BLEND FORMATION BETWEEN *HOMO*- AND *CO*-POLYMERS AT 298.15 K
PMMA-SAN blends

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Abstract

Solution heats in chloroform at 25°C have been measured experimentally for poly(methyl-methacrylate) (PMMA), samples of poly(styrene-co-acrylonitrile) (SAN) containing from 5 to 37 mass% of acrylonitrile, and some PMMA–SAN blends prepared inside the miscibility range. From these data the mixing enthalpies for blend formation were obtained. Use of the mixing heats values in the framework of the Prigogine–Flory–Patterson theory allowed to calculate values of the exchange energy parameters between the components of the blends much more negative than existing literature data. Calculation of binary interaction energy parameters between the single repeat units of the copolymer from the above data, and from model compounds, clearly indicates a strong increase of the intramolecular repulsive energy between nitrile and styrene units of SAN, as compared with the interaction between the corresponding free model molecules.

Introduction

Mixtures of poly(methylmethacrylate) (PMMA) with random poly(styrene-co-acrylonitrile) (SAN) represent one of the most studied partially miscible polymeric systems. It is in fact known that PMMA, polystyrene (PS) and poly(acrylonitrile) (PAN) are immiscible with each other, while PMMA and SAN result miscible within a specified range of compositions of the random copolymer (10–30 mass% of acrylonitrile) [1–3]. Many authors investigated this thermodynamic behaviour by using different techniques such as phase equilibrium [1–4], DSC [1, 5], spectroscopy [5, 6] and analogue calorimetry [7, 8] or predictive approaches based on Prigogine–Flory EOS [9, 10].

The energies of interaction of this system were recently investigated also by our group [11, 12] through the measurement of the excess enthalpies, H^E, of binary and ter-

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nary liquid mixtures of small molecules chosen as to simulate the repeat units of PMMA and SAN. In order to reach a more complete thermodynamic characterization of these polymeric mixtures, we deemed it useful to determine calorimetrically the mixing enthalpies for the formation of some blends inside the miscibility range of this system and thus supplement the information resulting from studies on model compounds.

In our previous work [12] a group contribution approach has been proposed based on the UNIQUAC model [13] which, with a few modifications with respect to the original model, allows to obtain an easy estimate of the mixing enthalpies of the macromolecules under study. The corresponding Gibbs energy values were evaluated through the approximate Flory–Huggins equation. The miscibility window calculated in these studies were in qualitative agreement with literature data [1–3] though slightly larger than those observed experimentally. A few tentative calculations with the UNIQUAC procedure, introducing changes of the surface areas of CH and CH_2 groups or of the coordination number z, provided interesting indications for improving the above agreement.

In the present work are reported measurements of the solution heats, $\Delta_{sol}H_i$, in chloroform of PMMA and SAN as well as of proper blends of these polymers characterized by a different acrylonitrile (AN) content in the copolymer (5–37 mass%). The heats of mixing, $\Delta_{mix}H$, associated with the formation of the amorphous polymeric blends starting from the single components were then calculated from the above solution heats through a simple thermodynamic cycle.

Calculation of the heats of mixing through methods which utilize the enthalpic behaviour of proper model compounds yielded negative $\Delta_{mix}H$ values much smaller in magnitude than the experimental ones. These differences can be reasonably attributed to the different interactions between the free molecules (model compounds) as compared with the repeat units constrained in the macromolecular chain. A quantitative justification of these differences is afforded by comparing values of binary interaction parameters calculated through the Prigogine–Flory EOS, applied both to solution and to mixing heats, with the analogous parameters calculated from model compounds.

Experimental

Solution heats

The calorimetric apparatus was a Calvet-type SETARAM mod. BT 200 calorimeter, modified and improved as already described [12]. A special cell was constructed for the dissolution of the polymers, equipped with a stirrer driven by a stepping motor capable of reproducible stirring rates in the range 20 to 80 rpm. In a single run from 20 to 200 mg of solid sample, powder or small thin layers, are introduced into a stainless steel (type 316) cylinder, integral with the stirrer. The cell volume is 8 cm^3 and was filled with solvent so as to minimize the vapor space. The cell was sealed by a PTFE cap which allows the external connection with the stirring device and with the cell-opening device, while preventing the evaporation of the solvent.

