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The Melting of Mixtures of Chemically Identical Polymers

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ABSTRACT: The melting of binary mixtures of low molecular weight fractions of linear polyethylene and of poly(ethylene oxide), crystallized in such a manner that cocrystallization does not take place, is considered from both a theoretical and experimental point of view. Utilizing the appropriate Flory-Huggins mixing expression for species that are chemically identical and assuming that the crystalline phase is pure, a melting temperature-composition relation is derived. This relation gives good agreement with new experimental results that are presented. Other melting temperature-composition relations that have been previously used to analyze this type of data are discussed in their proper perspective. The requirements that need to be satisfied by the mixture components are pointed out.

Introduction

The crystallization and melting of different kinds of polymer mixtures have been extensively studied. These systems can be divided into three main categories. These are (a) two polymers of different chemical types, where either one or both of the species crystallize;[1-18] (b) polymer-low molecular weight diluents (see ref 19 and 20 for a summary); and (c) mixtures of two chemically identical species that differ only in molecular weight.[21-23] Most of the systems studied consisted of a homogeneous liquid, or disordered state, wherein both components were miscible in all proportions, and only one polymer component crystallized. In a few specific cases, it was found that the crystalline phase did not remain pure.[24-27] The analysis of the case of a pure crystalline state can be accomplished in a straightforward manner. In all cases, the Flory-Huggins free energy of mixing expression is used to obtain the chemical potential per repeating unit of the crystallizing species in the disordered, liquid state.[28] When this expression is equated to the chemical potential of the repeating unit in the pure crystalline phase, which is given by

$$\mu_u^c - \mu_u^\circ = -\Delta G_u = -(\Delta H_u - T\Delta S_u) = -\Delta H_u\left(1 - \frac{T}{T_m^\circ}\right) \tag{1}$$

the melting temperature-composition relation is obtained. In eq 1, T_m° is the melting temperature of the pure crystallizing species; ΔS_u and ΔH_u are the entropy and enthalpy of fusion per repeating unit, respectively. The appropriate Flory-Huggins expression has to be used for each type mixture.

Nishi and Wang[1] derived a melting point relation for a mixture of two dissimilar polymers. They used Scott's expression for the mixing of two chemically dissimilar polymers and found that

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{RV_{2u}}{\Delta H_u V_{1u}}\left[\frac{\ln v_2}{x_2} + \left(\frac{1}{x_2} - \frac{1}{x_1}\right)(1 - v_2) + \chi_{12}(1 - v_2)^2\right] \tag{2}$$

Here v_2 is the volume fraction of the crystallizing species, 2, in the mixture; x_2 and x_1 are the number of segments per molecule of the crystallizing species and noncrystallizing polymer, 1, respectively; χ_{12} is the thermodynamic interaction parameter between the two species in the melt; and V_{2u} and V_{1u} are the molar volumes of the repeating units of species 1 and 2, respectively. (It has not been generally recognized that in this derivation[1] the implicit assumption has been made that the volume of a lattice cell in the Flory-Huggins derivation is equal to V_{1u}.) Equation 2 and its reduced form[1] have been used in analyzing the melting temperature of polymer-polymer mixtures.[21,22]

For mixtures of a crystallizing polymer with a low molecular weight diluent, the classical melting point depression is found[29,30] and is given by

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{R}{\Delta H_u}\frac{V_u}{V_1}\left[\frac{\ln v_2}{x} - \left(1 - \frac{1}{x}\right)(1 - v_2) + \chi_1(1 - v_2)^2\right] \tag{3}$$

Here T_m is the melting temperature of the polymer-diluent mixture; V_u and V_1 are the molar volumes of the polymer repeating unit and diluent, respectively; and χ_1 is the polymer-diluent interaction parameter. For high molecular weight, $x \to \infty$, eq 3 reduces to

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \frac{R}{\Delta H_u}[(1 - v_2) - \chi_1(1 - v_2)^2] \tag{4}$$

Several experimental studies of the melting temperature as a function of composition for chemically identical polymers have been reported.[21-23] If it is required that the crystalline phase remain pure, the assumption upon which all the analyses given above are based, then the experiments must be limited to low molecular weight species. If not, as has been shown in the case of linear polyethylene, cocrystallization of the species will take place.[31,32] Since we are concerned with equilibrium theory, extended chain crystallites are required. This requirement also requires the use of low molecular weight species. Thus, with these restraints experimental studies must be limited to mixtures of low molecular weight species.

In the analyses of the experimental data for linear polyethylene mixtures[21] as well as those for perfluoroalkanes,[22] eq 2, applicable only to two chemically dissimilar species, was used. The application of eq 2 to these sets of experimental data will be discussed subsequently (cf. seq.). It should be recognized at this point, however, that the mixing of two chemically identical species should be athermal. Hence, the appearance of χ_1 in the equation for this particular application should cause immediate concern.

