

Gel Permeation Chromatography of Polyoxymethylene

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Synopsis

Gel permeation chromatography of polyoxymethylene has been studied using N,N-dimethylformamide as the solvent. Polyoxymethylene samples used here are a copolymer of tetraoxane with 1,3-dioxolane and a commercial polyoxymethylene whose molecular weight distributions are moderately broad. Their intrinsic viscosities $[\eta]$ range from 1.4 to 2.8 dl/g. Factors affecting chromatograms are discussed, and the operating conditions were determined by using the analytical scale GPC. On the basis of these operating conditions, the molecular weight fractionation of polyoxymethylene was carried out by using the preparative scale GPC. It was found that polyoxymethylene can be effectively fractionated to give seven to ten fractions each of them containing the fractionated polymer ranging in weight from 0.2 to 8 mg when 40 mg polymer sample was used for a run of the measurement. The fractionated polymers were also found to have a narrow molecular weight distribution within a single peak, and their M_w/M_n values decrease with increasing molecular weight.

INTRODUCTION

Gel permeation chromatography has been used extensively to measure the molecular weight distribution of polymers and has been also applied in the molecular weight fractionation of polymers. In these cases, however, most studies have been confined to polymers that are easily soluble in the solvents at a relatively low temperature. There are only a few papers that report the molecular weight distribution or the molecular weight fractionation of polyoxymethylene.¹⁻³ No paper on the gel permeation chromatography of polyoxymethylene has been reported.

Although polyoxymethylene is a straight-chain polymer without branched or crosslinked chains, one of the major problems in the gel permeation chromatography of polyoxymethylene is the lack of suitable solvent in which polyoxymethylene can be easily dissolved at a relatively low temperature. Furthermore, polyoxymethylene is easily decomposed by heating or acids. Therefore, it is difficult to measure its molecular weight and its distribution. Measurement of the molecular weight or polyoxymethylene, in most cases, has been carried out at 60°C in *p*-chlorophenol con-

taining 2% α -pinene after the polymer had been dissolved at temperatures above 60°C.

Kobayashi et al.³ investigated the molecular weight fractionation of polyoxymethylene by mechanical agitation. They found that fibrous polymer was easily precipitated around the stirrer by agitation of a *p*-chlorophenol solution of polyoxymethylene, and high molecular weight polymer precipitated at an early stage. They applied this method to the fractionation of polyoxymethylene. However, the recovery of the fractionated polymer in this method is less than 60–70%.

We tried to measure the molecular weight distribution of polyoxymethylene by gel permeation chromatograph with a procedure using an analytical scale gel permeation chromatograph. Then we applied the procedure to the molecular weight fractionation of polyoxymethylene by using a preparative scale gel permeation chromatograph.

EXPERIMENTAL

Materials

Two kinds of polyoxymethylene were used; one was a commercial polyoxymethylene, Duracon M-90, obtained from Polyplastics Co. Ltd., and the other was a copolymer of tetraoxane with 1,3-dioxolane. The latter (POM-A—C) was produced by the solid-state copolymerization of tetraoxane with 1,3-dioxolane initiated by I₂.⁴ The molecular weight of the copolymer and its distribution were controlled by the addition of methylal to the polymeric system. Thermal stabilities of the copolymer, R_{222}^{60} , were higher than 96%, where R_{222}^{60} represents the percentage of residual weight after 60 min under a nitrogen stream at 222°C.⁵

N,N-Dimethylformamide (DMF) was used as obtained commercially.

Available polystyrene standards, narrow molecular weight distribution samples, used for calibration work were the polystyrene standards obtained from Pressure Chemical Company.

Sample Preparation

Polymer was dissolved in DMF at 140°C under bubbling nitrogen gas. The dissolution was performed within 10 min, and the solution was then filtered with the filter heated at 145°C in order to eliminate insolubles. After making sure that no polymer precipitates, the solution was injected into the GPC sample loop.

Analytical Scale GPC

A Waters Associates gel permeation chromatograph Model 200 was used for the determination of the molecular weight distribution. The four columns used were obtained from Waters Associates, and they were packed with porous gels of crosslinked polystyrene having controlled pore sizes of 3×10^3 , 3×10^4 , 10^5 , and 10^6 angstroms, respectively. The flow rate of

solvent (DMF) was 1.0 ml/min. Sample solutions were injected for a period of 2 min, that is, as a 2.0-ml injection volume. The operating temperatures were as follows: degasser, 135°C; surge tank, 140°C; columns, 140°C; sample injector, 140°C; refractometer, 140°C; siphon chamber, 140°C.

