Miscibility prediction based on the corresponding states theory: poly(ethylene oxide)/atactic poly(methyl methacrylate) system

S. Cimmino, E. Martuscelli* and C. Silvestre
Istituto di Ricerche su Tecnologia dei Polimeri e Reologia, CNR Via Toiano 6, 80072 Arco Felice, Napoli, Italy

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A version of the corresponding states theorem of Prigogine for a polymer liquid system has been applied to a poly(ethylene oxide) (PEO)/atactic poly(methyl methacrylate) (At-PMMA) mixture and found to afford a good prediction of miscibility for this system semi-quantitatively. A value of the contact energy term, X_{12}, of -0.3 J cm^{-3} was calculated by using independent literature values of interaction parameter, χ_{12}, computed at about 80°C. The shape of the curve of χ_{12}/V_1^* over temperature indicates that the PEO/At-PMMA mixture is miscible in the liquid state from 0 to 200°C. Extrapolation of χ_{12}/V_1^* curve predicts a lower critical solution temperature (LCST) of about 350°C for this system.

(Keywords: miscibility; corresponding states theorem; PEO; PMMA)

INTRODUCTION

The poly(ethylene oxide)/atactic poly(methyl methacrylate) (PEO/At-PMMA) mixture has been extensively studied by many researchers and it is generally reported as a miscible system in the melt state[1–11]. Martuscelli, Silvestre *et al.*[1,2] have studied this system using different techniques such as differential scanning calorimetry (d.s.c.), optical and electron microscopy and small angle X-ray scattering (SAXS). The result of these investigations has shown that the amorphous phase of PEO/At-PMMA presents only one glass transition and no separated domains of the two components are observed for any of the blend compositions investigated in the melt state at temperatures close to the melting temperature (T_m) of PEO. At temperatures below T_m, after PEO crystallization, a two-phase system characterized by PEO crystalline lamellae separated by amorphous layers containing At-PMMA and amorphous PEO is formed.

Observations on crystallization kinetics[3,4] were interpreted by assuming that the polymers are compatible in the undercooled melt, at least for the range of crystallization temperatures investigated. Using melting point depression measurements, the Flory–Huggins interaction parameter χ_{12} was calculated to be -1.9 (at 76°C) for the blends containing PEO $M_w = 2.0 \times 10^4$ (g mol^{-1}) and -0.35 (at 74°C) for those containing PEO with $M_w = 1.0 \times 10^5$ (g mol^{-1}). Very recently with the same method Alfonso[10] has obtained a $\chi_{12} = -0.15$ using blends with several molecular weights of PEO and At-PMMA.

Russell *et al.*[12,13] investigating PEO/At-PMMA mixtures by small angle neutron scattering (SANS) technique have found that the Flory–Huggins interaction parameter (calculated at 80°C) has a quite small negative value and it is composition dependent (see *Table 1*). The positive value (at $\phi_2 = 0.9$) reported in the table corresponds to the result obtained by Lefebvre *et al.*[14] on the system with high At-PMMA content. Direct evidence of miscibility of PEO and At-PMMA in the melt was obtained by Martuscelli *et al.*[5] by investigating the ^{13}C n.m.r. behaviour of blends at 60 and 90°C.

In addition Ramana Rao *et al.*[6], using vibrational spectroscopy, have investigated the nature of intermolecular interactions and the shape assumed by the molecules of PEO and At-PMMA in the blends. Their conclusions are that there cannot be a strong interaction between At-PMMA and PEO because the attractive forces between the negatively charged oxygen atoms of PEO and positively charged carbonyl carbon atoms of At-PMMA are weakened by the repulsive forces offered by the negatively charged oxygen atoms of At-PMMA. Due to the occurrence of both attractive and repulsive

Table 1 Contact energy term, X_{12}, calculated by equation (25) using the literature value of the interaction parameter, χ_{12}

ϕ_2 At-PMMA monomer fraction	χ_{12}	Source of X_{12} parameter (reference)	X_{12} (J cm^{-3})
0.1[a]	−0.0067	12	−0.26
0.3[a]	−0.0058	12	−0.26
0.5[a]	−0.0029	12	−0.26
0.7[a]	−0.0010	12	−0.26
0.9[a]	+0.0083	14	−0.26
[b]	−0.15	10	−0.30
[b]	+0.001	1	−0.26
[b]	−1.9	3	−0.78
[b]	−0.35	4	−0.35

