

## Crystallization and Melting of Copolymers of Polyoxymethylene

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### Synopsis

Copolymers of polyoxymethylene were prepared from trioxane in the presence of comonomers such as dioxolane, 1,3-dioxane, dioxepane and epichlorohydrin, boron trifluoride etherate being used as catalyst. Fusion and crystallization phenomena were studied on these copolymers by use of density measurement, differential thermal analysis, dilatometry, and microscopy. The spherulite growth rate and the induction period of the crystallization were determined. The temperature dependence of the growth rate was calculated assuming a two-dimensional surface nucleation mechanism.

### INTRODUCTION

Polyoxymethylene is a fairly highly crystalline polymer in which crystallization takes place at a rapid rate from the melt accompanied by formation of spherulites.<sup>1,2</sup> The problems of crystallization of the polymers are of considerable interest, because the various properties depend not only on the total crystallinity but also on the size and shape of crystallites and on other morphological characteristics of the crystals.

The high crystallinity of polyoxymethylene contributes to the high tensile strength, high stiffness, and high hardness, etc. of this polymer.<sup>3</sup> Polyoxymethylene dihydrate, however, is not stable at elevated temperatures and suffers thermal degradation above 150°C., with evolution of formaldehyde gas. In order to increase the thermal stability, the hydroxyl endgroups are usually converted to other more stable groups such as ether, ester, or urethane groups. The thermal stability is much improved by introducing  $(\text{CH}_2)_n\text{—O}$  units into the polyoxymethylene chain, where  $n$  is above 2. In addition, the introduction of different units results in the depression of the crystallinity of polyoxymethylene. We have studied the copolymerization of trioxane with various comonomers such as dioxolane, 1,3-dioxane, dioxepane, and epichlorohydrin which have adjacent carbon atoms.<sup>4</sup> The details of the copolymerization will be published in forthcoming papers.

Lal and Trick<sup>5</sup> synthesized a number of poly(methylene sulfide)  $[-(\text{CH}_2)_n\text{—S—}]_x$  and poly(methylene oxide)  $[-(\text{CH}_2)_n\text{—O—}]_x$  polymers in order to study the influence of sulfur and oxygen atoms on the melting temperature and the rate of crystallization. Though they showed that the

difference in melting point between the two series is highest for  $n = 2$  and decreases as the length of the polymethylene groups is increased, they could not draw any conclusion regarding the influence of the polymer structure upon the crystallization rate. Recently, Richardson, et al.<sup>6</sup> studied the crystallization and melting of copolymers of polymethylene by dilatometry.

In this paper, we report the crystallization and melting behavior of the copolymers of polyoxymethylene. The melting point, density, growth rate of the spherulites, and induction periods of crystallization were determined, and dilatometry and differential thermal analysis, were carried out.

## EXPERIMENTAL

### Preparation of Monomers

Trioxane was purified by recrystallization in methylene chloride dehydrated with calcium hydride. Dioxolane was synthesized from ethylene glycol and formaldehyde in benzene, *p*-toluenesulfonic acid being used as catalyst. 1,3-Dioxane was prepared from trimethylene glycol and paraformaldehyde in benzene with the use of the same catalyst. Dioxepane

TABLE I  
Viscosities of the Copolymers Used

Comonomer	Comonomer content, mole-% <sup>a</sup>	Inherent viscosity <sup>b</sup>
None	—	1.42
Dioxolane	2	1.38
"	4	1.29
"	6	1.30
"	7	1.12
1,3-Dioxane	1	1.35
"	2	1.30
"	4	1.32
"	6	1.28
"	8	1.21
Dioxepane	1	1.51
"	3	1.33
"	6	1.38
"	7	1.40
"	9	1.26
Epichlorohydrin	2 (2.2)	0.96
"	4 (3.8)	1.12
"	5 (5.3)	0.96
"	7 (6.7)	0.83
"	9 (8.4)	0.81

<sup>a</sup> Mole % of comonomer is expressed in charging ratio. Regarding epichlorohydrin, values in parentheses show that comonomer composition in the polymer calculated from the weight-% of chlorine included in the polymer.

<sup>b</sup> Inherent viscosity is determined from the solution viscosity of 0.5 g./100 cc. in *p*-chlorophenol at 60°C.

was synthesized from tetramethylene glycol and paraformaldehyde in the presence of *N*-phenyl-naphthylamine and *p*-toluenesulfonic acid.

