Thermodynamic Analysis on the Phase Behavior of Copolymer Blends: An Equation of State Approach

Won Ho Jo* and Moo Sung Lee

Department of Textile Engineering, Seoul National University, Seoul 151-742, Korea

Received March 1, 1991; Revised Manuscript Received October 1, 1991

ABSTRACT: A model of copolymer blends based on the Prigogine–Flory–Patterson equation of state theory is presented to understand quantitatively the effect of comonomer on the LCST behavior of copolymer blends. According to Patterson's treatment, the free volume effect was introduced to the Flory–Huggins interaction parameter χ_{AB} of copolymer blends. The model explains that the intramolecular interaction within copolymers contributes not only to the interactional term but also to the free volume term. Unlike its contribution to the interactional term, the repulsion is not always favorable to the free volume term which depends on the difference in the characteristic temperatures between blend components. Since the characteristic parameters P^* and T^* of the copolymers are a function of those of the copolymer components, the difference depends on the magnitudes of the characteristic parameters of selected comonomer as compared with those of base polymer. The applicability of the proposed model was examined for poly(vinyl methyl ether) (PVME)/styrene copolymer blends. The calculated variation of χ_{AB} with the copolymer composition at a given temperature was in agreement with the variation of the LCST with the copolymer composition and the type of comonomer.

Introduction

In recent years considerable attention has been paid to studies of the phase behavior of copolymer blends since a copolymer often controls the miscibility of the blends. Two bascially different approaches for enhancing miscibility of polymer pairs have been developed. First, miscibility can be achieved by incorporating specifically interacting species into the component polymers.[1] Second blends of random copolymers are miscible for a certain range of copolymer composition although there are no specific interactions between the monomeric units of copolymer blends. For example, styrene–acrylonitrile copolymers (SAN) are miscible with poly(methyl methacrylate) (PMMA),[2] poly(vinyl chloride) (PVC),[3] and poly(ϵ-caprolactone) (PCL)[4] over a certain range of acrylonitrile (AN) contents, but neither polystyrene (PS) nor polyacyrlonitrile (PAN) is miscible with PMMA, PVC, or PCL. This phenomenon is well interpreted by a binary-interaction model,[5–7] based on Flory–Huggins lattice theory. According to the model, miscibility of random copolymers with a homopolymer or copolymer is due to a repulsion between segments comprising the copolymers. In a mean-field approach, the net interaction parameter χ_{blend} can be simply expressed in terms of segmental interaction parameters and copolymer composition in volume fraction. For high molecular weight polymers, it is usually assumed that phase separation occurs when $\chi_{\mathrm{blend}} > 0$ at a given temperature.

A binary interaction model has been successfully applied to account for the effect of comonomers incorporated into one or both components of a miscible blend.[10–16] In many cases, the comonomers have caused a significant change in phase behavior of the miscible polymer blend. Especially, the temperature at which the blends phase separate on heating, i.e., the lower critical solution temperature (LCST), changes dramatically with comonomer content and type of comonomer.[8–15] In accord with these experimental results, a binary-interaction model predicts that an increase in the strength of the net interaction by a repulsion within copolymers leads to a higher temperature for phase separation. However, it has not been possible to obtain a quantitative prediction of experimental results.[12,13]

One of the reasons for this may be due to the fact that the interaction parameters include effects other than purely enthalpy. In the original Flory–Huggins theory, there is no entropic contribution to the χ parameter. However, an extra contribution is required to account for the phenomena that have been observed for polymer solutions and/or polymer blends: composition-dependent χ parameter, LCST, volume change on mixing, etc. Modern thermodynamic theories introduce the equation of state (EOS) contribution into χ.[17–20] This effect is due to a mismatch of the thermal expansivities of the components. We believe that a binary-interaction model should be extended by introducing the free volume or EOS effects to understand quantitatively the LCST behavior of copolymer blends.

Interesting efforts for applying an EOS theory to copolymer blend have been made: The formulations by Kammer[21] and Panayiotou[22] have appeared in the literature. The proposed models could be used for predicting the phase separation phenomena in random copolymer blends, at least in qualitative terms. Although one can see the global effect of free volume on the phase behavior of copolymer blends, their approaches do not give a systematic understanding of the effect of comonomer on the free volume term.

Recently, Wendland et al.[23] reported that the phase separation temperature of poly(vinyl methyl ether) (PVME)/P(styrene-*co*-maleic anhydride) (P(St-co-MA)) blends drops dramatically with increasing maleic anhydride (MA) content in the copolymer. Considering the strong repulsion between the styrene (St) and MA units, the phase behavior of this copolymer blend system may not be explained only by the concept of intramolecular repulsion. As shown in their experimental evidence that the difference between the thermal expansion coefficients of PVME and the copolymer becomes larger because the thermal expansion coefficient of the copolymer decreases with an increase in MA content, the EOS properties of component polymers may give an important contribution to the phase behavior of copolymer blends. Since the phase separation temperature of polymer mixtures has been viewed as a balance between an unfavorable free volume term and a favorable interactional term, the approach to

0024-9297/92/2225-0842$03.00/0

understand quantitatively the effect of comonomer on the free volume term as well as on the interactional term may offer more quantitative guidance on how to select comonomers for controlling the phase separation temperature.

