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Polymerization of Itaconic Acid Derivatives*

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Synopsis

The γ-ray-initiated polymerization of dimethyl itaconate was studied. Dimethyl itaconate was polymerized by γ-irradiation at temperatures where the monomer does not polymerize thermally; so long as the monomer is kept in a liquid state, even at temperatures below the melting point, the polymerization takes place. Itaconic anhydride was polymerized in the solid state with γ-irradiation or benzoyl peroxide. The molecular weight of the polymer increases with time or yield and is greater than that of polymer obtained by other methods. The kinetic study and crystallographic study indicate that the γ-ray-initiated solid-phase polymerization is a first-order reaction with respect to monomer and the rate-determining step changes as the polymerization proceeds.

INTRODUCTION

Itaconic acid can be easily obtained by fermentation, but no extensive research on the homopolymerization of itaconic acid and its derivatives has been carried out.

Some studies on the radical polymerization of various esters and the acid have been reported by Marvel[1] and Nagai,[2] the polymer of the anhydride has been investigated by Drouglas,[3] and the polymerization of substituted imides by Akashi.[4] Also, radiation grafting of the acid on nylon was reported by Zimmerman.[5]

In the present study we examined the homopolymerization of itaconic acid, itaconic anhydride, dimethyl itaconate, and itaconic amide, in the solid and liquid states; the solid-state polymerization was examined in more detail.

EXPERIMENTAL

Materials

Itaconic acid and itaconic anhydride were commercial products (Charles Pfizer Co., Inc.), recrystallized from water and benzene, respectively; the melting points of the purified materials were 161 and 67.2–68.0°C., respectively.

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Dimethyl itaconate, a commercial product of the same company, was distilled *in vacuo* (91–94°C./10–12 mm. Hg) before use.

Itaconic diamide was prepared from a solution of 9.6 g. of dimethyl itaconate (9.6 g.) and 1.2 g. of ammonium chloride in 10 ml. of methanol to which 15 ml. of concentrated aqueous ammonium hydroxide solution was added. The solution was agitated at room temperature for about 9 hr and then evaporated *in vacuo*. The crystals formed were recrystallized from ethanol; yield 32 mg.; m.p. 195.4–196.5°C. (lit.: 192°C.).

ANAL. Calcd.: C, 46.98%; H, 6.29%; N, 21.87%. Found: C, 46.68%; H, 6.26%; N, 21.38%.

Methods

Polymerization. Polymerization was conducted in sealed glass tubes which were previously flushed with nitrogen, the tubes being placed in a thermostat controlled within ±0.1°.

Irradiation polymerization, a 300-c. ^{60}Co source was used at a dose rate of 5.1×10^4 r./hr.

In the radical-catalyzed solid-state polymerization of itaconic anhydride, benzoyl peroxide was used as catalyst, and given amounts of monomer and peroxide were dissolved in benzene and freeze-dried at −78°C. so that the catalyst might disperse in the monomer uniformly.

The specimens thus obtained were immediately used in the experiments.

In the case of dimethyl itaconate, the polymerized mass was dissolved in benzene and the solution was poured into methanol and the precipitated poly(dimethyl itaconate) was filtered and dried.

In the case of itaconic anhydride, the product was extracted with anhydrous benzene and the residue dried *in vacuo*.

A high-pressure mercury lamp was used as the source for ultraviolet-initiated polymerization.

Crystallographic Analysis. In the x-ray analysis of crystal structure of single crystals of itaconic anhydride, a Geigerflex instrument (Rigakudenki Co., Model 3-DF, 35 kv., 15 ma., Cu anticathode, Ni filter) was used.

In microscopic observation, the polarizing microscope was used at a magnification of 100.

The crystallinity of itaconic anhydride irradiated was determined by the following method. After irradiation for a given time, 80 mg. of powdered anhydride and 200 mg. of beryllium oxide used as internal compensation were mixed and ground for 15 min. The diffraction intensity of the mixture due to the anhydride and beryllium oxide, was determined at $2\theta = 32.0°$ and at $2\theta = 69.5°$, respectively. The ratio of the two intensities was calculated.

Viscosity Measurement. Benzene and acetone were used as solvents for poly(dimethyl itaconate) and of poly(itaconic anhydride), respectively, and the reduced viscosity η_{sp}/c was measured at 25°C. (1 g./100 ml. solvent) with an Ostwald viscometer.

RESULTS AND DISCUSSION

Irradiation Polymerization of Dimethyl Itaconate

The polymerization was carried out under irradiation at 50°C. for a wide range of time. The relations between polymerization time and reduced viscosity of polymer are shown in Figure 1. The melting point of dimethyl itaconate was found to be 34°C., and so it is in a uniform liquid phase at 50°C. and its polymer was obtained in a transparent homogeneous state. It was confirmed also in other experiments that no polymer was obtained from the same monomer on heating at 50°C. for 48 hr. without radical catalyst in bulk.

As shown in Figure 1, an induction period of about 10 hr. was noted after the beginning of irradiation, which was followed by a linear increase in yield which reached its limiting polymerization yield about 70 hr.

No marked change in reduced viscosity not found within a comparatively short irradiation time, but with irradiation for a long time, a decrease in reduced viscosity was found which may indicate that degradation of polymer took place.

The relation between irradiation temperature and yield of polymerization is shown in Figure 2. The polymerization proceeds only in a liquid state, including supercooled liquid state, independent of the melting point.

It was made clear that the relation between polymerization temperature and yield is continuous over a wide range including the melting point, and

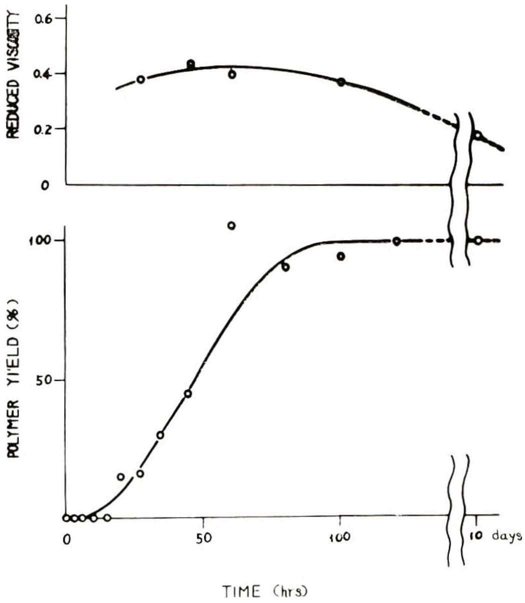


Fig. 1. Typical course of polymerization and reduced viscosity vs. time of irradiation in the polymerization of dimethyl itaconate initiated by γ-rays. Temperature, 50°C.; dose rate, 5.1×10^4 r./hr.

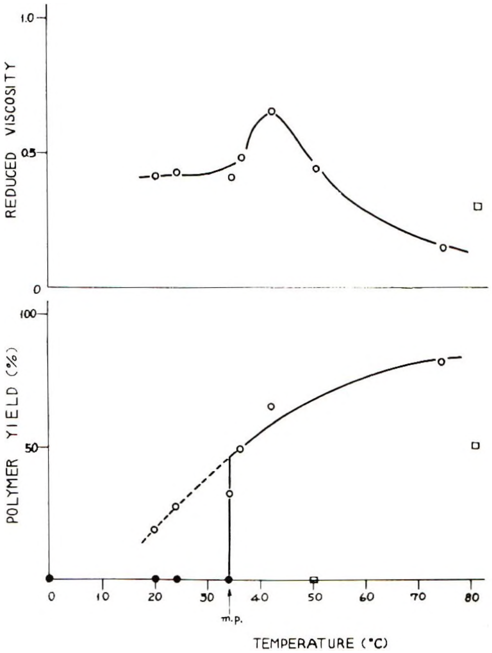


Fig. 2. Polymerizations of dimethyl itaconate initiated by γ-rays at various temperatures: (○) liquid state; (●) solid state; (□) heating without catalyst and irradiation. Time, 45 hr.; dose rate, 5.1×10^4 r./hr. The arrow indicates the melting point of the itaconate.

the condition of state, i.e., whether the monomer is a solid or a liquid, is a more important factor in effecting polymerization than the polymerization temperature.

The reduced viscosity, as shown in Figure 2, shows a maximum value at an irradiation temperature of 40°C. or so and becomes lower with increasing polymerization temperature.

The increase in product viscosity with temperature may be caused by a gel effect and the decrease may be due to degradation under irradiation.

The results of polymerization by heating without catalyst and irradiation in bulk are also plotted in Figure 2. No formation of polymer was found at 50°C. but a considerable amount of polymer was obtained at 80°C.

Polymerization of Itaconic Anhydride

Irradiation Polymerization. The influence of irradiation temperature on the yield and on the reduced viscosity of polymer was examined (Fig. 3).

In bulk, polymerization occurred rapidly at a temperature near 50°C., and polymerization is effected almost completely at 60–90°C. At a higher temperature (near 100°C.), the yield of polymer decreases considerably. The viscosity shows a maximum value in the polymer formed at 60°C.,

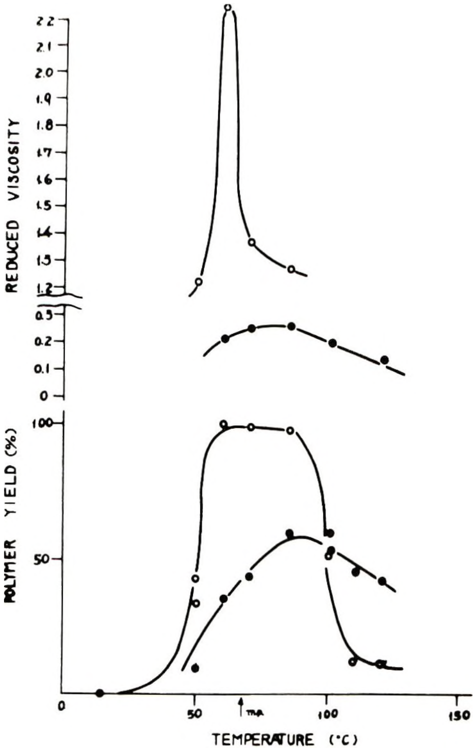


Fig. 3. Polymerization of itaconic anhydride initiated by γ-rays at various temperatures: (○) in bulk; (●) in benzene solution. Dose rate, 5.1×10^4 r./hr.; time, 48 hr. The arrow indicates the melting point of the itaconic anhydride.

which is slightly below the melting point of the monomer, and the viscosity of polymers formed at other temperature is considerably smaller than the maximum. When polymerization is carried out in benzene solution, the rate of polymerization is lower than that in bulk. Polymerization takes place at nearly 50°C. and attains its highest rate at about 90°C. If heated in solution at a higher temperature, the yield of polymer decreases but does not decrease so remarkably as in bulk. The viscosity is considerably lower, as compared with that of polymer obtained in bulk.

The reason why polymer cannot be obtained at high temperature is considered to be that isomerization from itaconic anhydride to citraconic anhydride takes place. Burb et al.[6] reported that isomerization from itaconic anhydride to citraconic anhydride takes place in bulk quantitatively at a temperature above the melting point.

For more detailed examination of this point, the relations between the thermal polymerization of itaconic anhydride and its transition to citraconic anhydride were studied; and results are shown in Figure 4. Quantitative determinations of citraconic and itaconic anhydrides were made on the basis of their characteristic absorptions in the infrared spectra at 699 and 809 cm.$^{-1}$, respectively. Thermal polymerization takes place in the

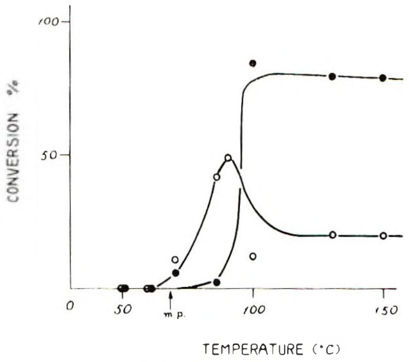


Fig. 4. Thermal polymerization and isomerization of itaconic anhydride: (○) yield of polymer based on monomer; (●) yield of citraconic anhydride based on monomer. The arrow indicates the melting point of the itaconic anhydride.

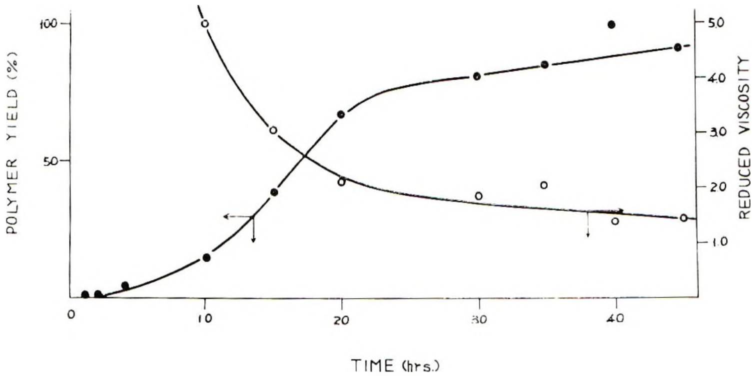


Fig. 5. Polymerization of itaconic anhydride initiated by γ-rays in the solid state: (●) polymer yield; (○) reduced viscosity. Temperature, 62°C.; dose rate, 5.1×10^4 r./hr.

liquid state, and the yield of polymer increases with increasing temperature, attains a maximum at 90°C., or so but decreases thereafter.

The isomerization begins to take place at about 90°C., and above 100°C. total unpolymerized monomer was found to be isomerized to citraconic anhydride. Thermal polymerization takes place at a temperature above the melting point and the yield of polymer increases with the elevation of temperature, but isomerization starts from about 90°C. and isomerization predominates at higher temperatures.

In addition, no polymer could be obtained even if a mixture (1:1 by weight) of itaconic anhydride and citraconic anhydride was heated with γ-irradiation, for example, at 62°C. for 18 hr. and, in another run, at 85°C. for 45 hr., where pure itaconic anhydride was polymerized at higher yield of polymer without isomerization, that is, some inhibitive effect of citraconic anhydride on polymerization of itaconic anhydride was observed.

The relation between yield of polymer and polymerization time in the case of radiation polymerization in a solid state is shown in Figure 5.

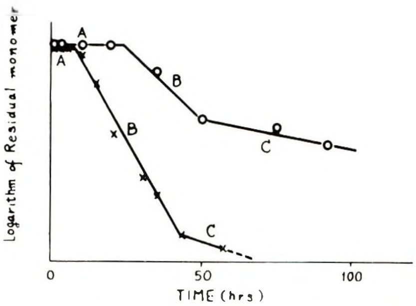


Fig. 6. Logarithm of unreacted monomer vs. time in polymerization of itaconic anhydride initiated by γ-rays: (○) at 50°C.; (×) at 62°C.

Polymerization takes place about 5 hr. after the beginning of irradiation and the yield increases linearly for 10 hr. to 20 hr. and thereafter slowly approaches a limiting value.

The viscosity reaches a quite large value, as high as 5.0, after irradiation time for 10 hr., but a marked decrease in viscosity is observed with longer irradiation time. When a polymer obtained by irradiation and having a reduced viscosity of 1.31 was again subjected to γ-irradiation at a dose rate of 5.1×10^4 r./hr. at 65°C. for 24 hr., its viscosity decreased to 0.55; this would indicate that the γ-irradiation at this temperature causes degradation of polymer and consequently a decrease in its viscosity.

The logarithms of residual monomer at polymerization temperaturss of 50 and 62°C., were plotted against time as shown in Figure 6; the relationships are shown by a series of lines of different slopes marked *A*, *B*, and *C*.

This polymerization may be considered to be a first-order reaction relative to monomer, and there exist three regions (*A*, *B*, and *C*) having different rate-determining steps which occur successively as the polymerization proceeds. First; in region *A*, there is an induction period during which the formation of crystal defect occurs but hardly any polymerization proceeds; the higher the temperature, the shorter this period is. In region *B*, the polymerization is stepped up and the propagation is the rate-determining step. In the last region, *C*, most of the monomer has been consumed, so that the rate of monomer uptake is very slow, migration of monomer which is difficult, may be the rate-determining step.

This is also supported by the information from the crystallographic study.

Crystallographic Study. It was found that if a single crystal of itaconic anhydride is subjected to γ-irradiation for a long time at a temperature below the melting point polymer can be obtained at a high yield without changing the apparent crystal form of monomer. The crystal pattern by x-ray and interference color by polarizing microscope were observed on irradiated single crystals.

It was found that the crystal pattern was caused by the residual unpolymerized monomer and the birefringence color was due to orientation

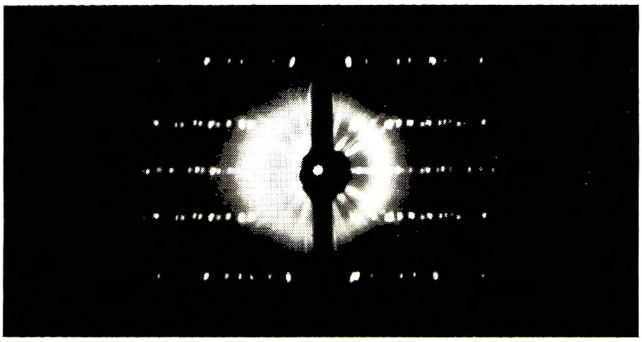
TABLE I

Indexing of Oscillation Photograph of Itaconic Anhydride by the Bernal Chart and Changes of Spot During Irradiation (λ = 1.542 A.)

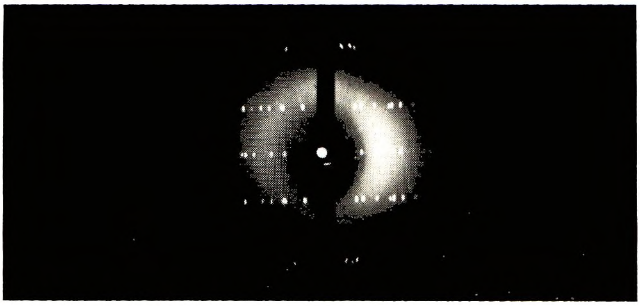
		Equator					1st layer line				2nd layer line			
		$10\lambda/d$			Spot after[a]		$10\lambda/d$		Spot after[a]		$10\lambda/d$		Spot after[a]	
Intensity	d, A.	Calcd.	Obs.	Indices	61 hr.	81 hr.	Obs.	Indices	61 hr.	81 hr.	obs.	Indices	61 hr.	81 hr.
							0.21	110	0	0	0.22	$\bar{1}20$	0	0
vs	6.10	0.25	0.23	$\bar{1}01$	0	0	0.24	$\bar{1}11$	0	0				
vs	3.52	0.44	0.40	$\bar{2}00$							0.39	$\bar{2}20$	0	
vs	3.18	0.49	0.45	$\bar{2}01$	0	0	0.46	$\bar{2}11$	0	0	0.45	$\bar{2}21$	0	
s	2.74	0.56	0.54	$\bar{2}02$	0		0.55	$\bar{2}12$	0	0	0.52	$\bar{2}22$	0	
s	2.45	0.63	0.61	$\bar{1}04$	0		0.60	$\bar{1}14$	0		0.60	$\bar{1}24$		
vs	2.31	0.67	0.65	005	0		0.64	015	0		0.63	025	0	
m	2.13	0.72	0.71	$\bar{1}05$	0		0.70	$\bar{1}15$	0		0.70	$\bar{1}25$	0	
s	1.99	0.77	0.74	$\bar{2}04$	0		0.73	$\bar{2}14$	0		0.73	$\bar{2}24$	0	
m	1.96	0.79	0.78	006	0						0.78	026	0	
							0.81	$\bar{3}13$	0		0.82	$\bar{3}23$	0	
w	1.77	0.87	0.89	$\bar{3}04$	0						0.88	$\bar{3}24$	0	
s	1.70	0.91	0.95	$\bar{2}07$	0		0.95	$\bar{2}17$	0		0.95	$\bar{2}27$	0	
s	1.50	1.03	1.01	$\bar{4}03$	0		1.02	$\bar{4}13$	0		1.02	$\bar{4}23$		
w	1.46	1.06	1.04	$\bar{1}08$										
w	1.43	1.08	1.07	$\bar{4}04$			1.07	$\bar{4}14$			1.07	$\bar{4}24$		
w	1.28	1.20	1.18	$\bar{2}08$							1.18	$\bar{2}28$		
w	1.21	1.27	1.25	$\bar{1}09$							1.26	$\bar{1}29$		

							1.28	610			1.28	620		
							1.31	416			1.31	426		
							0.21	110	0	0				
vs	6.41	0.24	0.25	002	0	0	0.25	012	0	0	0.25	022	0	0
			0.33	102	0	0	0.34	112	0	0	0.33	122	0	
vs	3.69	0.42	0.41	202	0		0.46	212	0	0	0.43	222	0	
vs	3.40	0.45	0.50	$20\bar{1}$	0	0	0.50	$21\bar{1}$	0	0	0.50	$22\bar{1}$	0	
vs	2.83	0.55	0.57	204	0		0.57	214	0		0.57	224	0	
s	2.51	0.62	0.61	300										
vs	2.35	0.66	0.67	303	0		0.68	313	0		0.67	323	0	
m	2.17	0.72	0.73	304	0		0.74	314	0		0.73	324	0	
vs	2.07	0.75	0.77	006	0		0.77	016	0		0.78	026	0	
s	1.90	0.81	0.81	206			0.80	216	0		0.80	226		
s	1.73	0.89	0.89	404			0.88	414			0.89	424		
m	1.61	0.96	0.92	207	0		0.91	217	0		0.91	227		
m	1.59	0.97	0.98	307	0		0.99	317	0		0.98	327	0	
m	1.48	1.04	1.05	504			1.05	514			1.05	524		
m	1.44	1.07	1.08	308										
m	1.29	1.20	1.18	505			1.19	515			1.12	525		
s	1.22	1.27	1.28	309							1.28	329		
s	1.17	1.32	1.30	604			1.30	614			1.30	624		

[a] Zero denotes spot without change after 61 and 81 hr. irradiation.



(a)



(b)

of residual monomer. After the residual monomer was removed from the polymer by extraction with anhydrous acetone, the polymer was completely amorphous and also showed no birefringence color.

The result of the x-ray analysis of the crystalline of itaconic anhydride obtained by recrystallization from benzene solution is shown in Table I.

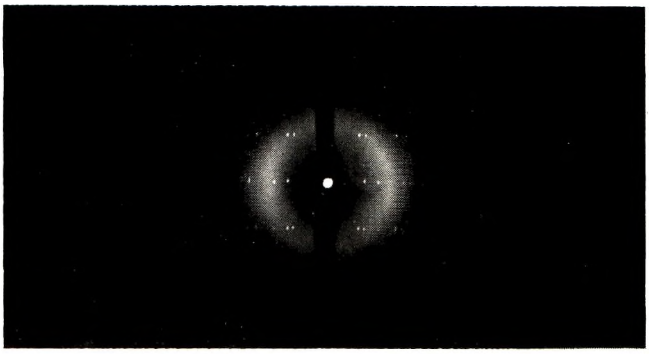
Itaconic anhydride was found to be monoclinic and belong to the space group of $C_2{}^2h = P_{21}/m$ with $a = 7.54$ A., $b = 5.16$ A., $c = 12.19$ A., $\alpha = \gamma = 90°$, and $\beta = 103° 6'$.

The density was found to be 1.38 g./cm.[3] and from this it was calculated that a unit cell contains 4 molecules.

Each crystalline pattern, by the 100° oscillation crystal method, of a small piece of single crystal after γ-ray irradiation for 61, 81, and 148 hr., is shown in Table I and Figure 7.

The morphological appearance of monomer does not change during the polymerization. There is no disappearance of the lattice point or lattice layer in the x-ray photograph up to 41 hr. in the initial stage of the polymerization. However, if polymerization progresses almost completely, some diffraction points of a higher order tend to disappear. A similar phenomenon has been reported in the case of heat vibration of inorganic compound.[5]

It might be considered, though this is not firmly established, that this is because a small amount of strain takes place on the boundaries of crystal as a result of thermal vibration among atoms.



(c)

(d)

Fig. 7. Oscillation photographs of itaconic anhydride single crystal; (*a*) initial; (*b*) after γ-irradiation for 61 hr. at 50°C.; (*c*) after γ-irradiation for 81 hr. at 50°C.; (*d*) after γ-irradiation for 148 hr. at 50°C.

A thin section of single crystal irradiated with γ-rays was observed by polarizing microscopy. The crystal in the initial stage shows a uniform interference color through the polarizing plate on the whole surface of crystal, and no defect can be observed even under magnifications of 80×. As polymerization progresses, the interference color slowly fades away but a uniform color remains until the yield reaches 80%. However, the interference color disappears and dark points appear on the whole surface when polymerization has gone to completion. Changes in x-ray diffraction intensity of the monomer crystal with irradiation time were determined, and the result is shown in Figure 8 together with the yield of polymer.

The diffraction intensity was indicated by the normalized ratio R of diffraction intensity at $2\theta = 32.0°$ (caused by the anhydride monomer), to that at $2\theta = 69.5°$ of beryllium oxide as internal standard. The relation between the ratio R and the polymer yield is shown in Figure 9.

The crystallinity of the monomer solid first decreases remarkably on the formation of a small amount of polymer, that is, the ratio comes down to about two-thirds of the original even at 5% of conversion of the monomer to polymer. Thereafter, this ratio decreases linearly with polymer for-

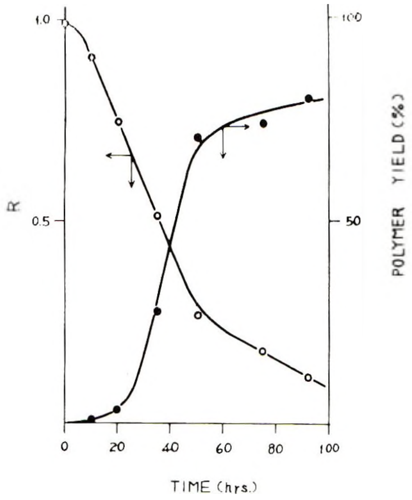


Fig. 8. Plots of change of (●) polymer yield and (○) ratio R of x-ray diffraction intensities with time in solid-state polymerization of itaconic anhydride under γ-irradiation. Polymer yield given as $R = I_{IA}/I_{BeO}$, where I_{IA} and I_{BeO} are the diffraction intensities of itaconic anhydride at $2\theta = 32.0°$ and of beryllium oxide at $2\theta = 69.5°$, respectively. Temperature, 50°C.; dose rate, 5.1×10^4 r./hr.

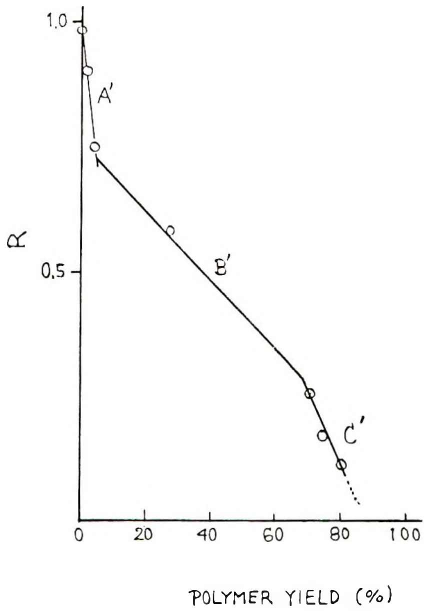


Fig. 9. Changes of the ratio of diffraction intensities R and of the polymer yield in the γ-ray-initiated polymerization of itaconic anhydride in the solid state. Temperature, 50°C.; dose rate, 5.1×10^4 r./hr.

mation until the yield is about 70%. As the yield exceeds 70%, the ratio decreases considerably again.

On comparing this observation with the relations in Figure 6, some interesting results are deduced. It seems that the regions *A*, *B*, and *C* in Figure 6 correspond to the lines *A′*, *B′*, and *C′* in Figure 9, respectively, and the two changes in slope are also located at corresponding points.

Region *A* denotes an induction period when the formation of crystal defect occurs but the polymerization does not take place. It is understood that both the radical formation and formation of some number of crystal defects, which corresponds to the transformation of the monomer crystal to a form able to migrate and polymerize are necessary for the initiation of polymerization. This mechanism may be applicable generally for solid-state polymerization.

When a sufficient number of defects have been formed, the polymerization starts and becomes dominant and the propagation is the rate-determining step in region *B*.

TABLE II

Radical-Catalyzed Polymerization of Itaconic Anhydride with Benzoyl Peroxide (1 Wt.-% Based on Monomer)

State	Temperature, °C.	Time, hr.	Yield, %	η_{sp}/c
Bulk, solid state	60	2	21.4	0.55
		4	48.8	2.29
		7	59.0	3.10
Bulk, molten	70	0.5	11.1	0.126
		1.0	20.2	0.082
		1.25	44.2	0.317
		2	77.1	0.385
		3	79.7	0.616
		7	98.1	0.88
Solution in benzene (1 g./10 ml.)	60	4	8.3	0.13
		7	12.5	0.15
		12	17.3	0.132
		15	22.1	0.132
		21	26.1	0.134

In this region, the defect formation accompanies polymerization but it occurs less extensively than in region A.

In region *C*, the defect formation is considerable in spite of the small amount of polymer formation, in other words, unless large defects occur, only little polymer can form.

Thus, in this region too, the formation of polymerizable monomer, that is, the defect formation is rate-determining.

Radical-Catalyzed Polymerization in Various States. Itaconic anhydride can be polymerized by radical catalyst too. The results obtained with benzoyl peroxide as catalyst are shown in Table II.

The relation between the yield and viscosity is shown in Figure 10. In a solution, even if the yield increases, the viscosity is constant and low.

When monomer containing the catalyst dispersed uniformly by freeze-drying was polymerized at a temperature below its melting point, no induction period could be observed, and a polymer of considerably higher viscosity was obtained in high yield. Furthermore, in solid-phase polymerization, the viscosity increases linearly with the yield. In the melted phase, the viscosity values are midway between those for solid and solution polymerization. While the yield is low, a slow rise in viscosity is seen, and when polymerization progresses and the reaction system near a solid phase, the increase of viscosity becomes sharp.

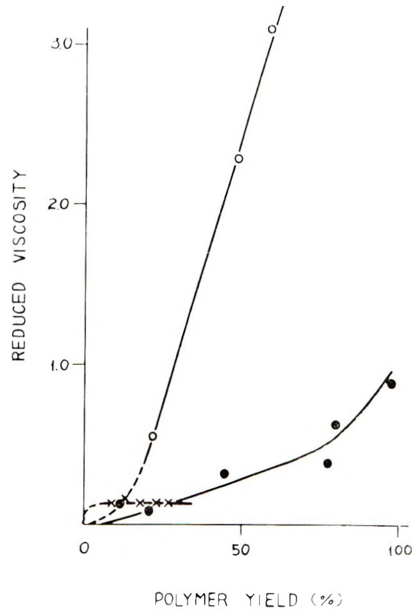


Fig. 10. Relations between reduced viscosity of polymer and yield in polymerizations of itaconic anhydride with benzoyl peroxide (1 wt.-% on monomer) in various states; (○) solid state at 60°C.; (●) molten state at 70°C.; (×) solution in benzene at 60°C.

Ultraviolet Irradiation Polymerization. Itaconic anhydride was polymerized by ultraviolet radiation in addition to γ-ray, heat, and radical catalyst. The results are shown in Table III. In a solid phase, polymerization progresses regardless of the existence of photosensitizer, but in a benzene solution, no polymer was obtained and partial isomerization to citraconic anhydride was found. However, the molecular weight of the polymer obtained in the solid phase was considerably lower, and the yield was also lower than with γ-ray or catalyzed solid-phase polymerization.

TABLE III
Polymerizations of Itaconic Anhydride with Ultraviolet Irradiation (Mercury Lamp, 1000 v., 300 ma.)[a]

Run no.	Temperature, °C.	Yield, %	η_{sp}/c	Remarks
PIA-124	55	16.1	0.208	Solid state containing 1 wt.-% of benzophenon
PIA-126	55	17.6	0.29	In solid state
PIA-127	55	0	—	In benzene solution (1 g./10 ml.) considerable isomerization was observed.

[a] After heating for 48 hr. under radiation.

Generally, in the case of itaconic anhydride, isomerization does not take place in a benzene solution or at a low temperature near about 55°C. with only heat. However, under ultraviolet irradiation, considerable isomerization occurred in solution at 55°C.

Attempted Polymerizations of Itaconic Acid and Itaconic Diamide

Polymerizations of itaconic acid and itaconic diamide by means of γ-ray irradiation at 50–100°C. for 6 days and with radical catalyst in the solid phase were attempted, but no polymer could be obtained under these experimental conditions.

Conclusions

Dimethyl itaconate does not polymerize thermally in liquid phase at a temperature below 50°C. However, the monomer polymerizes at a temperature below 50°C. under γ-irradiation as long as the monomer is kept in the liquid state, even at a temperature below the melting point.

Solid-state polymerization of dimethyl itaconate could not be observed; however, that of itaconic anhydride was confirmed. Itaconic anhydride was converted to polymer in high yield even at temperatures below the melting point under irradiation, and the polymer obtained by γ-irradiation at a temperature slightly below the melting point was found to have a much higher molecular weight than polymers obtained at other temperatures.

Itaconic anhydride polymerizes thermally only above the melting point, but at a temperature higher than 100°C. the monomer is converted to citraconic anhydride, and isomerization predominates over polymerization. However, monomers with dispersed uniformly benzoyl peroxide were polymerized in the solid state under heating, and polymers of quite high molecular weight were obtained. In this case, the viscosity of polymer increases linearly with the yield. On the basis of results of crystallographic study, may be concluded that in polymerization in a state in which molecular motions are limited, e.g., the solid state, only short-range reactions in crystal defects can take place. Therefore, monomer which can take part in the reaction is limited; on the other hand, termination reaction or chain transfer reactions do not take place at all or are quite rare, if any, in the crystal. In solid-state polymerization, the resultant polymer is of higher molecular weight than that obtained in solution, and the molecular weight increases with time, that is, with the yield.

In the γ-ray-initiated solid-phase polymerization of itaconic anhydride, the relationship between the rate of polymerization and crystal defects may be explained by considering the mechanism to consist of a first-order reaction relative to monomer having three rate-determining steps which depend on the formation of crystal defects.

The authors wish to express their gratitude to Assistant Professor Dr. S. Iwai of the Tokyo Institute of Technology for helpful guidance in the crystallographic analysis, to Mr. K. Yoshitake of our laboratory for performing the polarizing microscopy, to Dr. N. Kominami of our laboratory for useful discussion regarding the reaction mechanism, and to Dr. A. Suzuki, director of our laboratory, and Mr. R. Wakasa of our laboratory for encouragement throughout our research and permission to publish this paper.

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Résumé

La polymérisation initiée par rayons-γ del'itaconate de diméthyle a été étudiée. L'itaconate de diméthyle a été polymérisé par irradiation aux rayons-γ à une température à laquelle le monomère ne polymérise pas thermiquement et tant que le monomère est tenu à l'état liquide même en-dessous de la température de point de fusion, la polymérisation a lieu. L'anhydride itaconique a l'état solide a été polymérisé par irradiation aux rayons-γ ou en présence de peroxyde de benzoyle, et le poids moléculaire du polymère croît avec le temps ou avec le rendement et est plus élevé que par d'autres méthodes. Au départ des résultats cinétiques et d'une étude cristallographique on a montré que la polymérisation en phase solide initiée aux rayons-γ est une réaction de premier ordre en ce qui concerne le monomère et que l'étape déterminante de vitesse varie avec le degré d'avancement de la polymérisation.

Zusammenfassung

Die γ-Strahlen-initiierte Polymerisation von Dimethylitaconat wurde untersucht. Dimethylitaconat wurde durch γ-Bestrahlung bei einer Temperatur polymerisiert, bei welcher das Monomere thermisch nicht polymerisiert, und die Polymerisation findet statt, solange das Monomere in flüssigem Zustand gehalten wird, auch bei Temperaturen unterhalb des Schmelzpunktes. Itaconsäureanhydrid wurde in festem Zustand mit γ-Bestrahlung oder Benzoylperoxyd polymerisiert; das Molekulargewicht des Polymeren nimmt mit der Dauer oder dem Umsatz zu und ist so gross, wie es nach keiner anderen

Methode erhalten wird. Die Ergebnisse der kinetischen und kristallographischen Untersuchung zeigen, dass die durch γ-Strahlen initiierte Polymerisation in fester Phase eine Reaktion erster Ordnung bezüglich des Monomeren ist und dass sich der geschwindigkeitsbestimmende Schritt mit fortschreitender Polymerisation ändert.

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Synthesis of Polyaryloxysilanes by Melt-Polymerizing Dianilino- and Diphenoxysilanes with Aromatic Diols*

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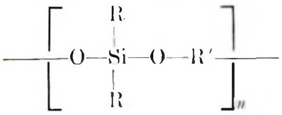
Synopsis

A series of polyaryloxysilanes was prepared from aromatic diols and dianilino- and diphenoxysilanes. High molecular weight polymers were obtained at temperatures of 200°C. or higher by using melt-polymerization procedures. The polymers, which combine the structures of silicones and polyaromatics, possessed high thermal stabilities and were obtained as materials which (*1*) failed to melt or soften at 350°C., (*2*) were gumlike at elevated temperatures, or (*3*) were soluble, film- and fiber-forming polymers capable of being processed as conventional thermoplastics and having potentially useful mechanical properties. The preparation of monomers, general polymerization procedures, and certain structure-property relationships for the thermoplastic polyaryloxysilanes are considered.

INTRODUCTION

The successful use of silicones in high-temperature applications for almost a quarter of a century has prompted extensive research efforts to provide improved polymers through modifications of the polysiloxane chain. Examples of the approaches followed include the total or partial replacement of the silicon atoms by various elements from Groups III to VI of the Periodic Table[1,2] of the oxygen atoms by nitrogen as in the polysilazanes,[3-6] and the inclusion of silicon-carbon linkages within the polymer chain as in the polysilphenylenes.[7,8]

The present paper is concerned with a class of silicon-containing polymers, the polyaryloxysilanes, which contain silicon-oxygen-carbon linkages in their main chains and have the general formula:



$$\left[-\mathrm{O}-\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{Si}}}-\mathrm{O}-\mathrm{R'}-\right]_n$$

where R′ is an aromatic unit and R may be either aromatic or aliphatic.

The polyaryloxysilanes should possess superior mechanical strength properties as compared to silicones because of the chain rigidity conferred

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by the aromatic rings included in the main valence chain. The same rigid rings should restrict the ability of the chain to elongate and provide a material having a relatively high surface hardness. In addition, the insertion of the rigid rings into the polymer's main chain should provide an enhanced resistance to thermal degradation, as compared with polysiloxane chains, by interfering with the degradation mechanism (breakdown to cyclic products) known to occur in the silicones. On the other hand, the highly flexible Si—O linkages in the main chain might be expected to limit the temperature at which the chain can retain its rigidity and exert a moderating influence on the mechanical strength of the polymer. The properties of the polyaryloxysilanes examined in this study appear to support these property predictions.

Polyaryloxysilanes have been prepared by the alcoholysis of dialkoxysilanes by aromatic diols[9] and the condensation of dihalosilanes with aromatic diols.[9,10] Polymers containing both aryloxysilane and silazane linkages in the main chain have been prepared by the condensation of cyclosilazanes with diols.[11] However, these procedures appear to have led only to relatively low molecular weight silicon-containing polymers having little technological utility.

Two promising synthetic routes to relatively high molecular weight polyaryloxysilanes were investigated in the present study. These depend upon the nucleophilic displacement of aniline from a dianilinosilane by an aromatic diol,[12]

$$(C_6H_5NH)_2SiR_2 + HO—R'—OH \rightarrow \left[O—Si(R)_2—O—R' \right]_n + C_6H_5NH_2\uparrow \qquad (1)$$

or displacement of phenol from a diphenoxysilane by an aromatic diol in the presence of a catalyst.[13]

$$(C_6H_5O)_2SiR_2 + HO—R'OH \xrightarrow{\text{Catalyst}} \left[O—Si(R)_2—O—R' \right]_n + C_6H_5OH\uparrow \qquad (2)$$

The polymers obtained by the two procedures are similar in nature and exhibit generally high thermal stabilities. The polyaryloxysilanes have been prepared as soluble, film- and fiber-forming thermoplastics, as materials that are gumlike at room or elevated temperatures, and as insoluble products that are nonfusible at 350°C. Polymers prepared by the reaction shown in eq. (1) are stressed in the present work, and the polymer in which R is phenyl and R′ is *p,p′*-biphenyl is discussed as a model system.

RESULTS AND DISCUSSION

Monomer Preparation

The methyl- and phenyl-substituted dianilino- and diphenoxysilane monomers I–IV (Table I) were prepared and condensed with a variety of aromatic diols. The dianilinosilane monomers I and II were prepared by a modification of the procedures of Anderson,[14] Curry and Byrd,[12] and

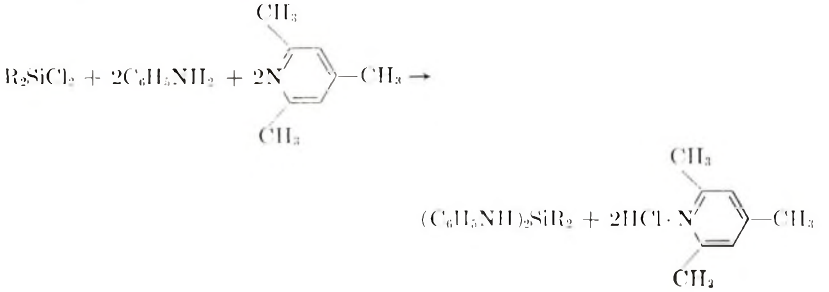
TABLE I
Properties of Silane Monomers

Monomer	Structure	Melting point, °C.	Calculated			Found		
			C, %	H, %	N, %	C, %	H, %	N, %
I	$(C_6H_5—NH)_2Si(C_6H_5)_2$	166–167	78.65	4.95	7.66	78.78	5.23	7.92
II	$(C_6H_5—NH)_2Si(CH_3)_2$	59–60	69.30	7.40	11.55	69.10	7.55	11.49
III	$(C_6H_5—NH)_2Si(CH_3)(C_6H_5)$	65.5–67.0	75.00	6.62	9.20	74.80	6.74	8.99
IV	$(C_6H_5O)_2Si(C_6H_5)_2$	64–65	78.25	5.47	—	78.14	5.23	—
V	$(C_6H_5O)_2Si(CH_3)_2$	132/4.8 mm. (b.p.)	68.86	6.59	—	69.15	6.39	—

Larsson and Smith[15] which involve the condensation of a dichlorosilane with excess aniline

$$R_2SiCl_2 + 4C_6H_4{-}NH_2 \rightarrow (C_6H_5NH)_2SiR_2 + C_6H_5NH_2\cdot HCl \qquad (3)$$

Anderson[14] and Benkeser[16] have shown that the conversion of a chlorosilane to an aminosilane is reversible. In the preparation of monomers I–III, the resulting equilibria produce appreciable quantities of the corresponding monoanilinochlorosilanes, $C_6H_5NH{-}Si(R)_2Cl$, which reduce the yields of the desired monomers and complicate their isolation as pure materials. Improved yields (up to 80%) of high purity monomers I–III were obtained by condensing 2 moles of aniline with 1 mole of the dichlorosilane in the presence of excess 2,4,6-trimethylpyridine (s-collidine). The collidine, which does not itself react with the chlorosilanes, is presumed to function as a preferential HCl acceptor because of its higher basicity than aniline and to form a hindered salt incapable of reacting with the dianilinosilane monomers to generate the monoanilinochlorosilanes.



(4)

The diphenoxysilane monomers IV and V were readily prepared by the condensation of the corresponding diphenyldichlorosilanes with phenol and were isolated and purified by vacuum distillation.

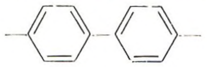
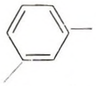
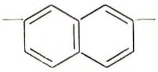
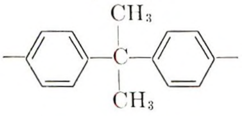
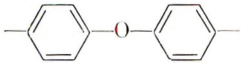
Polymer Preparation

Monomers I–III readily underwent melt polymerization with equimolar amounts of the various diols. The polymerizations were carried out in reaction vessels varying in size from 50-ml. polymerization tubes to a 10-gal. stainless steel reactor. In each case the vessels were equipped with a liquid takeoff condensing system and either a vacuum source or means for sweeping the system with dry nitrogen. The intimately mixed silane and diol monomers were heated under nitrogen until homogeneous melts were obtained, and the polymerizations were then carried out at temperatures ranging from 200 to 300°C. under a vacuum or nitrogen sweep. Agitation facilitated the release of aniline from the reaction mixtures but was not essential for the formation of high molecular weight polymers. Under similar polymerization conditions, monomers IV and V condensed only slowly. The rates of the polymerizations involving phenoxysilane monomers were greatly enhanced by the inclusion of catalytic amounts (about 1 part per 100 parts of monomer) of lithium, sodium, or potassium in the monomer mixtures. Several 11-kg. preparations of the polyaryloxysilane from monomer I and *p,p′*-biphenol were successfully accomplished under the same polymerization conditions used for laboratory-scale preparations.

Polymer Structure

The majority of the polyaryloxysilanes prepared were soluble in solvents such as tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, and 1,2,4-trichlorobenzene and are considered to be linear polymers corresponding to the general formula. Elemental analyses (Table II) of the polymers were in general agreement with the formulas.

TABLE II
Elemental Analyses of Type $\dagger O—Si(C_6H_5)_2—O—R'\dagger_n$ Polymers

R′	Calculated			Found		
	C, %	H, %	Si, %	C, %	H, %	Si, %
	78.65	4.95	7.66	78.13	4.94	8.7
	74.45	4.86	9.67	74.45	4.86	10.56
	77.75	4.71	8.20	77.67	4.74	9.92
	79.37	5.92	6.88	78.41	5.94	7.10
	75.33	4.74	7.34	75.46	4.67	7.96

Typical infrared spectra of polyaryloxysilanes containing common biphenyl chain components but differing silyl units are shown in Figure 1. The polymer containing the diphenylsilyl unit indicated several characteristic infrared bands (Fig. 1*A*). These included bands at 720 and 690 cm.$^{-1}$ arising from the monosubstituted aromatic rings attached to the silicon atom, and a sharp band at 1429 cm.$^{-1}$ and broad band at 1125 cm.$^{-1}$ attributed to the Si—C_6H_5 linkage. The 1,4-phenylene units in the chains showed absorption between 824 and 835 cm.$^{-1}$ due to C—H out-of-plane deformation. The Si—O linkages gave rise to a broad band system between 1200 and 1300 cm.$^{-1}$ which appeared in the spectrum of each polyaryloxysilane and is apparently characteristic of the phenoxy–silicon linkage. The replacement of the diphenylsilyl unit by methylphenylsilyl was accompanied (Fig. 1*B*) by the appearance of the C—H stretch absorption at about 2900 cm.$^{-1}$ and a decrease in the phenyl absorption at 3030 cm.$^{-1}$. This effect was intensified for those polymers containing dimethylsilyl chain units (Fig. 1*C*).

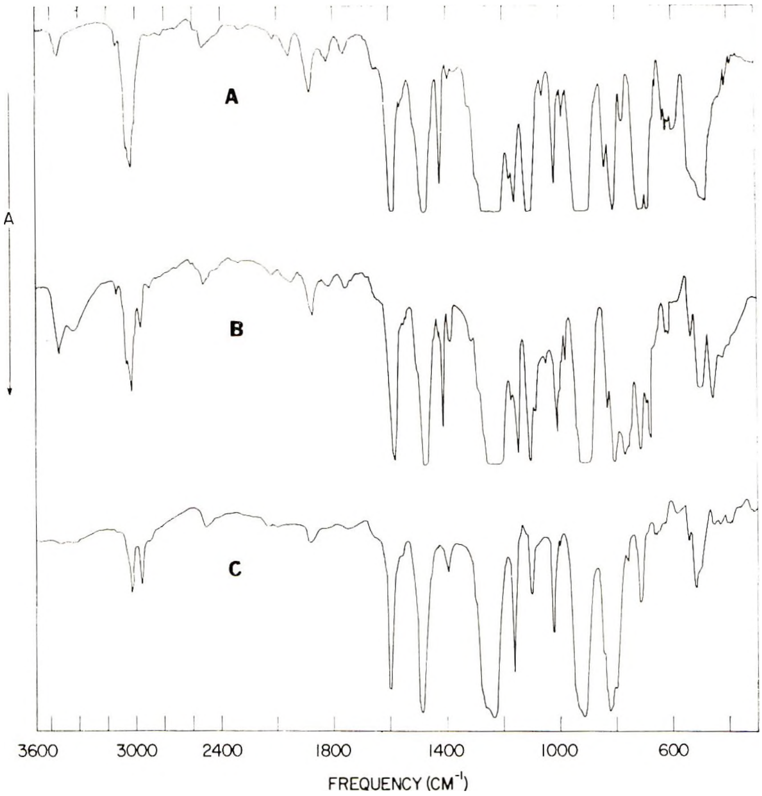


Fig. 1. Infrared spectra of polyaryloxysilanes containing (*A*) biphenyl and diphenylsilyl, (*B*) methylphenylsilyl, and (*C*) dimethylsilyl chain units.

The weight-average molecular weights $\bar{M}_w$ reported in this paper were based on data obtained by gel permeation chromatography (GPC) with 1,2,4-trichlorobenzene as the solvent and polymer repeating unit lengths determined from Stuart-Briegleb molecular models. Gel permeation chromatography proved to be a useful technique for determining the relative molecular weights of polyaryloxysilane specimens, and the weight-average values obtained by this method and by light scattering were found to be in good agreement. Typical correlations of values from the two molecular weight methods are shown in Table III.

TABLE III

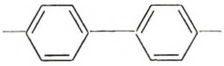
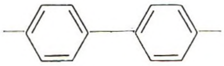
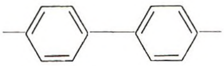
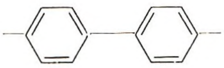
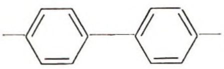
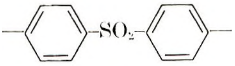
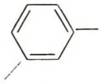
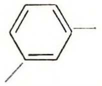
	Weight-average molecular weights	
	By GPC	By light scattering
Polymer sample A	78,000	88,000
Polymer sample B	38,000	31,000

General Properties

Typical polyaryloxydiphenylsilanes prepared by the above-described procedures from monomers I and IV and aromatic diols are shown in Table IV. The molecular weights indicated do not represent the maximum obtainable for the specific polymer structures shown. With the exception of the first preparation cited, the polymers described in Table IV were transparent, soluble thermoplastics. They varied from hard, brittle glasses to tough, flexible materials, depending upon their molecular weights. In each case, fibers could be drawn from the polymer melts. The polymers varied in color from light yellow to amber.

TABLE IV

Type $\left[O-Si(C_6H_5)_2-O-R \right]_n$ Polymers

Silane type[a]	R	Polymerization conditions		Polymer softening temp., °C.	$\bar{M}_n$[b]
		Time, hr.	Temp. °C.		
A		2	300[c]	>300[d]	—
A		2	300	150–155	81,000
B		5.5	200–300	145–150	38,000
A		2	200	135–140	28,000
B		2.5	250	115–120	16,000
A		1	250	130–135	6,000
A		6	250	65–70	24,000
B		2	250	65–70	13,000
A		6	250	65–70	30,000

[a] A = dianilino; B = diphenoxy.
[b] By gel permeation chromatography.
[c] Polymerized under air. All others were prepared under N_2.
[d] Crosslinked, insoluble, and nonfusible.

Crosslinked polyaryloxysilanes were obtained by prolonged heating or exposing the monomer mixtures to air at about 300°C. during polymerizations. The degree of crosslinking varied. For example, samples of polymers from monomer I and p,p'-biphenol were prepared which were insoluble and nonfiber-forming, but which could be compression-molded at moderate temperatures and pressures. More highly crosslinked forms of this polymer were obtained that were insoluble and did not soften or flow when attempts were made to compression-mold them at 350°C. under high pressures.

The polyaryloxysilanes appear to be amorphous materials which do not show true melting points. The x-ray diffraction patterns of the polymer from monomer I and p,p'-biphenol gave no indication of crystallinity. Differential thermal analyses of a sample of the same polymer (Fig. 2) showed no endotherms between 25 and 300°C. indicative of either a glass transition or a crystalline melting temperature. The polymer softening temperatures shown in Table IV indicate the temperatures at which the polymers soften and begin to stick to a heated metal surface and were determined by using a Fisher-Johns melting point apparatus. As might be expected, the larger, more rigid aromatic chain constituents provided polymers having higher polymer softening temperatures.

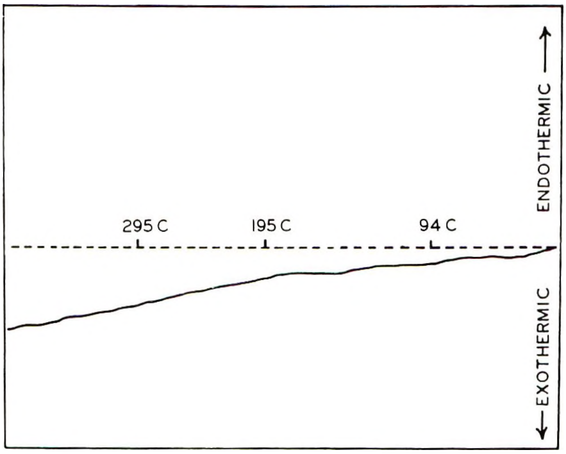
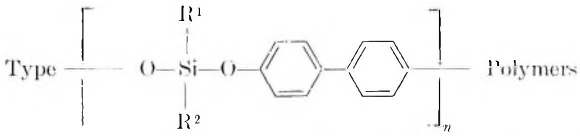


Fig. 2. Differential thermal analysis obtained for a polyaryloxysilane from monomer I p,p'-biphenol.

Representative polyaryloxysilanes prepared from p,p'-biphenol and monomers I–V are shown in Table V. These preparations illustrated that diphenyl-, phenylmethyl-, and dimethylsilyl-containing polyaryloxysilanes could be prepared with comparable ease by the same polymerization methods. As in the case of the polyaryloxydiphenylsilane polymers shown in Table IV, the polymers containing phenylmethyl- and dimethylsilyl chain units were obtainable as tough, transparent, soluble solids which could be molded and drawn into fibers. The replacement of the pendant groups on the polyaryloxysilane chains by methyl groups was observed to generally improve the flexibilities of the polymers, but to reduce their softening temperatures.

TABLE V



Silane type[a]	R^1	R^2	Polymerization conditions[b]		Polymer softening temp., °C.	$\bar{M}_w$[c]
			Time, hr.	Temp., °C.		
A	C_6H_5—	C_6H_5—	2	300	150–155	81,000
B	C_6H_5—	C_6H_5—	5.5	200–300	145–150	38,000
A	C_6H_5—	CH_3—	2	250	100–105	29,000
A	C_6H_5—	CH_3—	0.5	200	90–95	9,000
A	CH_3—	CH_3—	2	250	125–130	35,000
A	CH_3—	CH_3—	1	250	85–90	27,000
B	CH_3—	CH_3—	5	225–300	30–35	6,000

[a] A = dianilino; B = diphenoxy.

[b] The monomer mixtures were fused under nitrogen, then polymerized under a vacuum.

[c] By gel permeation chromatography.

The condensations of monomers I, II, and III with aromatic diols to produce high molecular weight polymers were rapid at polymerization temperatures of 200°C. or higher. For example, a conversion of equimolar

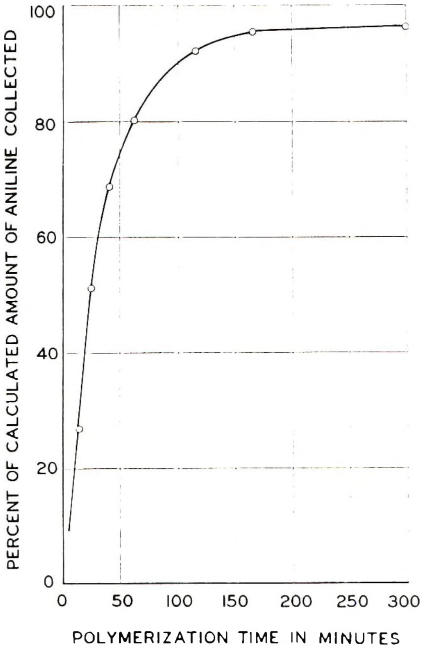


Fig. 3. Rate of aniline removal from and 11-kg. preparation of a polyaryloxysilane from monomer I and *p,p'*-biphenol at 250°C.

amounts of monomer I and *p,p′*-biphenol to provide 11 kg. of polymer was found to be essentially complete within about 180 min. at 250°C. (Fig. 3), as judged by the weight of the condensation side product, aniline, collected.

Thermal Stabilities

Representative thermogravimetric analyses of polyaryloxysilanes containing diphenylsilyl units are shown in Figure 4. These thermograms, obtained under nitrogen at a heating rate of 4°C./min., indicate thermal breakdown temperatures in the 400–500°C. range with appreciable polymer residues remaining up to 900°C. The thermal-oxidative resistance of the polyaryloxydiphenylsilanes appears to be exceptionally good. Thermal analyses under air and nitrogen of a polymer ($\bar{M}_w$ = 84,000) prepared from monomer I and *p,p′*-biphenol are shown in Figure 5. Thermal decom-

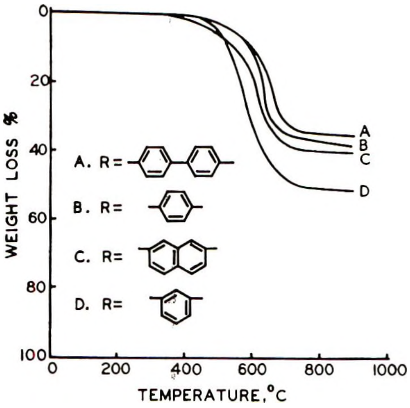


Fig. 4. Thermogravimetric analyses of type $\left[O—Si(C_6H_5)_2—O—R\right]_n$ polymers under nitrogen at a heating rate of 4°C./min.

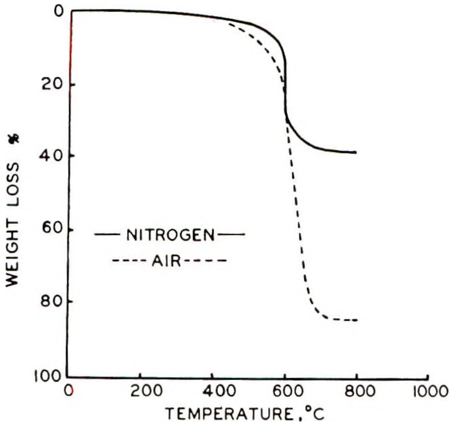


Fig. 5. Thermogravimetric analysis of polymer from monomer I and *p,p′*-biphenol under air and nitrogen.

TABLE VI

Characterization of Polymer I Specimens

Expt. no.	Polymerization conditions			Sample color	Solubility (0.5%) in 1,2,4-trichlorobenzene[a]	Moldability at 160°C.[b]	Strength of molded disk	Elemental analyses[c]			Molecular weights
	Atmosphere (heat-up/polym.)	Time, hr.	Temp., °C.					C, %	H, %	Si, %	$\bar{M}_w$ (by GPC)
1	Air/vac	2	300	Medium amber	—	—[d]	—	67.50	4.21	15.47	—
2	N_2/vac	2	300	Light amber	+	+	Nonbrittle	79.08	4.95	7.42	77,916
3	N_2/vac	2	300	Light yellow	+	+	Brittle	78.91	4.89	7.28	31,206
4	N_2/vac	6	300	Medium yellow	—	+	Nonbrittle	—	—	—	—
5	Air/air	2	300	Dark amber	—	—[e]	—	78.54	4.81	8.35	—
6	Air/air	2	300	Dark amber	—	+	Brittle	78.36	5.06	8.51	—
7	N_2/vac	4	300	Very light yellow	+	+	Nonbrittle	—	—	—	50,086
8	Air/air	0.3	285	Medium amber	+	+	Brittle	78.78	4.99	7.95	32,836
9	Air/air	2	250	Dark brown	—	+	Nonbrittle	78.89	5.00	7.20	—
10	N_2/vac	2	250	Very light amber	+	+	Nonbrittle	—	—	—	66,130
11	N_2/vac	4	250	Light amber	+	+	Nonbrittle	78.72	4.83	8.31	59,052
12	N_2/vac	6	250	Light amber	+	+	Nonbrittle	—	—	—	45,850
13	Air/air	2	200	Very dark amber	+	+	Nonbrittle	—	—	—	53,852
14	N_2/vac	4	200	Light amber	+	+	Nonbrittle	78.78	5.23	7.92	47,230
15	N_2/vac	6	200	Very light amber	+	+	Nonbrittle	—	—	—	47,454

[a] Soluble samples dissolved at room temperature; insoluble samples failed to dissolve in 24 hr. at 50°C. with agitation.

[b] Films pressed between aluminum foil between platens of laboratory press.

[c] Analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

[d] Nonmoldable also at 600°F. under high pressure.

[e] Can be sharply creased without cracking.

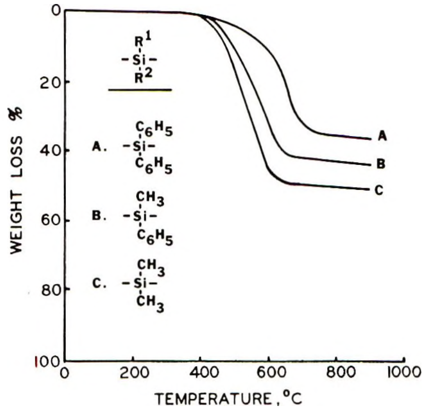
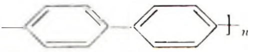


Fig. 6. Thermogravimetric analyses of type $-[-O-Si(R)_2-O-$  $]_n$ polymers under nitrogen at a heating rate of 4°C./min.

positions began under both conditions at about 400°C. However, the extent of degradation was more severe under air than under a vacuum.

Thermograms of polyaryloxysilanes containing diphenyl-, phenylmethyl-, and dimethylsilyl chain units (Fig. 6) indicate that polymers of each of these types exhibit high thermal stabilities. As would be expected, the fully aromatic substituted polyaryloxysilanes appeared to be the most stable.

Evaluation of a Model Polyaryloxysilane

A more thorough study was made of the polyaryloxysilane (designated polymer I) obtained from monomer I and *p,p'*-biphenol. As indicated in Table VI, high molecular weight forms of this model polymer were obtained from polymerizations carried out at 200–300°C. under either a vacuum or air. The polymers prepared under air were significantly darker in color than those prepared under a vacuum. This is attributed to the fact that the condensation side product, aniline, undergoes thermal-oxidative degradation readily at the polymerization temperatures used. In some cases, the presence of air during polymerizations or excessive heating at temperatures above about 250°C. caused crosslinked polymers to be obtained (as evidenced by their insolubility and/or lack of moldability).

The molding characteristics of each of the experimental polymer I specimens prepared were screened. Approximately 2-g. samples of the resins were pressed between sheets of aluminum foil between the platens of a laboratory press. In general, the polymers showed excellent melt flows and were readily formed into transparent films at 160°C. under moderate (1000 psi) pressure. Two samples that failed to mold at 160°C. also failed to mold at 320°C. under very high pressure. The same two polymers were insoluble in hot 1,2,4-trichlorobenzene and were considered to be highly crosslinked. Low degrees of crosslinking in certain other specimens were indicated by their ability to be compression-molded but not dissolved. The soluble polymer I specimens could readily be drawn into low-tenacity fibers from their melts. These fibers had average tenacities of about 0.5 g./den. and could not be cold-drawn. The films pressed from polymer specimens having weight-average molecular weights below about 45,000 were found to be brittle. However, those films from specimens having $\bar{M}_W$ values exceeding 45,000 were considerably stronger and could be creased sharply without breaking.

The possibility of increasing the molecular weight and attendant strength properties of polymer I specimens having $\bar{M}_W$ values less than about 45,000 was investigated. Remelting such specimens and heating them at 200–300°C. under a vacuum for prolonged periods of time proved unsuccessful. The general result of such post-polymerization treatments was to crosslink the polymers partially, rendering them insoluble, with no improvement in their mechanical strengths. However, it was found that the weight-average molecular weights of the polymer I specimens could be significantly increased by heating them with 5% of their weight of monomer I at 225–250°C. under a vacuum (Table VII). This procedure provided polymers having significantly higher molecular weights and which were totally soluble, tough thermoplastics. The upgrading process was applicable to

TABLE VII
Upgrading Brittle Polymer I Samples

		Conditions of Post-polymerization treatment				
Sample no.	Monomer added (5%)	Atmosphere	Time, hr.	Temp., °C.	$\bar{M}_W$[a,b]	Polymer properties[c]
1	—	—	—	—	41,000	Brittle
1A	Monomer I	Vacuum	0.66	225	63,000	Nonbrittle
1B	—	Vacuum	0.66	225	—	Brittle
1C	Monomer I	N_2 Sweep	2.0	225	42,000	Brittle
1D	Monomer I	Vacuum	1.0	250	53,000	Nonbrittle
1E	Monomer I + *p,p'*-biphenol (1:1)	Vacuum	1.0	250	—	Brittle
1F	—	Vacuum	1.0	250	38,000	Brittle
1G	Monomer I	Vacuum	1.0	250	54,000	Nonbrittle
2	—	—	—	—	37,000	Brittle
2A	Monomer I	Vacuum	1.0	250	58,000	Nonbrittle
3	—	—	—	—	32,000	Brittle
3A	Monomer I	Vacuum	1.0	250	61,000	Nonbrittle
3B[d]	Monomer I	Vacuum	1.0	250	84,000	Nonbrittle

[a] By gel permeation chromatography with 1,2,4-trichlorobenzene as solvent.

[b] All polymer specimens were soluble in 1,2,4-trichlorobenzene.

[c] Based on disks prepared by pressing polymers between aluminum foil in laboratory press at 160° C.

[d] An 11-kg. sample of polymer I was upgraded in this experiment.

both laboratory-scale (10–200 g.) and larger-scale (11 kg.) polymer I samples.

Attempts to prepare high molecular weight ($\bar{M}_w = 45{,}000$) Polymer I specimens by using an excess of monomer I in the initial monomer charges were unsuccessful. It is believed that a portion of the monomer I used in preparing polymer I is thermally destroyed or rendered inactive during the polymerizations and that the polymers formed are largely terminated by phenolic —OH groups. The coupling of such HO-terminated polyaryloxysilanes by the addition of fresh monomer I could explain the molecular weight increases observed.

Polymer I Properties

The mechanical properties of several thermoplastic Polymer I specimens prepared in this study were determined (Table VIII). The property data indicate that polymer I, or modifications thereof, show promise as structural plastics in specialized applications. These data were obtained on injection-molded test specimens prepared at a cylinder temperature of 160°C. and a ram pressure of about 1000 psi. The polymer I flowed well into cold molds and released from the molds easily. The polymer specimens did not undergo any apparent degradation during molding, and the scrap was remoldable.

TABLE VIII

Properties of Experimental Polymer I Specimens[a]

Specimen	$\bar{M}_w$	Flexural strength, psi × 10^{-3}	Tensile strength, psi × 10^{-3}	Heat deflection temp., °C.	Elongation at break, %	Impact strength, notched Izod, ft.-lb./in. of notch
A	49,000	3.1–3.6	3.0–5.8	101	5	0.15–0.23
B	72,000	5.6–6.1	6.0–7.4	95	5	0.38–0.47
C	56,000	7.8–10.5	7.1–8.0	108	5	0.15–0.43
D	84,000	3.1–5.0	7.0–7.7	95	5	0.15–0.40

[a] Injection-molded at 160°C., 1000 psi.

Polymer I specimens varying in $\bar{M}_w$ values from 49,000 to 84,000 are shown in Table VIII. Specimens having lower molecular weights were too brittle to withstand the necessary handling during testing. The specimens showed reasonable tensile and flexural strength values, ranging from about 3,000 to 10,000 psi for the former, and 3,000 to 8,000 psi for the latter.

The impact strengths (notched Izods) of the four polymer I specimens shown were low, fairly independent of molecular weight, and corresponded roughly to those of cast poly(methyl methacrylate) and general-purpose, heat-resistant polystyrene molding compounds.

In each case the heat deflection temperatures (264 psi) were near 100° C., regardless of the polymer's molecular weight. The elongation at break

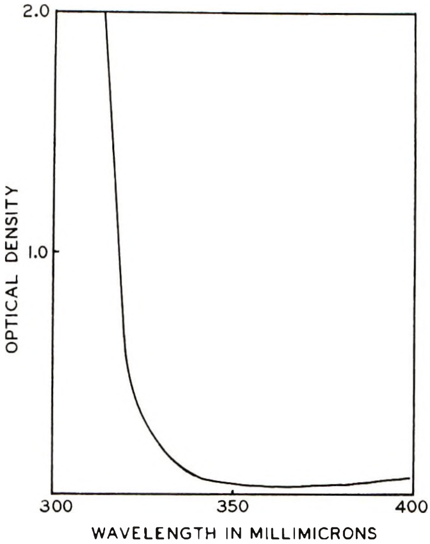


Fig. 7. Ultraviolet transmission of a 2-mil solvent-cast film of polymer I.

values for the specimens were low (4–5%) and consistent with the previous observation that polymer I fibers could not be effectively cold-drawn.

