Analysis of the Fractionation of Ethylene–Propylene Copolymerization Products

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Synopsis

The solution fractionation of ethylene–propylene copolymerization products was simulated by assuming an appropriate partition relationship for the polymer distribution between the two liquid phases and by using data for the molecular weight dependence of the solubility. Bivariate and log normal distribution functions were assumed for the polydispersities of the copolymer and the homopolymers, respectively. The products can be classified into five types: copolymer (EP), polyethylene–polypropylene (PE–PP), polypropylene–copolymer (PP–EP), polypropylene–copolymer–polyethylene(PP–EP–PE), and copolymer–polyethylene (EP–PE). The present work is mainly concerned with the latter three types. The experimental results, which could not be explained earlier in terms of pure EP or PE–PP blends, could be explained by the present computer analysis. Thus, even though the distribution curves vary in a complicated way with the component types and the ratios of amounts present, analysis of this kind should be useful for understanding the nature of unknown samples. Finally, the possibility of isolating pure components by solution fractionation is discussed.

INTRODUCTION

Copolymers are usually composed of various polymer species, each of which has a different molecular weight, chemical composition, monomer sequence, etc. Although a study of these factors as such is important, it is well to carry out the analysis of the copolymerization products at the same time since they contain homopolymers to a more or less extent.

In prior work, experimental results on solution fractionation and a computer analysis of the products were presented.[1–3] Some products showed the characteristics of pure ethylene–propylene copolymers (EP) or PE–PP blends,[1,2] whereas other products could not be explained in terms of these types. Further studies were therefore indicated.

In this paper, the analysis centered on products containing the homopolymers (PE and PP), the computer treatment of which is more complicated than for pure EP or PE–PP blends. An explicit computer analysis was achieved by incorporating the programs for pure EP and PE–PP into a single program. The experimental fractionation method was essentially the same as that used in the earlier work.

The experimental results, which could not be explained earlier in terms of pure EP or PE–PP blends, were compared with the results of the present

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computer analysis and were in good agreement with them.   Thus, a series of studies of this kind should be useful in understanding the behavior of the various components associated with ethylene–propylene copolymerization.

CALCULATIONS

Basis of the Calculations

A method similar to that used for pure EP or PE–PP blends can also be applied to the simulated fractionation of the copolymerization products. The fractionation in this simulation is performed for each component separately, and then the analysis for the product is treated by combining the results for each component.

Three fundamental factors (the characteristic parameters for the product, the solubility, and the partition relationship between two liquid phases) are required for the simulation.   A brief summary of these factors is presented below, with a more detailed discussion being available elsewhere.[1,2]   The following distribution function was adopted for the homopolymers[4-6]:

$$W(\ln M) = \frac{1}{\beta_h \sqrt{2\pi}} \cdot \exp\left[-\frac{1}{2\beta_h^2}(\ln M - \ln M_0)^2\right] \qquad (1)$$

where $W(\ln M)$ is the weight distribution function; β_h is the standard deviation for $\ln M$; and $\ln M_0$ is the peak position in the log normal distribution curve.   A bivariate normal distribution function[1] was adopted for the distribution of copolymers as follows:

$$W(\ln M, \alpha) = \frac{1}{2\pi \cdot \beta_M \cdot \beta_\alpha \cdot (1 - \rho^2)^{1/2}} \cdot \exp\left\{-\frac{1}{2(1-\rho^2)}\right.$$
$$\left.\cdot\left[\frac{(\ln M - \ln M_{EP})^2}{\beta_M^2} - \frac{2\rho(\ln M - \ln M_{EP})(\alpha - \alpha_0)}{\beta_M \cdot \beta_\alpha} + \frac{(\alpha - \alpha_0)^2}{\beta_\alpha^2}\right]\right\} \qquad (2)$$

where $W(\ln M, \alpha)$ is the distribution function for the copolymers; $\ln M$ is the logarithm of molecular weight; and α is the ethylene content; $\ln M_{EP}$ and α_0 are the peak positions for the molecular weight and the composition distributions, respectively; β_M and β_α are the standard deviations for $\ln M$ and α, respectively; and ρ is the correlation coefficient between $\ln M$ and α.

In the case of the solubility, a relationship between cloud point and molecular weight was applied in the following form:

$$M_c = 10^4\{[K_1 - K_2(X - K_3\alpha)]^{-2} + K_4\alpha\} \qquad (3)$$

where K_1, K_2, K_3, and K_4 are constants; M_c is the molecular weight; and X is the weight fraction of solvent in the eluent.   For the decalin–butyl carbitol system, for which all calculations in this work were carried out, the values were $K_1 = 0.57$, $K_2 = 2.79$, $K_3 = 0.22$, and $K_4 = 0.83$.[7]

For the partition relationship, a well-known equation derived from the Flory-Huggins theory[8] was used as follows:

$$f^E = \frac{Rf^R}{R + \exp{(\sigma \cdot \gamma)}} \tag{4}$$

where f^E and f^R are the volume fractions of γ-mer (each increment in γ) in the dilute phase and in the original product, respectively; R is the ratio of the volume of the dilute phase to that of the concentrated phase (a value of 200 is ordinarily applied in practice); γ is the degree of polymerization of polyethylene (in the copolymer or polypropylene it corresponds to the degree of polymerization of polyethylene showing the same cloud point as it); and σ is the partition coefficient of the γ-mer (each increment in γ) between the two liquid phases.

