

Heptane-Soluble Material from Atactic Polypropylene. II. Interaction with Liquids

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Synopsis

Reduced melting point and swelling measurements, involving heptane-soluble material from atactic polypropylene and over thirty liquids of differing chemical type, are reported. A value of 578 ± 40 cal. is obtained for the molar heat of fusion of a crystalline repeat unit which is much lower than values given for isotactic polypropylene. Some reasons for the low value are considered. Values of the polymer-solvent interaction parameter χ_1 for systems involving alkylbenzenes and *n*-alkanes suggest a solubility parameter of 7.9 ± 0.1 (cal./cc.)^{1/2} for the polymer. These values of χ_1 decrease with increasing molar volume of liquid. Polar liquids of comparable solubility parameter or molar volume are associated with higher values of χ_1 . Intrinsic viscosities and values of the slope constant k' are given for fractions in the molecular weight range 3,000-25,000 and six solvents at 25°C. The results suggest the following order of solvent power: cyclohexane \approx cyclohexene > methylcyclohexane > trichloroethylene > decalin > carbon tetrachloride. Intrinsic viscosities are higher than those generally obtained for flexible polymers of comparable molecular weight, and the values of the Mark-Houwink exponent appear to be high. Some reasons for these high values are considered.

INTRODUCTION

The fractionation of heptane-soluble material obtained from atactic polypropylene following prior extraction with ether was described in a previous paper.¹ It was pointed out that the material is likely to contain a mixture of polypropylenes of varying degrees of stereoregularity which should include stereoblock polypropylene. Although the material is soluble in a number of liquids at room temperature, little seems to be known of its interaction with liquids. This paper reports the results of swelling and reduced melting point measurements involving the fraction of highest molecular weight and dilute solution viscosity measurements on this and other fractions. Estimates are made of the polymer-solvent interaction parameter χ_1 for over thirty polymer-liquid systems. Some of the factors likely to affect the polymer-liquid interaction are discussed. Variations of intrinsic viscosities and values of the Huggins slope constant k' with solvent and polymer molecular weight are also considered.

EXPERIMENTAL

Materials

Six fractions of the heptane-soluble material, obtained as previously described,¹ were used. For convenience their molecular weights, densities, and melting points are given in Table I.

Cyclohexane, methylcyclohexane, cyclohexene, trichloroethylene, carbon tetrachloride, and decalin were used as solvents. Other liquids used in reduced melting point and swelling studies are given in Tables II and III. These and the solvents were dried and purified by appropriate methods and fractionally distilled before use.

TABLE I
Characteristics of Fractions

Fraction	Number-average molecular weight	Density (25°C.), g./ml.	Melting point, °C.
1	25,000	0.868	132
2	17,000	0.869	111.5
3	13,000	0.871	111.5
4	10,500	0.876	111.5
5	7,000	0.8875	112
6	3,400	0.888	116

TABLE II
Swelling Data

Liquid	20°C.		40°C.		T_m , °C.	χ_1 at T_m
	Q_m	χ_1	Q_m	χ_1		
Benzene	0.808	0.82	1.180	0.74	51	0.69
<i>n</i> -Amyl methyl ketone	0.388	1.07	0.487	0.98	97	0.76
Mesitylene	1.569	0.69	2.210	0.64	50	0.62
<i>n</i> -Butyl chloride	1.728	0.67	3.044	0.60	52.5	0.56
Tetralin	1.372	0.71	1.723	0.67	62	0.63
Bromobenzene	0.897	0.80	1.029	0.77	64	0.73

Experimental Methods

Reduced melting points of fraction 1 were determined by a method essentially that of Anagnostopoulos and Coran,^{2,3} involving determination of the temperature at which a swollen particle of polymer in excess liquid changed from a seemingly firm gel to a smooth-edged transparent drop. This temperature is regarded as the reduced melting point T_m of the polymer. According to Flory:^{4a}

$$1/T_m - 1/T_0 = RV_u(\phi_1 - \chi_1\phi_1^2)/\Delta H_u V_1 \quad (1)$$

where T_0 is the crystalline melting point of the polymer in absolute degrees, V_u and ΔH_u the molar volume and molar heat of fusion, respectively, of a