After recording a steady base line of the calorimetric signal under stirring, the cell is opened by applying a small pressure via a thin rigid steel wire. The working stirring rate was always 20 or 40 rpm. The fair solubility in $CHCl_3$ of the polymers, except for PAN which is insoluble, allowed to run experiments lasting at most 45 min. In any case, the complete dissolution of the sample was checked at the end of each run. Experimental heats were calculated from the surface areas of the curves, using a proportionality constant determined separately through a standard electrical calibration. Calibration of the instrument was periodically performed using the 1003.1 Ω calibration cell supplied by the manufacturer, applying an electrical current in the range 1–3.2 mA generated by a constant current feeder. Calibration times, never shorter than 300 s, were measured manually with a 0.1 s resolution chronometer.

The performance of the apparatus was checked by determining the heats of solution of KCl in water [14], resulting in an overall reproducibility of ± 0.05 J mol^{-1} and an accuracy better than 2%.

Materials

Poly(methylmethacrylate) (PMMA) was an atactic Aldrich product, and was used without further purification. Polystyrene (PS) was prepared in our laboratory via cationic polymerization. The product, characterized by a viscosimetric molecular mass $M_\eta =$ $2.5 \cdot 10^5$ and a glass transition temperature $T_g = 102°C$, was used with no further treatment.

Table 1 Physical properties of the polymers

Polymer	AN content/ mass% (mol%)	M_w	M_w/M_n	$T_g{}^a/°C$	$\Delta c_p{}^b/$ J g^{-1}K^{-1}
PMMA	–	120 000	–	104.0	0.34
PS	–	250 000	–	102.0	0.30
SAN5	4.5 (8.5)	153 800	1.62	106.6	0.31
SAN11	10.5 (18.7)	161 600	1.66	109.1	0.34
SAN16	15.6 (26.6)	142 700	1.65	109.8	0.38
SAN19	19.4 (32.1)	132 400	1.70	111.7	0.40
SAN25	25.0 (39.8)	78 600	1.64	112.7	0.41
SAN30	29.9 (45.6)	99 900	1.80	113.0	0.41
SAN34	33.8 (50.1)	78 400	1.68	113.1	0.40
SAN37	36.9 (53.4)	90 300	1.78	113.2	0.40

[a]Determined at midpoint of the transition
[b]$\Delta c_p = (c_{p,l} - c_{p,gl})$. Values determined at T_g by DSC, with uncertainties within 3%

Samples of poly(styrene-co-acrylonitrile) (SAN) were supplied by ENICHEM (Mantova, Italy). All samples were purified via double precipitation from THF solutions with ethanol/THF mixtures (90 vol% ethanol). The filtered product was dried in oven under vacuum for a few days at 80°C, and finally for 48 h at 140°C. The

acrylonitrile (AN) content, checked through elemental analysis, never differed substantially from that declared by the manufacturer. The characteristics of all products are reported in Table 1. Glass transition temperatures, T_g, were determined by DSC analysis with a Perkin Elmer DSC-2 apparatus interfaced to a PC for the recording and elaboration of DSC curves. The explored temperature range was 50–150°C and the gradient 20 K min^{-1}.

Table 2 Glass transition temperatures, T_g, and heat capacity changes, Δc_p, for the examined PMMA–SAN blends

Blend	SAN/mass%	T_g/°C	$\Delta c_p{}^a$/J g^{-1} K^{-1}
PMMA/SAN11	49.8	106.5	0.34
PMMA/SAN11	50.1	106.9	0.36
PMMA/SAN19	38.0	107.0	0.36
PMMA/SAN19	49.9	107.8	0.37
PMMA/SAN19	74.7	109.7	0.38
PMMA/SAN25	53.7	108.7	0.38

