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EVALUATION OF THE EFFICIENCY OF POLYMER FRACTIONATION BY THE COLUMN ELUTION METHOD

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SUMMARY

Three amorphous homopolymers were fractionated by the column elution-temperature gradient technique. The efficiency of the molecular-weight separations was determined by gel permeation chromatography. Three column-packing techniques were investigated. The most efficient method entailed preliminary bulk fractionation (four steps), and loading of the top fifth of the chromatographic column with the polymer-coated support. A cursory examination was made of the effect of sample size on column efficiency. Five grams of a POLA polyester (poly(4,4'-isopropylidene-diphenylene-1,1,3-trimethyl-3-phenylindan-4',5-dicarboxylate), a polystyrene, and a poly(methyl methacrylate) were fractionated by this technique. By optimizing conditions, ten fractions of nearly equal weight were obtained for each polymer, most fractions being of narrow molecular-weight distribution, *i.e.*, M_w/M_n 1.15 ± 0.10.

INTRODUCTION

BAKER AND WILLIAMS¹ introduced a chromatographic technique for the fractionation of polymers in the mid-1950's. Sample sizes range from centigrams²⁻⁴ to several hundred grams⁵⁻⁷ although the most common loading is 2 to 5 g. SCHNEIDER *et al.*^{8,9-10} have studied this technique extensively. However, there are few investigations of the interrelationship of column packing, sample size, and efficiency reported in the literature^{11,12}.

Fractions obtained by the column elution-temperature gradient technique¹ are generally characterized by viscosity and/or light-scattering measurements. The efficiency of the fractionation can be estimated by the breadth of the viscosity (or molecular weight) range and the regular increments of the viscosity (molecular weight) of the fractions. Gel permeation chromatography (GPC) enables one to characterize fractions in a more quantitative manner since it readily allows one to determine a relative molecular weight and characterize the breadth of the molecular-weight distribution by the ratio of the weight-average to number-average molecular weights (M_w/M_n).

In this study, several grams of polymer were fractionated under the same temperature and solvent conditions. Several column-packing methods were employed and the efficiency of the fractionation (minimum M_w/M_n) was established by GPC. The over-all objective was to fractionate a reasonable amount of polymer (5 g) while

maintaining high efficiency, *i.e.*, $M_w/M_n \sim 1.15$. These analyses were performed on a POLA polyester*, on polystyrene, and on poly(methyl methacrylate) samples to test whether the optimum packing method and sample size found for one polymer was applicable to other polymers.

EXPERIMENTAL

Materials

A moderate-molecular-weight POLA sample ($M_w \sim 50,000$) was prepared by an interfacial technique¹³, precipitated in a large excess of nonsolvent, filtered, and dried.

A polystyrene sample (Koppers SX, $M_w \sim 300,000$) was obtained from the Koppers Company, Pittsburgh, Pa., and used without preliminary purification.

The poly(methyl methacrylate) (PMMA) samples were obtained from the "polymer bank" administered by the Polytechnic Institute of Brooklyn. The samples were prepared, characterized, and supplied by the Rohm and Haas Company.

Cyclohexane, *p*-dioxane, and methanol were used for the various column fractionations without further purification. Tetrahydrofuran (THF) was used for the GPC measurements.

The column-packing material (silica) was 100-200 mesh (0.1 mm diameter) obtained from Agsco Corp., Patterson, N.J. The silica was treated thoroughly with hydrochloric acid to remove metallic impurities and then washed well with distilled water.

Fractionation analysis

The fractionating column and the solvent-mixing system are similar to those reported in the literature^{1,7}. The gold-plated, stainless-steel column was 5 ft. long and 1-in. I.D. A linear temperature gradient was imposed along the length of the column, and an exponential solvent gradient was used in all fractionations.

The fractionation conditions applicable for each polymer studied are described in Table I.

