Melting point depression in ethylene–vinyl acetate copolymer mixtures

N. E. Clough and R. W. Richards*
Interdisciplinary Research Centre in Polymer Science, University of Durham, Durham DH1 3LE, UK

and T. Ibrahim
Exxon Chemical, PO Box 1, Abingdon, Oxfordshire OX13 6BB, UK

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The miscibility of a random copolymer of ethylene and vinyl acetate with three other copolymers based on poly(ethylene glycol), poly(itaconic acid) and a vinyl acetate–fumaric acid ester has been investigated by d.s.c. and X-ray powder diffraction. Melting point depression data could be analysed using the full Nishi–Wang expression but additional entropy contributions to the miscibility were evident in some mixtures. These were attributed to the presence of long hydrocarbon substituents in the copolymers. For mixtures with the poly(ethylene glycol) based copolymer, a large negative value of the interaction parameter was obtained and there was cocrystallization of the ethylene–vinyl acetate copolymer with the docosyl end groups of the poly(ethylene glycol) based copolymer.

(Keywords: melting point depression; copolymer; miscibility)

INTRODUCTION

The miscibility of polymers is usually controlled by the enthalpy of mixing, since in general the entropic contribution to the free energy of mixing is negligible. Many miscible polymer mixtures are characterized by strong specific interactions between constituent groups which are the source of the favourable enthalpy of mixing[1]. Generally, the interactions between polymers are quantified by the value of the interaction parameter χ, since negative values are associated with miscible polymers. A number of methods can be used to evaluate values for χ, but none of them is particularly straightforward and each has its own particular limitations. The most direct method is to measure the heat evolved on mixing the two polymers together. This is restricted to materials with low viscosity and hence is usually confined to model compounds or oligomers[2]. Moreover, this method provides only the *enthalpic* contribution to χ, which strictly is a free energy term. Provided that phase separation takes place in an accessible temperature range, then determination of the spinodal curve[3] can be compared with predictions of equation of state theory to provide values of X, a term which plays the role of χ. Use of equation of state theory requires the coefficients of thermal expansion for each polymer and the mixture to be known and also their thermal pressure coefficients. However, some systems have been usefully analysed in this way[4–6]. Inverse phase gas chromatography and vapour sorption in an isopiestic still may be used[7,8] to provide values of χ. The former technique involves many sub-calculations and the final value can be subject to large errors. Vapour sorption is an absolute method but the times to reach equilibrium can be impracticably long. A method which has been used with great success on a variety of polymer mixtures is small angle neutron scattering[9–12]. This method is also absolute, provides the total χ and can be utilized to provide the temperature dependence of χ which is needed to define the location of the phase diagram. The limitation to small angle neutron scattering is the need to have one component deuterated and the scarcity of suitable instruments on which such experiments can be performed. A particularly straightforward method of obtaining χ when one component of the mixture is semicrystalline, is the depression of the melting point. Although straightforward, the composition and temperature dependence of χ are *not* obtainable by this method. Nonetheless, it is a method which is generally available and can provide a rationale of observed behaviour before recourse is made to other more demanding methods. We report here the results of melting point depression studies on mixtures of a random copolymer of ethylene and vinyl acetate (EVA copolymer) with a series of polymers. The common feature of the other component polymers is the presence of long hydrocarbon chains either at the ends or as the 'teeth' of comb polymers.

THEORY

The equilibrium melting point depression observed on mixing a compatible amorphous polymer with a semicrystalline polymer has been discussed by Nishi and Wang[13] using the Flory–Huggins thermodynamic theory of mixing. The equation obtained is:

$$1/T^0_{\mathrm{mb}} - 1/T^0_{\mathrm{m}} = (-R\bar{V}_{2\mathrm{u}}/\Delta H_{2\mathrm{u}})[(B/RT^0_{\mathrm{mb}})\phi_1^2 + \ln(1-\phi_1)/\bar{V}_2 + \phi_1(1/\bar{V}_2 - 1/\bar{V}_1)] \quad (1)$$

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[*] To whom correspondence should be addressed