$^a\Delta c_p=(c_{p,1}-c_{p,g1})$. Values determined at T_g by DSC, with uncertainties within 3%

The blends PMMA/SAN were prepared by dissolving in CHCl$_3$ proper quantities of the components up to a total 10 mass% content and kept under stirring for a few days. The solutions were then allowed to slowly evaporate under a pressure near to the solvent vapor pressure. The films thus obtained were dried in oven under vacuum for 24 h at 80°C and finally subjected to compression moulding for 2 min at 200°C. Blend formation could not be followed via DSC owing to the small difference of the glass transitions of PMMA and SAN ($T_{g,PMMA}$=104°C; $T_{g,SAN}$=106–112°C). Obtainment of perfectly transparent compact films was considered sufficient condition for the formation of a homogeneous single phase between the two polymers. The physical properties of the blends are listed in Table 2.

Theoretical background

The Prigogine–Flory–Patterson procedure

This treatment results from the Flory's extension to macromolecular systems [15] of the corresponding states equation devised by Prigogine [16] for pure fluids. The equation is:

$$\frac{\widetilde{P}\widetilde{V}}{\widetilde{T}}=\frac{\widetilde{V}^{1/3}}{\widetilde{V}^{1/3}-1}-\frac{1}{\widetilde{T}\widetilde{V}} \tag{1}$$

where $\widetilde{P}$, $\widetilde{V}$ and $\widetilde{T}$ are reduced variables defined by the ratios $\widetilde{P}=P/P^*$, $\widetilde{T}=T/T^*$ and $\widetilde{V}=V/V^*$, in which P^* T^* and V^* are the so-called characteristic variables. The vol-

ume V^* is the hard-core volume, i.e. the minimum volume occupied by the fluid, calculated as

$$\tilde{V} = \left(\frac{3+4\alpha T}{3+3\alpha T} \right)^3 \qquad (2)$$

where $\alpha = 1/V(\partial V / \partial T)_P$ is the isobaric coefficient for thermal expansion.

Other reduced variables $\tilde{T}$ and $\tilde{P}$ can be calculated from $\tilde{V}$ through the following relationships:

$$P^* = \gamma T \tilde{V}^2; \quad \tilde{T} = \frac{\tilde{V}^{1/3} - 1}{\tilde{V}^{4/3}} \qquad (3)$$

being $\gamma = (\partial P / \partial T)_v$.

Equation (1), substantially valid for pure compounds, has been extended by McMaster [17] to fluid mixtures and made applicable through some simplifications introduced by Patterson [18]. The simplifications are basically the following:

1) hard-core volumes are considered additive

2) intermolecular energies are expressed as simple functions of the contact surface areas between molecular segments and the solvent molecules.

In the case of mixtures the parameters P^* and T^* are calculated as

$$P^* = P_1^* \Phi_1^* + P_2^* \Phi_2^* - \Phi_1^* \vartheta_2 X_{12} \qquad (4)$$

$$T^* = \frac{P^*}{(P_1^*/T_1^*)\Phi_1^* + (P_2^*/T_2^*)\Phi_2^*} \qquad (5)$$

The quantities Φ_i and ϑ_i are the segment and surface fractions, respectively, of component i. Φ_i are expressed as:

$$\Phi_2^* = \frac{m_2 v_{sp_2}^*}{m_1 v_{sp_1}^* + m_2 v_{sp_2}^*} \qquad \Phi_1^* = 1 - \Phi_2^* \qquad (6)$$

where m_1 and m_2 are the masses of component 1 and 2 and v_{sp}^* the specific characteristic volume. The surface fraction ϑ_i is obtained by the relationship:

$$\vartheta_2 = 1 - \vartheta_1 = \frac{(s_2/s_1)\Phi_2^*}{\Phi_1^* + (s_2/s_1)\Phi_2^*} \qquad (7)$$

where the contact surfaces of the two components, s_1 and s_2, can be estimated through Bondi's atomic radii [19]. Parameter X_{12} of Eq. (4) has the dimensions of an energy per unit volume, and represents the density of interaction energy between components 1 and 2, even when the latter are repeat units of a random copolymer.

