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Analysis on the Fractionation of Polyethylene–Polypropylene Blends

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Synopsis

The hypothetical fractionation of polyethylene–polypropylene blends was carried out by assuming adequate molecular weight distribution and partition of polymer between two liquid phases for each homopolymer, and also by using the previously reported data of the molecular weight dependence on solubility. The experimental fractionation of blends was also carried out by the solvent gradient method, and the results were compared with those obtained by the hypothetical fractionation. Both results agreed fairly well in various distribution forms. Therefore, these results may provide valuable information for component or compositional analysis of unknown samples or copolymerization products.

INTRODUCTION

Homopolymers are generally incorporated more or less in copolymerization products. However, at the present stage, the complete separation of the products into homogeneous polymer species is impossible by the usual fractionation methods. Furthermore, it is practically not so easy even to distinguish pure copolymers from the products only by the experimental method. This is due to the fact that homopolymers, which are components of the products, have a molecular weight distribution, and that copolymers, which are also components of the products, have molecular weight and compositional distributions. Therefore, in the characterization of polymers it is a very extensive subject to establish the method for distinguishing copolymers from polymer blends.

Now, considering blended systems composed of ethylene–propylene copolymers (EP) and their homopolymers such as polyethylene (PE) and polypropylene (PP), these systems can be classified into the following four types: EP–PE, EP–PP, PE–EP–PP, and PE–PP. Though analysis is required for all blended systems to elucidate the composition of copolymerization products, PE–PP blends were taken up in this report, since this type is the most simple and representative of these four types.

The authors have already reported on the fractionation behavior of pure EP.[1] In this report, the behavior of PE–PP blends for solution fractionation were investigated by simulation and experiment. The difference in fractionation behavior between copolymers and homopolymer blends will be clarified through these investigations.

CALCULATIONS

The three factors, molecular weight distribution of the original polymer, solubility, and partition of polymer between two liquid phases, are required for hypothetical fractionation similar to the case of EP. With respect to these factors, adequate assumptions were made as follows. First, log normal distribution function, as expected by eq. (1), was adopted for the molecular weight distribution of original polymers by considering previously reported data[2-5]:

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

where $W(\ln M)$ is the weight distribution function, β is the standard deviation for $\ln M$, and $\ln M_0$ is the peak position in the log normal distribution curve.

Concerning the solubility of polymers, the relationships between molecular weight and cloud point were applied. Those for PP have already been given by eq. (2) or (3), as described in a previous paper[6]:

$$M = 10^4(0.57 - 2.79X)^{-2} \tag{2}$$

$$M = 10^4(1.47 - 3.25X)^{-2} \tag{3}$$

where eqs. (2) and (3) are for decalin–butyl carbitol and decalin–ethyl carbitol systems, respectively, and X is the weight fraction of solvent in the eluent. Similar relationships, as shown in eqs. (4) and (5), were used for polyethylene, which were estimated from the previous experimental results[6]:

$$M = 10^4\{[0.57 - 2.79(X - 0.22)]^{-2} + 0.83\} \tag{4}$$

$$M = 10^4\{[1.47 - 3.25(X - 0.19)]^{-2} + 0.24\} \tag{5}$$

where eqs. (4) and (5) are for decalin–butyl carbitol and decalin–ethyl carbitol systems, respectively. In addition, since these relationships are in liquid–liquid phase equilibrium, cloud point approximately corresponds to solubility point and in which equilibrium solubility of polymer is not generally influenced by coexistence of polymer. Therefore, the same relationships can be applied to the mixture of PE and PP described in this paper.

Concerning the partition of polymer between two liquid phases, the following well-known equation was used, which was derived from the Flory-Huggins theory[8]:

$$f_E = \frac{R}{R + \exp(\sigma \cdot \gamma)} \cdot f_R \tag{6}$$

where f_E and f_R are the volume fraction of γ-mer in the dilute phase and in the original polymer, respectively; R is the ratio of the volume of dilute phase to that of concentrated phase, and the value of 200 was ordinarily chosen; γ is the degree of polymerization in the case of polyethylene, while in polypropylene it corresponds to that of polyethylene which gives the same cloud points as polypropylene at a given solvent concentration; and σ is the partition coefficient between two liquid phases and was determined at each fractionation step (X) from eqs. (4) and (6) or (5) and (6), on the assumption that f_E/f_R = constant (Q), for which 0.5 was ordinarily applied.