For the analysis of the experimental melting temperature-composition data for binary mixtures of low molecular weight poly(ethylene oxide) fractions, eq 5 was used.[23,33] Here n is the number of repeating units in the molecule and x is the ratio of the molar volume of the two species.

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$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \frac{R}{n\Delta H_u}[-(\ln v_2) + (x-1)(1-v_2) + x\chi_1(1-v_2)^2] \quad (5)$$

It can be shown that eq 5 is equivalent to eq 3 for polymer–low molecular weight diluent mixtures.

The melting temperature–composition relation for two chemically identical species, only one of which crystallizes, can be calculated directly following the methods described above. The chemical potential of species x, μ_x, in a polydisperse mixture of the same chemical species and a low molecular weight diluent is given by[34]

$$\mu_x - \mu_x^\circ = RT\left[\ln v_x - (x-1) + v_2 x\left(1 - \frac{1}{\bar{x}_N}\right) + \chi_1 x(1-v_2)^2\right] \quad (6)$$

where v_x is the volume fraction of the x-mer and $\bar{x}_N$ the number-average degree of polymerization of the polymer mixture. For a pure polymer system, $v_2 \rightarrow 1$ so that the chemical potential per repeating unit, μ_{ux}, can be expressed as

$$\mu_{ux} - \mu_{ux}^\circ = RT\left\{\frac{\ln v_x}{x} + \left(\frac{1}{x} - \frac{1}{\bar{x}_N}\right)\right\} \quad (7)$$

Imposing the conditions of phase equilibrium, we find

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{R}{\Delta H_u}\left(\frac{\ln v_x}{x} + \frac{1}{x} - \frac{1}{\bar{x}_N}\right) \quad (8)$$

for the melting temperature–composition relation of the melting of a polymer in a mixture of chemically identical species. Equation 8 is apparently quite different from those which have been used previously for this problem.[21,23] The interaction parameter χ_1 does not appear at all in the correct expression. However, as would be expected from the structure of the Flory–Huggins lattice, eq 5 and 2 reduce to eq 8 when $\chi_1 = 0$ and $V_{2u} = V_{1u}$. (We thank one of the reviewers for pointing out the identity of eq 8 and 2 under these specific circumstances.)

In the present paper, we report the results of a study of the melting temperature–composition relations of binary mixtures of low molecular weight linear polyethylenes and of poly(ethylene oxides). These experimental results will be compared with the theoretical expectations described above and with the other equations that have been used in this problem.

Experimental Results

Samples. The samples used in this study were a set of low molecular weight polyethylene fractions, poly(ethylene oxide) fractions, and two n-alkanes. The molecular weights of the samples are listed in Table I. The lowest molecular weight polyethylene fraction, PE700, was purchased from Polysciences, Inc. The number-average molecular weight of this sample was determined by high-resolution solution carbon-13 NMR following procedures that were previously described in detail.[35] The M_n of this sample was found to be 725; GPC analysis of this sample indicates $M_w/M_n = 1.10$. Polymers designated PE1000 and PE2000 were obtained from the Petrolite Corp. These samples were used in a previous study and their molecular weights determined by GPC.[35] The poly(ethylene oxide) fractions were obtained from Hoechst Aktiengesellschaft Weik Gendorf. The molecular weights were supplied by the manufacturer, and the molecular weight distribution followed a Poisson distribution. The two normal hydrocarbons used, $C_{40}H_{82}$ and $C_{60}H_{122}$, were obtained from the Fluka Chemical Corp.

Preparation of Mixtures. The polyethylene mixtures were prepared by methods previously used in this laboratory.[31,32,36] The two components of the mixture were weighed out in the desired ratio and enough solvent, p-xylene, was added to bring the concentration of polymer in solution to approximately 0.2%. Once filled, the tubes were immersed in a thermostated oil bath at the desired mixing temperature. The samples were allowed to mix in the bath for 1 h under constant agitation provided by a Burrel wrist action shaker. After mixing for 1 h, the solutions were quench-precipitated into a dry ice saturated solution of methanol. The low temperature of the quenching agent combined with the nonsolvent effect of the methanol caused the polymer mixtures to precipitate immediately. After the quench procedures, the samples were allowed to warm to room temperature gradually. The crystals were then filtered through a scintered glass filter, washed with methanol several times, and dried for a minimum of 48 h under vacuum at room temperature. These solution-formed crystals were then melted and crystallized in the desired manner.

Table I
Characteristics of Polyethylene Fractions, n-Alkanes, and Poly(ethylene oxide) Fractions

sample	M_n	M_w/M_n	M_w	T_m
PE700	725	1.10		96.6
PE1000	1148	1.10		108.1
PE2000	1674	1.15		121.6
$C_{40}H_{82}$			563	
$C_{60}H_{122}$			843	102.4
poly(ethylene oxide) 1500	1490	≅1.07		54.7
poly(ethylene oxide) 2000	2040	≅1.07		
poly(ethylene oxide) 3000	3110	≅1.07		59.8

The poly(ethylene oxide) mixtures were prepared following the procedure described by Cheng and Wunderlich.[23] The two components were weighed out in the desired proportion in a DSC pan. After the aluminum DSC pans were sealed, the mixture was heated for about 0.5 h to a temperature about 30 °C above the melting temperature of the highest melting component.