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where T^0_{mb} is the melting point of the semicrystalline polymer in the mixture and T^0_{m} the melting point of the pure semicrystalline polymer. Subscripts 1 and 2 pertain to amorphous and semicrystalline polymer, respectively, and $\bar{V}_i$ is the molar volume of component i which has a volume fraction in the mixture of ϕ_i. The subscript u indicates the value of the parameter per repeat unit of the polymer, thus $\Delta H_{2\mathrm{u}}/\bar{V}_{2\mathrm{u}}$ is the enthalpy of fusion per unit molar volume of the repeat unit for the 100% crystalline component. The free energy density, B, in equation (1) is related to χ by:

$$\chi = B\bar{V}_{1\mathrm{u}}/RT^0_{\mathrm{mb}} \qquad (2)$$

Equation (1) can be rearranged to:

$$(1/T^0_{\mathrm{mb}} - 1/T^0_{\mathrm{m}})\Delta H_{2\mathrm{u}}/(R\bar{V}_{2\mathrm{u}}) + \ln(1-\phi_1)/\bar{V}_2 + \phi_1(\bar{V}_2^{-1} - \bar{V}_1^{-1}) = \frac{-B}{R}\frac{\phi_1^2}{T^0_{\mathrm{mb}}} \qquad (3)$$

In equation (3), the second and third terms on the left-hand side account for entropic contributions, particularly from chain ends, to the free energy of mixing. However, since $\bar{V}_i \approx M/\rho$, where M is the molecular weight and ρ the density of the polymer, then terms containing $\bar{V}_2^{-1}$ and $\bar{V}_1^{-1}$ approximate to zero for high molecular weight polymers and equation (3) becomes:

$$(1/T^0_{\mathrm{mb}} - 1/T^0_{\mathrm{m}}) = -(R\bar{V}_{2\mathrm{u}}/\Delta H_{2\mathrm{u}})(B\phi_1^2/RT^0_{\mathrm{mb}}) \qquad (4)$$

The use of equation (4) to obtain χ values for polymer mixtures has been critically reviewed recently[14]. Rigorously, the melting temperatures used should be the equilibrium temperatures; however Nishi and Wang[13] concluded that the absence of equilibrium conditions had little influence on the melting point depression. This is particularly true when the crystalline morphology is not significantly altered in the blends. Consequently a plot of the left-hand side of equation (4) as a function of ϕ_1^2 should be linear with an intercept of zero and from which a value of B, and hence χ, can be extracted from the slope which pertains to the temperature range over which the melting points as a function of ϕ_1 were obtained. For low molecular weight polymers, entropic effects may contribute significantly to the free energy of mixing and the full equation [equation (3)] should be used.

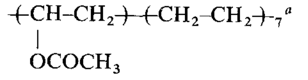
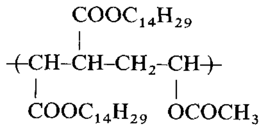
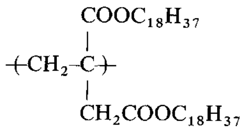
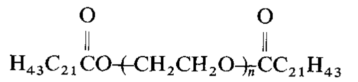
EXPERIMENTAL

Materials

All the polymers discussed here were supplied by Exxon Chemical Ltd, and their composition and molecular weight were obtained from n.m.r., combustion analysis and size exclusion chromatography. For the latter analysis, samples were dissolved in tetrahydrofuran and the chromatography performed using an instrument with a combined viscometric and differential refractometer detector (Viscotek 200). The results are reported in *Table 1*. The EVA copolymer is an amorphous random copolymer with an average molar ratio of ethylene to vinyl acetate of 7:1, whereas the copolymer of vinyl acetate and di-n-tetradecyl fumarate (FVA) is an alternating copolymer.

Mixtures of FVA, homopolymer of the di-n-octadecyl ester of itaconic acid (PI) or n-docosyl ester terminated poly(ethylene glycol) (PED) were prepared with EVA by dissolving both polymers in distilled chloroform such that the total polymer concentration was 10%. The solutions were then allowed to evaporate to dryness before being finally dried at 323K under vacuum for 24 h. Each mixture was then stored in a desiccator until required.

Table 1 Molecular weight and representative formulae

Polymer	Formula	$\bar{M}_{\mathrm{w}}$ ($\times 10^3$)	$\bar{M}_{\mathrm{n}}$ ($\times 10^3$)
EVA	 $\text{-(}\underset{\mathrm{OCOCH_3}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\text{)-(}\mathrm{CH_2}\text{-}\mathrm{CH_2}\text{)-}_7{}^a$	7.060	3.020
FVA	 $\text{-(}\underset{\mathrm{COOC_{14}H_{29}}}{\mathrm{CH}}\text{-}\overset{\mathrm{COOC_{14}H_{29}}}{\mathrm{CH}}\text{-}\mathrm{CH_2}\text{-}\underset{\mathrm{OCOCH_3}}{\mathrm{CH}}\text{)-}$	62.600	15.990
PI	 $\text{-(}\mathrm{CH_2}\text{-}\overset{\mathrm{COOC_{18}H_{37}}}{\underset{\mathrm{CH_2COOC_{18}H_{37}}}{\mathrm{C}}}\text{)-}$	11.240	9.900
PED	 $\mathrm{H_{43}C_{21}}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}\text{-(}\mathrm{CH_2CH_2O}\text{)-}_n\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{C_{21}H_{43}}$	1.315	1.200

[a] This formula indicates the molar ratio of the constituent units and is not meant to convey their organization in the molecule

Differential scanning calorimetry (d.s.c.)

