Polymer Fractionation by Repeated Extraction

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Synopsis

All current fractionation techniques—based on sol–gel equilibria—are characterized by a variation of the solvent power after each fractionation step in a discontinuous as well as in a continuous way. Overlapping of consecutive fractions is the consequence of this procedure. It can be shown that this overlapping can be diminished essentially by a multistage technique based on *complete* extraction at a given solvent power which then will be changed in discontinuous steps. As a further consequence, it is possible to obtain very homogeneous fractions of $\bar{M}_w/\bar{M}_n < 1.03$. A theoretical analysis of this technique on the basis of phase equilibrium data will be given, the results of which can be confirmed experimentally.

INTRODUCTION

The solubility of polymers in a binary solvent–nonsolvent mixture is known to be a function of the molecular weight M, the composition of the mixture γ, and of the temperature T.

Usually, turbidimetric titration[1] is used to obtain the so-called precipitation curve:

$$\gamma^* = f\,(\ln c),\ T = \text{constant},\ M = \text{constant}$$

In this connection, the term "solubility" is absolutely correct, because phase separation is the result of supersaturation above the equilibrium concentration c^*, related definitely to a given solvent power (γ, T). This has been proved experimentally.[2–4] (1) For certain values of γ and T, the polymer concentration c^* in the solution phase ("sol") and the composition of the precipitated phase ("gel") are independent of the total amount of polymer in the initial solution.[2,3] (2) The amount of polymer in the gel, determined experimentally, has been shown to be equal to the amount calculated from the precipitation curve.[3,4]

Thus, we can say the equilibrium sol–gel is an equilibrium between a dilute but saturated solution and a precipitated phase. The precipitation curve is the equilibrium curve of this two-phase system, assuming that the polymer is monodisperse (quasi-monodisperse[3]). The equilibrium conditions for phase separation in a polydisperse system can be shown[5] using the Claesson diagram,[6] where the equilibrium concentration c_i^* for each mono-

disperse species i is plotted against the molecular weight M_i. For a given solvent power (γ, T), the line connecting the saturation concentrations c^* of all polymer species M_i is called solubility line, sl.

The equilibrium can be established from both sides (Fig. 1):

1. Initially the whole polymer is in solution. Phase separation will be caused by lowering the solvent power from sl_3 to sl_2 (by adding nonsolvent and/or by lowering the temperature). Thus, part A of the initial polydisperse sample will precipitate and part B will remain in solution (precipitation fractionation).

2. Initially the whole polymer is precipitated. By increasing the solvent power from sl_1 to sl_2 (by adding solvent and/or by increasing the temperature), part B will be dissolved and part A will remain precipitated (solution fractionation).
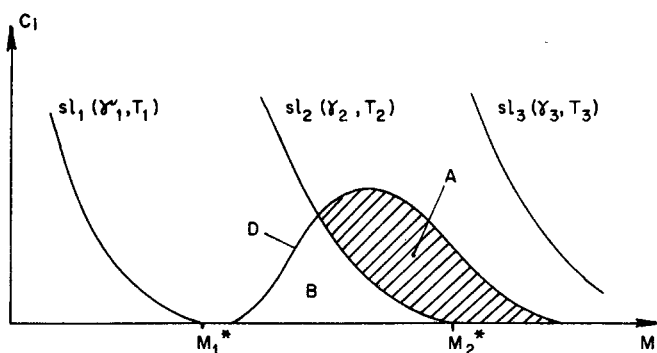

Fig. 1. Schematic Claesson diagram showing the principle of precipitation and solution fractionation: sl, solubility line; D, distribution curve of the polymer sample. Part A of the polymer sample (shaded area) is precipitated and part B is in solution.

There are, of course, some problems concerning the application of this scheme for the quantitative description of fractionation processes. This has been discussed in detail elsewhere.[5] Especially for the process described here, it is only interesting to know whether the solubility lines (γ, T) in the Claesson diagram have a point of intersection with the abscissa M, called M^*, or are approaching the abscissa asymptotically. This problem has already been discussed by Giesekus.[7]

Assuming the molecular weight M^* does exist, the polymer molecules can be divided into two parts: (1) Molecules $M_i < M^*$, which will be principally soluble; the amount of polymer which is soluble is given by the solubility line (γ, T). (2) Molecules $M_i > M^*$, which will be principally insoluble for the conditions (γ, T) given.

