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Chromatographic Fractionation of Polymers:* The Effect of Column Length

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Abstract

Two amorphous polymers, polystyrene and polyisobutene, have been fractionated in an attempt to optimize performance in column fractionation of polymers. We have studied the elution of the polymer from the glass beads on which the polymer is initially coated prior to passage through the column, and also varied the column length, i.e., the depth of the bed of uncoated glass beads in the column. The results that great care must be taken in this initial coating step, and that the length of column through which the polymer is eluted after this step is not of significant importance in achieving sharp fractions.

INTRODUCTION

A previous investigation (*1*) of the effect of temperature and temperature gradient on the chromatographic fractionation of polyisobutene led to the

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* Part XXIX of a series on Column Fractionation of Polymers.

conclusions that the lower temperature led to better fractionation, and the effect of a temperature gradient in the column did not produce a significant effect. These results were obtained when the polymer was selectively deposited on the beads (high molecular weight precipitated first). A similar study (*2*) dealing with the column fractionation of polystyrene produced the same conclusion for molecular weights below 6×10^5. The polymer was not selectively deposited for these experiments nor were molecular weight distributions (MWD) of the fractions determined by gel permeation chromatography (GPC). These authors concluded that fractionation was simply the elution of polymer off the support without precipitation. In one case where the polymer loaded onto the support was reduced to 1/5 of the usual amount, the polymer eluted according to phase equilibrium conditions of the Schulz theory (*3*). At the concentration used in all other experiments, 1 g of polymer/100 g of beads, the polymer eluted before the equilibrium composition of the solvent was reached. It was not experimentally determined which fractionation, the normal or low polymer loading, gave fractions with the narrowest MWD although the distributions for the original polymer calculated from the fractionations were similar.

Another recent study (*4*) deals with the effect of coating the polymer onto the beads and how it is loaded into the columns. This involved the separation of beads which had been selectively coated and packing these, which were covered with different molecular weight materials, in various ways into the fractionating column. The method which appeared to separate most effectively, followed by GPC, was when 80% of the column was filled with uncoated support and the polymer-coated support was separated into four molecular weight ranges. The lowest molecular weight material was on top of the uncoated support and so on to the support coated with the highest molecular weight material at the top of the column. Another interesting feature was that the narrowest MWD fractions were obtained where the maximum concentration of polymer was in the original distribution.

The purpose of the present work was to investigate the amount of fractionation occuring in the initial process of eluting the polymer from the coated beads and the amount which is produced by passing through the chromatographic column. If only elution off the beads without reprecipitation is involved, then clearly putting in uncoated beads has no value. The previous discussion shows the experimental evidence dealing with this to be contradictory.

EXPERIMENTAL

Polyisobutene Fractionation

A portion of the coated beads from the previous study (*1*) was packed into the short section of column as previously described and eluted at 0.25 ml/min at 30°C with methyl ethyl ketone to which was added benzene at 0.25 ml/min with mixing. Flow was in an upward direction, and the eluant was collected for 3 hr. These fractions were then dried and characterized by GPC using the columns and calibration curves as before (*1*). These results are referred to as the good coating study. Additionally, the same amount of polymer was coated to the same amount of glass beads by dissolving the polymer in 200 ml of chloroform and evaporating to dryness slowly with intermittent stirring. The polymer was eluted from these beads under identical conditions to the previous experiment, and this is termed the poor coating method. Calculations of the molecular weight averages and the distributions were performed with a computer program (*5*) which did not correct for band broadening.

Polystyrene Fractionation

For these experiments a glass column 60 cm × 4 cm ID was used fitted with a porous glass frit at the bottom. Fractionation was carried out by stepwise addition of a solvent gradient at the top of the column. A 25.6-g sample of commercial polystyrene was precipitated onto the glass beads (Superbrite #130), 2560 g, by dissolution in benzene which was slowly evaporated with stirring. Table 1 shows the columns and experimental conditions for three fractionations designated 1B, 2B, and 3B. An additional fractionation designated 1A was performed using beads which were coated in an exactly similar manner to the main lot. The fractions were analyzed by GPC using three columns 4 ft × 3/8 in. OD packed with Corning porous glasses. The separating range was found to be 10^4 to 2×10^6 for polystyrenes in tetrahydrofuran. The original polymer peak had a maximum concentration corresponding to 2.0×10^5.