Polymer I Film. Nonbrittle polymer I was solvent-cast into crystal clear, nearly colorless film from 20% solutions of the polymers in 1,2,4-trichlorobenzene or toluene. The films were cast on glass or polished aluminum plates, then heated at temperatures below 90°C. until solvent removal was completed. Solvent-free films approximately 2 mils in thickness

TABLE IX

Chemical Resistance and Reactivity of Polymer I[a]

Reagent	Results	
	7-day exposure	30-day exposure
Distilled water	No effect	Polymer bleached
Sulfuric acid (30%)	No effect	Polymer bleached
Sodium hydroxide (10%)	No effect	Reduced to white powder
Ethanol (absolute)	No effect	Polymer bleached
Acetone	Swollen	Swollen
Ethyl acetate	Swollen	Swollen
Carbon tetrachloride	Dissolved	Dissolved
Toluene	Dissolved	Dissolved
n-Octane	No effect	No effect
Sodium chloride soln. (10%)	No effect	Polymer bleached
Tetrahydrofuran	Dissolved	Dissolved
1,2,4-Trichlorobenzene	Dissolved	Dissolved
Benzene	Dissolved	Dissolved
Dimethylformamide	Dissolved	Dissolved
Dimethyl sulfoxide	Swollen	Swollen

[a] Sample with $\bar{M}_w = 84,000$. Tests at 23°C.

could be sharply creased without cracking and gave tensile values of 5,000–6,000 psi when pulled on an Instron testing machine at a crosshead speed of 0.2 in./min. The ultraviolet transmission of the polymer I film showed a sharp cutoff at about 313 mμ (Fig. 7).

Chemical Resistance. Qualitative tests of the chemical resistance of polymer I were carried out. The tests, shown in Table IX, consisted of placing particles (smaller than $^1/_8$ in.) of a representative polymer I specimen ($\bar{M}_w$ 84,000) in tubes containing the reagents under consideration. Appraisals of the samples were made after 7 and 30 days at 25°C. by observing any tendency of the polymers to dissolve, swell, and/or chemically react.

The 7-day tests showed that polymer I had good resistance to water, 30% sulfuric acid solution, 10% sodium hydroxide solution, absolute ethanol, aqueous sodium chloride, and *n*-octane. The polymer was soluble in a variety of organic solvents, but only swelled but did not dissolve in others.

After 30 days exposure to the reagents, the polymer specimens (originally amber-colored) in water, ethanol, and the aqueous reagents were bleached to a gray-white color. In addition, the sample exposed to the 10% sodium hydroxide solution had been reduced to a white powder. The absorption of water by, or hydrolysis of, polymer I did not occur rapidly, but was apparent after prolonged exposure at 25°C.

These results indicate that further studies of the hydrolytic stabilities of polyaryloxysilanes should be carried out, and that the development of crosslinked modifications of these polymers might be required if outstanding chemical and/or solvent resistance is to be achieved.

CONCLUSIONS

This study of polymer I has demonstrated that polymers of the polyaryloxysilane type can be readily prepared as high molecular weight materials, and that such polymers can possess uniquely useful engineering properties. Currently available data indicate that polymer I has an exceptionally high degree of thermal stability, as demonstrated by differential thermal and thermogravimetric analyses. However, the true test of a polymer's thermal stability is its retention of useful properties at elevated temperatures. To date, only linear, thermoplastic polymer I specimens have been explored in any depth. As a consequence of the large number of silicon–oxygen linkages in their chains, these materials have relatively high degrees of chain mobility and tend to undergo viscoelastic flow at moderate temperatures (100–200°C.). While the high degree of chain mobility might be highly useful in low-temperature applications, this property limits the practical use-temperature ceiling for polymer I for a number of potential applications, and also the ability to determine mechanical properties at elevated temperatures.

It is considered that the true high-temperature potentials of polyaryloxysilane-type polymers will be realized with crosslinked modifications.

These would include both elastomeric and tightly crosslinked thermoset materials. Polymers of these types would be expected to possess useful properties at higher temperatures than their linear, thermoplastic counterparts, and more fully utilize the inherent stability of the polyaryloxysilanes.

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Résumé

Une série de polyaryloxysilanes a été préparée au départ de diols aromatiques et de dianilino- et diphénoxysilanes. Des polymères de poids moléculaire élevé ont été obtenus à des températures de 200°C ou plus élevées, en utilisant le processus de polymérisation à l'état fondu. Les polymères, qui combinent les structures des silicones et polyaromatiques présentent des stabilités thermiques élevées et ont été obtenues comme matériaux (*1*) qui ne fondaient pas ou se ramolissaient à 350°C, (*2*) qui étaient gommeuses à des températures élevées, et (*3*) etaient solubles et filmogènes, ou formant des fibres capables d'être traitées comme des thermoplastics conventionnels et présentant potentiellement des propriétés mécaniques utiles. La préparation des monomères, des procédés généraux de polymérisation et certains rapports structure-propriétés pour les polyaryloxysilanes thermoplastiques ont été également considérés.

Zusammenfassung

Eine Reihe von Polyarylsiloxanen wurde aus aromatischen Diolen und Dianilino- und Diphenoxysilanen dargestellt. Mit Schmelzpolymerisations-verfahren wurden bei Temperaturen von 200°C und höher hochmolekulare Polymere erhalten. Die Polymeren, welche die Struktur von Silikonen und Polyaromaten vereinen, besassen hohe thermische Stabilität und wurden als Stoffe erhalten, die (*1*) bei 350°C noch nichtschmolzen oder erweichten, (*2*) bei höherer Temperatur gummiartig wurden oder (*3*) lösliche, film und faserbildende, wi ekonventionelle Thermoplaste verarbeitbare Polymere mit potentiell brauchbaren mechanischen Eigenschaften waren. Die Darstellung der Monomeren, die allgemeinen Polymerisationsverfahren sowie gewisse Struktur—Eigenschaftsbeziehungen für die thermoplastischen Polyaryloxylane werden diskutiert.

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Chemical Modifications of Polycyclopentadiene

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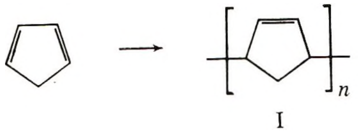
Synopsis

Polycyclopentadiene, which is known to undergo extremely fast autoxidation resulting in insoluble products, was chemically modified, leading to derivatives no longer sensitive to oxygen. Soluble and stable products can be obtained in high conversions by Diels-Alder addition of hexachlorocyclopentadiene (96.5 mole-%), by epoxidation (93.5 mole-%), and by addition of thioglycolic acid (97.9 mole-%). A prerequisite is an efficient purification of polycyclopentadiene via reprecipitations in an oxygen-free atmosphere. Other attempted alterations of the double bond were the hydroxyformylation and the free-radical addition of haloalkanes, which, however, resulted in completely insoluble products. Typical addition reactions were carried out with the epoxy derivative of polycyclopentadiene, e.g., additions of hydrogen chloride, monochloracetic acid, chlorophenol, thiophenol, piperidine, hydrolysis to glycols. Easily initiated polymerization of the epoxy group is believed to be a conversion-limiting side reaction in certain addition reactions, such as addition of hydrochloric acid or hydrolysis to glycols.

INTRODUCTION

Cyclopentadiene has been polymerized in these laboratories[1] by means of a homogeneous Ziegler system leading to soluble polymers of high molecular weight. As shown by NMR investigations,[1] it is possible that the polymer consists mainly of repeating units (I) resulting from 1,4-polymerization of cyclopentadiene.†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(1)

Although this process yields a polymer of higher molecular weight and probably of different structure than products reported in earlier work,[2–5] the extremely fast autoxidation of polycyclopentadiene (PCPD)[1,3,5] remains a disadvantage. The autoxidation very rapidly results in insoluble polymers and, therefore, militates against any practical utilization of polycyclopentadiene.

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† A private communication from Mrs. S.-P. S. Yen indicated that further work on the elucidation of the structure is required and planned.

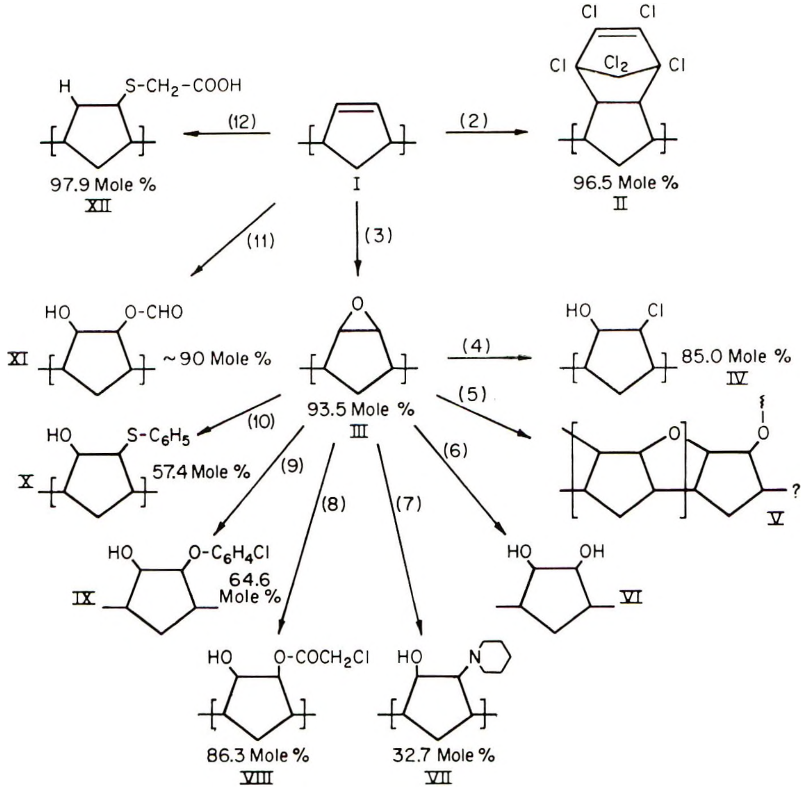


Figure 1.

Complete exclusion of oxygen is essential to maintain the solubility of the polymers. Addition of antioxidants[1] to inhibit autoxidation does give some protection during the work-up immediately after polymerization but is of very limited value during extended handling and storage. Unreasonably large quantities are needed to maintain solubility for several weeks. Chemical reactions, however, can lead to modified polymers that are no longer sensitive to oxygen and can be handled and stored in soluble form indefinitely.

It is the purpose of this paper to describe, with representative examples, reactions that lead to soluble, less sensitive derivatives of polycyclopentadiene by converting the double bond; namely, the Diels-Alder reaction, epoxidation, and the addition of thiols (Fig. 1). Hydroxyformylation by means of performic acid and free-radical addition of haloalkanes were also attempted but resulted in completely insoluble reaction products. Several reactions were also carried out with the epoxide derivative (III) of polycyclopentadiene (Fig. 1). The polymers obtained possess completely different properties than polycyclopentadiene. They cannot be obtained directly via polymerization since their corresponding monomers are either unknown or would give polymers of different structures.

Specially prepared low molecular weight polycyclopentadiene[1] was used for most of the reactions to reduce to a minimum the hazard of cross-linking during the reaction; however, the reactions can with proper care as well be carried out with polymers of much higher molecular weight.

RESULTS AND DISCUSSION

Prepurification of Polycyclopentadiene

Two different approaches were utilized in the purification of polycyclopentadiene. If the polymer was to be used shortly after purification and the reactions were not sensitive to antioxidants, three reprecipitations were carried out under a nitrogen blanket by adding a benzene solution to methanol containing 1–5% (based on the polymer) diphenylamine (DPA), phenyl-β-naphthylamine, or 4-*tert*-butylpyrocatechol. When stored at −20°C. in rubber capped ampules, the polymers remained soluble for about 2 weeks.

To prepare antioxidant-free polymers, especially for epoxidation and free-radical additions, four reprecipitations (benzene–methanol) in an argon-filled apparatus were found to be sufficient to remove the remains of the Ziegler-catalyst. After freeze drying from a benzene solution in high vacuum and sealing, these polycyclopentadiene samples stayed soluble over a test period of 18 months.

Diels-Alder Reaction

Hexachlorocyclopentadiene (HCCPD) is a solvent for PCPD, and its Diels-Alder reaction can therefore conveniently and most efficiently be carried out in an excess of this reactant. Analytically, HCCPD offers the advantage of introducing a high chlorine content into the polymer, which can be used for the determination of the conversion. This high chlorine content also makes it potentially one of the commercially most interesting dienes for Diels-Alder reactions since it confers fire-retardant properties on the polymers.

TABLE I
Diels-Alder Addition of Hexachlorocyclopentadiene (HCCPD) to Polycyclopentadiene (PCPD)[a]

Reaction PCPD/ HCCPD	Time, hr.	Cl content, %	Conversion, mole-%[b]	[η][c]	MW[d]
1	6	41.76	91.3	0.120	12,000
2	9	46.84	93.8	—	—
3	12	49.26	94.9	0.105	7,000
4	24	52.97	96.5	—	—

[a] Mole ratio HCCPD:PCPD = 10:1; 150°C.; nitrogen atmosphere.
[b] Based on $+C_5H_6+ \rightarrow +C_{10}H_6Cl_6+$; 100% conversion = 62.82% Cl.
[c] Concentration 0.5 g./100 ml. in tetrahydrofuran.
[d] Determined by vapor-phase osmometry.

In an inert atmosphere the addition of HCCPD [reaction (2) II] proceeds smoothly at temperatures of 140–150°C. A conversion of 91 mole-%, according to the chlorine content, is achieved after 6 hr. Prolonged heating increases the conversion only slightly (Table I) and is accompanied by strong discoloration and a slight degradation of the polymer. Partially converted samples (70 mole-% or less) still exhibit a strong tendency towards autoxidation and formation of insoluble products in the following work-up.

The reaction is confirmed by infrared data, shown by a shift and strengthening of the C═C stretching absorption (6.15–6.25 μ; HCCPD itself absorbs at 6.25 and 6.35 μ) and the strong decrease of the C═C—H stretching at 3.25 μ. Since the addition of HCCPD does not introduce additional protons into the polymer, the conversion can be followed by NMR via the decrease of olefinic protons. Unfortunately, an extremely low signal to noise ratio encountered with these samples made a quantitative determination impossible. This is due to the unfavorable low proton concentration in this polymer (6 protons per repeating unit with a molecular weight of 339), which requires unusually high concentrations resulting in weak signals with poor resolution.

No indication of pyrolysis of HCCPD[6] was observed under the conditions employed. Pyrolysis products of HCCPD would, in any case, be separated during the work-up as tested in blank reactions where pyrolysis was deliberately attempted. Secondary reactions of already converted repeating units, however, cannot be ruled out. If occurring at all, this would be only a very minor effect since in no case, even after unreasonably long reaction times, did the apparent conversion exceed 100%.

The polymers are obtained as yellow to brown powders. They are soluble in common organic solvents, e.g., chloroform, carbon tetrachloride, tetrahydrofuran, dioxane. Some nonsolvents are petroleum ether, ether, and acetone. The polymers form brittle, transparent films when cast from solution. The highly converted polymers remained soluble over a testing period of 30 months.

Partially converted products soften at temperatures between 200°C. and 250°C., depending on the degree of conversion. Products above 90 mole-% conversion neither discolor nor soften at temperatures up to 290°C. (5 min. in air). Prolonged heating at this temperature causes discoloration. Thermogravimetric analysis in air at a heating rate of 5°C./min. showed a weight loss of 8% at 310°C. with rapid decomposition setting in at this temperature; the weight loss is 46% at 325°C. The polymers are self-extinguishable when removed from a flame.

Epoxidation and Hydroxyacylation

Polycyclopentadiene was converted into the corresponding epoxide [reaction (3); III] by means of perbenzoic acid (PBA) in chloroform or methylene chloride solution (Table II).

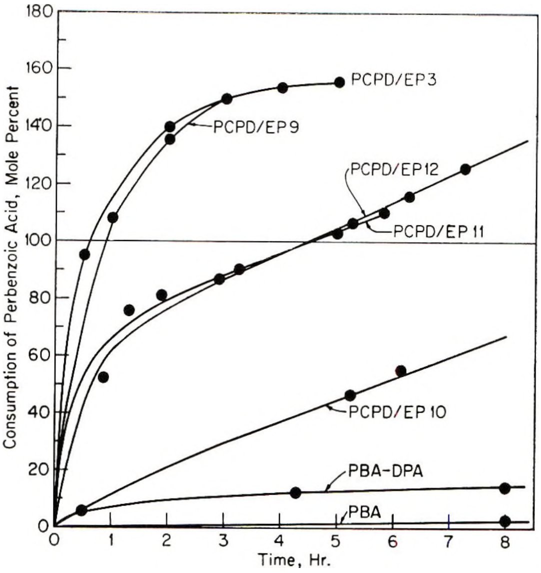


Fig. 2. Consumption of perbenzoic acid (PBA) in epoxidation of polycyclopentadiene in chloroform solution. Variation of temperature and sample history: (PCPD/EP3) no purification, no antioxidant, 0°C., 58 mole-% excess PBA; (PCPD/EP8), 1 reprecipitation in MeOH, DPA, −20°C., 100 mole-% excess PBA; (PCPD/EP9), 2 reprecipitations in MeOH, argon, 30°C., (in methylene chloride) 100 mole-% excess PBA; (PCPD/EP10), 2 reprecipitations in MeOH, argon; −20°C.; 100 mole-% excess PBA; (PCPD/EP11) 4 reprecipitations in MeOH, argon; 0°C.; 100 mole-% excess PBA; (PBA-DPA) 0°C.; 3 mole-% diphenylamine in perbenzoic acid; (PBA) 0°C.

The introduction of the epoxy group gives rise to three typical epoxide infrared absorptions, 8.15, 11.75, and 13.3 μ,[7,8] which are confirmed by the data on a model compound, 1,2-epoxycyclopentane, having absorptions at 8.25, 11.15, and 13.15 μ with the same intensity.[9] The presence of a weak carbonyl absorption at 5.8 μ, which was observed in all samples, is probably due to a small degree of hydroxyacylation.

Cyclopentene, when subjected to epoxidation in a model reaction under identical conditions, also yielded small amounts of 1,2-dihydroxycyclopentane monobenzoate and other higher-boiling carbonyl-containing fractions.[9] Isomerization of epoxy groups to keto groups[10] to a small extent can also not be ruled out as a source for carbonyl absorptions. However, none of these reactions is favored under the conditions chosen.

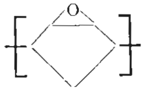
In the nuclear magnetic resonance spectra the protons of the epoxy group give rise to a strong peak centered at 6.55 ppm, with a half bandwidth of about 20 cps. 1,2-Epoxycyclopentane and 3,3′-bis(1,2-epoxycyclopentyl), which were used as model compounds, exhibit a singlet at 6.68 ppm or a multiplet centered at 6.65 ppm, respectively.[9]

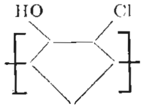
The purification of PCPD is essential in this reaction because of the rapid decomposition peracids undergo under the catalytic influence of heavy metal ions (remains of the Ziegler catalyst). Additional consumption and

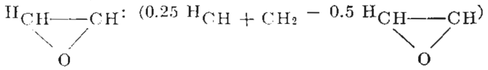
TABLE II
Epoxidation of Polycyclopentadiene (PCPD)

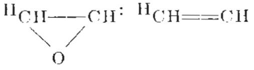
	PCPD							Analytical determinations								
								Elemental analysis					Conversion (based on HCl addition)			
Reaction PCPD /EP	Antioxidant	Prepurification	Wt., g.	Excess C_6H_5-COOH, mole-%	$CHCl_3$, ml.	Temp., °C.	Time, hr.	C, %	H, %	O, %	Conversion (based on oxygen content), mole-%	Conversion (based on HCl titration), mole-%	Cl content, %	Conversion, mole-%	Conversion (based on NMR), mole-%	Solubility in $HCCl_3$
1	DPA	None	2.0	58	200	0	0.5	76.75	7.83	—	—	53.6	16.00	67.3	—	
2	DPA	None	2.0	58	200	0	1.5	76.46	7.84	—	—	43.3	17.51	71.7	—	
3	DPA	None	2.0	58	200	0	5.5	76.32	7.72	—	—	53.5	18.76	79.1	—	
4	DPA	Extr. pet. ether, N_2	1.48	100	180	0	3.5	72.59	7.26	16.95	88.8	68.5	22.59	85.0	—	
5	DPA	2 rppts. benz./pet. ether; N_2	1.10	100	125	0	21.0	—	—	—	—	61.0	—	—	76.5[c]	
6	DPA	1 rppt. benz./ MeOH; N_2	1.77	100	190	−20	23.0	72.07	7.01	17.14	89.7	—	—	—	87.6[d]	Insol. after 1 day
7	DPA	1 rppt. benz./ MeOH; N_2	1.55	100	180	0	4.5	72.15	7.48	15.76	83.9	—	—	—	—	Insol. after 1 day

8	DPA	1 rppt. benz./MeOH; N_2	1.35	100	155	−20	11.5	—	—	16.14	85.6	—	—	—	—	
9	None	2 rppts. benz./MeOH; argon	0.95	100	300[e]	30	3.0	—	—	—	—	—	—	—	—	Insol. after 1 day
10	None	4 rppts. benz./MeOH; argon	2.40	100	240	−20	28.0	—	—	17.78	92.9	70.0	—	—	84.5[d]	Insol. after several months
11	None	4 rppts. benz./MeOH; argon	2.50	100	260	0	6.0	—	—	17.97	93.5	68.5	—	—	87.0[d]	Insol. after several months

[a] Calculated for  : C, 73.14%; H, 7.36%; O, 19.49%.

[b] Calculated for  : Cl, 29.66%.

[c] Based on  $0.5\,H_{\underset{O}{CH-CH}}$: $(0.25\,H_{CH} + CH_2 - 0.5\,H_{\underset{O}{CH-CH}})$

[d] Based on  $H_{\underset{O}{CH-CH}}$: $H_{CH=CH}$

[e] CH_2Cl_2.

decomposition of peracid is also caused by the presence of antioxidants although to a much smaller degree. Optimum conditions are attained when PCPD has been subjected to four reprecipitations in an argon atmosphere without the use of antioxidants. The epoxidation with perbenzoic acid is advantageously carried out at or below 0°C. (runs 10 and 11 in Table II).

Figure 2 shows the influence of a few parameters on the epoxidation. Decomposition of the peracid is virtually complete after 5 hr. even at 0°C., when unpurified, stabilized PCPD is used (PCPD/EP3). About the same rate of decomposition is observed in methylene chloride at 30°C. with a purified, antioxidant-free PCPD (PCPD/EP9). The conversion into the epoxide is not drastically reduced in these cases (Table II); however, the products become insoluble immediately after the work-up, owing to the extremely fast autoxidation of unreacted CPD units. The role of impurities is still important at −20°C. The reaction PCPD/EP8, carried out with less pure PCPD in the presence of antioxidant, shows a much faster disappearance of perbenzoic acid coupled with a lower conversion, than the reaction PCPD/EP10 of highly purified PCPD. The comparison of PCPD/EP 10 and 11, which both lead to high conversions and stable products, indicates that decomposition of perbenzoic acid is still considerable at 0°C. However, this does not endanger complete epoxidation of PCPD as long as an excess of peracid is supplied.

Highly epoxidized PCPD's are obtained in the form of white powders, which form somewhat brittle, transparent films when cast from solutions. These polymers are soluble in a variety of common solvents, e.g., halogenated hydrocarbons, dioxane, tetrahydrofuran, cyclohexanone, pyridine, epichlorohydrin. They dissolve at elevated temperatures, by undergoing reactions, in solvents with functional groups, e.g., amines, phenols, and thiols. Nonsolvents for the epoxidized PCPD are aliphatic and aromatic hydrocarbons, alcohols, acetone, and nitromethane. The polymer becomes sticky at 265–270°C. and discolors slightly at 270–280°C. (in air). Thermogravimetric analysis (nitrogen atmosphere, heating rate 5°C./min.) shows a weight loss of only 2% up to 252°C. with a very abrupt decomposition setting in at this temperature. The loss at 264°C. is 50%.

Monoperphthalic and *p*-nitroperbenzoic acid, both efficient epoxidizing agents,[11,12] yielded products that became insoluble shortly after isolation. In these reactions, the instability of the epoxidized products is attributed to the formation of the much stronger, sparingly soluble carboxylic acids, phthalic and *p*-nitrobenzoic acid, which are not easily separated from the precipitated polymer. They may subsequently cause crosslinking via epoxide polymerization.

A similar behavior was expected and observed when performic acid was used. In this case partial hydroxylation and hydroxyformylation [Fig. 1, reaction (10)] are further complications. The products became insoluble during the oxidation reaction, yet under conditions favorable for hydroxyformylation, infrared determinations showed a high degree of conversion.

Repeating units (XI) resulting from hydroxyformylation were indicated by the disappearance of unsaturation (C—H stretching at 3.25 μ) and the introduction of the formate (C=O stretching at 5.85 μ, C—O at 8.45 μ) as well as the hydroxy group. Epoxide absorptions were very weak or not observed at all. With the assumption of the sole formation of structural units XI, a calculation on the basis of the oxygen content gave 90 mole-% conversion.

Determination and Reactions of Polycyclopentadiene Epoxide

The quantitative determination of the epoxide content (Table II) by most methods is restricted to the polymer in solution and could therefore be carried out only on highly converted products. The accuracy of the determination is low compared to that reported for other polymeric epoxides,[13] since different values are obtained by different analytical methods. The determination on the basis of the oxygen content (maximum conversion: 94 mole-%) probably yields somewhat high values due to other oxygen sources, e.g., peroxides resulting from autoxidation. In the determination by nuclear magnetic resonance (maximum conversion: 88 mole-%) the ratio of olefinic protons (τ = 4.45 ppm) to newly formed epoxide protons (τ = 6.55 ppm) is used. When the absorption of residual olefinic protons becomes negligible upon high conversion, the amount of epoxide repeating units is determined by subtracting the corresponding aliphatic protons of these units from the total sum of aliphatic protons present. This latter method includes an additional inaccuracy; since it "sees" only epoxide and aliphatic protons, it does not discriminate between unreacted units and by-products. Nevertheless, the NMR determination seems to give the most reasonable values.

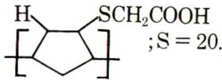
The commonly used method of epoxide determination, the addition of hydrogen chloride or bromide in dioxane or pyridine solution and back-titration of the excess acid,[13] gave consistently the lowest values (maximum conversion: 70 mole-%). Partial isomerization,[10] hydration,[13] or formation of epoxide from the intermediate chlorohydrin during back-titration[13] could be explanations for this behavior. A support for the latter hypothesis may be seen in the fact that determinations on the basis of the chloride content of the isolated chlorohydrin (IV), which was obtained under identical chlorination conditions, gave considerably higher values (maximum conversion: 84 mole-%). These latter values are comparable to those obtained from oxygen determination and NMR data.

Direct titration with hydrochloric or hydrobromic acid in an acetic acid medium[14] is not applicable because the polymer precipitates at the very beginning of the titration. The complete insolubility of the product indicates crosslinking due to epoxide polymerization. Polymerization is an epoxide-consuming reaction and would thus lower the chemically determinable epoxide. Deliberately attempted polymerizations of this polyepoxide, initiated by catalytic amounts of BF_3 etherate were undertaken as a test, and they yielded completely insoluble products. Infrared investigations

TABLE III
Epoxidation of Polycyclopentadiene (PCPD) with Thioglycolic Acid (TGA) at 60°C.

PCPD/TGA	Wt. PCPD, g.	Mole ratio TGA:PCPD	Solvent	DBPO[a]	Atmosphere	Time, hr.	S, %	Conversion, mole-%[b]
1	0.424	9:1	Benzene (50 ml.) + THF (4 ml.)	—	Air	8	19.27	97.9
2	1.117	8.5:1	THF (90 ml.)	2 mole-%	N_2	56	17.04	92.5

[a] Dibenzoyl peroxide, based on polymer.

[b] Calculated for 

;S = 20.73%.

revealed that the available epoxy groups were used up almost completely in this polymerization. Studies on model compounds,[9] such as 3,3-bis(1,2-epoxycyclopentyl), showed that the polymerization will not necessarily occur only intermolecularly but partially intramolecularly, to form blocks of ladder structures (V) in an otherwise crosslinked product.

The epoxide derivative of PCPD was subjected to further addition reactions leading to soluble products (Fig. 1). Rather high conversions were obtained in several instances, thus confirming the epoxide content determined by other methods (e.g., 85 mole-%, based on Cl in IV): addition of amines [e.g., piperidine; 32.7 mole-% conversion, reaction (7)]; addition of carboxylic acids [e.g., chloroacetic acid; 86.3 mole-% conversion, reaction (8)]; addition of phenols [e.g., chlorophenol, 64.6 mole-% conversion, reaction (9)]; addition of thiols [e.g., thiophenol; 57.4 mole-% conversion, reaction (10)]; acidic hydrolysis [reaction (6)] lead to insoluble products, presumably due to partial polymerization.

Reaction with Thioglycolic Acid

The reaction of PCPD with thioglycolic acid [Fig. 1, reaction (12)] proceeds smoothly at 60°C. when carried out in the presence of a limited amount of oxygen, e.g., an air-filled reaction apparatus, or a free-radical initiator (Table III). High-conversion products are obtained as yellow to brown powders, soluble in common organic solvents (methanol, acetone, dioxane, dimethylformamide, acetic acid, and pyridine); nonsolvents are petroleum ether, ether, carbon tetrachloride, chloroform, ethyl acetate, and acetonitrile. Films cast from solutions are transparent and brittle. The products become gradually insoluble over a period of several months.

The infrared spectrum confirmed the addition of thioglycolic acid, e.g., by the appearance of strong C═O stretching absorption (5.8 μ) and carboxylic OH stretching (3.75 μ).

Although it is generally assumed[15,16] that the reaction occurs via free-radical addition to the double bond, attack of an intermediate radical with abstraction of an allylic hydrogen is a possible side reaction. This should be especially likely in the case of polycyclopentadiene and should lead to higher conversions than anticipated on the basis of simple addition. However, here as in other reported instances,[15,16] the measured conversion approaches but never exceeds 100% (98 mole-% based on sulfur determination). This indicates that allylic substitution is, if it occurs at all, only a minor side reaction. Furthermore, crosslinking via recombination of carbon radicals should also occur whenever abstraction of allylic hydrogen is a significant side reaction. However, no gelation was observed.

EXPERIMENTAL

Source of Materials; Analyses; Instruments

Benzene, chloroform, and methanol (Baker Analyzed Reagent grade) were purged with argon and stored in bottles with serum caps under a slight argon pressure. Dioxane (Eastman) was refluxed over potassium hydroxide pellets under nitrogen for several hours prior to fractionation. The fraction boiling below 98°C. was discarded. Tetrahydrofuran (Eastman) was distilled from sodium–benzophenone under nitrogen shortly before use, a forerun of approx. 25% was discarded. Petroleum ether, b.p. 30–60°C., thioglycolic acid, piperidine, chloroacetic acid (Baker) were reagent grade and used without further purification. Hexachlorocyclopentadiene (Hooker) was used as obtained.

Perbenzoic acid was prepared from dibenzoyl peroxide (Lucidol) according to Brown[17] and Kolthoff[18] or from 94% hydrogen peroxide (DuPont, Electrochemical Division) and benzoic acid, following the procedure of Silbert et al.[19] *p*-Nitroperbenzoic acid was prepared from *p*-nitrobenzoic acid and 94% hydrogen peroxide.[19] Monoperphthalic acid was synthesized from phthalic anhydride and 30% hydrogen peroxide.[20] Performic acid was prepared *in situ* from formic acid and 30% H_2O_2.[21]

The spectroscopic investigations were performed with a Perkin-Elmer Infracord infrared spectrometer and Varian A60 NMR spectrometer. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Alfred Bernhardt, Mikroanalytisches Laboratorium, Mühlheim (Ruhr), Germany.

Prepurification of Polycyclopentadiene

With Addition of Antioxidant. Three precipitations were carried out by slowly pouring a 10% solution of polycyclopentadiene in benzene into the tenfold volume of methanol in an Erlenmeyer flask with a fast stream of nitrogen bubbling through the methanol. In each precipitation step three-fourths of the liquid was twice siphoned out and replaced by methanol purged with nitrogen. Antioxidants, 1–5% based on the weight of the polymer, were added to the precipitant. The polymer was finally dissolved in benzene, freeze-dried, and stored in rubber-capped ampules at −20°C. It was either used in this form or prior to use, transferred under nitrogen to a Soxhlet apparatus and extracted with petroleum ether for 2 hr. to remove the antioxidant.

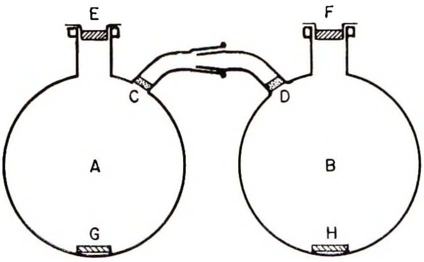


Fig. 3. Apparatus for purification of polycyclopentadiene in inert atmospheres: (A,B) 5-liter flasks; (C,D) sintered glass; (E,F) heavy-duty serum caps; (G,H) stirring bars.

Without Addition of Antioxidant. The polymerization apparatus[1] was equipped with one additional breakseal which also carried a rubber serum cap. The breakseal was broken by 18-gage stainless steel tubing, the apparatus filled with argon, and the polymer dissolved in a suitable solvent. The polymer solution was transferred via the same tubing into the argon-filled precipitation vessel A (Fig. 3) and precipitated in methanol. The supernatant liquid was first siphoned out and finally filtered off by rotating the whole apparatus and applying a weak vacuum to flask B. After washing with methanol, the polymer was redissolved in flask A and reprecipitated by running the polymer solution through the connecting tube into the methanol-filled flask B. This cycle was repeated four times. Solvents and precipitants were added and taken out by means of 18-gage stainless steel tubing. A slight positive pressure of argon was applied throughout the procedure. The polymer was finally dissolved in benzene, transferred into several ampules, freeze-dried, sealed off under high vacuum, and stored at −20°C.

The following procedures represent examples of PCPD reactions carried out under the optimum conditions tested.

Diels-Alder Addition of HCCPD

PCPD (1.83 g.) was dissolved in 44 ml. HCCPD at room temperature in a nitrogen atmosphere. After complete dissolution, the mixture was heated to 150°C. and samples taken at certain intervals (see Table 1). The polymer was precipitated by pouring 10 ml. of solution into 300 ml. petroleum ether. Two to three reprecipitations (dioxane–petroleum ether) were sufficient to obtain an odor-free product. The polymers were dried to constant weight (oil pump vacuum) at room temperature (Table I).

Epoxidation of PCPD

PCPD (2.5 g.) in a sealed ampule was dissolved in 60 ml. chloroform in an argon atmosphere. Perbenzoic acid (9.25 g. in 180 ml. $HCCl_3$) in a three-necked round-bottomed flask was purged and blanketed with argon and cooled to 0°C. The polymer solution was slowly transferred into the reaction flask through 18-gage stainless steel tubing by means of a slight argon pressure in the ampule. The reaction mixture was kept at 0°C., and samples were taken at certain intervals to determine the residual perbenzoic acid. The reaction was terminated by precipitation in petroleum ether. The polymer was redissolved in chloroform, or some other solvent, filtered from very small amounts of insoluble material and reprecipitated twice. The product was dried to constant weight (oil pump vacuum) at room temperature (Table II).

Reactions of PCPD-Epoxide

The following reactions were carried out in a nitrogen atmosphere in ampules sealed with serum caps.

Piperidine. PCPD-epoxide (0.2 g.) was dissolved at room temperature in 9 ml. dioxane, and 6 ml. piperidine was added. After 72 hr. at 80°C. the reaction was quenched by precipitation in petroleum ether. The product was purified by two reprecipitations (chloroform–petroleum ether) and dried to constant weight; N found, 1.35% (calcd. for VII, 8.38% N), conversion 32.7 mole-%.

Monochloroacetic Acid. PCPD-epoxide (0.2 g.) was dissolved at room temperature in 5 ml. methylene chloride and 5 ml. monochloroacetic acid was added. After 72 hr. at 80°C. the polymer was precipitated in methanol, purified by two reprecipitations (dioxane–methanol) and dried to constant weight. Nonsolvents were methylene chloride, chloroform, carbon tetrachloride, ether, benzene; Cl found, 12.0% (calcd. for VIII, 20.09% Cl), conversion 86.3 mole-%.

***p*-Chlorophenol.** PCPD-epoxide (0.2 g.) was dissolved at room temperature in 6 ml. dioxane and 12.8 g. *p*-chlorophenol was added. After 72 hr. at 80°C. the reaction was terminated by precipitating the polymer in petroleum ether. The product was purified by two reprecipitations (chloroform–petroleum ether) and dried to constant weight; Cl found, 6.13% (calcd. for IX, 16.85% Cl), conversion 64.6 mole-%.

Thiophenol. PCPD-epoxide (0.2 g.) was dissolved in 7 ml. thiophenol at room temperature and one drop of *N*,*N*-dimethylbenzylamine added as a catalyst. After 72 hr. at 80°C., the polymer was precipitated in methanol, reprecipitated twice from chloroform into petroleum ether, and dried to constant weight; S found 5.18% (calcd. for X, 16.67% S); conversion 57.4 mole-%.

Reaction of PCPD with Thioglycolic Acid

PCPD (0.424 g.) was dissolved at room temperature in a mixture of 4 ml. tetrahydrofuran and 50 ml. benzene. A 4-ml. portion of thioglycolic acid was added, and the solution was heated to 60°C. for 8 hr., during which time a yellowish-brown precipitate was formed. The supernatant liquid was decanted, the precipitate was dissolved in dioxane, and reprecipitated in ether. After three reprecipitations (dioxane–ether) the polymer was dried to constant weight (oil pump vacuum) at room temperature (Table III).

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Résumé

Le polycyclopentadiène qui est connu comme subissant extrêmement rapidement une autooxydation avec formation de produits insolubles a été modifié chimiquement pour former des dérivés insensibles à l'oxygène. Des produits solubles et stables peuvent être obtenus avec des hauts degrés de conversion par addition de Diels-Alder de hexachlorocyclopentadiène (96.5 mole %), par époxydation (93.5 mole %) et par addition d'acide thioglycolique (97.9 mole %). L'exigence préalable est une purification efficace du polycyclopentadiène au moyen de reprécipitation dans une atmosphère dépourvue d'oxygène. D'autres modifications de la double liaison ont été l'hydroxyformylation et l'addition radicalaire d'haloalkanes qui toutefois résultent dans des produits complètement insolubles. Les réactions d'addition typiques ont été effectuées avec un dérivé époxy du polycyclopentadiène p.e. additions d'acide chlorhydrique, d'acide monochloracétique, de chlorophénol, de thiophénol, de pipéridine, d'hydrolyse en glycols. Une polymérisation facilement initiée du groupe époxy constitue une réaction secondaire qui limite la conversion dans certaines réactions d'additions, telles que l'addition d'acide chlorhydrique ou l'hydrolyse dans le glycol.

Zusammenfassung

Polycyclopentadien, das mit extremer Leichtigkeit Autoxidationen unterliegt und daher in unlösliche Produkte übergeht, wurde durch chemische Reaktionen in Derivate überführt, die nicht länger empfindlich gegenüber Sauerstoff sind. Lösliche und be-

ständige Produkte können in hohen Umsätzen durch Diels-Alder-Addition von Hexachlorocyclopentadien (96,5 Mol-%), durch Epoxidierung (93,5 Mol-%) und durch Addition von Thioglykolsäure (97,9 Mol-%) erhalten werden. Eine Vorbedingung ist die sorgfältige Reinigung des Polycyclopentadiens durch Umfällung in sauerstoffreier Atmosphäre. Andere versuchte Modifizierungen der Doppelbindungen sind die Hydroxyformylierung und die Addition von Haloalkanen, die jedoch nur völlig unlösliche Produkte ergaben. Typische Additionsreaktionen wurden an den Epoxyderivaten ausgeführt, z.B. Addition von Chlorwasserstoff, Monochloressigsäure, Chlorphenol, Thiophenol, Piperidin, Hydrolyse zum Glykol. Es wird angenommen, dass die leicht auslösbare Polymerisation der Epoxygruppe eine den Umsatz begrenzende Seitenreaktion in bestimmten Additionsreaktionen, wie z.B. der Addition von Chlorwasserstoff und der Hydrolyse zum Glykol, darstellt.

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Kinetics of Nonequilibrium Methylsiloxane Polymerization and Rearrangement

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Synopsis

Nonrandom reactions were demonstrated experimentally during the polymerization of $(CH_3)_3SiOSi(CH_3)_3$ plus $[(CH_3)_2SiO]_4$ and the rearrangement of $(CH_3)_3SiO[(CH_3)_2SiO]_5Si(CH_3)_3$ or $(CH_3)_3SiO[(CH_3)_2SiO]_8Si(CH_3)_3$, using sulfuric acid-treated Fuller's earth as catalyst. Cyclic and linear reaction products were analyzed by gas–liquid chromatography. A four-step polymerization mechanism was proposed to account for the approach to equilibrium from either the forward or reverse direction. Reaction rate expressions for this mechanism were reduced to a finite set of nonlinear ordinary differential equations. These were solved by using a fourth-order Runge-Kutta numerical integration on a Burroughs B5500 computer. The calculated molecular weight distributions thus obtained were found to agree at all times with the distributions from polymerization and rearrangement experiments.

INTRODUCTION

Prior studies of the kinetics of siloxane polymerization can be grouped into two categories: (*1*) polymerization of D_4 [where D is a difunctional siloxane unit, $(CH_3)_2SiO$, and D_n is a cyclic containing n dimethylsiloxane units] to yield high molecular weight polymer, where kinetics of the acid- or base-catalyzed polymerization have been followed by determination of some gross parameter of the system (e.g., viscosity, vapor pressure[1–3]); (*2*) hydrolysis, polymerization, or rearrangement of a chlorosilane or siloxane monomer to yield low molecular weight polymer. Analyses of the polymer constituents as a function of time have been carried out by distillation,[4,5] NMR,[6] and endgroup analysis.[7] Lengyel and co-workers[4,5] rearranged a very low molecular weight linear siloxane, MODM [where M is a monofunctional chain terminator, $(CH_3)_3Si$], using concentrated H_2SO_4. Species MOM, MODM, MOD_2M, and MOD_3M were analyzed as a function of time. A random model, in which the probability of cleaving and reforming a single siloxane bond was assumed independent of bond location, was shown to fit the data. Carmichael and Heffel[8] showed that the distribution of linear species formed during the early stages of the acid clay-catalyzed reaction of D_4 and MOM is highly nonrandom. In that paper the experimental distributions were compared with the random theory at the same extent of reaction as a function of time.

In this paper experimental data are presented for the rearrangements of linear species MOD_5M and MOD_8M. Initial nonrandom reactions are demonstrated from the distribution data. A mechanism based on fundamental considerations of the various possible reactions is proposed. This mechanism is used to derive a set of kinetic rate expressions which simulate the D_4 + MOM reaction as well as the MOD_5M and MOD_8M rearrangement reactions. The simulated distributions are compared with the three sets of experimental data.

EXPERIMENTAL

The reaction D_4 + MOM was described in an earlier work.[8] The subsequent discussion of experimental conditions deals only with the rearrangement of MOD_5M and MOD_8M.

Materials

Hexadecamethylheptasiloxane (MOD_5M) and docosamethyldecasiloxane (MOD_8M) were distilled for use in rearrangement reactions. Gas–liquid chromatography indicated that each material was 99.8% pure. A sulfuric acid-treated Fuller's earth containing 15% free moisture and a H_2SO_4 equivalent of 16 mg. KOH/g. was used to catalyze each reaction.

Rearrangement Reactions

The rearrangements of MOD_5M and MOD_8M were carried out at 25°C. A typical experiment was as follows: 14.43 g. of MOD_8M and 0.0721 g. of acid clay catalyst were reacted in a tube 2 cm. in diameter and 8 cm. long with a 24/40 ground glass joint at the top and a side arm of 5 mm. diameter, through which the reaction mixture was sampled. The catalyst was removed by vacuum filtration. The sample was exposed to the vacuum for as little time as possible to minimize loss of volatile materials, particularly MOM.

Chromatography Analyses

The F and M Model 810 linear-temperature-programmed gas–liquid chromatograph was used for analyses. A 0–1 mv. Brown recorder equipped with a disk integrator was attached to the chromatograph. The column sets used were 2 ft. × $^1/_4$ in. stainless steel, packed with 9% diphenylsiloxane–dimethylsiloxane copolymer gum, prepared at Dow Corning Corporation, on 60–80 mesh Chromasorb W, non-acid washed. Column temperatures were programmed from 50 to 400°C. Other chromatography conditions were as follows: detector temperature, 350°C.; injection port temperature, 350–360°C.; bridge current, 140 ma.; column and reference He flow rates, 50 ml./min.

Calculation of Rearrangement Products

Response factors were determined from a known mixture of polymers $D_x (3 \leq x \leq 6)$ and MOD_yM $(0 \leq y \leq 9)$. The factors are listed elsewhere.[9]

Toluene was used as a marker. Response factors for higher cyclic and linear species were extrapolated by least-squares analysis.

Integrated areas for each component formed during rearrangement of MOD_5M and MOD_8M were converted to weight per cent by utilizing these response factors. The calculation was carried out as follows:

$$Q_i = (A_iR_i/\sum_{i=1}^{N} A_iR_i) \times 100$$

where Q_i is the weight per cent of the ith component, A_i is the GLC area of the ith component, R_i is the weight response factor of the ith component, and N is the number of components. The calculation of weight per cent from component areas and response factors was accomplished on the IBM 1401 computer with a FORTRAN program. Flow diagrams of the computer programs used for calculation and analyses of the chromatography data are illustrated in another paper.[9]

Reaction products are accurately calculated for the method described above for the MOD_5M rearrangement (see discussion of Fig. 10). However, significant errors are introduced into the weight per cent calculations of the MOD_8M rearrangement products (see discussion of Fig. 14). These errors arise from (*a*) incomplete elution of the high molecular weight linear polymer in the mixtures and (*b*) necessity of using uncertain extrapolated response factors for the large linear siloxanes.

For complete gas–liquid chromatographic (GLC) analysis of a polymer mixture with number-average molecular weight greater than 525, an alternative analytical method is recommended. Weight per cent compositions are obtained as follows:

$$Q_i = A_iQ_s/A_sR_i$$

where Q_i and A_i are previously defined, R_i is the weight response factor of the ith component relative to the internal standard, A_s is the area of the internal standard, and Q_s is the weight per cent of the internal standard.

MECHANISM

The proposed mechanism is based on consideration of the various chemical reactions which could occur and on an analysis of the chemical bonds which must be broken during these reactions.

$$P_n + I \underset{k_t}{\overset{k_i}{\rightleftharpoons}} P^*_n + M^* \qquad n \geq 0 \qquad (1)$$

$$P^*_0 + D_4 \underset{k_{d0}}{\overset{k_{p0}}{\rightleftharpoons}} P^*_4 \qquad (2)$$

$$P^*_n + D_4 \underset{k_d}{\overset{k_p}{\rightleftharpoons}} P^*_{n+4} \qquad n \geq 1 \qquad (3)$$

$$P^*_n + P_k \xrightarrow{k_r} P^*_m + P_{n+k-m} \qquad \begin{matrix} n \geq 0 \\ k \geq 0 \\ m \geq 0 \end{matrix} \qquad (4)$$

Here P_n denotes (MOD_nM), an unactivated linear species in solution with n-dimethylsiloxane units, P^*_n denotes (MOD_n--H), an activated linear species on the catalyst surface with n-dimethylsiloxane units, M^* denotes M--HSO_4 salt on the catalyst surface. I is the H_2SO_4-treated Fuller's earth catalyst. (Note that those starred species which are active during polymerization become terminated upon removal of the catalyst by filtration.)

k_d, k_{d0} are the depropagation rate constants when $n \geq 1$ and when $n = 0$, respectively; k_i is the initiation rate constant; k_p, k_{p0} are the propagation rate constants when $n \geq 1$ and $n = 0$, respectively; k_r is the rearrangement rate constant; and k_t is the termination rate constant. Reaction (1) is an initiation reaction in the forward direction and a termination reaction in the diverse direction. Reactions (2) and (3) are propagation reactions in the forward direction and depropagation reactions in the reverse direction. Reaction (4) is a rearrangement reaction which is the same in either direction since n, k, and m are arbitrary. Assumptions inherent in the mechanism are: (*1*) all reactions occur at the catalyst surface; (*2*) the solution contains P_n (i.e., MOD_nM) and D_4 only; (*3*) the catalyst surface is composed of I, M^*, and P^*_n (i.e., MOD_n--H) only; (*4*) since the Si—O bonds in $(CH_3)_3SiO$ are more basic than the Si—O bonds in $(CH_3)_2SiO$, H_2SO_4 reacts with $(CH_3)_3Si$—O bonds only; (*5*) $(CH_3)_2Si$—O bonds can react with P^*_n but not with M^*; (*6*) propagation and depropagation rate constants are independent of chain length for $n \geq 1$; (*7*) the only cyclic in the system is D_4; (*8*) all possible rearrangement reactions occur with equal probability.

Reaction Rate Expressions

By applying the law of mass action to reactions (1)–(4), we may write the following reaction rate expressions:

$$d[\mathrm{I}]/dt = -k_i[\mathrm{I}][\mathrm{P_T}] + k_t[\mathrm{M}^*][\mathrm{P}^*_\mathrm{T}] \tag{5}$$

$$d[\mathrm{M}^*]/dt = -\,d[\mathrm{I}]/dt \tag{6}$$

$$\begin{aligned} d[\mathrm{D}_4]/dt = {} & -k_{p0}[\mathrm{D}_4][\mathrm{P}^*_0] + k_{d0}[\mathrm{P}^*_4] - k_p[\mathrm{D}_4]\{[\mathrm{P}^*_T] - [\mathrm{P}^*_0]\} \\ & + k_d\{[\mathrm{P}^*_\mathrm{T}] - [\mathrm{P}^*_0] - [\mathrm{P}^*_1] - [\mathrm{P}^*_2] - [\mathrm{P}^*_3] - [\mathrm{P}^*_4]\} \end{aligned} \tag{7}$$

$$\begin{aligned} d[\mathrm{P}^*_0]/dt = {} & k_i[\mathrm{I}][\mathrm{P}_0] - k_t[\mathrm{M}^*][\mathrm{P}^*_0] - k_{p0}[\mathrm{D}_4][\mathrm{P}^*_0] + k_{d0}[\mathrm{P}^*_4] \\ & - k_r[\mathrm{P}^*_0]\sum_{m=0}^{\infty}(m + 1)[\mathrm{P}_m] + k_r\sum_{i=0}^{\infty}\sum_{k=0}^{k=i}[\mathrm{P}^*_k][\mathrm{P}_{i-k}] \end{aligned} \tag{8}$$

$$\begin{aligned} d[P^*_n]/dt = {} & k_i[\mathrm{I}][\mathrm{P}_n] - k_t[M^*][\mathrm{P}^*_n] - k_p[\mathrm{D}_4][\mathrm{P}^*_n] + k_d[\mathrm{P}^*_{n+4}] \\ & - k_r[\mathrm{P}^*_n]\sum_{m=0}^{\infty}(m + n + 1)[\mathrm{P}_m] + k_r\sum_{i=n}^{\infty}\sum_{k=0}^{k=i}[\mathrm{P}^*_k][\mathrm{P}_{i-k}] \\ & 1 \leq n \leq 3 \end{aligned} \tag{9}$$

$$d[\mathrm{P}^*_4]/dt = k_i[\mathrm{I}][\mathrm{P}_4] - k_t[\mathrm{M}^*][\mathrm{P}^*_4] + k_{p0}[\mathrm{D}_4][\mathrm{P}^*_0] - k_{d0}[\mathrm{P}^*_4] - k_p[\mathrm{D}_4][\mathrm{P}^*_4] + k_d[\mathrm{P}^*_8] - k_r[\mathrm{P}^*_4]\sum_{m=0}^{\infty}(m+5)[\mathrm{P}_m] + k_r\sum_{i=4}^{\infty}\sum_{k=0}^{k=i}[\mathrm{P}^*_k][\mathrm{P}_{i-k}] \quad (10)$$

$$d[\mathrm{P}^*_n]/dt = k_i[\mathrm{I}][\mathrm{P}_n] - k_t[\mathrm{M}^*][\mathrm{P}^*_n] - k_p[\mathrm{D}_4][\mathrm{P}^*_n] + k_d[\mathrm{P}^*_{n+4}] + k_p[\mathrm{D}_4][\mathrm{P}^*_{n-4}] - k_d[\mathrm{P}^*_n] - k_r[\mathrm{P}^*_n]\sum_{m=0}^{\infty}(m+n+1)[\mathrm{P}_m] + k_r\sum_{i=n}^{\infty}\sum_{k=0}^{k=i}[\mathrm{P}^*_k][\mathrm{P}_{i-k}] \qquad n \geq 5 \quad (11)$$

$$d[\mathrm{P}^*_\mathrm{T}]/dt = d[\mathrm{M}^*]/dt \quad (12)$$

$$d[\mathrm{P}_n]/dt = -k_i[\mathrm{I}][\mathrm{P}_n] + k_t[\mathrm{M}^*][\mathrm{P}^*_n] - k_r[\mathrm{P}_n]\sum_{m=0}^{\infty}(m+n+1)[\mathrm{P}^*_m] + k_r\sum_{i=n}^{\infty}\sum_{k=0}^{k=i}[\mathrm{P}^*_k][\mathrm{P}_{i-k}] \qquad n \geq 0 \quad (13)$$

$$d[\mathrm{P}_\mathrm{T}]/dt = d[\mathrm{I}]/dt \quad (14)$$

where

$$[\mathrm{P}_\mathrm{T}] = \sum_{n=0}^{\infty}[\mathrm{P}_n] \qquad [\mathrm{P}^*_\mathrm{T}] = \sum_{n=0}^{\infty}[\mathrm{P}^*_n]$$

The concentrations $[\mathrm{P}^*_n]$, $[\mathrm{P}^*_\mathrm{T}]$, $[\mathrm{P}_n]$, $[\mathrm{P}_\mathrm{T}]$, $[\mathrm{D}_4]$, and $[\mathrm{M}^*]$ are in units of moles/liter, but catalyst concentration $[\mathrm{I}]$ is in terms of weight per cent.

Computer Calculations

Equations (5)–(14) represent an infinite number of nonlinear ordinary differential equations. These were reduced to a finite number of equations by assuming an n_max, the number of D units in the largest linear polymer, such that $[\mathrm{P}_n] = [\mathrm{P}^*_n] = 0$ for $n \geq n_\mathrm{max}$.[10] This was feasible since the maximum n detected experimentally was $n = 34$ (See $\mathrm{MOD_5M}$ rearrangement data in Table I). The equations were solved by a fourth-order Runge-Kutta integration[11] procedure on a Burroughs B5500 digital computer. Input data for the program included initial concentration, weight per cent catalyst, and rate constants. The output included polymer distributions in weight per cent versus time, along with other pertinent time-dependent variables such as D_4, n_avg, (the average number of D units in the linear polymer), $\mathrm{P_T}$, $\mathrm{P^*_T}$, etc. Computer run time ranged from less than 1 min. up to four min. for each computer experiment, depending on initial conditions, size of time increment chosen, total polymerization time investigated, and n_max.

TABLE I
Rearrangement of MOD_5M: Experimental Molecular Weight Distribution as a Function of Time

Products	Distribution, wt.-%												
	2 hr.	4 hr.	26.5 hr.	67 hr.	142.5 hr.	145 hr.	240 hr.	335.5 hr.	427.5 hr.	503.5 hr.	595.5 hr.	673.5 hr.	765.5 hr.
Linear polymers													
MOM	0.34	0.25	0.95	3.22	4.27	4.39	4.63	5.34	5.29	4.49	4.72	5.16	5.00
MODM	0.15	0.11	0.72	2.40	4.12	4.04	5.89	7.09	7.51	6.93	6.81	7.69	7.18
MOD_2M	0.20	0.14	0.87	2.79	4.91	4.76	6.52	7.81	8.58	7.89	7.73	8.54	8.10
MOD_3M	0.20	0.17	1.04	3.34	5.85	5.70	7.53	8.65	9.20	8.42	8.14	8.91	8.23
MOD_4M	0.27	0.36	1.88	5.71	8.62	8.05	9.22	9.47	9.79	8.70	8.23	8.93	8.10
MOD_5M	95.98	96.86	82.63	49.28	25.66	27.89	18.19	11.33	10.42	8.71	8.14	8.59	7.59
MOD_6M	0.49	0.39	1.86	5.25	8.09	7.76	8.80	8.54	8.65	7.76	7.51	7.88	7.20
MOD_7M	0.17	0.11	0.91	2.60	6.33	5.05	6.50	7.19	7.65	7.12	6.74	7.14	6.65
MOD_8M	0.20	0.13	1.02	3.11	4.81	4.79	6.24	6.53	6.82	6.35	6.19	6.36	6.28
MOD_9M	0.30	0.23	1.27	3.58	4.85	4.88	6.10	5.63	5.85	5.52	5.48	5.34	5.45
$MOD_{10}M$	1.13	0.80	3.75	7.43	6.25	6.99	5.68	4.96	4.94	4.64	4.75	4.56	4.60
$MOD_{11}M$	0.15	0.13	0.85	2.62	3.55	3.56	3.62	3.83	3.50	3.92	3.99	3.64	3.72
$MOD_{12}M$	0.055	0.040	0.39	1.34	2.24	2.15	2.33	2.78	2.26	3.26	3.16	2.69	3.26
$MOD_{13}M$	0.041	0.024	0.29	1.06	1.75	1.81	1.68	1.87	1.56	2.63	2.72	1.97	2.83
$MOD_{14}M$	0.028	0.028	0.25	0.99	1.40	1.53	1.11	1.33	1.06	2.17	2.17	1.53	2.14
$MOD_{15}M$	0.047	0.038	0.31	1.14	1.29	1.36	0.78	0.98	0.55	1.74	1.86	1.18	1.75
$MOD_{16}M$	0.009	0.012	0.14	0.57	0.82	0.81	0.36	0.58	0.35	1.31	1.47	0.96	1.39
$MOD_{17}M$		0.004	0.081	0.32	0.49	0.53	0.20	0.32	0.21	0.92	1.15	0.70	1.06
$MOD_{18}M$			0.054	0.26	0.38	0.38	0.11	0.30	0.14	0.71	0.80	0.55	0.85

$MOD_{19}M$			0.031	0.17	0.21	0.27	0.056	0.23	0.068	0.53	0.62	0.42	0.67
$MOD_{20}M$			0.027	0.13	0.18	0.29	0.028	0.10	0.026	0.40	0.51	0.39	0.51
$MOD_{21}M$			0.010	0.093	0.091	0.10	0.008	0.067	0.005	0.30	0.39	0.29	0.39
$MOD_{22}M$				0.056	0.051	0.052		0.024		0.21	0.27	0.22	0.31
$MOD_{23}M$				0.038	0.021	0.035		0.013		0.17	0.21	0.18	0.25
$MOD_{24}M$				0.026	0.012	0.015				0.11	0.15	0.15	0.19
$MOD_{25}M$						0.013				0.075	0.13	0.098	0.14
$MOD_{26}M$										0.040	0.068	0.089	0.10
$MOD_{27}M$										0.040	0.061	0.069	0.062
$MOD_{28}M$										0.019	0.098	0.061	0.058
$MOD_{29}M$										0.014	0.030	0.056	0.056
$MOD_{30}M$											0.017	0.038	0.052
$MOD_{31}M$											0.019		
$MOD_{32}M$											0.015		
$MOD_{33}M$											0.012		
$MOD_{34}M$											0.010		
Cyclics													
D_3						0.008							0.086
D_4	0.054	0.044	0.31	0.83	1.54	1.56	2.21	2.68	3.08	2.72	2.70	3.11	2.98
D_5	0.10	0.068	0.41	1.26	1.71	1.87	2.02	2.03	2.21	1.83	2.32	2.15	2.10
D_6	0.010	0.029	0.030	0.11	0.17	0.13	0.23	0.31	0.33	0.32	0.43	0.35	0.53
D_7		0.025									0.23	0.072	0.14
D_8													
D_9	0.12	0.012											
D_{10}													
D_{11}		0.028											

The prime objective of this study was to simulate the nonequilibrium behavior of this system. Since the best rate constants for the assumed mechanism were not required, a trial and error approach was used. Rate constants were chosen for each computer run by comparison of previous computer runs with data. About 50 computer runs were made during the course of the present study. This many were needed because the experimental data available had been obtained at two different temperatures. A statistical method for obtaining the best set of rate constants in this and similar mechanisms is currently under study.

COMPARISONS OF CALCULATED AND EXPERIMENTAL DATA

MOM + D_4 Results

Figures 1–6 summarize the experimental and calculated results obtained when MOM and D_4 are charged into the system initially.

The initial conditions for the data and the computer simulation, along with the rate constants used, are summarized in Table II.

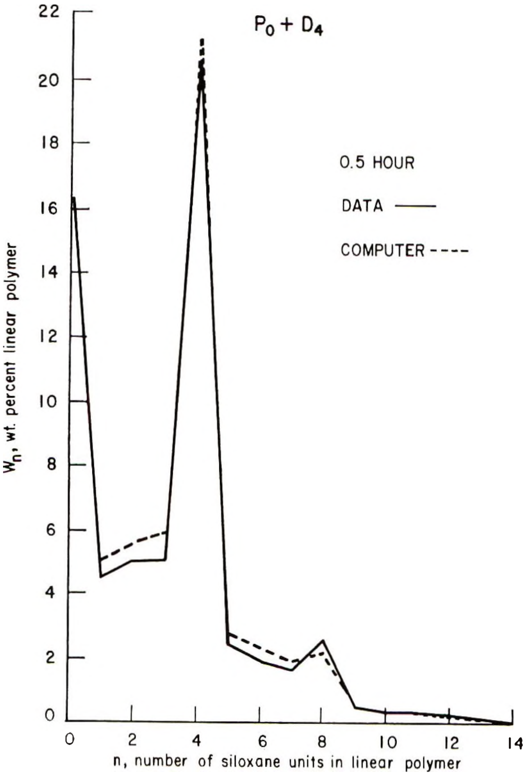

Fig. 1. $P_0 + D_4$, 0.5 hr.

TABLE II
Initial Experimental Conditions and
Rate Constants Used in Computer Simulation

	$P_0(MOM) + D_4$	$P_5(MOD_5M)$	$P_8(MOD_8M)$
Temperature, °C.	80	25	25
Polymer, g.-mole/l.	$P_0 = 1.807$	$P_5 = 1.687$	$P_8 = 1.224$
Cyclics, g.-mole/l.	$D_4 = 1.807$	0	0
Catalyst, wt.-%	0.5	0.5	0.5
Rate constants, g.-mole, liter, hr., wt.-% catalyst			
k_i	100	0.7	0.7
k_t	5	0.035	0.035
k_{p0}	15	0.05	0.05
k_p	5	0.035	0.035
k_{d0}	0.25	0.005	0.005
k_d	0.1	0.0007	0.0007
k_r	0.5	0.0015	0.0015

Figures 1 through 3 show the molecular weight distributions at various times prior to equilibration.

Early in the polymerization, significant peaks at $n = 4$ (MOD_4M) and $n = 8$ (MOD_8M) are observed (see Fig. 1). These result from initiation

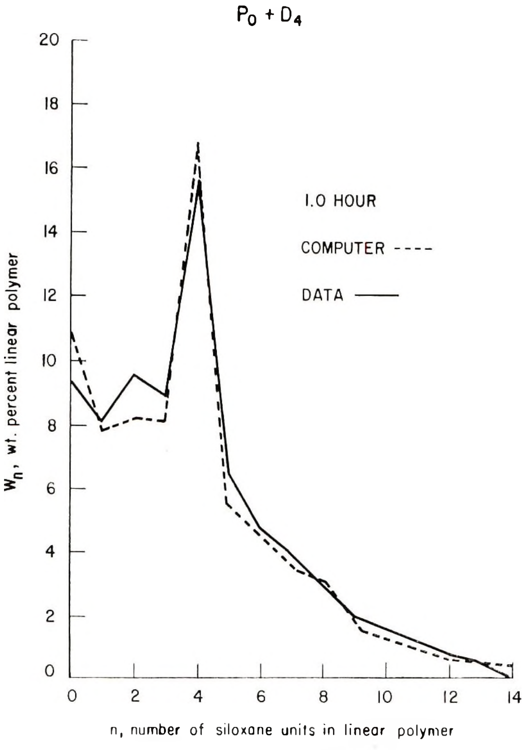

Fig. 2. $P_0 + D_4$, 1.0 hr.

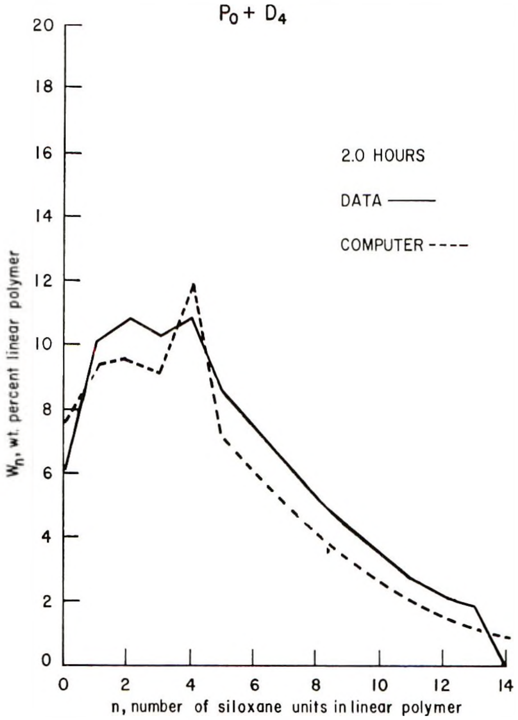

Fig. 3. $P_0 + D_4$, 2.0 hr.

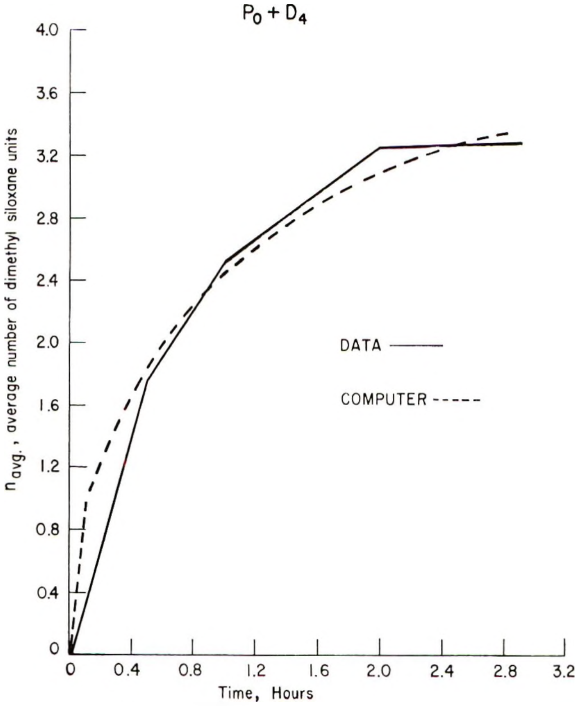

Fig. 4. $P_0 + D_4$.

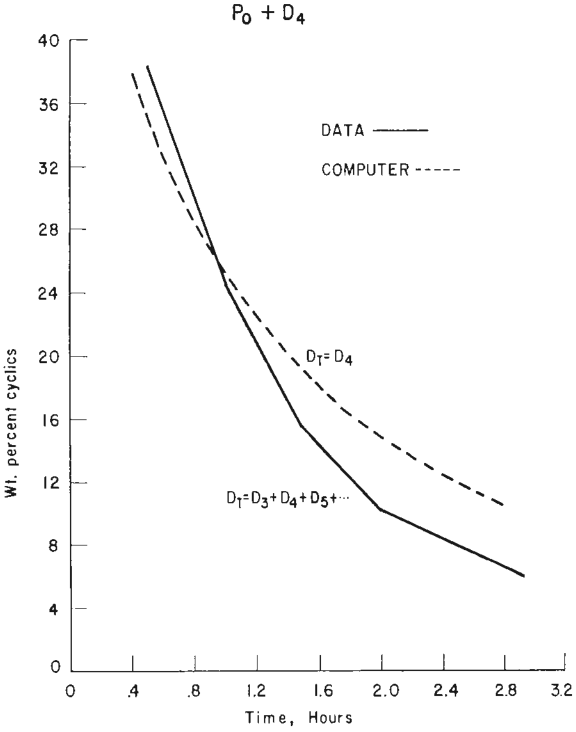

Fig. 5. $P_0 + D_4$.