[a] Interaction parameter calculated assuming a linear dependence on composition of χ_{12} values of references 12 and 14
[b] Interaction parameter assumed to be composition independent

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* To whom correspondence should be addressed

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forces, the interaction must be very weak and quite possibly of the magnitude of a van der Waals type. These experimental results as well as other results reported in the literature seem to indicate that PEO and At-PMMA form miscible blends. Because strong interactions between the two homopolymers should not exist, we must expect that the Flory–Huggins interaction parameter χ_{12} and the contact energy term X_{12} should be negative but very close to 0.

At present several theories, based on simple molecular models, may lead to useful predictions about the miscibility of polymer–polymer systems. The solubility parameter and group contribution approaches[15], the Flory–Huggins theory[15], the Patterson theory[16–18], the equation of state theory[11,15,19–21] and the lattice fluid theory[11] are examples of theories which give different levels of prediction. The reliability of the prediction depends on the amount of experimental data and the theory used.

The theoretical approach of group contributions and solubility parameters[15] has been applied by Martuscelli, Silvestre *et al.*[1] It was found that this theory predicts miscibility for PEO/At-PMMA blends at temperatures higher than PEO melting point.

This theoretical prediction of miscibility is in good agreement with a brief analysis made by Sanchez[11] where the pair PEO/At-PMMA is predicted to be miscible in accordance with the solubility parameter method (SPM) and lattice fluid theory (LFT) but not in accordance with Flory's equation of state theory. Sanchez[11] added that this comparison suggested that the equation of state theory is not so good as either the SPM or the LFT. However, Sanchez determined that this may be an erroneous conclusion because the equation of state theory had not yet been completely analysed.

The aim of this work is to apply the Patterson theory (see next section) to the PEO/At-PMMA system from 0 to 200°C in order to discover if this theory predicts miscibility for this system in the amorphous state under experimental conditions. Potentially, this theory has a higher level of prediction than the group contributions and solubility parameters approach. In fact the latter allows only a qualitative judgement of whether a system is miscible. In contrast, the Patterson theory, by taking into account the ever present disparity in size and shape between molecules and repeat units, gives a more quantitative prediction for miscibility.

THEORETICAL BACKGROUND

In the last twenty years, the Prigogine corresponding state theory (CST)[22] has attracted attention, particularly in the modified form of Flory and collaborators[23]. The main difference between Prigogine and Flory's (equation of state) theories lies in the volume dependence assumed for the molar configurational energy. Originally, Prigogine used a dependence inspired by the 6–12 Lennard-Jones potential. Flory[23] has used the inverse volume dependence characteristic of a van der Waals liquid.

Flory's equation of state theory was first applied by McMaster[24] to polymer mixtures and it was found that the free volume effects are of importance in polymer–polymer systems. However, the equations developed by McMaster are extremely complex because of the generalization of the theory. Patterson and collaborators[16–18], using the van der Waals dependence of the configurational energy on volume, have elaborated a simplified, but adequate, version of the corresponding state theory. This simplified version of CST is called the Patterson theory[25–28].

The expression of the interaction parameter in the Patterson theory takes the form:

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

Equation (1) contains the interactional and free volume terms, characterized by molecular parameters X_{12}/P_1^* and τ^2 respectively. The contact energy term, X_{12} is positive for dispersive forces and negative when specific interactions such as weak hydrogen bonds or charge–transfer complexes are present. The second term of equation (1) reflects differences in free volume between the components through the parameter

$$\tau=1-\frac{T_1^*}{T_2^*} \qquad (2)$$

and it is always positive, i.e. unfavourable to mixing. It becomes increasingly important at higher temperatures.

In the Patterson theory, as in Flory's equation of state, the basic quantities characterizing a liquid are the reduced temperature ($\tilde{T}$), volume ($\tilde{V}$) and pressure ($\tilde{P}$) defined by

$$\tilde{T}=T/T^* \qquad (3a)$$

$$\tilde{V}=V/V^*=v/v^* \qquad (3b)$$

$$\tilde{P}=P/P^* \qquad (3c)$$

The asterisked quantities are constant reference parameters. V^* and v^* are sometimes called hard-core volumes. They are the molar and specific volumes, respectively, at 0 K ($V^*=Mv^*$; where M is the molecular weight of the component).

