The Fractionation of Polypropylene by Extraction with Boiling Hydrocarbons with Increasing Boiling Points

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The fractionation of polypropylene is generally carried out either by the fractional solution method in a column or by the fractional extraction method in a Soxhlet-type apparatus. As to the column method, two techniques are known: the gradient elution fractionation is achieved at a given temperature by making use of solvents with gradually increasing solvent power, or the increasing temperature fractionation is performed with a given solvent at increasing temperatures. According to the findings on column techniques by Wijga and others,[1] the gradient elution method at a temperature (150°C) sufficiently near the melting point of the polymer separates fractions only according to molecular weight, whereas the increasing temperature method fractionates the polymer mainly according to tacticity. On the other hand, in the fractional extraction in a vapor-jacketed Soxhlet apparatus with boiling solvents with increasing boiling points, separation is considered to be conducted mainly by tacticity. However, in the reports[2-4] published so far, the solvents used for a series of fractional extractions of polypropylene have been comparatively few in number and, moreover, detailed information on the solubilities of polypropylene in these solvents has not been reported.

One of the present authors[5] previously fractionated polyethylene and its thermally degradated product by extraction with boiling hydrocarbons with increasing boiling points in a range from 45°C to 95°C, and pointed out that both the degree of crystallinity (density and melting point) and the molecular weight of the fractionated fraction increase with an increase in the boiling point of the hydrocarbons. Accordingly, this method of fractionation may be regarded as promising for polypropylene also.

In this study, 17 hydrocarbon fractions, mainly based on normal paraffins, with different boiling temperatures in the range from 35°C to 135°C, were used for the fractional extraction of polypropylene in a Soxhlet-type apparatus. With this method, successive fractionations are carried out with hydrocarbons, with different carbon numbers and with different solubilities, at different extraction temperatures corresponding to their boiling temperatures. Thus, fractionation, in this case, is conducted by two parameters. We will discuss the characteristic features of this method in comparison with other methods of fractionation and will also investigate the correlation between the solubility parameters of the solvents at their extraction temperatures and those of polymer fractions extracted at these temperatures, working with experimental findings on molecular weight, degree of crystallinity, tacticity, melting point, and extraction temperature.

Experimental

Material.—The polypropylene used was Moplen AS. Moplen AS pellets were dissolved in a low-boiling-range fraction of kerosene at 140~145°C and precipitated in powder form by cooling the solution to room temperature; then the solvent was evaporated in vacuo at 60°C. The powdered polypropylene thus obtained was used for the fractionation experiments.

Solvents for Extraction. — Purified petroleum ether, petroleum benzine and high-boiling-range ligroin were fractionated by fractional distillation to obtain hydrocarbon fractions with a sharp boiling range. 17 hydrocarbon fractions covering boiling temperatures of 35~130°C were prepared. The boiling temperature range of each hydrocarbon fraction is shown in the second column of Table I. Gas chromatographic examinations of these fractions disclosed that the main components in the fractions were normal paraffin hydrocarbons with carbon number from 5 to 8.

Fractionation Apparatus.—The fractional extraction was carried out in a vapor-jacketed Soxhlet-type apparatus, as is shown in Fig. 1, consisting of a extraction cell equipped with a G-1 glass filter, condensers and a solvent container. The outside of the apparatus was covered with asbestos to keep the temperature constant. With this apparatus, the extraction temperature (see Table I) were kept constant within ±0.3°C.

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[1] P. W. O. Wijga, J. van Schooten and J. Boerma, *Makromol. Chem.*, **36**, 115 (1960).

[2] G. Natta, *J. Polymer Sci.*, **34**, 531 (1959).

[3] S. Newman, ibid., **47**, 111 (1960).

[4] C. A. Russell, *J. Appl. Polymer Sci.*, **4**, 219 (1960).

[5] A. Nakajima, *Chem. High Polymers, Japan* (*Kobunshi Kagaku*), **7**, 64 (1950).

