

Preparative Fractionation of Polypropylene and Polyethylene

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Synopsis

According to the theory of solutional fractionation, simulation analyses were carried out for the fractionation of polypropylene and polyethylene. The results were compared with the experimental ones, which were obtained in fractionating 100-g samples. The experimental results were sufficiently explained by simulation. This fact demonstrated that these fractionations were carried out in the partition equilibrium between two liquid phases. Further, experimental conditions to obtain narrow distribution fractions were investigated by simulation techniques.

INTRODUCTION

Many studies have been performed concerning fractionation methods of homopolymers. At first, the methods were applied mainly for determining the molecular weight distribution of whole polymers by plotting the cumulative weight against the molecular weight of fractions. However, the emergence of gel permeation chromatography (GPC) brought about a depreciation of conventional fractionation methods for the determination of the distribution. Since narrow distributions are still required for the examination of physical and mechanical properties of polymers, we intended to prepare some characterized polymers having a variety of molecular weights by applying solutional fractionation. Our investigation in this paper was focused on the problem of preparative fractionation.

Polypropylene (PP) and polyethylene (PE) are saturated hydrocarbons having very similar crystalline properties and molecular structure. It is possible in principle to fractionate both polymers by almost the same method. Many investigations have been presented on column fractionation of these polymers. However, only a few were interested in the molecular weight distribution of fractions¹⁻⁶ evaluated by refractionation or determination of viscosity-average and other average molecular weights. Thus, more detailed discussions are required for preparative fractionation for these polymers. Tung,⁷ Koningsveld, and Staverman,⁸ and Kamide et al.,⁹ developed simulation techniques for solutional and precipitational fractionations. With suitable modification of these techniques, we performed simulation analyses for the solutional fractionation of these polymers. The experimental results will be discussed in detail on a theoretical basis.

EXPERIMENTAL

A large-scale fractionation apparatus was used to fractionate polymers. The operational conditions are almost the same as those described in previous papers.^{5,10} The number- and weight-average molecular weights of the fractions were determined by GPC. The apparatus used was a Shimadzu GPC-1A equipped with four columns (10^6 , 10^5 , 10^4 , and 10^3 Å). The experimental conditions adopted were as follows: flow rate, 1.0 ml/min; polymer concentration, 0.4 g/dl; solvent ODCB containing 0.2% Ionol; temperature, 135°C. The resolution efficiency of this combined column system was 1200 TPF with acetone at room temperature. The calibration curves for PP and PE were made by applying the universal rule¹¹ with narrow-distribution polystyrene samples (Pressure Chemical Co.).¹² The error known as the broadening effect was corrected by the method described in another paper.¹³

CALCULATION

Basis of Simulation

The molecular weight dependence of the partition of polymer species between two liquid phases, i.e., the concentrated phase (gel) and dilute phase (sol), is the basis for fractionation by elution. In principle, we can solve the problems of fractionation by equating chemical potentials between the two liquid phases. Then, in our experiments, a mixture of a good solvent and a nonsolvent is used as fractionation medium. Polymer fractions are obtained by varying the ratio of solvent and nonsolvent instead of varying temperature, as in the case of a single solvent system. However, the precise theoretical treatment of phase equilibrium for the polymer-solvent-nonsolvent system is very complicated. No complete calculation method has been found so far for fractionation in this system. As a first approximation, it seems admissible to study the fractionation carried out by lowering the temperature in solvent-polymer systems, instead of adding nonsolvent.^{14,15} Fractionation thus approximated corresponds to the most inefficient case in polymer-solvent-nonsolvent systems, although fractionation is still ideal.

According to the Flory-Huggins theory, the partial molar free energy of mixing for the solvent, $\Delta\mu_1$, and that for the X-mer, $\Delta\mu_x$, are

$$\Delta\mu_1 = RT[\ln(1 - \nu_p) + (1 - 1/\bar{X}_n)_p + \chi_0\nu_p^2] \quad (1)$$

$$\Delta\mu_x = RT[\ln \nu_x - (X - 1) + \nu_p(1 - 1/\bar{X}_n)X + (1 - \nu_p)^2X] \quad (2)$$

