

Polymer Deposition onto the Support in Column Fractionation

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Synopsis

The effects of the depositing condition in column fractionation of isotactic polypropylene were studied in detail. A good fractionation was accomplished not only in selective but also in nonselective deposition. Furthermore, it was found, in opposition to Kenyon's opinion, that the polymer was not spread uniformly over the support, but deposited onto the support in the state of particles and that fractionation was not successful in the case of large particles. From these facts, the particle size is regarded as an important factor to attain good fractionation of isotactic polypropylene.

INTRODUCTION

The solvent-gradient elution method is the most useful method for the fractionation of isotactic polypropylene.¹⁻⁶ This method is basically the application of extraction techniques in liquid-liquid phase equilibrium and has also been applied for many other polymers. Being analogous to the case of other fractionation methods, the fractionation by this method is considerably affected by the experimental conditions such as polymer deposition onto the support, fractionation temperature, packing the support into the column, solvent-nonsolvent system as eluent, elution rate, recovery of polymer from eluate, etc. With regard to these factors, many investigators have especially been interested in the mechanism of polymer deposition onto the support and in the effect of this factor on the fractionation results. The significance of selective deposition in achieving satisfactory fractionation was pointed out in many reports.^{2,4,7-9} On the other hand, Kamide also pointed out the importance of the depositing temperature in column fractionation of isotactic polypropylene in a solid-liquid system.¹⁰

Various methods have been adopted for selective deposition, and in the early stages it was believed that selective deposition was achieved by slow cooling of polymer solution in which the support was immersed, and that nonselective deposition was achieved by the evaporation of solvent from the polymer solution.^{2,7} Recently, however, while selective deposition is regarded to be attained by slow cooling of the solution composed of polymer, solvent, and nonsolvent, nonselective deposition is believed to be attained by the cooling of the solution without nonsolvent.^{4,8,9}

In this sense, the depositing method still remains ambiguous, and it is doubtful whether the polymer layers formed on the support by the selective deposition as presented by Kenyon⁷ are maintained during the fractionation. In this paper, the polymer depositing conditions were investigated and discussed in detail.

EXPERIMENTAL

Sample, Eluent, and Support

The molecular weight and its distribution of the samples used for fractionation and for the determination of phase diagrams are $\bar{M}_w = 3.7 \times 10^5$ and $\bar{M}_w/\bar{M}_n = 4.6$, respectively. Fractionation samples were used for the determination of cloud points and the polymer deposition by two steps (hereafter called the "reversed deposition"). The fractions used for the latter experiment had $\bar{M}_w = 7.3 \times 10^4$ and 3.2×10^5 ($\bar{M}_w/\bar{M}_n \leq 1.3$).

Decalin and butyl carbitol used were commercial grade. The commercially available support (Celite 545) was used after decantation with water; glass powder obtained by pulverizing glass fiber was also used as support for the observation of deposited state. The bulk densities of these supports are 0.40 g/ml (Celite) and 0.85 g/ml (glass powder), which are desirable sizes for the elution.

Determination of Cloud Points

Sofica 42000M light scattering instrument was used to study the dependence of cloud points on molecular weight. Measurement was performed in 1.5 mg/ml polymer solution in decalin-butyl carbitol mixtures. Turbidity in one direction (90°) was recorded as the solution was cooled gradually (0.3°C/min) from 150°C, and the cloud point was determined by extrapolation of the turbidity curve in the same manner as described previously.¹¹

Phase Diagram

A phase diagram for isotactic polypropylene, decalin, and butyl carbitol was determined. The sample was placed in a glass tube and allowed to stand at 160°C for 48 hr after sufficient stirring at a higher temperature, and then the two phases consisting of two mutually saturated solutions were formed. After the volumes of these solutions were measured, a small amount of these separated solutions was sampled and the ratio of solvent to nonsolvent was determined by the infrared method. The polymer was recovered by precipitation with acetone and weighed. The equilibrium point composed of polymer and butyl carbitol (nonsolvent) was determined by the method which is based on the melting behavior of two-component systems.¹² Thus, all points on the phase diagram were determined.

