S0032-3861(96)00453-3

Polymer Vol. 37 No. 26, pp. 5877–5882, 1996

Studies on miscibility in homopolymer/ random copolymer blends by equation of state theory

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(Received 4 December 1995; revised 19 February 1996)

The miscibility of poly(methyl methacrylate) (PMMA) and styrene-acrylonitrile random copolymers (SAN) blends was investigated on the basis of the Flory–Orwoll–Vrij equation of state theory. To obtain the equation of state parameters (P^*, V^*_{sp}, T^*: characteristic parameters), the pressure–volume–temperature (PVT) behaviour was measured for PMMA and a series of SANs with various acrylonitrile contents. The exchange energy parameter X_{ij} was also calculated by fitting the theory to some phase diagrams of PMMA/SAN blends. The Flory–Huggins interaction parameter χ was separated into two contributions based on the equation of state theory for mixtures: the exchange energy term χ_{inter} and the free volume term χ_{free}. Both the temperature and copolymer composition dependences of χ_{inter} and χ_{free} were estimated by calculations using the equation of state parameters. There exists a region in which χ_{inter} is negative, leading to a miscibility window in PMMA/SAN blends. However, the immiscibility at high temperatures in the blends cannot be explained only by χ_{inter}; it is caused by the free volume contribution, χ_{free}. The miscibility window behaviour in PMMA/SAN blends may be explained within the framework of the equation of state theory. Copyright © 1996 Elsevier Science Ltd.

(Keywords: miscibility window; equation of state; interaction parameter)

INTRODUCTION

For the last decade, extensive study of the miscibility window behaviour of blends containing random copolymers has been carried out. A homopolymer might form a miscible blend with random copolymer in a certain copolymer composition and temperature range, when there is a strong unfavourable interaction between comonomer units of copolymer, although all segmental interactions are positive.

The miscibility window behaviour has been reported for blends of poly(methyl methacrylate) (PMMA) and styrene-acrylonitrile random copolymers (SAN)[1]. In a previous paper we reported the temperature dependence of all three segmental (Flory–Huggins) interaction parameters, $\chi_{\text{S/MMA}}(T)$, $\chi_{\text{MMA/AN}}(T)$ and $\chi_{\text{S/AN}}(T)$, calculated from interfacial thickness data[2,3]. It was indicated that the phase behaviour of PMMA/SAN blends could be explained by a simple mean-field model considering the difference of the temperature dependence in $\chi_{ij}(T)$[4]. There is a possibility of LCST (lower critical solution temperature) behaviour, which is not driven by the free volume contribution.

Generally, LCST behaviour is explained by the free volume effect based on the equation of state (EOS) theories of polymers. From these theories χ can be separated into two contributions; an interactional term χ_{inter} and a free volume term χ_{free}, χ_{inter} corresponds to the exchange energy term of van Laar-type and χ_{free} reflects the difference of the free volumes or thermal expansions between components. Shiomi *et al.*[5] investigated the respective contributions of these terms to the miscibility in homopolymer/copolymer blends in detail by simulation based on Flory's equation of state theory. They indicated that the contribution of χ_{inter} was more important for the miscibility window behaviour but the LCST behaviour was driven by χ_{free}.

In this paper the miscibility in PMMA/SAN blends is investigated by separating χ into the two contributions on the basis of Flory–Orwoll–Vrij (FOV) theory[6]. Using the equation of state parameters determined from pressure–volume–temperature (PVT) measurements and the exchange energy parameters X_{ij} calculated from phase diagrams, the phase behaviour of PMMA/SAN blends is discussed from the viewpoint of thermodynamics.

THEORETICAL BACKGROUND

Here we employ the equation of state theory of Flory,

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Orwoll, and Vrij (FOV)[6]. EOS is given by

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

where $\tilde{P} = P/P^*$, $\tilde{V} = V_{\mathrm{SP}}/V^*_{\mathrm{SP}}$ and $\tilde{T} = T/T^*$ are reduced pressure, volume (V_{SP}: specific volume) and temperature, respectively. The quantities with asterisks are the characteristic or hard-core parameters which can be obtained from *PVT* measurements.