TABLE III
 Reduced Melting Point Data

Liquid	ϕ_1	$T_m, ^\circ\text{C.}$	χ_1
Trichloroethylene	0.950	5	0.37
Cyclohexane	0.892	16.5	0.36
Cyclohexene	0.870	18.5	0.31
Carbon tetrachloride	0.845	20	0.41
Decalin	0.984	24	0.13
Tetrachloroethylene	0.921	25.5	0.44
Methylcyclohexane	0.840	26.5	0.24
Chloroform	0.863	35.5	0.54
<i>n</i> -Heptane	0.925	41.5	0.33
Toluene	0.757	43.5	0.53
<i>n</i> -Hexane	0.929	44	0.44
<i>n</i> -Propyl bromide	0.785	45	0.66
<i>m</i> -Xylene	0.816	45.5	0.46
<i>n</i> -Butyl bromide	0.852	49	0.60
<i>sec</i> -Butyl chloride	0.772	49.5	0.60
<i>sec</i> -Butyl bromide	0.909	50	0.59
Mesitylene	0.835	50	0.44
Isopropyl bromide	0.854	50.5	0.67
<i>n</i> -Octane	0.900	51	0.34
Benzene	0.752	51	0.73
<i>n</i> -Butyl chloride	0.788	52.5	0.64
Nonane	0.880	54	0.29
Decane	0.860	57	0.25
Undecane	0.810	56	0.15
Tetralin	0.805	62	0.58
Dodecane	0.810	62.5	0.14
<i>s</i> -Tetrachloroethane	0.784	62.5	0.73
<i>o</i> -Bromotoluene	0.876	63	0.66
Bromobenzene	0.875	64	0.72
Di- <i>n</i> -butyl ether	0.863	65	0.46
Tridecane	0.797	66	0.12
<i>o</i> -Dichlorobenzene	0.816	67	0.74
Cyclohexanone	0.562	96	1.28
<i>n</i> -Amyl methyl ketone	0.714	97	0.95

crystalline repeat unit, R the gas constant and ϕ_1 and V_1 the volume fraction and molar volume, respectively, of the liquid.

The apparatus of Anagnostopoulos and Coran was slightly modified in order that volatile liquids could be used. A brass cylinder, about 0.8 cm. deep and 1 cm. in diameter, was provided with brass collars which could be screwed on to the ends of the cylinder. The collars held thin glass circles, between poly(ethylene terephthalate) washers, firmly against the ends of the cylinder, thus providing a closed cell which could be completely filled with liquid containing a roughly spherical particle of polymer. The cell was placed on a heating stage the temperature of which was raised at a rate of not more than 0.5°C./min. and the temperature noted at which the swollen particle, observed by means of a microscope, changed from an

apparently firm gel to a smooth-edged transparent drop. Such temperatures were reproducible to $\pm 2^\circ\text{C}$. In a few cases T_m was near or below room temperature, and in these the heating stage was cooled with a metal block which had been placed in a mixture of acetone and solid carbon dioxide. The stage was then allowed to slowly warm to room temperature. At least two determinations were made with each liquid. The volume fraction of liquid ϕ_1 was estimated from measurements of the particle before contact with liquid and of the transparent drop. Both particle and drop were assumed to be spherical. It was also assumed that swelling was isotropic and that no volume change occurred in mixing.

The use of eq. (1) to obtain values of χ_1 requires values for V_u and ΔH_u . The former can be obtained from the molecular weight of the repeat unit and the density of the polymer at T_m . If the density of the polymer is known at one temperature, the density at others may be obtained from the formula of Danusso et al.,⁵ assuming that the crystallinity does not change. A plot of $1/T_m$ against $RV_u(\phi_1 - \chi_1\phi_1^2)/V_1$ should be rectilinear with slope $1/\Delta H_u$ and ordinate intercept $1/T_0$. Values of χ_1 at T_m were therefore obtained independently from measurements of the swelling of films and the results used to obtain a value for ΔH_u .