TABLE I

FRACTIONATION CONDITIONS

Polymer	Solvent	Nonsolvent	V_f^a	T_{top} (°C)	T_{bot} (°C)
POLA	<i>p</i> -Dioxane	Cyclohexane	0.70 (0.55)	40	20
Polystyrene	<i>p</i> -Dioxane	Methanol	0.45 (0.30)	50	25
PMMA	<i>p</i> -Dioxane	Cyclohexane	0.60 (0.40)	50	25

^a V_f = volume fraction of nonsolvent initially. Values in parentheses represent volume fraction of nonsolvent at the end of the analyses.

* Poly(4,4'-isopropylidenediphenylene-1,1,3-trimethyl-3-phenylindan-4',5-dicarboxylate).

The solvent flow-rate was maintained constant at 7 ± 2 ml/min during each of the fractionations. The column effluent was monitored spectrophotometrically and test tubes (50 ml each) were combined appropriately to obtain ten fractions of nearly equal weight.

Gel permeation chromatography

A Waters Associates M-100 gel permeation chromatograph was employed in this study. Tetrahydrofuran at 23° was used as the eluting solvent at a flow-rate of 1.0 ± 0.1 ml/min. The column set consisted of 10^6 , 10^5 , 10^4 , and 10^3 -Å porosity (nominal values) columns. One milliliter of a 0.2 (w/v) % solution was injected from a standard 2-ml sample injection valve.

Corrections for axial dispersion (chromatographic band broadening) were made by TUNG's method¹⁴.

RESULTS AND DISCUSSION

POLA fractionation studies

Three column-loading procedures were employed in the POLA fractionation study. These procedures are shown schematically in Fig. 1. In method A, the column is packed in a 5-step process. The bottom portion of the column (20%) is packed with pure, acid-washed silica. A preliminary bulk fractionation of the polymer is

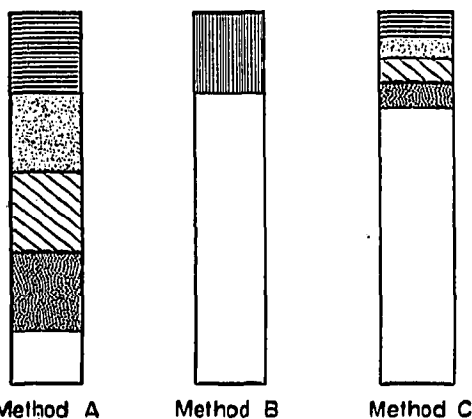


Fig. 1. Fractionation column as packed by methods A, B and C. (Schematic.)

then performed by the slow addition of nonsolvent to a well-stirred mixture of silica and dilute polymer solution. The four fractions are then packed sequentially with the lowest-molecular-weight components at the bottom of the column and highest-molecular-weight components at the top. Method B is a 2-step process wherein the column is first packed (80%) with the acid-washed silica and then with the polymer-coated silica. In this case the entire polymer is precipitated on to the silica in a single step.

Method C is a combination of A and B above in that a 4-step bulk fractionation is performed and that the column is first packed (80%) with pure, acid-washed silica.

A POLA polyester sample was fractionated by each of the column-packing

TABLE II
POLA FRACTIONATIONS

Fraction	Method A			Method B			Method C		
	W_f^a	P_w^b	R^c	W_f^a	P_w^b	R^c	W_f^a	P_w^b	R^c
1	0.10	15,100	1.37	0.06	8,100	1.61	0.18	30,200	3.06
2	0.13	26,900	1.16	0.11	22,100	1.20	0.05	23,600	1.18
3	0.08	38,400	1.15	0.11	34,200	1.09	0.05	30,300	1.06
4	0.10	46,700	1.11	0.12	45,700	1.10	0.09	40,700	1.08
5	0.09	60,800	1.10	0.09	56,000	1.07	0.09	48,600	1.06
6	0.10	71,700	1.12	0.10	67,500	1.07	0.10	61,600	1.05
7	0.11	85,400	1.10	0.08	73,200	1.06	0.12	76,000	1.07
8	0.10	94,700	1.12	0.09	96,000	1.17	0.10	94,700	1.07
9	0.10	125,000	1.20	0.19	139,000	1.16	0.08	111,000	1.08
10	0.09	163,000	1.30	0.05	166,000	1.19	0.14	171,000	1.16

^a Weight fraction of polymer.