In the case of solution fractionation, a repeated solution with constant solvent power would then lead to the complete dissolution of all molecules $M_i < M^*$, whereas all species $M_i > M^*$ would remain precipitated. According to this mechanism, vertical cuts through the initial sample would be possible, so that very sharp rectangular fractions could be prepared. In

this paper, a new fractionation procedure based on this principle shall be outlined and discussed in comparison with initial experimental results.

THEORY OF EXTRACTION PROCESS

Principles

The extraction process can be considered as a development of the usual solution fractionation. This will be discussed using the Claesson diagram (Fig. 2). The initial polymer sample is precipitated on glass beads packed into a column which has a temperature T_1. The free volume between the
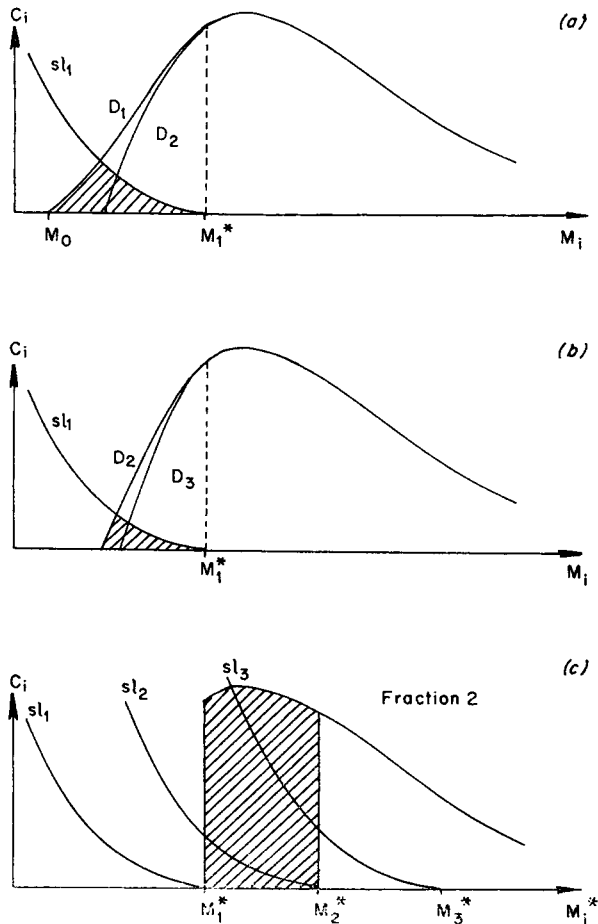

Fig. 2. Principle of the extraction process: sl, solubility line; M^*, critical molecular weight; D, distribution curve of the polymer sample;   (a) and (b), extraction of the first fraction;   solvent power of the solvent is represented by the solubility line sl_1;   (c), distribution of the second fraction (shaded area), which is extracted by a solvent whose solvent power is represented by the solubility line sl_2.

glass beads is filled up by solvent* of the composition γ_1, whose solvent power is represented by the solubility line sl_1. When equilibrium is established, the amount of polymer corresponding to the shaded triangle (Fig. 2a) will be dissolved by the solvent γ_1 and the eluate (solvent and polymer) will then leave the column as a saturated solution. The distribution curve of the polymer sample is being altered by this process: distribution 1 → distribution 2. Then, another volume of solvent will be filled into the column. But in contrast to the usual solution fractionation—where the second solution step is performed by a solvent of higher solvent power— the solvent has the same composition and temperature as the former one, so that sl_1 and M_1* remain constant. The amount of polymer dissolved in this second step is represented by the shaded triangle in Figure 2b. The addition of fresh solvent of constant solvent power will be repeated until all polymer will be dissolved. When the eluate of all solution steps will be combined, this fraction will contain all polymer molecules ranging from M_0 to M_1*.