### Preparation of Copolymers

Trioxane and comonomer were dissolved in cyclohexane, making 50% solution in a bottle with a stirrer. Boron trifluoride etherate (0.05–0.2 mole-%) as catalyst was added to the reaction mass. The polymerization was performed at a temperature of 55°C. for 3–20 hr. After the polymerization, 5% methanol solution of triethanolamine was poured in to kill the catalyst, and the reaction mass was then filtered. The copolymers of polyoxymethylene were obtained in the form of white powder after drying at 50–60°C. for 20–30 hr. in an air oven.

The specimens of the copolymers used in this experiment are tabulated in Table I. Figure 1 shows x-ray diffraction photographs of the copolymers, which indicate that high crystallinity is maintained in copolymers containing less than 10 mole-% of comonomers.

### Microscopy

The copolymer powders were heated on the hot stage of a polarizing microscope at a rate of heating of about 5°C./min. up to 20°C. below the melting point, and 0.5°C./min. near the melting temperature.

### Density

The density was measured at 25°C. by use of a density gradient tube. A mixture of toluene and carbon tetrachloride was used as the density gradient liquid. The polymer powder to be used for the measurement of the density was washed thoroughly with methanol and water and dried at 60°C. for 30 hrs.

### Dilatometry

For the measurement of the thermal expansion, a dilatometer was used which had a bulb of 6 mm. inner diameter and a length of 50 mm., the diameter of the capillary being 2 mm. The specimens were molded by compression molding into the form of rod, of 4.5–4.8 mm. in diameter 30 mm. in length. The rods were inserted into the bulb, then well purified mercury was added under vacuum. The expansions of the dilatometer bulb and mercury are compensated. The rate of temperature change was adjusted to 1–1.5°C./min.

### Differential Thermal Analysis

As reported in our previous paper,<sup>7</sup> the conventional differential thermal analysis, DT-10 Type apparatus, manufactured by Shimadzu Co., Kyoto, Japan, was used. The sample measured was in the form of powder. In each measurement, 50 mg. of the sample was taken. The melting and

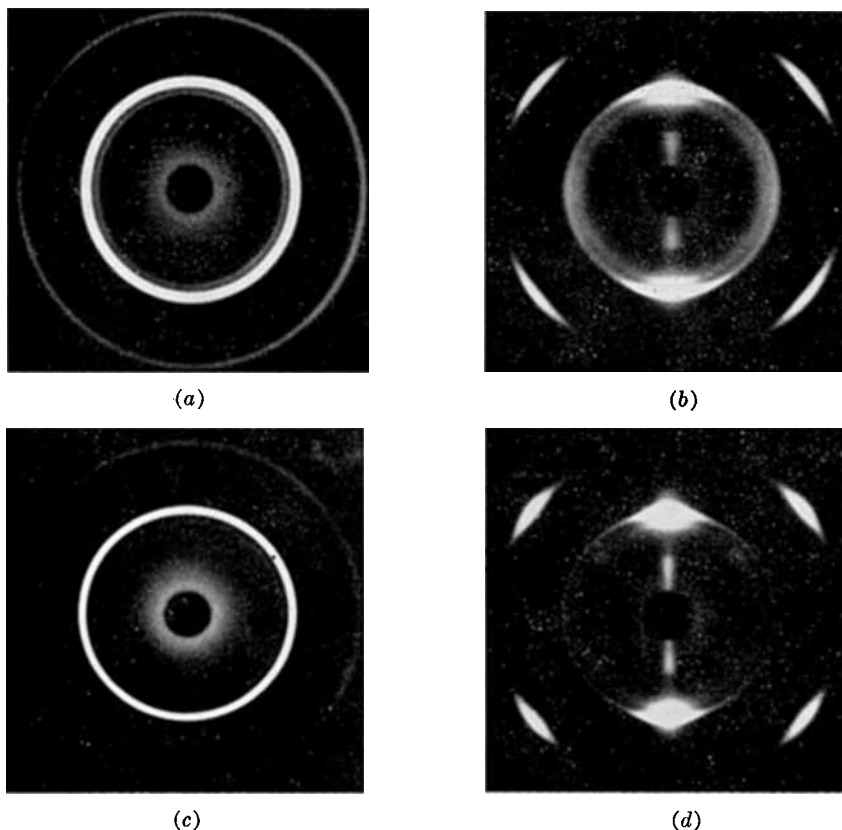


Fig. 1. X-ray diffraction photographs: (a) polyoxymethylene; (b) polyoxymethylene, hot drawn; (c) dioxolane, 4 mole-% copolymer; (d) dioxolane, 4 mole-% copolymer, hot drawn.

crystallization behaviors were studied by the observation of the endothermic and exothermic peaks, respectively.

