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Yoon Hur[ab]; Edward M. Barrall II[ac]; Julian F. Johnson[de]
[a] INSTITUTE OF MATERIALS SCIENCE UNIVERSITY OF CONNECTICUT, STORRS, CONNECTICUT [b] Addressograph-Multigraph, Guilford, Connecticut [c] IBM Research Laboratory, San Jose, California [d] IBM RESEARCH LABORATORY, SAN JOSE, CALIFORNIA [e] University of Connecticut,

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Preparatory Column Fractionation of Polymers: Selection of Solvent Gradient*

YOON HUR† and EDWARD M. BARRALL II‡

INSTITUTE OF MATERIALS SCIENCE
UNIVERSITY OF CONNECTICUT
STORRS, CONNECTICUT 06268

JULIAN F. JOHNSON§

IBM RESEARCH LABORATORY
SAN JOSE, CALIFORNIA 95193

Abstract

The use of a programmable solvent gradient attachment with a high-speed liquid chromatograph affords a rapid and precise method for evaluating the effects of a variety of solvent gradients on fractionation, a determination of the effect of flow rate on efficiency, and a ready procedure to establish conditions for producing approximately equal amounts of polymer in each fraction.

The ability to define rapidly a suitable gradient in terms of equal amounts of collected polymer opens up the possibility of efficiently scaling up the column chromatographic method. Previously, this has been unattractive because of the effort involved to carry out large-scale fractionations.

The use of high-speed gel permeation chromatography also facilitates the rapid and quantitative determination of the polydispersity of the fractions. It is interesting to note that the results indicated no variation in

*Part XXXIV of a series on Column Fractionation of Polymers.
†Current address: Addressograph-Multigraph, Guilford, Connecticut.
‡On leave from IBM Research Laboratory, San Jose, California.
§On leave from the University of Connecticut.

polydispersity over a wide range of molecular weights. Again, this would be desirable for large-scale fractionation.

INTRODUCTION

Polymers are inhomogenous with respect to molecular weight; therefore, there have been many fractionations carried out to obtain polymer samples containing a narrow molecular weight distribution for subsequent studies of physical and mechanical properties. A variety of methods for fractionation have been utilized. Two of these are often referred to as chromatographic or column fractionation methods.

Desreux (*1*) developed a method based on a single-stage selective fractional extraction using a solvent gradient. In this procedure the column is packed by various techniques with an inert support material coated with a thin layer of polymer. A poor solvent mixture is introduced into the top of the column at constant temperature. This solvent dissolves lower molecular weight portions of the polymer and flows down and out of the column. Repetition of the dissolution step with progressively better solvent properties gives a series of fractions with increasing molecular weights. The method has been employed with modifications by a number of workers (*2–4*).

Baker and Williams (*5*) utilized a column method employing both a temperature and solvent gradient. The inert support is packed into the fractionating column but only the upper portion is polymer coated. The lower portion is uncoated inert support. A temperature gradient is imposed on the column as well as a solvent gradient. The method is flexible in that both the temperature and solvent gradient can be varied separately or simultaneously. It has been extensively employed (*6–17*).

The polymer deposition step on the support material is known to influence the efficiency of fractionation (*16*, *18–21*). The effect of the deposition procedure was not examined in this work.

This research was undertaken to help evaluate the possibility of using the Desreux technique in a scaled-up version for preparatory fractionation of polymers. A rough comparison of the various methods for preparatory fractionation of polymers has been made (*28*) which indicates that this method with improvements deserves further evaluation.

The nature of the solvent gradient and its relationship to fractionation efficiency is not completely understood. Screaton (*19*) indicated that a linear solvent gradient gave superior fractionation efficiency for high-density polyethylene, and Guillet et al. (*22*) reported the same behavior

with low-density polyethylene. Hulme and McLeod (*23*) and others (*20*, *24–27*) recommended the widely used logarithmic gradient in general. On the usual scale of polymer fractionation by this method, 0.1 to 1.0 g, it is necessary to collect and evaluate fractions to determine the fraction size and efficiency as a function of solvent gradient. Using high-resolution liquid chromatographs coupled with high-speed gel permeation chromatography simplifies the task of evaluation.