By following the statistical thermodynamic treatment proposed by Patterson [18] the mixing enthalpy per unit mass $\Delta_{mix}H_{AB}$ for a mixture of a homopolymer A,

made up by type 1 units, and a copolymer B, made up by type 2 and 3 units, can be expressed as:

$$\Delta_{mix}H_{AB}=v^{*}_{sp}\left[\Phi_A P^{*}_A\left(\frac{1}{\widetilde{V}_A}-\frac{1}{\widetilde{V}}\right)+\Phi_B P^{*}_B\left(\frac{1}{\widetilde{V}_B}-\frac{1}{\widetilde{V}}\right)+\frac{\Phi_A \vartheta_B}{\widetilde{V}}X_{AB}\right] \qquad (8)$$

where X_{AB} is the interaction energy density parameter of the two species A and B.

The parameter X_{AB} can be finally expressed as a function of the analogous quantities X_{12}, X_{13} and X_{23}, relative to the interactions between the repeat units 1, 2 and 3, through the following expression proposed by Shiomi and Imai [20] and by Jo and Lee [21]:

$$X_{AB}=\vartheta^{(2)}_B X_{12}+\vartheta^{(3)}_B X_{13}-\chi X_{23} \qquad (9)$$

with
$$\chi=\frac{S_A}{S_B}\Phi^{(2)}_B \vartheta^{(3)}_B$$

where A and B are the main components and indexes 1, 2 and 3 refer, in our case, to the methylmethacrylate (MMA), styrene (S) and acrylonitrile (AN) units, respectively.

Group contributions through the modified UNIQUAC method

The procedure aims at providing a simple and sufficiently reliable prediction of the mixing enthalpy $\Delta_{mix}H$ of macromolecules. The latter is expressed as a function of the composition of the mixture, of the surface areas (Q_i) and the mutual energy interactions parameters (δ_{ij}) of all the groups which allow to build up the macromolecular structures. Values of group contributions, δ_{ij}, are calculated from a least square analysis of the mixing enthalpies of proper model compounds. The methodology is based on the UNIQUAC model [13] and was described in detail in a previous paper [12].

The procedure has been here applied to the (PMMA+SAN) system utilizing group contributions values reported in Table 4 of ref. [12]. A few values of the conventional surface areas, Q_i, have been modified with respect to the values reported in the known UNIFAC tables [22] in order to obtain a better agreement with experimental mixing heats of the binary model systems utilized to derive group contributions.

Results

Table 3 reports values of the solution heats in chloroform, $\Delta_{sol}H_i$, of PMMA, PS, and of SAN copolymers characterized by different acrylonitrile (AN) content.

Values of the solution heats, $\Delta_{sol}H_{AB}$, measured for the blends PMMA/SAN are instead reported in Table 4. The miscibility window reported in the literature by different authors [1–3] ranges approximately from 10 to 37% of AN mass content in SAN. All the blends are characterized by a SAN mass fraction, w_2, of about 50%. Only in the case of sample SAN19 have been examined also mixtures with w_2=0.380 and w_2=0.747.

Table 3 Solution enthalpies, $\Delta_{sol}H_i$, of polymers at 25°C[a]

Polymer	AN mass% in SAN	$-\Delta_{sol}H_i$/J g^{-1}
PMMA	–	73.2±0.7
PS	–	25.6±0.8
SAN5	4.5	50.3±0.5
SAN11	10.5	58.7±0.8
SAN16	15.6	61.8±0.4
SAN19	19.4	67.4±0.6
SAN25	25.0	68.1±0.9
SAN30	29.9	66.8±1.3
SAN34	33.8	73.4±0.5
SAN37	36.9	71.8±0.7

[a]The concentrations (mass fraction) ranged from 0.005 to 0.02. Enthalpy values are averages of at least five runs

The heats of formation of the blends, $\Delta_{mix}H_{AB}$, were obtained by proper combination of the solution heats of the polymers PMMA (A) and SAN (B), and of the corresponding blends, according to:

$$\Delta_{mix}H_{AB} = w_A \, \Delta_{sol}H_A + w_B \, \Delta_{sol}H_B - \Delta_{sol}H_{AB} \qquad (10)$$

where w_A and w_B are the mass fractions of A and B in the blend. A few measurements of the solution heats of some mechanical mixtures of these species yielded values equal to the sum of the weighted solution heats of the single polymers.

