

## Fractionation of Polypropylene by the Rising Temperature Method

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### Synopsis

Polypropylene having high isotacticity was fractionated by the rising temperature method. This method was then compared with the solvent gradient method through the characterization of fractions. It was found that the elution behavior in the rising temperature method was explainable by the equation of equilibrium between the polymer in dilute solution and the solid state polymer on the support, assuming that the heat of fusion and transition points for the deposited polymer were variable with polymer species.

### INTRODUCTION

Polypropylene having high isotacticity is generally fractionated by two column methods. One is the solvent gradient fractionation at a given temperature, the other is the rising temperature fractionation with a fixed solvent or a solvent-nonsolvent mixture. Considering these methods from the phase diagram viewpoint, the former belongs to the liquid-liquid phase equilibrium system and the polymer dissolves only according to molecular weight, because the solubility is almost independent of tacticity in these systems.<sup>1,2</sup> The latter method belongs to the solid-liquid phase equilibrium system, and it is expected that the polymer dissolves according to tacticity, because the free energy of fusion is closely related to the dissolution temperature.<sup>3,4</sup>

Fractionation of polypropylene by the rising temperature method was first reported in detail by Wijga et al.<sup>5</sup> The same types of experiments were also performed by other investigators.<sup>6-9</sup> Concerning the fractionation mechanism of this method, however, no proper study has been done. Thus, in this paper, the fractionation behavior was investigated from the thermodynamic point of view.

### THEORETICAL

A schematic representation of the polymer deposited onto the support is shown in Figure 1.<sup>10</sup> Each fractionation step in the rising temperature method represents the process of the dissolution of polymer from solid to eluent at a given temperature. We therefore must know the properties

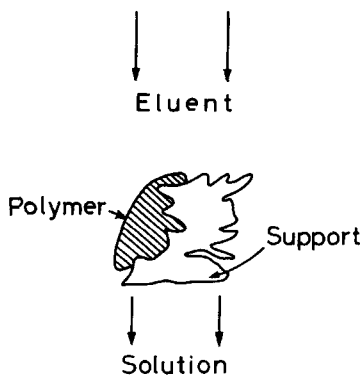


Fig. 1. Schematic representation of polymer deposited onto the support.

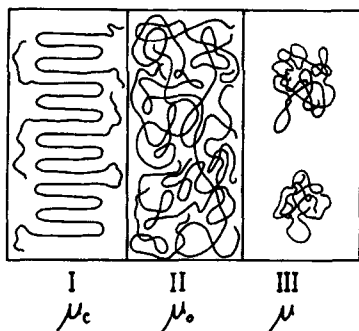


Fig. 2. Three polymer states for thermodynamic study: (I) imperfect crystal ( $\mu_c$ ); (II) melt (standard state) ( $\mu_o$ ); (III) dilute solution ( $\mu$ ).

of the solid and solution state of the polymers. The two phases and the standard state needed for thermodynamic study are schematically indicated in Figure 2, where the quantities  $\mu_c$ ,  $\mu_o$ , and  $\mu$  are the chemical potential per structural unit mole of imperfect crystal (I), melt (II), and dilute solution (III), respectively.

The treatment of the solid state is very important in discussing this fractionation. It is recognized by many investigators that crystalline lamellae are the basic structural elements of crystalline polymers. However, we cannot find any perfect crystals in actual polymers because of the presence of defects.<sup>11</sup> Furthermore, since the polymer is in solvent during the actual fractionation, it cannot be dealt with briefly.<sup>10,12</sup> However, in this experiment, to simplify the mechanism, the solid state polymer in solvent was assumed to be the same as the imperfect crystal in the solvent-free state. Model II in Figure 2 shows the melt of the polymer, and it is then defined as the standard state. Model III shows the dilute solution and also corresponds to the solution in Figure 1.

