

## Effects of the Combination of Solvent and Nonsolvent on the Fractionation of Polypropylene

TOSHIO OGAWA, SHOICHI TANAKA, and SADA O HOSHINO,  
*Hirakata Plastics Laboratory, Ube Industries Ltd., Hirakata, Osaka, Japan*

### Synopsis

The effects of the combination of solvent and nonsolvent on the column fractionation of polypropylene were investigated. Decalin, kerosene, and  $\alpha$ -chloronaphthalene were employed as the solvents, whereas ethyl and butyl carbitol were employed as the nonsolvents. It was found that the molecular weight distribution of the fractions was not very significantly affected by the combination of solvent and nonsolvent. By applying Caplan's theory, namely, that  $\bar{M}^{-1/2}$  is a linear function of the weight fraction of solvent contained in the eluent (where  $M$  is the average molecular weight of a fraction), we concluded that to conduct a good fractionation both the solvent and the nonsolvent should be poorer solvents for the polymer.

### INTRODUCTION

Column fractionation of a homopolymer generally has two purposes, one analytical and the other preparative. For the former, the measurement of the molecular weight distribution is the major purpose. A new technique, known as GPC, however, has become very popular; as far as the molecular weight distribution is concerned, the column technique is being replaced by GPC because of its simple and rapid operation. However, it is necessary in GPC to prepare a calibration curve for molecular weight ( $M$ ) versus elution counts ( $V_e$ ). To prepare the calibration curve, one should obtain very narrow fractions by column fractionation. Furthermore, the molecular weight distribution obtained by GPC usually has a tendency to be broader than the true one due to the broadening effect.<sup>1-3</sup> Therefore, one can say that the column technique is still important and valuable for the determination of molecular weight distribution.

The second purpose of the column technique is how efficiently we obtain large quantities of narrow fractions. Concerning this, the authors presented their work elsewhere.<sup>4</sup>

Many studies have been presented on the column fractionation of polypropylene<sup>4-10</sup> and the effects of experimental conditions, such as deposition onto the support, fractionation temperature, recovery of fractions, characterization, and so forth. In most papers, however, the conclusions were based on only a few runs of fractionation, and it seems necessary to carry out more detailed studies concerning the effects of fractionation conditions.

Among these fractionation conditions, the effect of solvent and non-solvent combination has not drawn much attention; there have been only a few papers concerned with this effect thus far.<sup>11-13</sup> Moreover, the authors of these papers evaluated the effect only with reference to whether the limiting viscosity number  $[\eta]$  increases in the order of the fraction numbers, especially in the higher molecular weight region, i.e., the occurrence of the reversal on the integral molecular weight distribution curve. No systematic study with regard to the combination effects of solvent and non-solvent has been reported. In this paper, we deal with this point and discuss the results from the viewpoint of both the molecular weight distribution of the original polymer and its fractions.

## EXPERIMENTAL

### Sample, Eluent, and Support

Polypropylene for commercial usage (M.F.I. = 5.4, unstabilized) was used as sample. Decalin,  $\alpha$ -chloronaphthalene, and kerosene were selected as solvents for the fractionation. The former two were both the high grades commercially available, and kerosene was also of commercial grade (bp 200°C,  $M = 158$ ). Butyl carbitol [ $C_4H_9O(CH_2CH_2O)_2H$ ] of commercial high grade was used as the nonsolvent. To prevent the degradation of the sample, 2,6-di-*tert*-butyl-*p*-cresol (Ionol) was added to the solution all through the fractionation processes. Silica particles (Celite 545) were used as the support in the columns. To eliminate the fine powder filtrable through the glass filter, the supporting materials were decanted three or four times and then washed with acetone before filling the columns.

### Apparatus

Almost the same fractionation apparatus as reported previously was used (Fig. 1),<sup>4</sup> with the following modification: In the previous column, heat transfer agent, i.e., cyclohexanol, evaporated in the flask (8), condensed in the vapor jacket (1), and was returned directly to the flask (8). In the present column, a condenser (4) was attached to the top of the straight tube. Condensed cyclohexanol returns to the flask (8) through the U-tube.

