

Molecular Weight Distribution of a Polyester

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Synopsis

Combined solvent composition and column temperature gradients were employed to effect the efficient fractionation of a polyester into several molecular weight fractions in about 16 hr. Mixtures of methyl ethyl ketone and cyclohexane were used as eluents for the fractionation which was conducted in a copper column packed with glass beads. In previously reported polymer fractionations with solvent and temperature gradients the temperatures at all points in the column have been either above or below the melting point of the polymer. This study demonstrates that hexanediol-succinic acid polyester may be efficiently fractionated by using a column temperature range which brackets the melting point of the polymer.

Introduction

In previous studies of fractionation of polymeric materials by chromatographic technique by use of temperature and solvent gradients the temperature in the column has been maintained at a level which insured that the condensed phase of the polymer was either a solid or a liquid at all times. Operation in this manner may necessitate use of a rather narrow temperature gradient in the column; e.g., the melting point of the polymer and the boiling point of the solvent system may be only a few degrees apart. Results of the present study indicate that with some polymers a rapid and satisfactory fractionation can be attained by using a temperature gradient which brackets the melting point of the polymer.

The theory and effect of the variables in chromatographic fractionation of polymers have been amply discussed elsewhere.¹⁻⁹ This method of fractionation has been applied to several polymers including polystyrene,^{1,4-6,9} polyethylene,² acrylonitrile,⁶ poly(ethylene terephthalate),¹⁰ butadiene polymers and copolymers,^{11,12} polyesters,¹³ and poly(methyl methacrylates).¹⁴ In all the studies mentioned above, except that of polyethylene by Guillet and Combs,² the temperature in the column was low enough to insure a solid polymer condensed phase. Guillet and Combs used a column temperature higher than the melting point of polyethylene, with a resulting decrease in fractionation time.

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Experimental

The fractionating column used in this study was constructed from a 3-ft. length of copper pipe having a wall thickness of 0.203 in. and inside diameter of 1.49 in. (Fig. 1). The well-insulated column was filled with fine glass beads having an average diameter of 75μ . A sintered glass disk was used to support the beads. The top of the column was wound with 4 ft. of heating tape rated at 48 w./ft., while the bottom of the column was provided with a cooling jacket to maintain the temperature at that point constant to within one degree.

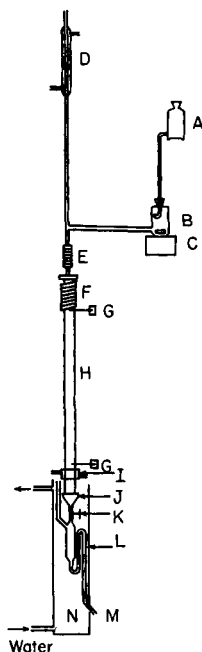


Fig. 1. Fractionating column. (A) good solvent supply; (B) mixing vessel; (C) magnetic stirrer; (D) condenser; (E) air removal heater; (F) column heater; (G) thermocouple; (H) column; (I) cooling jacket; (J) sintered disk holder; (K) needle valve; (L) siphon collector; (M) sample outlet; (N) water bath. Drawing not to scale. Column insulation not shown.

Solvent flow was regulated by a needle valve at the bottom of the column. To prevent precipitation of polymer in the needle valve and siphon collector, these items were immersed in a water bath maintained at a temperature higher than that at the bottom of the column. Some minor discoloration of the samples occurred in the apparatus described when the methyl ethyl ketone in the solvent exceeded 60 vol.-%; however, the quantitative effect of this was considered negligible under the conditions used for fractionation. The apparatus was also equipped with a heating tape wrapped around the solvent inlet tube to preheat the solvent for better

temperature control and to remove any dissolved gas prior to entry of the solvent into the column proper.

The polymer for this work was prepared by heating succinic acid and hexanediol at 197°C. without catalyst for four days. A vapor jacket from boiling ethylene glycol was used as a constant temperature heating bath for the reaction. This particular polymer has been thoroughly studied by Batzer.¹⁵⁻¹⁸

Preliminary solubility tests indicated 60 vol.-% methyl ethyl ketone with 40% cyclohexane was a suitable good solvent; the poor solvent, initially filling the 1-liter mixing vessel and the column, was 20 vol.-% methyl ethyl ketone with 80% cyclohexane.

The polymer samples were prepared for fractionation by coating 4-5 g. on 200-250 g. of the glass beads by means of the procedure of Jungnickel and Weiss.⁵ The coated beads were placed in the top of the column which had previously been filled with poor solvent.

After establishing the desired temperature gradient in the column, approximately fourteen 150-ml. fractions were collected. A mixing vessel at the top of the column permitted an exponential change in solvent composition from poor to good solvent. At a flow rate of 3-4 ml./min. the entire fractionation, including washing of the column with chloroform to remove the last traces of polymer, could be accomplished in 16 hr. Solvent was evaporated from the fractions by heating on a sand bath, and the samples then placed under vacuum until constant weight was achieved (ca. 2 days).

