

Thermodynamics of poly(ethylene oxide)–poly(vinyl acetate) blends

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(Received 8 July 1992)

Heat-of-mixing data, obtained on blends of poly(ethylene oxide) (PEO) with whole and fractionated poly(vinyl acetate) (PVAc), were used to feed Patterson's theory of polymer–polymer miscibility. Negative values of mixing enthalpy, contact-energy term, interaction parameter and excess volume were obtained only for blends with the lowest molecular weight PVAc fraction. These results show that miscibility of PVAc with PEO strongly depends on its molecular weight. The calculated unfavourable excess volume term of the Patterson equation is small in comparison with the absolute value of the interaction term. Therefore, miscibility of PEO and low-molecular-weight PVAc is dictated by the weak specific interactions between different repeat units and by the entropic gain in the mixing process.

(Keywords: miscibility; poly(ethylene oxide); poly(vinyl acetate); corresponding state theory; heat of mixing)

INTRODUCTION

Poly(ethylene oxide) (PEO) can act as a proton acceptor and form miscible blends with a variety of proton-donating polymers¹, since it has partial negative charge on the oxygen atoms². It can be expected that poly(vinyl acetate) (PVAc), which has a partial positive charge on the carbonyl carbon atom, may interact favourably with PEO and form a miscible pair.

In the last decade, several research groups have investigated the miscibility of PEO with PVAc. Munoz *et al.*³ performed a rheological and thermo-optical analysis and found that the apparent melt viscosity increases monotonically with the content of PEO at various shear stresses. An appreciable melting-point depression of PEO crystals grown from the blends was detected and attributed to mixing at the segmental level of the two components.

Kalfoglou^{4,5} studied the miscibility of this blend by dynamic mechanical analysis, optical microscopy, calorimetry and tensile tests. His results are consistent with partial miscibility of the components in the semicrystalline solid state and complete miscibility in the melt.

Martuscelli and Silvestre^{6–8} extensively studied the morphology, crystallization and thermal behaviour of PEO–PVAc blends by means of SAXS, d.s.c. and optical microscopy. A single glass transition temperature, intermediate between those of the pure polymers, was detected. The spherulitic growth rate and the overall crystallization kinetic constant decrease with the addition

of PVAc to PEO. Plain PEO crystals grow according to a regime I process, while crystals in blends grow with regime II mechanism. The amorphous content and the interphase thickness increase with increasing PVAc content, but the thickness of lamellae does not change with composition. From these observations, they suggested that amorphous PVAc is present in both interfibrillar and interlamellar regions of PEO spherulites.

The above results do not allow one to draw quantitative conclusions on miscibility of PEO with PVAc. A direct proof of miscibility can be obtained by measuring the enthalpy of mixing, ΔH_{mix} , since it represents the crucial contribution to the free-energy change associated with the mixing process⁹.

The main purpose of this work is to evaluate ΔH_{mix} by measuring the heats of solution of PEO, PVAc and their blends in a common solvent and applying Hess's law¹⁰. To investigate the influence of chain length on miscibility, experiments have been carried out using PVAc samples of different molecular weights. To describe the miscibility of PEO–PVAc blends quantitatively, the interaction parameter of the simplified Patterson theory¹¹ has been estimated from the heat of mixing data.

THEORETICAL BACKGROUND

The overall free energy of mixing of polymer blends can be expressed as:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (1)$$

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To have miscibility, two conditions must be fulfilled: ΔG_{mix} must be negative and the second derivative of ΔG_{mix} with respect to composition must be zero or positive. Since the combinatorial entropy terms are very small for high molecular weight polymers, the enthalpic contribution plays a dominant role in the sign of ΔG_{mix} . In other words, miscibility in polymer blends is a direct result of a negative heat of mixing contribution to the overall free energy of the process. When only weak dispersive or van der Waals forces act between the repeat units of the two polymers, the heat of mixing is positive. If specific interactions such as hydrogen bonds or dipole–dipole coupling are established, a negative ΔH_{mix} results. Therefore, evaluation of the heat of mixing is of prime relevance to understanding polymer–polymer miscibility.