where R is the molar gas constant; T is the absolute temperature; ν_p is the volume fraction of the polymer in solution; X is the degree of polymerization; \bar{X}_n is the number-average degree of polymerization (the molar volume of the monomer is assumed to be equal to that of the solvent); χ_0 is the polymer-solvent interaction parameter; and ν_x is the volume fraction of the X-mer in solution. When the two liquid phases are in thermodynamic equilibrium, the partial molar free energy for mixing each species must be equal between the two phases. As a result, the ratio of volume fraction of the X-mer in the concentrated solution, ν'_x , to that in the dilute one, ν_x , has been expressed by Flory¹⁶:

$$\nu'_x/\nu_x = \exp(\sigma X) \quad (3)$$

where

$$\sigma = \frac{2}{(\nu'_p + \nu_p)} \left\{ \ln \left[\frac{(1 - \nu_p)}{(1 - \nu'_p)} \right] + \left(1 - \frac{1}{\bar{X}_n} \right) \nu_p - \left(1 - \frac{1}{\bar{X}'_n} \right) \nu'_p \right\} - \ln \left[\frac{(1 - \nu_p)}{(1 - \nu'_p)} \right] \quad (4)$$

The prime indicates the concentrated phase. Since the X-mer is in the partition equilibrium between the two liquid phases, its amount in each phase must be determined. Now, let f_x^0 be the fraction of the X-mer in the original polymer; the fraction f_x^E of the X-mer in the dilute phase is given by

$$f_x^E = R f_x^0 / [R + \exp(\sigma X)] \quad (5)$$

where $R = V/V'$; V and V' represent the volumes of the two phases. In the fractionation, R and σ must be previously known. The procedure to determine R and σ is described in the following section.

Calculation Procedure

The molecular weight distribution of an original polymer is approximated by a log-normal distribution function,¹⁷ namely,

$$W(\ln M) = \frac{1}{(2\pi\beta^2)^{1/2}} \exp \left[- \left(\frac{1}{2\beta^2} \right) (\ln M - \ln M_0)^2 \right] \quad (6)$$

where $W(\ln M)$ is the weight distribution function as a function of $\ln M$ (M is molecular weight); β is the standard deviation for $\ln M$; and $\ln M_0$ is the peak position of log-normal distribution curve. One gram of the original polymer (density = 1.0 g/cm³) is hypothetically dissolved in V_0 ($= V + V' - 1$) ml of medium. The solution is brought to a temperature, by cooling, at which phase separation occurs, and the first fraction is obtained from the dilute phase. After this step is completed, the next fractionation step is carried out for the concentrated phase which is obtained in the penultimate step, the volume V_0 being kept constant. The operation is repeated until polymer species are almost completely removed from the concentrated phase. This process is schematically presented in Figure 1.

The actual calculation procedure is as follows. The flow chart for calculation is shown in Figure 2. The molecular weight distribution curve for $\ln M$ ranging

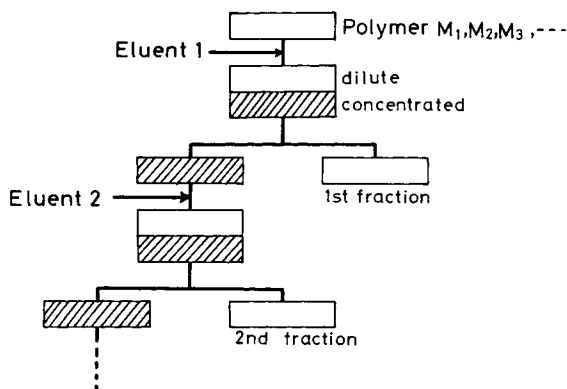


Fig. 1. Fractionation process in simulation. Solvent concentration of eluent 2 is higher than that of eluent 1.

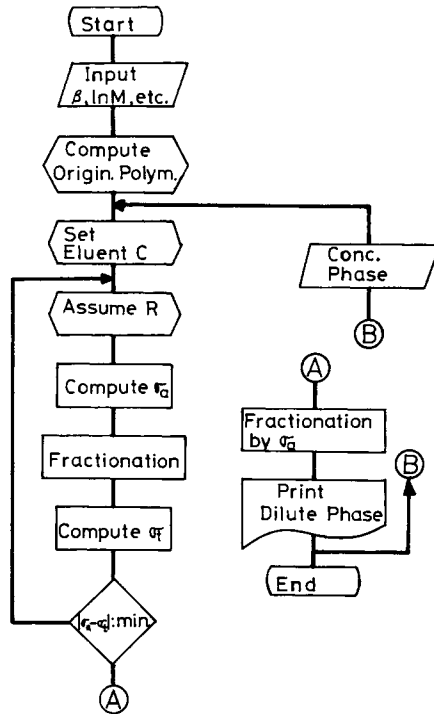


Fig. 2. Flow chart of hypothetical fractionation.