D.s.c. thermograms were obtained using a Perkin-Elmer DSC7. The general procedure adopted was to ascertain the melting point of each specimen by an initial temperature scan. A new specimen was then placed in the differential scanning calorimeter and heated at a rate of 200 K min^{-1} to 20 K above the melting point where it was held for 2 min. The specimen was then cooled at 10 K min^{-1} to the starting temperature for recording the thermogram, where it was again held for 2 min; generally this starting temperature was 263 K. D.s.c. thermograms were then obtained by heating at 10 K min^{-1} to 20 K above the maximum temperature of the melting endotherm. Each thermogram was recorded in triplicate using a new specimen each time and the melting points recorded here are the onset values of the melting endotherm. Heats of fusion were obtained from the area under the melting endotherm for the pure FVA, PI and PED polymers and their mixtures with EVA.

Wide-angle X-ray scattering (WAXS)

Powder diffraction X-ray scattering data were obtained at room temperature using a Siemens D5000 diffractometer. All the X-ray data were recorded at ambient temperatures, the entrance slit height was 1 mm and the collecting slit height was 2 mm and a monochromator before the detector removed any contribution from Kβ radiation of the Cu anode of the X-ray tube. The mixtures were spread as a 2 mm thick layer in the sample holder. As well as mixtures of the polymers with EVA, the powder diffraction patterns of the pure polymers were also obtained.

RESULTS

Differential scanning calorimetry

Figure 1 shows d.s.c. thermograms for the pure PED polymer. Three endotherms are evident, the melting point of the higher temperature endotherm becomes increasingly depressed as the EVA content increases in the PED/EVA mixture. In contrast, the lower temperature endotherms located at ~28°C are essentially unaffected as the EVA content increases. D.s.c. thermograms for pure PI and FVA polymers each have only a single endotherm which is depressed to lower temperatures as the EVA content increases. The melting point depression for these latter two polymers is by no means as marked as for the PED/EVA mixtures. *Figure 2* shows the melting points as a function of the volume fraction of EVA in each mixture.

WAXS and fractional crystallinity

Powder diffraction profiles obtained for PED/EVA and PI/EVA mixtures are shown in *Figures 3* and *4*. In the PI/EVA mixtures, there is a continual decrease in the peak amplitude as the EVA content increases, but the 2θ value of the maximum shows a negligible change. For PED/EVA mixtures, as well as a decrease in amplitude, there is a marked shift of the peaks to lower 2θ values (*Table 2*). For these two mixtures, fractional crystallinities were obtained by the internal comparison method. The crystalline peaks were fitted and their area obtained (A_c). In a similar way, the amorphous background was fitted and the area under the fitted curve obtained (A_a). The fractional crystallinity was then calculated from:

$$X_c = A_c/(A_c + A_a) \tag{5}$$

Figure 5 shows the dependence of fractional crystallinity for mixtures of EVA with PI and PED.

Since the FVA polymer has a melting point below ambient, this procedure could not be used for the FVA/EVA mixtures. Therefore the fractional crystallinity was estimated by comparing the heat of fusion with that for 100% crystalline polyethylene. This is justified by the crystallization in the FVA being effectively confined to the hydrocarbon side chains which are essentially identical to polyethylene molecules. By this means, the fractional crystallinity of pure FVA was obtained as 0.155. This method has been used by other workers[15] for various

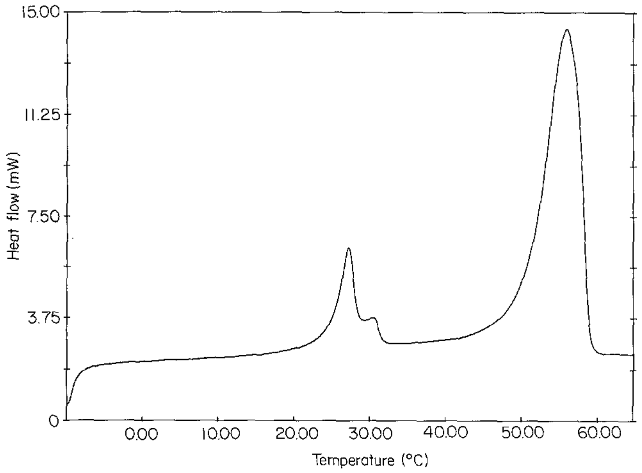


Figure 1 D.s.c. thermogram for the docosanyl ester of poly(ethylene glycol)