### Fractionation

For the polymer deposition onto the support, the stationary method (depositing the polymer without agitation, see ref. 4) was employed. A decalin-butyl carbitol (70:30 wt-%) mixture was used as the depositing solvent. The column temperature was kept at 161°C throughout the fractionation. Other procedures are the same as described in the previous paper.<sup>4</sup>

### Gel Permeation Chromatography

A Shimadzu Model GPC-1A mounted with  $10^6$ ,  $10^5$ ,  $10^4$  and  $10^3$  Å permeability columns was used for this work. The solvent was *o*-dichloro-

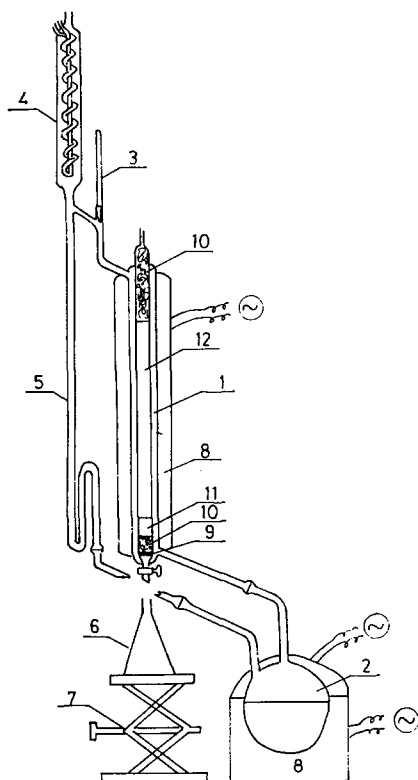


Fig. 1. Fractionation apparatus: (1) column, 27  $\phi$   $\times$  830 (inside), 47  $\phi$   $\times$  700 (outside); (2) flask; (3) thermometer; (4) condenser; (5) reflux pipe; (6) adapter; (7) laboratory jack; (8) heating mantle; (9) sintered glass filter (No. 2); (10) fiber glass; (11) Celite 545 (coarse); (12) Celite 545 coated with polymer.

benzene, the operation temperature was 135°C, and the elution rate was 1.0 ml/min. The polymer solution was prepared by dissolving polymer samples in *o*-dichlorobenzene containing 0.2% Ionol. The sample solution was filtered with the fluoro-resin filter VF-6 (German made, 0.45  $\mu$ ) mounted in a Millipore filter holder.

The calibration curve was made by plotting  $\log M$  versus  $V_e$  (elution count) using the polypropylene fractions prepared by large-scale column fractionation. Molecular weights of the fractions were determined by Kinsinger's equation,  $[\eta] = 1.10 \times 10^{-4} \bar{M}_w^{0.80}$ , 135°C, in decalin.<sup>14</sup> Since it was difficult to obtain the polypropylene fractions higher than  $1 \times 10^6$  in molecular weight by the fractionation, an extrapolated curve based on polystyrene was used in the higher molecular weight region by applying the relation that  $[\eta] \times M$  is independent of the polymer types concerning the elution count.<sup>1</sup> The calibration curve of polystyrene can be obtained by using commercially available high molecular weight fractions (maximum molecular weight  $1.8 \times 10^6$ ).

## RESULTS AND DISCUSSION

Looking at the polymer fractionation system from the standpoint of phase equilibrium, it belongs to the liquid-liquid system, i.e., the equilibrium between the polymer deposited on the support and the eluent solution surrounding it. In this case, the polymer on the support is considered to be in the form of gel or concentrated solution. Basically, the volume fraction of polymer species of size  $x$  in a dilute solution is given<sup>15</sup> by  $f(x)$ :

$$f(x) = \{R/(R + \exp(\rho x))\} \cdot f_0(x) \quad (1)$$

where  $f_0(x)$  is the volume distribution function of the original polymer,  $R$  is the volume ratio between the dilute and concentrated phases in equilibrium,  $x$  is the degree of polymerization, and  $\rho$  is a function of the volume fraction, degree of polymerization, and a solvent-polymer interaction parameter in each phase.

