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Morphological factor in the melting point depression of polypropylene by alkanes

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Abstract

Data of the melting point depression of isotactic polypropylene by *n*-alkanes ($n_C = 5$–30) reported by Hamada and Nakajima are analyzed. Anomalous values of the enthalpy of fusion per chain repeat unit and the polymer-diluent interaction parameter that have been obtained by applying the Flory equation for the melting point depression of crystalline polymers are attributed to the effect of diluent on the morphology of polymer crystals. Information on the magnitude of this effect is obtained. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The depression of the melting temperature of crystalline polymers by low-molecular-weight diluents is currently described by Eq. (1)

$$\Delta \equiv (1/T_m) - (1/T_m^0) = (R/\Delta H_u)(V_{2u}/V_1)(\varphi_1 - \chi\varphi_1^2) \qquad (1)$$

where T_m is the melting temperature of the polymer-diluent mixture, T_m^0 is the melting temperature of pure crystalline polymer, ΔH_u and V_{2u} are, respectively, the heat of fusion and the molar volume per chain repeat unit of the crystalline polymer, V_1 and φ_1 are, respectively, the molar volume and the volume fraction of diluent, and χ is the polymer-diluent interaction parameter. The equation offers a possibility to estimate the values of ΔH_u and χ. It is to be emphasized that it holds in the limit of high polymer molecular weights.

Eq. (1) and a similar relationship for mixtures of crystalline and amorphous polymers [2,3] have received large experimental verification with many systems, and in many cases both the ΔH_u and χ values obtained were in good agreement with those determined by other methods. Nevertheless, there are systems where the correspondence of χ values is not good [4]. An extreme disagreement has been found with mixtures of oligomers of ethylene oxide (crystalline) and propylene oxide (amorphous component) [5]. While the χ parameter determined from measurements of the melting point depression was negative and its absolute value was high, the values estimated by gas–liquid chromatography or from liquid–liquid equilibria were positive.

In search for χ values of isotactic polypropylene (IPP) we came across the paper by Hamada and Nakajima [6] who had studied the depression of the melting temperature of IPP by *n*-alkanes comprising $n_C = 5$–32 carbon atoms. Contrary to expectation, the ΔH_u values calculated with Eq. (1) were not constant but decreased from 8.33 kJ/mol for *n*-pentane to 5.31 kJ/mol for $n_C = 32$ and were considerably lower than those found by other methods (9.83–10.88 kJ/mol) [7]. By re-evaluating these data we found that not only the enthalpy of fusion but also the χ parameters are in strong disagreement with other information on these systems. This situation initiated the present note.

2. Results and discussion

Experimental data from Ref. [6] are plotted as Δ/φ_1 in Figs. 1 and 2. The slopes are negative for alkanes from *n*-pentane to *n*-octacosane ($5 < n_C < 20$) and close to zero for higher alkanes. That would indicate negative or zero χ-values. However, negative χ values are typical of systems with specific polymer–solvent interaction. In view of chemical similarity of IPP and *n*-alkanes, specific interactions can be excluded from considerations. This opinion is supported by a paper by Cowie and Ewen [8]. The authors studied liquid–liquid equlibria in solutions of IPP in *n*-pentane, *n*-hexane and *n*-octane at high temperatures and estimated the lower critical solution temperatures (LCST,

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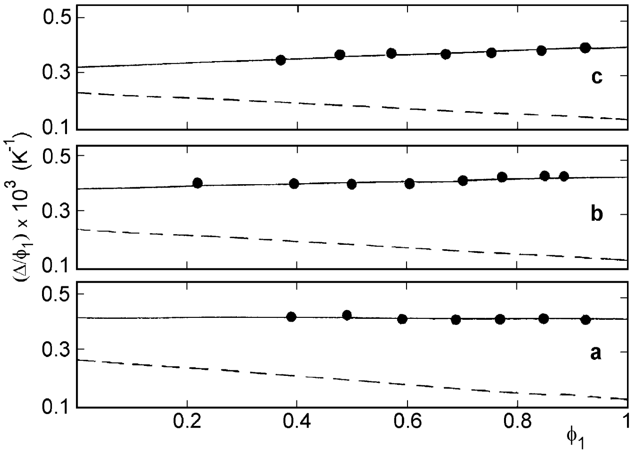

Fig. 1. Depression Δ of melting temperature of isotactic polypropylene (IPP) in *n*-pentane (a), *n*-hexane (b) and *n*-heptane (c) plotted as Δ/φ_1 vs. φ_1. Experimental data from Ref. [6]. Broken curves (*a–c*) calculated by means of Eq. (1) with $\chi = 0.51$, 0.47 and 0.41, respectively.