Procedure for Simulating the Fractionation

The fractionation was assumed to be carried out in the decalin–butyl carbitol system at 161°C. The fractionation process is represented in Figure 1. First, the solvent content X for each fractionation step was chosen and M_c was calculated from eq. (3). After M_c was converted into γ, σ was determined from eq. (4) by assuming that $f^E/f^R = $ constant (Q): the value of 0.5 was ordinarily chosen. Then, the extraction was performed using eq. (4) for each increment, for which a more detailed explanation will now be presented.

The distribution surface was divided into 810 increments: the range of α was from 0 to 1.0, and the range of ln M was from 7 to 19. For PP and PE, the curves were divided into 30 increments; the range of ln M was from 7 to 19. When the weight fraction for each increment (M_j) is given by $f_{PP}(\ln M_j)$, $f_{EP}(\ln M_j, \alpha_k)$, $f_{PE}(\ln M_j)$ for PP, EP, and PE, respectively, the molecular weight distribution $W(\ln M_j)_i$ of the ith fraction can be calculated by the equation

$$W(\ln M_j)_i = f_{PP}(\ln M_j) + \sum_{k=1}^{N} f_{EP}(\ln M_j, \alpha_k) + f_{PE}(\ln M_j). \tag{5}$$

The composition distribution $W(\alpha_k)_i$ of the ith fraction is as follows:

If $\alpha_k = 0$

$$W(0)_i = \sum_{j=1}^{K} f_{PP}(\ln M_j) \tag{6a}$$

If $0 < \alpha_k < 1.0$

$$W(\alpha_k)_i = \sum_{j=1}^{K} f_{EP}(\ln M_j, \alpha_k) \tag{6b}$$

If $\alpha_k = 1.0$
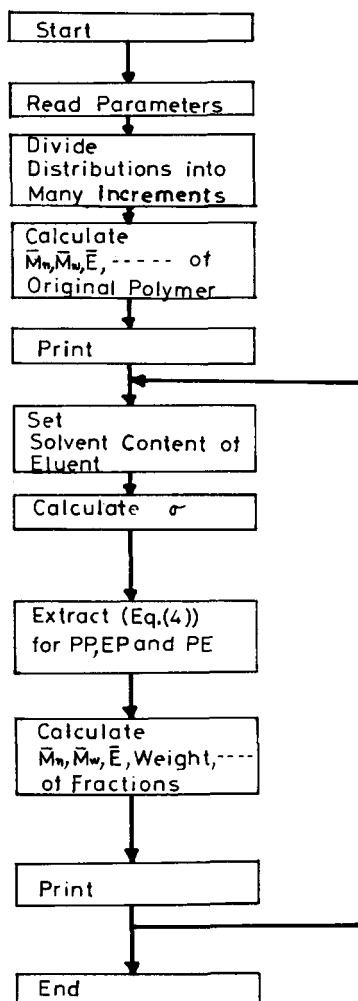
$$W(1)_i = \sum_{j=1}^{K} f_{PE}(\ln M_j) \tag{6c}$$

Fig. 1. Flow chart of computer simulation.

where K and N are the number of increments for the functions of $\ln M$ and α, respectively. Also, the quantity f^E in eq. (4) corresponds to $f_{PP}(\ln M_j)$, $f_{EP}(\ln M_j,\alpha_k)$, or $f_{PE}(\ln M_j)$. The quantity f^R in eq. (4) is expressed essentially by

$$(f^R)_i = f^{R0} - \sum_{l=1}^{i-1} (f^E)_l \tag{7}$$

where $(f^R)_i$ is the f^R of the ith fraction; f^{R0} is the f^R of the original product; $(f^E)_l$ is the f^E of the lth fraction. Therefore, the explicit result for eq. (7), for the (j,k)th increment, is shown in eqs. (8a), (8b), and (8c) as follows:

For PP and PE

$$f_{PP}^R(\ln M_j)_i = {}_{PP}{}^{R0}(\ln M_j) - \sum_{l=1}^{i-1} f_{PP}^E(\ln M_j)_l \qquad (8a)$$

$$f_{PE}^R(\ln M_j)_i = f_{PE}^{R0}(\ln M_j) - \sum_{l=1}^{i-1} f_{PE}^E(\ln M_j)_l \qquad (8b)$$

For EP

$$f_{EP}^R(\ln M_j, \alpha_k) = f_{EP}^{R0}(\ln M_j, \alpha_k) - \sum_{l=1}^{i-1} f_{EP}^E(\ln M_j, \alpha_k)_l \qquad (8c)$$

When WPP, WEP, and WPE are defined by

$$W\mathrm{PP} \equiv \sum_{j=1}^{K} f_{PP}^{R0}(\ln M_j) \qquad (9a)$$

$$W\mathrm{EP} \equiv \sum_{k=1}^{N} \sum_{j=1}^{K} f_{EP}^{R0}(\ln M_j, \alpha_k) \qquad (9b)$$

$$W\mathrm{PE} \equiv \sum_{j=1}^{K} f_{PE}^{R0}(\ln M_j) \qquad (9c)$$

the above functions are normalized as follows:

$$W\mathrm{PP} + W\mathrm{EP} + W\mathrm{PE} = 1. \qquad (10)$$

The ratios of components of PP, EP, and PP are

$$\mathrm{PP:EP:PE} = W\mathrm{PP}:W\mathrm{EP}:W\mathrm{PE} \qquad (11)$$

After one step, the ith fraction, was completed, the next fractionation, the $(i + 1)$th fraction, was performed at a higher solvent concentration for γ-mer of the concentrated phase from the preceding step, $(f^R)_i$. The fractionation was carried out until the polymer molecules were almost completely removed from the concentrated phase. The solvent concentration was increased stepwise in increments of 3.5%, and 13 fractions were obtained.