Only then will the solvent power of the solvent be increased by a small step $\Delta\gamma$ or ΔT, so that the solvent power now is given by a solubility line sl_2 (Fig. 2c). Thus, also a new value M_2* is fixed. The extraction will be repeated at a constant solvent power sl_2 until all molecules $M_i < M_2*$ will be dissolved. The combination of all the eluate corresponding to sl_2 will give a polymer fraction which contains all molecules between M_1* and M_2*.

The following fractions, M_2*–M_3*, M_3*–M_4*, etc., can be obtained by changing the solvent power step by step from sl_2 to sl_3, from sl_3 to sl_4, etc. and extracting to zero concentration as described above.

The stepwise discontinuous dissolution of the polymer sample leads itself well to describe the principle of the extraction process. In practice, however, the *discontinuous* process can be replaced by a *continuous* flow of solvent through the column.

Characteristics of the Process

The Elution Curve

The curve which shows the variation of the eluate concentration c_p as a function of the step numbers s is called elution curve. One step of dissolution is represented by a volume of solvent corresponding to the free volume between the glass beads in the column. The elution curve of the extraction of fraction 2 in Figure 2 (ranging from M_1* to M_2*) is shown in Figure 3. Figure 4 gives a schematic representation of the extraction process of this fraction in the Claesson diagram.

The eluate concentration c_p of the first steps is constant (see Fig. 3) and the amount of polymer dissolved in these steps is represented by the shaded area UVW (see Fig. 4). When the partial concentration of M_1* of the precipitated polymer sample will become smaller than its equilibrium con-

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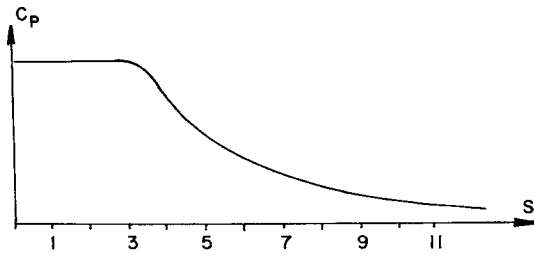* In the following, the term "solvent" will also be used for binary solvent–nonsolvent mixtures.

Fig. 3. Elution curve of the second fraction (see Fig. 2) (schematic picture): c_p, eluate concentration; s, step number.
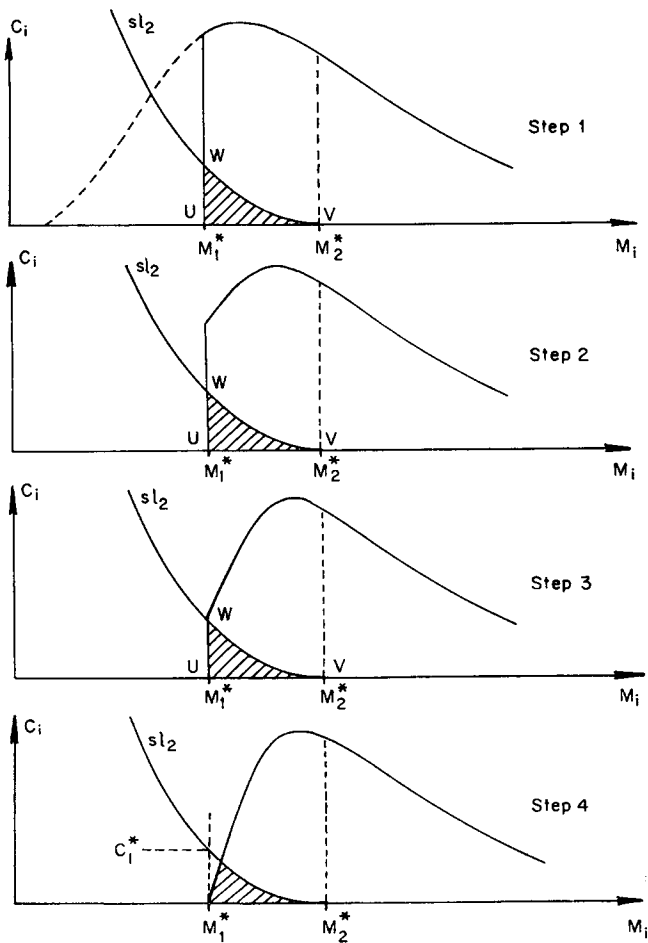

Fig. 4. Scheme of extraction process of second fraction: c_1^*, saturation concentration of M_1^* in a solvent with the solvent power corresponding to sl_2.

centration $c_1{}^*$, the eluate concentration c_p will decrease from extraction step to extraction step, and at the end of the process, c_p will essentially go to zero.