Crystallization and Melting. The melting behavior of the mixtures was studied by using a Perkin-Elmer DSC 2B scanning calorimeter operating at a heating rate of 10 K/min for the polyethylene mixtures and 5 K/min for the poly(ethylene oxide) mixtures. The instrument was calibrated with indium. The melting temperature was identified with the maximum of the endothermic peak in the thermograms. The melting temperatures of the pure species are given in the last column of Table I.

The theory under consideration is only applicable to equilibrium crystallites and requires the separate crystallization of each species. It is necessary, therefore, to adopt crystallization procedures that ensure that cocrystallization does not occur. For most of the mixtures, slow cooling from the melt was sufficient. After the mixtures were heated for 0.5 h at 30 °C above the melting temperature, the mixtures were cooled to room temperature at the rate of 10 K/min. For poly(ethylene oxide) mixtures containing the 3000 molecular weight species, an isothermal crystallization was carried out prior to cooling to room temperature. The poly(ethylene oxide) mixtures 1500/3000 and 2000/3000 were initially crystallized isothermally at 45 °C for 0.5 h before cooling.

Results and Discussion

The theoretical melting temperature relations that were presented here are compared in parts a and b of Figure 1 for two of the sets of polyethylene mixtures that were studied. Figure 1a is for mixtures of PE1000 and PE2000, while Figure 1b is for mixtures of PE700 and PE2000. The solid curve in each of the figures, which represents the case of $\chi_1 = 0$ and $V_{2u} = V_{1u}$, is the same under these circumstances for eq 2, 5, and 8 as has already been noted. The introduction of nonzero values of χ_1 in eq 2 (and eq 5 as well) results in significant changes in the melting temperature–composition relations. However, the use of a nonzero value for χ_1 is incorrect for mixtures of identical polymer species no matter how well its introduction improves the fit of the data.[21,37]

Since the analysis is predicated on the assumption that separate crystallization of the two species occurs, i.e., the fusion of the higher melting species is into the pure melt,

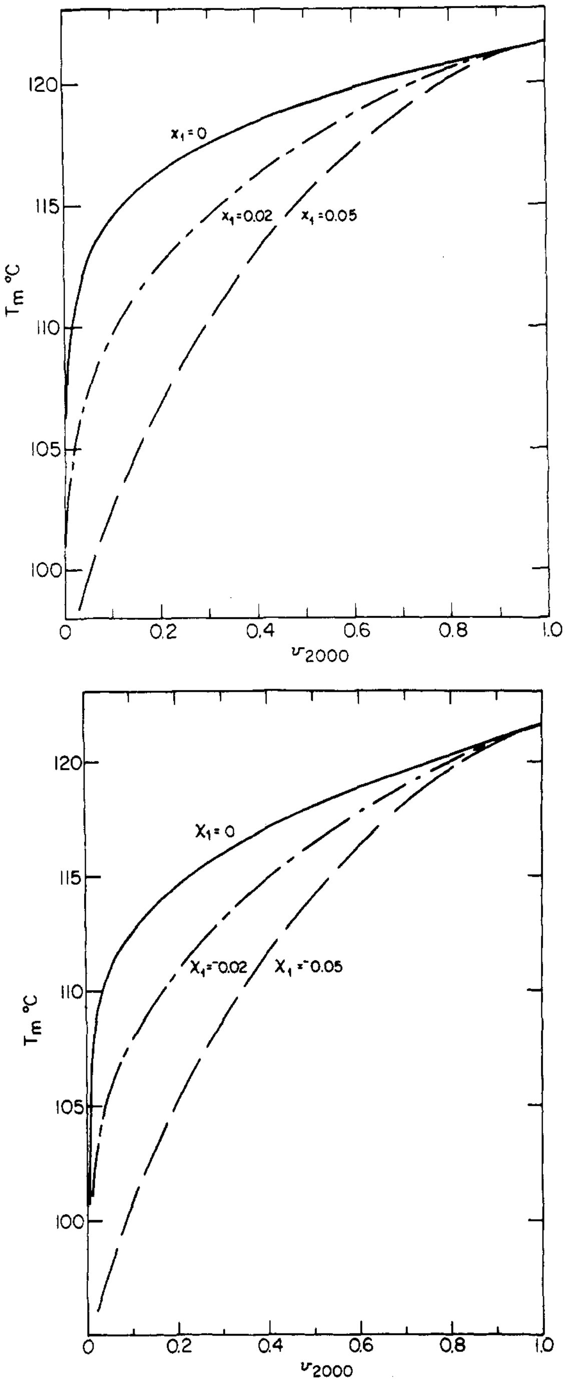

Figure 1. Plot of calculated melting temperatures against composition for binary mixtures of low molecular weight polyethylenes. (a, top) Mixtures of PE1000 and PE2000. (—) Calculated according to eq 8; (- - -) (– –) calculated according to eq 2 with indicated values of χ_1. (b, bottom) Mixtures of PE700 and PE2000. (—) Calculated according to eq 8; (- - -) (– –) calculated according to eq 2 with indicated values of χ_1.