Films of fraction 1 were prepared by casting from solutions in cyclohexane on to mercury, evaporation of solvent and further removal of solvent under vacuum. Weighed strips of film were immersed in excess benzene, *n*-amyl methyl ketone, mesitylene, *n*-butyl chloride, tetralin, and bromobenzene at 20 ± 0.05 and $40 \pm 0.05^\circ\text{C}$. until no further increase in weight occurred. Values of T_m and ϕ_1 with these liquids had previously been obtained. Values of χ_1 for each polymer-liquid combination at each temperature were obtained from:⁶

$$\ln(1 + 1/Q_m) = (1 + Q_m)^{-1} + \chi_1(1 + Q_m)^{-2} \quad (2)$$

where Q_m is the maximum volume of liquid imbibed by unit volume of polymer. It was assumed that the variation of χ_1 with temperature could be represented by:

$$\chi_1 = A + B/T \quad (3)$$

where T is the absolute temperature, A a temperature-independent term, and B a heat term. This relationship was used to obtain values of χ_1 at T_m from those at 20 and 40°C . for each of the polymer-liquid combinations used in swelling measurements. At least two determinations were made with each combination and the values of Q_m did not generally differ by more than 5%.

Viscosities of dilute solutions of the fractions in the concentration range 0.1–0.5 g./dl. were determined by using a suspended level capillary viscometer at $25 \pm 0.02^\circ\text{C}$. Plots of viscosity number η_{sp}/c against concentration c were used to obtain values of intrinsic viscosity $[\eta]$ and k' in the expression:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \quad (4)$$

RESULTS

Table II gives values of Q_m for the two temperatures at which swelling was measured and the corresponding values of χ_1 . Values of T_m obtained with the liquids used in swelling and estimated values of χ_1 at these temperatures are also given.

Uncertainty in the values of χ_1 from swelling measurements is estimated to be ± 0.05 .

Figure 1 shows a plot of $1/T_m$ against $RV_u(\phi_1 - \chi_1\phi_1^2)/V_1$ based on the values of T_m and χ_1 at T_m given in Table II. The plot, which is drawn to intercept the ordinate at $1/T_0$, shows some scatter and yields a value of 578 ± 40 cal./crystalline repeat unit for ΔH_u . The scatter may arise from at least two causes. The assumption that A , in eq. (3), is independent of temperature may not be entirely true. The values of ϕ_1 corresponding to Q_m are generally less than those referring to T_m , and it is quite possible that χ_1 will vary with concentration^{4b} as well as temperature. The estimated values of χ_1 at T_m may therefore be subject to some uncertainty. It may be significant that the point for *n*-amyl methyl ketone, the liquid associated with the highest value of T_m in Table II and the lowest value of ϕ_1 corresponding to Q_m , is the furthest from the line in Figure 1. The value of 578 cal. for ΔH_u must be regarded as approximate. It is also considerably less than might be expected. This latter point will be considered later. The value of 578 cal./repeat unit has, however, been used in eq. (1) to obtain values of χ_1 from the experimental values of T_m and ϕ_1 . Mean values of these and of χ_1 are given in Table III.

