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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Kobayashi, E. , Higashimura, T. and Okamura, S.(1967) 'Molecular Weight Distribution of Polyoxymethylene Obtained in Solid-State Polymerization of Trioxane Catalyzed by $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ ', Journal of Macromolecular Science, Part A, 1: 8, 1519 – 1529

To link to this Article: DOI: 10.1080/10601326708053789

URL: <http://dx.doi.org/10.1080/10601326708053789>

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Molecular Weight Distribution of Polyoxymethylene Obtained in Solid-State Polymerization of Trioxane Catalyzed by $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$

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Summary

To clarify the reaction mechanism of the solid-state polymerization of trioxane, the molecular weight distribution of polyoxymethylene is measured. High molecular weight polymer is precipitated around the stirrer in an early stage, then low polymer, while the *p*-chlorophenol solution of polyoxymethylene is violently rotated by a glass stirrer at about 60°C. To fractionate polymer, this phenomenon is applied for the polyoxymethylene produced in the solid-state polymerization catalyzed by $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ in *n*-hexane medium at 40 and 50°C. The polymer obtained at a low conversion contains a large amount of high polymer part, and the amount of high polymer decreases with increasing conversion. It is estimated that high polymer is produced only at the initial stage of the polymerization and that the decrease of molecular weight of polymer at a high conversion in the solid-state polymerization may be due to the formation of low polymer at a high conversion and also to the degradation of high polymer during the polymerization.

It was found that trioxane was easily polymerized in the solid state initiated by Friedel-Crafts catalyst (*I-3*). In the solid state, the polymerization proceeds from the surface toward the inner part of the crystal in which resultant polymer molecules are highly oriented. The polymer obtained in the initial stage of the polymerization contains the molecule having very high viscosity number and the viscosity number decreases with increasing the conversion of polymer. The formation of polyoxymethylene having a high molecular weight in the initial stage of the polymerization seems to be a

characteristic behavior in the solid state, since the molecular weight of polymer produced in the solution polymerization by $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ increases with increased conversion (1,4).

To explain the characteristics mentioned above, the high molecular weight polymer was considered to be formed only on the surface of crystal and not in the inner part. However, another possible explanation was the degradation of polymer during the polymerization (3).

The measurement of molecular weight distribution may be one of the effective methods to determine whether the decrease of the molecular weight of polymer at high conversion is due to the formation of low molecular weight polymer or comes from the degradation of high polymer. The fractionation of polyoxymethylene has scarcely been studied hitherto (5,6). As reported in the previous paper (7), high molecular weight polyoxymethylene was recognized to be precipitated in *p*-chlorophenol solution by stirring, in which the fractionation of polyoxymethylene became possible.

In this paper, polyoxymethylene obtained by solid-state polymerization is fractionated by stirring and the mechanism of the solid-state polymerization is discussed with the molecular weight distribution.

EXPERIMENTAL

Polymerization of Trioxane and Measurement of Intrinsic Viscosity

Trioxane is polymerized in the solid state, suspended in *n*-hexane at 40 and 50°C catalyzed by $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$. The techniques for polymerization and purification are the same as mentioned in the previous paper (1). Ammoniac methanol is added to the reaction system to stop the polymerization. The polymer is washed several times by methanol and is dried in vacuo at room temperature. The polymer thus obtained is immediately fractionated without stabilization of the end group of polymer molecules.

The intrinsic viscosity is measured by an Ostwald-type viscometer for *p*-chlorophenol solution containing 2% α -pinene at $60 \pm 0.01^\circ\text{C}$ (7). To prevent the effect of the degradation of polymer during dissolution, polymer is dissolved in *p*-chlorophenol under nitrogen by heating for 6 min at 110°C, as discussed in the previous paper (7).