it is important to establish experimentally that for the crystallization procedure adopted cocrystallization does not take place. Figure 2a shows that for cooling the PE1000/PE2000 system at 10 K/min two well-developed endothermic peaks are observed on subsequent heating. These peaks correspond to those found for the pure species and indicate separate crystallization of the two components. Similar results are found for the other mixtures studied. The thermograms in Figure 2b indicate that when these mixtures are quenched cocrystallization, at least in part, takes place. Clearly the situation of interest here is that represented by the crystallization procedure that yields the data of Figure 2a.

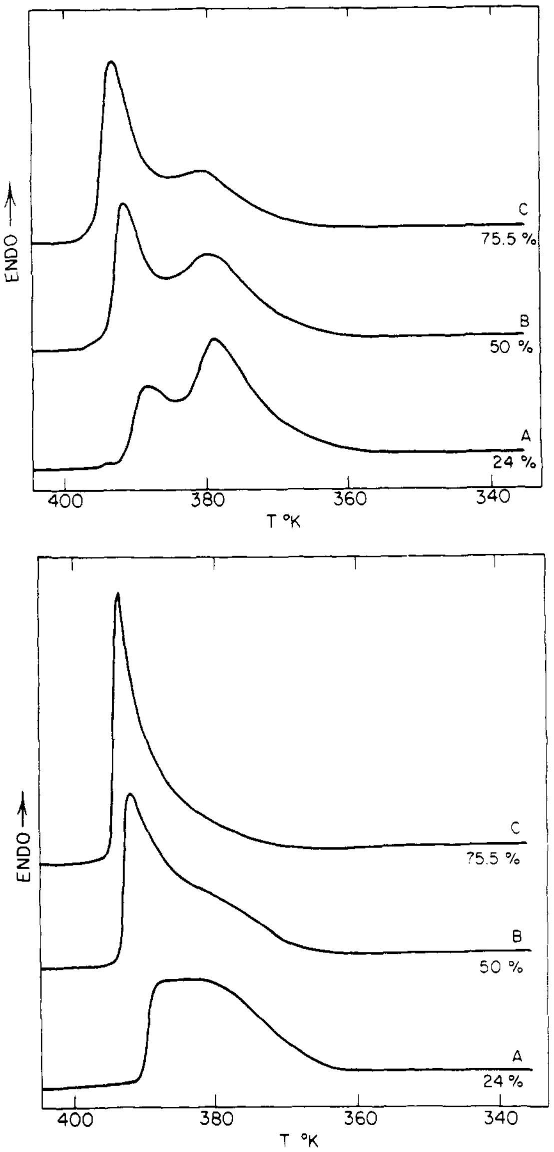

Figure 2. Differential scanning calorimetric thermograms for mixtures of PE1000 and PE2000 for indicated percent composition of PE2000. (a, top) Samples cooled at rate of 10 K/min. (b, bottom) Samples rapidly cooled, quenched.

With this background, we can examine the experimental results obtained with the mixtures. Figure 3 gives the experimental results for mixtures where PE2000 is the high molecular weight component. It is the melting temperature of this species as a function of composition that is of interest in the present context. The data in Figure 3a represent mixtures of PE1000/PE2000 and is the same system as that studied by Smith and Manley.[21] Their data are represented by the solid triangles in the figure. The dashed curve in the figure represents the theoretical expectation from eq 8. Very good agreement is obtained between theory and experiment at high concentrations of PE2000, i.e., to $v_{2000} \geq 0.50$. At lower concentrations of PE2000, the observed melting temperatures are 2–4 deg lower than expected. The melting temperatures can be well represented by a smooth curve. There is no evidence of a eutectic point, as has been reported for this system.[21] The melting temperature of the lower molecular weight component, PE1000, is essentially invariant with composition, as would be expected. (The pure PE1000 shows two endothermic peaks after slow cooling. One is located at 104 °C and the other at 108 °C.)