Molecular Weight Distribution of the Fractions

Neglecting the first and the last fractions, all intermediate fractions obtained by this extraction procedure should (1) be rectangular, and (2) not overlap each other.

Point (1) is important in obtaining fractions of very low polydispersity. The $\bar{M}_w/\bar{M}_n$ values of such rectangular fractions can be easily calculated. In Figure 5, some of these $\bar{M}_w/\bar{M}_n$ values are plotted against the average molecular weight $\bar{M}_w$ for selected ranges ΔM of the fractions.

Point (2) is important for the determination of distribution functions by fractionation, for all other fractionation procedures are characterized by a considerable overlapping of the fractions.[5,8—10]
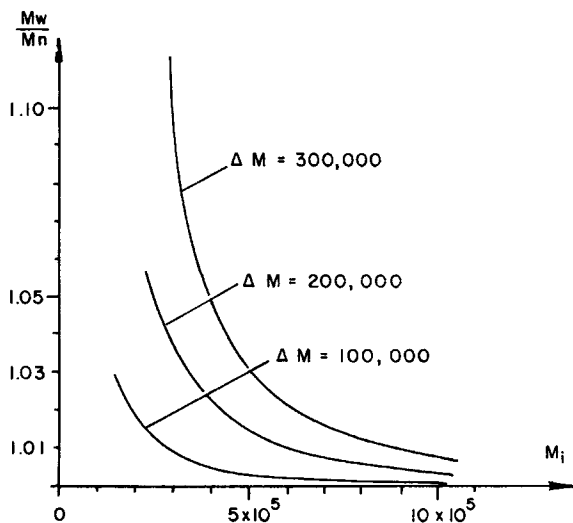

Fig. 5. Some calculated values $\bar{M}_w/\bar{M}_n$ for rectangular fractions, depending on the range ΔM of the fractions and their weight-average $\bar{M}_w$.

EXPERIMENTAL

Apparatus

The apparatus is shown in Figure 6. The essential part of the apparatus is the extraction column (1). The column used is a glass tube with a length of 530 mm and an internal diameter of 30 mm. Near the bottom of the column is a sintered-glass disc No. G2 (2). The column is packed with glass beads (3) of 0.1–0.15 mm diameter and a height of up to 350 mm. The free volume between the glass beads is 100 ml, therefore a solvent volume of 100 ml passing down the column is called one step. The polymer sample to be fractionated is placed on the glass beads. The space (4) over

the glass beads is provided for temperature conditioning of the solvent flowing at ambient temperature into the column. The column is temperature-controlled by a thermostat (5), and its temperature is measured with a thermometer (6). The whole column is insulated with asbestos string. The vessel (7) over the column contains the solvent, which is passing down
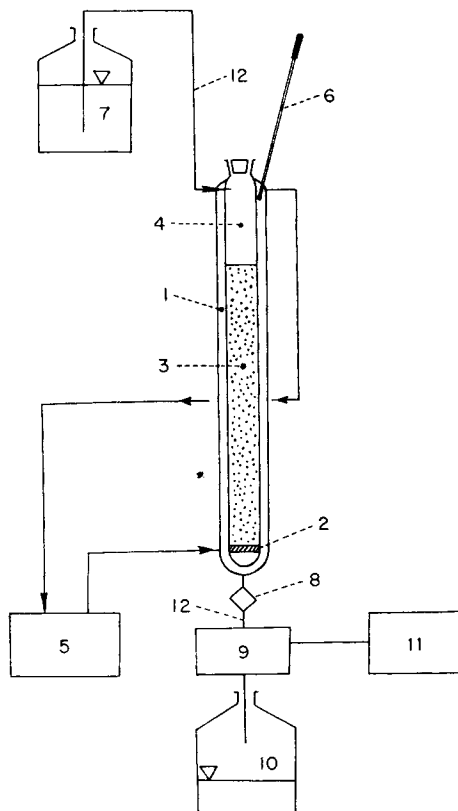