For a mixture of polymers A and B, the theory can be also applied and it is assumed that the hard-core mer volumes are equal for both components, $v^* = v^*_A - v^*_B$. The corresponding expression for the Gibbs free energy of mixing is given by[7,8]

$$\begin{aligned}\frac{\Delta G^M}{kT} = {} & N_{\mathrm{A}} \ln \phi_{\mathrm{A}} + N_{\mathrm{B}} \ln \phi_{\mathrm{B}} \\ & + \frac{rNv^*}{kT}\left[\phi_{\mathrm{A}} P^*_{\mathrm{A}}\left(\frac{1}{\tilde{V}_{\mathrm{A}}} - \frac{1}{\tilde{V}}\right) + \phi_{\mathrm{B}} P^*_{\mathrm{B}}\left(\frac{1}{\tilde{V}_{\mathrm{B}}} - \frac{1}{\tilde{V}}\right)\right. \\ & + 3\phi_{\mathrm{A}} P^*_{\mathrm{A}} \tilde{T}_{\mathrm{A}} \ln \frac{\tilde{V}_{\mathrm{A}}^{1/3} - 1}{\tilde{V}^{1/3} - 1} \\ & \left. + 3\phi_{\mathrm{B}} P^*_{\mathrm{B}} \tilde{T}_{\mathrm{B}} \ln \frac{\tilde{V}_{\mathrm{B}}^{1/3} - 1}{\tilde{V}^{1/3} - 1} + \frac{\phi_{\mathrm{A}} \theta_{\mathrm{B}} X_{\mathrm{AB}}}{\tilde{V}}\right]\end{aligned} \tag{2}$$

where the first two terms in equation (2) represent the combinatorial entropy of mixing and N is the total number of polymer chains given by $N = N_{\mathrm{A}} + N_{\mathrm{B}}$. The total number of segments r is given by $r = x_{\mathrm{A}} r_{\mathrm{A}} + x_{\mathrm{B}} r_{\mathrm{B}}$ with $x_{\mathrm{A}} = N_{\mathrm{A}}/N = 1 - x_{\mathrm{B}}$. Furthermore, the following relations are used

$$V^* = r_{\mathrm{A}} N_{\mathrm{A}} v^*_{\mathrm{A}} + r_{\mathrm{B}} N_{\mathrm{B}} v^*_{\mathrm{B}} = rNv^* \tag{3}$$

$$\theta_{\mathrm{A}} = s_{\mathrm{A}} r_{\mathrm{A}} N_{\mathrm{A}}/(srN) = 1 - \phi_{\mathrm{B}} \tag{4}$$

$$s = \phi_{\mathrm{A}} s_{\mathrm{A}} + \phi_{\mathrm{B}} s_{\mathrm{B}} \tag{5}$$

where ϕ_i and s_i are the site fraction and the number of contact sites per segment of component i, respectively. The ratio $s_{\mathrm{A}}/s_{\mathrm{B}}$ for the mixture is estimated by using Bondi's method[9]. X_{AB} is the exchange energy parameter and can be obtained by, e.g. calorimetric measurements or fitting a calculated critical temperature to an experimental one.

Comparing equation (2) with the Flory–Huggins (FH) equation for the free energy of mixing, the interaction parameter χ_{AB} is given by

$$\begin{aligned}\chi_{\mathrm{AB}} = {} & \frac{V^*_r}{\phi_{\mathrm{A}}\phi_{\mathrm{B}} RT}\left[\phi_{\mathrm{A}} P^*_A\left(\frac{1}{\tilde{V}_{\mathrm{A}}} - \frac{1}{\tilde{V}}\right) + \phi_{\mathrm{B}} P^*_{\mathrm{B}}\left(\frac{1}{\tilde{V}_{\mathrm{B}}} - \frac{1}{\tilde{V}}\right)\right. \\ & + 3\phi_{\mathrm{A}} P^*_{\mathrm{A}} \tilde{T}_{\mathrm{A}} \ln \frac{\tilde{V}_{\mathrm{A}}^{1/3} - 1}{\tilde{V}^{1/3} - 1} \\ & \left. + 3\phi_{\mathrm{B}} P^*_{\mathrm{B}} \tilde{T}_{\mathrm{B}} \ln \frac{\tilde{V}_{\mathrm{B}}^{1/3} - 1}{\tilde{V}^{1/3} - 1} + \frac{\phi_{\mathrm{A}} \theta_{\mathrm{B}} X_{\mathrm{AB}}}{\tilde{V}}\right]\end{aligned} \tag{6}$$

The last term in equation (6) represents the exchange energy contribution and the other terms the free volume contributions.