^b Weight average molecular weight in terms of the polystyrene calibrating standards.

^c Ratio \bar{P}_w/\bar{P}_n as described in the text.

procedures with the spectrophotometer set at 305 nm. During these studies, the same temperature gradient and solvent gradients were employed. Three grams of polymer were used in the A and B fractionations, whereas 5 g were used in method C. In all cases, ten fractions of nearly equal weight were collected. The weight fraction and polystyrene-equivalent weight-average molecular weights (\bar{P}_w) are shown in Table II. The ratio of polystyrene weight-average to number-average molecular weights, R , is also given. The data are also presented graphically in Fig. 2 wherein the polydispersity (\bar{P}_w/\bar{P}_n) is plotted as a function of log molecular weight (\bar{P}_w). The data should be expressed as "bands" owing to the limited number of data points and consideration of the experimental uncertainty in \bar{P}_w/\bar{P}_n . Such a "band" is shown for method A in Fig. 2.

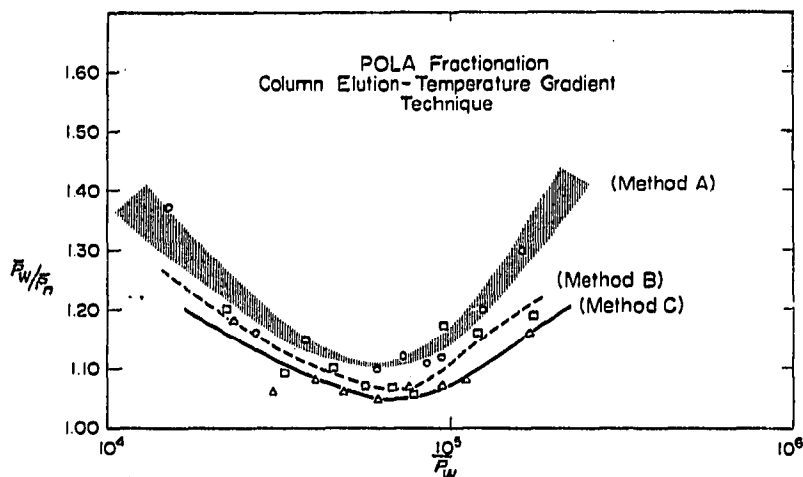


Fig. 2. Plot of \bar{P}_w/\bar{P}_n as a function of log molecular weight (P_w) for POLA fractionations.

The polystyrene-equivalent molecular weights (\bar{P}_w 's) for each of the fractionations increase systematically and the breadth of the molecular-weight distributions of the fractions are generally narrow (\bar{P}_w/\bar{P}_n 1.15 \pm 0.1). The first and last fractions show somewhat broader molecular-weight distributions in most cases. The 3-g fractionations by method A and B are nearly equivalent as estimated by the ratio (\bar{P}_w/\bar{P}_n) as a function of molecular weight. Method B appears somewhat more efficient, but the differences between the A and B fractionations are small.

Packing the column by method C clearly results in an increase in fractionation efficiency over methods A and B, as seen in Fig. 2. This is particularly significant in view of the fact that 5 g of the polymer was fractionated by this technique whereas only 3 g was fractionated by methods A and B. When 5 g of POLA was fractionated by method A, fractions having ratios of (\bar{P}_w/\bar{P}_n) 1.2 \pm 0.1 or higher were obtained. A 5-g fractionation by method B was attempted; however, surface coverage of the silica was poor. The silica exhibited extensive aggregation and the supernatant fluid was fairly turbid; therefore, the fractionation was discontinued. Subsequent 5-g fractionations utilizing this method were not performed owing to this aggregation problem.

