

Column Fractionation of Polymers. IV. Large-Scale Polyester Column Fractionation*

MANFRED J. R. CANTOW, ROGER S. PORTER, and JULIAN F. JOHNSON, *California Research Corporation, Richmond, California*

Synopsis

A small-scale fractionation of 9 g. and a large-scale fractionation of 90 g. of a polyester were carried out. The polymer was prepared by condensation of isophthalic acid, maleic anhydride, and propylene glycol in the mole ratio 1:2:3. Results from the two fractionations were in good agreement despite different fractionation conditions. By proton magnetic resonance measurements the fractions were found to have nearly constant chemical compositions. The Huggins' constant and the Staudinger relation for this polyester were determined from data on fractions in chloroform at 30°C. Integral and differential molecular weight distributions as well as various molecular weight averages for the polyester were obtained by a computer program. The fractionation data were applied to several popular distribution correlations. The experimental distribution was found to be in good agreement with that expected from the theory of polycondensation kinetics.

INTRODUCTION

The physical properties of a polymer of fixed chemical composition are markedly influenced by its molecular weight and molecular weight distribution. Systematic investigations in this field started quite early, as reviewed by Mark.^{1,2} A general correlation between number-average molecular weight and physical properties was derived by Flory.³ Recently, this was again checked by McCormick et al.⁴ on polystyrenes. The results deviated from the theoretical expectations. van Schooten et al.⁵ lately investigated the molecular weight dependence of several physical properties on a series of polypropylene fractions. Altogether, however, this field does not seem to have received the attention warranted by its technological importance. The reason for this is probably the amount of labor required in obtaining the necessary quantities of sharp fractions by conventional precipitation fractionation. In order to overcome this difficulty, we used the chromatographic method, proposed by Baker and Williams,⁶ which lends itself more easily to scaling up and to automation. This article describes a large-scale fractionation of 90 g. of polyester according to this technique.

* Based on a paper presented before the Polymer Division of the 145th National Meeting of the American Chemical Society, New York, September 1963.

TABLE I
Results of Polyester Fractionations

Fraction no.	Small-scale fractionation				Large-scale fractionation				
	Weight, g.	Per cent	\bar{M}_n	$I(M)$	Fraction no.	Weight, g.	Per cent	$[\eta]$	$I(M)$
a	0.255	2.83	460	0.01	1 + 2	2.7	3.0	0.036	0.02
b	0.474	5.27	1,250	0.05	3	4.3	4.8	0.062	0.05
c	2.092	23.24	3,200	0.20	4	10.1	11.2	0.09	0.13
d	1.743	19.37	5,600	0.41	5	9.4	10.5	0.11	0.24
e	1.068	11.87	7,900	0.57	6	10.5	11.7	0.13	0.35
f	0.557	6.19	9,200	0.66	7	7.3	8.1	0.17	0.45
g + h	0.624	6.93	10,500	0.72	8 + 9	9.4	10.4	0.19	0.55
i	0.705	7.84			10 + 11	6.1	6.8	0.22	0.63
k	0.457	5.07			12 + 13	4.1	4.6	0.25	0.69
					14	4.0	4.5	0.26	0.73
					15	16.5	18.4	0.34	0.85
					16	3.4	3.8	0.57	0.96

EXPERIMENTAL PROCEDURE

The polyester was obtained by condensation of isophthalic acid, maleic anhydride, and propylene glycol in the mole ratio 1:2:3. The glycol and the isophthalic acid reacted together at 230°C. for 7 hr. Then the charge was cooled to 150°C., the maleic anhydride added, and the reaction continued for 12 hr. at 215°C.

The large-scale, six-parallel column, chromatographic fractionator has already been described.⁷ A preliminary small-scale, single-column polyester fractionation showed that the system *n*-heptane-acetone was a suitable nonsolvent-solvent combination for large-scale operation. A 100-g. portion of the polyester was coated on 1000 g. of 3 M Superbrite glass beads, No. 130, average diameter 0.1 mm (Minnesota Mining and Manufacturing Company, St. Paul, Minnesota). For this purpose, the sample was dissolved in 200 cc.-acetone and treated with the same amount of *n*-heptane. Then the glass beads were added, and the mixture was slowly evaporated on a water bath under nitrogen. By working this way, it is assumed that the high molecular weight portion of the polyester is precipitated first on the beads, followed by deposition of decreasing molecular weights.