Shiomi *et al.*[5] and Jo *et al.*[10] suggested that X_{AB} can be calculated from segmental exchange energy parameters X_{ij} in the case of homopolymer A and random copolymer B, where homopolymer A is composed of monomer 1 and copolymer B of monomers 2 and 3;

$$X_{\mathrm{AB}} = \theta_{\mathrm{B}}^{(2)} X_{12} + \theta_{\mathrm{B}}^{(3)} X_{13} - \frac{s_{\mathrm{A}}}{s_{\mathrm{B}}} \phi_{\mathrm{B}}^{(2)} \theta_{\mathrm{B}}^{(3)} X_{23} \tag{7}$$

where $\phi_{\mathrm{B}}^{(\mathrm{i})}$ is the copolymer composition of monomer i ($\phi_{\mathrm{B}}^{(2)} + \phi_{\mathrm{B}}^{(3)} = 1$) and $\theta_{\mathrm{B}}^{(\mathrm{i})}$ is the site fraction of component i ($\theta_{\mathrm{B}}^{(2)} + \theta_{\mathrm{B}}^{(3)} = 1$). They also suggested that the characteristic parameters of copolymer **B** are given by

$$P^*_{\mathrm{B}} = \phi_{\mathrm{B}}^{(2)} P^*_2 + \phi_{\mathrm{B}}^{(3)} P^*_3 - \phi_{\mathrm{B}}^{(2)} \theta_{\mathrm{B}}^{(3)} X_{23} \tag{8}$$

$$V^*_{\mathrm{SPB}} = m_{\mathrm{B}}^{(2)} V^*_{\mathrm{SP2}} + m_{\mathrm{B}}^{(3)} V^*_{\mathrm{SP3}} \tag{9}$$

$$T^*_{\mathrm{B}} = \frac{P^*_{\mathrm{B}}}{\phi_{\mathrm{B}}^{(2)}(P^*_2/T^*_2) + \phi_{\mathrm{B}}^{(3)}(P^*_3/T^*_3)} \tag{10}$$

where m_{i} is the mass fraction ($m_{\mathrm{B}}^{(2)} + m_{\mathrm{B}}^{(3)} = 1$). It is important to note that equations (8), (9) and (10) for copolymer are identical to the equations for binary homopolymer blends consisting of components 2 and 3.

EXPERIMENTAL

The polymers used in this study are listed in *Table 1*. The densities of the samples at 25°C under atmospheric pressure were measured by a density gradient column prepared by aqueous potassium nitrate solution and a specific-gravity bottle. The change in density with temperature and pressure was measured using a *PVT* apparatus from Gnomix Research[11]. The sample cell was filled with approximately 1 g polymer and mercury as a confining fluid. The cell was closed at one end by a flexible bellows and the expansion was measured with changing temperature and pressure in order to determine the volume. In the isothermal mode, the volume measurements were carried out at fixed pressure intervals (10 MPa) in the range from 10 to 200 MPa. The process was repeated for temperature intervals of approximately 10°C. The *PVT* apparatus had an absolute accuracy of 1–$2 \times 10^{-3}\,\mathrm{cm^3\,g^{-1}}$, but volume change in the order of magnitude of 1–$2 \times 10^{-4}\,\mathrm{cm^3\,g^{-1}}$ could be resolved. The *PVT* behaviour was measured for all polymers in *Table 1*.

To obtain the characteristic or hard core parameters P^*, V^*_{sp} and T^*, the experimental *PVT* data were fitted to the EOS (equation (1)). A nonlinear least squares fit was carried out by minimizing the quantity d^2 [12]

$$d^2 = \sum_i \{P_i(\mathrm{data}) - P_i(\mathrm{fit})\}^2/(N-3) \tag{11}$$

where N is the number of data points, $P_{\mathrm{i}}(\mathrm{data})$ is the

Table 1 Characteristics of polymer specimens

Polymer	M_{w} ($\mathrm{g\,mol^{-1}}$)[b]	$M_{\mathrm{w}}/M_{\mathrm{n}}$[b]	Source
PS	185 000	2.7	DIC
SAN-5.7[a]	259 000	2.2	Mitsubishi Monsanto
SAN-22.4[a]	119 000	2.1	Mitsubishi Monsanto
SAN-32.6[a]	107 000	2.1	Mitsubishi Monsanto
SAN-50.1[a]	63 600	1.8	Mitsubishi Monsanto
SAN-59.3[a]	49 500	1.8	Mitsubishi Monsanto
SAN-73.6[a]	51 200	2.2	Mitsubishi Monsanto
PAN	150 000	–	Polysciences
PMMA	75 000	1.9	TOSOH

