Miscibilities in binary copolymer systems

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A lattice theory is presented for liquid–liquid equilibria in binary systems containing random copolymers. This theory takes into account deviations from random mixing through a non-randomness factor which follows from a generalization of Monte-Carlo calculations for the three-dimensional Ising model. While the lattice remains incompressible, the effect of specific interactions (hydrogen bonding) is introduced by superimposing on the non-random (Ising model) expression for the Helmholtz energy of mixing a correction based on the lattice–gas model by ten Brinke and Karasz. The resulting theory can predict immiscibility caused by lower critical solution temperatures. Several theoretical miscibility maps at fixed temperature were computed; these are compared with those predicted by the random-mixing Flory–Huggins theory. Theoretical miscibility maps are also compared with experiment for a few systems with strong specific interactions.

(Keywords: lattice model; miscibility; phase equilibria)

INTRODUCTION

There is considerable interest in the liquid–liquid equilibria of binary polymer blends containing random copolymers because such blends can exhibit a variety of mechanical, electrical, thermal, optical and other properties. Many homogeneous materials having desired properties can be obtained by mixing copolymers to make a blend. In addition to their potential for new materials, random copolymers are also used as compatibilizers for blends of homopolymers that are immiscible without compatibilizers.

Miscibility of copolymers is often achieved through favourable specific interactions such as hydrogen bonding. Although a fundamental understanding of the pertinent thermodynamics plays a crucial role in the preparation of copolymer blends, there are few useful molecular–thermodynamic models for copolymer blends with specific interactions; a major exception is the association model developed by Coleman *et al.*[1]. The objective of this work is to develop an approximate but theoretically based molecular–thermodynamic model for predicting phase equilibria of copolymer blends including specific interactions within the framework of a lattice model. Theoretical miscibility maps are compared with experiment for blends of random copolymers containing vinyl phenol and methyl acrylate segments reported by Coleman *et al.*[1]. This work is confined to binary mixtures of random copolymers at ordinary temperatures where the free-volume effect is negligible[2,3].

THEORY

Lattice model

The most frequently used lattice theory is that of Flory–Huggins which is based on a particularly simple mean-field approximation[4]. In this theory, in the absence of specific interactions, the Helmholtz energy of mixing, $\Delta_{\text{mix}}A$, is given by:

$$\frac{\Delta_{\text{mix}}A}{N_r kT}=\frac{\phi_1}{r_1}\ln\phi_1+\frac{\phi_2}{r_2}\ln\phi_2+\frac{z}{2\tilde{T}}\phi_1\phi_2 \qquad (1)$$

where N_r is the total number of lattice sites, k is the Boltzmann constant, T is the absolute temperature, r_i and ϕ_i are the number of segments per molecule and volume fraction, respectively, of component i, z is the lattice coordination number ($z=6$ in this study), and $\tilde{T}$ is a reduced temperature defined as:

$$\tilde{T}\equiv\frac{kT}{\tau_{12}} \qquad (2)$$

Here τ_{12} is the copolymer interchange energy which depends on the type of mixture[5–7]. For a mixture of type $(\text{A}_X\text{B}_{1-X})_{r_1}/(\text{A}_Y\text{B}_{1-Y})_{r_2}$, where X and Y are the surface fractions of segment A in components 1 and 2, respectively, τ_{12} is given by:

$$\tau_{12}=(X-Y)^2\omega_{\text{AB}} \qquad (3)$$

where ω_{AB} is the pair interchange energy (excluding specific interactions) defined as:

$$\omega_{\text{AB}}\equiv 2\varepsilon_{\text{AB}}-\varepsilon_{\text{AA}}-\varepsilon_{\text{BB}} \qquad (4)$$

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where ε_{ij} is the non-specific potential energy of a non-bonded *i–j* interaction. For a mixture of type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$, τ_{12} is given by:

$$\tau_{12}=X^2\omega_{AB}+XY(\omega_{AC}-\omega_{AB}-\omega_{BC})+Y^2\omega_{BC} \qquad (5)$$

where

$$\omega_{ij}=2\varepsilon_{ij}-\varepsilon_{ii}-\varepsilon_{jj} \qquad (i,j=\text{A, B C}) \qquad (6)$$

The advantage of the Flory–Huggins theory lies in its remarkably simple form. The Flory–Huggins theory, however, is based on the assumption of random mixing which is a poor assumption whenever intermolecular forces in the mixture include specific forces such as hydrogen bonding.