The optimization of the solvent gradient requires a definition of the desired results. For preparatory fractionation we have chosen to consider a solvent gradient that gives an equal amount of polymer in each equal volume increment of solvent as the desirable one.

This choice is debatable. For large-scale fractionation it is convenient to collect fractions of approximately equal amounts. If subsequent testing is to be undertaken, this allows tests to be performed over as wide a molecular range as possible. The effect of such a gradient on the width of the molecular weight distribution has not previously been reported and is considered here.

EXPERIMENTAL

Glass beads (Super Brite by 3M Company, Quinn, Alabama) were washed with hot hydrochloric acid until the supernants were clear, then washed four times with hot nitric acid, with distilled water to neutralize, then twice with acetone, and dried in air.

In order to obtain a narrow range of size distribution, the dried beads were screened through a U.S. standard testing sieve, No. 230 (250 mesh), and then screened through No. 100 (100 mesh) so that the beads size ranged between 60 and 150 μm. These beads were dried in a vacuum oven at 100°C for 48 hr and cooled in a dessicator until used.

The *polymer deposition* method used a decreasing temperature and solvent evaporation with agitation. In this procedure, 3.00 g of polystyrene (as obtained, PS-1 Dow Chemical Co., Midland, Michigan), 300.0 g of glass beads, and 900 ml of methylcyclohexane was charged into a reaction kettle equipped with mechanical stirrer, thermometer, and nitrogen inlet, and the kettle was placed in a constant temperature water bath. A slow stream of nitrogen was passed through the reactor during the polymer deposition. The nitrogen was also used to evaporate solvent later. After stirring for 30 min until the system was in thermal equilibrium (preliminary experiments showed that 30 min was adequate time for the polymer to go into solution), the reactor was cooled at an average rate of 0.2°C/min.

When the reactor temperature reached 12 to 13°C, solvent evaporation was started by blowing with nitrogen first, followed by cold air on the outside of the reactor which helped to lower the temperature to 5°C.

At this point a small aliquot sample of solvent was titrated against ethanol which showed that no polymer remained in the solvent. The solvent was then evaporated to dryness, the contents transferred into a tared beaker, and the beaker and beads were dried in a vacuum over for 24 hr at 40°C.

The reactor and stirrer were thoroughly washed with benzene and the residual glass beads were washed several times with benzene, dried, and weighed. The calculated average weight of polymer coated on the beads was 1.0015% of the total weight of glass beads plus polymer.

The *polymer fractionation* column was packed with polymer-coated glass beads on the top and uncoated glass beads in the bottom of the column, and it was thermostated in a constant temperature water bath at 38°C. A precolumn was placed in front of the fractionation column for thermal equilibration of the solvent–nonsolvent mixture before it entered the fractionation column. A schematic diagram is shown in Fig. 1. The fractionation column was charged with coated and uncoated beads, Fig. 1.

A Varian Liquid Chromatograph Series 4200 with dual pumps and a solvent gradient controller was used both for the Desreux column experiments and for the gel permeation chromatography. Cyclohexane of spectroquality and reagent grade was blended 40:60 v/v in order to minimize base line drift on solvent composition change. Pure nonsolvent was pumped through the column until a stable baseline was established and then the solvent gradient program was started. The Varian UV detector operating at 254 nm was used for the fractionation experiments and gel permeation chromatography.

An Isco Model 1200 Pup fraction collector using a time base collected 4 ml fractions. Each fractionation yielded 20 to 30 fractions. The solvent from the fractions was evaporated at 35°C at about 75 Torr. The polymer residue was dissolved in 0.5 ml of chloroform for determination of the molecular weight distribution. Table 1 lists the operating parameters of the gel permeation chromatograph.