The extent of polymer–polymer interactions can be qualified by means of a thermodynamic interaction parameter. The Prigogine–Flory theory¹² arrives at a correct expression for the interaction parameter of polymer–solvent systems. McMaster¹³ extended this theory to polymer mixtures, but the derived equations are very complex and of little utility for experimental verification. Patterson^{14,15} developed a simplified corresponding-state theory, leading to the following expression for the interaction parameter:

$$\frac{X_{12}}{V_1^*} = \frac{P_1^*}{RT_1^*} \left[\frac{\tilde{v}_1^{1/3}}{\tilde{v}_1^{1/3} - 1} \left(\frac{X_{12}}{P_1^*} \right) + \frac{\tilde{v}_1^{1/3}}{2(4/3 - \tilde{v}_1^{1/3})} \tau^2 \right] \quad (2)$$

The first term on the right hand side of equation (2) is the ‘interaction’ term, which is defined by X_{12}/P_1^* . The contact energy term, X_{12} , is a measure of the interchange energy between unlike units. X_{12} can be positive or negative, depending on whether dispersion forces or specific interactions—such as hydrogen bonds or dipole–dipole interaction—are dominating in the mixture, respectively. $X_{12} > 0$ implies unfavourable mixing; $X_{12} \leq 0$ must be fulfilled to attain a thermodynamically stable mixture of the polymer pair.

The second term represents the ‘free-volume’ term. It is dependent on:

$$\tau = 1 - T_1^*/T_2^* \quad (3)$$

and, always being positive, gives an unfavourable contribution to polymer–polymer miscibility.

The state parameters T^* , P^* and v^* in the above equations are defined by the actual and the reduced temperature (\tilde{T}), pressure (\tilde{P}) and specific volume (\tilde{v}):

$$\tilde{T} = T/T^* \quad (4)$$

$$\tilde{P} = P/P^* \quad (5)$$

$$\tilde{v} = v/v^* \quad (6)$$

A molar hard-core volume can be defined as:

$$V_i^* = M_i v_i^* \quad (7)$$

where M_i is the molecular weight of the i th component.

Reduced volume and temperature are related to the thermal expansion coefficient α through the equations:

$$\tilde{v} = [(3 + 4\alpha T)/(3 + 3\alpha T)]^3 \quad (8)$$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \quad (9)$$

The reference characteristic pressure (P^*) is related to the thermal coefficient of pressure, $\gamma = (\partial P/\partial T)_v$, by the equation:

$$P^* = \gamma T \tilde{v}^2 \quad (10)$$

X_{12} can be obtained either from the heat of mixing of the two polymers^{16,17}:

$$\Delta H_{\text{mix}} = x_1 P_1^* V_1^* (1/\tilde{v}_1 - 1/\tilde{v}) + x_2 P_2^* V_2^* (1/\tilde{v}_2 - 1/\tilde{v}) + x_1 V_1^* \Theta_2 X_{12}/\tilde{v} \quad (11)$$

or from the reduced temperature of the mixture:

$$\tilde{T} = (\varphi_1 P_1^* \tilde{T}_1 + \varphi_2 P_2^* \tilde{T}_2)/(\varphi_1 P_1^* + \varphi_2 P_2^* - \varphi_1 \Theta_2 X_{12}) \quad (12)$$

The parameters φ_i (segmental fraction) and Θ_2 (site fraction) in equations (11) and (12) are defined as:

$$\varphi_2 = 1 - \varphi_1 = x_2/(x_2 + x_1 r_1/r_2) \quad (13)$$

$$\Theta_2 = \varphi_2/(\varphi_2 + \varphi_1 S_1/S_2) \quad (14)$$

where

$$r_1/r_2 = V_1^*/V_2^* \quad (15)$$

$$S_1/S_2 = (V_1^*/V_2^*)^{-1/3} \quad (16)$$

and x_1 and x_2 are mole fractions of components 1 and 2, respectively.