On hypothetical fractionation, the distribution function was divided into 40 parts in ln M ranging from 8 to 18 ($\Delta \ln M = 0.25$). For each part, the fractionation was performed according to eqs. (2), (4), and (6) or eqs. (3), (5), and (6). Other procedures are the same as reported previously.[1]

EXPERIMENTAL

Fractionation. Sample A was prepared by blending commercial PE and PP in the ratio of 45:55; a 5-g sample was fractionated by the solvent gradient method at 161°C in decalin–ethyl carbitol system. Sample B was prepared in heptane by introducing propylene, hydrogen, and ethylene in order in the presence of $AlEt_2Cl$–$TiCl_3$ (activated), and the ethylene content in the product was 31 wt-%. A 40-g sample was fractionated at 161°C in decalin–butyl carbitol system. Details of the fractionation procedure are the same as described elsewhere.[5]

Characterization. The limiting viscosity numbers of the fractions were determined at 135°C for decalin solution with an Ubbelohde-type viscometer. Ethylene content of fractions was determined by Corish's method, which is based on using the ratio of the intensity at 1380 cm^{-1} to that at 1460 cm^{-1} in infrared spectra.[7,9] A Shimadzu GPC Model 1A was employed with a combination of four columns, i.e., crosslinked polystyrene gel of 1×10^6, 1×10^5, 1×10^4 and 1×10^3 Å permeability. *o*-Dichlorobenzene was used as solvent at 135°C. Other experimental conditions were the same as reported previously.[6]

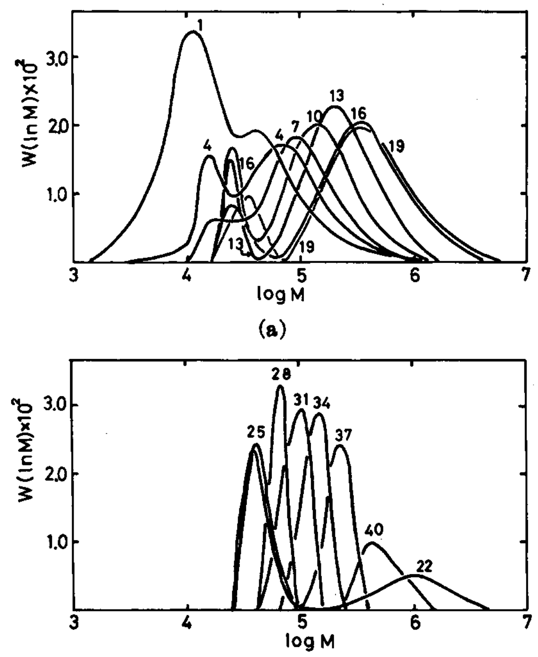
RESULTS AND DISCUSSION

Fractionation Behavior

Simulation of fractionation (hypothetical fractionation) was carried out in decalin–butyl carbitol and decalin–ethyl carbitol systems, and both systems fundamentally led to almost the same results. Thus, the fractionation results in the decalin–butyl carbitol system will be mainly described here. Furthermore, the results will be discussed below, comparing them with those for EP[1] at the same time.

The fractions in this system gave the characteristic molecular weight distribution curves shown in Figure 1. The curves of the fractions obtained by eluent of 1% to 22% in decalin indicate the two peaks, i.e., one in a lower molecular weight region, which arises from the polyethylene part, and the other in a higher molecular weight region, which arises from the polypropylene part. Fractions obtained by higher concentrations show a peak due to PE only, because PP has already been eluted completely.

As shown in Figure 2, $\bar{M}_w/\bar{M}_n$ of the fractions also varies abnormally according to above fractionation behavior. In other words, $\bar{M}_w/\bar{M}_n$ in intermediate fractions shows extremely high values, while in the latter half of the fractions, it shows a value under 2.0, as in the case of homopoly-



(a)

(b)

Fig. 1. Molecular weight distribution curves for fractions (hypothetical fractionation). Numbers indicate per cent decalin in eluent. Character of the original polymer is: PE, ln M_0 = 10.8, β = 1.25; PP, ln M_0 = 12.0, β = 1.25; PE:PP = 45:55 (wt).

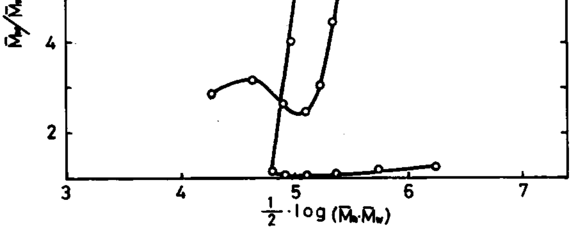


Fig. 2. $\bar{M}_w/\bar{M}_n$ for fractions obtained from original polymer showing 45 wt-% in ethylene content (hypothetical fractionation).