The purpose of the present paper is to introduce the free volume term to the χ parameter, retaining the framework of a binary-interaction model for miscibility criterion: The pair is miscible at a given temperature provided χ is less than a critical value χ_{crit} or zero in the limit of high molecular weights. In this work, we will apply the Prigogine–Flory–Patterson EOS theory to copolymer blends and show that the intramolecular repulsion contributes to the free volume term as well as to the interactional term. Although Patterson's version of the Prigogine–Flory EOS theory seems to be oversimplified, this theory provides a convenient and readily acceptable insight into the two factors controlling the phase behavior of polymer blends. The results from the new model is compared with experimental data of PVME/styrenic copolymer blends, for which variations of LCST with the type of comonomer and copolymer composition are well reported.

Theoretical Background

a. Flory's EOS Theory. Flory's equation of state for chain molecules can be expressed in a reduced form as

$$\frac{\hat{P}\hat{v}}{\hat{T}} = \frac{\hat{v}^{1/3}}{\hat{v}^{1/3} - 1} - \frac{1}{\hat{v}\hat{T}} \tag{1}$$

where $\hat{v} = v/v^*$ is the reduced specific volume, $\hat{P} = P/P^*$ is the reduced pressure, and $\hat{T} = T/T^*$ is the reduced absolute temperature. The quantities with asterisks reflect the molecular characteristics of the chain molecule. At atmospheric pressure, eq 1 reduces to eq 2. All $\hat{v}^{1/3}$ values

$$\hat{T} = \frac{\hat{v}^{1/3} - 1}{\hat{v}^{4/3}} \tag{2}$$

are found between the extremes of 1 and $^4/_3$ due to the limit of the thermal expansion of chain molecules. If an additional interaction parameter, which arises from the difference in interaction energy between like and unlike segment pairs, is introduced, Flory's EOS is extended to liquid mixtures.

b. Patterson's Approach for Phase Separation Behavior. Patterson[24] derived a general relation from the Prigogine's corresponding state theory for the χ_{AB} parameter, normalized to a reference molecule

$$\chi_{\text{AB}} = -\frac{U_{\text{A}}}{RT}\left[\frac{X_{\text{AB}}}{P_{\text{A}}^*}\right] + \frac{C_{p,\text{A}}}{2R}\tau^2 \tag{3}$$

where U_{A} is the molar configuration energy of reference molecule (component A) and $C_{p,\text{A}}$ is the configurational heat capacity. In the first term, X_{AB} is a measure of the intermolecular interaction between the component molecules. The second term of eq 3 reflects the difference in free volume between the components through the parameter τ:

$$\tau = 1 - T_{\text{A}}^*/T_{\text{B}}^* \tag{4}$$

It is helpful to note that τ depends on the ratio of the characteristic temperature T^* of each component, which is closely related to the thermal expansion coefficient of the component. In using a van der Waals model, U_{A} and $C_{p,\text{A}}$ can be expressed in terms of the reduced volume $\hat{v}_{\text{A}}$ of the reference molecule

$$-U_{\text{A}} = \frac{P_{\text{A}}^* V_{\text{A}}^*}{\hat{v}_{\text{A}}} \tag{5}$$

$$C_{p,\text{A}} = \frac{\hat{v}_{\text{A}}^{1/3}}{^4/_3 - \hat{v}_{\text{A}}^{1/3}}\left[\frac{P_{\text{A}}^* V_{\text{A}}^*}{T_{\text{A}}^*}\right] \tag{6}$$

where V_{A}^* is the characteristic volume of molecule A. By use of eqs 5 and 6, χ_{AB} is expressed as

$$\frac{\chi_{\text{AB}}(T)}{C_{\text{A}}} = \frac{\hat{v}_{\text{A}}^{1/3}}{\hat{v}_{\text{A}}^{1/3} - 1}\left[\frac{X_{\text{AB}}}{P_{\text{A}}^*}\right] + \frac{\hat{v}_{\text{A}}^{1/3}}{2(^4/_3 - \hat{v}_{\text{A}}^{1/3})}\left[1 - \frac{T_{\text{A}}^*}{T_{\text{B}}^*}\right]^2 \tag{7}$$

where C_{A} satisfies the relation $C_{\text{A}} = P_{\text{A}}^* V_{\text{A}}^*/RT_{\text{A}}^*$ and reflects the flexibility of molecule A. Since the reduced volume is related with the reduced temperature by the equation of state, eq 7 is a function of temperature. The first term on the right of eq 7 is the interactional contribution, and the second is the free volume contribution. As the temperature (or the reduced volume) increases, the interactional term decreases and the free volume term increases in an appropriate manner. Therefore, the free volume term always tends to destabilize the mixtures at high temperature. The critical value of χ_{AB} is given by

$$\frac{\chi_{\text{AB,crit}}}{C_{\text{A}}} = \frac{RT_{\text{A}}^*}{2P_{\text{A}}^*}\left[\frac{1}{V_{\text{A}}^{*1/2}} + \frac{1}{V_{\text{B}}^{*1/2}}\right]^2 \tag{8}$$

Patterson[25] describes the essential features of phase separation behavior as follows: The temperature at which $\chi_{\text{AB}}(T) = \chi_{\text{AB,crit}}$ is the phase separation temperature. The system is miscible for temperatures at which $\chi_{\text{AB}}(T) < \chi_{\text{AB,crit}}$ and immiscible otherwise.