Preparative Scale GPC

A preparative scale gel permeation chromatograph was assembled from commercially available components, the flow diagram is shown in Figure 1. The capacity of the apparatus is about ten times that of the analytical scale GPC, and the maximum flow rate is 20 ml/min. The apparatus was equipped with a 16-ml sample loop, a 250-ml fraction bottle, and a 50-liter solvent tank. The main flow is separated into two parts by the splitter valve located at the outlet of the column system; one is led to the refractometer and the other, to the fraction bottle. The flow rate to the refractometer can be controlled by the splitter valve. The fraction collector is operated electrically at regular time intervals.

The column system used consists of four 4-ft-long, 1 in. in diameter columns packed with Styragels having pore sizes of 3×10^3 , 3×10^4 , 10^5 , and 10^6 angstroms.

Operating conditions used mainly were as follows; flow rate of solvent was 12.3 ml/min, flow rate to the refractometer was 1.3 ml/min, injection time was 6 min, and the operating interval of the fraction collector was 6 min.

The operating temperatures were the same as those in the analytical scale GPC.

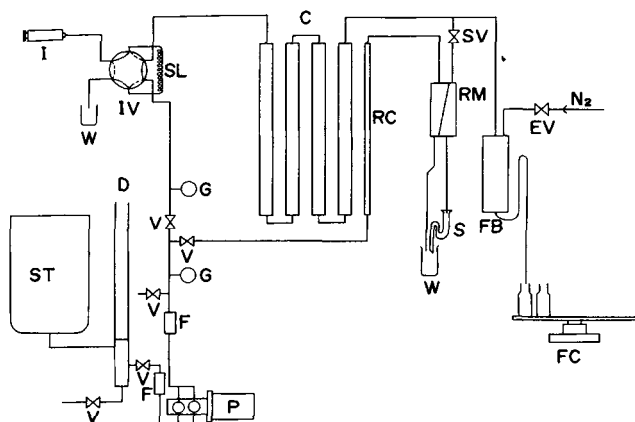


Fig. 1. Flow diagram for preparative scale GPC: ST, solvent tank; F, filter; P, pump; G, pressure gauge; V, valve; I, injector; W, bottle for waste solvent; IV, injection valve; SL, sample loop; C, column system; RC, reference column; SV, splitter valve; RM, refractometer; S, syphon; FB, fraction bottle; FC, fraction collector; EV, electromagnetic valve.

The main solution which eluted from the columns and was collected by the fraction collector was evaporated to recover the fractionated polymers. The polymers were washed with acetone and ethyl ether several times and were weighed after drying in vacuo.

The molecular weight and distribution of the fractionated polymer were determined when necessary. The latter was carried out by using the analytical scale GPC. The solution viscosity was measured at 60°C in *p*-chlorophenol containing 2% α -pinene after the polymer sample was dissolved at 115°C within 15 min. The molecular weight of the sample was calculated¹ by using the equation

$$[\eta] = 5.43 \times 10^{-4} \bar{M}_n^{0.66}.$$

RESULTS AND DISCUSSION

When measuring the molecular weight distribution of a polymer by gel permeation chromatography, there are many operating factors to be decided, such as choice of solvent, polymer concentration of sample solution, flow rate, injection time, choice of column system, operating temperature of the instrument, and so on. In the case of gel permeation chromatography of polyoxymethylene, however, it is essentially impossible to greatly vary the factors, because there are only a few solvents in which polyoxymethylene is soluble at a relatively low temperature. The polymer is also unstable to acids and to heating. Consequently, we could determine the operating conditions for the gel permeation chromatography of polyoxymethylene only after carrying out a few experiments.

As mentioned above, *N,N*-dimethylformamide (DMF) was used as solvent in this work. Although DMF is one of the solvents for high molecular weight polyoxymethylene, it is necessary to heat the system at a temperature above 135°C to dissolve polyoxymethylene in DMF.⁶ However, the boiling point of DMF is 153°C, and it is well known that the higher the temperature, the larger the heat decomposition of polyoxymethylene. Therefore, most operating temperatures chosen in this work were constant at 140°C, and we did not try to vary them.

The calibration work was carried out by using the narrow molecular weight distribution polystyrene standards, since it is impossible to obtain commercial polyoxymethylene standards whose molecular weight distribution is known. In this work, the molecular weight of polyoxymethylene eluted from the column system was indicated by the chain length of polystyrene. Figure 2 shows the relationship between the elution count and the chain length of polystyrene. It was found that a straight line was obtained over the entire range of the chain lengths of polystyrene standards used. In order to determine the molecular weight distribution curve of polyoxymethylene sample, the chain length of polystyrene at a given elution count was determined on the basis of the relationship given in Figure 2, and the weight fraction of the eluted polyoxymethylene at a