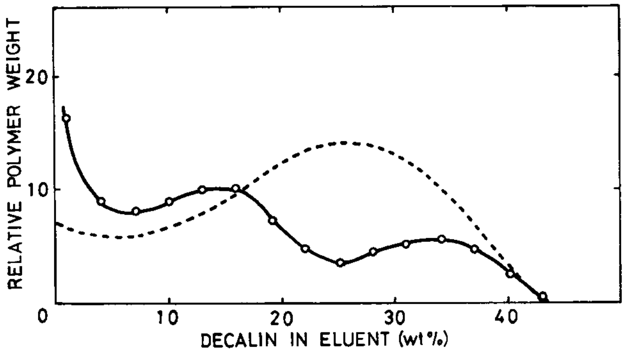


Fig. 3. Elution behavior concerning polymer weight (hypothetical fractionation): (———) blends; the character is the same as that shown in Fig. 1; (– – – – – – – –) copolymers, ethylene content of original polymer = 48 wt-%.[1]

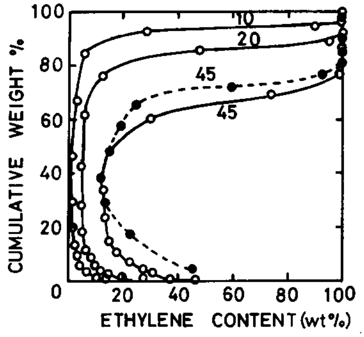


Fig. 4. Cumulative weight distribution curves vs. ethylene content (hypothetical fractionation). Numbers indicate ethylene content of original polymer by weight: (– – –●– –) decalin–butyl carbitol system; (——O——) decalin–ethyl carbitol system.

mers.[6] Such characteristic pattern could not be detected in the simulation for EP.[1] Therefore, it is expected to distinguish homopolymer blends from copolymers by applying such behavior.

Some other characteristic patterns will be discussed below. Figure 3 shows the elution behavior concerning polymer weight. Two peaks were observed in the blends. One at a concentration of 15% decalin, was assigned to PP and another, at 34% decalin, to PE, but only one peak was observed in the case of EP.

Next, the distribution of the original polymer was evaluated in cumulative form. The cumulative weight distribution curve against ethylene content is shown in Figure 4, which was drawn by Shulz's method.[10] Remarkable variations of ethylene content in fractions were observed at around 70% cumulative weight in the base of blends (45 wt-% PE). Furthermore, as shown in Figures 4 and 5, since such a pattern was kept even in the simulation of the original polymer with other ethylene content and also confirmed in experiment, this is concluded to be the characteristic of blends.

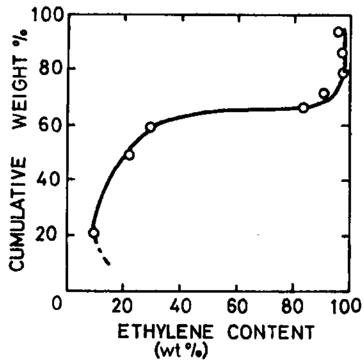


Fig. 5. Cumulative weight distribution curve vs. ethylene content obtained in decalin-ethyl carbitol system (experimental fractionation). Sample A, ethylene content of original polymer = 45 wt-%.

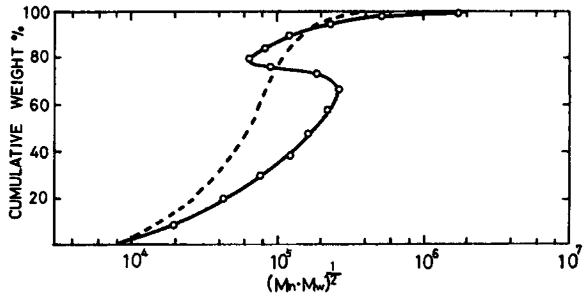


Fig. 6. Cumulative weight distribution curves vs. molecular weight (hypothetical fractionation): (———) blends; the character is the same as that shown in Fig. 1; (– – – – –): copolymers, ethylene content = 48 wt-%.

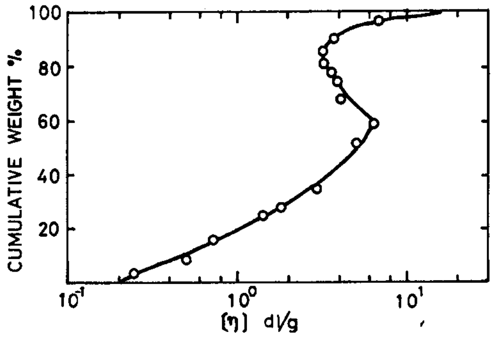


Fig. 7. Cumulative weight distribution curve vs. limiting viscosity number (experimental fractionation). Sample A.