The reduced volume ($\tilde{V}$) and temperature ($\tilde{T}$) are related to the experimental value of the thermal expansion coefficient (α) through the equations:

$$\tilde{V}^{1/3}-1=\alpha T/3(1+\alpha T) \qquad (4)$$

$$\tilde{T}=T/T^*=(\tilde{V}^{1/3}-1)/\tilde{V}^{4/3} \qquad (5)$$

where

$$\alpha=(\partial \ln V/\partial T)_p \qquad (6)$$

The constant reference parameters T^*, V^* are calculated by equations (3a) and (3b). P^* can be calculated by the following equation[29]:

$$P^*=\gamma T\tilde{V}^2 \qquad (7)$$

where $\gamma=(\partial P/\partial T)_v$ is the thermal pressure coefficient.

In the case of polymers, γ can be estimated from solubility parameters (δ), which themselves are related to the cohesive energy density (CED) and hence to the strength of the internal pressure of the structural molecules[30]:

$$\gamma = \frac{\delta^2}{T} m \tag{8}$$

where m assumes a value close to 1 for polymer systems.

The critical value of χ_{12}/V_1^* beyond which phase separation occurs is given by the following expression:

$$\left[\frac{\chi_{12}}{V_1^*}\right]_{\mathrm{crit}} = \frac{1}{2}\left[\frac{1}{(V_1^*)^{1/2}} + \frac{1}{(V_2^*)^{1/2}}\right]^2 \tag{9}$$

This equation uses χ_{12} per unit core volume of the interacting molecules.

As $M \rightarrow \infty$ ($V^* = Mv^* \rightarrow \infty$), the quantity $(\chi_{12}/V_1^*)_{\mathrm{crit}}$ tends rapidly to zero, so that the total of interactional and free volume contributions must be negative to achieve miscibility.

Figure 1 shows the prediction that can be obtained by the Patterson theory for a polymeric mixture with a negative interaction parameter ($X_{12} < 0$) and finite molecular weights. Because the interaction term is negative and favourable to mixing, it balances the unfavourable free volume term and an S-shaped χ_{12}/V_1^* curve is obtained. At low temperatures the system is compatible. However, as the temperature is increased the magnitude of the favourable interactional term decreases rapidly until it can no longer outweigh the unfavourable free volume term to give a negative value of χ_{12}/V_1^*. A lower critical solution temperature (LCST) occurs at $\chi_{12}/V_1^* = (\chi_{12}/V_1^*)_{\mathrm{crit}}$ followed by incompatibility at higher temperature. In this case, the LCST is caused primarily by the interactional term becoming less negative. However, a U-shaped temperature dependence of χ_{12}/V_1^*, resulting in both an upper critical solution temperature (UCST) and an LCST, occurs in the case of a system of two polymers with a positive interaction contribution ($\chi_{12} > 0$).

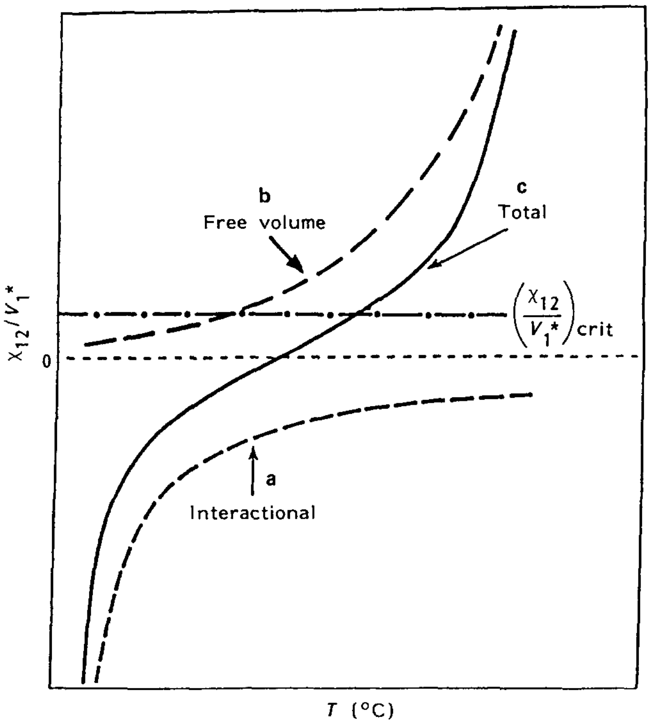

Figure 1 Schematic representation of the free volume (curve b) and interactional contributions (curve a) to the χ_{12}/V_1^* parameter (curve c) against temperature in the case of specific interactions between the blend components. The horizontal line corresponds to the critical value of χ_{12}/V_1^*