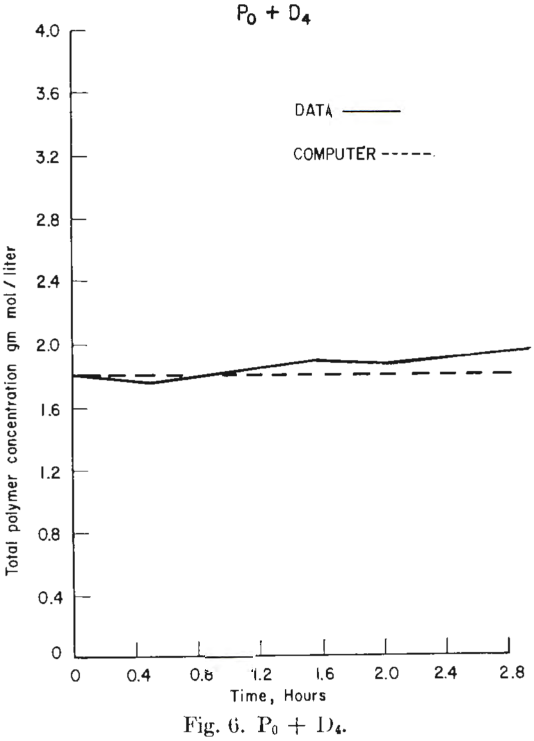

Fig. 6. $P_0 + D_4$.

of MOM followed by addition of D_4 through propagation. Termination may occur during polymerization via step (1) in the mechanism. Those species which are active in the polymerization vessel become terminated upon removal of the catalyst by filtration.

Rearrangement, however, is not negligible, even in the early stages of polymerization, since linear species with every n up to 14 are observed. As the polymerization proceeds, the combined effects of termination, reinitiation, and rearrangement all work toward decreasing the predominance of the $n = 4$ and $n = 8$ peaks, until finally the distribution of linear polymers approaches its random equilibrium shape. It should be noted that the simulation of the data is excellent during the early stages of polymerization but as time goes on the simulation does not approach randomness as rapidly as the experimental data. This is most likely due to improper choice of the combination of rate constants. Since the average chain length is closely simulated as a function of time (Fig. 4), but the weight per cent cyclics (Fig. 5) is not, the ratio of propagation to depropagation rate constants is particularly in question. This explains the excellence of the simulation during early stages of polymerization when the concentration of cyclic $[D_4]$ is high enough so that the depropagation reaction does not play a significant role.

Figure 6 represents the total linear polymer concentration, $\{[P_T] + [P^*_T]\}$, versus time. The experimental and simulation data compare

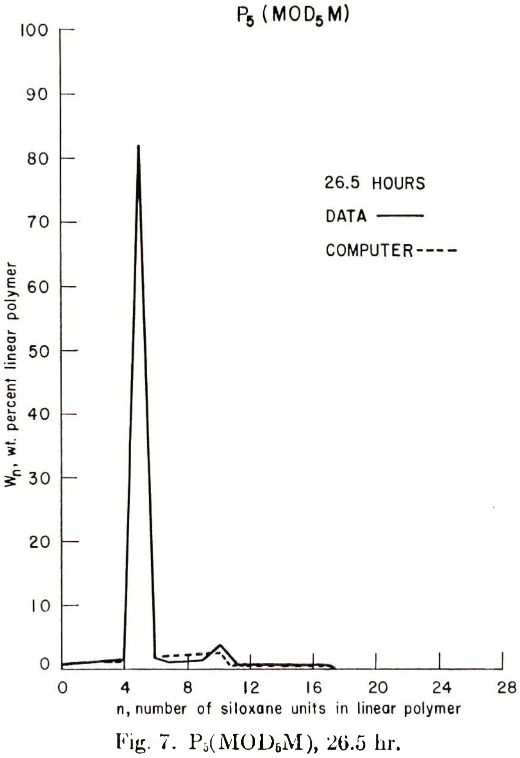

Fig. 7. $P_5(MOD_5M)$, 26.5 hr.

within 8% over the entire time range of the polymerization. The deviation of the experimental $\{[P_T] + [P_T^*]\}$ from the simulation is a measure of the experimental accuracy of the data as a function of time.

MOD_5M and MOD_8M Results

Figures 7–14 compare the experimental and calculated behavior of the system when the system is initially charged with MOD_8M. During the early stages of the reaction (see Figs. 7 and 11) the primary species formed by rearrangement of MOD_xM ($x = 5, 8$) is $MOD_{2x}M$. This indicates that activated linear species formed by the initiation step couples with MOD_xM by the rearrangement step. Assumption *4* (only end siloxane bonds are initiated) is thus borne out by the experimental observations. Persisting excess $MOD_{3x}M$ over either of its neighbors later in the reaction (see Tables I and III) indicates further selective attack of $MOD_{2x}M$ at the end siloxane bond.

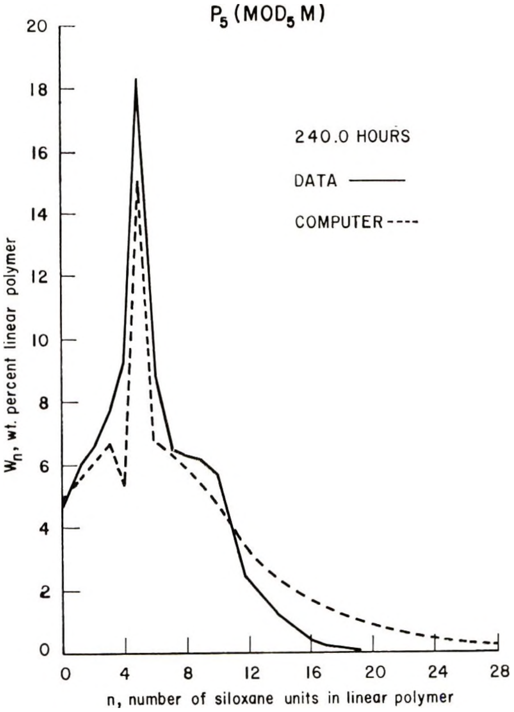

Fig. 8. $P_5(MOD_5M)$, 240.0 hr.

As time proceeds, rearrangement is an increasingly important step. After 1.5 hr., 20% of the MOD_8M which reacted was $MOD_{16}M$, while the remaining 80% was identified as 19 linear and 4 cyclic species (see Table III). After the reaction has proceeded for a long period of time, the combined effects of initiation and rearrangement along with termination,

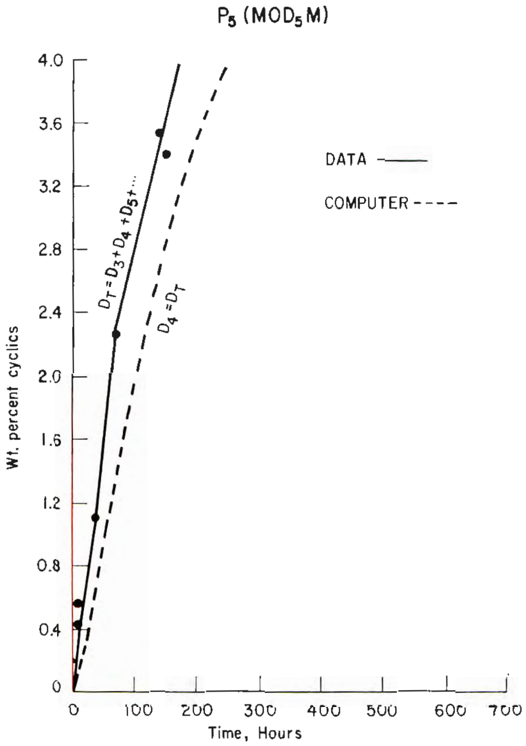

Fig. 9. $P_5(MOD_5M)$.

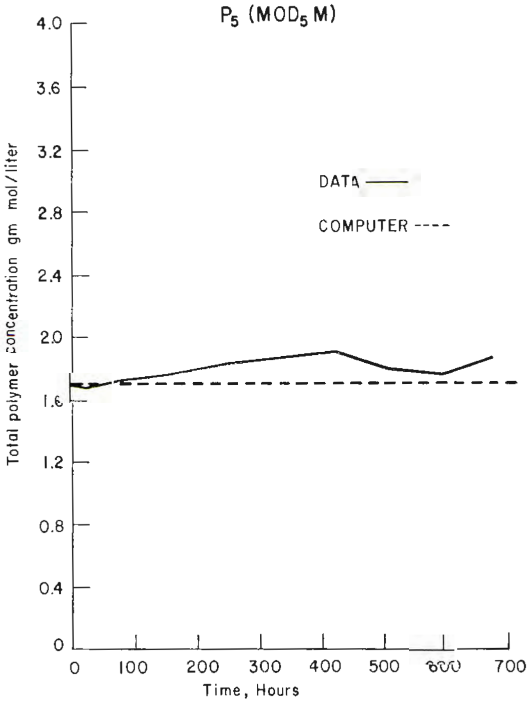

Fig. 10. $P_6(MOD_5M)$.

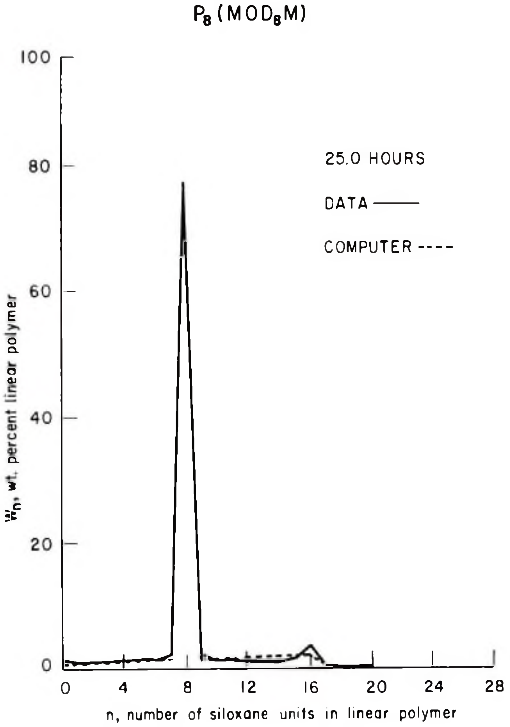

Fig. 11. $P_8(MOD_8M)$, 25.0 hr.

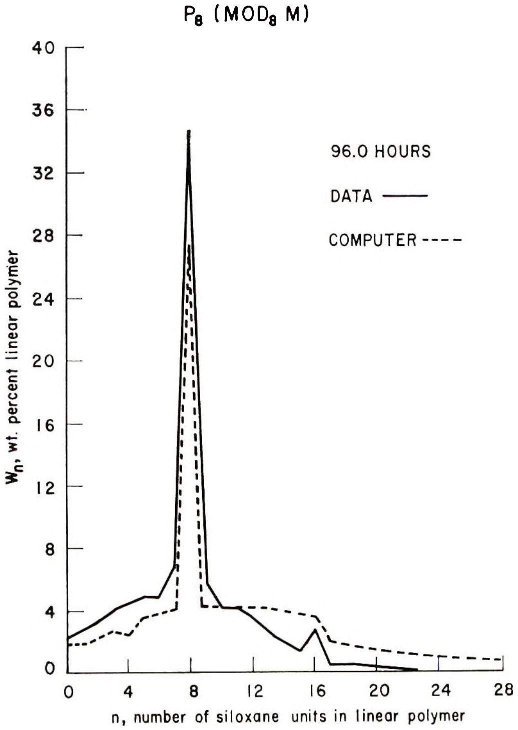

Fig. 12. $P_8(MOD_8M)$, 96.0 hr.

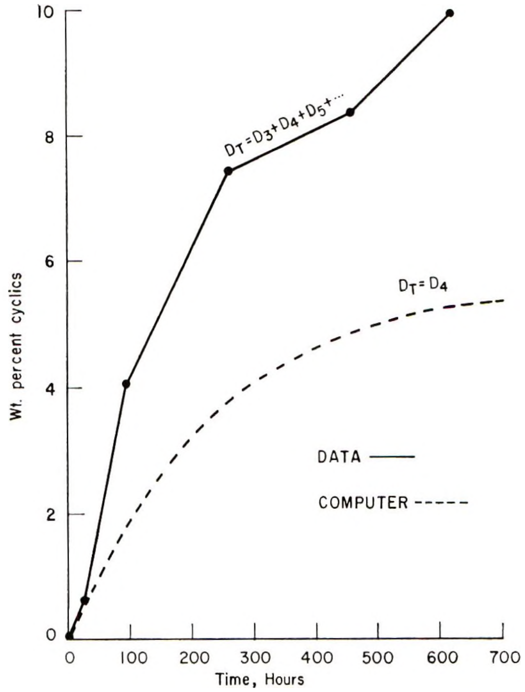

Fig. 13. $P_8(MOD_8M)$.

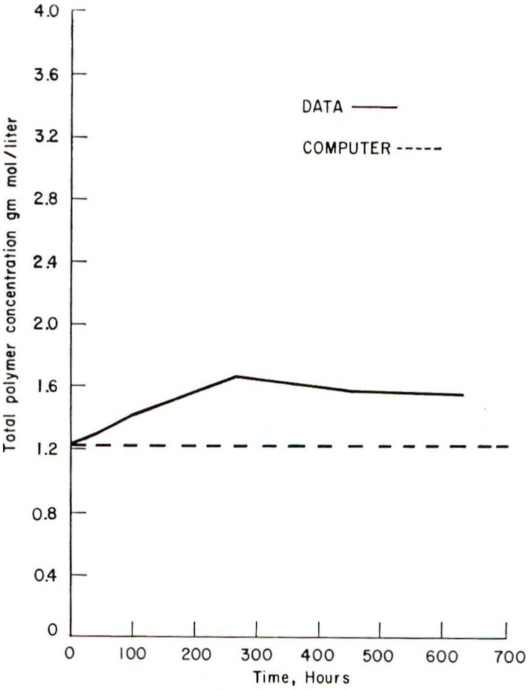

Fig. 14. $P_8(MOD_8M)$.

TABLE III
Rearrangement of MOD_8M:
Experimental Molecular Weight Distribution as a Function of Time

	Distribution, wt.-%						
Products	0.5 hr.	1.5 hr.	25 hr.	96 hr.	265 hr.	450.5 hr.	620.5 hr.
Linear polymers							
MOM	0.18	0.062	0.79	2.19	2.72	2.89	3.27
MODM	0.11	0.063	0.64	2.67	5.66	5.52	5.23
MOD_2M	0.15	0.088	0.78	3.15	7.06	6.73	6.28
MOD_3M	0.21	0.12	1.09	4.03	7.97	7.40	6.79
MOD_4M	0.24	0.15	1.17	4.34	8.29	7.53	7.11
MOD_5M	0.28	0.16	1.26	4.79	8.42	7.25	6.98
MOD_6M	0.22	0.17	1.15	4.75	8.51	7.20	7.38
MOD_7M	0.20	0.29	1.80	6.99	8.59	7.02	7.32
MOD_8M	95.64	97.25	77.83	35.33	9.66	6.65	6.90
MOD_9M		0.25	2.41	6.01	7.23	5.36	5.79
$MOD_{10}M$	0.26	0.12	1.11	4.27	5.71	4.81	5.24
$MOD_{11}M$	0.21	0.14	1.23	4.18	4.08	4.32	4.05
$MOD_{12}M$	0.22	0.075	1.04	3.60	2.31	3.17	3.25
$MOD_{13}M$	0.23	0.12	0.99	2.75	2.07	2.90	3.26
$MOD_{14}M$	0.20	0.12	0.79	1.94	1.41	2.87	2.24
$MOD_{15}M$	0.26	0.14	1.00	1.47	0.97	1.74	1.75
$MOD_{16}M$	0.076	0.50	3.29	2.75	0.63	1.62	1.43
$MOD_{17}M$	0.086	0.049	0.44	0.54	0.44	1.40	1.07
$MOD_{18}M$	0.030	0.010	0.17	0.48	0.31	1.15	0.90
$MOD_{19}M$	0.024	0.015	0.15	0.43	0.21	0.89	0.70
$MOD_{20}M$	0.007	0.007	0.094	0.30	0.15	0.69	0.63
$MOD_{21}M$	0.004		0.063	0.19	0.069	0.59	0.53
$MOD_{22}M$			0.032	0.11	0.036	0.46	0.35
$MOD_{23}M$			0.038	0.081	0.020	0.43	0.33
$MOD_{24}M$			0.038	0.070		0.32	0.25
$MOD_{25}M$				0.007		0.24	0.23
$MOD_{26}M$						0.16	0.15
$MOD_{27}M$						0.11	0.14
$MOD_{28}M$						0.10	0.13
$MOD_{29}M$						0.053	0.12
$MOD_{30}M$						0.044	0.099
$MOD_{31}M$						0.023	0.084
$MOD_{32}M$							0.066
Cyclics							
D_4	0.05	0.03	0.34	1.42	4.25	4.65	4.74
D_5	0.02	0.02	0.14	0.64	2.11	2.57	2.81
D_6	0.01	0.01	0.052	0.16	0.76	0.86	0.92
D_7	0.03			0.15	0.32	0.26	0.35
D_8	0.04	0.03	0.074	0.18			0.15

propagation and reinitiation lead to a random distribution of linear polymers (see Table III).

While the computer simulation follows the same pattern of behavior as the experimental data, there are some significant differences.

The $MOD_{2x}M$ and $MOD_{3x}M$ peaks are not as pronounced in the simulation, even in the early stages of reaction. This is a reflection of assumption *8* (equal reactivity for all possible rearrangement reactions). Assumption *8* was made for mathematical convenience and is in contradiction with the experimentally demonstrated fact that end siloxane bonds are the most susceptible to attack, i.e., rearrangement as well as initiation takes place preferentially at the end siloxane bond.

Cyclic tetramer was assumed to be the only cyclic present in the simulation. This accounts for the lag in formation of cyclics observed in Figures 9 and 13. It also no doubt accounts for differences in the simulated and observed distribution of linears especially at large times (see Fig. 8 and 12). However, a good deal of the discrepancy in Figures 8 and 12 can be explained by experimental error, as shown in Figures 10 and 14. These figures present experimental and simulated total polymer concentration versus time for MOD_5M and MOD_8M, respectively. Substantial experimental error is present in the MOD_8M data at long times.

CONCLUSIONS

(*1*) The nonrandom behavior of acid-catalyzed polymerization of cyclic and rearrangement of linear siloxanes can be explained by a four-step addition polymerization mechanism: initiation, propagation, termination, and rearrangement.

(*2*) The above behavior can be simulated by solution of the equations derived from the assumed mechanism by judicious choice of rate constants. The experimental behavior can probably be quantitatively simulated by further refinement of the rate constants chosen for this study. Such refinement should especially include: (*a*) adjustment of the ratio of depropagation to propagation; (*b*) separation of the rate of rearrangement at end siloxane bonds from rearrangement at interior siloxane bonds; (*c*) inclusion of the rate of formation and consumption of cyclics other than D_4.

(*3*) The combination of well-planned experimental studies, computer data reduction, and computer simulation can be extremely effective for understanding and quantitatively describing the chemical and physical phenomena observed during polymerization of siloxane systems. This understanding is not limited to an equilibrium situation but can be used to relate molecular weight distributions to the operating variables of a polymerization system as a function of time during the approach to equilibrium. Further, the insight gained in interpreting siloxane reactions prior to attainment of equilibrium should be generally applicable to studies of other labile inorganic polymers such as silazanes, silthians, germoxanes, germthians, phosphonitriles, and metalloxosiloxanes.

Thanks are due to Mr. D. J. Gordon, who performed the rearrangement reaction experiments and analyses, and to Mr. J. Ostahowski, who distilled the linear siloxane fluids.

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Résumé

Des réactions non-statistiques ont été démontrées expérimentalement au cours de la polymérisation de $(CH_3)_3SiOSi(CH_3)_3$ avec $[(CH_3)_2SiO]_4$ et le réarrangement de $(CH_3)_3$-$SiO[(CH_3)_2SiO]_4Si(CH_3)_3$ ou $(HC_3)_3SiO[(CH_3)_2SiO]_8Si(CH_3)_3$ utilisant comme catalyseur la terre de Fuller-acide sulfurique. Des produits de réactions cycliques et linéaires ont été analysés par chromatographie gaz-liquide. Un mécanisme de polymérisation à quatre étapes a été proposé pour rendre compte de l'atteinte des équilibres au départ soit d'une direction, soit de la direction inverse. Les expressions de vitesses de réaction pour ce mécanisme sont ramenées à un système fini non-linéaire, différentiel ordinaire. Celles-ci ont été résolues en utilisant une intégration numérique de quatrième ordre Runge-Kutta sur un calculateur Burroughs B-5000. Les distributions de poids moléculaires calculées sont en accord avec les distributions au départ des expériences de polymérisation et de réarrangement.

Zusammenfassung

Nicht-statistische Reaktionen wurden experimentell bei der Polymerisation von $(CH_3)_3SiOSi(CH_3)_3$ plus $[(CH_3)_2SiO]_4$ und bei der Umlagerung von $(CH_3)_3SiO$-$[(CH_3)_2SiO]_4Si(CH_3)_3$ oder $(CH_3)_3SiO[(CH_3)_2SiO]_8Si(CH_3)_3$ mit schwefelsäure-behandelter Fullererde als Katalysator nachgewiesen. Cyclische und lineare Reaktionsprodukte wurden mittels Gas-Flüssig-Chromatographie analysiert. Ein vierstufiger Polymerisationsmechanismus wurde zur Erklärung der Gleichgewichtsannäherung aus beiden Richtungen, vorwärts und rückwärts, vorgeschlagen. Die Geschwindigkeitsausdrücke für diesen Reaktionsmechanismus wurden auf eine endliche Zahl nicht-linearer gewöhnlicher Differentialgleichungen reduziert. Diese wurden mit einer numerischen Runge-Kutta-Integration vierter Ordnung auf einem Burroughs B-5000 Computer gelöst. Die so erhaltenen berechneten Molekulargewichtsverteilungen stimmten bei allen Versuchsdauern mit den Verteilungen bei den Polymerisations- und Umlagerungsversuchen überein.

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Role of Heterogeneous $Cr(AcAc)_3$–$AlEt_3$ Catalyst System in Isoprene Polymerization

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Synopsis

Polymerization of isoprene in presence of a heterogeneous Ziegler-type catalyst system, $Cr(AcAc)_3$–$AlEt_3$, has been studied in benzene medium. The rate of polymerization is first-order with respect to catalyst as well as monomer concentration. The rate studies, activation energy, and polymer microstructures are reported in order to follow the probable mechanism of polymerization.

Introduction

In an earlier communication,[1] polymerization of styrene with a homogeneous $Cr(AcAc)_3$–$AlEt_3$ catalyst system was studied. Similarly, Bawn et al.[2] have described the polymerization of butadiene with this homogeneous catalyst system. In the polymerization of isoprene, this catalyst system was found to be ineffective at low concentrations. However, higher concentration of catalyst system polymerized isoprene but due to the precipitation of a fine black precipitate during the preparation of catalyst, it did not remain homogeneous. The formation of the precipitate of the catalyst complex by the concentration of its dilute solution has been observed by Sartori et al.[3] The catalyst system at higher concentrations thus behaves as a heterogeneous system. In the present paper, results of a kinetic study of the polymerization of isoprene in benzene at 40°C. with this catalyst system under heterogeneous conditions are reported.

Experimental

Preparation of catalyst components, purification of solvent, and the method of polymerization have been described in the earlier publication.[1] The polymerizations were conducted in a lightly stoppered, 50-ml. Erlenmeyer flask and the reactants were added in the following order: solvent, $Cr(AcAc)_3$, $AlEt_3$, and monomer. The reaction mixture was stirred vigorously; ±5% reproducibility was obtained.

Isoprene (Phillips) was purified from *tert*-butylcatechol by washing with 10% alkali solution followed by washing with a large quantity of water. It was distilled and later stored over anhydrous magnesium sulfate. The required amount of monomer was redistilled over sodium under nitrogen prior to use.

On mixing the catalyst components, a fine black precipitate was formed which completely settled at the bottom of the flask during the usual aging period of 10 min. The color of the soluble phase remained brown-black as reported[1] previously for this catalyst system under homogeneous condition.

The polymerization reaction was stopped by adding the reaction mixture to an excess of methanol containing 10% glacial acetic acid, whereupon the polymer precipitated out. It was further purified and then stabilized with 0.2% α-naphthylamine inhibitor.

For the characterization of the polymer, its limiting viscosity number was determined in benzene at 25°C. These measurements were carried out on the ungelled samples as soon as they were removed from methanol and dried; hence the gel content of the samples was not estimated. Infrared absorption spectra of thin films obtained by spreading the resinous sample between plates were obtained with a Perkin-Elmer Infracord 137 B spectrophotometer.

Results and Discussion

The rate of polymerization was studied at various ratios of combination of triethyl aluminum with chromium acetylacetonate, the $Cr(AcAc)_3$ concentration being kept constant at a level nearly 4.5 times higher than that used in homogeneous system.

The rate of polymerization increased up to an Al/Cr ratio of 4 and then attained nearly a constant value at higher ratios of Al/Cr (Fig. 1 and Table I). This would indicate that the maximum activity of the catalyst complex is obtained beyond an Al/Cr ratio of 4, which is higher than the optimum

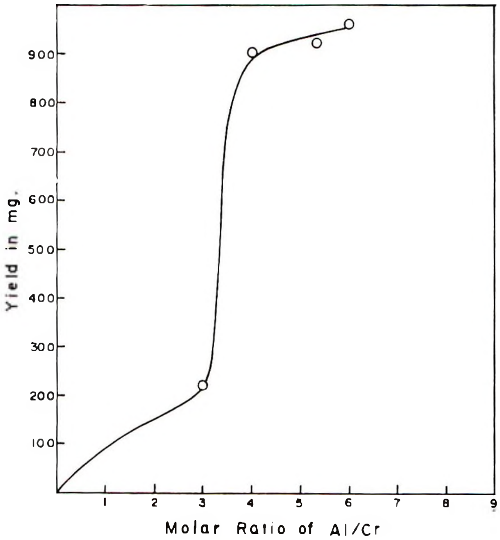

Fig. 1. Yield vs. molar ratio of Al/Cr. $Cr(AcAc)_3$ concn., 4.5×10^{-2} mole/l.; monomer concn., 4.997 mole/l.; 40°C.; 2 hr.

TABLE I[a]

Al/Cr ratio	$Cr(AcAc)_3$ concn., mole/l.	$AlEt_3$ concn., mole/l.	Yield, mg.
3	0.045	0.135	227.2
4	0.045	0.18	906.35
5.3	0.045	0.24	918.35
6	0.045	0.27	953.30

[a] Reaction conditions: monomer concn., 4.99 mole/l., 2 hr., 40°C.

ratio (Al/Cr = 3) established earlier in the polymerization of styrene with the very catalyst system under homogeneous conditions. This higher value of the ratio of maximum activity could be attributed to the heterogeneous nature of the catalyst system. (In this connection we may compare the Al/Cr ratio of maximum activity of 3.5 for the heterogeneous $Cr(AcAc)_3$–$AlEt_2Br$ catalyst system and the Al/Cr ratio of 3.0 for the homogeneous catalyst system of $Cr(AcAc)_3$–$AlEt_3$ obtained in the polymerization of styrene.) At the Al/Cr ratio of 5.3, the rate of polymerization was constant for 4 hr., which shows no change in the catalytic activity during this period (Fig. 2). Correspondingly, further rate studies were carried out at 2 hr. reaction time and the yield was held to 12% conversion in order to keep monomer concentration unchanged.

In view of this, the rate of polymerization was found to be first-order with respect to monomer (Fig. 3, Table II) and catalyst (Fig. 4, Table III) concentrations and such a linear dependence is well known for typical

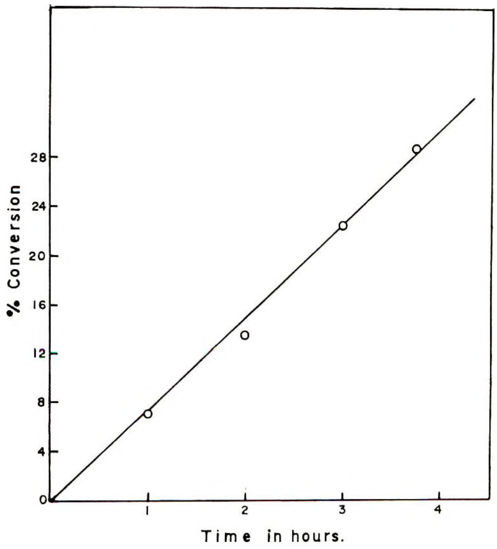

Fig. 2. Yield of polymer variation with time. Al/Cr = 5.3; $Cr(AcAc)_3$ concn., 4.5×10^{-2} mole/l.; monomer concn., 4.997 mole/l.; 40°C.

TABLE II[a]

Monomer concn., mole/l.	$R_p \times 10^5$, mole/l. sec.	$[\eta]$, dl./g.
4.997	9.363	0.158
2.498	4.693	0.071
1.499	2.504	—

[a] Reaction conditions: Al/Cr = 5.3; $Cr(AcAc)_3$ concn., 0.075 mole/l.; $AlEt_3$ concn. 0.24 mole/l.; 40°C., 2 hr.

TABLE III[a]

$Cr(AcAc)_3$ concn., mole/l.	$AlEt_3$ concn., mole/l.	$R_p \times 10^5$, mole/l.	$[\eta]$, dl./g.
0.045	0.24	9.393	0.158
0.037	0.20	12.34	0.089
0.030	0.16	7.577	0.068
0.023	0.12	5.75	—

[a] Reaction conditions: monomer concn., 4.99 mole/l.; Al/Cr = 5.3; 40°C.; 2 hr.

Ziegler type catalyst systems of heterogeneous nature. Similarly, the value of 11.50 kcal./mole (Fig. 5) for the activation energy of polymerization, obtained from the plot of log rate of polymerization in the temperature range of 30–50°C. versus reciprocal of absolute temperature, is also in agreement with the value reported for a typical Ziegler catalyst in the polymerization of isoprene[4] under heterogeneous condition.

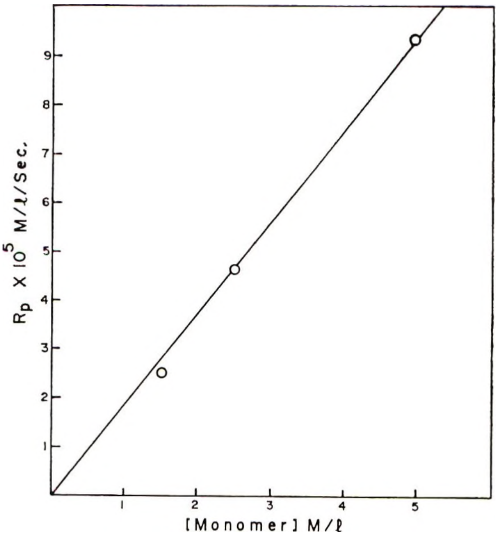

Fig. 3. Variation of rate of polymerization with monomer concentration. Al/Cr = 5.3; $Cr(AcAc)_3$ concn., 4.5×10^{-2} mole/l.; 2 hr.; 40°C.

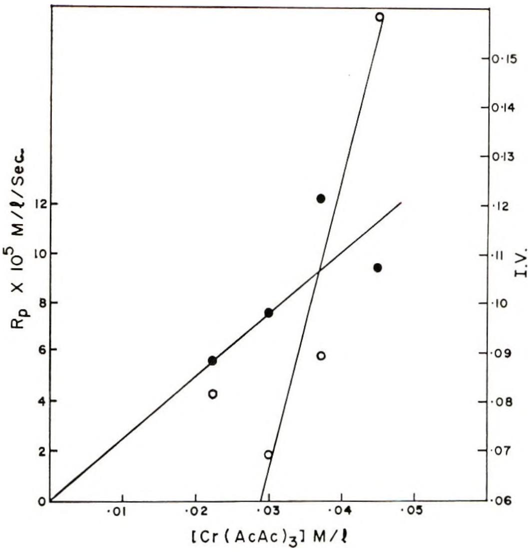

Fig. 4. Variation of (●) rate of polymerization and (○) intrinsic viscosity with Cr(AcAc)$_3$ concentration. Al/Cr = 5.3; monomer concn., 4.997 mole/l.; 2 hr.; 40°C.

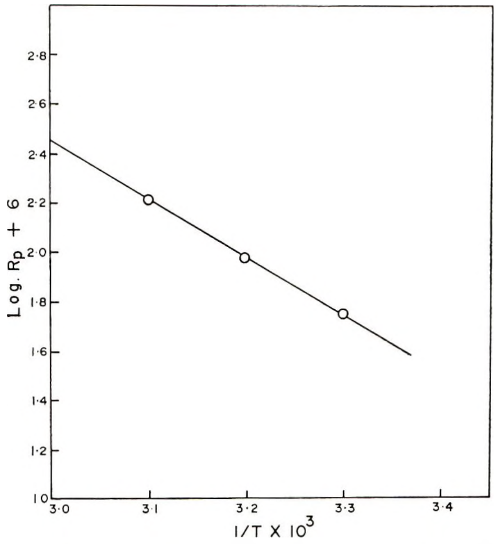

Fig. 5. Plot of log R_p + 6 vs. reciprocal of absolute temperature Al/Cr = 5.3; Cr(AcAc)$_3$ concn., 4.5 × 10^{-2} mole/l.; monomer concn., 4.997 mole/l.; 2 hr.

The limiting viscosity number of the polymer solution does not decrease with increasing concentration of monomer and catalyst (Fig. 3, Tables II and III). This suggests that the termination reaction may occur by hydride transfer only. The characteristic absence of chain transfer with the catalyst indicates that the catalyst complex is either completely precipitated out or the soluble catalyst complex species are unable to take part in chain transfer.

It is apparent from the above observation that at high concentrations this catalyst system is similar in behavior to a normal Ziegler catalyst. The presence of strong absorption at 10.9 and 11.2 μ for vinyl and isopropenyl groups, respectively, in the infrared spectrum of polymer shows the predominance of the 1,2 and 3,4 microstructures (Fig. 6). Also, entirely new bands at 4.5 and 6.5 μ obtained may be due to the partial cyclized ladder structure as suggested recently by Binder.[5] It would follow that the mechanism of polymerization is likely to be a coordinate anionic. Kennedy et al.[6] have also attributed the formation of 1,2 structure in the polymerization of butadiene to a coordinate anionic mechanism (1,4-*cis* and *trans* structures are possible with all mechanisms of polymerization).

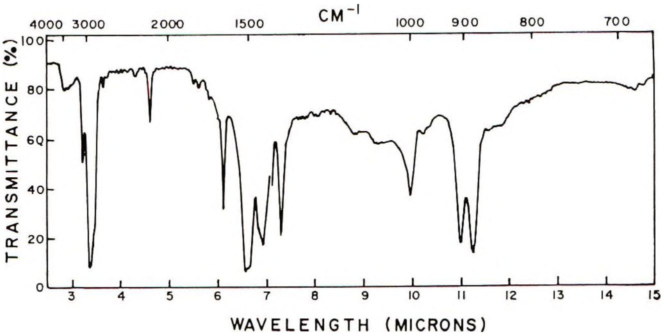

Fig. 6. Infrared absorption spectrum of a thin film of polymer showing 3,4 and 1,2 microstructures.

Further studies to collect more evidence in support of above investigations are envisaged.

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Résumé

On a étudié la polymérisation de l'isoprène en présence d'un catalyseur de Ziegler hétérogène (système $Cr(AcAc)_3$–$AlEt_3$) dans un milieu benzènique. On a trouvé que la vitesse de polymérisation était de premier ordre par rapport à la concentration en catalyseur et à la concentration en monomère. On décrit l cinétique, l'énergie d'activation et la microstructure du polymère en vue de suivre le mécanisme probable de cette polymérisation.

Zusammenfassung

Die Polymerisation von Isopren in Gegenwart des heterogenen Katalysatorsystems vom Ziegler-Typ $Cr(AcAc)_3$–$AlEt_3$ wurde in Benzol untersucht. Die Polymerisationsgeschwindigkeit ist in Bezug auf Katalysator- und Monomerkonzentration von erster Ordnung. Zur Aufklärung des Reaktionsmechanismus werden Geschwindigkeitsuntersuchungen sowie die Aktivierungsenergie und die Mikrostruktur des Polymeren herangezogen.

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Molecular Parameters of Sodium Cellulose Xanthate in Dilute Solution

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Synopsis

Molecular parameters of sodium cellulose xanthate in NaOH solution have been determined by means of light scattering and viscometry. The effect of the degree of substitution on the molecular configuration of sodium cellulose xanthate has been studied for three series of samples of varying degree of substitution. The expansion factor has been determined from the expression due to Orofino and Flory. The effective bond length b and the ratio of the unperturbed dimension to the dimension assuming free rotation of the chain units $(\bar{R}_o^2/\bar{R}_f^2)^{1/2}$, have also been determined. It is concluded that sodium cellulose xanthate in dilute solution is a loosely coiled molecule, comparable to other cellulose derivatives in chain stiffness.

Viscose, a solution of sodium cellulose xanthate, has been the subject of extensive investigation, and numerous papers have been published, mainly on the technical aspects of this commercially important cellulose derivative. Though some attempts have recently been made to elucidate the physicochemical properties of cellulose xanthate with the help of modern techniques like ultracentrifugation,[1,2] electron microscopy,[3] and light scattering,[4] the present state of knowledge of its molecular and configurational properties is still inadequate. Recently, detailed studies on these lines have been carried out with other cellulose derivatives like hydroxyethyl cellulose,[5] ethyl hydroxyethyl cellulose,[6] carboxymethyl cellulose,[7] and cellulose nitrate,[8] but such studies with sodium cellulose xanthate have only very recently been undertaken[9] with particular reference to the degree of substitution (DS) and its relation to its distribution at the C_2, C_3, and C_6 hydroxyls of the anhydroglucose unit of the cellulose molecule.

The present work aims at a general evaluation of the configurational and hydrodynamic parameters of sodium cellulose xanthate in dilute solution, and particularly, the influence of the overall degree of substitution on these parameters.

EXPERIMENTAL

Preparation of Sodium Cellulose Xanthates

The sodium cellulose xanthates were prepared in the laboratory by the following method. Three batches (I, II, and III) each containing 6 g.

of cotton cellulose, were mercerized in 18% NaOH solution for 30 min. at 25°C. The alkali cellulose was pressed to a press-weight ratio of 1:3. The three batches of alkali celluloses were then shredded and allowed to degrade in air at 25°C. for different periods (batch I, 0 hr.; batch II, 24 hr.; batch III, 48 hr.). Each batch of alkali cellulose was then divided into four equal parts (a, b, c, and d) and then treated with various quantities of CS_2: a, 0.4 ml./g. of cellulose; b, 0.8 ml./g. of cellulose; c, 2.4 ml./g. of cellulose; d, 3.6 ml./g. of cellulose. The requisite amount of CS_2 was added in installments to the alkali cellulose in a closed bottle at definite intervals. The yellow crumbs of cellulose xanthate were then dispersed in 1*N* NaOH solution and shaken for 2-3 hr. The resulting solutions were kept at 0°C. for 24-hr., filtered through a grade 2 sintered glass filter and thereafter stored in stoppered bottles at −5°C.

In order to obtain a uniform distribution of degree of polymerization, the the samples were fractionated into five fractions by the method described by Ghosh[10] with the use of methanol as the nonsolvent. Measurements were performed with the middle fraction only. In spite of the rigorous fractionation procedures employed, some amount of polydispersity cannot be ruled out, and this might introduce some uncertainty into the results. The fractions were washed with methanol till free from alkali, washed again with ether, dried in air, and finally redissolved in 1*N* NaOH solution. The degree of substitution of the samples was determined by a standard method.[11]

Viscosity

The viscosity measurements were made in a Ubbelohde capillary viscometer with an efflux time of 133.0 sec. for 4 ml. of 1*N* NaOH solution. All measurements were made in a thermostat maintained at 30 ± 0.1°C. Kinetic energy corrections, being negligible, were not undertaken.

Refractive Index Increment

The refractive index increments were measured at 546 mμ in a Brice-Phoenix differential refractometer, calibrated with KCl solution at 25°C. The values of *dn/dc* for cellulose xanthates have been determined with samples having different degrees of substitution to show the dependence of

TABLE I
Refractive Index Increment for Cellulose Xanthates of Different Degrees of Substitution in 1*N* NaOH Solution at 546 mμ

Sample	Degree of substitution	*dn/dc*, ml./g.
1a	0.25	0.205
1b	0.48	0.275
1c	0.77	0.300
1d	0.91	0.425

dn/dc on the degree of substitution. The determination of exact dn/dc of viscose solution is difficult due to the presence of various by-product thio salts in the solution. This difficulty has been obviated by precipitating the cellulose xanthate with methanol and redissolving it in alkali. The dn/dc values for sodium cellulose xanthate were also determined by Tait et al.[13] (0.212 ml./g.), Claesson and Bruun[1] (0.230 ml./g.), and Onyon[4] (0.20 ± 0.02 ml./g.). Values obtained in the present work for cellulose xanthate of different degrees of substitution are shown in Table I.

Light-Scattering Measurements

Solutions for light-scattering studies were prepared by dilution of the stock solution with 1N NaOH to cellulose concentrations below 0.5%. Clarification of the solutions was carried out by filtering through ultrafine sintered-glass filters. Measurements were made only when the solutions appeared to be optically clear on visual examination at low angles.

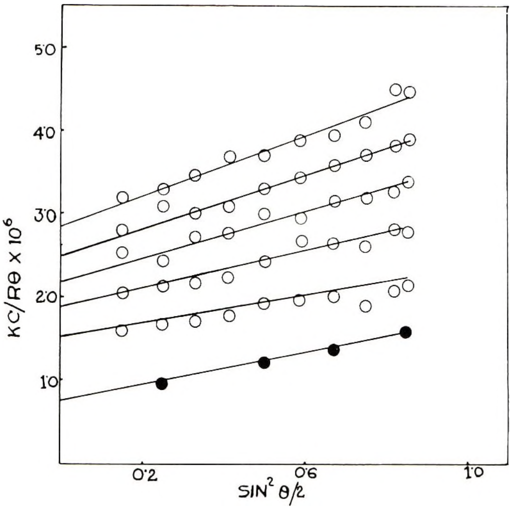

Fig. 1. Plot of $Kc/R\theta$ vs. $\sin^2 \theta/2$ for sodium cellulose xanthate (sample 1b) in dilute NaOH solution.

Dilutions were made directly in the light-scattering cell with solvents filtered through ultrafine sintered-glass filters. The wavelength of light used was 546 mμ. Measurements were made in a Brice-Phoenix universal light-scattering photometer, Series 1999-10. Calibrations were made with Cornell standard polystyrene (Styron 1960), 0.00122 cm.$^{-1}$ being taken as the absolute 90° excess turbidity.

Measurements of the scattering intensities were made from 45° to 135° by using a cylindrical cell of the Wittnauer-Scherr[12] type. The data were treated in the usual way to obtain values of $Kc/R\theta$. The scattering of the solvent was similarly determined and deducted from that of the solution.

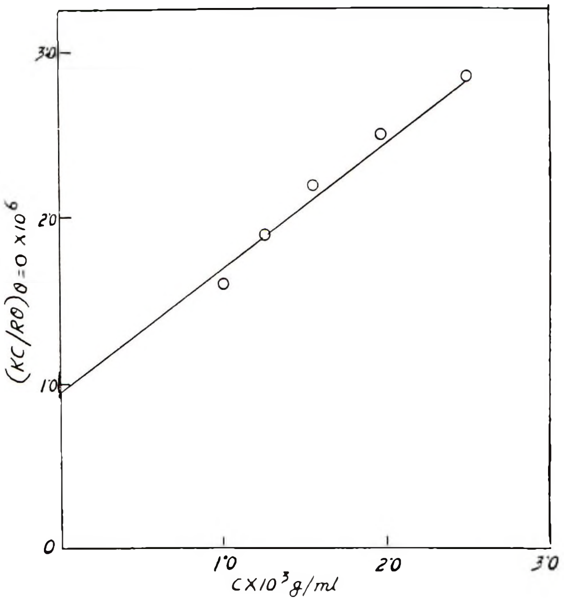

Fig. 2. Concentration dependence of $(Kc/R\theta)_{\theta=0}$ for sodium cellulose xanthate in dilute NaOH solution.

No fluorescence could be detected, and the correction for depolarization, being very small, was not applied.

Values of $Kc/R\theta$ were plotted against $\sin^2 \theta/2$ as shown in Figure 1. The zero angle intercepts from Figure 1 were plotted against concentration in Figure 2. Data for selected constant angles were plotted against concentration in the same way as zero-angle data and the intercepts at zero concentration plotted against $\sin^2 \theta/2$ (filled circles in Fig. 1). From the slope of such a line, the radius of gyration $(\bar{S}^2)_z^{1/2}$ was calculated according to the relationship

$$(\bar{S}^2)_z^{1/2} = \frac{3}{16\pi^2}\left(\frac{\lambda}{\eta_0}\right)^2 \frac{\text{Initial slope}}{\text{Intercept}}$$

λ/n_0 being the wavelength of light in the solution of refractive index n_0.

RESULTS AND DISCUSSION

Figure 3 shows a double logarithmic plot of intrinsic viscosity versus weight-average degree of polymerization, DP_w for sodium cellulose xanthate at the DS level 0.5. The relation between $[\eta]$ and DP_w may be expressed according to the Mark-Houwink equation:

$$[\eta] = 1.29 \times 10^{-2}\mathrm{DP}_w^{0.42}$$

In Figure 4 are plotted the $[\eta]$ values of three different samples of cellulose xanthates having varying molecular weights against degree of substitution.

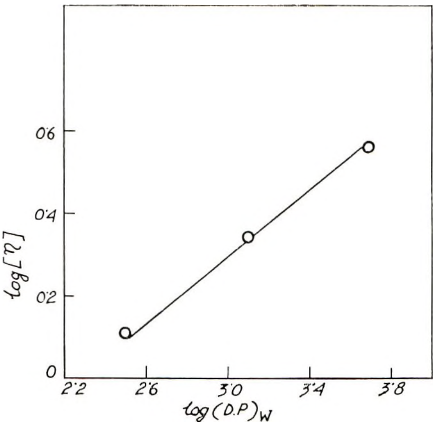

Fig. 3. Dependence of intrinsic viscosity on degree of polymerization.

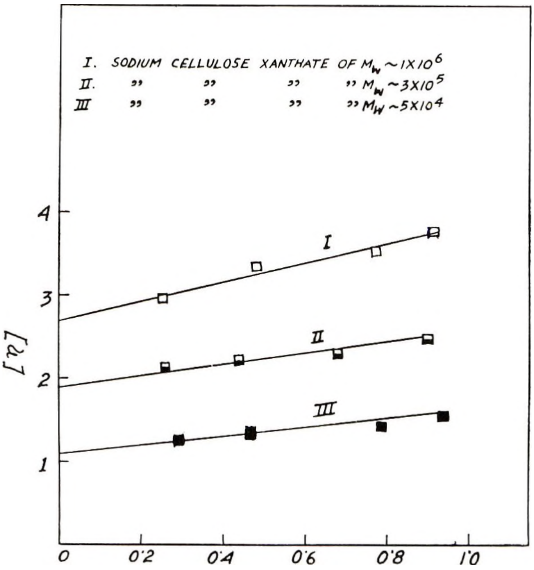

Fig. 4. Intrinsic viscosity of sodium cellulose xanthate vs. degree of substitution.

It will be observed that in all cases, the [η] values show an increase with increasing degree of substitution. It is well known that for flexible polymers, the variation of [η] with solvent power is related to differences in chain configurations. Although the chains of the cellulose derivatives are much stiffer, some flexing or kinking is possible, and the observed variations of [η] with degree of substitution may be explained on this basis. When the degree of substitution is low, the interaction between solvent and solute molecules is small, polymer–polymer contacts are favored, and the polymer chains coil up, leading to a smaller hydrodynamic volume. However, as the number of —CSSNa groups in the chain increases, the

TABLE II

Molecular Parameters of Sodium Cellulose Xanthate in Dilute NaOH Solution

Sample no.	DS	$[\eta]$, dl./g.	$\bar{M}_w$	$(\bar{S}^2)_z^{1/2}$, A.	$A_2 \times 10^4$, cm.^{3}/g.^{2}	α	$(\bar{R}^2)_z^{1/2}$, A.	$(\bar{R}_0^2)_z^{1/2}$, A.	$\Phi \times 10^{-21}$
1a	0.25	3.00	1.08×10^6	900.3	1.22	1.02	2205	2161	2.97
1b	0.48	3.55	1.02×10^6	949.3	3.75	1.05	2325	2214	2.88
1c	0.77	3.60	1.05×10^6	972.5	4.22	1.05	2382	2269	2.86
1d	0.91	3.70	1.14×10^6	1025.0	4.31	1.03	2498	2425	2.69
2a	0.26	2.15	3.12×10^5	539.1	1.75	1.01	1320	1303	2.92
2b	0.42	2.20	2.63×10^5	551.6	2.10	1.02	1351	1324	2.35
2c	0.69	2.25	2.78×10^5	561.3	3.62	1.01	1374	1361	2.41
2d	0.90	2.45	3.33×10^5	598.4	4.94	1.02	1466	1436	2.59
3a	0.29	1.30	5.26×10^4	155.8	2.27	1.01	382	378	1.28
3b	0.47	1.30	5.71×10^4	153.8	3.12	1.03	377	366	1.44
3c	0.79	1.40	5.56×10^4	162.1	4.75	1.03	398	386	1.24
3d	0.94	1.55	5.88×10^4	174.1	5.00	1.03	426	414	1.18

interaction between a polymer segment and solvent molecules adjacent to it increases, and the polymer molecule tends to expand so as to reduce the frequency of contacts between pairs of polymer segments. The influence of the added steric restrictions to rotation about the chain bonds with increasing degree of substitution is presumably overshadowed by the increased polymer–solvent interaction.

The $(\bar{S}^2)_z^{1/2}$ values (Table II) show a similar trend towards increased chain dimensions with increasing degrees of substitution. It may be mentioned here that Cornell and Swenson,[14] while studying the solution properties of diethylacetamide cellulose xanthate in 90% dimethyl sulfoxide have observed that the polymer–solvent interaction is primarily responsible in determining the configuration in solution.

The hydrodynamic parameter Φ was calculated from the Flory equation $\Phi = [\eta]M_w/(\bar{R}^2)_z^{1/2}$, the end-to-end distance $(\bar{R}^2)_z^{1/2}$ being obtained from the relation for randomly coiled polymers $(\bar{R}^2)_z^{1/2} = 6^{1/2}(\bar{S}^2)_z^{1/2}$. The values of Φ obtained varies from 1.2×10^{21} to 2.9×10^{21}. Considering the range of molecular weights investigated and that no correction for polydispersity has been applied, the data obtained seem to be satisfactory.

The expansion factor α was calculated by use of the relationship due to Orofino and Flory:[15]

$$A_2 = 16(\pi/3^{3/2})[N_A(\bar{S}^2)^{1/2}/M] \ln [1 + (\pi^{1/2}/2)(\alpha^2 - 1)]$$

The values of α shown in Table I are of the order of 1.02. The expansion factor is seen to be practically independent of molecular weight and is smaller than the values obtained for synthetic polymers.[16] The inherent stiffness of the cellulose chain is responsible for the nearly negligible expansion $(\alpha - 1)$. This has also been observed with other cellulose derivatives, such as cellulose trinitrate[8] $(\alpha = 1.03)$ and hydroxyethyl cellulose[5] $(\alpha = 1.04)$. The value of α for sodium cellulose xanthate obtained by us $(\alpha = 1.02)$ is close to the α values for other cellulose derivatives.

An important parameter for characterizing the stiffness of a polymer chain is the effective bond length b. This was calculated as

$$b = (\bar{R}_0^2)^{1/2}/(\mathrm{DP}_w)^{1/2}$$

and was found to be 29 A. for sample 1a. Data for the extension parameters of some cellulose derivatives and of polystyrene are presented in Table III. This provides some important information. The effective bond length of sodium cellulose xanthate is seen to be much higher than that of polystyrene, indicating a higher degree of coiling in the latter. However, compared to those of cellulose trinitrate and sodium carboxymethyl cellulose, the effective bond length of cellulose xanthate is smaller, which shows that cellulose xanthate is more flexible than cellulose trinitrate and sodium carboxymethyl cellulose.

By employing the relationship for *trans*-1,4′-polysaccharides[17]

$$(\bar{R}_f^2)^{1/2} = 7.75(\mathrm{DP}_w)^{1/2}$$

TABLE III
Extension Parameters for Sodium Cellulose Xanthate and Other Systems

System	b, A.	$(\bar{R}_0^2/\bar{R}_f^2)^{1/2}$	Reference
Sodium carboxymethyl cellulose in NaCl	37.4	—	7
Cellulose trinitrate in ethyl acetate	35	4.5	8
Sodium cellulose xanthate in NaOH	29.0	3.8	Present work
Cellulose in cadoxen	19	2.7	18
Polystyrene	8.6	2.2	19

the end-to-end distances assuming free rotation about all chain bonds can be calculated. The ratio of the unperturbed coil dimension to that determined with free rotation of the chain bonds, $(\bar{R}_0^2/\bar{R}_f^2)^{1/2}$ is accepted as a characteristic of the flexibility of the polymer chains. In Table III this ratio for sodium cellulose xanthate in NaOH is seen to be higher than that of polystyrene and cellulose in cadoxen[18] but lower than that of cellulose trinitrate. This lends further support for our earlier conclusions arrived at from considerations of the effective bond length.

Thus, from the information provided by the parameters and α, b, and $(\bar{R}_0^2/\bar{R}_f^2)^{1/2}$ it appears that sodium cellulose xanthate in dilute solution behaves as an extended, loosely coiled molecule, substantially stiffer than the synthetic polymers, but comparable to other cellulose derivatives in chain flexibility.

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Résumé

Les paramètres moléculaires du xanthate sodique de cellulose ont été déterminés par diffusion lumineuse et viscosimétrie en solution d'NaOH. On a étudié l'effet du degré de substitution sur la configuration moléculaire du xanthate sodique de cellulose en considérant trois séries d'échantillons de degrés de substitution différents. On a déterminé le facteur d'expansion à partir de l'équation d'Orofino et Flory, ainsi que la longueur reélle de liaison *b* et le rapport entre la partie non rotative et la partie rotative des unités de chaînes $(\bar{R}_o^2/\bar{R}_f^2)^{1/2}$. La conclusion était que lanthate sodique de cellulose en solution diluée est une molécule en spirale étendue comparable à d'autres dérivés de cellulose en ce qui concerne la rigidité de la chaîne.

Zusammenfassung

Molekülparameter von Cellulosenatriumxanthogenat wurden in NaOH-Lösung durch Lichtstreuung und Viskosimetrie besimmt. Der Einfluss des Substitutionsgrades auf die Molekülkonfiguration von Cellulosenatriumxanthogenat wurde an drei Reihen von Proben mit verschiedenem Substitutionsgrad untersucht. Der Espansionsgrad wurde mit der Beziehung von Orofino und Flory berechnet. Auch die effektive Bindungslänge, *b*, und das Verhältnis der ungestörten Dimension zur Dimension bei freier Rotation der Kettenbausteine, $(\bar{R}^2{}_o/\bar{R}_f^2)^{1/2}$ wurde bestimmt. Man kommt zu dem Schluss, dass Cellulosenatriumxanthogenat in verdünnter Lösung ein lokker geknäueltes Molekül mit einer den anderen Cellulosederivaten vergleichbaren Kettensteifigkeit ist.

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Kinetics of the γ-Radiation-Induced Polymerization of Methyl Methacrylate in the Solid State

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Synopsis

Studies have been made of the γ-radiation-induced polymerization of methyl methacrylate in bulk, in the solid state at a temperature of −65°C. and a radiation intensity of 346,000 rad/hr. The reaction was found to have an extremely long induction period (~50 hr.) when pure monomer was used, and to be first-order with respect to polymer concentration. This first-order dependency was confirmed by a series of irradiations in which 0.6% poly(methyl methacrylate) was dissolved in the monomer before irradiation. These irradiations showed no induction period. Nuclear magnetic resonance spectroscopy indicated a much more heterotactic polymer than that obtained in the liquid state at −49°C.

Introduction

Although the current literature reflects a great amount of investigation into radiation-induced, solid-state polymerization, there are no reports of the successful polymerization of pure methyl methacrylate (m.p. ~ −50°C.) under these conditions.[1,2] However, methyl methacrylate has been successfully polymerized when irradiated in a solid mixture with mineral oil.[10] Since the kinetics of the γ-radiation-induced polymerization of methyl methacrylate in the temperature range of −19° to −49°C. has been studied in these laboratories,[3] it was considered that it would be of interest to attempt to polymerize this monomer in the solid state.

Experimental

The irradiation facility used in these experiments is similar to that described previously,[4] and the ferrous ion dosimetry technique was that of Weiss.[5,6] The methyl methacrylate was obtained from the Matheson, Coleman and Bell Company.

The purification of the monomer and the degassing procedure used in the preparation of the monomer samples is identical to that previously used.[3] The stainless steel cooling jacket, which contained the sample cell in the radiation chamber, allowed cold methanol to be circulated in direct contact with the sample vial. This methanol was cooled by pumping it through a cooling coil immersed in acetone–Dry Ice. The temperature was found to stabilize at −65 ± 2°C. after about 30 min. of precooling before starting the irradiation. The Dry Ice reservoir held approximately 200 lb. of Dry Ice; this amount was sufficient for about 16 hr. of operation.

The amount of polymer produced was determined gravimetrically by precipitation in methanol.[7,8] The reaction mixture was kept frozen after removal from the irradiation facility. The cell was opened and the frozen mixture was allowed to drip as it melted into a beaker containing hydroquinone dissolved in a small amount of acetone. After the vial had drained, it was rinsed with acetone and the polymer was precipitated by adding copious amounts of methanol. This procedure was designed to minimize any post-irradiation polymerization. Control samples irradiated 40 hr. showed no polymer formation when this procedure was followed.

Nuclear magnetic resonance spectra were obtained by using a Varian Associates V-4302 dual purpose 60 Mc./sec. instrument in connection with a heated probe. A 15% (w/v) solution in spectrograde chloroform was used, and peak areas were approximated by triangulation. Final peak area reported is the average of several spectra.

Rates of Polymerization

Irradiation of frozen methyl methacrylate for 24 and 31.5 hr. at an average intensity of 346,000 rad/hr. yielded no polymer; however after 48 hr. of irradiation, a trace amount of polymer was produced. The presence of this trace of polymer led to longer irradiations and these results are tabulated in Table I. A plot of weight per cent conversion versus time irradiated yielded a logarithmic curve. The shape of this curve suggested that the reaction was first-order in polymer concentration, so a series of irradiations was made in which 0.6% of poly(methyl methacrylate) was dissolved in the monomer before irradiation. The results of this series are shown in Table II. A graph of the results of this series also yielded a logarithmic curve which was almost identical to that obtained with the pure monomer except that the induction period was eliminated.

If first-order kinetics were governing the reaction, the rate of polymerization would be proportional to the concentration of the polymer [P], as well

TABLE I
Results of the Polymerizations of Pure Methyl Methacrylate in the Solid State at an Average Intensity of 346,000 rad/hr.

Irradiation time, hr.	Conversion, wt.-%
24.0	0.00
31.5	0.00
48.0	Trace
52.0	~0.04
74.3	2.37
81.3	7.50
89.5	14.96
96.0	~100

TABLE II

Results of the Polymerization of Mixtures of Methyl Methacrylate and Poly(methyl Methacrylate) in the Solid State at an Average Intensity of 324,000 rad/hr.

Irradiation time, hr.	Conversion, wt.-%	Total polymer, wt.-%
2.3	0.09	0.52
16.3	1.25	1.89
24.0	3.93	4.54
30.6	20.0	20.6

as to the intensity raised to some power, I^a. Mathematically this would be expressed as

$$d[\mathrm{P}]/dt = kI^a[\mathrm{P}] \qquad (1)$$

but, since I^a is essentially constant, it can be combined with the proportionality constant to yield a new constant, K. Equation (1) would then become

$$d[\mathrm{P}]/dt = K[\mathrm{P}] \qquad (2)$$

which on integration gives

$$\ln [\mathrm{P}] = Kt + C \qquad (3)$$

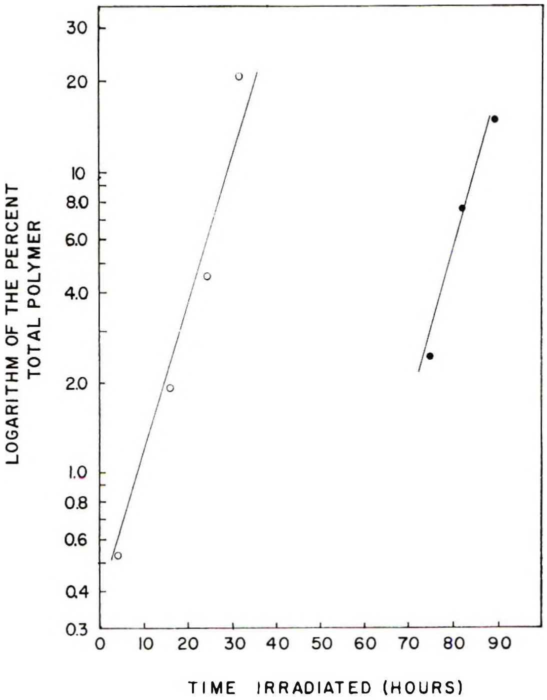

Fig. 1. Logarithm of per cent total polymer vs. time irradiated.

where C is the constant of integration. According to this equation a plot of the logarithm of the concentration of polymer versus time should give a straight line with the slope equal to K, if the reaction is first-order in polymer concentration. In addition, the value of K for both series should be the same. This graph is shown in Figure 1, a plot of the logarithm of the weight per cent of total polymer present versus time. In the case of the pure monomer, the per cent polymer present is the same as the per cent conversion; however, in the case where polymer was added to the monomer, Figure 1 represents the weight per cent of total polymer present, including the added polymer. This is necessary to satisfy the above equation. The plot of the experimental results do in fact yield straight lines. The slopes of these lines, K, were calculated by the method of least squares to be 0.115 for the pure monomer and 0.124 for the runs with added polymer. The value of K for the polymerization of the pure monomer is in close agreement with value of K for the polymerizations carried out with added polymer. This is a strong indication that the important reaction is first-order in polymer concentration. This equation would hold only after polymerization has been initiated, since the equation does not account for the initial formation of polymer. Apparently, during the long induction period minute amounts of polymer are formed, perhaps at crystal defects or at surfaces.

TABLE III
Relative Fraction of Syndiotactic Configuration as a Function of Irradiation Temperature and Physical State

Temperature, °C.	Fraction syndiotactic
−19	0.77[a]
−29	0.82[a]
−39	0.85[a]
−49	0.88[a]
−65	0.64

[a] Data of Lipscomb and Weber.[3]

The molecular weights of low conversion runs (7.50 and 14.96% conversion) were found to be 2.3×10^5, while the molecular weight of the polymer produced from the run that gave 100% conversion was 5.6×10^5. These are comparable to molecular weights obtained from the liquid state at higher temperatures.[3]

Bovey and Tiers[9] have previously obtained NMR spectra of poly(methyl methacrylate) and have assigned τ values for the α-methyl peaks corresponding to different configurations. The peak at 8.78 τ was attributed by them to the isotactic configuration of the form *ddd* or *lll*. The peak at 9.09 τ was attributed to the syndiotactic configuration of the forms *dld* or *ldl*. The α-methyl groups of the heterotactic configuration, *ldd*, *dll*, *ddl, or lld,* were assigned the peak at 8.95τ. The NMR data for the polymers produced in this work gave τ values of 8.78, 8.94, and 9.07 for the isotactic, heterotactic, and syndiotactic configurations, respectively.

The relative fraction of syndiotactic configuration is shown in Table III. For purposes of comparison, data from previous work[3] on the low temperature liquid-state polymerizations are included. The relative fraction of the contribution of the syndiotactic configuration was calculated based on the total area of the syndiotactic and heterotactic peaks. The isotactic peak was not included because the area was essentially the same in all spectra and would not affect any trends; in addition, it was very small. It is interesting to note that the relative fraction of syndiotactic contribution increases with decreasing temperature when the polymer is produced above the freezing point of the monomer but polymer produced in the solid state reverses this trend.

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Résumé

On a étudié la polymérisation induite par des radiations du méthacrylate de methyle en bloc, à l'état solide et à la température de −65°C, sous une intensité de radiation de 346.000 rads/heure. On a trouvé que la réaction avait une très longue période d'induction (50 heures), lorsqu'on utilisait du monomère pur et qu'elle était du premier ordre par rapport à la concentration en polymère. Cette dépendance du premier ordre a été confirmée par une série d'irradiations dans lesquelles 0,6% de polyméthacrylate de méthyle était dissous dans le monomère avant l'irradiation. Ces irradiations ne montrent pas de période d'induction. La résonance magnétique nucléaire montre une plus grande hétérotacticité du polymère que celui obtenu à l'état liquide à −49°C.

Zusammenfassung

Eine Untersuchung der γ-Strahlen-induzierten Polymerisation von Methylmethacrylat in Substanz, in fester Phase bei −65°C und einer Strahlungsintensität von 346000 rad/h wurde durchgeführt. Die Reaktion besitzt bei Verwendung von reinem Monomeren eine extrem lange Induktionsperiode (50 Stunden) und ist von erster Ordnung in Bezug auf die Polymerkonzentration. Die Abhängigkeit erster Ordnung wurde in einer Bestrahlungsreihe bestätigt, in welcher 0.6% Polymethylmethacrylat vor der Bestrahlung im Monomeren gelöst wurde. Diese Versuche zeigten keine Induktionsperiode. Kernmagnetische Resonanzspektroskopie liess ein viel stärker heterotaktisches Polymeres erkennen als das in flüssiger Phase bei −49°C erhaltene.

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Identification of Volatile Products Produced During the Peroxide Vulcanization of Poly(vinyl Alkyl Ethers)

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Synopsis

Volatile products are produced during vulcanization of the polymers of vinyl methyl, ethyl, isopropyl and *n*-butyl ethers with dicumyl peroxide, both in the presence and, absence of added sulfur. They were identified and estimated by gas-liquid chromatography and mass spectrometry. The principal products formed during the vulcanization of poly(vinyl ethyl ether) with dicumyl peroxide were ethane and acetaldehyde and to a lesser extent methane. The addition of sulfur in the curing recipe resulted in a sharp increase in the proportion of ethyl alcohol, a large increase in methane, and a large decrease in ethane. The formation of these volatile products and the observed changes due to the presence of sulfur in the curing recipe can be accounted for on the basis of side-chain scission of the polymer radicals produced during vulcanization. The length and/or shape of the alkyl group in poly(vinyl alkyl ether) determine the composition of the volatile products. The data are in harmony with the postulated chemistry of vulcanization of these polymers.

INTRODUCTION

During the past few years, we have studied the vulcanization of poly(vinyl alkyl ethers) and dynamic properties of their gum vulcanizates.[1-4] In the course of these investigations, it was observed that stabilizer-free poly(vinyl alkyl ethers) on curing with dicumyl peroxide gave porous or foamy vulcanizates. The addition of small amounts of elemental sulfur in the compounding recipes eliminated the apparent porosity in the resulting elastomers. In the present study, we identify the major volatile products formed during vulcanization. In addition, the effect of the length and/or shape of the alkyl group in poly(vinyl alkyl ethers) on the composition of the volatile products has been determined. These data are viewed in terms of the chemistry of vulcanization of these polymers.

EXPERIMENTAL

Materials

Monomers. Vinyl *n*-butyl ether and vinyl isopropyl ether were obtained and purified as reported previously.[5]

Polymers. A sample of poly(vinyl methyl ether), PVME, was kindly supplied by Dr. John A. Manson of Air Reduction Company and was used without any purification. Poly(vinyl ethyl ether), PVEE, was obtained from Union Carbide Chemicals Company as an antioxidant-free cement in hexane. It was carefully dried under vacuum. Poly(vinyl isopropyl ether), PVi-PE, and poly(vinyl *n*-butyl ether), PVBE, were prepared from the corresponding monomers by polymerization with aluminum hydrosulfate hydrate[6] catalyst in dry pentane. The polymers were precipitated in methanol, isolated, and dried under vacuum.

Compounding and Vulcanization

The polymers were compounded on a two-roller mill according to the recipes shown in Table I. The vulcanizations were carried out under 10^{-5} Torr for 80 min. in glass tubes. The latter were suspended in an oil bath maintained at 144°C.

TABLE I
Vulcanization Recipe

	Parts (by weight)
Rubber	100
Dicumyl peroxide (95%)	4
Sulfur	Variable
Cure: 80 min./144°C.	

Analysis of Volatile Products

The volatile products of vulcanization present in the upper portion of the glass tube were identified and estimated by mass spectrometry and/or gas-liquid chromatography (GLC). A 26 ft. × 1/8 in. GLC column containing 20% UCON–di-*n*-decyl phthalate was used for separating the components in the analytical sample. For comparison, the retention times were determined for authentic samples of the various compounds which were suspected to be formed as the volatile products during vulcanization.

RESULTS

In Table II, GLC data are shown for the volatile products formed during the vulcanization of PVEE with dicumyl peroxide alone and with dicumyl peroxide plus sulfur. In the absence of sulfur, ethane and acetaldehyde constitute the major products together with a small amount of methane. The presence of sulfur in the vulcanization recipe profoundly affects the chemistry of vulcanization as attested by the following changes: (*1*) a large increase in the relative amount of methane; (*2*) a sharp increase in the proportion of ethyl alcohol; (*3*) a large decrease in the relative amount of ethane; (*4*) substantial increases in the proportions of acetone, and probably methyl ethyl ketone and isopropyl alcohol.