Molecular weights of the fractions were determined by measuring the specific viscosity of polymer-chloroform solutions with a Cannon-Fenske type viscometer of ASTM size 25. The constants for the molecular weight versus specific viscosity relation for hexanediol-succinic acid polyester in chloroform have been determined by Batzer,^{17,18} and these constants were accepted for use in this study. The concentration of polymer in chloro-

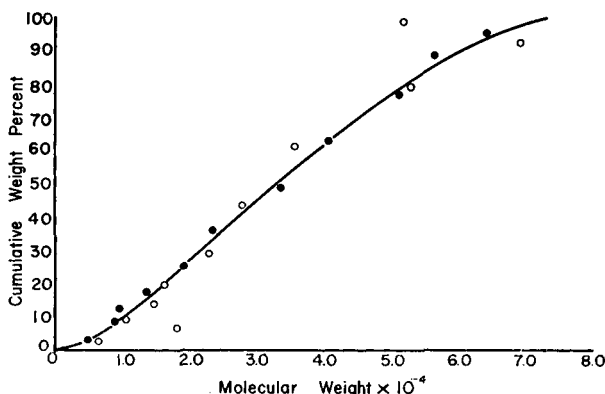


Fig. 2. Molecular weight distribution of hexanediol-succinic acid polymer: (O) sample 1; (●) sample 2. Data are plotted as midpoints of each fraction.

form for the viscosity measurements was adjusted to give a specific viscosity of approximately 1.5.

Results and Discussion

The molecular weight distributions of two samples taken from the same batch of polymer are shown in Figure 2 and Tables I and II. The fractionations were performed by using column temperature gradients of 70 to 40°C. for sample 1 and 70 to 27°C. for sample 2. The melting point of hexanediol-succinic acid polyester is 58°C.¹⁷ Inspection of Figure 2 indicates that reproducible fractionations were obtained by using a range of column temperatures which bracketed the melting point of the polymer.

TABLE I
Fractionation of Hexanediol-Succinic Acid Polyester, Sample 1^a

Fraction no.	Mass of fraction, g.	Part of total, %	Cumulative wt.-%	Molecular weight
1	0.1910	5.189	5.189	6,660
2	0.0873	2.372	7.561	18,150 ^b
3	0.1512	4.108	11.669	10,820
4	0.1704	4.630	16.299	14,920
5	0.2691	7.312	23.611	16,300
6	0.4254	11.560	35.171	23,000
7	0.6326	17.190	52.361	28,000
8	0.6575	17.865	70.226	35,800
9	0.6907	18.766	88.992	53,000
10	0.2872	7.802	96.794	69,300
11	0.0403	3.206	100.000	52,000 ^c
12	0.0231			
13	0.0546			

^a Initial sample size: 4.22 g.; polymer recovered: 3.68 g.; column temperature: 40–70°C.

^b Small amount of fraction made an accurate viscosity measurement difficult.

^c Fractions 11, 12, and 13 were combined for molecular weight determination. Fraction 13 contained polymer removed from column by chloroform.

As a further check on the success of the method, one of the fractions obtained in the initial fractionation of sample 1 was refractionated. The results of this refractionation, presented in Table III, demonstrate that an efficient fractionation was obtained. All the measurable fractions obtained, representing 97% of the tested fraction, had molecular weights intermediate between those of the fractions preceding and following the tested fraction.

The efficient fractionation obtained with the operating conditions used in this study may be attributed to a combination of factors. At the top of the column the polymer is above its melting point. As it passes down the column into the region which is below its melting point it may form a gel rather than a crystalline or amorphous solid. Transfer of polymer molecules between the gel and the solution would occur more readily. Another

factor of possibly greater significance is the increased adsorption power of some smooth surfaces, glass in particular, as the molecular weight increases.^{6,19,20} If the adsorption power is great enough fractionation will

TABLE II
Fractionation of Hexanediol-Succinic Acid Polyester, Sample 2^a

Fraction no.	Mass of fraction, g.	Part of total, %	Cumulative wt.-%	Molecular weight
1	0.2470	6.236	6.236	5,000
2	0.0426	1.075	7.311	^b
3	0.1179	2.977	10.288	9,000
4	0.1793	4.527	14.815	9,850
5	0.2477	6.254	21.069	13,650
6	0.3633	9.173	30.242	19,200
7	0.4636	11.706	41.948	23,600
8	0.5572	14.069	56.017	33,700
9	0.5600	14.140	70.157	40,800
10	0.5562	14.044	84.201	51,400
11	0.3719	9.390	93.591	56,700
12	0.1428	3.606	97.197	64,200
13	0.0511	1.290	98.487	^b
14	0.0599	1.513	100.000	^b

^a Initial sample size: 4.23 g.; polymer recovered: 3.96 g.; column temperature: 27–70°C.

^b Fractions were too small for viscosity measurement. Fraction 14 contained polymer removed from column by chloroform.