#### Growth Rate of Spherulites and Induction Periods of Crystallization

The polymer samples in the form of powder were melted at temperatures  $20^{\circ}\text{C}$ . above the melting points for 2–3 min. between glass microscope cover slips on a hot plate to form a sandwich in which the polymer thickness is about  $20\ \mu$ . In order to study the kinetics of spherulite growth, the melts were quickly transferred ( $<0.5$  sec.) to a hot stage mounted on a polarizing microscope. The temperature of the hot stage was adjusted within  $0.5^{\circ}\text{C}$ . of the desired crystallization temperature. The growth of spherulites was followed with a motion picture camera mounted on the microscope. From the film records of the spherulite growth, the radius of an individual spherulite was determined as a function of time by measuring the image from the film projected at  $500\times$  total magnification. Film speeds were 16–42

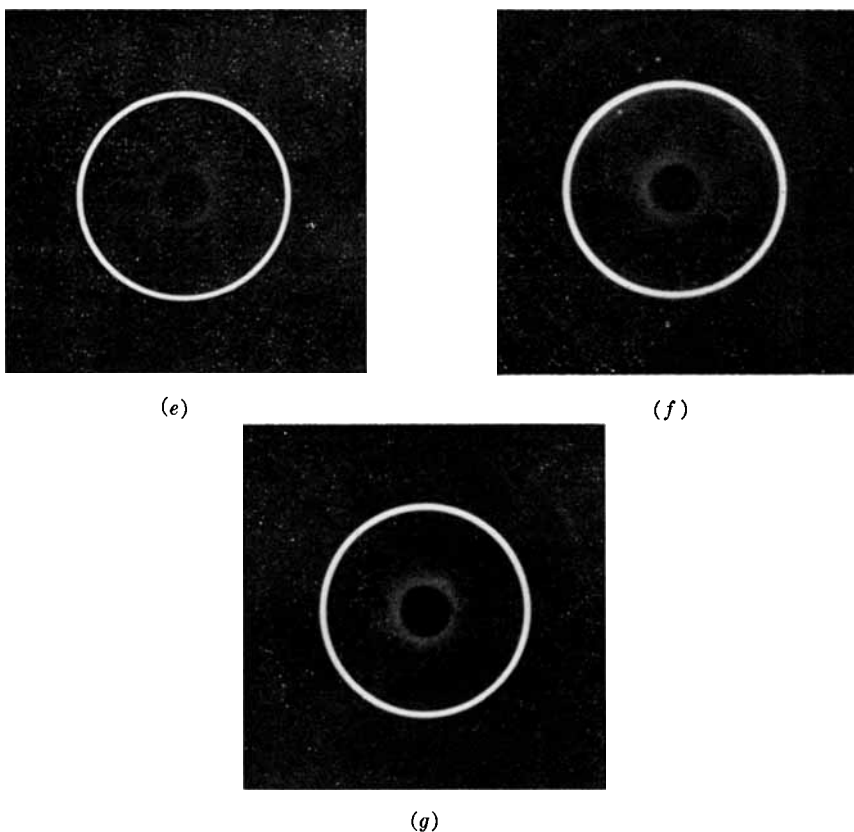


Fig. 1 (*continued*). X-ray diffraction photographs: (e) 1,3-dioxane, 4 mole-% copolymer; (f) dioxepane, 3 mole-% copolymer; (g) epichlorohydrine, 5 mole-% copolymer.

frames/sec. depending on the growth rate at a given crystallization temperature.

The induction period was taken as the crystallization time required just to produce a birefringent sparkle, from which a spherulite grows. The measurements were repeated several times for each set of experimental conditions.

