsewhere.[24] The irradiations were performed at ambient temperature. For these experiments a dose rate of 1 Mrep/hr. was employed to give a final dosage of 10 Mrep. Field intensities were measured by using ferrous sulfate dosimeters.[25] The liquid acrylonitrile became a solid polymer upon irradiation and was stored at −78°C. prior to pressurization.

Conventional Polyacrylonitrile

Acrylonitrile was polymerized in a slurry polymerization with a redox catalyst system.[26] The following system was heated at 30°C. under nitrogen with slow stirring: water, 200 g.; acrylonitrile, 10.0 g.; potassium persulfate, 0.4 g.; sodium bisulfite, 0.15 g. White flocculent polymer began to form almost immediately. After stirring for 2 hr., the polymer was filtered, washed, and air-dried. The white polyacrylonitrile was then dried *in vacuo* over P_2O_5 at 50°C. The infrared spectrum of this material showed no foreign absorption bands and was identical with the spectrum of polymer produced by irradiation of acrylonitrile.

Analyses

Carbon, hydrogen and nitrogen analyses were made by the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York.

Infrared spectra were obtained on a Perkin-Elmer Infracord spectrometer with NaCl optics. The extent of reaction of the nitrile to amide group was measured by infrared techniques. A comparison of the relative intensities of the —NH and —CN bands was made. Standard mixtures, composed of irradiated polyacrylonitrile and commercially available polyacrylamide, were prepared. A plot of the percentage composition of the standard mixtures against the ratio of the absorption bands of —NH and —CN was then used to determine unknown compositions. All spectra were obtained as KBr disks.

Pressurization

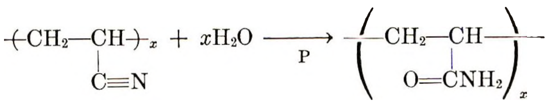
Pressurization of the irradiated polyacrylonitrile was accomplished in two high pressure dies. For very high pressures, 34,000 atm., a modified belt-type die was utilized. It consists of a tungsten carbide linear containing 12–15% cobalt surrounded by heat-shrunk steel retaining rings which have been treated to maximum hardness. A thermocouple is used to measure the temperature of the sample. Two pistons made from sintered tungsten carbide containing 6% cobalt impinge upon a sample which is 0.5 in. in diameter and about 0.5 in. long. Hydraulic ram force for the apparatus was provided by a single-piston 200-ton press.

Lower pressure reactions up to 10,000 atm. were carried out in a die constructed of a hardened steel drill bushing with heat-shrunk steel retaining rings. Pistons were 0.5-in. diameter hardened steel pins. A 20-ton Carver laboratory press provided the motive force for the pistons. Band heaters with a thermocouple-activated temperature controller provided the heating unit.

Irradiated polymer and water (1:1 mole ratio) were enclosed in polyethylene capsules for pressurizations. Polyethylene was found suitable for work up to 100°C. These capsules had polyethylene covers which we heat-sealed into place after they were loaded with reactants. At higher temperatures, Teflon capsules of similar design were employed.

RESULTS AND DISCUSSION

Irradiated polyacrylonitrile was reacted with water (1:1 mole) over a pressure range of 5,130–34,200 atm. at temperatures between 85 and 200°C. The polyacrylonitrile was found to be hydrated rather easily by the water to produce polyacrylamide [eq. (1)].



$$\left(\mathrm{CH_2{-}}\underset{\displaystyle \mathrm{C{\equiv}N}}{\mathrm{CH}}\right)_x + x\mathrm{H_2O} \xrightarrow[\mathrm{P}]{} \left(\mathrm{CH_2{-}}\underset{\displaystyle \mathrm{O{=}CNH_2}}{\mathrm{CH}}\right)_x \qquad (1)$$

The solubility of the product in water was found to be a function of the applied pressure in the hydrolysis step. At very high pressures (34,200 atm.), the product appears to be completely insoluble in either hot or cold water. These high pressure products were yellow. Examination of this material did not reveal any softening or discoloration up to 350°C.

Polyacrylamide formed at lower pressures such as 7,520 atm. exhibited solubility in hot water and limited solubility in cold water. Lower pressures invariably produced material of lighter color, usually off-white to pure white. Lower temperatures also resulted in whiter product.

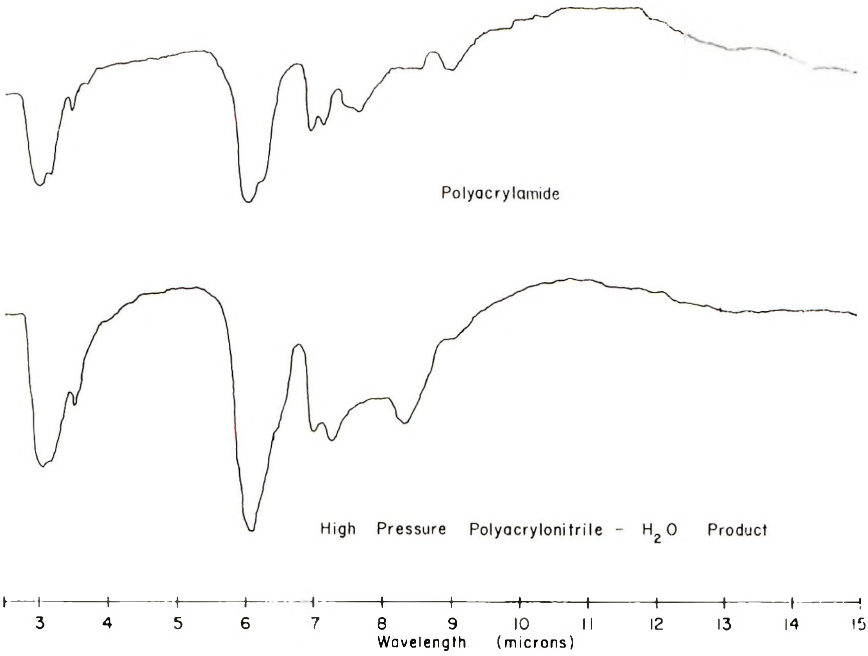


Fig. 1. Infrared spectra of polyacrylamide and high-pressure hydrolysis product

The irradiated polyacrylonitrile high pressure hydrolysis product was examined by x-ray powder diffraction and did not reveal any crystallinity. Examination of a number of polyacrylamide samples produced by this high pressure hydrolysis of conventional polyacrylonitrile with added peroxide did not exhibit any crystallinity. This is in agreement with results obtained by the solid-state polymerization of acrylamide which results in an amorphous polymer.[27] The infrared spectrum of the irradiated polyacrylonitrile was in agreement with that reported for the head-to-tail structure.[28]

The polymer produced by hydrolysis of polyacrylonitrile was analyzed for its elements. Both high and low-pressure products (at approximately 100% hydrolysis) were found to be similar to conventional polyacrylamide. A typical analysis is as follows.

ANAL. Calcd. for $(C_3H_5NO)_x$: C, 50.69%; H, 7.09%; N, 19.71%. Found: C, 50.81%; H, 7.03%; N, 19.49%.

The infrared spectrum of the high pressure hydrolysis product and authentic polyacrylamide (PAM-100, American Cyanamid Company) were virtually identical. These are shown in Figure 1. Note the complete absence of nitrile absorption at 4.45 μ in the high-pressure product.

Polyacrylonitrile prepared by a redox catalyst as described above was pressurized with water (1:1 mole) at 7,520 atm. and 85°C. for periods ranging from 1 to 4 hr. Examination of the infrared spectra of these samples revealed that no amide groups had formed by hydrolysis of nitrile groups. Additional experiments conducted at 150°C. also resulted in no reaction. It should be pointed out at this time that irradiated acrylonitrile gave about 98% conversion to polyacrylamide after 1 hr. at 150°C. and 7,520 atm.

To test the role of added peroxides on this unique hydrolysis reaction, several experiments were performed with both irradiated and nonirradiated polyacrylonitrile. *tert*-Butyl hydroperoxide was chosen as the peroxide for its well-known ease in initiating free-radical reactions.

Irradiated polyacrylonitrile was reacted with water at 5,130 atm. and 150°C. to give 79.3% conversion to polyacrylamide. Addition of 1% *tert*-butyl hydroperoxide (by weight) increased the yield to 98.7% under the same conditions. Nonirradiated polyacrylonitrile did not react with water under the same conditions of temperature and pressure. However, addition of 1% *tert*-butyl hydroperoxide resulted in a 33.0% conversion of nitrile groups to produce a partially hydrolyzed polymer. These results are summarized in Table I.

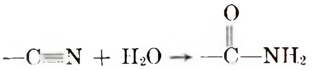
TABLE I
Peroxide Effect on Hydrolysis[a]

Polyacrylonitrile	Concn. *tert*-butyl hydroperoxide, wt.-%	Hydrolysis, %[b]
Irradiated	0	79.3
Irradiated	0.1	98.7
Nonirradiated	0	0.0
Nonirradiated	0.1	33.0

[a] Reaction conditions: 3 hr., 5,130 atm., 150°C.

[b] Determined from infrared spectra of reaction mixture.

The rate of the hydrolysis of polyacrylonitrile to polyacrylamide at 85°C. was measured by using infrared spectra measurements on dried samples. A stoichiometric quantity of water was used to react with the nitrile groups according to eq. (2).



$$—C{\equiv}N + H_2O \rightarrow —\overset{\overset{\displaystyle O}{\|}}{C}—NH_2 \qquad (2)$$

The hydrolysis reaction was assumed to be quenched effectively upon release of the pressure since no further reaction was observed over a period of several days.

TABLE II
Rate of Hydrolysis of Irradiated Polyacrylonitrile at 7,520 atm., 85°C.

Time, min.	Conversion to polyacrylamide, %
15	2.8
30	3.2
60	5.7
90	11.4
120	17.9
150	28.1
180	42.8
210	83.6

Table II contains the data obtained from a number of experimental runs at 7,520 atm. and 85°C. At 150°C. the reaction was found to be very rapid. After only 30 min. the reaction was 93% complete. Insufficient data are at hand to determine the kinetics of this heterogeneous reaction.

The high-pressure product (34,200 atm.) is a hot water-insoluble form which may be mildly degraded. The extensive formation of a condensed aromatic ring structure similar to "black Orlon"[28] is highly unlikely on the basis of the color of the products. These structures require a dehydrogenation reaction for their formation which is improbable under these very high pressure conditions.

Nitriles have been found to undergo unique cyclization reactions under high-pressure conditions. Cairns et al. showed[29] that acetonitrile, propionitrile, *n*-valeronitrile, 2,2-dichloropropionitrile, and benzonitrile, when heated at 60–125°C. and 7,000–8,500 atm. in the presence of methanol or of weak bases, form symmetric triazines. Bengelsdorf[30] studied the formation of trimers from benzonitrile in the absence of solvents. Quantitative and rapid formation of a cyclic trimer from benzonitrile can be achieved by heating for a few minutes at about 400°C. at 35,000–50,000 atm. More recently, Johns[31] studied the high-pressure condensation of nitriles to produce polymers containing triazine structures.

These triazine structures may result from reactions of polyacrylonitrile under very high pressure. However, no substantial evidence for their formation, under the reaction conditions encountered in this study has been found by studying the ultraviolet spectra of typical high pressure products dissolved in dimethylformamide.

Experimental results obtained from this study suggest that the hydrolysis reaction is radical in nature. Evidence supporting this proposed mechanism may be found in the observation that irradiated polyacrylonitrile will undergo hydrolysis, whereas nonirradiated polymer does not react. Trapped radicals in the polyacrylonitrile chain formed during irradiation and stable at low temperatures for extended periods of time are proposed as the reactive species.

In order to differentiate between the trapped acrylonitrile radicals and peroxy radicals (formed by exposure to air) initiating the hydrolysis reac-

TABLE III
Effect of Air on Hydrolysis Reaction of Irradiated Polyacrylonitrile at 7,520 atm., 85°C.

Experimental atmosphere	Time, min.	Conversion to polyacrylamide, %
Air	60	5.7
Air	150	28.1
Air	210	83.6
Helium	60	6.1
Helium	150	32.3
Helium	210	87.4

tion the following experiments were performed. Several hydrolysis reactions were carried out in which great care was taken to insure the rigorous exclusion of air to the irradiated polyacrylonitrile. The sample preparations and subsequent pressurizations were conducted under an atmosphere of dry helium. These results are summarized in Table III.

Acrylonitrile radicals are capable of initiating the polymerization of acrylonitrile and styrene at 60°C. and above.[32] However this activity is destroyed by exposure to atmospheric oxygen. The exposure times to atmospheric oxygen in the above experiments were short, about 5 min. required for sample preparation. Exclusion of oxygen resulted in small increases in the yield of hydrolysis product thus indicating that the trapped acrylonitrile radicals, not peroxy radicals, are the free-radical source in this reaction. If the reverse were true, then hydrolysis conversions should have been lower under a helium atmosphere.

The observation that the rate of hydrolysis of irradiated polyacrylonitrile is dependent upon the polymerization dose rate is also offered as evidence for the role of trapped acrylonitrile radicals as the free-radical source. The rate of polymerization of acrylonitrile in bulk has been found to increase with dose rate in a logarithmic relationship.[33–35] It has been shown that the probability that a given radical is trapped in unit time rises with the polymerization rate.[36,37] The trapping mechanism was suggested as involving coalescence of the growing chains. Hydrolysis reactions

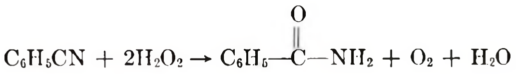
TABLE IV
Effect of Dose Rate on the Hydrolysis of Irradiated Polyacrylonitrile at 7,520 atm., 85°C.

Dose rate of polymer preparation Mrep/hr.[a]	Hydrolysis time, min.	Conversion, %
1.0	60	5.7
1.0	150	28.1
1.0	210	83.6
0.48	60	3.9
0.48	150	18.4
0.48	210	72.7

[a] Total dosage was 10 Mrep in all cases.

were carried out with samples irradiated at two dose rates to the same total dosage. Results are summarized in Table IV.

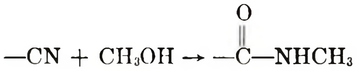
Further support for this radical mechanism arises from the marked effect of added catalytic quantities of *tert*-butyl hydroperoxide (see Table I). Not only was the extent of reaction increased for irradiated polymer, but normally nonreactive conventional polymer was caused to react. A study of the mechanism of the reaction of benzonitrile with peroxide has revealed that the peroxide anion is an effective nucleophilic agent in its reaction with benzonitrile.[38] The stoichiometry of this reaction requires two moles of peroxide to one of benzonitrile [eq. (3)].



$$C_6H_5CN + 2H_2O_2 \rightarrow C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2 + O_2 + H_2O \qquad (3)$$

The initial step in the process is attack of the carbon atom of the nitrile group by the peroxide anion. The resulting ion, after being protonated, reacts with hydrogen peroxide to give the amide. Therefore, the addition of the *tert*-butyl hydroperoxide may induce a nucleophilic reaction; however, the requirement of a stoichiometric quantity of peroxide renders this an unlikely possibility in the case of catalytic amounts of peroxide producing large increases in conversion.

Preliminary evidence was also obtained for the reaction of methyl alcohol with polyacrylonitrile under similar conditions to produce a poly-*N*-methacrylamide.



$$-CN + CH_3OH \rightarrow -\overset{\overset{\displaystyle O}{\|}}{C}{-}NHCH_3 \qquad (4)$$

An impure product was obtained after 2 hr. at 7,520 atm. and 130°C. Examination of the infrared spectrum of the yellowish polymer revealed the presence of the amide carbonyl group and a primary amide hydrogen. Efforts at purification were unsatisfactory. Secondary and tertiary alcohols have been reported to react with acrylonitrile to give the corresponding *N*-substituted acrylamides.[39] Further work will be directed to an extension of this reaction.

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Résumé

Le polyacrylonitrile préparé au départ de monomères irradiés aux rayons-γ réagit facilement avec l'eau dans un domaine de pression de 5.130 à 34.200 atm. pour fournir le polyacrylamide. Les vitesses de réaction à 85°C et 150°C ont été mesurées; l'hydrolyse était extrêmement rapide à température plus élevée. Les résultats indiquent le nature radicalaire de la réaction. La pression exerce un effet sur les propriétés du polyacrylamide résultant.

Zusammenfassung

Aus γ-bestrahltem Monomeren hergestelltes Polyacrylnitril reagiert in einem Druckbereich von 5130 bis 32200 Atm leicht mit Wasser unter Bildung von Polyacrylamid. Die Reaktionsgeschwindigkeit wurde bei 85°C und 150°C gemessen; bei der höheren Temperatur verlief die Hydrolyse extrem rasch. Die Ergebnisse sprechen für einen radikalischen Verlauf der Reaktion. Der Druck beeinflusste die Eigenschaften des gebildeten Polyacrylamides.

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Polymerization of Thietane

CHARLES C. PRICE and E. ALLAN BLAIR, *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

Synopsis

Grignard reagent-initiated polymerization of thietane gave a soluble crystalline polymer melting at 59°C. Oxidation of the polymer with one or two equivalents of hydrogen peroxide gave the sulfoxide and sulfone, respectively. The sulfoxide was noncrystalline and insoluble in all common solvents at room temperature and softened at 185–200°C. The sulfone was partially crystalline and insoluble.

DISCUSSION

The action of various acids on thietane (trimethylene sulfide) has been reported to give low polymers or insoluble polymers.[1,2] Our attempts to carry out the polymerization by using various Lewis acids under mild conditions and low concentrations gave low conversions to gel polymers which could not be dissolved. It is assumed that these gels are very highly branched polymers in which the branching takes place through sulfonium groups. Each branch would consume a molecule of catalyst, resulting in the exhaustion of the catalyst before all of the monomer is consumed. The reaction was very fast and exothermic, and the product was a rubbery gel when swelled with excess monomer or a solvent. However, it dried to a hard solid which melted to a viscous tacky gum below 100°C.

Treatment of thietane with methylmagnesium iodide or other Grignard reagents resulted in very slow polymerization to a linear, crystalline, soluble polymer.* At room temperature it required about 6 months for the polymerization to go to completion. The rate of polymerization was accelerated by increasing the temperature, and both the rate of polymerization and the molecular weight depend on the amount of catalyst.

The crude polymer obtained with 10% catalyst was insoluble at room temperature and contained chemically bound magnesium and halogen. At temperatures above its melting point (59°C.), it dissolved in dimethylformamide and other powerful solvents and was crystalline according to x-ray diffraction patterns. Treatment of a warm solution of the polymer in butyrolactone with concentrated HCl, followed by precipitation with water gave a product which was ash-free and had an excellent analysis. The melting point was unchanged from that of the crude polymer. The

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* This polymer (MW 2000, m.p. 56–57°C. has been reported earlier from the reaction of sodium with bis(γ-chloropropyl) sulfide by Hurd and Wilkinson.[3]

intrinsic viscosity was somewhat increased. The polymer could also be purified by heating it with dioxane containing a small amount of concentrated hydrochloric acid. The polymer slowly dissolved. After dissolving, the polymer was precipitated with dilute hydrochloric acid and freeze-dried from benzene.

The intrinsic viscosities of the purified polymers were 0.10 for the polymer made with 15% butylmagnesium bromide, 0.16 for 5% initiator, and 0.18 for 1% initiator. With 15% initiator at 100°C. the polymerization was complete in 4 hr., with 5% initiator it took 5 days, and with 1% initiator it took 6 weeks.

Polythietane was easily converted to the corresponding sulfoxide by addition of one equivalent of hydrogen peroxide to a dioxane solution of the sulfide polymer. The sulfoxide slowly precipitated from the dioxane solution. It was noncrystalline, melting at 185–200°C., and was insoluble in all common solvents at room temperature. The analysis was correct for C_3H_6SO and the infrared spectrum showed that it contained a very small amount of sulfone.

The sulfone was prepared by a similar reaction by using two equivalents of hydrogen peroxide. The insoluble sulfone precipitated slowly. The analyses and infrared spectrum showed it to be essentially pure sulfone. It carbonized at 200°C. but did not melt at 300°C.[4]

EXPERIMENTAL

Polymerization of Thietane with Acid Catalysts

Thietane (0.5 ml., Eastman White Label or synthesized according to Bordwell and Pitt[5]) was placed in a test tube and 5 μl. of dimethyl sulfate was mixed in. The mixture became warm and viscous, and after 8 hr. it gelled. The product was weak and rubbery and smelled strongly of thietane. On standing in air, the product dried to a solid which was insoluble in all solvents, but swelled in most organic solvents. It softened at about 60°C. A similar gel formed with boron fluoride etherate catalysis.

Polymerization of Thietane with Grignard Reagents

Thietane (0.5 ml.) was sealed in a tube with 5 ml. of 20% methylmagnesium iodide in ether. After standing for 6 months at room temperature, the thietane had polymerized to a benzene-soluble product.

Thietane (2 ml.) was sealed in a Carius tube with 1 ml. of 30% butylmagnesium bromide and heated at 70°C. for 3 days. The solid product obtained after allowing the ether to evaporate was insoluble in all solvents at room temperature. It dissolved in hot dimethylformamide, dimethyl sulfoxide and butyrolactone, but precipitated on cooling, $[\eta] = 0.043$ dl./g. in DMF at 120°C. m.p. 61°C. X-ray diffraction showed strong crystallinity. Considerable ash was left when the polymer was burned. The observed analysis could be reconciled with the calculated by assuming the presence of 14.5% $MgBr_2$ and 4.5% Et_2O.

ANAL. Calcd. for C_3H_6S: C, 48.7%; H, 8.11%; S, 43.2%. Found: C, 42.22%; H, 7.62%; S, 35.70%.

Preparation of Polythietane with 5% Catalyst

In a test tube with a constricted neck, 10 g. of thietane and 3.2 g. of 1*M* butylmagnesium bromide were sealed under vacuum at Dry-Ice temperature. After 4 hr. at 100°C., polymerization had begun. The tube was left for 4 days at 100°C. The polymer was dissolved with difficulty in dioxane and concentrated hydrochloric acid by boiling. The hot dioxane solution was precipitated by pouring into water. The precipitated polymer was dissolved in dioxane again and was reprecipitated by addition of dilute hydrochloric acid. The precipitated polymer was freeze-dried from benzene. The yield was 82.7%, $[\eta] = 0.16$ dl./g., m.p. 59°C.