When the column fractionation is carried out at a given temperature, ( $T$ ) the chemical potential of the solid state polymer has to be equal to that of

the dissolved polymer, and this is expressed in eq. (1). At a certain temperature,  $\mu_c$  becomes equal to  $\mu_0$  as expressed in eq. (2), and this temperature is defined as the transition point ( $T_m$ ) of the deposited polymer:

$$\mu_c - \mu = (\mu_c - \mu_0) + (\mu_0 - \mu) = 0 \quad (1)$$

$$\mu_c - \mu_0 = -(\Delta H_u - T_m \Delta S_u) = 0 \quad (2)$$

where  $\Delta H_u$  and  $\Delta S_u$  are heat and entropy of fusion per unit mole, respectively. According to Flory's equation for dilute solution of polymer,<sup>13</sup> eq. (1) can be expressed as

$$(1/T) - (1/T_m) = \frac{R}{\Delta H_u} \times \frac{V_u}{V_1} \times \left\{ \left(1 - \frac{1}{X}\right) v_1 - \frac{BV_1}{RT} v_1^2 - \frac{\ln(1 - v_1)}{X} \right\} \quad (3)$$

where  $V_u$  is the molar volume of structural unit mole,  $V_1$  is the molar volume of solvent,  $X$  is the ratio of the molar volume of polymer to that of solvent,  $v_1$  is the volume fraction of solvent, and  $B$  is the thermodynamic interaction parameter for polymer-solvent systems.<sup>14</sup> In this work, it is assumed that  $\Delta H_u$  is not confined to the value for a perfect crystal. In this respect, this equation is different from Flory's equation. Furthermore,  $\Delta H_u$  and  $\Delta S_u$  are assumed to be independent of temperature in deriving eq. (3).

## EXPERIMENTAL

### Apparatus

The apparatus for the rising temperature fractionation consists of a column and an oil bath, as shown in Figure 3. The lower part of the column was packed to a height of 5 cm with coarse particles of sea sand (40–80 mesh), and then the column was packed with Celite to a height of 30 cm, on which the polymer had been deposited. The top of the column was filled with glass fiber. The apparatus for the solvent gradient fractionation is the same as that described in the previous paper.<sup>15</sup>

### Fractionation

An outline for the rising temperature fractionation is as follows. Five grams of commercial polypropylene (M.F.I. = 5.4) was used. The polymer was dissolved in a decalin (269 g)-butyl carbitol (115 g) system. The solution was poured into Celite heated to 160°C, and the polymer was deposited on it by cooling.<sup>15</sup> Fractionation was started from 30°C with decalin, and the column temperature was raised in increments. A change-over to a higher temperature setting was made after the eluent failed to show turbidity in excess acetone.<sup>5</sup>

An outline for the solvent gradient fractionation is as follows. Polymer deposition was carried out in the same way as the rising temperature

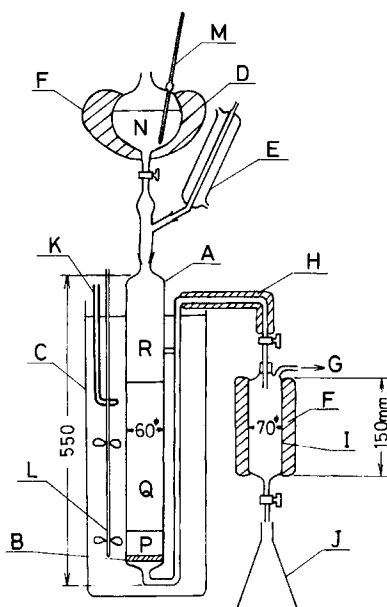


Fig. 3. Apparatus: (A) Column body; (B) sintered glass (No. 4); (C) oil bath; (D) eluent reservoir; (E) reflux condenser; (F) heating mantle; (G) aspirator; (H) band heater; (I) adapter; (J) flask; (K) heater; (L) stirrer; (M) thermometer; (N) eluent; (P) sea sand (40–80 mesh); (Q) Celite, on which polymer deposited; (R) glass fiber.

method. After the column was filled with Celite on which the polymer had been deposited, the fractionation was carried out at 161°C in a decalin-ethyl carbitol system. Other conditions are the same as those described in the previous paper.<sup>15</sup>

### Differential Scanning Calorimetry (DSC)

Fractionated samples were dissolved in hot decalin-ethyl carbitol. The solution was cooled to room temperature and allowed to precipitate. The precipitate obtained in such a way is regarded to be in the same crystalline