The fractionator was charged with 988 g. of the selectively coated beads containing 89.9 g. of polyester. The bottom 85% of each column was filled with clean, uncoated glass beads. A temperature gradient from 50°C. to 27°C. was maintained down the column. The solution flow rate was set at 1.6 cc./min. The fractionation required 112 hr. This corresponds to an average polymer concentration of 0.84 vol.-%. During this time, 16 cuts were taken, some of which were recombined to give 12 fractions, as summarized in Table I. The fractions add up to 87.8 g., corresponding to a recovery of 97.8% of the original charge.

Table I also gives the results of the preliminary small-scale fractionation. In this case the average polymer concentration was only 0.5 vol.-%. The recovery was 88.6% of the original 9-g. charge.

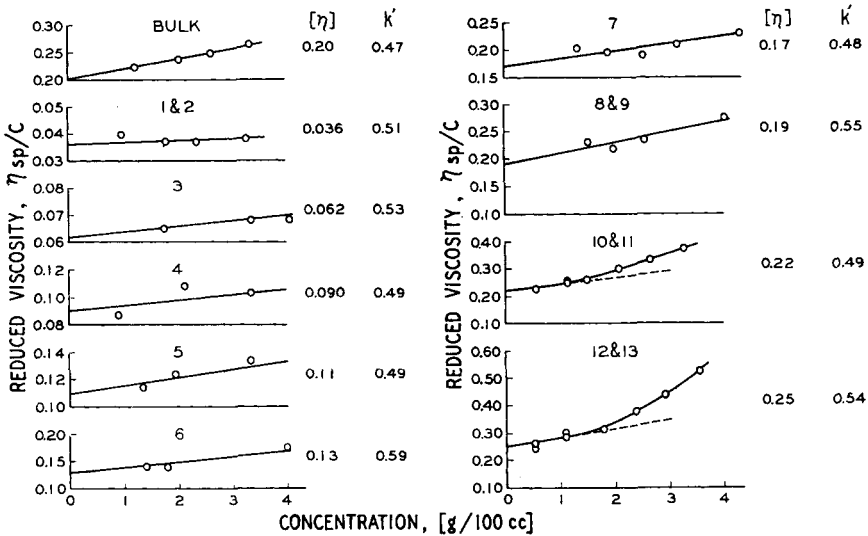
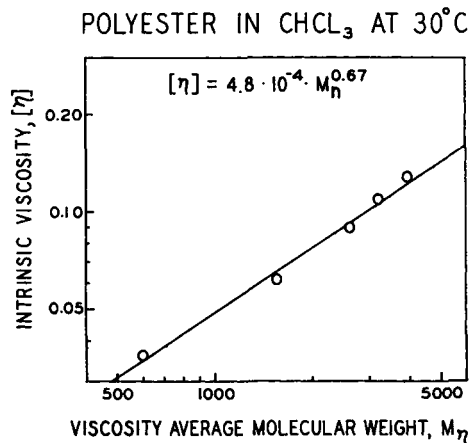
DETERMINATION OF MOLECULAR WEIGHTS

A. Viscometric Measurements

The intrinsic viscosities $[\eta]$ of the fractions were determined in chloroform at 30°C., with the use of crossarm, capillary viscometers⁸ (the dimension of $[\eta]$ is 100 cc./g.). The extrapolations are shown in Figure 1. A Huggins' constant of 0.53 ± 0.04 was obtained for these conditions.

B. Molecular Weight Determination

No Staudinger relation for this polyester is readily available. To determine the molecular weight, a commercial apparatus was used (Osmometer, Mechrolab, Inc., Mountain View, California) which is based on the Hill-Blades vapor tension apparatus.⁹ Since this method depends upon

Fig. 1. Polyesters in CHCl_3 at 30°C .Fig. 2. Polyester in CHCl_3 at 30°C .

the difference in vapor pressure between solvent and solution, a number-average molecular weight is obtained.