ANAL. Calcd. for C_3H_6S: C, 48.7%; H, 8.11%; S, 43.2%. Found: C, 48.52%; H, 8.19%; S, 43.32%.

The infrared spectrum showed thioether absorption at 830 cm.$^{-1}$ in addition to C—C and C—H absorption. Powder x-ray diffraction gave a good pattern with spacings (in Angstroms) at 4.42 s, 4.08 w, 3.53 w, 2.98 s, 2.56 m, 2.24 w, 2.15 m, 1.95 w, 1.68 w.

Preparation of Poly(thietane Oxide)

Purified polythietane (1.00 g., 13.5 meq. sulfur) was dissolved in 50 ml. of dioxane at room temperature. To this solution was added 1.52 g. of 30% hydrogen peroxide (13.5 meq.). The mixture slowly became cloudy and solid precipitated over a period of 2 hr. The solution was evaporated under vacuum, yielding a white powder softening at 185–200°C. which was not soluble in any common solvent at room temperature. The infrared spectrum showed the sulfoxide band at 1050 cm.$^{-1}$. X-ray diffraction showed no crystallinity.

ANAL. Calcd. for C_3H_6SO: C, 40.00%; H, 6.67%; S, 35.56%. Found: C, 40.00%; H, 6.48%; S, 35.44%.

Preparation of Poly(thietane Dioxide)

Purified polythietane (1.00 g., 13.5 meq. sulfur) was dissolved in 50 ml. of dioxane and 3.04 g. of 30% hydrogen peroxide (27 meq.) was added all at once. The solution immediately became cloudy and a solid precipitated. The solution was allowed to stand for 2 hr. and was then heated to boiling. The dioxane was evaporated under vacuum leaving a white powder which turned black at 200°C. but did not melt up to 300°C. In a flame, it melted briefly then changed to a glassy black mass which burned slowly. X-ray diffraction showed faint crystallinity with spacings (in Angstroms) of 3.86 w, 2.28 m, 2.12 m, and 1.95 m, and the infrared spectrum showed the sulfone doublet at 1325 and 1160 cm.$^{-1}$.

ANAL. Calcd. for $C_3H_6SO_2$: C, 33.96%; H, 5.66%; S, 30.19%. Found: C, 34.19%; H, 5.72%; S, 30.09%.

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Résumé

La polymérisation du thiétane initié par des réactifs de Grignard fournit un polymère cristallin soluble fondant à 59°C. L'oxydation de ce polymère avec un oudeux équivalents de peroxyde d'hydrogène fournit le sulfoxyde et la sulfone respectivement. Le sulfoxyde n'était pas cristallin et était insoluble dans le plupart des solvants à température de chambre et se ramolissait à 185 à 200°C. La sulfone était partiellement cristalline et insoluble.

Zusammenfassung

Die mit Grignard-Reagens gestartete Polymerisation von Thietan lieferte ein lösliches, kristallines, bei 59°C. schmelzendes Polymeres. Die Oxydation des Polymeren mit einem oder zwei Äquivalenten Wasserstoffperoxyd ergab das Sulfoxyd bzw. das Sulfon. Das Sulfoxyd war nicht-kristallin, in allen üblichen Lösungsmitteln bei Raumtemperatur unlöslich und erweichte bei 185–200°C. Das Sulfon war teilweise kristallin und unlöslich.

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Isotactic Sequence Lengths by Ozonation of Poly(propylene Oxide)

CHARLES C. PRICE and ANTHONY L. TUMOLO, *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104,* and *the Welsbach Corporation, Philadelphia, Pennsylvania*

Synopsis

Ozonation followed by lithium aluminum hydride reduction cleaved high molecular weight isotactic poly(propylene oxide) to crystalline polyglycols. From the melting point and molecular weight of the latter, the molar freezing point depression produced by endgroups is found to be ca. 18°C./mole, as compared to that estimated for poly(ethylene glycols), $K_f = 12$°C./mole, from earlier data. By assuming syndiotactic placements (or other irregularities) would produce the same molar depression, the melting point of isotactic poly(propylene oxides) produced by various catalysts has been used to estimate the isotactic sequence lengths.

DISCUSSION

Earlier investigation of the ozonation of simple ethers[1] has been extended to the ozonation of several simple polyepoxides. Ozone is readily and nearly completely consumed, especially by poly(propylene oxide) and poly-1,2-epoxybutane with tertiary ether hydrogens available for ozone attack.

Analysis for a variety of functional groups present in the ozonated PPO showed the results summarized in Table I. The results compare favorably with those reported earlier for a simple ether.[1]

TABLE I

Functional Groups in Ozonated Ether and Poly(propylene Oxide)

Group	*n*-Propyl isopropyl ether, mole-%/mole O_3	Poly(propylene oxide), mole-%/mole O_3
Ester	83	93
Alcohol	33	37
Carbonyl	23	40
Acid	8	42

The wide variety of oxidized groups indicated in Table I were all converted to hydroxyl by reduction with lithium aluminum hydride (LAH), giving a series of poly(propylene glycols), as summarized in Table II. The

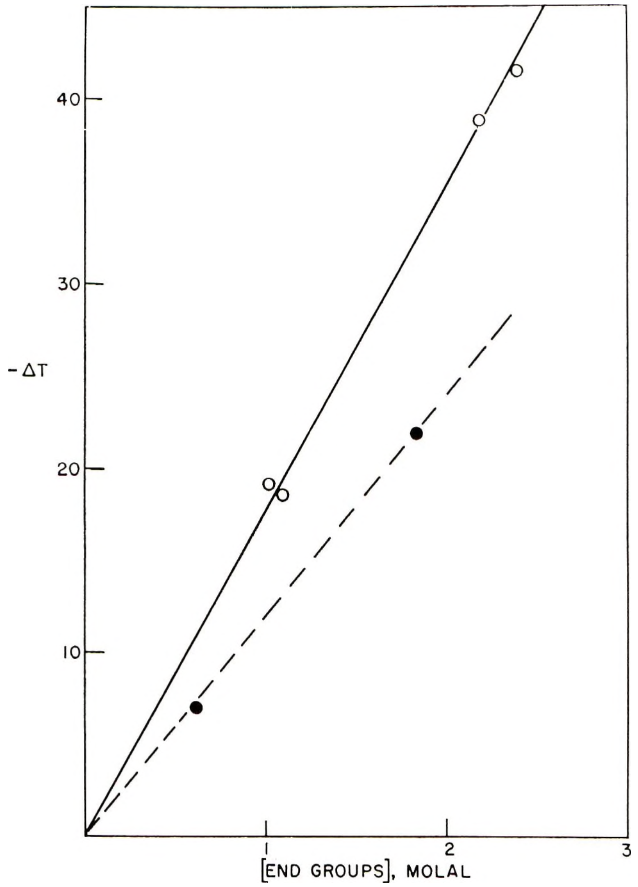
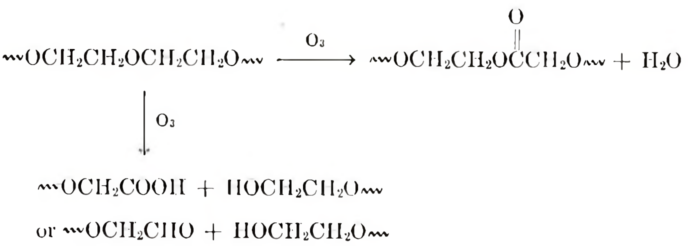


Fig. 1. Melting point depression for isotactic (○) poly(propylene glycols) and (●) poly-(ethylene glycols).

variation in molecular weight with ozone consumed in the degradation fits very satisfactorily with the postulate that, following reduction, one ether link has been cleaved for each ozone consumed. When the reduction step was omitted for ozonated poly(ethylene oxide), the observed molecular weight was nearly twice that calculated from ozone consumed. This would be in accord with the view that about half the ozone attack produced an ester group rather than direct cleavage.



$$\sim\!\sim OCH_2CH_2OCH_2CH_2O\sim\!\sim \xrightarrow{O_3} \sim\!\sim OCH_2CH_2O\overset{\overset{O}{\|}}{C}CH_2O\sim\!\sim + H_2O$$

$$\downarrow O_3$$

$$\sim\!\sim OCH_2COOH + HOCH_2CH_2O\sim\!\sim$$

or $\sim\!\sim OCH_2CHO + HOCH_2CH_2O\sim\!\sim$

TABLE II
Ozone–LAH Degradation of Isotactic Poly(propylene Oxide)

PPO, g.	O_3, mg.	PPG, g.	M.p., °C.	Molecular weight Osmometric	Molecular weight Calculated[a]
3.14	10.2	2.94	64.5	18,000[b]	15,000
4.15	99.3	3.9	56.0	1940 (2180)[c]	2,000
0.98	23.3	1.00	56.5	1800	2,000
2.10	187	1.64	36.0	920	540
1.01	93	1.05	33.5	833	520

[a] Calculated assuming one chain cleaved per molecule of O_3 consumed by the equation M.W. = mg. PPO × 48/mg. O_3.

[b] Viscometric molecular weight.

[c] By hydroxyl endgroup determination, assuming two hydroxyl groups per molecule.

TABLE III
Melting Point Data for Isotactic Poly(propylene Glycols) and Poly(ethylene Glycols)

Polymer	M.p., °C.	Avg. mol. wt.	m[a]	$-\Delta T$, °C.
PEO	64.8–65[b]	200,000	0.01	—
	54–58[c]	3,270	0.61	7
	40–43	1,090	1.83	22
	20–22	536	3.73	43
	9–11	424	4.72	54
PPO	74–75[d]	200,000	0.01	—
	64.5	18,000	0.11	10
	56	1,940	1.03	19
	56.5	1,800	1.11	18.5
	36	920	2.18	39
	33.5	833	2.41	41.5

[a] Molal concentration of endgroups, m = 2000/avg. mol. wt.

[b] Data of Miller and Price.[3]

[c] Data of Perry and Hibbert.[2]

[d] Data of Price and Osgan.[4]

The data in Table II can be used to evaluate a molar freezing point depression for endgroups as "contaminants" in isotactic poly(propylene oxide). In the expression for freezing point depression, $-\Delta T = K_f m$,* the molal concentration m of endgroups, may be calculated from the number-average molecular weights. The results are summarized in Table III and plotted in Figure 1 and indicate K_f = 18°C. molal for isotactic poly(propylene oxide). For comparison, similar data on melting points for poly(ethylene glycols)[2] has been plotted in the same figure, indicating a value for K_f = 12°C. molal for poly(ethylene oxide).

Based on this value for K_f it is also possible to evaluate the molal concentration of "contaminants," i.e., imperfections in structure, in high

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* This is only a convenient approximation for the more exact equation,

$$(1/T_m) - (1/T_m^\circ) = -(R/\Delta H_u)\ln N_A$$

molecular weight isotactic poly(propylene oxide) from melting points. On the basis of a melting point of 75°C. for the "best" isotactic poly(propylene oxide), which also seems to be in excellent accord with the extrapolated melting point data in Figure 1, the sequence lengths for polymer prepared earlier are summarized in Table IV.

TABLE IV
Sequence Lengths in Isotactic Poly(propylene Oxide) from the Melting Point

Catalyst	M.p., °C.[a]	m	Sequence length[b]
$FeCl_3(PO)_4$[c]	74–75	0.0555	>370
$Al(i\text{-}PrO)_3 \cdot ZnCl_2$[d]	68	0.39	44
$Et_2Zn \cdot H_2O$[e]	64	0.61	28

[a] Data of Chu and Price.[5]

[b] Calculated from molality of imperfections, $m = (75 - \text{m.p.})/18$, assuming even distribution of imperfections; sequence length $= 1000/58m$.

[c] Data of Pruitt and Baggett.[6]

[d] Data of Price and Osgan.[4]

[e] Data of Sakata et al.[7]

These sequence lengths are appreciably longer than, but in the same order, as estimated by Aggarwal[8] by another method, i.e., 122 for the iron catalyst and 12.5 for diethylzinc–water.

The isotactic PPO prepared by Price and Osgan[9] from optically pure monomer had a molecular weight of ca. 3000 and a melting point of 56°C. The melting point indicates an isotactic sequence length of about 2000 molecular weight units. This is in close enough accord with the molecular weight to indicate very few other imperfections in the sequence. On the other hand, ozonation down to diglycol units has indicated as much as 10% of head-to-head units in KOH-catalyzed PPO.[10]

EXPERIMENTAL

Ozonation Techniques

These were generally as described previously.[1]

Functional Group Analyses

Total carbonyl was determined by hydroxylamine hydrochloride, acid by alkaline titration, ester by saponification, after converting aldehyde to oxime and correcting for acid, alcoholic hydroxyl by phthalic anhydride, and active oxygen by potassium iodide in acetic acid.

Characterization

Melting points were determined on a Fisher-Johns apparatus, viscosities in benzene at 30°C. in an Ubbelohde viscometer, and molecular weights on a

Mechrolab vapor pressure osmometer, Model 301A, in benzene after calibration with 0.004 and 0.015M phenanthrene in benzene.

Preparation of Isotactic Poly(propylene Oxide)

Isotactic poly(propylene oxide) was prepared by an adaptation of the procedure of Price and Osgan.[4] The reactor was a stainless steel pressure vessel wrapped with heating wire. The temperature was measured by a thermocouple placed in a well extending into the center of the reactor. The temperature was controlled by an on-off controller connected to the thermocouple and heating wires. The temperature varied between 80 and 90°C. during the experiment. A glass liner was used in the reactor, and a lead gasket was used to seal the reactor.

The liner was charged with 300 g. (5.17 mole) of propylene oxide (purified by refluxing over CaH_2 and distilling), 200 ml. of heptane, 1.54 g. (1.88 mmole) of aluminum isopropoxide (Matheson, Coleman and Bell, distilled at 135–138°C./8 mm.), 1.50 g. (11.0 mmole) of zinc chloride (Baker's Analyzed Reagent grade, fused immediately before use).

The sealed vessel was heated for 90 hr. Approximately 75 ml. of material distilled out of the glass liner and was discarded. The product remaining in the liner was dissolved in 3.65 l. of acetone by refluxing for 10 hr. A stabilizer (0.1 g. of hydroquinone) was added to the acetone solution to inhibit oxidation during handling. Then 75 ml. of water was added and the solution refluxed for 1 hr. The isotactic polymer was separated from the atactic material by cooling to -30°C. A thick gel (ca. 1200 ml.) formed. It was separated by centrifuging while still cold. The gel was dissolved in 2.50 l. of acetone and fractionated again. The gel was dissolved in 1500 ml. of benzene and 0.5 g. of hydroquinone was added. The benzene solution was washed with 500 ml. of dilute hydrochloric acid, with 500 ml. of water, 500 ml. of 5% aqueous sodium bicarbonate and then three times with 500 ml. of water. The product was isolated by freeze-drying the benzene solution. The yield was 65.6 g. (23% of theory) of crystalline polymer, m.p. 68.5°C., intrinsic viscosity 2.53, corresponding to a molecular weight of 215,000.*

Ozonation of Poly(propylene Oxide) and Analyses of Functional Groups Formed

The ozonator controls were adjusted to deliver 6.5 mg. ozone/min. A solution containing 3.34 g. of isotactic poly(propylene oxide) (mol. wt. 215,000) in methylene chloride was treated with 552 mg. of ozone and 524 mg. was absorbed. The solution was treated with 0.1 g. of 5% platinum on carbon which decomposed most of the peroxides present. The remaining peroxides were reduced by treating with hydrogen at a pressure of about 1 m. of water. The mixture was evaporated under vacuum on a rotary evaporator. Aliquot portions were analyzed by the procedures given in the

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* Determined from the equation[11] $[\eta] = 1.4 \times 10^{-4} M^{0.8}$.

section on functional group analyses. Based on moles of ozone consumed, the yields found were: ester, 93%; total carbonyl, 42%; acid, 40%; alcohol, 37%.

Ozone Degradation to Crystalline Poly(propylene Glycol) (Mol. Wt. 1940)

The ozonator controls were adjusted to deliver 7.07 mg. ozone/min. A solution of 4.15 g. of isotactic poly(propylene oxide) (mol. wt. 215,000) in 110 ml. of methylene chloride (Fisher Certified 99 mole-% pure) in a gas washing bottle with a fritted-glass inlet was treated at room temperature with 109 mg. of ozone. It absorbed 99.3 mg. The solution was diluted with 130 ml. of dry ether and 0.55 g. of lithium aluminum hydride in 550 ml. of ether was slowly added. The mixture was allowed to react overnight. The next day 15 ml. of water was added and the solution was washed with 50-ml. portions of 5% aqueous hydrochloric acid, 5% aqueous sodium bicarbonate, and few times with water. The solution was evaporated under vacuum on a rotary evaporator, dissolved in benzene and freeze-dried. The yield was 3.9 g. (94% of theory) of crystalline polymer, m.p. 56.0°C., molecular weight 1940 by vapor-phase osmometry, molecular weight 2180 by hydroxyl endgroup determination. This and other similar ozonation results are summarized in Table II.

Ozone Degradation of Poly-1,2-epoxybutane

Similar to the previous example, 2.00 g. of poly-1,2-epoxybutane having a reduced viscosity of 7.5 was treated with 48.3 mg. of ozone. It absorbed 44.9 mg. The material was reduced with lithium aluminum hydride and isolated as described in previous experiments. The yield was 1.8 g. (90% of theory) of product having a molecular weight of 2100 by vapor-phase osmometry (calcd. on O_3 consumed, 2140).

Ozone Degradation of Poly(ethylene Oxide)

A solution of 0.50 g. of polyethylene oxide (Union Carbide Polyox WSR-301, mol. wt. > 500,000) in 89 ml. of chloroform was treated with 53.2 mg. of ozone. It absorbed 35.4 mg. The product was isolated directly, without reduction, by evaporation and freeze-drying. The yield was 0.53 g. (100% of theory) having a molecular weight of 1160 as determined by vapor-phase osmometry (calculated on O_3 consumed, 680). Note that the ozone was appreciably less completely consumed by poly(ethylene oxide) than by poly(propylene oxide) and poly-1,2-epoxybutane, in accord with the earlier observation[1] that tertiary ether hydrogens are more readily attacked than secondary. Also note that the omission of reduction gave a higher molecular weight product than calculated from ozone consumed. This is presumably due to the presence of ester links in the polymer chain.

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Résumé

L'ozonisation suivie d'une réduction à l'hydrure d'aluminium-lithium rompt l'oxyde de polypropylène isotactique de poids moléculaire élevé en polyglycols cristallins. Au départ du point de fusion et du poids moléculaire de ce dernier, l'abaissement molaire du point de congélation, produit par les groupes terminaux, était d'environ 18°C/mole comparé à la valeur préalablement trouvée pour le polyéthylène glycol, $K_f = 12°C/mole$, au départ de résultats antérieurs. En admettant un agencement syndiotactique (ou d'autres irrégularités) qui produirait une dépression molaire semblable, le point de fusion, de l'oxyde de polypropylène isotactique produit par divers catalyseurs a été utilisé pour évaluer la longueur des séquences.

Zusammenfassung

Ozonisierung mit darauffolgender Lithiumaluminiumhydrid-Reduktion führte zur Spaltung von hochmolekularem, isotaktischem Polypropylenoxyd in kristalline Polyglykole. Aus dem Schmelzpunkt und dem Molekulargewicht der Polyglykole berechnet sich die durch die Endgruppen hervorgerufene molare Gefrierpunktsernierrigung zu etwa 18°C/Mol im Vergleich zu der aus früheren Versuchen für Polyäthylenglykole bestimmten von $K_f = 12°C/Mol$. Unter der Annahme, dass eine syndiotaktische Anordnung (oder andere Unregelmässigkeiten) die gleiche molare Depression erzeugen, wurde der Schmelzpunkt von mit verschiedenen Katalysatoren erzeugtem Polypropylenoxyd zur Bestimmung der isotaktischen Sequenzlänge herangezogen.

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Copolymerization of Trioxane by γ-Radiation

S. RÖSINGER, H. HERMANN, and K. WEISSERMEL,
Farbwerke Hoechst AG., Frankfurt (Main)-Höchst, Germany

Synopsis

High molecular copolymers of trioxane with different cyclic ethers and formals were produced by γ-radiation from a ^{60}Co source. It was polymerized in the solid state at 53°C. Polymerization does not occur in the melt. Irradiation was carried out with exclusion of air at a dose rate of 7×10^3 rad/hr. The polymerization rate was increased very considerably in the presence of 1,3-dioxolane and epichlorhydrin; the addition of other comonomers may reduce the yield. The concentration of the comonomer is generally higher in the polymer than in the initial mix. These comonomers which increase the polymerization rate are introduced preferentially into the polymer chain; this is proved by the unstable polymer part and the thermal stability. Experiments with the trioxane–1,3-dioxolane system revealed that the unstable polymer part is markedly reduced and the heat stability considerably inproved with rising concentrations of this monomer. The thermal stability and the reduced viscosity of these copolymers are within the range of technical processability.

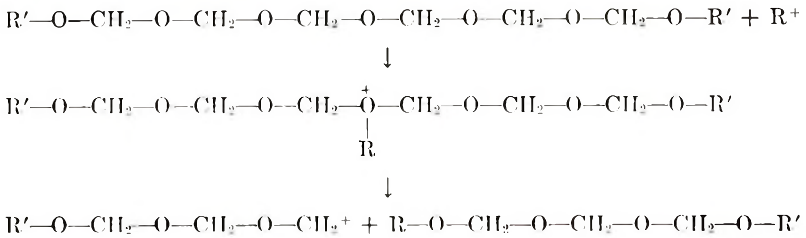
EINLEITUNG

Nachdem es gelungen war, Polyoxymethylene zur Herstellung nicht nur harter und steifer, sondern auch zäher Kunststoffe heranzuziehen, haben diese Polymeren in den letzten Jahren zunehmende Bedeutung erlangt.[1]

In den Laboratorien der Farbwerke Höchst A.G.[2] gelang es erstmals, Polyoxymethylene durch Einwirkung von γ-Strahlung auf Trioxan herzustellen. Wenig später kamen japanische Forscher zu ähnlichen Ergebnissen.[3-8] Inzwischen hat die strahlenchemische Polymerisation des Trioxans zunehmendes Interesse gefunden.[9,10]

Nach dem Verfahren wird ein Polymeres erhalten, das bei Einwirkung von Wärme unbeständig ist. Verantwortlich für diese Instabilität sind die Halbacetalendgruppen des Polymeren, die leicht Formaldehyd abspalten. Über eine "Reissverschlussreaktion" kann dies zum vollständigen Zerfall der Polymermoleküle führen.