Another currently available theory is Guggenheim's quasichemical approximation[8] which takes deviation from random mixing into account. Although this theory is known to provide a lattice theory somewhat better than that of Flory–Huggins, the expression for $\Delta_{\text{mix}}A$ for copolymer systems is complex and inconvenient.

Our approach is different from that of the Flory–Huggins theory and Guggenheim's quasichemical approximation. We begin with the internal energy of mixing for a random mixture, $\Delta_{\text{mix}}U^*$, given by:

$$\Delta_{\text{mix}}U^*=\tfrac{1}{2}N^*_{12}\tau_{12} \qquad (7)$$

where N^*_{12} is the number of 1–2 pair interactions for a random mixture. For a real (non-random) mixture, the internal energy of mixing, $\Delta_{\text{mix}}U$, is given by:

$$\Delta_{\text{mix}}U=\tfrac{1}{2}\Gamma_{12}N^*_{12}\tau_{12} \qquad (8)$$

where Γ_{12} is the non-randomness factor which takes into account deviations from random mixing. In the Flory–Huggins theory, Γ_{12} is unity.

Based on Monte–Carlo calculations for a cubic Ising lattice (a mixture of equal-sized molecules A and B)[9], we obtained the following expression for Γ_{12}:

$$\Gamma_{12}\equiv 1-0.8031x_1x_2\left[\exp\left(\frac{\omega_{AB}}{kT}\right)-1\right] \qquad (9)$$

where x_i is the mole fraction of component *i*. Equation (9) is simpler than the corresponding equation of Guggenheim[8]:

$$\Gamma_{12}\equiv\frac{2}{1+\sqrt{1+4x_1x_2\left[\exp\left(\frac{\omega_{AB}}{kT}\right)-1\right]}} \qquad (10)$$

Application to copolymer systems was made by replacing x_i and ω_{AB} by the surface fraction, $\theta_i\equiv x_iq_i/(x_1q_1+x_2q_2)$, and τ_{12}, respectively, where q_i is the surface area parameter which is related to the number of surface contacts per molecule: $zq_i\equiv(z-2)r_i+2$.

Γ_{12} is therefore assumed to be:

$$\Gamma_{12}\equiv 1-0.8031\theta_1\theta_2\left[\exp\left(\frac{\tau_{12}}{kT}\right)-1\right] \qquad (11)$$

In the following, expressions for the Helmholtz energy of mixing based on equation (11) are called the Ising-model approximation.

Specific interactions

Following ten Brinke and Karasz[10] and Sanchez and Balazs[11], we assume that each contact point of a molecule interacts either in a specific manner (e.g. hydrogen bonding) with interaction energy $\varepsilon_{ij}+\delta\varepsilon_{ij}$ or in a non-specific manner with interaction energy ε_{ij} where *i* and *j* denote segments. Both ε_{ij} and $\delta\varepsilon_{ij}$ are negative and independent of temperature. We also assume that a fraction, f_{ij}, of the *i–j* interactions is specific and $1-f_{ij}$ is non-specific. Here f_{ij} depends only on temperature and is independent of composition. Under these assumptions, we consider as an example a mixture of type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ with specific interactions between segments A and A as well as between segments A and C.

