

Estimation of Molecular Weights of Epichlorohydrin-Bisphenol A Polymers by Gel Permeation Chromatography

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Synopsis

During a program to evaluate the gel permeation chromatography (GPC) technique for measuring the molecular size distribution of polymers, three experimental epichlorohydrin-bisphenol A polymers were sent to Waters Associates for analysis with the commercially available instrument. The resulting distribution curves were used to calculate weight-average and number-average chain lengths of the samples. These values were found to give good straight-line correlations with weight-average and number-average molecular weights measured by absolute methods. Thus the GPC method gives meaningful information about the molecular size distribution of polymers which can be used to obtain rapid estimates of molecular weight.

Introduction

The gel permeation chromatography (GPC) technique developed by Moore has been described in the literature.¹ Briefly, the method consists of injecting a dilute solution of polymer into a solvent stream flowing through a column packed with porous beads of inert, crosslinked polymer gel. The polymer sample is fractionated in the column according to molecular size depending on the depth to which each molecular species penetrates the gel. Hence, the largest species penetrates the gel least and is eluted first.

The volume of solvent eluting from the column and the difference in the refractive index of solvent and solvent-solute streams is continuously recorded.

Columns to be used in a separation are calibrated by examining the elution volume of materials with very narrow molecular weight distributions. A graph is prepared from the results showing the elution volume to sample peak versus the theoretical extended chain length of a molecule of the solute.

The epichlorohydrin-bisphenol A polymers examined here have very broad molecular weight distributions. Intrinsic viscosity and weight-average molecular weight measurements on high molecular weight fractions of the polymers indicate that they contain branched molecules. In gel

permeation chromatography, it is not unlikely that branched and linear polymer molecules having the same molecular weight but different apparent molecular size exhibit different elution volumes. For this reason, molecular weights of the samples have not been calculated directly from the curves as has been done in other cases involving linear polymers.² Rather, average chain lengths have been calculated from the curves and the values related to the measured molecular weights.

Experimental Procedures and Results

Properties of the samples examined are given in Table I.

TABLE I
Molecular Weights of Polymer Samples

Product properties	Polymer I	Polymer II	Polymer III
\bar{M}_w	198,000	101,500	350,000
\bar{M}_n	11,900 (14,100)	8,300 (8,570)	6,300
\bar{M}_w/\bar{M}_n	16.6	12.2	55.6

The weight-average molecular weights \bar{M}_w were determined by light scattering; the number-average molecular weights \bar{M}_n by ebulliometry. Also, polymers I and II were fractionated by a coacervation technique into seven and six parts, respectively. Number-average molecular weights were measured by ebulliometry on the low molecular weight fractions and by osmometry on the high molecular weight fractions. The results recombined mathematically are shown in parentheses in Table I, and lend validity to the ebulliometric measurements on the whole polymers.

Three columns were used in the separations. The upper permeability limit of the first two columns was about 10^6 Å, while that of the third column was about 10^4 Å. In each measurement 1 ml. of a 1 wt.-% polymer solution was used. Tetrahydrofuran at room temperature was used as the solvent. The flow rate through the columns was 1 ml./min. The time required for a sample to pass completely through the system was about $2\frac{1}{2}$ hr.

The molecular size distribution curves and the calibration for this system of columns between extended chain length and elution volume obtained by Waters Associates are shown in Figure 1.

Discussion

The breadth of the molecular size distribution curves shown in Figure 1 are in agreement with the distribution ratios, \bar{M}_w/\bar{M}_n , of the polymers. It can be shown by calculation that the curves fall in the proper sequence according to the measured number-average and weight-average molecular weights. Consider, for example, that for a given polymer species, i , there