from 7 to 18 is divided into a number of equal increments. Each increment f_x^0 in eq. (7) is expressed as $W(\ln M)$ in eq. (6), where $X = M/m$ (m = molecular weight of a polymer chain unit). Then f_x^0 is normalized as follows:

$$\sum_{i=1}^n (f_x^0)_i = 1 \quad (7)$$

where n is the number of increments, usually 100.

For the hypothetical fractionation, the parameter R and σ in eq. (5) have to be known before each fractionation step is executed. In other words, the problem of hypothetical fractionation is how to obtain a self-consistent R - σ pair. Now, actual fractionation is accomplished by varying the solvent concentration in the medium. However, in the actual system it is impossible to determine the pair directly only from solvent concentration. The value of the concentration, i.e., the medium composition, must be converted into another variable. For this purpose, the relation between molecular weight and medium composition at cloud point is determined by adding nonsolvent to the polymer-solvent system at constant temperature. These relations are shown in Figures 3 and 4 for PP and PE, respectively. By varying this relation, the molecular weight, i.e., the degree of polymerization at cloud point,¹² is determined from a given solvent concentration in the medium for each fractionation point. A self-consistent R - σ pair is calculated on the assumption that $R/[R + \exp(\sigma X)] = 0.5$ for each fractionation point, i.e., for the fixed degree of polymerization obtained above, where it is not important to set the value but for the value to be constant. The hypo-

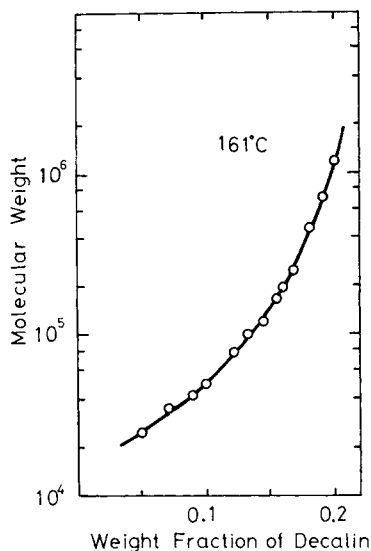


Fig. 3. Relation between molecular weight and solvent concentration at cloud point in decalin-butyl carbitol system for PP.

thetical fractionation for all the increments is performed in the first place using a certain $R-\sigma(\equiv \sigma_a)$ pair. The value $R-\sigma(\equiv \sigma_t)$ is recalculated by eq. (4) from the results of the simulation, σ_t is compared with σ_a . Thus, by repeating this calculation, the $R-\sigma$ pair is singled out, minimizing the absolute value of $\sigma_a - \sigma_t$. One step of the fractionation is accomplished using this $R-\sigma_a$ pair. The operation for the next step begins in a similar manner to that of the penultimate step and is repeated until most polymer species in the concentrated phase are eluted.

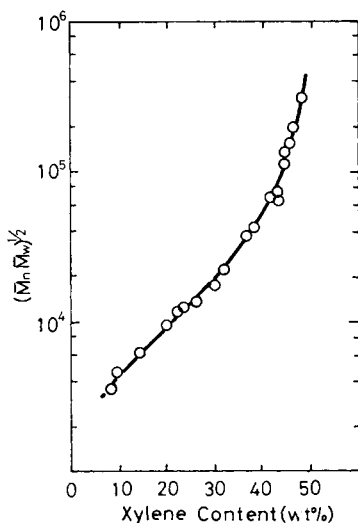


Fig. 4. Relation between molecular weight and solvent concentration at cloud point in xylene-butyl cellosolve system for PE.