TABLE I. RESULTS OF FRACTIONATION EXPERIMENTS

No.	Solvent b. p., °C	Extr. °C	Main comp.	Extr. g.	$[\eta]$	$\bar{P}$	d^{30}	D_{995}/D_{974}	T_m, °C
1	35～ 38	36.0	Pentane	0.413	0.400	672	0.851	0	none
2	50～ 55	50.0		0.521	0.390	652	0.862	0	none
3	60～ 65	60.5		0.463	0.435	765	0.876	0.327	101
4	65～ 70	65.0		0.282	0.360	590	0.875	0.537	118
5	70～ 75	71.0	Hexane	0.274	0.275	421	0.884	0.653	120
6	75～ 80	75.5		0.651	0.345	645	0.891	0.752	128
7	85～ 90	89.0		0.502	0.382	635	0.891	0.758	138
8	90～ 95	92.5		0.209	0.410	694			
9	95～100	99.5	Heptane	0.360	0.485	856	0.897	0.794	139
10	102～104	102.5		2.730	1.150	2517	0.911	0.926	159.5
11	106～108	106.0		0.340	1.634	3905	0.912	0.929	163.0
12	110～112	111.0		3.149	2.520	6712	0.912	0.955	163.0
13	114～116	115.0		1.418	3.60	10478	0.912	0.962	172.0
14	118～120	119.0		0.105	4.86	15254	0.912		
15	122～124	123.5		2.883	4.60	13444	0.913	0.970	178.0
16	124～126	126.0	Octane	1.079	6.50	21317	0.911	0.979	178.0
17	126～130	128.5		0.282	7.38	25541	0.913	0.968	178.5

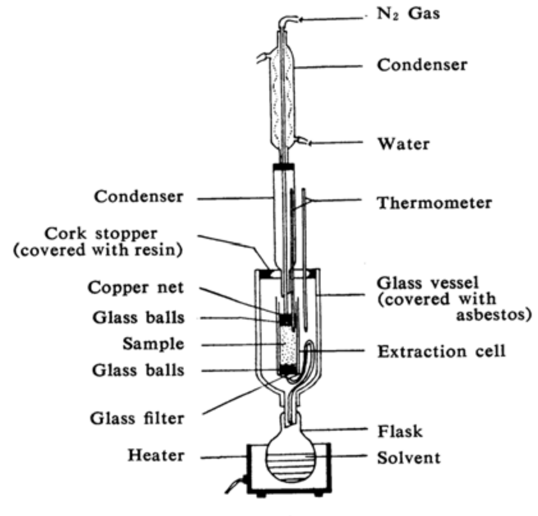

Fig. 1. Extraction apparatus.

Fractionation.—Fifteen grams of a sample was placed in the extraction cell. The extraction of each fraction was performed in 10 hr. by circulating the solvent under flushing (100 cc./min.) nitrogen. The amount of solvent placed in the flask was 400 ～500 ml., and the time needed for one cycle of solvent circulation through the cell was about 10 min. In cases of extractions at above 100°C, 2, 6-di-*t*-butyl-*p*-cresol was added (0.5% of the amount of solvent) to prevent the thermal decomposition of the polymer. The polymer fractions extracted below 100°C were recovered by evaporating the solvent, while those extracted above 100°C were collected in acetone to remove the stabilizer, filtered, and dried in a vacuum oven. The amount of fractions extracted is given in the fifth column of Table I.

Molecular Weight Determination. — The molecular weights, M, of the fractions were estimated by determining the limiting viscosity numbers in decalin, including a small amount of 2, 6-di-*t*-butyl-*p*-cresol, at 135°C, with the equation :[6]

$$[\eta]=1.10\times10^{-4}M^{0.8} \tag{1}$$

where the limiting viscosity number, $[\eta]$, is given in dl./g. units. The viscosity measurements were carried out in a nitrogen atmosphere.

Density Measurement.—Samples were molded in film form under the same conditions and were thoroughly annealed at temperatures suited to the fractions. Density measurements were then carried out by the flotation method in a water-methanol system at 30°C. The degree of crystallization at 30°C, X_c, was estimated by means of Eq 4.