As a zeroth approximation we consider the case where the distribution of segments is random, designated by a superscript asterisk. For that case $\Delta_{\text{mix}}U^*$ is given by:

$$\Delta_{\text{mix}}U^*=\tfrac{1}{2}N^*_{12}\Psi_{12} \qquad (12)$$

where Ψ_{12} is the copolymer interchange energy with specific interactions:

$$\Psi_{12}\equiv\tau_{12}+XY(2f_{AC}\delta\varepsilon_{AC})-X^2(f_{AA}\delta\varepsilon_{AA}) \qquad (13)$$

where τ_{12} is given by equation (5). Similarly, for a mixture of type $(A_XB_{1-X})_{r_1}/(C_YD_{1-Y})_{r_2}$ with specific interactions between segments B and B as well as between segments B and D, Ψ_{12} is given by:

$$\Psi_{12}\equiv\tau_{12}+(1-X)(1-Y)(2f_{BD}\delta\varepsilon_{BD})-(1-X)^2(f_{BB}\delta\varepsilon_{BB}) \qquad (14)$$

where

$$\tau_{12}=XY\omega_{AC}+(1-X)Y\omega_{BC}+X(1-X)\omega_{AD}$$
$$+(1-X)(1-Y)\omega_{BD}-X(1-X)\omega_{AB}-Y(1-Y)\omega_{CD} \qquad (15)$$

We assume that f_{ij} is given by the Boltzmann distribution law:

$$\frac{1-f_{ij}}{f_{ij}}=g_{ij}\exp\left\{-\frac{[\varepsilon_{ij}-(\varepsilon_{ij}+\delta\varepsilon_{ij})]}{kT}\right\} \qquad (16)$$

where g_{ij} is the ratio of the degeneracy of non-specific *i–j* interactions to that of specific *i–j* interactions; f_{ij} is therefore given by:

$$f_{ij}=\frac{1}{1+g_{ij}\exp(\delta\varepsilon_{ij}/kT)} \qquad (17)$$

Now consider the more realistic case where the distribution of segments is not random. For a non-random mixture, $\Delta_{\text{mix}}U$ is given by:

$$\Delta_{\text{mix}}U=\tfrac{1}{2}\Gamma_{12}N^*_{12}\Psi_{12} \qquad (18)$$

To obtain Γ_{12} in the presence of specific interactions[12], replace τ_{12} by Ψ_{12} in equation (11).

Helmholtz energy of mixing

The Helmholtz energy of mixing, $\Delta_{\text{mix}}A$, for the Ising-model approximation is obtained by integrating the Gibbs–Helmholtz equation using Guggenheim's athermal entropy of mixing as the boundary condition:

$$\frac{\Delta_{\text{mix}}A}{N_rkT}=\int_0^{1/\tilde{T}}\frac{\Delta_{\text{mix}}U}{N_r\tau_{12}}\,\mathrm{d}\left(\frac{1}{\tilde{T}}\right)+\left(\frac{\Delta_{\text{mix}}A}{N_rkT}\right)_{1/\tilde{T}=0} \qquad (19)$$

where

$$\left(\frac{\Delta_{\mathrm{mix}}A}{N_r kT}\right)_{1/\tilde{T}=0}=\frac{\phi_1}{r_1}\ln\phi_1+\frac{\phi_2}{r_2}\ln\phi_2 +\frac{z}{2}\left(\phi_1\frac{q_1}{r_1}\ln\frac{\theta_1}{\phi_1}+\phi_2\frac{q_2}{r_2}\ln\frac{\theta_2}{\phi_2}\right) \quad (20)$$

Use of Γ_{12} given by equation (11) has an operational advantage over the use of Guggenheim's Γ_{12} [equation (10)] because, in the presence of specific interactions, the expression for the Helmholtz energy of mixing given by equation (19) is much simpler than that which would be obtained using equation (10).

For comparison, we also make calculations using the random-mixing Flory–Huggins theory with specific interactions. With the assumptions $\Gamma_{12}=1$ and $\theta_i=\phi_i$, $\Delta_{\mathrm{mix}}A$ for the Flory–Huggins theory with specific interactions is obtained using the same procedure as that used to obtain $\Delta_{\mathrm{mix}}A$ for the Ising-model approximation.