TABLE I
Results of Experimental Fractionation of Polypropylene^a

Fraction no.	Weight, g	Weight, %	$(\bar{M}_n \bar{M}_w)^{1/2}$	<i>D</i>
1	5.595	5.12	1.66×10^4	1.45
2	5.890	5.39	1.99×10^4	1.23
3	5.166	4.73	3.25×10^4	1.16
4	7.395	6.76	5.03×10^4	1.12
5	10.594	9.69	7.38×10^4	1.16
6	13.315	12.18	1.19×10^5	1.12
7	15.446	14.13	1.77×10^5	1.21
8	14.452	13.23	2.62×10^5	1.23
9	12.149	11.11	2.82×10^5	1.12
10	8.163	7.47	4.64×10^5	1.21
11	4.059	3.71	4.93×10^5	1.20
12	3.765	3.45	5.73×10^5	1.36
13	3.316	3.04	6.35×10^5	1.92
Total	109.30 (recovery 96.5%)			

^a Original polymer: $\bar{M}_n = 7.56 \times 10^4$, $\bar{M}_w = 3.62 \times 10^5$, $D = 4.79$.

RESULTS AND DISCUSSION

Experimental and Simulated Fractionations

Based on the previous experiments,⁵ we succeeded in fractionating PP in amounts from 50 to 100 g using decalin–butyl carbitol mixtures as eluent. The average molecular weights and *D* values of fractions were determined by GPC. The typical experimental results for a commercial PP are shown in Table I and Figure 5. Table I shows that most *D* values are close to 1.3, and generally bear a good fractionation. However, a considerably large *D* value was confirmed in the higher molecular weight region. Furthermore, we could not obtain any fractions having an $(\bar{M}_n \bar{M}_w)^{1/2}$ more than 2.0×10^6 , although at least ten fractionation experiments were attempted. This phenomenon may be attributed to be the same development as the “backlash,” i.e., return to lower molecular weight of fractions, which was found in many column fractionation experiments.^{18,19}

We carried out the hypothetical fractionation for this system. The parameters of eqs. (5) and (6) were chosen as close as possible to the experimental ones: $\ln M_0 = 12.0$ and initial concentration of polymer = 1.5%. The calculated results

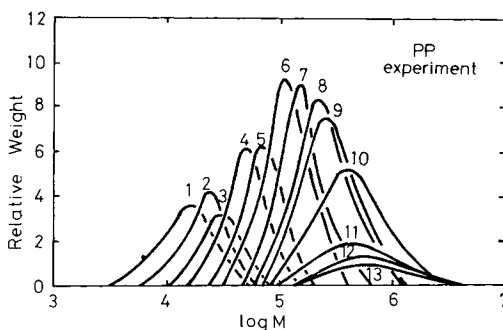


Fig. 5. Molecular weight distribution curves of fractions for PP (experiment). Numbers indicate the order of fractions.

TABLE II
Results of Hypothetical Fractionation of Polypropylene^a

Fraction no.	Weight, %	$(\bar{M}_n \bar{M}_w)^{1/2}$	D
1	6.93	1.85×10^4	1.51
2	2.77	2.32×10^4	1.34
3	2.07	3.06×10^4	1.21
4	2.60	4.00×10^4	1.15
5	4.03	5.16×10^4	1.14
6	6.17	6.70×10^4	1.15
7	8.09	8.65×10^4	1.17
8	9.89	1.15×10^5	1.19
9	11.52	1.59×10^5	1.22
10	12.85	2.30×10^5	1.25
11	13.19	3.47×10^5	1.30
12	11.73	5.67×10^5	1.36
13	6.90	1.11×10^6	1.48
14	1.00	2.83×10^6	1.66

^a Original polymer: $\bar{M}_n = 7.47 \times 10^4$, $\bar{M}_w = 3.55 \times 10^5$, $D = 4.76$.

are shown in Table II and Figure 6. The simulated D values of fractions have a minimum at a certain molecular weight. This tendency and the D values are in agreement with the experimental ones, except for a few fractions in a higher molecular weight region. This discrepancy is discussed in detail in the following section.

The fractionation of PE was as difficult as that of PP in experiment. This was accomplished in xylene-butyl cellosolve mixture as eluent at 130°C. The results for 93 g of a commercial high-density PE in the load is shown in Table III. The D values of the fractions are generally smaller than those of PP. However, the steep increase in D values occurs faster than that for PP in higher molecular weight fractions. The location of this increase may depend on the polymer properties in solution.

The simulation for PE as in the case of PP was carried out on the assumption that $\log M_0 = 10.8$ and $\beta = 1.25$, which were estimated from the experimental results, and that the initial concentration of polymer is 0.5%. As shown in Table IV, the results agreed well with the experimental ones, except for higher molecular weight fractions.