X_{12} can be calculated from the characteristic values of pure components by simultaneously solving, by a trial-and-error method, equations (9), (11) and (12). Alternatively, equation (11) can be directly applied if the excess volume of mixing, V^E , is available from specific volume measurements of pure components and blends:

$$V^E = [\tilde{v} - (\varphi_1 \tilde{v}_1 + \varphi_2 \tilde{v}_2)](x_1 V_1^* + x_2 V_2^*) \quad (17)$$

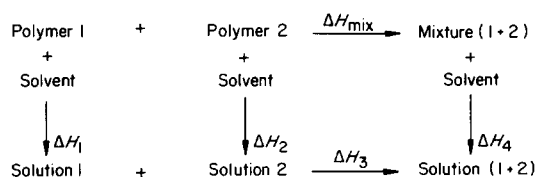
or

$$V^E/V^0 = \tilde{v}/\tilde{v}_0 - 1 \quad (18)$$

where \tilde{v}_0 is the weighted sum of the volumes of the pure components:

$$\tilde{v}_0 = \varphi_1 \tilde{v}_1 + \varphi_2 \tilde{v}_2 \quad (19)$$

Owing to the very small heat effect and to the slow interdiffusion of the components, it is very difficult to measure directly the heat of mixing for polymer–polymer systems. A more convenient approach is to follow an indirect route according to the following thermodynamic cycle based on Hess’s law^{18,19}:



From the above cycle, ΔH_{mix} is calculated from:

$$\Delta H_{\text{mix}} = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 \quad (20)$$

EXPERIMENTAL

Materials

PEO and PVAc were purchased from Fluka and Aldrich-Chemie, respectively. Their molecular weights are given in Table 1.

PVAc was purified and fractionated by using the following procedure. A solution in acetone at a concentration of 2 g/100 ml was filtered at room temperature on a G4 sintered glass funnel and precipitated by adding an excess of petroleum ether. The

same solvent/non-solvent system was used to fractionate PVAc by a step precipitation method. All fractions were washed with petroleum ether and dried in a vacuum oven for 4 days at 323 K. The molecular characteristics of the fractions were determined by g.p.c. and are reported in Table 1.

Sample preparation

Blends were prepared by dissolving appropriate amounts of the two components in chloroform at an overall concentration of 2% w/v. Solutions were cast on glass plates and quickly transferred to an oven with forced air circulation at 323 K until dry. Films were then completely dried *in vacuo* for 48 h.

Heat of solution measurements

Heat of solution measurements of pure components and blends were carried out by means of a Setaram C80D calorimeter using cyclohexanone as common solvent.

In order to get the heat of mixing of components in the liquid state, measurements were performed at a temperature higher than both the glass transition of PVAc and the melting point of PEO. A temperature of 343 ± 0.1 K was used throughout all the experiments.

Reversal mixing equipment was adopted to improve the dissolution speed. According to the recommended procedure, the sample was placed in the lower container and the solvent in the upper one of the measuring cell. A mercury seal and a lip were used to separate the two containers and the same quantities of solvent and mercury were placed in the reference vessel. Sample mass and solvent volume were established to obtain final concentrations of less than 0.2% w/v.

Repeated experiments under the same conditions indicate that the heat of solution measurements were affected by an error of less than 5%. The reported heats of solution were calculated from the average of at least four measurements on the same sample.

The heats of mixing of blends were calculated by using the following equation:

$$\Delta H_{\text{mix}} = w_1 \Delta H_1 + w_2 \Delta H_2 + \Delta H_3 - \Delta H_4 \quad (21)$$

Table 1 Average molecular weights of PEO, PVAc and fractions of PVAc measured by g.p.c.