RESULTS AND DISCUSSION

Theoretical coexistence curves and miscibility maps

In the absence of specific interactions, coexistence curves for mixtures of type $(\mathrm{A}_X\mathrm{B}_{1-X})_{r_1}/(\mathrm{A}_Y\mathrm{B}_{1-Y})_{r_2}$ calculated from the Ising-model approximation are very close to those calculated from Guggenheim's quasichemical approximation[13]. For example, for $r_1=r_2=100$; $X=0.3$; $Y=0.7$, the critical composition (ϕ_c) and reduced temperature ($\tilde{T}_c$) predicted by the Ising-model approximation are 0.5 and 100, respectively, while Guggenheim's quasichemical approximation gives $\phi_c=0.5$ and $\tilde{T}_c=99$. However, Flory–Huggins theory gives $\phi_c=0.5$ and $\tilde{T}_c=150$.

By including specific interactions between dissimilar segments, the Ising-model approximation is able to predict the closed-loop phase diagram where a lower critical solution temperature (*LCST*) lies below an upper critical solution temperature (*UCST*). Upon also including specific interactions between similar segments, the model predicts a variety of phase diagrams. *Figure 1* shows the theoretical coexistence curves predicted by the Ising-model approximation for a mixture of homopolymer 1 consisting of segment A and homopolymer 2 consisting of segment B ($r_1=r_2=500$) where specific interactions can be formed between segments A and A as well as between segments A and B. The solid curves represent the phase diagram where an *UCST* is predicted below a closed-loop coexistence curve. The broken curve is an hour-glass shaped coexistence curve.

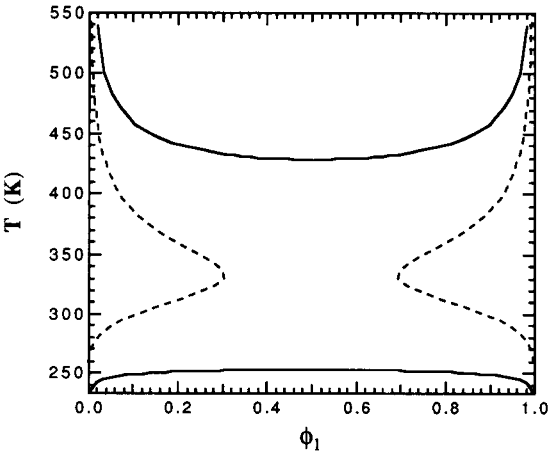

Figure 1 Theoretical coexistence curves from the Ising-model approximation for a mixture of type $\mathrm{A}_{r_1}/\mathrm{B}_{r_2}$ ($r_1=r_2=500$). Specific interactions between segments A and A as well as those between segments A and B are included. $\omega_{\mathrm{AB}}=0.456\ \mathrm{kJ\ mol^{-1}}$, $\delta\varepsilon_{\mathrm{AB}}=-2.74\ \mathrm{kJ\ mol^{-1}}$, $g_{\mathrm{AB}}=10$, $g_{\mathrm{AA}}=40$. The values of $\delta\varepsilon_{\mathrm{AA}}$ for solid and broken curves are -5.07 and $-5.13\ \mathrm{kJ\ mol^{-1}}$, respectively

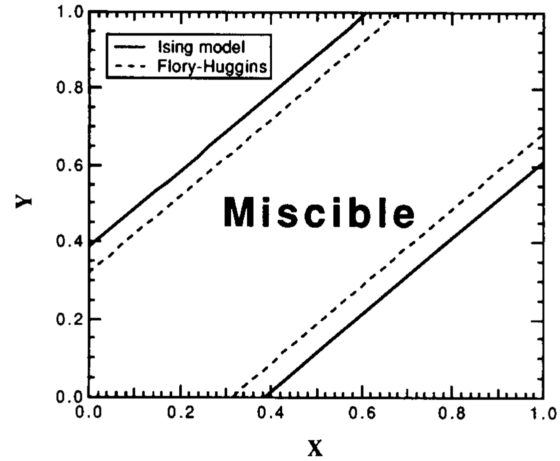

Figure 2 Miscibility map for a $(\mathrm{A}_X\mathrm{B}_{1-X})_{r_1}/(\mathrm{A}_Y\mathrm{B}_{1-Y})_{r_2}$ mixture: $r_1=r_2=1000$, $\chi_{\mathrm{AB}}=0.02$. Solid and broken curves are calculated with the Ising-model approximation and the Flory–Huggins theory, respectively