RESULTS AND DISCUSSION

Figure 2 shows the amount of polymer eluted as a function of time using a linear solvent gradient. Typically, the amount of polymer varies markedly with time, in this case showing maxima at about 52, 62, and 66

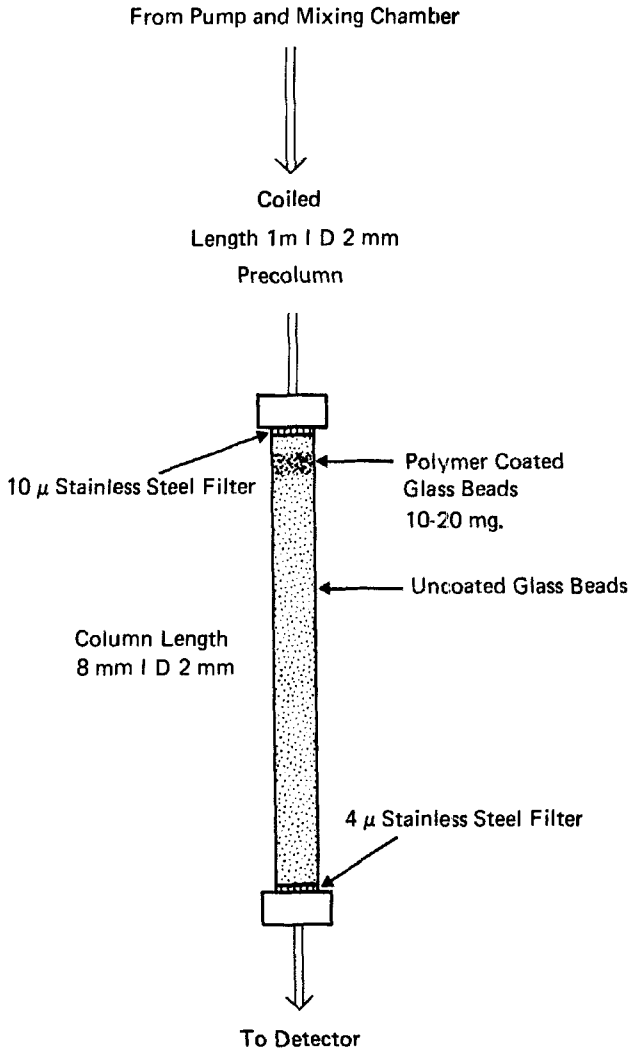

FIG. 1. Schematic diagram of column configuration.

TABLE 1

Operating Parameters of the Gel Permeation Chromatograph[a]

Column no.	Particle size (μm)	Mean pore diameter (Å)	Pore volume (cm^3/g)	Pore distribution (%)	Nominal operating range molecular weight
1	36–44	84	0.53	8.7	650–28,000
2	36–44	171	0.78	5.6	1,050–68,000
3	36–44	660	0.82	5.7	15,000–300,000
4	36–44	1933	0.87	6.8	120,000–650,000

[a]Chromatograph: Varian LC4200. Room temperature. Solvent: Chloroform. Flow rate: 1 ml/min. Inlet pressure: 3000 psi. Sample concentration: 0.06 mg/20 μl. Injection volume: 20 μl. Columns: 4 columns in series, each 50 cm long, 2.6 mm i.d., stainless steel, VIT-X Porous Glass Packing.

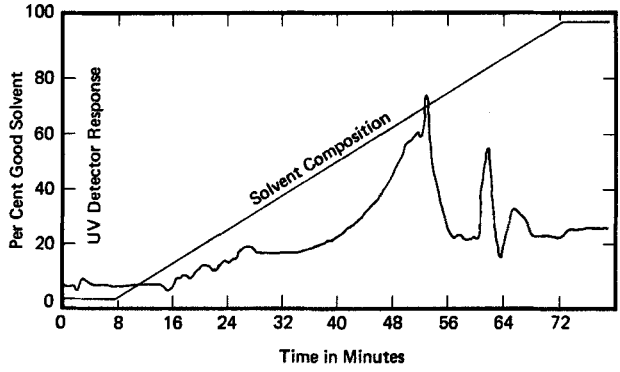

FIG. 2. Elution concentration of polymer using a linear solvent gradient.

min. By trial and error an approximation to the desired "equal amount" gradient was obtained. This is shown in Fig. 3. While not exact, the amount of polymer eluted in unit time is fairly uniform. The solvent gradient program is given in Table 2.