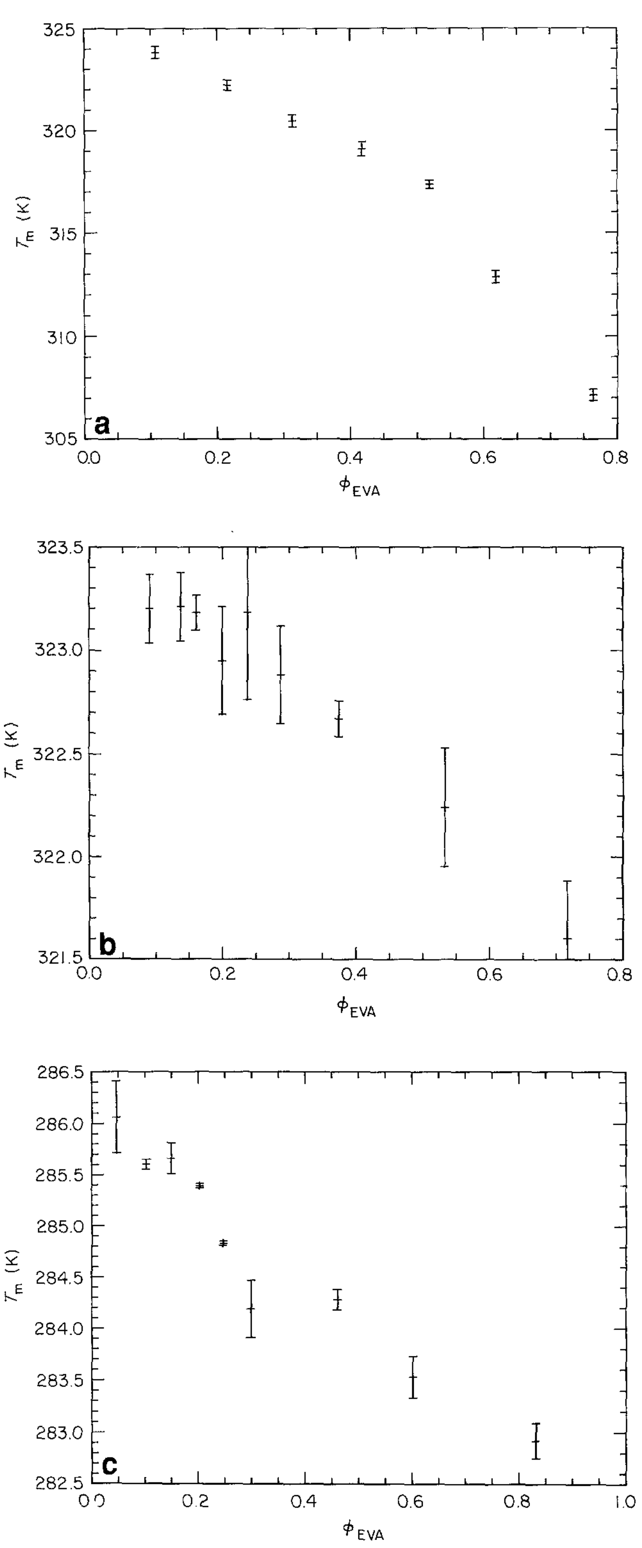


Figure 2 Melting point depression in mixtures with EVA copolymer: (a) PED/EVA; (b) PI/EVA; (c) FVA/EVA

Table 2 Lattice plane spacings for PED/EVA mixtures

	Lattice plane spacing (Å)	
PED weight fraction	Peak A	Peak B
1	4.045	3.633
0.8	4.145	3.697
0.6	4.123	3.708
0.4	4.202	3.756

polyitaconates and we note here that its use for the PI polymer produces a value of X_c of 0.33 which agrees well with the value of 0.36 obtained from the powder diffraction profile of the pure PI polymer.