Many papers theoretically deal with fractional solutions in systems involving a solvent and a single or two different molecular species based on eq. (1).<sup>16-18</sup> Especially Huggins assumed that the average size of the polymer in the dilute and the concentrated phases is equal. However, the discussion under those conditions does not apply so much to the system dealt with in this paper because of its complexity.

Therefore, as a first step of the study concerning the fractional solution in the practical system, we will take into account the effect of the composition of eluent.

We estimated the solubility of polypropylene in various solvent-nonsolvent systems from the behavior of cloud points of the solvent-nonsolvent-polypropylene systems in the previous report<sup>19</sup> and found that the performance of ethylene glycol derivatives used as the nonsolvent for polypropylene fractionation was as follows (this order coincides with the order of  $\theta$  temperature of these derivatives):

methyl carbitol > ethyl carbitol

>  $C_4H_9O(CH_2CH_2O)_2COCH_3$  > butyl carbitol

Among these, methyl carbitol is not miscible with decalin at low temperature. Other esters and glycols such as dioctyl sebacate,  $C_4H_9O(CH_2CH_2O)_2C_4H_9$ , and  $C_4H_9OCH_2CH_2OH$  have better solvent power than the above ethylene glycol derivatives and dissolve polypropylene at a temperature below 160°C; therefore, they are not very useful as nonsolvent in polypropylene fractionation.

On the other hand, the order of solubility parameter of pure and chlorinated hydrocarbons used as the solvent in fractionation of polypropylene was<sup>19</sup>

$\alpha$ -chloronaphthalene > *o*-dichlorobenzene > chlorobenzene

> tetralin > decalin or kerosene > *n*-hexadecane

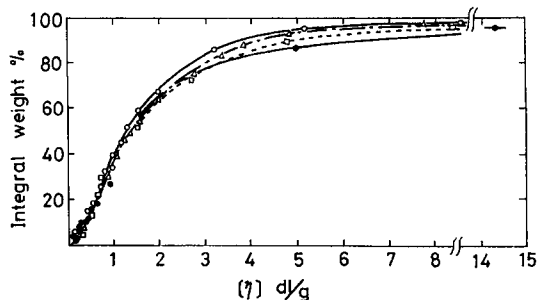


Fig. 2. Molecular weight distribution for the polymer obtained in various solvent-nonsolvent systems: ( $\square$ ) decalin-butyl carbitol, polymer load 5 g; ( $\Delta$ ) decalin-ethyl carbitol, polymer load 5 g; ( $\bullet$ ) kerosene-butyl carbitol, polymer load 9 g; ( $\circ$ )  $\alpha$ -chloronaphthalene-butyl carbitol, polymer load 5 g.

In the present work, we applied several combinations of solvent and nonsolvent described above to the fractionation. The results are shown in Figure 2, where the integral weight fraction is plotted against  $[\eta]$  of each fraction. While they indicate a similar tendency, in general, it is noteworthy that the fractionation with the decalin-ethyl carbitol system gives the highest molecular weight fraction,  $[\eta] = 14.5$  dl/g, among the four combinations employed in this work.

Molecular weight distributions of these fractions were measured by GPC, and the results are shown in Figures 3 to 6 and Tables I to IV. The calibration curve used for the calculations is shown in Figure 7. In general, the separation efficiency of GPC decreases in the higher molecular weight region, or lower elution count. For this reason, the  $D$  value ( $\bar{M}_w/\bar{M}_n$ ) of fractions having molecular weights greater than  $2 \times 10^6$  usually becomes larger than the true one. The  $D$  value of fractions located in the linear region of the calibration curve (Fig. 7) is also influenced by the error known as the broadening effect.

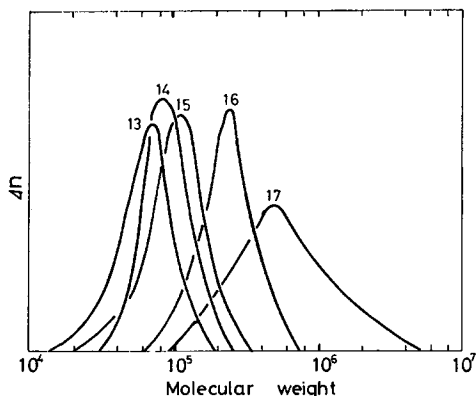


Fig. 3. Molecular weight distribution for fractions obtained in decalin-ethyl carbitol system. Polymer load, 5 g.