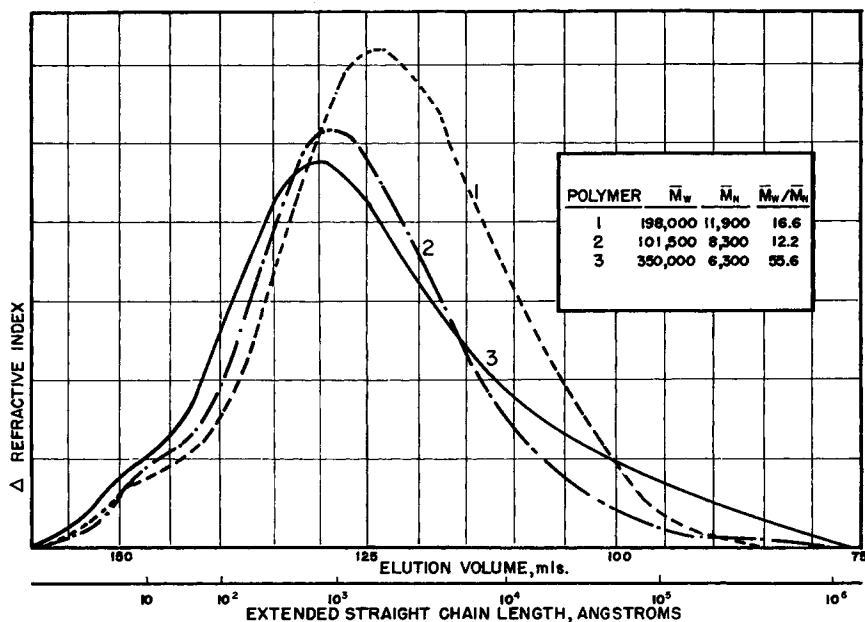


Fig. 1. Molecular size distribution of polymer samples by GPC.

should exist a relation between molecular weight, M_i , and extended straight chain length in angstroms, A_i , such that

$$M_i = k A_i$$

where k is the coefficient of mass per unit chain length for a given homologous series. The number-average molecular weight \bar{M}_n of the entire polymer can be calculated by summing the grams of each species, g_i , and dividing by the sum of moles of each species in the polymer:

$$\bar{M}_n = \frac{\sum_{i=1}^n g_i}{\sum_{i=1}^n g_i/M_i} = \frac{\sum_{i=1}^n g_i}{\sum_{i=1}^n g_i/kA_i}$$

Defining \bar{A}_n as the number-average chain length of the entire polymer, one obtains

$$\bar{A}_n = \frac{\bar{M}_n}{k} = \frac{\sum_{i=1}^n g_i}{\sum_{i=1}^n g_i/A_i}$$

Thus a plot of \bar{M}_n versus \bar{A}_n should be a straight line with slope k which intercepts the origin. By a similar argument, it can be shown that the relation between the weight-average molecular weight \bar{M}_w and weight-average chain length, \bar{A}_w , is

$$\bar{M}_w = k\bar{A}_w$$

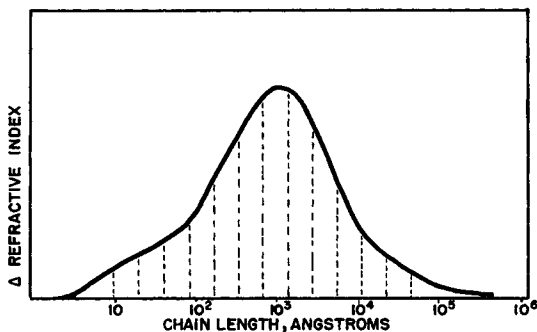


Figure 2.

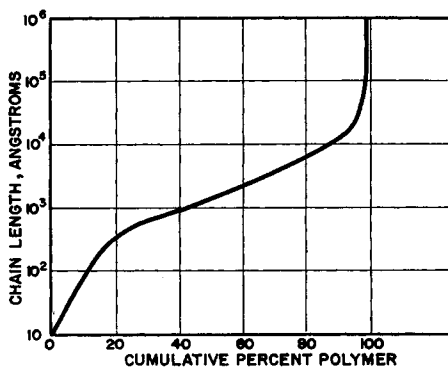


Figure 3.

Both \bar{A}_n and \bar{A}_w were calculated from the GPC distributions as follows: (1) the curve was divided into several segments, arbitrarily selected, as shown in Figure 2; (2) the area under the entire curve and under each segment was measured by using a planimeter; (3) a graph was constructed from the information obtained of log extended chain length versus cumulative per cent area polymer which was assumed to be cumulative per cent weight polymer (Fig. 3); (4) chain length values were taken from the graph at 5%, 15%, 25%, . . . , 95% polymer for the calculation of \bar{A}_n and \bar{A}_w .

The \bar{A}_n and \bar{A}_w calculated from the GPC curves are shown plotted against measured \bar{M}_n and \bar{M}_w , respectively, in Figures 4 and 5. Excellent straight-line correlations are obtained between the molecular weights of the polymers and the calculated values.