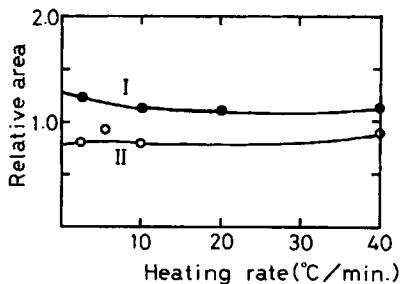


Fig. 4. Effect of heating rate on the relative area under the DSC curve: (I) (peak area in  $M = 5.96 \times 10^6$ )/(peak area in  $M = 2.07 \times 10^6$ ); (II) (peak area in  $M = 8.09 \times 10^6$ )/(peak area in  $M = 5.96 \times 10^6$ ).

state as when deposited onto the support. The transition point and the relative heat of fusion for the precipitate were measured by using a Perkin Elmer Model DSC-1B in 10 mg at a heating rate of 10°C/min. The area under the DSC curve largely depends on the heating rate, but the relative area is almost independent of it, as shown in Figure 4. Therefore, the relative area is a reasonable parameter for indicating the variation of  $\Delta H_u$  with tacticity or molecular weight.

### Gel Permeation Chromatography (GPC), Osmometry, and Light Scattering

A Shimadzu GPC Model-1A was employed with a combination of four columns: crosslinked polystyrene gel  $1 \times 10^6$ ,  $1 \times 10^5$ ,  $1 \times 10^4$ , and  $1 \times 10^3$  Å permeability. A Hewlett Packard Model-502 high-speed membrane osmometer was employed to determine the number-average molecular weight. Determinations were made at 130°C for tetralin solution. A Sofica 42000M light-scattering instrument was employed to determine the weight-average molecular weight. Measurements were made at 140°C for  $\alpha$ -chloronaphthalene solution. Other experimental conditions for these methods are the same as described in the previous paper.<sup>16</sup>

### Determination of Tacticity Parameter

Fractionated sample was dissolved in hot xylene and brought into 5–10 wt-% xylene solution. The solution was poured onto the glass microslide. The glass was cooled to room temperature and was annealed at 120°C for 6 hr under vacuum. Thus, a thin film was obtained to determine the tacticity parameter. The intensity ratio ( $D_{998}/D_{974}$ ) of the band 998  $\text{cm}^{-1}$  to that of 975  $\text{cm}^{-1}$  in infrared absorption spectra was used as the tacticity parameter.<sup>17</sup>

## RESULTS AND DISCUSSION

Polypropylene having high isotacticity was fractionated by the two methods described above, and the tacticity parameters of these fractions were determined and compared. As shown in Figure 5, the tacticity parameter increased with molecular weight more rapidly in the rising temperature method than in the solvent gradient method. From this fact, it is expected that the fractions in the rising temperature method have molecular weight polydispersity, if it is a group of molecules having merely the same tacticity. Thus, the molecular weight distribution of the fractions was measured by GPC and is shown in Figure 6 and Table I. The  $\bar{M}_w/\bar{M}_n$  of fractions in the rising temperature method is approximately two times as large as that in the solvent gradient method. Therefore, these results can be explained by assuming that this fractionation was carried out mainly according to tacticity.

Discussing the rising temperature method from the thermodynamic point of view, eq. (3) is the most suitable function. Several parameters included are as follows:  $T_m$  is the transition point of the pure solid polymer,

TABLE I  
Molecular Weight Distribution of Fractions Determined by GPC

Method	$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
R.T.	7.40	2.92	2.53
R.T.	21.1	7.68	2.75
R.T.	21.1	9.99	2.11
R.T.	32.1	14.5	2.23
R.T.	46.3	17.3	2.68
S.G.	6.22	4.68	1.28
S.G.	8.53	7.85	1.09
S.G.	9.62	8.56	1.13
S.G.	24.8	18.2	1.36
S.G.	70.3	39.6	1.78

