Thermodynamics of poly(ethylene oxide)–poly(methyl acrylate) blends: prediction of miscibility based on the Prigogine–Flory theory

E. Pedemonte* and G. Burgisi
Istituto di Chimica Industriale, Università di Genova, e Centro di Studi Chimico-Fisici di Macromolecole Sintetiche e Naturali, CNR, Corso Europa 30, 16132 Genova, Italy
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The misicibility of poly(ethylene oxide) (PEO) with poly(methyl acrylate) (PMA) is demonstrated by using the Prigogine–Flory theory in Patterson's approximation. Negative values of enthalpy of mixing, contact-energy term and interaction parameter were obtained for the blend with 75/25 weight ratio. The temperature dependence of χ_{12}/V_1^* indicates that PEO–PMA mixtures are miscible in the liquid state over the accessible temperature range.

(Keywords: poly(ethylene oxide); poly(methyl acrylate); miscibility)

INTRODUCTION

Poly(ethylene oxide) (PEO) can act as a proton acceptor and form miscible blends with proton-donating polymers[1], since it carries an excess negative charge on the oxygen atom[2]. It can be expected that poly(methyl acrylate) (PMA), which has a partial positive charge on the carbonyl carbon atom, may interact favourably with PEO and form a miscible pair: similar to the poly(methyl methacrylate)–poly(ethylene oxide) (PMMA–PEO) system[3] we can expect that the PEO–PMA system is miscible in the liquid state.

A direct proof of miscibility can be achieved by measuring the enthalpy of mixing of the two polymers, ΔH_{mix}, since it represents the crucial contribution to the free-energy change associated with the mixing process. The main purpose of this work is to evaluate ΔH_{mix} through direct measurements of enthalpies of solution of PEO, PMA and their blends in a common solvent and application of Hess's law.

The Prigogine–Flory theory[4,5], in Patterson's approximation[6,7], was used to describe quantitatively the miscibility of this polymer pair. The interaction parameter χ_{12}/V_1^* of the simplified theory was estimated from the heat-of-mixing data and from the characteristic temperature T^* of the blend.

EXPERIMENTAL

Materials

PEO and PMA were purchased from Fluka and Aldrich, respectively; their molecular weights are given in *Table 1*. Binary blends of PEO and PMA with 75/25 weight ratio (PEO–PMA 75/25) were prepared by casting from chloroform solution at room temperature. Solvent was completely removed by keeping samples under vacuum at 50°C for two days.

Table 1 Molecular characteristics of polymers

Polymer	M_w (g mol^{-1})	M_n (g mol^{-1})	M_w/M_n
PEO	24 800	13 600	1.82
PMA	30 600	17 486	1.75

Dilatometry

A glass dilatometer was used for specific-volume measurements[8,9]. The dilatometer cell was connected to a glass capillary of constant internal diameter and was placed in an oil thermostat with a temperature control of ±0.05°C. The height of mercury inside the capillary was measured by a cathetometer with a precision of ±0.005 cm.

Calorimetry

Owing to slow polymer interdiffusion and to the small heat effects associated with the formation of polymer–polymer interactions, it is impossible to measure directly the heat of mixing. A convenient approach is to follow the indirect route suggested by the following thermodynamic cycle based on Hess's law:

$$\begin{tikzcd}
\begin{array}{c}\text{PEO}+\text{PMA}\\ +\text{solvent}\end{array} \arrow[rr, "\Delta H_{\text{mix}}"] \arrow[dr, "\Delta H_1"'] & & \begin{array}{c}\text{Mixture}\\ +\text{solvent}\end{array} \arrow[dl, "\Delta H_2"] \\
& \text{Solution} &
\end{tikzcd}$$

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* To whom correspondence should be addressed

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Then ΔH_{mix} is given by

$$\Delta H_{\mathrm{mix}} = \Delta H_1 - \Delta H_2 \tag{1}$$

where ΔH_1 is the heat of solution of a mechanical mixture of small pieces of polymer films in the proper weight ratio and ΔH_2 is the heat of solution of the solvent-cast blend with the same composition.