The results for the $C_{60}H_{122}$/PE2000 mixture, which are given in Figure 3b, show very good agreement between

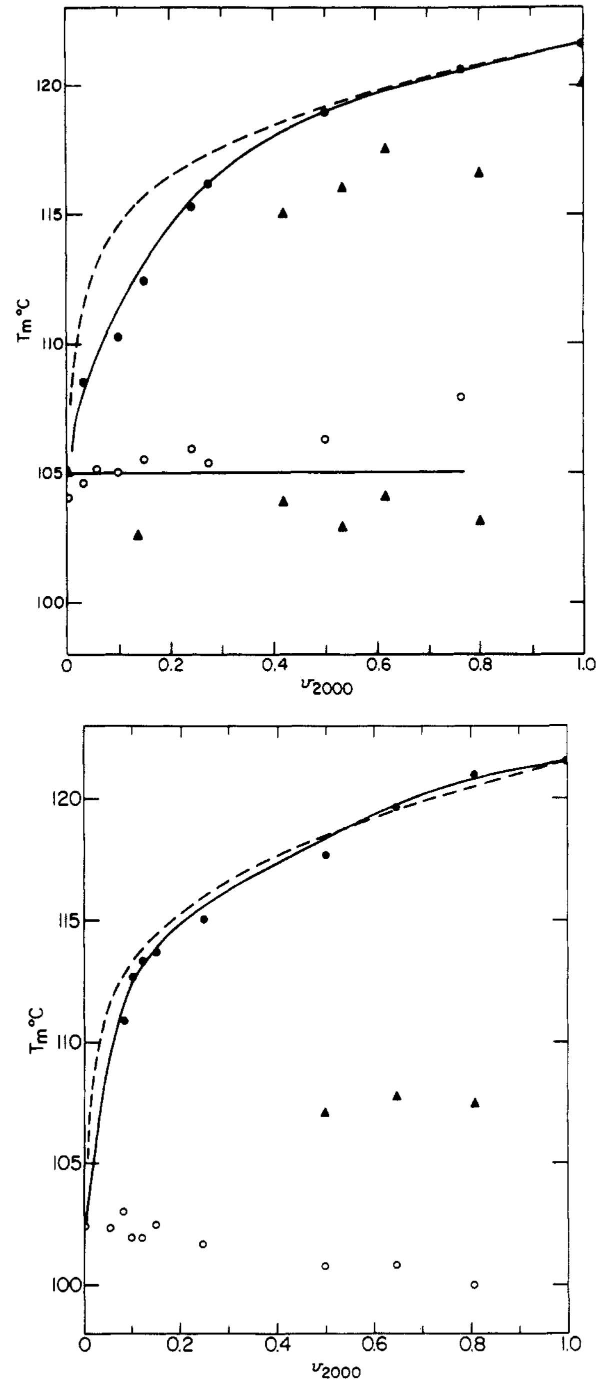

Figure 3. Plot of experimentally observed melting temperatures as function of composition for binary mixtures in which PE2000 is the highest molecular weight component. (a, top) Mixtures of PE1000 and PE2000. (---) Calculated from eq 8; (●) (○) data from this work; (▲) (△) data from ref 21. (b, bottom) Mixtures of $C_{60}H_{122}$ with PE2000. (---) Calculated from eq 8. All symbols experimental data from this work.

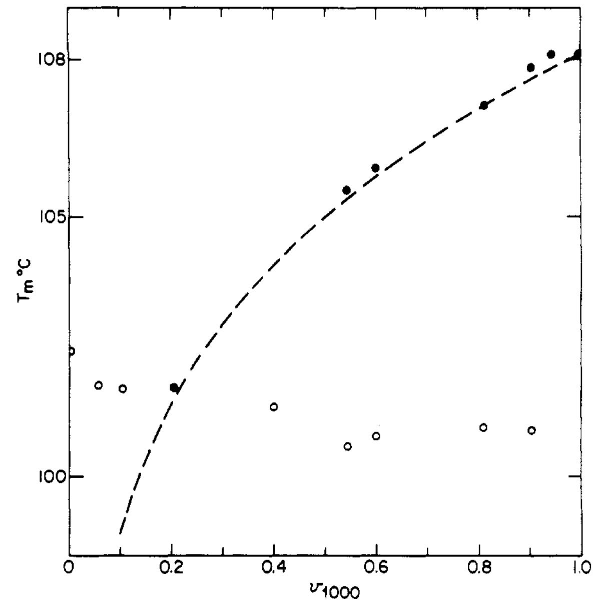

Figure 4. Plot of experimentally observed melting temperatures as function of composition for mixtures of $C_{60}H_{122}$ and PE1000. All symbols experimental data from this work. (---) Calculated from eq 8.