Fractionation of Polyoxymethylene

Polyoxymethylene is fractionated by the method of successive separation of a precipitated polymer by stirring the solution. The details of the fractionation process are reported elsewhere (7), so only the procedure is described briefly in this paper. A solution of polyoxymethylene (1 g/100 ml of *p*-chlorophenol containing 2% α -pinene) is kept in the glass vessel shown in Fig. 1 at a constant temperature, usually about 60°C. While the glass stirrer is rotated at 1350 rpm, a fibrous polymer begins to precipitate around the stirrer after several minutes. After stopping the rotation of the stirrer, the polymer precipitated is taken out of the solution and washed several times by *p*-chlorophenol containing α -pinene at 60°C. Then it is washed by acetone to remove *p*-chlorophenol and is dried under reduced pressure at room temperature.

Residual solution is successively fractionated at the same or a lower temperature by the same method. As the low molecular weight polymer cannot be precipitated by stirring, the residual polymer solution is poured into a large amount of methanol, and the total amount of polyoxymethylene is recovered.

RESULTS AND DISCUSSION

Fractionation of Polyoxymethylene

Fractionation based on a molecular weight is examined in this paper for the stirring method. As shown in Tables 2 and 3, the polymer precipitated after stirring for a short time gives a high value of

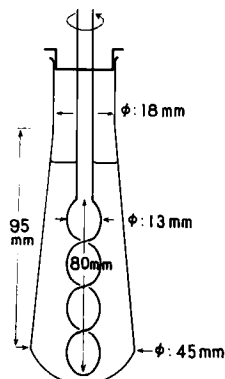


FIG. 1. Schematic diagram of fractionation apparatus.

intrinsic viscosity $[\eta]$, showing the effectiveness of fractionation of polyoxymethylene. It was already observed that crystallization of polyethylene occurred by stirring the solution (8,9). It is also reasonable to consider that polyoxymethylene molecules orient in the solution in which the crystallization is accelerated by adding the stress for molecules from one direction (e.g., the rotation of a solution). If the high molecular weight part of the polymer molecules more easily orients than the low polymer part, crystallization of polyoxymethylene molecules seems to start in the high $[\eta]$ part, inducing the fractionation mentioned above.

Solid polyoxymethylene precipitated around the stirrer gives an X-ray diagram having a partially oriented pattern. This fact supports the contention that a polymer is crystallized and precipitated due to the orientation of polymer molecule in the solution by stirring.

Molecular Weight Distribution and Reaction Mechanism

As reported in the previous papers, polyoxymethylene having a high molecular weight was produced in the initial stage of the solid-state polymerization of trioxane and the viscosity number of polymer decreases with increasing the conversion. There are three possible mechanisms to explain the decrease of molecular weight.

1. High polymer is produced only in the initial stage of polymerization, and thereafter the molecular weight of resultant polymer lowers. The degradation of polymer by acidic catalysts does not occur during polymerization.

2. High polymer is produced in the whole range of polymerization. However, the polymer is decomposed by acidic catalysts during polymerization.

3. High polymer is produced only in the initial stage, and the polymer is decomposed simultaneously.

These three mechanisms cannot be distinguished only by consideration of the relationship between the conversion and the $[\eta]$ values. If the molecular weight distribution of polymer can be measured, the mechanism seems to be confirmed. In the case of mechanism 1, the amount of a high polymer part may be constant through the whole conversion and the amount of a low polymer part may increase with increasing conversion. In the case of mechanism 2, the high polymer part can be observed in the whole range of reaction. In mechanism 3, the amount of the high polymer part decreases

with increasing conversion or the high polymer disappears at high conversion.

It seems difficult to distinguish mechanism 2 from mechanism 1 without knowing the relative rates of polymer formation and degradation. However, mechanism 3 may be examined qualitatively.

Fractionation of Polyoxymethylene Obtained in Solid-State Polymerization

To confirm the reaction mechanism of solid-state polymerization, polyoxymethylenes obtained in the solid state are fractionated. Polymerization conditions are summarized in Table 1. One of the characteristics of solid-state polymerization is the formation of high molecular weight polymer even at high temperature (1). Polymers prepared at different temperatures are also fractionated here to study the effect of polymerization temperature.

Results of the fractionation are shown in Tables 2 and 3. Integral molecular weight distribution curves calculated from these tables are given in Figs. 2 and 3, respectively.