## RESULTS AND DISCUSSION

### Fusion and Crystallization Phenomena

Figure 2 shows the melting points of the copolymers measured by use of the polarizing microscope. The melting points are linearly depressed independently of the kind of comonomers as the composition of the comonomers is increased. The specific volume of the copolymers is illustrated in Figure 3, which indicates that the copolymers have quite sharp melting points, and that the specific volumes of the amorphous parts of

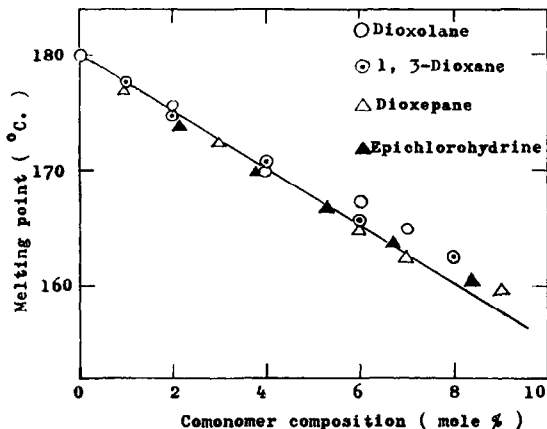


Fig. 2. Melting points of polyoxymethylene copolymers by microscopy.

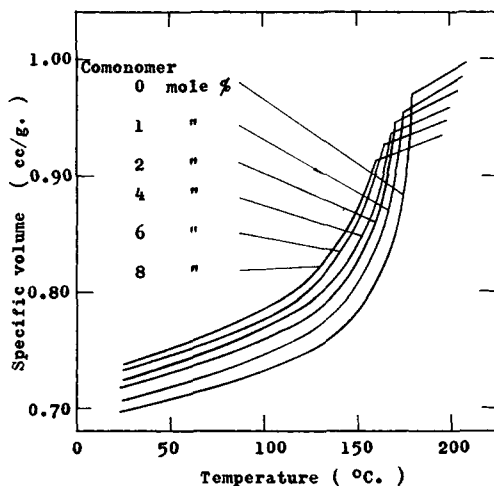


Fig. 3. Specific volumes of polyoxymethylene copolymers by dilatometry. Comonomer: 1,3-dioxane.

polyoxymethylene and the copolymers at 25°C. are almost equal, as estimated by extrapolating the specific volumes of the melts. Figure 4 is an example of the thermograms of the fusion and crystallization by differential thermal analysis. As the comonomer content increases, both the melting peak temperature and its area are decreased.

As shown in Table II, the melting points by dilatometry agree fairly well with those obtained by differential thermal analysis. The peak area is proportional to the crystallinity of the specimens, corresponding to the density, as shown later. With increase of the comonomers contents, the difference between the specific volume at the melting point and that at 25°C. is decreased.

TABLE II  
Melting Points and Specific Volumes of the Copolymers of Polymethylene

Comonomer	Differential thermal analysis			Dilatometry	
	Comonomer content, mole-%	Melting peak temperature, °C.	Peak area (relative)	Melting temperature, °C.	Specific volume difference between at 25°C. and at m.p., cc./g.
None		179	380	180	0.272
Dioxolane	2	176	345	176	0.245
"	4	170	290	172	0.226
"	6	168	275	169	0.205
"	7	164	270	165	0.191
1,3-Dioxane	1	176	352	175	0.250
"	2	174	325	173	0.238
"	4	169	285	170	0.208
"	6	166	270	165	0.192
"	8	163	262	163	0.176
Dioxepane	1	178	345	177	0.245
"	3	173	310	173	0.233
"	6	165	272	166	0.215
"	7	163	265	162	0.193
"	9	160	260	160	0.184
Epichlorohydrin	2	175	330	176	0.240
"	4	172	295	172	0.216
"	5	168	270	169	0.208
"	7	165	265	166	0.198
"	9	163	260	165	0.181

The melting temperatures of copolymers,  $T_m$ , are given by the Flory's equation:<sup>8,9</sup>

$$(1/T_m) - (1/T_m^0) = - (R/\Delta H_u) \ln X_a \quad (1)$$

where  $T_m^0$  is the melting temperature of the homopolymer,  $\Delta H_u$  is the heat of fusion per mole of crystallizing unit,  $R$  is the gas constant, and  $X_a$  is the mole fraction of the crystallizing unit. We obtained a value of 1490 cal./mole for  $\Delta H_u$  by application of our data of the melting points to eq. (1). This value of the heat of fusion is consistent with a value of 1590 cal./mole which is obtained from the depression of the melting point of polyoxymethylene by diluents.<sup>10</sup>

Figure 5 shows the densities of the copolymers of polyoxymethylene at 25°C.