Bei den durch kationische Katalysatoren ausgelösten Trioxanpolymerisation ist es leicht möglich, eine Stabilisierung der Polymerketten zu erreichen.[11] Hierzu werden geringe Mengen von cyclischen Äthern oder cyclischen Acetalen mit Trioxan copolymerisiert. Das Überraschende bei dieser Copolymerisation ist, dass dabei meist chemisch sehr einheitlich aufgebaute Copolymerisate erhalten werden. Eine eingehende Untersuchung dieses Phänomens führte zur Aufklärung einer wichtigen Neben-reaktion. Während der Polymerisation und Copolymerisation des Trioxans findet eine ständige Spaltung und Neuverknüpfung der Polymerketten statt, die sich wie folgt formulieren lässt:



$$R'{-}O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}R' + R^+$$
$$\downarrow$$
$$R'{-}O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}\underset{\displaystyle R}{\overset{+}{O}}{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}R'$$
$$\downarrow$$
$$R'{-}O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2^{\,+} + R{-}O{-}CH_2{-}O{-}CH_2{-}O{-}CH_2{-}O{-}R'$$

R^+ = Polymerkation
R' = Polymerrest

Diese Transacetalisierung, die besonders gut bei der Copolymerisation des Trioxans in Substanz und in flüssiger Phase zu beobachten ist, führt zwangsläufig zu einer Vereinheitlichung der Polymeren. Sie wird dadurch bewiesen, dass bei der Polymerisation des Trioxans in Gegenwart eines linearen Polyformals ein einheitliches Copolymeres entsteht.

Diese Copolymeren können nun auf einfache Weise stabilisiert werden. Behandelt man beispielsweise ein Copolymeres aus Trioxan und 1,3-Dioxolan mit Wärme oder Alkali, so beginnt vom Kettenende her unter Abspaltung von Formaldehyd ein Abbau, der jedoch bei der ersten Oxyäthyleneinheit zum Stillstand kommt. Das resultierende Polymere ist gegen Wärme oder Alkali stabil. Schon ein geringer Zusatz von 1,3-Dioxolan bei der Polymerisation genügt, um den instabilen Anteil des Polymeren wesentlich zu senken. Die Herstellung beständiger Polyoxymethylene durch kationisch katalysierte Copolymerisation des Trioxans hat erhebliche technische Bedeutung erlangt. Es ergab sich nun für uns die Frage, ob sich diese Copolymerisation auch durch energiereiche Strahlung auslösen lässt und ob dieser Syntheseweg gegenüber dem bekannten Verfahren Vorteile bietet.

EXPERIMENTELLER TEIL

Das Trioxan und die Comonomeren wurden vor jeder Polymerisation scharf getrocknet, erneut unter Stickstoff destilliert und danach gaschromatisch geprüft.

Die Proben (je etwa 100 g) wurden so hergestellt, dass dem flüssigen Trioxan die Comonomeren unter Luftausschluss zugegeben wurden. Dann wurde das Gemisch bis zur völligen Homogenisierung bei 70°C gerührt und in gasdichten Reaktionsrohren polymerisiert. Als Strahlenquelle diente eine ^{60}Co-Quelle von 500 Curie; die Dosisleistung lag bei den Versuchen zwischen 5×10^3 und 2×10^4 rad/Std. Die Temperatur war einheitlich 53 ± 2°C, lag also unterhalb des Schmelzpunkts von Trioxan. Die verwendeten Comonomeren waren bei dieser Temperatur flüssig (die Zweiphasensysteme Trioxan-Cokomponente sind nicht genau bekannt).

Nach der Bestrahlung wurden die Proben sofort abgekühlt und nicht weiter thermisch nachbehandelt.

Um eine gleichmässige Aufarbeitung zu gewährleisten, wurden alle Proben nach der Bestrahlung in einer Schlagmühle gemahlen, dann 30 Minuten mit Methanol am Rückflusskühler gekocht und anschliessend 3 Stunden bei 50°C im Vakuum getrocknet. Das Polymerisat (10 Gew. Teile) wurde in Benzylalkohol (90 Gew. Teile), dem 2 Gew.-% Triäthanolamin zugesetzt waren, 30 Minuten bei 150°C behandelt. Der nach der Abkühlung ausfallende Niederschlag konnte leicht abgetrennt, gewaschen und getrocknet werden. Der hierbei beobachtete Gewichtsverlust wird der Zersetzung der instabilen Kettenenden zugeschrieben und als instabiler Polymeranteil bezeichnet. Zur Charakterisierung der thermischen Beständigkeit des stabilen Polymeranteils wurde der mittlere Gewichtsverlust pro Minute in Prozent angegeben, der nach einer Behandlung von 45 Minuten bei 230°C an Luft in Gegenwart von Stabilisatoren entsteht.

Die reduzierte Viskosität wurde in einer Lösung von 0,5 g Polymeren in 100 cm^3 eines Gemisches aus γ-Butyrolacton und 2 Gew.-% Diphenylamin bei 140°C bestimmt. Die Schmelzpunkte wurden auf der Koflerbank gemessen.

Die Menge der Cokomponenten im Polymerisat wurde durch Elementaranalyse ermittelt, wobei die Bestimmung über den Chlorgehalt mit höherer Genauigkeit möglich war als über die Kohlenstoff-Wasserstoff-Werte. Bei den Copolymerisaten mit 1,3-Dioxolan war die Bestimmung mit Hilfe des Infrarot-spektrums möglich, und zwar bei einer Wellenlänge von 7,32 μ durch Vergleich mit einem Homopolymerisat des 1,3-Dioxolans.

ERGEBNISSE

Copolymerisation von Trioxan mit verschiedenen Comonomeren

Einfluss von Dosis und Temperatur auf den Verlauf der Polymerisation. Im allgemeinen erhöhte sich mit steigender Dosis der Umsatz bei der Polymerisation in Gegenwart von Comonomeren ebenso wie bei der Polymerisation des Trioxans allein. In Abbildung 1 ist der Polymerisationsverlauf im festen Zustand in Abhängigkeit von der Dosis für Trioxan in Gegenwart von 4-Chlormethyl-1,3-Dioxolan aufgezeichnet.

Auch der Einfluss der Temperatur war bei der Copolymerisation ähnlich wie bei der Homopolymerisation. In der Schmelze konnten unter den gewählten Bedingungen keine Polymerisate erhalten werden. Die günstigsten Polymerisationstemperaturen lagenetwas unterhalb des Schmelzpunktes. Weiteres Absenken der Temperatur hat auch eine Verringerung des Umsatzes zur Folge.

Einfluss von Art und Konzentration der Comonomeren auf die Polymerisationsgeschwindigkeit. Es war ein deutlicher Einfluss der Art des Comonomeren auf die Polymerisation von Trioxan zu verzeichen. Abbildung 2 zeigt den Einfluss der Konzentration einzelner Comonomerer

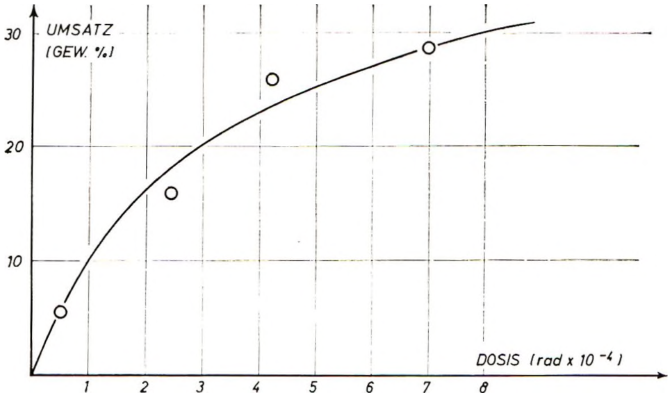


Abb. 1. Copolymerisation von Trioxan mit 4-Chlormethyl-1,3-dioxolan (Konz. 2%, 53°C, Dosisleistung 5 × 10^3 rad/Std.).

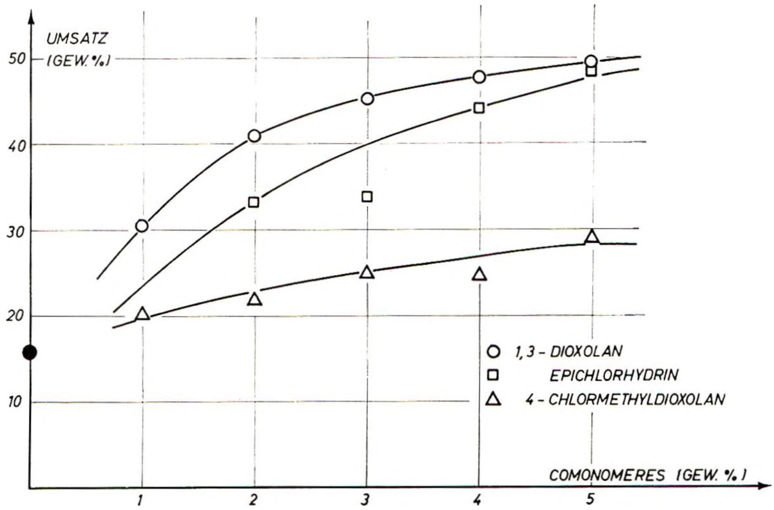


Abb. 2. Copolymerisation von Trioxan. Abhängigkeit des Umsatzes von der Konzentration der Comonomeren (53°C, Dosisleistung 5 × 10^3 rad/Std., Bestrahlungszeit 15 Std.).

auf den Umsatz. Überraschend ist der Anstieg des Umsatzes in Gegenwart steigender Mengen von 1,3-Dioxolan und Epichlorhydrin. Auch 4-Chlormethyl-1,3-Dioxolan bewirkte noch eine beachtliche Erhöhung der Polymerisationsgeschwindigkeit. Die strahlenchemische Ausbeute wird als *G*-Wert definiert (Zahl der umgesetzten Moleküle pro 100 eV absorbierter Strahlenenergie). Während dieser Wert bei der Polymerisation von Trioxan etwa bei 3 × 10^4 liegt, stieg er in Gegenwart von 5% 1,3-Dioxolan auf 8,1 × 10^4 und von Epichlorhydrin auf 7,9 × 10^4. Nicht alle untersuchten Comonomeren hatten aber einen fördernden Einfluss auf die Polymerisation. Als Gegenbeispiel ist in Abbildung 3 der Zusammenhang zwischen Umsatz und Konzentration von 1,3-Dioxacyclohepten-(5), 3,3-Bischlormethyloxacyclobutan und 1,3,6-Trioxacyclooctan aufgetragen. Eine ausreichende Erklärung für die Erhöhung der Polymerisationsgeschwindigkeit kann noch nicht gegeben werden. Vielleicht spielt eine Störung im Kristallgitter des Trioxans eine Rolle.

Aufbau der Copolymerisate. Auf Grund der Kurven auf den Abbildungen 2 und 3 lässt sich noch nicht entscheiden, ob eine Copolymerisation eingetreten ist. Eine Klärung dieser Frage konnte nur eine genaue Charakterisierung der Polymerisate bringen. Die Ergebnisse sind der Tabelle I zu entnehmen. Aus Spalte 2 und 3 geht deutlich hervor, dass diejenigen Comonomeren, welche die Polymerisationsgeschwindigkeit steigern, auch die höchsten reduzierten Viskositäten des Copolymerisats bewirken. In Spalte 4 ist der Gehalt der Cokomponente im Polymerisat angegeben. Er liegt, mit Ausnahme von 4-Chlormethyl-1,3-Dioxolan, im Polymeren höher als in der Ausgangsmischung. Besonders deutlich kann dies bei Epichlorhydrin gezeigt werden. Bricht man unter gleichen Bestrahlungsbedingungen wie in Tabelle 1 die Polymerisation statt nach 15 Std. schon nach 1 Std. ab, so erhält man bei einem Umsatz von etwa 10% ein Polymeres mit ca. 30% Epichlorhydrin.

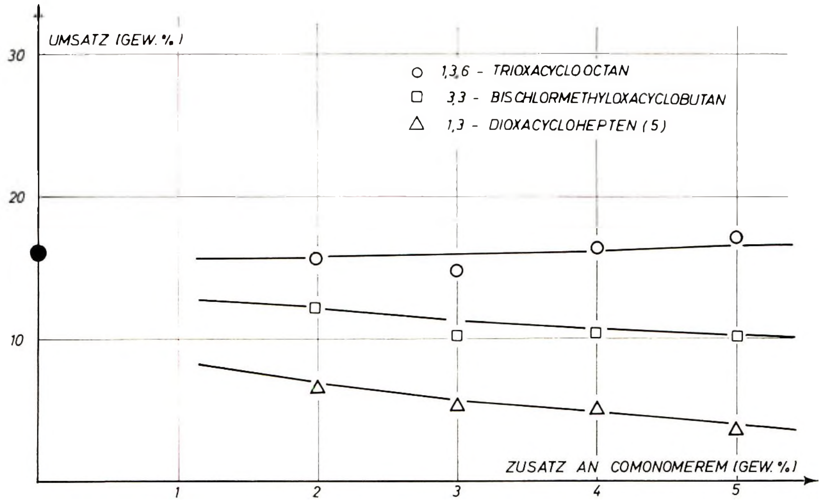
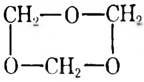
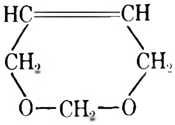
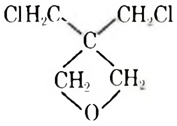
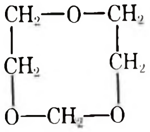
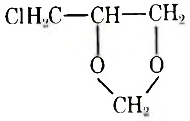
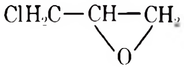
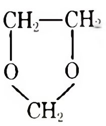


Abb. 3. Copolymerisation von Trioxan. Abhängigkeit des Umsatzes von der Konzentration der Comonomeren (53°C, Dosisleistung 5 × 10³ rad/Std., Bestrahlungszeit 15 Std.).

Eine Entscheidung, ob chemisch einheitliche Copolymere vorliegen, ist natürlich aus der analytischen Zusammensetzung allein nicht möglich. Aufschluss darüber gibt die Extraktion des Polymeren mit einem für das Homopolymerisat der Cokomponente selektiven Lösungsmittel, z.B. Aceton. Unter den von uns gewählten Bedingungen konnte bei dieser Behandlung kein löslicher Polymeranteil isoliert werden.

TABELLE I
Copolymerisation von Trioxan mit verschiedenen Comonomeren[a]

Comonomeres	Umsatz, Gew.-%	Reduzierte Viskosität, dl/g	Gehalt der Cokomponente im Polymeren, Gew.-%	Instab. Polymeranteil, Gew.-%	Gew. Verlust bei 230°C, Gew.-%/Min
	17	0.55	0	82	0.058
	4	0.41	—	78	0.187
	11	0.34	7.8	62	0.098
	17	0.37	10	38	0.020
	29	0.52	3.6	30	0.164
	48	0.66	7.5	14	0.099
	51	0.65	5.6	12	0.008

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[a] Bestrahlungstemperatur 53°C, Bestrahlingszeit 15 Std. Dosisleistung 5 × 10^3 rad./Std., 5 Gew.-% Comonomeres.

Weitere Hinweise lieferte die Bestimmung des instabilen Polymeranteiles. Ein Copolymeres, in dem die eingebauten Einheiten der Cokomponente statistich verteilt sind, wird bei der alkalischen Behandlung nur einen geringen Gewichtsverlust erleiden. Ein Polymergemisch oder ein uneinheitlich aufgebautes Polymerisat wird sich unter gleichen Bedingugnen zu einem erheblichen Teil zersetzen. Die Menge des instabilen Anteiles erlaubt somit eine Aussage über die Einheitlichkeit. Im Falle des 1,3-

TABELLE II
Copolymerisation von Trioxan mit, 1,3-Dioxolan[a]

1,3-Dioxolan, Gew.-%	Umsatz, Gew.-%	Gehalt an Dioxolan im Polymeren, Gew.-%	Reduzierte Viskosität, dl/g	Instab. Polymerant., Gew.-%	Gewichts-Verlust bei 230°C., Gew.-%/Min.	Schmelzpunkt, °C
0	17	—	0.55	82	0.058	175
1	30	2.8	0.43	38	0.023	168
2	41	2.9	0.47	27	0.017	168
3	45	3.6	0.50	20	0.012	166
5	51	5.6	0.65	12	0.008	166

[a] Polymerisationsdauer 15 Std., 53°C, Dosisleistung 5 × 10^3 rad/Std.

Dioxacycloheptens-(5), des 3,3-Bischlormethyloxacyclobutans, des 1,3,6-Trioxacyclooctans lagen sehr uneinheitliche, im Fall von 4-Chlormethyl-1,3-Dioxolan und Epichlorhydrin dagegen entstanden einheitliche Copolymerisate. Vergleicht man nun die Spalten 2 und 5, so findet man einen überraschenden Zusammenhang. Diejenigen Copolymeren die nach einer vorgegebenen Zeit mit dem höchsten Umsatz erhalten wurden, hatten auch den geringsten instabilen Polymeranteil. Offensichtlich wurden diejenigen Comonomeren, welche die Polymerisationsgeschwindigkeit erhöhen, auch bevorzugt und gleichmässig in das Polymermolekül eingebaut. Die thermische Beständigkeit wurde nur an solchen Produkten gemessen, die vorher einem alkalischen Abbau unterworfen waren. Aus der Tabelle I ist zu ersehen, dass alle chlorhaltigen Copolymeren mehr oder weniger instabil waren. Die Produkte, die mit 1,3-Dioxolan hergestellt wurden, besassen demgegenüber eine beachtliche Wärmebeständigkeit.

Die Copolymerisation von Trioxan mit 1,3-Dioxolan

Aus der Tabelle I ist zu erkennen, dass von allen untersuchten Monomeren das 1,3-Dioxolan die günstigsten Ergebnisse bei der Copolymerisation erbrachte. Es wurden daher diese Copolymerisate einer eingehenden Untersuchung unterzogen. Die Versuchsergebnisse enthält Tabelle II. Mit steigendem 1,3-Dioxolangehalt im Monomerengemisch wurde mehr 1,3-Dioxolan eingebaut und die Polymerisationsgeschwindigkeit nahm zu. Die reduzierte Viskosität änderte sich allerdings kaum. Dagegen nahm mit steigendem 1,3-Dioxolangehalt der instabile Anteil im Polymeren stark ab. Die thermische Beständigkeit der stabilen Polymeranteile verbesserte sich im gleichen Verhältnis. Der Schmelzpunkt des Polytrioxans liegt bis 175°C. Er sinkt mit zunehmender Konzentration an 1,3-Dioxolan bis auf 166°C ab.

DISKUSSION DER ERGEBNISSE UND BEURTEILUNG DES VERFAHRENS

Die Polymeren, die durch strahlenchemische Polymerisation mit 1,3-Dioxolan hergestellt werden, besitzen, wie die Versuche gezeigt haben, wertvolle Eigenschaften. In bezug auf ihre thermische Beständigkeit und ihren geringen instabilen Anteil sind sie durchaus vergleichbar mit den heute technisch durch ionische Copolymerisation hergestellten Hochpolymeren des Trioxans. Darüber hinaus enthalten sie nach der Polymerisation keine Katalysatorreste, die einen unerwünschten Abbau der Polymeren hervorrufen. Im Vergleich zur katalytischen Polymerisation ergeben sich aber auch Nachteile. Trotz Erhöhung der Polymerisationsgeschwindigkeit im festen Zustand durch Zusatz von Comonomeren verläuft die Polymerisation wesentlich langsamer als bei dem katalytischen Verfahren in der Schmelze. Vorläufig ist auch die Herstellung einheitlicher Polymerer auf strahlenchemischem Wege weniger leicht möglich. Die wesentlichsten Gründe dürften wohl darin liegen, dass bei der Polymerisation im festen Zustand keine ideale Mischung der Komponenten mehr vorliegt. Häufig ist der Zugang der Cokomponente, z.B. bei 1,3-Dioxacyclohepten-(5), zu den polymerisierenden Molekülen behindert. Durch die verschiedene Struktur der Comonomeren kann dieser sterische Faktor mehr oder weniger stark ausgeprägt sein.

Daneben tritt aber auch eine Behinderung der Transacetalisierungsreaktion zwischen den Polymermolekülen ein, da die Beweglichkeit der im kristallinen Trioxan eingebetteten Polymermoleküle wesentlich geringer ist als im geschmolzenen Zustand. Diese Störung konnte auch bei der katalytischen Polymerisation in fester Phase beobachtet werden. Da diese Transacetalisierung wesentlich zur Bildung einheitlich aufgebauter Copolymerer beiträgt, dürften die auf strahlenchemischem Wege hergestellten Copolymerisate die Einheitlichkeit der auf katalytischem Wege dargestellten nur in Ausnahmefällen erreichen.

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Résumé

Des copolymères de poids moléculaire élevé du trioxane avec divers éthers cycliques et formals ont été obtenus par radiation-γ au Co^{60}. La polymérisation avait lieu a l'état solide a 53°C. Elle ne se passe pas a l'état fondu. L'irradiation était effectuée en absence d'air a des vitesses de doses de 7×10^3 rad/h. La vitesse de polymérisation était accrue très considérablement en présence de 1,3-dioxolane et d'épichlorhydrine; l'addition d'autres comonomères peut réduire le rendement. La concentration en comonomère est la plupart du temps plus elevée dans le polymère que dans le mélange initial. Ces comonomères qui accroissent la vitesse de polymérisation sont introduits préférentiellement dans la chaîne polymérique; ceci est prouvé par la partie instable du polymère et par la stabilité thermique. Ces expériences avec le trioxane, 1,3-dioxolane révelènt que la partie instable est notablement diminuée et la stabilité thermique considérablement améliorée en augmentant la concentration de ce monomère. La stabilité thermique et la viscosité réduite de ces copolymères sont dans le domaine d'utilisation habituel des processus techniques.