However, all polymers are characterized by a glass transition temperature T_g much higher than the working temperature (T_0=25°C). Therefore, the solution heats of the compounds in the glassy state were transformed into the corresponding heats of solution of the liquid compounds through the relationship:

$$\Delta_{sol}H_{i,l} = \Delta_{sol}H_{i,gl} + \Delta c_{p,i} \, (T_{g,i} - T_0) \qquad (11)$$

and consequently the mixing enthalpies of the liquid A and B species are given by:

$$\Delta_{mix}H_{AB,l} = \Delta_{mix}H_{AB} + [w_A \, \Delta c_{p,A} \, (T_{g,A} - T_0) + \\ + w_B \, \Delta c_{p,B} \, (T_{g,B} - T_0) - \Delta c_{p,AB} \, (T_{g,AB} - T_0)] \qquad (12)$$

where $\Delta c_{p,i}$ are the specific heat differences of the various i species, between the liquid and the glassy state at the T_g temperature. Values of the quantities $\Delta c_{p,i}$ have been determined by DSC for all the compounds and the blends here considered and are reported in Tables 1 and 2, respectively.

When the solution experiments are performed at temperatures much lower than the glass transition, and the T_g value of the various polymers cover a large temperature range, the correction term within square brackets of Eq. (12) may reach large values. Moreover, as it is not easy to determine precise c_p values for both the glassy and the liquid state, this

correction may lead to large uncertainties of the values of $\Delta_{mix}H_{AB}$. Fortunately, in the present case the T_g temperatures are confined within a very small range and values of $\Delta c_{p,i}$ of the blends are not far different from those of the single constituents. Therefore, this correction does not critically influence the $\Delta_{mix}H_{AB}$ values.

The solution heats in chloroform of various SAN copolymers, corrected according to Eq. (11), are represented in Fig. 1. They show a rather clear linear dependence on the acrylonitrile content of the copolymer, with increasingly negative values down to $\Delta_{sol}H = -37$ J g^{-1} for a SAN sample containing 37 mass% of AN. The figure also shows, for comparison, $\Delta_{sol}H_{AB}$ values for some blends, together with the corresponding mechanical mixtures with the same composition.
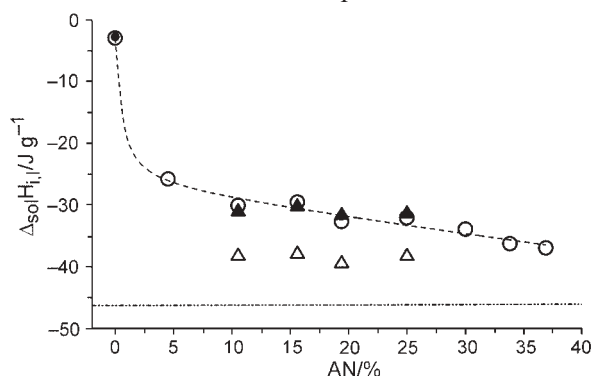

Fig. 1 Heats of solution, $\Delta_{sol}H_i$, of polymers and blends as a function of AN content (mass%) in SAN copolymers: ⊙ – SAN; ○ – polystyrene; ▲ – PMMA–SAN blends 50 mass%; △ – PMMA+SAN mechanical mixtures; – · – · – – PMMA

Values of the heats for blend formation, $\Delta_{mix}H_{AB}$, calculated for the glassy state (Eq. (10)) and for the liquid state (Eq. (12)) are reported in Table 4. These data may be assigned an uncertainty generally lower than 15%, which should not surprise if one takes into account that these are small numbers resulting from the algebraic sum of Eq. (10).