Θ_L) and the entropy-of-mixing parameters ψ ($\Theta_L = 397$, 449, 437 K and $\psi = -0.3$, -0.33 and -0.43 for $n_C = 5$, 6 and 7, respectively). Using the equation

$$\chi = 1/2 - \psi(1 - \Theta_L/T) \tag{2}$$

we have computed approximate χ values for these three systems ($\chi = 0.51$, 0.47 and 0.41) at the temperature $T =$ 400 K which corresponds to the middle of the interval of T_m values. The parameters χ are positive and much higher than those calculated from the melting point depression (Fig. 3).

For the sake of comparison, we have compiled χ values for polyethylene in *n*-alkanes (Fig. 3). Unlike IPP, almost all of them are positive irrespective of the method of estimation, and those calculated from the melting point depression are in fair agreement with those obtained by other methods (liquid–liquid equlibria, gas–liquid chromatography [9–14]).

The plots of Δ/φ_1 vs. φ_1 for IPP in *n*-pentane, *n*-hexane and *n*-heptane in Fig. 1 are completed by curves computed with Eq. (1) and the χ parameters mentioned above. The differences Y between the experimental and calculated values of Δ/φ_1 are large. As can be seen in Fig. 4, they can be well fitted by the equation

$$Y = Y_0 + Y_1\varphi_1 \tag{3}$$

where the Y_0 and Y_1 values depend on the length of alkane chains. Combining Eqs. (1) and (3) we obtain an empirical modification of Eq. (1)

$$\Delta/\varphi_1 = a + b\varphi_1 \tag{4}$$

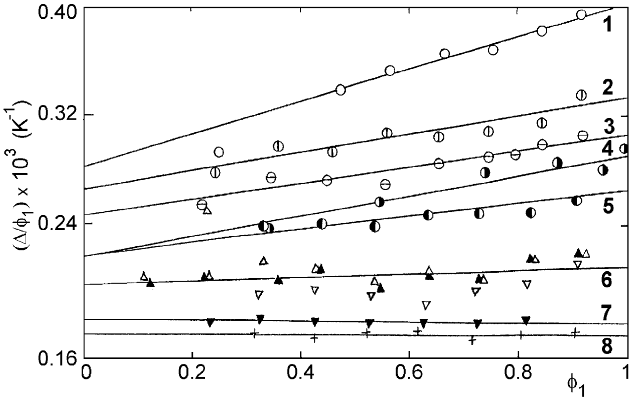

Fig. 2. Depression Δ of melting temperature of IPP in *n*-alkanes. Experimental data from Ref. [6]. Curves 1–5 for n_C (number of C atoms in alkane chain)= 8, 9, 10, 12, 14, curve 6 for $n_C = 16$, 18, 20, curves 7 and 8 for $n_C = 22$ and 28.