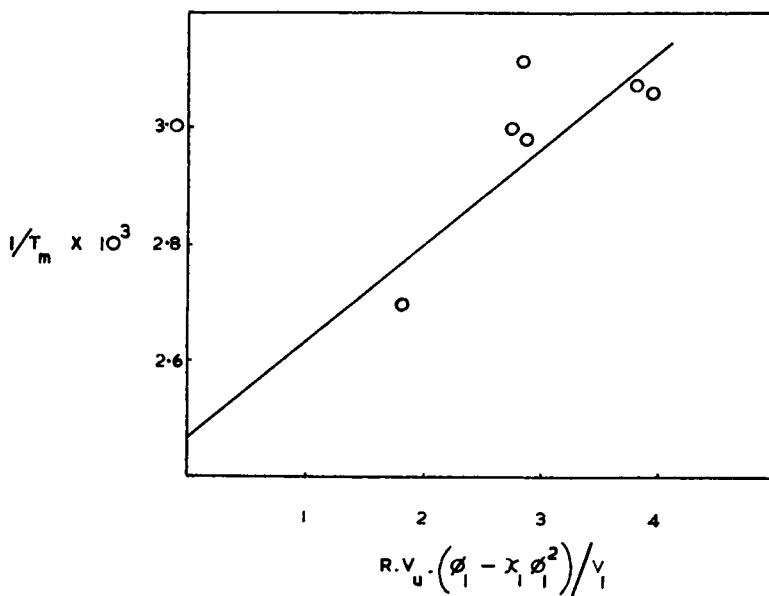


Fig. 1. $1/T_m$ as a function of $RV_u(\phi_1 - \chi_1\phi_1^2)/V_1$.

Figure 2 shows plots of η_{sp}/c against c at 25°C. Table IV gives values of intrinsic viscosity.

Table V gives values of the slope constant k' for Fractions 1 and 2. The small slopes of the η_{sp}/c against c plots for the other fractions precluded accurate estimation of k' .

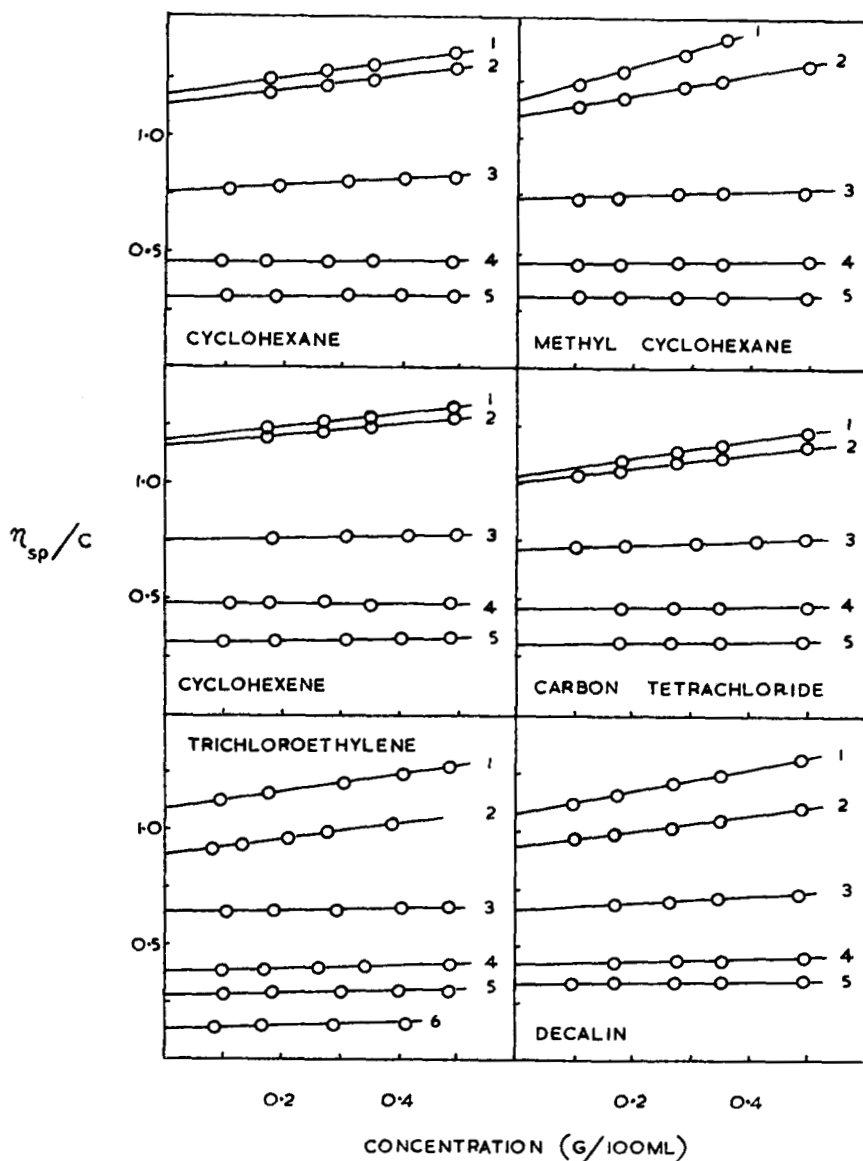


Fig. 2. η_{sp}/c vs. c plots for fractions in different solvents.