[a] Number means weight fraction of acrylonitrile in SAN
[b] Determined by g.p.c.

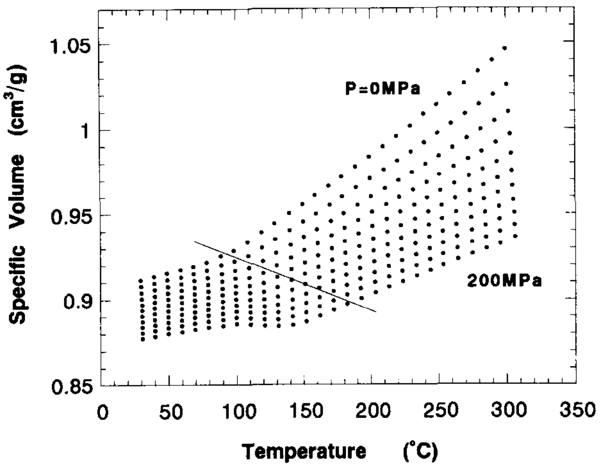

Figure 1 *PVT* data for SAN-32.6. Pressure-dependent glass transition (full line) can be observed. The isobars range from 0 MPa at the top to 200 MPa at the bottom in steps of 20 MPa (data for 0 MPa are obtained by extrapolation)

measured pressure at a given data set of (V, T) and P_i (fit) is the predicted value from the EOS.

RESULTS AND DISCUSSION

Equation of state parameters

Figure 1 shows an example of *PVT* measurements (SAN-32.6). It indicates a typical behaviour of amorphous polymer, showing a change of the slope in V–T relation at the glass transition temperature T_g. The pressure-dependent T_g (solid line) can also be distinguished clearly. For all samples only the data of the liquid state were used to obtain the characteristic parameters by fitting the *PVT* data to the EOS as described above. The temperature range of *PVT* data used for fitting was taken from T_g to 200°C for SAN, to 190°C for PAN. The pressure range was taken from 0 MPa to 200 MPa except for the data below T_g.

In *Figure 2* the experimental values of P^* and V^*_{sp} are plotted against the core volume fraction of acrylonitrile in SAN, ϕ_2:

$$\phi_2 = \frac{m_2 V^*_{sp2}}{m_2 V^*_{sp2} + m_3 V^*_{sp3}} = 1 - \phi_3 \qquad (12)$$

The dotted curves in *Figure 2* depict the P^* and V^*_{sp} as a function of ϕ_2, calculated by equations (8) and (9), respectively. P^* may be related to the mean intermolecular energy per contact pair. The calculated curve exhibits a slightly negative deviation from additivity. This is due to the unfavourable interaction between different comonomers in SAN, $X_{S/AN} (= X_{23})$. The stronger unfavourable interaction renders more negative deviation according to equation (8). As can be seen in *Figure 2*, the values of P^* estimated from *PVT* measurements are almost on the dotted curve calculated by using the value of $X_{S/AN}$ in *Table 2*. Equation (8), which is obtained from the assumption of random mixing may be applicable to SAN, although the experimental error is large. The contribution of large positive $X_{S/AN}$ for the copolymer composition dependence of P^* is not so large because the dotted curve is close to a straight line.

The calculated line for the ϕ_2 dependence of the hard-core volume, $V^*_{SP} - \phi_2$, from equation (9) is straight as shown by the dotted line, while the values of V^*_{sp} estimated from *PVT* measurements are lower than that line.