The exothermic peaks in crystallization by differential thermal analysis are shown in Table III. The exothermic peak areas by crystallization are nearly equal to the endothermic areas by fusion. In Table III,  $\Delta T$  is the difference between the melting peak temperature  $T_m$  and the crystallization

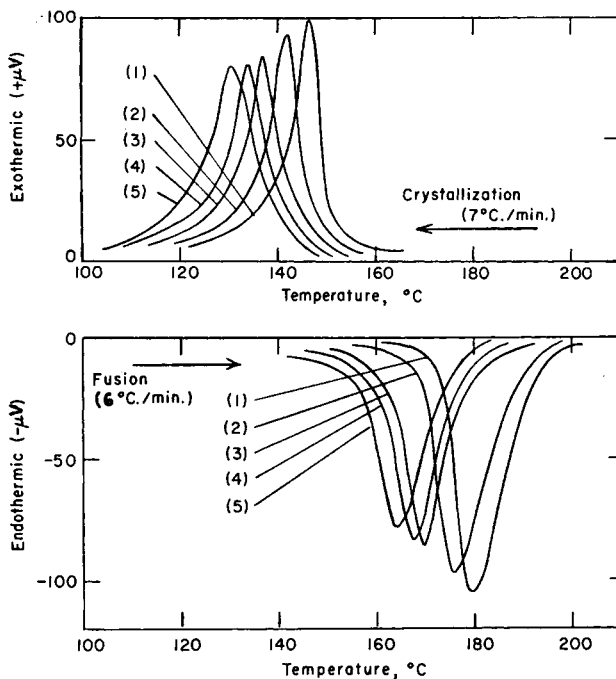


Fig. 4. Thermograms of fusion and crystallization of polyoxymethylene copolymers with dioxolane with various comonomer contents: (1) 0 mole-%; (2) 2 mole-%; (3) 4 mole-%; (4) 6 mole-%; (5) 7 mole-%.

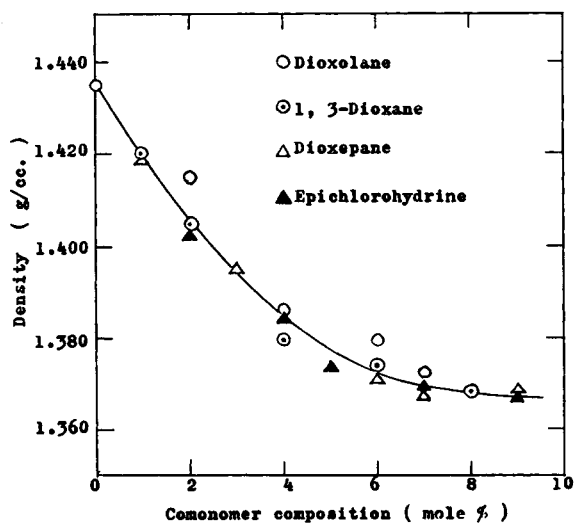


Fig. 5. Densities of polyoxymethylene copolymers (25 $^{\circ}\text{C}$ .).



TABLE III  
Differential Thermal Analysis of Crystallization of  
the Copolymers of Polyoxymethylene

Comonomer	Comonomer content, mole-%	Crystallization peak temp. $T_c$ , °C.	Crystallization peak area (relative)	$\Delta T =$ $T_m - T_c$ , °C.
None		147	365	32
Dioxolane	2	142	332	34
"	4	137	275	33
"	6	134	258	34
"	7	132	256	35
1,3-Dioxane	1	141	340	35
"	2	138	312	36
"	4	133	260	36
"	6	129	257	37
"	8	126	250	37
Dioxepane	1	142	332	36
"	3	137	300	36
"	6	128	259	37
"	7	125	250	38
"	9	122	247	38
Epichlorohydrin	2	140	318	35
"	4	137	282	35
"	5	132	255	36
"	7	129	250	36
"	9	127	250	37

peak temperature,  $T_c$ , which is increased at higher composition of comonomers and on increasing the adjacent carbon atoms of the comonomers.