TABLE IV
 Intrinsic Viscosities at 25°C.

Solvent	[η], dl./g.					
	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Fraction 6
Cyclohexane	1.18	1.13	0.77	0.45	0.32	
Methylcyclohexane	1.14	1.08	0.73	0.45	0.32	
Cyclohexene	1.17	1.14	0.75	0.48	0.32	
Decalin	1.08	0.91	0.67	0.43	0.33	
Trichloroethylene	1.08	0.89	0.64	0.42	0.29	0.14
Carbon tetrachloride	1.03	1.01	0.70	0.46	0.32	

 TABLE V
 Values of k'

Solvent	k'	
	Fraction 1	Fraction 2
Cyclohexane	0.25	0.29
Methylcyclohexane	0.36	0.38
Cyclohexene	0.24	0.24
Trichloroethylene	0.39	0.34
Decalin	0.40	0.45
Carbon tetrachloride	0.42	0.34

DISCUSSION

The value of 578 cal./repeat unit for ΔH_u , although approximate, is much less than those of 2370 and 2600 cal./repeat unit given for isotactic polypropylene.^{7,8} Although the fraction used may contain material of differing and lower degrees of stereoregularity,¹ a higher value for ΔH_u might be expected, since it refers to a crystalline repeat unit. A value approaching those for isotactic polypropylene, with the experimental values of T_m , would lead to negative values of χ_1 which seem improbable, at least with nonpolar liquids. It is possible that the values of T_m are too low. Coran and Anagnostopoulos³ have suggested that the temperature at which a transition occurs from a seemingly firm gel to a liquid drop may be lower than the true value of T_m . Even if this were so, the values of T_m obtained with the liquids used in swelling would have to be considerably higher than those given in Table II to correspond to values of ΔH_u closer to those for isotactic polypropylene. It is possible that both T_0 and T_m are reduced by amorphous material. Although melting point is not normally depressed very much on mixing amorphous and crystalline polymer, the fraction used may be of sufficiently low molecular weight for amorphous material to act as solvent for crystalline and reduce the value of T_0 . Amorphous material and liquid together may similarly reduce the value of T_m below

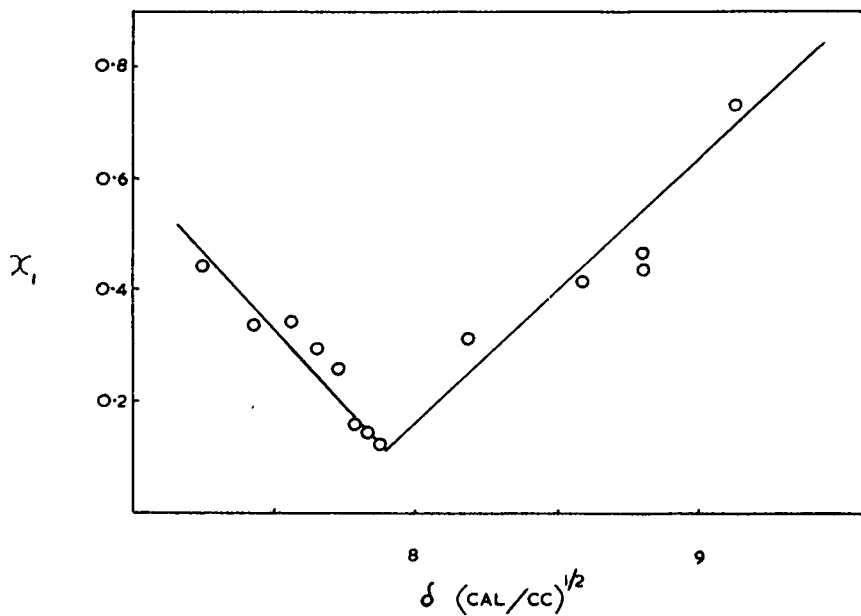


Fig. 3. χ_1 as a function of solubility parameter of nonpolar liquids.