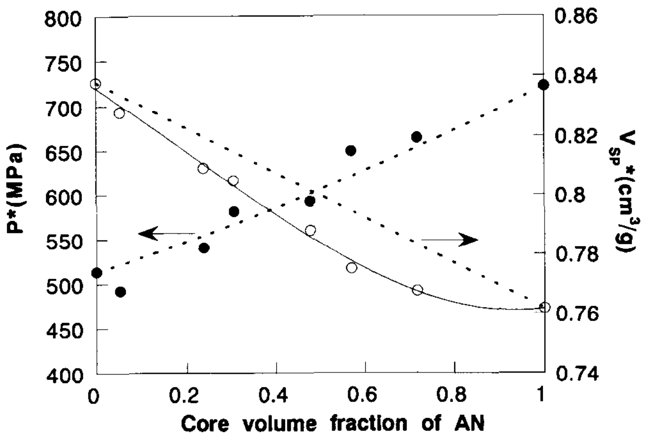

Figure 2 Copolymer composition dependence of P^* and V^*_{sp} in SAN estimated from *PVT* measurements (●; P^*; ○; V^*_{sp}). Dotted curves are calculated from equations (8) and (9), respectively

Table 2 Values of segmental exchange energy parameters used for calculation of X_{AB}

	S/MMA	MMA/AN	S/AN
X_{ij} (J cm^{-3})	3.4	24.9	45.1

Kubota *et al.* showed that the concentration dependence of V^*_{sp} deviated from an additivity in poly(dimethyl siloxane)/benzene mixture[13]. Shiomi *et al.*[14] assumed that the core volumes per segment were different between unlike segments, i.e., $v_1^* \neq v_2^*$, and that the core volume per segment in mixtures was given by

$$v^* = \phi_1^2 v_1^* + 2\phi_1 \phi_{12}^* v_{12}^* + \phi_2^2 v_2^* \qquad (13)$$

where

$$v_{12}^* = \xi[(v_1^{*1/3} + v_2^{*1/3})/2]^3 \qquad (14)$$

where ξ is unity for rigid spheres. They also used equation (13) for random copolymers[15,16]. In order to obtain v_i^*s, one has to use some assumption. Even if one applies V^*_{spi}s to equation (13) instead of $v_i^*s (\xi = 1)$, the large deviation of V^*_{sp} from the dotted line in *Figure 2* cannot be explained. Shiomi *et al.*[14] indicated that the result of Kubota *et al.*[13] could be explained by the deviation from an additivity in the external degree of freedom with respect to the segment fraction. However, there is presently no obvious reason for the large deviation in SAN. The fact that different segments are linked by covalent bonds may have an effect.

Figure 3 shows the ϕ_2 dependence of T^*, which is a parameter reflecting the flexibility of the polymer chain. The values of T^* determined from *PVT* measurements are much smaller than those indicated by the dotted curve calculated from equation (10). T^* is related to other parameters by the following equation,

$$T^* = P^* v^* / ck = \frac{P^* V^*_{sp}}{R(c/M_0)} \qquad (15)$$

where $3c$ is the number of external degrees of freedom per segment and M_0 is molecular weight of segment. From equation (15) and the results of *Figure 2*, the lower T^* of SAN cannot be explained only by effect of smaller

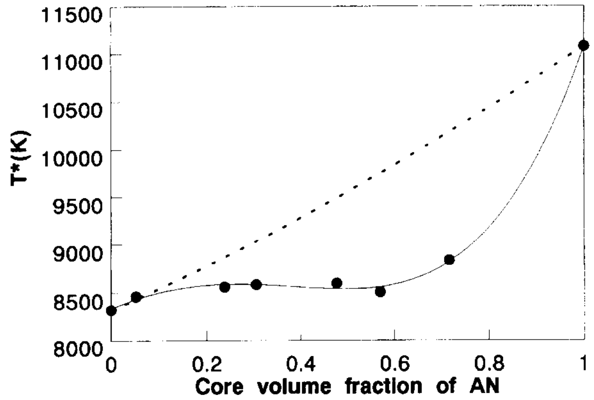

Figure 3 Copolymer composition dependence of T^* in SAN estimated from *PVT* measurements (●). Dotted curve is calculated from equation (10)