c. Formulations of X_{AB} for Copolymer Blends and Characteristic Parameters of Copolymer. Consider a mixture of polymer A and copolymer B. Copolymer B is a random copolymer of monomers 2 and 3, and polymer A is composed entirely of a different monomer 1. Let N_i be the number of monomer i in the mixture. r_i is the number of segments per monomeric unit of component i. s_i is the number of contact sites per segment, and c_i is the number of external degrees of freedom per segment. The segment fraction ϕ_i and site fraction θ_i for component i with i = 1–3 in the mixture are given respectively by

$$\phi_i = \frac{r_i N_i}{r_1 N_1 + r_2 N_2 + r_3 N_3} = \frac{r_i N_i}{rN} \tag{9a}$$

$$\theta_i = \frac{r_i N_i s_i}{r_1 N_1 s_1 + r_2 N_2 s_2 + r_3 N_3 s_3} = \frac{r_i N_i s_i}{rNS} \tag{9b}$$

The segment fraction Φ_{A} and site fraction Θ_{A} of polymer A in the mixture are defined respectively as

$$\Phi_{\text{A}} = \frac{r_1 N_1}{rN} = \phi_1 \tag{10a}$$

$$\Theta_{\text{A}} = \frac{r_1 N_1 s_1}{rNs} = \theta_1 \tag{10b}$$

Similarly, the segment fraction Φ_{B} and site fraction Θ_{B} of copolymer B in the mixture are defined, respectively, as

$$\Phi_B = \frac{r_2N_2 + r_3N_3}{rN} = \phi_2 + \phi_3 \qquad (11a)$$

$$\Theta_B = \frac{r_2N_2s_2 + r_3N_3s_3}{rNs} = \theta_2 + \theta_3 \qquad (11b)$$

The mean numbers of contact sites s per segment and of external degrees of freedom c per segment in the mixture are given by

$$s = \phi_1s_1 + \phi_2s_2 + \phi_3s_3 \qquad (12a)$$

$$c = \phi_1c_1 + \phi_2c_2 + \phi_3c_3 \qquad (12b)$$

Similarly, the segment fraction and site fraction for component i with $i = 2$ or 3 in the copolymer B are given by

$$\phi_B{}^{(i)} = \frac{r_iN_i}{r_2N_2 + r_3N_3} = \frac{r_iN_i}{r_BN_B} \qquad (13a)$$

$$\theta_B{}^{(i)} = \frac{r_iN_is_i}{r_2N_2s_2 + r_3N_3s_3} = \frac{r_iN_is_i}{r_BN_Bs_B} \qquad (13b)$$

Simple additivity of s_B and c_B is assumed for pure copolymer. Thus, the average quantities per segment for copolymer B are defined as

$$s_B = s_2\phi_B{}^{(2)} + s_3\phi_B{}^{(3)} \qquad (14a)$$

$$c_B = c_2\phi_B{}^{(2)} + c_3\phi_B{}^{(3)} \qquad (14b)$$

Parameters with subscript 1 are the same as those with subscript A.

To obtain expressions for X_{AB} of copolymer blends and characteristic parameters of copolymers, appropriate mixing rules analogous to those of ref 26 are required. With the above definitions and appropriate mixing rules, the mean potential energy of the mixture can be written in the following form

$$-E_o = \frac{N_{11}\eta_{11}+N_{22}\eta_{22}+N_{33}\eta_{33}+N_{12}\eta_{12}+N_{13}\eta_{13}+N_{23}\eta_{23}}{\nu} \qquad (15)$$

where N_{ij} is the number of i–j pair interactions, each being characterized by the interaction energy η_{ij}/ν. If random mixing is assumed, then

$$N_{11} = \frac{(r_1N_1s_1)^2}{2rNs} \qquad N_{22} = \frac{(r_2N_2s_2)^2}{2rNs} \qquad (16)$$

$$N_{33} = \frac{(r_3N_3s_3)^2}{2rNs} \qquad N_{12} = \frac{r_1N_1s_1r_2N_2s_2}{rNs}$$

$$N_{13} = \frac{r_1N_1s_1r_3N_3s_3}{rNs} \qquad N_{23} = \frac{r_2N_2s_2r_3N_3s_3}{rNs}$$

The mean potential energy may then be written as

$$-\frac{E_o}{rN} = \frac{(\nu^*)^2}{\nu}[\Phi_AP_1{}^* + \Phi_B\phi_B{}^{(2)}P_2{}^* + \Phi_B\phi_B{}^{(3)}P_3{}^* - \Phi_A\Theta_B\theta_B{}^{(2)}X_{12} - \Phi_A\Theta_B\theta_B{}^{(3)}X_{13} - \Phi_B\Theta_B\phi_B{}^{(2)}\theta_B{}^{(3)}X_{23}] \qquad (17)$$

where $\Delta\eta_{ij} = \eta_{ii} + \eta_{jj} - 2\eta_{ij}$, $P_i{}^* = s_i\eta_{ii}/2\nu^{*2}$, and $X_{ij} = s_i\Delta\eta_{ij}/2\nu^{*2}$. Equation 17 can be reduced as follows:

$$-\frac{E_o}{rN} = \frac{\nu^*}{\nu}[\Phi_AP_1{}^* + \Phi_B[\phi_B{}^{(2)}P_2{}^* + \phi_B{}^{(3)}P_3{}^* - \phi_B{}^{(2)}\theta_B{}^{(3)}X_{23}] - \Phi_A\Theta_B[\theta_B{}^{(2)}X_{12} + \theta_B{}^{(3)}X_{13} - (s_A/s_B)\phi_B{}^{(2)}\theta_B{}^{(3)}X_{23}]] \qquad (18)$$

