

## Studies of the Fractionation of Polyoxymethylene

EIICHI KOBAYASHI and SEIZO OKAMURA, *Department of Polymer Chemistry, Kyoto University, Kyoto Japan*, and RUDOLF SIGNER, *Institute of Organic Chemistry, Berne University, Berne, Switzerland*

### Synopsis

The precipitation of polyoxymethylene in *p*-chlorophenol solution and the molecular weight fractionation of the polymer by mechanical agitation were investigated. The agitation of the solution was carried out in a glass vessel with a stirrer, usually at 60°C. After agitation for several minutes a fibrous polymer precipitated. High molecular weight polymer precipitated around the stirrer in an early stage, and therefore the method might be applied to the fractionation of polyoxymethylene. The method was applied to the fractionation of polyoxymethylene prepared in a solid-state and in a solution polymerization of trioxane, catalyzed by  $\text{BF}_3 \cdot \text{OEt}_2$ . It was found that the polymer from the solid state contained a small amount of extremely high molecular weight fraction, and that obtained from the solution had a relatively narrow distribution of molecular weight.

### INTRODUCTION

In a preceding paper<sup>1</sup> the preparation of polyoxymethylene solution in *p*-chlorophenol and some anomalous behaviors of the solution were reported, one of which was the instability of the solution. The present investigation deals with the precipitation phenomenon of polyoxymethylene in the solution and the molecular weight fractionation of polyoxymethylene by mechanical agitation.

Fibrous polymer was easily precipitated around the stirrer by agitation of *p*-chlorophenol solution of polyoxymethylene. The intrinsic viscosity of the residual polymer solution was less than that of the original solution. A high molecular weight fraction of polyoxymethylene may be precipitated during the agitation of the solution. This fact was supported by measurement of the intrinsic viscosity of the polymer precipitated.

A few papers have been published concerning the fractionation of polyoxymethylene.<sup>2,3</sup> The methods were of the elution type. A new method of fractionation has now been developed and is reported herein: agitation of the polymer solution and precipitation.

### EXPERIMENTAL

#### Polymerization

The polyoxymethylene was prepared by solid-state polymerization of trioxane with  $\text{BF}_3 \cdot \text{OEt}_2$  catalyst at 40°C.,<sup>4</sup> and by solution polymerization

of trioxane in nitrobenzene at 9°C.<sup>5</sup> The trioxane was purified in a manner similar to that previously described.<sup>4</sup>

The polymer produced is isolated from the reaction mixture by filtration and washed repeatedly with methanol containing a small amount of ammonia and then again with methanol. It is dried under reduced pressure at room temperature. The results of polymerization in the solid state are summarized in Table I.

TABLE I  
Polymerization in Solid State<sup>a</sup>

Polymer no.	Polymerization time, min.	Polymer yield, %	$[\eta]$ , dl./g.
1	0.5	3.6	2.55
2	1	5.0	2.29
3	3	7.5	1.92
4	6	10.2	1.73
5	15	18.5	1.43

<sup>a</sup> Trioxane, 2 moles in 1 liter of hexane;  $\text{BF}_3 \cdot \text{OEt}_2$ , 10 mmoles/l.

### Preparation of Polymer Solution

The polymer is used without any stabilizing reaction. It is dissolved in *p*-chlorophenol containing 2%  $\alpha$ -pinene, at 110°C. for 6 min. under a nitrogen atmosphere. The *p*-chlorophenol is purified by distillation over a marble chip under reduced pressure (b.p. 83–85°C. at 4–5 mm. Hg).

### Measurement of Viscosity

The viscosity of the solution was measured by an Ostwald type of viscometer at  $60 \pm 0.01^\circ\text{C}$ . The intrinsic viscosity  $[\eta]$  was calculated from

$$\eta_{sp}/c_{t \rightarrow 0} = [\eta] + k'C[\eta]^2 \quad (1)$$

where Huggins' constant  $k'$  was 0.40. The  $\eta_{sp}/c_{t \rightarrow 0}$  can be determined graphically from the intersection on the time axis  $t = 0$  of the curve of  $\eta_{sp}/c_t$  versus time, as described in the next section.

### Fractionation of Polymer

Figure 1 shows four kinds of vessel used in the experiments. In the case of types 1 and 4 air bubbles are formed in the solution during agitation. After agitation for several minutes a fibrous polymer precipitates around the stirrer at over 700 rpm. The polymer precipitated is washed several times with *p*-chlorophenol containing 2%  $\alpha$ -pinene, at 60°C., and then with acetone at its boiling temperature. The polymer is finally dried under reduced pressure at room temperature.