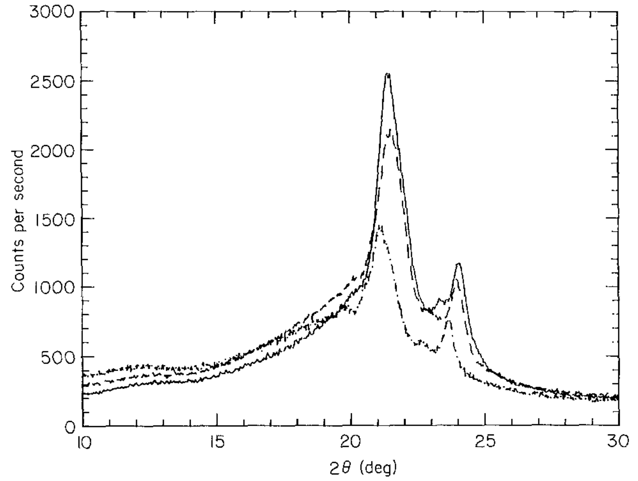


Figure 3 X-ray diffraction profiles for PED/EVA mixtures with differing weight percentages of PED: (——) 80% PED; (– –) 60% PED; (– ·) 40% PED

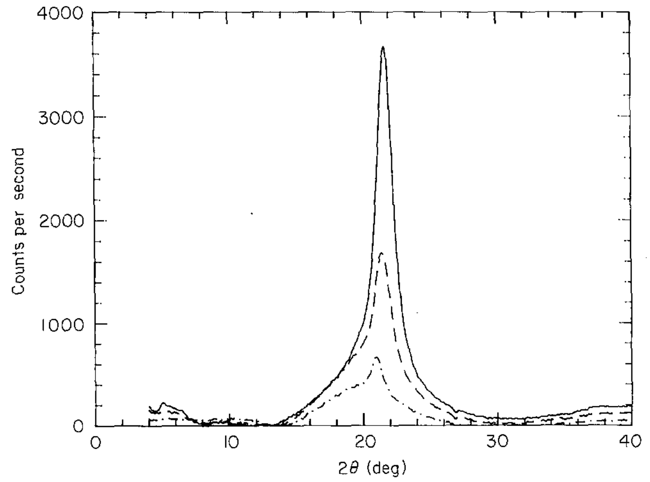


Figure 4 X-ray diffraction profiles for PI/EVA mixtures with differing weight percentages of PI: (——) 85% PI; (– –) 45% PI; (– ·) 27% PI

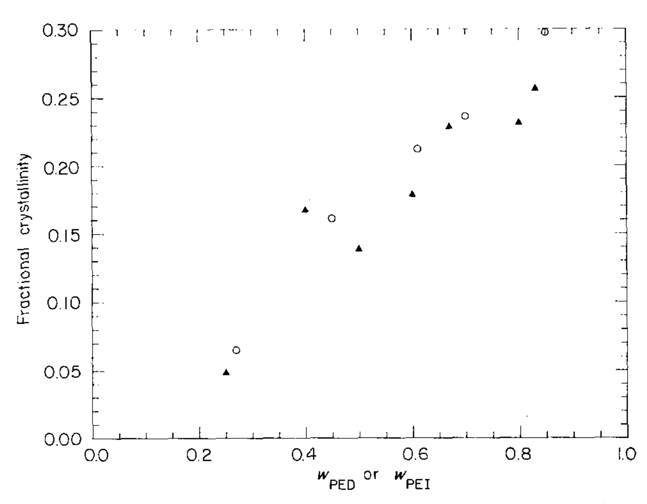


Figure 5 Fractional crystallinity in EVA mixtures: (▲) PED/EVA mixtures; (○) PI/EVA mixtures

DISCUSSION

Evaluation of χ

Before discussing the evaluation of χ from the melting point data, the d.s.c. thermograms of PED/EVA mixtures are discussed further here. We noted earlier that these thermograms displayed three endotherms. The dihydroxy terminated poly(ethylene glycol), i.e. before esterification with docosanoic acid, has a melting point of 250 K. We also note that poly(ethylene oxide) is immiscible with EVA copolymers whose vinyl acetate content is below a critical value[16]. The EVA copolymer studied had a vinyl acetate content far less than this critical value and therefore we anticipate that the ethylene oxide 'block' in the PED polymer is rejected from EVA-rich regions. The EVA copolymer has sufficiently long ethylene sequences which are able to crystallize with the docosyl end groups thereby depressing the melting point of the docosyl groups. (Docosanoic acid has a melting point of 353.3 K). Consequently, in the subsequent discussion of PED/EVA mixtures our attention is confined to the higher melting endotherm alone.

Because of the low number-average molecular weights of the polymers used, the possibility of a considerable entropic contribution to the mixing must be accounted for. Therefore, the full equation, equation (3), has been used to evaluate χ. The left-hand side of this equation requires a value of ΔH_{2u}, the enthalpy of fusion per monomer unit of the fully crystalline polymer. For PI, FVA and PED, this quantity has been calculated from the observed enthalpies of fusion and the fractional crystallinities obtained from the powder diffraction profiles (for PI and PED) and by the comparison method (for FVA). The molar volume of the repeat unit has been approximated by the ratio of the molecular weight of the repeat unit to the density of the polymer. *Figures 6, 7* and *8* show the melting point depression data, for the three types of mixtures investigated, plotted according to equation (3) and the linear least squares fits to the data. *Table 3* summarizes the data obtained from the plots and gives the values of χ obtained. These values of χ indicate that the FVA and PI polymers are only just miscible with EVA at the melting point, whereas the PED polymer is quite definitely miscible because χ is large and negative.