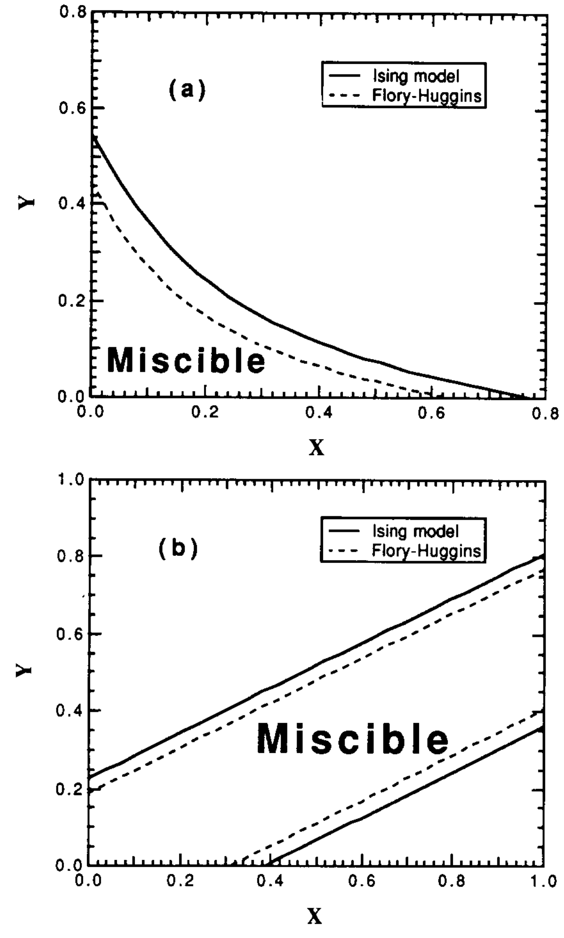

Figure 3 Miscibility map for a $(\mathrm{A}_X\mathrm{B}_{1-X})_{r_1}/(\mathrm{C}_Y\mathrm{B}_{1-Y})_{r_2}$ mixture: $r_1=r_2=1000$; (a) $\chi_{\mathrm{AB}}=0.005$, $\chi_{\mathrm{AC}}=0.06$, $\chi_{\mathrm{BC}}=0.01$; (b) $\chi_{\mathrm{AB}}=0.02$, $\chi_{\mathrm{AC}}=0.01$, $\chi_{\mathrm{BC}}=0.058$. Solid and broken curves are calculated with the Ising-model approximation and the Flory–Huggins theory, respectively

Figures 2, *3* and *4* show theoretical miscibility maps at fixed temperature in the absence of specific interactions