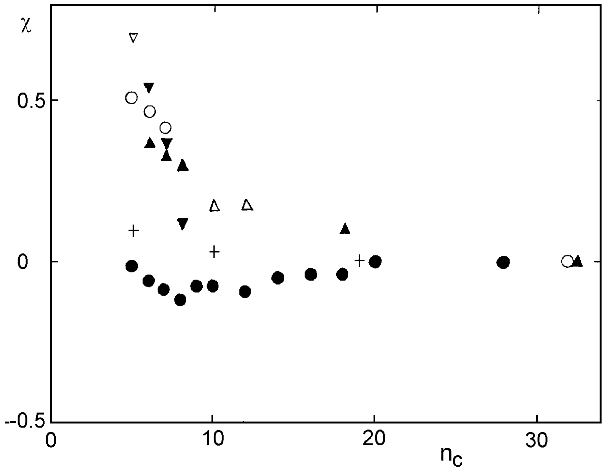

Fig. 3. χ-parameter for polyethylene (PE) and isotactic polypropylene in *n*-alkanes at 400–410 K. Data points for IPP: ● this paper (apparent values estimated from the slopes of plots in Figs. 1 and 2 according to Eq. (1)), ○ calculated with Eq. (2) as described in text. Data points for PE calculated from melting point depression [11,13] (▲ +), liquid–liquid equlibria [12,13] (▽▼), gas–liquid chromatography [9] (△). Highly negative value ($\chi = -1.3$) for PE in dotriacontane as obtained by Ke [10] from the melting point depression is not included.

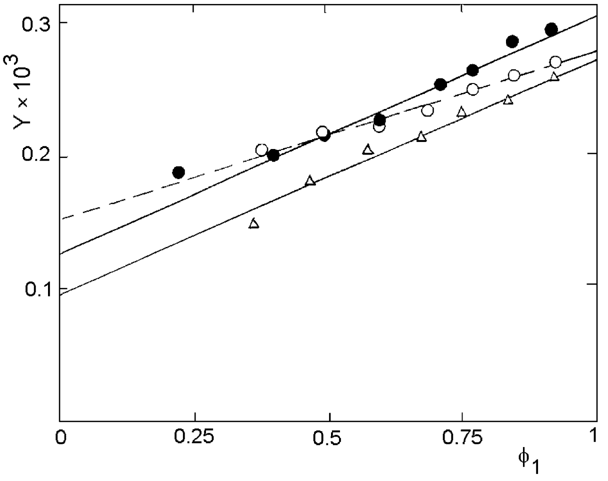

Fig. 4. Plot of Y (defined by Eq. (3)) vs. diluent concentration φ_1 for IPP in *n*-pentane (○), *n*-hexane (●), *n*-heptane (△).

where

$$a = (RV_{2u}/\Delta HV_1) + Y_0 \qquad (5)$$

and

$$b = Y_1 - (RV_{2u}/\Delta H_u V_1)\chi \qquad (6)$$

We assume that Eq. (4) also holds for higher alkanes where direct estimation of Y_0 and Y_1 by the method similar to that used with lower alkanes is impossible because the χ values in the range of the melting temperatures are unknown.

The a and b values are equal, respectively, to the intercepts and slopes of plots in Figs. 1 and 2. As shown in Fig. 5 the a values increase with an increase in V_1^{-1}. At $n_C > 8$ the dependence is nearly linear, the intercept being 0.08×10^{-3} K^{-1}. As follows from Eq. (5) the (initial) slope of this plot should be equal to $RV_{2u}/\Delta H_u$. With this assumption we obtain $\Delta H_u = 9.83 \times 10^3$ J/mol in good agreement with the values mentioned above [7].

The b values are positive for $n_C < 16$ and close to zero for higher alkanes. The dependence of b on n_C (Fig. 6) is more involved than that of the a parameter. It has a maximum at $n_C \approx 10$. At $n_C > 16$ the b parameter is equal to zero due to the compensation of the terms in Eq. (6).

The difference in ΔH_u has been attributed to the impact of the diluents on the morphology of polymer crystals [6]. As follows from the theory [1] the dependence of the melting temperature on the concentration of diluent follows from three contributions to the free energy changes. They are due to the fusion of polymer crystals, mixing of components and morphological effects. Eq. (1) is a simplified form of a more general equation derived by Flory [1] where not only the polymer–diluent interaction but also the equilibrium crystallite length ξ was taken into account ('morphological factor'). This factor depends on the polymer concentration and the nucleation parameter connected with the end-interfacial free energy but cannot be predicted by the theory [1].