Since the energy for a binary mixture of two components A and B defined as

$$-\frac{E_o}{r_AN_A + r_BN_B} = \frac{\nu^*}{\nu}[\Phi_AP_A{}^* + \Phi_BP_B{}^* - \Phi_A\Theta_BX_{AB}] \qquad (19)$$

eq 18 leads to a definition of $P_B{}^*$ for copolymer B of the form

$$P_B{}^* = \phi_B{}^{(2)}P_2{}^* + \phi_B{}^{(3)}P_3{}^* - \phi_B{}^{(2)}\theta_B{}^{(3)}X_{23} \qquad (20)$$

and the effective contact energy parameter X_{AB} for the mixture

$$X_{AB} = \theta_B{}^{(2)}X_{12} + \theta_B{}^{(3)}X_{13} - (s_A/s_B)\phi_B{}^{(2)}\theta_B{}^{(3)}X_{23} \qquad (21)$$

In this case, $X_{ij} \neq X_{ji}$ $(=s_j\Delta\eta_{ij}/2\nu^{*2})$ due to $s_i \neq s_j$. If it assumed that the number of contact sites per segment is the same for all segments, eq 21 can be reduced to the form identical with a binary interaction model for homopolymer/copolymer blend:

$$X_{AB} = \phi_B{}^{(2)}X_{12} + \phi_B{}^{(3)}X_{13} - \phi_B{}^{(2)}\phi_B{}^{(3)}X_{23} \qquad (22)$$

In this case, $X_{ij} = X_{ji}$. From a relation between the characterstic parameters $P^*\nu^* = ckT^*$ and eq 14b, the characteristic temperature $T_B{}^*$ for copolymer B is given by

$$T_B{}^* = \frac{\phi_B{}^{(2)}P_2{}^* + \phi_B{}^{(3)}P_3{}^* - \phi_B{}^{(2)}\theta_B{}^{(3)}X_{23}}{\phi_B{}^{(2)}P_2{}^*/T_2{}^* + \phi_B{}^{(3)}P_3{}^*/T_3{}^*} \qquad (23)$$

It is noteworthy that eqs 20 and 23 for copolymers are identical with eqations for binary mixtures. The effective contact energy parameter for mixing a copolymer A of monomers 1 and 2 with a copolymer B of 3 and 4 can be written as eq 24.

$$X_{AB} = \phi_A{}^{(1)}\theta_B{}^{(3)}X_{13} + \phi_A{}^{(1)}\theta_B{}^{(4)}X_{14} + \phi_A{}^{(2)}\theta_B{}^{(3)}X_{23} + \phi_A{}^{(2)}\theta_B{}^{(4)}X_{24} - \phi_A{}^{(1)}\theta_A{}^{(2)}X_{12} - (s_A/s_B)\phi_B{}^{(3)}\theta_B{}^{(4)}X_{34} \qquad (24)$$

Analysis of Results

The characteristic parameters for pure components should be predetermined for analysis of thermodynamic properties of polymer mixtures. Temperature-independent parameters can be obtained from fitting P–V–T data directly to an equation of state over a wide range of pressures and temperatures. In this work, T^* and ν^* are determined by fitting the experimental zero-pressure V–T data in eq 2. P^* is determined from the experimental zero-pressure isothermal compressibility $\beta(T)$ according to Zoller's procedure.[27] The characteristic parameters of the polymers, except for PAN, are evaluated from the P–V–T data taken from the literature. Since no overall P–V–T data are available for PAN, the characteristic parameters are obtained from the thermal expansion coefficient α, specific volume, and solubility paramter δ instead of thermal pressure coefficient γ. In the case of polymers, γs can be estimated from solubility parameters:[31] $\gamma = m\delta^2/T$, where m assumes a value close to 1 for polymers.

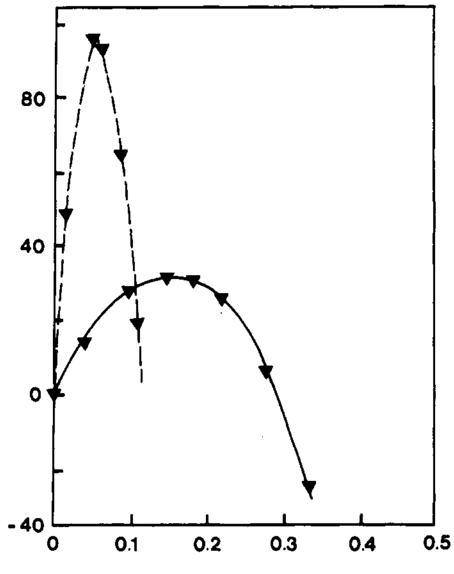

Figure 1. Variations of the LCST with the copolymer composition for PVME/styrenic copolymer blends. The LCST of PVME/PS is chosen as a reference. The symbols are the experimental points taken from ref 12 and 13: solid line, PVME/SMMA blends; broken line, PVME/SAN blends.