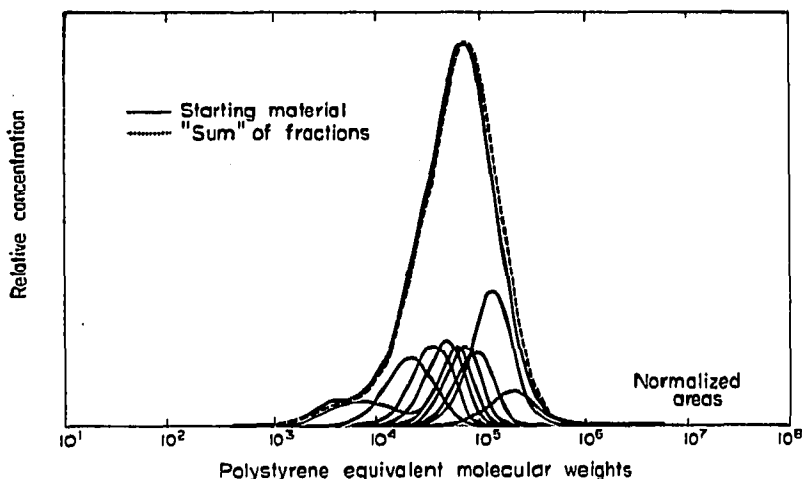


Fig. 3. GPC traces of the POLA polyester fractions and original starting material.

A typical GPC study of one of the fractionations is shown in Fig. 3. The original polymer is shown (solid line) as well as the fractions. The area under each curve of the fractions is proportional to the weight fraction it represents of the whole polymer. The "sum" of these areas, shown as dashes, agrees well with the curve of the original polymer. This demonstrates that little, if any, degradation has occurred during the course of the fractionation and recovery processes. It also indicates that the weight-fraction determinations are reasonably accurate and that the GPC analyses of the data are self-consistent.

A commercial polystyrene sample and a PMMA blend were examined to determine the effect of the column-packing method and fractionation efficiency. In these studies 5 g of the polymer were fractionated by methods A and C.

TABLE III

POLYSTYRENE FRACTIONATIONS

Fraction	Method A			Method C		
	W_f	P_w	R	W_f	P_w	R
1	0.16	205,000	3.16	0.05	108,000	4.60
2	0.08	84,700	1.63	0.04	47,400	1.17
3	0.04	77,200	1.16	0.05	68,100	1.13
4	0.06	123,000	1.13	0.07	93,200	1.08
5	0.12	160,000	1.15	0.12	134,000	1.06
6	0.09	226,000	1.15	0.10	179,000	1.07
7	0.12	314,000	1.24	0.12	229,000	1.09
8	0.13	418,000	1.28	0.14	289,000	1.12
9	0.11	435,000	1.50	0.17	404,000	1.15
10	0.10	386,000	1.57	0.12	593,000	1.23

Polystyrene fractionation studies

During these fractionations, the spectrophotometer was used at 272 nm. The GPC and weight-fraction data for this study are shown in Table III and Fig. 4. Examination of Fig. 4 indicates that packing the column by method C does produce fractions having narrower molecular-weight distributions than does packing by method A. This increase in efficiency is rather pronounced in the high-molecular-weight range. The GPC analyses were examined in the manner shown in Fig. 3. The "sum" of the fractions agreed very well with that of the original polymer in both cases. Note that \bar{M}_w 's and \bar{M}_n 's are reported in this study since the gel permeation chromatography has been previously calibrated with appropriate polystyrene standards.