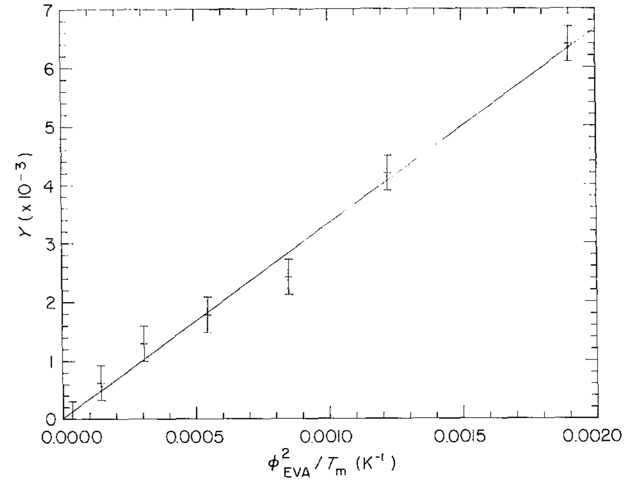


Figure 6 Melting point depression data for PED/EVA mixtures plotted according to equation (3). The solid line is the linear least squares fit. Y is the left-hand side of equation (3)

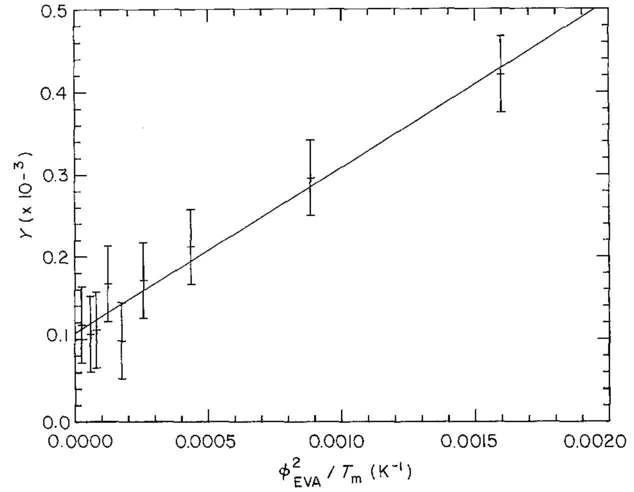


Figure 7 Melting point depression data for PI/EVA mixtures plotted according to equation (3). The solid line is the linear least squares fit. Y is the left-hand side of equation (3)

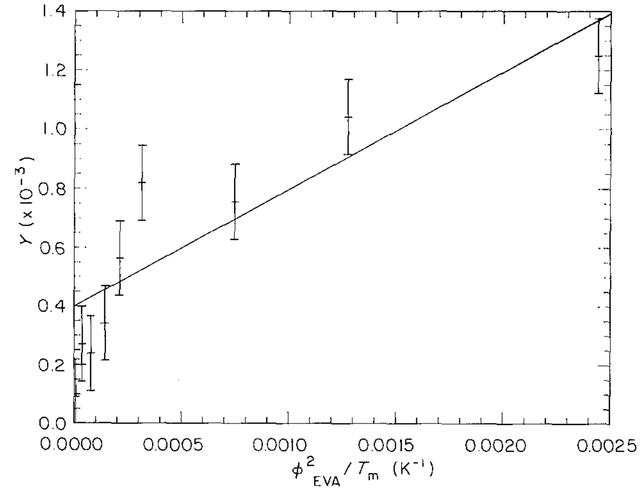


Figure 8 Melting point depression data for FVA/EVA mixtures plotted according to equation (3). The solid line is the linear least squares fit. Y is the left-hand side of equation (3)

For the PED/EVA mixture, the intercept in *Figure 6* is essentially zero, indicating that the entropic contributions have been fully accounted for. However, for FVA/EVA and PI/EVA mixtures finite positive intercepts are obtained which are indicative of some additional entropy contribution. Similar additional entropy contributions have been noted in mixtures of linear and branched polyethylenes[17]; it appears most probable that the hydrocarbon side chains in PI and FVA are the source of the additional entropy. Since no additional entropy contributions in PED/EVA mixtures were noted, the acetate substituent makes a negligible contribution to this additional entropy. In principle, the PI polymer would be expected to lead to a higher additional entropy contribution since the 'grafting' density of hydrocarbon substituents is higher than that of FVA. Moreover, the length of the substituents in the PI polymer is longer and consequently the configurational contribution to the entropy would be expected to be larger. What is observed instead is that the FVA/EVA mixture has the larger additional entropy contribution. Although the grafting density is lower, the hydrocarbon substituents are on