Figure 1 shows how the LCSTs of PVME/styrenic copolymer blends vary with the copolymer composition. The copolymer composition is expressed in volume fractions. The data points are taken from the experimental work of Chien et al.[12] for PVME/styrene-methyl methacrylate copolymer (SMMA) blends and from the work of Min and Paul[13] for PVME/SAN blends. SAN copolymers have a more limited range of miscibility with PVME than SMMA copolymers: The limit of the miscibility window lies between 36 and 40 vol % MMA for SMMA copolymers and between 10 and 11 vol % AN for SAN copolymers. However, the maximum rise in the LCSTs for SMMA copolymers is much less than for SAN copolymers. If we assume that the LCST reflects the interaction between blend components, the existence of a maximum in the LCSTs requires a minimum in the interaction parameters. The observations clearly suggest that the absolute value of the intramolecular repulsion is much larger than those of the two remaining segmental interactions and that the repulsion between the St-AN pair is much stronger than that between the St-MMA pair. Although the shape of the net interaction parameter is determined by the difference in interactional strength between interacting segments, the main factor for controlling the curvature is the intramolecular interaction, namely the repulsion within copolymers. It seems that there is a mismatch between the shape of LCSTs for PVME/SMMA blends and the segmental interaction parameter from the binary interaction model for the St-MMA pair:[15] The value of the repulsive interaction parameter of the St-MMA pair is not so large as to cause a considerable raise of LCST, i.e., to make the net interaction parameter more negative and show a minimum.

The problem now is to find the segmental contact energy parameters X_{ij}s from the copolymer composition-LCST data for PVME/styrenic copolymer blends. The calculations are iterative because X_{ij}s can only be calculated after X_{AB}s at the given copolymer compositions have been determined: The method of successive approximations must be used. In the first approximations, X_{23} is set equal to zero in eq 23. Then, X_{AB}s are found from the LCST data with the copolymer composition, and thereafter three X_{ij}s are computed from the regression using eq 22. The entire calculation is then repeated except that the new value of X_{23} is now used in eq 23. One proceeds in this way until the calculated values of X_{ij}s are converged to exact values. The iteration results are shown in Figure 2 and Table II. The X_{ij}s evaluated from the assumption of equal contact site, i.e., eq 22, are also listed in Table II. Note that PVME homopolymer is chosen as a reference polymer. The value of X_{12} was estimated to be −5.7 J/cm^3, and this value is comparable with the values (−1.76, −9.0 J/cm^3) reported by other workers.[33,34] As shown in Table II, the repulsion for the St-AN pair is much stronger than that for the ST-MMA pair.

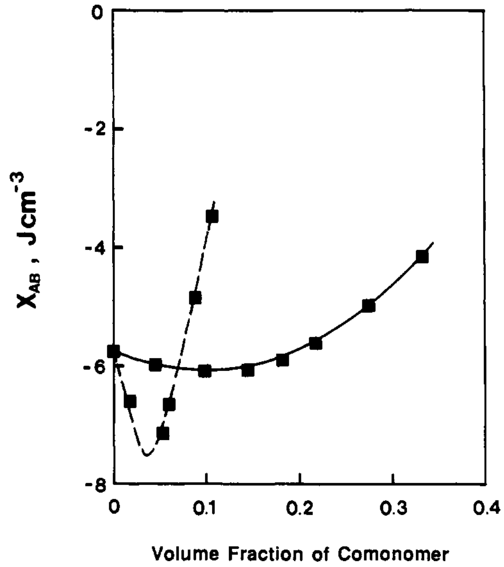

Figure 2. Dependence of the effective contact energy parameter X_{AB} on the copolymer composition: solid line, PVME/SMMA blends; broken line, PVME/SAN blends. The solid and broken lines are least-squares fits to the data points according to eq 21.

Table I
Characteristic Parameters of Pure Polymers

polymer	v^*, cm^3/g	P^*, J/cm^3	T^*, K	s_i/s_{PS}[d]
PS[a]	0.8466	453	8982	1.00
PMMA[a]	0.7643	562	8474	1.20
PVME[b]	0.8051	524	6598	1.17
PAN[c]	0.7798	810	11680	1.12

[a] Reference 28. [b] Reference 29. [c] Reference 30. [d] Calculated from Bondi's table.[32]

Table II
Segmental Contact Energy Parameters

	X_{ij}, J/cm^3	
segmental pair	from eq 21	from eq 22
VME/St	−5.7	−5.8
VME/MMA	16.9	22.6
VME/AN	610.0	693.0
St/MMA	25.1	34.5
St/AN	574.0	745.0

Here, we should point out assumptions for simplifying the calculation. First, it is well-known that phase separation temperatures of PVME/PS blends are sensitive to the molecular weight and molecular weight distribution of each polymer.[33,35] In reality, the two papers,[12,13] which are used as the references for the experimental data in Figure 1, show a difference of about 10 °C in the LCST of PVME/PS: The LCST of PVME/PS in the PVME/SAN series is about 110 °C whereas the LCST of PVME/PS in the PVME/SMMA series is about 120 °C. This is no doubt the result of a difference in molecular weight of components, more specifically the molecular weight of

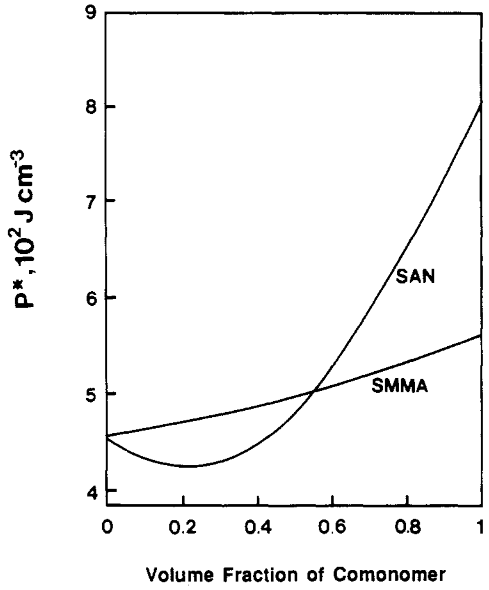

Figure 3. Theoretically calculated characteristic pressures of the copolymers as a function of copolymer composition: curve A, SMMA copolymers; curve B, SAN copolymers.