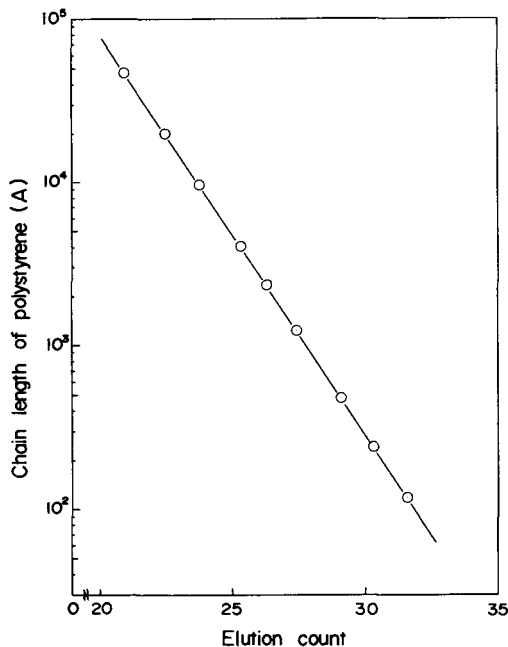


Fig. 2. Calibration curve for analytical scale GPC: columns, $3 \times 10^3 \text{ \AA}$, $3 \times 10^4 \text{ \AA}$, 10^5 \AA , 10^6 \AA ; solvent, DMF; flow rate, 1.0 ml/min; temperature, 140°C .

given elution count was determined from the height of the GPC chromatogram.

At first, the influence of solution concentration was investigated. It is known that solution concentration can affect elution time,⁷ i.e., the chromatogram of a sample solution at a higher concentration differs from the chromatogram obtained at a dilute solution. On the other hand, when a sample solution at too low a concentration is used, exact analysis becomes increasingly difficult. Since the chromatogram is a function of polymer concentration of the solution eluted from the columns, an error in reading becomes large. Therefore, it is necessary to determine a suitable concentration of polymer in the sample solution. Figure 3 shows the chromatograms obtained at polymer concentrations of 0.5% and 0.25%. It was found that the chromatograms are somewhat influenced by the solution concentration, and the chromatogram obtained at a higher concentration was shifted to the lower molecular length side, i.e., the higher the concentration, the later elution of the fractionated polymer. Preliminary experiments revealed that the maximum concentration of high molecular weight polyoxymethylene dissolved in DMF at 140°C was ca. 0.5%, and the larger the molecular weight of the polymer, the lower the maximum concentration. When the sample solution at the maximum concentration was used, the polymer precipitated easily before the injection so that the resulting chromatograms were unreliable. In the worst case, the columns may be clogged

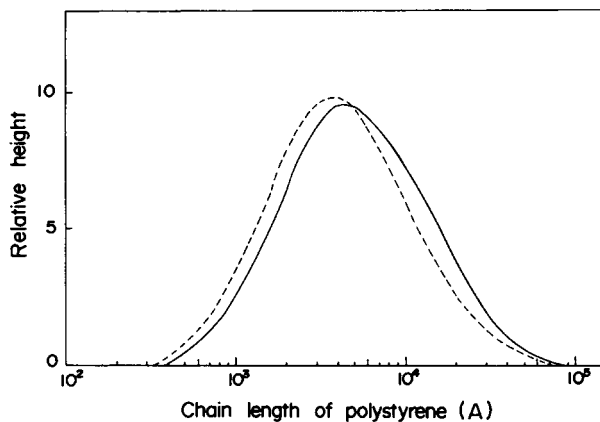


Fig. 3. GPC curves of polyoxymethylene at concentrations of 0.25% (solid line) and 0.5% (dashed line).

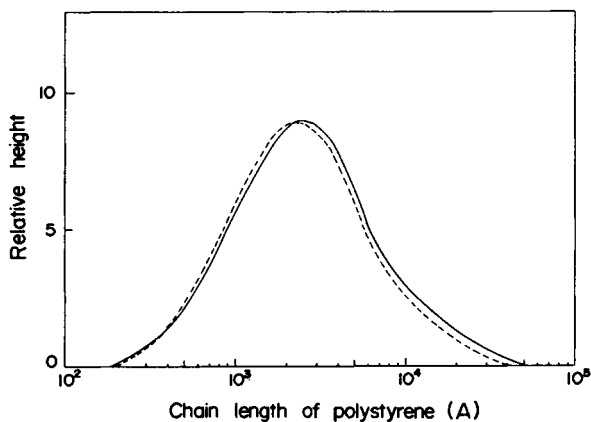


Fig. 4. GPC curves of polyoxymethylene; sample solutions were kept at 140°C for 10 min (solid line) and 90 min (dashed line) before injection.

with the precipitates. For these reasons, subsequent experiments were carried out at a constant concentration of 0.25%.