EXPERIMENTAL

Samples designated as EPA and EPB were used for the experimental fractionations. The sample EPA is a commercial polypropylene developed for high-impact service: the ethylene content $(\bar{E})$ of the sample was 8.6 wt-%. The sample EPB was prepared in heptane by introducing propylene, nitrogen, and ethylene, in that order, in the presence of AlEt$_2$Cl–TiCl$_3$ (activated); the $\bar{E}$ of the product was 46 wt-%. A 10-g sample of EPA and a 20-g sample of EPB were fractionated by the solvent gradient method, at a temperature of 164°C in a decalin–butyl carbitol system. A large-scale fractionation column (80 mm diam. × 1000 mm), made of

stainless steel and designed for exact control of the flow rate and column temperature,[3] was used.

The limiting viscosity numbers of the fractions were determined at 135°C in the decalin solutions, using an Ubbelohde-type viscometer. The $\bar{E}$ of the fractions was determined by Corish's method,[9] which is a method based on using the ratio of the infrared intensity at 1380 cm^{-1} to that at 1460 cm^{-1}.

RESULTS AND DISCUSSION

Table I shows the parameters for each component, which were assumed for the simulated fractionation. The overall characteristic values for the products are given in Table II.

Because of the complexity of the combined system, a classification into three types of components was made to provide better understanding of the fractionation behavior. The three types, i.e., PP–EP, PP–EP–PE, and EP–PE, will be described individually with respect to the cumulative weight distribution curves and the characteristics of the fractions. In addition, at the end of this section, the possibility of isolating or purifying individual components will be discussed in terms of the three types of systems.

PP–EP Type

Figures 2 and 3 show the cumulative weight distribution curves as a function of ethylene content and molecular weight, respectively. The curves with ethylene content as the abscissa have a characteristic convex shape. Also, it should be noted that the curve obtained even in the case of a sample of low $\bar{E}$ (EPA-3) shows a broad distribution and, in this respect, is fundamentally different from EP.

The curves as a function of molecular weight at the higher ratios of EP to PP (EPA-1 and EPA-2) are similar to those for the homopolymers, but for the lower ratios of EP (EPA-3) they show a reversal; that is, the curves show behavior identical to that of the blend PE–PP.[2]

As shown in Figure 4, the standard deviation of the ethylene content shows a maximum for intermediate fractions. Also in this case, since the standard deviation generally shows high values, sufficient composition fractionation can be expected only in the higher molecular weight regions. As shown in Figure 5, the molecular weight distributions of the fractions are generally broad, having $\bar{M}_w/\bar{M}_n$ values in the range of 2 to 3. Accordingly, we can distinguish the PP–EP type from pure EP or PE–PP by using figures of this kind, although precise experimental data are needed.

PP–EP–PE Type

Figures 6 and 7 show the cumulative weight distribution curves. The behavior in these three component types is extremely complicated. Only a few examples are shown here. The curves obtained at low ratios of EP

TABLE I
Assumed Characteristic Parameters for the Components in the Products

Type of blend	Simulation no.	Weight ratios			PP		EP					PE	
		PP	EP	PE	β_P^a	$\ln M_P^b$	β_α	α_0	β_M	$\ln M_{EP}$	ρ	β_E^a	$\ln M_E^b$
PP–EP	EPA-1	0.2	0.8	0.0	1.25	12.0	0.362	0.435	1.25	12.0	0.25	—	—
	EPA-2	0.4	0.6	0.0	1.25	12.0	0.362	0.435	1.25	12.0	0.25	—	—
	EPA-3	0.8	0.2	0.0	1.25	12.0	0.362	0.435	1.25	12.0	0.25	—	—
PP–EP–PE	EPB-1	0.4	0.2	0.4	1.25	12.0	0.362	0.435	1.25	12.0	0.25	1.25	11.0
	EPB-2	0.4	0.3	0.3	1.25	12.0	0.362	0.435	1.25	12.0	0.25	1.25	11.0
	EPB-3	0.2	0.6	0.2	1.25	12.0	0.362	0.435	1.25	12.0	0.25	1.25	11.0
	EPB-4	0.2	0.6	0.2	1.25	12.0	0.100	0.435	1.25	12.0	0.25	1.25	11.0
	EPB-5	0.2	0.6	0.2	1.25	12.0	0.700	0.435	1.25	12.0	0.25	1.25	11.0
EP–PE	EPC-1	0.0	0.6	0.4	—	—	0.362	0.435	1.25	12.0	0.25	1.25	11.0
	EPC-2	0.0	0.3	0.7	—	—	0.362	0.435	1.25	12.0	0.25	1.25	11.0
	EPC-3	0.0	0.8	0.2	—	—	0.362	0.435	1.25	12.0	0.25	1.25	11.0
PE–PP	EPD-1	0.54	0	0.46	1.25	12.0	—	—	—	—	—	1.25	11.0

a In eq. (1), it corresponds to β_A.
b In eq. (1), it corresponds to $\ln M_0$.