Infrared Spectra. — Samples were dissolved in ligroin with a high boiling point and then cast in films, ca. 20 μ thick, by evaporating the solvent. Infrared absorption spectra were obtained for these films by using a Shimadzu spectrometer (Type AR-275-2S). The ratio of optical densities at 995 cm^{-1} and 974 cm^{-1}, D_{995}/D_{974}, was used to estimate the isotacticity X_i of the samples according to the method of Luongo.[7]

Melting Point Measurement.—The melting points of the samples were determined by visual observations on sufficiently-annealed samples sealed in capillary tubes by raising the temperature at a rate of about 1°C/hr.

Results and Discussion

Fractionation. — Table I shows the boiling temperatures of the solvents, the extraction temperatures, the main components of the solvents, the amounts of the polymer fractions extracted, the limiting viscosity numbers, the degrees of polymerization (P), the densities

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[6] J. B. Kinsinger and R. E. Hughes, *J. Phys. Chem.*, **63**, 2002 (1959).

[7] J. P. Luongo, *J. Appl. Polymer Sci.*, **3**, 302 (1960).

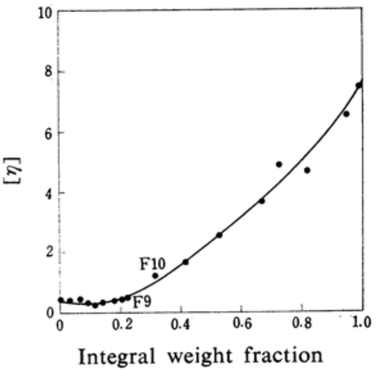

Fig. 2. Integral weight fraction plotted against the intrinsic viscosity.

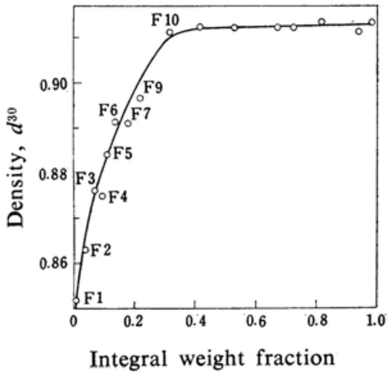

Fig. 3. Integral weight fraction plotted against the density of the fractions.

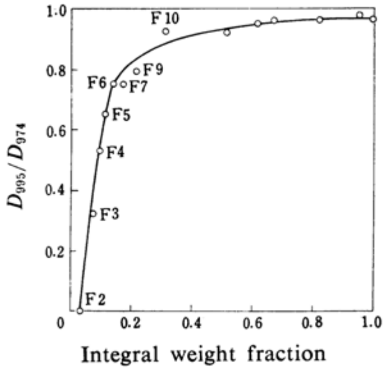

Fig. 4. Integral weight fraction plotted against D_{995}/D_{974}.

(d^{30}), the optical density ratios, and the melting points of the fractions.

In Figs. 2, and 4, the integral weight fraction is plotted against the limiting viscosity number, the density, and the optical density ratio of the fractions respectively. A characteristic feature of the curve shown in Fig. 2 is that the limiting viscosity number of the fractions is almost constant up to about a 0.2 integral weight fraction. This means that the fractionation in the low molecular weight range did not occur according to the molecular weight of the polymer. On the other hand, the curve shown in Fig. 3 or 4 means that the fractionation in the low molecular weight range (F1–F9) was rather determined by the crystallinity or tacticity of the fractions, but that the fractions above F10 were fractionated according to molecular weight and have almost the same crystallinity or tacticity. The integral weight fraction at above 0.3 is abruptly increased with an increase in the density or in the optical density ratio. This behavior is similar in the low molecular weight range to the results obtained for increasing temperature fractionation by the column technique and in the high molecular weight range to those obtained by the gradient elution method. Compared with the increasing temperature method, the maintenance of a constant temperature in the method used here was much easier. Between the melting points of the fractions and the extraction temperatures, a linear relationship was obtained, as is shown in Fig. 5. Presumably, the extraction was carried out at or near the critical solution temperatures of the corresponding polymer fractions. To confirm this,

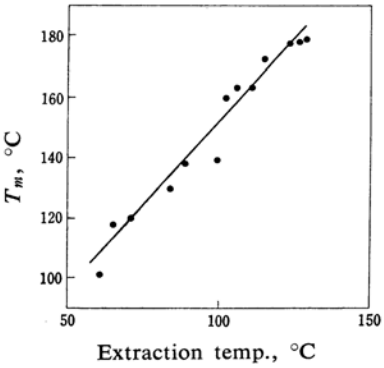

Fig. 5. Melting points of the fractions plotted against the extraction temperature.