Zusammenfassung

Mit Hilfe von ^{60}Co γ-Strahlung konnten hochmolekulare Copolymere des Trioxans mit verschiedenen zyklischen Äthern und Formalen durch Polymerisation im festen Zustand bei 53°C hergestellt werden. In der Schmelze tritt keine Polymerisation ein. Die Bestrahlungen wurden unter Luftausschluss bei einer Dosisleistung von 7×10^3 rad/Std. ausgeführt. In Gegenwart von 1,3-Dioxolan und Epichlorhydrin gelang es, die Polymerisationsgeschwindigkeit ganz wesentlich zu steigern; Zusätze anderer Comonomerer können die Ausbeute senken. Die Konzentration der Cokomponente ist im Polymeren meist höher als in der Ausgangsmischung. Durch Bestimmung des instabilen Polymeranteils und der thermischen Beständigkeit konnte nachgewiesen werden, dass die Comonomeren, welche die Polymerisationsgeschwindigkeit steigern, auch bevorzugt in das Polymere eingebaut werden. Detaillierte Untersuchungen mit dem System Trioxan–1,3-Dioxolan ergaben, dass mit steigender Konzentration an 1,3-Dioxolan der instabile Polymeranteil deutlich verringert und die Wärmebeständigkeit wesentlich verbessert wird. Die Polymerisate liegen hinsichtlich der thermischen Stabilität und der reduzierten Viskosität im Bereich technischer Verarbeitbarkeit.

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The Initiation Process in the Polymerization of Tetrahydrofuran with Carbonium Ion Salts*

IRVING KUNTZ,
Enjay Polymer Laboratories, Linden, New Jersey 07036

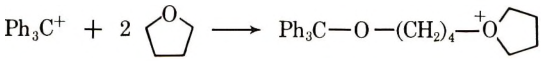
Synopsis

The initiation process for the polymerization of tetrahydrofuran with $(C_6H_5)_3C^+SbCl_6^-$ has been studied. Two mechanisms have been considered: a cation-addition process, and a process in which tetrahydrofuran donates a hydride ion to the cation of the initiator to form triphenylmethane. The biscarbonium salt $[(C_6H_5)_2C^+C_6H_4CH_2]_2(SbCl_6^-)_2$ has been synthesized and used to initiate the polymerization of tetrahydrofuran. The results are consistent with the hydride-ion mechanism but may be inconclusive because of chain transfer. NMR experiments with 0.05–0.2*M* solutions of initiator in tetrahydrofuran show that triphenylmethane is rapidly produced in an amount equal to the molar amount of initiator originally present. Some NMR evidence for the presence of an acetal endgroup in the polymer has been obtained. It is concluded that the initiation process in this system definitely involves the formation of triphenylmethane, although a detailed, unique mechanism cannot be selected at this time.

INTRODUCTION

This paper discusses our research to elucidate the mechanism of the initiation process in the ring-opening polymerization of tetrahydrofuran (THF) to poly(tetramethylene oxide), triphenylcarbonium antimony hexachloride ($Ph_3C^+SbCl_6^-$) being used as initiator. Two experimental approaches have been used: the first was the synthesis of a biscarbonium ion salt and its use as initiator, the second used NMR spectroscopy to directly study the initiation process. Preliminary reports of this research have appeared.[1]

This polymerization system was first discussed by Bawn et al.[2] In another publication, Bawn et al.[3] considered the details of the initiation process. Two possible initiation schemes were recognized. One route would be the addition of the Ph_3C^+ cation to THF, as shown in eq. (1).



(1)

A second possible initiation process would involve the formation of triphenylmethane by hydride-ion abstraction from a THF molecule [eq. (2)]. The hydride abstraction mechanism has been postulated for the dimeriza-

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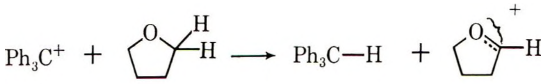
tion of styrene oxide with $Ph_3C^+SbCl_6^-$.[4] The cation formed in eq. (2) can react with another molecule of THF. Shown in eq. (3) is the product of reaction at one of the α carbon atoms which would produce a cyclic acetal endgroup in the polymer. (If reaction occurred at the other α carbon atom an aldehyde endgroup would be produced.)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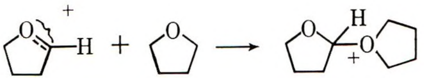
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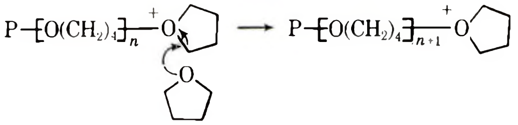

(4)

The oxonium ion of eq. (1) or (3) can now propagate. Propagation can involve a series of nucleophilic displacements by THF monomer on the α carbon atom of a macromolecular oxonium ion [eq. (4)].

EXPERIMENTAL

4,4′-Bis[diphenylcarbonium]bibenzyl Bis(antimony hexachloride) (I)

In a glove box under nitrogen 2.69 g. of freshly prepared 4,4′-bis(diphenylchloromethyl)bibenzyl[5] was dissolved in 135 ml. of CCl_4 and then added to a solution of 1.35 ml. of $SbCl_5$ in 135 ml. of CCl_4. The brown precipitate which was deposited was allowed to stand for 15 min., then filtered off and washed with CCl_4, and then with hexane. After drying in the vacuum oven 5.32 g. (98% yield) of brown solid was obtained. It was purified by solution in CH_2Cl_2 and slow precipitation by adding hexane and isolated as before.

ANAL. Calcd. for $C_{40}H_{32}Cl_{12}Sb_2$: C, 40.65%; H, 2.73%; Cl, 36.01%. Found: C, 40.94, 40.97%; H, 2.82, 2.74%; Cl, 35.65, 35.96%.

4,4′-Bis(diphenylmethyl)bibenzyl (II)

The structure of I was confirmed by its transformation to II by reaction with cycloheptatriene. I (1.99 g.) was dissolved in 50 ml. of CH_2Cl_2 and added to 1.4 g. of cycloheptatriene. The red-brown color of the solution faded and solid, colorless tropylium antimony hexachloride was deposited and isolated (1.18 g., 83%); ultraviolet absorption spectrum in reagent sulfuric acid: 268 mμ (log ε) 2.725; 274 mμ, 2.778; 279 mμ, 2.714. The filtrate was evaporated to give 0.72 g. (83%) of II, m.p. 144–147°C. Recrystallization from benzene gave colorless crystals, m.p. 157–159°C., ultraviolet absorption spectrum in methylcyclohexane: 263 mμ, (log ε)

3.501; 270 mμ, 3.394; 275 mμ, 3.236. NMR measurements of II in C_6D_6 gave excellent agreement with the anticipated structure.

ANAL. Calcd. for $C_{40}H_{34}$: C, 93.34%; H, 6.66%. Found: C, 93.56%; H, 6.50%.

n-Butyl Triphenylmethyl Ether

The ether was prepared from the alcohols, toluenesulfonic acid being used as catalyst.[6] A viscous liquid which slowly deposited crystals was obtained, b.p. 160°C./(0.28 mm.), n_D^{18} 1.5902.

ANAL. Calcd. for $C_{23}H_{24}O$: C, 87.30%; H, 7.64. Found: C, 87.27, H, 7.54.

Polymerizations

THF (J. T. Baker Chemical Co.) was distilled from NaOH, then from lithium metal dispersion. Immediately before use it was refluxed over and distilled from CaH_2 into a receiver containing sodium naphthalene and finally distilled therefrom. $Ph_3C^+SbCl_6^-$ was prepared as described in the literature.[4] Polymerizations were carried out with 10-ml. portions of THF in screw-capped ampules at 25°C. for 48 hr. Polymers were isolated by precipitation into ice-water and drying *in vacuo*. Intrinsic viscosities were determined promptly in benzene at 30°C.

NMR Experiments

The 60 Mc. Varian Associates A60 instrument was used at room temperature. In certain experiments it was used with a time-averaging computer. Tetramethylsilane (TMS) was introduced in trace amounts for use as an internal standard; for some measurements the 1.8 ppm peak of THF was used.

DISCUSSION AND RESULTS

Biscarbonium Ion Experiments

The polymerization of THF by $Ph_3C^+SbCl_6^-$ is reported to be characterized by rapid initiation involving complete use of catalyst and little or no termination except at higher temperatures.[2] The polymerization appears to yield "living polymers" with the added feature that monomer–polymer equilibria occur at ordinary temperatures (approximately 73% conversion to polymer is observed at 25°C. with undiluted monomer).[2] In a polymerization system with these characteristics the use of a biscarbonium ion salt should permit the identification of the initiation process between the models which involve addition of the cation to the monomer [eq. (1)] or hydride-ion abstraction [eqs. (2) and (3)]. For the first mechanism, two independently growing macromolecular oxonium ions should be formed and give a final polymer product of double the molecular weight obtained with the mono-salt $Ph_3C^+SbCl_6^-$. For the second mechanism the bis salt and the mono salt should both yield the same molecular weight product. We

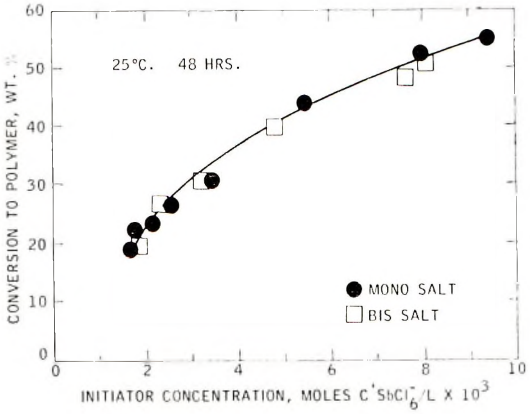


Fig. 1. Bulk polymerizations of THF with $Ph_3C^+SbCl_6^-$ and I at 25°C. for 48 hr.

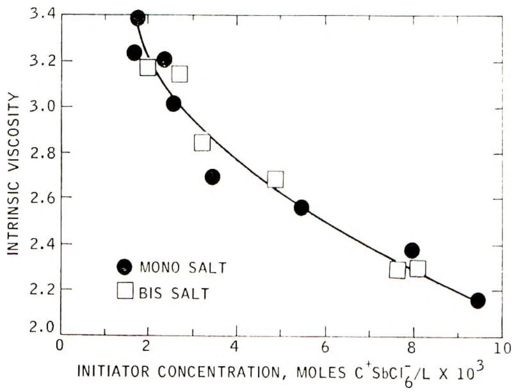
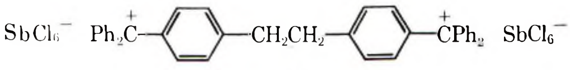


Fig. 2. Intrinsic viscosities (in benzene at 30°C.) of the polymers of Fig. 1.

synthesized the biscarbonium salt I and have used it to initiate the polymerization of THF.



I

Figure 1 shows the results of polymerizations of THF in bulk carried out at 25°C. for 48 hours with varied concentrations of the mono salt and the bis salt (I). These results show that each $>C^+ SbCl_6^-$ center of I is as effective a polymerization initiator as $Ph_3C^+SbCl_6^-$. (In our results we have not yet reached the equilibrium conversion obtained by Bawn and co-workers in approximately 48 hr.) Figure 2 shows the results where polymer molecular weight as measured by intrinsic viscosity is plotted as a function of initiator concentration for the mono and bis salts. The intrinsic viscosities of both series of polymers are experimentally indistinguishable.

These results are consistent with the hydride-ion abstraction mechanism [eqs. (2) and (3)] and do not support the cation-addition mechanism [eq. (1)]. However, after this research was complete, Bawn et al. reported results[7] that indicated chain transfer may be important in the polymerization of THF with $Ph_3C^+SbCl_6^-$. Therefore, the results with the bis salt I cannot serve as a firm basis for selecting the initiation mechanism.

NMR Experiments

We have examined freshly prepared solutions of $Ph_3C^+SbCl_6^-$ in THF by NMR spectroscopy to determine if Ph_3CH was produced as demanded by the hydride-ion abstraction mechanism [eqs. (2) and (3)], or, alternately, if we could use this technique to detect the endgroup demanded by eq. (1), the cation-addition mechanism.

Figure 3 shows the NMR spectrum of an authentic sample of triphenylmethane dissolved in THF. The chemical shifts at 1.7 ppm (downfield from tetramethylsilane at 0 ppm) and 3.7 ppm are due to THF; the former is assigned to the methylene groups β to the ether oxygen, the latter to the methylene groups α to the ether oxygen. The chemical shift at 7.3 ppm is due to the aromatic protons of Ph_3CH, and that at 5.7 ppm to the tertiary hydrogen. The theoretical ratio of aromatic protons to the tertiary hydrogen is 15/1 and integration of spectra such as that shown give this ratio within experimental error. Instrumental amplification is available as shown in the offset curve in Figure 3 to help in detecting the peak at 5.7 ppm.

As a model compound for the endgroup predicted by the cation addition mechanism [eq. (1)] the *n*-butyl ether of triphenylmethanol was prepared by the method of Pratt and Draper.[6] The spectrum is seen most simply in CCl_4 as shown in Figure 4. The chemical shifts can be assigned to the various hydrogen atoms as shown in the figure and the quantitative integration agrees with the theoretical values. It will be noted that no chemical

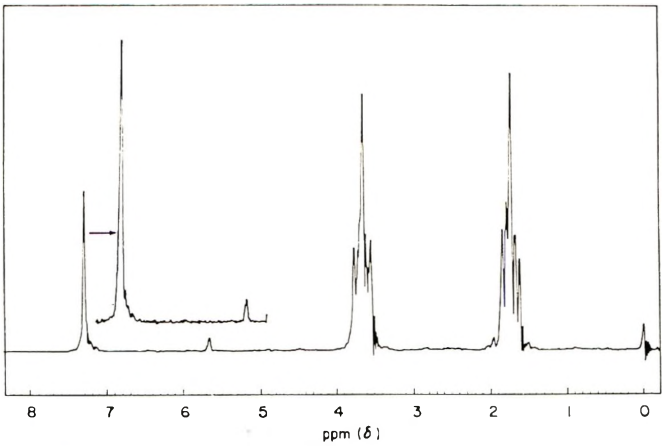


Fig. 3. NMR spectrum of authentic Ph_3CH (approximately 20 wt.-%) in THF.

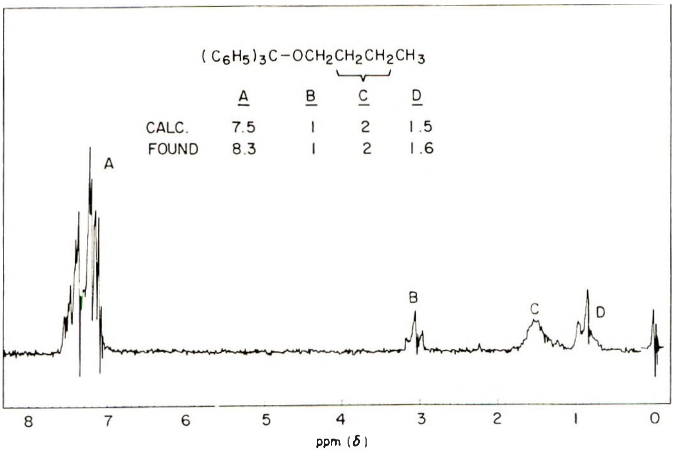


Fig. 4. NMR spectrum of n-BuOCPh$_3$ in CCl$_4$. The chemical shifts are identified by the letters and integrated areas ratios and calculated values are shown.

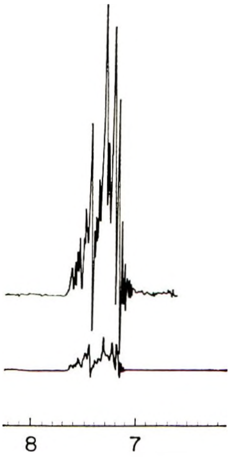


Fig. 5. NMR spectrum of aromatic protons of n-BuOCPh$_3$ in THF.

shift is observed at 5.7 ppm. n-BuOCPh$_3$ in THF shows no peaks in the area of 5.7 ppm and the aromatic protons show a complicated multiplet as shown in Figure 5. (Note in Fig. 3 that the aromatic protons of Ph$_3$CH appear as a singlet at 7.3 ppm.) We have determined the NMR spectrum of Ph$_3$C$^+$SbCl$_6^-$ in nitromethane as shown in Figure 6. The aromatic proton multiplet in the carbonium ion salt is about 7.8 ppm. The nitromethane solvent masks the 5.7 ppm region but studies by other investigators[4] make us confident that no absorption for Ph$_3$C$^+$SbCl$_6^-$ will appear in this region in THF. These results with authentic samples show that small amounts of Ph$_3$CH can be detected in THF solution by taking advantage of the chemical shift at 5.7 ppm.

With this background experiments were now carried out in which solutions of Ph$_3$C$^+$SbCl$_6^-$ of varied concentrations were prepared and examined

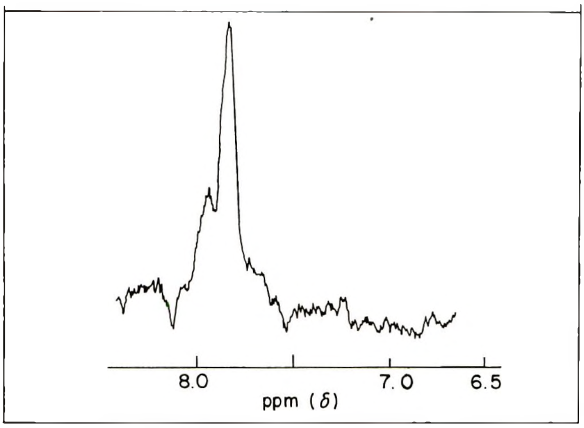


Fig. 6. NMR spectrum of $Ph_3C^+SbCl_6^-$ in nitromethane.

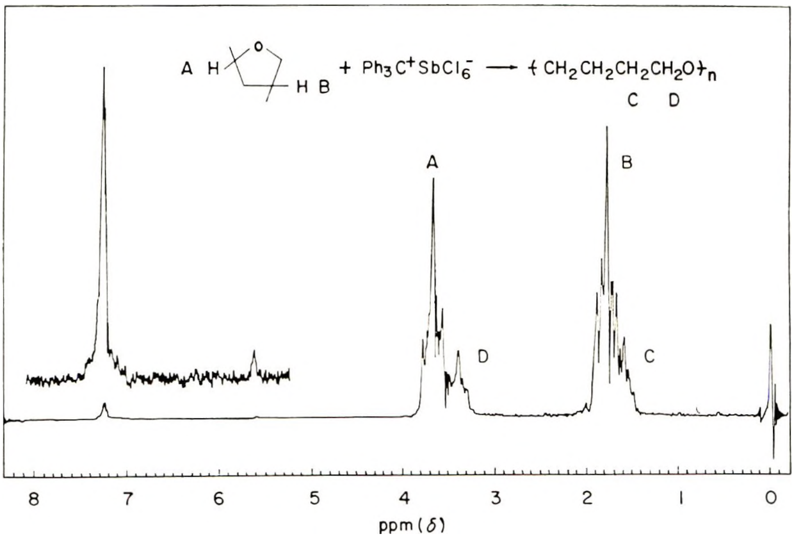


Fig. 7. NMR spectrum of 0.2M $Ph_3C^+SbCl_6^-$ in THF obtained 0.6 hr. after mixing. The letters identify the chemical shifts of the monomer and polymer.

in the NMR spectrometer at varying time intervals. The temperature in the instrument in the area of the sample was 28°C. A typical result is shown in Figure 7. Here, the spectrum of a 0.2M solution of $Ph_3C^+SbCl_6^-$ in THF is shown 0.6 hours after mixing. Several features are clear. Aromatic protons are seen at 7.3 ppm, and the characteristic peak assigned to the tertiary hydrogen of Ph_3CH is seen at 5.7 ppm. The integration of the scan showed the ratio of aromatic protons to the tertiary hydrogen was 15 within experimental error. The peak at 7.3 ppm is similar to the singlet observed with authentic samples of Ph_3CH (Fig. 3) and does not resemble the multiplet observed with the ether n-$BuOCPh_3$ (Fig. 5). Results similar to those shown in Figure 7 were obtained in many experiments.

These results lead us to conclude that Ph_3CH is formed in polymerizing solutions of THF initiated with $Ph_3C^+SbCl_6^-$.

Shown in Figure 7 are the chemical shifts of the protons of poly(tetramethylene oxide) polymer relative to those of THF. The values are the same observed when preformed polymer is dissolved in THF, and are similar to those observed with 1,4-butanediol.[9] We have been able, therefore, to conveniently measure conversion to polymer by comparing the relative area of the peak at 3.4 ppm to the total integrated area between 3 and 4 ppm.

Table I summarizes the results of a number of experiments. In the fourth column of Table I we show the ratio of the protons of the $—CH_2\text{-}OCH_2—$ group obtained from the 3–4 ppm region to the aromatic protons at 7.3 ppm determined by integration of the experimental scans. The values in parentheses are the calculated values obtained from the nominal concentrations assuming that $Ph_3C^+SbCl_6^-$ yields an equal molar amount of Ph_3CH. The last column of the table shows the observed ratio of the aromatic protons to the tertiary proton at 5.7 ppm, compared to the theoretical ratio of 15 demanded by Ph_3CH.

Several conclusions can be drawn from the data shown in Table I. Initiation is rapid under our experimental conditions where the ratio of THF to initiator is high. In all our experiments we have not been able to detect any evidence for the persistence of the Ph_3C^+ cation. In one ex-

TABLE I
THF Polymerization Studies by the NMR Technique[a]

$Ph_3C^+SbCl_6^-$ concentration, M	Reaction time, hr.	Conversion, %	$\frac{\Sigma CH_2OCH_2}{Ph_3}$	$\frac{Ph_3}{C—H}$
0.052	—	—	(63)[b]	(15)[b]
	0.7	11	71	—
	2.2	21	79	—
	4.25	29	63	—
	5.2	30	72	—
0.20	—	—	(17)[b]	(15)[b]
	0.4	15	16	17
	0.6	18	—	—
	1.1	29	15	15
	2.0	33	15	14
	3.7	38	17	16
	4.2	40	15	12
0.09	—	—	(35)[b]	(15)[b]
	0.5	12	33	—
	1.3	25	38	16
	2.4	31	36	18
	3.0	35	38	—
0.12	—	—	(28)[b]	(15)[b]
	0.05	3	30	20

[a] THF was $12M$ in all experiments.

[b] Parenthetical values are ratios calculated from nominal concentrations.