The agreement between the simulated and experimental values suggests that the fractionations take place in the partition equilibrium between two liquid

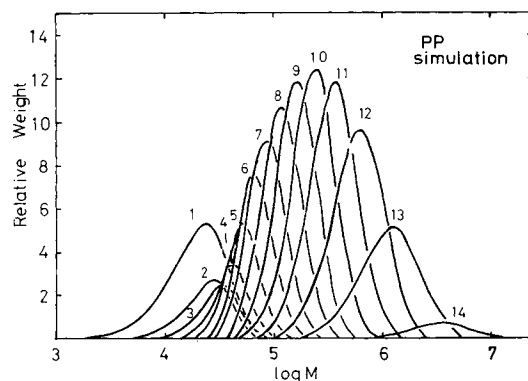


Fig. 6. Molecular weight distribution curves of fractions for PP (simulation).

TABLE III
Results of Experimental Fractionation of Polyethylene

Fraction no.	Weight, g	Weight, %	$(\bar{M}_n\bar{M}_w)^{1/2}$	<i>D</i>
1	1.466	1.57	1.98×10^3	1.16
2	4.074	4.36	3.57×10^3	1.15
3	2.423	2.59	5.63×10^3	1.05
4	2.024	2.16	7.13×10^3	1.05
5	3.356	3.59	1.00×10^4	1.06
6	3.512	3.76	1.06×10^4	1.05
7	4.380	4.69	1.15×10^4	1.04
8	5.540	5.93	1.39×10^4	1.05
9	9.628	10.30	2.20×10^4	1.03
10	4.552	4.87	2.70×10^4	1.05
11	3.185	3.41		
12	2.767	2.96	3.12×10^4	1.06
13	2.669	2.86	3.57×10^4	1.07
14	2.051	2.19	3.64×10^4	1.10
15	3.577	3.83		
16	3.317	3.55	4.30×10^4	1.10
17	5.900	6.31	6.70×10^4	1.09
18	7.060	7.55	7.29×10^4	1.15
19	6.782	7.26	1.14×10^5	1.28
20	2.186	2.34	1.37×10^5	1.30
21	4.681	5.01	1.48×10^5	1.33
22	5.631	6.02	2.02×10^5	1.35
23	2.036	2.18		
24	0.653	0.70	3.62×10^5	1.75
Total	93.449 (recovery 99.4%)			

phases. Furthermore, the slight discrepancy between them in the higher molecular weight region may be due to a fundamental defect of column elution for fractionation. Details concerning this defect are described in the following section.

Broad Distribution Fractions

Abnormally large *D* values were obtained for the end fractions in the order of elution in the experiments. Two reasons are considered for these values: one may be due to the insufficient phase equilibrium between the two liquid phases, and the other may be due to the escape of polymer droplets from the support material.¹⁰

As shown in Figure 5, the molecular weight distribution curves of the end fractions for PP have almost common peaks around 5.0×10^5 in molecular weight, while in simulation the peak molecular weight increases in the order of elution, as shown in Figure 6. This fact implies that insufficient fractionation has apparently been carried out. Further, the molecular weight distribution of these fractions could not be so narrowed by refractionation taking a long enough period to achieve fractionation in phase equilibrium. As described above, we have never obtained a PP fractions having an $(\bar{M}_n\bar{M}_w)^{1/2}$ of more than 2.0×10^6 , and could not obtain such fractions for PE either.

In the following, this phenomenon is mainly discussed from the viewpoint of the escape of polymer droplets in the column. First, the polymer concentration,

TABLE IV
Results of Hypothetical Fractionation of Polyethylene^a

Fraction no.	Weight, %	$(\bar{M}_n \bar{M}_w)^{1/2}$	<i>D</i>
1	1.62	2.66×10^3	1.16
2	1.74	4.44×10^3	1.11
3	2.32	6.26×10^3	1.09
4	2.91	8.25×10^3	1.09
5	3.34	1.05×10^4	1.08
6	3.58	1.29×10^4	1.08
7	3.77	1.55×10^4	1.08
8	3.94	1.85×10^4	1.07
9	4.22	2.18×10^4	1.07
10	4.74	2.58×10^4	1.07
11	5.59	3.10×10^4	1.08
12	6.86	3.80×10^4	1.08
13	8.55	4.84×10^4	1.09
14	10.34	6.47×10^4	1.10
15	11.48	9.18×10^4	1.12
16	10.98	1.40×10^5	1.14
17	8.26	2.36×10^5	1.16
18	3.49	4.65×10^5	1.25
19	1.61	6.50×10^5	1.40
20	0.46	9.03×10^5	1.66
21	0.09	1.16×10^6	1.97
22	0.01	1.32×10^6	2.21