Polymer	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n
PEO ^a	24 800	13 600	1.82
PVAc ^b	151 000	56 400	2.68
PVAc-1	169 000	108 000	1.56
PVAc-2	63 100	45 400	1.39
PVAc-3	41 800	20 800	2.00

^aViscosity parameters of PEO in chloroform at 25°C²³; $K = 0.206 \text{ cm}^3 \text{ g}^{-1}$, $a = 0.50$

^bViscosity parameters of PVAc in tetrahydrofuran at 35°C²⁴; $K = 1.56 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$, $a = 0.708$

Table 2 Calorimetric data of PEO–PVAc blends measured at 343 K

PEO/PVAc (mole ratio)	M_n (PVAc)	$w_1 \Delta H_1 + w_2 \Delta H_2 + \Delta H_3$ (J g ⁻¹)	ΔH_4 (J g ⁻¹)	ΔH_{mix} (J g ⁻¹)	ΔH_{mix} (J mol ⁻¹)
28/72	108 000	18.0	17.7	0.3	≈ 0
28/72	45 400	17.8	17.9	-0.1	≈ 0
28/72	20 800	16.9	21.4	-4.5	-84 600
50/50	20 800	16.8	20.1	-3.3	-56 600
75/25	20 800	16.0	18.4	-2.4	-36 900

where w_1 and w_2 are the weight fractions of PEO and PVAc in a blend, respectively. The unit of ΔH_{mix} is J g⁻¹.

Thermal pressure coefficient measurements

The home-made apparatus sketched in Figure 1 was used to measure the thermal pressure coefficients (γ) of PEO and PVAc^{20–22}. The cell was connected to a pressure balance and placed in an oil thermostat, with a temperature control at ± 0.005 K. The parameter γ was obtained from the slope of the pressure *versus* temperature plot.

RESULTS AND DISCUSSION

The average experimental calorimetric data determined in two complementary steps are shown in Table 2. The first step provides the total heat effect associated with dissolution of polymer 1 ($w_1 \Delta H_1$), dissolution of polymer 2 ($w_2 \Delta H_2$) and mixing of the two resulting solutions

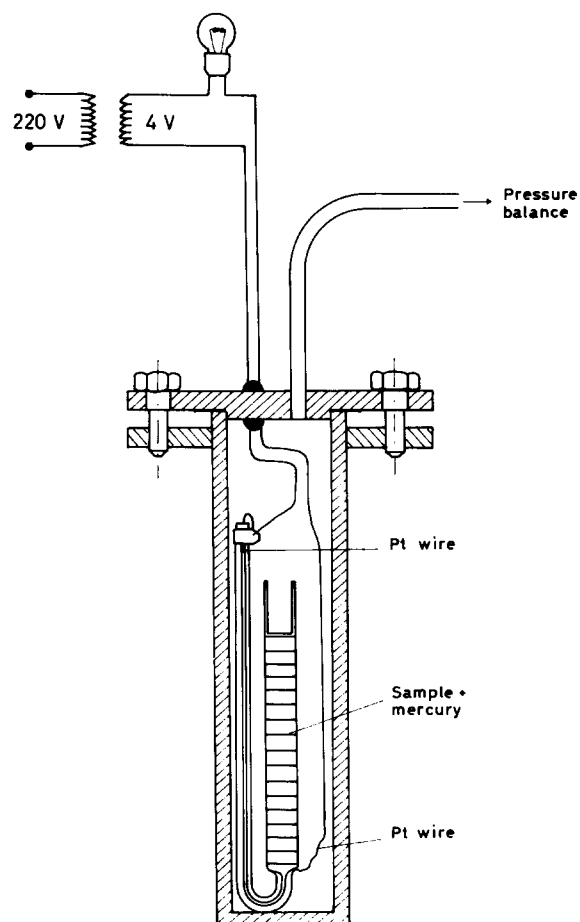


Figure 1 Home-made apparatus used for thermal pressure measurement

(ΔH_3). This experiment is performed using a *mechanical mixture* of polymer films, cut into small pieces, and in the proper weight ratio. In the second independent step, the enthalpic change due to dissolution of a *blend* (ΔH_4), prepared according to the above-mentioned procedure, is measured.