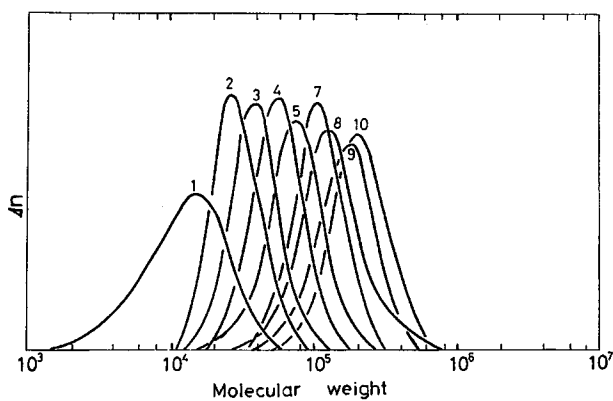


Fig. 4. Molecular weight distribution for fractions obtained in  $\alpha$ -chloronaphthalene-butyl carbitol system. Polymer load, 5 g.

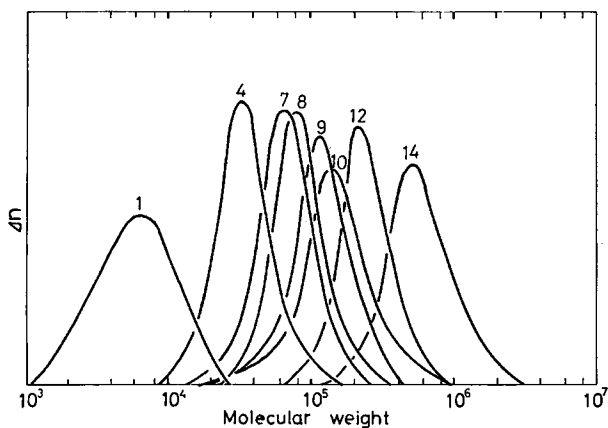


Fig. 5. Molecular weight distribution for fractions obtained in kerosene-butyl carbitol system. Polymer load, 9 g.

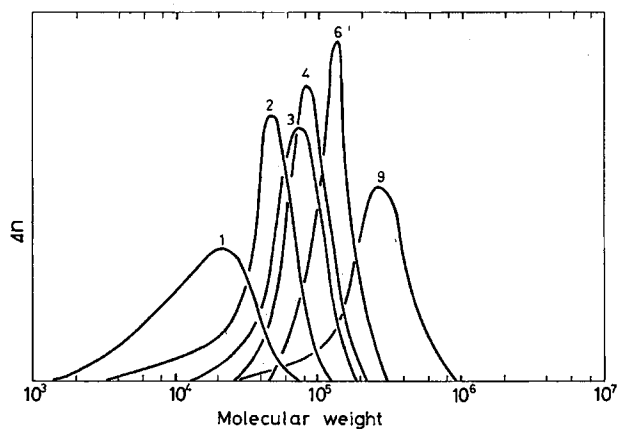


Fig. 6. Molecular weight distribution for fractions obtained in decalin-butyl carbitol system. Polymer load, 5 g.

TABLE I  
Molecular Weight and Its Distribution for Fractions  
Obtained in  $\alpha$ -Chloronaphthalene-Butyl Carbitol System<sup>a</sup>

Fraction no.	$\bar{M}_w \times 10^{-4}{}^b$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	
				Observed	Corrected
1	1.26	0.95	1.51	1.58	1.49
2	2.70	2.68	3.13	1.17	1.12
3	4.00	3.68	4.41	1.20	1.15
4	6.50	5.17	6.14	1.19	1.14
5	6.90	6.38	8.03	1.26	1.21
7	10.9	9.27	11.3	1.22	1.15
8	12.9	10.4	13.9	1.34	1.26
9	15.8	14.0	17.6	1.25	1.15
10	20.7	18.2	22.9	1.26	1.13

<sup>a</sup> Polymer load, 5 g.