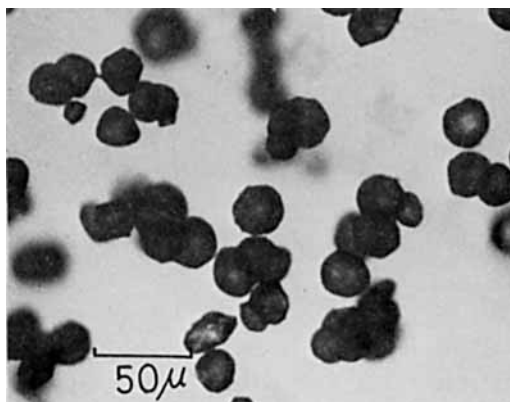
Fractionation

The same apparatus as reported previously (700 × 27 mm ϕ) was used.^{5,13} The fractionation was carried out in a decalin-butyl carbitol system at

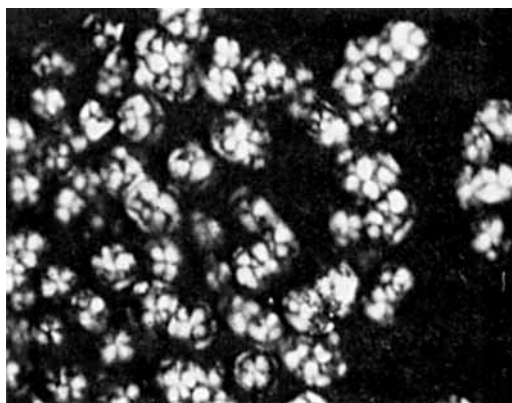
161°C. Solvent concentration was varied stepwise by 300-g increments of eluent. Other conditions and procedures are the same as those reported previously.⁶

Deposition and Mixing of Polymer with Support

Deposition onto the support was made by the same method as adopted in the fractionation.⁶ On the other hand, the following unique method was also applied in order to change the depositing conditions. The polymer particles used for mixing with the support were prepared by cooling of 3.0 g/l. decalin solution. The polymer particles obtained after drying were spherulites having a uniform size of 30 μ in diameter, as shown in Figure 1. The mechanical mixture of polymer particles with the support was packed by the procedure as shown in Figure 2. The reversed deposition was carried out as follows. The polymer particles previously obtained from the



WHITE LIGHT



POLARIZED

Fig. 1. Polymer particles precipitated from decalin solution (3 g/l.).

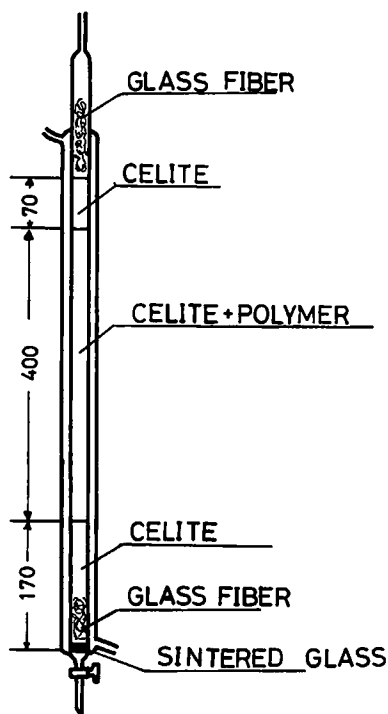


Fig. 2. Packing of mixture of polymer particles and Celite into a column.

fraction having lower molecular weight ($\bar{M}_w = 7.3 \times 10^4$) was poured into a 2.5% (w/w) decalin solution of polymer having higher molecular weight ($\bar{M}_w = 3.7 \times 10^5$), whose temperature had been maintained just below the precipitation temperature. Thus, the polymer particles obtained by rapid cooling of this solution were used for column fractionation.

Microscopic Observation

The state of the deposited or precipitated polymer was observed by natural or polarized light at a magnification of 100.

Gel Permeation Chromatography (GPC)

A Shimadzu GPC Model 1-A was used, with the column consisting of four sections packed with crosslinked polystyrene resins of 10^6 , 10^5 , 10^4 , 10^3 Å permeability, respectively. Other conditions are the same as those described previously.¹³

RESULTS

The authors have already reported that good fractionation was attained even in polymer deposition from the concentrated solution (5–10%), in which selective deposition was not expected.⁶ Thus, it was considered to

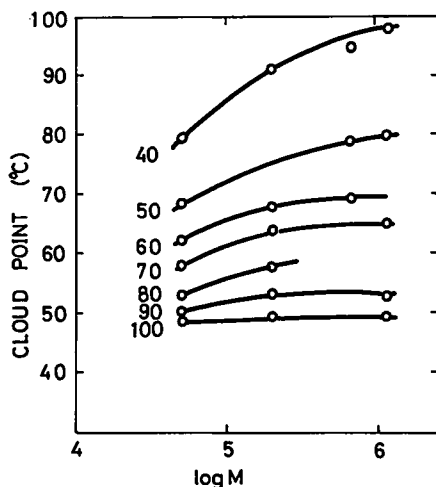


Fig. 3. Dependence of cloud point on molecular weight in polypropylene-decalin-butyl carbitol system. Data points are decalin per cent (by volume).