### Kinetics of Spherulite Growth

Figure 6 shows typical plots of the radial growth rate of spherulites versus crystallization temperatures. We used specimens having almost the same viscosities, as shown in Table I. The temperature ( $T_{\max}$ ) at which the growth rate is maximum is depressed with increasing comonomer contents. As the melting points of the copolymers are lower than those of the homopolymers, we examined values of  $T_{\max}/T_m$ . The results are shown in Table IV. The values of  $T_{\max}/T_m$  are 0.82 in natural rubber, 0.86 in polybutene-1,<sup>11</sup> and 0.83 in nylon 6.<sup>12</sup>

In order to describe the temperature dependence of the growth rate  $G$ , we have plotted  $\log (G/T)$  against  $T_m/T(\Delta T)$  in the region of temperature of  $T_{\max} < T < T_m$ , and  $\log (G/T)$  against  $1/T$  in the region of temperature of  $T < T_{\max}$ . As shown in Figures 7 and 8, they are all in linear relations. This means that the growth proceeds through two-dimensional surface nucleation.<sup>13-15</sup> Therefore, the growth rate can be expressed by eqs. (2):

$$\log (G/T) = \log G_0 - (E_d / 2.3kT) - [\pi L \sigma_s^2 / 2.3k (\Delta h_u) T_m / T(\Delta T)] \quad (2)$$

or

$$\log (G/T) = \log G_0 - (A/T) - BT_m/T(\Delta T) \quad (3)$$

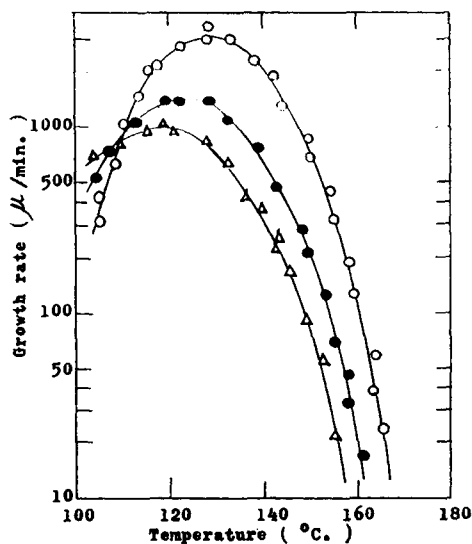


Fig. 6. Growth rate of spherulites of polyoxymethylene copolymers with dioxolane with various comonomer contents: (O) 0 mole-%; (●) 4 mole-%; (▲) 7 mole-%.

TABLE IV  
Temperatures at Which the Growth Rates Have Maximum Values

Comonomer	Comonomer content, mole-%	$T_m$ , °K.	$T_{max}$ , °K.	$T_{max}/T_m$
None		453	398	0.887
Dioxolane	4	443	398	0.898
"	7	436	393	0.901
1,3-Dioxane	1	451	399	0.886
"	3	443	394	0.890
"	6	438	392	0.899
Dioxepane	3	445	394	0.887
"	6	437	387	0.891
"	9	433	386	0.893
Epichlorohydrin	2	447	398	0.892
"	5	443	396	0.895
"	7	436	392	0.900

where

$$A = E_d / 2.3k$$

$$B = \pi L \sigma_s^2 / 2.3k(\Delta h_u)$$

$G_0$  is a constant,  $E_d$  is the apparent activation energy for viscous flow,  $L$  is disk thickness,  $\sigma_s$  is the interfacial free energy per unit area,  $\Delta h_u$  is the heat of fusion per unit volume of repeating unit, and  $k$  is the Boltzman constant.

The values of  $A$  and  $B$  indicate the temperature dependence of the crystallization rate, and both are decreased with increase of comonomer