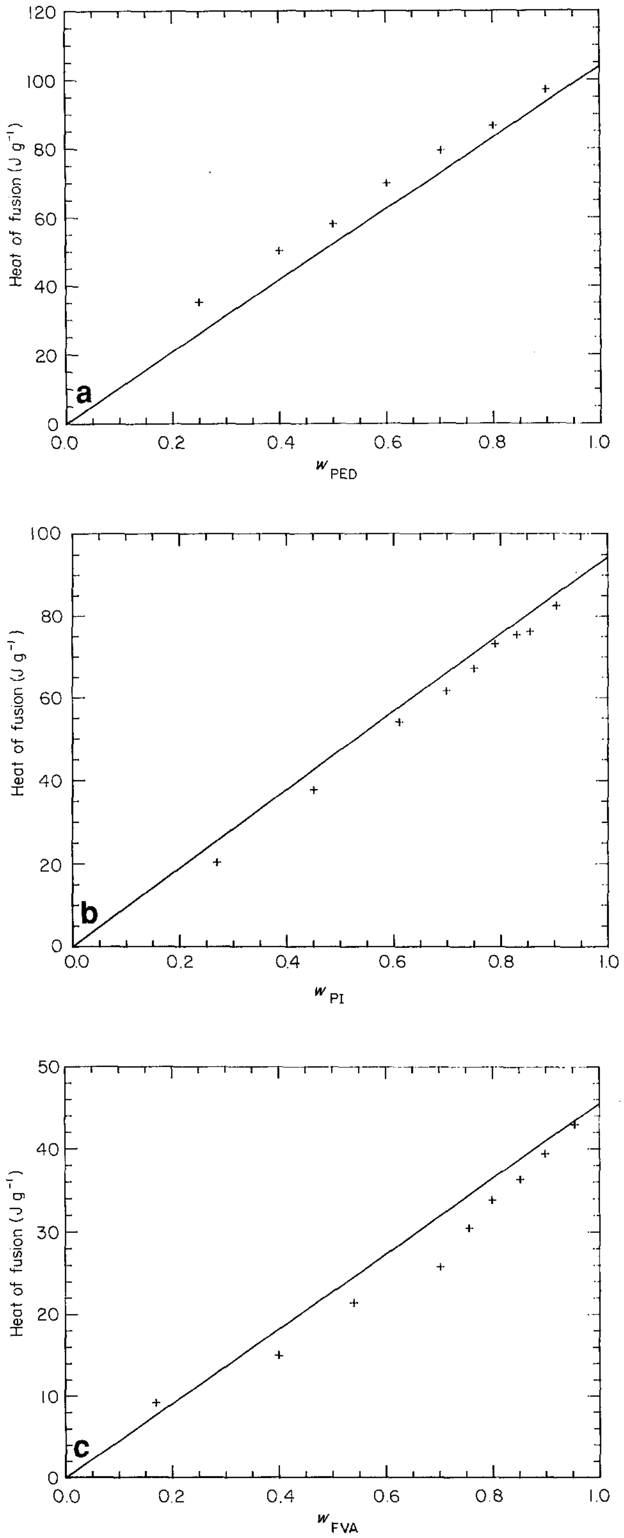


Figure 9 Dependence of the enthalpy of fusion on the weight fraction of crystallizable polymer in the mixtures. The straight line connects the enthalpy of fusion equal to zero to the enthalpy of fusion when the weight fraction of crystallizable polymer is 1: (a) PED/EVA; (b) PI/EVA; (c) FVA/EVA

Table 3 Parameters from least squares fits to Nishi–Wang plots

Blend description	Slope	Intercept ($\times 10^{-3}$)	B (J cm^{-3})	χ
FVA/EVA	0.43±0.09	0.34±0.08	−3.6±0.7	−0.06
PI/EVA	0.20±0.01	0.11±0.01	−1.7±0.1	−0.02
PED/EVA	3.32±0.15	0.01±0.14	−27.6±4.11	−0.38

different carbon atoms. Consequently there will be a greater number of available rotational states about the main chain bonds, which will increase the configurational entropy contribution and hence this may be the source of the increased additional entropy contribution. Additionally, hydrocarbon substitution may also alter the crystalline morphology more effectively than its effect on the change in the entropy of mixing.