With the type 2 stirrer there are no air bubbles in the solution during agitation. The diameter of the type 2 stirrer is in the range of 11.2–16.5 mm.

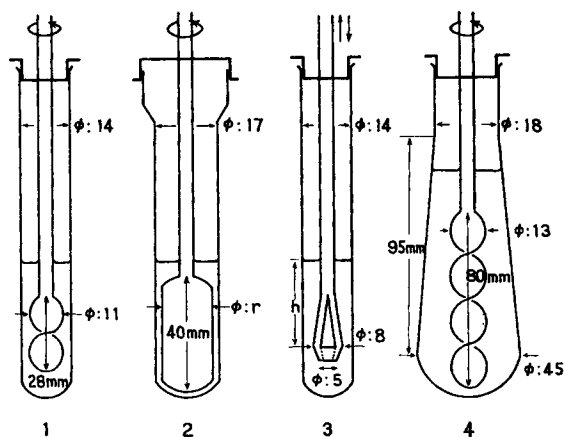


Fig. 1. Schematic diagram of fractionation apparatus;  $r = 11.2\text{--}16.5$  mm.

## RESULTS AND DISCUSSION

### Measurement of Intrinsic Viscosity

The polymer is precipitated from *p*-chlorophenol solution by agitation, and the intrinsic viscosity of the remaining solution is found to decrease with increasing time of agitation. It is not certain, however, whether degradation of the polymer is accelerated by agitation or whether precipitation of the high molecular weight part of the polymer occurs.

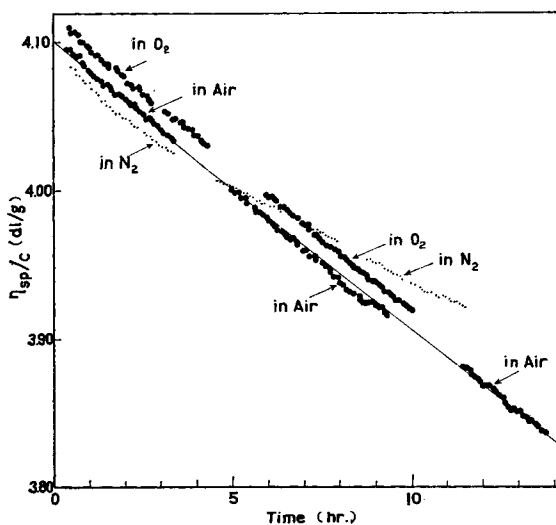


Fig. 2. Effect of atmosphere in viscometer on viscosity number versus time at  $60^{\circ}\text{C}$ . Rate constant of decrease of viscosity number at polymer concentration of  $0.6$  g./dl. calculated from eq. (2):  $k = 0.81 \times 10^{-2} \% \text{ min.}^{-1}$ .

The effect of atmosphere in the viscometer on the viscosity of the solution was investigated, and the results are shown in Figure 2. The rate of decrease in the viscosity number both in air and in oxygen is well represented by eq. (2). In nitrogen it is a little less than in air or oxygen. Figure 2 shows a plot of eq. (2), in which  $k$  is the rate constant of decrease of the viscosity number and corresponds to the first-order reaction con-

$$\eta_{sp}/c_t = \eta_{sp}/c_{t \rightarrow 0} e^{-kt} \quad (2)$$

stant. The following experiments were done in an atmosphere of air, and the viscosity number  $\eta_{sp}/c_{t \rightarrow 0}$  was obtained by using eq. (2) and the  $k$  value evaluated above.

### Fractionation by Various Types of Apparatus

**Type 1.** The experimental results are summarized in Table II. The intrinsic viscosity of the remaining solution gradually decreases with increasing amounts of deposited polymer. This suggests that the part of the polymer having the highest molecular weight may be preferentially precipitated by agitation.

In Table II the temperature of the solution of Br, evolutions per minute of stirrer of C, and the molecular weight of polymer of D were varied.