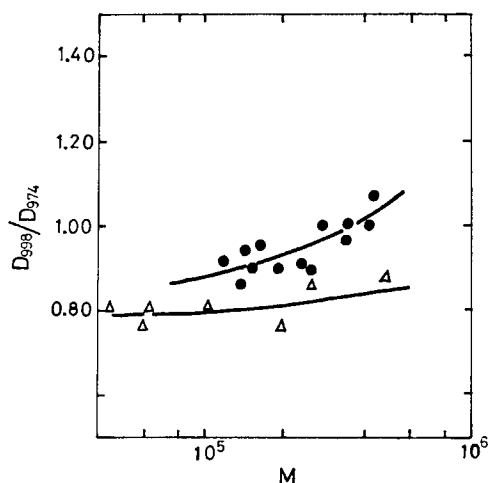


Fig. 5. Dependence of tacticity on molecular weight.  $M$  ( $= \sqrt{\bar{M}_n \bar{M}_w}$ ) was determined by GPC ( $M$  in other figures has also the same meaning): (●) fractions in the rising temperature method; (Δ) fractions in the solvent gradient method.

and the peak position in the DSC curve was adopted as  $T_m$ . It is somewhat doubtful whether the peak position is the true  $T_m$  of deposited polymer. However, the use of the peak position is satisfactory for demonstrating the mutual relationship of transition points, as shown in Figure 7. Parameter  $B$  was estimated from the data, in the decalin-polypropylene system, given by Tamura et al.<sup>18</sup> Using 15 for the  $B$  value,  $0.42 \times 10^{-3} \text{ deg}^{-1}$  for  $R/\Delta H_u \times (V_u/V_1)$ , and eq. (3), the dependence of elution temperature on molecular weight was calculated as shown in Figure 8. The experimental points in the *n*-decane-polypropylene system<sup>19</sup> are also shown for reference. The curves do not so much deviate from experimental points in the decalin-polypropylene system, thus the  $B$  value adopted is shown to be pertinent. Accordingly, a value of 15 was used for  $B$  thereafter. Since the fractionation is performed in equilibrium with the pure

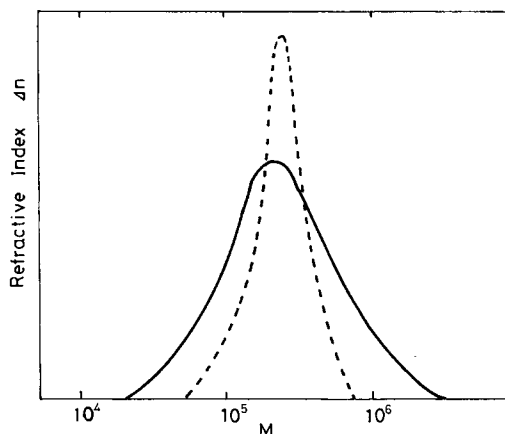


Fig. 6. Molecular weight distribution of fractions determined by GPC: (—) A fraction in the rising temperature method; (---) A fraction in the solvent gradient method.

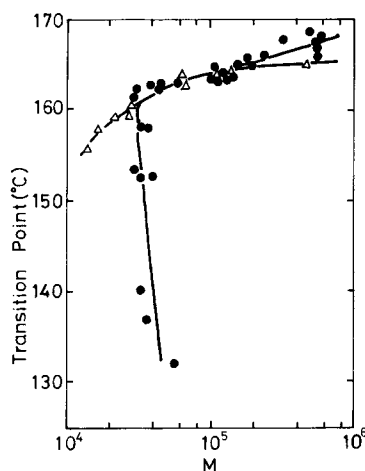


Fig. 7. Relationship between transition point and molecular weight: (●) fractions in the rising temperature method; (Δ) fractions in the solvent gradient method.

solid polymer and dilute solution, each fractionation step corresponds to the behavior of the elution temperature  $T$  in eq. (3). Here,  $v_1 = 0.99$  was conveniently used for calculations.