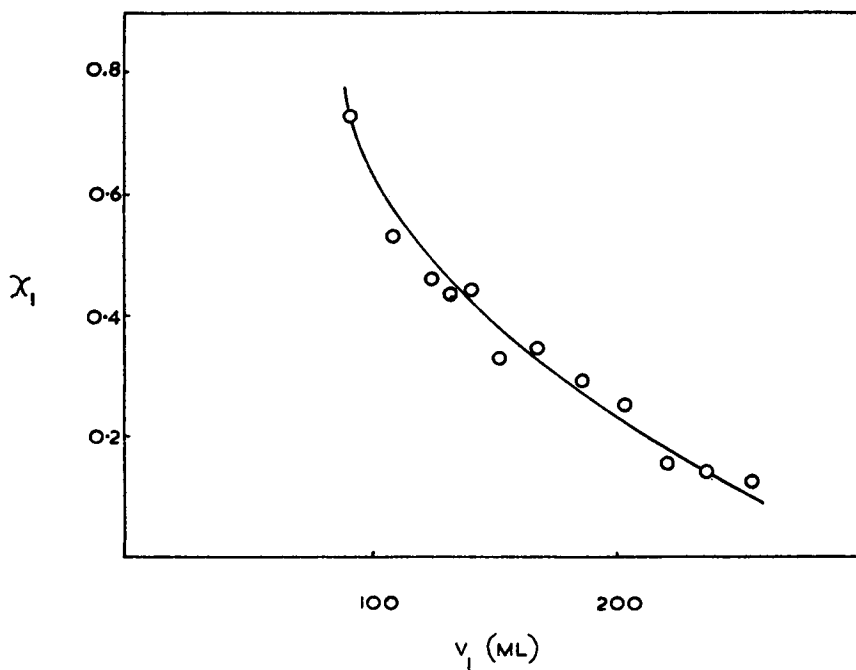


Fig. 4. χ_1 as a function of molar volume for alkylbenzenes and *n*-alkanes.

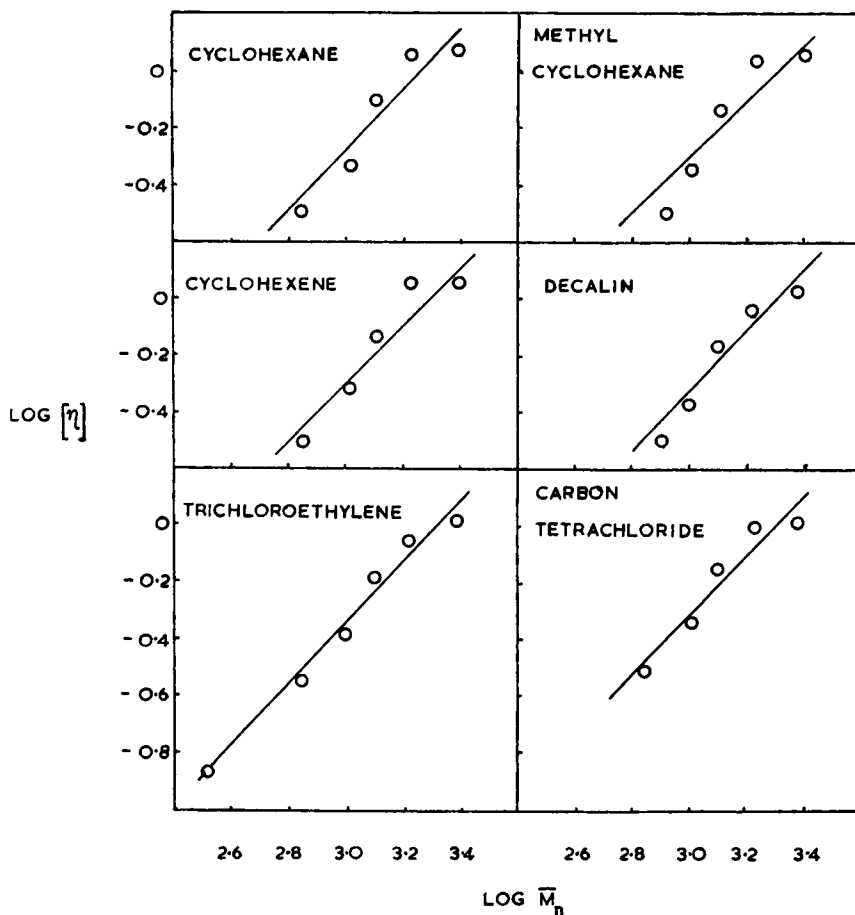


Fig. 5. $\log [\eta]$ as a function of $\log \bar{M}_n$ for different solvents.