The use of the small column combined with the ease of selection of solvent composition by use of the solvent programmer makes the determination of the desired gradient relatively easy. The final 30-min interval is primarily to ensure that all polymer is removed and could undoubtedly be shortened.

Fractions were collected and the breadth of distribution evaluated using gel permeation chromatography. Table 3 shows results on a typical

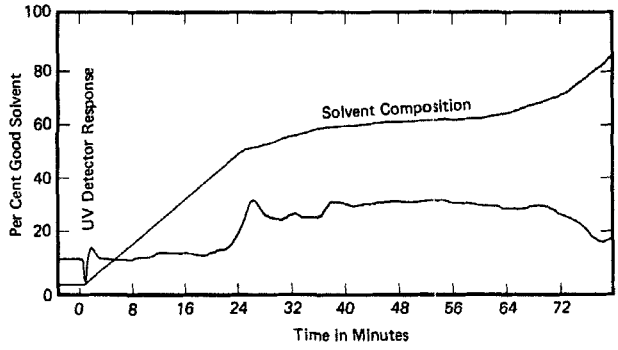

FIG. 3. Elution concentration of polymer using an "equal amount" solvent gradient.

TABLE 2

"Equal Amount" Solvent Gradient Profile[a]

Time interval (min)	Increase of B (%/min)	Percent of B in mixture	
		Start	Finish
25	2.0	0	50.0
1	0.5	50.0	50.5
3	1.0	50.5	53.5
5	0.8	53.5	57.5
6	0.4	57.5	59.9
9	0.1	59.9	60.8
1	0.4	60.8	61.2
4	0.8	61.2	64.4
7	1.0	64.4	71.4
15	2.0	71.4	100
30	—	100	100

[a]Poor solvent A, ethanol; good solvent B, cyclohexane.

run. Molecular weight refers to the molecular weight calculated from the elution volume to the maximum of the GPC peak using Eq. (1) established by calibration with narrow known molecular weight fractions of polystyrene:

$$\log M = -0.763V + 11.11 \tag{1}$$

The ratio of weight-average to number-average molecular weight was determined by measuring σ, the peak width at half height, and calculating

TABLE 3

Typical Fractionation Results, Fractionation Flow Rate 1.0 ml/min

Fraction no.	Elution volume (ml)	Molecular weight $\times 10^{-3}$	σ $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
D 1	8.500	42.1	21.1	1.25
D 3	8.437	47.1	23.6	1.25
D 5	8.312	58.6	27.6	1.22
D 7	8.187	73.0	34.4	1.22
D 8	8.187	73.0	36.4	1.25
D 9	8.062	90.8	42.8	1.22
D10	8.000	101	47.7	1.22
D11	8.000	101	50.7	1.25
D13	7.750	157	78.5	1.25
D15	7.687	176	87.7	1.25
D16	7.625	196	97.8	1.25
D17	7.562	219	109	1.25
D19	7.562	219	103	1.22
D21	7.437	273	136	1.25
D23	7.250	379	189	1.25
D25	7.125	472	222	1.22
D27	7.062	527	263	1.25
D29	6.937	656	328	1.25
D31	6.937	656	328	1.25

$\bar{M}_w/\bar{M}_n$ from Eq. (2). In this equation, $\bar{M}_n$ is assumed to be the same as that calculated from Eq. (1). This results in values of $\bar{M}_w/\bar{M}_n$ that are lower than the actual values. As no corrections for band broadening were made, this error is partially offset. In any case, the values are used only for comparative purposes.

$$\frac{\bar{M}_w}{\bar{M}_n} = \left[\frac{\sigma}{\bar{M}_n}\right]^2 + 1 \tag{2}$$

The results in Table 3 show about a 15-fold change in molecular weight. The ratio $\bar{M}_w/\bar{M}_n$ is essentially constant over the entire molecular weight range within experimental error. This was also the case for other fractionations carried out at several flow rates as shown in Table 4. The decrease in fractionation efficiency with increase in flow rate at flow rates of 1.5 ml/min and higher is marked and in agreement with other reported results (*6*, *24*).