Kwei and Frisch [15] have derived a similar equation which is more practical for use. The morphological term is expressed as the difference $(2\sigma/\xi) - (2\sigma/\xi)^0$, where the symbol 2σ stands for the surface free energy of segments in a crystal lamella. It has been defined 'in a broad sense to include the contributions from surface induced defects'. Superscripts 0 refer to zero diluent concentration. Based on some experimental observations the authors described the concentration dependence of this difference by equations

$$\xi = \xi^0(1 - q\varphi_1) \qquad (7)$$

and

$$(2\sigma/\xi) - (2\sigma/\xi)^0 = (2\sigma/\xi)^0 q\varphi_1 \qquad (8)$$

where

$$q \ll 1 \quad \text{and} \quad (2\sigma/\xi) \approx (2\sigma/\xi)^0 \qquad (9)$$

Walsh and Singh [16] pointed out that higher order terms in φ_1 may also appear in Eq. (8). Therefore we write

$$(2\sigma/\xi) - (2\sigma/\xi)^0 \approx C_1\varphi_1 + C_2\varphi_1^2 \qquad (10)$$

Combining Eqs. (1), (4) and (10) we obtain, after rearrangement

$$\Delta/\varphi_1 = (RV_{2u}/\Delta H_u)(V_1^{-1} + C_1/TV_{2u}) + [(C_2/\Delta H_u T_m) - (RV_{2u}/\Delta H_u V_1)\chi]\varphi_1 \qquad (11)$$

If the morphological term is negligible, Eq. (11) reduces to Eq. (1). It can be seen from Eq. (11) that the ratio Δ/φ_1 should not be a linear function of the diluent concentration because the χ parameter depends on temperature and the melting temperature T_m depends on concentration. However, as follows from Ref. [6] the T_m values for the highest and lowest concentrations differ by less than 10%, so the T_m values on the right hand side of Eq. (11) may be replaced by their arithmetic mean $\bar{T}_m$. For the same reason the variation of χ with temperature may be neglected. These approximations simplify the treatment of data without significantly affecting the conclusions.

In this approximation the plot of Δ/φ_1 should be linear, the intercept a and the slope b being given by equations

$$a = (RV_{2u}/\Delta H_u)V_1^{-1} + (RC_1/\Delta H_u \bar{T}_m) \qquad (12)$$

and

$$b = (C_2/\Delta H_u \bar{T}_m) - (RV_{2u}/\Delta H_u V_1)\chi \qquad (13)$$

It can be seen that, unlike Eqs. (5) and (6), the intercept a should be a linear function of the reciprocal of V_1 and the slope b may be positive even if the χ value is not negative. Thus the variation of ΔH_u with the alkane chain length as reported in Ref. [6] is only an apparent one.

The shape of the plot in Fig. 5 indicates that, for $V_1^{-1} < 5 \times 10^{-3}$ (i.e. for $n_C > 9$), the term $(RC_1/\Delta H_u \bar{T}_m)$ is approximately constant and equal to $a_0 = 8 \times 10^{-5}$. Using this value, $\bar{T}_m = 420$ K (which is practically invariant with respect to temperature) and $\Delta H_u = 9.83$ kJ/mol we estimate $C_1 \approx 39$ for these alkanes. The C_1 values for lower alkanes ($n_C < 9$) are higher (Fig. 5). This means that longer alkane

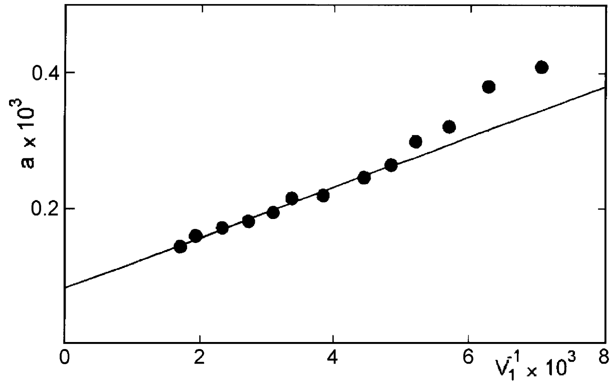

Fig. 5. Plot of the a parameter (cf. Eqs. (5) and (6)) of IPP vs. reciprocal value of the molar volume of alkanes. Curve 1 fits data points for $n_C > 8$.