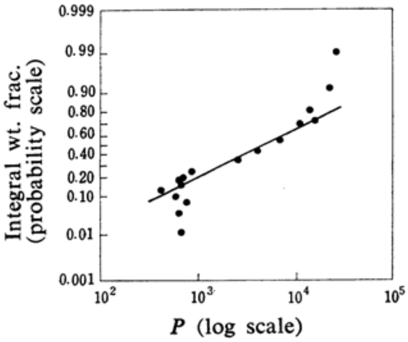

Fig. 6. Integral weight fraction plotted on logarithmic paper. *P* denotes the degree of polymerization.

some experiments were undertaken. In Fig. 6, the integral weight fraction is plotted against the degree of polymerization on logarithmic probability paper after Wesslau.8) A straight line was obtained from about a 0.1 to a 0.8 integral weight fraction. Taking into account the fact that the fractionation up to a 0.3 integral weight fraction is carried out according to the degree of crystallinity, it may be concluded that the molecular weight distribution of the sample is given approximately by a log-normal molecular weight distribution except in a sufficiently high molecular weight range. From the slope of the straight line, the ratio of the weight average to the number average degree of polymerization, P_w/P_n, is obtained by using the expression:

$$P_w/P_n=\exp\sigma^2 \tag{2}$$

were σ is the standard deviation of the Gaussian distribution of the weight fractions against the logarithm of the molecular weight of the fractions; it is determined by the equation: $\sigma=[\sqrt{2\pi}P(\mathrm{d}I/\mathrm{d}P)_{P=P_0}]^{-1}$, in which I denotes the integral weight fraction and P_0 is the degree of polymerization at $I=0.5$. The value of P_w/P_n obtained was 13, which falls in the range of $P_w/P_n=12\sim35$ found1) for some commercial polypropylene samples.

The Characterization of the Fractions.—Before discussing the solubility of polypropylene, we should refer to the stereoregularity and crystallinity of the fractions. Luongo,7) after taking into account the fact that the degree of crystallinity of samples with the same tacticity is scarcely affected by the method of sample preparation, obtained a relationship between the tacticity of polypropylene and the D_{974}/D_{995} value from data obtained for a series of mixtures composed of a 100% isotactic and a 100% atactic sample. In this study, the isotacticity, X_i, was obtained from D_{974}/D_{995} using Luongo's method.

On the other hand, the crystallinity, X_c, was calculated from the density of the fractions at 30°C by using the relation:

$$\frac{1}{d}=X_c\frac{1}{d_c}+(1-X_c)\frac{1}{d_a} \tag{3}$$

in which d_c and d_a are the densities of crystalline and amorphous polypropylene respectively. With $d_c=0.936$, which was obtained by Natta et al.9) from X-ray data, and with $d_a=0.850$, also obtained by Natta et al.,10) Eq. 3 becomes:

$$X_c=11.68-(9.966/d) \tag{4}$$

The linear relationship shown in Fig. 7 was obtained between X_i and X_c, from which it is known that the intermediate fractions are different in their tacticities. The extrapolated value of X_c to $X_i=1$ is about 0.8. Since X_i indicates the fraction of maximum crystallizable component, the result means that about 80% of a crystallizable component is really crystallized.

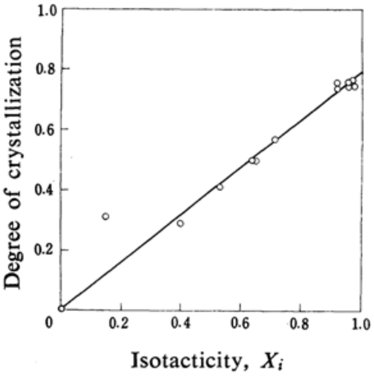

Fig. 7. Relation between the degree of crystallization and the isotacticity of the fractions.