Table 2 Molecular characteristics of polymers

Polymer	Source and trade name	M_w	M_n	M_v
Poly(ethylene oxide) (PEO)	PEO2 (Fluka AG)	2.0×10^4		1.96×10^4 [a]
Atactic poly(methyl methacrylate) (At-PMMA)	BDH	1.3×10^5	5.8×10^4	1.2×10^5 [b]

[a] In water at 30°C (ref. 32): (dl/g) $= 1.25 \times 10^{-4} \bar{M}_v^{0.78}$
[b] In chloroform at 25°C (ref. 32): (dl/g) $= 5.81 \times 10^{-5} \bar{M}_v^{0.79}$

EXPERIMENTAL

Materials

The molecular characteristics together with the source and the code of the polymers used are reported in *Table 2*. Before the determination of the specific volume the At-PMMA and PEO were kept under vacuum for 24 h at 140 and 80°C respectively.

Dilatometry

For dilatometric measurements a common glass dilatometer was used. The dilatometer was placed in an oil thermostat, with a temperature control at ±0.1°C. Specific volumes were determined at intervals of about 10°C throughout the temperature range between 30 and 170°C. Four series of measurements were carried out using separate samples. A close agreement amongst the four sets of measurements resulted. The specific volumes (V) of the homopolymers were calculated using the relation:

$$V = \frac{V_b(T) - (m_{\mathrm{Hg}} - \Delta m_{\mathrm{Hg}})V_{\mathrm{Hg}}(T)}{m_p} \tag{10}$$

where m_p and m_{Hg} are the masses of the polymer and of the mercury in the dilatometer; $V_b(T)$ is the bulb volume and $(m_{\mathrm{Hg}} - \Delta m_{\mathrm{Hg}})V_{\mathrm{Hg}}(T)$ is the volume occupied by the mercury at the different temperatures below the reference mark of the cell; Δm_{Hg} is the mass of Hg in the capillary above the reference mark and $V_{\mathrm{Hg}}(T)$ is the specific volume of mercury[1,32].

In the calculation we set:

$$V_b(T) = V_b(30°\mathrm{C})[1 + \alpha\Delta T] \tag{11a}$$

$$\Delta m_{\mathrm{Hg}} = (L - L_0)S/V_{\mathrm{Hg}}(30°\mathrm{C}) \tag{11b}$$

where α is the thermal expansion coefficient of Pyrex glass[1]: ($\alpha = 9.9 \times 10^{-6}\,\mathrm{K}^{-1}$); ΔT is equal to $(T - T_0)$ where T_0 is the reference temperature ($T_0 = 30$°C); V_b(30°C) is the volume of the bulb measured at 30°C; L and L_0 are the measured heights of the mercury in the capillary at T and 30°C, respectively, and S is the section of the capillary.

RESULTS AND DISCUSSION

The parameters relating to individual components PEO and At-PMMA are presented here by the indices 1 and 2,

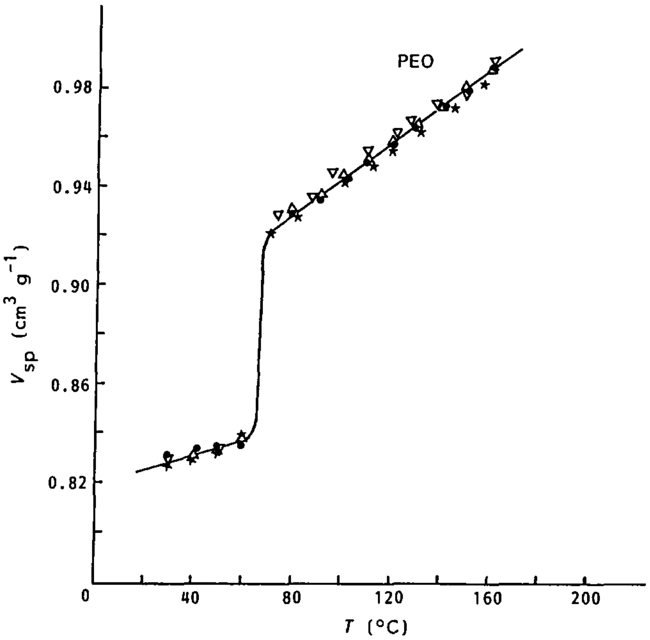

Figure 2 Specific volumes of PEO against temperature. The symbols indicate different sets of measurements