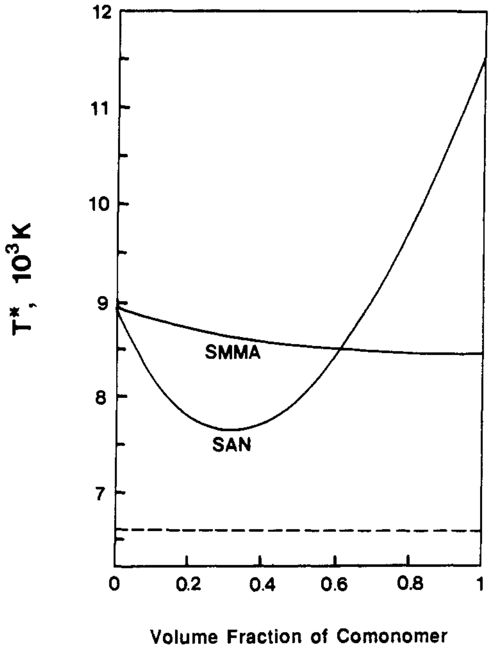

Figure 4. Theoretically calculated characteristic temperatures of the copolymers as a function of copolymer composition: curve A, SMMA copolymers; curve B, SAN copolymers; dotted line, characteristic temperature of PVME.

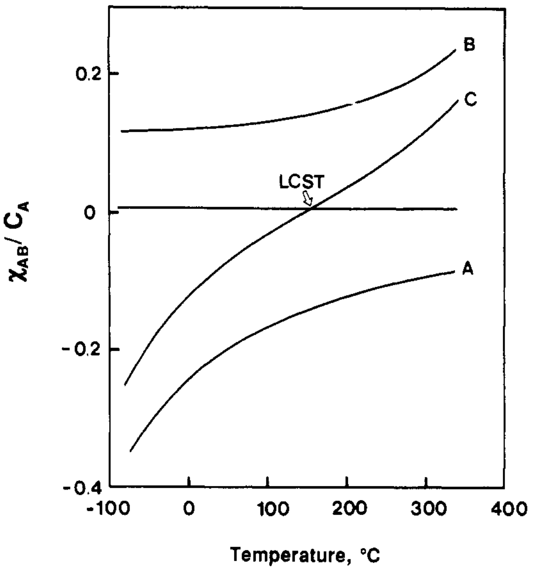

Figure 5. Variation of the interactional (A) and free volume (B) contributions to the χ_{AB} parameter (C) as a function of temperature for PVME/SMMA (86.5 vol % St). The horizontal line corresponds to the critical value of χ_{AB}/C_A, assuming that the characteristic volume of the copolymer is simple additive to those of components.

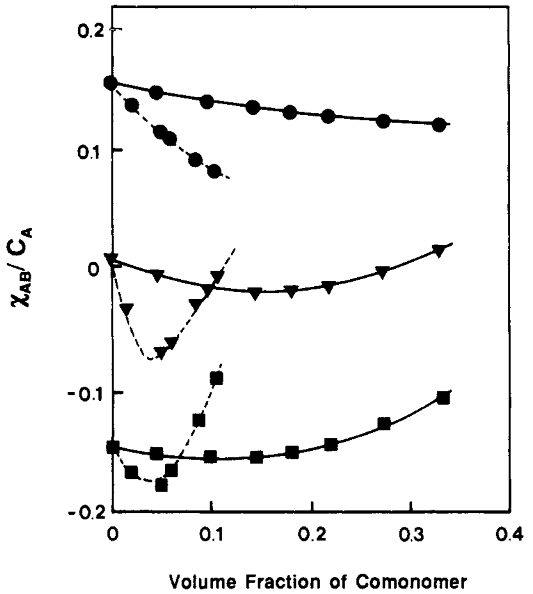

Figure 6. Variation of the interaction (■) and free volume (●) contributions to the χ_{AB} parameter (▼) as a function of copolymer composition at the LCST of PVME/PS. The solid lines are calculated ones for the SMMA series and the broken lines for the SAN series.

PVME used in each study. It is desirable to exclude its contribution to the LCST for the proper comparison of LCSTs of two series. Thus, the LCSTs for PVME/SAN series were corrected by an adding factor, 10 °C, corresponding to the effect of molecular weight on the LCST. Second, it should be noted that there is a difference, though small, between the segment fraction and volume fraction of comonomer in the copolymer. In this work we used volume fractions to characterize the copolymer composition.

Figures 3 and 4 demonstrate that the predicted values for the characteristic parameters P^* and T^* of the two copolymers SMMA and SAN exhibit nonadditive variations with the copolymer composition. The negative deviation from additivity in P^* and T^* is the result of the repulsion within copolymers. Since the free volume term is proportional to τ^2, it is noticeable that the larger the difference in the characteristic temperature of each component, the more positive is the free volume term, i.e., more unfavorable for mixing. Recalling T^* of 6598 K for PVME, we know that the difference rather decreases with increasing comonomer content to some extent.