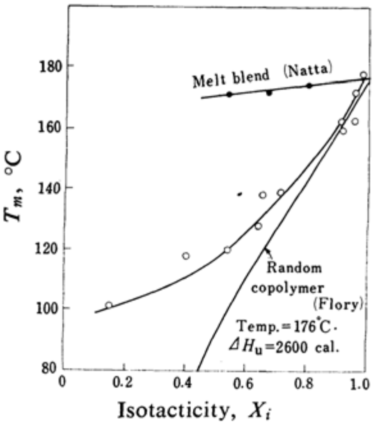

Fig. 8. Melting point-isotacticity relation.

Figure 8 shows the relation between the melting points of the fractions and their isotacticities, together with the results obtained on melt blends of amorphous and crystalline polymers by Natta.11) Obviously, the melting points of our fractions are much lower than those of melt blends of the same isotacticity. This may mean that our intermediate fractions are composed of copolymers which are built up of components of *d*- and *l*-configurations. Now, we shall apply Flory's12) equation, proposed for a random copolymer composed of

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8) H. Wesslau, *Makromol. Chem.*, **20**, 111 (1956).
9) G. Natta, P. Corradini and M. Cesari, *Lincei-Rend. Sc. fis. mat. e nat.*, **22**, 11 (1957).
10) G. Natta, F. Danusso and G. Moraglio, *Angew. Chem.*, **69**, 686 (1957).
11) G. Natta, *J. Polymer Sci.*, **34**, 531 (1959).
12) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

crystalline and amorphous components, to the polypropylene fractions. For the present case, the melting point depression should be a function of X_i, instead of the mole fraction of crystalline component in the case of the random copolymer. Thus, we have:

$$\frac{1}{T_m}-\frac{1}{T_m{}^0}=-\frac{\boldsymbol{R}}{\Delta H_u}\ln X_i \qquad (5)$$

in which T_m and $T_m{}^0$ donote the melting point of the fractions and that of $X_i=1$ respectively, and in which ΔH_u indicates the heat of the melting of the polymer.

The curve, T_m against X_i, calculated with $T_m{}^0=176°\mathrm{C}$ and $\Delta H_u=2600$ cal./mol., a value obtained by Danusso,[13] is given also in Fig. 8. A comparison between the observed and calculated curves shows that the two coincide at higher values of X_i, but at lower values of X_i the observed melting points are higher than the calculated ones for a random copolymer. Such results may suggest that these fractions are composed of stereoblock copolymers (as designated by Natta), which are built up, in a somewhat different fashion in the low X_i range from usual random copolymers, of sequences of *d*- and *l*-configurations of various lengths. In other words, the distribution of such stereoregular-sequence length may differ from that of crystalline-sequence length in random copolymers.

The Fractionation Mechanism in Connection with Solubility Parameters of Solvents.—The solvents used for extraction and the polymer are both aliphatic hydrocarbons, so the solvent-polymer interaction may be approximated by the geometrical mean of the solvent-solvent interaction and the polymer-polymer interaction. Thus, we may discuss the mechanism of the extraction fractionation in connection with the solubility parameter of the solvent, δ_s, and of the polymer, δ_p. Since the partial molar heat of dilution, $\Delta\overline{H}_1$, for the polymer solution is related[14] to the heat parameter, κ_1, by the equation:

$$\kappa_1=\frac{\Delta\overline{H}_1}{\boldsymbol{R}Tv_2{}^2} \qquad (6)$$

where v_2 denotes the volume fraction of the polymer in solution, the equation given by Hildebrand;[15]

$$\Delta\overline{H}_1=V_1(\delta_s-\delta_p)^2v_2{}^2 \qquad (7)$$

is rewritten in the form:

$$\frac{\kappa_1}{V_1}=(\delta_s-\delta_p)^2/\boldsymbol{RT} \qquad (8)$$

in which V_1 represents the molar volume of the solvent, and in which the solubility parameter of solvent, δ_s, is calculated by the equation:[16]