Heat-of-solution measurements were carried out by means of a Setaram C80D calorimeter using cyclohexanone as common solvent. In order to obtain the heat of mixing of components in the liquid state, measurements were performed at 80.0±0.1°C, i.e. above the glass transition of PMA and the melting point of PEO.

RESULTS AND DISCUSSION

In the discussion here, the indices 1, 2 and 12 refer to PEO, PMA and mixture, respectively.

The specific-volume data of PEO and PMA in the liquid state were taken from the literature. According to Cimmino *et al.*[8] and Brunacci *et al.*[9], respectively:

$$V_{1,l} = 0.8781 + 5.67 \times 10^{-4} T + 6.82 \times 10^{-7} T^2 \tag{2}$$

$$V_{2,l} = 0.8363 + 5.34 \times 10^{-4} T + 3.52 \times 10^{-7} T^2 \tag{3}$$

in which V and T are in cm^3 g^{-1} and °C, respectively. We estimated that the above equations fit experimental data with an accuracy of $\pm 9.6 \times 10^{-4}$ and $\pm 2.7 \times 10^{-4}$ cm^3 g^{-1}, respectively.

Dilatometric measurements on the PEO–PMA 75/25 blend show that its specific volume in the liquid state depends on temperature according to the equation:

$$V_{12,l} = 0.8638 + 2.85 \times 10^{-4} T + 2.07 \times 10^{-6} T^2 \tag{4}$$

in which V and T are in cm^3 g^{-1} and °C, respectively. Experimental data deviate from those calculated from equation (4) by less than $\pm 2 \times 10^{-4}$ cm^3 g^{-1}.

It should be noted that the specific volume of the blend, $V_{12,l}$, is smaller than the weighted sum of $V_{1,l}$ and $V_{2,l}$, as should be expected since specific interactions are active between PEO and PMA.

The thermal expansion coefficients in the liquid state can be obtained from the above data. Their temperature dependence is:

$$\alpha_{1,l} = 6.54 \times 10^{-4} + 9.70 \times 10^{-7} T \tag{5}$$

$$\alpha_{2,l} = 6.38 \times 10^{-4} + 4.23 \times 10^{-7} T \tag{6}$$

$$\alpha_{12,l} = 6.64 \times 10^{-4} + 7.96 \times 10^{-8} T + 7.1 \times 10^{-9} T^2 \tag{7}$$

where α and T are expressed in °C^{-1} and °C, respectively.

The thermal pressure coefficients (γ) were given in previous papers[3,9,10]. In the explored temperature range, the following relations were found:

$$\gamma_{1,l} = 3.58 - 5.90 \times 10^{-3} T - 1.09 \times 10^{-6} T^2 \tag{8}$$

$$\gamma_{2,l} = 25.10 - 0.137 T + 1.96 \times 10^{-4} T^2 \tag{9}$$

where γ is in J cm^{-3} K^{-1} and T in K.

From the experimental calorimetric data, the mean value of the enthalpy of mixing was calculated as:

$$\Delta H_{\mathrm{mix}} = \Delta H_1 - \Delta H_2 = -1.9 \text{ J g}^{-1}$$

and the error on ΔH_{mix} is about ±10%.

Similarly to poly(ethylene oxide)–poly(vinyl acetate) (PEO–PVAc)[10] and PEO–PMMA[2,3] mixtures, the negative value of mixing enthalpy should be attributed to dipole–dipole interactions between the oxygen atom of the polyether and the carbonyl carbon atom of PMA.

In *Tables 2* and *3* the calculated[3] values of reduced volume ($\tilde{v}$) and characteristic parameters (v^*, V^*, T^* and P^*) at several temperatures in the range from 70 to 100°C are reported for PEO and PMA, respectively. In agreement with the behaviour of other polymers[11], it is noted that the value of characteristic parameters are slightly affected by temperature, although the theory defines them as temperature-independent; this is further discussed elsewhere[8,9]. For all calculations we have used the values of characteristic parameters measured at 80°C; the value of $\tilde{v}$ for the blend at 80°C is 1.2154, and the parameters used in the calculations are listed in *Table 4*.