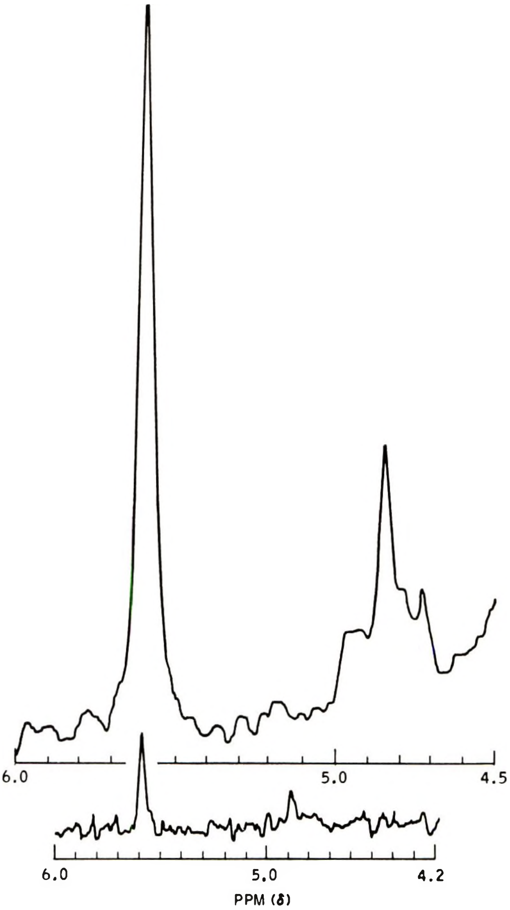


Fig. 8. NMR spectrum of THF solution originally 0.21*M* in $Ph_3C^+SbCl_6^-$ when about 15% conversion to polymer had taken place. Lower curve is original; the upper curve was made by using the time-averaging computer for 20 scans.

periment we obtained a spectrum 3 min. after a sample had been prepared. We would estimate that only about 3% conversion to polymer had occurred in this interval (this corresponds to the polymerization of 3 molecules of THF per molecule of initiator) and yet, as shown by the last entry in Table I, the amount of Ph_3CH produced agreed with the theoretical value predicted by the nominal solution concentration. That initiation is rapid and complete is further supported by the experimental invariance of the Σ CH_2OCH_2/Ph_3 proton ratio as a function of conversion within each experiment. The agreement between observed and calculated concentrations of Ph_3CH suggest that only a mode of initiation is operative that produces this compound. In all experiments the amount of Ph_3CH produced was equivalent to the molar amount of $Ph_3C^+SbCl_6^-$ originally present.

We have tried to elucidate the nature of the polymer endgroup using the NMR technique with solutions of THF undergoing polymerization. As mentioned previously, an alternate to the acetal endgroup shown in eq. (3) would be an aldehyde endgroup. Aliphatic aldehydic protons show a chemical shift in the 9.7–9.8 ppm region. This area was examined under high amplification conditions and also using the time-averaging computer technique in several of our samples. In these experiments, we could find no evidence for the presence of aldehydic protons.

We have also looked for the acetal endgroup shown in eq. (3). In 1,1-diethoxyethane the acetal hydrogen shows a chemical shift at 4.7 ppm. As a possibly better model compound for the cyclic acetal shown in eq. (3) we obtained the NMR spectrum of 2-ethoxy-3,4-dihydro-2-H-pyran and found the acetal hydrogen appeared as a triplet at 4.9 ppm. Figure 8 shows the NMR spectrum of a solution of THF originally 0.21*M* in $Ph_3C^+SbCl_6^-$. About 15% conversion to polymer had occurred at the time of measurement. The curve obtained with the time-averaging computer shows a multiplet in the 4.8–4.9 ppm region. This observation, duplicated in other experiments, supports the formation of an acetal endgroup in the polymer as demanded by the mechanism shown in eq. (3). However, integration of the peaks shown in Figure 8 indicates about 0.6 acetal hydrogen for each tertiary hydrogen present in Ph_3CH; according to the mechanism shown the number of these two hydrogens should be equal. At this time, we do not consider that the nature of the endgroup of the polymer is completely established.

CONCLUSIONS

The results of the NMR experiments clearly show that triphenylmethane is produced when $Ph_3C^+SbCl_6^-$ is used to initiate the polymerization of tetrahydrofuran. These results support the hydride-ion mechanism of eqs. (2) and (3). The results with the biscarbonium ion salt I are also consistent with this initiation model but may be less critical because of chain transfer. No evidence for the cation-addition mechanism of eq. (1) was observed. Some evidence for the presence of an acetal endgroup in the polymer has been obtained, none for the presence of an aldehyde endgroup.

As formulated in eq. (2), THF can donate a hydride ion to the Ph_3C^+ cation to yield a species in which the carbonium ion is stabilized by neighboring oxygen.[10] The recent results of the Liverpool group show that the anion plays an important role in the initiation process.[7] The transformations shown in eqs. (2) and (3) may take place by a concerted process in which the anion plays a critical part.

The nature of the endgroup in the polymer has not been firmly established. Therefore, it cannot be said that the mechanism shown in eqs. (2) and (3) is the unique initiation process in this system. However, it appears certain that the formation of triphenylmethane is an essential feature of the initiation mechanism.

We would like to thank Drs. A Ledwith, B. E. Hudson, Jr., and F. P. Baldwin for most helpful discussions.

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Résumé

Le processus d'initiation de la polymérisation du tétrahydrofurane avec$(C_6H_5)_3C^+$-$SbCl_6^-$ a été étudié. Deux mécanismes ont été considérés: un processus d'addition cationique et un processus dans lequel le tétrahydrofuranne fournit un ion hydride au cation de l'initiateur pour former le triphénylméthane. Le sel bis-carbonium $[(C_6H_5)_2$-$C^+C_6H_4CH_2]_2(SbCl_6^-)_2$ a été synthétisé et utilisé pour l'initiation de la polymérisation du tétrahydrofuranne. Les résultats sont en accord avec le mécanisme par ions hydrures mais pas entièrement conclusifs par suite d'un transfert de chaînes. Les expériences NMR avec des solutions à 0.05 à 0.2 molaires d'initiateur dans le tétrahydrofuranne montrent que le triphénylméthane est rapidement produit en une quantité égale à la quantité molaire d'initiateur généralement présente. Le NMR montre également la présence d'un groupe terminal métallique dans le polymere. On en conclut que le processus d'initiation dans ce systeme comporte définitivement la formation de triphénylméthane bien qu'un mécanisme détaillé et unique ne puisse pas encore être présenté en ce moment.

Zusammenfassung

Der Startvorgang bei der Polymerisation von Tetrahydrofuran mit $(C_6H_5)_3C^+SbCl_6^-$ wurde untersucht. Zwei Mechanismen wurden in Betracht gezogen: ein Kationenadditionsprozess und ein Prozess, bei welchem Tetrahydrofuran als Hydridiondonator zum Starterkation unter Bildung von Triphenylmethan fungiert. Das Bis-carboniumsalz $[(C_6H_5)_2C^+C_6H_4CH_2]_2(SbCl_6^-)_2$ wurde synthetisiert und zum Start der Polymerisation von Tetrahydrofuran verwendet. Die Ergebnisse lassen sich mit dem Hydridionenmechanismus deuten, sind aber wegen der Kettenübertragung nicht schlüssig. NMR-Versuche mit 0,05 bis 0,2 molaren Lösungen des Starters in Tetrahydrofuran zeigen, dass Triphenylmethan rasch in einer der Menge des ursprünglich vorhandenen Starters äquivalenten Menge erzeugt wird. NMR lieferte auch Hinweise auf das Vorhandensein einer Acetalendgruppe im Polymeren. Es ergibt sich der Schluss, dass der Startprozess in diesem System mit der Bildung von Triphenylmethan verknüpft ist, ein eindeutiger. detaillierter Mechanismus kann aber derzeit noch nicht angegeben werden.

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Polymerization with Heterogeneous Metalorganic Catalysts. VI.* Differences in Polymerization Activity of α-Olefins and Some Kinetic Results on Butene-1 Polymerization

H. SCHNECKO, W. LINTZ, and W. KERN, *Organisch-Chemisches Institut, Universität Mainz, Germany*

Synopsis

Relative changes in polymerization activity of ethylene, propylene, and butene-1 in Ziegler-Natta polymerization were compared by use of $TiCl_3$ samples contaminated with O_2 and H_2O to various extents. Catalyst depletion varied for the three monomers, which supported the existence of different active centers. In butene-1 polymerizations with the system $Al(C_2H_5)_2Cl$–$TiCl_3$, the formation of active centers involves an irreversible and a reversible (adsorption) reaction, the former pertaining to the formation of $Al(C_2H_5)Cl_2$ and dependent upon the purity of the $TiCl_3$. The kinetic treatment of the rate curves suggests a mixed order of catalyst deactivation and again points to the importance of $Al(C_2H_5)Cl_2$.

Introduction

Up to now the question of the exact nature and structure of active centers in heterogeneous Ziegler-Natta polymerizations remains unsolved. Promising approaches have been proposed,[1-6] but they differ in essential details. It is not our intention to add another hypothesis to the many existing already, but rather to confirm with our results one or the other of them.

In a previous communication[7] we were able to show that there are different centers in the polymerization of ethylene, propylene, and butene, respectively. Additional results can be obtained by intentional deactivation of the catalyst and the varying influence on the different monomers. On the other hand, questions related to the nature of active centers can be explored advantageously with butene-1 as a monomer. The greater specificity of active centers which can be expected in butene polymerization permits a more accurate observation of elementary processes of catalyst formation and depletion.

Experimental

Most of the experimental procedures, materials, and apparatus have been described previously.[8]

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* For Part V, cf. ref. 7.

TABLE I

Decrease of Polymerization on Addition of O_2 and H_2O to $TiCl_3$ for Three Monomers[a]

Monomer	Pressure, torr	Temp., °C.	Al compound	Amt. Al compound, mmole	Vol. $TiCl_3$ suspension, ml.[b]	O_2 added to $TiCl_3$, mole-%	H_2O added to $TiCl_3$, mole-%	Monomer consumption, ml./hr.	Relative polymerization activity, %[c]
Ethylene	250	50	$Al(C_2H_5)_3$	2.64	3	—	—	2375	100
						2.25	—	2225	94
						2.42	6.8	2055	87
Propylene	400	50	$Al(C_2H_5)_3$	4.40	5	—	—	2340	100
						2.25	—	2090	89
						2.42	6.8	1655	71
Butene-1	350	50	$Al(C_2H_5)_3$	2.64	3	—	—	1485	100
						2.25	—	1440	97
						2.42	6.8	980	66
Ethylene	400	60	$Al(C_2H_5)_2Cl$	4.40	5	—	—	2065	100
						2.25	—	1900	92
						2.42	6.8	1440	70
Propylene	720	60	$Al(C_2H_5)_2Cl$	8.80	10	—	—	3070	100
						2.25	—	2480	81
						2.42	6.8	1670	54
Butene-1	500	60	$Al(C_2H_5)_2Cl$	8.80	10	—	—	1540	100
						2.25	—	1040	67
						2.42	6.8	605	39

[a] Exp. in 100 ml. Sinarol.

[b] 1 ml. suspension = 0.13 mmole $TiCl_3$.

[c] Relative to initial activity for a given set of reaction conditions.

In this work different $TiCl_3$ samples were originally obtained from one Stauffer $TiCl_3$-AA catalyst. Notation and treatment of the $TiCl_3$ suspensions are as follows. $TiCl_3$-I denotes pure $TiCl_3$-AA suspended in Sinarol in a nitrogen bag directly from the original contact. $TiCl_3$-II was a $TiCl_3$-AA suspension (preparation as $TiCl_3$-I) which had been exposed unintentionally to air and humidity. $TiCl_3$-III was a $TiCl_3$-AA suspension which had been contaminated intentionally with fixed amounts of O_2 and H_2O, (Table I). Oxygen was admitted to the unstirred suspension with a syringe under slight vacuum. Subsequent addition of H_2O was done in fine drops very slowly (syringe, thin needle) to the unstirred suspension so that preferential reaction in the solution was obtained. $TiCl_3$-IV was obtained by treatment of a pure $TiCl_3$-AA suspension with an excess of $Al(C_2H_5)_2Cl$ under polymerization conditions, i.e., at 60°C. for 20 hr., in absence of monomer followed by thorough washings with Sinarol and preparation of a new suspension.

Since complications of the polymerization system are even more pronounced when $Al(C_2H_5)_3$ is used as cocatalyst, due to the possibility of a reduction of $TiCl_3$, $Al(C_2H_5)_2Cl$ was used throughout, except for comparative measurements (Table I).

Activity Changes of Different Monomers

Several studies have dealt with the influence of oxygen on the catalyst in Ziegler-Natta polymerizations. Increasing as well as decreasing polymerization activity is claimed after treatment of the catalyst with oxygen. The most comprehensive study on the reaction of $TiCl_3$ with O_2 has been published by Martin and Blanck,[9,10] who were also able to explain some of the discrepancies which appeared in the literature. According to their findings, older $TiCl_3$ samples in which the crystals have conglomerated will exhibit a higher activity if they are oxidized by O_2 to Ti^{4+}, which in turn is reduced to a $TiCl_3$ of smaller crystal size and larger surface, i.e., of higher activity.[10]

Our findings support Martin and Blanck's conclusions. In several cases $TiCl_3$ samples with reduced activity gave an activity increase up to the original polymerization value. This reaction could be obtained either by addition of oxygen or by increased stirring (mechanical cleaving of clustered $TiCl_3$ crystals).

Moreover, we believed that the intentional deterioration of the catalyst by addition of O_2 and H_2O ($TiCl_3$-III) would give further clues as to the difference of active centers in Ziegler-Natta polymerization, since the reaction of the $TiCl_3$ surface with O_2 and H_2O should preferentially occur at centers of higher polymerization activity. Our results are seen in Table I and can be summarized as follows.

(*a*) With new samples of $TiCl_3$-I of optimal activity no increase in polymerization was observed as a result of addition at O_2. (*b*) On adding certain amounts ($\sim$2 mole-% of $TiCl_3$-III) the action of oxygen resulted in an activity decrease of the $TiCl_3$. (*c*) After addition of O_2 the activity decrease is less than the decrease of the titrated (Ce^{+4}) value of $TiCl_3$; this discrepancy can be related to the fact that part of the Ti^{+4} formed by oxidation is still active in polymerization, but cannot be detected by titration. (*d*) Additional amounts of H_2O, introduced to the $TiCl_3$ suspension (after quantities of oxygen had been added) in order to achieve hydrolysis of oxidized $TiCl_3$, increased deactivation. (*e*) In the system $Al(C_2H_5)_2Cl$–$TiCl_3$-III the activity decrease occurred earlier; i.e., with smaller quantities of O_2 and H_2O, and the decrease was more pronounced than in the system $Al(C_2H_5)_3$–$TiCl_3$. (*f*) With both cocatalysts, the rates of polymerization of the monomers are affected by the deterioration of $TiCl_3$ in the following ascending order: ethylene, propylene, butene-1.

These results confirm qualitatively the existence of centers of different activity. However, there still exist at least two possible explanations as to the nature of these active centers. (*1*) There can be a gradual difference in the accessibility of these centers for the monomers, i.e., all centers that polymerize butene will also be active for propylene and the more so for ethylene,[7] but not vice versa. (*2*) Alternatively, there may be specific centers which are different for each monomer, i.e., any center which polymerizes ethylene does not polymerize propylene or butene, respectively. This latter case should, however, be discarded since the well-known formation of block copolymers in Ziegler-Natta polymerization cannot be explained if each monomer requires its own type of active center.

For the first possibility, one can, by a crude approximation, calculate the relative amounts of centers effective for the different monomers from the results of Table I, provided that the centers of highest activity are the first to be destroyed by O_2–H_2O. One finds that, in polymerizations with $Al(C_2H_5)_2Cl$, 1.3 and 2 times as many centers as in butene polymerizations are active in propylene and ethylene polymerization, respectively. Actually, these numbers may be much higher if it is assumed that the high reactivity of oxygen towards $TiCl_3$ may affect centers of lower activity prior to complete destruction of highly active sites.

Catalytic Activity in Butene-1 Polymerization

Differences in $TiCl_3$ samples, e.g., changes in the catalyst activity on aging,[7] can be better observed from changes of incremental rate curves than from changes in total monomer consumption/hr. (VB_{60}). A combination of incremental rate and total consumption curves gives a better insight into the formation process of active centers.

We have only a limited number of butene-1 polymerizations with constant incremental rate curves, in particular for low activity. In order to simplify the polymerization system, primarily in the hope of obtaining constant rate curves, we pretreated the catalyst ($TiCl_3$-IV). Pretreatment of this sort has been described,[5,6] and has been successful with respect to constant rate curves in cases of low catalyst activity.

Typical forms of rate–time curves of a pure $TiCl_3$-I for varying Al/Ti ratios can be seen from Figure 1. When the Al/Ti ratio is less than 4

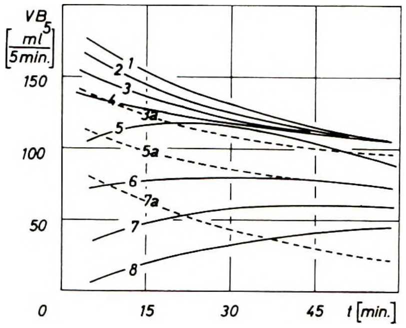

Fig. 1. Rate–time curves for polymerization of butene-1 with AlR$_2$Cl–TiCl$_3$–I. (*1*) Al/Ti = 15.3; (*2*) Al/Ti = 11.5; (*3, 3a*) Al/Ti = 7.7; (*4*) Al/Ti = 3.8; (*5, 5a*) Al/Ti = 1.9; (*6*) Al/Ti = 1.2; (*7, 7a*) Al/Ti = 0.77; (*8*) Al/Ti = 0.38. 100 ml. Sinarol; 60°C.; pressure of butene-1 = 500 torr; TiCl$_3$ = 1.15 mmole.

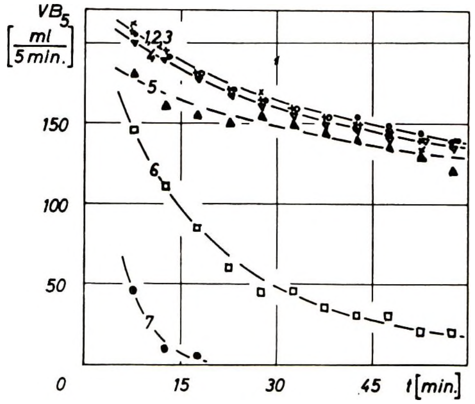

Fig. 2. Rate–time curves for polymerization of butene-1 with AlR$_2$Cl–TiCl$_3$–IV: (*1*) Al/Ti = 12.1; (*2*) Al/Ti = 6.1; (*3*) Al/Ti = 3.0; (*4*) Al/Ti = 1.5; (*5*) Al/Ti = 0.61; (*6*) Al/Ti = 0.30; (*7*) Al/Ti = 0. 100 ml. Sinarol; 60°C.; pressure of butene-1 = 500 torr; TiCl$_3$ = 1.45 mmole.

(Fig. 1, curves *5–8*), the rate during polymerization initially increases, reaches a maximum, and then begins to decrease. For higher Al/Ti ratios (Fig. 1, curves *1–4*) the decrease is observed immediately. Aging of the premixed catalyst produces diminishing rate–time curves for the entire range of Al/Ti ratios studied (Fig. 1, curves *3a, 5a, 7a*).

Similar curves, i.e., those showing decreasing rate with time for all Al/Ti ratios, are obtained for the pretreated TiCl$_3$-IV (Fig. 2). With this catalyst, however, the activity at low Al/Ti ratios was much higher (cf. Fig. 3 below). In addition, at an Al/Ti ratio of 0 (curve *7*, no Al(C$_2$H$_5$)$_2$Cl added after pretreatment), a small initial activity was measured which, however, subsided rapidly; presumably it results from residual Al(C$_2$H$_5$)$_2$Cl which had not been washed out completely. These results confirm that the center-forming reaction is time-consuming;[7] at low Al concentrations and without aging increasing rate curves indicate the build-up of centers during the first hour

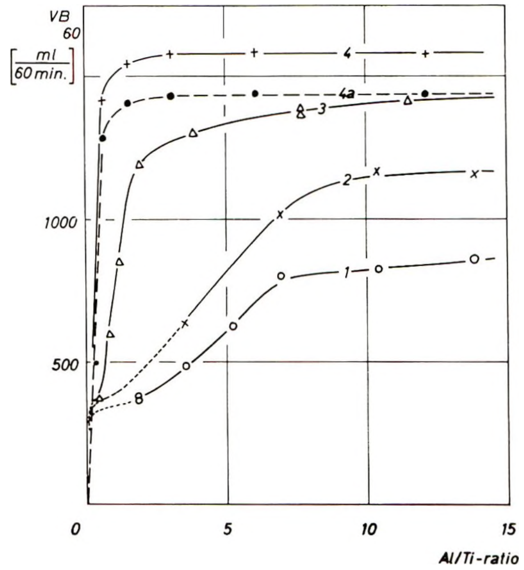

Fig. 3. Polymerization activity (VB_{60}) vs. Al/Ti ratio for polymerization of butene-1 with AlR_2Cl–$TiCl_3$: (*1*, *2*) $TiCl_3$-II; (*3*) $TiCl_3$-I; (*4*, *4a*) $TiCl_3$-IV. 100 ml. Sinarol; 60°C.; pressure of butene-1 = 500 torr; $TiCl_3$ = 1.15 mmole.

of polymerization. At higher Al/Ti ratios or with aging or pretreatment of the catalyst, the formation of active centers is almost complete at the beginning of the polymerization.

The pronounced differences in the rate curves with $TiCl_3$-I and $TiCl_3$-IV at low Al/Ti ratios (< 2) indicate an irreversible reaction between solid $TiCl_3$ and $Al(C_2H_5)_2Cl$ in solution, in addition to the assumed reversible adsorption of the cocatalyst. If the reaction of catalyst formation were totally reversible, as it should be assumed for a pure adsorption process,[11] there should be no difference between treated and untreated $TiCl_3$. In a normal untreated $TiCl_3$ both reactions occur on addition of the Al–organic compound. The importance of the reversible adsorption of $Al(C_2H_5)_2Cl$ can be seen from the exact conformance to the Eley-Rideal relationship[11] between polymerization activity and Al/Ti ratio for the pretreated $TiCl_3$-IV, whereas with the other $TiCl_3$ samples the exclusive existence of the adsorption reaction is not verified qualitatively and quantitatively (adsorption equations not applicable); for the pretreated $TiCl_3$-IV only the irreversible reaction is completed.