Calculating the elution temperature from the properties of deposited polymer, as in the first case, it was assumed that  $\Delta H_u$  was independent of molecular weight. In addition,  $\Delta H_u$  was fixed in such a way that the calculated elution temperature agreed with an experimental point at  $M = 5.0 \times 10^4$ . In this manner, the curves calculated by eq. (3) show a slight increase with molecular weight, as shown in Figure 9 (curves A and B). But when  $M$  changes from  $5 \times 10^4$  to  $1 \times 10^6$ , the change in experimental elution temperature is  $25^\circ\text{C}$  while that in this calculation is only  $2^\circ\text{C}$ . This

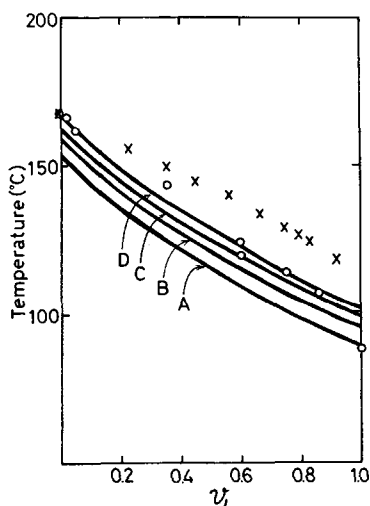


Fig. 8. Dissolution temperature of polymer: (O) by Tamura et al.<sup>18</sup>;  $M = 3.7 \times 10^6$  in decalin; (X) by Hamada et al.<sup>19</sup>;  $M = 3.4 \times 10^6$  in *n*-decan; (A–D) calculated curves obtained by using eq. (3): A,  $M = 1 \times 10^4$ , B,  $M = 2 \times 10^4$ , C,  $M = 5 \times 10^4$ , D,  $M = 1 \times 10^6$ , in decalin.

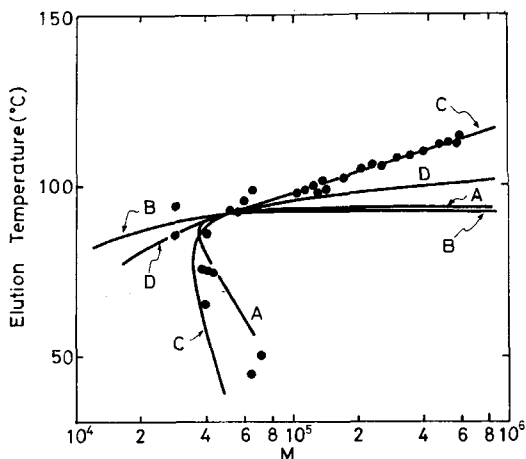


Fig. 9. Comparison of calculated curves with experimental points: (A) data used obtained by fractions in the rising temperature method, where  $\Delta H_u$  was assumed to be constant; (B) data used obtained by the fractions in the solvent gradient method, where  $\Delta H_u$  was assumed to be constant; (C) data used obtained by the fractions in the rising temperature method, where  $\Delta H_u$  was assumed to vary with polymer species (Fig. 10); (D) data used obtained by the fractions in the solvent gradient method, where  $\Delta H_u$  was assumed to vary with polymer species (Fig. 10).

means that the fractionation behavior cannot be explained by the assumption that  $\Delta H_u$  is constant.

In the second case, it was assumed that  $\Delta H_u$  changed with the fractionation steps. The dependence of  $\Delta H_u$  on molecular weight was obtained by measuring the area under the DSC curve, which was standardized by using



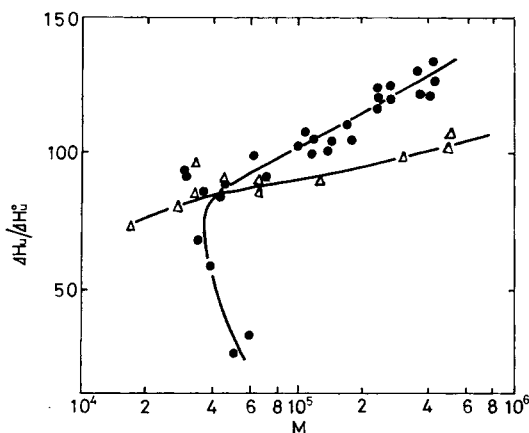


Fig. 10. Dependence of relative heat of fusion on molecular weight: (●) fractions in the rising temperature method; (Δ) fractions in the solvent gradient method;  $\Delta H_u^0$  = heat of fusion (peak area, 100) in  $M = 5 \times 10^4$ .