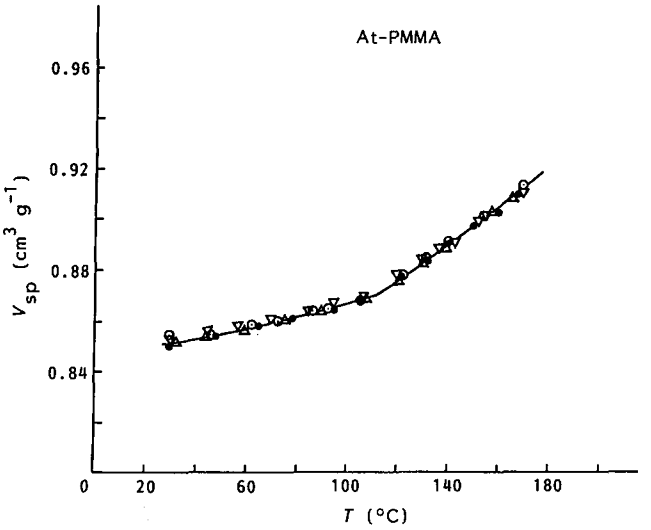

Figure 3 Specific volumes of At-PMMA against temperature. The symbols indicate different sets of measurements

respectively. Those relating to mixtures bear the index 12.

The experimental specific volumes of PEO (V_1) and At-PMMA (V_2) are presented in *Figures 2* and *3* respectively. The plot in *Figure 2* shows that the first order phase transition of PEO is about 65°C, as expected. *Figure 3* indicates that the second order transition of At-PMMA is at about 115°C.

In order to calculate the thermal expansion coefficients (α) and hence, all the parameters relative to the liquid state of the homopolymers as required by the Patterson theory, average values of specific volumes must be computed. The experimental specific volumes of PEO and At-PMMA were subjected to a multiple regression analysis. It was determined that the data were best represented by the following quadratics for PEO and At-PMMA, respectively:

$$V_{1,l}=0.87812+5.6755\times10^{-4}\,T+6.8174\times10^{-7}\,T^2 \tag{13}$$

$$V_{2,l}=0.81643+4.1374\times10^{-4}\,T+8.1194\times10^{-7}\,T^2 \tag{14}$$

Coefficients of correlation and relative average error are equal to $0.996\pm9.6\times10^{-4}$ (cm^3 g^{-1}). The letter l indicates that the value is relative to the liquid state of the homopolymers.

The expressions for the thermal expansion coefficient of PEO (α_1) and At-PMMA (α_2) obtained from equations (13) and (14) by applying equation (6) are:

$$\alpha_1=6.546\times10^{-4}+9.703\times10^{-7}\,T \tag{15}$$

$$\alpha_2=5.182\times10^{-4}+1.438\times10^{-6}\,T \tag{16}$$

The relative average error is $\pm8.0\times10^{-7}$ (°C^{-1}).

Because specific volumes may depend on polymerization condition, molecular weight and purification procedure, equations (13), (14), (15) and (16) are simply mathematical devices for accurate representation of our experimental results and have no status as fundamental equations of state.

The specific volumes (V_1), the thermal expansion coefficient (α_1), the reduced volume ($\tilde{V}_1$) and the constant reduction parameters (v_1^*, V_1^*, T_1^*, P_1^*) of PEO calculated in the range of temperature from 80 to 170°C, that is the range of temperature where the experimental specific volumes relative to the liquid state of PEO have been measured, are reported in *Table 3*. The specific volumes were calculated by equation (13). α_1 values were calculated by equation (15); the reduced volume by equation (4) and the constant reduction parameters by equations (3), (5) and (7).

The parameters relative to the liquid state of At-PMMA are shown in *Table 4*. Here the range of temperature is obviously different from that of PEO because of the presence of a T_g of At-PMMA at about 115°C. All the parameters for At-PMMA were computed in the same way as explained above for PEO.