be doubtful that selective deposition was necessary by all means. In this paper, the dependence of cloud point on molecular weight was first determined in various ratios of solvent to nonsolvent, in order to seek the most favorable condition for selective or nonselective deposition. As shown in Figure 3, the dependence of cloud point on molecular weight was considerable in the 40% (v/v) system and diminished as the solvent ratio increased. The dependence ultimately disappeared in the 100% (v/v) system.

The fractionations were carried out in 40, 70, and 100% (v/v) systems, in order to study the influence of the depositing conditions. The results are shown in Figure 4. Further, it is shown in Figure 5 that the fractionation in the case of reversed deposition is also sufficiently performed, and that the distribution curve is in agreement with that by GPC determined for reference. The molecular weight distributions of these fractions are shown as D values ($= \bar{M}_w / \bar{M}_n$) in Figure 6, and any difference cannot be con-

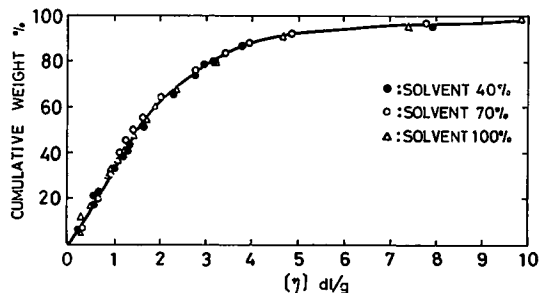


Fig. 4. Cumulative weight distribution curves of polymer deposited in 40% (v/v), 70% (v/v), and 100% (v/v) solvent concentrations. Polymer particles as shown in Fig. 1 were used only in the case of 100% (v/v) and packed by the method of Fig. 2.

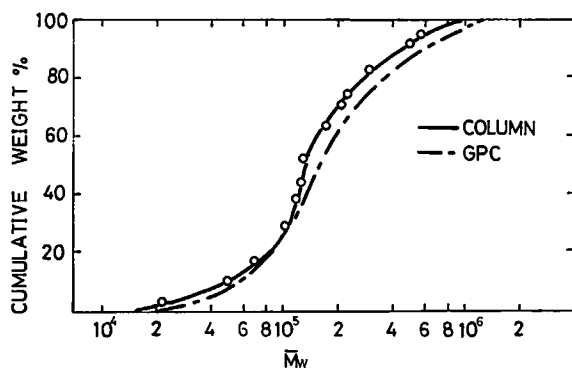


Fig. 5. Cumulative weight distribution curve obtained in reversed deposition.

firmed among these fractionations. Therefore, it can be said that the selective deposition is not so important a factor to attain good fractionation if performed under the recommended conditions, which are concerned with many experimental factors other than deposition.

DISCUSSION

Firstly, the fractionation process should be discussed from the standpoint of phase equilibrium. The phase diagram consisting of decalin, butyl carbitol, and isotactic polypropylene is shown in Figure 7. From this figure, it is clear that the state of the deposited polymer at a given fractionation temperature corresponds to the concentrated phase shown by tie line, because the fractionation is performed in liquid-liquid phase equilibrium systems. Therefore, it is expected that a large amount of solvent and nonsolvent is included in this phase (liquid drop) which will be described below. This phase may also correspond to polypropylene gel in phase distribution chromatography as reported by Casper.¹⁴

On the other hand, the state of the deposited polymer on the support, at room temperature, is shown in Figure 8. From this figure, it can be con-

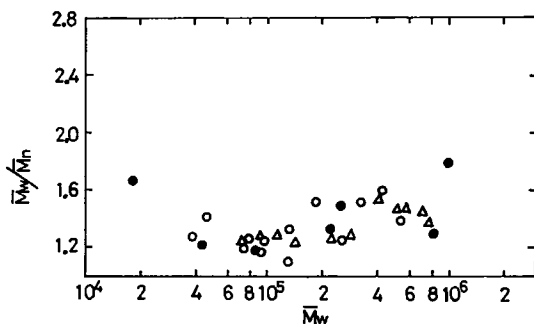


Fig. 6. \bar{M}_w/\bar{M}_n of fractions: (●) fractions obtained for 100% (v/v) solvent concentration; (○) fractions obtained for 70% (v/v) solvent concentration; (Δ) fractions obtained in reversed deposition.