For this irreversible reaction it is possible either that $Al(C_2H_5)_2Cl$ dissolves components of the $TiCl_3$ lattice and thus creates new active surface sites on the $TiCl_3$ or that alkylation of $TiCl_3$[5] or of $AlCl_3$[6] (cocrystallized in the $TiCl_3$ lattice) takes place with formation of active centers containing adsorbed $Al(C_2H_5)_2Cl$ and production of $Al(C_2H_5)Cl_2$. It is conceivable that this heterogeneous reaction at low Al/Ti ratios is slow and not completed before the polymerization is started, unless aging or pretreatment has been conducted. The fact that the rate curves decrease does not prove that, even at high starting activity, active site formation is completed, but only that site destruction is predominating. In accordance with Caunt,[6] we think that increasing amounts of $Al(C_2H_5)Cl_2$ are responsible for deactivating active sites. The appearance of $Al(C_2H_5)Cl_2$ can also be seen from the Al/Ti curves (Fig. 3), where, with the untreated impure $TiCl_3$-II at low ratios of Al/Ti a shoulder is observed which is the more pronounced the more impurities are present in the $TiCl_3$; with pretreated $TiCl_3$-IV no inflection point exists. It can be assumed that at low Al/Ti ratios a great part of the $Al(C_2H_5)_2Cl$ present will react with impurities (i.e., soluble oxidation products) to form $Al(C_2H_5)Cl_2$ which, in turn, will compete with $Al(C_2H_5)_2Cl$ for active centers at the $TiCl_3$ surface. Adsorption of $Al(C_2H_5)Cl_2$, however, will result in centers of much lower, if any, polymerization activity. With increasing Al/Ti ratios the $Al(C_2H_5)Cl_2/Al(C_2H_5)_2Cl$ ratio is diminished, and the adsorption equilibria between $Al(C_2H_5)_2Cl$ and $Al(C_2H_5)Cl_2$ will be shifted towards $Al(C_2H_5)_2Cl$ which then follows its own adsorption curve. Competitive adsorption between two cocatalysts of different activating power has been studied earlier with similar results.[12]

The difference in the limiting height (Fig. 3) of the curves must be explained by (*a*) the total amount of $Al(C_2H_5)Cl_2$ present in the system, (*b*) an irreversible destruction of active sites by O_2/H_2O. Again, the pretreated $TiCl_3$-IV yields the highest level, indicating the lowest amount of $Al(C_2H_5)Cl_2$. However, in pretreated $TiCl_3$ no $Al(C_2H_5)Cl_2$ should be present at all since all reactions causing its formation have been completed prior to polymerization. We still find decreasing rate curves.

Catalyst Deactivation during Butene Polymerization

What explanations are possible to interpret decreasing rate curves in the essentially unterminated Ziegler-Natta polymerizations? In the literature the following possibilities are considered: (*a*) diffusion-controlled monomer admission to the active centers by viscosity increase, (*b*) decrease of monomer solubility by polymer formed, (*c*) blocking of centers by polymer, (*d*) transfer reactions with simultaneous destruction of centers, (*e*) rearrangement of the active complex into an inactive form during the polymerization.

We were able to verify experimentally that in our system under our conditions cases (*a*)–(*c*) can be eliminated. Accordingly, it had to be assumed that the rate decrease was connected with a loss of active centers.

We then tried to interpret our rate curves kinetically. Friedlander, in a recent paper,[13] considers different orders of decay. Our rate data do not fit second-order curves. It seems that a second-order termination[14] would be difficult to explain in heterogeneous polymerization. By plotting our data assuming a first-order termination, it is possible to obtain straight lines. However, a comparison between the half-time polymerization activity calculated from the Friedlander straight line (integral curve) and that calculated from the differential curve reveals differences of 100% (e.g., 75 vs. 150 min.); thus, with the constants evaluated, it is not possible to construct a theoretical differential curve fitting the experimental rate curve. Obviously, the representation is not sufficiently sensitive, particularly if the limiting value of the polymerization rate has to be determined from very short polymerization times.

The shape of both our differential and integral rate curves suggests a mixed order in which only part of the active centers disappears. Friedlander discusses a mixed order without using a linear representation. The rate equation for a mixed order

$$\log (d[\mathrm{P}]/dt - k'_p[\mathrm{M}][\mathrm{C}_s^*]) = \log (k_p[\mathrm{M}][\mathrm{C}_0^*]) - k_d t \tag{1}$$

(where [P] is polymerized monomer volume, $d[\mathrm{P}]/dt$ is rate of polymerization; $[\mathrm{C}_0^*]$ is concentration of unstable active centers at beginning of polymerization; $[\mathrm{C}_s^*]$ is corresponding concentration of stable centers, and k'_p, k_p, [M] are constants), can be written in the form

$$\log (x - a) = \log b - k_d t \tag{2}$$

where x is the polymerization rate at time t, a is that at infinite time (which has to be extrapolated or calculated by trial and error), and b the fraction of the rate of polymerization initiated by $[\mathrm{C}_0^*]$.

By plotting $\log (x - a)$ versus t our data yield a straight line (Fig. 4, curve *1*) from which k_d can be evaluated and, with eq. (2), our rate curve can be verified theoretically (Fig. 4, curve *2*); however, as can also be seen from the rate curves directly (e.g., Figs. 1,2) there is no constant slope of the different straight lines, i.e., k_d still varies. Thus, the kinetic treatment of our rate curves shows that there is only a partial deactivation of the active sites; this would be expected either if there is only a limited disappearance of sites (competition with a site-forming reaction) leading to an

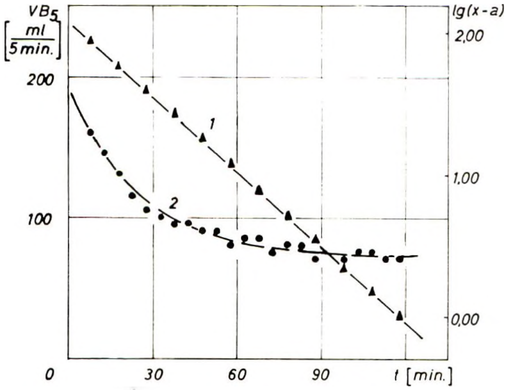

Fig. 4. Plot of rate curve for mixed order of catalyst deactivation for polymerization of butene-1 with $\mathrm{AlR_2Cl{-}TiCl_3{-}I}$: (*1*) log $(x-a)$ vs. t; (*2*) found (points) and calculated rate curve, VB_5 vs. t. 100 ml. Sinarol; 60°C.; pressure of butene-1 = 500 torr; $\mathrm{TiCl_3}$ = 1.15 mmole; $\mathrm{AlR_2Cl}$ = 8.8 mmole.

equilibrium concentration, or if there are sites of different reactivity and stability of which only the most active disappear.

From the literature two types of reaction can be adopted: Kohn et al.[3] describe a rearrangement of the active polymerization complex to an active plus an inactive complex. The active complex, however, should again be subject to disproportionation unless certain restrictions exist to prevent a complete decay. More suitable to our observations is the proposal of Caunt[6] to consider a transfer reaction of the active center with $Al(C_2H_5)_2Cl$, in the course of which $Al(C_2H_5)Cl_2$ is formed. Again the $Al(C_2H_5)Cl_2$ will compete with $Al(C_2H_5)_2Cl$ for active sites until an equilibrium population at these sites is achieved. The variation of k_d is also in agreement with this concept, since the rate of formation of $Al(C_2H_5)Cl_2$ varies with the $Al(C_2H_5)_2Cl$ concentration. Attempts to determine propagation and chain transfer rate constants are in progress.

We were able to calculate $[C_0^*]$, the concentration of initially active centers in butene polymerization terminated with I_2[6] by a modified ultramicro iodine determination[15] which will be described elsewhere. A concentration of 1×10^{-3} mmoles of active centers/mmole $TiCl_3$ was found, a value which is ca. 4 times lower than that found by Caunt[6] for propylene polymerization. We intend to check our result by termination with BuO_3H.

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Résumé

On a comparé les changements relatifs d'activités de polymérisation de l'éthylène, du propylène et du butène-1 dans des polymérisations Ziegler-Natta en utilisant des échantillons de $TiCl_3$ contaminés progressivement avec de l'oxygène et de l'eau. L'épuisement du catalyseur variait pour les trois monomères, ce qui supporte l'existence de différents centres actifs. Dans la polymérisation du butène-1 avec le système $Al(C_2H_5)_2Cl/TiCl_3$, la formation de centres actifs comprend à la fois une réaction irréversible, une réaction réversible (d'adsorption), la première conduisant à la formation de $Al(C_2H_5)Cl_2$ et dépendant de la pureté du $TiCl_3$. Le traitement cinétique des courbes de vitesses suggère un ordre mixte de désactivation du catalyseur et de nouveau souligne l'importance de $Al(C_2H_5)Cl_2$.

Zusammenfassung

Die relative Änderung der Polymerisationsaktivität eines Ziegler-Natta-Katalysators bei der Polymerisation von Äthylen, Propylen und Buten-1 wurde verglichen unter Verwendung einer $TiCl_3$-Probe, die sukzessive mit O_2 und H_2O verunreinigt wurde. Die Verringerung der Katalysatoraktivität, die für die drei Monomeren unterschiedlich gross war, liess die Existenz verschieden aktiver Zentren vermuten. Bei der Polymerisation von Buten-1 mit dem System $Al(C_2H_5)_2Cl/TiCl_3$ wurde gezeigt, dass die Bildung aktiver Zentren in einer irreversiblen und einer reversiblen Reaktion (Adsorption) besteht, und dass bei der irreversiblen Reaktion in Abhängigkeit von der Reinheit des $TiCl_3$ $Al(C_2H_5)Cl_2$ gebildet wird. Die kinetische Auswertung der Geschwindigkeitskurven ergibt eine gemischte Ordnung für die Katalysator-Desaktivierung und lässt wiederum auf den Einfluss von $Al(C_2H_5)Cl_2$ schliessen.

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Influence of Preparative Conditions on Molecular Weight and Stereoregularity Distributions of Polypropylene

R. L. COMBS,* D. F. SLONAKER, F. B. JOYNER, and H. W. COOVER, JR., *Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee*

Synopsis

The influence of preparative conditions on the molecular weight and stereoregularity distributions of polypropylene was investigated. The stereoregularity distribution is narrowed by using a highly stereospecific catalyst, by decreasing the polymerization temperature, and for the three-component catalyst by keeping the mole proportion of the electron-donating third component at 0.5. The molecular weight distribution can be narrowed by using a highly stereospecific catalyst, a high monomer concentration, and a high polymerization temperature, and by having a lower conversion, particularly at low monomer concentration. The possibility of long-chain branching in polypropylene was indicated by data from the fractionation of tritium-labeled polymers.

INTRODUCTION

There have been many papers[1-3] on the influence of catalysts on the molecular structure of polypropylene but only a few[4-7] on the influence of catalysts on the molecular weight distribution. This investigation was concerned with both the molecular weight and the stereoregularity distributions of the polypropylene molecules. The preparation variables studied were monomer concentration, temperature, conversion, and different catalysts having varying stereospecificities. The catalysts studied were $Al(C_2H_5)_3$–α-$TiCl_3$ (hereafter referred to as $TiCl_3$), $Al(C_2H_5)_2Cl$–$TiCl_3$, and $AlC_2H_5Cl_2$–hexamethylphosphoric triamide (HPT)–$TiCl_3$.

EXPERIMENTAL

Preparation Variables

The catalysts studied were $Al(C_2H_5)_3$–$TiCl_3$, $Al(C_2H_5)_2Cl$–$TiCl_3$, and $AlC_2H_5Cl_2$–HPT–$TiCl_3$; the purity of the materials used was described previously.[2] The $TiCl_3$ was obtained from Stauffer Chemical Co. and was hydrogen-reduced (HA), Lot No. HA 71-747. The ratio of the electron-donating third-component, hexamethylphosphoric triamide, to AlC_2-

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* To whom inquiries should be addressed.

H_5Cl_2 was studied in the range of 0.2 to 0.7. The conversion varied from 1 to 64 g. polymer/g. $TiCl_3$. The propylene concentration varied from 0.47 to 2.59 mole/l., in a temperature range of 40–70°C. The apparatus was described previously.[2]

Molecular Weight Distribution

The molecular weight fractionation technique was discussed in previous publications.[8,9] In the molecular weight fractionation, the polymer is extracted continuously above its melting point. The lowest molecular weight molecules are eluted first.

In plots of molecular weight distributions, I is one-half of the weight per cent of the fraction studied plus the sum of the weight per cent of all the preceding fractions. The molecular weight ($\bar{M}_v$) is calculated by using the Kinsinger and Hughes equation[10] and the inherent viscosity of a 0.1% (w/v) solution in Tetralin at 145°C. The molecular weight distribution is best described as a ratio of weight-average molecular weight to number-average molecular weight. This ratio is given the symbol U. U is calculated from a log $\bar{M}_v$ versus I probability plot.[11] The standard deviation of U at a value of 13.4 was found to be 7% of the average value. The larger the value of U, the broader the molecular weight distribution. It should be noted that this definition $U = \bar{M}_w/\bar{M}_n$ is different from that proposed by Schulz;[12] his definition was $U' = (\bar{M}_w/\bar{M}_n) - 1$.

Stereoregularity Distribution

In the stereoregularity fractionation, a chromatographic extraction at increasing temperatures as much below the melting point of the polymer as possible elutes the lowest stereoregular molecules first. A comparison of this technique with the molecular weight fractionation technique is given in Table I. There are some interactions between the stereoregularity and molecular length which influence the results in these two fractionation techniques. These techniques do show, however, different distributions which can be interpreted.

The stereoregularity fractionation procedure is as follows. A 2.000-g. portion of polymer is dissolved in 160 ml. of nitrogen-saturated Tetralin which has been stabilized with 0.1% Santonox R at 170 ± 10°C. The Pyrex fractionation column is 41 mm. o.d. by 950 mm. long. It is filled to

TABLE I

Polypropylene Chromatographic Fractionation

	Fractionation	
	Stereoregularity	Molecular weight
Initial solvent	Tetralin	90/10 Butyl Carbitol/Tetralin
Final solvent	Tetralin	50/50 Butyl Carbitol/Tetralin
Initial temp., °C.	20	165
Final temp., °C.	150	165

within 6.5 in. of the top with 100-μ glass beads (Superbrite No. 130, Minnesota Mining and Manufacturing Co.) and Tetralin is added to occupy the free volume. The column is heated to 150°C. and the polymer solution is added to the 6.5-in.-deep free space at the top. After the polymer solution is digested onto the column, the dissolving flask is rinsed with 40 ml. of Tetralin near 170°C. which is added to the column. The flow is stopped at the bottom of the column, and the column is cooled to room temperature with cold water. The desired temperature and time programs for the fractionation are established on the control unit. The fractionation is started by connecting the top of the column to a Tetralin reservoir and allowing the Tetralin to flow through the column continuously. A heated capillary is used at the bottom of the column for flow control. Fifteen fractions are collected stepwise at increasing temperatures in 1-liter beakers. Approximately 600-ml. portions of solvent are collected at each temperature when the fractionation is complete, and a volume of acetone 1.5 times the amount of solvent collected is added to each portion to precipitate the polymer. After standing overnight, each fraction is filtered in a sintered glass funnel. The residual polymer is washed at least twice with acetone and then stabilized by saturating with a 0.1% solution of Santonox R. The antioxidant solvent is allowed to evaporate, and the polymer fractions are then dried at 50°C. for at least 6 hr. at less than 3 mm. Hg pressure. The fractions are then weighed and removed from the funnels.

In stereoregularity distributions, S is the sum of the weight per cent of all preceding fractions and the weight per cent of the fraction being measured. The melting point is defined as the temperature at which the last crystalline phase disappears; it is measured by using polarized light on a hot stage microscope and a heating rate of 1°C./min. Although this melting point could be altered by subjecting the fractions to grossly different thermal histories, the melting point values of the fractions in the normal form of precipitated powder were quite reproducible. The experimental error in terms of an average 2σ limit for fractions was found to be $\pm 1.6\%$ of the actual melting point value. The melting points obtained in the manner described were converted into percentage stereoregularity of the polymer molecules by using Flory's equation:[13]

$$-(R/\Delta H) \ln (\omega/100) = (1/T_m) - (1/T^\circ_m) \qquad (1)$$

where R is the gas constant, $\Delta H = 2600$ cal./mole, T_m is the melting point of the fraction, $T^\circ_m = 170$°C. (443°K.), and ω is the percentage stereoregularity. To establish the overall reproducibility of the fractionation method in establishing the stereoregularity distribution curve, analyses were done on duplicate samples in which the pellets from sample A were split in half to give samples A-1 and A-2. The average standard deviation for any given point on the curve was found statistically to be 1°C. This reproducibility was adequate to detect significant differences in the distribution of melting points of different pellets which were sampled from the same container of a commercial film-grade polypropylene. The molecular weight, as indicated by the inherent viscosity, as well as the melting point varied in these fractions. With the exception of the most soluble, low-melting first fraction, which had an inherent viscosity of about 0.7, the inherent viscosities of the fractions increased from 0.3 to 3.5 as the melting points increased. This relationship of the high-melting fractions having the highest inherent viscosities was not changed by degradation of these materials to a lower average inherent viscosity. Results obtained from using this fractionation technique will be discussed more fully in a later paper. The crystallinity index[1] is a measure of the average stereoregularity and is the percentage of the polypropylene which is insoluble in refluxing 4-methyl-2-pentanone.

Studies of Radioactive Polypropylene

The techniques used in the investigation of radioactive polypropylene were described previously.[3] $\bar{M}_t$ is the molecular weight calculated from the radioactivity of the sample. This calculation is based on the assumptions that every polymer molecule has one metal–carbon bond and that the isotope effect (rate of hydrogen reaction/rate of tritium reaction = 1.56) is not affected by the molecular weight of the polymer molecule attached to the metal atom. The isotope effect was determined by splitting the radioactive polymer prepared in a single preparation into four batches. Two of these batches were deactivated in the normal manner. The other two batches were deactivated slowly over a 15-min. period and the results obtained are shown in Table II.

TABLE II

Deactivation	Radioactivity, μc./mg.
Normal	2.70×10^{-3}
Normal	2.23×10^{-3}
Equilibrium	4.18×10^{-3}
Equilibrium	3.50×10^{-3}

The isotope effect (1.56) calculated from these results is similar to that (1.3) found by Kohn and co-workers[14] using similar techniques. The inherent viscosities of the radioactive fractions were determined on smaller than normal samples (5 mg. rather than 50 mg.).

RESULTS AND DISCUSSION

Stereoregularity Distribution

Figure 1 shows the stereoregularity distributions for polypropylenes prepared with the three catalysts studied. The higher the stereospecificity of the catalyst the narrower the stereoregularity distribution. The crystallinity indexes of the polymers are given in Figure 1 for comparison.

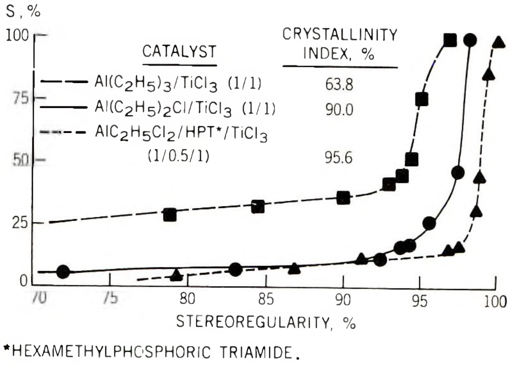


Fig. 1. Effect of catalyst on stereoregularity distribution.

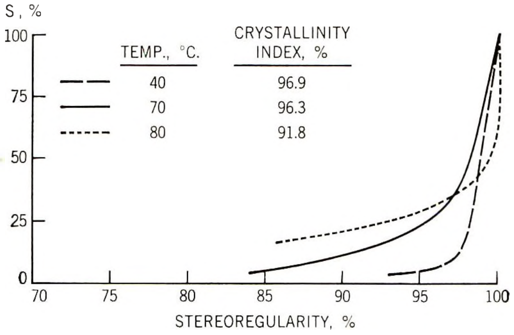


Fig. 2. Effect of temperature on stereoregularity distribution.

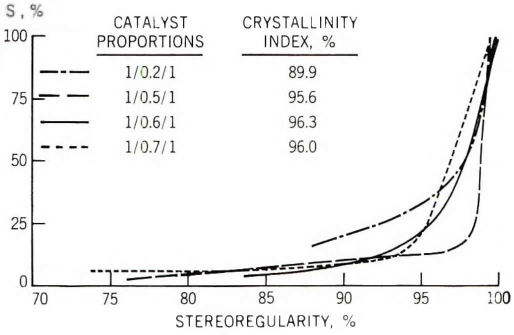


Fig. 3. Effect of third component of $AlC_2H_5Cl_2$–HPT–$TiCl_3$ catalyst on stereoregularity distribution.

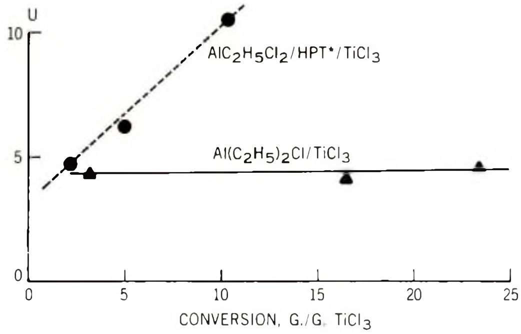
The effect of polymerization temperature on the stereoregularity distribution of polypropylene prepared with the three-component catalyst is illustrated in Figure 2. Lowering the temperature narrows the distribution and increases the crystallinity index.

The narrowest stereoregularity distribution is shown by polymer prepared with the three-component catalyst having an HPT/$AlC_2H_5Cl_2$ ratio of 0.5 (Fig. 3). The distribution is broader when this ratio is increased or decreased. This indicates that the catalyst producing the polymer having the narrowest stereoregularity distribution is composed of $AlC_2H_5Cl_2$–HPT–$TiCl_3$ in mole proportions of 1/0.5/1.