Under B at a temperature above 75°C. the solution becomes fairly stable to agitation; polymer is not precipitated at 80°C., in the solution of which

TABLE II  
Effects of Experimental Conditions and  $[\eta]$  of Original Polymer on Amount of Deposition of Polymer ( $P_{dep}$ ) and Change in Intrinsic Viscosity of Remaining Solution<sup>a</sup>

Group no.	$[\eta]_{orig}$ , dl./g.	rpm	Agitation		$P_{dep}/P_0$ , wt.-%	$[\eta]$ , dl./g.
			Time, min.	Temp., °C.		
A	2.55	1350	0	60	0	2.55
			5		4.2	2.52
			15		7.5	2.49
			30		11.6	2.46
B	2.55	1350	15	60	7.5	2.49
				70	1.7	2.53
				75	trace	2.54
				80	0	2.54
C	2.55	0	30	60	0	2.55
		470			0	2.54
		700			trace	2.53
		1000			4.2	2.50
		1350			11.6	2.46
D	1.43 <sup>b</sup>	1350	30	60	0	1.42
	1.73				1.5	1.70
	2.55				11.6	2.46

<sup>a</sup> Polymer concentration of original solution, 0.6 g./dl.; volume of solution, 5 ml.

<sup>b</sup> After agitation for 60 min. deposition of polymer was not observed.

the intrinsic viscosity is found to be the same within the experimental error before and after agitation. The result indicates that the degradation of polymer is not accelerated by agitation even under in air at 80°C.

Below 700 rpm the solution is stable, as shown in C. Air bubbles are not observed in the solution at rpm's below 1000. The role of air bubbles formed in the solution and of shearing stress were examined by using different kinds of stirrers; the results are described in the following sections.

Group D shows that the amount of polymer deposited depends on the molecular weight of the polymer. This result supports that the fractionation possibly effected by agitation of the polymer solution.

**Type 2 and Type 3.** The intrinsic viscosity of the remaining solution gradually decreases, and the amount of polymer deposited increases with increasing time of agitation, as shown by group A, Table III. The polymer seems certainly to be precipitated only by agitation and not by adsorption on air bubbles.

TABLE III  
Effect of Type of Apparatus on Amount of Deposition of Polymer ( $P_{\text{dep}}$ ) and Change in Intrinsic Viscosity of Remaining Solution<sup>a</sup>

Group no.	Diam. of rod (mm., group A) or position of rod (cm., group B)	Agitation time, min.	$P_{\text{dep}}/P_0$ , wt.-%	$[\eta]$ , dl./g.	
A <sup>b</sup>	11.2	30	2.5	2.23	
	13.1	30	2.9	2.21	
	15.2	0	0		2.29
		10	trace		2.20
		20	2.5		2.22
		30	3.8		2.19
16.5	30	1.3	2.28		
B <sup>c</sup>	0.2	30	13.8	2.11	
	1	30	15.8	2.10	
		0	0		2.29
	2	5	2.9		2.27
		15	7.5		2.12
		30	17.9		2.03

<sup>a</sup> Polymer concentration of original solution 0.6 g./dl.; volume of solution, 5 ml.; temperature, 60°C.

<sup>b</sup> At 1350 rpm; type 2 vessel.

<sup>c</sup> At 50 cps; type 3 vessel.

The effect of the diameter of the stirrer on the efficiency of agitation was studied. The efficiency of the fractionation seems to depend on the diameter, but the relationship is not clear.

Vibrating experiments with type 3 vessels were undertaken with different amounts of air bubbles by changing the position of the rod. The solution is agitated by vibrating the rod vertically at 50 cps. The precipitation of

polymer is observed after several minutes. The amount of polymer precipitated depends on the height of the rod, as shown by B in Table III.

The effect of time of agitation is clear, as shown in B in Table III. The characteristics of the phenomena are quite similar to those of A in Tables II and III.

### Fractionation of Polyoxymethylene Obtained in Different Conditions

For the molecular weight distribution under different polymerization conditions the fractionation of polymers prepared both in solid-state and in solution polymerization was studied. The type 4 apparatus is suitable for the fractionation of a large amount of polymer. After a specified time the deposited polymer is taken out from the vessel. The amount of polymer precipitated is regulated by lowering the temperature and shortening the time of agitation. This procedure is repeated several times; see Tables IV and V. The polymer is washed and weighed after drying.

In both cases the first fractions contain polymer of higher molecular weight than those in the following fractions. The integral molecular weight distribution curves obtained are shown in Figure 3.