TABLE II
Effect of Sulfur on the Volatile Products Formed during the Vulcanization of Poly(vinyl Ethyl Ether) With Dicumyl Peroxide (GLC Analysis)

	Product, %	
	Peroxide alone	Peroxide + sulfur[a]
Methane	4.6	32.2
Ethane	66.7	4.4
Ethylene	0.2	—
Dimethyl ether	0.3	—
Acetaldehyde	25.7	20.8
Methanol	0.3	2.6
Acetone	0.4	5.8
Ethyl alcohol	0.03	14.0
Isopropyl alcohol (?)	0.9	12.3
Methyl ethyl ketone (?)	0.8	3.5
Six unidentified peaks		4.6
Total	99.93	100.2

[a] 0.5 weight parts per 100 parts of rubber.

TABLE III
Effect of Sulfur on the Volatile Products Formed during the Vulcanization of Poly(vinyl *n*-Butyl Ether) with Dicumyl Peroxide (Mass Spectrometric Analysis)

	Product, mole-%	
	Peroxide only	Peroxide + sulfur[a]
Methane	5	1
Butane	54	—
n-Butanol	—	28
Propane	15	—
Butyraldehyde	9	37
Air	0.8	—
Carbon dioxide	—	24
Carbon monoxide	16	5
Water	0.1	—
Carbon disulfide (?)	—	5

[a] 0.4 weight parts per 100 parts of rubber.

In Table III, mass spectrometric data are shown for the volatile products generated during the vulcanization of poly(vinyl *n*-butyl ether) with dicumyl peroxide and dicumyl peroxide plus sulfur. In addition to the types of chemical products observed by GLC, air, carbon monoxide, water, and probably carbon disulfide also show up.

The data in Table IV show the effect of sulfur concentration in the compounding recipe of poly(vinyl ethyl ether) on the volatile products formed. The significantly lower values of the pressure produced in the sample tube by the volatile products when sulfur is present in the recipe is consistent

TABLE IV
Effect of Sulfur Concentration on the Volatile Products Formed during the Vulcanization of Poly(vinyl Ethyl Ether) with Dicumyl Peroxide (Mass Spectrometric Analysis)

	Product, mole-%		
	Peroxide (pressure 72.1 μ)	Peroxide + sulfur[a] (pressure 33.9 μ)	Peroxide + sulfur[b] (pressure 41.9 μ)
Methane	7.0	48.1	15.1
Ethane	22.9	2.2	—
Ethyl alcohol	0.8	4.5	13.9
Acetaldehyde	20.6	15.2	13.9
Methyl mercaptan	—	Trace	0.8
Hydrogen Sulfide	—	Trace	3.7
Air	1.2	1.4	8.9
Nitrogen and/or carbon monoxide	46.4	9.9	—
Water	0.4	7.0	21.6
Not identified (Mass = 86)	Trace	6.5	10.3
Not identified (Mass = 84)	Trace	3.1	6.8

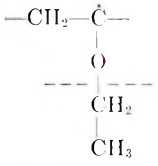
[a] 0.5 weight parts per 100 parts of rubber.
[b] 2.0 weight parts per 100 parts of rubber.

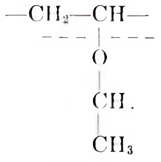
with our observations of bubbles and porosity in the vulcanizates of antioxidant-free poly(vinyl alkyl ethers) in the sulfur-free recipes. As the sulfur concentration in the recipe increases, ethane and carbon monoxide decrease while ethyl alcohol, water, and sulfur compounds increase.

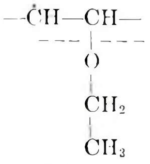
DISCUSSION

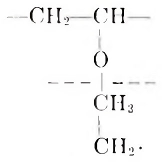
Some idea about the reactions of poly(vinyl alkyl ethers) with free radicals and the fate of the resulting radicals may be obtained from literature data on the abstraction of unactivated hydrogen atoms by alkoxy radicals. Unactivated hydrogen atoms are abstracted by *tert*-butoxy radicals at rates which are in the order:[7] primary < secondary < tertiary, the relative rates being 1:20:28. Cumyloxy radicals are more selective[8] than *tert*-butoxy radicals; tertiary hydrogens are abstracted 6–7 times faster than secondary hydrogens at 153°C. Hydrogen atoms adjacent to an ether group are activated and their abstraction is facilitated. The activating effect is more pronounced for primary hydrogen and is considerably less for tertiary hydrogen.[9] The ease of abstraction of hydrogens in poly(vinyl ethyl ether) and poly(vinyl *n*-butyl ether) is expected to be in the order $CH^* > CH_2^* > CH_2 > CH_3$, where CH^* and CH_2^* refer to the groups activated by the presence of an adjacent ether linkage.

From PVEE, several different radicals may be formed by reaction with cumyloxy radicals:


Type A


Type B


Type C


Type D

Volatile fragments could result by side-chain scission at the respective β positions indicated by the broken lines. Type A radical would give an ethyl radical which would yield principally ethane by abstracting a hydrogen atom. Occasionally, it yields ethylene and ethane if it disproportionates with another ethyl radical, or butane if it combines. The analytical data show that these latter reactions are not significant under the conditions of our experiments. Type B radical would lead to the formation of acetaldehyde, which is one of the major products (Table II). During electron irradiation of polyethylene and other saturated hydrocarbon polymers, paraffin hydrocarbons, which are characteristic of short side chains in the polymers, have been identified and estimated by GLC and mass spectrometric techniques.[10,11] The virtual absence of ethyl alcohol in the volatile products from the sulfur-free recipe indicates that the side-chain scission of nonactivated secondary radical of type C is not favored. Presumably, nonactivated secondary radicals, whether on the polymer chain or on the pendant alkyl group, such as n-butyl, react with other polymer radicals to yield crosslinks or disproportionated molecules. The increased[3] efficiency of crosslinking of poly(vinyl n-octyl ether) compared to that of poly(vinyl n-butyl ether) supports this hypothesis. Similarly, nonactivated primary radicals of type D do not undergo side chain splitting and hence are available for coupling reactions.

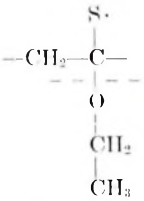
According to the above mechanism, the side chain scissions of radicals of types A and B from poly(vinyl n-butyl ether) should result in the formation of n-butane and n-butyraldehyde. As shown in Table III, these products are indeed formed. The formation of propane and carbon monoxide could be explained from further reaction of butyraldehyde with another radical as shown in eq. (1).

$$\begin{array}{c} CH_3CH_2CH_2CHO + R\cdot \rightarrow CH_3CH_2CH_2\dot{C}O + RH \\ \downarrow \\ R'\cdot + CH_3CH_2CH_3 \xleftarrow{R'H} CH_3CH_2CH_2\cdot + CO \end{array} \qquad (1)$$

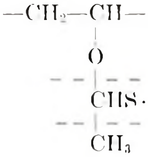
Effect of Sulfur

Wanless et al.[12] have reported that the principal high-boiling products of the reaction of 2,5-dimethylpentane, sulfur, and di-*tert*-butyl peroxide at 160–180°C. were disulfides and/or polysulfides, most of which were formed from the isoparaffin starting material. Based on this model compound work, Wei and Rehner[13] have proposed a mechanism for the vulcanization of saturated hydrocarbon elastomers by the peroxide–sulfur system. We have previously shown[2] that chemically bound sulfur is present in the vulcanizates of poly(vinyl ethyl ether) prepared with dicumyl peroxide and sulfur. Vulcanizates from recipes similar to the one shown in Table II contained only a small proportion, if any, of polysulfidic structures.

It may be necessary to write many different radical reactions to illustrate all that could be taking place during vulcanization. The large increase in the relative amount of methane and the sharp increase in the proportion of ethyl alcohol in the volatile products (Table II) as a result of the presence of sulfur in the compounding recipe could result from β-scissions of radicals of types A′ and B′.



Type A′



Type B′

The mechanism of formation of these radicals is not known with certainty. They may be formed by reaction of a type A or type B radical with sulfur:

$$\mathrm{R}\cdot + \mathrm{S}_8 \rightarrow \mathrm{RS}_8\cdot \xrightarrow[\text{sulfur}]{\text{additional}} \mathrm{RS}_x\cdot \rightleftharpoons \mathrm{RS}\cdot + \cdot\mathrm{S}\cdot_{x-1} \qquad (2)$$

or by the cleavage of disulfidic and/or polysulfidic crosslinks by free radicals:

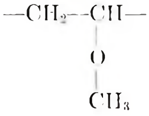
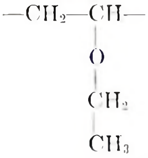
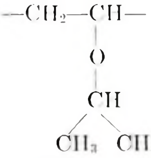
$$\mathrm{R{-}S}_y\mathrm{{-}R} + \mathrm{R}'\cdot \rightarrow \mathrm{R{-}S}\cdot + \mathrm{R}'\mathrm{{-}S}_{y-1}\mathrm{{-}R} \qquad y \geqslant 2 \qquad (3)$$

Type A′ radical, on side-chain splitting, would yield ethoxy radical and subsequently ethyl alcohol. The formation of type A′ radical from type A would result in the suppression of side chain scission from type A radical and a decrease in the amount of ethane would be observed. The significant increase in the amount of methane evolved, when sulfur is present in the recipe, suggests that scission of type B′ radical to give methyl radical must be playing an important role. The alternate mode of scission would yield thioacetaldehyde, which is expected to polymerize to a nonvolatile compound and escape detection. The formation of methyl ethyl ketone is probably due to further reactions among the fragment radicals.

An increase in the concentration of sulfur from 0.5 part to 2 parts in the compounding recipe further increases the proportion of ethyl alcohol and virtually eliminates ethane. The relative proportion of acetaldehyde is also suppressed. Qualitatively, these data can be rationalized on the basis of reactions outlined earlier in the paper. The observed decrease in methane is presumably due to the reaction of methyl radicals with elemental sulfur or other polysulfidic compounds which are formed during vulcanization. Apparently, this reaction competes with the abstraction of hydrogen by methyl radicals.

A comparison of the volatile products produced during the vulcanization of three different poly(vinyl alkyl ethers) with the use of identical curing recipes is shown in Table V. The effect of the length and/or shape of the alkyl group in poly(vinyl alkyl ether) in determining the products formed during vulcanization is quite evident. Methane and methanol were the principal products produced from PVME, together with a smaller amount of an unidentified product which was not formaldehyde. It is quite possible that formaldehyde might also have been formed but polymerized rapidly to nonvolatile polyformaldehyde. Methane, ethyl alcohol, and acetaldehyde were the main products from PVEE, as also indicated in Table II; however, the quantitative agreement is less than desirable. In the case of PVi-PE, the chief products were methane, acetone, and isopropyl alcohol.

TABLE V
The Effect of Alkyl Group in Poly(vinyl Alkyl Ether) on the Volatile Products Formed During Vulcanization with Dicumyl Peroxide and Sulfur (Analysis by GLC)[a]

	Volatile products, %		
	PVME  $-CH_2-CH(OCH_3)-$	PVEE  $-CH_2-CH(OCH_2CH_3)-$	PVi-PE  $-CH_2-CH(OCH(CH_3)_2)-$
Methane	76.7	32.8	19.5
Ethane	—	—	1.1
Unidentified peak	4.2	0.2	0.4
Acetone	—	1.6	57.4
Isopropyl alcohol	—	—	19.1
Unidentified peak	—	—	0.5
Ethyl alcohol	—	21.5	—
Methanol	16.6	—	—
Acetaldehyde	—	43.0	—

[a] 0.5 weight parts per 100 parts of rubber.

These products are consistent with the postulated chemical reactions discussed earlier in the paper. The formation of acetaldehyde from PVEE and of acetone from PVi-PE suggests that some radicals of type B undergo cleavage before they have a chance to participate in reactions that produce type B′ radicals. In the presence of sulfur, acetone is expected to be formed due to the ionic[14] cleavage of dicumyl peroxide. The data in Tables II and V show that acetone constitutes a minor proportion of the volatile products that are formed during the vulcanization of the polymers of vinyl methyl and ethyl ethers. Hence, in the vulcanization of poly(vinyl isopropyl ether) acetone is formed primarily by the β-scission of type B radicals. The volatile products from the vulcanization of PVME, PVEE, and PVi-PE with dicumyl peroxide and sulfur were also examined with the aid of mass spectrometer. Qualitatively, they were in agreement with the data in Table V. In addition, carbon monoxide was also found in all the three cases.

We are grateful to J. L. Patrick and R. D. Board for GLC analyses, to J. K. Phillips for analyses by mass spectrometry, and to Dr. K. W. Scott and Professor W. J. Bailey for valuable discussions.

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Résumé

Des produits volatils sont produits durant la vulcanisation des polymères des vinyle, méthyle, éthyle, isopropyle et n-butyl éthers avec le dicumyl peroxyde, tous deux en présence ou en absence de soufre. Ces substances ont été identifiées et dosées par G.L.C. et par spectrométrie de masse. Les principaux produits formés durant la vulcanisation du poly-vinyl-éthyl-éther avec le dicumyl peroxyde sot l'éthane, l'acétaldéhyde et en quantité moindre, le méthane. De l'addition de soufre au cours de la réaction, il résulte: une grande augmentation de la proportion d'alcool éthylique formé, une grande augmentation de la formation de méthane et une importante diminution de la quantité d'éthane formé. On peut rendre compte de la formation de ces produits volatils ainsi que des changements observés en présence de soufre dans la réaction sur la base de la production de radicaux formés sur les chaînes latérales du polymère durant la vulcanisation. La longueur et/ou la forme du groupe alcoyl dans le polyvinyl alcoyl éther détermine la composition des produits volatils. Les résultats sont en harmonie avec les données de la chimie générale de vulcanisation de ces polymères.

Zusammenfassung

Bei der Vulkanisation der Polymeren von Methyl-, Äthyl-, Isopropyl-, und n-Butylvinyläther mit Dicumylperoxyd mit und ohne Schwefelzusatz entstehen flüchtige Produkte. Sie wurden mittels GLC und Massenspektrometrie identifiziert und quantitativ bestimmt. Die bei der Vulkanisation von Polyvinyläthyläther mit Dicumylperoxyd gebildeten Hauptprodukte waren Äthan und Acetaldehyd und in geringerem Ausmass Methan. Der Zusatz von Schwefel zum Vulkanisationsansatz führte zu einer scharfen Zunahme des Anteils an Äthylalkohol, einer grossen Zunahme an Methan und einer grossen Abnahme anÄtham. Die Bildung dieser flüchtigen Produkte sowie die

bei Schwefelzusatz zum Vulkanisationsansatz beobachteten Änderungen können durch Seitenkettenspaltung in den bei der Vulkanisation gebildeten Polymerradikalen erklärt werden. Die Länge und Gestalt der Alkylgruppe in Polyvinylalkyläthern bestimmen die Zusammensetzung der flüchtigen Produkte. Die Ergebnisse stehen mit dem angenommenen Vulkanisationschemismus in Einklang.

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Effect of Temperature and Solvents on Stereospecific Polymerization of Vinyl Alkyl Ethers Catalyzed by Aluminum Sulfate–Sulfuric Acid Complex

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Synopsis

The effect of polymerization temperature and solvents was determined on the crystallinity of polymers of vinyl isobutyl ether and of vinyl *n*-butyl ether prepared with aluminum sulfate–sulfuric acid complex catalyst. Principally, the methyl ethyl ketone (MEK)-insoluble fractions of these polymers were used for characterization. Density, per cent crystallinity by x-ray diffraction, infrared ratio, and dilatometric volume contraction of these polymer fractions were used as criteria of crystallinity. The MEK-insoluble fractions of poly(vinyl *n*-butyl ethers) prepared in carbon disulfide in the temperature range of −30 to +25°C. did not show any significant difference in the values of the above crystallinity parameters. The polymer obtained at 50°C. was less crystalline than the rest of the polymers. The MEK-insoluble fractions of poly(vinyl isobutyl ethers) prepared at 0–50°C. in carbon disulfide and *n*-heptane solvents also did not significantly differ in their degree of crystallinity. They were, however, decidedly less crystalline than the MEK-insoluble fractions of the corresponding polymers obtained at −20°C. These data indicate that on increasing the temperature of polymerization the crystallinity of the polymers was either unchanged or decreased slightly. The polymerizations of vinyl *n*-butyl ether and vinyl isobutyl ethers were also carried out in binary mixtures of carbon disulfide with *n*-heptane, chlorobenzene, and MEK. Generally, increasing the concentration of carbon disulfide increased the inherent viscosities of polymers as well as the weight percentage of their MEK-insoluble fractions. The MEK-insoluble fraction of poly(vinyl isobutyl ether) prepared in carbon disulfide–MEK mixture (volume ratio 2:1) was isotactic and highly crystalline. Likewise, the MEK-insoluble fractions of two polymers of vinyl *n*-butyl ether prepared in MEK itself were also isotactic and highly crystalline. Compared to poly(tetramethylene oxide), these latter fractions exhibited less dependence of rate of crystallization upon temperature. Consequently, at low degrees of supercooling they crystallize much more rapidly than does poly(tetramethylene oxide).

INTRODUCTION

Until recently, most polymerizations of vinyl alkyl ethers had to be carried out at low temperatures to obtain stereoregular polymers of high molecular weight. Polymers of irregular structure were usually obtained at higher temperatures. We had previously reported[1,2] that the reaction product of ferric sulfate hydrate and sulfuric acid catalyzed polymerization of vinyl alkyl ethers at room temperature to high molecular weight, crystallizable polymers. We further showed[2,3] that the polymers of vinyl alkyl ethers prepared at room temperature with Mosley's[4] catalyst, viz., the reaction product of an aluminum sulfate hydrate and sulfuric acid, were crystallizable, isotactic materials. Okamura and co-workers[5-7] have determined the effect of polymerization temperature on the stereoregularity of poly(vinyl isobutyl ether). In these studies, vinyl isobutyl ether was polymerized in hexane solvent with the use of catalysts obtained from several metal sulfates and sulfuric acid. From the weight per cent of the polymer fraction insoluble in methyl ethyl ketone, which was used as the measure of the degree of stereoregularity, it was concluded[5-7] that the stereoregularity of the polymer generally increased slightly when the temperature of polymerization was increased from −40 to 50°C. The relative degree of stereoregularity as measured by an infrared technique also increased as the temperature of polymerization was increased from −40 to 20°C. but decreased for the polymer prepared at 40°C.[7] In our studies on the polymerization of vinyl alkyl ethers with the aluminum sulfate–sulfuric acid complex, hereafter also referred to as AHS, we have also determined the effect of polymerization temperature on the stereoregularity of the polymers. In addition, the effect of several polymerization solvents and solvent mixtures on the characteristics of the polymers has been examined.

EXPERIMENTAL

Materials

The purification of the monomers was reported previously.[2] Heptane (purified by sulfuric acid treatment) and methyl ethyl ketone (MEK) were distilled over calcium hydride. Carbon disulfide and chlorobenzene were dried by passing through a column of silica gel.

Aluminum hydrosulfate hydrate (AHS) was prepared by a slight modification of the procedure described by Mosley.[4] A 60-g. portion of finely powdered aluminum sulfate octadecahydrate and 300 ml. of concentrated sulfuric acid were placed in a 500-ml. flask fitted with a drying tube containing Drierite. The mixture was stirred with a glass-coated magnetic stirrer and maintained at 90°C. for 4 hr. After cooling, it was carefully added under a nitrogen blanket to 1 gal. of stirred anhydrous diethyl ether. The white precipitate was filtered under a blanket of nitrogen, washed with additional anhydrous ether three times and dried for 64 hr. at 35°C. and 1 torr. A yield of 45 g. of white powder was obtained.

ANAL. Found: Al, 10.45%; S, 25.7%; H_2O, 9.85%; acid as H_2SO_4, 20.75%.

A 2% AHS suspension in dried mineral oil was used for catalyzing polymerizations in cleaned and dried 8-oz. bottles. The average size of the catalyst particles in the oil suspension was about 5 μ. The volume ratio of solvent to monomer in the polymerization recipe was either 6:1 or 1.7:1. The polymerizations were terminated with methanol containing phenyl β-naphthylamine stabilizer and the entire reaction mass was dried under vacuum.

Polymer Characterization

Inherent viscosity was measured at 30°C. on a 0.1% solution of polymer in toluene. The solution was filtered to remove insoluble polymer and catalyst residues. Therefore, the inherent viscosity values are for toluene-soluble fraction of polymers. The concentration of dissolved polymer in filtered solution was determined by drying an aliquot sample. From this value, the fraction of original polymer insoluble in toluene was calculated.

The weight fraction of polymer insoluble in MEK at 25°C. was determined as indicated in Tables I–VI.

Densities of the polymers were measured with a density-gradient tube. Specimens which were molded at about 155°C. for 15 min. and were free from bubbles when viewed under a magnifying glass were kept at 25°C. for 72 hr. before use.

Per cent crystallinity was determined by x-ray diffraction on molded specimens, 0.03 in. thick, which had also been kept at 25°C. for 72 hr. A relative index of crystallinity was also determined from the infrared spectrum obtained on the polymer film cast from carbon disulfide. For poly(vinyl isobutyl ether) fractions of high crystallinity, which were insoluble in carbon disulfide, the films were cast from hot *o*-dichlorobenzene. In the case of poly(vinyl *n*-butyl ether) the ratio D_{968}/D_{978}, representing the ratio of the optical densities of the absorption bands at 968 and 978 cm.$^{-1}$ and measured from a baseline drawn from the curves at 920–1205 cm.$^{-1}$, was used as a measure of crystallinity. The ratio D_{985}/D_{962} was used similarly for poly(vinyl isobutyl ether). The optical density measurements were made from a baseline drawn from the curves at 930–1225 cm.$^{-1}$.

Melting points and rates of crystallization were measured on MEK-insoluble fractions of two samples of poly(vinyl *n*-butyl ether). Standard dilatometric techniques were employed with mercury as the confining fluid. For melting point determination, slow heating rates were used in an attempt to maintain equilibrium conditions during the melting cycle. Before measuring rates of crystallization, the samples were pretreated for 30 min. at about 20°C. above the melting point. The experimental results are given in Table VIII. For comparison purposes some similar results on poly(tetramethylene oxide)[8] are included.

The volume contraction of poly(vinyl *n*-butyl ether) was measured dilatometrically as the per cent change in volume at 60°C. between the rapid cooling curve (15°C./hr.) and the slow heating curve (10°C./day).

RESULTS AND DISCUSSION

Effect of Polymerization Temperature on Stereoregularity of Polymers

The data on poly(vinyl *n*-butyl ether) prepared in carbon disulfide are shown in Table I. The ratio D_{968}/D_{978} for the unfractionated polymers prepared at −30 and −20°C. was slightly greater than the corresponding value for the polymer obtained at 0°C. This suggests that the latter polymer may be slightly less crystallizable than the other two polymers prepared at lower temperatures. The values of density, per cent crystallinity by x-ray diffraction, the ratio D_{968}/D_{978}, and per cent volume contraction at 60°C. were determined on the MEK-insoluble fraction of the polymer. As the temperature of polymerization is increased from −30 to 25°C., none of these parameters which are dependent on the stereoregularity and crystallinity of the polymer showed any significant difference. The corresponding per cent volume contraction and density values for the polymer prepared at 50°C. were significantly lower than the values for the remaining polymers and suggest a lower degree of crystallizability for this polymer. The weight fraction of MEK-insoluble polymer increased somewhat as the polymerization temperature was increased from −30 to 0°C. and decreased thereafter. Russian investigators[9] reported that increasing the temperature from 0 to 40°C. in such a polymerization system in heptane solvent had no significant effect on the weight percentages of polymer fractions insoluble in MEK and boiling acetone. For poly(vinyl isobutyl ethers) obtained in the polymerization temperature range of 0–50°C. (Table II), the values of various crystallinity parameters measured on MEK-insoluble fractions did not change significantly, but they were decidedly lower than the corresponding values for the two polymers obtained at −20°C. in heptane and carbon disulfide solvents. In other words, increasing the polymerization temperature from −20 to 0°C. decreased the crystallinity of the MEK-insoluble fraction of poly(vinyl isobutyl ether), and increasing the temperature from 0 to 50°C. had virtually no effect. It is noteworthy that the weight fraction of the MEK-insoluble (or toluene-insoluble) polymer decreased as the temperature of polymerization was increased from −20 to 50°C. If this weight fraction were to be used as a measure of stereoregularity, it could be concluded that the effect of increasing the polymerization temperature was to reduce the stereoregularity of the polymer obtained.

The conclusions from our data are not in accord with those of Okamura and co-workers, who emphasized that the stereoregularity of poly(vinyl isobutyl ether) increased slightly on increasing the temperature of polymerization. The coordination[2] of the ether oxygen atoms of the vinyl ether monomer and of the growing end of the polymer molecule to the metal centers in the heterogeneous counteranion of the metal sulfate complex catalyst was deemed important in the formation of isotactic polymers. It would be expected that increasing the polymerization temperature would

TABLE I

Effect of Polymerization Temperature on Stereoregularity of Poly(vinyl *n*-Butyl Ether)[a]

	Unfractionated polymer			MEK-insoluble polymer				
Polymerization temperature, °C.	Polymer conversion, %	Inherent viscosity, dl./g.	Infrared ratio[b]	Insolubles, wt.-%[c]	Density, g./cc.	Crystallinity (x-ray), %	Infrared ratio[b]	Volume contraction, (100 $\Delta V/V$ at 60°C.), %
−30	20	8.5	0.81	31	0.919	7	0.82	—
−20	35	9.3	0.80	40	0.923	11	0.81	0.16
0	96	7.2	0.75	43	0.922	10	0.81	0.13
25	97	3.9	—	25	0.921	8	0.81	0.19
50	94	3.0	—	9	0.921	—	0.76	<0.07

[a] Polymerization conditions: 100 ml. carbon disulfide, 60 ml. vinyl *n*-butyl ether, 0.1 ml. AHS suspension (2%); polymerization time variable.

[b] D_{968}/D_{978} (46 hr. after film casting).

[c] Polymer (1 g.) suspended in 200 ml. MEK at 25°C. for 100 hr. Contents shaken occasionally.

TABLE II

Effect of Polymerization Temperature on Stereoregularity of Poly(vinyl Isobutyl Ether)[a]

Polymerization temperature, °C.	Polymerization solvent	Unfractionated polymer		MEK-insoluble polymer				
		Polymer conversion, %	Inherent viscosity, dl./g.	Insolubles, wt.-%[b]	Density, g./cc.	Crystallinity (x-ray), %	Infrared ratio[c]	
							A	B
−20	Heptane	50	—	35	0.932	59	1.12	1.16
25	Heptane	87	2.1[d]	20	0.918	20	0.58	0.60
50	Heptane	87	2.3[e]	—	0.914	24	0.66	0.68
−20	Carbon disulfide	60	0.5	52	0.931	56	1.07	1.15
0	Carbon disulfide	89	4.7[f]	50	0.918	28	0.74	0.80
25	Carbon disulfide	88	3.6[g]	37	0.918	31	0.75	0.86
50	Carbon disulfide	88	2.6[e]	24	0.922	29	0.87	0.92

[a] Polymerization conditions: 100 ml. solvent, 60 ml. vinyl isobutyl ether, 0.1 ml. AHS suspension (2%); polymerization time variable.

[b] Polymer (1 g.) suspended in 200 ml. MEK at 25°C. for 100 hr. Contents shaken occasionally.

[c] D_{985}/D_{962}: (A) 46 hr. after film casting; (B) annealed 66 hr. at 115°C. in vacuum.

[d] 5.4% polymer insoluble in toluene.

[e] Polymer almost completely soluble in toluene.

[f] 35% polymer insoluble in toluene.

[g] 19% polymer insoluble in toluene.

lessen this control on stereospecific polymerization and thereby lead to the formation of lesser crystallizable polymers. Higashimura et al.[7] have reported that in the polymerization of vinyl isobutyl ether with boron trifluoride etherate and ethylaluminum dichloride as catalysts in hydrocarbon solvents, the relative isotacticity of the polymer measured by the infrared technique decreased on raising the polymerization temperature from −80 to −20°C. Again, a decrease in the stereoregularity of poly(vinyl *tert*-butyl ether) prepared with boron trifluoride etherate was reported by Higashimura and co-workers.[7,10] The isotactic polymer prepared in toluene and the syndiotactic polymers prepared in nitroethane and methylene dichloride solvents became less regular as the polymerization temperature was raised from −80 to −30°C.

Effect of Solvent

The nature of solvent employed for the polymerization of vinyl alkyl ethers has an important influence on the properties of polymers. We have previously reported that polymers obtained are more crystalline if polymerization is carried out in carbon disulfide instead of pentane.[3] The effect of the presence of carbon disulfide in binary mixtures with three different solvents has been determined for the polymerization of vinyl *n*-butyl ether and vinyl isobutyl ether. The data on the polymerization of vinyl *n*-butyl ether in CS_2–heptane mixture solvents are shown in Table III. All the polymers were obtained in better than 90% conversion and had high inherent viscosity values. As the concentration of CS_2 in the polymerization solvent was increased, the fraction of polymer insoluble in MEK, representing more easily crystallizable material, increased at

TABLE III
Polymerization of Vinyl *n*-Butyl Ether at 0°C.[a]

Solvent				
CS_2, ml.	Heptane, ml.	Polymer yield, %	Inherent viscosity, dl./g.	MEK-insoluble, %[b]
0	50	96	6.3	10.1
1	49	99.5	5.9	8.1
2	48	97.5	6.2	9.9
3	47	98	6.2	10.6
5	45	92.5	7.2	—
8	42	95.5	7.1	13.2
10	40	93.5	6.2	11.5
15	35	96	6.6	15.4
20	30	94.5	6.2	14.6
30	20	96	6.4	14.6
50	0	92.5	6.8	16.6

[a] Polymerization conditions: monomer 30 ml., solvent 50 ml., AHS catalyst 0.1 ml. (0.008 parts/100 weight parts monomer); polymerization time 15.5 hr.

[b] Molded samples were conditioned for 10 days at room temperature. Total time for extraction = 10 days. Solvent changed after 3 and 6 days.

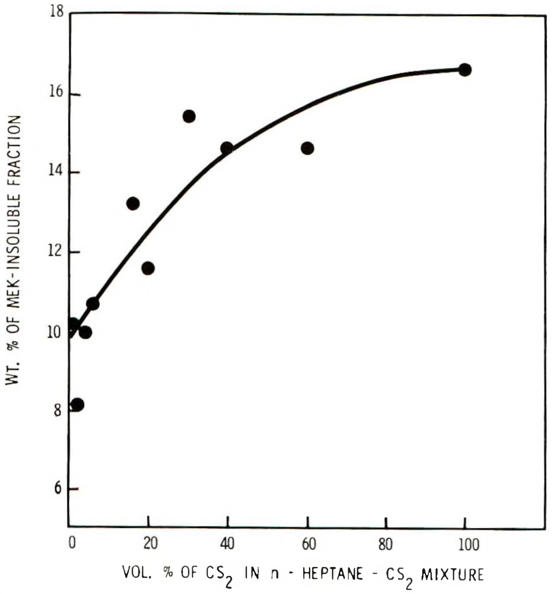

Fig. 1. Effect of the addition of carbon disulfide to *n*-heptane polymerization solvent on the weight per cent of MEK-insoluble fraction of poly(vinyl *n*-butyl ether). Vinyl *n*-butyl ether polymerized at 0°C. with aluminum hydrosulfate hydrate catalyst. Data of Table III.

first and then tended to level off, as shown in Figure 1. Improvements in the inherent viscosity and yield of the MEK-insoluble fraction of poly(vinyl *n*-butyl ether) due to the addition of CS_2 when chlorobenzene was the solvent, are shown in Table IV and Figure 2. The MEK-insoluble fraction was less than 1% when either chlorobenzene alone was used as the polymerization solvent or when the volume ratio of CS_2 to chlorobenzene

TABLE IV
Polymerization of Vinyl *n*-Butyl Ether at 25°C.[a]

Solvent				
CS_2, ml.	Chloro-benzene, ml.	Polymer yield, %	Inherent viscosity, dl./g.	MEK-insoluble, %[b]
0	120	96	4.2	0.15
20	100	96.5	4.3	0.45
40	80	96	4.6	9.1
60	60	97	5.3	5.1
80	40	95	5.2	7.3
100	20	97	5.4	17.6
120	0	97.5	6.3	21.5

[a] Polymerization conditions: monomer 20 ml., solvent 120 ml., AHS catalyst 0.2 ml. (0.016 parts/100 parts monomer); polymerization time 19 hr.

[b] Molded samples were conditioned for 5 days at room temperature. Total time for extraction = 72 hr. Solvent changed after 24 and 48 hr.

was 1:5. Improvements in the inherent viscosity and yield of the MEK-insoluble fraction of polymer due to the addition of CS_2 were also observed when vinyl isobutyl ether was polymerized in CS_2–chlorobenzene mixture solvent (Table V). These values of inherent viscosity are significantly lower than the corresponding values obtained for polymers of vinyl *n*-butyl ether in Table IV. This may be partly due to the fact that in preparing solutions of poly(vinyl isobutyl ether) samples in toluene for measurement of viscosities about 30% of the material did not dissolve. Presumably, this

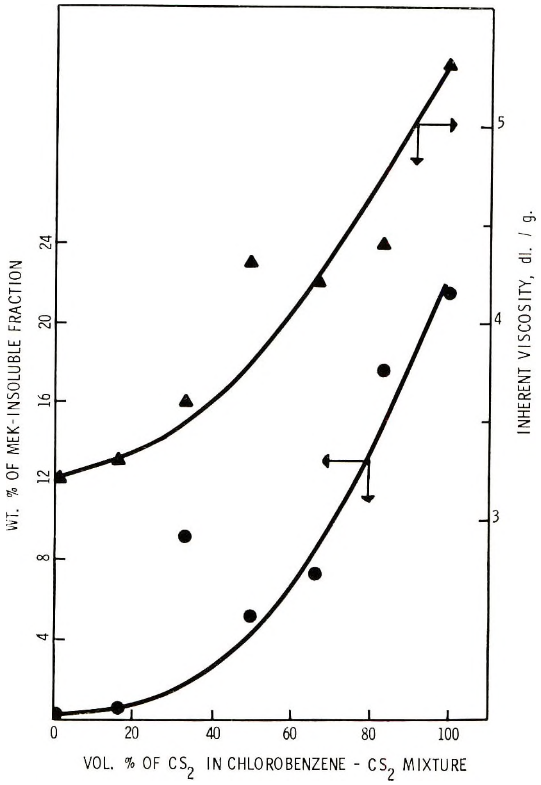

Fig. 2. Effect of the addition of carbon disulfide to chlorobenzene polymerization solvent on (●) the weight per cent of MEK-insoluble fraction and (▲) inherent viscosity of poly(vinyl *n*-butyl ether). Vinyl *n*-butyl ether polymerized at 25°C. with aluminum hydrosulfate hydrate catalyst. Data of Table IV.

insoluble material was highly crystalline and also high in molecular weight. During polymerization, the polymerization bottles contained two phases: a homogeneous phase of viscous solution of polymer and a heterogeneous phase of polymer granules dispersed in the homogeneous phase. On drying, heterogeneity persisted in the solid mass and the powdery polymer was found dispersed in an elastomeric matrix. The powdery polymer remained insoluble when the entire mass was treated with MEK for the deter-

TABLE V
Polymerization of Vinyl Isobutyl Ether at 25°C.[a]

Solvent		Polymer yield, %	Inherent viscosity, dl./g.	Toluene-insoluble, wt.-%	MEK-insoluble, wt.-%[b]
CS_2, ml.	Chlorobenzene, ml.				
0	120	89	1.4	27	41.6
20	100	91	1.4	29	51
40	80	91	1.7	14	45
60	60	96	1.5	31	46
80	40	97	1.7	31	50
100	20	96	2.0	30	50
120	0	97	1.9	27	50

[a] Polymerization conditions: monomer 20 ml., solvent 120 ml., AHS catalyst 0.2 ml. (0.016 parts/100 parts monomer); polymerization time 48 hr.

[b] Suspension in MEK stirred with a magnet for 72 hr. Solvent changed after 30 and 54 hr.

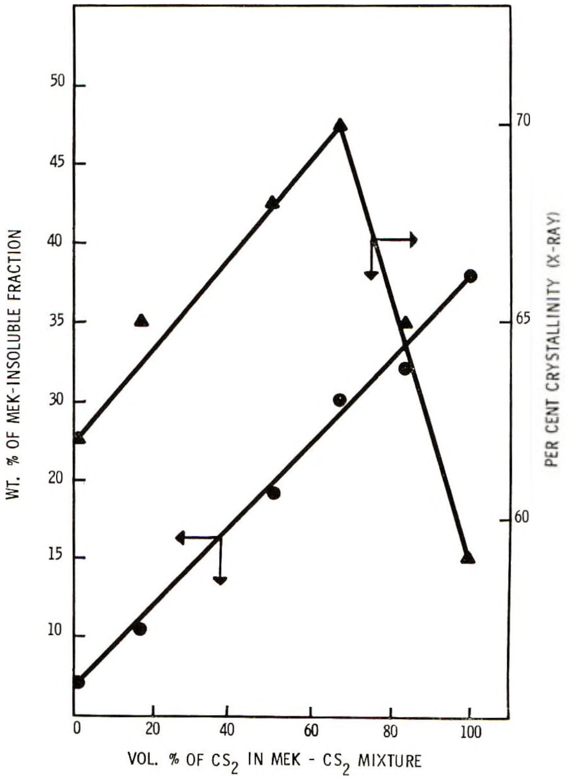

Fig. 3. Effect of the addition of carbon disulfide to methyl ethyl ketone polymerization solvent on (●) the weight per cent of MEK-insoluble fraction and (▲) per cent crystallinity of poly(vinyl isobutyl ether). Vinyl isobutyl ether polymerized at 25°C. with aluminum hydrosulfate hydrate catalyst. Data of Table VI.

TABLE VI
Polymerization of Vinyl Isobutyl Ether at 25°C.[a]

Solvent		Unfractionated polymer			MEK-insoluble		
CS$_2$, ml.	MEK, ml.	Polymer yield, %	Inherent viscosity, dl./g.	Toluene-insoluble, wt.-%	Insoluble, wt.-%[b]	Crystallinity (x-ray), %	Density, g./cc.
0	120	64	0.1	14	12	62	0.936
20	100	67	0.1	17	15.6	65	0.937
40	80	78	—	—	—	—	—
60	60	93	0.1	18	24.2	68	0.943
80	40	92	0.26	17	30.4	70	0.943
100	20	97	0.24	11	32.1	65	0.938
120	0	99	0.72	20	38.1	59	0.933

[a] Polymerization conditions: monomer 20 ml., solvent 120 ml., AHS catalyst 1 ml. (0.125 parts/100 parts monomer); polymerization time 70 hr.

[b] Suspension in MEK stirred with a magnet for 96 hr. Solvent changed after 24, 48, and 72 hr.

mination of the MEK-insoluble fraction. It is noteworthy that poly(vinyl isobutyl ether) prepared in chlorobenzene alone had a sizable yield of the MEK-insoluble fraction.

In Table VI, data are listed for the polymerization of vinyl isobutyl ether in CS_2–MEK mixture solvent. Here again, heterogeneity of the type described above was observed during polymerization. On drying, lumps of powdery polymer were dispersed in a matrix of viscous liquid having a low inherent viscosity value. In preparing solutions for viscosity measurements, about 15–20% of the material, presumably of high crystallinity and high molecular weight, failed to dissolve in toluene. Increasing the concentration of carbon disulfide in the solvent mixture somewhat increased the inherent viscosity values of the soluble portion of the polymer and linearly increased the yield of the MEK-insoluble fraction (Fig. 3). The x-ray diffraction of these MEK-insoluble fractions showed them to be highly crystalline. The values of per cent crystallinity (precision ±3) are listed in Table VI and shown in Figure 3. According to these data, the solvent mixture containing 2:1 volume ratio of carbon disulfide and MEK gives optimum crystallinity. This is in accord with the density values of the MEK-insoluble fractions. The density of 0.943 g./cc. was the highest value obtained by us. This value is surprisingly higher than the value of 0.940 g./cc. calculated[11] by using the elementary cell data of Natta and co-workers.[12] Kern et al.[13] have also reported a density value of 0.946 g./cc. for the benzene-insoluble fraction of poly(vinyl isobutyl ether).

In Table VII, the crystallinity parameters of three polymers of vinyl isobutyl ether described in Tables V and VI are compared with those of two other polymers prepared in pentane with ethylaluminum dichloride catalyst at 25°C. and boron trifluoride etherate catalyst at −78°C. The polymer obtained with ethylaluminum dichloride was amorphous (x-ray diffraction) and was completely soluble in MEK. The polymer prepared with boron trifluoride etherate catalyst was 35% crystalline (x-ray diffraction); its infrared ratio was 0.73. On extraction with MEK, the per cent crystallinity and infrared ratio of the MEK-insoluble portion increased as compared to the corresponding values of the unfractionated polymer. However, this MEK-insoluble fraction was considerably less crystalline than the MEK-insoluble fractions of the three other polymers prepared with the aluminum hydrosulfate hydrate catalyst. These latter fractions were found to be isotactic by comparison of their x-ray diffraction patterns with that reported by Natta and co-workers[12] for the polymer obtained with boron trifluoride etherate catalyst. The polymers prepared with the aluminum hydrosulfate hydrate catalyst in chlorobenzene and CS_2–MEK mixture contained appreciable amounts of benzene-insoluble fractions which melted at 170°C. (polarizing microscope). Vandenberg and co-workers[14,15] have also reported melting temperatures of 165 and 170°C. for crystalline fractions of polymers prepared with stereospecific catalysts.

TABLE VII

Comparison of Crystallinity Parameters of Vinyl Isobutyl Ether Polymers Prepared Under Different Conditions

		MEK-insoluble fraction				
Polymerization conditions	Infrared ratio[a]	Weight-%	Density, g./cc.	Infrared ratio[a]	Crystallinity (x-ray), %	Melting temperature, °C.
AHS catalyst, 25°C., CS_2–MEK (2:1) solvent mixture	b	30.4[c]	0.943	1.32	70	140–170,[d] 163[e]
AHS catalyst, 25°C., chlorobenzene	b	41.6[f]	0.931	—	57	160[d]
AHS catalyst, 25°C., CS_2	0.85	38.1	0.933	1.13	59	158–168,[d] 164[e]
$BF_3 \cdot O(C_2H_5)_2$, −78°C., pentane	0.73	27	0.929	0.86	47	95[e]
$C_2H_5AlCl_2$, 25°C., pentane	0.46	0	—	—	—	—

[a] D_{985}/D_{962} (annealed for 66 hr. at 115°C. in vacuum).

[b] Two discrete phases present in the isolated polymer.

[c] This fraction on further extraction with benzene contained 57% insoluble polymer having the infrared ratio of 1.47 and melting at 170°C.

[d] Observed on the hot stage of a polarizing microscope.

[e] Peak temperature of DTA thermogram.

[f] This fraction on further extraction with benzene contained 82% insoluble polymer having 68% crystallinity (x-ray), infrared ratio of 1.33, and melting at 170°C.

TABLE VIII

Comparison of the Crystallization of Highly Stereoregular Poly(vinyl *n*-Butyl Ether) with Poly(tetramethylene Oxide)

Polymer	Crystallinity (x-ray), %	Infrared ratio[a]	Dilatometric melting point, °C.	Crystallization data: Temperature, °C.	Crystallization data: $t_{1/2}$, min.	Crystallization data: Volume Contraction (100 $\Delta V/V$), %
A[b]	36[c]	1.17	81	60	45	0.70
				56	22	—
B[b]	28	1.11	~70	60	470	0.76
				56	290	0.81
				52	155	0.86
Poly(tetramethylene oxide)[d]	—	—	43	23	700	5.4
				19	66	5.4

[a] D_{968}/D_{978}.

[b] MEK-insoluble fractions from two separate polymers. A solution of vinyl *n*-butyl ether in methyl ethyl ketone (volume ratio 1:3) was polymerized at 0°C. with the aluminum hydrosulfate hydrate catalyst.

[c] This sample had a density of 0.930 g./cc. at 30°C. (lit.[16] $d_4^{25} = 0.93$ g./cc.).

[d] Data of Trick and Ryan.[8]

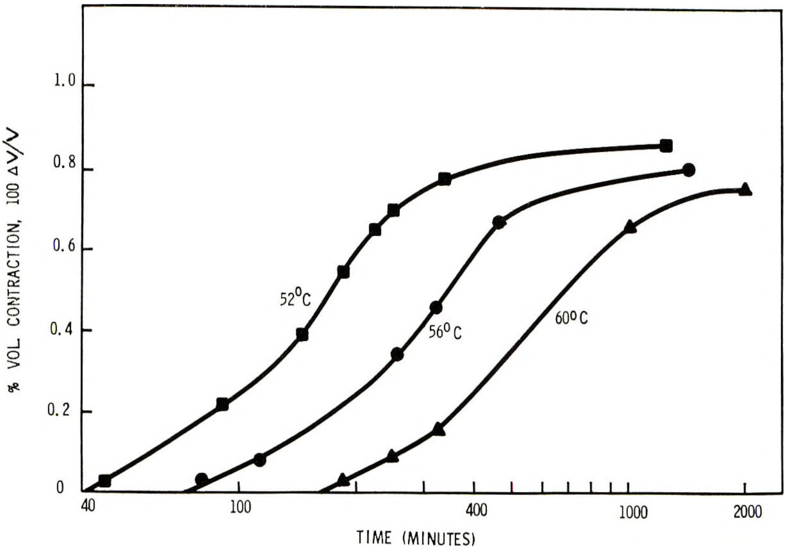

Fig. 4. Volume contraction of a sample of highly stereoregular poly(vinyl *n*-butyl ether) at three crystallization temperatures as a function of time. See also Table VIII.

Poly(vinyl *n*-butyl ether) prepared with the aluminum hydrosulfate hydrate catalyst at 0°C. in CS_2–MEK mixture (volume ratio 2:1) contained about 3% MEK-insoluble fraction. The infrared ratio of this fraction was 1.25. A film prepared from this fraction necked down readily on stretching. When the polymerization was carried out in MEK, the resulting polymer yielded about 5% MEK-insoluble fraction which was also highly crystalline and was isotactic[16] (x-ray diffraction). In Table VIII are given crystallization data on two such fractions, designated A and B. They were isolated from two separate polymers prepared under otherwise similar conditions. Some differences in these fractions may be due to the thoroughness of extraction with MEK. These fractions are significantly more crystalline than the polymers described in Table I. The dilatometric melting temperature of 81°C. recorded for A is significantly higher than the melting temperatures of 64 and 68–69°C. in the literature.[15,2]

Typical crystallization rate curves for polymer B (Table VIII) are shown in Figure 4. The usual sigmoidal shape is observed, but because of the difficulties[17] associated with analyzing curves of this type, particularly for polymers that probably are not pure in microstructure, no attempt has been made to obtain information on the kinetics of crystallization from the shape of the curves. Compared to other polymers, such as poly(tetramethylene oxide),[8] the two experimental polymers show considerably less dependence of rate of crystallization upon temperature. Consequently, at low degrees of supercooling the experimental polymers crystallize much more rapidly than does poly(tetramethylene oxide).

The per cent crystallinity (x-ray) and infrared ratio do not appear to correlate well with the relative volume contractions measured diatometrically but this may be due to the measurements being made at different temperatures. It appears possible that the experimental polymers are nonrandom in composition and their first-order transition behavior would be quite sensitive to the exact experimental conditions employed.

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Résumé

On a déterminé l'effet de la température de polymérisation et des solvants sur la cristallinité des polymères du vinyl isobutyl éther et du vinyl *n*-butyl éther préparés avec le complexe catalytique sulfate 'aluminium–acide sulfurique. On a utilisé principalement les fractions de polymères insolubles dans le méthyléthyl cétone (MEK) pour la caractérisation. La densité, le pourcentage de cristallinité par diffraction aux R.X., les rapports I.R. et la contraction de volume par dilatométrie sur ces fractions de polymères furent utilisées comme critère de cristallinité. Les fractions insolubles dans la MEK du poly(vinyl *n*-butyléther) préparé dans le sulfure de carbone dans le domaine de température de -30 à $+25$°C ne présentent pas de différence significative avec les valeurs des paramètres de cristallinité cités plus haut. Le polymère obtenu à 50°C était moins cristallin que les autres polymères. Les fractions insolubles dans la MEK du poly(vinyl isobutyl éther) préparé à -50°C dans le sulfure de carbone et l'heptane normal comme solvant ne diffèrent guère non plus dans leur degré de cristallinité. Elles furent cependant moins cristallines que les fractions insolubles de la MEK des polymères obtenus à -20°C. Ces résultats indiquent que en augmentant la température de polymérisation, la cristallinité des polymères était soit inchangée ou baissait lentement. Les polymérisations du vinyl n-butyl éther et du vinyl isobutyl éther furent également faites dans un mélange binaire de sulfure de carbone avec l'heptane-*n*, le

chlorobenzène et la MEK. Généralement, en augmentant la concentration du sulfure de carbone on augmentait les viscosités inhérentes des polymères ainsi que le pourcentage en poids de leur fraction insoluble dans la MEK. La fraction insoluble dans la MEK du poly(vinyl isobutyl éther) préparé dans le mélange sulfure de carbone–MEK (rapport de volume 2:1) était isotactique et hautement cristalline. De même, les fractions insolubes dans la MEK de deux polymères du vinyl *n*-butyl éther préparés dans la MEK elle-même étaient également isotactiques et hautement cristallines. Comparées au poly(tetraméthylène oxyde), ces dernières fractions ne montrent aucune dépendance de la vitesse de cristallisation avec la température. En conséquence, à des bas degrés de refroidissement, ils cristallisent plus rapidement que le poly(tétraméthylène oxide).

Zusammenfassung

Der Einfluss von Polymerisationstemperatur und Lösungsmittel auf die Kristallinität der mit dem Aluminiumsulfat-Schwefelsäurekomplex als Katalysator dargestellten Vinylisobutylätherund Vinyl-*n*-butylätherpolymeren wurde untersucht. Hauptsächlich wurden die methyläthylketon-(MEK)-unlöslichen Fraktionen dieser Polymeren zur Charakterisierung verwendet. Als Kristallinitätskriterien dienten Dichte, röntgenographisch bestimmte prozentuelle Kristallinität, Infrarotverhältnis und dilatometrische Volumskontraktion dieser Polymerfraktionen. Die in Schwefelkohlenstoff im Temperaturbereich von −30 bis +25°C hergestellten MEK-unlöslichen Polyvinyl-*n*-butylätherfraktionen zeigten keine signifikanten Unterschiede in den Werten der angeführten Kristallinitätsparameter. Das bei 50°C erhaltene Polymere war weniger kristallin als die übrigen. Die MEK-unlöslichen, bei 0 bei 50°C in Schwefelkohnelstoff und *n*-Heptan als Lösungsmittel hergestellten Polyisobutylvinylätherfraktionen unterschieden sich ebenfalls nur wenig in ihrem Kristallinitätsgrad. Sie waren aber entschieden weniger kristallin als die MEK-unlöslichen Fraktionen der entsprechenden, bei −20°C erhaltenen Polymeren. Diese Ergebnisse zeigen, dass mit steigender Polymerisationstemperatur die Kristallinität der Polymeren entweder ungeändert blieb oder schwach abnahm. Die Polymerisation von Vinyl-*n*-butyläther und Vinylisobutyläther wurde auch in binären Mischungen von Schwefelkohlenstoff mit *n*-Heptan, Chloroform und MEK ausgeführt. Im allgemeinen stieg bei einer Erhöhung der Schwefelkohlenstoffkonzentration die Viskositätszahl der Polymeren und der prozentuelle Anteil ihrer MEK-unlöslichen Fraktion an. Die MEK-unlösliche Fraktion des in einer Schwefelkohlenstoff–MEK-Mischung (Volumsverhältnis 2:1) hergestellten Polyvinylisobutyläthers war isotaktisch und hochkristallin. In gleicher Weise waren die MEK-unlöslichen Fraktionen zweier in MEK selbst hergestellten Vinyl-*n*-butylätherpolymerer ebenfalls isotaktisch und hochkristallin. Im Vergleich zu Polytetramethylenoxyd zeigten letztere Fraktionen eine geringere Temperaturabhängigkeit der Kristallisationsgeschwindigkeit. Infolgedessen kristallisieren sie bei geringer Unterkühlung viel rascher als Polytetramethylenoxyd.

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Linear Polymers of Acrylic Monomers Containing an Acetylenic Moiety

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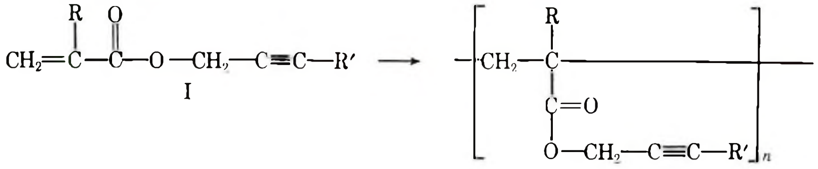
Synopsis

1-Acryloxy-2-butyne and 1-methacryloxy-2-butyne were synthesized and polymerized by means of anionic initiators to soluble linear polymers containing acetylenic bonds in the pendant side chains. In contrast, insoluble, crosslinked polymers were formed when cationic and radical initiators were used. The unpolymerized acetylenic bonds in the resulting linear polymers were shown to be present by infrared spectroscopic methods and by the following post-reactions of these bonds: (*1*) the thermal- and radical-initiated crosslinking of the linear polymers through the acetylenic bonds; (*2*) the post-bromination of the acetylenic bonds; and (*3*) the reaction of decaborane with the acetylenic bonds. The anionic copolymerization of both monomers with a number of selected monomers was performed and the copolymer reactivity ratios for several of the comonomer pairs were determined. Dibromination of the linear polymers affords self-extinguishing polymers with apparently good hydrolytic stability. Decaboronation of the linear polymers yields soluble polymers which do not soften up to 300°C. The linear polymers and copolymers, as well as their partially brominated and partially decaboronated products, may be classified as "self-reactive" polymers which yield thermosetting polymers.

INTRODUCTION

Recently the necessity of preparing a new class of polymers arose. This class of polymers can be represented by the general structure II, where $R =$ H or CH_3 and $R' =$ H, lower alkyl, or substituted alkyl.



$$\underset{\text{I}}{CH_2{=}\overset{R}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_2-C{\equiv}C-R'} \longrightarrow \underset{\text{II}}{\left[-CH_2-\overset{R}{\overset{|}{C}}\left(-C({=}O)-O-CH_2-C{\equiv}C-R'\right)-\right]_n}$$

II

This polymer is a linear polyacrylate containing acetylenic groups in the pendant side chains. Although polyacrylates are well known and are commonly prepared by the polymerization of acrylic esters,[1] there are no known cases of linear polyacrylates which contain an acetylenic bond in the pendant side chain. It can be seen that the repeating unit in polymer II is derivable theoretically from an acrylic monomer of general structure I

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which contains two unsaturated and potentially reactive polymerization sites. However, these sites exist in different structural environments; the acetylenic moiety is isolated from any resonance effects, while the vinyl moiety is flanked by and is in conjugation with the electron-withdrawing carbonyl group. Thus, in order to use such a monomer to obtain the desired polymer, it is necessary to utilize these differences in chemical environment and to choose an initiator which will react preferentially with the vinyl group.

Since both acetylenic and vinyl groups are generally susceptible to attack by either radical or cationic initiators, one would expect the cationic or radical polymerization of I to lead to an insoluble crosslinked product.[2] Anionic initiators also polymerize some multivinyl monomers such as ethylene diacrylate and ethylene dimethacrylate to insoluble, infusible polymers because both unsaturated moieties react with the initiator.[3] Still, marked differences are found in the reaction of an anionic-type initiators on different vinyl moieties.[1,4,5] Though the polymerization of a nonconjugated triple bond by means of anionic initiators has not been reported, it is known that double bonds in conjugation with an electron-withdrawing group are generally susceptible to anionic initiation[6] and that the vinyl moieties in acrylic esters polymerize to high molecular weight polymers if anionic initiators are used.[7-11] Consequently, it appears that the acetylenic group and the vinyl group in I would show a sufficient difference in chemical reactivity toward anionic initiators to permit selective polymerization of the vinyl group.

In order to test this assumption, it was necessary to prepare suitable monomers and subject them to the appropriate polymerization reactions. The monomers chosen for this study were 1-acryloxy-2-butyne (AB) and 1-methacryloxy-2-butyne (MAB). It was believed that these monomers could be conveniently prepared and, since they do not contain a terminal acetylenic group, the possibility is eliminated that the labile $\equiv$C—H bond might be attacked by the anionic initiator, thus complicating the polymerization.

The purpose of this study is to prepare linear polymers and copolymers of AB and MAB by means of appropriate initiators, and this paper describes the synthesis of these two monomers and their polymerization under the influence of various radical, cationic, and anionic initiators. The chemical and spectroscopic methods used in determining the structure of the resulting polymers are given. Also described are the anionic copolymerization of AB and MAB with various vinyl monomers. The monomer reactivity ratios, as determined for several of the common pairs, are discussed.

RESULTS AND DISCUSSION

Polymerization Reactions

It has been postulated that both the radical- and cationic-initiated polymerization of AB and MAB would lead to crosslinked, insoluble polymers since both the vinyl and the acetylenic groups are susceptible to these types of initiators. In order to demonstrate this point, AB and MAB were subjected to both radical and cationic polymerization reactions using benzoyl peroxide and aluminum chloride, respectively, as the initiators. In all cases, insoluble, crosslinked polymers were formed indicating that both potential reaction sites had participated in the polymerization.

On the other hand, it was believed that the anionic polymerization of AB and MAB would lead to linear soluble polymers with pendant acetylenic groups. These linear polymers would be the result of selective polymerization through the vinyl groups of the respective monomers. In order to demonstrate this point, AB and MAB were subjected to anionic polymerization reactions with the use of three different anionic initiators: *n*-butyllithium, sodium naphthalene, and sodium benzalaniline, the latter two representing the class of radical-anion initiators. The polymers formed in each case were soluble in a number of organic solvents and softened to viscous liquids or masses at higher temperatures. That the acetylenic group did not polymerize readily with these same anionic initiators was indicated by the failure of 1-acetoxy-2-butyne to yield polymer products under the same conditions. That the polymerization was occurring substantially through the vinyl groups was indicated by the fact that ethylene diacrylate (EDA) and ethylene dimethacrylate (EDMA) yielded crosslinked polymers.

The formation of soluble polymers from AB and MAB in contrast to the formation of insoluble, crosslinked polymers from EDA and EDMA points to an essential difference between these two classes of monomers. All of these monomers have two unsaturated polymerizable groups; however, both AB and MAB have only one vinyl group activated by an electron-withdrawing structure, whereas EDA and EDMA each has two such activated vinyl groups and, therefore, the latter pair yield crosslinked polymers.

In the case of MAB, a comparison of the infrared spectrum of the monomer with that of the corresponding polymer disclosed the disappearance of the olefinic band at 6.15 μ and the shift of the ester band from 5.83 to 5.77 μ due to the loss of conjugation with the olefinic bond. However, the acetylenic band at 4.50 μ remained unchanged.[12] Similar evidence was obtained in the case of AB. Both the physical character of the polymers formed and the infrared spectra obtained are strong evidence that polymerization occurred almost exclusively through the double bond without appreciably affecting the acetylenic bond.

Since both sodium naphthalene and sodium benzalaniline exist as radical-anions,[13–17] it was believed that the polymerizations initiated by these compounds might exhibit some radical character and would differ from those initiated by *n*-butyllithium. Differences, especially in the solubilities of the resultant polymers, might have been expected, since some radical polymerization of the triple bond and subsequent crosslinking of the polymer could possibly have occurred. If such was the case, the degree of radical

TABLE I
Anionic Polymerization of AB and MAB

Monomer	Solvent[a]	Initiator[b]	Temperature, °C.	Time, min.	Conversion, %	$[\eta]$
AB	THF	*n*-BuLi	−78	90	90.3	0.348
AB	THF	*n*-BuLi	−40	90	74.1	0.219
AB	THF	*n*-BuLi	−20	90	70.7	0.087
AB	TN	SBA	−78	90	93.8	0.504
AB	TN	SN	−78	90	94.1	0.447
AB	TN	SN	−20	90	76.6	0.122
MAB	TN	*n*-BuLi	−78	60	95.4	0.594
MAB	THF	SBA	−78	60	98.6	0.648
MAB	THF	SN	−78	60	90.1	0.615
MAB	THF	SN	−40	60	76.4	0.283
MAB	THF	SN	−20	60	62.2	0.094

[a] THF = tetrahydrofuran; TN = toluene.

[b] *n*-BuLi as a 15.03% solution in hexane; SN = sodium naphthalene, 0.511*N*; SBA = sodium benzalaniline, 0.609*N*.

polymerization was so small as not to appreciably influence the polymer solubility.

Due to the inherent differences between a radical-anionic and a strictly anionic initiator, other differences in the polymerizations certainly are expected to have occurred. However, this investigation, at this time, was not intended to explore this aspect of the anionic polymerizations but only to establish the validity of the concept that a monomer containing an acetylene moiety and a vinyl moiety flanked by an electron-withdrawing group can be predominantly polymerized through the vinyl double bond by means of an anionic initiator.

The results of the polymerizations given in Table I indicate that the polymerization is occurring only through the acrylyl or methacrylyl moiety. The difference in conversions of AB and MAB to polymers is similar to the difference found in the anionic polymerizations of the alkyl methacrylates and acrylates[8,18] and of allyl methacrylate and allyl acrylate.[3] Allyl methacrylate,[3] methyl methacrylate[8,18] and 1-methacryloxy-2-butyne can be polymerized substantially quantitatively at −78°C., whereas the conversions of AB are not quantitative and more sensitive to temperature. In this respect, AB is similar to isopropyl acrylate.[8,18] The conversions reported are based on the sum of the amounts of hexane-insoluble polymer precipitated from the reaction solution by addition to hexane and of the hexane-soluble low molecular weight polymers isolated from the hexane solution on evaporation. At a polymerization temperature of −78°C., the low molecular weight polymers obtained were less than 0.5%, while at −40°C. they averaged about 3% and at −20°C. about 8%. Appreciable amounts of hexane-soluble polymers were found by Wiles and Bywater in their work[19] on the anionic polymerization of methyl methacrylate with *n*-butyllithium; these results were attributed to side reactions involving attack of butyllithium on the carbonyl of the monomer. This attack was more evident the higher the polymerization temperatures.

The molecular weight distribution of poly(methyl methacrylate) prepared by anionic initiators has been shown to be broad,[8,19,20] and undoubtedly is also broad in these acetylenic ester polymers as evidenced by the presence of low molecular weight polymers.

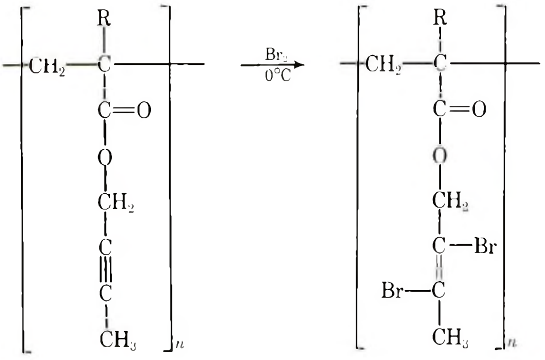
The intrinsic viscosities given in Table I are those of the hexane-insoluble polymers, and some relative values of their molecular weights may be estimated from other viscosity–molecular weight relationships. Meyerhoff[21] derived the relationship $[\eta] = 7.15 \times 10^{-5} M^{0.75}$ for poly(butyl acrylate) in acetone; for poly(methyl methacrylate) in chloroform Chinai[22] used $[\eta] = 3.4 \times 10^{-5} M^{0.83}$, and Glusker developed the equation $[\eta] = 5.2 \times 10^{-5} M^{0.76}$ in benzene. From these equations, it is estimated that of the polymers in Table I, the highest molecular weight for the MAB polymers prepared is of the order of about 175,000 and the lowest molecular weight is of the order of about 15,000; and for AB, the highest molecular weight is about 140,000 and the lowest about 13,500.

Kinetic measurements to determine the effects of monomer and initiator concentrations on molecular weight rate, of polymerization, and microstructure of the polymers are in progress.

The linear polymers of AB and MAB are relatively stable in air and gave no evidence of crosslinking when exposed in air for one week. This is in contrast to the linear polymers of allyl acrylate and allyl methacrylate, which on exposure to air crosslink unless they contain inhibitors.[3]

Post-Reactions of the Linear Polymers

Several of the linear polymers prepared from AB and MAB were subjected to various post-reactions of the pendant acetylenic group. The primary purpose of these post-reactions was to lend support to the proposed linear structures by characterizing the products formed from these reactions. Among the reactions employed were the bromination of the acetylenic group, the radical and thermal crosslinking of the polymers through the acetylenic group, and the reaction of the acetylenic group with decaborane to form linear polymers with "carborane" structures in the pendant side chains.



$$\left[-CH_2-C(R)(C(=O)-O-CH_2-C\equiv C-CH_3)-\right]_n \xrightarrow[0°C]{Br_2} \left[-CH_2-C(R)(C(=O)-O-CH_2-C(Br)=C(Br)-CH_3)-\right]_n \qquad (1)$$

The linear polymers obtained by the anionic polymerization of AB and MAB were subjected to bromination with bromine as the brominating agent [eq. (1), R = H, CH_3].

To assure reaction to the dibromo derivatives, the reaction was allowed to continue for at least 7 days at 0°C. in the dark. No evidence of tetrabromination was found under these conditions. The amount of bromine found in the brominated polymers is in good agreement with the expected values. Short bromination times yielded polymers which contained unreacted residual acetylenic groups still available for other reactions. Larger excesses of bromine and higher temperatures introduced more bromine than required for the dibromo derivative. A comparison of the infrared spectrum of the initial polymers and those of the brominated product disclosed the disappearance of the acetylenic peak at 4.50 μ and the subsequent appearance of a peak at 6.03 μ attributable to a carbon–carbon double bond.[12] When ignited in the flame of a bunsen burner and withdrawn from the flame, all of the post-brominated polymers were found to be self-extinguishing. Thus, post-bromination offers a convenient method for preparing self-extinguishing polymers and avoids the problems associated with polymerizing the equivalent monomer, $CH_2{=}C(R)COOCH_2CBr{=}CBrCH_3$. When a film of the polymer was ignited after boiling in water for 48 hr., no loss of the self-extinguishing property was apparent.

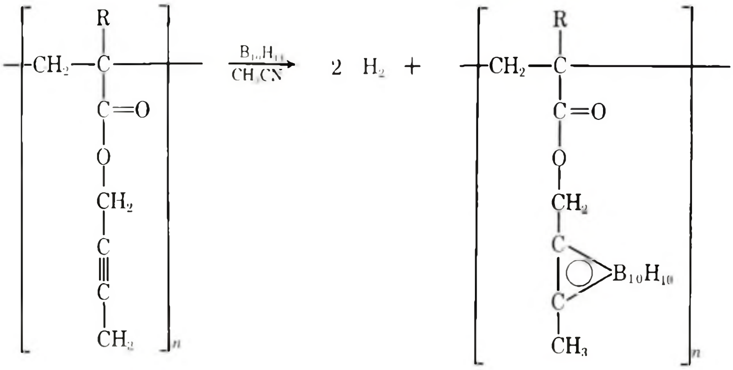
Further confirmation of the linear structure of these polymers and of the reactivity of the free acetylenic bond was obtained by both the thermal- and radical-induced crosslinking of the polymers through the triple bonds. The major portion of the radical-induced post-reactions consisted of casting films of the polymer from solutions containing benzoyl peroxide and then heating the solvent-free films at 60–80°C. to produce insoluble, crosslinked films. The thermal-induced post-reactions were conducted in a similar manner except that benzoyl peroxide was not included in the polymer solutions and heating was carried out at temperatures in excess of 100°C. Crosslinked films were also obtained in these reactions. The infrared spectra of the crosslinked polymers showed a decrease in the band at 4.50 μ indicating the disappearance of some of the $—C{\equiv}C—$ functions.

Similarly, when thermally or radically crosslinked, the partially brominated MAB polymers yielded insoluble, infusible, crosslinked polymers which were self-extinguishing when lighted and withdrawn from the flame source.

The thermal- and radical-induced crosslinking of acrylonitrile–AB and acrylonitrile–MAB copolymers were also facile. Strips of the films of the acrylonitrile copolymers containing 60 wt.-% or more of acrylonitrile could be cold-drawn before crosslinking. The drawn films could be crosslinked similarly to the undrawn films.

The AB–methyl acrylate, the AB–methyl methacrylate, the MAB–methyl acrylate and the MAB–methyl methacrylate copolymers as well as the MMA–MAB and the styrene–MAB block copolymers also could be crosslinked easily. Solvent extraction for 6 hr. of the crosslinked block copolymers with refluxing acetone, followed by drying of the extracted films to constant weight in a vacuum oven showed losses of approximately 2.1% for the MMA and 3.4% for the styrene block copolymers, respectively.

The linear polymers from the anionic polymerizations of AB ([η] = 0.219) and MAB ([η] = 0.283) were both subjected to reactions with decaborane with acetonitrile being used as the catalyst [eq. (2), R = H, CH_3]. Elemental analyses indicated that the reaction had been substantially complete. The infrared spectrum indicated the loss of the acetylenic peak at 4.50 μ and the presence of the B–H peak at 3.92 μ.[12,23]



(2)

The decaboronated polymers failed to melt when heated to 300°C. on a Fisher-Johns melting apparatus and gave no external evidence of decomposition at this temperature. This appears to be in accord with previous findings[24] that the 1,2-dicarbaclovodecaborane-(12) nucleus exhibits a high degree of oxidative, hydrolytic, and thermal stability. That the decaboronated polymers were not crosslinked was shown by their solubility in benzene, toluene, and acetone.

