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# Polymer Fractionation by Column Methods

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► The principal factors which control the fractionation of polymers by the elution and thermal gradient methods are discussed. Applications of both methods to estimations of molecular weight distributions in a variety of polymers are mentioned, including polystyrene, poly(methyl methacrylate), polyolefins, polyesters, and polypeptides. Basic differences are noted between batch and column methods.

**A**UTOMATIC methods of polymer fractionation have long been sought for making the determination of molecular weight distributions a direct and more accessible task. The method of Desreux (2), in which the polymer sample was dispersed on a finely divided support and extracted in a column using a single solvent at successively higher temperatures, may be considered the forerunner of two column methods in current use for polymer fractionation. The first of these, a direct descendent of Desreux's procedure, is the elution method as modified by Francis, Cooke, and Elliott (5) for the fractionation of polyethylene. In this method the polymer is precipitated rather than dried on the support and extraction is carried out at a single temperature, using solvent-nonsolvent mixtures of increasing solvent power, a procedure which admits of somewhat greater flexibility and control than varying the temperature of extraction. This method has been widely used in the fractionation of

polyethylene (5, 8, 10) as well as isotactic and atactic polypropylene (20). It has given remarkably good results, especially when viewed in the original but erroneous context of depending only on the selectivity of the extraction step.

The second method is the thermal gradient (chromatographic) method, devised by Baker and Williams (1) as a means of bringing a multistage fractional extraction and precipitation process to the column. As the title used here implies, the key feature of this method is a thermal gradient maintained in the column by a metal jacket which is heated at the top and cooled at the bottom. The purpose of the thermal gradient is to bring about a selective precipitation from the polymer fractions as they flow down the column into cooler zones. This precipitated polymer is later re-extracted by further enriched solvent fed to the column by a mixing vessel-reservoir system. In this way, each fraction may be assumed to undergo a repeated sequence of fractional extraction and precipitation steps during its course down the column. The method has been used successfully on a variety of amorphous polymers including polystyrene (1, 9, 13, 18), poly(methyl methacrylate) (21), polyisobutylene (12), and atactic poly( $\alpha$ -olefins) (9) as well as for polyesters and polypeptides (14), and in one laboratory is used in the routine fractionation of polyethylene (6).

The main purpose of this paper is to call attention to some of the principal

factors which appear to control the fractionation. In addition, some basic differences between the column and batch methods of fractionation are briefly indicated, as well as some unsolved problems in the operation of these columns. A previous review (7) and the original papers should be consulted for material not included here, especially the operation and construction of the columns and the conditions of fractionation for individual polymers.

## ELUTION METHOD

Both the column designed by Francis and coworkers and the method of operation have been adopted by later workers with little modification. Two exceptions are worth noting. Recently, a column which employs upward solvent flow has been described by Shyluk (20). This system offers better control over the flow rate, while reducing channeling in the column. The second important modification is the procedure employed by Henry (8) for scaling up the fractionation from 2- to 50-gram polyethylene samples by using Celite rather than sand as a support to circumvent an unmanageable increase in column size. The advantage of Celite, in addition to its greater surface area, arises from the fact that it is light enough to disperse readily. This makes it possible to stir a large volume of polymer solution with the Celite during the cooling step which precipitates the polymer on the support.

The precipitation rather than the

drying of the polymer on the support has proved to be an important factor in the fractionation. For crystalline polymers which are insoluble at room temperature, this is carried out by the simple expedient of pouring the polymer solution onto the heated column and, after the solution has wet the support, permitting the column to cool to room temperature. It was first pointed out by Kenyon and Salyer (10) that a preliminary fractionation would be expected as the column temperature decreased and this might result in a crude arrangement according to molecular weight of the precipitated polymer on the support. They found that satisfactory results were obtained from a precipitated polyethylene sample, whereas, under the same conditions, very poor fractionation resulted with a sample dried on the support. This indicated that the selective deposition of the polymer on the support, occurring in the initial precipitation step, made an important contribution to the fractionation. Further studies (20) of the role of selective deposition, using an atactic polypropylene sample, have clearly shown that failure of the fractionation without selective deposition is due to the slow rate of diffusion of the soluble polymer through the swollen sample.