The heats of mixing listed in the last column are computed from the heats of mixing per total polymer weight (J g^{-1}) by using the relation:

$$\Delta H_{\text{mix}} (\text{J mol}^{-1}) = [\Delta H_{\text{mix}} (\text{J g}^{-1})] / (w_1 v_1^* / V_1^* + w_2 v_2^* / V_2^*) \quad (22)$$

It can be appreciated that blends with high molecular weight PVAc ($M_n = 108\,000$ and $45\,400$) exhibit negligibly small absolute values of heat of mixing for the composition PEO/PVAc = 28/72 (mole ratio). Since these values are within experimental error, it can be considered that the heat of mixing is zero. Specific interactions do not provide a thermodynamic force leading to miscibility of the components. On the other hand, when the lower molecular weight PVAc ($M_n = 20\,800$) is used, an appreciable and negative heat of mixing is measured.

These experimental results suggest that miscibility between PEO and PVAc is very strongly affected by the molecular weight of the PVAc. Such a strong dependence can hardly be justified on the basis of the number-average molecular weights reported in Table 2. However, a closer inspection of our g.p.c. results reveals that PVAc-3 contains about 17% of chains whole molecular weight is lower than 10000, while only 2% and $\approx 0\%$ of those chains are detected in PVAc-2 and PVAc-1, respectively.

Measurements of ΔH_{mix} have been performed also on blends with different PEO/PVAc ratio for the lower molecular weight PVAc. As shown in Table 2, the absolute value of heat of mixing decreases with increasing PEO content. This suggests that miscibility increases on decreasing the content of PEO in the mixture.

A negative heat of mixing implies that specific interactions are active between PEO and PVAc. In their paper on poly(ethylene oxide)–poly(methyl methacrylate) (PEO–PMMA) blends, Zerbi *et al.*² suggested that the oxygen atom of PEO has a negative charge ($\Delta q(\text{O}) = -0.3e$) (Figure 2a) and behaves as a proton acceptor. PMMA may behave either as a proton acceptor through the negative oxygen ($\Delta q(\text{O}) = -0.3e$), or as a proton donor owing to the influence of the positive carbon atoms of the carbonyl groups ($\Delta q(\text{carbonyl carbon}) = +0.45e$) (Figure 2b). On the other hand, it might be sterically possible to form a dipole–dipole interaction between the oxygen atom of PEO and the carbonyl carbon atom of PMMA.

The molecular structure of PVAc has some similarities to that of PMMA. Its main chain is similar to that of n-alkanes. Carbonyl carbons in sp^2 hybridization could be strongly positive ($\Delta q = +0.45e$) (as shown in Figure 2c); therefore, the methyl group on the side-chains may act as a proton donor. Hydrogen bonds might be formed between the oxygen of PEO and one of the hydrogens of the $-\text{CH}_3$ group of PVAc. In addition, dipole–dipole interactions between the oxygen in the polyether chain and the carbonyl carbon of PVAc can be conceived. Both hydrogen bonds and dipole–dipole interactions may contribute to intimate mixing of the two polymers.

By using conformational models (see Figures 2b and 2c) it can be argued that, between the carbonyl carbon

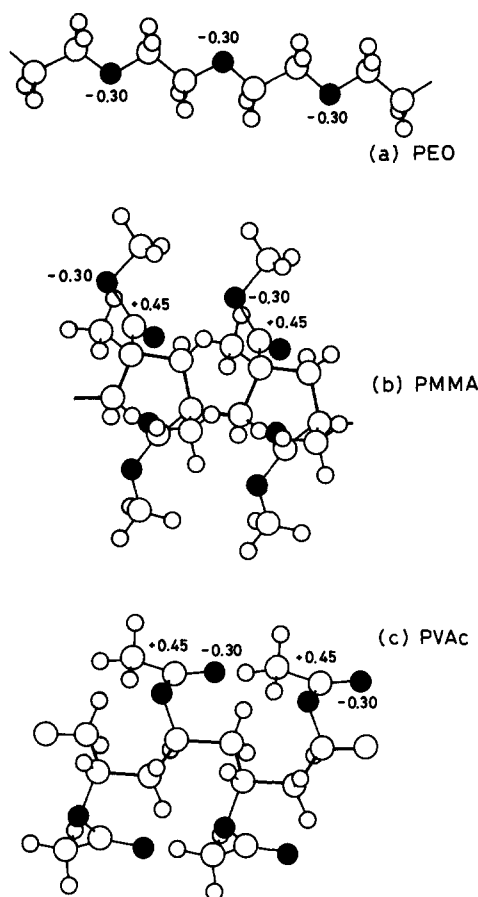


Figure 2 Atomic charges in (a) PEO, (b) PMMA and (c) PVAc

Table 3 Thermal expansion coefficient (α), thermal pressure coefficient (γ), specific volume (v), reduced volume (\bar{v}) and reduced state parameters (v^* , V^* , T^* , P^*) for PEO and PVAc at 343 K