Conversion has only a minor effect on the stereoregularity distribution of polymers prepared with the three-component catalyst. There are indications that the higher the conversion the narrower the distribution, although the crystallinity index of the low-conversion polymer is slightly higher than that of the high-conversion polymer. Monomer concentration appears to have little or no influence on the stereoregularity distribution.

Molecular Weight Distribution

The influence of the preparation variables on the molecular weight distribution of polypropylene may be seen from Table III. At the higher monomer concentration, the molecular weight distribution decreases as the catalysts increase in stereospecificity (Table III, runs a, b, and g). These data are not in agreement with those of Hirooka et al.,[4] who used a higher monomer concentration and hydrogen as a chain-transfer agent for the $Al(C_2H_5)_2Cl$–$TiCl_3$ catalyst system. Also, these investigators probably went to high conversion, although this was not discussed. They found that the addition of a third component to the $Al(C_2H_5)_3$–$TiCl_3$ and to the $Al(C_2H_5)_2Cl$–$TiCl_3$ catalyst systems did not influence the molecular weight distribution of the polymer greatly. It should be pointed out that no chain-transfer agents were added to our systems, and the catalysts were compared under substantially the same conditions.



*HEXAMETHYLPHOSPHORIC TRIAMIDE.

Fig. 4. Effect of conversion on molecular weight distribution ([M] = 0.47 mole/l.).

In this investigation the monomer concentration was found to influence the molecular weight distribution of the polymers; whereas, Chien[7] reported that it did not. This is evident from Table III if one compares runs d and b for the $Al(C_2H_5)_2Cl$–$TiCl_3$ catalyst system at high conversion, and runs f and c for the same catalyst system at low conversion. The in-

TABLE III

Effect of Preparation Variables on the Molecular Weight Distribution

Run	Catalyst	Temp., °C.	Monomer concn.		Conversion, g./g. $TiCl_3$	$\{\eta\}^a$	U
			Mole/l.	Psig			
a	$Al(C_2H_5)_3–TiCl_3$[b]	70	1.39	40	21.7	2.05	41.0
b	$Al(C_2H_5)_2Cl–TiCl_3$[b]	70	1.39	40	57.7	2.90	5.9
c	$Al(C_2H_5)_2Cl–TiCl_3$[b]	70	1.39	40	5.1	2.00	3.9
d	$Al(C_2H_5)_2Cl–TiCl_3$[b]	70	0.47	10	23.3	1.85	4.7
e	$Al(C_2H_5)_2Cl–TiCl_3$[b]	70	0.47	10	16.4	1.87	4.2
f	$Al(C_2H_5)_2Cl–TiCl_3$[b]	70	0.47	10	3.2	1.38	4.4
g	$AlC_2H_5Cl_2$–HPT–$TiCl_3$[c]	70	1.39	40	64.2	4.25	5.4
h	$AlC_2H_5Cl_2$–HPT–$TiCl_3$[c]	70	1.39	40	5.2	3.20	3.8
i	$AlC_2H_5Cl_2$–HPT–$TiCl_3$[c]	70	0.47	10	10.3	2.38	10.5
j	$AlC_2H_5Cl_2$–HPT–$TiCl_3$[c]	70	0.47	10	5.0	1.70	6.2
k	$AlC_2H_5Cl_2$–HPT–$TiCl_3$[c]	70	0.47	10	2.2	1.74	5.0
l	$AlC_2H_5Cl_2$–HPT–$TiCl_3$[c]	40	1.10	10	1.0	3.97	30.0
m	$AlC_2H_5Cl_2$–HPT–$TiCl_3$[c]	80	1.01	40	29.0	2.72	2.0
n	$AlC_2H_5Cl_2$–HPT–$TiCl_3$[c]	70	1.39	40	33.0	3.61	2.0
o	$AlC_2H_5Cl_2$–HPT–$TiCl_3$[c]	60	1.78	40	26.0	4.00	3.0
p	$AlC_2H_5Cl_2$–HPT–$TiCl_3$[c]	40	2.59	40	17.0	5.34	8.0

[a] $\{\eta\}$ = inherent viscosity of a 0.1% (w/v) Tetralin solution at 145°C.

[b] Mole ratio of 1/1.

[c] Mole proportions of 1/0.6/1.

fluence of monomer concentration for the catalyst system $AlC_2H_5Cl_2$–HPT–$TiCl_3$ may be seen at high conversion by comparing runs i and g, and at low conversion by comparing runs j and h. At low conversion, increasing the monomer concentration decreases the distribution. This indicates that the monomer is a chain-transfer agent which narrows the molecular weight distribution.

The conversion or the concentration of the dead or nongrowing polymer molecules influences the distribution as shown in Figure 4. At low monomer concentration the U value of polymer prepared with the three-component catalyst increases greatly as the conversion increases. However, at higher monomer concentration, conversion appears to have less influence (Table III, runs g and h) and appears to have little or no influence on the U value of polymer prepared with the $Al(C_2H_5)_2Cl$–$TiCl_3$ catalyst. This influence of conversion is most easily explained by the chain-transfer reaction previously proposed [eq. (2)]:[3]

$$Ti^*Cl_3(AlX_2P) + AlX_3 + C_3H_6 \rightarrow Ti^*Cl_3(AlX_3) + AlX_2C_3H_6P \qquad (2)$$

where X is an alkyl or halogen group, P is the polymer chain, and Ti* is the active site. Thus, the dead polymer molecules, which are $AlX_2C_3H_6P$ at high conversion, evidently slow down the chain-transfer reaction.

Our results for increasing temperature agree with those reported by Chien.[7] As the temperature increases, a decrease in U indicates that more chain transfer occurs at the higher temperatures. The decrease in U is illustrated in Table III by runs l and k for low monomer concentrations and by runs m–p for high monomer concentrations. The distributions at low monomer concentrations were measured at low conversion to eliminate the effect of conversion. The broadening of the molecular weight distribution due to decreasing temperature is even larger than indicated in runs l and k, since the increase in monomer concentration tends to reduce this distribution.

Studies of Radioactive Polypropylene

According to eq. (2), the chain-transfer equation, there are at least two types of metal–polymer bonds in the polymerization system. One type is present at the active site and the other at the dead polymer molecule which has been transferred from the active site. If this system is treated with tritiated methanol, both active and dead polymer molecules will be labeled with a tritium atom. This technique was used to calculate the number of active sites.[3] Four of these radioactive polymers prepared to high and low conversions with the monochloride, and the three-component catalyst systems were fractionated on a molecular weight basis.

The fractionation results for the polypropylene prepared to high conversion with the three-component catalyst are given in Figure 5. I is plotted on a normal probability scale. The molecular weight is plotted on a log scale and is calculated by two methods. $\bar{M}_v$ is the molecular weight calculated from the inherent viscosity in Tetralin at 145°C. by using the

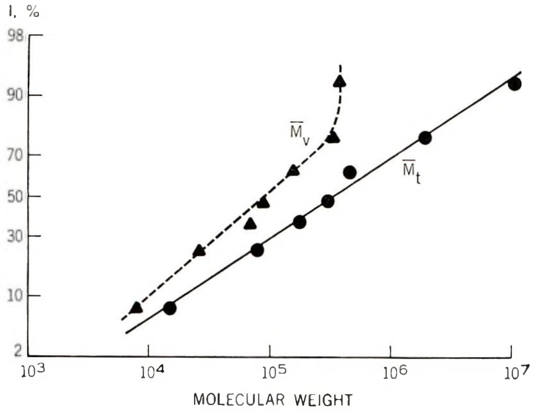


Fig. 5. Molecular weight distribution of high-conversion polypropylene (8.8 g./g. $TiCl_3$) with $AlC_2H_5Cl_2$–HPT–$TiCl_3$(1/0.6/1) at 70°C. (0.47 mole propylene/l.).

Kinsinger-Hughes equation:[10] ($\{\eta\} = 1.38 \times 10^{-4}M^{0.80}$). $\overline{M}_t$ is the molecular weight calculated from the radioactivity of the fraction by assuming that every polymer molecule has a metal–carbon bond, and that the isotope effect (1.56) is not affected by the molecular weight of the polymer molecule. It is evident that one of these assumptions is incorrect or that there is some other effect causing the difference between $\overline{M}_v$ and $\overline{M}_t$ shown in Figure 5. It should be noted that these lines diverge as the molecular weight increases. A possible explanation of this difference could be that the inherent viscosity-molecular weight relationship used was incorrect. The equation necessary to bring these two lines together would have a slope of 0.65 ($\{\eta\} = 3.98 \times 10^{-4}M^{0.65}$). This slope is outside the range of 0.77–1.0 found by four other investigators[15] for solvents (Decalin and Tetralin) and temperature (135°C.) similar to those we used, and thus this does not appear to be a likely explanation for the divergence. Other explanations such as long-chain branching and another chain-transfer reaction are discussed later.

The upturn in the $\overline{M}_v$ curve (Fig. 5) at the high molecular weight end has been observed before, and several explanations have been proposed.[9] Among these explanations are inefficient fractionation at the high molecular weight end and termination of the high molecular weight molecules by a different mechanism. Degradation has also been suggested as an explanation of this upturn. In these fractionations, however, the sum of the weight per cent of each fraction times this fraction's inherent viscosity gave no indication of degradation when compared with the original inherent viscosity of the whole polymer except in the following case. In Figure 6 the same type curves are given for the polypropylene prepared to low conversion with the three-component catalyst. In this case, there is no upward curvature in the $\overline{M}_v$ line, but the lines are diverging. The experimental error for these radioactive fractionations is larger than that for the standard fractionations since the inherent viscosities were deter-

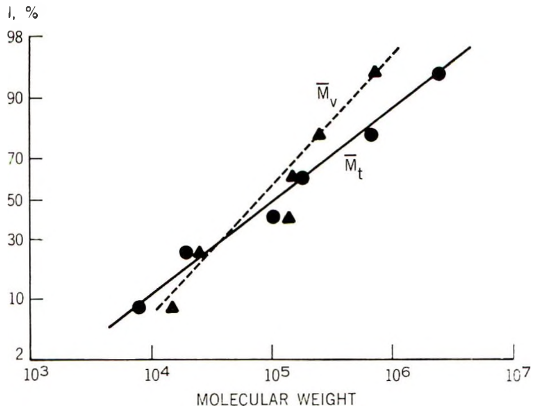
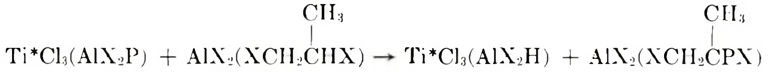


Fig. 6. Molecular weight distribution of low-conversion polypropylene (2.15 g./g. $TiCl_3$) with $AlC_2H_5Cl_2$–HPT–$TiCl_3$ (1/0.6/1) at 70°C. (0.47 mole propylene/l.).

mined on smaller samples. The $\bar{M}_v$ curve for polypropylene prepared to high conversion (23.3 g./g. $TiCl_3$) with the monochloride catalyst also has an upward curvature, while once again the $\bar{M}_t$ curve is a straight line. The curves for polypropylene prepared to low conversion (3.24 g./g. $TiCl_3$) with the monochloride catalyst represent the only fractionation which had curvature in both lines, and this curvature could be due to inefficient fractionation or degradation. In only this one case the sum of the weight per cent of each fraction times this fraction's inherent viscosity (1.06) was lower than the original inherent viscosity (1.20) of the whole polymer. For both of these polymers there was a divergence of the $\bar{M}_v$ and $\bar{M}_t$ lines with increasing molecular weight.

In two cases, both with high conversion polymers, there was an upward curvature in the $\bar{M}_v$ line and no curvature in the $\bar{M}_t$ line. These two cases cannot be explained as inefficient fractionation or a different termination mechanism. The most likely explanation is that when prepared to high conversion the high molecular weight molecules have long-chain branching which gives them the same solution viscosity as a more linear molecule of a lower molecular weight. This would affect the calculation of $\bar{M}_v$ but not that of $\bar{M}_t$.

Three possible explanations of the divergence of the $\bar{M}_v$ and $\bar{M}_t$ lines observed in all four fractionations are considered. If the isotope effect were a function of the polymer molecular weight and if the tritium isotope reacted slower, proportional to this molecular weight, than the hydrogen isotope then the observed divergence would be explained. This explanation, however, appears unlikely. It has also been suggested[16] that when the tritiated agent is added, it reacts preferentially with the alkyl aluminum compounds in solution, and then it reacts with the more available portions of the solid. During this time, the hydrogen isotope is reacting faster than the tritium isotope (probably three times as fast, not the observed average of 1.56). Thus, the last portions of the solid to react will be the most highly tritiated. These portions could also have the lowest molecular weight because of difficulty in the diffusion of the monomer to the most unavailable site. This explanation, using a different isotope effect for different active sites, would explain the divergence but not the sharp upturn in the $\bar{M}_n$ curve for high-conversion polymers. A possible method of confirming this proposed mechanism would be the use of iodine labeling. As a second possibility, there could be another chain-transfer reaction or a termination reaction which does not leave a metal–carbon bond on the dead polymer molecule. In order to explain the results observed, however, this reaction would have to be a function of the polymer molecular weight. Several chain-transfer reactions with monomer, with monomer plus the titanium compound, and with other metal alkyls have been proposed.[17] None of these, however, has been suggested to be a function of the length of the polymer chains. If there were another chain-transfer or termination reaction which did not leave a metal–carbon bond and which was not a function of the polymer chain length, parallel lines would be expected rather than the diverging lines observed. In the kinetic studies[3] the amount of chain transfer was found to decrease with conversion. However, the divergence was observed at both high and low conversions, and thus the chain-transfer reaction must still be a function of the molecular weight in order to explain the results. As a third possibility, a long-chain-branching reaction is proposed [eq. (3)].



$$\mathrm{Ti^{*}Cl_3(AlX_2P) + AlX_2(XCH_2\overset{CH_3}{\overset{|}{C}}HX) \rightarrow Ti^{*}Cl_3(AlX_2H) + AlX_2(XCH_2\overset{CH_3}{\overset{|}{C}}PX)} \qquad (3)$$

This reaction does not give another metal–carbon bond in the polymer chain. The rate of the reaction is proportional to the number of tertiary carbon atoms and consequently to the molecular weight of the dead polymer molecule. Thus, long-chain branching in the polypropylenes investigated could explain both the divergence of the $\bar{M}_n$ and $\bar{M}_t$ fractionation curves as well as the sharp upturn in the $\bar{M}_n$ curve with high-conversion polymers. This appears to be the most likely explanation of these fractionation results on the radioactive polymers.

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Résumé

On a étudié l'influence des conditions de synthèse sur la distribution des poids moléculaires et de la stéréorégularité du polypropylène. La distribution de la stéréorégularité devient plus étroite lorsque l'on utilise un catalyseur hautement périodique, lorsque l'on décroit la température de polymérisation et pour les systèmes catalytiques a trois composants lorsque l'on tient le rapport molaire du troisième composant électrodonneur a 0.5. On peut diminuer la largeur de la distribution des poids moléculaires en utilisant un catalyseur hautement stéréospécifique, à une concentration en monomère élevée et une température de polymérisation élevée, et en se limitant à de faibles taux de conversion. Ceci en particulier lorsque la concentration en monomère est basse. On a quelques indications relatives à une possibilité de branchement à longue chaine dans le cas du polypropylène grâce à des fractionnements de polymères marqués au tritium.

Zusammenfassung

Der Einfluss der Darstellungsbedingungen auf Molekulargewichts- und Stereoregularitätsverteilung von Polypropylen wurde untersucht. Die Stereoregularitätsverteilung wird durch Verwendung eines hochstereospezifischen Katalysators, durch Herabsetzung der Polymerisationstemperatur und beim DreiKomponenten-Katalysator durch Einhalten eines Molverhältnisses 0,5 für die dritte Elektronendonatorkomponente verengt. Die Molekulargewichtsverteilung kann durch Verwendung eines hochstereospezifischen Katalysators, eine hohe Monomerkonzentration und eine hohe Polymerisationstemperatur sowie, besonders bei niedriger Monomerkonzentration, durch Einhalten eines niedrigen Umsatzes verengt werden. Fraktionierungsergebnisse an tritiummarkierten Polymeren liessen das Auftreten einer Langkettenverzweigung bei Polypropylen als möglich erscheinen.

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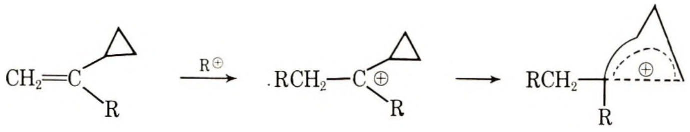
NOTES

Rearrangements of the Propagating Chain End in the Cationic Polymerization of Vinylcyclopropane and Related Compounds

The polymerization of vinylcyclopropane and some of its derivatives by Ziegler-Natta catalysts and by free-radical initiators has been described in some detail.[1-5] There has, however, been only one brief reference to the cationic polymerization of these materials.[5]

Polymerization initiated by Friedel-Crafts reagents is of particular interest because the initially formed cyclopropyl carbinyl cation which constitutes the propagating chain end will rearrange to the nonclassical, resonance-stabilized bicyclobutonium ion or, alternatively, be in equilibrium with a number of rapidly interconverting classical carbonium ions.[6] However, since the initially formed cyclopropyl carbinyl cation is, of necessity, either a secondary or tertiary carbonium ion, the major contributing canonical structure in the resonance hybrid would be expected to be that in which the charge is localized mainly on the α-carbon. Thus the ion formed in the cationic polymerization of vinylcyclopropane itself is probably similar to that formed in the reaction of 1-cyclopropylethanol with acidic methanol which, because of the rapid rate, is assumed to involve a bicyclobutonium ion yet yields an unrearranged product.[7] Likewise the rapid solvolysis of phenyl cyclopropylcarbinyl *p*-nitrobenzoate[8] and of dicyclopropyl carbinyl *p*-nitrobenzoate[9] lead exclusively to unrearranged products. On the basis of electronic considerations alone, therefore, we would expect vinylcyclopropane and its 1-alkyl and 1-aryl derivatives to yield unrearranged polymers with the cyclopropyl rings as pendant groups on the chain.



However, it is extremely unlikely that such polymers can exist, except in the case of polyvinylcyclopropane itself, due to the great steric compression between these pendant groups.[10] Recently there have been a number of examples of polymerizations in which rearrangement of a secondary to a more stable tertiary carbonium ion occurs in the propagation step.[11-13] In all of these, relief of steric strain is probably also a driving force. Relief of steric strain in the case of vinylcyclopropane polymerization, on the other hand, could only arise by attack of the incoming monomer unit on one of the electronically less favored positions of the bicyclobutonium ion.

We have polymerized vinylcyclopropane, 1,1-dicyclopropylethylene, and a number of α-cyclopropylstyrenes at −78° with $AlBr_3$ catalyst in dry ethyl chloride as solvent. In all cases, > 90% yields of polymer were obtained in 15 min. The polymers were precipitated by addition of their solutions to methanol and dried under vacuum. Molecular weights ranged from 4000–16,000.* Structures for these polymers are proposed on the basis of infrared and PMR spectra.

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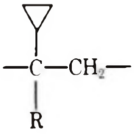
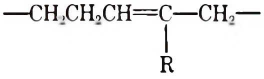
* Number-average molecular weights, determined using a Mechrolab Vapor Pressure Osmometer.

Table I shows the integral data for PMR signals arising from aromatic, vinyl, saturated (including allylic and cyclobutyl), and cyclopropyl protons. On the basis of this data the contributions of the structures:

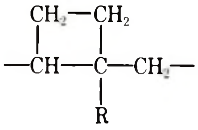


I



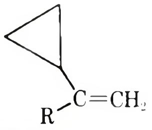
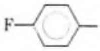
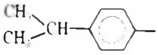
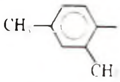
$$-CH_2CH_2CH{=}\underset{\displaystyle R}{\underset{|}{C}}-CH_2-$$

II



III

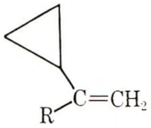
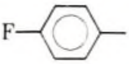
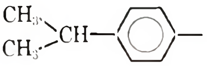
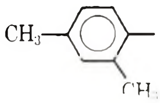
TABLE I
PMR Spectra[a] of Polymers Obtained from 1-Alkyl and 1-Aryl-1-cyclopropylethylenes

	Integral ratios for various types of protons			
	Aromatic	Vinyl	Saturated CH_2 + allylic + cyclobutyl	Cyclopropyl
R = H	—	1.0 (4.6τ)	31 (5–9.1τ)	12.5 (>9.1τ)
	—	1.0 (4.2τ)	17.5 (5–9.0τ)	27.5 (>9.0τ)
	7.6 (3–3.5τ)	1.0 (4.6τ)	11.0 (5–9.3τ)	1.5 (>9.2τ)
	1.9 (3–3.5τ)	0.0	7.7 (5–9.0τ)	0.0 (>9.0τ)
	4.4 (3–3.5τ)	1.0 (4.8τ)	19.7 (5–9.0τ)	0.0 (>9.0τ)

[a] Spectra obtained in perchlorobutadiene at 190°. Tetramethylsilane reference. Varian A-60A instrument.

have been calculated (Table II). Qualitative confirmations of the structures were obtained by the presence or absence of infrared absorptions at 1015 cm.$^{-1}$ and 1045 cm.$^{-1}$ (cyclopropyl),[14] at 915 cm.$^{-1}$ and 1235 cm.$^{-1}$ (cyclobutyl),[15] and 1620–1630 cm.$^{-1}$ (C=C stretching).

TABLE II
Relative Contributions of Unrearranged and Rearranged Structures in Polymer Chains

	R=	H				
Structure	I	60	73	20	0	0
	II	10	27	50	0	60
	III	30	0	30	100	30

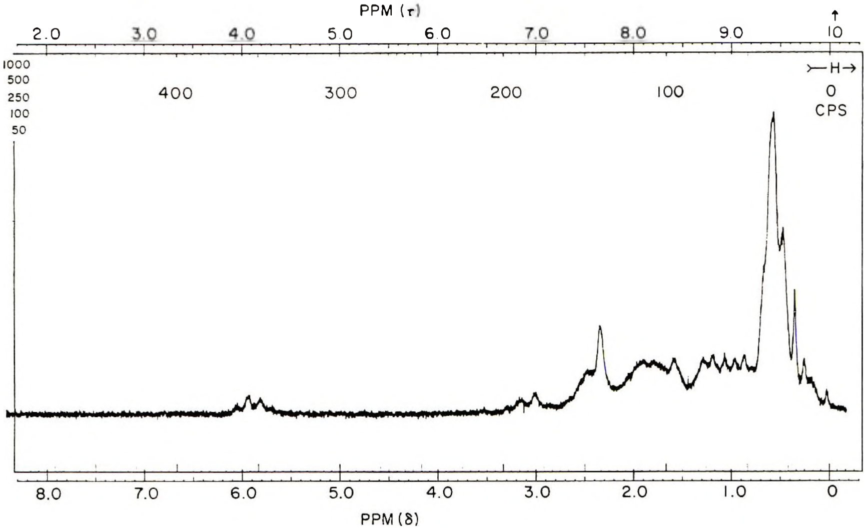


Fig. 1. The PMR spectrum of the polymer of 1,1-dicyclopropylethylene.