that which would be obtained for crystalline material and liquid only. Examination of eq. (1) shows that reduction of T_0 and T_m in this way would lead to a lower value for ΔH_u .

Although the values of χ_1 given in Table III, because of the uncertainty with respect to the value of ΔH_u , may also be subject to uncertainty, they should place the liquids in the correct order as regards interaction with the polymer. An approximate correlation of the values of χ_1 obtained with nonpolar liquids with the solubility parameter⁹ δ of the liquid is shown in Figure 3. The values of δ refer to 25°C. Although the values of χ_1 refer to different temperatures it may suffice, as Hildebrand and Scott¹⁰ suggest, to have consistent values of δ at one temperature. Figure 3 suggests a minimum at 7.9 ± 0.1 (cal./cc.)^{1/2}, presumably corresponding to the solubility parameter of the polymer. Calculation of this by Small's method¹¹ gives 7.75 (cal./cc.)^{1/2}. Assuming the entropy contributions to χ_1 with the nonpolar liquids to be not very different, the data are in accord

with Hildebrand's view that the heats of mixing are related to the differences between the solubility parameter of the polymer and those of the liquids.⁹ The plot shown in Figure 3 is much more scattered if the data for polar liquids is included. Figure 4 shows a plot of χ_1 against the molar volume of liquid V_1 for alkylbenzenes and *n*-alkanes. χ_1 decreases with increasing values of V_1 . Similar results have been obtained with polyethylene-liquid systems.² Table III shows that nonpolar liquids are associated with lower values of χ_1 than are polar liquids of comparable molar volume.

The values of $[\eta]$ in Table IV suggest the following order of solvent power at 25°C.: cyclohexane \approx cyclohexene > methylcyclohexane > trichloroethylene > decalin > carbon tetrachloride. The variation of $[\eta]$ with solvent, however, is small. A similar order is suggested by the values of k' . These orders are not those which might have been expected from the values of χ_1 in Table III which refer, however, to different concentrations and somewhat different temperatures. The values of $[\eta]$ are considerably greater than those to be expected for flexible polymers, and the comparatively low values of k' suggest that association of polymer is not responsible.¹² The value for $[\eta]$ of 1.18 for fraction 1 in cyclohexane may be compared with 0.29 for polyisobutene of the same molecular weight in the same solvent, calculated from the appropriate viscosity-molecular weight relationship.¹³ Moraglio and Danusso¹⁴ found the intrinsic viscosities of atactic polypropylene to be unusually high. The high values of $[\eta]$ suggest that the chains may be considerably extended in solution, and this might account for the small variation of $[\eta]$ with solvent.

Figure 5 shows plots of $\log [\eta]$ against $\log \bar{M}_n$. The lines are drawn with a slope of unity. The points may suggest higher values, but these are improbable on theoretical grounds.¹⁵ Assuming the relationship $[\eta] = KM^a$ to apply, with the exponent a equal to unity, we obtain the values of K in Table VI. A value of similar magnitude to these was obtained by Ciampa¹⁶ for stereoblock polypropylene in tetralin at 135°C.