TABLE IV  
Results of Fractionation of Polyoxymethylene  
Prepared in Solution Polymerization by Agitation<sup>a</sup>

Fract. no.	Agitation		Polymer wt.-%	[ $\eta$ ], dl./g.	$I_p^b$ wt.-%
	Temp., °C.	Time, min.			
1	60	0-15	1.3 <sub>8</sub>	3.96	0.6 <sub>9</sub>
2	"	15-45	2.7 <sub>7</sub>	3.70	2.7 <sub>6</sub>
3	"	45-75	2.3 <sub>9</sub>	3.64	5.3 <sub>4</sub>
4	"	75-135	2.6 <sub>3</sub>	3.45	7.8 <sub>8</sub>
5	"	135-195	4.4 <sub>6</sub>	3.28	11.4 <sub>0</sub>
6	"	195-285	6.5 <sub>1</sub>	3.08	16.8 <sub>9</sub>
7	58	285-345	2.7 <sub>2</sub>	3.04	21.5 <sub>0</sub>
8	56	345-405	4.2 <sub>3</sub>	2.85	24.9 <sub>8</sub>
9	55	405-465	5.2 <sub>2</sub>	2.75	29.7 <sub>0</sub>
10	54	465-525	5.0 <sub>7</sub>	2.67	34.8 <sub>4</sub>
11	53	525-585	5.1 <sub>7</sub>	2.61	39.9 <sub>6</sub>
12	51.6	585-645	8.4 <sub>9</sub>	2.58	46.7 <sub>0</sub>
13	50.2	645-705	6.6 <sub>9</sub>	2.55	54.3 <sub>8</sub>
14	49	705-765	4.3 <sub>6</sub> <sup>c</sup>	2.53	59.9 <sub>0</sub>
		Total	62.0 <sub>9</sub>		
15 <sup>d</sup>			37.9 <sub>1</sub>	2.25	

<sup>a</sup> Polymer concentration 1 g./dl.; volume of solution, 100 ml.; 1350 rpm; [ $\eta$ ]<sub>orig</sub> = 2.48 dl./g.; [M<sub>0</sub>] = 3.5 moles/l., [BF<sub>3</sub> · OEt<sub>2</sub>] = 2.5 mmoles/l.

<sup>b</sup> Polymerization conditions,  $I_p$ , integral weight per cent of polymer fraction.

<sup>c</sup> Polymer deposited was partly dispersed in solution, so collection of deposited polymer was not complete.

<sup>d</sup> Residual polymer removed by precipitation into methanol.

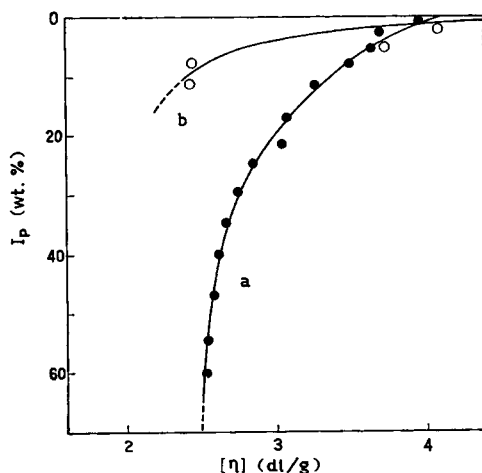


Fig. 3. Integral molecular weight distribution curves (from Tables IV and V) for in (a) polymer prepared solution polymerization and (b) in solid-state polymerization.

The original intrinsic viscosity of the polymer prepared in solid state was found to be 1.92. The result of fractionation, however, indicates that the polymer contains a small amount of very high molecular weight fraction, as shown in Table V. On the other hand, the polymer obtained in solution polymerization shows a relatively narrow distribution of molecular weight. This fact agrees well with the results obtained by melt viscosity.<sup>6</sup> However, there is no independent confirmation of this result, such as the ratio of number-average to weight-average molecular weight. Therefore, the conclusion that polymer prepared in solid-state polymeriza-

TABLE V  
Results of Fractionation of Polyoxymethylene (Polymer No. 3) Prepared in Solid State by Agitation at 60°C.<sup>a</sup>

Fraction no.	Agitation time, min.	Polymer wt.-%	$[\eta]$ , dl./g.	$I_p$ , wt.-%
1	0-30	4.3 <sub>8</sub>	4.09	2.1 <sub>9</sub>
2	30-60	1.9 <sub>1</sub>	3.73	5.3 <sub>4</sub>
3	60-90	1.4 <sub>6</sub>	2.43	7.5 <sub>8</sub>
4	90-120	1.1 <sub>2</sub>		
5	120-150	0.7 <sub>9</sub>	2.42	11.1 <sub>3</sub>
6	150-210	1.6 <sub>9</sub>		
7	210-270	1.2 <sub>4</sub>		
8	270-330	0.9 <sub>6</sub>		
	Total	13.4 <sub>9</sub>		
9 <sup>b</sup>		86.5 <sub>1</sub>	1.70	

<sup>a</sup> Polymer concentration, 1 g./dl.; volume of solution, 50 ml.; 1350 rpm;  $[\eta]_{orig} = 1.92$  dl./g.