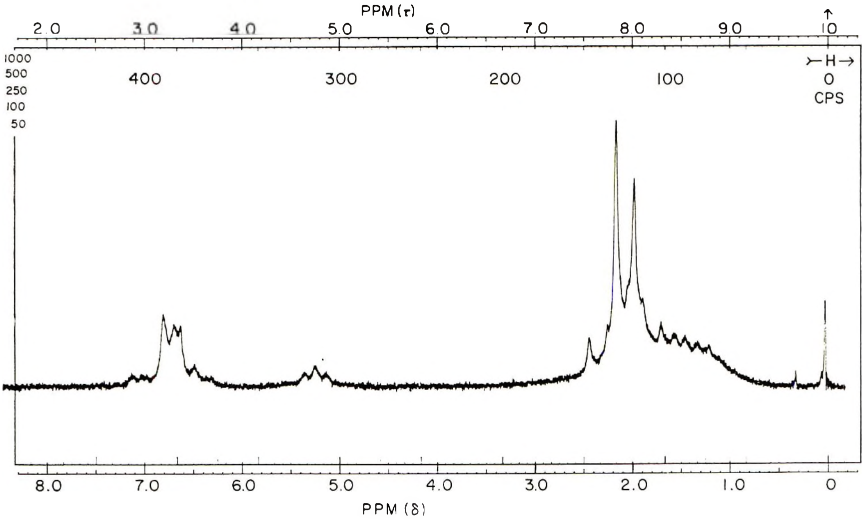


Fig. 2. The PMR spectrum of the polymer of 1-(2,4-dimethylphenyl)-1-cyclopropylethylene.

In the polymers from vinylcyclopropane and 1,1-dicyclopropylethylene a major portion of the cyclopropyl groups remain intact as shown by the large absorptions at $> 9\tau$ in the PMR spectrum (Fig. 1). In the aryl-substituted compounds the cyclopropyl groups are largely or wholly destroyed, the PMR spectra showing little or no absorption at $< 9\tau$ (Fig. 2). Apparently, the most likely point of attack of the incoming monomer upon the bicyclobutonium ion will depend both the charge distribution in the ion and the steric factors. Thus 1,1-dicyclopropylethylene gives a less rearranged polymer than vinylcyclopropane despite the difficulty of incorporating a *gem*-dicyclopropyl group in the chain. Here, the charge density on the α-carbon compensates for the steric interaction. When the α-hydrogen or cyclopropyl is replaced by an aryl substituent, especially aryl groups carrying bulky substituents such as isopropyl, the steric interactions involved in adding the monomer unit to the α-carbon of the chain end become so great that addition to some other position of the bicyclobutonium must take place if propagation is to proceed.

Whether the incoming monomer will attack the methylene position of the bicyclobutonium ion to give II or the methinyl position to give III will probably depend upon the conformation of this ion with respect to that of the pendant group in the penultimate chain unit. At present, our data do not allow us to predict which mode of attack will be most likely for a given monomer.

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A. D. Ketley
A. J. Berlin
L. P. Fisher

Washington Research Center
W. R. Grace & Co.
Clarksville, Maryland 21029

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Direct Determination of ε-Caprolactam in the Presence of Nylon 6 and Its Oligomers by Infrared Spectroscopy

Introduction

Rapid determination of the monomer (ε-caprolactam) and oligomer content in nylon 6 is quite necessary for the study of ε-caprolactam polymerization and/or quality control of nylon 6. The methods described in the literature are time-consuming indirect determinations, generally based on weight differences, and requiring the extraction of the monomer and the oligomers with hot water from the sample, followed by drying of the residue. Recently Bukač et al.[1] determined the equilibrium content by ultraviolet and infrared spectroscopy, based on the estimation from the difference in results between the per cent of the water extractables and the per cent of the monomer obtained by UV and IR. As the key bands of the monomer, the absorption bands at 870 cm.$^{-1}$ (IR) and 196 mμ (UV) were used. Anton[2] reported the direct determination of the cyclic oligomer content in the presence of the monomer by infrared spectroscopy. This method involves evaporation of the water extract of nylon 6 and dissolving the residue in tetrafluoropropanol, followed by determination of the absorbance at 6.4 μ due to NH deformation of the oligomers.

In this paper the rapid direct determination of the monomer in nylon 6, without any extraction of the sample, is described. In this method, the sample is dissolved in *o*-chlorophenol, and the absorbance at 892 cm.$^{-1}$ is determined by the base-line method. The band at 892 cm.$^{-1}$ is the key band of ε-caprolactam. The reproducibility of this method is about ± 1.4% as a relative error. The oligomer content of the sample is estimated by knowing the per cent of the dimethyl sulfoxide extractable and the per cent of the monomer in the original nylon 6.

Experimental

Instrument. Infrared spectra were measured with a Nihon-Bunko Model IR-S double-beam infrared spectrophotometer equipped with KBr optics. Quantitative measurements were taken at the following instrument settings: power 4 (0.95 A.), sensitivity 70, wave number expansion × 2, transmittance range expansion × 5, and medium speed. Two matched potassium bromide sealed cells with a spacing of 25 μ were used in the analysis.

Material. ε-Caprolactam was refined by redistillation. Cyclic dimer, trimer, and tetramer standards were obtained by the usual method. Melting points of the monomer, trimer, and tetramer were 68.4, 236.2, and 259.8°C., respectively, and these materials were confirmed to be pure substances.[3,4] Cyclic dimer was also certified by paper chromatography. The nylon 6 used for the construction of a calibration curve was extracted with water at 95°C. for 24 hr., and then dried in a vacuum oven at 100°C., for 24 hr. *o*-Chlorophenol was reagent grade, and dimethyl sulfoxide was redistilled.

Infrared Spectra. Infrared spectra of the monomer, the dimer, the trimer, the tetramer, and the polymer (nylon 6) were measured by the KBr pressed disk technique. A calibration curve was constructed by dissolving 100 mg. of the mixtures of the monomer and the nylon 6, in which the oligomers were extracted, into 1 ml. of *o*-chlorophenol in 10-ml. glass-stoppered Erlenmeyer flasks. The solution was injected into the sealed KBr cell and the infrared spectra were recorded between 1000 cm.$^{-1}$ and 700 cm.$^{-1}$ with *o*-chlorophenol in the reference cell. The absorbance at 892 cm.$^{-1}$ was determined by the base-line method.

Polymerization of ε-Caprolactam. ε-Caprolactam polymerization was carried out at 235 ± 2°C. by controlling water content of the caprolactam to 0.388 wt.-%, and sealing it in an ampule after flushing air with nitrogen. Polymerization time of the samples was 2 to 7.5 hr., and the six samples of different polymerization times were prepared.

Determination of the Monomer in Nylon 6. For analyzing the monomer content in the caprolactam polymerizates shown in the previous section, a 100-mg. quantity of the sample was dissolved into 1 ml. of *o*-chlorophenol in a 10-ml. glass-stoppered Erlenmeyer flask, and the infrared spectrum was recorded according to the previous instuctions. The per cent of the monomer in the sample was determined by means of the calibration curve.

For determining the monomer and oligomer content in the samples, a 2.0-g. quantity of the sample was dissolved in 20 ml. of dimethyl sulfoxide in a 100-ml. Erlenmeyer flask with a reflux condenser, and then the mixture was heated for 10 min. After cooling to room temperature, it was transferred to a 1-liter beaker containing 500 ml. of hot water at about 90°C., and extracted by shaking intermittently on a water bath at 90°C. for 20 min. The solution was then filtered through a sintered glass filter 1G-3 and the residue was collected and dried in a vacuum oven at 60–80°C. for 24 hr. The per cent of the monomer and the oligomers in the sample was determined by the following relationship:

$$\%\text{ monomer and oligomers in the sample (w/w)} =$$
$$100\cdot\frac{[\text{wt. extractables (g.)}] - [\text{wt. sample taken (g.)}][\text{H}_2\text{O content in the sample }(\%)/100]}{[\text{wt. sample taken (g.)}]\ [100 - \text{H}_2\text{O content in the sample }(\%)]}$$

Results and Discussion

The infrared spectra in the region of 1800 cm.$^{-1}$ to 400 cm.$^{-1}$ of the monomer, the oligomers, and the polymer are shown in Figure 1. The spectrum of the tetramer is the

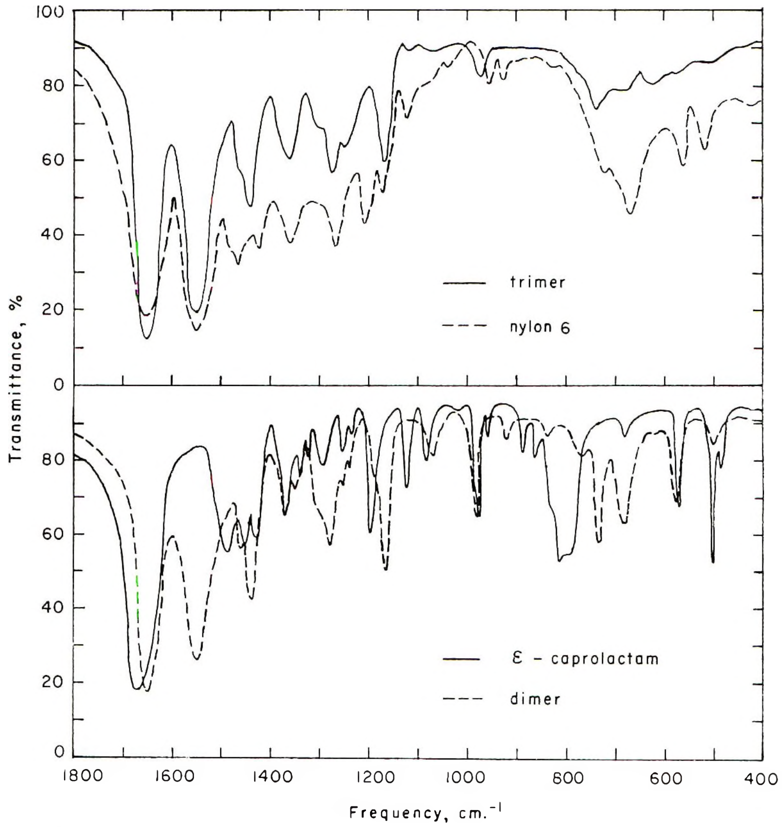

Fig. 1. Infrared spectra of ε-caprolactam, dimer, trimer, and nylon 6. (KBr pellet.)

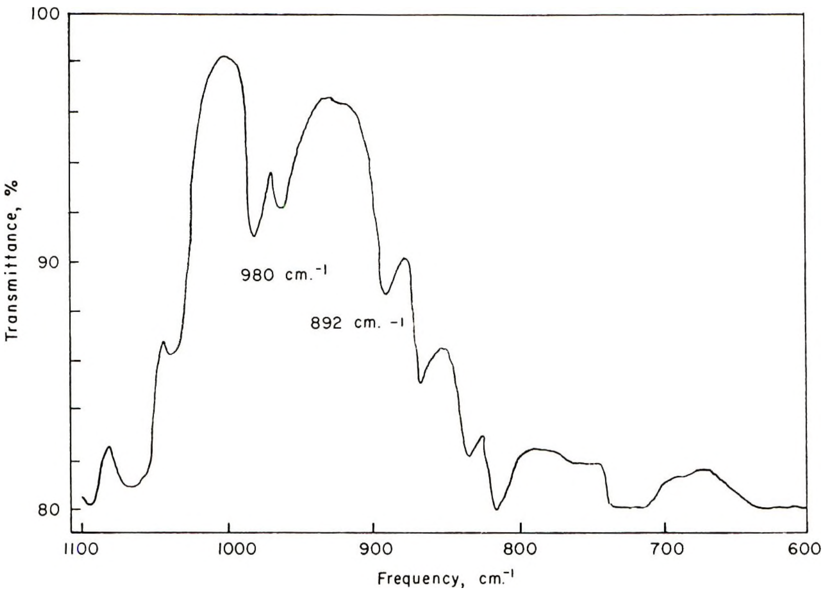

Fig. 2. Infrared spectrum of ε-caprolactam and nylon 6 in *o*-chlorophenol; concentration: ε-caprolactam 8%, nylon 6 2%. Spectrum of the solvent is compensated.

same as that of the trimer. Comparing with these spectra, it is possible to select key bands from the bands at 1484 cm.$^{-1}$, 892 cm.$^{-1}$, 867 cm.$^{-1}$, 824 cm.$^{-1}$, 805 cm.$^{-1}$, or 488 cm.$^{-1}$ of the monomer, it is discriminated from the oligomers and the polymer; the band at 745 cm.$^{-1}$ of the dimer and those at 578 cm.$^{-1}$ and 523 cm.$^{-1}$ of the polymer are the key bands; the monomer does not have such a band at 1170 cm.$^{-1}$ of the oligomers

TABLE I
Precision and Accuracy of Direct Infrared Determination of Monomer in the Presence of Nylon 6

	Monomer concentration, %					
	Precision of cal. curve		Replicability		Reproducibility	
	Theoretical	Observed	Theoretical	Observed	Theoretical	Observed
	50	50	80	78	80	83
	60	59	80	81	80	80
	70	71	80	79	80	79
	80	79	80	80	80	82
	90	88	80	81	80	81
	100	101				
Mean				79.8		81.0
Standard deviation		1.1		1.0		1.3
t Value		0.19				
Relative error				±1.1		±1.4

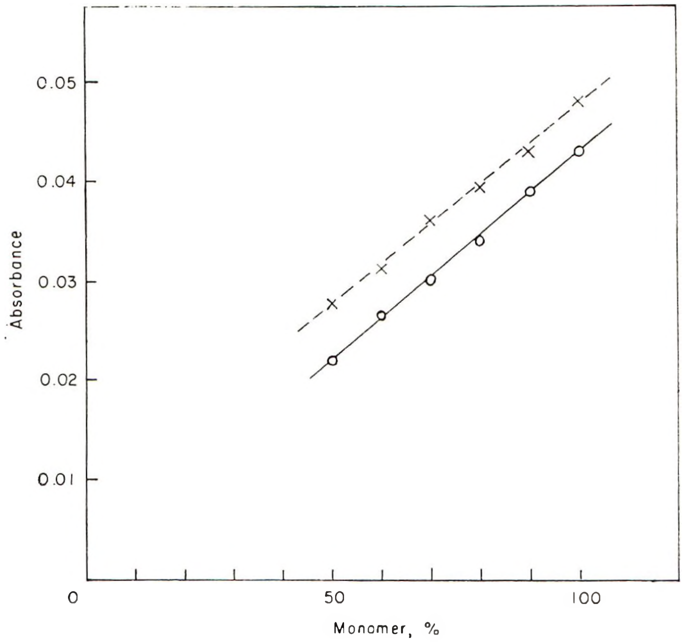

Fig. 3. Calibration curve for determination of monomer of nylon 6: (X) 892 cm.$^{-1}$ band; (O) 980 cm.$^{-1}$ band.

and the polymer. *o*-Chlorophenol is transparent at 920–860 cm.$^{-1}$ where the band at 892 cm.$^{-1}$ of the monomer can be used as the key band, whereas the cyclic oligomers and the polymer do not give such a band in that region (Fig. 2).

The accuracy of the method was determined by testing the precision of the calibration curve (Fig. 3) by means of the Youden method.[5] The statistical *t* value between the theoretical and the observed values indicates that this method is not significant at the 5% level of significance and that this is an accurate and precise method. Reproducibility and replicability of the method were also determined by analyzing the same five concentration samples of known weight of the monomer mixed with known weight of the polymer. The relative precision and accuracy of the method are indicated in Table I.

TABLE II
Comparison of the Infrared and Dimethyl Sulfoxide Extraction Methods of Determining Monomer and Oligomers in Nylon 6[a]

Polymerization time, hr.	Infrared method, monomer, %	Dimethyl sulfoxide extraction, monomer and oligomers, %
2	96.5	99.9
4	96.0	99.3
5.5	91.0	92.8
6.5	82.5	87.0
7.0	82.5	84.8
7.5	78.8	78.7

[a] Preheat time (0.5 hr.) is excluded in the numerical value of polymerization time.

Table II is a compilation of data obtained on caprolactam polymerizates of both infrared and dimethyl sulfoxide extraction methods. In the infrared method, the per cent of the oligomers is obtained from the difference between the dimethyl sulfoxide extractable and the per cent of the monomer found. It indicates no oligomers exist after 7.5 hr. polymerization. These data may indicate an inaccuracy in the monomer–oligomer determination, and details are now under investigation.

To determine the accuracy and precision of the dimethyl sulfoxide extraction method, the extraction of a known weight of the monomer mixed with a known weight of the polymer was carried out, in which the monomer and the oligomers were extracted previously. The result is shown in Table III.

TABLE III
Dimethyl Sulfoxide Extraction of Preparative Samples[a]

Theoretical		Observed
Monomer, %[b]	Polymer, %[b]	Monomer, %[b]
95	5	95.1
90	10	90.1
90	10	90.1
90	10	90.8
90	10	90.0
90	10	90.1
80	20	80.1
70	30	69.8
50	50	49.9

[a] Standard Deviation, 0.25; *t* value, 1.18.

[b] Relative error, 0.2%.

Standard deviation and *t* value are calculated by means of the Youden method. The precision of the extraction method, as indicated in Table III, is about ± 0.2% as a relative error, and the accuracy is within ± 0.2% as a bias (an absolute error) except one sample. The *t* value indicates that it is not significant at the 5% level of significance. In this paper the monomer content determined is between 50–100% in nylon 6. The limitation of quantitative monomer determination under this method is regarded to be 30% monomer in nylon 6 considering the results of the calibration curve and the infrared spectra. For the determination of lower-monomer content in nylon 6 (smaller than 30%), a cell of longer path length should be used, because the limitation of the polymer concentration in *o*-chlorophenol is up to 8% at the most, owing to the increase of the viscosity of the solution, which makes the determination difficult. The transmittance of *o*-chlorophenol at 892 cm.$^{-1}$ is greater than 70% in a cell of path length 25 μ, and about 30% in a cell of path length 100 μ. The 10% monomer in nylon 6 was determined by using a cell of path length 100 μ in the similar way, but the precision was worse. If a longer path length cell is used, lower monomer concentration could be measured, but the precision would become much worse.

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Sadao Mori
Kaoru Okazaki

Technical Development Department
Toyo Rayon Co., Ltd.
Nagoya, Japan

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BOOK REVIEW

Macromolecules in Solution (High Polymers, Volume XXI). HERBERT MORAWETZ. Interscience, New York, 1965. xvi + 495. $16.50.

This book grew out of the author's course in "Solution Properties of Polymers." Its spirit and motivation are expressed in the Preface: "Since Flory's classical book on Polymer Chemistry was published in 1953, two revolutionary developments have had a profound impact on the field. The first was the discovery of techniques for the synthesis of stereoregular vinyl polymers. This development broadened the field of study of solution properties of macromolecules, with increased emphasis on techniques which might characterize the stereoregularity of a sample. It also had the effect of stimulating a more careful theoretical analysis of the conformations of chain molecules. The second major development was the discovery of the existence of systems in which chain molecules assume in solution precisely defined helical conformations. . . . With the realization that (such behavior) is not confined to the realm of biological macromolecules, the *de facto* separation of the fields of natural and synthetic macromolecules became an absurdity and a serious impediment to progress. This book was written, therefore, with the idea of bringing the exciting facts of modern protein and nucleic acid research to the attention of the chemist whose work is mostly concerned with synthetic macromolecules." Morawetz also had in mind the large body of chemists, biologists, and other workers with macromolecules who have to rely heavily on physicochemical techniques but whose workaday desires may not often extend beyond semiquantitative comprehension and a feeling for the physical significance of the underlying theory.

The nine chapters bear the following titles: I. General Considerations (Comparison of Methods for the Study of Small and Large Molecules; Distribution Functions of Chain Length and Composition; Relation of the Study of Macromolecules in Solution and in Bulk). II. The Solubility of Macromolecules. III. Configuration and Conformation of Chain Molecules. IV. Equilibrium Properties of Dilute Solutions. V. Spectroscopy, Optical Activity, and the Scattering of Light and X-Rays. VI. Frictional Properties of Dissolved Macromolecules. VII. Polyelectrolytes. VIII. Molecular Association. IX. The Reactivity of Macromolecular Solutions.

It is a fearsome job to compress up-to-date discussions of all the above topics into a volume of modest size and in a form accessible to the wide circle of potential readers contemplated. To do so, the author sticks rather closely to chemistry as distinct from technological or biological applications, and he has to avoid extensive theoretical and mathematical details. Of course the danger is that shallow, unreliable, or even misleading notions may be conveyed by such deliberately limited expositions. A great burden rests on the author to make his descriptions succinct and to fortify the chosen equations with critical, incisive explanations. The references for further study must also be the more carefully selected and easily accessible. In the reviewer's opinion, Morawetz brings it off remarkably well. No major errors have been detected, and no disagreements in matters of taste seem worthy of note here.

This work deserves wide trial as a textbook for introductory graduate courses in polymer science, supplemented of course in areas chosen for special emphasis. The last three chapters may be especially valuable to the synthetic-polymer chemist, for they deal with subject matter which he is not likely to know well but which is likely to prove of practical importance to him at some time. As this section of the book deals with many of the author's own major research interests, the treatment is especially authoritative. The mission undertaken in the Preface has been well accomplished.

Walter H. Stockmayer

Department of Chemistry
Dartmouth College
Hanover, New Hampshire 03755

INFORMATION FOR CONTRIBUTORS

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