^a Original polymer: $\bar{M}_n = 2.32 \times 10^4$, $\bar{M}_w = 1.07 \times 10^5$, $D = 4.60$.

namely, the polymer gel in the column, is estimated by fractionation simulation. Polymer concentration C_j in the gel phase is given by the following equation:

$$C_j = \frac{1}{V_j} \left[1.0 - \sum_{k=1}^j \sum_{i=1}^n (f_i^E)_k \right] \quad (8)$$

where

$$V_j \simeq \frac{V_0}{1 + R_j} \quad (9)$$

where f_i^E is the fraction of i th increment polymer in the dilute phase; V_j is the volume of the concentrated phase of j th fraction; R_j is the ratio of the volume of dilute phase to that of the concentrated phase. C_j can also be determined experimentally using the phase diagram of solvent–nonsolvent–polymer system¹⁰ and the fractionation data. As shown in Figure 7, the C_j , the concentrated phase, decreased from 25–30 to 1.5 g/l. with increase in molecular weight, although there was somewhat of a difference between the experiment and the simulation, which was probably caused by experimental error. These facts demonstrate that it is too dilute for liquid droplets to stick to support material in the column when the $(\bar{M}_n \bar{M}_w)^{1/2}$ of polymer species in the droplets is higher than 6×10^5 . Almost the same behavior was confirmed for the case of PE. Furthermore, as described above, the undesirable results were not improved by the refractionation. Although the effect of insufficient partition equilibrium cannot be neglected completely, the appearance of abnormally broad distribution fractions is attributed mainly to a fundamental defect of the column elution—the escape of

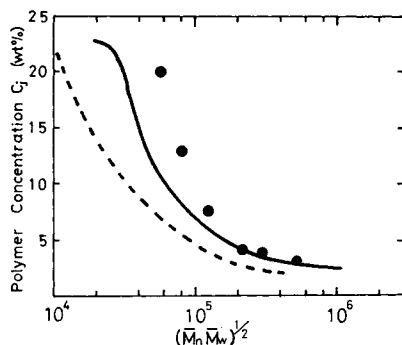


Fig. 7. Polymer concentration of liquid droplets in fractionation column as a function of molecular weight: (—) PP (simulation); (- - -) PE (simulation); (●) experimental points (PP).

polymer droplets. Therefore, it is essentially impossible to obtain all the fractions in narrow distribution.

Amount of Eluent

To conduct a preparative fractionation, it is most desirable to obtain narrow distribution fractions. There are several elution techniques for preparing narrow distribution fractions: the use of a large amount of eluent for each fraction, the increase of a number of fractions by eluents having a variety of component ratios, and so on. We studied the effect of these techniques on the D values of fractions by simulation. As a results, the D values of fractions were almost independent of these elution techniques when the total amount of eluent was fixed for a given polymer weight loaded. In other words, the D values varied mainly depending on the total amount of eluent. Therefore, the relation between the D values and the amount of eluent was examined in detail. The results are shown in Figures 8 and 9 for PP and PE, respectively. In the figures the relations were expressed as a function of D values in two molecular weights, respectively. The facts demonstrate that the D values of fractions decrease in a straight decline with increase in the amount of eluent. The simulated D values agree approximately with those obtained by experiment. Therefore, the increase in the amount is the most effective way to reduce the D values of fractions. Additionally, the experimental errors due to temperature variation and chaneling phenomena in the column become considerable compared with the effect of amount of eluent.

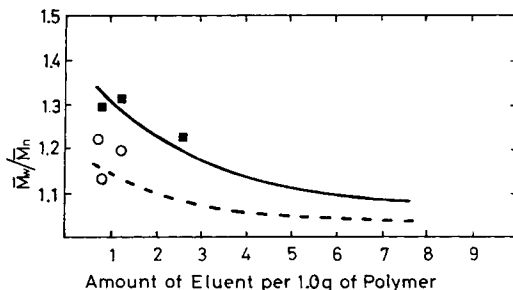


Fig. 8. D values of fractions as a function of amount of eluent in liter for PP: (- - -) simulated curve at $(\overline{M}_n\overline{M}_w)^{1/2} = 3 \times 10^4$; (—) simulated curve at $(\overline{M}_n\overline{M}_w)^{1/2} = 3 \times 10^5$; (O) experimental points at $(\overline{M}_n\overline{M}_w)^{1/2} = 3 \times 10^4$; (■) experimental points at $(\overline{M}_n\overline{M}_w)^{1/2} = 3 \times 10^5$.