Since it is well known that polyoxymethylene is not heat stable, it is necessary to take into account the thermal decomposition of the polymer when polyoxymethylene is handled at an elevated temperature. Although thermally stable polyoxymethylene copolymers were used in this work, it was found, as shown in Figure 4, that a slight decrease in the height of the chromatogram at the higher molecular weight side was recognized when the sample solution was maintained at 140°C for a longer period before injection. In order to obtain an exact chromatogram, it is preferable to shorten the heating time of the sample solution as much as possible. Therefore, the heating time interval for the preparation of sample solution before the injection was kept constant at 10 min.

TABLE I
Operating Conditions of GPC for Polyoxymethylene

Sample Solution:

Solvent, DMF
Concentration, 0.25% (wt/v)
Dissolution time, 10 min
Dissolution temp., 140°C
Filtration temp., 145°C

Operating Conditions:

Solvent, DMF
Flow rate, 1.0 ml/min
Sample loop, 2.0 ml
Injection time, 120 sec
Column porosities, 3×10^3 , 3×10^4 , 10^5 , 10^6 Å

Operating Temperatures:

Each part of the GPC instrument, except the solvent tank and degasser, is kept at 140°C, solvent tank and degasser are kept at room temperature and at 135°C, respectively.

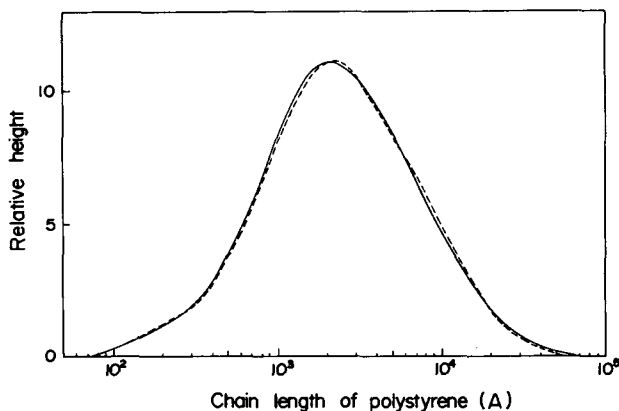


Fig. 5. Reproducibility of GPC curves obtained under operating conditions listed in Table I.

In all cases, a flow rate of 1.0 ml/min was used, and the sample solution was injected for a period of 2 min, since the injection volume was 2 ml. By these means, the standard operating conditions for the gel permeation chromatography of polyoxymethylene were determined and are listed in Table I.

Figure 5 shows that reproducible chromatograms can be obtained under the standard operating conditions listed in Table I. It is concluded that the molecular weight distribution of polyoxymethylene can be determined by using the analytical scale GPC under suitable operating conditions.

We considered that the preparative fractionation of polyoxymethylene can be carried out with the GPC technique, since the molecular weight

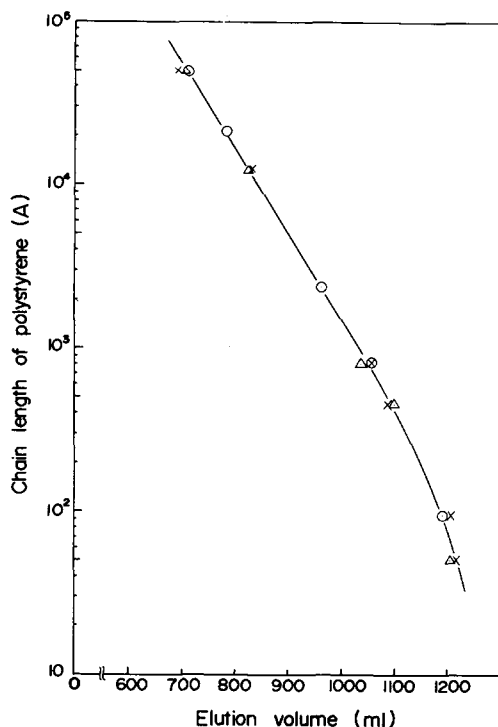


Fig. 6. Calibration curve for preparative scale GPC: columns, $3 \times 10^3 \text{ \AA}$, $3 \times 10^4 \text{ \AA}$, 10^5 \AA , 10^6 \AA ; solvent, DMF; temperature, 140°C ; flow rates, (Δ) 12.3 ml/min, (\times) 17.4 ml/min, (\circ) 20.2 ml/min.

distribution of polyoxymethylene can be easily obtained under suitable GPC operating conditions. Because large amounts of sample are required for the determination of the molecular weight distribution and solution viscosity of the fractionated polymer, a large-scale GPC, preparative scale GPC, was used. The apparatus and its operating conditions were already described in the experimental section.