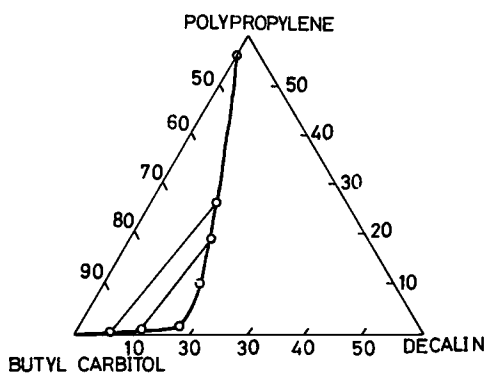


Fig. 7. Phase diagram for decalin, butyl carbitol, and isotactic polypropylene.

cluded, in opposition to Kenyon's opinion, that the polymer is not uniformly spread on the support in the order of molecular weight, but deposited in the state of particles. Further, the particles at a given fractionation temperature are regarded as being present in the state of liquid

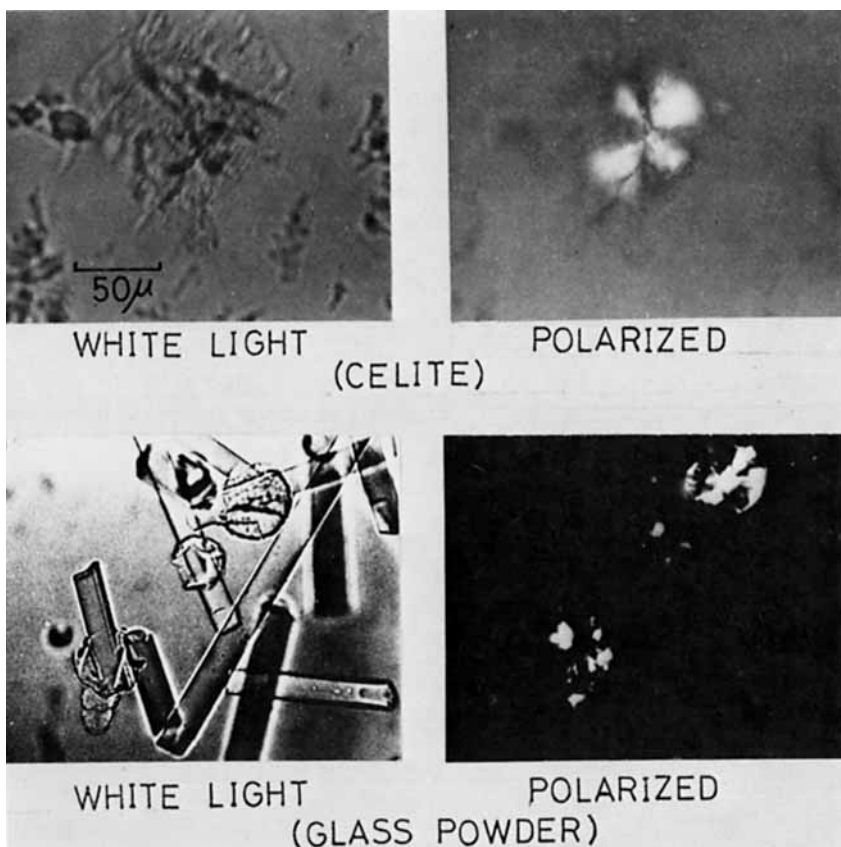


Fig. 8. Particles of isotactic polypropylene deposited onto support.

drops, in which such quantities of solvent and nonsolvent are absorbed as expected by the phase diagram (Fig. 7). Therefore, the fractionation process can be studied by the same method as solvent extraction, such as spray tower or packed tower. In these apparatuses, it is well known that increasing the contact surface of liquid drops with solvent considerably improves the extraction efficiency; and the time when solute diffusing from the center to the surface of a liquid drop is proportional to the square of the radius, which is also obvious from the equation of one-dimensional diffusion, as shown by eq. (1):

$$t \propto \frac{r^2}{D} \quad (1)$$

where t is the time for solute to diffuse from center to surface of the drop, r is the radius of the drop, and D is the diffusion constant.