$$\delta_s=\frac{\Delta H_v-\boldsymbol{RT}}{V_1} \qquad (9)$$

where ΔH_v is the heat of the vaporization of the solvent at temperature T. Our extraction fractionation was carried out at the boiling points of hydrocarbons with different boiling points. Now we shall estimate the solubility parameters of solvents at their boiling points. It is possible to estimate the heat of vaporization from the boiling point, provided the liquid is nonpolar, by the aid of the "Hildebrand rule." Between the heats of vaporization at the normal boiling point, $\Delta H_{v,b}$ (cal./mol.), and the normal boiling points, T_b (°K), the following relation was found by Scott:[17]

$$\Delta H_{v,b}=17.0\,T_b+0.009\,T_b{}^2 \qquad (10)$$

Thus, we can estimate δ_s at the boiling point of the solvent, the temperature regarded as the extraction temperature, with Eqs. 9 and 10 if the molal volume of the liquid at the boiling point is known.

In Table II, the boiling point, T_b, the molar volume, V_1, of the liquid at T_b, and the solubility parameter of the solvent at T_b are listed. The numerical values of V_1 for the solvents used here were obtained in the following way. At first, the values of V_1 at the boiling points of *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane were calculated using the equation proposed by Sakurada and one of the present authors:[18]

$$V_1=1.143+0.00089\,t+\frac{1}{(0.50-0.00110\,t)n} \qquad (11)$$

where n is the number of carbon atoms in normal paraffin and t is the temperature in °C. Plotting these V_1-values against the boiling temperatures of the corresponding paraffins, we obtained the V_1 values of the solvents used here by interpolation. The δ_s values of normal paraffins at their boiling points are plotted against their boiling points in Fig. 9 (the broken line less sloped). In Fig. 9 also the δ_s values of normal paraffins at temperatures up to their boiling points are plotted against the temperatures (the broken lines more sloped). Our extractional fractionation is carried out along the former broken line; on the other hand, the increasing temperature

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[13] F. Danusso, G. Moraglio and E. Flores, *Lincei-Rend. Sc. fis. mat. e nat.*, **25**, 520 (1958).

[14] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y. (1953), p. 523.

[15] J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd. ed., Reinhold Pub. Corp., N. Y. (1950), p. 180.

[16] Ibid., p. 424.

[17] Ibid., p. 427.

[18] I. Sakurada and A. Nakajima, *Chem. High Polymers, Japan* (*Kobunshi Kagaku*), **3**, 95 (1946).

method, using a given solvent and the column technique, is performed along a curve as shown by the latter broken lines. In both cases, δ_s decreases with an increase in the temperature; however, the slopes of the curves are different.

TABLE II. SOLUBILITY PARAMETERS OF SOLVENTS AT BOILING POINTS

No.	T_b, °C	V_1 at T_b	δ_s at T_b
1	36.0	118	6.90
2	50.0	128	6.80
3	60.5	135	6.78
4	65.0	138	6.74
5	71.0	142	6.70
6	75.5	146	6.67
7	89.0	156	6.60
8	92.5	159	6.58
9	99.5	164	6.54
10	102.5	166	6.52
11	106.0	170	6.50
12	111.0	174	6.47
13	115.0	177	6.44
14	119.0	180	6.42
15	123.5	184	6.40
16	126.0	186	6.39_5
17	128.5	188	6.39

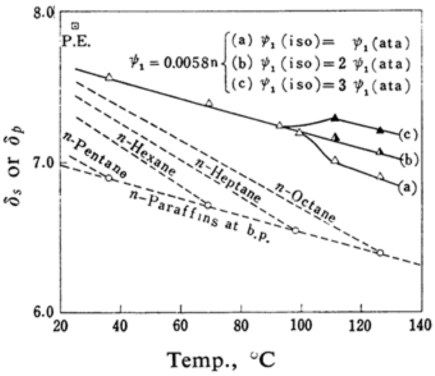

Fig. 9. Cohesive energy density of solvent, δ_s (broken line), and of polymer, δ_p (solid line), as a function of temperature.