<sup>b</sup> From limiting viscosity number.

TABLE II  
Molecular Weight and Its Distribution for Fractions Obtained in  
Decalin-Butyl Carbitol System<sup>a</sup>

Fraction no.	$\bar{M}_w \times 10^{-4}{}^b$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	
				Observed	Corrected
1	1.88	1.11	1.90	1.71	1.64
2	4.85	3.31	4.68	1.41	1.35
3	7.45	6.13	7.43	1.21	1.16
4	10.0	7.67	8.80	1.15	1.09
6	13.1	11.9	13.0	1.09	1.02
9	31.1	19.2	32.8	1.71	1.48

<sup>a</sup> Polymer load 5 g.

<sup>b</sup> From limiting viscosity number.

Since the broadening effect is independent of the type of the polymer according to the fundamental rule of GPC, the correction curve for polystyrene was applied to polypropylene in this work. For example, the value 1.20 for the standard polystyrene expressed as  $D \leq 1.20$  was used for the  $D$  value in the correction term  $(D_0 - D)/D$ , in which  $D_0$  is the experimental value obtained by GPC. The value for each fraction is plotted against the peak count of fractions, as shown in Figure 8. Thus, the  $D$  value was corrected ranging from 1.0 to 1.7 irrespective of the combination of solvent and nonsolvent. In general, the molecular weight distribution of the first fraction is broader than other fractions due to the presence of low molecular weight species. The average and the standard deviations of the  $D$  values (listed in Tables I to IV) are shown in Table V, where the value  $2\sigma$  for each combination corresponds to a statistical level of significance of 5%. In Table V, the average of the  $D$  value ranges from 1.09 to 1.24, which is not significant statistically at the 5% level. This proves that the combination of solvent and nonsolvent has no significant effect on the molecular weight

TABLE III  
Molecular Weight and Its Distribution for Fractions  
Obtained in Decalin-Ethyl Carbitol System<sup>a</sup>

Fraction no.	$\bar{M}_w \times 10^{-4}{}^b$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	
				Observed	Corrected
13	4.6	4.86	6.22	1.28	1.23
14	9.2	7.85	8.53	1.09	1.04
15	8.7	8.56	9.62	1.13	1.07
16	15.8	18.2	24.8	1.36	1.22
17	66.4	39.6	70.3	1.78	1.14

<sup>a</sup> Polymer load 5 g.

<sup>b</sup> From limiting viscosity number.

TABLE IV  
Molecular Weight and Its Distribution for Fractions  
Obtained in Kerosene-Butyl Carbitol System<sup>a</sup>

Fraction no.	$\bar{M}_w \times 10^{-4}{}^b$	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	
				Observed	Corrected
A-1	2.4	0.49	0.70	1.49	1.38
A-4	3.6	3.09	3.89	1.26	1.22
A-7	7.8	5.99	7.44	1.24	1.20
A-8	7.8	7.59	9.38	1.24	1.20
A-9	10.4	9.98	13.2	1.32	1.27
A-10	13.0	12.3	18.7	1.52	1.46
A-12	19.3	22.1	26.8	1.21	1.14
A-14	44.7	44.9	61.6	1.37	1.22
B-1	2.4	1.83	2.16	1.18	1.10
B-2	3.8	3.66	4.32	1.18	1.13
B-3	5.2	6.28	7.05	1.12	1.08
B-4	5.8	7.96	8.53	1.07	1.03
B-5	15.7	9.83	11.6	1.18	1.11

<sup>a</sup> Polymer load, 9 g for fractions A-1 through A-14, 5 g for fractions B-1 through B-5.

<sup>b</sup> From limiting viscosity number.

distribution of each fraction, although, at first sight, the values in the decalin-ethyl carbitol system have a tendency to be narrower than in others.

We have been looking for a suitable method to characterize the various eluent systems employed for the fractionation of polypropylene. After a number of trials, we found that our results can be characterized satisfactorily by a theory proposed by Caplan.<sup>20</sup> Caplan assumed that the  $\theta$  temperature of eluent is a linear function of the volume fraction of the solvent. Since the cloud points in solvent-nonsolvent-polypropylene systems form a straight line with the weight fraction of the solvent, we checked if Caplan's theory is applicable to our systems by substituting weight fraction for volume fraction.