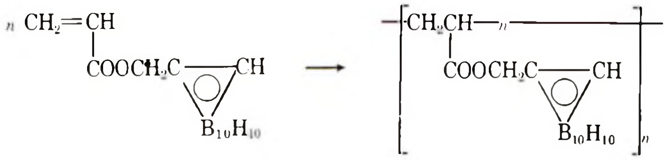
The partially decaboronated MAB polymer ([η] = 0.615) in which about 37.5% of the acetylenic groups were converted to the dicarbaclovodecaborane structure also failed to melt at 300°C., apparently contributing a high degree of thermal stability to the polymer even though about two-thirds of the original polymer had not reacted. The infrared spectrum of the product exhibited a reduced peak at 4.50 μ attributable to the unreacted acetylenic bonds.[12] The presence of these acetylenic bonds was further confirmed by the radical-induced crosslinking of the product. Substantially quantitative reaction with decaborane was also obtained in the case of the 20.2:79.8 mole-% MAB–methyl acrylate copolymer ([η] = 0.246) and of the 32.4:67.6 mole-% of the AB–methyl methacrylate copolymer ([η] = 0.276).

Several attempts were made to increase the amount of decaboronation of the same MAB ([η] = 0.615) polymer by using decaborane in appreciable excess and by extending the reaction time to 140 hr. without noticeable improvement. The high conversions of the other AB and MAB polymers may be attributable to differences in molecular weights since the AB polymer ([η] = 0.219) and the MAB polymer ([η] = 0.283) reacted with decaborane substantially quantitatively, whereas the maximum conversion obtained with the MAB polymer ([η] = 0.615) was about 40% even when very high dilution techniques were used. Incomplete decaboronation was also experienced in the MAB polymers of [η] = 0.594 and 0.648.

Though this would indicate the acetylenic sites were less available for reaction in the high molecular weight polymers even though high dilution techniques were used, many post-reactions of polymers are known to be less than quantitative because of other factors[25] such as tacticity, etc.; none of these factors was examined at this time.

The decaboronated polymers burned slowly with a greenish smoky flame when ignited, but burned rapidly with an intense greenish-white flame when mixed in powdered form with ammonium perchlorate; hence, they may be of interest as propellants. The boronated polymers may also be of interest in the field of radiation because of the variation[26] with neutron energy of the cross section (Barns) of boron for the (n,α) reaction.

Decaboronation of AB and MAB polymers and copolymers offers a convenient method of preparing soluble, tractable, boron-containing polymers in relatively high yields. Radical polymerization of the corresponding acrylic monomer,[27,28] yielded a mixture of polymers insoluble in benzene, toluene, and acetone, and a soluble fraction from which only brittle films could be cast. Most probably these results are due to radical transfer reactions that occur during polymerization with the abundant hydrogen atoms in the carborane structure.



(3)

Copolymerizations

The effect of the pendant acetylenic groups on the copolymerization reactivities of AB and MAB was not known; and hence, they were subjected to anionic copolymerizations with styrene, acrylonitrile, methyl acrylate, and methyl methacrylate. Further, if linear, soluble copolymers

TABLE II
Copolymerization of AB and Methyl Acrylate (MA)

AB (M_1), mole-%	MA (M_2), mole-%	Conversion, %	Br, %	C, %[a]	AB in copolymer, mole-%	MA in copolymer, mole-%[a]
13.8	86.2	8.6	43.12	62.21	40.4	59.6
18.7	81.3	9.2	44.74	62.66	44.9	55.1
50.0	50.0	6.3	48.11	63.98	59.3	40.7
61.5	38.5	7.9	51.10	64.97	68.5	31.5

[a] Before bromination.

TABLE III
Copolymerization of AB and Methyl Methacrylate (MMA)

AB, (M_1), mole-%	MMA (M_2), mole-%	Conversion, %	Br, %	C, %[a]	AB in copolymer, mole-%	MMA in copolymer, mole-%
95.5	4.5	8.9	55.71	66.58	98.2	1.8
57.7	42.3	7.4	53.10	66.32	80.5	19.5
50.8	49.2	4.1	51.83	65.09	75.5	24.5
20.0	80.0	5.3	42.39	64.46	43.5	56.5
11.8	88.2	6.8	36.42	62.95	32.4	67.6

[a] Before bromination.

TABLE IV
Copolymerization of MAB and Methyl Acrylate (MA)

MAB, (M_1), mole-%	MA (M_2), mole-%	Conversion, %	Br, %	C, %[a]	MAB in copolymer, mole-%	MA in copolymer, mole-%
94.5	5.5	5.1	52.10	68.18	87.20	12.8
82.4	17.6	4.6	48.67	66.78	70.20	29.8
50.0	50.0	6.2	42.88	63.96	46.40	53.6
15.0	85.0	9.0	28.85	59.82	20.20	79.8
10.0	90.0	6.8	24.79	58.83	14.65	85.35
5.8	94.2	7.8	16.81	57.62	9.05	90.95

[a] Before bromination.

TABLE V
Copolymerization of MAB and Methyl Methacrylate (MMA)

MAB (M_1), mole-%	MMA (M_2), mole-%	Conversion, %	Br, %	C, %[a]	MAB in copolymer, mole-%	MMA in copolymer, mole-%
69.1	30.9	7.1	46.46	66.54	59.1	40.9
61.3	38.7	5.0	40.83	64.28	44.2	55.8
50.0	50.0	4.6	43.16	65.40	49.8	51.2
17.9	82.1	9.8	23.96	62.26	16.9	83.1
15.6	84.4	6.8	31.88	63.18	26.8	73.2

[a] Before bromination.

TABLE VI
Copolymerization of AB and Acrylonitrile (AN)

AB (M_1), mole-%	AN (M_2), mole-%	N, %[a]	AB in copolymer, mole-%	AN in copolymer, mole-%
76.7	23.3	5.45	61.6	38.4
50.0	50.0	10.17	39.4	60.6
45.4	54.6	11.38	35.5	64.5
5.7	94.3	23.42	5.1	94.9

[a] Corrected value.

were obtained, this would demonstrate that the acetylenic monomers polymerized similarly to alkyl acrylates and that the acetylenic group did not participate to any appreciable degree in the polymerization. The copolymerization data are summarized in Tables II–IX. Intersect plots of r_1 versus r_2 were made according to the method of Lewis and Mayo.[29] The monomer reactivity ratios were determined from these plots and are given in Table X. The data of Tables II–V for the acrylate and methacrylate copolymers with AB and MAB show that the resulting copolymers contained appreciable amounts of the comonomers.

In both the AB–MA and AB–MMA copolymerizations, the reactivity ratios indicated that the acetylenic monomers were incorporated preferentially into the copolymers. This would seem to indicate that the acetylenic group enhanced the reactivities of these monomers when compared

TABLE VII
Copolymerization of MAB and Acrylonitrile (AN)

MAB (M_1), mole-%	AN (M_2), mole-%	N, %[a]	MAB in copolymer, mole-%	AN in copolymer, mole-%
71.4	28.6	8.76	44.6	55.4
65.5	34.5	10.21	38.8	61.2
50.0	50.0	11.59	34.4	65.6
16.5	83.5	18.36	14.5	85.5
9.6	90.4	20.59	8.8	91.2

[a] Corrected value.

TABLE VIII
Copolymerization of AB and Styrene (S)

AB (M_1), mole-%	S (M_2), mole-%	Conversion, %	C, %	H, %	AB in copolymer, mole-%
82.2	17.8	5.5	68.10	6.41	~100
80.5	19.5	6.7	67.63	6.48	~100
47.9	52.1	8.1	67.40	6.54	~100
32.9	67.1	4.2	67.51	6.59	~100
24.0	76.0	7.3	67.38	6.62	~100

TABLE IX
Copolymerization of MAB and Styrene (S)

MAB (M_1), mole-%	S (M_2), mole-%	C, %	H, %	MAB in copolymer, mole-%	S in copolymer, mole-%
65.8	34.2	74.34	6.74	72.6	27.4
54.8	45.2	76.11	6.84	64.6	35.4
38.8	62.0	79.71	7.16	51.5	48.5
9.3	90.7	86.13	7.35	18.3	81.7

TABLE X
Monomer Reactivity Ratios of AB or MAB (r_1) with Respective Vinyl Monomer (r_2)

Comonomers			
M_1	M_2	r_1	r_2
AB	Methyl acrylate	0.60 ± 0.14	0.09 ± 0.015
AB	Methyl methacrylate	2.78 ± 0.45	0.26 ± 0.05
MAB	Methyl acrylate	0.35 ± 0.05	0.56 ± 0.08
MAB	Methyl methacrylate	0.35 ± 0.06	0.34 ± 0.04
AB	Acrylonitrile	0.30 ± 0.07	1.14 ± 0.25
MAB	Acrylonitrile	0.04 ± 0.01	1.10 ± 0.20
AB	Styrene	—	—
MAB	Styrene	1.20 ± 0.16	0.40 ± 0.05

to the acrylic and methacrylic esters of saturated alcohols. Such an effect was not apparent, however, in the MAB–MA and the MAB–MMA copolymerizations. In the MAB–MA the reactivity ratios indicated that MA was incorporated slightly preferentially, whereas the reactivity coefficients of MAB and MMA were almost identical.

In order to gain additional insight into the reactivities of AB and MAB as they may be influenced by the pendant acetylenic group, both of these monomers were subjected to anionic copolymerization reactions with acrylonitrile and styrene. The data for the AB–acrylonitrile and the MAB–acrylonitrile copolymerizations are given in Tables VI and VII, respectively, in which the compositions were determined from their corrected nitrogen content. In order to account for low nitrogen values due to any incomplete combustion of the copolymers, it was necessary to establish a correction factor.

Three separate samples of polyacrylonitrile were prepared by means of sodium naphthalene initiator and their nitrogen contents determined. The average of the ratios of nitrogen calculated to nitrogen found was 1.15, and this factor was used in calculating the copolymer compositions.

In both the AB–acrylonitrile and MAB–acrylonitrile copolymerizations, acrylonitrile is preferentially incorporated into the copolymer. These values are comparable with those obtained in other anionic copolymerizations involving acrylonitrile and acrylate or methacrylate esters[30,31] and do not indicate any enhanced reactivity of AB and MAB.

The AB–styrene copolymerization yielded the expected results and the data are shown in Table VIII. The copolymers consisted almost exclusively of AB, despite the fact that large excesses of styrene were used in some of the copolymerizations. These results compare well with the sodium naphthalene- and sodium benzalaniline-initiated copolymerizations of styrene and methyl methacrylate. Other investigators have found that the resulting copolymers contained almost exclusively methyl methacrylate.[14,32]

However, the results of the MAB–styrene copolymerizations, shown in Table IX, were somewhat surprising, in that an appreciable amount of styrene appeared in the copolymers. Since this copolymerization can also be compared to the anionic copolymerization of styrene and methyl methacrylate, results similar to the AB–styrene and the MMA–styrene copolymerizations had been expected. To assure the correctness of these findings and to verify data in the literature,[14,32] styrene and methyl methacrylate were copolymerized with sodium naphthalene and sodium benzalaniline as initiators. The resulting copolymers analyzed very closely as poly(methyl methacrylate). Since these copolymerizations did not deviate appreciably from those[14,32] reported in the literature, it appears that the copolymerization data obtained for the MAB–styrene system in this investigation are valid. On the basis of the preceding results, it is not possible at this time to explain the anomalies encountered in the MAB–styrene copolymerizations. However, it is known that in the ketyl-initiated copolymerizations[14,33] of styrene and methyl methacrylate that copolymer compositions are obtained which contain styrene, but in this specific case, the anomaly has been attributed to the metal component of the initiator system, in that the lower the electropositivity of the metal, the higher the degree of incorporation of styrene in the copolymer.

EXPERIMENTAL

Materials

Reagent-grade tetrahydrofuran was refluxed over potassium hydroxide pellets for several hours,[34] distilled, then redistilled off of lithium aluminum hydride into glass receivers which had been flamed prior to use and which contained calcium hydride. Then it was saturated with helium.

Toluene, A.R. grade, previously treated with sulfuric acid, sodium hydroxide and dried, was refluxed over calcium hydride, distilled, and saturated with helium, and stored over calcium hydride.

Commercial styrene, acrylonitrile, methyl acrylate, and methyl methacrylate were refluxed over and distilled off calcium hydride. They were stored over calcium hydride in glass receivers which had been flamed, then saturated with helium, and were generally used within 24 hr.

Initiators

n-Butyllithium, as a 15.03% hexane solution, was obtained from the Foote Mineral Company. Only relatively fresh bottles were used. Sodium naphthalene was prepared by the method of Scott et al.,[35] stored under helium in tightly sealed vials and in the absence of light, and used as soon as possible after preparation. Sodium benzalaniline was prepared by the method of Ringsdorf,[14] stored in a similar manner, and also used as soon as possible after preparation.

The initiator concentrations were determined after hydrolysis for sodium hydroxide or lithium hydroxide.

Monomers

AB. Into a 300-ml., round-bottomed, three-necked flask fitted with a Dean-Stark trap, nitrogen inlet and outlet, a reflux condenser, and a thermometer were placed 2-butyn-1-ol (35.0 g., 0.5 mole) as prepared by the method of Schulte and Reiss,[36] glacial acrylic acid (36.0 g., 0.5 mole) and *p*-toluenesulfonic acid (2.0 g.). *p-tert*-Butyl catechol (0.2 g.) was added as an inhibitor. These chemicals were dissolved in 60 ml. of dry benzene, placed under a slight nitrogen pressure and refluxed for 36 hr. until about 8 ml. of water was collected in the Dean-Stark trap. The reaction mixture was then neutralized with a saturated aqueous sodium carbonate solution and dried over anhydrous sodium carbonate. After the sodium carbonate was filtered off, the benzene was stripped off under reduced pressure and distillation yielded AB (46.0 g.) in a 74% yield. Vapor-phase chromatographic analysis (UCON 50-HB-200, 190°C., flow rate 50 ml./min.) indicated the presence of approximately 0.5% impurities. It was then refluxed over and fractionally distilled from calcium hydride, collected over calcium hydride in a sealed flask which had been flamed prior to use and then saturated with helium. Vapor-phase chromatographic analysis showed less than 0.1% impurity.

An infrared spectrum was recorded on the sample having the following physical constants: $n_D^{20} = 1.4605$; g.p. 49°C./4 mm.

ANAL. Calc'd. for $C_7H_8O_2$: C, 67.74%; H, 6.45%. Found: C, 68.01%; H, 6.65%.

MAB. This monomer was obtained in 60% yield by a method similar to that described above. The following physical constants were recorded: $n_D^{20} = 1.4680$; b.p. 59°C./4 mm. and 110°C./65 mm. It was also stored over calcium hydride and saturated with helium.

ANAL. Calc'd. for $C_8H_{10}O_2$: C, 69.56%; H, 7.25%. Found: C, 69.75%; H, 7.39%.

1-Acryloxymethylcarborane. It was prepared in a 28.1% yield from propargyl acrylate and decaborane by a previously published method.[23,24]

Polymerizations

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

In polymerization of 1-acryloxymethylcarborane, a solution of 3.0 g. of 1-acryloxymethylcarborane and 0.06 g. of benzoyl peroxide in 50 ml. of dry purified toluene was refluxed for 24 hr. while a slow stream of dry deoxygenated nitrogen was bubbled through the solution while it was agitated by means of a magnetic stirrer. An insoluble product formed which was removed by filtration, extracted with heptane and dried; yield 0.915 g. (30.5%). The filtrate was then poured into 150 ml. of rapidly stirred heptane, the precipitated polymer isolated by filtration, extracted with heptane, and dried; yield 1.43 g. (47.6%). A film of the soluble polymer cast from toluene solution was brittle and friable. Neither the insoluble nor the soluble polymer showed signs of melting when heated to 300°C. on a Fisher-Johns melting point apparatus.

Anionic Homopolymerization. A typical anionic polymerization using a modification of previously described procedures[7,8] is given as follows. The reaction vessel attached to a high vacuum manifold consisted of a five-necked glass flask fitted with an externally driven magnetic stirrer, a sidearm to which was attached a 25-ml. round-bottomed flask, a stopcock crowned with a serum cap, and a helium inlet tube.

The solution of monomer, 10.0 g. in 30 ml. of tetrahydrofuran or toluene, stored over calcium hydride in the round-bottomed flask for at least 8 hr., was degassed twice at 3×10^{-6} mm. Hg and distilled into the reaction vessel, which had been previously flamed in a stream of helium. The system was then pressured with helium to slightly above atmospheric pressure. The reaction vessel was then cooled to −78°C. with a Dry Ice–acetone bath. Then, the initiator, at a 1:400 mole ratio to monomer, was injected volumetrically by means of a hypodermic syringe through the serum cap. The polymerization was terminated by injecting methanol.

The polymer was isolated by filtration after pouring the polymer solution slowly into vigorously stirred hexane. The isolated polymer was washed with hexane, and dried to constant weight in a vacuum oven at 25°C. It was soluble in chloroform. Low molecular weight polymers soluble in the precipitant were isolated by evaporation of the solvent at 15 mm. Hg pressure. The infrared spectra of the monomers and the polymers were recorded and the intrinsic viscosities of representative samples of linear poly-1-acryloxy-2-butyne and poly-1-methacryloxy-2-butyne.

In addition to AB and MAB, 1-acetoxy-2-butyne, ethylene diacrylate, and ethylene dimethacrylate which had been purified and saturated with helium, were subjected to polymerization conditions at −40°C. as 30% solutions in THF with butyllithium and sodium naphthalene as initiators. Polymerization did not occur in the case of 1-acetoxy-3-butyne, whereas infusible, insoluble polymers were obtained from ethylene diacrylate and ethylene dimethacrylate.

Copolymerizations. The general procedure described above for the anionic polymerization was used to prepare the copolymers. The copolymerizations were carried out in a 50% solution of tetrahydrofuran at −40°C. with sodium benzalaniline as the initiator. The initiator to comonomer mole ratio was 1:300. Copolymerizations were generally carried out to about 10% conversion, the time required varying from a few minutes to 1 hr., depending on the composition of the monomer mixture. Generally, the copolymerizations were allowed to proceed until a noticeable increase in viscosity occurred before they were terminated. If the conversion was found to exceed 10%, the polymerization was repeated and terminated at a shorter reaction time. The polymers were isolated by precipitation in a nonsolvent, redissolved, and reprecipitated three times in a suitable solvent–nonsolvent system; the polymer solutions were filtered through sintered disks before reprecipitation. For the purification of the acrylonitrile copolymers, dimethylformamide was used as the solvent and methanol as the precipitant. In the remainder of the copolymerizations, benzene was used as the solvent and heptane as the precipitant. The isolated copolymers were dried to constant weight in a vacuum oven at 25°C.

Block Copolymers. The apparatus described above for the homopolymerization was used for preparing the block copolymers. The procedure described by Baer[37] of first polymerizing one monomer at −78°C. with sodium naphthalene and then adding the second monomer was followed. The monomer systems used were styrene–MAB and methyl methacrylate–MAB. Termination, isolation, purification, and drying of the polymer were as described above.

The styrene–AMA block copolymer was prepared by first polymerizing 16.64 g. (0.16 mole) styrene as a 25% solution in tetrahydrofuran for 4 hr., at a sodium naphthalene–styrene mole ratio of 1:100; conversion, 99.6%; $[\eta]$ in toluene = 0.287. Then 5.32 g. (0.04 mole) of MAB was injected through the serum cap by means of a hypodermic needle, the reaction allowed to proceed for 1 hr., terminated with methyl alcohol, and the polymer isolated. Then it was treated with refluxing acetonitrile to extract the homopolymer of MAB and dried; yield 21.5 g. (98%); $[\eta] = 0.402$.

The MMA–MAB block copolymer was similarly prepared by first polymerizing 15.0 g. (0.15 mole) MMA with a sodium naphthalene–MMA mole ratio of 1:300 (conversion 99.2%, $[\eta] = 0.503$), followed by the addition of 6.9 g. (0.05 mole) AMA; yield, 21.1 g. (96.2%); $[\eta] = 0.597$.

Viscosity Determinations

The intrinsic viscosities of the acrylic and methacrylic homopolymers prepared in this investigation were determined in benzene solution by use of semimicro Ubbelohde dilution viscometers. The bath temperature was maintained at 20.00 ± 0.02°C., and flow times were determined for at least three solution concentrations.

Post-Reactions

Bromination of the Linear Polymer of MAB. Into a 125-ml. glass-stoppered flask was placed 0.680 g. of polymer dissolved in 3 ml. of carbon tetrachloride. To this was added twice the theoretical amount of bromine (0.781 g.). The reaction mixture was mixed well, stoppered, and placed in the refrigerator at 0°C. for 1 week. At that time the soluble polymer was precipitated in 15 ml. of heptane, isolated by filtration, and redissolved and reprecipitated twice, with carbon tetrachloride as a solvent and heptane as a precipitant.

ANAL. Calc'd. for $C_8H_{10}O_2Br_2$: C, 32.20%; H, 3.42%; Br, 53.61%. Found: C, 32.76%; H, 3.63%; Br, 51.75%.

Bromination of Linear Polymer of AB. The same procedure as used for the MAB polymer was used for the AB polymer.

ANAL. Calc'd. for $C_7H_8O_2Br_2$: C, 29.57%; H, 2.82%; Br, 56.33%. Found: C, 29.49%; H, 2.88%; Br, 55.87%.

Excess Bromination of Linear Polymer of AB. Approximately 0.330 g. of the polymer was dissolved in 2 ml. of chloroform and approximately a threefold excess of bromine (1.170 g.) was added in the cold and absence of light. This reaction mixture was kept at 20°C. for one month, at which time the brominated polymer was precipitated by means of 10 ml. of heptane and isolated by filtration. The polymer was then dissolved in 3 ml. of chloroform and reprecipitated in 15 ml. of heptane. After isolation by filtration, it was dried in a vacuum oven at room temperature.

ANAL. Calc'd. for $C_7H_8O_2Br_2$: C, 29.57%; H, 2.82%; Br, 56.33%. Calc'd. for $C_7H_8O_2Br_4$: C, 18.93%; H, 1.80%; Br, 72.04%. Found: C, 22.06%; H, 2.62%; Br, 63.30%.

Partial Bromination of Linear MAB Polymer. The procedure described above for the MAB polymer was used, except that the reaction time was 12 hr.

ANAL. Calc'd. for 80.19:19.81 mole-% MAB: (MAB-Br_2): C, 54.01%; H, 5.52%; Br, 22.32%. Found: C, 53.62%; H, 5.49%; Br, 21.79%.

Bromination of Methyl Methacrylate–MAB Copolymers. The same procedure used above for the MAB polymer was used also in this case, and the copolymer compositions calculated from the halogen analyses.

Bromination of Styrene–MAB Block Copolymer (80:20 mole-% Feed. The procedure described above was used.

ANAL. Calc'd. for 82.0:18.0 mole-% styrene: (MAB-Br_2): C, 64.75%; H, 5.72%; Br, 24.48%. Found: C, 64.03%; H, 5.89%; Br, 23.34%.

Bromination of Methyl Methacrylate–MAB Block Copolymer (75:25 mole-% Feed). The procedure described above was used.

ANAL. Calc'd. for 78.1:21.9 mole-% MMA:(MAB-Br_2): C, 47.63%; H, 5.96%; Br, 23.86%. Found: C, 47.76%; H, 6.13%; Br, 24.49%.

Crosslinking of Polymers

Thermal Crosslinking. Approximately 1.0 g. of each of the linear polymers of AB and MAB was dissolved in 5 ml. of benzene. Films were cast on glass plates, the solvent allowed to evaporate at room temperature for 24 hr., and then placed in an oven at 110°C. for 6 hr. The resulting films were found to be insoluble in acetone, benzene, chloroform, carbon disulfide, and dimethylformamide.

Approximately 0.25 g. of the linear polymers of AMA and AA were heated at 250°C. for 5 min. on a Fisher-Johns melting point apparatus. The polymers softened and formed films which were found to be insoluble in chloroform and dimethylformamide.

Radical Crosslinking. Approximately 0.25 g. of each of the linear polymers of AB, MAB, and the partially brominated polymer of MAB (21.79% Br) was dissolved in 5 ml. of dry benzene and 0.002 g. of benzoyl peroxide was added. After being thoroughly mixed, the solution was poured onto glass plates, the solvent allowed to evaporate at room temperature for 24 hr. then placed in a 100°C. oven for 3 hr. The resulting films were found to be insoluble in acetone, benzene, chloroform, and dimethylformamide.

Similar solutions containing benzoyl peroxide were prepared in benzene of the MMA–MAB copolymers and of the block copolymers of MMA–MAB and styrene–MAB. The films cast from them and treated at 100°C. for 2 hr. were found also to be insoluble and infusible. Similar solutions containing benzoyl peroxide were prepared in dimethylformamide of the acrylonitrile–AB (69.5:30.5 mole-%) and of acrylonitrile–MAB (89.5:10.5 mole-%). The heated, cast-films were insoluble in dimethylformamide.

Decaboronation of the Linear Polymers

Reaction of Decaborane with the Linear Polymer of AB. Into a 500-ml., round-bottomed, three-necked flask fitted with a reflux condenser, a mechanical stirrer, and a nitrogen inlet was placed 4.0 g. of polymer ($[\eta] = 0.219$) and the decaborane (5.0 g., 0.041 mole) so that the decaborane would be present in about 50% excess of the theoretical amount. To this was added acetonitrile (1.8 g., 0.0436 mole) dissolved in 200 ml. of dry toluene along with 0.1 g. of di-*tert*-butyl-*p*-cresol as an inhibitor. This reaction mixture was refluxed for 84 hr., at which time the clear solution was poured into 500 ml. of rapidly stirred heptane. The precipitated polymer was isolated by filtration and extracted with heptane to remove any unreacted decaborane. The product was insoluble in carbon tetrachloride, chloroform, and carbon disulfide, but was soluble in toluene and acetone from which clear, tough films could be cast. The polymer was purified twice by dissolving it in benzene, filtering the solution, and precipitating it in heptane. The isolated polymer was then dried in the vacuum oven at room temperature. The pale yellow product when heated on a Fisher-Johns melting point apparatus showed no appreciable softening up to 300°C.

ANAL. Calc'd. for $C_7H_{18}B_{10}O_2$: C, 34.41%; H, 7.43%. Found: C, 33.49%; H, 7.68%.

Reaction of Decaborane with Linear Polymer of MAB. Into a 250-ml. round-bottomed, three-necked flask fitted with a mechanical stirrer, a reflux condenser, and a nitrogen inlet was placed 2.62 g. of the polymer ($[\eta] = 0.283$) and decaborane (3.66 g., 0.030 mole) so that the decaborane would be in about 50% excess of the theoretical amount. To this was added acetonitrile (1.22 g., 0.030 mole) dissolved in 200 ml. of dry toluene with a little di-*tert*-butyl-*p*-cresol as an inhibitor. The reaction mixture was refluxed for 140 hr. at which time it was poured into 250 ml. of vigorously stirred heptane and the polymer precipitated and separated by filtration. The product was insoluble in chloroform, carbon tetrachloride, and carbon disulfide, but was soluble in acetone and toluene from which clear films could be cast. After the polymer was dissolved in 50 ml. of toluene and reprecipitated by 150 ml. of heptane, it was isolated by filtration and dried in a vacuum oven at room temperature. The cream-colored product showed no softening up to 300°C. when heated on a Fisher-Johns melting point apparatus.

ANAL. Calc'd. for $C_8H_{20}B_{10}O_2$: C, 37.50%; H, 7.81%. Found: C, 36.73%; H, 7.97%.

Partial Decaboronation of Linear Polymer of MAB. The procedure given above for the reaction of decaborane with the MAB polymer was repeated, except that the $[\eta]$ of the polymer was 0.615 and the reaction mixture was refluxed for 36 hr., and the cream-colored reaction product isolated and purified as above. The decaboronated polymer showed no softening up to 300°C. when heated on a Fisher-Johns melting point apparatus. The infrared spectrum exhibited a peak at 4.65 μ attributable to the unreacted acetylenic bonds.

ANAL. Calc'd.: C, 37.50%; H, 7.81%. Found (for 37.5% conversion): C, 58.31%; H, 6.17%.

Approximately 0.20 g. of the polymer was dissolved in 10 ml. of toluene and 0.002 g. of benzoyl peroxide was added. After being thoroughly mixed, the solution was poured onto a glass plate, the solvent allowed to evaporate at room temperature 36 hr., then the plate was placed in a 120°C. oven for 8 hr. The resulting film was found to be insoluble in toluene and acetone.

Reaction of Decaborane with MAB–Methyl Acrylate Copolymer. The procedure given above was repeated with a 73.1:26.9 mole-% MAB–methyl acrylate copolymer, $[\eta] = 0.214$.

ANAL. Calc'd.: C, 39.65%; H, 7.70%. Found: C, 40.07%; H, 7.44%.

Elemental analyses were performed by Midwest Microlab, Indianapolis, Indiana and by the Schwartzkopf Microanalytical Laboratory, Woodside, New York.

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Résumé

Le 1-acryloxy-2-butyne et le 1-méthacryloxy-2-butyne ont été synthétisés et polymérisés, au moyen d'initiateurs anioniques pour donner des polymères linéaires solubles. Contenant des liens acétylèniques dans les chaînes latérales. Au contraire, on a obtenu des polymères insolubles ramifiés en utilisant des initiateurs cationiques et radicalaires. On a prouvé la présence des liens acétylèniques non polymérisés dans les polymères linéaires, par spectroscopie infra-rouge et par toute une série de réactions caractéristiques de ces liaisons. (*1*) les polymères linéaires se pontent au moyen des liens acétylèniques par initiation thermique et radicalaire, (*2*) les liens acétylèniques ont été bromés, (*3*) on a effectué la réaction du décaborane avec les liens acétylèniques. On a réalisé la copolymérisation anionique des deux monomères avec un nombre de monomères choisis et on a déterminé les rapports des réactivités pour chacune des paires de comonomères envisagées. La débromation des polymères linéaires donnent naissance à des polymères auto-extincteurs à avec une stabilité hydrolytique apparemment bonne. La décaboronation des polymères linéaires donne de polymères solubles qui ne se ramollissent pas jusque 300°C. Les polymères et copolymères linéaires aussi bien que leurs produits de bromuration partielle et de décaboronation partielle, peuvent être classifiés comme des polymères autoréactifs qui douent des polymères thermostables.

Zusammenfassung

1-Acryloxy-2-butin und 1-Methacryloxy-2-butin wurden synthetisiert und mit anionischen Initiatoren zu löslichen linearen Polymeren mit Acetylenbindungen in der Seitenkette polymersiert. Im Gegensatz dazu wurden bei Verwendung kationischer und radikalischer Initiatoren unlösliche, vernetzte Polymere gebildet. Die unpolymeren wurden infrarotspektroskopisch und durch folgende Reaktionen dieser Bindungen Nachgewiesen: (*1*) die thermisch und radikalisch gestartete Vernetzung der linearen Polymeren durch die Acetylenbindungen; (*2*) die Nachbromierung der Acetylenbindungen; und (*3*) die Reaktion von Dekaboran mit den Acetylenbindungen. Die anionische Copolymerisation beider Monomerer mit einer Zahl ausgewählter Monomerer wurde durchgeführt und die Copolymer-Reaktivitätsverhältnisse einiger Comonomerpaare wurde bestimmt. Dibromierung der linearen Polymeren liefert selbstlöslichende Polymere mit offenbar guter hydrolytischer Stabilität. Dekaboranierung der linearen Polymeren führt zu löslichen, bis hinauf zu 300°C nicht erweichenden Polymeren. Die linearen Polymeren und Copolymeren sowie ihre partiell bromierten und dekaboranierten Produkte können als "selbst-rektive" Polymere bezeichnet werden, welche wärmehärtende Polymere liefern.

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Determination of Kinetic Parameters for Pyrolysis of Cellulose and Cellulose Treated with Ammonium Phosphate by Differential Thermal Analysis and Thermal Gravimetric Analysis

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Synopsis

Activation energy E, pre-exponential factor k_0, and reaction order n for the pyrolysis of α-cellulose and cellulose modified with dihydrogen ammonium phosphate were determined by means of TGA and DTA. The results obtained are $E = 53.5$ kcal./mole, $k_0 = 10^{18.8}$ min.$^{-1}$, $n = 1$ for α-cellulose and $E = 32$ kcal./mole, $k_0 = 10^{12}$ min.$^{-1}$, $n = 1$ for modified cellulose. A new theory of DTA was also developed. This theory, in which it is concluded that the peak value of DTA curve coincides with the maximum rate of reaction, may be used not only for the present work but is generally applicable to DTA studies. Detailed procedures of experiment and theory are described.

INTRODUCTION

Pyrolysis of cellulose treated with flame retardants such as ammonium phosphate, borax and boric acid, and tetrakishydroxymethyl-phosphonium chloride has been studied by many investigators. Browne[1] has given an extensive survey covering the significant developments in this field, and Broido and Kilzer[2] suggested an interesting mechanism on the pyrolysis of pure cellulose. Also Tang et al.[3,4] studied the effect of some inorganic salts on the pyrolysis of cellulose by means of differential thermal analysis (DTA) and thermal gravimetric analysis (TGA), and determined the overall activation energy and the reaction heat for pyrolysis of treated cellulose. The results obtained by Tang and his collaborators are of use for a quantitative evaluation of the effect of flame retardants and an estimation of the retarding process. However in this work,[3,4] it seems that no attention was paid to three components contained within the treated cellulose; untreated cellulose, free chemical, and modified cellulose.

Then in our study, each component of cellulose treated with dihydrogen ammonium phosphate was confirmed on DTA curve and the kinetic parameters, i.e., reaction order, activation energy, and pre-exponential factor, of the pyrolysis reaction were determined in the light of DTA and TGA theory including a new method developed by authors.

THEORETICAL BASIS

Determination of Kinetic Parameters by TGA

In general, rate of weight loss for pyrolysis of cellulosic materials may be expressed by

$$dw/dt = k_0 \exp\{-E/RT\} \cdot (w_0 - w)^n \tag{1}$$

where w is the weight decomposed by time t, w_0 is the decomposable weight of reactant, E is the activation energy of the pyrolysis reaction, n is the order of reaction, T the temperature of material, k_0 the pre-exponential factor of the Arrhenius equation, and R the gas constant.

If it is assumed that the temperature is increased with a linear relation $T = T_0 + \phi t$ (T_0 is the initial temperature and ϕ is the constant rate of temperature rise), the maximum rate is given by

$$(dw/dt)_m = [(w_0 - w_m)/n](E\phi/RT_m^2) \tag{2}$$

where the subscript m denotes the state of maximum rate.

Thus if reaction order n is known, we can calculate directly the activation energy by inserting $(dw/dt)_m$, $(w_0 - w_m)$, T_m, and ϕ obtained from the TGA curve into eq. (2).

On the one hand, combining eqs. (1) and (2) and rearranging, we get

$$\ln\left(\frac{\phi}{T_m^2}\right) = \ln [(nR/E)k_0(w_0 - w_m)^{n-1}] - (E/RT_m) \tag{3}$$

and hence eq. (3) can also be used for the determination of activation energy. This method presented originally by Kissinger[5] is superior to the above method in the respect that activation energy E is determined without a knowledge of reaction order n and initial weight w_0, but it seems to us that plotting of ln (ϕ/Tm^2) and $1/T_m$ is not necessarily exact enough because of the small variation of T_m at the usual rate of temperature rise in DTA. In this study, eq. (2) was used for determination of activation energy of materials made from a single component, and eq. (3) was used

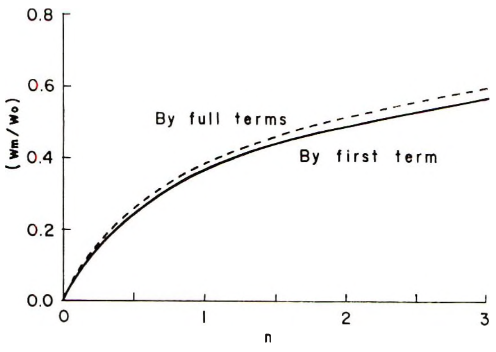

Fig. 1. Relation between n and (w_m/w_0).

for the multicomponent materials for which it is difficult to obtain $(dw/dt)_m$ and w_0 from TGA curves. In either case, the pre-exponential factor in the Arrhenius equation k_0 can be calculated from eqs. (1) and (2).

Now in order to determine the reaction order n, we integrate eq. (1) as

$$\int_0^w \frac{dw}{(w_0 - w)^n} = \frac{k_0}{\phi} \int_0^T \exp\left\{-\frac{E}{RT}\right\} dT \tag{4}$$

The right-hand side of eq. (4) has no exact integral, but by making a partial integration and using eq. (3), we obtain

$$\ln\left(1 - \frac{w_m}{w_0}\right) = \frac{1}{n-1} \ln\left\{1 - \frac{n-1}{n}\left[1 - 2\left(\frac{RT_m}{E}\right) + 6\left(\frac{RT_m}{E}\right)^2 - \ldots\right]\right\} \qquad n \neq 1 \tag{5}$$

$$\ln\left(1 - \frac{w_m}{w_0}\right) = -\left[1 - 2\left(\frac{RT_m}{E}\right) + 6\left(\frac{RT_m}{E}\right)^2 - \ldots\right] \qquad n = 1 \tag{6}$$

As is well known, though the asymptotic series contained in eqs. (5) and (6) does not converge sharply except for $RT_m/E \ll 1$, it is easy to show that the error committed in truncating the series after the second term is very small for the range of E and T_m in this study. Then eqs. (5) and (6) can be approximated reasonably as by eqs. (7) and (8), respectively.

$$[1 - (w_m/w_0)]^{1-n} \simeq n \qquad n \neq 1 \tag{7}$$

$$[1 - (w_m/w_0)] \simeq e^{-1} \qquad n = 1 \tag{8}$$

In Figure 1, the relations between n and (w_m/w_0) calculated by both kinds of equations, namely eqs. (5) and (6) and (7) and (8), are given for the case of $E = 50$ kcal./mole and $T_m = 500°$K.

Thus the reaction order can be estimated by above procedure if only the ratio of the weight of reactant at maximum rate to the initial one will be known from TGA curves. Similar methods are also presented by Coats and Redfern[6] and Horowitz and Metzger.[7]

Freeman and Carroll[8] have given the following equation involving the use of the difference of reaction rate at two different temperatures:

$$\Delta \ln (dw/dt) = -(E/R)(\Delta T^{-1}) + n\Delta \ln w \tag{9}$$

According to eq. (9), E and n may be obtained from plots of $\Delta(\ln dw/dt)$ and $\Delta(1/T)$ and of $\Delta(\ln dw/dt)$ and $\Delta(\ln w)$, respectively. Although this procedure, named the difference method by Farmer[9] and applied to the pyrolysis of cellulosic materials by Tang and Neill,[4] is convenient in that E and n may be determined simultaneously and easily, we have hesitation in using this equation for fear that the errors contained in experimental data will be amplified by the procedures.

New Theory of DTA

Theories of differential thermal analysis have been given by Kissinger,[5] Borchardt and Daniels,[10] Reed et al.[11] and others. These theories are useful for analysis of the DTA curve in many cases, but we believe there is a different conclusion on the relation between the DTA peak and the maximum rate of reaction. To elucidate this problem, we tried to develop a new mathematical treatment of DTA.

Fundamental Equations. If it is assumed that the vessel is regarded as an infinite cylinder, that the effects of temperature and material consumption upon the thermal diffusivity are negligible, and that the final weight loss of reactant is not so large compared to the total sample weight (this assumption may be attained by mixing some standard material into the reactant), the fundamental equations for DTA for standard cell and sample cell are expressed by eqs. (10) and (11), respectively.

$$\frac{\partial T_1}{\partial t} = \kappa_1\left(\frac{\partial^2 T_1}{\partial r^2} + \frac{1}{r}\frac{\partial T_1}{\partial r}\right) \tag{10}$$

$$\frac{\partial T_2}{\partial t} = \kappa_2\left(\frac{\partial^2 T_2}{\partial r^2} + \frac{1}{r}\frac{\partial T_2}{\partial r}\right) + \frac{Q}{C_2 w_2}\left(\frac{dw}{dt}\right) \tag{11}$$

where T_1 and T_2 are the temperatures in the standard cell and sample cell, respectively, r the radial coordinate, t the time, κ_1 and κ_2 the thermal diffusivities of materials packed in both cells, Q the heat of reaction, c_2 and w_2 the specific heat and the weight of sample material, respectively, and (dw/dt) is the pyrolysis rate of reactant.

Initial and boundary conditions are given commonly by

$$(T)_{t=0} = T_0 \tag{12}$$

$$(T)_{r=a} = T_0 + \phi t \tag{13}$$

where a is the radius having the same value in both cells. Boundary condition (13) is obtained by neglecting the thermal effect of small gaps existing between packed materials and cell walls, but it seems this assumption is reasonable for usual DTA.

Heat Source Term. As will be mentioned later, the reaction order of cellulosic materials is equal to unity. Hence, provided that a reaction is first order and the temperature rise in sample cell is small in comparison with the heating temperature, eq. (1) may be rewritten as

$$(dw/dt) \simeq k_0 \exp\{-E/RT_0\}\cdot\exp\{(E\phi/RT_0^2)\cdot t\}(w_0 - w) \tag{14}$$

Integrating eq. (14) and making the substitution $A = k_0 \exp\{-E/RT_0\}$ and $\alpha = E\phi/RT_0^2$, we get

$$(w_0 - w) \simeq w_0 \exp(A/\alpha)\cdot\exp\{-(A/\alpha)\exp(\alpha t)\} \tag{15}$$

The second exponential term of right-hand side in eq. (15) may also be expressed as

$$\exp\left\{-(A/\alpha)\cdot\exp(\alpha t)\right\} = 1 - (A/\alpha)e^{\alpha t} + {}^1/_2(A/\alpha)^2e^{2\alpha t}$$

$$- {}^1/_6(A/\alpha)^3e^{3\alpha t} + \ldots \; = \sum_{l=0}^{\infty} \frac{(-1)^l}{l!}\cdot(A/\alpha)^l \exp\left\{l\alpha t\right\} \qquad (16)$$

Therefore, by combining eqs. (14)–(16), we get the following equation as the heat source term of equation (11).

$$\frac{Q}{C_2w_2}\cdot\frac{dw}{dt} = \delta\sum_{l=0}^{\infty}\frac{(-1)^l}{l!}\cdot\left(\frac{A}{\alpha}\right)^l\cdot\exp\left\{(l+1)\alpha t\right\} \qquad (17)$$

where $\delta = (Qw_0/C_2w_2)A\ \exp\left\{A/\alpha\right\}$.

Temperature Profile in Sample Cell. From eq. (17), the fundamental equation for sample cell becomes

$$\frac{\partial T_2}{\partial t} = \kappa_2\left(\frac{\partial^2 T_2}{\partial r^2} + \frac{1}{r}\frac{\partial T_2}{\partial r}\right) + \delta\sum_{l=0}^{\infty}\frac{(-1)^l}{l!}\left(\frac{A}{\alpha}\right)^l \exp\left\{(l+1)\alpha t\right\} \qquad (18)$$

To solve this equation under the conditions (12) and (13), we first make the transformation

$$T_2 = \Theta(r,t) + \frac{\delta}{\alpha}\sum_{l=0}^{\infty}\frac{(-1)^l}{l!}\cdot\frac{1}{l+1}\cdot\left(\frac{A}{\alpha}\right)^l\cdot e^{(l+1)\alpha t} \qquad (19)$$

then we obtain

$$\frac{\partial\Theta}{\partial t} = \kappa_2\left(\frac{\partial^2\Theta}{ar^2} + \frac{1}{r}\frac{\partial\Theta}{\partial r}\right) \qquad (20)$$

$$(\Theta)_{t=0} = T_0 - \frac{\delta}{\alpha}\sum_{l=0}^{\infty}\frac{(-1)^l}{(l+1)\cdot l!}\cdot\left(\frac{A}{\alpha}\right)^l \qquad (21)$$

$$(\Theta)_{r=a} = T_0 + \phi t - \frac{\delta}{\alpha}\sum_{l=0}^{\infty}\frac{(-1)^l}{(l+1)\cdot l!}\cdot\left(\frac{A}{\alpha}\right)^l e^{(l+1)\alpha t} \qquad (22)$$

Again by making the transformation

$$\Theta = \theta_2 + T_0 - \frac{\delta}{\alpha}\sum_{l=0}^{\infty}\frac{(-1)^l}{(l+1)\cdot l!}\cdot\left(\frac{A}{\alpha}\right)^l \qquad (23)$$

eqs. (20), (21), and (22) simplify to:

$$\frac{\partial\theta_2}{\partial t} = \kappa_2\left(\frac{\partial^2\theta_2}{\partial r^2} + \frac{1}{r}\frac{\partial\theta_2}{\partial r}\right) \qquad (24)$$

$$(\theta_2)_{t=0} = 0 \qquad (25)$$

$$(\theta_2)_{r=a} = \phi t - \frac{\delta}{\alpha}\sum_{l=0}^{\infty}\frac{(-1)^l}{(l+1)\cdot l!}\cdot\left(\frac{A}{\alpha}\right)^l\cdot e^{(l+1)\alpha t} + \frac{\delta}{\alpha}\sum_{l=0}^{\infty}\frac{(-1)^l}{(l+1)\cdot l!}\cdot\left(\frac{A}{\alpha}\right)^l$$

$$(26)$$

Since these equations can be solved by Stokes' method[12] by using the approximation

$$1/[(1+l)\alpha + (\kappa_2\lambda s^2/a^2)] \simeq (a^2/\kappa_2\lambda s^2)[1-(1+l)(a^2\alpha/\kappa_2\lambda s^2)] \tag{27}$$

and the known relations on Bessel function,

$$\sum_{s=1}^{\infty} \frac{J_0(\lambda s\cdot r/a)}{\lambda s J_1(\lambda s)} = \frac{1}{2} \tag{28}$$

$$\sum_{s=1}^{\infty} \frac{J_0(\lambda s\cdot r/a)}{\lambda s^3 J_1(\lambda s)} = \frac{a^2-r^2}{8a^2} \tag{29}$$

we get the solution:

$$\begin{aligned}\theta_2 = \frac{2\kappa_2}{a^2}\sum_{s=1}^{\infty}\frac{\lambda s\cdot J_0(\lambda s\cdot r/a)}{J_1(\lambda s)}&\left\{\frac{a^4\phi}{\kappa_2{}^2\lambda s^4}\left[\frac{\kappa_2\lambda s^2}{a^2}\cdot t-1+e^{-(\kappa_2\lambda s^2/a^2)t}\right]\right.\\ &-\frac{\delta}{\alpha}\sum_{l=0}^{\infty}\frac{(-1)^l}{(l+1)\cdot l!}\cdot\left(\frac{A}{\alpha}\right)^l-\frac{a^2}{\kappa_2\lambda s^2}\left[1-(l+1)\frac{a^2\alpha}{\kappa_2\lambda s^2}\right]\\ &\times\left[e^{(l+1)\alpha t}-e^{-(\kappa_2\lambda s^2/a^2)t}\right]+\frac{\delta}{\alpha}\sum_{l=0}^{\infty}\frac{(-1)^l}{(l+1)\cdot l!}\cdot\left(\frac{A}{\alpha}\right)^l\cdot\frac{a^2}{\kappa_2\lambda s^2}\\ &\left.\times\left[1-e^{-(\kappa_2\lambda s^2/a^2)t}\right]\right\}\end{aligned}\tag{30}$$

Turning the variable θ_2 to T_2, eq. (30) becomes

$$\begin{aligned}T_2 = T_0+\phi t-\frac{\phi}{4\kappa_2}(a^2-r^2)&+\frac{2a^2\phi}{\kappa_2}\sum_{s=1}^{\infty}\frac{J_0(\lambda s\cdot r/a)}{\lambda s^3 J_1(\lambda s)}\cdot\exp\left\{-\frac{\kappa_2\lambda s^2}{a^2}\cdot t\right\}\\ &+\frac{\delta}{4\kappa_2}(a^2-r^2)\cdot\exp(\alpha t)\cdot\exp\left\{-\frac{A}{\alpha}\exp(\alpha t)\right\}\\ &-\frac{2a^2\delta}{\kappa_2}\exp\left\{-\frac{A}{\alpha}\right\}\sum_{s=1}^{\infty}\frac{J_0(\lambda s\cdot r/a)}{\lambda s^3\cdot J_1(\lambda s)}\exp\left\{-\frac{\kappa_2\lambda s^2}{a^2}\cdot t\right\}\end{aligned}\tag{31}$$

where J_0 and J_1 denote the Bessel functions of zero order and first order, respectively, and λs denotes the sth root of the equation $J_0(r) = 0$.

Temperature Profile in Standard Cell. The solution of eq. (10) under the conditions (12) and (13) is easily obtained through the transformation $\theta_1 = T_1 - T_0$ by the same method. The result is given by

$$T_1 = T_0+\phi t-\frac{\phi}{4\kappa_1}(a^2-r^2)+\frac{2a^2\phi}{\kappa_1}\sum_{s=1}^{\infty}\frac{J_0(\lambda s\cdot r/a)}{\lambda s^3 J_1(\lambda s)}\cdot\exp\left\{-\frac{\kappa_1\lambda s^2}{a^2}\cdot t\right\}\tag{32}$$

Temperature Difference (DTA Curve). The DTA curve corresponds to the difference of temperatures in the sample cell and the standard cell. Therefore by obtaining the difference of eqs. (31) and (32), we can obtain the equation;

$$
\begin{aligned}
\Delta T &= T_2 - T_1 \\
&= \frac{\phi}{4}(a^2 - r^2)\left(\frac{1}{\kappa_1} - \frac{1}{k_2}\right) - 2a^2\phi \sum_{s=1}^{\infty} \frac{J_0(\lambda s \cdot r/a)}{\lambda s^3 J_1(\lambda s)} \\
&\quad \cdot\left[\frac{1}{\kappa_1}\exp\left\{-\frac{\kappa_2\lambda s^2}{a^2}t\right\} - \frac{1}{\kappa^2}\exp\left\{-\frac{\kappa_1\lambda s^2}{a^2}t\right\}\right] \\
&\quad + \frac{\delta}{4\kappa_2}(a^2 - r^2)\cdot\exp\{\alpha t\}\exp\left\{-\frac{A}{\alpha}\exp(\alpha t)\right\} \\
&\quad - \frac{2a^2\delta}{\kappa_2}\exp\left(-\frac{A}{\alpha}\right)\cdot\sum_{s=1}^{\infty}\frac{J_0(\lambda s\cdot r/a)}{\lambda s^3 J_1(\lambda s)}\exp\left\{-\frac{\kappa_2\lambda s^2}{a^2}t\right\}
\end{aligned}
\tag{33}
$$

Equation (33) is a mathematical expression of the DTA curve by this theory, and the first and second terms of the right-hand side of the equation show the deviation from the base line in the DTA curve. If the thermal diffusivities of sample material and standard material are equal or nearly equal ($\kappa_1 \simeq \kappa_2$), these terms will be eliminated and no deviation of the base line will appear. In practice, since the thermal diffusivities of the sample material and the standard material used in our experiment do not differ widely as a result of some standard material being added to the reactant in sample cell, the above assumption is fairly satisfied. Moreover it may be found from a numerical calculation that the last term of eq. (33) is negligibly small in comparison to the third term.

Thus eq. (33) can be written as

$$\Delta T \simeq \frac{\delta}{4\kappa_2}(a^2 - r^2)\cdot\exp(\alpha t)\cdot\exp\left\{-\frac{A}{\alpha}\exp(\alpha t)\right\} \tag{34}$$

$$= \frac{a^2 - r^2}{4\kappa_2}\cdot\frac{Q}{C_2 w_2}\cdot\left(\frac{dw}{dt}\right) \tag{35}$$

In transformation from eq. (34) to (35), the following relation obtained from eqs. (14) and (15) was used.

$$\frac{dw}{dt} = w_0 A \exp\left\{\frac{A}{\alpha}\right\}\cdot\exp\{\alpha t\}\cdot\exp\left\{-\frac{A}{\alpha}\exp(\alpha t)\right\} \tag{36}$$

Also differentiating eq. (35), we get

$$\frac{d}{dt}(\Delta T) \simeq \frac{(a^2 - r^2)}{4\kappa_2}\cdot\frac{Q}{C_2 w_2}\cdot\left(\frac{d^2 w}{dt^2}\right) \tag{37}$$

Equation (35) means that the temperature difference in DTA is indirectly proportional to the reaction rate, and eq. (37) shows that the peak of DTA curve just coincides with the inflection point of the TGA curve, namely the maximum rate. The later conclusion is in agreement with Kissinger's[5] and seems to be useful for determining the inflection point of a complicated TGA curve.

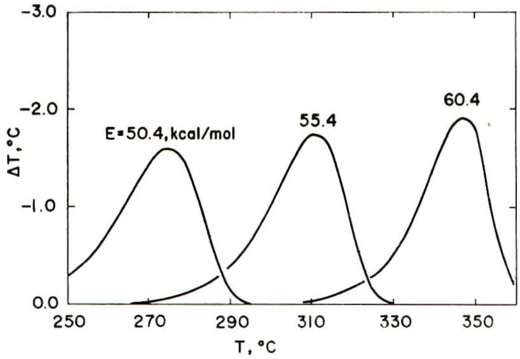

Fig. 2. Effect of E on DTA curve. $\phi = 0.95$°C./min.; $T_0 = 215$°C.; $k_0 = 10^{19}$ min.$^{-1}$; other conditions as in Fig. 7.

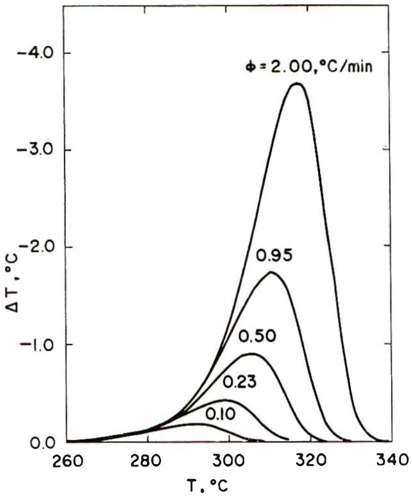

Fig. 3. Effect of ϕ on DTA curve. $E = 55.4$ kcal./mole; $T_0 = 215$°C.; $k_0 = 10^{19}$ min.$^{-1}$; other conditions as in Fig. 7.

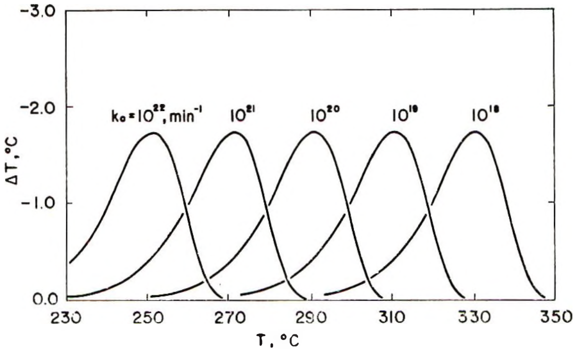

Fig. 4. Effect of k_0 on DTA curve. $E = 55.4$ kcal./mole; $T_0 = 215$°C.; $\phi = 0.95$°C./min.; other conditions as in Fig. 7.

In Figures 2, 3, and 4, the dependence of the activation energy E, heating rate ϕ, and pre-exponential factor k_0 on the temperature rise–heating temperature diagram calculated from eq. (34) are illustrated for a representative case of α-cellulose.

EXPERIMENTAL

Apparatus

An apparatus with which the weight loss and the temperature change of reactant (cellulose) in sample cell can be measured simultaneously was used for our experiment. It is based on a recording balance with differential transformer for measuring weight loss together with a recording thermocouple (0.3 mm. diameter, a.c.) having partly a very fine wire (50 μ) which permits measurement of the temperature in the sample material without affecting weight change. The quartz cell is shown in Figure 5 and it was put in a beryllium oxide block for homogeneous heating. Samples of 100–200 mg. were used at all times, and aluminum oxide (α-Al_2O_3) was selected for the most cases as the reference material in the standard cell. For the ambient atmosphere, vacuum conditions (under 10^{-1} Torr) were used in many experiments, and air or flowing nitrogen was in some. Nitrogen gas was supplied to the cells through a reducer and a flow meter from a cylinder.

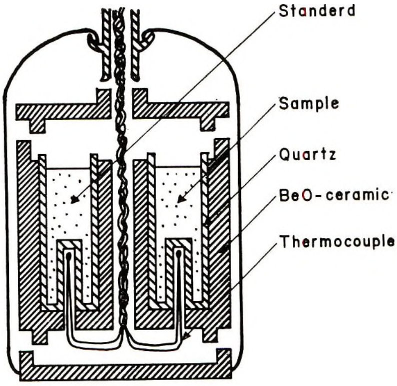

Fig. 5. Schematic diagram of sample holder.

Preparation of Samples

The cellulose used was a quantitative ash-free filter paper.

The cellulose was treated by soaking it in an aqueous solution of dihydrogen ammonium phosphate (cp. grade) of 10^{-3}–1.6M concentration, and after which each treated cellulose sample was powdered and packed into the sample cell with aluminum oxide.

RESULTS AND DISCUSSIONS

DTA and TGA Curves of α-Cellulose

Typical DTA and TGA curves of α-cellulose in vacuum, nitrogen, and air are shown in Figure 6. DTA curves of pure cellulose in vacuum show a deep endotherm corresponding to rapid weight loss of TGA curve in the range of 300–350°C., and the result in nitrogen is similar to that *in vacuo*. In air, however, the endotherm is masked by a following sharp exotherm which seems to be due to an oxidation of pyrolysis products and hence the curve becomes more or less complicated compared with those obtained in nonoxidative atmospheres. Therefore, the thermograms in vacuum which may be considered as a curve indicating a fundamental pyrolysis reaction, were used for the present analysis.

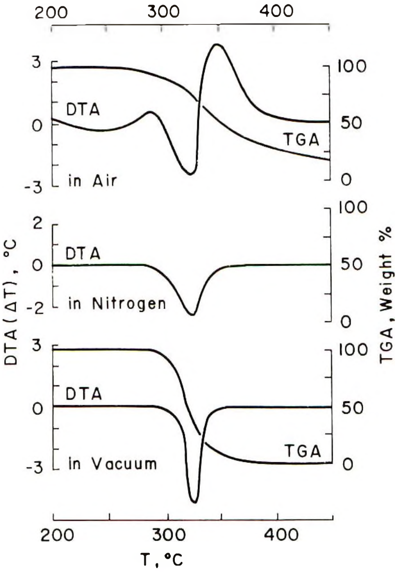

Fig. 6. DTA and TGA curves of α-cellulose in air, in nitrogen, and *in vacuo*. ϕ = 5°C./min.

Reaction Order, Activation Energy, and Pre-exponential Factor of α-Cellulose

By applying the ratio (w_m/w_0) obtained from eight different TGA curves having different heating rate ϕ to eqs. (7) and (8), reaction order n for pyrolysis of cellulose was calculated. The results are given in Table I. The average of n is nearly equal to unity, so the pyrolysis reaction is found to be first-order as is accepted generally.[4,13] Next by using w_m, $(dw/dt)_m$, and T_m obtained from the same TGA curves and eq. (2), E for various ϕ was determined. The results are also given in Table I. The activation energy is undoubtedly independent of heating rate and the average is 53.5 kcal./

TABLE I
Kinetic Parameters for Pyrolysis of α-Cellulose

No.	ϕ, °C./min.	w_m/w_0 $\times 10^{-2}$	T_m, °K.	$t_m \times 10^{-2}$, min.	n	E, kcal./mole	log k_0, min.$^{-1}$
1	2.40	38.5	598	6.92	0.97	43.4	18.8
2	2.20	39.4	603	6.51	1.02	54.3	18.9
3	0.95	40.1	587	3.03	1.05	54.2	19.1
4	0.94	39.4	588	2.84	1.02	53.3	18.7
5	0.50	40.9	579	1.64	1.10	52.5	18.4
6	0.47	40.0	578	1.58	1.05	55.2	19.5
7	0.24	39.4	568	0.83	1.02	53.0	18.7
8	0.23	42.4	570	0.78	1.20	52.2	18.3
				Average	1.054	53.51	18.80
				Standard deviation	0.065	0.94	0.36

mole with a standard deviation of 0.94 kcal./mole. This value is in good agreement with the result obtained by Madorsky et al.[14] for cotton cellulose rather than other results in the literature.[15] Moreover, the average pre-exponential factor of Arrhenius equation calculated from eq. (1) was $10^{18.8}$ min.$^{-1}$, as shown in Table I.

Comparison Between Theory and Experiment for the DTA Curve of α-Cellulose

An experimental DTA curve for pyrolysis of cellulose was compared to the calculated one based on the new theory. The experiment was carried out at the condition of $\phi = 0.25$°C./min. and $w_0 = 76$ mg. ($w_2 = 198$ mg.), and the calculation was performed by using eq. (34) and the numerical values; $E = 53.5$ kcal./mole, $k_0 = 10^{18.8}$ min.$^{-1}$, $n = 1.0$, $T_0 = 265$°C., $Q = -88$ cal./g., $a = 0.28$ cm., $r = 0$ cm. (at center), $c_2 = 0.30$ cal./g.-deg. (estimated), $\kappa_2 = 5.1 \times 10^{-2}$ cm.^{2}/min., where the heat of endothermic pyrolysis Q was quoted from Tang's paper,[4] and the initial temperature T_0 was chosen as the temperature measured just prior to an observable departure of DTA curve from the base line. Also the thermal diffusivity κ_2 was obtained by dividing the thermal conductivity of the sample material $K_2 = 0.012$ cal./cm.-min.-deg. (estimated) by the product of specific heat c_2 and density $\rho_2 = 0.80$ g./cm.^{3}. Results are given in Figure 7.

Although this comparison is nothing but an example, it seems the theoretical curve agrees well with the experimental one. Thus it is found that the theory developed here is sufficiently reliable in the range of our study, notwithstanding many assumptions are contained.

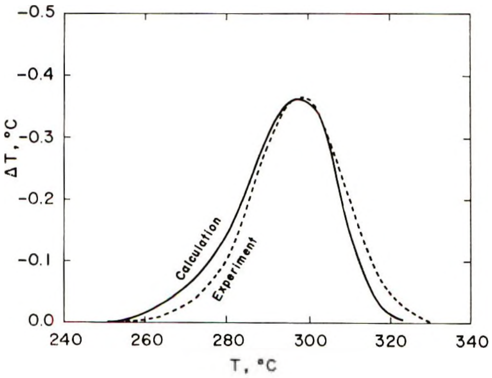

Fig. 7. Comparison between theory and experiment. $E = 53.5$ kcal./mole; $\phi = 0.25$°C./min.; $T_0 = 265$°C.; $n = 1$; $k_0 = 10^{18.8}$ min.$^{-1}$; $Q = -88$ cal./g.; $\kappa_2 = 5.1 \times 10^{-2}$ cm.^{2}/min.; $c_2 = 0.30$ cal./g.-deg.; $(w_0/w_2) = 0.38$; $a = 0.28$ cm.; $r = 0$ cm. (at center).

DTA and TGA Curves of α-Cellulose Treated with Ammonium Phosphate

As mentioned above, it is expected that a cellulose treated with aqueous solution of inorganic salt is not a compound but a kind of mixture consisting of free chemical, residual cellulose, and cellulose modified by salt. Therefore the thermograms of DTA and TGA for this material must indicate the characteristics of their components. In fact, the results obtained from our measurement show four endotherm peaks on a DTA curve as is known from an example given in Figure 8. The problem then becomes

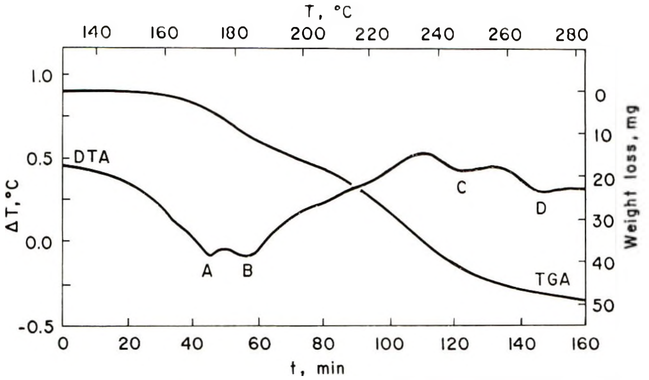

Fig. 8. Typical DTA and TGA curves of cellulose treated with ammonium phosphate. Heating rate: 1°C./min.; atmosphere: 0.1 Torr.

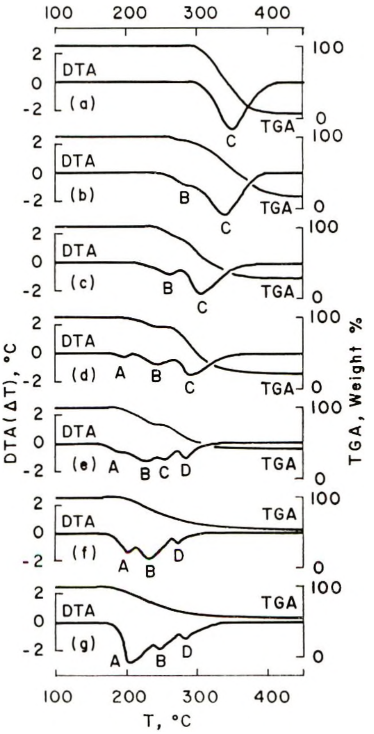

Fig. 9. DTA and TGA curves of cellulose treated with aqueous solution of ammonium dihydrogen phosphate of different concentrations: (*a*) $0.001M$; (*b*) $0.01M$; (*c*) $0.10M$; (*d*) $0.15M$; (*e*) $0.50M$; (*f*) $0.90M$; (*g*) $1.5M$. 5°C./min., 3 Torr.

that of to identifying each of the endotherm. It is convenient for this purpose to use some curves of cellulose treated with solutions of different concentration. That is, if the quantity of salt added to cellulose increases, the area of the endotherm of untreated cellulose in the DTA curve should decrease and conversely the endotherms due to free chemical and modified cellulose should increase. The variation of DTA curves are given in Figure 9, and the relations between the area of endotherms and concentration of aqueous solutions of dihydrogen ammonium phosphate are shown in Figure 10. Thus it was confirmed that the first peak (*A*) which appears at the lowest temperature region corresponds to the decomposition of ammonium phosphate; the next peak (*B*) corresponds to the pyrolysis of modified cellulose, the third peak (*C*) to the pyrolysis of residual cellulose, and the last peak (*D*) to the secondary reactions of products generated from the pyrolysis of modified cellulose.

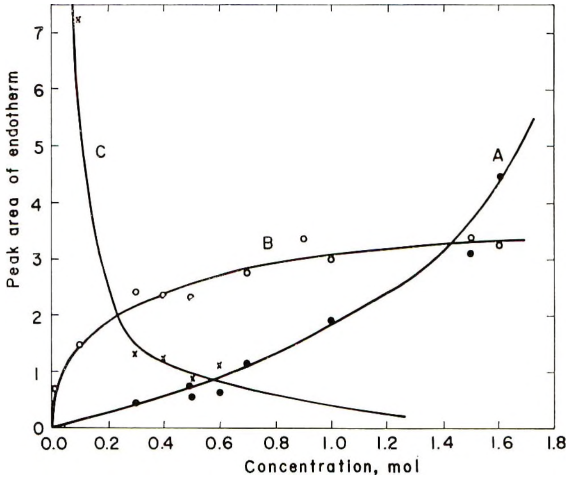

Fig. 10. Dependence of concentration of aqueous solution on peak area of DTA for pyrolysis of cellulose treated with ammonium phosphate.

According to Figure 9, moreover, the peak value of the DTA curve for each component has a tendency to move toward the low temperature side with increases in the quantity of added salt. This result agrees with an opinion[16] presented previously that the pyrolysis rate of cellulose is accelerated by adding flame retardants. Further, it is of interest that the concentration of aqueous solution at which the area of endothrm of modified cellulose attains a limiting value just coincides with the limit below which good performance for flame retardation is unavailable by usual impregnating method, and that when a treated cellulose is washed sufficiently with water, the thermogram obtained is much similar to those of untreated cellulose. Perhaps the later phenomenon suggests that modified cellulose is produced after heating of the sample.

Kinetic Parameters of Cellulose Treated with Ammonium Phosphate

In determining the activation energy and the pre-exponential factor for the pyrolysis reaction of each component, eqs. (3) and (1) were used for the reasons mentioned above, and the determination of T_m required for calculation was carried out on the basis of the fact that the maximum rate of pyrolysis reaction should, in theory, agree with the peak of DTA curve. The result for cellulose treated with dihydrogen ammonium phosphate is given in Figure 11. A plot of ln (ϕ/T_m) versus $(1/T_m)$ on each component shows a linear relation in every case, and the slopes of the lines give activation energies of 54 kcal./mole for residual cellulose, 32 kcal./mole for modified cellulose, and 41 kcal./mole for ammonium phosphate. Also the pre-exponential factors of Arrhenius equations corresponding to these activation energies are 10^{19} min.$^{-1}$ for residual cellulose, 10^{12} min.$^{-1}$ for modified cellulose, and 10^{18} min.$^{-1}$ for ammonium phosphate. The kinetic parameters of the second-stage reaction of modified cellulose were not determined because of the low accuracy of the DTA and TGA curves.