Thus, polymer particles having an average diameter of 100μ were packed in the column together with Celite by the method as shown in Figure 2, and fractionated in the same manner as described above for the purpose of confirming the effect of particle size on fractionation efficiency. The result of this fractionation is shown in Figure 9, in which only 30–40% of the packed polymer was fractionated in order, while in the small polymer particles (30μ in diameter) good fractionation was achieved as shown in Figure 4. This fact demonstrates that the dispersibility of polymer in the column is the most important factor for good fractionation. This concept is also in agreement with the fact that the extraction of polymer coated on wire gauze gave better results than that on aluminum leaf as was reported by Fuchs¹⁶ and Bersniewicz.¹⁷ Therefore, depositing condition to make the particle size small should be recommended in any case.

Next, the particle sizes of the deposited polymer under various conditions were observed under the microscope. As Figures 10 and 11 show, the deposited polymer particles on glass powder are smaller than the ones on Celite. Here, the size of the liquid drop formed by the particles of this

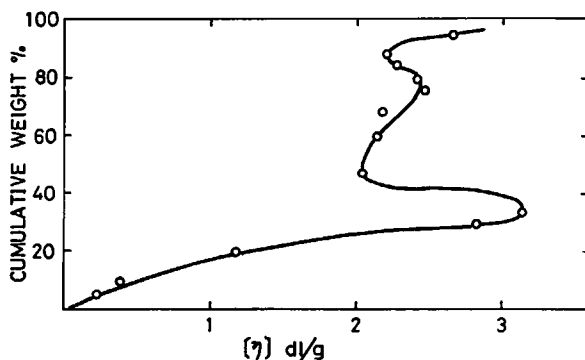


Fig. 9. Cumulative weight distribution curve obtained for polymer particles 100μ in diameter (polymer load 5 g).

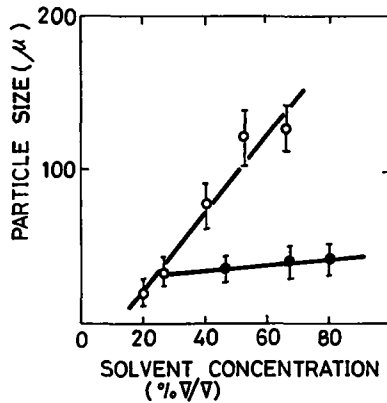


Fig. 10. Dependence of particle size on solvent concentration, determined in 0.4 g polymer; and (O) 10 g Celite or (●) 21 g glass powder.

polymer cannot be compared with that formed by the particles shown in Figure 1, because the precipitated polymer without support is different from the deposited polymer with respect to the shape and bulk density. The particle size on glass powder was hardly dependent on solvent concentration and on the amount of polymer, as shown in Figures 10 and 11. Although further investigations are required in connection with the shape and dimension of these supports, the glass powder is a superior support for the fractionation of isotactic polypropylene as far as we can determine. It is also a noteworthy fact that the support has an important effect upon the size of deposited polymer and further upon the fractionation efficiency. On the other hand, in the case of Celite, the particle size decreased as the solvent concentration decreased. Therefore, that the deposition from a thermodynamically poor solvent gave good fractionation⁴ should be attributed to the effect of particle size rather than that of the selective deposition.

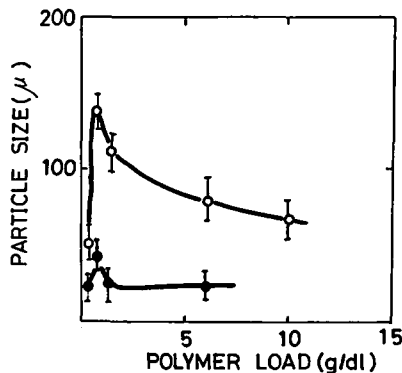


Fig. 11. Dependence of particle size on polymer load, determined in 60% (v/v) solvent concentration and (O) 10 g Celite or (●) 21 g glass powder.

As described in the introduction, there are many factors which should be studied for achieving a satisfactory fractionation. Of these factors, the particle size, which has been discussed in this report, is in competition with the fractionation temperature (T), and T is generally related to the diffusion constant D_0 by the following expression:

$$D_0 = k_1 \cdot \exp\left(-\frac{k_2}{T}\right) \quad (2)$$

where k_1 and k_2 are constants. From eq. (1) and (2), for example, it is estimated that a 10°C rise in a fractionation temperature is expected to decrease the diffusion time 30% on the basis of the diffusion data in a poly-(acrylic acid)-methyl acetate system.¹⁶ The same effect will be attained by a 15% decrease in particle size, and the decrease in particle size is not accompanied by any trouble resulting from the increase in temperature. Thus, the particle size of the deposited polymer is the most critical experimental factor in the fractionation of crystalline polymers whose fractionation temperature range is very narrow.

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