Parameters	PEO	PVAc
α (10^{-4} K^{-1})	7.2252 ^a	6.7000 ^b
γ ($\text{J cm}^{-3} \text{ K}^{-1}$)	1.44	0.78
v ($\text{cm}^3 \text{ g}^{-1}$)	0.9212 ^a	0.8662 ^b
\bar{v}	1.2120	1.1987
v^* ($\text{cm}^3 \text{ g}^{-1}$)	0.7600	0.7226
V^* ($\text{cm}^3 \text{ mol}^{-1}$)	10336	15175
T^* (K)	6696	7014
P^* (J cm^{-3})	726	384

^aFrom ref. 25

^bFrom ref. 26

atoms of PVAc and the oxygen atoms of PEO, less steric hindrance and charge shielding (repulsive forces due to the negatively charged oxygen atoms) are operative than in the case of PMMA and PEO. Therefore, it can be assumed that interactions between PEO and PVAc are stronger than those formed in PEO–PMMA blends.

As previously noted, miscibility can be expressed quantitatively in terms of the value of the interaction parameter, χ_{12}/V_1^* , which can be estimated from Patterson's equation. We denote PEO and PVAc with indices 1 and 2, respectively. The parameters used in the calculations are listed in Table 3.

Contact-energy terms X_{12} , reduced volumes \bar{v} , interaction parameters χ_{12}/V_1^* and excess volumes V^E/V^0 calculated by solving the simultaneous equations (9), (11) and (12), and equations (2) and (12), are given

Table 4 Contact energy term (X_{12}), interaction parameter (χ_{12}/V_1^*), excess volume (V^E/V^0) and reduced volume (\bar{v}) of PEO–PVAc blends

PEO/PVAc (mole ratio)	\bar{M}_n (PVAc)	X_{12} (J cm ⁻³)	χ_{12}/V_1^* (mol cm ⁻³)	V^E/V^0	\bar{v}
28/72	108 000	0	5.4×10^{-3}	1.3×10^{-3}	1.2031
28/72	45 400	0	5.4×10^{-3}	1.3×10^{-3}	1.2031
28/72	20 800	-37.0	-1.1×10^{-2}	-1.8×10^{-3}	1.1994
50/50	20 800	-18.9	-5.4×10^{-3}	-2.4×10^{-4}	1.2038
75/25	20 800	-15.2	-4.3×10^{-3}	-5.8×10^{-5}	1.2075

in Table 4. As expected from the signs of the heats of mixing, positive values of X_{12} , χ_{12}/V_1^* and V^E/V^0 were obtained for the blends with high molecular weight PVAc (PVAc-1, PVAc-2), whereas negative values of these parameters resulted at all compositions when the low molecular weight PVAc-3 fraction was used. Calculations provide a further indication that miscibility in the PEO–PVAc system is strongly conditioned by the molecular weight, thus suggesting a relevant contribution of mixing entropy to the interaction parameter²⁷.

In Table 4 the values of the calculated thermodynamic quantities, relative to different compositions of PEO/PVAc-3, are also reported. In line with the expectations from the equation-of-state theory²⁸, they indicate a composition-dependent miscibility not accounted for in Patterson's simplified theoretical treatment.

The negative excess volumes calculated for the blends with the lowest molecular weight PVAc suggest that a slight densification is associated with the formation of specific interactions between polymers.