Fig. 6. Apparatus: (1) column; (2) sintered-glass disc; (3) glass beads; (4) space for temperature conditioning of the solvent; (5) thermostat; (6) thermometer; (7) vessel; (8) valve; (9) absorptiometer; (10) vessel; (11) recorder; (12) polyethylene hoses.

the column by force of gravity. The flow rate of the solvent through the column is regulated by a valve (8). When passing down the column, the solvent is dissolving part of the polymer placed on the glass beads. The solution passing out from the column is controlled by an ultraviolet absorptiometer (9) ($\lambda = 2537$ Å), with which polymer concentrations as low as $10^{-4}\%$ are detectable.

Materials

Butyl acetate and n-propanol were used as solvent and nonsolvent, respectively. Both were purified by rectification. For the experiments

described here, a "solvent" of constant 70/30% composition (γ = 0.3) was used.

The polymer samples were the industrial polystyrene PS VI (supplied by BASF) and f3 obtained by fractional precipitation of PS VI. They were purified by reprecipitation from concentrated benzene solution into a tenfold volume of methanol under constant stirring. The fibrously precipitating polymer was separated by filtering and then drying at 50°C under vacuum. High-speed membrane osmometry and sedimentation analysis by ultracentrifugation were used[11] to obtain average molecular weights and molecular distributions of the original samples. The values are given in Table I. The glass beads were purified with chromosulfuric acid, then washed with distilled water, and finally dried at 80°C.

TABLE I
Characteristic Data of Polystyrene Samples Used in Fractionation

Sample	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
PS VI	450,000	170,000	2.6
f3	212,000	181,000	1.18

Fractionation

A 1.8-g sample of polystyrene was dissolved in 100 ml of solvent at about 80°C, and this solution was decanted into the empty column which also had a temperature of 80°C. To prevent air inclusions, the glass beads were added last. By slowly cooling the column to the experimental temperature, nearly the whole polymer precipitated as gel, covering the glass beads as a thin film.

Then, by opening the valve (8), the solvent of the vessel (7) passed down the column and down the absorptiometer (9) with a flow rate of 1–2 ml/min into the collecting vessel (10). Thus, the first fraction of the applied polymer was dissolved. The dissolution of the first fraction was finished when no more polymer could be registered in the solvent passing out from the column. The needed volume of solvent was several liters.

For dissolving the second fraction, the solvent power was increased by raising the experimental temperature. To isolate the polymer, the solution of each fraction was evaporated.

RESULTS

In the experimental series II, the industrial polystyrene PS VI was fractionated. From fraction to fraction, the solvent power of the butyl acetate–propanol mixture was increased by temperature increases of about 2°C. The results of series II are complied in Table II. In the experimental series III, the polystyrene sample f3 was fractionated. To get fractions of low polydispersity, small temperature steps of about 0.5°C were taken. The results of series III are compiled in Table III. The molecular weight

TABLE II
Characteristic Data of Experimental Fractionation Series II[a]

Fraction	$T_1 - T_2$, °C	ΔT, °C	Amount, g	Amount, %	$\bar{M}_n$ (U.C.)	$\bar{M}_w/\bar{M}_n$ (U.C.)
II1	−15.7	—	0.58	32.2	—	—
II2	15.7–17.6	1.9	0.11	6.1	186.000	1.03
II3	17.6–19.6	2.0	0.10	5.6	210,000	1.015

[a] Polymer: PS VI; amount deposited: 1.8 g; butyl acetate/n-propanol mixture $\gamma = 0.3$. (The series was stopped after fraction II3).