Now we would like to speculate about the solubility parameter of the polymer, δ_p. We assume that extraction is carried out at the critical solution temperature, T_c, of the extracted polymer fraction with regard to the hydrocarbon used for extraction. According to Flory,[14] the heat parameter, κ_1, is related to the entropy parameter, ψ_1, and the free energy parameter, χ_1, by $\chi_1=0.5+\kappa_1-\psi_1$, and the value of χ_1 at the critical temperature is expressed by the equation:

$$\chi_{1,c}=\frac{(1+x^{1/2})^2}{2x} \tag{12}$$

Accordingly, by combining these equations with Eq. 8, we obtain:

$$(\delta_s-\delta_p)^2{}_{T=T_c}=\frac{RT_c}{V_1}\left[\frac{1}{2x}+\frac{1}{x^{1/2}}+\psi_1\right] \tag{13}$$

where x means the ratio of the molar volume of the polymer to that of the solvent. As the entropy parameter, ψ_1, is independent of the temperature, if ψ_1 is known for the corresponding solvent-polymer system, then we can calculate the δ_p at $T=T_c$ from Eq. 13.

So far we do not have any information about the ψ_1 of polypropylene in aliphatic hydrocarbons. However, the results obtained by Fox[19] for the ψ_1 of polyisobutylene-aliphatic hydrocarbon systems may serve as a reference. The relationship obtained between ψ_1 and the number of carbon atoms in aliphatic hydrocarbons, n, is

$$\psi_1=0.0058\,n \tag{14}$$

The δ_p values, calculated from Eq. 13 by the use of the ψ_1 values obtained by assuming Eq. 14 for polypropylene, are plotted against the temperature as curve a in Fig. 9. The curve shows that δ_p is abruptly changed at the fraction (F10) extracted near 100°C. This change in δ_p may be due to the change in T_c arising from the marked effect in tacticity. As is obvious from Fig. 3, the densities of the fractions above F10 are quite high and are almost all the same. Previously we pointed out, on the basis of experiments on polymethyl methacrylate in several solvents,[20] that the ψ_1 of the isotactic polymer is always larger than that of the atactic polymer. If we apply this fact for polypropylene and assume $\psi_1(\text{iso})=2\psi_1(\text{atac})$ and $\psi_1(\text{iso})=3\psi_1(\text{atac})$, then we obtain curves b and c in Fig. 9. In these estimations, we regarded the fractions extracted at above 100°C as isotactic and used the $\psi_1(\text{iso})$ value, and the fractions extracted at below 100°C as atactic and used the $\psi_1(\text{atac})$ value, the value calculated by Eq. 14. In the case of curve b, δ_p was nearly linearly decreased with the temperature, but in the case of c, the δ_p of the fractions above F10 were located higher than those given by curve b. If we extrapolate the linear portion of these curves for higher fractions, then we have, at a given temperature, $\delta_p(\text{iso})\gtreqless\delta_p(\text{atac})$ according to the condition of a, b, and c. In the present polymer-solvent system, the case c means that the energy interaction between the crystalline segment and the solvent is larger than that between the amorphous segment and the solvent. Such a case is the same as the model

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[19] T. G. Fox, *Polymer*, **3**, 111 (1962).

[20] I. Sakurada, A. Nakajima, O. Yoshizaki and K. Nakamae, *Koll-Z.*, **186**, 41 (1962).

introduced by Oyama[21] for a crystalline polymer solution. Thus, the condition as given in c seems most probable so far as Eq. 14 is concerned.

So far as Eq. 14 is concerned, the δ_p value of polypropylene at 25°C is estimated as 7.6. This value may be compared to $\delta_p=7.9$ for polyethylene[21] and $\delta_p=8.05$ for polyisobutylene.[22] Taking into account the value obtained here for polypropylene at 25°C, the solubility parameter, δ_s, of *n*-octane or *n*-nonane at 25°C is very close to that of polypropylene at that temperature.

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[21] T. Oyama, *Chem. High Polymers, Japan* (*Kobunshi Kagaku*), **18**, 420, 426 (1961).

[22] M. Magat, *J. Chim. Phys.*, **46**, 344 (1949); H. A. Stuart, "Das Makromolekül in Lösungen," Springer-Verlag, Berlin (1953), p. 204.