Table II shows the relationship between the flow rate to the fraction bottle and the flow rate to the refractometer. These values were obtained when the splitter valve (see Fig. 1) was opened fully. The data indicate that the flow rate in the refractometer increases with increasing flow rate to the fraction bottle. The relationship between the elution volume in the fraction bottle and the chain length of the polystyrene standards at the various flow rates are shown in Figure 6. The plots deviated from a straight line only at the range of the especially lower chain length of polystyrene standard. However, it may be concluded that the effect of flow rate on the calibration curve (Fig. 6) is negligible, since the data obtained with the various flow rates could be plotted on the same calibration curve. Consequently, the preparative fractionation of polyoxymethylene was carried out at flow rates of about 11 and 1.3 ml/min for the fraction bottle

TABLE II
Flow Rates to Fraction Bottle and to Refractometer^a

Flow rate to fraction bottle, ml/min	Flow rate to refractometer, ml/min	Pressure in column, psi
6.7	1.2	50
11.0	1.3	50 ~ 80
15.8	1.6	60 ~ 95
18.4	1.8	75 ~ 115

^a Solvent, DMF; temperature, 140°C.

TABLE III
Polymer Recovery in the Preparative Scale GPC^a

Sample	Batch	Number of fractions recovered	Polymer weight injected, mg	Polymer recovery		Polymer sample	
				mg	%	Intrinsic viscosity $[\eta]$, dl/g	Thermal stability R_{222}^{60} , %
POM-A	15	10-19	600	520.6	86.8	2.8	96.9
POM-B	5	12-19	200	175.6	87.8	1.4	98.2
POM-C	1	1-25	40	32.6	81.5	1.4	99.4
Duracon M-90	5	12-18	200	172.3	86.2	1.4	98.8

^a Solvent, DMF; temperature, 140°C; volume of one fraction, 66 ml; volume of one injection, 16 ml; concentration, 0.25%.

and the refractometer, respectively. In this case, as well as in the analytical scale GPC, the polystyrene chain length was used as an indication of the molecular weight of the fractionated polyoxymethylene on the basis of the calibration curve given in Figure 6.

Table III shows the results in the molecular weight fractionation of the polyoxymethylene samples. The numbers given in the third column of the table indicate the fraction number in which the fractionated polymer was recovered. Under the operating conditions mentioned above, the polyoxymethylene samples used in this work were fractionated into seven to ten fractions according to the width of the molecular weight distribution. Of course, the polymer can be fractionated into more than ten fractions by shortening the operating time intervals of the fraction collector. However, it is better not to greatly increase the number of fractions recovered, because amount of polymer recovered from one fraction decrease with increasing number of fractions, consequently, further analytical studies of the fractionated polymer become difficult.

On the other hand, as can be seen from the fractionation results of POM-C in Table III, even when all fractions (fractions 1 to 25) were collected into a vessel and the polymer it contained was recovered by the evaporation of solvent, the recovery of polymer did not differ too much from those recovered from the 7-10 fractions. It was considered that most unrecovered

TABLE IV
 GPC Data Obtained with POM-A^a

Fraction number	Polystyrene chain length Å	Polymer recovery	
		mg	%
10	1.4×10^5	2.10	0.4
11	6.9×10^4	20.63	4.0
12	3.2×10^4	64.32	12.4
13	1.5×10^4	75.94	14.6
14	7.1×10^3	83.22	16.0
15	3.4×10^3	117.12	22.5
16	1.6×10^3	100.06	19.2
17	7.1×10^2	43.48	8.4
18	2.9×10^2	13.22	2.5
19	9.0×10	0.51	0.1
	Total	520.60	

^a For operating conditions, see Table III.

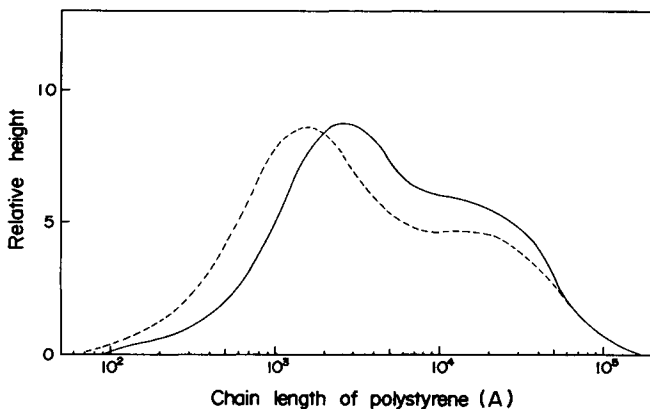


Fig. 7. GPC curves of POM-A obtained with preparative scale GPC (solid line) and analytical scale GPC (dashed line).

polymer was drained out after passing through the refractometer, because the amounts of the unrecovered polymer approximated those of the polymer contained in the solution which passed through the refractometer and drained out. Consequently, it was reasonable to conclude that decomposition of polymer during the measurement of GPC was negligible.