These results focus attention on the control of the precipitation step. For crystalline polymers precipitation should be carried out under conditions which ensure the separation of an amorphous rather than a crystalline phase (3). In this respect it is interesting that the selective deposition of polyethylene is usually carried out in xylene, although the equilibrium phase diagram exhibits only a crystalline solid phase in this solvent (15). Presumably, the success of the fractionation in this solvent is due to the fact that the polymer droplets which separate are initially liquid. But it would still seem worthwhile to try precipitation from a solvent such as amyl acetate, in which the precipitated phase has been shown to be amorphous (15). In addition to the above requirement, the rate of cooling should be slow and precipitation should be carried out from dilute solution and at lower concentrations for higher molecular weight polymers. Since implementation of the last condition is limited by the volume of the column, it may be useful to point out that an isotactic polypropylene sample,  $M_w = 1 \times 10^6$ , could be fractionated when precipitated from a 1% solution by increasing the time for the cooling step from 1 to 6 hours (20).

In the extraction step, the principal requirement is that the column temperature be above the crystalline melting point of the polymer in the solvent system used for extraction. This does

not preclude the fractionation of all polymers with very high melting points, since in a suitable solvent some of these undergo a sufficient depression in melting point to bring the fractionation temperature into a usable range (4). With polyethylene, Francis and co-workers found that satisfactory fractionation could be effected over a wide temperature range. However, Shyluk found that with the high molecular weight polypropylene sample mentioned above, there was only a narrow temperature range, 8° C., consistent with acceptable fractionation. At the lower temperatures crystallization appeared to interfere, while at higher temperatures, the polymer swelled to such an extent that it flowed off the column without being fractionated; an occurrence to which reference will be made later.

The other elution conditions should be adjusted according to the molecular weight of the sample. For higher molecular weight polymers, the flow rate must be slower, the increments in solvent concentration smaller, and the eluting volumes larger, to secure proper fractionation.

#### THERMAL GRADIENT METHOD

A critical step in this method, and the primary one that differentiates it from the elution method, is the reprecipitation of polymer as it flows down the column into the cooler zones. Although Baker and Williams assumed that the thermal gradient was highly efficient, Hall (7) has questioned the effectiveness of the precipitation stages of the column. A more recent examination of this problem has been made (18) by comparing the fractionation of two high molecular weight polystyrene samples with and without a thermal gradient. The molecular weights of the final fractions from the thermal gradient column were about 50% higher than those from the elution column. This is reassuring evidence of the effectiveness of the thermal gradient. However, this study left important questions unanswered, including an explanation of the unusual degree of fractionation observed, under certain conditions, with the single temperature column. At least three versions of the thermal gradient column, differing in important respects from the original, have been described (9, 16, 21).

Since no preliminary fractionation of the sample is attempted in this method—that is, the polymer is dried rather than precipitated on the support—it might be expected that the success of the fractionation will be more sensitive to conditions than in the elution method. Pepper and Rutherford (13) have pointed out that the most important

single factor controlling the success of the fractionation is the concentration of the polymer in the fractions eluted from the column as represented by the concentration of the maximum size fraction. This conclusion was supported by the results of a study of the fractionation of high molecular weight polystyrene samples covering a tenfold range of molecular weights (17). Moreover, in this work the highest concentration of eluted polymer, consistent with satisfactory fractionation, depended strongly on the molecular weight of the largest fraction, varying inversely as  $M^{1/2}$ .