As evident in Figures 6 and 7, the occurrence of the reversal was observed in the cumulative weight distribution curve against molecular weight, or limiting viscosity number while such a pattern could be observed neither in simulation nor in experiment in the case of EP. And also, as shown in Figure 4, it is evident that the reversal corresponds to the inflection point from the PP-rich fraction to the PE-rich fraction. Therefore, these patterns are concluded to be very useful for identification of homopolymer blends.

Example

Valuable information for the elucidation of polymer components and composition is obtained by such patterns in various forms as described above and also in connection with the results for EP. The unknown sample in the component (sample B) was fractionated in decalin–butyl carbitol system. The results are shown in Figures 8 to 11 and were evaluated concerning the components as follows. Experimental results such as elution behavior (Fig. 8) and cumulative weight distribution curves (Figs. 9 and 10) were in good agreement with those of simulation for blends. However, GPC curves shown in Figure 11 did not indicate two clear peaks, while in simulation the molecular weight distribution curves for most fractions had two peaks. This is due to the fact that the calibration curve for PE in GPC is situated in lower counts than that for PP.[7] Details concerning this will be described in another paper.

In this sample, other system, i.e., PE–EP–PP, may also be taken into consideration. However, the fractionation behavior in this system was

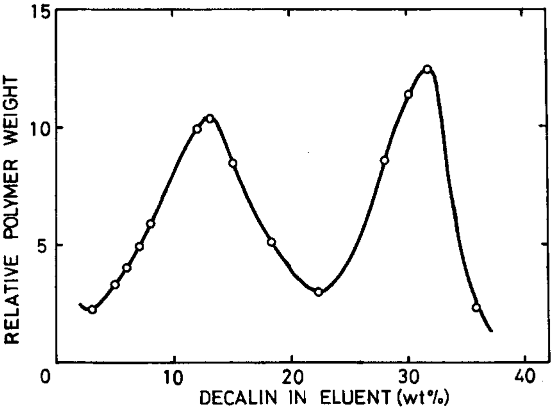


Fig. 8. Elution behavior concerning polymer weight (experimental fractionation). Sample B.

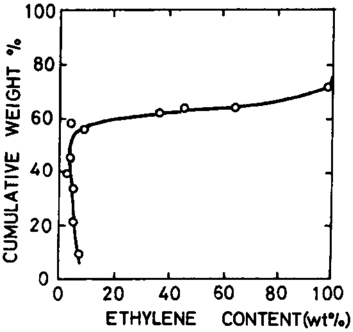


Fig. 9. Cumulative weight distribution curve vs. ethylene content (experimental fractionation). Sample B.

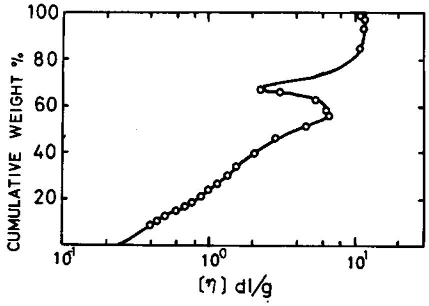


Fig. 10. Cumulative weight distribution curve vs. limiting viscosity number (experimental fractionation). Sample B.

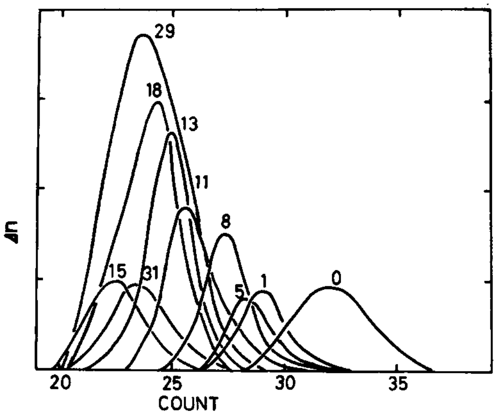


Fig. 11. GPC curves for fractions (experimental fractionation). Sample B. Numbers indicate per cent decalin in eluent.

substantially different from that in Figures 8 to 11, especially from that of Figure 9. Details concerning this will be described elsewhere because more cases that differ from PE–PP must be discussed. Thus, it is estimated that this sample consists of PE and PP, but does not contain EP.

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