TABLE III
Characteristic Data of Experimental Fractionation Series III[a]

Fraction	$T_1 - T_2$, °C	ΔT, °C	Amount, g	Amount, %	$\bar{M}_n$ (osmosis)	$\bar{M}_w/\bar{M}_n$ (U.C.)
III1	−15.5	—	0.28	15.5	100,000	1.06
III2	15.5–16.6	0.4	0.20	11.1	150,000	1.02
III3	15.9–16.6	0.7	0.43	23.9	195,000	1.01
III4	16.6–17.1	0.5	0.26	14.4	265,000	1.01
III5	17.1–	—	0.45	25.0	320,000	1.01

[a] Polymer: f3; amount deposited: 1.8 g; butyl acetate/n-propanol mixture $\gamma = 0.3$.

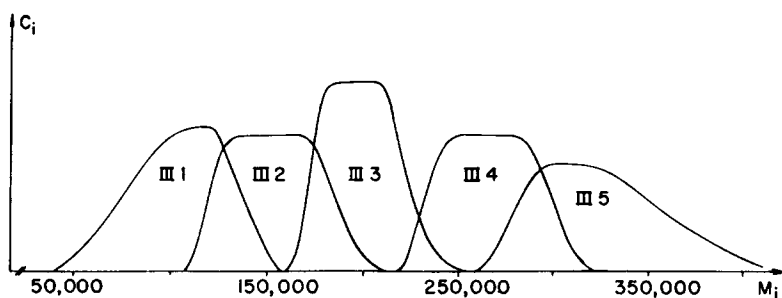distribution curves of the fractions of series III obtained by sedimentation analysis[11] are shown in Figure 7.

Fig. 7. Distribution curves of the fractions of polymer sample f3 from sedimentation analysis (c_i is given in relative units) (see Table III).

DISCUSSION

The "Critical" Molecular Weight M^*

The only assumption underlying the extraction mechanism outlined above was the existence of a critical molecular weight M^*, defined as the intersection point of a solubility line with the abscissa. Theoretically, however, this is not quite exact. Each solution that is in equilibrium with a precipitate will contain some molecules of each molecular weight as solute.
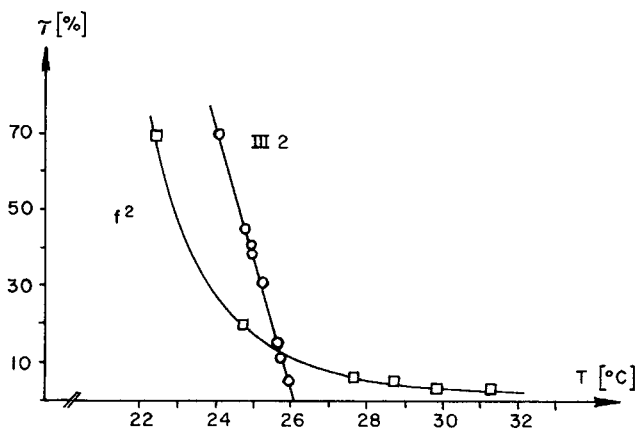
Fig. 8. Turbidity curves of polymer samples f2 and III2 (see Fig. 9): τ, turbidity; T, temperature; solvent, composition 70/30% of butyl acetate/propanol; concentrations, $c_{f_2} = 0.097\%$, $c_{III_2} = 0.11\%$.

The solution concentration may be very small, but it exists nevertheless. So, the solubility line will never cut or touch the abscissa, but will approach it asymptotically.

But, in practice, the equilibrium concentrations of all $M_i > M^*$ are very small and therefore negligible, so that the concept of a critical M^* can be considered as permissible approximation. The following facts are confirming this:

1. The elution curves have the same shape as theoretically predicted. From experimental data we can state the final concentration to be about $10^{-4}\%$, so that the eluate concentration is essentially going to zero.

2. The distribution curves of the fractions are characterized by very steep slopes on both sides. These distribution curves were determined by the ultracentrifugation method. With this method, however, tails with small partial concentrations of high or low molecular weight species are not detectable.