TABLE II
Characteristic Values for the Hypothetical Products

| Type of blend	Simulation no.	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	Ethylene, wt-%	S.D.[a]
PP–EP	EPA-1	7.91	35.7	4.51	37.6	28.9
	EPA-2	7.83	35.6	4.55	28.2	29.8
	EPA-3	7.66	35.6	4.65	9.4	21.7
PP–EP–PE	EPB-1	4.76	26.6	5.59	49.4	46.0
	EPB-2	5.28	28.9	5.47	44.1	43.6
	EPB-3	5.96	31.2	5.24	48.2	36.9
	EPB-4	5.83	31.1	5.33	46.1	32.7
	EPB-5	5.99	30.7	5.12	49.4	37.8
EP–PE	EPC-1	4.82	26.7	5.54	68.2	32.1
	EPC-2	3.72	19.9	5.35	84.1	27.7
	EPC-3	7.01	30.1	4.29	57.6	30.5
PE–PP	EPD-1	4.48	25.2	5.62	46.0	49.8

[a] Standard deviation of ethylene content (%).
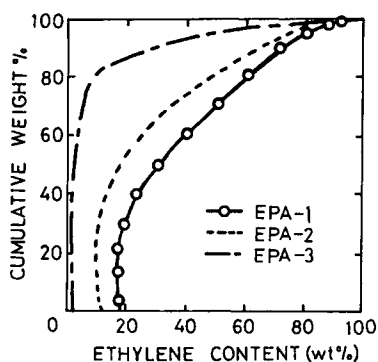
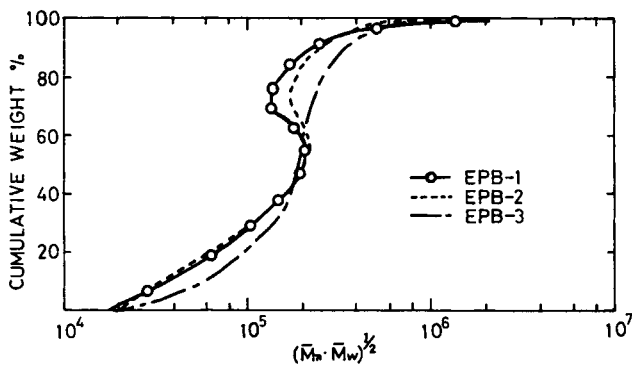Fig. 2. Cumulative weight distribution curves as a function of ethylene content; PP–EP type.
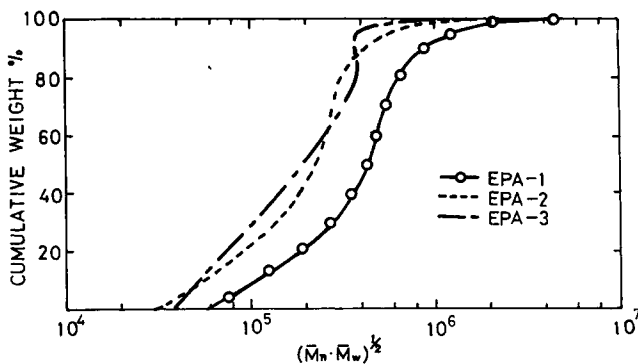
Fig. 3. Cumulative weight distribution curves as a function of molecular weight; PP–EP type.
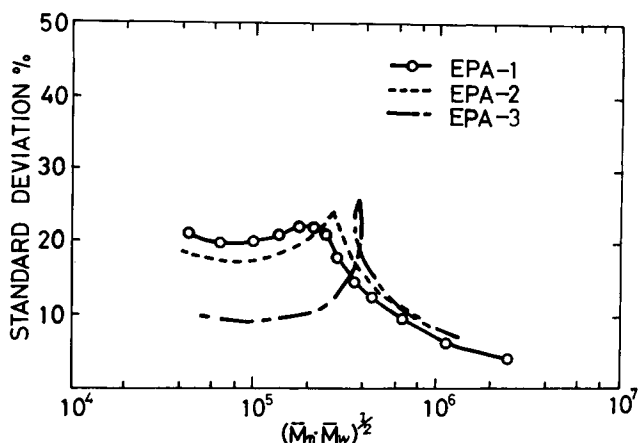
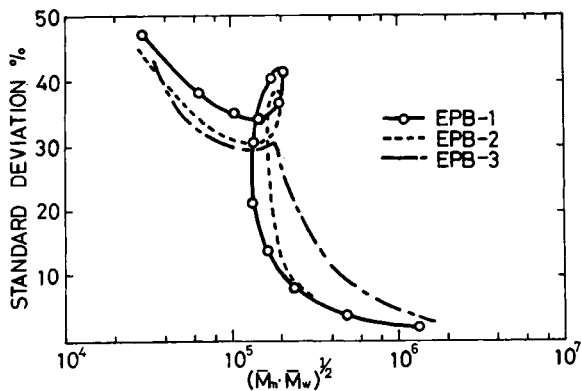Fig. 4. Standard deviation of the ethylene content of the fractions; PP–EP type.
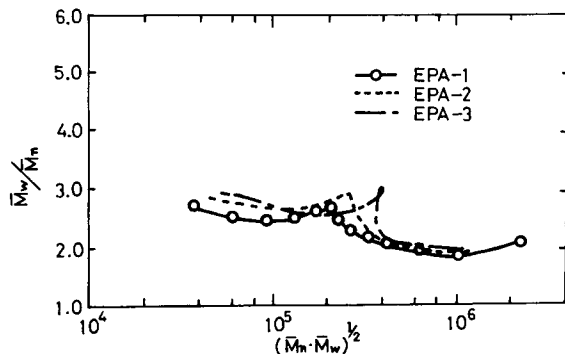
Fig. 5. $\bar{M}_w/\bar{M}_n$ of the fractions; PP–EP type.