The high value for the exponent a is in accord with the suggestion of extended chains and exponents of unity at low molecular weights have been suggested for cellulose derivatives,¹⁷⁻¹⁹ the chains of which are known to be extended. It may, however, be doubtful to what extent concepts applicable at higher molecular weights can be applied to the low molecular

TABLE VI
Values of K

Solvent	$K \times 10^6$
Cyclohexane	5.25
Methylcyclohexane	4.6
Cyclohexene	4.8
Carbon tetrachloride	4.95
Trichloroethylene	4.5
Decalin	4.6

weight polymers concerned here. Theory²⁰⁻²² predicts an exponent of unity for completely draining Gaussian chains at lower molecular weights, but deviations to a lower exponent are to be expected at higher molecular weights.¹⁵ The reverse behavior is, however, shown by polystyrene¹⁵ and poly(methyl methacrylate).²³ It is possible that the high value of the exponent a is a consequence of differing molecular weight distributions in the fractions,²⁴ and the relatively low values of K may tend to support this view. Differing molecular weight distributions might also account for the scatter of the points in Figure 5.

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Résumé

Des mesures de points de fusion réduits et des mesures de gonflement, comportant la détermination de matériaux solubles dans l'heptane au départ de polypropylène atactique et comportant au delà de 30 liquides de type chimique différent, ont été rapportés dans le présent travail. Une valeur de 578 ± 40 cal. a été obtenue pour la chaleur de fusion molaire de l'unité périodique cristalline, ce qui est beaucoup plus faible que les valeurs indiquées pour le polypropylène isotactique. Certaines raisons pour ces faibles valeurs sont soumises à considération. Les valeurs du paramètre d'interaction χ_1 du polymère-solvant pour les systèmes comportant des alkyle-benzènes et des *N*-alkanes suggèrent un paramètre de solubilité de 7.9 ± 0.1 (cal./cc.)^{1/2} pour le polymère. Ces valeurs de χ_1 décroissent avec un volume molaire croissant du liquide. Les liquides polaires de paramètres de solubilité comparables ou de volume molaire comparable sont associés avec des valeurs plus élevées de χ_1 . Les viscosités intrinsèques et les valeurs des tangentes k' sont

déterminées pour les fractions de poids moléculaires variant de 3.000 à 25.000 et six solvants à 25°C. Les résultats suggèrent l'ordre suivant du pouvoir solvant: cyclohexane \approx cyclohexène > méthyl cyclohexane > trichloréthylène > décaline > tétrachlorure de carbone. Les viscosités intrinsèques sont plus élevées que celles généralement obtenues pour les polymères flexibles de poids moléculaires comparables et les valeurs de l'exposant de l'équation de Mark-Houwink sont élevées. Certaines raisons pour ces valeurs élevées sont considérées.

Zusammenfassung

Über die Messung des reduzierten Schmelzpunkts und der Quellung von heptanlöslichem Material aus ataktischem Polypropylen in über 30 Flüssigkeiten von verschiedenem chemischen Charakter wird berichtet. Ein Wert von 578 ± 40 cal wird für die molare Schmelzwärme des kristallinen Kettenbausteins erhalten, was viel niedriger als die für isotaktisches Polypropylen angegebenen Werte ist. Einige Gründe für den niedrigen Wert werden untersucht. Die Werte des Polymer-Lösungsmittel-Wechselwirkungsparameters χ_1 für Systeme mit Alkylbenzolen und *n*-Alkanen ergeben für das Polymere einen Löslichkeitsparameter von $7,9 \pm 0,1$ (cal/cc)^{1/2}. Die Werte von χ_1 nehmen mit steigendem Molvolumen der Flüssigkeit ab. Polare Flüssigkeiten mit vergleichbarem Löslichkeitsparameter oder Molvolumen besitzen höhere χ_1 -Werte. Viskositätszahlen und Werte der Neigungskonstanten k' werden für Fraktionen im Molekulargewichtsbereich von 3000 bis 25 000 und 6 Lösungsmitteln bei 25°C angegeben. Die Ergebnisse liefern folgende Reihenfolge der Lösungsmittelgüte: Zylohexan \approx Zylohexen > Methylzylohexan > Trichloräthylen > Dekalin > Tetrachlorkohlenstoff. Die Viskositätszahlen liegen höher als sie allgemein für flexible Polymere von vergleichbarem Molekulargewicht erhalten werden und die Werte für den Mark-Houwink-Exponenten scheinen hoch zu sein. Gründe für diesen hohen Werte werden diskutiert.

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