TABLE III
Refractionation of Fraction 7, Sample 1

Fraction no.	Mass of fraction, g.	Part of total, %	Cumulative wt.-%	Molecular weight
1	0.0079	1.320	1.320	^a
2	0.0029	0.484	1.804	^a
3	0.0056	0.936	2.740	^a
4	0.0121	2.022	4.762	26,000 ^b
5	0.0384	6.416	11.178	
6	0.1412	23.592	34.770	32,300
7	0.2432	40.635	75.405	29,900
8	0.0497	8.304	83.709	29,700
9	0.0975	16.291	100.000	33,300

^a Fractions 1, 2, and 3 were too small for viscosity measurement.

^b Fractions 4 and 5 were combined for viscosity measurement.

occur even when the eluting solvent is not saturated with polymer, i.e., the separation occurs, in principle, like vapor-phase chromatography.

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References

1. Baker, C. A., and R. J. P. Williams, *J. Chem. Soc.*, **1956**, 2352.
2. Guillet, J. E., R. L. Combs, D. F. Slonaker, and H. W. Coover, Jr., *J. Polymer Sci.*, **47**, 307 (1960).
3. Bock, R. M., and N. Ling, *Anal. Chem.*, **26**, 1543 (1954).
4. Caplan, S. R., *J. Polymer Sci.*, **35**, 409 (1959).
5. Jungnickel, J. L., and F. T. Weiss, *J. Polymer Sci.*, **49**, 437 (1961).
6. Krigbaum, W. R., and J. E. Kurz, *J. Polymer Sci.*, **41**, 275 (1959).
7. Schneider, N. S., L. G. Holmes, C. F. Mijal, and J. D. Loconti, *J. Polymer Sci.*, **37**, 551 (1959).
8. Schneider, N. S., J. D. Loconti, and L. G. Holmes, *J. Appl. Polymer Sci.*, **5**, 354 (1961).
9. Pepper, D. C., and P. P. Rutherford, *J. Appl. Polymer Sci.*, **2**, 100 (1959).
10. Bruck, S. D., *J. Polymer Sci.*, **32**, 519 (1958).
11. Cooper, W., G. Vaughan, D. E. Eaves, and R. W. Madden, *J. Polymer Sci.*, **50**, 159 (1961).
12. Cooper, W., G. Vaughan, and J. Yardley, *J. Polymer Sci.*, **59**, 52 (1962).
13. Pope, M. T., T. J. Weakley, and R. J. P. Williams, *J. Chem. Soc.*, **1959**, 3442.
14. Weakley, T. J., R. J. P. Williams, and J. D. Wilson, *J. Chem. Soc.*, **1960**, 3963.
15. Batzer, H., *Makromol. Chem.*, **5**, 5 (1950).
16. Batzer, H., *Makromol. Chem.*, **12**, 145 (1954).
17. Batzer, H., and B. Mohr, *Makromol. Chem.*, **8**, 217 (1952).
18. Batzer, H., and G. Weissenberger, *Makromol. Chem.*, **12**, 1 (1954).
19. Koral, J., R. Ullman, and F. R. Eirich, *J. Phys. Chem.*, **62**, 541 (1958).
20. Stromberg, R. R., and G. M. Kline, *Mod. Plastics*, **38**, No. 8, 130 (1961).

Résumé

On a employé différents mélanges de solvants et différents gradients de température de colonne pour effectuer un fractionnement d'un polyester et ses fractions de poids moléculaire; ce résultat a été obtenu en environ 16 heures. On a employé des mélanges de méthyléthylcétone et de cyclohexane comme éluants pour le fractionnement qu'on a effectué dans une colonne en cuivre remplie de perles en verre. Dans les fractionnement de polymère rapportés précédemment et utilisant des solvants et des gradients de température, on gardait à tous les points de la colonne une température soit plus haute, ou juste inférieure au point de fusion du polymère. Cette étude montre que le polyester de hexanediol-acide succinique peut être fractionné efficacement en employant dans la colonne des températures aux environs du point de fusion du polymère.

Zusammenfassung

Mit gleichzeitigem Lösungsmittelzusammensetzungs- und Säulentemperaturgradienten wurde eine wirksame Fraktionierung eines Polyesters in mehrere Molekulargewichtsfractionen in etwa sechzehn Stunden erreicht. Mischungen von Methyläthylketon und Cyclohexan wurden als Eluierungsmittel zur Fraktionierung in einer mit Glaskügelchen gepackten Kupfersäule verwendet. Bei früheren Polymerfraktionierungen mit Lösungsmittel- und Temperaturgradienten lag die Temperatur in allen Teilen der Säule entweder oberhalb oder unterhalb des Schmelzpunktes des Polymeren. Die vorliegende Untersuchung zeigt, dass ein Hexandiol-Bernsteinsäure-Polyester bei einem Temperaturbereich der Säule, welcher den Schmelzpunkt des Polymeren umfasst, erfolgreich fraktioniert werden kann.

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