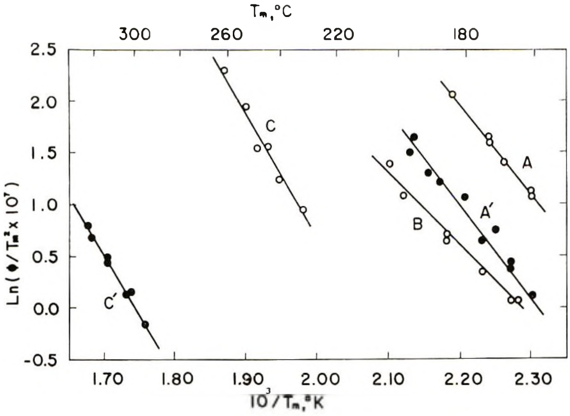

Fig. 11. Plots of ln (ϕ/T_m) vs. $1/T_m$: (*A*) free ammonium phosphate in treated cellulose; (*B*) modified cellulose in treated cellulose; (*C*) residual cellulose in treated cellulose; (*A′*) ammonium phosphate alone; (*C′*) cellulose alone.

In these results, E and k_0 for residual cellulose and free chemical are in good agreement with the results given in Table I, i.e., $E = 53.5$ kcal./mole and $k_0 = 10^{18.8}$ min.$^{-1}$ for pure cellulose, and with results obtained by the same procedure on both the separate components, i.e., $E = 53$ kcal./mole, $k_0 = 10^{18}$ min.$^{-1}$ for cellulose; and $E = 40$ kcal./mole, $k_0 = 10^{17}$ min.$^{-1}$ for ammonium phosphate. Plots for the separate materials are shown in Figure 10. Thus the identification of peaks in the DTA curve was confirmed, and then the activation energy and the pre-exponential factor for pyrolysis of modified cellulose was determined as 32 kcal./mole and 10^{12} min.$^{-1}$ respectively. This activation energy is more or less different from the result presented by Tang,[4] but agrees with Madorsky's conclusion[14] that the activation energy of cellulose decreases on chemical modification.

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Résumé

On a déterminé au moyen de TGA et DTA, l'énergie d'activation E, le facteur pré-exponentiel k_0 et l'ordre de réaction n pour la pyrolyse de l'α-cellulose et de la cellulose modifiée avec du dihydrogénophosphate d'ammonium. Les résultats obtenus pour la cellulose modifiée sont: $E = 53.5$ Kcal/mole, $k_0 = 10^{18.8}$ min^{-1} et $n = 1$. Dans le domaine de l'analyse, une nouvelle théorie de l'analyse thermique différentielle a été développée. Cette théorie arrive à la conclusion que le point maximum de la courbe de la DTA coïncide avec la vitesse maximum de la réaction, elle ne peut être utilisée non seulement dans le cas présent, mais également pour un emploi général de la DTA. Les procédés détaillés des expériences ainsi que de la théorie sont décrits dans cet article.

Zusammenfassung

Aktivierungsenergie E, präexponentieller Faktor k_0 und Reaktionsordnung n für die Pyrolyse von α-Cellulose und mit Dihydrogenammoniumphosphat modifizierte Cellulose wurden mittels TGA und DTA bestimmt. Die erhaltenen Ergebnisse sind $E = 53$ Kcal/Mol, $k_0 = 10^{18.8}$ min^{-1}, $n = 1$ für α-Cellulose und $E = 32$ Kcal/Mol, $k_0 = 10^{12}$ min^{-1}, $n = 1$ für modifizierte Cellulose. Bei der Analyse wurde auch eine neue DTA-Theorie entwickelt. Diese Theorie führt zu dem Schluss, dass das Maximum der DTA-Kurve mit dem Maximum der Reaktionsgeschwindigkeit zusammenfällt, was nicht nur in der vorliegenden Arbeit Verwendung finden kann sondern allgemein für DTA anwendbar ist. Experimentelle und theoretische Verfahren werden in ihren Einzelheiten beschrieben.

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NMR Studies on the Stereospecific Polymerization of Methyl Vinyl Ether. Part I. Polymerization by Metal Halides: Penultimate Effect

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Synopsis

Methyl vinyl ether (MVE) was polymerized under various conditions by $BF_3 \cdot O(C_2H_5)_2$ and $SnCl_4 \cdot CCl_3CO_2H$ catalysts. The effect of polymerization conditions on the steric structure of poly(methyl vinyl ether) (PMVE) was studied by NMR spectra. It was found that the triad isotacticity of PMVE decreased and the syndiotacticity and heterotacticity increased with increasing polarity of the solvent and increasing polymerization temperature. This result coincided with the qualitative conclusion estimated from softening point and infrared spectra. However, the variation of tacticity by the change of the polarity of a solvent was not so large as expected. There was no large difference between the behavior of $BF_3 \cdot O(C_2H_5)_2$ and $SnCl_4 \cdot CCl_3CO_2H$ as catalysts. From the relation between the difference of free energy of monomer addition due to the steric structure of the polymer and the polymerization temperature, it was concluded that the penultimate effect really existed and was due to only the difference in enthalpy in the MVE–$BF_3 . O(C_2H_5)_2$ or MVE–$SnCl_4 \cdot CCl_3CO_2H$ systems. The penultimate effect was not greatly changed by the polymerization conditions in these systems.

INTRODUCTION

Crystalline poly(methyl vinyl ether) (PMVE) has been obtained at low temperature by "activated" polymerization, i.e., polymerization with addition of chloroform or methylene chloride as an activator in aliphatic hydrocarbon solution of methyl vinyl ether (MVE) and BF_3 catalyst.[1] We found that in the cases in which the resultant PMVE was soluble in the reaction system the polymerization of MVE at low temperature proceeded without chlorinated hydrocarbon as an activator.[2,3] As the method for determining the stereoregularity of PMVE had not yet been confirmed at that time, only a qualitative comparison was carried out in these studies.[1-3]

Recently, the triad and diad tacticity of PMVE has been quantitatively determined by means of NMR spectra.[4,5] Therefore, one of the purposes of this investigation is to clarify quantitatively the relationship between the steric structure of PMVE and polymerization conditions. If the triad tacticity in PVME is measured, it is possible to discuss, on the basis of the results, the effect of a penultimate unit for the steric structure of an entering monomer. In a previous paper[6] we pointed out that the α value given by eq. (1) is a suitable measure of the penultimate effect, where P_{ii} etc.

$$\alpha = P_{si}/P_{ii} \qquad (1)$$

are the probabilities of monomer addition considering the steric structure of the penultimate unit. The second object of this paper is to elucidate the penultimate effect in stereospecific polymerization of MVE under various conditions.

EXPERIMENTAL

Polymerization was carried out under dry nitrogen. Solvent and catalyst were introduced into a 100-ml. flask sealed with a rubber cap. The monomer solution was introduced with a syringe to the catalyst solution. At a specified time, the polymerization was stopped by addition of ammoniacal methanol, and the resultant polymer was separated, washed with hot water, and dried *in vacuo* at 40°C. To clarify the effect of temperature on the regularity of the polymer, the polymerization temperature was measured by a thermocouple inserted into the reaction vessel.

The NMR spectra of PMVE were measured in nitromethane solution (10%, w/v) at 80°C. and 60 Mc./sec. (Varian Associate HR-60). As the PMVE obtained in these experiments had a relatively high molecular weight $\{[\eta]$ (in benzene, 30°C.) $> 0.2\}$, there is no obstacle to determining the stereoregularity by NMR spectra. Also, the tacticity of PMVE did not change during the polymerization. Figure 1 shows typical spectra of protons in a methoxyl group of PMVE. These peaks were assigned as triads for syndiotactic, heterotactic, and isotactic structure with increasing magnetic

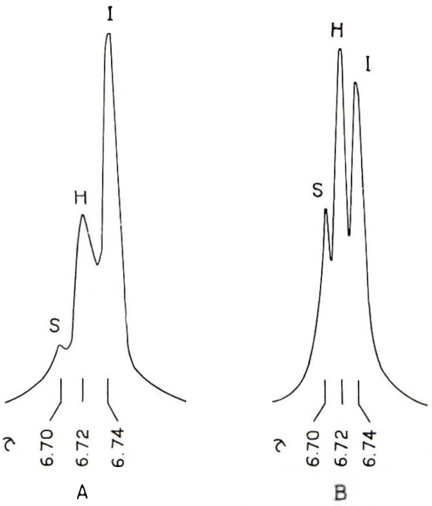

Fig. 1. NMR spectra of the methoxyl region of poly(methyl vinyl ethers): (*A*) polymer prepared with $BF_3 \cdot O(C_2H_5)_2$ in *n*-hexane and toluene (50/50, v/v) at −78°C.; (*B*) polymer prepared with $BF_3 \cdot O(C_2H_5)_2$ in methylene chloride at −20°C.

field strength.[4,5] The fraction of the isotactic triad of PMVE in Figure 1A was 58.7%, and that in Figure 1B was 36.9%. Reproducibility of the peak area of PMVE was good and the experimental error was less than 1% for PMVE obtained in this paper. For a more stereoregular polymer, the experimental error for a peak area increased.

Purification of materials was carried out by the same procedure as in the previous papers,[2,3] and water content was several millimoles per liter in this polymerization system.

RESULTS

Effect of Kind of Solvent and Catalyst

It has been found that the steric structure of poly(vinyl alkyl ethers) is remarkably affected by the polarity of a solvent in cationic polymerization.[3,7] Therefore, the effect of the polarity of the solvent was studied first. Figure 2 shows the relationship between the triad tacticity of PMVE and the composition of solvent in the polymerization catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in the toluene–methylene chloride mixed solvent. In this figure, P_I, P_H, and P_S represent the fractions of isotactic, heterotactic, and syndiotactic material, respectively. The isotactic fraction decreased linearly, and the heterotactic and syndiotactic fractions increased with increasing content of methylene chloride in the solution. However, the isotactic fraction was always more than the syndiotactic fraction, even in PMVE obtained in pure methylene chloride solvent.

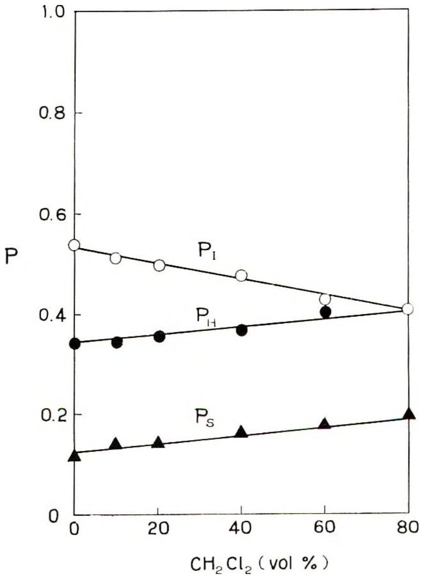

Fig. 2. Relationship between tacticity for poly(methyl vinyl ether) and solvent, composition at −78°C. $[M_0]$ = 20 vol.-%; $[BF_3 \cdot O(C_2H_5)_2]$ = 1 mmole/l.; solvent toluene–methylene chloride.

The tacticity of PMVE obtained by $SnCl_4$ is shown in Figure 3. In this system, trichloroacetic acid was added to $SnCl_4$ as a cocatalyst in equimolar amounts. On comparing Figures 3 and 2, it is seen that the iso-

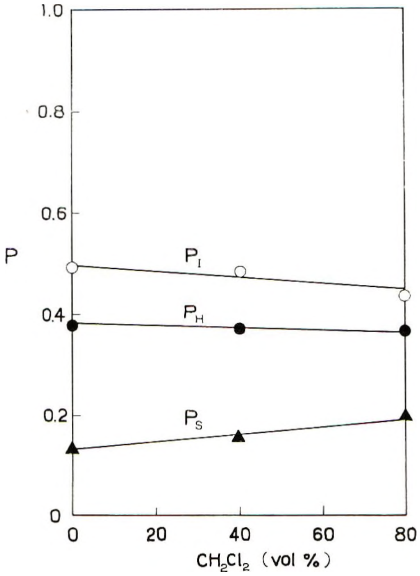

Fig. 3. Relationship between tacticity for poly(methyl vinyl ether) and solvent composition at −78°C. $[M_0]$ = 20 vol.-%; $[SnCl_4 \cdot CCl_3CO_2H]$ = 1 mmole/l.; solvent, toluene–methylene chloride.

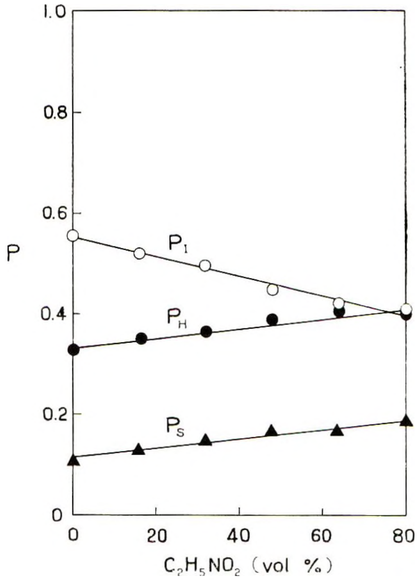

Fig. 4. Relationship between tacticity for poly(methyl vinyl ether) and solvent composition at −78°C. $[M_0]$ = 20 vol.-%; $[BF_3 \cdot O(C_2H_5)_2]$ = 1 mmole/l.; solvent, toluene–nitroethane.

tactic and heterotactic fraction in PMVE obtained with $BF_3 \cdot O(C_2H_5)_2$ was changed more markedly than that obtained with $SnCl_4 \cdot CCl_3CO_2H$ with increasing the polarity of a solvent. In the cationic polymerization of *tert*-butyl vinyl ether, the change in the tacticity of the polymer by the polarity of the solvent was larger in $BF_3 \cdot O(C_2H_5)_2$ than in $SnCl_4$ or $TiCl_4$.[8]

A more polar solvent, nitroethane, was used instead of methylene chloride, the dielectric constant of nitroethane being larger than that of methylene chloride. Nevertheless, the effect of nitroethane was almost the same as that of methylene chloride for the same solvent composition (volume ratio), as shown in Figure 4.

Effect of Polymerization Temperature

It is well known in many instances that the isotacticity of poly(vinyl alkyl ether) decreases with increasing polymerization temperature. The change of the triad tacticity with polymerization temperature gives important knowledge regarding the penultimate effect. Therefore, the effect of polymerization temperature on the triad tacticity was studied in detail.

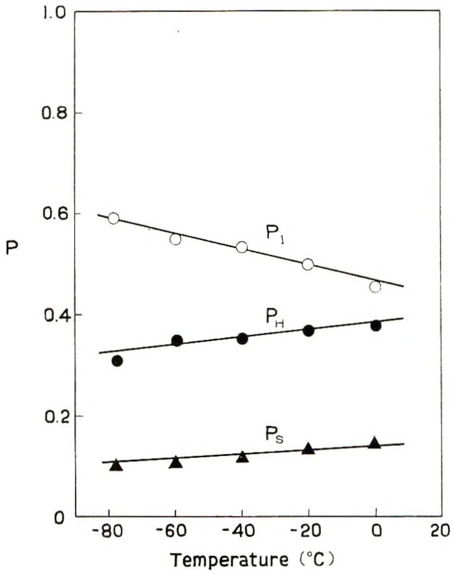

Fig. 5. Effect of polymerization temperature on tacticity for poly(methyl vinyl ether) obtained with $BF_3 \cdot O(C_2H_5)_2$ in *n*-hexane–toluene (50/50, v/v). $[M_0]$ = 20 vol.-%; $[BF_3 \cdot O(C_2H_5)_2]$ = 1 mmole/l.

Figures 5 and 6 show the steric structure of PMVE obtained with $BF_3 \cdot O(C_2H_5)_2$ and $SnCl_4 \cdot CCl_3CO_2H$ in a toluene–*n*-hexane mixed solvent. On adding *n*-hexane to toluene, the isotactic fraction of polymer increased. This result confirms quantitatively the observation[3] that isotactic poly(vinyl alkyl ether) is produced in a solvent with low dielectric constant in a homogeneous system. The change of tacticity due to the polymerization temperature was larger with $SnCl_4 \cdot CCl_3CO_2H$ than with $BF_3 \cdot O(C_2H_5)_2$.

Similar experiments were carried out over a wide range of temperature

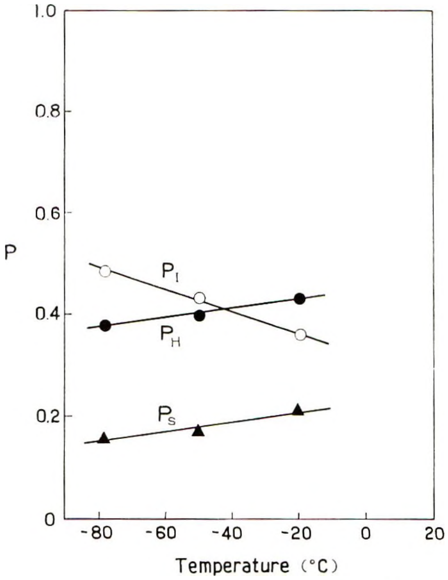

Fig. 6. Effect of polymerization temperature on tacticity for poly(methyl vinyl ether) obtained with $SnCl_4 \cdot CCl_3CO_2H$ in n-hexane–toluene (50/50, v/v). $[M_0]$ = 20 vol.-%; $[SnCl_4 \cdot CCl_3CO_2H]$ = 1 mmole/l.

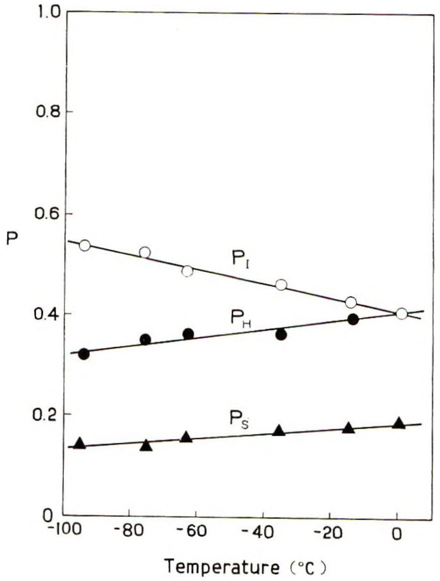

Fig. 7. Effect of polymerization temperature on tacticity for poly(methyl vinyl ether) obtained with $BF_3 \cdot O(C_2H_5)_2$ in toluene. $[M_0]$ = 10 vol.-%; $[BF_3 \cdot O(C_2H_5)_2]$ = 1 mmole/l.

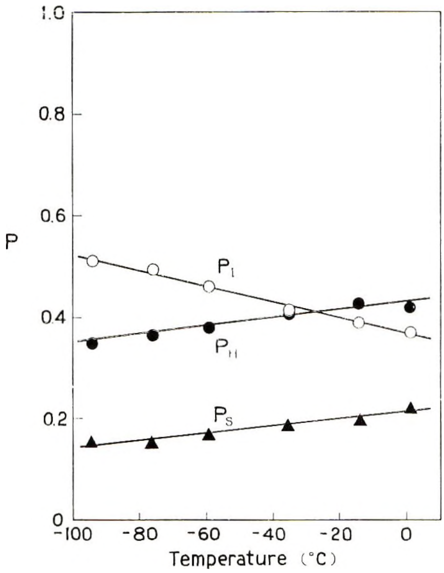

Fig. 8. Effect of polymerization temperature on tacticity for poly(methyl vinyl ether) obtained with $BF_3 \cdot O(C_2H_5)_2$ in methylene chloride. $[M_0] = 10$ vol.-%; $[BF_3 \cdot O(C_2H_5)_2] = 1$ mmole/l.

(from −95 to 0°C.) in toluene and methylene chloride with $BF_3 \cdot O(C_2H_5)_2$ as a catalyst, as shown in Figures 7 and 8. In both solvents, the isotactic fraction of PMVE decreased and the syndiotactic and heterotactic fractions increased with increasing temperature.

Physical Properties and Tacticity of PMVE

In the previous papers,[2,3] the melting point or softening point was used as a qualitative measurement of tacticity of PMVE. As mentioned above,

TABLE I
Relationship Between Tacticity and Softening Point of Poly(methyl Vinyl Ether) Catalyzed by $BF_3 \cdot O(C_2H_5)_2$

Polymerization conditions				
Solvent	Polymerization temperature, °C.	Nature	Triad isotacticity, %	Softening point, °C.
Toluene	−78	White solid	52.5	~70
Methylene chloride	−78	Slightly tacky and rubbery solid	45.9	~53
Toluene	−40	Slightly tacky and rubbery solid	42.8	~47

the tacticity of PMVE obtained in various conditions was determined from the NMR spectra and the melting (or softening) point of PMVE was compared with the tacticity. The softening point and appearance of PMVE were clearly changed by the tacticity, as shown in Table I.

Amorphous PMVE in which the isotactic fraction was less than 40% was tacky or viscous material. On the other hand, PMVE containing more than 40% isotactic fraction was a rubbery, slightly tacky, solid, and PMVE having more than 50% isotactic fraction was a white solid.

DISCUSSION

Effect of Polymerization Conditions on the Steric Structure of PMVE

The polymerization of MVE was carried out by using various catalysts and solvents over a wide range of polymerization temperature. From the measurement of a triad tacticity, it was confirmed that the conclusion estimated from the softening point, infrared spectra or x-ray diffraction pattern was reasonable, that is, the isotacticity of PMVE decreases with increasing polarity of the solvent and increasing polymerization temperature. The maximum isotacticity of PMVE obtained by $BF_3 \cdot O(C_2H_5)_2$ at −78°C. was about 60% and was not so high as expected. This fact does not agree with the Brownstein's result[4] that almost 100% isotactic PMVE could be obtained with $BF_3 \cdot O(C_2H_5)_2$.

In the polymerization of MVE, the decrease of the tacticity due to the increase in polarity of the solvent is not so large, as shown in Figures 2–4. This behavior is very different from that of *tert*-butyl vinyl ether[8,9] and methyl methacrylate[10] in which syndiotactic-rich polymer is produced by the addition of a polar solvent. We have at present no real explanation for this characteristic behavior of the stereospecific polymerization of MVE.

Activation Energy Difference between Isotactic and Syndiotactic Additions

From the triad tacticity, the diad isotacticity P_i and syndiotacticity P_s can be easily calculated as shown in eq. (2). Using eq. (3) for the rela-

$$\begin{aligned} P_i &= P_I + {}^1/_2\, P_H \\ P_s &= P_S + {}^1/_2\, P_H \end{aligned} \qquad (2)$$

$$\ln (P_s/P_i) = -(\Delta H_s - \Delta H_i)/RT + (\Delta S_s - \Delta S_i)/R \qquad (3)$$

tionship between the value of (P_s/P_i) and polymerization temperature, we can calculate the difference of activation energy for the syndiotactic and isotactic addition irrespective of the steric structure of the end unit. Figure 9 shows the plots calculated from Figures 5, 7, and 8; results are summarized in Table II.

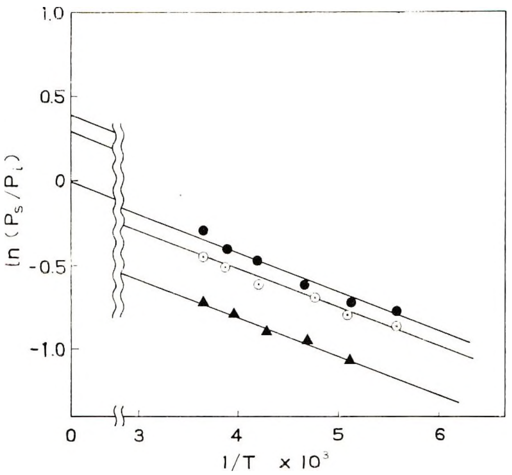

Fig. 9. Relationship between $1/T$ and ln (P_s/P_i) of poly(methyl vinyl ether) obtained with $BF_3 \cdot O(C_2H_5)_2$ in various solvents: (○) toluene; (●) methylene chloride; (▲) *n*-hexane–toluene (50/50, v/v).

As shown in Figure 9, ln (P_s/P_i) shows a good linear relation with $1/T$. The values of $(\Delta H_s - \Delta H_i)$ in the cationic polymerization of MVE are constant irrespective of the kind of solvent. These values derived from NMR measurements were found to be smaller than the corresponding values estimated from softening points.[3] The absolute value of enthalpy difference was almost the same as that in the radical polymerization of vinyl chloride[11] and methyl methacrylate,[12] although the sign of $(\Delta H_s - \Delta H_i)$ was positive.

TABLE II
Activation Energy and Activation Entropy of Diad Addition

Monomer	Polymerization conditions	$\Delta H_s - \Delta H_i$, cal./mole	$\Delta S_s - \Delta S_i$, e.u.
MVE	$BF_3 \cdot O(C_2H_5)_2$; *n*-hexane–toluene (50/50, v/v)	450 ± 20	0.0 ± 0.05
MVE	$BF_3 \cdot O(C_2H_5)_2$; toluene	“	0.6 ± 0.05
MVE	$BF_3 \cdot O(C_2H_5)_2$; methylene chloride	“	0.8 ± 0.05
Vinyl chloride[a]	Radical polymerization	−600	—
Methyl methacrylate[b]	“	−775 ± 75	0.0 ± 0.

[a] Data of Fordham et al.[11]

[b] Data of Bovey.[12]

Penultimate Effect

The tacticity of PMVE obtained in this paper was not consistent with the one-parameter model applied to the radical polymerization of methyl methacrylate,[13] because α was not unity. The α-values defined in eq. (1) were calculated from the results of Figures 2 and 4; these α values increased slightly with increasing amount of a polar solvent, as shown in Figure 10. In the case of the anionic polymerization of methyl methacrylate in a nonpolar solvent, the addition of a small amount of a polar solvent markedly increases the α value.[14] The difference of this behavior suggests a different reaction mechanism (probably the penultimate effect) for the two systems.

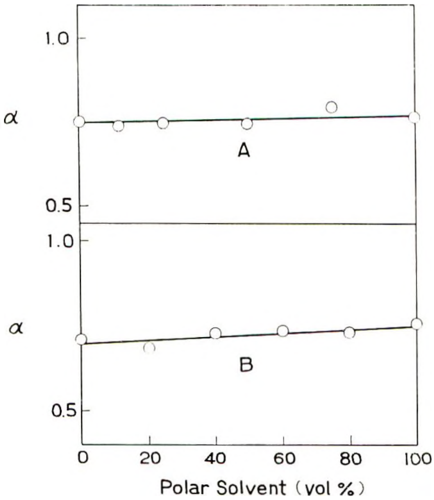

Fig. 10. Effect of polar solvent on α value of poly(methyl vinyl ether) obtained with $BF_3 \cdot O(C_2H_5)_2$ at −78°C.: (*A*) toluene–methylene chloride system; (*B*) toluene–nitroethane system.

The fact that α is smaller than unity means that the steric structure of an adding monomer is determined not only by the end unit of a growing chain, but by other factors, e.g., the penultimate unit. However, even in the case where α is smaller than unity, there is a problem whether the penultimate effect really exists during the polymerization.[15] Recently, Chujyo[16] derived eq. (4) from a statistical treatment according to the Ising model,

$$\begin{aligned}\Delta\epsilon &= \epsilon_I + \epsilon_S - 2\epsilon_H \\ &= -RT \ln\,[4(N_I/N)(N_S/N)/(N_H/N)^2] \qquad (4)\end{aligned}$$

where ϵ_I, ϵ_S, and ϵ_H are free energy in isotactic, syndiotactic, and heterotactic addition, respectively, and (N_I/N), (N_S/N), (N_H/N) are the fraction of a triad tacticity. In this equation, when $\Delta\epsilon$ is equal to zero, the configuration of an adding monomer is determined only by the chain end

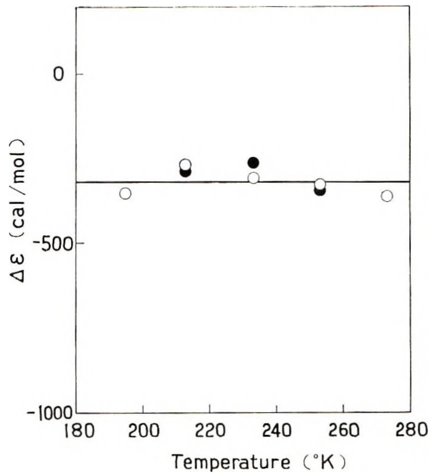

Fig. 11. Relationship between polymerization temperature and $\Delta\epsilon$ of poly(methyl vinyl ether) obtained with $BF_3\cdot O(C_2H_5)_2$ and $SnCl_4\cdot CCl_3CO_2H$ in *n*-hexane–toluene (50/50, v/v): (○) with $BF_3\cdot O(C_2H_5)_2$; (●) with $SnCl_4\cdot CCl_3CO_2H$. $[M_0]$ = 20 vol.-%; [Cat] = 1 mmole/l.

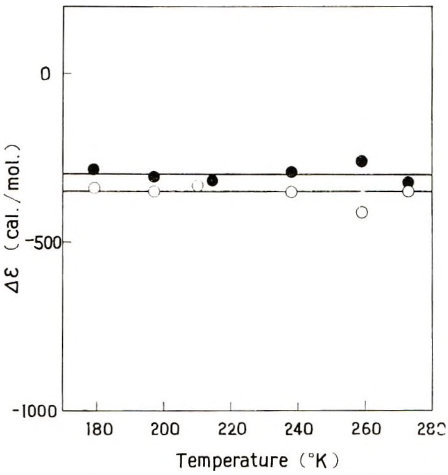

Fig. 12. Relationship between polymerization temperature and $\Delta\epsilon$ of poly(methyl vinyl ether) obtained with $BF_3\cdot O(C_2H_5)_2$: (○) in toluene; (●) in methylene chloride. $[M_0]$ = 10 vol.-%; $[BF_3\cdot O(C_2H_5)_2]$ = 1 mmole/l.

unit, i.e., the system is consistent with Bovey's model. On the other hand, when $\Delta\epsilon \neq 0$ and the plot of $\Delta\epsilon$ against polymerization temperature is a straight line, the penultimate effect really exists. For example, in the case of $\Delta\epsilon$ = constant, the result means that $\Delta\epsilon$ is controlled only by enthalpy difference.

Our experimental results (Figs. 5–8) were calculated according to equation (4). $\Delta\epsilon$ was independent of polymerization temperature irrespective of the polymerization solvent, whether $BF_3\cdot O(C_2H_5)_2$ or $SnCl_4\cdot CCl_3CO_2H$

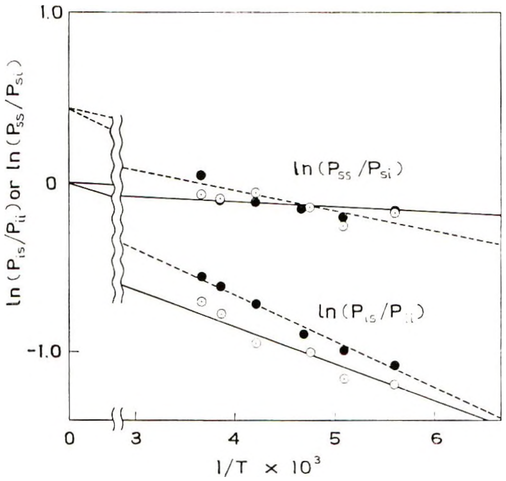

Fig. 13. Relationship between $1/T$ and ln (P_{is}/P_{ii}) and ln (P_{ss}/P_{si}) of poly(methyl vinyl ether) obtained with $BF_3 \cdot O(C_2H_5)_2$: (○) in toluene; (●) in methylene chloride.

was used as a catalyst, as shown in Figures 11 and 12. As the range of polymerization temperature was narrow, the result for $SnCl_4 \cdot CCl_3CO_2H$ catalyst is not clear. However, these figures show clearly that $\Delta\epsilon$ was constant in both the polar and the nonpolar solvent. Two important conclusions can be obtained from this result according to eq. (4): one is that the penultimate effect really exists in these systems, and the other is that the free energy difference ($\Delta\epsilon$) leading an adding monomer to the different steric configuration is caused only by the enthalpy term in the MVE–$BF_3 \cdot O(C_2H_5)_2$ system. As reported elsewhere,[17] in the polymerization of MVE by $Al(C_2H_5)Cl_2$ catalyst the plot of $\Delta\epsilon$ against polymerization temperature is a straight line through the origin, that is, $\Delta\epsilon$ in the MVE–$Al(C_2H_5)Cl_2$ system is controlled only by entropy difference.

By means of eq. (3), the effect of the penultimate unit on the energy differences between different tactic placements of the last monomer unit can be calculated. In this case, eq. (3) is modified to eqs. (5) and (6). The tacticity of PMVE obtained by $BF_3 \cdot O(C_2H_5)_2$ in toluene and methylene chloride was plotted by these equations. The results are summarized in

TABLE III

Activation Enthalpy and Activation Entropy of Triad Addition

Polymerization conditions	$\Delta H_{ii} - \Delta H_{is}$, cal./mole	$\Delta H_{ss} - \Delta H_{si}$, cal./mole	$\Delta S_{ii} - \Delta S_{is}$, e.u.	$\Delta S_{ss} - \Delta S_{si}$ e.u.
$BF_3 \cdot O(C_2H_5)_2$; toluene	-430 ± 20	60 ± 20	0.0 ± 0.05	0.0 ± 0.05
$BF_3 \cdot O(C_2H_5)_2$; methylene chloride	-550 ± 20	240 ± 20	-0.9 ± 0.05	0.9 ± 0.05

$$\ln (P_{is}/P_{ii}) = -(\Delta H_{is} - \Delta H_{ii})/RT + (\Delta S_{is} - \Delta S_{ii})/R \qquad (5)$$

$$\ln (P_{ss}/P_{si}) = -(\Delta H_{ss} - \Delta H_{si})/RT + (\Delta S_{ss} - \Delta S_{si})/R \qquad (6)$$

Figure 13 and Table III. In both systems, the entering monomer showed preferentially isotactic addition to the syndiotactic addition, irrespective of the steric structure of the penultimate unit. Isotactic addition to an end unit of an isotactic–isotactic structure seems to be energetically most favorable.

Although many reaction mechanisms for stereospecific polymerization of vinyl ethers have been proposed, there is no explanation considering that the penultimate effect is due mainly to the enthalpy term or entropy term. The reaction mechanism considering such a result will have to be discussed in the future.

We wish to express our thanks to Drs. Chujyo and Sato of Toyo Spinning Co. Ltd. for the measurement and the discussion of NMR spectra.

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Résumé

Le méthyl-vinyl éther (MVE) fut polymérisé sous différentes conditions par $BF_3 \cdot O(C_2H_5)_2$ et $SnCl_4 \cdot CCl_3COOH$ comme catalyseurs. L'effet des conditions de polymérisation sur la structure stérique du poly(méthyl vinyl éther) (PMVE) fut étudiée par spectre NMR. On a trouvé que la triade d'isotaticité du PMVE diminuait et que sa syndiotacticité et hétérotacticité augmentaient en augmentant la polarité du solvant et la température de polymérisation. Ce résultat coincide avec la conclusion qualitative estimée à parti du point de ramollissement et du spectre IR. Cependant, la variation de tacticité en hangeant la polarité du solvant fut très faible comme inespéré. Il n'y

avait pas de grande différence entre le comportement des catalyseurs $BF_3O(C_2H_5)_2$ et $SnCl_4 \cdot CCl_3$ COOH. Or la relation entre la différence et énergie libre de l'addition d'un monomère due à la structure stérique du polymère et la température de polymérisation, on a conclu que le pénultième effet existait réellement et cet effet était dû uniquement à la différence d'enthalpie dans le système MVE-$BF_3 \cdot O(C_2H_5)_2$ ou MVE-$SnCl_3 \cdot CCl_3$-CO_2H. Le pénultième effet ne changeait pas beaucoup avec les conditions de polymérisation dans ces systèmes.

Zusammenfassung

Methylvinyläther (MVE) wurde unter verschiedenen Bedingungen mit $BF_3 \cdot O(C_2H_5)_2$ und $SnCl_4 \cdot CCl_3CO_2H$ als Katalysator polymerisiert. Der Einfluss der Polymerisationsbedingungen auf die sterische Struktur von Polymethylvinyläther (PMVE) wurde NMR-spektroskopisch untersucht. Die Triaden-Isotaktizität von PMVE nahm mit steigender Polarität des Lösungsmittels und steigender Polymerisatinstemperatur ab, während seine Syndiotaktizität und Heterotaktizität zunahm. Dieses Ergebnis stimmt mit der qualitativen Schlussfolgerung aus Erweichungspunkt und IR-Spektren überein. Die Abhängigkeit der Taktizität von der Polarität des Lösungsmittels war jedoch unerwarteter Weise sehr gering. Im Verhalten von $BF_3 \cdot O(C_2H_5)_2$ und $SnCl_4 \cdot CCl_3CO_2H$ als Katalysatoren bestand kein grosser Unterschied. Aus der Beziehung zwische dem durch die sterische Struktur des Polymeren bedingten Unterschied der freien Energie der Monomeraddition und der Polymerisationstemperatur wurde geschlossen, dass tatsächlich ein Einfluss der vorletzten Gruppe besteht und dass dieser Einfluss nur durch den Enthalpieunterschied der MVE-$BF_3 \cdot O(C_2H_5)_2$- und MVE-$SnCl_4 \cdot CCl_3CO_2H$-Systeme bedingt ist. Die Polymerisationsbedingungen hatten bei diesen Systemen nur einen geringen Einfluss auf den "Vorletzten-Gruppen-Effekt".

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NMR Studies on the Stereospecific Polymerization of Methyl Vinyl Ether. Part II. Polymerization by Sulfuric Acid–Aluminum Sulfate Complex: Enantiomorphic Catalyst Sites Model

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Synopsis

Highly crystalline poly(methyl vinyl ether) (PMVE) was produced in toluene in a temperature range of 0 to −20°C. with the use of sulfuric acid–aluminum sulfate complex (SA catalyst). It was found from the NMR spectra that these polymers contained more than 50% of the triad isotactic fraction and the melting point of the unfractionated polymer was about 130°C. However, PMVE contaning a large amount of the isotactic fraction was insoluble in nitromethane, so the triad tacticity of highly crystalline PMVE could not be quantitatively determined. The molecular weight of PMVE increased with increasing conversion and increasing polymerization temperature. This behavior is different from that in metal halide catalysts. Also, the stereoregularity of PMVE decreased with increasing monomer concentration. However, addition of a polar solvent and increasing the polymerization temperature had little effect on the stereoregularity of the polymer. The increase in the isotactic fraction at high catalyst concentration and the difference in the monomer composition in the copolymerization of methyl vinyl ether with 2-chloroethyl vinyl ether by SA catalyst from that obtained by $BF_3 \cdot O(C_2H_5)_2$ suggest that the absorption of MVE on a catalyst surface is an important step in the propagation step by SA catalyst. The fraction of the triad tacticity calculated from the enantiomorphic catalyst sites model[8] coincided with the experimental results. This fact shows that the steric structure of the adding monomer is determined only by the nature of the catalyst irrespective of the nature of a growing chain end. It is concluded, on considering also the results of the previous paper, that completely different factors can control the steric structure of a polymer even for the same monomer when different catalysts are used.

INTRODUCTION

In the cationic polymerization of alkyl vinyl ethers catalyzed by metal halides or metal alkyl halides which are soluble to a reaction system, crystalline polymers have been obtained in a nonpolar solvent only at low temperature. On the other hand, it was reported that highly crystalline polymers were produced at high temperature by heterogeneous catalyst. Modified Ziegler type catalysts,[1] chromium oxide,[2] sulfuric acid–metal sulfates,[3–5] and fluoroaluminum gel[6] are examples of heterogeneous catalysts which produce a crystalline polymer at room temperature. In polymerizations by such heterogeneous catalysts, although a study of the relation between polymerization conditions and the stereoregularity of polymer has been carried out, little information regarding the reaction mechanism was obtained. One of the reasons was the lack of a quantitative knowledge of the steric structure of the resultant polymer. As reported in the previous paper,[7] methyl vinyl ether (MVE) is a suitable monomer for this purpose, because the triad tacticity of poly(methyl vinyl ether) (PMVE) can be determined by NMR spectroscopy.

The object of the present study is to elucidate the mechanism by which the steric structure of a monomer is controlled in the polymerization catalyzed by the sulfuric acid–aluminum sulfate complex (SA catalyst). In this system, highly isotactic PMVE was produced in the temperature range of 0 to −20°C. The content of the triad tacticity of PMVE obtained by SA catalyst agreed with the value calculated from the enantiomorphic catalyst sites model.[8] This means the factor controlling the steric structure of an adding monomer in SA catalyst is only the catalyst. The case is altogether different from that with $BF_3 \cdot O(C_2H_5)_2$ catalyst,[7] where the growing chain end and the penultimate unit determine the steric structure of an approaching monomer.

EXPERIMENTAL

Polymerization

MVE was polymerized under dry air without stirring. MVE was added at fixed temperature by means of a syringe to a suspension of the catalyst in a solvent in a polymerization tube sealed with a rubber cap. It was observed that the polymerization immediately proceeded from the catalyst surface as in the case of polymerization of isobutyl vinyl ether.[4] Polymerization was stopped by an addition of concentrated aqueous ammonia solution. PMVE was isolated from the reaction system with petroleum ether and purified by precipitating a benzene solution of the material in cold methanol.

Materials

Materials were purified as described in previous papers.[3,4,7] 2-Chloroethyl vinyl ether (Union Carbon & Carbide Corp.) was washed with aqueous NaOH solution and distilled over CaH_2 after drying with KOH. SA catalyst was obtained by adding concentrated H_2SO_4 to $Al_2(SO_4)_3 \cdot 18H_2O$ and washing with diethyl ether.[4] The composition of the catalyst determined by the alkali titration method[9] corresponded to $Al_2(SO_4)_3 \cdot 2.5H_2SO_4 \cdot 9.1H_2O$.

Measurement of Properties of Polymers

The triad tacticity of PMVE was determined in nitromethane solution from the NMR spectra under the same conditions as in the previous paper.[7]

However, when the isotactic fraction of PMVE was over 70%, the tacticity could not be measured, since the highly crystalline PMVE was partially insoluble in nitromethane. With other solvents for the measurement of NMR spectra, the triplet absorption of the methoxyl group was incompletely resolved and we could not find other suitable solvents.

As NMR spectra could not be measured for all PMVE, the tacticity of PMVE was qualitatively compared by infrared spectra of a film which was dried over Hg at room temperature and without a heat-treatment. As reported by Kern and Calfee,[6] the ratio of 12.40μ/12.65μ absorption (*D* value) was used as a measure of tacticity. An increase in *D* value means an increase in the isotacticity of PMVE. Even in this method, a film of highly isotactic PMVE was opaque due to the crystallization and we could not obtain *D* values with good reproducibility. Therefore, the *D* values have only a qualitative meaning.

The intrinsic viscosity $[\eta]$ was measured in benzene solution at 40°C. The composition of a copolymer of MVE with 2-chloroethyl vinyl ether was determined by elementary analysis of carbon, and the melting point was measured by a micro-melting point measurement apparatus (Yanagimoto Co.).

RESULTS

Relationship Between Polymerization Conditions and Properties of PMVE

In the polymerization of MVE in toluene, the surface of the catalyst became yellowish-brown immediately after the addition of MVE. Conversion increased monotonically with reaction time. As control of the

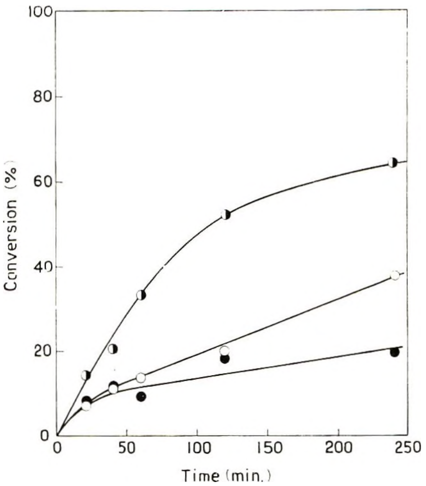

Fig. 1. Time–conversion curve of poly(methyl vinyl ether) obtained in toluene at various polymerization temperatures: (◑) 0°C.; (○) −10°C.; (●) −20°C. $[M_0]$ = 20 vol.-%; [Cat] = 0.4 g./100 ml.

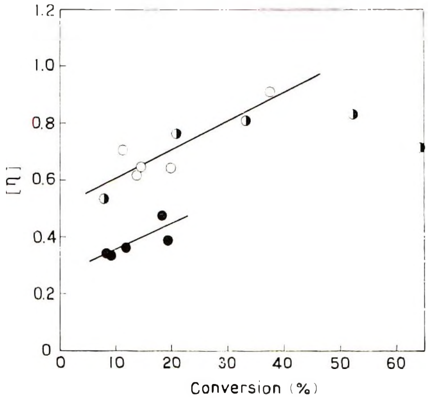

Fig. 2. Relationship between conversion and $[\eta]$ of poly(methyl vinyl ether) obtained in toluene at various polymerization temperatures: (◑) 0°C.; (○) −10°C.; (●) −20°C.

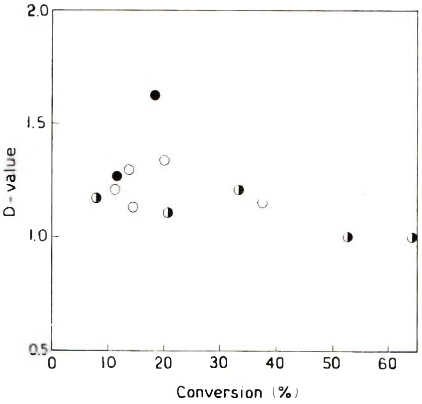

Fig. 3. Relationship between conversion and D value of poly(methyl vinyl ether) obtained in toluene at various polymerization temperatures: (◑) 0°C.; (○) −10°C.; (●) −20°C.

size of the catalyst particles was difficult, the yields of PMVE were scattered, as shown in Figure 1. From this figure, it is found that the increasing of polymerization temperature accelerates the rate of polymerization as expected.

As shown in Figure 2, the molecular weight of PMVE increased with increasing conversion up to about 40% and with increasing polymerization temperature. This behavior is very different from that in the usual homogeneous catalyst $[\mathrm{BF_3 \cdot O(C_2H_5)_2}$ or $\mathrm{SnCl_4 \cdot CCl_3CO_2H}]$. The D value of PMVE decreased slightly with increasing conversion and polymerization temperature, although this tendency was not so clear, as shown in Figure 3.

An increase of the catalyst concentration also increased the stereoregularity of PMVE at both high and low conversions, as shown in Figure 4. However, at more than 0.4 g./100 ml., catalyst concentration, the tac-

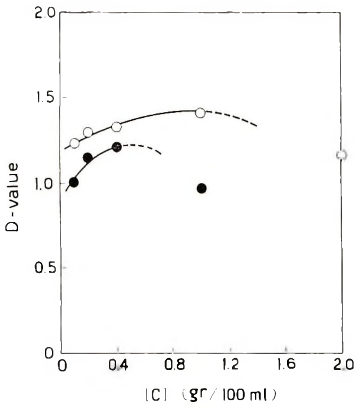

Fig. 4. Effect of catalyst concentration on *D* value of poly(methyl vinyl ether) obtained in toluene at -10°C.: (○) low conversion (4–10%); (●) high conversion (25–50%). $[M_0]$ = 20 vol.-%.

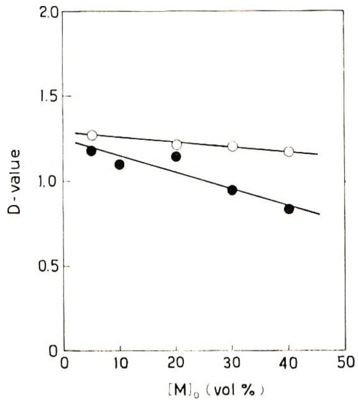

Fig. 5. Effect of monomer concentration on *D* value of poly(methyl vinyl ether) obtained in toluene at -10°C.: (○) low conversion (4–10%); (●) high conversion (25–50%). [Cat] = 0.4 g./100 ml.

ticity of PMVE decreased with increasing catalyst concentration. In PMVE obtained at a high catalyst concentration, the infrared spectra indicated the presence of a carbonyl group. MVE or PMVE may be partially decomposed by sulfuric acid isolated from a large amount of catalyst, and so the stereoregularity of PMVE may be decreased.

Figure 5 shows the effect of monomer concentration on the stereoregularity of PMVE. As an increase in the monomer concentration causes an increase of the polarity of the reaction system, the regularity of the polymer will be decreased. Figure 5 shows clearly that the regularity of PMVE at high conversion was less than that at low conversion. On the other hand, the addition of methylene chloride to toluene very slightly decreased the stereoregularity of PMVE. The change of the steric structure was much less than that in the homogeneous polymerization.[10]

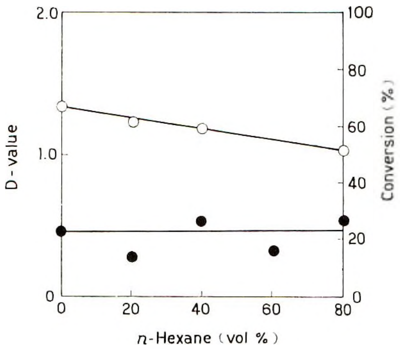

Fig. 6. Effect of solvent composition on conversion and D value of poly(methyl vinyl ether) at −10°C.: (○) D value; (●) conversion. $[M_0]$ = 20 vol.-%; [Cat] = 0.4 g./100 ml.; polymerization time, 90 min.; solvent, toluene–n-hexane.

The polymerization behavior in toluene–n-hexane mixed solvent is very interesting, because n-hexane is less polar than toluene and a nonsolvent for the resultant PMVE. As shown in Figure 6, although the polymer yield at specified intervals was not affected, the stereoregularity of PMVE was decreased by an addition of n-hexane. This behavior is similar to that in the stereospecific polymerization of *tert*-butyl vinyl ether[11] and α-methylstyrene[12] by $BF_3 \cdot O(C_2H_5)_2$. Therefore, it was concluded that the steric structure of PMVE was affected by both the polarity and the homogeneity of the reaction system.

Copolymerization of MVE with 2-Chloroethyl Vinyl Ether

The absorption of the monomer on the catalyst surface seems to be one reason why a highly isotactic polymer is produced by such a heterogeneous catalyst, because the stereoregularity of PMVE increased with increasing catalyst concentration under conditions where side reactions do not occur. Similar ideas were discussed by Lal[5] and Vandenberg.[1] To clarify this point,

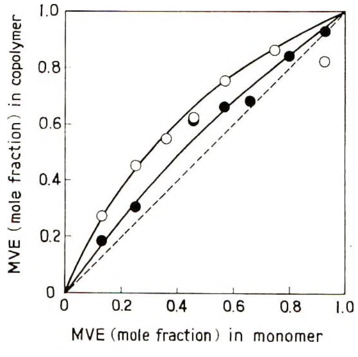

Fig. 7. Copolymer composition curve for copolymerization of methyl vinyl ether in toluene at −10°C. with various catalysts: (○) $Al_2(SO_4)_3$–H_2SO_4 complex, 0.4 g./100 ml.; (●) $BF_3 \cdot O(C_2H_5)_2$, 1 mmole/l.

TABLE I
Physical Properties of PMVE Obtained with Various Catalysts

Polymerization conditions			Triad isotacticity, %	*D* value	Melting point, °C.
Catalyst	Solvent	Temperature, °C.			
$Al_2(SO_4)_3$–H_2SO_4 complex	Toluene	−20	>70	>2	~130
Vandenberg catalyst[1]	Ether + *n*-Heptane	30	—	—	130–144
AlF_3 gel in CH_2Cl_2[6]	*n*-Hexane + CH_2Cl_2	−35 to 40	—	>2	—
$BF_3 \cdot O(C_2H_5)_2$[7]	Toluene	−78	~50	0.8	~70

MVE was copolymerized with 2-chloroethyl vinyl ether in toluene by SA catalyst and $BF_3 \cdot O(C_2H_5)_2$. As shown in Figure 7, the content of MVE in the copolymer obtained by SA catalyst was larger than that in the case of $BF_3 \cdot O(C_2H_5)_2$.

Properties of Resultant PMVE

Properties of PMVE obtained by SA catalyst were very different from those of polymer prepared with $BF_3 \cdot O(C_2H_5)_2$. PMVE polymerized by SA catalyst was a nontacky, hard solid which had a high crystallinity according to its x-ray diffraction pattern. The solubility and other physical properties of the unfractionated PMVE were similar to those of polymer obtained with a fluoroaluminum catalyst as reported by Kern and Calfee.[6] Since PMVE containing an isotactic fraction of more than 70% was insoluble in nitromethane and since a film of PMVE having a *D* value higher than 2 was opaque, the isotacticity could not be quantitatively compared as described in the experimental section. The physical properties of an unfractionated PMVE are summarized in Table I.

Unfractionated PMVE obtained with SA catalyst shows a high melting point, and this fact coincides with the result that resultant PMVE does not contain much of an amorphous (viscous liquid) part.

DISCUSSION

It was found that MVE was polymerized to highly crystalline PMVE in toluene at relatively high temperature with SA catalyst. According to the NMR spectra, these polymer contain an isotactic fraction of more than 50%.

An increase in polarity of the solvent or of the monomer concentration decreases the isotacticity of PMVE. This tendency is similar to the case of stereospecific polymerization of alkyl vinyl ethers in the homogeneous system. On the other hand, the molecular weight of PMVE increases with increasing conversion and increasing polymerization temperature. These phenomena are characteristic of a heterogeneous polymerization, and this behavior is the same as in the polymerization of isobutyl vinyl ether by the same catalyst.[4]

The most important point is the fact that a greater isotactic portion was produced at a high catalyst concentration and that the composition of a copolymer of MVE with 2-chloroethyl vinyl ether obtained by SA catalyst is very different from that of the copolymer obtained with $BF_3 \cdot O(C_2H_5)_2$. The former result suggests that the catalyst surface plays an important role in the stereospecific polymerization. Generally, in the cationic polymerization of vinyl monomer by homogeneous catalysts, the copolymer composition is slightly affected by the kind of catalyst.[13,14] Therefore, such a large difference in the composition of copolymers obtained with a homogeneous and a heterogeneous catalyst may be due to the stronger interaction of the catalyst surface with the MVE than with the

2-chloroethyl vinyl ether. If the counterion is a simple charged particle, 2-chloroethyl vinyl ether should easily form a complex with the counterion since it is a monomer with a weak electron-donating alkyl group. However, the copolymer contains more MVE than 2-chloroethyl vinyl ether units although the electron-donating ability of the alkyl group of MVE is higher. This fact suggests that the counterion in SA catalyst is not a simple negatively charged particle.

To elucidate the reaction mechanism in more detail, the factors which control the steric structure of an adding monomer were studied according in the same way, as presented in the previous paper.[7] In PMVE obtained with SA catalyst, α is smaller than unity and $\Delta\epsilon$ is negative. However, the plot of $\Delta\epsilon$ against polymerization temperature is not a straight line, although the experiment does not cover a wide range of temperature. Therefore, it is concluded that the steric structure of an adding monomer is not determined by the structure of the end unit and/or a penultimate unit in a growing chain end. We have to consider that the penultimate effect does not exist in the SA catalyst system, in spite of the fact that $\alpha < 1$.

As α is smaller than unity, of course, these results cannot be explained by the one-parameter model proposed by Bovey.[15] On the other hand, for a system where the configuration of the monomer is determined by the catalyst, a treatment based on the enantiomorphic catalyst sites model was proposed by Fueno et al.[8] In this model, each fraction of the three kinds of triads is expressed by persistence probability σ_2, as shown by eqs. (1)–(3).

$$I = 1 - 3(\sigma_2 - \sigma_2^2) \tag{1}$$

$$S = \sigma_2 - \sigma_2^2 \tag{2}$$

$$H = 2(\sigma_2 - \sigma_2^2) \tag{3}$$

The triad tacticity measured by NMR spectra of PMVE which was soluble in nitromethane is summarized in Table II. From the observed values of the isotactic fraction, we can obtain the persistence probability σ_2. By using this value of σ_2, the triad syndiotactic and heterotactic fraction can be calculated from eqs. (2) and (3). The observed values of each fraction of the three kinds of triad were in surprisingly good agreement with the theoretical values calculated from the enantiomorphic catalyst sites model. As shown in Table II, the steric configuration of not only the unfractionated PMVE but also PMVE fractionated with methanol coincided with this model, and this fact suggests that the steric structure of all resultant PMVE was controlled by the same mechanism.

The steric configuration of PMVE obtained by metal halide catalysts cannot be applied to this model. As shown in Figure 8, the observed values for PMVE obtained with $BF_3 \cdot O(C_2H_5)_2$ do not agree with the theoretical curve calculated from the enantiomorphic catalyst sites model. Fueno et al. checked their theory by using the results of Brownstein

TABLE II

Tacticity of PMVE Obtained with $Al_2(SO_4)_3$–H_2SO_4 complex

Expt. no.	Polymerization conditions: Polymerization temperature, °C.	Polymerization conditions: Conversion, %	Observed tacticity: I, %	Observed tacticity: H, %	Observed tacticity: S, %	Calculated from Bovey model: σ_1	Calculated from Bovey model: H, %	Calculated from Bovey model: S, %	Calculated from enantiomorphic model[4]: σ_2	Calculated from enantiomorphic model[4]: H, %	Calculated from enantiomorphic model[4]: S, %
1[a]	0°C.	50%	50.7	32.5	16.8	0.712	41.0	8.3	0.793	32.8	16.4
2[a]	−10	3	69.9	21.0	9.1	0.836	27.4	2.7	0.887	20.0	10.0
3[a]	−10	9	54.2	30.7	15.1	0.736	38.8	7.0	0.812	30.5	15.3
4[a]	−10	20	55.8	29.2	15.0	0.747	37.8	6.4	0.821	29.4	14.7
5[a]	−20	9	59.6	27.2	13.2	0.772	35.2	5.2	0.840	26.9	13.4
4-1	MeOH-soluble portion (at 0°C.) of No. 4		45.5	36.0	18.5	0.675	43.9	10.6	0.761	36.4	18.2
4-2	MeOH-insoluble portion (at 0°C.) of No. 4		67.5	22.1	10.4	0.882	29.3	3.2	0.876	21.7	10.9

[a] [Cat] = 0.4 g./100 ml., $[M]_0$ = 20 vol.-%; solvent, toluene.

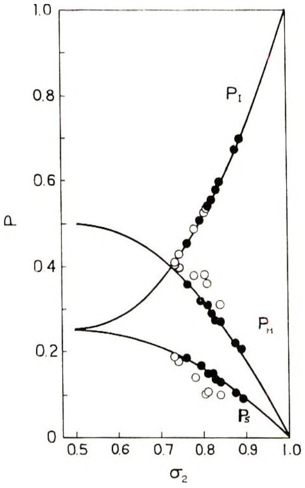

Fig. 8. Relationship between σ_2 and tacticity of poly(methyl vinyl ether) with various catalysts: (●) $Al_2(SO_4)_3$–H_2SO_4 complex, toluene; (○) $BF_3 \cdot O(C_2H_5)_2$, toluene. Curves: theoretical values calculated from the enantiomorphic catalyst sites model.

et al.[16] However, it could not be clearly concluded what system their theory can be applied to, as there were few experimental results. From our experimental results, it is conclusively confirmed that the steric structure of adding monomer in the presence of SA catalyst is controlled only by a catalyst site.

This conclusion of the statistical treatment coincides with other experimental results (Figs. 4 and 7) which confirm that the adding monomer was adsorbed on the catalyst surface before the bond formation of monomer with a growing chain end. It is very important that different factors control the polymer configuration even in the polymerization of the same monomer if different catalyst systems are used.

The authors thank Drs. Chujyo and Sato of Toyo Spinning Co. Ltd. for the measurement and the discussion of NMR spectra.

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Résumé

En utilisant le complexe acide sulfurique/sulfate d'aluminium (catalyseur SA) comme catalyseur, du poly(méthylvinyl éther) (PMVE) hautement cristallin fut fabriqué dan le toluène dans un domaine de température de 0° à 20°C. On a trouvé par spectre NMR que ces polymères contenaient des fractions de triade isotactique à plus de 50% et que le point de fusion d'un polymère non fractionné était environ 130°C. Cependant, du PMVE contenant une grande quantité de fraction isotactique était insoluble dans le nitrométhane dès lors la tacticité de la triade du PMVE hautement cristallin n'a pas pu être déterminée quantitativement. Le poids moléculaire du PMVE augmente avec l'augmentation de la conversion et de la température de polymérisation. Ce comportement est différent de celui ou le catalyseur est un halogénure métallique. De même la stéréorégularité du PMVE décroît avec l'accroissement de la concentration en monomère. Cependant l'addition d'un solvant polaire et l'élévation de la température de polymérisation affecte à peine la stéréorégularité du polymère. L'accroissement de la fraction isotactique à une haute concentration en catalyseur et la différence de composition en monomère dans la copolymérisation du méthyl vinyl éther avec le 2-chlorométhyl vinyl éther par catalyse SA par rapport à celle obtenue par $BF_3 \cdot O(C_2H_5)_2$ suggère que l'absorption du MVE sur la surface du catalyseur est une étape importante dans l'étape de propagation par catalyse SA. La fraction de tacticité des triades calculée à partir du modèle des sites du catalyseur énanthiomorphe coincidait avec les résultats expérimentaux. Ce fait montre que la structure stérique d'un monomère ajouté est déterminé uniquement par la nature d'un catalyseur ne respectant pas la nature d'une fin de chaîne en croissance. Il est conclu conjointement avec les résultats des publications précédentes que le facteur complétement différent peut contrôler la structure stérique d'un polymère résultant même dans le monomère en utilisant les différents catalyseurs.

Zusammenfassung

Mit dem Schwefelsäure-Aluminiumsulfatkomplex (SA-Katalysator) als Katalysator wurden in Toluol im Temperaturbereich von 0° bis −20°C hochkristalline Polymethylvinyläther (PMVE) hergestellt. NMR-spektroskopisch wurde festgestellt dass diese Polymeren die isotaktische Triadenfraktion zu mehr als 50% enthalten; der Schmelzpunkt des unfraktionierten Polymeren lag bei etwa 130°C. Da jedoch PMVE mit einem hohen Gehalt an isotaktischer Fraktion in Nitromethan unlöslich war konnte die Triadentaktizität von hochkristallinem PMVE nicht quantitativ bestimmt werden. Das Molekulargewicht von PMVE nahm mit steigendem Umsatz und steigender Polymerisationstemperatur zu. Dieses Verhalten unterscheidt sich von demjenigen bei Metallhalogenidkatalysatoren. Weiters nahm die Stereoregularität von PMVE mit steigender Monomerkonzentration ab. Der Zusatz eines polaren Lösungsmittels und die Erhöhung der Polymerisationstemperatur hateen jedoch kaum einen Einfluss auf die Stereoregularität des Polymeren. Die Zunahme der isotaktischen Fraktion bei hoher Katalysatorkonzentration und der Unterschied in der Zusammensetzung der mit dem

SA-Katalysator und der mit $BF_3 \cdot O(C_2H_5)_2$ erhaltenen Methylvinyläther- 2-Chloräthyläthercopolymeren sprechen dafür dass die Adsorption von MVE an der Katalysator-oberfläche einen wichtigen Schritt bei der Wachstumsreaktion mit dem SA-Katalysator bildet. Der aus dem Modell der enantiomorphen Katalysatorplätze berechnete Bruchteil an Triadentaktizität fällt mit den Versuchsergebnissen zusammen. Dieser Umstand beweist, dass die sterische Struktur eines sich addierenden Monomeren nur durch die Natur des Katalysators bestimmt ist und die Natur des wachsenden Kettenendes keinen Einfluss hat. Zusammen mit den Ergebnissen der früheren Arbeit kommt man zu dem Schluss, dass auch beim gleichen Monomeren bei Verwendung verschiedener Katalysatoren völlig verschiedene Faktoren die sterische Struktur des entstehenden Polymeren bestimmen können.

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Pulse Radiolysis Studies of Styrene

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Synopsis

We have applied the pulse radiolysis technique of studying short-lived, radiation-produced intermediates to a study of pure, dry liquid styrene. We have observed at least three distinct species. The most rapidly decaying species ($\tau_{1/2}$ = 4 μsec., $\lambda_{\max}$ ≈ 370 mμ) exhibits an apparent first-order decay which is slowed down in the presence of dry oxygen, occurs too rapidly to be measured in the presence of water, and has a temperature coefficient of approximately 1 kcal./mole between 25 and 45°C. We have tentatively identified the species as the styryl anion with a G value for formation of approximately 0.15. A second species ($\tau_{1/2}$ = 220 μsec. $\lambda_{\max}$ ≈ 320–330 mμ) exhibits a first-order decay which appears to be independent of oxygen and water. From its spectrum, we have tentatively identified it as the styryl radical. The third species ($\lambda_{\max}$ ≈ 310 and 320 mμ) is relatively stable in the dark, but is readily photolyzed by the analyzing light of the usual experimental set-up for pulse radiolysis studies. The formation of this species appears to be independent of the water and oxygen content of the styrene.

INTRODUCTION

In the past few years the pulse radiolysis technique has proved to be a powerful tool in the investigation of radiolytic processes.[1] The technique has been applied in detail mainly to aqueous systems; however, the absorption spectra of radicals, ions, and excited species have also been observed in pure organic compounds. The technique should be applicable to and provide information of radiolytic processes in the radiation-induced polymerization of vinyl monomers.

We have chosen styrene as a test study as it can be polymerized by free radicals, anions, and cations, and the spectrum of the styrene negative radical ion has been reported in the literature.[2–5] Two of us (D. J. Metz and R. C. Potter) are also presently engaged in a detailed study of the γ-radiation-induced polymerization of this monomer, and we have studied the effects of various additives such as oxygen and water on the observed polymerization kinetics.[6,7]

EXPERIMENTAL

Sample Preparation

Styrene was purified by a procedure already given in detail elsewhere.[7,8] The method of sample preparation is also identical, except that the sample holder, (Fig. 1), was either substituted for the dilatometer used in kinetic studies or mounted in parallel with a dilatometer. Basically, the preparative scheme is to fill a reaction vessel which has been previously baked at 500°C. under a vacuum of 10^{-8}–10^{-9} torr for 24–36 hr. with monomer which has been distilled through a 6-ft. packed column at reduced pressure under a blanket of dry helium. The monomer, after degassing, is dried over silica gel, which is in a vessel between the distilled monomer and the reaction vessel and which has been subjected to the same baking operation as the reaction vessel.

Figure 1 shows the arrangement of the final sample holder. All of the glassware, with the exception of the irradiation chamber, was of Pyrex brand glass. The cylindrical, 4-cm. long, irradiation cell (A) is made of Supracil fused quartz and is connected to the remainder through a graded

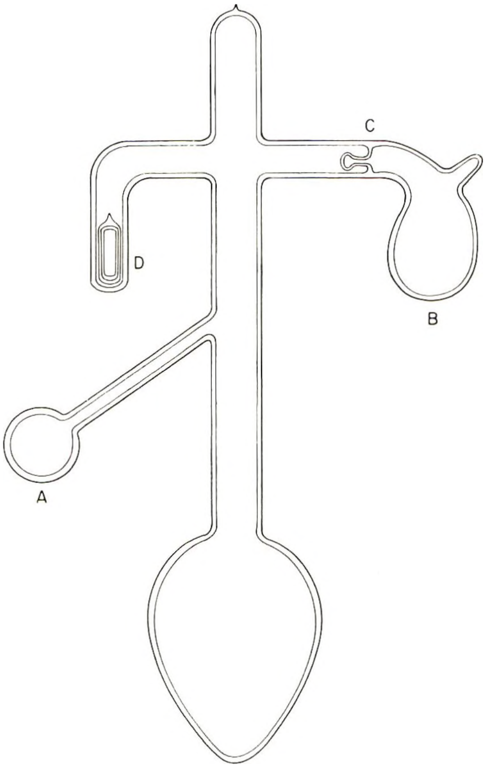

Fig. 1. Sample vessel for pulse radiolysis studies: (A) (quartz) irradiation cell; (B) side arm (optional) containing additive; (C) glass breakseal; (D) glass-encased magnetic hammer.

seal. The bulb on the side arm, labeled (B), is isolated from the sample by the breakseal (C), and can contain a known amount of an additive. Addition of the "impurity" is accomplished by manipulation of the glass encased soft iron "hammer" (D) with a strong magnet.

Pulse Radiolysis

The pulse radiolysis apparatus has been described,[1,9] and here it suffices to briefly outline the procedure, with reference to the schematic diagram (Fig. 2). The sample cell is irradiated by a 1.0-μsec. pulse of 15-M.e.v., electrons from the Argonne linear accelerator. An analyzing light beam, from a high-pressure xenon lamp, passes twice through the cell, giving an effective path length of 8 cm., and then to a Bausch and Lomb monochromator. The wavelength selected by the monochromator is monitored by a 1P28 photomultiplier tube. The signal from the phototube is amplified and displayed on a Tektronix 555 oscilloscope. The species produced during the radiolysis absorb a portion of the analyzing light causing a change in the output of the photomultiplier tube, the change being registered by the shape of the oscilloscope trace. These traces are photographically recorded on Polaroid 3000 ASA film.