In this procedure, the low polymer part cannot be precipitated only by stirring. It is observed, however, that the polymer obtained in the initial stage of polymerization contains an extremely high molecular weight fraction and has a wide molecular weight distribution. The polymer obtained at lower conversion contains a larger amount of high polymer part than that obtained at higher conversion.

For example, in sample 1a, obtained at 4% conversion, about 24% of a resultant polymer is a high polymer with $[\eta]$ more than 4.

TABLE I

Polymerization Conditions of Polyoxymethylene Used for Fractionation
 ($[M]_0$, 2.0 moles/liter; $[BF_3 \cdot O(C_2H_5)_2]$, 10 mmoles/liter; $[H_2O]$ in medium,
 1.2 mmoles/liter; medium, *n*-hexane)

Sample	Polymerization temp., °C	Reaction time, min	Conversion, %	$[\eta]$
1a	40	0.5	4.0	3.06
1b	40	2.0	8.0	2.18
2a	50	0.5	8.0	3.77
2b	50	2.0	16.0	2.53
2c	50	20	42.1	1.75

TABLE 2
Fractionation of Polyoxymethylene by Stirring Method (Sample 1)

Fraction	Stirring		Wt. % polymer ^a	[η], dl/g	I_p , %
	Temp., °C	Time, min			
(a) Sample 1a					
1	60	0-15	1.3 ₃	5.80	0.6 ₇
2	60	15-45	2.9 ₇	5.54	2.8 ₂
3	60	45-75	2.5 ₈	5.29	5.5 ₉
4	60	75-135	4.0 ₆	4.96	8.9 ₁
5	60	135-195	3.1 ₅	4.80	12.5 ₂
6	60	195-285	4.5 ₄	4.56	16.3 ₉
7	58.7	285-345	3.2 ₆	4.34	20.2 ₆
8	57.4	345-405	2.7 ₇	4.05	23.2 ₈
9	56.4	405-465	4.3 ₅	3.92	26.8 ₄
10	55.8	465-525	3.3 ₄	3.86	30.6 ₈
11	55.4	525-585	3.0 ₉	3.68	33.8 ₉
12	54.8	585-645	3.4 ₉	3.64	37.1 ₉
13	54.5	645-705	3.2 ₀	3.54	40.5 ₃
14	53.9	705-765	3.0 ₅	3.44	43.6 ₆
15	53.3	765-825	2.4 ₂	3.44	46.3 ₉
16	52.8	825-885	2.6 ₄	3.36	48.9 ₂
17	52.4	885-945	2.6 ₆	3.34	51.5 ₇
18	51.7	945-1005	2.6 ₉	3.30	54.2 ₅
19	50.7	1005-1065	2.7 ₅	3.20	56.9 ₇
20	50.0	1065-1125	3.8 ₃	3.14	60.2 ₆
			62.1 ₇		
	Residual polymer		37.8 ₃	2.24	
(b) Sample 1b					
1	60	0-30	0.4 ₉ }	4.65	0.4 ₈
2	60	30-60	0.4 ₇ }		
3	60	60-120	1.4 ₇	4.20	1.7 ₀
4	59.1	120-180	1.2 ₈	3.74	3.0 ₇
5	58.2	180-240	1.8 ₇	3.57	4.6 ₈
6	57.3	240-300	3.1 ₉	3.39	7.1 ₉
7	56.8	300-360	3.1 ₁	3.30	10.3 ₄
8	56.6	360-420	3.4 ₉	3.21	13.6 ₄
9	56.1	420-480	3.4 ₁	3.09	17.0 ₉
10	55.2	480-540	3.8 ₁	3.00	20.7 ₀
11	54.6	540-600	2.7 ₄	2.89	23.9 ₇
12	54.1	600-660	3.5 ₄	2.82	27.1 ₁
13	53.6	660-720	5.2 ₄	2.78	31.5 ₀
14	53.4	720-780	4.6 ₄	2.70	36.4 ₄
15	52.9	780-850	2.0 ₆	2.56	39.7 ₉
			40.8 ₀		
	Residual polymer		59.2 ₀	2.35	

^a Recovery, 96% in sample 1a; 84% in 1b.