Table 4 Solution enthalpies in CHCl$_3$, $\Delta_{sol}H_{AB}$, and mixing enthalpies, $\Delta_{mix}H_{AB}$, of some PMMA–SAN blends at 25°C[a]

Blend	SAN/ mass%	SAN/ mol%	$-\Delta_{sol}H_{AB}$/ J g^{-1}	$-\Delta_{mix}H_{AB,gl}$[b]/ J g^{-1}	$-\Delta_{mix}H_{AB,l}$[b]/ J g^{-1}
PMMA/SAN11	49.8	51.2	58.8±0.3	7.2	7.2
PMMA/SAN16	50.1	52.6	59.8±0.7	7.7	7.6
PMMA/SAN19	38.0	77.1	63.7±0.5	7.3	7.0
PMMA/SAN19	49.9	53.1	62.4±0.6	7.9	7.8
PMMA/SAN19	74.7	41.2	62.3±0.8	6.6	6.1
PMMA/SAN25	53.7	58.8	63.4±1.1	7.8	7.9

[a]Enthalpy values are averages of at least three runs. Errors are given as standard deviation
[b]*gl*=glassy state; *l*=liquid state

$\Delta_{mix}H_{AB}$ values were utilized in Eq. (8) in order to calculate the exchange energy parameter X_{AB}. Characteristic data of single compounds necessary for the application of Eq. (8) are reported in Table 5. In Table 6 are listed the analogous data for the polymeric blends, together with values of X_{AB}. Values of the latter parameter are plotted in Fig. 2 as a function of χ (Eq. (9)).

The linear trend of the function $X_{AB}= f(\chi)$ (Fig. 2) over the range investigated suggests to identify the slope of this function with X_{23}, thus allowing to calculate the energy interaction parameter of S and AN in the copolymer as $X_{AN-S}=180$ J cm^{-3} (procedure (I)).

Table 5 Characteristic properties of the compounds used in the application of Prigogine–Flory EOS[a]

Compound	v_{sp}^*/cm^3 g^{-1}	P^*/bar	T^*/K	v_{sp}/cm^3 g^{-1}	$s \cdot 10^{-9}$/ cm^2 mol^{-1}
PMMA	0.724	5885	7926	0.954	7.790
PS	0.838	5150	8450	0.955	7.250
PAN	0.761	7200	11080	0.855	4.110
SAN5	0.835	5228	8555	0.951	6.984
SAN11	0.830	5250	8696	0.945	6.662
SAN16	0.826	5425	8817	0.940	6.413
SAN19	0.823	5493	8907	0.937	6.241
SAN25	0.819	5596	9043	0.931	6.007
SAN30	0.815	5687	9162	0.927	5.818
SAN34	0.812	5761	9258	0.923	5.677
SAN37	0.810	5820	9335	0.920	5.571
Chloroform[b]	0.495	6559	3549	0.644	6.030
Toluene[b]	0.918	5795	3970	1.160	7.450
Acetonitrile[b]	0.977	6574	3398	1.287	4.310
Methyl i-butyrate[c]	0.901	5965	4184	1.130	9.130

[a]Except otherwise indicated, all data were obtained from [9]
[b]All characteristic properties were calculated using data of isobaric thermal expansivity, isothermal compressibility and density taken from [23]
[c]The value of v^* has been obtained from thermal expansivity, $\alpha=10.39$ K^{-1}, estimated using the Peng–Robinson EOS. Value of the pressure P^* has been evaluated from $\gamma=1.3\ \delta^2/T$ (Eq. (3)) following a procedure indicated by Voeks [24]

For the sake of comparison the binary interaction parameters X_{ij} have been also calculated using, instead of the experimental data of $\Delta_{mix}H_{AB}$, the corresponding values calculated through the UNIQUAC group contribution method described above. In this procedure (II) we utilized all SAN samples of Table 5, in view of the fact that the UNIQUAC method yielded negative $\Delta_{mix}H_{AB}$ values for all SAN samples here examined [12]. In a further procedure (III) the X_{ij} values were derived from excess heat enthalpies of the binary mixtures of proper model compounds: methyl i-butyrate for