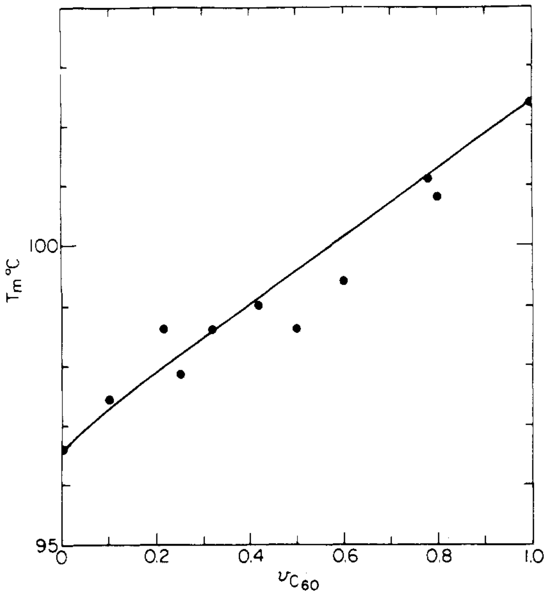

Figure 5. Plot of experimentally observed melting temperatures as a function of composition for mixtures of PE700 and $C_{60}H_{122}$.

theory and experiment. The differences between observed and expected melting temperatures are quite small even in the dilute range for this case. The low melting species gives the expected invariance of melting temperature with composition, and there is no indication of any eutectic temperature. We also note that for this system that when $\upsilon^2 \geq 0.5$ a third endothermic peak, which is independent of composition, is observed in the vicinity of 107 °C. This endotherm is only observed when the crystallization temperature is below 100 °C (the melting temperature of the low-melting component). When mixtures of this composition were crystallized above 100 °C, only the high-melting endotherm was observed. This result is consistent with the idea that the cocrystallization of a small portion of the high- and low-melting species takes place.

Figure 4 gives the melting temperature–composition results for the $C_{60}H_{122}$/PE1000 mixture. The dashed line is calculated according to eq 8. The agreement between theory and experiment is very good in this case. A eutectic temperature is predicted in the vicinity of $\upsilon_2 \cong 0.2$.

Although the results for the PE700/$C_{60}H_{122}$ mixture, plotted in Figure 5, do not fall into the specific purpose of this paper, they are included here because of general interest. Over the complete composition range of this mixture, only one endothermic peak was observed. This peak increased monotonically with increasing concentration of the $C_{60}H_{122}$ species. This result is indicative of the cocrystallization of the two species over the complete composition range. The cocrystallization of these species could have been anticipated because of the close similarity in molecular weights.

Figures 6, 7, and 8 give the results for the three mixtures

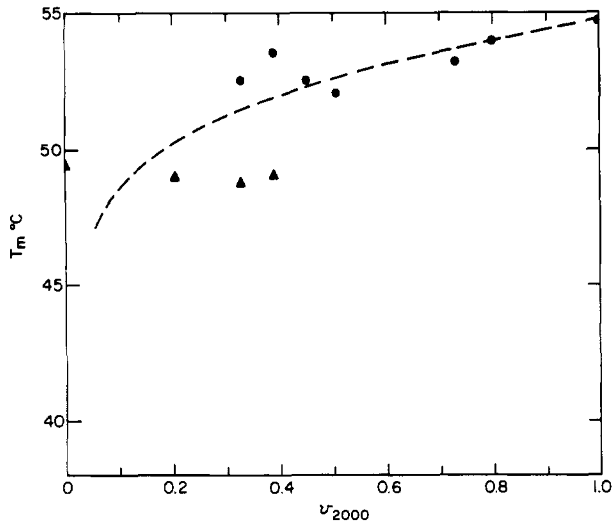

Figure 6. Plot of experimentally observed melting temperatures as a function of composition for poly(ethylene oxide) mixtures of molecular weight fractions 1500 and 2000. Dashed line calculated according to eq 8.

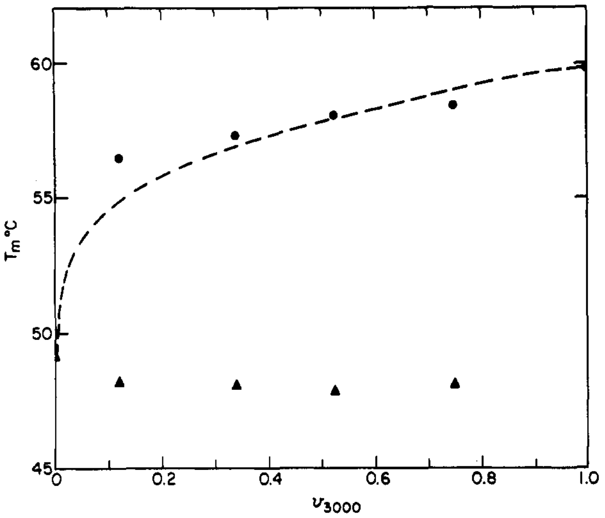

Figure 7. Plot of experimentally observed melting temperatures as a function of composition for poly(ethylene oxide) mixtures of molecular weight fractions 1500 and 3000. Dashed line calculated according to eq 8.

of the low molecular weight poly(ethylene oxide) fractions that were studied. For all three of these systems, very good agreement was obtained between the predictions of eq 8 and the experimental results. For two of these poly(ethylene oxide) mixtures, 1500/2000 and 2000/3000, eutectic points are predicted. The agreement between theory and experiment for the poly(ethylene oxide) mixtures is somewhat better than that found for the polyethylenes. This may be due to the fact that the poly(ethylene oxide) samples have narrower molecular weight distributions than the polyethylenes.