A typical example of the detailed result obtained in the molecular weight fractionation of polyoxymethylene is shown in Table IV. It was found that this polymer sample, POM-A, has a considerably wide molecular weight distribution, with a discernible shoulder at the larger molecular weight side and can be fractionated into ten fractions. In any case, it is too difficult to completely recover the fractionated polymer corresponding to both terminal positions of the chromatogram, since the amounts of polymer contained in the solutions are too small. However, the amounts

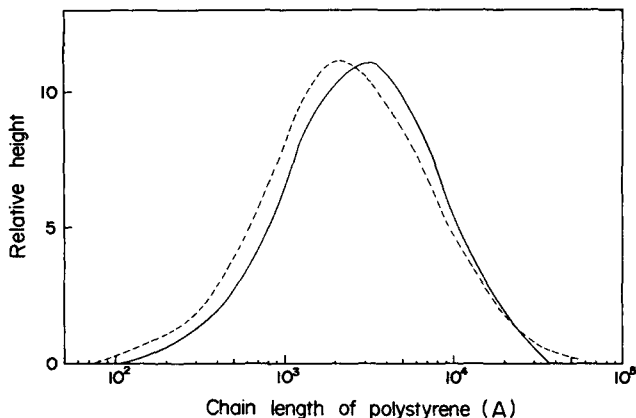


Fig. 8. GPC curves of POM-B obtained with preparative scale GPC (solid line) and analytical scale GPC (dashed line).

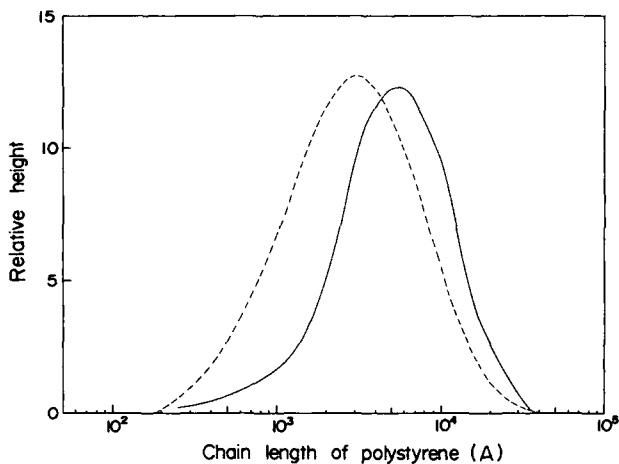


Fig. 9. GPC curves of Duracon M-90 obtained with preparative scale GPC (solid line) and analytical scale GPC (dashed line).

of the polymer in the fractions near the peak of the chromatogram are large enough to determine their molecular weight distribution by the analytical scale GPC and their solution viscosities. The molecular weight distribution curve can be obtained by plotting the weight fractions of the recovered polymer against the chain length of polystyrene obtained from the elution volume. The molecular weight distribution curves thus obtained are shown in Figures 7, 8, and 9 in comparison with those obtained by the analytical scale GPC. Although the molecular weight distribution curves in the preparative scale GPC shifted to the larger molecular weight side as compared with those resulting from the analytical scale GPC, the shapes of the curves were similar. This implied that significant fractionation according to molecular weight was accomplished by the preparative

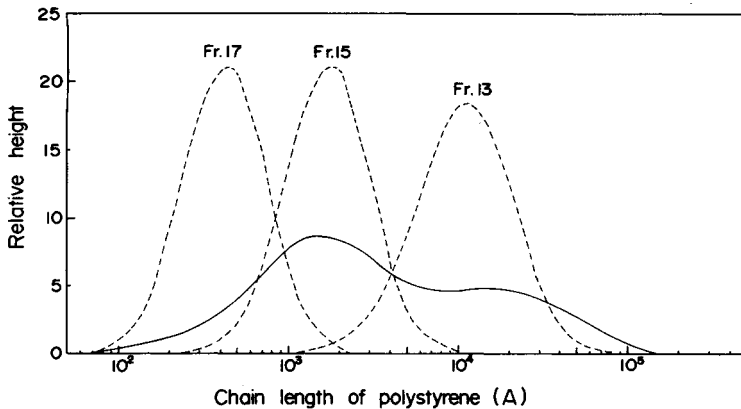


Fig. 10. GPC curves of unfractionated POM-A (solid line) and fractions of POM-A recovered by preparative scale GPC (dashed lines).