Two approaches can be used to calculate the contact-energy term of the mixture. In the first one it can be obtained from T^* of the mixture using the following equation:

$$X_{12} = \frac{1}{\Theta_2 \Phi_1} \left[\Phi_1 P_1^* + \Phi_2 P_2^* - T^* \left(\frac{\Phi_1 P_1^*}{T_1^*} + \frac{\Phi_1 P_1^*}{T_2^*} \right) \right] \tag{10}$$

and a value of $X_{12} = -3.04$ J cm^{-3} is obtained. The contact-energy term can also be calculated from the equation:

$$X_{12} = \frac{\tilde{v}}{w_1 v_1^* \Theta_2} [\Delta H_{\mathrm{mix}} - w_1 v_1^* P_1^* (\tilde{v}_1^{-1} \tilde{v}^{-1}) - w_2 v_2^* P_2^* (\tilde{v}_2^{-1} - \tilde{v}^{-1})] \tag{11}$$

and $X_{12} = -14 \pm 5$ J cm^{-3} is obtained. The two values are of the same order of magnitude and seem to be in good agreement.

The negative values of X_{12} and excess volume suggest that slight densification is associated with the formation of specific interactions between the repeat units of the two polymers.

Table 2 Characteristic parameters of PEO

T (K)	$\tilde{v}$	v^* (cm^3 g^{-1})	V^* (cm^3 mol^{-1})	T^* (K)	P^* (J cm^{-3})
343	1.213	0.761	10 350	6696	726
353	1.220	0.761	10 350	6730	706
363	1.227	0.761	10 350	6730	672
373	1.235	0.762	10 363	6770	677

Table 3 Characteristic parameters of PMA

T (K)	$\tilde{v}$	v^* (cm^3 g^{-1})	V^* (cm^3 mol^{-1})	T^* (K)	P^* (J cm^{-3})
343	1.1977	0.7309	12 780	7039	607
353	1.2036	0.7322	12 803	7093	629
363	1.2095	0.7335	12 826	7147	671
373	1.2153	0.7350	12 852	7203	677

Table 4 Parameters used in calculations

Parameters	PEO	PMA
$\tilde{v}$ (cm^3 g^{-1})	0.761	0.7309
V^* (cm^3 mol^{-1})	10 350	12 803
T^* (K)	6730	7093
P^* (J cm^{-3})	706	629
Θ_2		0.23
Φ	0.76	0.24

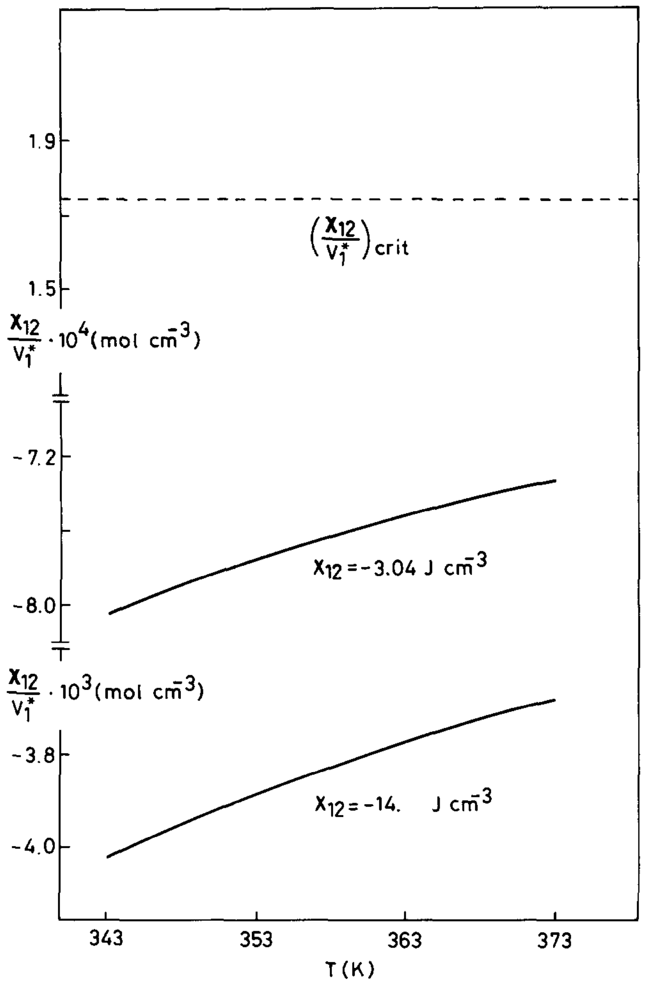

Figure 1 Total interaction parameter χ_{12}/V_1^* calculated with $X_{12}=-3.04\ \mathrm{J\ cm^3}$ and with $X_{12}=-14\pm5\ \mathrm{J\ cm^{-3}}$ as a function of temperature for blends with 75/25 weight ratio. The critical interaction parameter is represented by the horizontal broken line