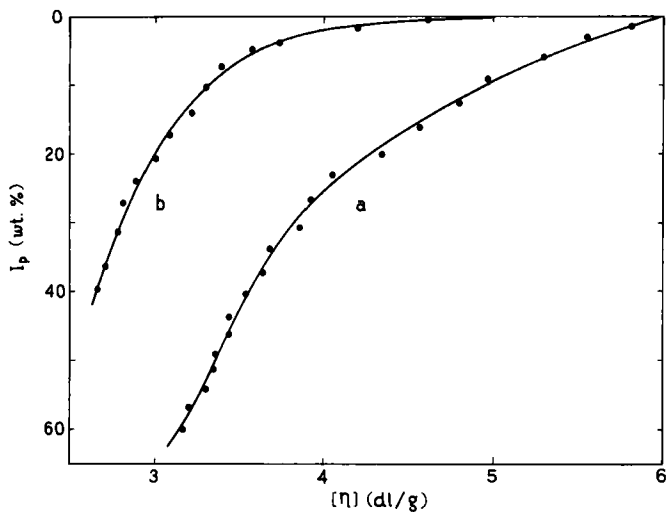


FIG. 2. Integral molecular weight distribution of polyoxymethylene (sample 1) prepared in the solid state at 40°C. (Sample number is the same as in Table 1.)

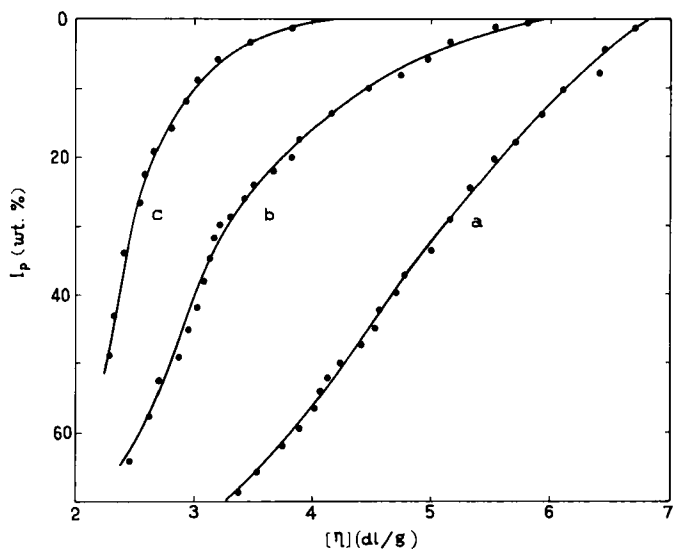


FIG. 3. Integral molecular weight distribution of polyoxymethylene (sample 2) prepared in the solid state at 50°C. (Sample number is the same as in Table 1.)

TABLE 3
 Fractionation of Polyoxymethylene by Stirring Method (Sample 2)