to homopolymers (EPB-1 and EPB-2) are similar to those for PE–PP or PP–EP. The sample EPB-3, which contains relatively large amount of EP component, is similar to EP.

As shown in Figure 8, the behavior of the standard deviation of the ethylene content is similar to that of pure EP, and composition fractionation can be expected in the higher molecular weight regions, namely, in the latter half of the fractionation steps.   In Figure 9, the maximum in the $\bar{M}_w/\bar{M}_n$ curves, at about $(\bar{M}_n \cdot \bar{M}_w)^{1/2} = 2.0 \times 10^5$, is very striking; maxima of this type seem to be a very characteristic feature of blended materials.   That is, the amount of polyethylene showing lower molecular weight increases in the fractions, with a decrease in the amount of polypropylene showing higher molecular weight.

In addition, the analysis was carried out for products which contain an EP component having either narrower or broader composition distributions than those discussed above, and the results are shown in Figures 10 and 11.   These analyses correspond to Figures 6 and 7.   It should be noted
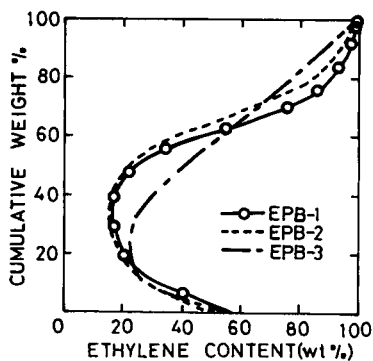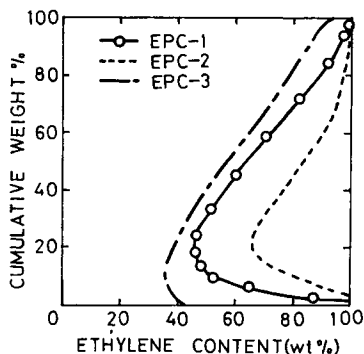
Fig. 6. Cumulative weight distribution curves as a function of ethylene content; PP–EP–PE type.

Fig. 7. Cumulative weight distribution curves as a function of molecular weight; PP–EP–PE type.

Fig. 8. Standard deviation of the ethylene content of the fractions; PP–EP–PE type.
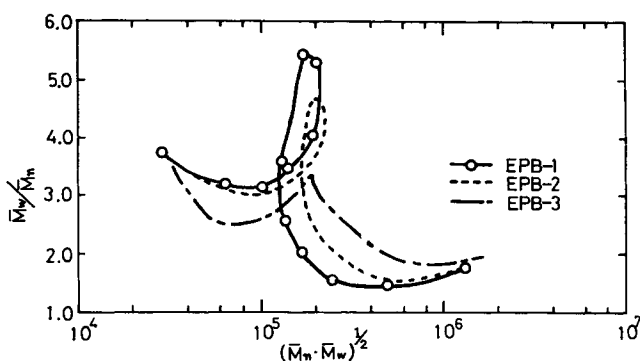
Fig. 9. $\bar{M}_w/\bar{M}_n$ of the fractions; PP–EP–PE type.
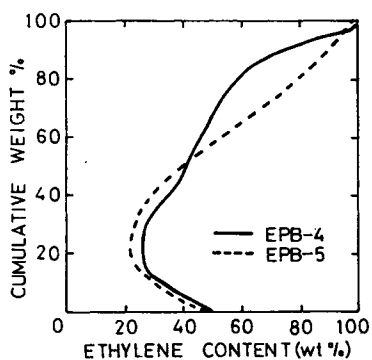
Fig. 10. Cumulative weight distribution curves as a function of ethylene content; PP–EP–PE type. These curves were obtained from products which contain an EP component with either a narrower or a broader composition distribution than in the previous figures.
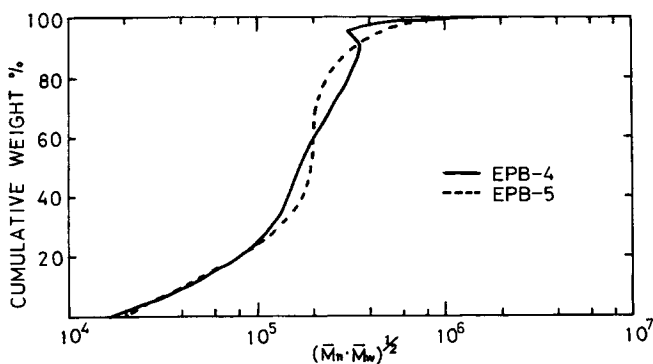
Fig. 11. Cumulative weight distribution curves as a function of molecular weight; PP–EP–PE type. The characteristics of the products are the same as those shown in Fig. 10.

that a change in distribution only causes a complex variation in the cumulative weight distribution curves. Especially, in the case of a narrower composition distribution of the EP component (EPB-4), the occurrence of a reversal is very striking in Figure 11. Thus, since the behavior of the three-component types is very complex, one needs very accurate data to investigate the nature of unknown samples.