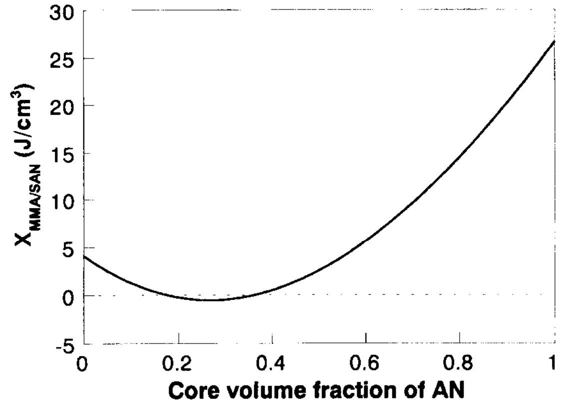

Figure 4 Copolymer composition dependence of $X_{SAN/PMMA}$ calculated from equation (7) by using each segmental exchange energy parameters listed in *Table 2*

V^*_{sp}. A larger c in the copolymer chains leading to the increase of flexibility is expected[17]. Equation (10) is derived by assuming an additivity of c with respect to the copolymer composition. However, in general, c of mixtures is given by[18]

$$c = \phi_1 c_1 + \phi_2 c_2 - \phi_1 \phi_2 c_{12} \tag{16}$$

c in copolymers should be also expressed by equation (16)[15,16], and c_{12} is generally non-zero. Though the values of c_i depend on the size of segment, it is clear that c_{12} in SAN is large and negative. This may result from the fact that the different segments are linked by covalent bonds as in the case of P^*, but the details are not clear. The detailed investigation of this behaviour will be presented in a later paper. The behaviour of T^* could affect the free volume terms of the free energy of mixing.

Exchange energy parameter

In order to calculate χ the values of the exchange energy parameter X_{AB} are also necessary. The segmental X_{ij}s can be obtained by measurements of the heat of mixing for low molecular weight analogues[19,20]. However, it is difficult to measure for polymer–polymer mixtures. In this work we obtained them by fitting the calculated phase diagrams to the experimental one. It is possible to calculate the binodal curve within the framework of the EOS theory by using the expression of the chemical potentials derived from equation (2). For this calculation, the values of the characteristic parameters and X_{AB} are necessary. As described above, the characteristic parameters can be determined from *PVT* measurements. Where the phase diagram is known we can use X_{AB} for the calculation of phase diagrams as the only fitting parameter. Because the shape of the phase diagram calculated by EOS theory is often different from the experimental one, we find the values of X_{ij} matching the bottom (or top) temperature of the two-phase region in the calculated phase diagram with that of the experimental cloud point curve[3,21]. For example, using the values of 588.5 (MPa), 0.7241(cm^3 g^{-1}) and 7925.7(K) for P^*, V^*_{SP} and T^* in PMMA, respectively, the value of $X_{S/MMA}$ was determined to be 3.0 to 3.8 (J cm^{-3})[3,21]. In order to calculate X_{AB} from equation (7) in PMMA/SAN blends, the values of $X_{S/AN}$ and $X_{MMA/AN}$ are also necessary. However, the values of $X_{S/AN}$ and $X_{MMA/AN}$ could not be calculated from phase diagrams by fitting calculated results to experimental ones because the phase diagrams of PS/PAN and PMMA/PAN cannot be measured experimentally, even for low molecular weight mixtures.

Some phase diagrams of PMMA with SANs which have different AN contents have been reported[22]. From those phase diagrams, one can obtain the values of $X_{MMA/SAN\text{-}i}$ by the fitting procedure indicated above. By using the values of $X_{MMA/SAN\text{-}i}$ estimated from the phase diagrams of PMMA/SAN-28.2 and PMMA/SAN-34.4 in the literature[22], we can obtain the values of $X_{S/AN}$ and $X_{MMA/AN}$ from equation (7) and $X_{S/MMA} = 3.4$ (J cm^{-3}). *Table 2* shows the values of X_{ij} obtained. We use them for the calculation of the copolymer composition dependence of X_{AB}. $X_{S/AN}$ is the largest of the three segmental contact pairs and it implies that there exists a strong unfavourable interaction between styrene and acrylonitrile segments in SAN copolymer.

Figure 4 shows the copolymer composition dependence of $X_{MMA/SAN}$ calculated from equation (7) by using the values in *Table 2*. This curve does not depend on temperature according to Flory's EOS. Although all X_{ij}s are positive, there appears a region in which $X_{MMA/SAN}$ is negative. The negative $X_{MMA/SAN}$ is caused by repulsion between S and AN in SAN copolymer. Thus, the miscibility window appears in the $T - \phi_2$ phase diagram because of the segmental exchange energy effect.