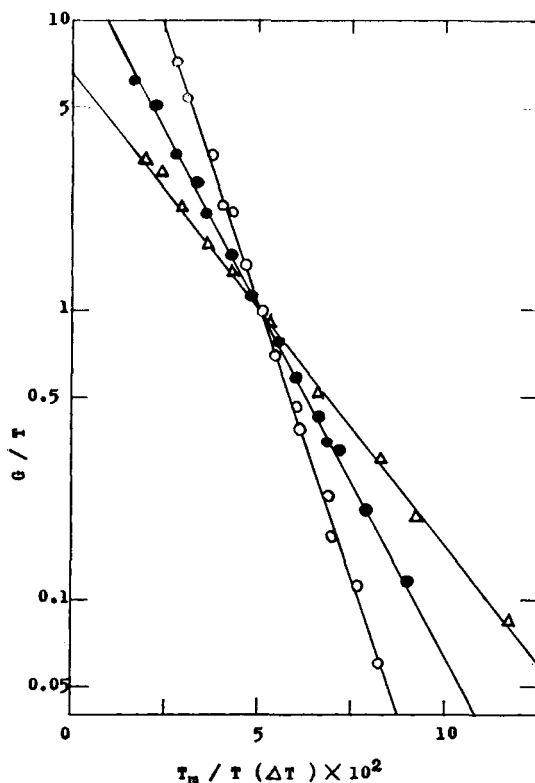


Fig. 7. Plots of  $G/T$  against  $T_m/T(\Delta T)$  in polyoxymethylene copolymers with dioxolane with various comonomer contents: (O) 0 mole-%; (●) 4 mole-%; ( $\Delta$ ) 7 mole-%.

composition. This tendency is more marked with increasing the adjacent carbon atoms of the comonomers.

To calculate the values of  $E_d$  and  $\sigma_s$  from the growth rate data, the value of the thickness of the surface nucleus,  $L$  and the heat of fusion per unit volume of repeating unit  $\Delta h_u$  are required. The value of  $\Delta h_u$  can be calculated from the heat of fusion per mole of repeating unit,  $\Delta H_u$  and the molar volume at  $T_m$ . In this paper, we obtained 1490 cal./mole for  $\Delta H_u$  by application of the melting point data of the copolymers of polyoxymethylene to eq. (1), and 28.5 cm.<sup>3</sup>/mole for the average molar volume at  $T_m$  by dilatometry.  $\Delta h_u$  is calculated to be  $2.19 \times 10^9$  erg/cm.<sup>3</sup> per unit from these data, and a value of 10 Å. for  $L$  was used. From the values of  $A$  and  $B$  determined, the corresponding values of  $E_d$  and  $\sigma_s$  are computed. These values are reported in Table V.

The values of approximately 10–20 kcal./mole for the apparent activation energy of viscous flow is reasonable and in good agreement with the value estimated from the temperature dependence of the melt viscosity in the vicinity of the melting point.<sup>16</sup>  $E_d$  decreases with increasing comonomer contents.

TABLE V  
 $E_d$  and  $\tau_s$  of the Copolymers of Polyoxymethylene

Comonomer	Comonomer content, mole-%	$E_d$ , kcal./mole		$\sigma_s$ , erg./cm. <sup>2</sup>
		A	B	
None		5150	48.2	10.2
Dioxolane	4	3620	34.0	8.6
"	7	2450	25.5	7.4
1,3-Dioxane	1	4500	43.5	9.7
"	3	3300	34.0	8.6
"	6	2400	24.5	7.3
Dioxepane	3	3200	35.0	8.7
"	6	2150	22.5	7.0
"	9	1550	20.5	6.6
Epichlorohydrin	2	4550	40.2	9.4
"	5	3150	30.5	8.2
"	7	2400	22.5	7.0

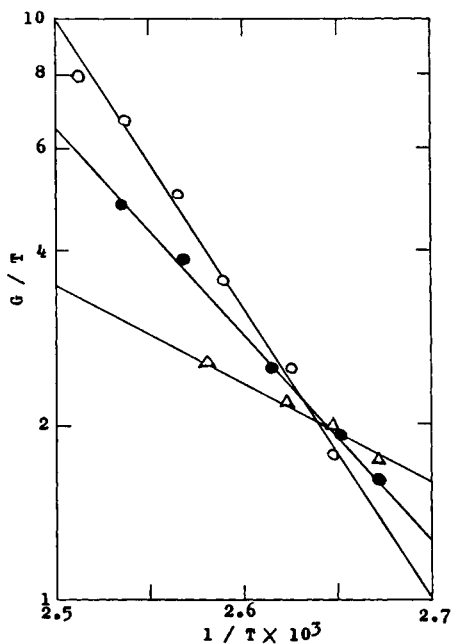


Fig. 8. Plots of  $G/T$  against  $1/T$  in polyoxymethylene copolymers with dioxolane with various comonomer contents: (O) 0 mole-%; (●) 4 mole-%; ( $\Delta$ ) 7 mole-%.