EP–PE Type

The results for EP–PE type are shown in Figures 12 to 15. The curves generally resemble those for pure EP. However, the cumulative weight distribution curve in EPC-2 with high $\bar{E}$ (Fig. 12) shows appreciable curvature, while the curve for pure EP lies approximately parallel to the ordinate.[1] Therefore, this pattern may be useful for distinguishing between EP–PE and pure EP. The cumulative weight distribution-versus-molecular weight curves are not distinctive. Figure 14 shows that a fair extent of composition fractionation can be attained in the higher molecular weight regions. The molecular weight distributions of fractions

Fig. 12. Cumulative weight distribution curves as a function of ethylene content; EP–PE type.
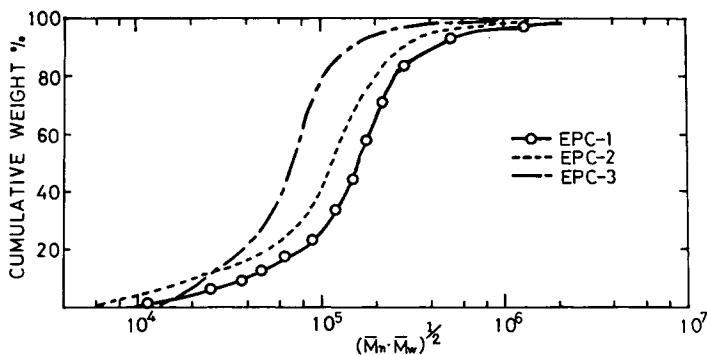

Fig. 13. Cumulative weight distribution curves as a function of molecular weight; EP–PE type.
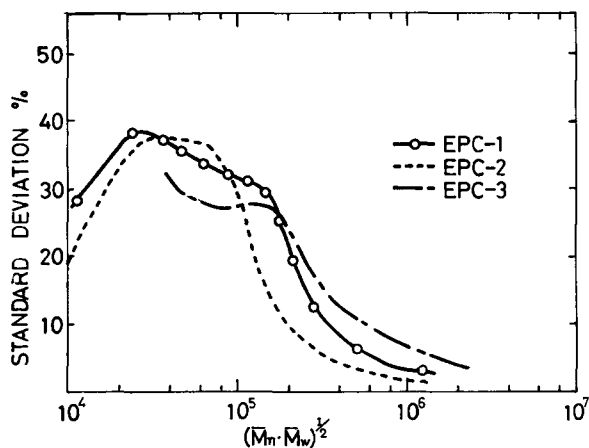
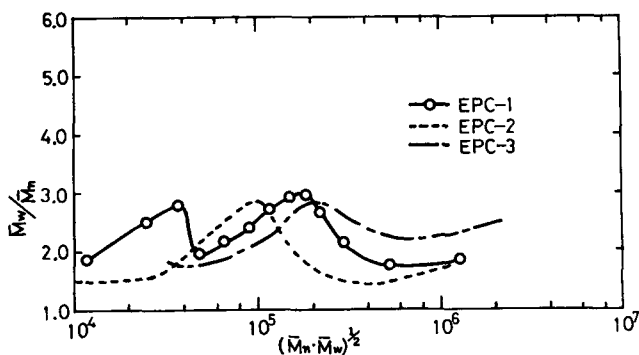Fig. 14. Standard deviation of the ethylene content of the fractions; EP–PE type.

Fig. 15. $\bar{M}_w/\bar{M}_n$ of the fractions; EP–PE type.

shown in Figure 15 do not vary with molecular weight and, therefore, very satisfactory molecular weight fractionation cannot be expected.

Elution Behavior

The elution curve for the products is usually expressed as the sum of the curves for the components. In the case of pure polymers, the elution curves show the following peaks: PP at 15% decalin, PE at 34% decalin, and EP at 26% decalin.[2]