Prud'homme[37] studied the melting temperature of mixtures of two poly(ethylene oxide) fractions, M_n = 3636 and 1181, respectively. The data could be fitted quite well with the general polymer–diluent relation by taking $\chi_1 = -0.09$. This procedure is not physically meaningful. Moreover, the higher melting species was not crystallized in extended form. For this latter reason, we have not compared these experimental results with eq 8 for chemically identical species.

In summary, the experimental results that are given here show, in general, very good agreement with the theory developed from the Flory–Huggins mixing expression appropriate to chemically identical species, which differ only in chain length. Minor deviations are found from theory in some of the mixtures at high dilution of the higher melting species. These discrepancies can be attributed to the uncertainties in the mixing expression, particularly in the dilute range. The relation derived is the same as for polymer–diluent mixtures and for two dissimilar polymers when $\chi_1 = 0$ and the molar volumes of the units are the same. However, the general presentation of these two cases is not appropriate to the present problem.

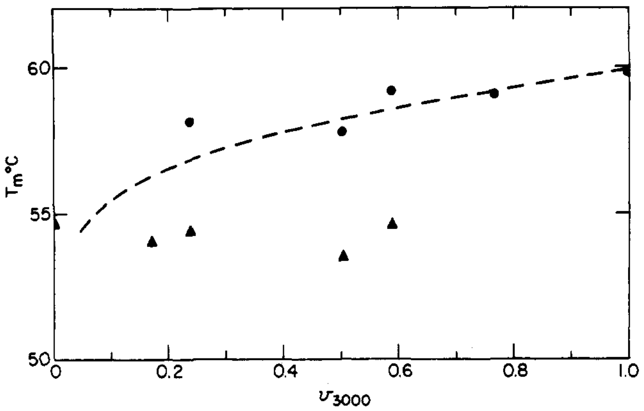

Figure 8. Plot of experimentally observed melting temperatures as a function of composition for poly(ethylene oxide) mixtures of molecular weight fractions 2000 and 3000. Dashed line calculated according to eq 8.

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Registry No. PE, 9002-88-4; $C_{60}H_{122}$, 7667-80-3; poly(ethylene oxide), 25322-68-3.

References and Notes

(1) Nishi, T.; Wang, T. T. *Macromolecules* **1975**, *8*, 909.
(2) Imken, R. L.; Paul, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1976**, *16*, 593.
(3) Morra, B. S.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2243.
(4) Cruz, C. A.; Paul, D. R.; Barlow, J. W. *J. Appl. Polym. Sci.* **1979**, *23*, 589.
(5) Jonza, M. J.; Porter, R. S. *Macromolecules* **1986**, *19*, 1946.
(6) Berghmans, H.; Overbergh, N. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1757.
(7) Paul, D. R.; Barlow, J. W. Polymer Alloys. In *Polymer Science and Technology*; Klemper, D., Frisch, K. C., Eds.; Plenum Press: New York, 1980; Vol. 1, p 239.
(8) Aref-Azar, A.; Hay, J. N.; Marsden, B. J.; Walker, N. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 637.
(9) Bélongey, G.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 191.
(10) Aubin, M.; Bédard, Y.; Morrissette, M.; Prud'homme, R. E. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 233.
(11) Rim, P. B.; Runt, J. P. *Macromolecules* **1983**, *16*, 762.
(12) Martuscelli, E.; Pracella, M.; Yue, W. P. *Polymer* **1984**, *25*, 1097.
(13) Li, X.; Hsu, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1331.
(14) Guerra, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1986**, *19*, 1935.
(15) Alfonso, G. C.; Russell, T. P. *Macromolecules* **1986**, *19*, 1143.
(16) Zhang, H.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *24*, 723.
(17) Hu, S. R.; Kyu, T.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 71.
(18) Kyu, T.; Hu, S. R.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 89.
(19) Mandelkern, L. *Crystallization of Polymers*; McGraw-Hill: New York, 1963; p 38ff.
(20) Mandelkern, L. In *Comprehensive Polymer Science. V.2. Polymer Properties*; Bouth, C., Poricen, C., Eds.; Pergamon Press: New York, 1989; Chapter 11.
(21) Smith, P.; Manley, R. St. John *Macromolecules* **1979**, *12*, 483.
(22) Smith, P.; Garner, K. H. *Macromolecules* **1985**, *18*, 1222.