Fraction	Stirring		Wt. % polymer ^a	[η], dl/g	I_p , %
	Temp., °C	Time, min			
(a) Sample 2a					
1	60	0-15	2.6 ₇	6.70	1.3 ₄
2	60	15-30	3.6 ₂	6.44	4.4 ₈
3	60	30-45	3.1 ₈	6.40	7.8 ₈
4	60	45-60	2.3 ₂	6.11	10.6 ₃
5	60	60-90	4.4 ₉	5.91	14.0 ₄
6	60	90-120	2.9 ₀	5.71	17.7 ₃
7	60	120-150	2.6 ₉	5.52	20.5 ₃
8	60	150-210	5.0 ₄	5.33	24.3 ₉
9	60	210-270	5.0 ₁	5.15	29.4 ₂
10	60	270-330	3.4 ₅	5.00	33.6 ₅
11	58.8	330-390	3.3 ₇	4.77	37.0 ₆
12	57.9	390-450	2.1 ₈	4.70	39.8 ₂
13	57.2	450-510	2.8 ₈	4.57	42.3 ₄
14	56.3	510-570	2.3 ₄	4.52	44.9 ₅
15	55.5	570-630	2.3 ₅	4.41	47.3 ₀
16	54.6	630-690	2.5 ₅	4.24	49.7 ₅
17	53.8	690-750	1.7 ₁	4.10	51.8 ₈
18	53.0	750-810	2.2 ₄	4.06	53.8 ₅
19	52.2	810-885	2.9 ₅	4.02	56.4 ₅
20	51.5	885-945	2.5 ₁	3.89	59.1 ₈
21	50.7	945-1005	3.1 ₄	3.74	62.0 ₀
22	50.3	1005-1065	3.3 ₈	3.52	65.2 ₆
23	49.5	1065-1125	3.6 ₁	3.37	68.7 ₆
			70.5 ₆		
	Residual polymer		29.4 ₄	3.24	
(b) Sample 2b					
1	60	0-15	0.5 ₈	5.80	0.2 ₉
2	60	15-35	1.5 ₃	5.53	1.3 ₃
3	60	35-65	2.4 ₃	5.15	3.3 ₅
4	60	65-95	2.5 ₁	4.97	5.8 ₃
5	60	95-125	1.7 ₈	4.75	8.0 ₁
6	60	125-170	2.5 ₁	4.46	10.1 ₆
7	60	170-230	4.3 ₈	4.16	13.6 ₀
8	60	230-290	3.1 ₄	3.88	17.3 ₆
9	59.1	290-350	2.1 ₃	3.82	20.0 ₀
10	58.1	350-410	1.8 ₄	3.68	21.9 ₈
11	57.1	410-470	2.2 ₁	3.50	24.0 ₁
12	55.7	470-540	1.8 ₉	3.42	26.0 ₆
13	54.6	540-600	1.8 ₃	3.30	27.9 ₂

TABLE 3 (Continued)

Fraction	Stirring		Wt. % polymer ^a	[η], dl/g	I_p , %
	Temp., °C	Time, min			
14	53.4	600-660	1.7 ₄	3.21	29.7 ₀
15	53.0	660-720	2.5 ₂	3.15	31.8 ₃
16	52.4	720-780	3.4 ₃	3.12	34.8 ₁
17	51.8	780-840	3.3 ₇	3.09	38.2 ₁
18	51.2	840-900	3.5 ₁	3.02	41.6 ₅
19	51.0	900-960	3.9 ₁	2.96	45.3 ₆
20	50.6	960-1020	3.3 ₃	2.87	48.9 ₈
21	50.2	1020-1080	3.9 ₅	2.70	52.6 ₂
22	49.6	1080-1140	7.0 ₂	2.63	58.1 ₀
23	49.3	1140-1200	5.2 ₉	2.47	64.2 ₆
			66.9 ₀		
Residual polymer			33.1 ₀	2.14	
(c) Sample 2c					
1	60	0-20	0.4 ₆	—	0.2 ₃
2	60	20-80	1.5 ₉	3.82	1.2 ₆
3	58.1	80-140	2.2 ₃	3.46	3.1 ₇
4	56.9	140-200	2.7 ₀	3.19	5.6 ₃
5	56.4	200-260	3.4 ₂	3.02	8.6 ₉
6	55.8	260-320	3.2 ₇	2.93	12.0 ₄
7	55.4	320-380	4.0 ₈	2.81	15.7 ₁
8	55.2	380-440	3.0 ₇	2.67	19.2 ₉
9	54.9	440-500	3.5 ₇	2.57	22.6 ₁
10	54.4	500-570	4.1 ₃	2.54	26.4 ₆
11	53.9	570-690	10.9 ₂	2.43	33.9 ₈
12	53.5	690-750	7.0 ₃	2.32	43.0 ₀
13	53.2	750-810	4.5 ₈	2.29	48.7 ₆
			51.0 ₅		
Residual polymer			48.9 ₅	2.16	

^a Recovery, 93% in sample 2a; 90% in 2b; 85% in 2c.