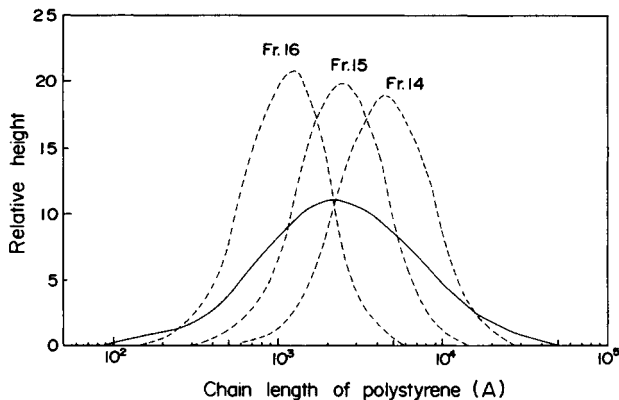


Fig. 11. GPC curves of unfractionated POM-B (solid line) and fractions of POM-B recovered by preparative scale GPC (dashed lines).

scale gel permeation chromatography. The disagreement seen in Figures 7, 8, and 9 can be mainly attributed to the time gap between the detection of the eluted polymer in the refractometer and the recovery of the polymer by the fraction collector; moreover, the time gap itself may differ in the polystyrene standards and the polyoxymethylene samples.

The molecular weight distribution of the polymer thus fractionated was measured again by the analytical scale GPC, and the results are shown in Figures 10, 11, and 12. The measurement was carried out under the operating conditions shown in Table I. The values of M_w/M_n determined from the molecular weight distribution curves⁸ and the solution viscosity $[\eta]$ of the fractionated polymer are listed in Table V. From these results, it was proved that each polymer fraction has a narrow distribution molecular weight and that fractionation was carried out effectively according to the molecular size of polymer. For example, as shown in Figure 10,

TABLE V
Analytical Data for Fractionated Polymer

POM-A:				
	Fraction 13	Fraction 15	Fraction 17	Original sample
Chain length, Å	1.15×10^4	1.8×10^3	4.4×10^2	1.6×10^3
M_w/M_n	1.43	1.34	1.31	
Intrinsic viscosity [η], dl/g	4.5	1.1	0.35	2.8
POM-B:				
	Fraction 14	Fraction 15	Fraction 16	Original sample
Chain length, Å	4.5×10^3	2.5×10^3	1.25×10^3	2.2×10^3
M_w/M_n	1.42	1.38	1.33	2.92
Intrinsic viscosity [η], dl/g	2.1	1.2	0.9	1.4
Duracon M-90:				
	Fraction 13	Fraction 15	Original sample	
Chain length, Å	6.0×10^3	2.2×10^3	3.1×10^3	
M_w/M_n	1.59	1.44	2.23	
Intrinsic viscosity [η], dl/g		1.2	1.4	

* Chain length of polystyrene.

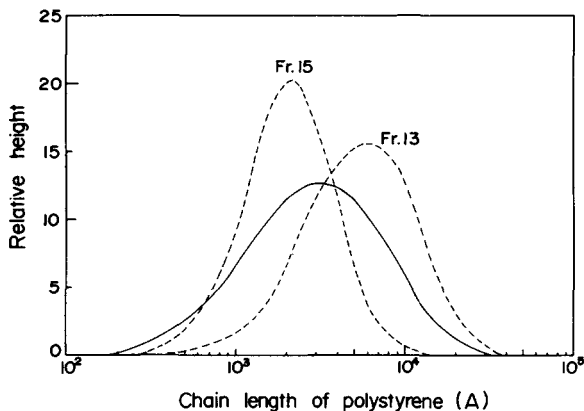


Fig. 12. GPC curves of unfractionated Duracon M-90 (solid line) and fractions of Duracon M-90 recovered by preparative scale GPC (dashed lines).

the original polymer sample, POM-A, has a wide molecular weight distribution curve with a shoulder, but each polymer fractionated has a very narrow distribution curve with a single peak. It was also found that the polymer, which has a considerably narrow molecular weight distribution, can be fractionated to give the fractionated polymer with a more sharp distribution curve by the preparative scale GPC as shown in Figures 11 and 12.

The fractionation was performed more effectively in the smaller molecular weight region, since the molecular weight distribution curve obtained at

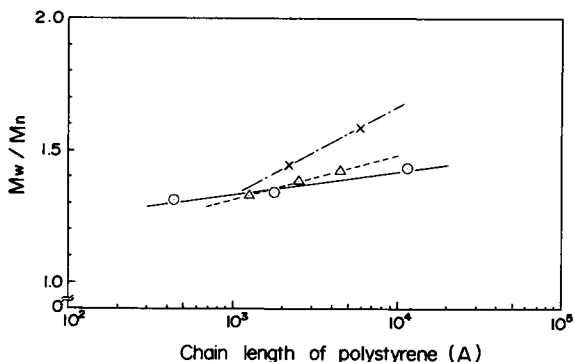


Fig. 13. Changes in M_w/M_n values of fractionated polyoxymethylene as a function of chain length of polystyrene: (○) POM-A; (△) POM-B; (×) Duracon M-90.