χ parameter

For a comprehensive discussion on the miscibility of PMMA/SAN blends, one has to come back to the χ parameter given by equation (6). The last term in the bracket of equation (6) represents the effect of the exchange energy (X_{AB}) and we denote this term as χ_{inter}. The other terms which vanish at $\tilde{V} = \tilde{V}_A = \tilde{V}_B$ correspond to the free volume effect and are denoted as χ_{free}. In the calculations we use the values of the characteristic parameters for each SAN determined by fitting to *PVT* data (*Figures 2 and 3*). Since χ depends on ϕ from equation (6), we calculate χ for PMMA/SAN = 50/50 in *Figures 5 to 7*.

Figure 5 shows χ_{inter} calculated as a function of copolymer composition (core volume fraction) of AN in SAN at three temperatures, using the copolymer composition dependence of $X_{MMA/SAN}$ shown in *Figure 4*.

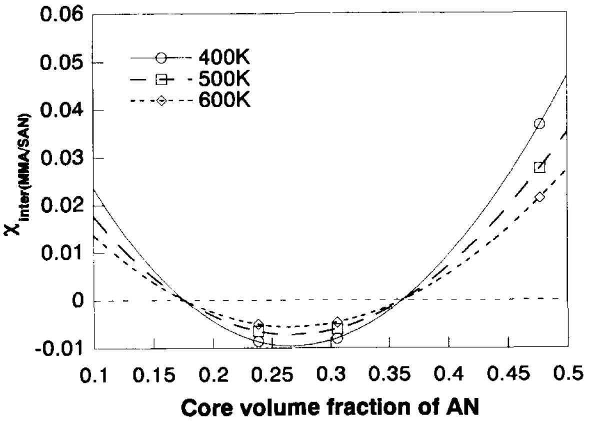

Figure 5 Copolymer composition dependence of χ_{inter} at 400 K, 500 K and 600 K

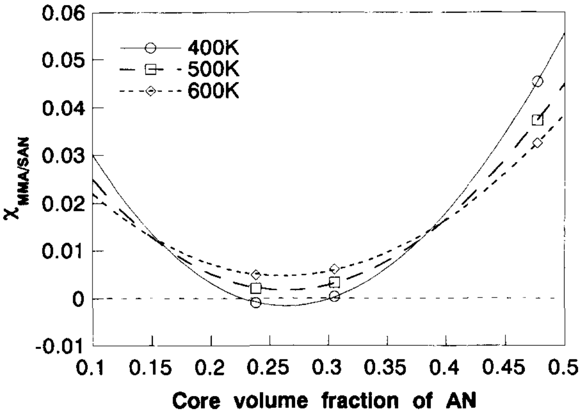

Figure 7 Copolymer composition dependence of total χ parameter at 400 K, 500 K and 600 K