(23) Cheng, S. Z. D.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 577.
(24) Factor, A.; Heinsohn, G. E.; Vogt, L. H., Jr. *J. Polym. Sci., Polym. Lett. Ed.* **1969**, *7*, 205.
(25) Schultz, A. R.; McCullough, C. R. *J. Polym. Sci., Part A-2* **1969**, *7*, 1577.
(26) Shu, P. H. C.; Burchell, D. J.; Hsu, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1421.
(27) Robitaille, C.; Marques, S.; Boilo, D.; Prud'homme, J. *Macromolecules* **1987**, *20*, 3023.
(28) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 507ff.
(29) Flory, P. J. *J. Chem. Phys.* **1949**, *17*, 223.
(30) Reference 28, p 568ff.
(31) Jackson, J. F.; Mandelkern, L. In *Analytical Calorimetry*; Johnson, J., Porter, R., Eds.; Plenum Press: New York, 1968.
(32) Glaser, R. H.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 221.
(33) Prime, R. B.; Wunderlich, B. *J. Polym. Sci., Part A-2* **1969**, *7*, 2073.
(34) Reference 28, p 513.
(35) Prasad, A.; Mandelkern, L. *Macromolecules* (in press).
(36) Alamo, R. G.; Glaser, R. H.; Mandelkern, L. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 2169.
(37) Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 307.

Conformational Properties of Poly(vinyl bromide) and Poly(vinyl fluoride)

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ABSTRACT: The conformational properties of molecules modeling poly(vinyl bromide) (PVB) and poly(vinyl fluoride) (PVF) dimers and trimers have been analyzed using the molecular mechanics method of Boyd et al., which takes into account both steric and electrostatic energies. The geometric and energy results show that the steric effects of changing the halide are greater than the electrostatic effects. Total conformational energies were used to determine a set of intramolecular interaction energies that by means of the rotational isomeric states model allowed estimation of the characteristic ratio, C_r, and dipole moment ratio, C_m, of PVB and PVF. The results agree satisfactorily with available experimental values.

Introduction

It is of great interest to find out how the physical properties of polymers are related to their conformational properties.[1] This is especially so in the case of poly(vinyl halides) $(-CH_2CHX-)_n$, whose important electrical and mechanical properties are to be related to the steric strains and electrostatic interactions of their molecules. This article describes a study of the conformational properties of poly(vinyl bromide) (PVB) and poly(vinyl fluoride) (PVF) by means of a recently published molecular mechanics method including parameters for polar molecules,[2] which has been successfully applied to poly(vinyl chloride)[3a] and poly(vinylidene chloride).[3b] We also calculated characteristic ratios, $C_r = \langle r^2\rangle_0/2xl^2$, and dipole moment ratios, $C_m = \langle \mu^2\rangle_0/xm^2$ (where x is the degree of polymerization, l the length of the C–C bond, and m the dipole moment of the carbon–halogen bond).

The general plan of the calculations performed has been described elsewhere.[3,4] The method used is such that energy minimization (by a modified Newton–Raphson procedure) can involve variation of not only the torsion angles, ϕ_{ijkl}, but also the bond lengths, r_{ij}, and valence angles, θ_{ijk}, of all the atoms of the molecules studied, which in this case were molecules modeling dimers and trimers of PVB and PVF.

The steric energy, DE + NB, is determined by a transferable force field that includes bond stretching terms, $U(r_{ij})$, bending terms, $U(\theta_{ijk})$, twisting terms, $U(\phi_{ijkl})$, and terms for interactions between nonbonded atom pairs (NB). The total conformational energy, ET, is considered to be the sum of the steric contribution, DE + NB, and the electrostatic contribution, EE.

In order not to prolong the calculations, the optimal geometry is taken to be the structure obtained by minimizing the steric energy, DE + NB, while simulating the electrostatic energy, EE, by fixed partial charges; once the sterically optimal geometry has been determined, the total energy is obtained after calculating the electrostatic energy correctly for this structure. For this latter calculation, it is assumed that the carbon–halogen bonds have intrinsic dipole moments, μ_0, that create an electric field, giving rise to induced dipole moments, μ, in each bond, that the induced moments in turn induce further moments in other bonds, and so on. The total moment of each bond is obtained by solving a system of equations,[3a] and the electrostatic energy, EE, is given by the work done on polarization and the energy of interaction between dipoles.

The conformational properties of the most important poly(vinyl halide), poly(vinyl chloride) (PVC), have been studied by Flory and Williams[5] and Mark,[6] who related statistical weight parameters obtained from experimental data to interactions among the bonds of the polymer chain, a procedure that can be generalized to other vinyl polymers. Specifically, they considered three-bond "gauche" and "skew" interactions and the four-bond interactions w, w', and w''. In his molecular mechanics study of PVC, Boyd and Kesner[3a] subsequently introduced the four-bond interaction, w_p, that arises when two adjacent C–X bonds and their corresponding intermediate C–C bonds are all coplanar (Figure 1). Since the statistics used in the present study conform to the rotational isomeric states model,[5,6] which refers to diadic interactions in the polymer, the short-range gauche (g) and skew (sk) interactions are the most important. The energy $E_n = E_{sk} - E_g$ provides the statistical weight parameter, n, that Flory and Williams[5] obtained from data for the stereochemical equilib-

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