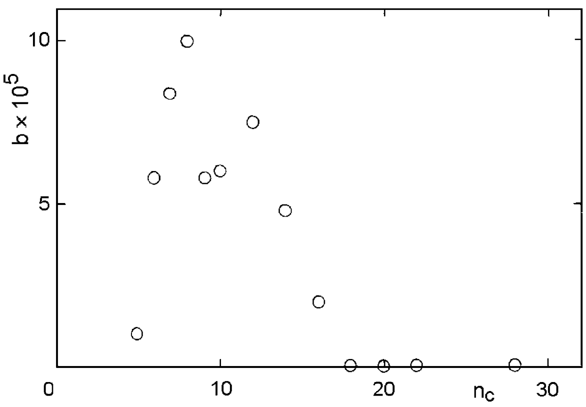

Fig. 6. Plot of the b parameter (cf. Eqs. (5) and (7)) vs. n_C for IPP in n-alkanes.

chains have a weaker impact on the morphology of polypropylene than the short ones (at least at very low concentrations of diluents). Inspection of Fig. 5 shows that the term $(RC_1/\Delta H_u\bar{T}_m)$ which corresponds to the free energy changes due to morphological effects is comparable in magnitude to the term $(RV_{2u}/\Delta H_u V_1)$ reflecting the free energy changes due to fusion (at $\varphi_1 \to 0$).

The b parameter comprises a morphological contribution in addition to that related to the polymer–diluent interaction. The sign of the slope of the plots of Δ/φ_1 vs. φ_1 and the possibility of estimating the χ parameter depends on the proportion of these terms. This possibility exists only if $C_2 = 0$. In other cases it is impossible to resolve the b values into these contributions Fig. 6.

As the χ parameter of IPP in n-pentane, n-hexane and n-heptane is positive (Fig. 2), positive b values give evidence of prevalence of the morphological effect. This conclusion can be extrapolated to higher alkanes. At $n_C > 20$ both effects match rendering b equal to zero.

Using the χ parameters for the lowest alkanes (pentane–heptane) we have estimated the coefficient C_2. Taking again, as we have done above, the arithmetic mean $\bar{T}_m$, we obtain $C_2 = 2.7$ with no indication of a dependence on the number of carbon atoms in alkanes.

3. Concluding remarks

The present analysis shows that the anomalous values of the enthalpy of fusion and polymer–diluent interaction parameter observed with IPP and n-alkanes can be attributed to the effect of diluent on the morphology of polymer crystals. It is noticeable that two terms in Eq. (10) are sufficient to describe the concentration dependence of the morphological factor. An experimental conformation of this effect is desirable.

It is interesting that Ke [10] obtained a highly negative χ value for polyethylene in dotriacontane ($\chi = -1.3$) from the melting point depression. That may have a similar reason.

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References

[1] Flory PJ. J Chem Phys 1949;17:223.
[2] Mandelkern L. Crystallization of polymers. New York: McGraw-Hill, 1964.
[3] Olabisi O, Robeson LM, Shaw MT. Polymer–polymer miscibility. New York: Academic Press, 1970.
[4] Riedl B, Prud'homme RE. Polym Engng Sci 1984;24:1291.
[5] Bohdanecký M, Šimek L, Petřík S. Polymer 1990;31:137.
[6] Hamada F, Nakajima A. Chem High Polym Japan 1965;22:577 (see also 583).
[7] Van Krevelen DW. Properties of polymers, their estimation and correlation with the molecular structure. 2nd ed. Amsterdam: Elsevier, 1976.
[8] Cowie JMG, Mc Ewen IJ. J Polym Sci Polym Phys Ed 1974;12:441.
[9] Patterson D, Tewari YB, Schreiber HP, Guillet S. Macromolecules 1971;4:356.
[10] Ke B. J Polym Sci 1961;50:79.
[11] Nakajima A, Hamada F. Kolloid-Z 1965;205:55.
[12] Nakajima A, Hamada F. Rep Progr Polym Phys Japan 1966;9:41.
[13] Kodama Y, Swinton FL. Br Polym J 1978;10:191.
[14] Sawodny M, Asbach GI, Kilian HG. Polymer 1990;31:1859.
[15] Kwei TK, Frisch HL. Macromolecules 1978;11:1267.
[16] Walsh DJ, Singh VB. Makromol Chem 1984;185:1979.