Table 6 Characteristic quantities of the blends used in the application of Prigogine–Flory procedure and values of the binary interaction parameter $X_{\text{PMMA–SAN}}$ (Eq. (8))

Blend[a]/A/B	v_{sp}^{*}/cm^3 g^{-1}	ϕ_A	ϑ_A	$\widetilde{V}$[b]	$\widetilde{V}_B$[c]	χ	X_{AB}/J cm^{-3}
PMMA/SAN11 (49.8)	0.7768	0.4679	0.5069	1.2224	1.1385	0.0602	−51.7
PMMA/SAN16 (50.1)	0.7751	0.4661	0.5147	1.2218	1.1380	0.0904	−59.1
PMMA/SAN19 (38.0)	0.7616	0.5894	0.6417	1.2441	1.1385	0.1129	−61.1
PMMA/SAN19 (49.9)	0.7734	0.4690	0.5243	1.2225	1.1385	0.1129	−62.3
PMMA/SAN19 (74.7)	0.7979	0.2295	0.2710	1.1796	1.1385	0.1129	−60.3
PMMA/SAN25 (53.7)	0.7750	0.4325	0.4971	1.2150	1.1367	0.1458	−67.7

[a]Within parentheses is indicated the SAN mass percent.
[b]Calculated under the hypothesis of excess volume V^E=0
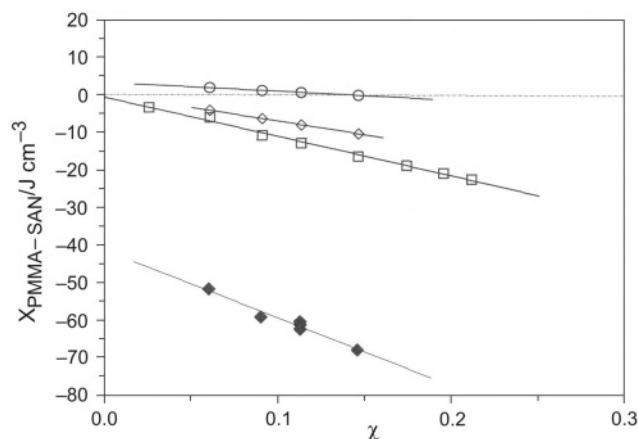[c]Reduced volume of component A is a constant value $\widetilde{V}_A$=1.3177

Fig. 2 Trend of $X_{PMMA-SAN}$ parameter, calculated through various procedures, as a function of the variable χ (Eq. (9)); ◆ – from Eq. (8) using experimental $\Delta_{mix}H_{AB}$ values for all the blends examined; □ – from Eq. (8) and $\Delta_{mix}H_{AB}$ from UNIQUAC group contribution procedure, using all SAN copolymers and blends with 50 mass% of PMMA; ◇ – from Eq. (9) using specific parameters X_{MMA-S}, X_{MMA-AN} and X_{AN-S} obtained from excess enthalpies of the model compounds (only blends with 50 mass% of PMMA); ○ – calculated from Eq. (9) using the specific parameters X_{MMA-S}, X_{MMA-AN} and X_{AN-S} reported by Shimomai et al. [9] (only blends with 50 mass% of PMMA)

PMMA, acetonitrile and toluene for the nitrile and styrene repeat units of SAN. Values of these interaction parameters can be compared with existing literature data (IV), calculated by Shimomai et al. [9] from binodal curves of phase diagrams following a procedure suggested by Shiomi and Imai [20] and Jo and Lee [21]. Values of the X_{ij} parameters calculated through all these procedures are summarized in Table 7.