Examples for the products are shown in Figure 16. The curve for EPA-1, the main component of which is EP, exhibits a peak at 22% decalin. In the curve for EPB-1, two peaks are observed, at 14% and 35% decalin, corresponding to PP and PE, respectively. In the case of EPC-1, being in the ratio of 6:4 for EP to PE, the peak appears at 31% decalin, which corresponds to an intermediate point between EP and PE. Thus, an elution curve will probably be useful in determining the components.
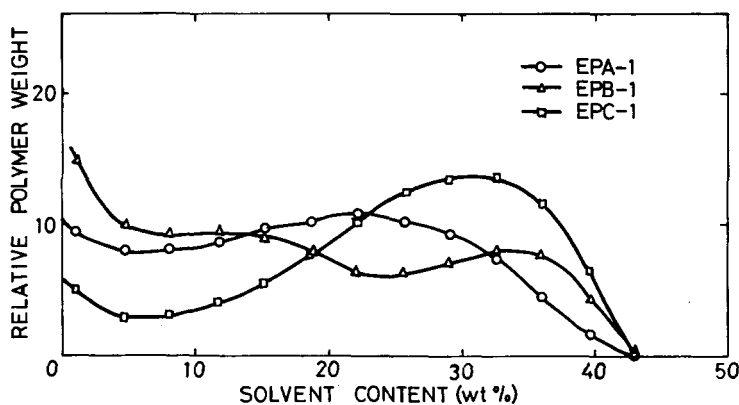
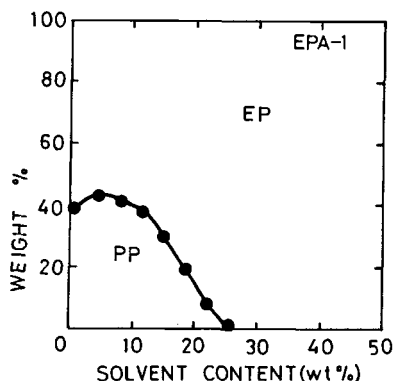Fig. 16. Elution behavior in terms of polymer weight.

Fig. 17. Ratios of the components of the fractions; PP–EP type.

However, one should note that these curves are sensitive to some extent to the method of applying the solvent gradient.

Next, the use of fractionation as a preparative tool will be discussed. In homopolymers, the conditions required for carrying out a satisfactory preparation are generally related to the technical problem of attaining a large amount of material, and also, in the case of copolymerization products, with the problem of further isolation of the components.

The per cent ratios of the components in the polymer eluted were plotted against the decalin concentration, as shown in Figures 17 to 20. In the PP–EP type (Fig. 17), two components, i.e., PP and EP, were simultaneously eluted up to 25% decalin. The EP component only was eluted at a high decalin concentration, and therefore one can obtain the isolation of pure EP in this case. In the PP–EP–PE type (Fig. 18), three components are always present in the polymer eluted at any given per cent decalin. The behavior of the components in the EP–PE type (Fig. 19) is analogous to the situation described above. In the PE–PP type (Fig. 20, obtained from the data in a previous work[2]), the behavior is very similar to that of the PP–EP type, and the PE component can be isolated. A

summary of the possibilities for isolating the various components is shown in Table III.   One sees that, in general, purification is very difficult, and in only two cases, i.e., PP–EP and PE–PP, can one separate a pure component.
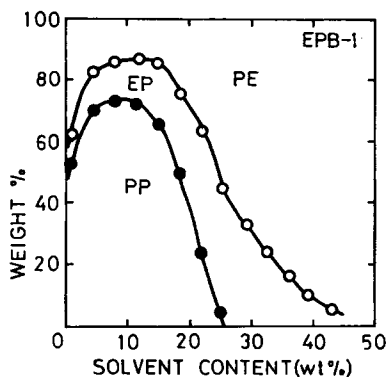

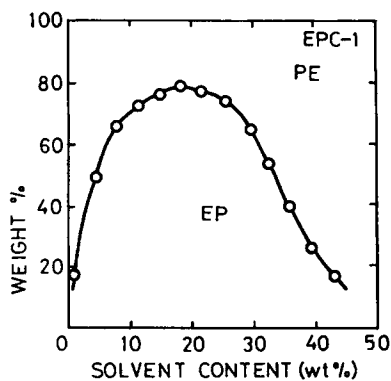Fig. 18. Ratios of the components of the fractions; PP–EP–PE type.

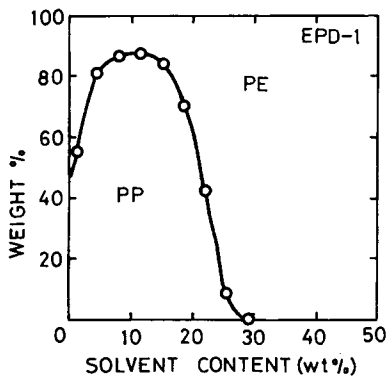Fig. 19. Ratios of the components of the fractions: EP–PE type.

Fig. 20. Ratios of the components of the fractions; PE–PP type.

However, the same conclusion cannot be applied to products constituted of components of narrow composition or of narrow molecular weight distributions. In this case, isolation of pure components becomes easier, although the ease of the separation depends on the breadth of the distributions. This is clear from the curves of cloud point versus molecular weight, as described elsewhere.[3]

APPLICATIONS

Sample EPA

When the different kinds of patterns described above are used together with those for the EP[1] or PE-PP[2] type, the ratios of the amount or the characteristics of the components in an unknown sample can be deduced. The cumulative weight distribution curves obtained experimentally are shown in Figures 21 and 22. The curves were compared with those obtained from a simulation based on EP, PE-PP, and PP-EP. It is clear from Figures 21 and 22 that the curves for both composition and molecular weight are not in agreement with the curves calculated for EP. Furthermore, in the case of the PE-PP type, the difference between the experimental and simulated curves exceeds the estimated experimental errors, and therefore the sample must not be of the PE-PP type.