the smaller molecular weight was more sharp than that at the larger molecular weight, i.e., the value of M_w/M_n decreased with increase in fraction number, as seen in Table V. Plots of the value of M_w/M_n against peak of the molecular weight distribution curve obtained by the analytical scale GPC are found to be linear, as shown in Figure 13. It was also found that the larger the molecular weight of the fractionated polymer, the larger the value of M_w/M_n . As seen from Figure 13, there is a small difference in this relationship between the polyoxymethylene samples POM-A and POM-B, obtained by the solid-state polymerization of tetraoxane and the commercial polyoxymethylene Duracon, which was obtained by the liquid-state polymerization of trioxane. Although the molecular weight distribution of POM-B is similar to that of Duracon, the straight line of POM-B in Figure 13 is similar to that of POM-A rather than Duracon. Therefore, the behavior mentioned above may be attributed not to the difference in the molecular weight distribution of the sample but to the essential properties of polymer, which mainly depend on the polymerization method. For example, it is suggested that the samples used in this work may differ in the distribution of -C-C-O- groups in the polymer chain, because the samples POM-A and POM-B were obtained by the solid-state copolymerization of tetraoxane with 1,3-dioxolane, and Duracon is the commercial polyoxymethylene which was obtained by the liquid-state copolymerization of thioxane with ethylene oxide. However, it is beyond this paper to discuss these problems in further detail, and further studies on the gel permeation chromatography of polyoxymethylene will be continued in our laboratory.

Figure 14 shows logarithmic plots of the molecular weight and the solution viscosity of the fractionated polymer against the chain length of polystyrene corresponding to the chromatogram peak of the fractionated polymer. It was found that each plot gives only a straight line, irrespective of the polymerization methods by which the polymer samples were produced. Therefore, a calibration curve for the GPC of POM can be

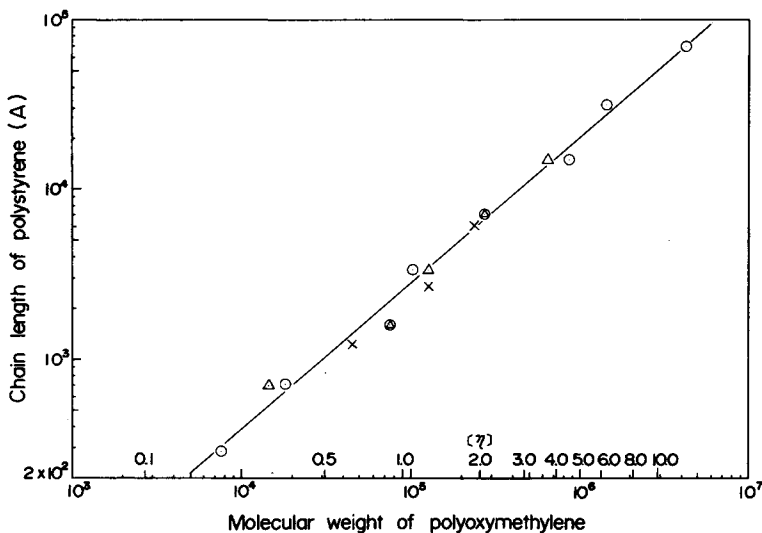


Fig. 14. Relationship between molecular weight or intrinsic viscosity of polyoxymethylene and chain length of polystyrene: (\odot) POM-A; (Δ) POM-B; (\times) Duracon M-90.

easily obtained from this relationship. It is also possible to determine the solution viscosity and molecular weight of polyoxymethylene sample from the peak of GPC chromatogram when it is not so broad, i.e., the value of M_w/M_n is less than about 1.5.

SUMMARY

The results and discussion above can be summarized as follows. As polyoxymethylene is unstable at a higher temperature and there is no good solvent in which polyoxymethylene can be easily dissolved at a relatively low temperature, it is very difficult to vary widely the various factors in the gel permeation chromatography of polyoxymethylene. However, it was proved that the molecular weight distribution of polyoxymethylene can be determined by the analytical scale GPC, and its operating conditions are described. In the preparative scale GPC, polyoxymethylene can be effectively fractionated into seven to ten fractions according to the molecular weight distribution of polymer sample, i.e., each fraction contains the fractionated polymer ranging in weight from 0.2 to 8 mg, when 40 mg polymer sample was used for a run of the measurement. Each fractionated polymer has a very narrow distribution molecular weight. It was found that the decomposition of polyoxymethylene during the measurement was negligible, since the recovery of polymer eluted from the column system was found to be reasonable.

We believe that gel permeation chromatography of polyoxymethylene is one of the most useful techniques for the elucidation of reaction mechanism. In our laboratory we are studying extensively the reaction mecha-

nism of solid-state copolymerization of tetraoxane and trioxane with 1,3-dioxolane by using gel permeation chromatography, differential scanning calorimetry, gas chromatography, and nuclear magnetic resonance spectroscopy, and we will report them elsewhere in the near future.

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