It is noteworthy to observe in *Table 4* that there is no dependence of the constant reduction parameters of At-PMMA on temperature. However, in the case of PEO (see *Table 3*) we found a little dependence of the constant reduction parameters on the temperature. This discrepancy between theory and experiment has been reported by several researchers. For example, Flory *et al.*[20] found that the characteristic parameter v^*, T^* and P^* for polystyrene (PS) changed greatly with temperature. They attributed the variation to the unavoidable deficiency of the theory. Because our values change little with temperature we felt it justified to compute average values and use them in the Patterson theory.

The average values of the constant reduction parameters of PEO and At-PMMA are reported in *Table 5*. If we conform to the experimental results, the Patterson theory should be applied in the range of temperature of the experimental measurement of specific volumes. However, we have widened these limits from 0 to 200°C by calculating the required $\tilde{V}_1$ from 0 to 60°C and 170 to 200°C (see equation (5)) by extrapolating specific volumes of PEO using equation (13). We did not go further with the extrapolation to avoid higher uncertainties of further extrapolated values of specific volume. The only parameter still needed in order to apply equation (1) is χ_{12}.

Table 3 Specific volumes (v), thermal expansion coefficient (α), reduced volume ($\tilde{V}$) and constant reference parameters (v^*, V^*, T^*, P^*) of PEO computed in the range of temperature from 80 to 170°C

T (K)	v ($cm^3 g^{-1}$)	$\alpha \times 10^4$ (K^{-1})	$\tilde{V}$	v* ($cm^3 g^{-1}$)	V* ($cm^3 mol^{-1}$)	T* (K)	P* ($J cm^{-3}$)
353	0.928	7.324	1.220	0.761	15220	6730	534
363	0.935	7.419	1.227	0.761	15220	6750	534
373	0.942	7.516	1.235	0.762	15240	6770	532
383	0.949	7.613	1.243	0.763	15260	6800	531
393	0.956	7.710	1.251	0.764	15280	6830	529
403	0.964	7.807	1.259	0.766	15320	6870	527
413	0.971	7.904	1.267	0.767	15350	6900	525
423	0.979	8.001	1.275	0.768	15360	6940	524
433	0.987	8.098	1.283	0.769	15380	6970	523
443	0.995	8.195	1.291	0.771	15420	7010	520

Table 4 Specific volumes (v), thermal expansion coefficient (α), reduced volume ($\tilde{V}$) and constant reference parameters (v^*, V^*, T^*, P^*) of At-PMMA computed in the range of temperature 120–170°C

T (K)	v ($cm^3 g^{-1}$)	$\alpha \times 10^4$ (K^{-1})	$\tilde{V}$	v^* ($cm^3 g^{-1}$)	V^* ($cm^3 mol^{-1}$)	T^* (K)	P^* ($J cm^{-3}$)
393	0.878	6.906	1.229	0.714	92800	7270	508
403	0.884	7.050	1.238	0.714	92800	7260	508
413	0.890	7.194	1.247	0.714	92800	7260	508
423	0.897	7.338	1.256	0.714	92800	7260	508
433	0.903	7.482	1.265	0.714	92800	7260	508
443	0.910	7.625	1.274	0.714	92800	7270	508

Table 5 Characteristic parameters of PEO and At-PMMA

Polymer	v^* ($cm^3 g^{-1}$)	V^* ($cm^3 mol^{-1}$)	T^* (K)	P^* ($J cm^{-3}$)
PEO	0.765±0.003	15 300±70	6860±90	528±5
At-PMMA	0.714	92 800	7260	508

The contact energy term, X_{12}, can be calculated by determination of enthalpy of mixing[33]. However, no one has so far reported a calorimetric experiment involving the direct mixing of two polymers, although measurements of ΔH_M for oligomeric analogues have been employed[34].

In this paper we report a procedure that permits an estimated value of the X_{12} contact energy term to be computed if the χ_{12} interaction parameter has been calculated at a fixed temperature by different methods. This is possible because in the Patterson theory the X_{12} contact energy term is considered to be independent of temperature.

In order to apply this procedure we have utilized the values of the χ_{12} parameters reported in literature (see *Table 1*). The χ_{12} values from references 1, 12 and 14 were computed at 80°C; the others were computed at equilibrium melting point, i.e. very close to 80°C.