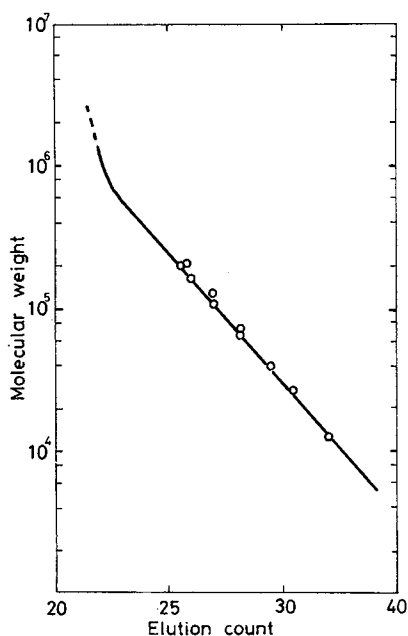


Fig. 7. Calibration curve of molecular weight vs. peak count in GPC.

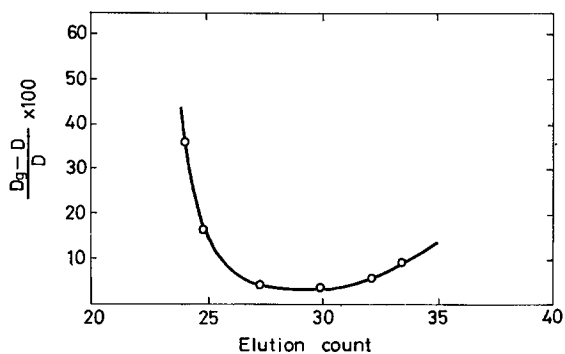
Fig. 8. Correction curve for observed  $D$  values.

TABLE V  
Average of  $D$  Values and Standard Deviations for Fractions

Solvent	Nonsolvent	$N^a$	Average $D^b$	$2\sigma^c$
$\alpha$ -Chloronaphthalene	butyl carbitol	8	1.16	0.08
Decalin	butyl carbitol	5	1.22	0.32
Decalin	ethyl carbitol	5	1.14	0.15
Kerosene	butyl carbitol	7	1.24	0.18
		4	1.09	0.07

<sup>a</sup> Number of fractions used for calculation.

<sup>b</sup>  $D = \bar{M}_w / \bar{M}_n$ , calculated from the last columns of Tables I through IV.

<sup>c</sup>  $\sigma$  = Standard deviation of  $D$ .

TABLE VI  
Comparison of Solvent and Nonsolvent Based on Eq. (2)

Solvent	Nonsolvent	$\psi/K$	$\{[(\psi + \tau) - T]/KT\} \times 10^3$
$\alpha$ -Chloronaphthalene	butyl carbitol	8.12	0.66
Decalin	butyl carbitol	12.1	0.57
Decalin	ethyl carbitol	14.1	1.47
Kerosene	butyl carbitol	15.3	0.80

Caplan's theory in our case can be expressed by the following equation using weight fraction ( $W_1$ ) instead of volume fraction:

$$\bar{M}^{-1/2} = \frac{(\psi + \tau) - T}{KT} - \frac{\psi}{KT} \cdot W_1 \quad (2)$$

where  $T$  is the fractionation temperature,  $(\psi + \tau)$  and  $\tau$  are the  $\theta$  temperature of nonsolvent and solvent, respectively,  $K$  is a constant and  $\bar{M}$  is the average molecular weight of a fraction.  $\bar{M}^{-1/2}$  is plotted against  $W_1$  with the four series of solvent-nonsolvent systems as shown in Figure 9. One can find that eq. (2) holds for these systems quite sufficiently, and that the reproducibility of the data is also satisfactory, as indicated in the  $\alpha$ -chloronaphthalene-butyl carbitol and kerosene-butyl carbitol systems. Consequently, one can say that eq. (2) is quite suitable to evaluate the combination effects of solvent-nonsolvent systems for column fractionation (Table VI). It turns out that, as a rule, the following two conditions are required for a good fractionation to be carried out: (1) a narrow molecular weight distribution of fractions over the whole molecular weight range; and