In theory, the coefficient of mass per unit chain length (k value) for a linear epichlorohydrin-bisphenol A polymer should be about 17 g./A.-mole. The repeating unit for this type of epoxy resin has a molecular weight of 284 and an extended chain length of about 17 Å. Hence,

$$284/17 = 17 \text{ g./Å.-mole}$$

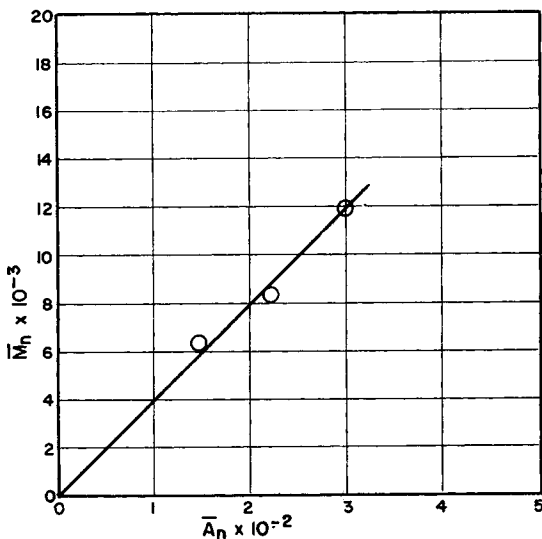


Fig. 4. Relationship between the ebulliometric number-average molecular weight and GPC number-average chain length.

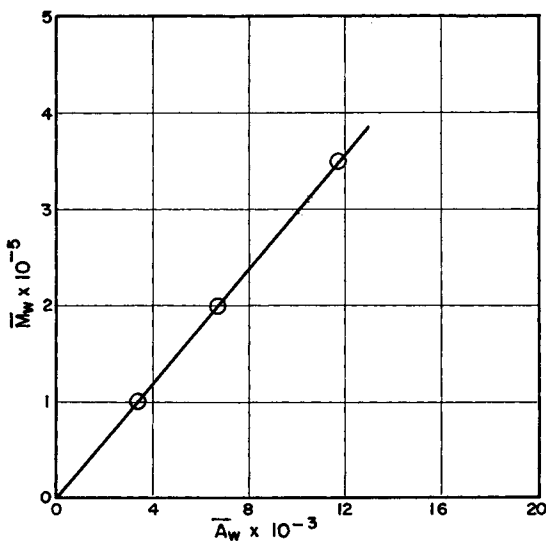


Fig. 5. Relationship between the light-scattering weight-average molecular weight and GPC weight-average chain length.

Naturally, the value would be greater if the polymer were branched as the samples in these experiments are believed to be. The slopes of the lines in Figures 4 and 5 do give greater k values; 40 and 30 g./A.-mole, respectively. It is not understood why different values are obtained. More work will be necessary to resolve this question.

Conclusions

The results show that good estimates of \bar{M}_n , \bar{M}_w , and hence the distribution ratio, \bar{M}_w/\bar{M}_n , can be obtained from the GPC distribution curves. Since the curves are in proper sequence according to average molecular weights, it appears that they do present pictures which are representative of the distributions of the samples.

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References

1. Moore, J. C., *J. Polymer Sci.*, **A2**, 835 (1964).
2. Maley, L. E., paper presented at Seminar for Users of GPC, Sponsored by Waters Associates, January 19, 20, 1965, Cleveland, Ohio.

Résumé

Afin d'évaluer la chromatographie par perméation sur gel (GPC) du point de vue de la mesure de la distribution des grandeurs moléculaires des polymères, trois polymères d'épichlorhydrine-bisphénol A ont été envoyés à Waters Associates à des fins d'analyse avec leur instrument commercial disponible. Les courbes de distributions résultantes ont été utilisées pour calculer les longueurs de chaînes moyennes en poids et en nombre des échantillons. Ces valeurs donnent des relations linéaires satisfaisantes avec les poids moléculaires moyens en poids et en nombre déterminés par des méthodes absolues. Par conséquent la méthode fournit des informations significatives concernant la distribution des grandeurs moléculaires des polymères qui peut être utilisées pour obtenir rapidement une estimation du poids moléculaire.

Zusammenfassung

Im Rahmen eines Versuchsprogramms zur Anwendung der Gelpermeationschromatographie (GPC) zur Messung der Molekülgrößenverteilung von Polymeren wurden drei Epichlorhydrin-Bisphenol-A-Polymere an Waters Associates zur Analyse mit ihrem im Handel erhältlichen Instrument gesandt. Die erhaltenen Verteilungskurven wurden zur Berechnung des Gewichts- und Zahlenmittelwerts der Kettenlänge der Proben verwendet. Diese Werte zeigten eine gute lineare Beziehung zu den nach Absolutmethoden bestimmten Gewichts- und Zahlenmittelwerten des Molekulargewichts. Die GPC-Methode liefert daher eine sinnvolle Information über die Molekülgrößenverteilung von Polymeren, welche für eine rasche Molekulargewichtsabschätzung brauchbar ist.

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