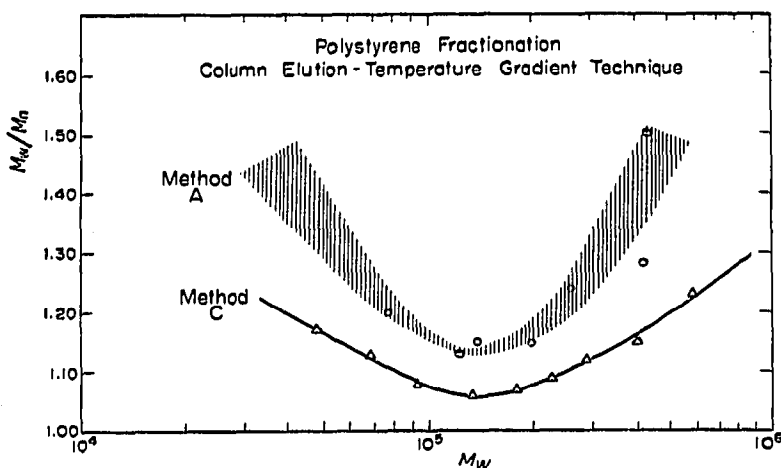


Fig. 4. Plot of \bar{M}_w/\bar{M}_n as a function of log molecular weight (\bar{M}_w) for the polystyrene fractionations.

PMMA fractionations

The PMMA sample was a blend (equal weight) of two samples having log normal molecular-weight distributions and weight-average molecular weights of 50,000 and

260,000. The resulting molecular-weight distribution (MWD) was somewhat broader than those examined thus far. We wished to determine what effect, if any, the MWD might have on the efficiency of the fractionation.

TABLE IV
PMMA FRACTIONATIONS

Fraction	Method A			Method C		
	W_f	P_w	R	W_f	P_w	R
1	0.51	47,400	1.35	0.38	35,800	1.76
2	0.04	32,500	1.07	0.07	62,500	1.06
3	0.03	47,900	1.04	0.06	80,100	1.06
4	0.04	58,900	1.04	0.08	109,000	1.11
5	0.04	71,300	1.05	0.07	141,000	1.11
6	0.07	90,400	1.06	0.05	216,000	1.08
7	0.05	120,000	1.08	0.07	231,000	1.12
8	0.08	162,000	1.12	0.08	272,000	1.16
9	0.09	240,000	1.16	0.06	316,000	1.26
10	0.05	339,000	1.26	0.04	334,000	1.44

A preliminary examination of the data in Table IV suggests that method A is preferred to method C in this investigation. However, fraction 1 of the method A analysis contained 51% (2.5 g) of the original sample. The large amount of polymer collected in the first few hundred milliliters is symptomatic of column overloading. Since less polymer remained on the column an "apparent" increase in efficiency was obtained.

During the course of the method C fractionation, a greater volume of eluate was collected to represent fraction 1. This fraction contained *ca.* 38% of the original polymer. A great difficulty was encountered in qualitatively monitoring the polymer concentration spectrophotometrically (230 nm). This was partly responsible for the large amount of polymer being taken as fraction 1 during the two analyses. A further improvement of the fractionation could be obtained if one were to start the solvent gradient at a composition slightly richer in nonsolvent. In view of these difficulties the efficiency of PMMA fractionation by the A and C techniques should be considered equivalent.

CONCLUSION

The column elution-temperature gradient technique has been successfully applied to samples of POLA, polystyrene, and poly(methyl methacrylate). GPC analysis has shown the fractions to have very narrow molecular-weight distributions when chromatographic conditions are optimized. Five grams of polymer can be adequately fractionated for further characterization by light scattering, viscometry, and osmometry.

The method of column packing affects the efficiency of the fractionation, method C being equal to or better than the other two procedures.

The polystyrene equivalent molecular weights for the POLA and PMMA samples have been converted to absolute molecular weights using BENOIT's¹⁶ hydro-

dynamic volume concept. This transformation does not influence our results and the details of these studies will be reported elsewhere¹⁶.

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