In summary, the use of a programmable solvent gradient attachment with a high-speed liquid chromatograph affords a rapid and precise method for evaluating the effects of a variety of solvent gradients on

TABLE 4

Fractionation Efficiency as a Function of Flow Rate

Column flow rate (ml/min)	$\bar{M}_w/\bar{M}_n$ of fractions	
	Minimum	Maximum
0.25	1.20	1.22
0.50	1.20	1.31
0.75	1.20	1.24
1.00	1.22	1.25
1.50	1.28	1.34
3.00	1.31	1.53

fractionation and for establishing the experimental parameters for scaling up the fractionation.

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REFERENCES

1. V. Desreux, *Rev. Trav. Chim. Pays-Bas., 68*, 789 (1949).
2. P. M. Henry, *J. Polym. Sci., 36*, 3 (1959).
3. P. S. Francis, R. C. Cooke, and J. H. Elliot, *Ibid., 31*, 453 (1958).
4. A. Mular and L. Chinellato, *Eur. Polym. J., 6*, 1 (1970).
5. C. A. Baker and R. J. P. Williams, *J. Chem. Soc., 1956*, 2352.
6. W. R. Krigbaum and J. E. Kurz, *J. Polym. Sci., 41*, 275 (1959).
7. M. J. R. Cantow, R. S. Porter, and J. F. Johnson, *Nature, 192*, 752 (1961).
8. A. S. Kenyon, I. O. Salyer, J. E. Kurz, and D. R. Brown, *J. Polym. Sci., C, 8*, 205 (1965).
9. D. F. Slonaker, R. L. Combs, J. E. Guillet and H. W. Coover, Jr., *J. Polym. Sci., 4*, 523 (1966).
10. M. J. R. Cantow, R. S. Porter, and J. F. Johnson, *Ibid., 1*, 187 (1963).
11. M. J. R. Cantow, R. S. Porter, and J. F. Johnson, *J. Appl. Polym. Sci., 8*, 2963 (1964).
12. J. F. Henderson and J. M. Hulme, *Ibid., 11*, 2349 (1967).
13. J. Polacek, *Eur. Polym. J., 6*, 81 (1970).
14. T. Ogawa, S. Tanaka, and S. Hoshino, *J. Appl. Polym. Sci., 16*, 2257 (1972).
15. T. Ogawa, Y. Suzuki, and T. Inaba, *J. Polym. Sci., Polym. Chem. Ed., 10*, 737 (1972).
16. T. Ogawa, S. Tanaka, and T. Inaba, *J. Appl. Polym. Sci., 17*, 779 (1973).
17. T. Ogawa, S. Tanaka, and T. Inaba, *Ibid., 17*, 319 (1973).
18. R. S. Porter and J. F. Johnson, in *Polymer Fractionation* (M. J. R. Cantow, ed.), Academic, New York, 1967, Chap. B3.

19. A. S. Kenyon and I. O. Salyer, *J. Polym. Sci., 43,* 427 (1960).
20. N. S. Schneider, J. D. Loconti, and L. G. Holmes, *J. Appl. Polym. Sci., 5,* 354 (1961).
21. A. Chapiro, P. Cordier, J. Jazeforwicz, and J. Sebban-Danon, *J. Polym. Sci., C, 4,* 491 (1963).
22. J. E. Guillet, R. L. Combs, D. F. Slonaker, and H. W. Coover, Jr., *J. Polym. Sci., 47,* 307 (1960).
23. J. M. Hulme and L. A. McLeod, *Polymer, 3,* 153 (1963).
24. D. C. Pepper and P. P. Rutherford, *J. Appl. Polym. Sci., 2,* 100 (1959).
25. R. S. Alm, R. J. P. Williams, and A. Tiselius, *Acta Chem. Scand., 6,* 826 (1952).
26. L. M. Marschall, K. O. Donalson, and F. Friedberg, *Anal. Chem., 24,* 775 (1952).
27. G. Meyerhoff and J. Romatowski, *Makromol. Chem., 74,* 222 (1964).
28. J. R. Martin and J. F. Johnson, *Separ. Sci., 8,* 619 (1973).

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