The interaction parameter χ_{12}/V_1^* for the PEO–PMA 75/25 blend was calculated from 70 to 100°C using Patterson's equation[6,7]:

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

The critical value of χ_{12}/V_1^*, above which phase separation is expected, was computed from:

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

$$=1.74\times10^{-4}\ \mathrm{mol\ cm^{-3}}$$

The sign of χ_{12}/V_1^* does not change using the two different values of X_{12} in equation (12), but only the absolute value changes: this is shown in *Figure 1*, where the values of χ_{12}/V_1^* are plotted against *T*. A plot of χ_{12}/V_1^* *versus* *T* calculated with $X_{12}=-14\pm5\ \mathrm{J\ cm^{-3}}$ is shown in *Figure 2*; the interactional and free-volume contributions are also shown. The total term is under the critical condition and therefore miscibility can be predicted over the whole temperature range studied.

CONCLUSIONS

A negative enthalpy of mixing for PEO–PMA 75/25 blend has been measured. This result suggests that specific interactions are active between PEO and PMA, as previously shown for PEO–PMMA. Mixing is also associated with a volume contraction. The analysis of experimental data indicates that the interaction parameter is negative; this implies miscibility between the two polymers over the temperature range studied.

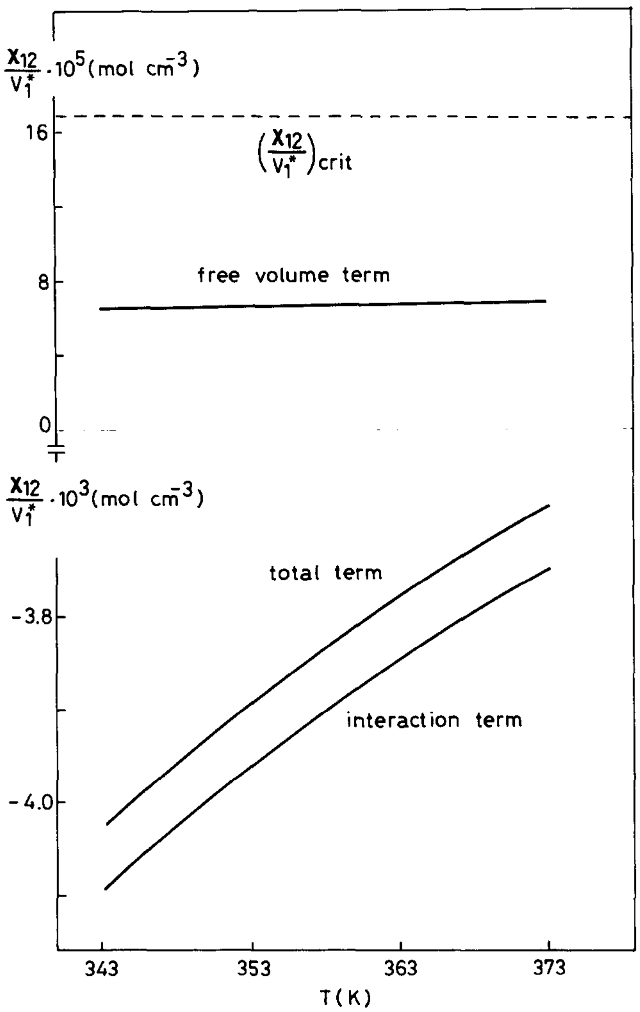

Figure 2 Total interaction parameter χ_{12}/V_1^*, interaction term and free-volume term as functions of temperature for blends with 75/25 weight ratio. The critical interaction parameter is represented by the horizontal broken line

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