In Figure 5, χ_{AB}/C_A for PVME/SMMA (86.5 vol % St) is plotted against temperature. The interactional and free volume term are also shown in this figure. As the temperature increases, the magnitude of the favorable interactional term with $X_{AB} = -6.1$ J/cm^3 decreases while that of the unfavorable free volume term increases. At the temperature of about 150 °C, where the free volume term cancels the interactional contribution, an LCST occurs.

In Figure 6, χ_{AB}/C_A, calculated at 394 K (the LCST of PVME/PS), is plotted against the copolymer composition. The calculated value for PVME/PS is nearly zero since the combinatorial term is negligibly small. The free volume terms are always positive as expected, but decrease with the copolymer composition. These effects make χ_{AB} more negative and consequently LCST higher. SAN copolymers are more effective in reducing the unfavorable free volume term than SMMA copolymers. The interactional term, the counterpart of the free volume term for miscibility, is proportional to the effective contact energy parameter X_{AB} at a given temperature (compare with Figure 2). The minimum values in the plot of the interactional term versus copolymer composition are attributable to the strong repulsion between St and comonomer. The curvature for SMMA series is less than that for SAN series, which means that the repulsion between St and MMA is weaker than that between St and AN. The χ_{AB} parameters for two-blend series are given by the sum of the interactional and free volume term of each series. The interactional term seems to be the controlling factor for χ_{AB} because this term is a quadratic function of the composition; however, the free volume term is also important to make χ_{AB} more negative.

Discussion

We may examine the relative ability of the proposed model to describe specific systems by comparing the theoretically predicted values with the characteristic parameters P^* and T^* of copolymers experimentally determined by the direct P–V–T measurement. However, it is not easy to obtain the parameters within meaningful error limits due to lack of accuracy of experimental data. In fact, experimental data are rare for the composition-dependent characteristic parameters of blends. Moreover, there are problems for the treatment of the copolymer as a blend, especially for the interpretation of the characteristic parameters. Zoller et al.[36] has discussed the difference between the experimental data and theoretical prediction in terms of the segment sequential distribution in the copolymer chain and the nonadditivity of the external degree of freedom for copolymer.

Although the contact energy parameter X_{ij} is free from the free volume effect, the X_{ij} has a similar physical meaning to the B_{ij} in the Flory–Huggins theory: the net change in cohesive energy density upon mixing at the hard core state. ten Brinke et al.[6] have qualitatively discussed the temperature dependence of the interactional contribution to the χ_{AB} parameter on the basis of the first term of eq 7. The importance of negative X_{AB} for polymer–polymer miscibility has been discussed in terms of a binary-interaction model, but the effect of comonomer on the free volume term has not been discussed. According to an extended version of a simple binary-interaction model,[37] one can equate the composition of the maximum in the locus of the LCSTs to that of the minimum value of the net interaction parameter in the plot of copolymer composition versus net interaction parameter. Although, in a qualitative sense, the net interaction parameter calculated from the extended version parallels the experimental LCST results, the variation of the net interaction parameter with the copolymer composition and the type of comonomer does not quantitatively correlate with that of the LCST's.[38] The free volume term of copolymer blends introduced in this study seems to be simply an adding factor for a binary interaction model, but this term is essential to describe the LCST behavior of copolymer blends, i.e., phase diagram of copolymer blends. Moreover, as shown in Figure 6, the effect of comonomer on the free volume term of copolymer blends is important to fit the χ_{AB} parameter to experimental LCST data as compared with the case that considers only the effect on the interactional term. The variation of the free volume term with the copolymer composition is negligible only when the difference in T^* of each blend component is small and the intramolecular interaction within copolymers is weak.

The present model explains that the repulsion within copolymers contributes to the free volume term as well as to the interactional term of Flory–Huggins interaction parameter. The repulsion is always favorable for the interactional term, i.e., make X_{AB} more negative. However, its contribution to the free volume term is rather complex. The characteristic temperatures for copolymers are determined not only by the intramolecular interaction within a copolymer but also by the characteristic parameters of each component in the copolymer (see eq 23). Since the free volume contribution depends upon a difference in T^* of the blend components, it is possible that the repulsion may cause a larger difference in the characteristic temperatures of blend components and act unfavorably on the free volume term. To our knowledge, no experimental data for this case have been reported. We have shown in the previous section that the repulsion between St and comonomer plays an important role in raising the LCST of PVME/styrenic copolymers. In this case, the repulsion contributed favorably to both the interactional and free volume terms. Although the free volume term is important to χ_{AB}, the effective contact energy parameter X_{AB} must be negative for miscibility since the free volume term does not favor phase stability.

In the context of the above formulation, site fraction is introduced to account for the difference in molecular shape of each component. As a consequence, $X_{ij} \neq X_{ji}$. Unfortunately, this limits their usefulness as fundamental molecular parameters dependent only on the chemical structures of component molecules. As shown in Table II, somewhat different results are obtained depending on whether the effect of surface area differences is considered. Generally, the surface to volume ratio affects the skewness of the spiniodal curve and has little effect on the LCST.[39]

As discussed in detail by Patterson and Robard,[20] the simple version of the Prigogine–Flory EOS theory by Patterson contains some oversimplifications; it does not consider any variation of χ_{AB} with blend ratio. As a consequence, eq 7 cannot predict the details of phase diagram, e.g., shape of spinodal or binodal, although the variation of LCSTs with X_{AB}, molecular weight, and the difference in characteristic parameters of blend components has been well and simply predicted.