100 for  $\Delta H_u$  at  $M = 1 \times 10^5$ . As shown in Figure 10,  $\Delta H_u$  depends on the fractionation method, and the dependence of  $\Delta H_u$  on molecular weight shows to be more pronounced in the rising temperature method than in the solvent gradient method. As discussed above, these dependences are mainly due to tacticity rather than to molecular weight. Thus, when  $\Delta H_u$  of fractions in the rising temperature method was used, the curve agreed very closely with experimental points, while the curve by the data in the solvent gradient method did not agree with them. This fact means that the behavior in the rising temperature fractionation cannot be explained by molecular weight, but mainly by the character of tacticity. In any case, it is certain that  $\Delta H_u$  and  $T_m$  of each fraction are important factors in explaining the elution temperature of each fractionation step.

With regard to the fractionation mechanism of the rising temperature method, the deviation of experimental points from the calculated curves at a temperature below 85°C has not been intended to be accounted for. The fractionation eluted in this region of temperature shows lower transition points and smaller heat of fusion than expected. As a reason for the deviation, it is considered that the relative area under the DSC curve and  $T_m$  depends on the heating rate because of lower tacticity.

### CONCLUSIONS

The rising temperature fractionation of polypropylene was carried out, and thermodynamic analysis was applied to this method. As a result, it was confirmed that the elution temperature in each fractionation step could be estimated from the properties of solid state polymer, in which heat of fusion and transition points were variable with polymer species. Accordingly, in the rising temperature method, fractionation is by tacticity, whereas in the solvent-nonsolvent method, fractionation is by molecular weight only.

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### References

1. A. Kotera, K. Takamizawa, T. Kamata, and H. Kawaguchi, *Rep. Progr. Polym. Phys.*, **4**, 131 (1961).
2. P. Parrini, F. Sebastiano, and G. Messina, *Makromol. Chem.*, **38**, 27 (1960).
3. P. J. Flory, R. R. Garret, S. Newman, and L. Mandelkern, *J. Polym. Sci.*, **12**, 97 (1954).
4. E. M. Cernia, C. Mancici, and A. Saini, *Kobunshi Kagaku*, **24**, 738 (1967).
5. P. W. O. Wijga, J. van Schooten, and J. Boerma, *Makromol. Chem.*, **36**, 115 (1960).
6. M. Sato and O. Ishizuka, *Kobunshi Kagaku*, **23**, 799 (1966).
7. H. Sato, *Kogyo Kagaku Zasshi*, **65**, 385 (1962).
8. A. Saijyo, S. Hayashi, F. Hamada, and A. Nakajima, *Kobunshi Kagaku*, **24**, 775 (1967).
9. A. Nakajima and H. Fujiwara, *Bull. Chem. Soc. Japan*, **37**, 909 (1964).
10. T. Ogawa, S. Tanaka, and T. Inaba, *J. Appl. Polym. Sci.*, **17**, 779 (1973).
11. R. K. Eby, *J. Appl. Phys.*, **34**, 2442 (1963).
12. A. S. Kenyon and I. O. Salyer, *J. Polym. Sci.*, **43**, 427 (1960).
13. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y., 1953, p. 513.
14. P. J. Flory and W. R. Krigbaum, *Ann. Rev. Phys. Chem.*, **2**, 383 (1951).
15. T. Ogawa, Y. Suzuki, S. Tanaka, and S. Hoshino, *Kobunshi Kagaku*, **27**, 356 (1970).
16. T. Ogawa, Y. Suzuki, and T. Inaba, *J. Polym. Sci. A-1*, **10**, 737 (1972).
17. J. P. Luongo, *J. Appl. Polym. Sci.*, **3**, 602 (1960).
18. K. Tamura, K. Nakatsuka, and R. Fujishiro, *Bull. Chem. Soc. Japan*, **39**, 20 (1966).
19. F. Hamada and A. Nakajima, *Kobunshi Kagaku*, **22**, 577 (1965).

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