The contact energy term X_{12} (see *Table 1*) was computed by the following expression which is equation (1) worked out for X_{12}.

$$X_{12}=\chi_{12}\frac{RT_1^*}{V_1^*}\cdot\frac{(\tilde{V}_1^{1/3}-1}{\tilde{V}_1^{1/3}}-P_1^*\frac{(\tilde{V}_1^{1/3}-1)}{2(4/3-\tilde{V}_1^{1/3})}\left(1-\frac{T_1^*}{T_2^*}\right) \tag{17}$$

The contact energy term is practically constant except the value calculated from the χ_{12} interaction parameter from reference 3. This constancy is due to the small magnitude of the first term in comparison with the second term on the right hand side of equation (17).

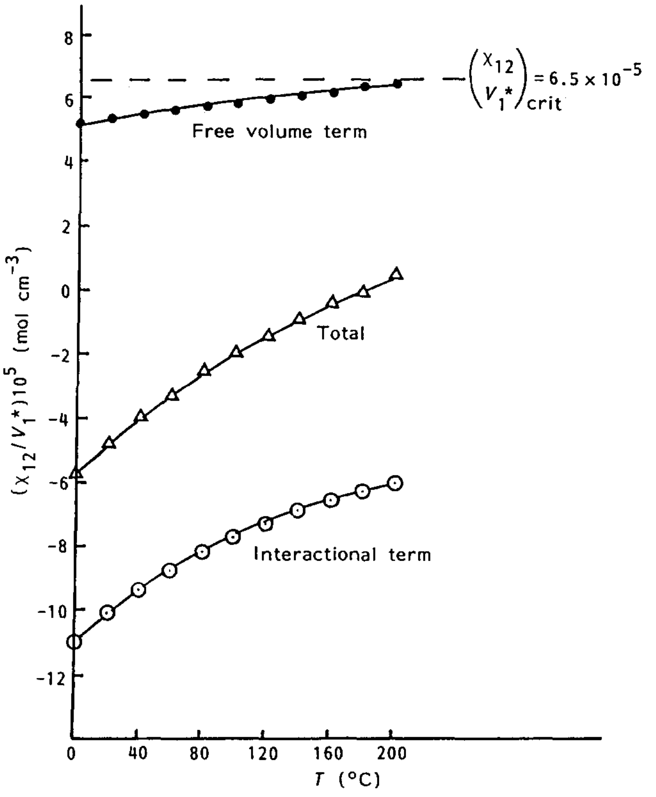

Figure 4 χ_{12}/V_1^* parameter (△), interaction term (○) and free volume term (●) as a function of temperature for the PEO/At-PMMA system. The calculation was performed setting $X_{12}=-0.3$ ($J cm^{-3}$). The horizontal line corresponds to the critical value of χ_{12}/V_1^*

From the above results we used a value of $X_{12}=-0.3$ J cm^{-3} for our calculation. This computed contact energy term is in agreement with our expectation of a small negative value representative of a very weak interaction between the two homopolymers as found experimentally[6]. In *Figure 4*, χ_{12}/V_1^*, calculated by equation (1), is plotted against the temperature. The dashed line represents the critical value of χ_{12}/V_1^* beyond which phase separation occurs. The interactional and free volume terms are also shown in this figure. The free volume term is always positive, as expected, and increases with temperature. Because the contact energy term X_{12} is negative, the interactional term is negative and favourable to mixing. It balances the unfavourable free volume term and the total χ_{12}/V_1^* curve obtained is representative of a miscible polymer–polymer system. Therefore the PEO/At-PMMA system is predicted to be miscible in the amorphous state in the range of temperature 0–200°C. Of course, as the temperature is increased the magnitude of the favourable interactional term decreases until it can no longer outweigh the unfavourable free volume term and a LCST occurs at $\chi_{12}/V_1^* = (\chi_{12}/V_1^*)_{\mathrm{crit}}$ followed by incompatibility at higher temperature. Equating equation (1) to the critical value, given by equation (9), and calculating T from equation (5), the LCST is predicted to be at about 350 ± 70°C.

Of course, we did not expect an accurate prediction of a critical solution temperature but only an indicative value due to the simplification of the theory and the inevitable uncertainties of reference parameters.

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