Discussion

Computation of the interaction parameters has been carried out by using Prigogine–Flory EOS via Eqs (8) and (9) with the experimental heats of mixing $\Delta_{mix}H_{AB}$. The overall interaction parameter $X_{PMMA-SAN}$ and the intermolecular, X_{MMA-AN} and X_{MMA-S}, and intramolecular X_{AN-S} parameters, relative to pair interactions between the several groups on the macromolecular chains, measure the intensity of the attractive or repulsive interactions between the components. A correction from the glassy to the liquid state (Eq. (12)) is necessary for a proper application of the above equation of state, but fortunately introduces in our case a small uncertainty. However, this uncertainty might slightly affect the trend of the function expressed by Eq. (9).

The values of parameter $X_{PMMA-SAN}$ obtained through this procedure (I) are reported in Table 6. Large negative values are observed for all the blends, as it would be expected for compositions lying inside the miscibility window. The different trends of this parameter as a function of χ (Eq. (9)), calculated through the procedures I–IV,

are represented in Fig. 2. Both the actual values of $X_{PMMA-SAN}$ and the slopes of the function, calculated using experimental $\Delta_{mix}H_{AB}$ data, result noticeably more negative than in case they are obtained through indirect procedures (phase diagrams, model compounds, group contributions).

A general picture of the parameters representing the single interactions MMA–S, MMA–AN and AN–S is reported in Table 7. Values of X_{AN-S} and X_{MMA-AN} are positive, while those of X_{MMA-S} are near zero. Clear differences are observed between values calculated in this work through calorimetric data and literature values obtained from phase diagrams. In particular, our data of the AN–S parameter, which measures intramolecular interaction energies between the styrene and nitrile units of the copolymer, are much larger than Shimomai's value, and exhibit an increasing trend when going from the model system towards the real system.

Table 7 Comparison between values of the Prigogine–Flory–Patterson interaction parameters X_{ij} calculated by different procedures

	Reference system	Thermodynamic data	$X_{MMA-S}/$ J cm^{-3}	$X_{MMA-AN}/$ J cm^{-3}	$X_{AN-S}/$ J cm^{-3}
I	Real blends	calorimetric $\Delta_{mix}H$	–	–	180
II	Real polymers	UNIQUAC $\Delta_{mix}H$	~0	26	132
III	Model compounds	H^E	~0[a]	11[b]	83[c]
IV	Real blends[d]	phase equilibria	3.4	24.9	45.1
V	SAN+CHCl$_3$	$\Delta_{sol}H$	–	'–'	40

[a]from mixtures (methyl-*i*-butyrate+toluene)
[b]from mixtures (methyl-*i*-butyrate+acetonitrile)
[c]from mixtures (toluene+acetonitrile)
[d][9]

In our opinion it is important to put attention on the comparison between the real systems and the model compounds, rather than attributing soundness to the single values. Data of Table 7 put in evidence how values of parameters X_{AN-S}, X_{MMA-S} and X_{MMA-AN} change as a function of the reference system and of the calculation procedure. The value of X_{AN-S}, which refers to the repulsive intramolecular interaction inside the copolymer, is largest when calculated from the calorimetric heat of mixing of the real blends and results 1.5 times the value obtained from group contributions and more than twice that obtained from the binary model (acetonitrile+toluene).

The above picture certainly provides a valid contribution to the understanding of macromolecular interactions, in that it puts in evidence unequivocally the increase of the repulsion between the different repeat units mutually linked in the copolymer as compared with the same interactions exerted between model molecules.

Calorimetric data for the solution of polymers in chloroform, when treated according to an equation analogous to Eq. (8) but valid for infinite dilution [25], also lead to some interesting results. In fact the solution heats of the SAN copolymers give a value of the energy density parameter, X_{AN-S}, which is similar to that obtained from

excess enthalpies of the model system (acetonitrile+toluene). This fact appears consistent with the assumption that pendant group of the macromolecule, surrounded by a large excess of solvent, exhibit a thermodynamic behaviour substantially similar to that of the model molecules, though being not as accessible to the solvent as are the free molecules. The above value results to be also very similar to that obtained by Shimomai *et al*. [9].

The trends above observed for X_{ij} parameters might suggest a criterion for correcting the UNIQUAC group contributions, strictly valid for small molecules, in order to let them better describe the mixing enthalpies of macromolecules.

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