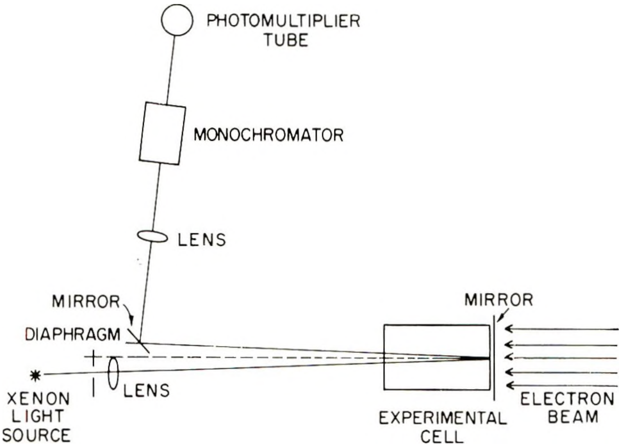

Fig. 2. Schematic diagram of components used in pulse radiolysis studies.

The photographs are enlarged and subjected to analysis as described below.

Dosimetry

Dosimetry was performed by the direct observation of I_2^- formed radiolytically in $10^{-3}M$ aerated aqueous potassium iodide solution in a cell identical to that used for styrene. Previous studies on this system have established that I_2^-, with a radiolytic yield $G_{I_2^-} = 2.40$, has an extinction coefficient of 14,000 at 385 mμ. The dose received by the styrene samples was 91% of that measured by I_2^- due to the greater electron density of the aqueous iodide solution.

EXPERIMENTAL RESULTS

Decay Curves

Figure 3 illustrates the oscilloscope tracings of the transients observed in the pulse radiolysis of pure, dry styrene. The decay processes observed may be conveniently divided into three time regions. Figure 3*a* shows a decay over a period of 70 μsec.; Figure 3*b* shows a further decay over 1 msec., leading to a permanent absorption which, under favorable conditions, can last for minutes.

Initial Decay over 30 μsec. The premise is made that the initial absorption consists of three distinct absorbing species with different rates of

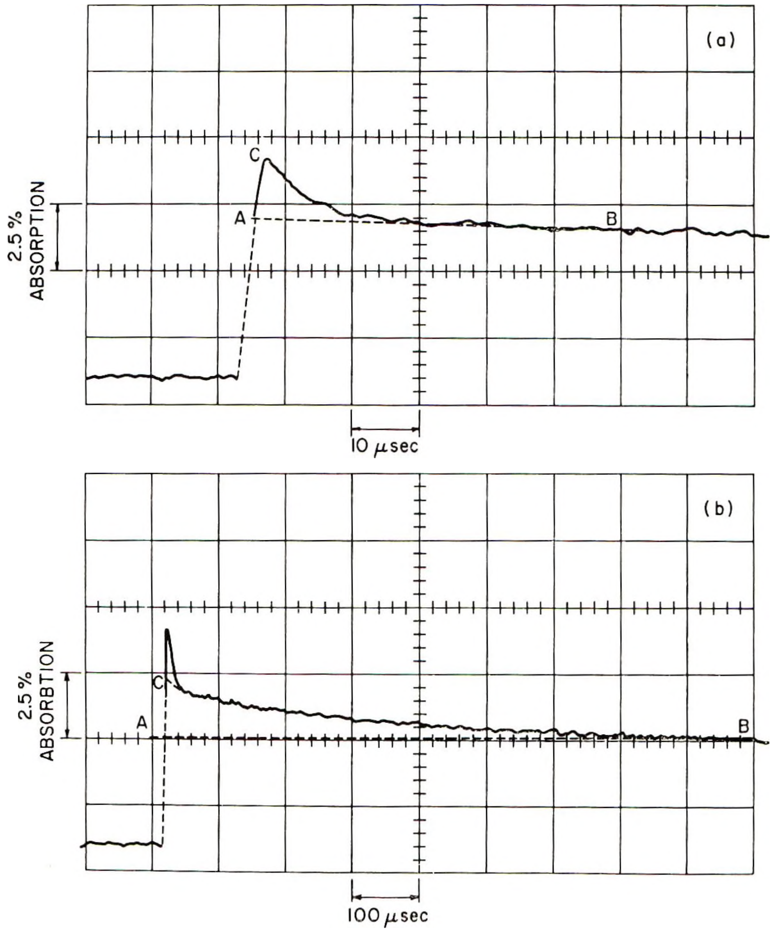

Fig. 3. Decay curves in pulsed pure styrene measured at 350 mμ: (*a*) at 10 μ sec. per scale division; (*b*) at 100 μ sec. per scale division.

decay. Hence, the initial decay in Figure 3*a* is obtained by extrapolating the flat portion of the trace at *B* back to *A*, thereby making *AB* the base line for the curve *ACB*. The displacement of the curve *CB* from line *AB*

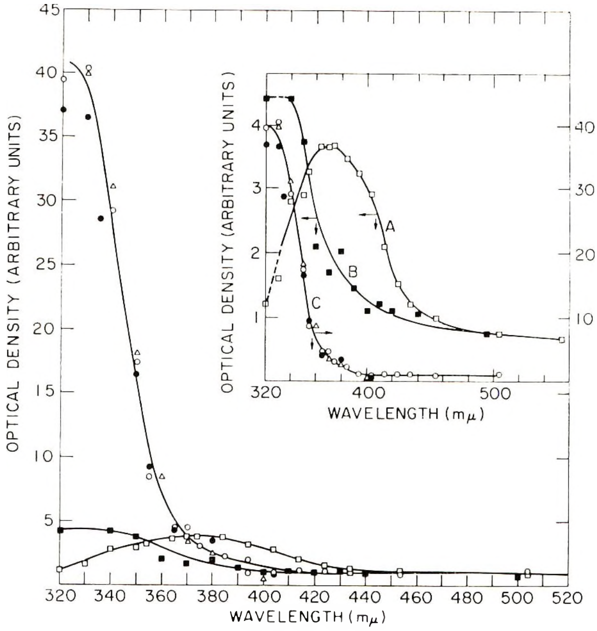

Fig. 4. Spectra of species observed in pulse radiolysis of styrene: (○, □, △) pure dry styrene; (●, ■) styrene saturated with water.

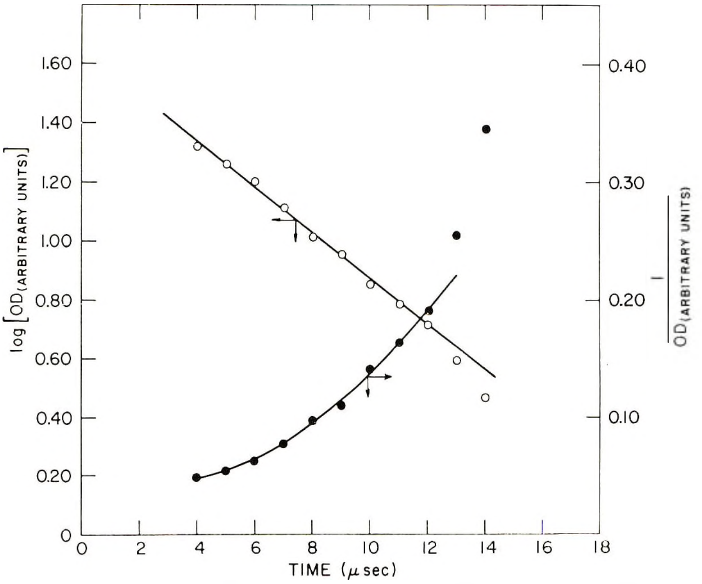

Fig. 5. Analysis of decay of short-lived species in pulse radiolysis of pure styrene: (○) first-order; (●) second-order.

at any time, t, is I_t', proportional to the intensity of absorbed light. Thus, if I_0 is the initial light intensity, the optical density of the solution is given by

$$\mu = \text{Optical density} = \log\,[I_0/(I_0 - I_t)]$$

Based on this procedure, the spectrum of this rapidly decaying species is shown in curve A of Figure 4. The rate of decay of this species measured at 350 mμ fits a first-order kinetic plot, shown in Figure 5, with a half life of approximately 4 μsec.

Decay over 0.5 msec. Following the same rationale and procedure as above, curves such as Figure 3*b* can be analyzed to reconstruct the spectrum of this species. This spectrum is shown as curve B in Figure 4, and the decay of this species measured at 350 mμ is best represented by a first-order plot with an apparent half life of approximately 220 μsec., as shown in Figure 6.

Permanent Absorption

When the permanent absorption, indicated at the end of curves such as shown in Figure 3*b*, is plotted versus wavelength, the spectrum labeled C in Figure 4 results. A slow decay of this species, over seconds, can be observed, but it is due to photolysis of the species in the highly intense analyzing light. Under lower light levels, the absorption lasted for several minutes.

It is possible to produce the same absorption by the much lower intensity ^{60}Co γ-radiolysis of styrene. The spectrum obtained after absorption

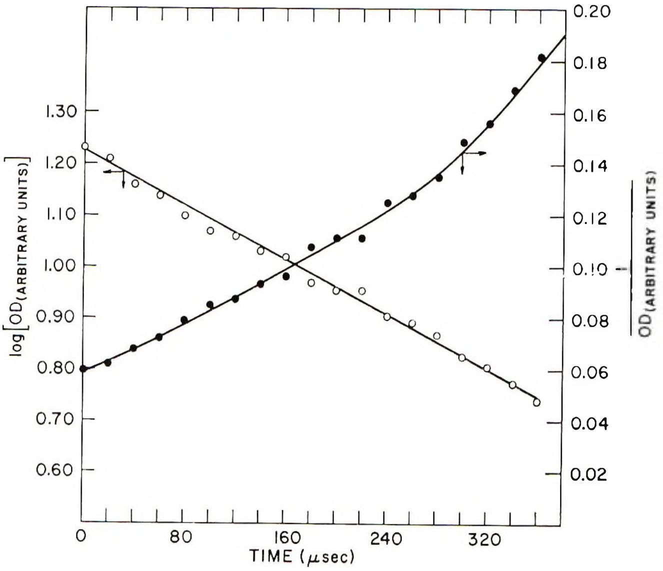

Fig. 6. Analysis of decay of intermediate species in pulse radiolysis of pure styrene: (○) first-order; (●) second-order.

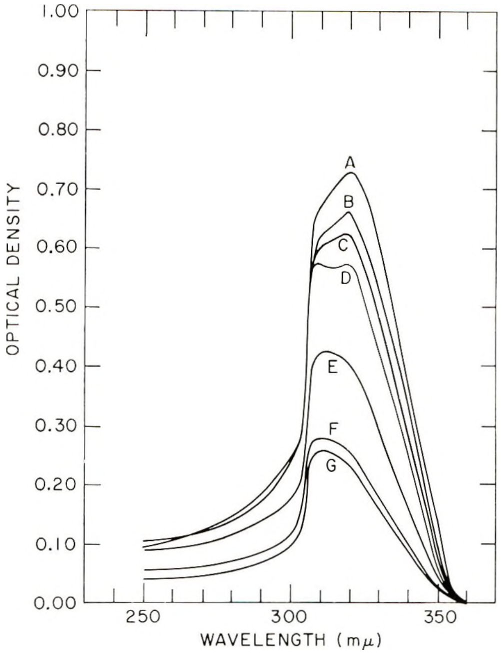

Fig. 7. Spectrum observed in γ-irradiation styrene (open to the atmosphere) and its change on standing in the dark at room temperature: (*A*) 4 min.; (*B*) 10 min.; (*C*) 20 min.; (*D*) 30 min.; (*E*) 1 hr. 30 min.; (*F*) 8 hr. 42 min.; (*G*) 26 hr. Dose, 35×10^4 rad, delivered at 7.75×10^6 rads/hr.

of approximately 350 Krad in a 7.75 Mrad/hr. cobalt source in air and water saturated styrene is shown in Figure 7. Also shown is the decay of the spectrum over a period of 26 hr. These spectra were obtained by using a Beckman DK-2 recording spectrophotometer, and the data are corrected for differences in cells used for irradiated styrene and a blank styrene sample. The light from the hydrogen lamp source was not allowed to illuminate the samples other than during a spectral run.

Effects of Additives

Nitrous oxide, introduced at a pressure of approximately $^1/_5$ atm., appears to have no effect on either the permanent absorption nor on the transients decaying over 30 μsec. and 0.5 msec. This behavior was noted in both bulk styrene and $10^{-3}M$ solutions of styrene in cyclohexane.

Oxygen, introduced at a pressure of approximately $^1/_5$ atm., does not appear to have any effect on the permanent absorption or the intermediate decay, over 0.5 msec. However, oxygen does seem to have an effect on the very short-lived species, as can be seen from Figure 8, in that the presence of oxygen appears to modify the initial height of the absorption, and also its decay rate. The curves in Figure 8*a* and 8*b* were analyzed as described above, and the rates of decay measured at 370 mμ are shown in Figure 9. In the absence of oxygen, the half life is the same as was reported above, approximately 4 μsec. In the presence of oxygen, there is an apparent change in behavior, and the decay rate shows a first-order half life of approximately 11 μsec.

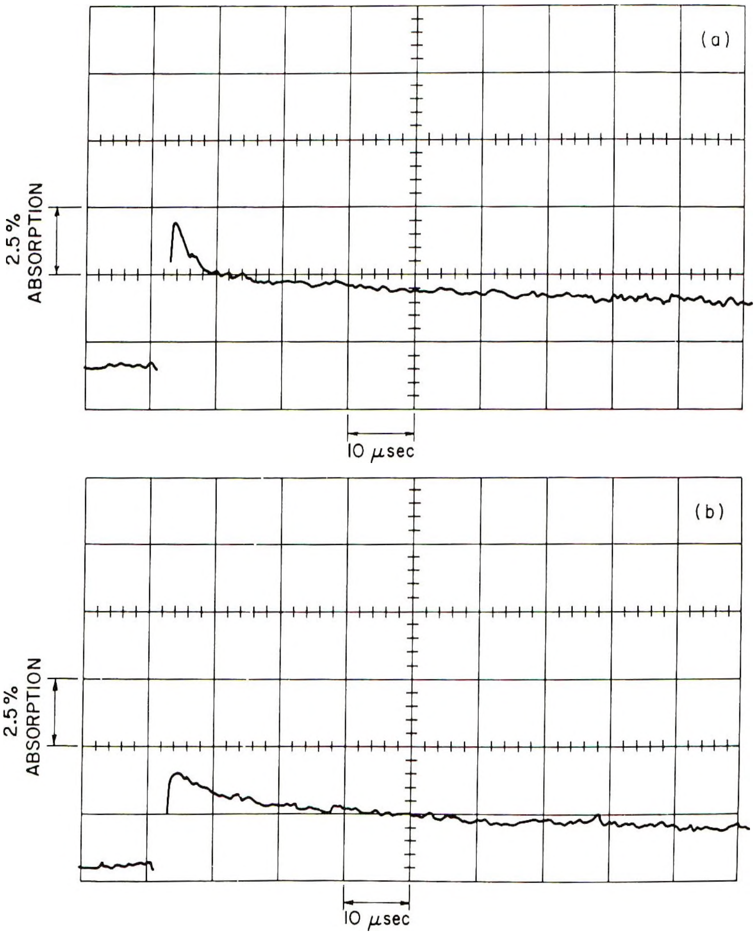

Fig. 8. Decay curves in pulsed styrene measured at 370 mμ: (*a*) pure styrene; (*b*) oxygen added.

Water has a most dramatic effect on the very short-lived species. Styrene saturated with water shows absolutely no very short-lived species, while the behavior of the intermediate species and the permanent absorption are unaffected. In addition, we have noticed that occasionally a sample that is presumably dry will also exhibit the absence of this very short-lived species. This behavior we attribute to minute traces of water impurity.

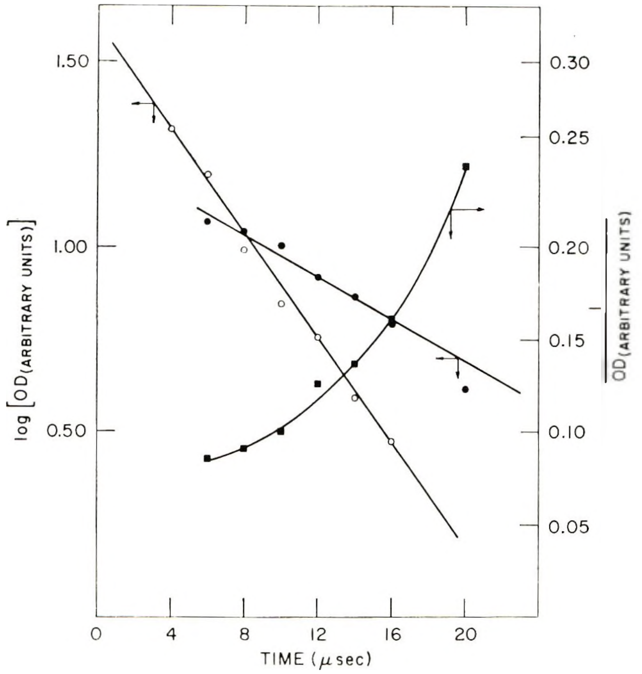

Fig. 9. Analysis of decay of short-lived species in styrene before and after addition of oxygen: (○) pure styrene, first-order; (●) after oxygen addition, first-order; (■) after oxygen addition, second-order.

Effect of Temperature

We have observed the decay rate of the very short-lived species at 25 and at 45°C. The relative rates of decay over this temperature differential, based on first-order kinetics, leads to an apparent temperature coefficient of approximately 1 kcal./mole.

DISCUSSION

At least three distinct species are produced in the radiolysis of styrene. These species are distinguishable by their rates of decay, their relative sensitivities to water and oxygen, and by their absorption spectra.

The shortest-lived species has a spectrum with a maximum around 370 mμ. Its sensitivity to water suggests that it may be an ion. The absorption spectrum of the negative ion-radical of styrene has been observed in low-temperature γ-ray irradiation of organic glasses containing styrene, and a maximum absorption of 400 mμ is reported.[4] The same workers attribute a maximum absorption at 460 mμ to the (styrene)$^+$ radical-ion. Tetrahydrofuran and dioxane solutions of the alkali metal salts of styrene, which lead to the formation of "living" polymer chains wth terminal (styrene)$^-$ ends are brilliantly colored and give an absorption spectrum with a maximum between 335 and 345 mμ, depending on counterion and solvent.[5] Similar results have also been reported by Bywater et al.[3] On the other hand, Kuwata reports[2] a spectrum for the sodium salt of "living" polystyrene in toluene which shows two absorption peaks, one at 510 mμ and another at approximately 370 mμ.

Recently, Katayama[10] has reported a transient in pure, dry α-methylstyrene ($\lambda_{\max} = 350$) and ascribed it to the $(\alpha\text{-MS})^-$ carbanion-radical.

The normal carbonium ion of styrene, formed by proton addition, has been reported to have an absorption spectrum exhibiting a broad maximum at 435 mμ[11] and 430 mμ,[12] where most of the phenyl-substituted ethylene carbonium ions absorb. In 1,1-diphenylethylene an additional band appears at 600 mμ in weakly acidic media, which has been attributed[13] to the $(\text{styrene})^+$ carbonium ion-radical, formed by oxidation of the hydrocarbon.

Basing our judgment on these assignments, we suggest that the species with the spectrum (curve *A*) in Figure 2 is $(\text{styrene})^-$ formed through electron capture by a styrene molecule. This view is further supported by our observation that in a $10^{-3}M$ solution of styrene in cyclohexane there is formed a very short-lived species which is extremely sensitive to water and whose spectrum is very similar to curve *A*, Figure 2, except, perhaps, slightly shifted to a higher wavelength.

If we accept, for the moment, this tentative assignment, it is instructive to calculate the radiolytic yield of $(\text{styrene})^-$, $G(\text{styrene}^-)$. At a dose rate of 1.32×10^{20} e.v./l. pulse (1.0 μsec./pulse), based on $G_{\text{I}_2^-} = 2.4$ (See section on dosimetry), we measure an initial optical density for the fast decaying component of 0.026 at 370 mμ. This optical density μ is given by

$$\mu = \epsilon c d = 0.026$$

where c is the molar concentration of the absorbing species and d is the light path length through the cell (8.0 cm.). In addition,

$$c = \frac{\text{Dose rate} \times G}{100 \times 6.02 \times 10^{23}} = 2.2 \times 10^{-6} G$$

Therefore,

$$G\epsilon \times 2.2 \times 10^{-6} \times 8 = 0.026$$

and

$$G\epsilon = 1.5 \times 10^{3}$$

Taking $\epsilon_{(\text{styrene}^-)}$ as approximately 1.0×10^4, a value consistent with those in the literature,[8,9] we find

$$G_{(\text{styrene}^-)} \approx 0.15$$

The species decaying over the time interval of several hundred microseconds can be tentatively identified as a radical. It has an absorption maximum at approximately 320–330 mμ and is unaffected by the presence of even large amounts of water. An absorption maximum at approximately 320 mμ has been reported[14] in the γ-irradiation of α-bromoethylbenzene in methyltetrahydrofuran glass, and attributed to the radical $C_6H_5—\dot{C}H—CH_3$. Also, Porter[15] has attributed an absorption maximum at 322 mμ to the same radical formed in the photolysis of ethylbenzene in frozen glasses.

Based on the previous dosimetry value of 1.32 × 10²⁰ e.v./l. per pulse, and a G value for radical formation in styrene of 0.35,[16] we calculate an instantaneous production of

$$1.32 \times 10^{20} \frac{\text{e.v.}}{\text{l.}} \times 0.0035 \frac{\text{radicals}}{\text{e.v.}} \times \frac{1 \text{ mole}}{6.02 \times 10^{23} \text{ radicals}}$$

$$\approx 7.7 \times 10^{-7} \text{ mole/l.}$$

The initial optical density of this intermediate species at 320 mμ is found to be 0.041. Thus, we would calculate an extinction coefficient for this species, assuming it to be a styryl radical, of

$$\epsilon = \frac{\mu}{cd} = \frac{0.041}{7.7 \times 10^{-3} \times 8} \approx 7. \times 10^{3}$$

The extinction coefficient given by Hamill[14] for the styryl radical in methyltetrahydrofuran glass is 12 × 10³. The agreement is reasonably good.

The decay of this species, however, exhibits two characteristics that are difficult to understand, if it is indeed a radical. In the first place, it appears to decay according to first-order kinetics. This behavior can be explained by assuming that it is undergoing a pseudo-first-order transformation to a species which absorbs outside of the spectral region covered in this investigation. More disturbing, however, is the apparent insensitivity of this species to oxygen. No explanation for this behavior can be offered on the basis of presently available experimental data.

The permanent absorption, which we have also observed in the pulse radiolysis of dilute solutions of styrene in cyclohexane, was found to behave in an unexpected fashion. We originally believed that we were observing the decay of a radical species over some tenths of seconds, until we found that the species is quite stable when the intensity of the analyzing light is either severely reduced or the light is turned off completely. In addition, as far as we can discern, water, oxygen, and nitrous oxide have no appreciable affect on its formation. Schneider and Swallow have also reported the observation of a long-lived species in the pulse radiolysis of styrene.[17]

Referring to Figure 7, it is apparent that the spectrum is composed of at least two overlapping peaks, with an apparent maxima at 320 mμ and at 310 mμ, the former showing a more rapid decay rate than the latter. It is not possible to specify the type of kinetics exhibited, but it is obvious that we are observing one or more species that decay, in the dark, over many hours. Similar to the behavior in the analyzing light of the pulse radiolysis samples, the spectrum is completely bleached after less than a 15-min. exposure to a mercury vapor lamp.

Electron spin resonance studies[18] have shown that substituted cyclohexadienyls are formed during the irradiation of polystyrene. It is possible that the permanent absorption observed in our studies is arising from a similar process. The details of the formation, decay, and identity of this absorption peak in irradiated styrene is presently under further investigation.

For the sake of comparison, it should be mentioned that we have also conducted a very preliminary investigation of α-methylstyrene, using the same method of purification and sample preparation as for styrene. In general, α-methylstyrene behaves quite similarly to styrene, in that it shows at least the same three general types of absorbing species at approximately the same wavelengths. A brief report on our findings were recently presented.[19] At the time of this presentation, we were not aware of the photolysis of the longest-lived species, and we interpreted our data incorrectly. One interesting correlation, however, is tentatively offered with respect to the findings of Katayama et al.[10] with this monomer. It was reported by Katayama that, upon admission of moist air, the transient species observed under dry conditions practically disappeared. In view of our findings, namely that water removes only the very short-lived species in α-methylstyrene, we were originally perplexed. Considering, however, the similarity in behavior between styrene and α-methylstyrene and our recent finding concerning the photolytic behavior of the long-lived species, Katayama's results in the presence of water are not surprising. These latter observations were recorded by using a photographic plate, which calls for very intense analyzing illumination. We suggest that the water removed the short-lived species and the longer-lived species was probably photolyzed during observation.

Finally, we would like to be able to correlate the data obtained by pulse radiolysis and both our own[6,7] kinetic data on the polymerization of styrene under these conditions of extreme purity and dryness, as well as similar studies made by Okamura.[20] Our kinetic results and, in regions where they overlap, also those of Okamura, can best be interpreted as indicative of one or more ionic polymerization processes, the relative amounts of which are governed by the concentration of water in the system. The mechanism which is tentatively under experimental scrutiny involves both cationic and anionic propagation. It has been somewhat disappointing, then, that the present study has not uncovered any species that can reasonably be suspected of being a carbonium ion, either normal or free radical.

Indeed, if anions are formed, and we have here tentatively identified the (styrene)$^-$ ion-radical, somewhere there must be positively charged species. If, as is suggested by the work of Leftin and Hall[13] the (styrene)$^+$ ion-radical might be expected to absorb at wavelengths >600 mμ, then our investigation sould be extended to this region of the spectrum. Experimental difficulties confined us, in this study, to wavelengths ≤ 600 mμ.

On the basis of decay times at several fixed wavelengths, Katayama[21] has recently reported the observation of a water-sensitive species in α-methylstyrene at 3663 and 5461 A., attributed to the radical-anion, and a water-insensitive species at 3663 A., ascribed to a radical. Our own spectral studies on styrene failed to show any indication of an absorbing species in the vicinity of 550 mμ. The observation of both a radical-ion and a free radical at lower wavelengths by Katayama agrees with our findings.

In conclusion, we believe that we have been able to identify at least three species in the pulse radiolysis of pure, dry styrene, which absorb between 310 and 550 mμ. The shortest-lived species is probably an ion and is partially responsible for the kinetics of polymerization observed under extremely dry conditions. Water completely removes this absorbing species in the pulse radiolysis study and, it has also been shown that addition of water to styrene exhibiting the novel ionic kinetics causes the kinetics to revert to the normal free-radical mechanism.[22] In addition, we have found in this study that oxygen does have some marked affect on this very short-lived species, which parallels the findings on the effect of adding oxygen to ultrapure, ultradry styrene.[22] We have tentatively identified the species with an absorption maximum at 370 mμ as the styrene radical-anion.

From its spectrum, the species decaying over a millisecond could be reasonably ascribed to a free radical. It does not however, show any sensitivity towards oxygen.

The longest-lived absorbing species is probably a relatively stable chemical species which is very readily photolyzed and which also shows a very slow thermal rate of decay at room temperature.

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Résumé

Nous avons appliqué la technique de radiolyse par pulsation pour l'étude d'intermédiaires à courte durée de vie produits par irradiation de styrène pur à l'état liquide. Nous avons observé au moins trois espèces distinctes. L'espèce, de durée de vie la plus courte, ($\tau_{1/2}$ = 5 microsecondes, $\lambda_{\max}$ = 370 mμ) montrait une disparition apparente du premier ordre qui diminuait en présence d'oxygène sec; elle se passe trop rapidement pour être mesurée en présence d'eau et présente un coefficient thermique d'environ 1 Kcal/mole entre 25° et 45°C. Nous avons tenté d'identifier la nature d'un ion styryle avec une valeur de *G* pour la formation d'environ 0.15. Une seconde espèce ($\tau_{1/2}$ = 220 microsecondes, $\lambda_{\max} \approx$ 320–330 mμ) manifestait une disparition du premier ordre qui était indépendante de la présence d'oxygène ou d'eau. Au départ de son spectre, nous avons essayé d'identifier le radical styryle. La troisième espèce ($\lambda_{\max} \approx$ 810 et 320 mμ) est relativement stable à l'obscurité mais est facilement photolysée par la lumière incidente utilisée au cours de l'expérience habituelle pour les études de radiolyse par pulsation. La formation de cette espèce apparaît être indépendante de la présence d'oxygène et d'eau du styrène.

Zusammenfassung

Das Pulse-Radiolyseverfahren zur Untersuchung kurzlebiger, strahlungserzeugter Zwischenprodukte wurde auf reines trockenes flüssiges Styrol angewedet. Es wurden mindestens drei verschiedene Spezies beobachtet. Die am raschesten verschwindende Spezies ($\tau_{1/2}$ = 5 Mikrosekunden, $\lambda_{\max}$ = 370 mμ) zeigt einen Abfall nach erster Ordnung, der durch Anwesenheit von trockenem Sauerstoff verlangsamt wird in Gegenwart von Wasser zu rasch ist, um gemessen zu werden und zwischen 25 und 45°C einen Temperaturkoeffizienten entsprechend etwa 1 Kcal/Mol besitzt. Diese Spezies wurde versuchsweise als Styrylanion mit einem Bildungs-*G*-Wert von angenähert 0,15 identifiziert. Eine zweite Spezies ($\tau_{1/2}$ = 220 Mikrosekunden, $\lambda_{\max} \approx$ 320–330 mμ) zeigt einen Abfall erster Ordnung, der von Sauerstoff und Wasser unabhängig zu sein scheint. Nach ihrem Spektrum wurde sie versuchsweise als Styrylradikal identifiziert. Die dritte Spezies ($\lambda_{\max} \approx$ 310 und 320) ist im Dunkeln verhältnismässig stabil, wird aber durch das Analysenlicht in der üblichen Versuchsanordnung für Pulse-Radiolyseuntersuchungen leicht photolysiert. Die Bildung dieser Spezies scheint von Wasser- und Sauerstoffgehalt des Styrols unabhängig zu sein.

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Polymerization of β-Isovalerolactone

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Synopsis

The polymerization of β,β′-dimethyl-β-propiolactone with various catalysts was investigated. A detailed study on the heterogeneous polymerization initiated by triethyl aluminum was carried out. A reaction mechanism is suggested on the basis of chemical analysis of the polymer.

INTRODUCTION

The polymerization of β-propiolactone (PL) has been extensively studied with acidic,[1,2] basic,[3,4] or organometallic catalysts.[5,6] The polymerization of α-substituted β-propiolactone with either tertiary amines or betaines as catalysts is also reported.[7] Only few papers have appeared on the polymerization of β-substituted β-propiolactones. Etienne and Fischer[8] report that the β-substitution in PL seems to decrease the melting point and the degree of polymerization of the polymers. We have studied the polymerization of β,β′-dimethyl-β-propiolactone (DMPL) with different catalytic systems. A more detailed investigation was carried out with triethyl aluminum as an initiator in order to clarify the polymerization mechanism.

EXPERIMENTAL

Reagents

Triethyl aluminum (Texas Alkyls Inc., Pasadena), 17.5% (w/v) in *n*-hexane, was used without further purification. Metal halides (C. Erba, Milan) were used without further purification. *n*-Hexane (C. Erba, Milan) was dried by refluxing for half an hour over phosphorus pentoxide, and then distilled; a fraction was collected at 68.7°C. Dioxane (C. Erba, Milan) was dried by refluxing for $^1/_2$ hr. over calcium hydride and then fractionally distilled. A fraction was collected at 102°C. Deoxygenated ($O_2 \leqslant 10$ ppm), anhydrous nitrogen was used. DMPL was obtained by allowing ketene to react with acetone.[9] The product was purified by several redistillations under high vacuum (b.p. 23.7°C./0.2 mm. Hg).

ANAL. Calc'd. for $C_5H_8O_2$: C, 60.0%; H, 8.0%. Found: C, 59.9%; H, 8.1%.

Heterogeneous Polymerization

DMPL was usually polymerized in the solid, crystalline state at temperatures below its melting point and in the presence of an inert suspending medium (*n*-hexane), in which the initiator was (at least partially) soluble. The solid-state polymerization at low temperatures was also employed by Okamura et al.[10] and Baccaredda et al.[11] This type of polymerization was necessary in our case since the monomer DMPL easily decomposes at room temperature to carbon dioxide and isobutene. The decomposition by acids can be very fast and explosive; this situation prevents the bulk polymerization at room temperature. A four-necked, 100-ml. flask, equipped with stirrer, Hg valve, nitrogen inlet, and rubber stopper for sampling, was dried by flaming under vacuum. To 50 ml. of *n*-hexane as suspending medium, 0.05 mole monomer and catalyst were added under nitrogen atmosphere and under stirring at the chosen polymerization temperature.

Analytical Determinations on Polymers Obtained by $AlEt_3$, Initiation

At the end of the polymerization analytical determinations were carried out on the polymers according to two different procedures.

Procedure A

The suspending medium was withdrawn with a syringe under nitrogen atmosphere. The residual polymer was washed twice with 10 ml. of *n*-hexane and was dissolved in anhydrous dioxane in a 50-ml. volumetric flask. From this solution samples were analyzed for total acidity, double bond content, aluminum content, and for ethyl groups of the initiator.

Total Acidity. A sample containing approximately 0.02–0.04 meq. of acid groups was used, which was diluted with diethyl ether (neutral to phenolphthalein) and titrated to phenolphthalein with 0.02*N* sodium hydroxide alcoholic solution.

Double Bond Content. The double bond content was determined either by hydrogenation (in glacial acetic acid, catalyst Pd 5% on coal) or by bromination. In the latter method, to a sample containing approximately 0.04–0.08 meq. double bonds, 5 ml. water was added with stirring in order to decompose residual unconverted monomer to isobutene and carbon dioxide.[9] After standing, the solution was diluted with 100 ml. of titration solvent, which had the following volumetric composition: glacial acetic acid, 81%; carbon tetrachloride, 15%; 5*N* sulfuric acid, 2%; mercuric chloride (10% in methanol), 2%. The solution thus obtained was cooled to 5°C. and titrated by constant current potentiometry with platinum electrodes, by using an aqueous 0.02*N* bromide–bromate solution.

Aluminum Determination. A sample of solution containing polymer and approximately 10–15 mg. of aluminum was added dropwise to a platinum cup containing 10 ml. of ethanol and 0.3 ml. of 36N sulfuric acid. The solvents were evaporated under an infrared lamp. The organic material was then decomposed at 500°C. The residual aluminum sulfate was weighed.

Determination of Ethyl Groups of the Initiator. The ethyl group content of the initiator was determined by measuring the ethane content of the gases evolved by decomposition of the sample with water. The polymer solution (1–2 ml.) was poured into a 20-ml. flask containing 10 ml. of sodium chloride in a saturated aqueous solution under a carbon dioxide atmosphere. The amount of evolved gases was determined with a nitrometer over potassium hydroxide solution. The mixture of gases was then analyzed by gas chromatography. A gas chromatographic apparatus, Model B (C. Erba), equipped with a 8-m. long column of γ-butyrrolactone on C-22 Celite at 20°C. was used; helium was the carrier gas.

Procedure B

After removal of the suspending medium, the bulk polymer was dissolved in 50 ml. of chloroform; the solution was then added to 700 ml. of methanol containing 3 ml. of 12N hydrochloric acid to dissolve the decomposed initiator; finally 120 ml. water was added dropwise. After a few hours the polymer was filtered, reprecipitated, and dried under vacuum. The conversion was obtained by weighing the dried polymer. The relative viscosity was determined at 25°C. in an Ostwald viscometer. Solutions containing 1% of polymer in chloroform were used. The molecular weights were determined at 37°C. in benzene solution with a Mechrolab vapor-pressure osmometer (Model 301A). Total acidity and terminal double bonds were determined as in Procedure A. Stability toward hydrolysis was determined according to Thiebaut et al.[12] Only 2% of the polymer underwent alkaline hydrolysis, showing a stability similar to that of poly(ethylene terephthalate). The observed melting point of the polymer (determined with a polarizing microscope) was about 60°C.

Infrared Spectra

Infrared spectra of poly(DMPL) were obtained with a Perkin-Elmer Model 21 spectrophotometer, equipped with NaCl prism. The band characteristic of esters at 1735 cm.$^{-1}$ was observed. The vibrations characteristic of —C—O— were observed in the range of 1150–1250 cm.$^{-1}$. The 1450 cm.$^{-1}$ band was assigned to the vibration of methyl group deformation, while the splitting at 1380 cm.$^{-1}$ indicated the presence of β-*gem*-methyl groups.

RESULTS AND DISCUSSION

The results of several polymerization runs with different initiators are reported in Table I. It may be observed that, whatever the initiator, low molecular weight polymers were obtained. Moreover, only cationic

TABLE I
Polymerization of DMPL with Various Initiators[a]

Run no.	Initiator: Nature	Initiator: Concentration, mole/100 mole DMPL	Temperature, °C.	Polymerization time, hr.	Conversion, %	η_{rel}
43	$SbCl_5$	2.5	−35	9	50	1.12
80	$SbCl_5$	2.5	−78	7	40	1.11
34	$SbCl_5$	5	−35	7	35	1.11
45	$SnCl_4$	2.5	−35	7	30	1.10
47	$SnCl_4$	5	−35	23	47	1.12
47a	$SnCl_4$	5	−40	6	36	1.12
49	$[CH_3CO]^+[SnCl_5]^-$	2.5	−35	10	30	1.11
42	$TiCl_4$	2.5	−35	23	42	1.10
42a	$TiCl_4$	2.5	−40	6	38	1.11
44	$[CH_3CO]^+[TiCl_5]^-$	2.5	−35	8	35	1.11
74	$TiCl_4/BuLi$	2.5/2.5	−35	20	No polymerization	
51	BF_3	2.5	−35	20	40	1.12
56	BF_3	1.25	−35	8	30	1.12

46	BF_3/H_2O	2.5/2.5	−35	21	12	1.09
86[b]	$[CH_3OCH_2]^+[AlCl_4]^-$	2.5	−35	21	38	1.12
57	$FeCl_3$	2.5	−35	20	39	1.12
76[c]	$[CH_3OCH_2]^+[FeCl_4]^-$	4	−35	21	40	1.10
158	FeF_3	3	−40	19	17	1.11
185	PF_5	3.6	−40	17	30	1.12
62[d]	$[CH_3CO]^+[ClO_4]^-$	0.1	−35	22	40	1.13
53[e]	$[CH_3CO]^+[ClO_4]^-$	0.1	−35	23	52	1.11
54[e]	$[CH_3CO]^+[ClO_4]^-$	0.5	−35	23	60	1.08
85	CF_3COOH	2	−40	15	20	1.10
20	BuLi	2.5	−35	23	No polymerization	
21[f]	BuLi	2.5	+20	22	No polymerization	
22	$N(C_2H_5)_3$	3	−35	18	No polymerization	
23[f]	$N(C_2H_5)_3$	3	+20	18	No polymerization	
17[f]	Betaine	3	+20	19	No polymerization	

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[a] Rate of stirring 350 rpm; suspending medium *n*-hexane.

[b] Molecular weight 3600.

[c] Molecular weight 3300.

[d] Initiator was used as 0.7% (w/v) nitrobenzene solution.

[e] Initiator was used as 1% (w/w) toluene solution.

[f] Bulk polymerization.

TABLE II
Effect of the Rate of Stirring on the Molecular Weight and Conversion[a]

Run no.	Initiator concentration, mole/100 mole DMPL	Rate of stirring, rpm	Conversion, %	η_{rel}
245	1.5	350	19	1.16
246	1.5	350	19	1.16
242a	5	350	77	1.13
243a	5	350	78	1.13
250	5	350	72	1.13
258a	5	200	42	1.14
250a	5	100	25	1.14
251	5	100	26	1.15

[a] Initiator $Al(C_2H_5)_3$; suspending medium n-hexane; temperature −40°C.; polymerization time 3 hr.; samples precipitated by adding 450 ml. of water.

TABLE III
Effect of Temperature on the Molecular Weight and Conversion[a]

Run no.	Initiator		Temperature, °C.	Conversion, %	η_{rel}	M.W.
	Nature	Concentration, mole/100 mole DMPL				
239a	$Al(C_2H_5)_3$	3	−110	40	1.15	—
239	"	5	−110	45	1.14	4500
221	"	5	−78	46	1.14	4500
227	"	5	−78	45	1.13	4200
230a	"	5	−40	47	1.14	—
249	"	5	−40	42	1.14	4300
254	"	5	−40	45	1.14	—
258	"	5	−40	39	1.14	—
270a	"	3	−40	41	1.16	—
240	BF_3	2.5	−110	47	1.13	—
51	"	2.5	−35	40	1.12	—

[a] Polymerization time 3 hr.; rate of stirring 350 rpm; suspending medium n-hexane.

initiators were found to be effective for polymerization; all anionic initiators failed to induce polymerization. This is in agreement with the electron-donating nature of the lactone molecule. In order further to investigate the cationic nature of DMPL polymerization, we carried out some experiments using $AlEt_3$ as an initiator.

$AlEt_3$ is very soluble in n-hexane at low temperatures and is well known to act as a cationic initiator of the polymerization of cyclic ethers.[13] Table II shows that the conversion and the molecular weight of the polymer are both dependent on the rate of stirring; it indicates better diffusion of the initiator into the monomer with increasing rate of stirring. For

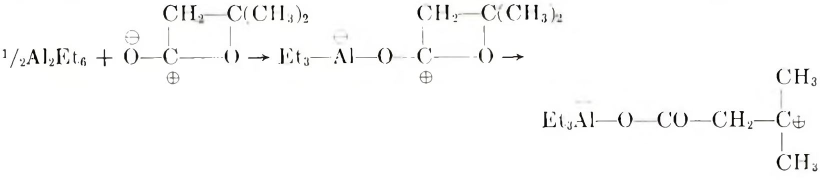
TABLE IV
Influence of Polymerization Time on the Molecular Weight and Conversion[a]

	Initiator					
Run no.	Nature	Concentration, mole/100 mole DMPL	Polymerization time, hr.	Conversion, %	η_{rel}	M.W.
224	$Al(C_2H_5)_3$	5	0.5	25	1.13	4000
228	"	5	0.5	28	1.14	—
229	"	5	1	40	1.14	—
266[b]	"	5	1	50	1.13	—
230	"	5	2	41	1.14	—
238	"	5	2	43	1.13	—
203	"	5	3	46	1.14	4500
208	"	5	3	41	1.15	4800
230a	"	5	3	47	1.14	—
249	"	5	3	42	1.14	4300
254	"	5	3	45	1.14	—
258	"	5	3	39	1.14	—
204	"	5	6	45	1.15	4900
205	"	5	9	48	1.14	4500
210	"	5	9	49	1.15	4850
47a	$SnCl_4$	5	6	36	1.12	—
47[c]	"	5	23	47	1.12	—
42a	$TiCl_4$	2.5	6	38	1.11	—
42[c]	"	2.5	23	42	1.10	

[a] Rate of stirring 350 rpm; temp. −40°C.; suspending medium *n*-hexane.
[b] Purified by one precipitation.
[c] Temperature −35°C.

this reason all the polymerization experiments were carried out at the fixed rate of stirring of 350 rpm. Tables III, IV, and V show, respectively, the effects of temperature, polymerization time, and $AlEt_3$ concentration on the conversion and on the molecular weight of the polymers. The temperature effect appears to be very small (Table III). This fact leads to the conclusion that the overall activation energy involved in the process is quite low. From Table IV it appears that both conversion and molecular weight reach a maximum value in a short time. After 3 hr. practically no further change in molecular weight and conversion is observed. For this reason most of the polymerization experiments were stopped after 3 hr. Finally it can be seen from Table V that conversion increases and molecular weight decreases with increasing initiator concentration.

On the basis of the cationic nature of $AlEt_3$ we can assume that the initiation of the DMPL polymerization occurs according to the reactions:



$$\tfrac{1}{2}\mathrm{Al_2Et_6} + \begin{array}{l}\quad\mathrm{CH_2{-}C(CH_3)_2}\\ \quad\,|\qquad\quad |\\ \overset{\ominus}{\mathrm{O}}{-}\underset{\oplus}{\mathrm{C}}{-\!-\!-}\mathrm{O}\end{array} \rightarrow \begin{array}{l}\qquad\qquad\quad\mathrm{CH_2{-}C(CH_3)_2}\\ \qquad\qquad\quad\,|\qquad\quad |\\ \mathrm{Et_3{-}\overset{\ominus}{Al}{-}O{-}\underset{\oplus}{C}{-\!-\!-}O}\end{array} \rightarrow \mathrm{Et_3\overset{-}{A}l{-}O{-}CO{-}CH_2{-}}\overset{\displaystyle \mathrm{CH_3}}{\underset{\displaystyle \mathrm{CH_3}}{\overset{|}{\underset{|}{\mathrm{C}^{\oplus}}}}} \qquad (1)$$

TABLE V

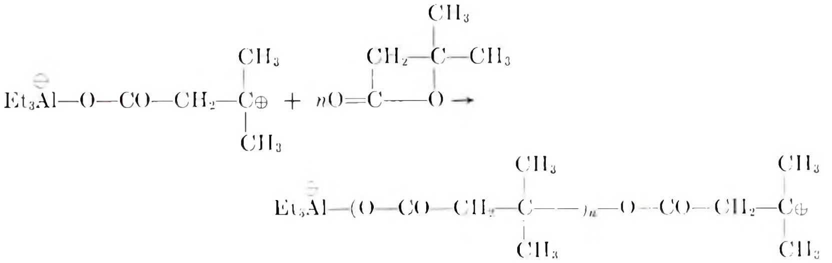
Influence of $Al(C_2H_5)_3$ Concentration[a]

Run no.	Initiator concentration, mole/100 mole DMPL	Conversion, %	η_{rel}	M.W.
234	1.5	16	1.18	—
234a	1.5	15	1.17	—
245[b]	1.5	19	1.16	—
246[b]	1.5	19	1.16	—
269	1.5	22	1.18	6650
233	1.5	36	1.16	—
233a	3	38	1.15	—
270	3	41	1.16	—
270a	3	41	1.16	—
203	5	46	1.14	4500
208	5	41	1.15	4800
230a	5	47	1.14	—
249	5	42	1.14	4300
254	5	45	1.14	—
258	5	39	1.14	—
241	7	60	1.12	4000

[a] Temperature −40°C.; rate of stirring 350 rpm; polymerization time 3 hr.; suspending medium *n*-hexane.

[b] Precipitated by adding 450 ml. of water.

This scheme involves a DMPL ring cleavage at the alkyl–oxygen bond according to Liang and Bartlett.[14] For the propagation step we can write eq. (2):



(2)

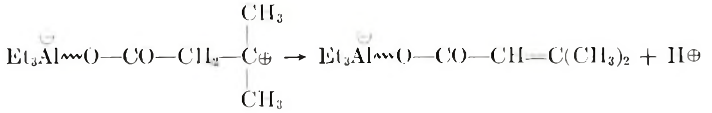
where the growth of macromolecular chains is due to the tertiary carbon ion. The fact that chemical analysis shows that in every macromolecule one aluminum atom corresponds to one carboxyl group (Table VI) lends support to eqs. (1) and (2). The mechanism of eqs. (1) and (2), indicating large charge separation, is certainly incorrect for the cationic polymerization of olefins; however, in our case, there is a possibility of a stable cyclic configuration of the growing macromolecule, due to chain flexibility about the carbon–oxygen bond, as suggested by Plesch[15] for the cationic polymerization of formaldehyde. Moreover, it is probable that the dielectric constant of the monomer medium could allow some charge separation of the ion pair.

TABLE VI
Runs Analyzed by Methods Described in Procedure A[a]

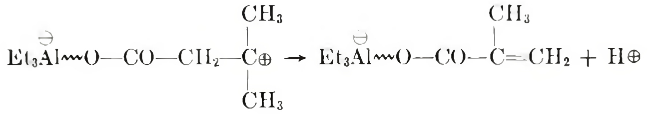
Run no.	Aluminum, mole × 10^3	—COOH groups, mole × 10^3	Double bonds, mole × 10^3		Ethane, mole × 10^3	Molar ratio ethane/aluminum
			Br_2	H_2		
259	1.6	1.9	1.3	1.4	3.2	2.00
260	1.3	1.6	0.8	0.9	2.4	1.85
260a	1.8	2.1	1.6	1.7	3.7	2.06
260b	1.4	1.6	1.0	0.9	2.7	1.93

[a] Suspending medium *n*-hexane; rate of stirring 350 rpm; polymerization time 18 hr.; temperature −40°C.; initiator concentration, 5 mole/100 mole DMPL; DMPL 0.05 mole.

Similar mechanisms were advanced by Colclough and Wilkinson[13] for the cationic polymerization of propylene oxide with $(CH_3)_3Al$ as catalyst and by Kern and Jaaks[16] for the cationic polymerization of trioxane with BF_3. The termination step must involve a charge recombination and, in agreement with the terminal groups experimentally found, we can postulate the termination mechanism shown in eqs. (3a) and (3b).



$$\mathrm{Et_3\overset{\ominus}{Al}\sim O{-}CO{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}\oplus \rightarrow Et_3\overset{\ominus}{Al}\sim O{-}CO{-}CH{=}C(CH_3)_2 + H\oplus} \tag{3a}$$



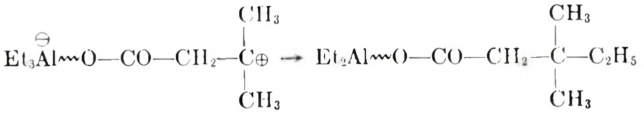
$$\mathrm{Et_3\overset{\ominus}{Al}\sim O{-}CO{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}\oplus \rightarrow Et_3\overset{\ominus}{Al}\sim O{-}CO{-}\overset{CH_3}{C}{=}CH_2 + H\oplus} \tag{3b}$$

In our opinion, reaction (3a) is more probable, owing to conjugation of double bond with the carbonyl group; furthermore, the protonation of terminal —CH_2— is favored by the adjacent ester group.

The protons formed in reactions (3a) and (3b) can react as shown in eq. (4) with consequent ethane evolution.

$$\mathrm{Et_3\overset{\ominus}{Al}\sim + \overset{\oplus}{H}\rightarrow \rightarrow C_2H_6 + Et_2Al\sim} \tag{4}$$

However, not all the polymeric chains terminate with double bonds (Table VI). Therefore we can propose, as a hypothesis, that the remaining macromolecules are terminated by the reaction (5)



$$\mathrm{Et_3\overset{\ominus}{Al}\sim O{-}CO{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}\oplus \rightarrow Et_2Al\sim O{-}CO{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{C}}{-}C_2H_5} \tag{5}$$

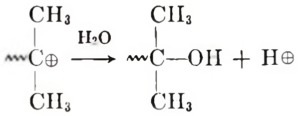
in agreement with the fact that we have found an ethane/aluminum molar ratio of 2 (Table VI).

In our opinion, reaction (5) can occur owing to the low stability of the Al complex with coordination 4 which tends to be transformed into a more stable trivalent form by splitting of an ethyl anion.

Unfortunately we were not able to follow ethane evolution during the polymerization in order to determine quantitatively the ratio between the two termination reactions (4) and (5). In fact, the presence of $AlEt_3$ in the suspending medium prevented chromatographic analysis.

The other endgroups which were determined in polymer samples are carboxyl groups (procedure B). These are formed by hydrolysis of $>\!Al{-}O{-}CO{-}$ which is itself formed in the postulated initiation step. However, it was impossible to show in purified polymer that every macromolecule is terminated with a carboxyl endgroup. In fact, aqueous acid methanol can partially esterify carboxyl groups[2,17] and the degree of esterification changes on standing.

Hydroxyl groups, which might be formed in a termination reaction of polymeric chains with adventitious moisture [eq. (6)]



$$\sim\!\overset{CH_3}{\underset{CH_3}{C}}{}^{\oplus} \xrightarrow{H_2O} \sim\!\overset{CH_3}{\underset{CH_3}{C}}{-}OH + H^{\oplus}$$

have not been detected either by chloroformate[18] or by infrared spectroscopy. The literature contains evidence of terminal hydroxyl groups in the polymerization of unsubstituted propiolactone[1] or α-substituted propiolactone;[7] they are formed by acyl–oxygen cleavage of the lactone ring.

We wish to thank Dr. G. Ribaldone for monomer preparation, Dr. G. Carraro for molecular weight determination, Dr. L. Biasin for chromatographic analyses, and Dr. B. Minasso for infrared spectra.

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Résumé

La polymérisation du β-β′ diméthyl β propiolactone avec différents catalyseurs a été étudiée. Une étude détaillée de la polymérisation hétérogène initiée par le diéthylaluminium a été effectuée. On a suggéré un mécanisme de réaction sur la base de l'analyse chimique du polymère.

Zusammenfassung

Die Polymerisation von β,β′-Dimethyl-β-propiolactam mit verschiedenen Katalysatoren wurde untersucht, und zwar besonders eingehend die durch Triäthylaluminium gestartete heterogene Polymerisation. Ein auf der chemischen Analyse des Polymeren beruhender Reaktionsmechanismus wird vorgeschlagen.

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Poly-1,6-diselenahexamethylene, 1,2-Diselenane, and Their Effects on Vinyl Polymerizations

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Synopsis

Poly-1,6-diselenahexamethylene has been prepared, and some of its properties and those of its depolymerization product, 1,2-diselenane, have been studied. Depolymerization probably occurs by a free-radical mechanism. The effects of these organoselenium compounds on the thermal polymerization of styrene, methyl methacrylate, vinyl acetate, and acrylonitrile at 60°C. in the presence and absence of 2,2′-azobisisobutyronitrile and on the direct photopolymerization of these vinyl monomers at 25°C. has been examined. Various reaction mechanisms are suggested to explain the experimental results.

INTRODUCTION

Initiation of polymerization of vinyl monomers by monoradicals generated by thermal or photochemical breakdown of initiators such as organic peroxides, hydroperoxides, and azo compounds is now well established.[1,2]

Most cyclic peroxides and cyclic azo compounds which would be expected to give diradicals on decomposition are poor thermal and photoinitiators for vinyl monomers. A few cyclic peroxides, such as cyclohexanone peroxide, dihydroascaridole, and ascaridole, which under certain conditions can act as efficient initiators appear, from measurements of rates and degrees of polymerization, to form initiating monoradicals rather than diradicals. The initially formed diradicals are assumed to be rapidly converted to monoradicals or else undergo cyclization after adding a few monomer molecules.[3,4]

Linear disulfides may sometimes act as monoradical initiators,[5] but experimental studies of polymerization with cyclic disulfides are limited. However, the ring disulfide, 1-oxa-4,5-dithiacycloheptane has some initiating ability[6] and can also undergo chain transfer with polymer radicals by copolymerization.[7,8] This paper reports a study of the chemistry of poly-1,6-diselenahexamethylene and a ring diselenide, 1,2-diselenane (1,2-diselenacyclohexane) and of their effects on various vinyl polymerizations. The six-membered nonplanar ring in 1,2-diselenane,[9] as in other cyclic diselenides and disulfides,[5] is under considerable strain.

EXPERIMENTAL

Materials

The initiator 2,2′-azobisisobutyronitrile,[10] (AZBN), dimethylformamide[11] (DMF), and styrene[12] were purified as described previously. Conventional techniques were used to purify acrylonitrile[13] and methyl methacrylate.[14]

Vinyl acetate (Koch-Light) was fractionally distilled at atmospheric pressure under oxygen-free nitrogen. The middle fraction, distilling at 72.0–72.5°C., was collected and prepolymerized to about 5% conversion by means of ultraviolet light. The monomer–polymer mixture was degassed and monomer distilled off under vacuum. The middle fraction was retained for further use.

All monomers were used as quickly as possible after purification, being stored at −78°C. until required.

Commercial grade chloroform was shaken with concentrated sulfuric acid and then with 10% sodium carbonate and distilled water. It was dried successively over anhydrous calcium chloride (1 hr.) and anhydrous calcium sulfate (overnight), and distilled under oxygen-free nitrogen at atmospheric pressure. The middle fraction distilling at 61.0°C. was retained and stored under oxygen-free nitrogen in the dark. Many of the reactions studied involving chloroform as a solvent proceeded at rates markedly dependent on its purity. Chloroform used within 2 hr. of the final distillation is described as "pure" chloroform in this paper, all other purified samples being designated simply chloroform. Some experiments involved the use of unpurified commercial grade chloroform.

Bromoform (B.D.H.) was purified by washing with water, drying over anhydrous sodium sulfate, and fractionally distilling under vacuum. It was stored under oxygen-free nitrogen in the dark and used as soon as possible after distillation.

Low molecular weight poly-1,6-diselenahexamethylene $\lbrack Se(CH_2)_4Se \rbrack_n$ was prepared in low yield by the method of Burstall and Morgan,[15] who previously assumed that 1,2-diselenane $(CH_2)_4Se_2$ alone had been synthesized. The method involved the air oxidation of 1,4-tetramethylene diselenocyanate $NCSe(CH_2)_4SeCN$ (I) in an alkaline medium. I was synthesized by reacting 1,4-dibromobutane (II) with potassium selenocyanate, (III). II was prepared by reacting 1,4-butanediol with hydrobromic acid in the presence of concentrated sulfuric acid[16] and was dried and fractionally distilled (73.8–75.6°C./10 mm. pressure) before use. III was obtained as colorless needles in almost theoretical yield by reaction of potassium cyanide with selenium.[17]

Poly-1,6-diselenahexamethylene was isolated as a yellow powder with a noncrystalline appearance and had a low solubility in all solvents examined except chloroform. It was purified by dissolving in warm chloroform and then cooling the solution in ice. Material remaining in solution was discarded. This process was repeated twice, and the final material, when dry, melted at 38–39°C. with decomposition. Microanalysis gave: C, 23.37%; H, 4.18%; Se, 70.9%; O, 1% (approx.); Na and N, traces. The solid appeared stable when stored in the dark.

Procedure

Poly-1,6-diselenahexamethylene and Its Depolymerization. The molecular weights of the poly-1,6-diselenahexamethylene and of the products formed by its depolymerization were determined by the freezing point depression method with the use of bromoform as solvent and a Beckman thermometer. The apparatus was shielded from light during the experiment. The depolymerization in bromoform at 60°C. was also followed viscometrically in subdued daylight in an Ubbelohde viscometer.

Ultraviolet and visible spectrum measurements were recorded by using a Perkin-Elmer 4000A Spectracord or a Cary-14 spectrophotometer. The effects of temperature, oxygen, and light on rates of depolymerization of poly-1,6-diselenahexamethylene in chloroform solutions were ascertained by experimental procedures that usually involved removal of samples from a bulk solution at known times. All samples removed were quench-cooled to room temperature before spectral analysis. The use of a darkroom and reaction vessels covered with aluminum foil, when needed, proved advantageous.

The direct photochemical depolymerization of poly-1,6-diselenahexamethylene at 25°C. was followed with the use of a stoppered silica spectroscopic cell as a reaction vessel. A Hanovia fluorescence lamp (Model 16) provided light of predominantly 2537 and 3660 A. wavelength. Changes in the spectrum were recorded after known times of exposure to light.

The effect of purity of the chloroform on the rates of depolymerization was also assessed, and a few measurements were made with a Varian EPR spectrograph.

Effects of Poly-1,6-diselenahexamethylene and Its Depolymerization Products on Vinyl Polymerizations. Rates of polymerization with or without added AZBN were measured gravimetrically or dilatometrically at 60°C. in the usual way,[10] in the presence and absence of poly-1,6-diselenahexamethylene. In many experiments the latter compound was used as a saturated solution in the appropriate monomer. Solubility in all monomers was low, being for example, 1.7×10^{-3} g./l. for a saturated solution in vinyl acetate at room temperature. When necessary, operations were carried out in the dark with ampules and dilatometer bulbs covered with aluminum foil.

Photochemical polymerization of vinyl monomers without added AZBN was carried out in Pyrex or silica dilatometers at room temperature (about 25°C.) both in the presence and absence of poly-1,6-diselenahexamethylene. A Hanovia fluorescence lamp fitted with a Wood's glass filter confined light to wavelengths of about 3600 A. Conversions were calculated at known time intervals by placing the dilatometers in a reference bath at 30°C.

All the above polymerizations were performed to conversions of less than 10%, but with an excess of polymeric diselenide some high conversion polymerizations were carried out, and the resulting polymers were analyzed for selenium content and examined spectroscopically.

The disappearance of poly-1,6-diselenahexamethylene in polymerizing monomers was also followed spectroscopically.

Vinyl polymers were isolated by precipitation in a suitable nonsolvent containing a trace of hydroquinone. After washing with nonsolvent, the polymers were dried in vacuum. Intrinsic viscosities were determined at 30°C. in an Ubbelohde viscometer in the usual way.[12] The solvents used were toluene for polystyrene, chloroform for poly(methyl methacrylate), acetone for poly(vinyl acetate), and *N,N*-dimethylformamide for polyacrylonitrile.

RESULTS AND DISCUSSION

Poly-1,6-diselenahexamethylene and Its Depolymerization

The molecular weight of the polymeric diselenide in a freshly prepared solution of bromoform, 0.237% by weight, was found by the cryoscopic method to be 516.3, ignoring any extrapolation of data to zero concentration. This value is a minimum value, since freezing point redeterminations indicated that the molecular weight in solution decreased rapidly with time in air in the dark. When the solution was maintained at 60°C. in the dark for 24 hr., the molecular weight reached a steady value of 209.7.

A decrease in molecular weight with time was also indicated by viscosity measurements on a bromoform solution of poly-1,6-diselenahexamethylene at 60°C. in air in subdued daylight. Figure 1 shows the results.

The ultraviolet spectrum of a freshly prepared solution of poly-1,6-diselenahexamethylene in chloroform gave an absorption maximum at 3080 A. characteristic of the Se—Se bond in linear diselenides.[9] Slight changes in wavelength of the absorption maximum occurred in other solvents such as bromoform, benzene, and vinyl monomers. On allowing chloroform solutions of poly-1,6-diselenahexamethylene to stand at 60°C. in the presence or absence of air, the peak at 3080 A. disappeared and another maximum at 3640 A. appeared, as shown in Figure 2. The latter absorption maximum is characteristic of the Se—Se bond in the cyclic 1,2-diselenane $(CH_2)_4Se_2$, and is in agreement with a value of 3650 A., recorded for the same compound in chloroform solution prepared by a depolymerization method by Bergson.[9] The fact that cyclic compounds, including disulfides and diselenides, show an absorption maximum at slightly longer wavelengths than their straight-chain analogs is well substantiated.[18]

Further evidence of the conversion of polymeric diselenide to cyclic diselenide was provided by the fact that bromoform solutions at the end of both the viscometric and freezing point depression experiments gave a single peak at 3690 A. The molecular weight of the species in those solutions was 209.7, which is close to the value of 214.0 expected for 1,2-diselenane. Depolymerization of other polymers to give 1,2-dithiolane[19] and 1,2-diselenolane[9,19] has been observed previously, while polymeric products together with 1-thia-2-selenacyclopentane-4-carboxylic acid have been formed in the aqueous air oxidation of propane-1-thiol-3-selenol-2-carboxylic acid.[20]

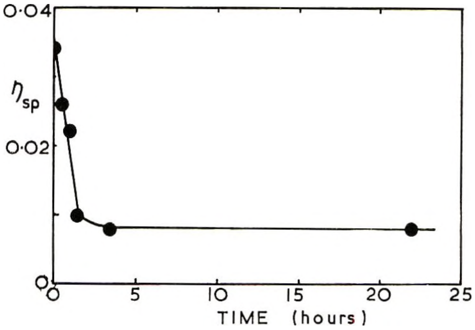


Fig. 1. Specific viscosity η_{sp} at 60°C. of a bromoform solution containing initially 0.5 wt.-% of poly-1,6-diselenahexamethylene as a function of time. The experiment was performed in air and subdued daylight.

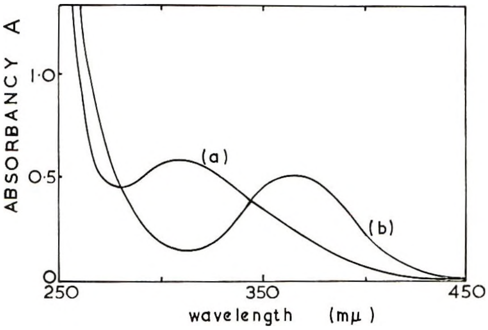


Fig. 2. Absorbancy A vs. wavelength for a chloroform solution of poly-1,6-diselenahexamethylene: (*a*) freshly prepared solution; (*b*) after 30 min. at 60°C. The experiment was performed in the absence of air and light; 1 cm. path length; initial concentration of poly-1,6-diselenahexamethylene = 2.30×10^{-2} g./dl.

An infrared spectrum in the range 2–16 μ of the solid poly-1,6-diselenahexamethylene gave a slight absorption at 4.35 μ characteristic of HSe-- endgroups,[21] but the other endgroups were unidentified, although analytical results suggest that they may include HO_2Se-, NaO_2Se-, and unreacted NCSe- groups.

Observations of changes in spectra, particularly at 3080 and 3640 A., established that for the thermal depolymerization in solution in the absence of light an increase of temperature increased the rate of depolymerization under any conditions.

$$\left[\!\!-Se(CH_2)_4Se-\!\!\right]_n \rightarrow n(CH_2)_4Se_2 \qquad (1)$$

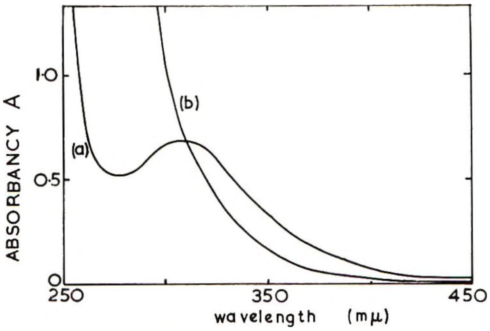


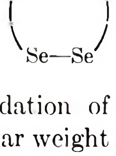
Fig. 3. Depolymerization of poly-1,6-diselenahexamethylene in chloroform solution at room temperature in direct sunlight: (*a*) freshly prepared solution; (*b*) after 30 min. exposure. The experiment was performed in the presence of air; 1 cm. path length; initial concentration of poly-1,6-diselenahexamethylene = 2.63×10^{-2} g./dl.

Also, impurities in the chloroform retarded the depolymerization rate. Indeed, in very pure chloroform, even at room temperature in air, the depolymerization was extremely rapid and was almost complete by the time the solid material had dissolved. Oxygen in the air acts as a retarder for the depolymerization reaction under any conditions. For example, at 60°C. under oxygen-free nitrogen in chloroform solution in the dark, poly-1,6-diselenahexamethylene was almost completely depolymerized to 1,2-diselenane after 10 min.

Similar experiments in the presence of sunlight showed that photochemical depolymerization also occurred at a rate strongly dependent on the purity of the chloroform, and it was retarded by oxygen. Although in diffuse sunlight the peak at 3080 A. was replaced by one at 3640 A., in very strong sunlight the latter peak was not observed at all, as indicated in Figure 3. This suggests that two photochemical processes may occur:

$$\left[Se(CH_2)_4Se \right]_n + h\nu \rightarrow n(CH_2)_4Se_2 \qquad (2a)$$

and



$+ h\nu' \rightarrow$ products containing no Se—Se bonds (2b)

Photolytic degradation of solid poly(alkylene polysulfides) *in vacuo* to form low molecular weight products has also been noted.[22]

These observations suggest that depolymerization proceeds by a free-radical mechanism, both photochemically and thermally. Electron spin resonance spectra for solutions of poly-1,6-diselenahexamethylene in chloroform in the presence of traces of oxygen gave *g* values of 2.000 characteristic of radicals, but the experiments were not reproducible.

There was no indication that 1,2-diselenane in chloroform solution at 0–60°C. exists in equilibrium with poly-1,6-diselenahexamethylene or that polymerization occurs on standing. This does not necessarily imply that the polymeric diselenide is above its ceiling temperature,[1,23] since a catalyst, as with cyclic poly(methylene disulfide),[24] or a higher temperature, as with α-lipoic acid[25] may be required to induce polymerization.

Solutions of poly-1,6-diselenahexamethylene in ethanol depolymerized much more rapidly in the presence of an added trace of sodium hydroxide, although the 1,2-diselenane initially formed was later consumed by other reactions. This type of nucleophilic attack on Se—Se bonds by added OH^- is paralleled by nucleophilic attack by OH^-, RS^-, and other anions on S—S bonds in disulfides[5] and disulfide polymers.[26,27]

Beer's law was obeyed by freshly prepared solutions of poly-1,6-diselenahexamethylene in commercial grade chloroform at 3080 A. and by the depolymerization products at 3640 A. $E^{1\%}_{1\,\text{cm}}$ values for the peaks at 3080 and 3640 A. were 26.2 and 17.5 100 ml./g.-cm., respectively, over the concentration range 0–3 × 10^{-2} g./100 ml.

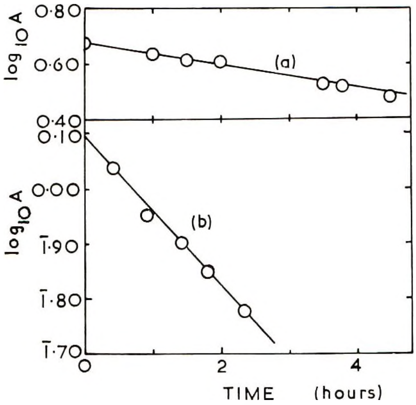


Fig. 4. Plot of log A as a function of time for the depolymerization of poly-1,6-diselenahexamethylene in chloroform solution: (a) in the absence of light and presence of air at 60°C., initial concentration of poly-1,6-diselenahexamethylene = 0.183 g./dl.; (b) in the presence of ultraviolet light and air at room temperature, initial concentration of poly-1,6-diselenahexamethylene = 4.72 × 10^{-2} g./dl.