Strictly speaking, though it was not correct for us to use the heat of fusion of polyoxymethylene for  $\Delta H_u$ , and 10 A. for  $L$ , the errors in the value of  $\sigma_s$  will not be serious, since  $\sigma_s$  is related to the square root of both  $L$  and  $\Delta h_u$ . Values of 6–10 erg/cm.<sup>2</sup> are found for  $\sigma_s$  in the series of copolymers of polyoxymethylene. The literature values of  $\sigma_s$  for other crystalline polymers are as follows: 18.1 erg/cm.<sup>2</sup> and 27.4 erg/cm.<sup>2</sup> for nylon 6,<sup>12,17</sup> 10.8

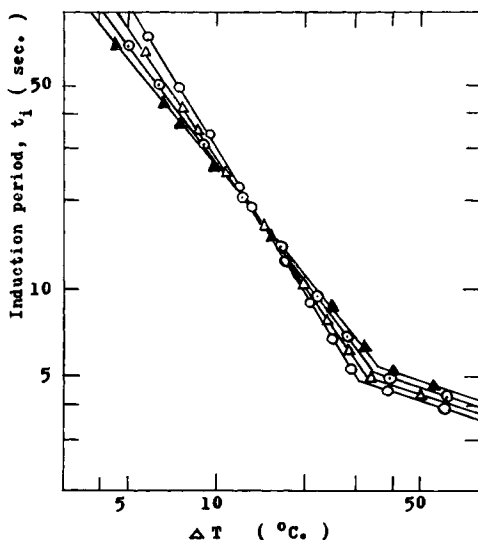


Fig. 9. Induction period of crystallization in polyoxymethylene copolymers with dioxepane with various comonomer contents: (O) 0 mole-%; ( $\Delta$ ) 3 mole-%; ( $\odot$ ) 7 mole-%; ( $\blacktriangle$ ) 9 mole-%.

erg/cm.<sup>2</sup> for polychlorotrifluoroethylene,<sup>18</sup> and 8.03 erg/cm.<sup>2</sup> for isotactic polystyrene.<sup>19</sup>

### Induction Period of Crystallization

Figure 9 shows the relationship of the induction period of crystallization,  $t_i$ , with the supercooling,  $\Delta T$ , on a logarithmic scale. Similar results are obtained for all the copolymers examined. The linearity of the relationship is expressed in eq. (4) as

$$t_i = k(\Delta T)^{-n} \quad (4)$$

where  $k$  and  $n$  are constants. Kantrovitz<sup>20</sup> developed theoretically a similar relationship for the induction period of the development of the spherical nuclei in a condensed system. As shown in Figure 9, the relation between the induction period and the supercooling is linear on a logarithmic scale. The temperature dependence of the induction period seems discontinuous at some temperatures,  $T_i$ . In the case of nylon 6,<sup>21</sup> it is shown that above  $T_i$ , the nucleation of the spherulite is sporadic in time, and below  $T_i$ , it is simultaneous or predetermined in time. The induction period in the copolymers of polyoxymethylene is much shorter than that in nylon 6, so the data obtained in this experiment are not always reliable for further discussion.

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## Résumé

On a préparé des copolymères de polyoxyméthylène au départ de trioxane et de comonomère tels le dioxolane, le 1,3 dioxane, le dioxépane et l'épichlorhydrine, en utilisant l'éthérate du trifluorure de bore comme catalyseur. On a étudié les phénomènes de fusion et de cristallisation de ces copolymères par des mesures de densité, par analyse thermique différentielle par dilatométrie et par microscopie. La vitesse de croissance des sphérolites et la période d'induction de la cristallisation ont été déterminées. La dépendance de la vitesse de croissance vis-à-vis de la température a été calculée sur la base d'un mécanisme de nucléation superficielle à deux dimensions.

## Zusammenfassung

Copolymere von Polyoxymethylen wurden aus Trioxan in Gegenwart von Comonomeren wie Dioxolan, 1,3-Dioxan, Dioxepan und Epichlorhydrin mit Borfluorid-Ätherat als Katalysator dargestellt. Schmelz- und Kristallisationserscheinungen wurden an diesen Polymeren durch Dichtemessungen, Differentialthermoanalyse, Dilatometrie, und Mikroskopie verfolgt. Die Wachstumsgeschwindigkeit der Sphärolithe und die Induktionsperiode der Kristallisation wurden bestimmt. Die Temperaturabhängigkeit der Wachstumsgeschwindigkeit wurde unter Annahme eines zweidimensionalen Oberflächenkeimbildungsmechanismus berechnet.

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