In the Patterson theory, the contact energy term was treated as temperature independent. Accordingly, the variation of the interaction parameter χ_{12}/V_1^* with temperature can be estimated directly from equation (2). The values of χ_{12}/V_1^* for the blend with PEO/PVAc = 50/50 were calculated in the temperature range 323–443 K and are shown in Figure 3. The critical value of χ_{12}/V_1^* , above which phase separation is expected, was computed from:

$$(\chi_{12}/V_1^*)_c = \frac{1}{2} [1/(V_1^*)^{1/2} + 1/(V_2^*)^{1/2}]^2 \quad (23)$$

and corresponds to the horizontal broken line in Figure 3.

The free-volume term is always positive and does not favour mixing; on the other hand, the interaction term is negative. Since the absolute value of the interaction term is much higher than that of the free-volume term, the net value of χ_{12}/V_1^* is negative. Therefore, miscibility can be predicted in this temperature range.

Both interaction and free-volume contributions to the parameter χ_{12}/V_1^* increase with increasing temperature, thus implying that a lower critical solution temperature (LCST) behaviour is to be expected in the phase diagram of PEO–PVAc.

CONCLUSIONS

We have measured a negative heat of mixing in blends of PEO and low molecular weight PVAc. Miscibility is likely to be due to hydrogen bonds and dipole–dipole interactions that, on the basis of a conformational model, can act between different repeat units. The analysis of experimental data according to the simplified Patterson equation indicates that the free-volume term has a much smaller absolute value than the interaction term. Both

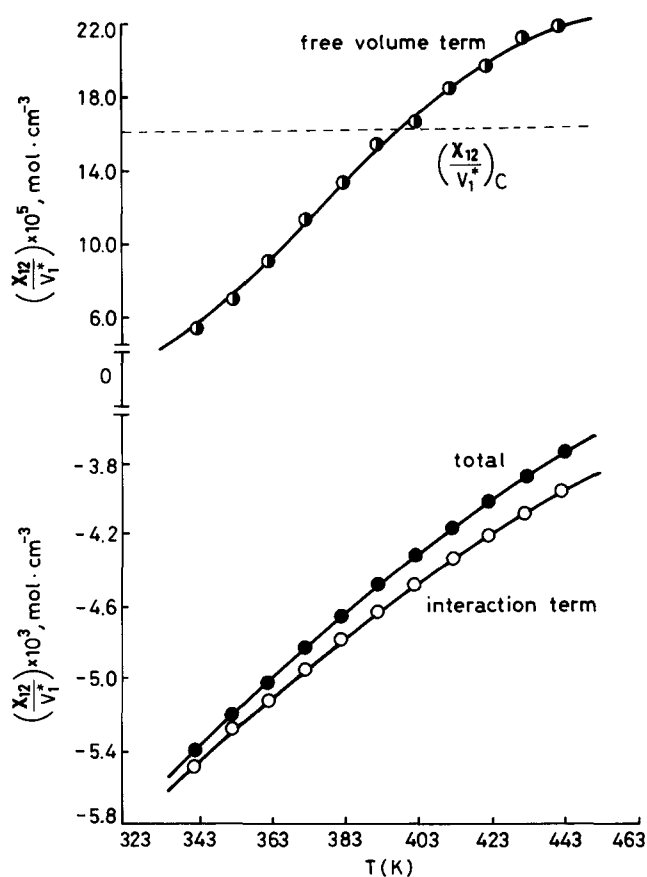


Figure 3 Total interaction parameter χ_{12}/V_1^* , interaction term and free-volume term of χ_{12}/V_1^* as functions of temperature for blends with PEO/PVAc = 50/50 (mole ratio). The critical interaction parameter is represented by the horizontal broken line

contributions to the interaction parameter increase with temperature, leading to the prediction of LCST behaviour in the phase diagram of PEO–PVAc blends.

ACKNOWLEDGEMENTS

We are indebted to Professor Li Bincai for his critical reading of the manuscript and for his suggestions. This work has been carried out in the framework of the CNR (Italy)–Academia Sinica (PRC) Cooperation Agreement. Both institutions are gratefully acknowledged. This research was supported by 'Progetto Finalizzato Chimica Fine e Secondaria II', CNR, Italy.

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