The rate of the purely thermal depolymerization of poly-1,6-diselenahexamethylene in commercial grade chloroform at 60°C. in the dark and in the presence of air was measured by following the decrease in height of the absorption peak at 3080 A. as a function of time. In the initial stages of depolymerization, assuming negligible overlap of peaks due to polymeric and monomeric diselenides, first-order kinetics were obeyed, as shown in Figure 4. Under these conditions, the first-order velocity constant was 2.75 × 10^{-5} sec.$^{-1}$. Figure 4 also indicates that the photochemical depolymerization at 25°C. in chloroform solution, with light predominantly of 2537 and 3660 A., was also first-order in polymeric diselenide concentration with a velocity constant of 8.96 × 10^{-5} sec.$^{-1}$.

Effects of Poly-1,6-diselenahexamethylene and Its Depolymerization Products on Vinyl Polymerizations

Saturated or partially saturated solutions of poly-1,6-diselenahexamethylene in various monomers were prepared at room temperature and used in all later experiments. Negligible depolymerization of the polymeric diselenide occurred before the ampules and dilatometers were used in experimental studies.

Thermal Reactions at 60°C. in the Dark in the Absence of AZBN. The results are summarized in Table I. Since spectroscopic studies showed that poly-1,6-diselenahexamethylene depolymerized to 1,2-diselenane at 60°C. in all four monomers, it appears that organoselenium radicals produced by reaction (3) are incapable of adding to vinyl acetate or acrylonitrile.

$$\sim\!\sim\!\text{—Se(CH}_2)_4\text{Se—Se(CH}_2)_4\text{Se—}\sim\!\sim \xrightarrow{k_1} \sim\!\sim\!\text{—Se(CH}_2)_4\text{Se}\cdot + \cdot\text{Se(CH}_2)_4\text{Se—}\sim\!\sim \qquad (3)$$

The possibility that organoselenium radicals abstract hydrogen atoms from vinyl monomers to form selenol endgroups is unlikely, although hydrogen atom abstraction from other solvents can occur with thiyl radicals.[28] Although organoselenium radicals may have some reactivity towards methyl methacrylate, the large decrease in $[\eta]$ and hence the degree of polymerization, $\overline{\text{DP}}$, for the polymerization of this monomer and styrene suggests that polymer radicals, $\text{R}_r\cdot$, may undergo transfer reactions with 1,2-diselenane which is present in the polymerizing vinyl systems:

$$\text{R}_r\cdot + (\text{CH}_2)_4\text{Se}_2 \rightarrow \text{R}_r\text{Se(CH}_2)_4\text{Se}\cdot \qquad (4)$$

The organoselenium radicals would be relatively inactive towards styrene and cause a rate decrease. Transfer reactions involving copolymerization similar to that of eq. (4) have been observed with the cyclic disulfide, 1-oxa-4,5-dithiacycloheptane.[7,8]

Polyvinyl radical attack on poly-1,6-diselenahexamethylene in the polymerization of methyl methacrylate and styrene would also be expected to occur:

$$\text{R}_r\cdot + \sim\!\sim\!\text{—Se(CH}_2)_4\text{Se—Se(CH}_2)_4\text{Se—}\sim\!\sim \rightarrow$$
$$\underset{(\text{X})}{\sim\!\sim\!\text{—Se(CH}_2)_4\text{Se—R}_r} + \cdot\text{Se(CH}_2)_4\text{Se—}\sim\!\sim \qquad (5)$$

since polymer (and other) radical displacement reactions on disulfides by reaction (6) are well known.[1,5]

$$\text{R}_r\cdot + \text{R}'\text{—S—S—R}' \rightarrow \text{R}_r\text{—S—R}' + \cdot\text{S—R}' \qquad (6)$$

Thermal Reactions at 60°C. in the Dark in the Presence of AZBN. The results of experiments performed at 60°C. in the presence of AZBN at a concentration of 1×10^{-3} mole/l. are summarized in Table I. There was no observable effect on the rates of polymerization for styrene and methyl methacrylate, but retardation occurred with acrylonitrile and to a very marked extent with vinyl acetate as shown in Figure 5. The addition of

TABLE I. Effects of Poly-1,6-diselenahexamethylene and Its Depolymerization Products on Vinyl Polymerizations

			Intrinsic viscosity at 30°C. [η], dl./g.[a]	
Type of reaction	Monomer	Effect of adding poly-1,6-diselenahexamethylene to reaction mixture	Polymer formed in absence of poly-1,6-diselenahexamethylene	Polymer formed in the presence of poly-1,6-diselenahexamethylene
Thermal reaction at 60°C. in the dark (no added AZBN)	Styrene	Rate decreased	1.64	1.48
	Methyl methacrylate	Rate slightly increased	10.00	7.60
	Vinyl acetate	No polymerization with or without poly-1,6-diselenahexamethylene	—	—
	Acrylonitrile	No polymerization with or without poly-1,6-diselenahexamethylene	—	—
Thermal reaction at 60°C. in the dark at [AZBN] = 1.0 × 10^{-3} mole/l.	Styrene	No observed effect	3.50	1.92
	Methyl methacrylate	No observed effect	4.60	4.40
	Vinyl acetate	Extreme retardation	1.63	—[b]
	Acrylonitrile	Slight retardation	16.20	10.00
Photochemical reaction at 25°C. with wavelength about 3600 A. (no added AZBN)	Styrene	Rate increased	2.10	0.76
	Methyl methacrylate	Rate increased	4.00	1.10
	Vinyl acetate	Rate increased	2.70	2.27
	Acrylonitrile	Rate increased	1.50	c

[a] Solvents used were toluene for polystyrene, chloroform for poly(methyl methacrylate), acetone for poly(vinyl acetate), and *N*,*N*-dimethylformamide for polyacrylonitrile; [b] not enough polymer isolated during retardation period for viscosity analysis; [c] polymer had too low a molecular weight to be isolated by precipitation.

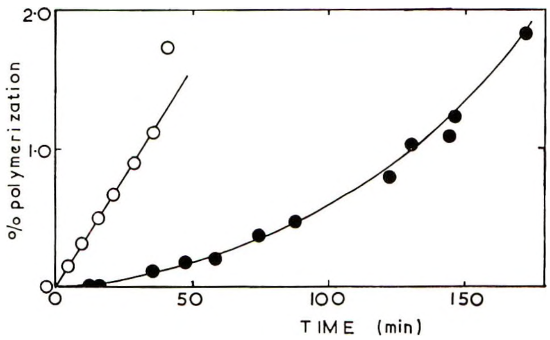


Fig. 5. Thermal polymerization of vinyl acetate at 60°C. with [AZBN] = 1.0 × 10^{-3} mole/l.: (○) in the absence of poly-1,6-diselenahexamethylene; (●) in the presence of added poly-1,6-diselenahexamethylene at an initial concentration of ca. 1.0 × 10^{-3} g./dl.

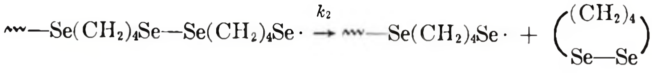
N,*N*-dimethylformamide to the system decreased the polymerization rate as expected.

Polystyrene and poly(methyl methacrylate) prepared at 60°C. in the presence of AZBN at a concentration of 1 × 10^{-3} mole/l. to 40% conversion in the presence of excess polymeric diselenide were found by microanalysis to contain about 0.5% of selenium. Spectroscopic analysis of such polymers, however, showed no absorption peak at about 3100 A. characteristic of Se—Se bonds. This suggests the importance of reaction (4) but does not rule out the possibility that induced depolymerization of poly-1,6-diselenahexamethylene occurs by reaction (5), followed by subsequent thermal rupture of Se—Se bonds in structures such as (X), or polymer radical attack on (X), to give more 1,2-diselenane.

Experiments were therefore performed with styrene and methyl methacrylate at 60°C. in which the disappearance of polymeric diselenide and 1,2-diselenane was followed spectroscopically, both in the presence and absence of AZBN. In all cases, the concentration of polymeric diselenide decreased relative to the 1,2-diselenane concentration at a greater rate when AZBN was present, indicating the importance of reaction (5), particularly in the initial stages of the reaction.

A more detailed study was made of the thermal polymerization of vinyl acetate at 60°C. initially saturated with poly-1,6-diselenahexamethylene with [AZBN] = 1.0 × 10^{-3} mole/l. Retardation was severe, and over the first 150 min. of the reaction the polymerization rate was too small to be measured accurately by dilatometry. Spectroscopic studies with the use of a reference cell filled with vinyl acetate with AZBN at 1.0 × 10^{-3} mole/l. showed that during this period a peak at 2800 A. characteristic of the polymeric diselenide gradually disappeared, and a peak characteristic of 1,2-diselenane appeared at 3620 A., reached a maximum intensity after 90 min. of reaction, and subsequently decreased in intensity. The rate of decrease of absorbancy at 2880 A., $-dA/dt$, was found to be linearly proportional to A at various times t during this 150-min. period of retardation.

These results can be rationalized by using a conventional type of retardation scheme[29] with rate of initiation I, vinyl propagation with velocity constant k_p, reaction of poly(vinyl acetate) radicals and two types of retarder given by reactions (4) and (5) with associated velocity constants k_z' and k_z, respectively; thermal breakdown of Se—Se bonds in polymeric diselenides, and structures such as (X) produced in the reaction (5), to give organoselenium radicals, with common velocity constant k_1; depolymerization of polymeric organoselenium radicals to give 1,2-diselenane, by an unzippering process:



$$\sim\!\!—\mathrm{Se(CH_2)_4Se—Se(CH_2)_4Se}\cdot \xrightarrow{k_2} \sim\!\!—\mathrm{Se(CH_2)_4Se}\cdot + \left(\begin{matrix}\mathrm{(CH_2)_4} \\ \mathrm{Se—Se}\end{matrix}\right) \qquad (7)$$

and lastly a termination process:

$$\sim\!\!—\mathrm{Se}\cdot + \cdot\mathrm{Se}—\!\!\sim \xrightarrow{k_{zt}} \sim\!\!—\mathrm{Se—Se}—\!\!\sim \qquad (8)$$

Since poly-1,6-diselenahexamethylene and 1,2-diselenane are insufficient by themselves to cause polymerization of vinyl acetate, one can ignore the reaction involving addition of monomer to organoselenium radicals (velocity constant k_{zp}), and termination steps other than that of eq. (8) are probably relatively unimportant during the period of severe retardation[29] when $[\mathrm{R_r}\cdot] \ll [\cdot\mathrm{Se}—\!\!\sim] \ll [\sim\!\!—\mathrm{Se—Se}—\!\!\sim]$ or $[(\mathrm{CH_2})_4\mathrm{Se_2}]$. Unfortunately the uncertainty in measuring the rate of polymerization during extreme retardation precluded the possibility of evaluating k_z'/k_p and k_z/k_p.

Photochemical Reactions at 25°C. in the Absence of AZBN. The results of irradiating monomers with light of wavelength predominantly 3600 A. at 25°C. with no added azo initiator are shown in Table I. In all experiments the initial presence of the polymeric diselenide caused an in-

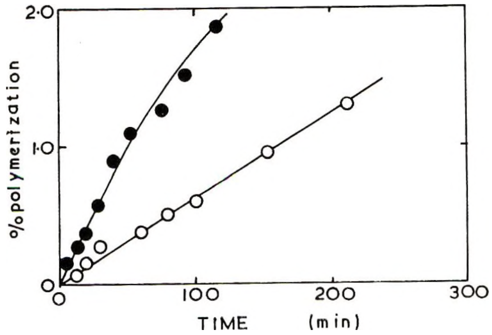


Fig. 6. Photochemical polymerization of styrene at 25°C.: (○) in the absence of poly-1,6-diselenahexamethylene; (●) in the presence of added poly-1,6-diselenahexamethylene at an initial concentration of ca. 1.0 × 10^{-2} g./dl. Light at predominantly 3600 A.

creased rate of polymerization and a corresponding decrease in $\overline{DP}$. A typical rate effect is shown in Figure 6. The behavior resembles that of many linear disulfides that show little activity as thermal initiators of vinyl polymerization but are excellent photoinitiators.[30]

Spectroscopic experiments indicated that although initially both polymeric diselenide and 1,2-diselenane were present in the vinyl systems, after a few minutes irradiation, the absorption peak at about 3640 A. disappeared completely, showing that 1,2-diselenane was being removed. Therefore the concentration of poly-1,6-diselenahexamethylene decreased throughout the reaction but the 1,2-diselenane, which presumably was continuously thermally formed was destroyed by photochemical reactions. There was no evidence of the photopolymerization of 1,2-diselenane to give poly-1,6-diselenahexamethylene, although such a photoreaction has been observed with the cyclic trimethylene disulfide even at low temperatures.[31]

Vinyl polymers prepared photochemically in the presence of a large excess of polymeric diselenide were shown spectroscopically to contain no Se—Se bonds. Since selenium-ended radicals produced thermally at 60°C. are not capable of initiating polymerization of vinyl monomers (except possibly for methyl methacrylate) the results cannot be explained by assuming an initiation process:

$$(CH_2)_4Se_2 + h\nu' \rightarrow \cdot Se(CH_2)_4Se\cdot \qquad (9)$$

unless the resulting diradicals possessed exceptional reactivity due to excess electronic and vibrational energies. Again, cyclization would be expected after addition of a few monomer units.[3,4]

Now there is evidence from kinetic investigations, spectroscopic work including ESR, and other studies, that the S—S bond in linear disulfides, R—S—S—R, usually breaks homolytically on pyrolysis or photolysis.[5,32–35] There is some evidence, however, that vapor-phase pyrolysis of alkyl disulfides produces two types of sulfur radical, RSS· and RS·.[36] Recent ESR studies indicate that on photolysis diselenides behave differently from disulfides. The Se—Se bond need not rupture but other radicals usually located on a methylene carbon are formed.[35] Hence an acceptable explanation for the photolytic results involving 1,2-diselenane is that light in the region of 3600 A. is absorbed by Se—Se bonds but that adjacent C—Se bonds are broken [eq. 10].

$$(CH_2)_4Se_2 + h\nu' \rightarrow \cdot CH_2(CH_2)_3{-}Se{-}Se\cdot \qquad (10)$$

The resulting radical would be expected to behave virtually as a monoradical with respect to vinyl monomers, since rapid addition of monomer molecules could only occur from the methylene radical end. An increased rate of polymerization and decrease in DP would result. The high reactivity of 1,2-diselenane as a photoinitiator may be associated also with the high quantum yields which would be expected on photolysis by analogy with the behavior of strained five-membered ring disulfides.[37]

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Résumé

On a préparé le poly-1,6-disélénahexaméthylène et certaines de ses propriétés et celles de son produit de dépolymérisation, 1,2-disélènane ont été étudiées. La dépolymérisation se passe probablement par un mécanisme radicalaire. Les effets des composés organo-séléniques sur la polymérisation thermique du styrène, du méthacrylate de méthyl, de l'acétate de vinyle et l'acrylonitrile à 60°C en présence et en absence de 2,2'-azobisisobutyronitrile et sur la photopolymérisation directe de ces monomères vinyliques à 25°C ont été étudiés. Différents mécanismes de réaction sont suggérés pour expliquer les résultats expérimentaux.

Zusammenfassung

Poly-1,6-diselenahexamethylen wurde dargestellt und einige seiner Eigenschaften sowie diejenigen seines Depolymerisationsproduktes, 1,2-Diselenan, wurden untersucht. Die Depolymerisation verläuft wahrscheinlich über einen radikalischen Mechanismus. Der Einfluss dieser selenorganischen Verbindungen auf die Wärmepolymerisation von Styrol, Methylmethacrylat, Vinylacetat und Acrylnitril bei 60°C mit und ohne Zusatz von 2,2′-Azobisisobutyronitril und auf die direkte Photopolymerisation dieser Vinylmonomeren bei 25°C wurde untersucht. Reaktionsmechanismen zur Erklärung der Versuchsergebnisse werden vorgeschlagen.

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NOTES

Polymerization of Propylene Oxide with a Dialkylzinc–Hydrazine Catalyst

The polymerization of propylene oxide by use of catalysts consisting of dialkylzinc and an oxygen-containing compound, e.g., water, alcohols, etc., has been reported.[1-3] Other two-component catalyst systems based on dialkylzinc–sulfur[4] and dialkylzinc–amines[3] were found active in the polymerization of olefin oxides and lead to high molecular weight polymers which are mainly amorphous. Aggarwal et al.,[5] during a study on the effect of stereosequence length on the crystallization kinetics of poly(propylene oxide), found that a modification of the dialkylzine–water catalyst system with isopropylamine caused a substantial change in the average length of the uncrystallizable sequence with relatively small change in the average length of the crystallizable sequence.

A two-component catalyst system consisting of dialkylzinc and hydrazine has been found to be an active system for the polymerization of propylene oxide to a high molecular weight, rubbery polymer. The catalyst in general is somewhat slower than dialkylzinc–water and the resulting polymer exhibits different solubility and swelling characteristics in acetone which suggest a broader distribution of the crystalline sequences among polymer chains.

The polymerization of propylene oxide by the dialkylzinc–hydrazine catalyst was carried out in solution. Propylene oxide, 30 ml. in 100 ml. solution in benzene, which was dried by passing over silica gel under nitrogen, was charged with 0.135 ml. of anhydrous hydrazine (4.4×10^{-3} mole) followed by 4.0 ml. of 1.55*M* solution of diethylzinc. Under polymerization conditions of 50°C. for 24 hr. a solid polymer yield of 90% was obtained. The polymer had an inherent viscosity of 25 dl./g. and was completely soluble in benzene.

The activity of the dialkylzinc–hydrazine catalyst depends on the ratio of hydrazine to dialkylzinc. Best results were achieved at a hydrazine/dialkylzinc molar ratio in the range 0.70–0.75. The system is not limited to hydrazine alone. Derivatives such as dimethylhydrazine or diphenylhydrazine in combination with organozinc compounds are also active polymerization catalysts for olefin oxides.

Amorphous poly(propylene oxide) is known to be soluble in acetone at room temperature while crystalline poly(propylene oxide) is insoluble. Hence, acetone extraction is widely used to separate amorphous from crystalline poly(propylene oxide). A polymer specimen of mixed structure, with crystallizable sequences distributed among the chains, will partially dissolve in acetone and the insoluble portion will swell. One may use the solubility and swelling characteristics in acetone as a convenient indicator of the degree of crystallinity and the distribution of crystalline sequences among the poly(propylene oxide) chains. A polymer with all of its crystalline portion concentrated in a relatively few chains will display a high solubility, while the insoluble portion will swell very little. On the other hand, a polymer with a similar degree of crystallinity but with the crystalline sequences widely distributed among many chains will be less soluble, yet the insoluble fraction will swell more in acetone. The acetone-soluble portion will consist of poly(propylene oxide) chains having on the average less than one crystalline sequence per weight-average molecular weight molecule.

The poly(propylene oxide) obtained by the diethylzinc–hydrazine combination consists of an 80% acetone-insoluble portion which has a swelling value of 20.0. The swelling value here is defined as the ratio of the weights of the acetone-swollen polymer to the dried polymer. In comparison, poly(propylene oxide) prepared by the combina-

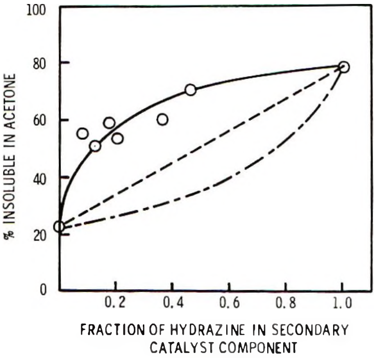

Fig. 1. Dependence of the acetone-insoluble portion of poly(propylene oxide) on the mole fraction of hydrazine in the hydrazine–water mixture used as the secondary catalyst component in combination with diethylzinc.

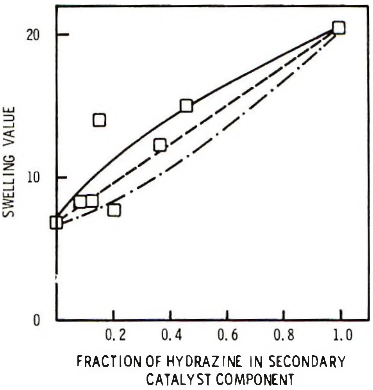

Fig. 2. Dependence of the swelling value of the acetone-insoluble portion of poly(propylene oxide) on the mole fraction of hydrazine in the hydrazine–water mixture used as the secondary catalyst component in combination with diethylzinc.

tion, dialkylzinc–water, consists of a 22% acetone-insoluble portion that has a swelling value of 7.8. The densities of the insoluble fractions were found to be 1.0275 g./cc. and 1.0400 g./cc. for the dialkylzinc–hydrazine and dialkylzinc–water polymers, respectively. A highly crystalline poly(propylene oxide) prepared using an iron trichloride–propylene oxide complex[6] consists of a 98% acetone-insoluble portion and a low swelling value of 1.33. The density of the insoluble fraction of the last polymer was found to be higher than 1.0500 g./cc. A study of the dependence of the insoluble fraction on molecular weight suggests that the differences in the acetone-insoluble fractions of the above polymers are due primarily to differences in their distribution of crystallinity rather than molecular weight. The polymer obtained with the dialkylzinc–water catalyst is characterized by moderate crystalline sequence lengths confined to about a fourth of the polymer chains on a weight basis, while the crystalline sequence lengths are more uniformly distributed among all polymer chains with the other catalysts, the length being short with the dialkylzinc–hydrazine catalyst and long for the iron trichloride–propylene oxide complex catalyst.

By using mixtures of water and hydrazine as the secondary component in combination with dialkylzinc, it is possible to prepare poly(propylene oxides) with varying solubility and swelling values in acetone. Figures 1 and 2 illustrate plots of per cent of polymer insoluble in acetone and swell value versus the fraction of hydrazine in the secondary component. The type of nonlinear dependence in both plots suggests that the system dialkylzinc–water–hydrazine is not acting as a simple mixture of dialkylzinc–water and dialkylzinc–hydrazine catalysts. If the latter were the case, considering the lower activity of the dialkylzinc–hydrazine system, one should expect a behavior of the qualitative appearance shown by the dash-dotted lines in Figures 1 and 2, i.e., a curve convex to the abscissa. The solid lines in the figures, which represent the average observed dependence of per cent of poly(propylene oxide) insoluble in acetone and the swelling value on the fraction of hydrazine in the secondary component, are actually concave to the abscissa.

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Polymerization of 9-Ethynylanthracene

The low-temperature, cationic polymerization of 9-vinylanthracene was shown earlier to proceed 1,6 through the center ring of the anthracene nucleus, and the product was easily rearranged to poly-9,10-dimethyleneanthracene.[1] A similar path for 9-ethynylanthracene would result in an allenic polymer which should rearrange to a completely conjugated polymer in which anthracene and ethylene units alternate. The more conventional route of 1,2 polymerization would give a completely conjugated polymer with the anthracene groups pendent from the backbone. Cyclic trimers and tetramers are possible also by 1,2 polymerization. A third process involving successive Diels-Alder additions of the ethynyl group of one molecule across the 9,10-position of another molecule could conceivably occur as well.

We have found that the cationic polymerization of 9-ethynylanthracene gives predominantly 1,2 polymer containing some unidentified dihydroanthracene structure(s). Ziegler-type catalysis gives exclusively 1,2 polymers which have lower molecular weights than the cationic polymers and may contain some cyclic trimer and tetramer.

DISCUSSION

The objective of this study was to synthesize 9-ethynylanthracene and to examine its polymerization by cationic and Ziegler-type systems.

9-Ethynylanthracene was prepared from 9-acetylanthracene by conversion to 9-(α-chlorovinyl)anthracene followed by dehydrohalogenation. The reaction of 9-acetylanthracene with phosphorus pentachloride at elevated temperatures, either neat or in phosphorus oxychloride, results in chlorination at the 10-position. If the reaction, however, is carried out in phosphorus trichloride, which represses the dissociation of phosphorus pentachloride, the desired product is obtained in satisfactory yield.

The polymerization procedures are described in the Experimental section. Table I summarizes the cationic polymerizations, which were initiated with $TiCl_4$ in methylene chloride at room temperature and −70°C. Conversions were highest at room temperature. Some products were separated into methylene chloride-soluble and insoluble fractions.

The Ziegler-type polymerizations with triisobutylaluminum–titanium tetrachloride are summarized in Table II. Here too, the products were partially fractionated. Molecular weight was not very sensitive to monomer–catalyst ratio but the yield was (compare G and I). The yield was optimum at an $AlR_3/TiCl_4$ ratio of 2:1 (compare K, L, M). Increased temperature with concomitant reduction in time had little effect on the molecular weight of the methylene chloride soluble fraction (compare F and K).

The maximum molecular weight measured for cationic polymer was 2840 (DP = 14). Although the structure of this polymer has not been fully elucidated, some conclusions can be reached. There were only minor differences between the infrared spectra of the various cationic preparations and fractions. A typical spectrum is shown in Figure 1. The most prominent absorption at 13.7 μ indicates that the polymerization is largely 1,2, giving pendent 9-anthryl groups. The bands at 13–13.5 μ could arise from 9,10-dihydrostructures as in the allenic 1,6 polymer and in the Diels-Alder polymer, or from the 9,10-disubstituted anthracene resulting from the aromatization of 1,6 polymer. A 50% reduction in the characteristic anthracene ultraviolet absorptions at ~370 mμ makes us favor the dihydro structures which do not absorb in this region. There is no distinct allenic infrared absorption at 5.1 μ. On the other hand, such absorption falls into the region of the aromatic overtones and could easily be hidden. Therefore, we are not in the position at this time to decide whether the allenic 1,6 polymer or the Diels-Alder polymer is present.

The Ziegler-type polymers were distinctly different structurally from the cationic polymers. The 13.7 μ infrared band (see Fig. 1), as well as the ultraviolet absorption at 370 mμ attest to their simple 9-anthryl structure.

TABLE I

Cationic Polymerization of 9-Ethynylanthracene

Run	CH_2Cl_2, ml.[a]	Monomer, g. mmole	$TiCl_4$, mmole[b]	Time, hr.	Temp., °C.	CH_2Cl_2 soluble, g.	CH_2Cl_2 insoluble, g.	Analysis[c] C, %	Analysis[c] H, %	Molecular weight[d]
A	10	0.25(1.2)	0.18	2	−70	0.02 (8%)	—			
B	10	0.25(1.2)	0.09	12	−75	Trace	—			
C	9	0.23(1.1)	0.18	10	−73	0.07 (30%)	—	94.74	5.35	1980
D	10	0.25(1.2)	0.18	2	Room temp.	0.09 (36%)	0.03 (12%)			
E	9[e]	0.23(1.1)	0.18	10	Room temp.[f]	0.10 (48%)	0.04 (17%)	91.38 (no ash)	5.09[g]	2845

[a] Dried over silica gel.

[b] $0.92M$ solution in cyclohexane.

[c] Calculated for $C_{16}H_{10}$: C, 94.76%; H, 5.07%.

[d] Measured in benzene by Mechrolab vapor-phase osmometer on methylene chloride-soluble fraction.

[e] Solvent deaerated.

[f] Run in serum bottle on shaker apparatus.

[g] Analysis of soluble fraction.

TABLE II
Ziegler-Type Polymerization of Ethynylanthracene

Run	Solvent[a]	Monomer solution, ml.[b]	Monomer, g. (mmole)	$Al(R)_3$, mmole[c]	$TiCl_4$ mmole[c]	Time, hr.	Temp., °C.	Product, g.		Analysis[e]			Molecular weight[f]
								Crude	Separated[d]	C, %	H, %	Ash, %	
F	*n*-Heptane	8.5	0.43(2.2)	0.1	0.05	21.5	Room	0.34	A 0.10	94.16	5.06	1.33	—
							temp.	(78%)	B 0.18	94.58	5.08	0	758
G	*n*-Heptane	8.5	0.43(2.2)	0.2	0.1	21.5	Room	0.35	A 0.08	93.33	5.24	1.71	1180[g]
							temp.	(82%)	B 0.20	94.85	5.31	0	792
H	Toluene	10	0.50(2.5)	0.1	0.05	21.5	Room	0.41	A 0.12	—	—	—	—
							temp.	(82%)	B 0.23	—	—	—	687
I	*n*-Heptane	30	1.56(7.7)	0.15	0.075	22	Room	0.81	A 0.27	92.93	5.00	1.1	943[g]
							temp.	(52%)	B-1 0.24	94.75	5.19	0	661

J	*n*-Heptane	6	0.30(1.5)	—	—	5	60	Only a trace of heptane insolubles						
K	*n*-Heptane	7.5	0.38(1.9)	0.1	0.05	5	60	0.30 (79%)	A	0.06	89.76	4.82	4.24	—
									B	0.19	94.86	5.35	0	685
L	*n*-Heptane	8.5	0.43(2.2)	0.05	0.05	5	60	0.07 (16%)						
M	*n*-Heptane	8.5	0.43(2.2)	0.2	0.05	5	60	0.12 (28%)						

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[a] Dries over silica gel.

[b] Deaerated in a closed serum bottle by sparging with dry nitrogen through hypodermic needles.

[c] $0.5M$ in *n*-heptane, R = isobutyl.

[d] A = methylene chloride-insoluble; B = methylene chloride-soluble.

[e] Calculated for $C_{16}H_{10}$: C, 94.76%; H, 5.07%.

[f] Measured in benzene by Mechrolab Vapor Phase Osmometer.

[g] Measured in chlorobenzene. Accuracy is limited by solubility. The polymer had been purified by dissolving it in hot chlorobenzene, filtering, and precipitating with methanol.

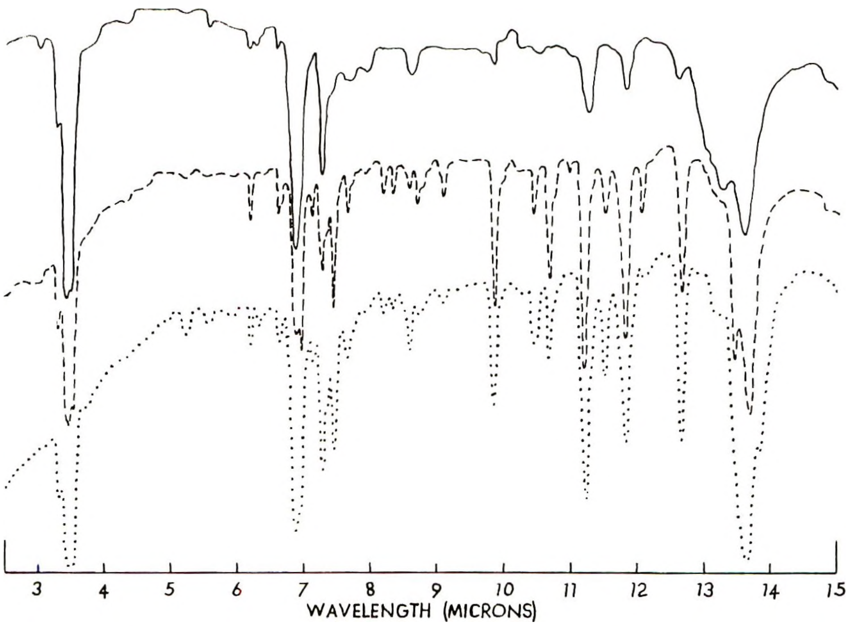

Fig. 1. Infrared spectra of poly-9-ethynylanthracene (in Nujol); (——) cationic polymer; (- -) CH_2Cl_2-insoluble Ziegler-type polymer; (· ·) CH_2Cl_2-soluble Ziegler-type polymer.

The methylene chloride-insoluble polymer has a molecular weight of 940–1180 (DP = 4.6–5.9). Since it is larger than tetramer (M.W. 808) it must be linear 1,2 polymer. The absence of significant aliphatic C—H absorption in its infrared spectrum (halocarbon mull) is surprising, since one might expect aluminum trialkyl to be involved in the initiation.

The molecular weight of the methylene chloride-soluble fractions ranged from 660 to 790. Here, too, no alkyl endgroups are indicated by either the infrared or NMR spectra. Extraction with hot methanol leaves residues (M.W. 910) which are probably linear polymer because they are larger than tetramer (M.W. 808), but the more soluble material (M.W. 660) isolated by cooling and partially evaporating the methanol could be predominantly cyclic trimer (M.W. 606). Our data are not adequate to resolve this question.

EXPERIMENTAL

9-(α-Chlorovinyl)anthracene

A one-liter, three-necked flask equipped with a stirrer, a Glascol mantle, and a condenser with a drying tube was charged with 62 g. 9-acetylanthracene,[2] 600 ml. phosphorus trichloride, and 65 g. phosphorus pentachloride. This mixture was refluxed 48 hr. and then poured on ice. The product was extracted with ether. The ether layer was washed with aqueous sodium carbonate and water and was then dried over sodium sulfate. The ether was removed on a vacuum evaporator, and the oily residue was taken up in hexane. The hexane solution was chromatographed on neutral alumina. The carbonyl-free fractions (infrared spectrum) were combined and taken up in one liter methanol.* The

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* A methanol-insoluble residue was separated. It appeared to be a polymeric material.

solution was decolorized with charcoal. Repeated reduction in volume and chilling to −16°C. gave several fractions of yellow crystals which, on further recrystallization from methanol and thorough drying (room temperature and reduced pressure for 72 hours), totaled 16 g. The purest of these melted at 60.5–62°C., the least pure at 56.5–58.5°C.

From time to time, a lower-melting form (50°C.) was isolated which on remelting also melted at ~60°C. There was no noticeable difference in the infrared spectra of these polymorphs.

Analysis and spectra confirmed the composition of the compound.

ANAL. Calcd. for $C_{16}H_{11}Cl$: C, 80.50%; H, 4.65%; Cl, 14.85%. Found: C, 80.08%; H, 4.65%; Cl, 14.98%.

The NMR spectrum in carbon disulfide showed two olefinic protons (*cis* and *trans* to chlorine) at τ = 4.50 and 3.83. Absorption for 9 aromatic protons was found near $\tau \cong 2.5$.

The infrared spectrum indicated that the compound was a 9-substituted anthracene (13.7 μ band).

9-ETHYNYLANTHRACENE

Into a two-liter, three-necked flask equipped with a stirrer, nitrogen inlet, dropping funnel, and drying tube outlet were charged 400 ml. liquid anhydrous ammonia. A 13-g. portion of sodium was converted to sodamide (a small amount of ferric chloride was used as catalyst). To this solution was added 12.7 g. 9-(α-chlorovinyl)anthracene in 150 ml. dry tetrahydrofuran over 1 hr. The ammonia was then allowed to evaporate under a rapid stream of nitrogen over a period of 2 hr. Ether (500 ml.) was added, as well as some ice. The ether layer was separated. The water layer was extracted once more, and the ether extracts were combined and dried over sodium sulfate. The ether was removed on a vacuum evaporator. The residue was repeatedly extracted with low boiling petroleum ether. Stepwise, evaporation of the solvent and chilling to −50°C. gave the following fractions which were dried at room temperature and reduced pressure: 3.25 g., m.p. 75–76°C.; 3.28 g., m.p. 73.5–74.5°C.; 1.17 g., m.p. 73–74°C.; 1.28 g., m.p. 72.5–74°C.

The composition of this compound was confirmed by analysis and spectroscopy.

ANAL. Calcd. for $C_{16}H_{10}$: C, 95.02%; H, 4.98%. Found: C, 94.76%; H, 5.07%.

The infrared spectrum showed absorptions for acetylenic hydrogen at 3 μ and for a 9-substituted anthracene at 13.7 μ.

Monomer Stability: "Spontaneous" Polymerization

It should be pointed out that the instability of the monomer necessitated purification before use. After less than a week of storage at ambient conditions, a brown polymeric contaminant was present which was not soluble in aliphatic hydrocarbons. This material had a molecular weight of ~1800, an infrared spectrum similar to the cationic polymer, and a low carbon-hydrogen analysis which implied the presence of oxygen. Storage at −16°C. under nitrogen in the dark appeared to slow down this "spontaneous" polymerization but did not inhibit it completely. Solutions were prepared from freshly recrystallized material, or, in the case of polymerizations in aliphatic hydrocarbons, the solutions were filtered before initiation. A control run for the Ziegler-type polymerization at 60°C. (Run J, Table II) showed that "spontaneous" polymerization is not fast enough to contaminate the products under investigation.

Cationic Polymerization

The cationic polymerizations were run in a flame-dried, 100-ml., four-necked flask equipped with a stirrer, a drying tube, a dry nitrogen inlet, an injection port, and cooling bath. Freshly recrystallized monomers and dry methylene chloride were introduced. In the case of low-temperature polymerizations, the flask was cooled in a Dry Ice–isopropyl alcohol bath. The initiator was injected. The polymerization was blanketed with dry nitrogen throughout until terminated with a solution of 5 ml. concentrated hydrochloric acid in 50 ml. ethanol. The solids were isolated by filtration and separated into methylene chloride soluble and insoluble material. The soluble material was recovered by precipitation with methanol or by evaporation of the methylene chloride followed by extraction of the residue with methanol to remove monomer and very low molecular weight material. The products were dried at room temperature and reduced pressure. They were brown and did not melt below 300°C.

Note that one polymerization (E) was run in a serum bottle in carefully deaerated solvent in order to check the effect of traces of oxygen. None was noted in the polymerization or the product.

Ziegler-Type Polymerization

The Ziegler-type polymerizations were run in an oven-dried, nitrogen-filled serum bottle containing a magnetic stirring bar. The initiator solutions were injected in the order, triisobutylaluminum first, titanium tetrachloride second. The mixture was stirred 5 min. at room temperature before injecting a deaerated solution of monomer. The bottles for 60°C. runs were immersed in an oil bath and the stirring was continued. The reactions were terminated with alcoholic hydrochloric acid. The alcohol insoluble solids were extracted with refluxing 5% aqueous hydrochloric acid for 2 hr., dried at room temperature at reduced pressure, and weighed. The methylene chloride solubles were separated by extraction with 15 ml. solvent and recovered by precipitation with ethanol. All products were dried at room temperature and reduced pressure.

The insoluble polymers were generally dark grey and infusible below 300°C. The soluble polymers were brown and melted at 270–300°C.

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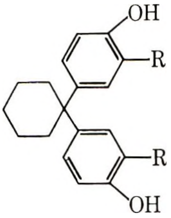
Elastomers Based on Cyclohexylidene Bisphenol Polycarbonates

The recent paper[1] by Perry et al. reported on the interesting properties of block copolymer elastomers based on polycarbonate hard segments derived from 4,4′-(2-norbornylidene) bis(2,6-dichlorophenol) (I). These polymers represented a unique class of elastomers, inasmuch as there was no evidence of the presence of any of the usual forms of crosslinking, i.e., covalent crosslinks, intermolecular hydrogen bonding, or hard segment crystallinity. Perry stated[1] that bulky, bicyclic groups, such as norbornylidene, imparted elastomeric behavior to these polymers by hindering the motion of chain segments. Shortly after hearing the preliminary report[2] on this subject, it was speculated that cyclohexylidene groups might be as effective as norbornylidene, since the spatial requirements of these two radicals are somewhat similar. One may consider that norbornane is derived from "boat" cyclohexane by replacement of the axial hydrogens at the "bow" and "stern" positions (C_1 and C_4 of norbornane) by a methylene bridge (C_7 of norbornane). Molecular models of "chair" cyclohexane (the normal conformation) and of norbornane confirm that the two groups are almost equally effective in their volume-filling ability, contrary to previously published[3] viewpoints. Because of the commercial availability of cyclohexanone, it seemed appropriate to prepare elastomers based on bisphenols derived from this chemical, and to compare their properties with those derived from norcamphor, which had been reported by Perry.[1]

Accordingly, a series of block copolymer elastomers was prepared with hard segments composed of the polycarbonate of 1,1-bis(4-hydroxyphenyl)cyclohexane (IIA), or 1,1-bis(4-hydroxy-3-methylphenyl)-cyclohexane (IIB), and a polyester soft segment.



IIA, R = H
IIB, R = CH_3

The polyester segment was Mobay's Multron R-16, a commercially available hydroxyl-terminated poly(diethylene glycol adipate) of approximately 2500 molecular weight. In one case, a polytetrahydrofuran soft segment was employed. Polymer preparation was effected by a modified Goldberg[4] technique, which consisted of bubbling phosgene through a pyridine–methylene chloride (50:50) solution of the bisphenol and the hydroxyl-terminated soft segment until solution viscosity increased to the point at which stirring became impossible. The polymers were then precipitated in isopropyl alcohol, carefully washed with alcohol and water, and dried *in vacuo*. Properties were evaluated on films cast from methylene chloride or on fibers dry-spun from this solvent.

In Table I, film properties of the best polymers obtained are compared to the properties of elastomers based on other polycarbonate hard segments. (Compositions containing significantly higher bisphenol to soft segment mole ratios were not snappy; those prepared using much lower ratios than those reported here were sticky and had uninterestingly low tensile strengths.) The significance of the data of Table I is that none of the block polycarbonate elastomers based on IIA and IIB showed any increase in tensile strength with mechanical orientation, although an identical mechanical orientation procedure produced twofold to approximately tenfold increases in tensile strength in the other block copolycarbonate elastomers studied. That the IIA and IIB block polycarbonate elastomers did not increase their tenacities upon mechanical orientation

TABLE I
Comparison of Physical Properties of Polycarbonate Elastomers (Film Data)

		Non-oriented film properties			Oriented film properties		
Polycarbonate Segment Based on Bisphenol	Soft segment	Tensile strength, psi	Elongation, %	Immediate elastic recovery, %	Tensile strength, psi	Elongation, %	Immediate elastic recovery, %
1,1-Bis(4-hydroxyphenyl)cyclohexane, 8 moles	Multron R-16 polyester, 1 mole	4930	930	97	4700	960	97
1,1-Bis(4-hydroxy-3-methylphenyl)-cyclohexane, 6 moles	Multron R-16 polyester, 1 mole	3480	930	97	3490	1020	97
1,1-Bis(4-hydroxyphenyl)cyclohexane, 9 moles	Multron R-16 polyester, 1 mole	4600	733	95	4840	763	94
Toluhydroquinone, 4 moles	Multron R-16 polyester, 1 mole	2290	2170	98	4820	850	99
Bisphenol A, 9.17 moles	Multron R-16 polyester, 1 mole	2110	990	96	8310	529	98
Bisphenol A, 3.7 moles	MW1061 Poly THF 1 mole	1380	1080	96	15600	228	99
p,p'-Diphenol, 3.5 moles	Multron R-16 polyester, 1 mole	580	1600	100	3930	1600	100

TABLE II
Typical Fiber Properties of the Block Copolymers of II Bisphenol

Polycarbonate segment based on Bisphenol	Soft segment	As-spun properties				Properties of boiled-off fibers			
		Tenacity				Tenacity			
		g./den.	psi	Elongation, %	Permanent set, %	g./den.	psi	Elongation, %	Permanent set, %
1,1-Bis-(4-hydroxy-3-methyl-phenyl)-cyclohexane, 6 moles	Multron R-16 polyester, 1 mole	0.56	8,600	460	25	0.33	5,060	490	53
1,1-Bis-4-hydroxy-phenyl)cyclohexane, 8 moles	Multron R-16 polyester, 1 mole	1.01	15,500	470	15	0.42	6,450	490	37
1,1-Bis-4-hydroxy-phenyl)-cyclohexane, 8 moles	MW2700 Poly THF, 1 mole	1.49	22,800	160	—	0.33	5,060	430	34
1,1-Bis-4-hydroxy-phenyl)-cyclohexane, 9 moles	Multron R-16 polyester, 1 mole	0.73	11,200	355	—	0.52	8,000	456	33

may be a consequence of the noncrystallizability of these polycarbonate hard segments. X-ray examination of the elastomers based on IIA and IIB showed them to be completely amorphous, regardless of whether they were stretched, unstretched, or steam-treated. In these respects they are similar to the I block polycarbonate elastomers of Perry et al. Apparently, the cyclohexylidene group exerts an influence on elastomeric properties which is equivalent to that of a norbornylidene group, and permits the formation of strong, snappy elastomers which do not contain classical type tie-points.

The IIA and IIB block polycarbonate elastomers were dry-spun from methylene chloride solutions.

Optimum properties, obtained by adjusting process variables, are recorded in Table II. As-spun tensile properties are higher than would be expected on the basis of film properties, indicating that some orientation had occurred in the spinning and drawing process. This orientation, however, could not be "locked in" by hard segment crystallization, and boiling reduced fiber tenacities to the approximate corresponding film tensile strengths. It is interesting that the general level of tensile properties of the IIA and IIB block polycarbonate elastomers is approximately in the same range as the properties reported[1] for the elastomers based on I, although there is a large disparity in the second-order transition temperatures of the homopolycarbonates of these two types of bisphenols. The polycarbonates of IIA and IIB have T_2 = 179°C.[3] and 137°C.,[5] respectively, whereas I polycarbonate has T_2 = 290°C.[3] This nondependence of elastomeric properties on hard-block homopolymer transition temperatures suggests that the interchain interactions of the hard segments are of an unusual nature.

In summary, we have found that it is not necessary to use bisphenols containing polycyclic rings to obtain elastomeric block copolycarbonates having noncrystallizable hard segments. Indeed, hard segments of IIA or IIB polycarbonate, having cyclohexylidene pendant groups, behave similarly to the I polycarbonate hard segments, reported by Perry et al.[1,2] which have norbornylidene pendant groups. The results are somewhat unexpected, inasmuch as the homopolycarbonates of bisphenols IIA and IIB are described in the literature[5,6] as crystalline, whereas that of bisphenol I is amorphous.[3]

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The Kinetics of Depolymerization of Hyaluronic Acid by L-Ascorbic Acid, and the Inhibition of This Reaction by Anions of the Lyotropic Series

The depolymerization of hyaluronic acid by L-ascorbic acid in oxygenated aqueous solutions (ORD reaction[1]) is inhibited by six inorganic potassium salts. The inhibiting power is shown in this paper to follow the approximate order of the anions in the lyotropic (Hofmeister) series.[2] The inhibitions appear to arise from variations in the abilities of the anions to compete with the polymer for free radicals generated by the ascorbic acid. Evidence is presented that the active species is the hydroxyl radical.

Hyaluronic acid was prepared in a purified state (less than 5% w/w protein) from cattle synovial fluid, after removal of contaminants by successive treatments with ethanol, cetylpyridinium chloride, and Fuller's earth.[3] The final product (intrinsic viscosity 30 dl./g.) was diluted to 0.4 mg./ml. for all experiments. During depolymerizations, viscosity changes were followed as described in earlier papers from this laboratory[3,4] in Cannon-Manning viscometers, type 100, at 30 ± 0.01°C. The initial concentration of L-ascorbic acid was always 0.31 *mM*. The ionic strength of all solutions was $0.2M$ at a pH of 7.4 using appropriate quantities of phosphate buffer. When the results were plotted as specific fluidity (ϕ) against time, straight lines were obtained for all experiments conducted either in the presence or absence of potassium salts. Typical results are shown in Figure 1, and are similar to those obtained by Smidsrød et al. for the depolymerization of alginic acid by L-ascorbic acid.[5] They may be expressed as

$$d\phi/dt = \text{const.} \tag{1}$$

We explain these results as follows: for aqueous solutions of hyaluronic acid a linear relationship exists between specific viscosities (η_{sp}) at different concentrations and the intrinsic viscosity $[\eta]$ of the polymer, as indicated by the theory of viscosity of such molecules[6,7] $[\eta] = \eta_{sp}\,(1/c - a)$, where c is the concentration in units conventionally as g./dl. As the concentration remains the same during any one depolymerization, changes in specific viscosity may be related to the number of chain breaks (N) occurring in a random process, using in addition Laurent's value[8] of 0.78 for the exponent in the Staudinger equation $[\eta] = k[\text{M.W.}]^{\alpha}$. Such calculations show that over the initial stages of such reactions $d\phi/dt \sim dN/dt$. Earlier papers from this and other laboratories have given experimental data that indicate the free-radical nature of the reactions studied here.[9,10]

We consider that the following mechanism represents the method of generation of the organic free radical that leads to the degradation of the hyaluronic acid in the presence of inhibitor.

$$\text{RH} + \dot{\text{Z}} \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} \dot{\text{R}} + \text{ZH} \tag{2}$$

$$\text{X}^- + \dot{\text{Z}} \xrightarrow[k_1]{} \dot{\text{X}} + \text{Z}^- \tag{3}$$

where $\dot{\text{Z}}$ is the active free radical produced in ORD reactions by the autoxidant, X^- is the added anion, and $\dot{\text{R}}$ is the polymer radical which is rapidly degraded leading to a decrease in viscosity. The species Z^- and $\dot{\text{X}}$ are considered to lead to no further depolymerization. Because the concentration of the autoxidant L-ascorbic acid was the same for all the experiments, at steady-state conditions the rate of production of $\dot{\text{Z}}$ is the same constant value for all experiments, C. From eqs. (2) and (3) we have

$$C - k_0(\dot{\text{Z}})(\text{RH}) + k_{-0}(\dot{\text{R}})(\text{ZH}) = 0$$

$$(\dot{\text{Z}}) = \{C + k_{-0}(\dot{\text{R}})(\text{ZH})\}/k_0(\text{RH})$$

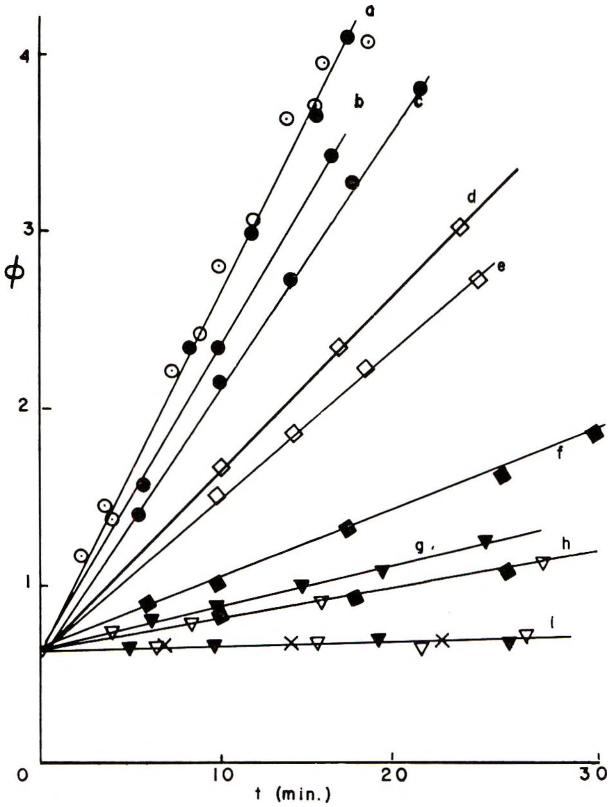

Fig. 1. Typical fluidity/time relationships during the depolymerization of hyaluronic acid (0.4 mg./ml.) by L-ascorbic acid (0.31 *mM*) in the presence of various concentrations of inhibiting anions of potassium: (⊙) no added anion; (●) KCl (*a*) 0–2 *mM*, (*b*) 11 *mM*; (*c*) 30 *mM*; (◇) KNO_3, (*d*) 9 *mM*, (*e*) 18 *mM*; (◆) KBr, (*f*) 5 *mM*, (*h*) 10 *mM*; (▼) KCNS, (*g*) 2 *mM*, (*i*) 5 *mM*; (▽) KI, (*h*) 6.7 *mM*, (*i*) 13.3 *mM*; (×) $K_4Fe(CN)_6$ 4.2 *mM*.

in the absence of inhibitor, and

$$C - k_0(\dot{Z})'(RH) + k_{-0}(\dot{R})'(ZH)' - k_1(\dot{Z})'(X^-) = 0$$

$$(\dot{Z})' = [C + k_{-0}(\dot{R})'(ZH)']/[k_0(RH) + k_1(X^-)]$$

in the presence of inhibitor. Since we consider $d\phi/dt \propto dN/dt$, both of which are proportional to $(RH)(\dot{Z})$, $\Delta\phi_0/\Delta\phi = (\dot{Z})/(\dot{Z})'$ where $\Delta\phi$ is the change in specific fluidity over an arbitrary time interval (taken as 10 min.) in the presence of inhibiting anion, and $\Delta\phi_0$ has the same significance in the absence of inhibiting anions. Then,

$$\Delta\phi_0/\Delta\phi = (\dot{Z})/(\dot{Z})' = [C + k_{-0}(\dot{R})(ZH)] \times [k_0(RH) + k_1(X^-)]/[k_0(RH)][C + k_{-0}(\dot{R})'(ZH)'] \quad (4)$$

We see that if $C \gg k_{-0}(\dot{R})(ZH)$ and also $\gg k_{-0}(\dot{R})'(ZH)'$, as would be expected when $\dot{R}$ is rapidly and irreversibly oxidized, eq. (4) reduces to

$$\Delta\phi_0/\Delta\phi = 1 + [k_1/k_0(RH)](X^-)$$

so that when $(\Delta\phi_0/\Delta\phi) - 1$ is plotted against (X^-), a series of linear curves should be produced, all passing through the origin.

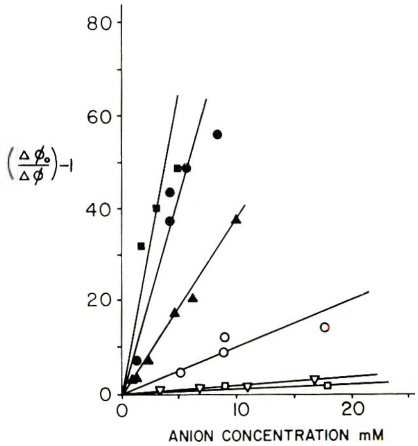

Fig. 2. $[(\Delta\phi_0/\Delta\phi) - 1]$ vs. concentration (mM) of various inhibiting anions. The inhibiting powers of the anions are proportional to the slopes of the curves: (■) ferrocyanide; (▲) iodide; (○) bromide; (▽) chloride; (□) nitrate; (●) thiocyanate. The results for chloride ions are plotted as $10[(\Delta\phi_0/\Delta\phi) - 1]$ vs. chloride concentration (mM).

The experimental data follow this relationship as shown in Figure 2. The slopes of the curves are therefore proportional to the k_1's for the respective anions reacting with the active species, and are also proportional to the inhibiting abilities of the anions. This order, with the most efficient inhibitor first, is $Fe(CN)_6^{4-}$, CNS^-, I^-, Br^-, NO_3^-, Cl^-, the anions appearing in their order in the classical lyotropic series.[11]

As the hydroxyl radical is a plausible choice for the unidentified species $\dot{Z}$, we have obtained values of k_1/k_0 (RH) from the slopes of the plots in Figure 2, and used published values for the rates of attack of the hydroxyl radical upon the various anions studied.[12-14] k_0 (now assumed to be the rate constant for the reaction: $\dot{O}H$ + hyaluronic acid → products) has a satisfactorily constant value for four out of the five reactions for which data are available (Table I).

Our study, then, indicates that the changes in viscosity of hyaluronic acid solutions in the presence of L-ascorbic acid are initiated by some free-radical species. The evidence suggests that the species is the hydroxyl radical. We further consider that the

TABLE I

Evaluation of k_0 from the Data of Figure 2, Using Values of k_1 Found in the Literature for Hydroxyl Radical Reactions[12-14]

Competing anion	k_1/k_0 RH [a]	$k_1 \times 10^{-8}$, M^{-1} sec.$^{-1}$ [b]	$k_0 \times 10^{-8}$, M^{-1} sec.$^{-1}$ [c]
Ferrocyanide	13.8	110	6.6
Thiocyanate	8.8	60	5.7
Iodide	3.8	120	26
Bromide	0.9	9	8.3
Nitrate	0.1	—	—
Chloride	0.02	0.2	8.3

[a] Values of the slopes of the curves in Fig. 2.

[b] Weighted averages of recent values recorded in the literature 12–14 from pulse radiolysis results.

[c] RH is 1.2 mM when expressed as disaccharide units. k_0 is calculated on this basis and therefore the figures also refer to disaccharide units.

inhibitions produced by addition of various anions are results of their ability to compete with the polymer for the free-radical species. We further suggest that similar phenomena reported as following the lyotropic series (e.g., the retrogradation of soluble starch solutions[11]) should be reconsidered as also arising from this type of irreversible oxidation rather than from variations in the solvolytic properties of the anions.

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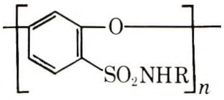
Poly-m-phenoxylene Sulfonamides

A series of polymers of the general structure



has been prepared and its properties investigated. These modified poly-*m*-phenoxylenes were prepared from a sulfonyl chloride derivative which could undergo reaction with various amines to form the sulfonamide derivatives.

The basic polymer, poly-*m*-phenoxylene, was synthesized* according to a previously reported method[1] which involved the polymerization of the potassium salt of *m*-chlorophenol in the presence of copper powder.

Initially, the intermediate sulfonyl chloride derivative was to have been made from the corresponding sulfonic acid derivative. Accordingly, the sulfonic acid group was introduced into poly-*m*-phenoxylene by means of sulfuric acid in acetic anhydride as the sulfonating agent. However, attempts to convert the sulfonic acid to the sulfonyl chloride derivative met with only fair success. Although various methods were used, elemental analyses indicated conversions of less than 40% in all cases. This lack of success could be attributed partly to difficulties encountered during work-up of the reaction mixtures and the subsequent hydrolysis of the sulfonyl chloride groups during these purification procedures.

As an alternate route, the sulfonyl chloride was prepared by reaction of poly-*m*-phenoxylene with chlorosulfonic acid. If protolytic solvents were avoided during the work-up procedures, sulfonyl chloride groups constituted as much as 85% of the sulfur-containing groups. The products of a number of these reactions were combined to form a uniform starting material which was then carefully purified. It had approximately 1.4 sulfur-containing substituents per repeating unit, 1.0 of these being sulfonyl chloride groups. The remaining sulfur-containing substituents were probably sulfonic acid groups which either were formed as an intermediate in the sulfonyl chloride synthesis or resulted from hydrolysis during the work-up procedure.

The sulfonyl chloride derivative was reacted with ammonia and a series of amines (i.e., aniline, carbazole, 4-amino-*p*-terphenyl, dodecylamine, and allyl amine) to form sulfonamide derivatives. The weight ratio (sulfonamide derivative/sulfonyl chloride derivative) varied from 0.6 to 1.1.

Pyridine was used as an acid acceptor in the majority of the reactions. The resulting pyridine hydrochloride could be eliminated from the polymer more easily than the hydrochloride salts of a number of other potential acid acceptors.

A small amount of insoluble, crosslinked polymer was isolated from some of the reactions. It was found that crosslinking was held to a minimum if reaction temperatures of less than 65°C. were used.

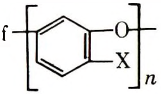
In the majority of the reactions, dimethyl sulfoxide was used as a reaction medium, since the products were soluble in that solvent and stayed in solution during the course of the reaction. Attempts to use tetrahydrofuran as a solvent resulted in the formation of crosslinked products.

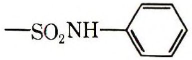
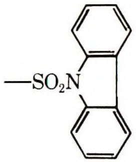
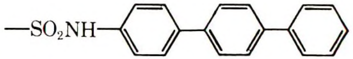
Properties of the Polymers

The poly-*m*-phenoxylene used in this investigation was a tan powder with an inherent viscosity in benzene of 0.16. Vapor-pressure osmometry molecular weight determinations in that solvent indicated a molecular weight of approximately 5100.

* Prepared by Wyandotte Chemicals Corporation, Wyandotte, Michigan under AF Contract.

TABLE I

Physical Properties of 

X	Appearance	Solvents	Number of X units per ring[a]	η_{inh} (solvent)
—H	Tan powder	C_6H_6, THF, $CHCl_3$, DMF	1.0	0.16 (C_6H_6)
—SO_2Cl	Light tan powder	THF, DMF, DMSO	1.0	0.84 DMSO
—SO_2NH_2	Light brown powder	HCOOH, H_2O, DMSO, DMF	1.0	1.74 (DMSO)
	Olive powder	DMSO, HCOOH, DMF, THF	0.9	1.25 (DMSO)
	Tan powder	DMSO, HCOOH, DMF	0.6	0.60 (DMSO)
	Tan powder	DMSO	0.8	0.66 (DMSO)
—$SO_2NH(CH_2)_{11}CH_3$	Tan powder	THF, acetone, DMSO, DMF	1.0	0.25 (DMSO)
—$SO_2NHCH_2CH{=}CH_2$	Light tan powder	DMSO, HCOOH, DMF	1.0	1.14 (DMSO)

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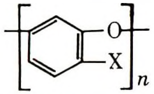
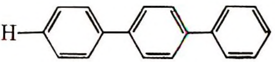
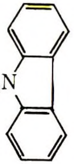
[a] As determined from elemental analysis.

TABLE II
DTA Transitions and TGA Inversion Points for



X	DTA transitions, °C.[a,b]					Inversion point(s) of the TGA curve, °C.
—H	53(−)	[135(−)]			*580*(+)	*545*
—SO_2Cl	95(−)	135(−)	215(+)	*255*(+)	430(−)	(120), *270*
—SO_2NH_2	90(−)	135(−)		*367*(−)	[475(−)]	*345*, 475
—$SO_2NH(CH_2)_{11}CH_3$	[60(−)]	135(−)		*312*(−)		*300*
—$SO_2NHCH_2CH{=}CH_2$	60–80(−)	[135(−)]	265(+)	*300*(−)		*280*
—SO_2NH 	80(−)	140	235(+)	*385*(−)		*310*
—SO_2NH— 	75–85(−)	130(−)	245(+)	*350*(−)	370(−)	*300*
—SO_2N 	90(−)	135(−)	220(−)	*255*(−)	295(+), 315(−)	*285*

[a] + = exotherm; − = endotherm; [ ] = questionable.

[b] Italics denote decomposition temperature.

In general, the various derivatives were tan or olive-colored powders. Elemental analyses of the products indicated that conversion of the sulfonyl chloride group to the desired substituent varied from 60 to 100% (0.6 to 1.0 of the desired substituent per repeating unit). The various modified polymers exhibited inherent viscosities in dimethyl sulfoxide ranging from 0.25 to 1.74. This wide range in values can be attributed partly to the varying degrees of interaction of the different substituents with the solvent. In addition, many of the products were inadvertently fractionated during the purification procedures, the higher molecular weight fractions being retained. However, the possibility that chain extension or branching may have occurred should not be overlooked.

In general, the infrared spectra of the polymers were consistent with their assigned structures. In all cases, the spectra exhibited bands at ~1450 and ~1600 cm.$^{-1}$, indicative of the phenyl nucleus, and at ~1250 cm.$^{-1}$, indicative of the diaryl ether linkage. The sulfonic acid derivative gave rise to bands at 1040 and 1200 cm.$^{-1}$, attributable to the sulfonic acid group. These bands could be seen in many of the other spectra, thus demonstrating the presence of unreacted $-SO_3H$ groups in these polymers. The sulfonyl chloride derivative exhibited bands at 1180 and 1390 cm.$^{-1}$ indicative of the $-SO_2Cl$ group while the sulfonamide derivatives all gave rise to bands in the regions 1120–1230 and 1310–1420 cm.$^{-1}$ attributable to the $-SO_2$-stretching vibrations.[2] NMR spectroscopy indicated that the sulfur-containing substituents were primarily in positions *ortho* to the first and *para* to the second ether linkage. The composition, appearance, solubility and inherent viscosities of the polymers are given in Table I.

The reversible and irreversible thermal transitions of the polymers were determined by subjecting them to softening under load, thermogravimetric analysis, and differential thermal analysis. Comparison of the data obtained by these three methods allows one to distinguish between the reversible transitions connected with the melting process and the irreversible transitions from decomposition of the polymers. The starting material melts is the range 40–90°C. The sulfonyl chloride and the primary sulfonamide soften only to a limited extent in this range. The rest of the sulfonamide polymers have softening ranges around 200°C.

Differential thermal analysis shows a rather complex pattern. All of the polymers have two endotherms (between 53 and 90°C. and between 130 and 140°C.) which are connected with the melting process. A number of the polymers have a transition (mostly exothermic) between 215 and 265°C. Another transition (between 255 and 385°C. and mostly endothermic) can be related to the decomposition temperature. This temperature is also reasonably close to the inversion point of the TGA curve (Table II).

In general, the substitution of the polymer with sulfonamide groups increased the softening point, but decreased the thermal stability. No improved mechanical properties were noted.

Experimental

Preparation of Starting Materials. Poly-*m*-phenoxylene[3] was found to contain substantial amounts of mineral oil. The polymer was subjected to several dissolution–reprecipitation treatments, tetrahydrofuran being used as a solvent and petroleum ether as a precipitant. In order to obtain the polymer in a tractable condition, it was necessary to carry out a final reprecipitation in methanol. The polymer was dried in a vacuum oven at 35°C. for 48 hr.

ANAL. Calcd. for C_6H_4O: C, 78.26%; H, 4.34%; O, 17.38%; Cl, 0.00%; Cu, 0.00%. Found: C, 76.25%; H, 4.40%; O, 17.34%; Cl, 0.45%; Cu, 0.19%.

4-Amino-*p*-terphenyl was prepared by the Monsanto Research Corporation under Air Force contract and was used as received, m.p. 198–201°C. (lit.[4] m.p.: 201°C.). The remaining starting materials were obtained through commercial sources.

Chlorosulfonation of Poly-*m*-phenoxylene. Approximately 160 ml. of chlorosulfonic acid was cooled to 0–5°C. by means of an ice bath. Then 10 g. of poly-*m*-phenoxylene was added slowly with vigorous stirring. The reaction mixture was allowed to warm to room temperature and was then heated at 65°C. for 18 hr. After being allowed to cool to room temperature, the reaction mixture was added slowly with stirring to 800 ml. of cooled absolute ether. The solvent–nonsolvent mixture was decanted, and 1 liter of chloroform was added to the syrupy residue. After several minutes of vigorous stirring, the polymer took on a tan color and could be isolated as fine particles by filtration. The filtrate was stirred with an additional 500 ml. of ether. Additional polymer precipitated and was also isolated by filtration. The polymer was dried in a vacuum desiccator for 48 hr. A total of 19.0 g. of product was obtained.

The products of a number of trials similar to the above were dissolved together in tetrahydrofuran (THF) and reprecipitated with ether. The isolated polymer was redissolved in THF, the polymer solution filtered, and the polymer reprecipitated with pet. ether. The polymer was isolated by filtration and dried in a vacuum desiccator for 60 hr.

ANAL. Found: C, 30.6%; H, 1.6%; S, 18.4%; Cl, 15.5%.

Reaction of the Sulfonyl Chloride Derivative with 4-Amino-*p*-terphenyl. The following is an example of a preparation of a sulfonamide derivative. The sulfonyl chloride derivative (2.0 g.) was dissolved in 30 ml. of anhydrous DMSO at room temperature. With vigorous stirring being maintained, a solution of 4-amino-*p*-terphenyl (2.0 g.) and dried pyridine (2.0 g.) in 20 ml. of DMSO was added dropwise. A precipitate formed almost immediately but dissolved when the reaction temperature was raised to 60°C. After 2 hr., the reaction mixture was allowed to cool to room temperature and was stirred for 4 hr. more. The polymer was precipitated with 500 ml. of acetone and was isolated by filtration. It was then redissolved in 100 ml. of DMSO and reprecipitated with 800 ml. of THF. After drying, the polymer was extracted in a Soxhlet with THF for 75 hr. and with methanol for 8 hr. After drying in a vacuum over at 100°C. for 125 hr., 2.1 g. of product was obtained.

ANAL. Found: C, 55.7%; H, 3.9%; S, 12.0%; N, 3.7%; Cl, 0.5%.

Determination of Softening Range. The softening range of the polymers was obtained in the following manner. A sample holder was filled with the powdered polymer to a depth of 0.04 in. The sample was then placed under a load of 1 kg. covering an area of 0.049 in.^{2}. Heating was performed at a constant rate of 150°C./hr. The softening range was determined from a plot of temperature versus penetration.

Thermogravimetric Analysis (TGA). Determinations were carried out in a nitrogen atmosphere on a modified Chevenard thermobalance at a constant heating rate of 150°C./hr.

Differential Thermal Analysis (DTA).* The instrument used was a specially designed aluminum block connected to an Aminco thermobalance. The determinations were performed under a helium atmosphere at a heating rate of 8°C./min. The sample was mixed with Al_2O_3 with the reference material also being Al_2O_3.

The authors wish to thank Miss Mary Ryan for her valuable assistance in interpreting the NMR spectra.

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* Performed by U. S. Rubber Company under Air Force Contract.

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Stress–Strain Behavior of Elastic Materials. Selected Problems of Large Deformations. O. H. Varga. Interscience, New York, 1966. x + 190 pp. $11.00.

In this book the author presents a rigorous mathematical development of necessarily valid stress–strain relationships in isotropic incompressible materials, applicable to any assumed strain-energy functions. He then shows that "the simplest principal stress–strain law," consistent with these relationships, is in agreement with the elastic behavior of vulcanized rubber, as measured experimentally in various ways, up to extensions of about 100%. For larger extensions this simplest law is not applicable, but for many problems of interest and importance it will surely be useful.

Structural and kinetic theories of elasticity are not considered, yet the fundamental relationships derived and presented here will certainly be used by others wishing to test their theoretical ideas and equations and to apply them to actual materials and industrial problems.

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