The simulated curve most similar to the experimental data is of the PP-EP type. Here, the PP-EP-PE type may be needed, but even if the

TABLE III
Possibility of Isolating Individual Components

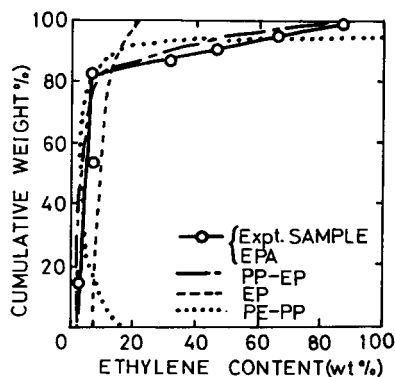| Type of blend	Isolation of PP or PE	Isolation of EP
PP-EP	impossible	possible
PP-EP-PE	impossible	impossible
EP-PE	impossible	impossible
PE-PP	possible (PE)	—

Fig. 21. Cumulative weight distribution curves as a function of ethylene content. Experimental data (sample EPA) and simulated curves.

sample contains the PE component, it will include less PE than EP. This may be seen in Figures 21 and 22. Therefore, sample EPA is thought to be composed of PP and EP.

Sample EPB

The cumulative weight distribution curves are shown in Figures 23 and 24. The curves do not coincide with any curve obtained from a simulation based on EP or PE–PP blends, even though the parameters were varied over wide ranges. Further, the experimental curves are fundamentally different from those simulated by the PP–EP or EP–PE analysis, which are shown in Figures 2, 3, and 12 to 15. Finally, this sample was considered to be of the PP–EP–PE type.

Therefore, the simulated results for different ratios of PP, EP, and PE components must, in the first analysis, be compared with experimental
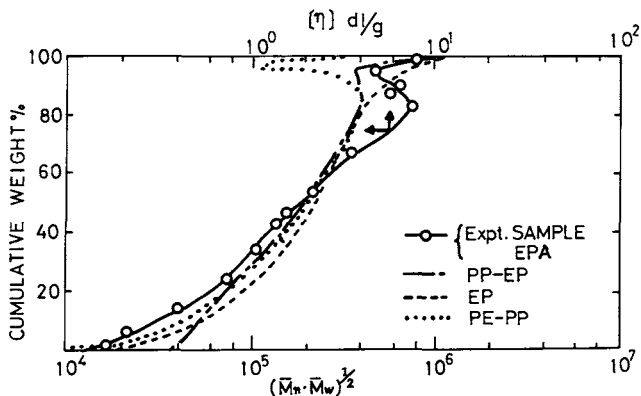

Fig. 22. Cumulative weight distribution curves as a function of molecular weight or limiting viscosity number. Experimental data (sample EPA) and simulated curves.
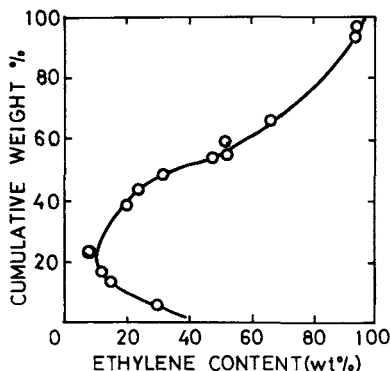

Fig. 23. Cumulative weight distribution curve as a function of ethylene content. Experimental data (sample EPB).
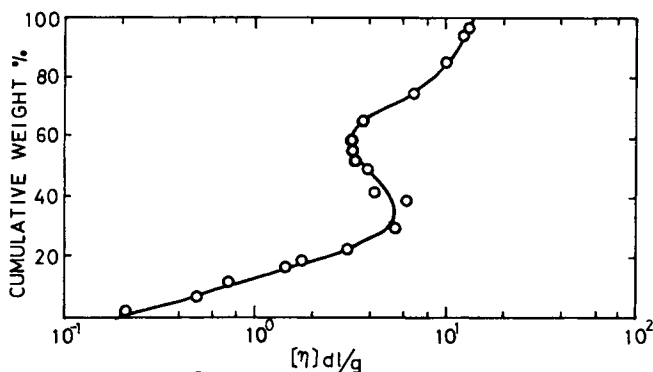
Fig. 24. Cumulative weight distribution curve as a function of limiting viscosity number. Experimental data (sample EPB).

data. In this case, as the $\bar{E}$ of the sample is already known, the ratios of the components can be estimated to a certain extent. A detailed comparison of the results for the hypothetical product shows reasonable agreement with the experimental data, that is, in the ratio 4:2:4 or 4:3:3. Finally, sample EPB is estimated to be composed of PP, EP, and PE in the ratio 4:2–3:4–3.

CONCLUSIONS

The behavior of solution fractionation, as related to ethylene–propylene copolymerization products, was examined by computer simulation. The products were classified into five types, i.e., EP, PE–PP, PP–EP, PP–EP–PE, and EP–PE, with the latter three types being the main ones treated in this paper.

The behavior varies in a complicated way with respect to the kinds and ratios of components. Although the determination of components in the present work is more difficult than distinguishing between pure EP and PE–PP,[1,2] such an analysis can be made if the results are studied from several points of view. From the present work, one can understand the results in terms of blends of the copolymers and the homopolymers, even though they could not be understood in terms of pure EP or PE–PP blends.

Finally, some discussion is presented for using solution fractionation as a means for separating products in the decalin–butyl carbitol (or similar) system into pure components. It was concluded that such a separating is usually impossible, except possibly for two cases.

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