The measurements were carried out in chloroform at 39.0°C . For reasons discussed elsewhere¹⁰ only the fractions up to No. 6 and the unfractionated polymer could be measured in this system. Figure 2 shows a double logarithmic plot of \bar{M}_η as a function of $[\eta]$. The following relation results:

$$[\eta] = 4.8 \times 10^{-4} \bar{M}_\eta^{0.67} \quad (1)$$

This is the first equation for this commercially important polyester. By use of this relation, the molecular weights of the higher fractions were

calculated from the intrinsic viscosities. The results are compiled in Table I.

MOLECULAR WEIGHT DISTRIBUTION

The chemical homogeneity of the fractions was investigated by use of a Varian A-60 proton spectrometer. High resolution nuclear magnetic resonance spectra have been obtained on fractions in chloroform. Each of the three compounds forming the polyester was identified and determined by characteristic proton contributions. Duplicate analyses confirmed approximately the stoichiometry of the synthesis with a 12–15% decrease in isophthalic acid content with increasing molecular weight from fractions 4 to 14. This indicates that this acid might have a lower reactivity than maleic anhydride.

The cumulative weights of the fractions $I(M)$ were calculated according to the procedure given by Schulz¹¹ (see Table I). An attempt was made to fit fractionation data on a Wesslau plot.¹² The data scattered considerably and allowed no unequivocal interpretation. Graphical representation of the data according to Tung's method¹³ gave two intersecting lines.

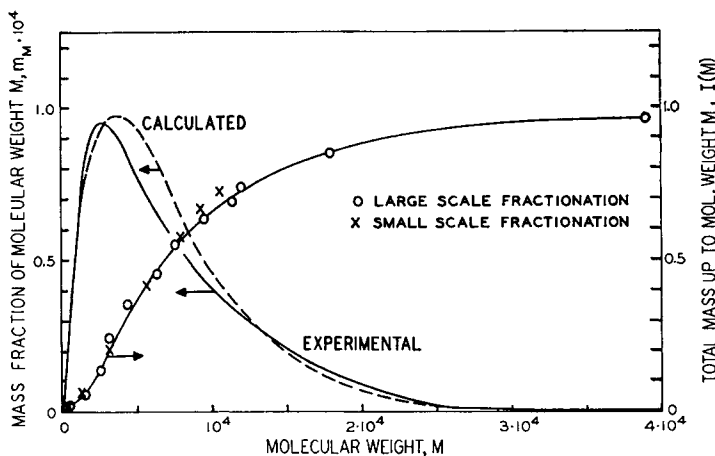


Fig. 3. Molecular weight distribution of polyester.

Figure 3 shows a conventional plot of the integral molecular weight distribution curve. The crosses represent the small-scale, the circles the large-scale results. The solid line was obtained by fitting the large-scale points with the equation

$$I(M) = \frac{a_1 M^2 + a_2 M^3 + a_3 M^4 + a_4 M^5}{M^2 + a_5} \quad (2)$$

by using a Datatron computer program. For this empirical relation, the program selected a suitable set of coefficients a_1 to a_5 . The coefficient of

correlation was 0.9981. An additional program calculated the differential molecular weight distribution, represented by the solid line in Figure 3, and the number-average, viscosity-average, and weight-average molecular weights collected in Table II.

TABLE II
Comparison of Experimental and Calculated Values from Polyester Fractionation

	Measured	Calculated	
		From distribution	From kinetics
\bar{M}_n	3100	3850	—
\bar{M}_η	8000	8400	—
\bar{M}_w	—	9500	7500
\bar{M}_w/\bar{M}_n	—	2.5	1.955
$[\eta]$	0.20	0.20	—

The expected molecular weight distribution was calculated according to the statistical derivations given by Schulz¹⁴ and Flory.¹⁵ From the stoichiometry of the synthesis an average acid-glycol base unit molecular weight of 173 was assumed. The computations were based on the calculated number-average molecular weight of 3850 from Table II. The dashed curve on Figure 3 represents the expected distribution. The agreement with the experiment is satisfactory. The calculated averages are compiled in Table II.

CONCLUSION

It has been shown that up to 90-g. batches of polyester can be rapidly fractionated by a large-scale, multiple-column method. The large-scale fractionation was shown to be as efficient as a small single-column scaled run. Analyses by NMR indicate a small change in chemical composition with fraction molecular weight. The applicability of the statistics of polycondensation was proved even for a rather complicated polymer as this three-component system. Several published methods for distribution interpretation failed satisfactorily to interpret data on the narrow polyester fractions obtained from the large-scale segregation. The polyester molecular weight distribution was treated successfully by a computer-generated empirical power law function.