The concentration of polymer in the fractions can be decreased to the required level by providing a larger eluting volume to cover the range of solvent concentration over which the sample is eluted. With the closed mixing vessel-reservoir system commonly used with this method, this can be accomplished either by increasing the mixing vessel size or reducing the concentration of solvent in the reservoir. In one study (18) it was shown that the response of the fractionation pattern to such adjustments in the solvent gradient is in qualitative accord with prediction. A further point of interest from this work is the pronounced increase in the molecular weight of the highest fraction of a polystyrene sample, from  $1.3 \times 10^6$  to  $2.0 \times 10^6$ , that was obtained with the more extended solvent gradients.

Although these results furnish an empirical basis for the selection of proper fractionation conditions, it cannot be claimed that the factors which control the fractionation are completely understood. Thus, while many of the runs in which there is a regression of molecular weight in the terminal fractions can be improved by lowering the concentration of the fractions, this does not prove to be an effective remedy in all cases. The nearly critical dependence on the concentration of eluted polymer over a small (twofold) range of concentration has no counterpart in batch fractionation and remains a puzzling factor. Finally, the efficiency of the fractionation may depend on the specific solvent used in the fractionation (19). For polystyrene, conditions which gave acceptable fractionation using methyl ethyl ketone (2-butanone) gave poor fractionation with benzene.

#### DIFFERENCES BETWEEN BATCH AND COLUMN METHODS

The most important difference between batch and column methods is the requirement that the polymer remain in place on the support and not flow with the solvent. Since the sample swells continuously during the fractionation, as the solvent power of the eluent increases, any adverse effects of sample

mobility would be most pronounced in the terminal fractions of a run or in the fractionation of high molecular weight polymers. The difficulties experienced in the fractionation of polypropylene, mentioned earlier, as well as reported difficulties with higher molecular weight poly(methyl methacrylate) samples (21), indicate that polymer mobility may sometimes be a critical problem. On the basis of these considerations and the observation that the polystyrene precipitate is 60% more swollen in benzene than in methyl ethyl ketone (19), it appears that the difference in efficiency of these two solvents may arise from the greater swelling and, therefore, greater mobility of the polymer in benzene. This interpretation, if correct, indicates the desirability of using poor solvents to limit the swelling of the sample.

A second difference from batch methods is due to the possible adsorption of polymer on the support. The occurrence of a reversible adsorption of polystyrene on sand has been shown by its effect on the solubility of the polymer (11), but it is not certain what role this might play in the fractionation. On Celite there was a pronounced irreversible adsorption of the higher molecular weight portion of the same sample. This would appear to rule out the use of Celite for small samples, except in special cases such as that described by McLeod and Hulme (12), where the sample was deposited on Celite to eliminate plugging of the column with rubbery polymers such as polyisobutylene, the remainder of the column being filled with the usual 0.1-mm.-diameter glass beads. However, even in this case it was necessary to pre-treat the Celite with a high molecular weight sample to minimize adsorption of the sample being analyzed.

## CONCLUSIONS

The column methods of fractionation have proved their value for the routine fractionation of a variety of polymers, giving sufficient detail, in many cases, to permit an estimation of the molecular weight distribution curve. Although it is not certain that all polymers which yield to batch fractionation can be handled equally well on a column, the increasing variety of polymers that are being fractionated in this way suggests that the column methods are applicable to most samples of moderate molecular weight and polydispersity. However, it must be admitted that unsolved difficulties persist in the fractionation of polymers of very narrow molecular weight distribution or of very high molecular weight or in attempting to define the terminal portion of the sample (above 95% cumulative weight). In regard to the thermal gradient method, the efficiency of the thermal gradient needs to be evaluated more critically and it would be useful to have a careful comparison of the results from this method with those from the elution method employing selective deposition. With regard to the latter method, it is important to determine whether selective deposition is equally effective with amorphous polymers and, in particular, to learn whether Henry's method of scaling up the fractionation using Celite offers a general approach to preparative scale fractionation on a column. In any case, to take full advantage of these methods requires a more complete understanding of the processes that control fractionation. This, in turn, depends on a more basic and varied approach which goes beyond the goal of finding a single set of conditions which give acceptable fractionation for a particular sample.

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