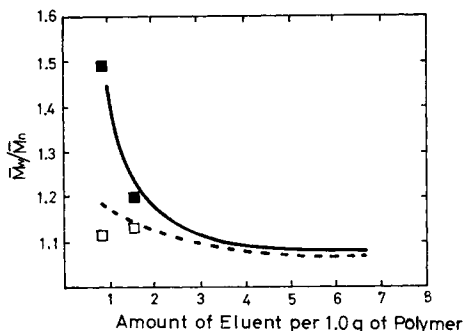


Fig. 9. D values of fractions as a function of amount of eluent in liter for PE: (---) simulated curve at $(\overline{M}_n\overline{M}_w)^{1/2} = 1 \times 10^4$; (—) simulated curve at $(\overline{M}_n\overline{M}_w)^{1/2} = 6 \times 10^4$; (□) experimental points at $(\overline{M}_n\overline{M}_w)^{1/2} = 1 \times 10^4$; (■) experimental points at $(\overline{M}_n\overline{M}_w)^{1/2} = 6 \times 10^4$.

In practice, the D values will not be as improved by the use of extreme amounts of eluent as expected by simulation.

CONCLUSIONS

The experimental results were compared with those obtained by simulation from the viewpoint of D values of fractions. The results gave almost the same values as expected by simulation, except for the end fractions in the order of elutions. This exception was considered to be mainly caused by the escape of polymer liquid droplets from the support material.

The following factor affecting the D values of fractions was examined using simulation techniques, namely, the relation between the D values of fractions and the amount of eluent. The D values decreased with an increase in the amount of eluent. This result is essentially valuable for preparing narrow distribution fractions.

References

1. P. M. Henry, *J. Polym. Sci.*, **36**, 3 (1959).
2. J. E. Guillet, R. L. Combs, D. F. Slonaker, and H. W. Coover, Jr., *J. Polym. Sci.*, **47**, 307 (1960).
3. D. F. Slonaker, R. L. Combs, J. E. Guillet, and H. W. Coover, Jr., *J. Polym. Sci. A-2*, **4**, 523 (1966).
4. V. Kokle and F. W. Billmeyer, Jr., *J. Polym. Sci. C*, **8**, 217 (1965).
5. T. Ogawa, Y. Suzuki, S. Tanaka, and S. Hoshino, *Kobunshi Kagaku*, **27**, 356 (1970).
6. S. Saeda, *Kobunshi Kagaku*, **31**, 367 (1974).
7. L. H. Tung, *J. Polym. Sci.*, **61**, 449 (1962).
8. R. Koningsveld and A. J. Staverman, *J. Polym. Sci. A-2*, **6**, 305 (1968).
9. K. Kamide and K. Sugamiya, *Makromol. Chem.*, **156**, 259 (1972).
10. T. Ogawa, S. Tanaka, and S. Hoshino, *J. Appl. Polym. Sci.*, **17**, 779 (1973).
11. Z. Grubisic, P. Rempp, and H. Benoit, *J. Polym. Sci. B*, **5**, 753 (1967).
12. T. Ogawa, S. Tanaka, and T. Inaba, *J. Appl. Polym. Sci.*, **17**, 319 (1973).
13. T. Ogawa, S. Tanaka, and S. Hoshino, *J. Appl. Polym. Sci.*, **16**, 2257 (1972).
14. T. Ogawa and S. Hoshino, *Kobunshi Kagaku*, **28**, 348 (1971).
15. R. A. Mendelson, *J. Polym. Sci. A*, **1**, 2361 (1963).
16. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.
17. H. Wesslau, *Makromol. Chem.*, **20**, 111 (1956).
18. P. S. Francis, R. C. Cooke, Jr., and J. H. Elliott, *J. Polym. Sci.*, **31**, 453 (1958).
19. S. Shyluk, *J. Polym. Sci.*, **62**, 317 (1962).

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