On the other hand, the amount of such a high polymer ($[\eta] > 4$) is only 2.4% in sample 1b, which was obtained at 8% conversion. Also, sample 1b does not contain extremely high molecular weight polymer (for example, $[\eta] > 5$), which is observed in sample 1a. The same result is confirmed in sample 2, obtained at different temperatures.

It is estimated from these results that the mechanism of solid-state polymerization is perhaps in mechanism 3. The high molecular weight polymer seems to be produced in the initial stage of the

polymerization, and this high polymer decomposes during polymerization. The formation of the high polymer part only at the initial stage means that the high polymer may be produced only at the surface of the crystal. This estimation agrees with the reaction mechanism (2,3) assumed from the kinetic results and X-ray diffraction pattern.

In the previous papers (1,2), the decrease of molecular weight of polymer during polymerization was explained only by the production of low polymer in an inner part of the crystal. The decrease of molecular weight of polymer during polymerization is also due to the degradation of polymer molecules by acidic catalysts as well as the formation of low polymer.

Another characteristic of solid-state polymerization is the formation of high polymer at high temperature. Curve b in Fig. 2 and curve a in Fig. 3 show the molecular weight distribution of polyoxymethylene obtained at the same conversion (8%) at temperatures of 40 and 50°C, respectively. From these curves it is concluded that the high $[\eta]$ of the polymer obtained at high temperature is due to the formation of the high polymer part at high temperature, both at the initial and later stages of polymerization.

As already reported (10), in the solid-state polymerization of trioxane by high-energy radiation the orientation of monomer molecule greatly affects the polymerization. The disturbance of alignment of monomer molecules in crystals by the formation of polymer causes a decrease of molecular weight at high conversion. As the high polymerization temperature makes the movement of monomer molecule easier, the high polymer shall be easily produced even at high conversion.

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Zusammenfassung

Zur Klärung des Reaktionsmechanismus der Festkörperpolymerisation von Trioxan wurde die Molekulargewichtsverteilung von Polyoxymethylenen gemessen. Hochmolekulare Polymere scheiden sich während des Anfangsstadiums am Rührer ab, später dann niederpolymere Produkte, während die p-Chlorphenollösung der Polyoxymethylene intensiv mit einem Glasrührer bei 60° gerührt wird. Um die Polymeren zu fraktionieren, wurde dieses Verfahren auf die mit $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ katalysierten und im Festzustand polymerisierten Polyoxymethylene in n-Hexan bei 40 und 50° angewendet. Das bei geringem Umsatz erhaltene Polymere enthält einen grossen Anteil an Hochpolymerem, wobei dieser Anteil mit steigendem Umsatz abnimmt. Es wird angenommen, dass das Hochpolymere nur im Anfangsstadium der Polymerisation gebildet wird und dass die Abnahme des Molekulargewichtes des Polymeren bei zunehmendem Umsatz in der Festkörperpolymerisation auf die Bildung von Niederpolymeren bei hohem Umsatz und auch auf einen Abbau von Hochpolymerem während der Polymerisation zurückzuführen ist.

Résumé

En vue d'éclaircir le mécanisme réactionnel de la polymérisation à l'état solide du trioxanne on a mesuré la distribution de la masse moléculaire du polyoxyméthylène. Un polymère à poids moléculaire élevé précipite au voisinage de l'agitateur plutôt qu'un polymère à poids moléculaire bas, lorsque la solution de polyoxyméthylène en p-chlorophenol est agité vigoureusement avec un agitateur en verre à 60°C environ. Pour le fractionnement du polymère, ce phénomène est appliqué au polyoxyméthylène produit dans la polymérisation à l'état solide, catalysée par le $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ dans le n-hexane à 40° et 50°C. Le polymère obtenu à conversion basse contient une grande quantité de hauts polymères et cette quantité diminue avec l'accroissement de la conversion. On pense que le polymère haut est produit seulement dans le stade initial de la polymérisation et que l'abaissement de la masse moléculaire à conversion élevée dans la polymérisation à l'état solide est peut être du à la formation d'un polymère bas et aussi à la dégradation des hauts polymères au cours de la polymérisation.

Received by editor July 16, 1967

Submitted for publication August 18, 1967