RESULTS AND DISCUSSION

Polyisobutene Fractionation

The results of the cumulative percent polymer eluted versus the fraction number (approximately 45 ml) are plotted in Fig. 1. There is quite a

TABLE 1

Fractionation Conditions for Polystyrene Fractionations

Code	Non-solvent	Solvent gradient	Average flow rate (ml/min)	Amount of uncoated beads on top of column (cc)	Amount of coated beads (g)	Amount of uncoated beads below coated beads (cc)
1B	Methanol	Methyl ethyl ketone, 0 to 100% in 6% increments	20.0	125	129.2	400
1A	Methanol	Methyl ethyl ketone, 0 to 100% in 6% increments		125	129.2	200
2B	Methanol	Benzene, 0 to 100% in 6% increments		125	129.2	400
3B	Methanol	Methyl ethyl ketone, 66 to 100% in 13 steps	40.0	125	129.2	0

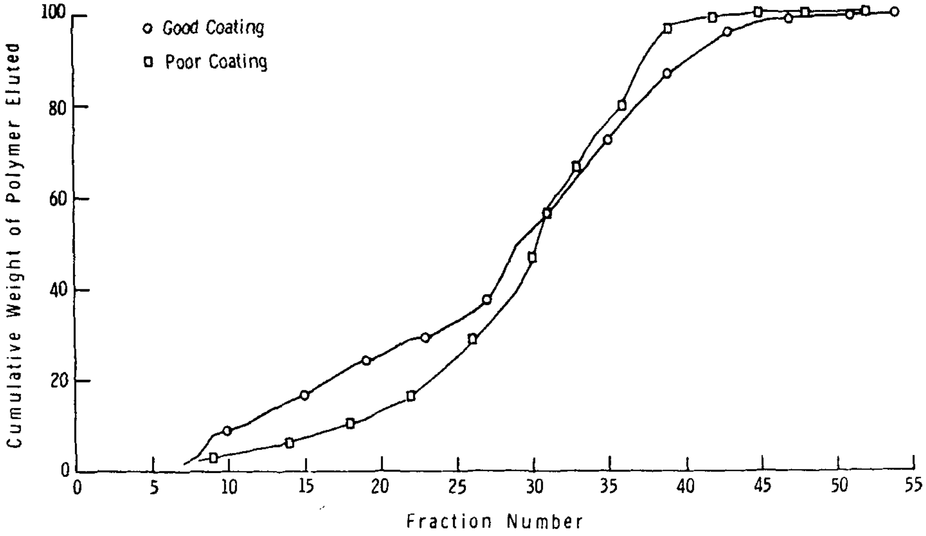

FIG. 1. Elution of polybutene LMMS from glass beads using a solvent gradient at 30°C.

drastic difference in the way the polymer is eluted. In the poor coating experiment, the polymer is not spread out over such a range of elution volume as in the good coating experiment. This is consistent with there being a considerable amount of fractionation, the highest molecular weights being deposited first in the good coating method. The lowest molecular weight material is coated on last and is thus readily available for elution, which is the required order for column fractionation. It appears that insufficient fractionation has taken place in the poor coating or that the polymer is not coated on the beads in thin layers but may be in clumps of considerable size in-between the glass beads. The smaller molecules are unable to diffuse out of the swollen gel and are thus retarded in elution compared with the good coating experiment.

A completely different behavior is noticed when the polydispersity, $\bar{M}_w/\bar{M}_n$, is plotted against weight-average molecular weight $\bar{M}_w$ (Fig. 2). The fractions obtained with good coated beads and the use of a column (120 cm × 3.7 cm i.d.) exhibit a minimum in the value of polydispersity at a value of 60,000 molecular weight, $\bar{M}_w$. For the good coated beads with no column, the polydispersities of the fractions are more constant with increasing molecular weight. The poor coated beads give poorer fractionations expressed in terms of polydispersity of the fractions. In the poor coating experiments it appeared that some backlash had occurred at the

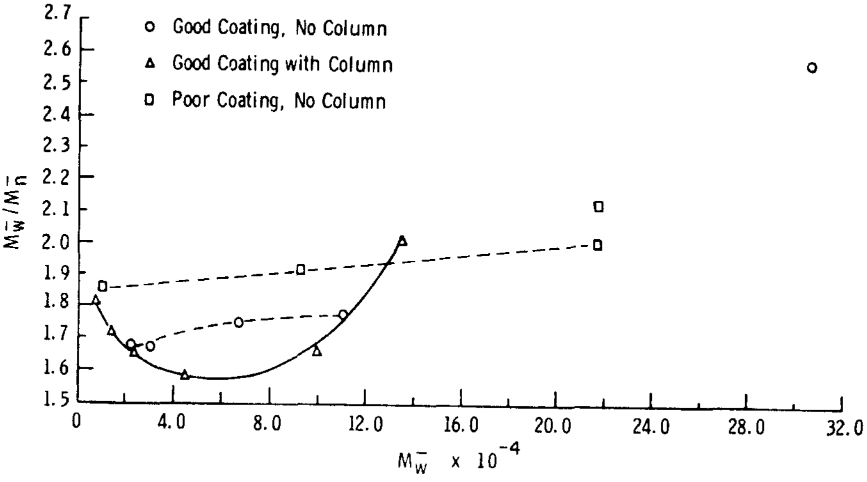

FIG. 2. Plot of polydispersity, $\bar{M}_w/\bar{M}_n$, of fractions from various polyisobutene fractionations vs weight-average molecular weight $\bar{M}_w$.

highest molecular weights. The important feature of this plot is that the polydispersity of the fractions from the good coated beads are approximately the same whether a column is used or not. It appears then that the critical part of the fractionations is in the initial elution from the coated beads and not the passage through the column afterward. Indeed, any further fractionation occurring in the column may be cancelled out by the dispersion associated with flow through a packed column, as experienced, for example, in GPC.