We are indebted to Dr. G. B. Johnson and Dr. P. H. Parker for providing the polyester samples and to Mr. G. G. Bejarano for help with the Datatron program.

References

1. Mark, H., *Chemie und Physik der Cellulose*, Springer, Berlin, 1932.
2. Mark, H., *Ind. Eng. Chem.*, **34**, 1343 (1943).
3. Flory, P. J., *J. Am. Chem. Soc.*, **67**, 2048 (1945).
4. McCormick, H. W., F. M. Brower, and L. Kin, *J. Polymer Sci.*, **39**, 87 (1959).
5. van Schooten, J., H. van Hoorn, and J. Boerman, *Polymer*, **2**, 1961 (1961).

6. Baker, C. A., and R. J. P. Williams, *J. Chem. Soc.*, **1956**, 2352.
7. Cantow, M. J. R., R. S. Porter, and J. F. Johnson, *Nature*, **192**, 752 (1961).
8. Cantow, M. J. R., R. S. Porter, and J. F. Johnson, *J. Polymer Sci.*, **C1**, 187 (1963).
9. Johnson, J. F., R. L. LeTourneau, and R. Matteson, *Anal. Chem.*, **24**, 1505 (1952).
10. Hill, A. V., *Proc. Roy. Soc. (London)*, **A127**, 9 (1930).
11. Cantow, M. J. R., R. S. Porter, and J. F. Johnson, *J. Polymer Sci.*, **A2**, 2547 (1964).
12. Schulz, G. V., *Z. Physik. Chem.*, **B32**, 27 (1936).
13. Wesslau, H., *Makromol. Chem.*, **20**, 111 (1956).
14. Tung, L. H., *J. Polymer Sci.*, **20**, 495 (1956).
15. Schulz, G. V., *Z. Physik. Chem.*, **A182**, 127 (1938).
16. Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953.

Résumé

On a effectué un fractionnement à petite échelle de 9 g et un fractionnement à grande échelle de 90 g d'un polyester. On a préparé le polymère par condensation de l'acide isophthalique, l'anhydride maléique et le propylène glycol dans un rapport molaire de 1:2:3. Les résultats obtenus à partir des deux modes de fractionnement sont en concordance malgré les conditions différentes. Des mesures de résonance magnétique nucléaire ont montré que les compositions chimiques des différentes fractions étaient presque constantes. On a déterminé la constante d'Huggins et la relation de Staudinger pour ce polyester sur la base de données obtenues sur des fractions dans le chloroforme à 30°C. On a obtenu par calcul, pour ce polyester les distributions intégrées et différentielles des poids moléculaires ainsi que divers poids moléculaires moyens. On a appliqué les données de fractionnement à diverses corrélations de distribution connues. On a trouvé que la distribution expérimentale concordait avec celle que la théorie des cinétiques de polycondensation prévoyait.

Zusammenfassung

Eine Fraktionierung mit geringer Substanzmenge von 9 g und eine mit grosser von 90 g eines Polyesters wurde ausgeführt. Das Polymere wurde durch Kondensation von Isophthalsäure, Maleinsäureanhydrid und Propylenglycol im Molverhältnis 1:2:3 hergestellt. Die Ergebnisse der beiden Fraktionierungen stimmen trotz der verschiedenen Fraktionierungsbedingungen gut überein. Wie durch protonenmagnetische Resonanzmessungen gezeigt wurde, haben die Fraktionen fast konstante Zusammensetzung. Die Huggins-Konstante und die Staudinger-Beziehung wurde für diese Polyester aus Ergebnissen an Fraktionen in Chloroform bei 30°C bestimmt. Integrale und differentielle Molekulargewichtsverteilung sowie verschiedene Molekulargewichtsmittel wurden für die Polyester durch ein Computerprogramm erhalten. Die Fraktionierungsergebnisse wurden auf verschiedene bekannte Verteilungsbeziehungen angewendet. Die experimentelle Verteilung steht in guter Übereinstimmung mit der nach der Theorie der Polykondensationskinetik erwarteten.

Received January 10, 1964