Concluding Remarks

We have presented a simple version of the Prigogine–Flory–Patterson theory that predicts quantitatively the effect of comonomer on the LCST behavior of copolymer blends. The model explains that the intramolecular interaction within copolymers contributes to the free volume term as well as to the interactional term of Flory–Huggins interaction parameter. Unlike its contribution to the interactional term, the repulsion is not always favorable to the free volume term, which depends on several factors, including the characteristic parameters of components in copolymers and the intramolecular interaction. The present model predicts well that the dependence of χ_{AB} on the copolymer composition at a given temperature is in agreement with the variation of LCST with the copolymer composition. This model may give prior guidance on how to select comonomers that are used for controlling the phase separation temperature. Although the model may not predict precisely the composition dependence of the characteristic parameters for copolymers, the agreement between model prediction and experimental LCST data is satisfactory. In a further study, we will confirm the various theoretical possibilities for the free volume effect by using appropriate experiments.

References and Notes

(1) Smith, P.; Hara, M.; Eisenberg, A. *Current Topics in Polymer Science*; Ottenbrite, R. M., Utracki, L. A., Inoue, S., Eds.; Macmillan Publishing: New York, 1987.
(2) Suess, M.; Kressler, J.; Kammer, H. W. *Polymer* **1987**, *28*, 957.
(3) Kim, J. H.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 2211.
(4) Chiu, S. C.; Smith, T. G. *J. Appl. Polym. Sci.* **1984**, *29*, 1797.
(5) Kambour, R. P.; Bendler, J.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(6) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(7) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(8) Kwei, T. K.; Pearce, E. M.; Min, B. Y. *Macromolecules* **1985**, *18*, 2326.
(9) Walsh, D. J.; Sham, C. K. *Macromolecules* **1989**, *22*, 3799.
(10) Fernandes, A. C.; Barlow, J. W.; Paul, D. R. *Polymer* **1986**, *27*, 1788.
(11) Min, K. E.; Paul, D. R. *Macromolecules* **1987**, *20*, 2828.
(12) Chien, Y. Y.; Pearce, E. M.; Kwei, T. K. *Macromolecules* **1988**, *21*, 1616.
(13) Min, K. E.; Paul, D. R. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 2257.
(14) Min, K. E.; Lee, D. H.; Jung, H. M. *Polym. Bull.* **1990**, *24*, 221.
(15) Nishimoto, M.; Keskkula, H.; Paul, D. R. *Macromolecules* **1990**, *23*, 3633.
(16) Jo, W. H.; Lee, S. C. *Macromolecules* **1990**, *23*, 2261.
(17) Prigogine, I. *The Molecular Theory of Solutions*; North-Holland Publishing: Amsterdam, 1957.
(18) Flory, P. J. *Discuss. Faraday. Soc.* **1970**, *49*, 7.
(19) Patterson, D. *Rubber Chem. Technol.* **1967**, *40*, 1.
(20) Sanchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145.
(21) Kammer, H. W. *Acta Polym.* **1986**, *37*, 1.
(22) Panayiotou, C. G. *Makromol. Chem.* **1987**, *188*, 2733.
(23) Wendland, C.; Klotz, S.; Krieger, V.; Cantow, H. J. *Am. Chem. Soc., Polym. Prepr.* **1988**, *30*(2), 109.
(24) Patterson, D. *J. Polym. Sci., Part C* **1968**, *16*, 3379.
(25) Patterson, D.; Robard, A. *Macromolecules* **1978**, *11*, 690.
(26) Sanchez, I. C. *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Chapter 3.
(27) Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 897.
(28) Simha, R.; Wilson, P. S.; Olabisi, O. *Kolloid Z. Z. Polym.* **1973**, *251*, 402.
(29) Uriarte, C.; Eguiazabal, J. I.; Lianos, M.; Iribarren, J. I.; Iruin, J. J. *Macromolecules* **1987**, *20*, 3038.
(30) Chiang, R. *J. Polym. Sci., Part A* **1963**, *1*, 2765.
(31) Allen, G.; Gee, G.; Mangaray, D.; Sins, D.; Wilson, G. J. *Polymer* **1960**, *1*, 467.
(32) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(33) Walsh, D. J.; Dee, G. T.; Halary, J. L.; Ubiche, J. M.; Millequant, M.; Lesse, J.; Monnerie, L. *Macromolecules* **1989**, *22*, 3395.
(34) Shiomi, T.; Hamada, F.; Nasako, T.; Yoneda, K.; Imai, K.; Nakajima, A. *Macromolecules* **1990**, *23*, 229.
(35) Nishi, T.; Kwei, T. K. *Polymer* **1975**, *16*, 285.
(36) Zoller, P.; Jain, R. K.; Simha, R. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 687.
(37) Cowie, J. M. G.; McEwen, I. J.; Nadvornik, L. *Macromolecules* **1990**, *23*, 5106.
(38) Lee, M. S. Ph.D. Thesis, Seoul National University, Seoul, 1991.
(39) Walsh, D. J.; Rostami, S. *Adv. Polym. Sci.* **1985**, *70*, 119.

Registry No. PVME (homopolymer), 9003-09-2; SMMA (copolymer), 25034-86-0; SAN (copolymer), 9003-54-7.