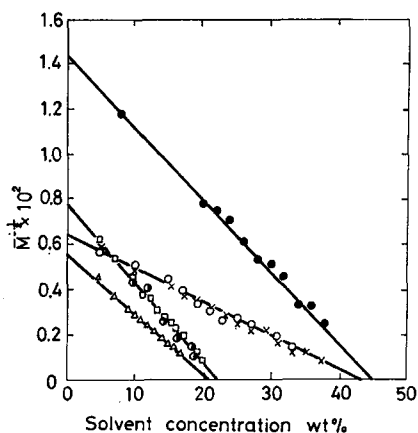


Fig. 9. Plots of eq. (2) for experimental results: (O, X)  $\alpha$ -chloronaphthalene-butyl carbitol system, polymer load 5 g, 9 g; ( $\Delta$ ) decalin-butyl carbitol system, polymer load 5 g; ( $\bullet$ ) decalin-ethyl carbitol system, polymer load 5 g; ( $\square$ ,  $\bullet$ ) kerosene-butyl carbitol system, polymer load 9 g, 5 g.

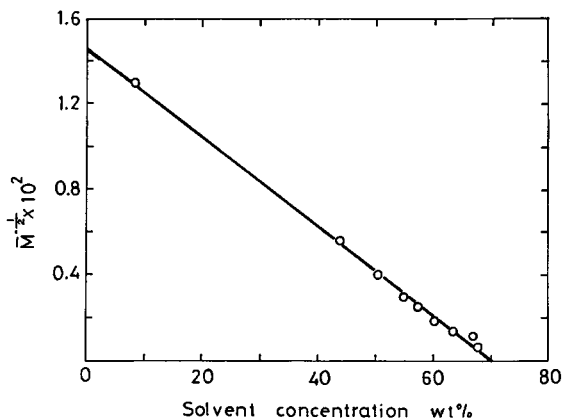


Fig. 10. Plots of eq. (2) for the fractionation results in  $\alpha$ -chloronaphthalene–methyl carbitol system.

(2) the eluent composition must be variable in a wide range to facilitate the fractionation procedure.

At first, in eq. (2), the greater the term  $(\psi + \tau)$ , the higher the first term of the right-hand member is. If one wishes to obtain polymer fractions with the molecular weight distribution as narrow as possible, it is preferable to have a higher intercept in Figure 9, because we can magnify the differences between the molecular weight of adjacent fractions by that, and this will satisfy the first requirement described above.

Secondly, the higher the  $\tau$  value, the lower the coefficient of the second term of eq. (2) is when  $(\psi + \tau)$  is kept constant. This means a decrease in the slope of the curve expressed by eq. (2), and it then becomes possible to vary the composition of the eluent over a wide range. This satisfies the second requirement.

In this regard, it is evident that the mixture of decalin–ethyl carbitol is preferable for the fractionation of polypropylene because of the higher intercept in Caplin's plot than in other three eluent combinations used in this work, as shown in Figure 9. According to this principle, we can further conclude that the combination of  $\alpha$ -chloronaphthalene and methyl carbitol would be the most favorable for the fractionation of polypropylene among the solvents and nonsolvents described above. This was also verified by the result obtained with this combination as shown in Figure 10.

To summarize, it seems that it is preferable to make  $(\psi + \tau)$  as large as possible and  $\psi$  as small as possible to conduct a good fractionation. In other words, in the binary eluent system (solvent–nonsolvent system), both solvent and nonsolvent should be poorer with regard to solubility for polypropylene.

Horowitz<sup>14</sup> found that a butyl cellosolve–butyl carbitol system gave a good result for fractionation of polypropylene at 165°C. As is commonly known, these two carbitols belong to the nonsolvent for polypropylene.

However, since a certain difference between these two glycols is recognized in the solubility of polypropylene it seems reasonable from our conclusion that one works as the solvent and the other as the nonsolvent in the above system. Horowitz himself did not speculate about this.

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