<sup>b</sup> Residual polymer removed by precipitation into methanol.

tion has a broader molecular weight distribution than that obtained in the solution polymerization should be regarded as tentative.

### Discussion

The fractionation of high molecular weight polyoxymethylene diacetate has been studied<sup>2</sup> by the equilibrium elution process, with phenol ethylcellosolve as solvent and Kisselite as adsorption carrier for the polymer. The results were not satisfactory enough because of an accompanying degradation of high molecular weight polymer.

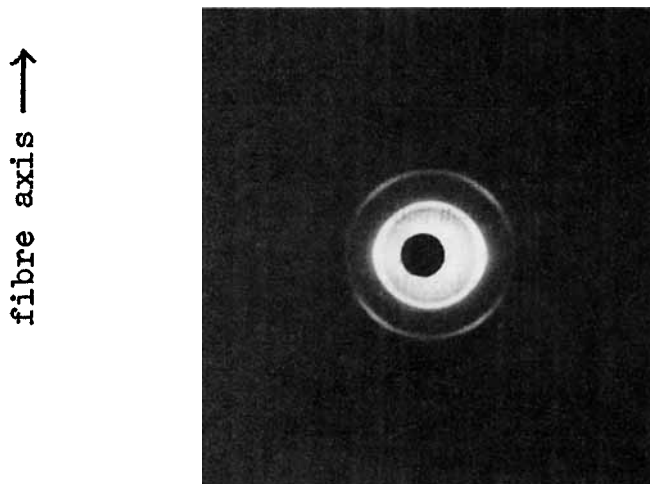


Fig. 4. X-ray diffraction diagram of fibrous polymer obtained from *p*-chlorophenol solution by agitation; fiber axis is vertical.

Recently it was reported<sup>7,8</sup> that a partial fractionation of polyethylene was observed in the course of preparative experiments on single crystals of the polymer. According to Pennings and Kiel,<sup>8</sup> laminar flow accelerates the formation of ribbon-like crystals, and uniformly stretched and fibrous polyethylene crystals were observed in an electron microscope. These reports suggest that the fractionation of polyoxymethylene by means of agitation may be caused by a process of crystallization under molecular orientation: the shearing stress applied in polymer solution promotes the molecular orientation, the formation and the growth of crystal nuclei.

In the case of polyoxymethylene, it is observed that the fibrous polymer precipitated from solution by agitation shows a slightly higher melting point (182–184°C.) than usual (180°C.)<sup>9</sup> and shows strong birefringence in a polarizing microscope. The x-ray diffraction diagram of the fibrous polymer prepared by agitation at 60°C. and 1350 rpm indicates that the polymer chains are oriented along the fiber axis as shown in Figure 4. The *d* spacings of this pattern illustrate that the *c* axis is parallel to the fiber axis. Details of x-ray analysis will be reported elsewhere.



We thank Dr. T. Higashimura for his helpful discussion of the work and Dr. E. Stirne-  
mann for his kindness in giving us the opportunity to carry out this study.

### References

1. E. Kobayashi and R. Signer, *J. Polymer Sci. B*, **3**, 491 (1965).
2. A. Kakiuchi and W. Fukuda, *Kogyo Kagaku Zasshi*, **66**, 964 (1963).
3. J. Majer, *Makromol. Chem.*, **86**, 253 (1965).
4. S. Okamura, E. Kobayashi, K. Takeda, M. Tomikawa, and T. Higashimura, in *Macromolecular Chemistry, Paris 1963 (J. Polymer Sci. C, 4)*, M. Magat, Ed., Interscience, New York, 1964, p. 827.
5. T. Miki, T. Higashimura, and S. Okamura, *Bull. Chem. Soc. Japan*, **39**, 41 (1966).
6. T. A. Koch and P. E. Lindvig, *J. Appl. Polymer Sci.*, **1**, 164 (1959).
7. T. Kawai and A. Keller, *J. Polymer Sci. B*, **2**, 333 (1964); T. Kawai, *High Polymer (Japan)*, **15**, 898 (1966).
8. A. J. Pennings and A. M. Kiel, *Kolloid-Z. Z. Polymere*, **205**, 160 (1965).
9. M. Inoue, *J. Appl. Polymer Sci.*, **8**, 2225 (1964).

Received October 10, 1967

Revised December 18, 1967