Therefore, the extraction fractions were also analyzed by turbidimetric titration.[1] Since the turbidity curves are very steep and have a point of intersection with the abscissa, they are a real proof that molecules $M_i > M^*$ may be dissolved at most in quantities that can be neglected in practice (Fig. 8). The solvent–nonsolvent system butyl acetate–n-propanol shows to be in agreement with this approximation. Other solvents or solvent mixtures will give the same results. But generally this cannot be stated without experimental tests.

Quality of Fractions

As seen from Figure 7, the fractions obtained by the extraction process are very symmetric and nearly nonoverlapping and have very steep slopes on both sides (except the first and the last fraction). The values of the ratio
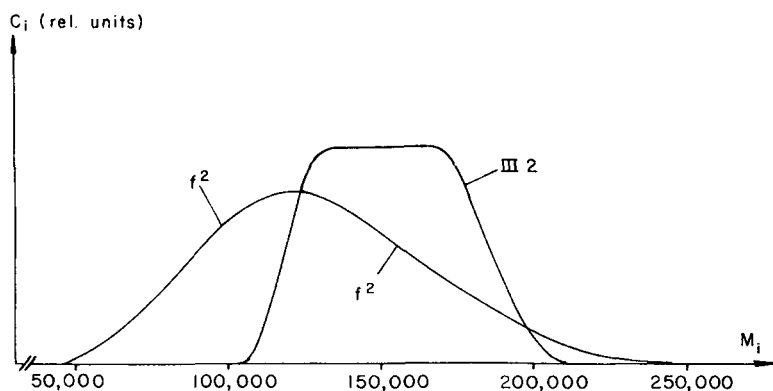
Fig. 9. Distribution curves of fractions f2 and III2 from sedimentation analysis. Fraction f2 was obtained by repeated precipitation fractionation; III2, by the extraction process.

$\bar{M}_w/\bar{M}_n$, being definitely smaller than 1.03, show that the fractions are much more homogeneous than those obtained by any other fractionation method, which generally have a dispersity limit of $\bar{M}_w/\bar{M}_n$ of about 1.05.

The progress can well be demonstrated by comparing an extraction fraction with one obtained by repeated precipitation fractionation (Fig. 9). But, obviously, the shape of the distribution curves of the fractions obtained experimentally deviates from the rectangular shape predicted in the theoretical part. This can be explained as follows:

To obtain fractions with rectangular shapes, the complete dissolution of all molecules $M_i < M^*$ would be necessary. According to the shape of the solubility lines, the saturation concentrations c_i^* are diminishing with increasing molecular weight M_i. Therefore, for the complete dissolution of the highest molecular weights of each fraction, a very large amount of solvent and a large expense of time would be necessary, so that in practice the dissolution always will remain incomplete and lead to the trapezoid shape of the fractions. This aspect will be discussed quantitatively in another paper. Further evidence that the concept of complete extraction at a given solubility line is justified is incorporated in the studies of polymer degradation by Wegner,[9] who reported a series of successful fractionations using the method described in this paper.

CONCLUSIONS

1. In spite of the problem of theoretical exactness, the experimental results are encouraging proof of the usefulness of the new method.

2. Advantages of the method are: (a) the compact shape and the homogeneity of the fractions, which have not been obtained before; (b) the small overlapping of fractions—compared with other fractionation methods— which is important for the analytical determination of molecular weight

distributions by fractionation; and (c) the rather simple equipment and procedure.

3. Disadvantages of the method are: (a) To get samples of low poly-dispersity, the solubility steps $(\Delta\gamma, \Delta T)$ have to be very small and therefore the solution leaving the column will become very dilute. The isolation of the polymer fractions from very dilute solutions includes procedures such as evaporation, solution, precipitation, and drying, and might therefore lead to degradation of the polymer molecules. (b) Moreover, the elution must be as complete as possible; therefore much time and solvent is needed by this method.

4. The most important characteristic of this procedure is the repeated extraction at constant solubility conditions until complete dissolution is achieved. Thus, we can say the extraction process has to be interpreted as a *multistage process*, as is known from the liquid–solid extraction. In the writer's opinion, this is the first real multistage process reported for polymer fractionation on the basis of sol–gel equilibrium.

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