Enthalpy of fusion

The dependence of the enthalpy of fusion on the weight fraction of crystallizable polymer in the mixtures is shown in *Figure 9*. For both PI/EVA and FVA/EVA mixtures there is a small reduction in the enthalpy of fusion compared to that expected for a simple dilution of the crystalline component by the presence of the EVA. It appears that the small favourable interaction between EVA and these polymers, frustrates the crystallization of the hydrocarbon side chains. For PED/EVA mixtures, the heats of fusion observed are greater than the prediction of simple dilution. In this situation there appears to be a cocrystallization of long ethylene sequences with the docosyl ends of the PED polymer. This view is supported by the expansion in the lattice plane spacings as the EVA content of the blend increases (*Table 2*); no such expansion was noted in the PI/EVA mixtures. *Figure 10* shows the powder diffraction profiles of PED and a high molecular weight poly(ethylene oxide); the peak centred at $2\theta = 21.5°$ in the PED is attributed to the crystallization of the docosyl residues and that at $2\theta \simeq 24°$ is due to the poly(ethylene oxide) part of the molecule but whose organization has been modified by the presence of the docosyl ends. Since the EVA copolymer used here is not compatible with poly(ethylene oxide), it is surprising that the lattice plane spacing associated with the separate crystallization of the poly(ethylene oxide) units is modified by the presence of the EVA. We can only speculate that the cocrystallization of docosyl residues with ethylene sequences has also induced the crystallization of the poly(ethylene oxide) units to larger lattice plane spacings. Starkweather[18] has discussed the influence of a second polymer on the crystallization of a semicrystalline component in a mixture of two polymers. There is no general rule by which one can predict the influence of miscibility on crystallinity; the extent of crystallinity may be either increased or decreased. For the mixtures studied here both types of behaviour are evident. There is an enhancement of crystallinity for the PED/EVA mixture which appears to be due to some cocrystallization indicating that the polymers are miscible both in the crystalline and amorphous regions, whereas in the PI/EVA and FVA/EVA mixtures a small decrease in the crystallinity is noted arising from a frustration of the crystallization process.

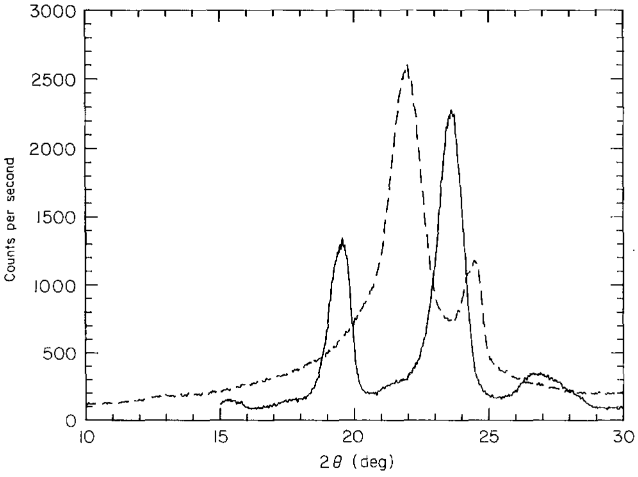


Figure 10 X-ray powder diffraction profiles for PED (--) and pure poly(ethylene oxide) homopolymer (——)

CONCLUSIONS

The random EVA copolymer investigated here has been found to mix with a docosyl ester terminated (at both ends) low molecular weight poly(ethylene glycol). This interaction appears to take place via a cocrystallization of the docosyl ends with ethylene sequences in the EVA copolymer. Supporting data for this viewpoint is provided by the expansion of the lattice planes as more EVA polymer is incorporated. We also note that this cocrystallization forces some change in the lattice plane spacing of the separately crystallized poly(ethylene oxide) part of the PED polymer. The average length of the poly(ethylene oxide) unit in the PED polymer corresponds to about nine ethylene oxide units. This is rather too short for chain folding to become important and it therefore appears that the PED polymer is aggregated into clusters, the cores being ethylene oxide units and coronas composed of docosyl ends and ethylene sequences in EVA cocrystallized together.

No such cocrystallization takes place with the FVA or PI polymers, rather the crystallization of the side chains is frustrated. This may arise from the inability to assimilate long ethylene sequences in the side chain crystalline regions of FVA or PI due to the higher molecular weight of these polymers and the higher frequency of hydrocarbon substituent chains in these polymers. These prevent optimization of the packing of EVA with the hydrocarbon substituents; in its turn presence of the EVA severely reduces the possibility of side chain crystallization. The enthalpic interactions between EVA and FVA and more so for EVA and PI are insufficiently negative to overcome these entropic restrictions, and as a consequence the polymers are only just miscible.

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