Polystyrene Fractionations

The molecular weight analyses are summarized in Table 2 for the four fractionations made. The molecular weight corresponding to the point of maximum concentration in the chromatogram is recorded together with

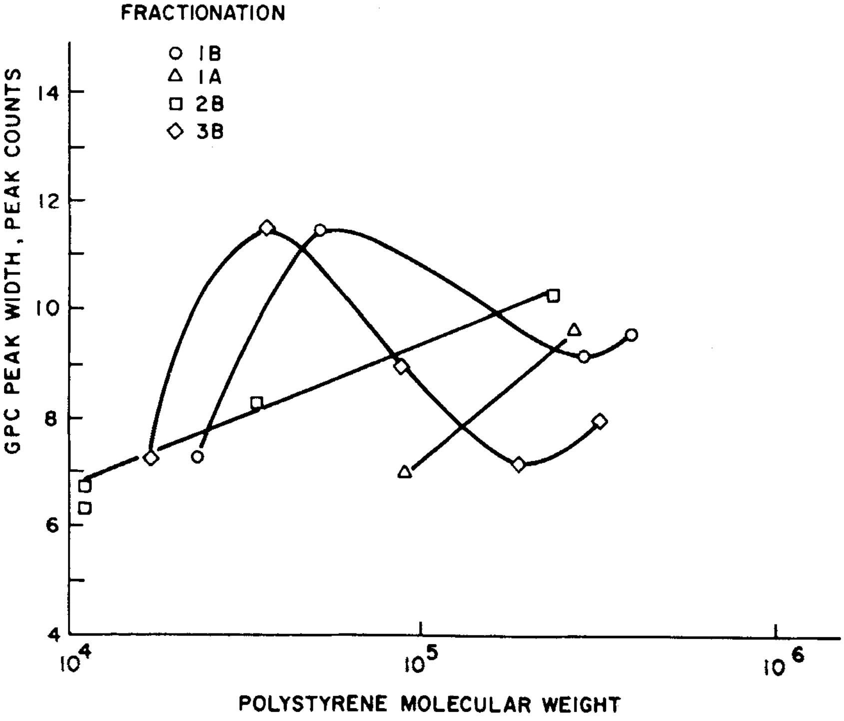

FIG. 3. Plot of GPC peak width of polystyrene fractions from various fractionations against weight-average molecular weight $\bar{M}_w$.

TABLE 2

Summary of Fractionation Data for Polystyrene Fractionations

Fractionation	Fraction No.	Molecular weight at peak maximum $\times 10^{-4}$	Peak width at the base (peak counts)
1B	15	2.3	7.34
	16	5.1	11.42
	17	10.0	—
	18	29.0	9.10
	19	39.0	9.54
1A	14	4.0	—
	15	9.0	6.96
	16	27.0	9.57
	17	25.0 (backlash)	10.74
2B	12	1.1	6.32
	13	1.1	6.75
	14	3.4	8.22
	16	13.0	—
	17	24.0	10.19
	18	17.0 (backlash)	12.18
	19	20.0 (backlash)	12.17
3B	3	1.7	7.26
	4	3.6	11.53
	5	8.8	8.94
	6	19.0	7.13
	7	32.0	7.97
	8	20.0 (backlash)	11.53

the width of the chromatogram measured at the base. The narrower the peak width, the better is the fractionation efficiency. This data is plotted in Fig. 3. The data where backlash occurred, noted in Table 2, are not plotted. The other points for a given fractionation are connected by lines for convenience and have little significance. From Fig. 3 the following general features are apparent. No particular fractionation appeared to be more successful overall than the others. Fractionations 2B and 1B, which both had 400 cc of uncoated beads below the coated beads, differed only in the identity of the good solvent benzene versus methyl ethyl ketone. The fractionation using benzene did not produce fractions with exceptionally wide peak widths in the molecular weight range 3.5×10^4 as did the methyl ethyl ketone. Limited data from Run 1A, with only 200 cc of uncoated beads below the coated beads and methyl ethyl ketone as the good solvent, suggest that a better fractionation was obtained. Fractionation 3B, which had only coated beads present and also an improved choice of solvent gradient, showed performance equivalent to the other fractionations and produced the narrowest MWD fractions at higher molecular weights.

CONCLUSIONS

For both of the amorphous polymers used in this study we have not found any dramatic effect of the bed depth in a fractionation column. We concur with others that, as normally carried out, column fractionation is simply elution from the originally coated beads. Future work in the area of polymer fractionation, particularly large-scale separations, should be directed toward the coating procedure.

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