LETTERS TO THE EDITORS

Chromatographic Fractionation of High Molecular Weight Polystyrenes

The recent paper of Pepper and Rutherford[1] on the conditions for large-scale chromatographic fractionation of low to moderate molecular weight polystyrenes properly stresses the concentration of the polymer in the eluant as the most important single factor governing the success of fractionation. The results presented in this note display the operation of this principle in the fractionation of high molecular weight polystyrenes. Furthermore, these results give a more definite picture of the decrease in the maximum permissible concentration of polymer with increasing molecular weight suggested by some of the results in the above paper.

The chromatographic system used in our experiments and the determination of molecular weights by single-point viscosity analyses have been described previously.[2,3] In all fractionations ethyl alcohol was used as the nonsolvent and methyl ethyl ketone as the solvent. In conformity with the criterion used by Pepper and Rutherford, fractionation was considered successful if the molecular weight of successive fractions increased in a regular manner. Table I lists our results on five polystyrene samples whose viscosity-average molecular weights, M_v, are given in column 2. The third and fourth columns list the molecular weight, M_{max}, and concentration in the eluant, C_{max}, of the fraction of maximum size. These results are from successful fractionations in all cases except for sample 3, where resolution ceased at about 75% of the sample weight. From the trend of C_{max} with molecular weight, it is expected that complete fractionation would be obtained in sample 3 by decreasing C_{max} by 20 to 30% by using a smaller sample or larger mixing vessel. In this respect there is a difference in behavior with increasing molecular weight. In the high molecular weight polymers resolution ceases abruptly a few fractions beyond the fraction of maximum size if C_{max} is excessive, while in the lower molecular weight polymers an excess ratio of polymer to eluant usually results in successive fractions having a lower molecular weight than under proper conditions, but the differences between fractions may continue to 90% or more of the sample. With regard to the accuracy of C_{max}, it should be stated that the conditions of fractionation were arrived at by an arbitrary decrease in the sample size for a given eluant volume. Therefore, the maximum permissible concentration may be somewhat greater than the reported values of C_{max}. In any case, the strong dependence of C_{max} on molecular weight is clearly shown in Table I.

Flory[4] has suggested that the maximum concentration for efficient fractionation should be proportional to $M^{-1/2}$ which derives from the molecular weight dependence of the critical concentration for phase separation in polymer solvent systems. The constancy of the product $C_{max}M_{max}^{1/2}$ in the next to the last column is consistent with this suggestion although such a comparison cannot be quantitative considering the looseness with which C_{max} was determined. In the last column we show the mixing vessel size, V, required for

TABLE I
Conditions for the Fractionation of High Molecular Weight Polystyrenes

Sample[a]	$M_v \times 10^{-6}$	$M_{max} \times 10^{-6}$	C_{max}, %	$C_{max}M_{max}^{1/2} \times 10^{-2}$	V, cc.
1	0.30	0.59	0.45	3.4	220
2	0.50	0.94	0.38	3.7	250
3	0.87	1.63	0.28	3.6	500
4	3.8	5.70	0.10	2.5	2000
5	5.0	7.60	0.11	2.9	2000

[a] Description of polystyrene samples: 1 and 2 are commercial Styron samples; 3 is one of a set of fractions obtained from the Dow Chemical Company; 4 and 5 were obtained at different times from a quantity of inhibited styrene that polymerized during prolonged storage.

the fractionation of a 0.4-g. sample of polymer with 100% methyl ethyl ketone in the reservoir. The fractionations of samples 4 and 5 were actually carried out on 0.2-g. samples, using a 500-cc. mixing vessel and 90-10 mixture of methyl ethyl ketone–ethyl alcohol in the reservoir, but the comparison of mixing vessel sizes given here serves to emphasize the large volumes required in the fractionation of the very high molecular weight polymers.

One consequence of the foregoing remarks deserves emphasis. The eluant volume required for successful fractionation will depend on the molecular weight distribution as well as on the average molecular weight of the sample, since a sample of narrow distribution will require a larger elution volume to maintain a sufficiently low value for C_{max}.

A discussion of other factors which affect fractionation and further details of the above determinations will be presented in a later paper dealing with a comparison of chromatographic and elution fractionation.

References

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