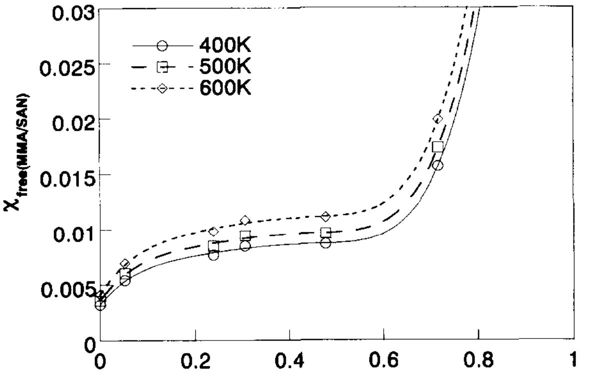

Figure 6 Copolymer composition dependence of χ_{free} at 400 K, 500 K and 600 K

The blend should be miscible in the range where χ is smaller than χ_{cr} which is χ at the critical point in the phase diagram. χ_{cr} can be found from equation (2) by the condition that the second and third derivatives of ΔG^{M} with respect to the composition are zero. Although it is a very complex equation, because χ depends on the composition, it is clear that χ_{cr} depends on r_{A} and r_{B} as well as a case that χ is composition independent[23]. χ_{cr} is always positive and decreases with increasing molecular weight of the components, becoming zero for a mixture of infinite molecular-weight polymers. The copolymer composition dependence of χ_{inter} is parabolic owing to the strong unfavourable interaction between S and AN segments in SAN copolymers. For the particular composition for which χ_{AB} vanishes (0.17 and 0.37, core volume fraction of AN in SAN), χ_{inter} also vanishes and does not depend on temperature. In the copolymer composition range from 0.17 to 0.37, χ_{inter} is negative and increases with increasing temperature, but the sign never changes from negative to positive. This means that χ never becomes greater than χ_{cr} when χ increases with increasing temperature; therefore, the miscibility window can be explained, but the LCST behaviour observed in some PMMA/SAN blends cannot. Conversely, outside the negative χ region, χ_{inter} is positive and decreases with increasing temperature. This leads to UCST (upper critical solution temperature) behaviour if the value of χ crosses χ_{cr}. This agrees with the experimental finding that the lower molecular weight mixtures of PMMA with SAN that have low AN content (and PS) show UCST behaviour[4].

In *Figure 6* the copolymer composition dependence of χ_{free} is shown. The values of χ_{free} were calculated by using the values of T^* in *Figure 3* for each PMMA/SAN-*i* and curves were drawn by a nonlinear least-squares fit. For all copolymer compositions χ_{free} is positive and increases monotonically with increasing temperature. At an AN content of about 60% it increases suddenly. This is caused due to the ϕ_2 dependence of T^* in SAN as shown in *Figure 3*.

Figure 7 shows the copolymer composition dependence of total χ ($\chi = \chi_{\mathrm{inter}} + \chi_{\mathrm{free}}$) at three temperatures. There is a copolymer composition range in which χ increases with increasing temperature and its sign changes from negative to positive. In the region where χ increases, χ crosses the value of χ_{cr} and LCST behaviour can appear—the LCST behaviour can be explained only by considering both χ_{inter} and χ_{free}.

Both the LCST and UCST behaviour of PMMA/SAN blends can be explained qualitatively by *Figure 7*, although the calculated results deviate slightly from the experimental ones. This deviation may be due to a small error included in the values of χ_{ij} in *Table 2*.

CONCLUDING REMARKS

The contributions of the exchange energy and free volume terms to the χ parameter in PMMA/SAN blends were discussed by the FOV equation of state (EOS) theory. It was shown that the miscibility in the limited copolymer composition range was explained by the copolymer composition dependence of only χ_{inter}, but χ_{free} was necessary to explain the LCST behaviour. The results indicated in this paper were qualitatively similar to those calculated by other EOS theories—a lattice fluid model by Sanchez and Lacombe[24,25], the cell and modified cell model by Dee and Walsh[12,26] and the model by Simha and Somcynsky[27].

We discussed the miscibility by using the description for homopolymer/copolymer mixtures suggested by Shiomi *et al.*[5] and Jo *et al.*[10], and the miscibility of PMMA/SAN blends was consistent with results simulated by Shiomi *et al.*[5]. As more general expression, however, χ_{AB} of homopolymer/copolymer mixtures is given by

$$\chi_{AB} = \phi_B^{(2)}\chi_{12} + \phi_B^{(3)}\chi_{13} - \phi_B^{(2)}\phi_B^{(3)}\chi_{23} \qquad (17)$$

Each segmental interaction χ_{ij} can be also given by the expression shown in equation (6)—one can estimate the temperature and copolymer composition dependences of χ_{AB} from the temperature dependence of each χ_{ij}. We also calculated χ_{AB} for PMMA/SAN blends in this way. The result was similar to that indicated in this paper and the free volume term was also necessary to explain the LCST behaviour. However, the effect that the different comonomers are randomly linked in copolymer is not taken into account in χ_{AB} calculated from the temperature dependence of each χ_{ij} by equation (17): it is not reflected in χ_{AB} that the values of T^* in SAN copolymers deviate remarkably from the additivity for the copolymer composition, as shown in *Figure 3*. The contribution of the free volume term to χ obtained from the experimental result of *Figure 3* is different from the one obtained by equation (17). This implies that the properties of random copolymers do not always exhibit simple additivity for copolymer composition and it should be considered carefully for the discussion of the miscibility. Where χ is calculated by equation (17) it is possible that the LCST behaviour appears by considering only the exchange energy term without the free volume effect since equation (7) is not used.

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