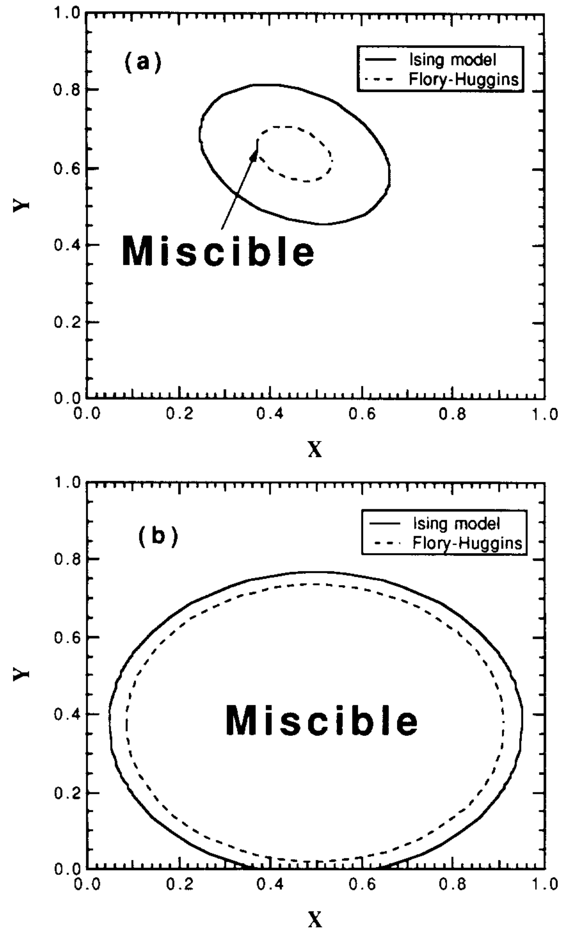

Figure 4 Miscibility map for a $(A_XB_{1-X})_{r_1}/(C_YD_{1-Y})_{r_2}$ mixture: $r_1=r_2=1000$; (b) $\chi_{AB}=0.03$, $\chi_{AC}=0.02$, $\chi_{AD}=0.01$, $\chi_{BC}=0.02$, $\chi_{BD}=0.01$, $\chi_{CD}=0.04$; (a) $\chi_{AB}=0.03$, $\chi_{AC}=0.02$, $\chi_{AD}=0.02$, $\chi_{BC}=0.01$, $\chi_{BD}=0.03$, $\chi_{CD}=0.04$. Solid and broken curves are calculated with the Ising-model approximation and the Flory–Huggins theory, respectively

for mixtures of types $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$, $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ (ref. 14) and $(A_XB_{1-X})_{r_1}/(C_YD_{1-Y})_{r_2}$ (ref. 15), respectively. Here, χ_{ij} is the Flory pair interaction parameter defined as:

$$\chi_{ij}\equiv\frac{z}{2\tilde{T}_{ij}} \tag{21}$$

where $\tilde{T}_{ij}$ is the pair reduced temperature defined as:

$$\tilde{T}_{ij}\equiv\frac{kT}{\omega_{ij}} \tag{22}$$

If a pair of copolymers with X and Y is in the miscible region, the mixture forms a single homogeneous phase in all proportions. For mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$, the theory predicts that the miscibility depends only on the composition difference $|X-Y|$. The miscibilities of some real mixtures of this type, however, were found to deviate from theoretical prediction[16]. In the absence of specific interactions, the theory predicts an *UCST* only and the miscible region increases with rising temperature. The miscible region predicted by the Ising-model approximation is larger than that obtained from Flory–Huggins theory.

Figure 5 shows a theoretical miscibility map with specific interactions at two different absolute temperatures for a mixture of type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ where specific interactions can be formed between segments A and C. Ψ_{12} is given by equation (13) with $\delta\varepsilon_{AA}=0$. The energy parameters are chosen such that the ratio of absolute temperatures is 1.1. If we set ω_{AC} to $0.836\,\mathrm{kJ\,mol^{-1}}$, $\delta\varepsilon_{AC}=-3.01\,\mathrm{kJ\,mol^{-1}}$, the mixture of homopolymer 1 consisting of segment A and homopolymer 2 consisting of segment C ($r_1=r_2=1000$) exhibits a *LCST* at ~400 K (ref. 10). Except for the pair of copolymers with X and Y near the origin where immiscibility is caused by an *UCST*, for this mixture the miscible region decreases as temperature rises because this system has a *LCST*.

Comparison with experiment

We compare the theoretical miscibility maps by the Ising-model approximation with experiment for blends of random copolymers containing vinyl phenol (VPh) and methyl acrylate (MA) segments reported by Coleman *et al.*[1,17]. In systems containing VPh and MA segments, specific interactions between VPh segments (self-association) as well as those between VPh and MA segments (solvation) must be considered.

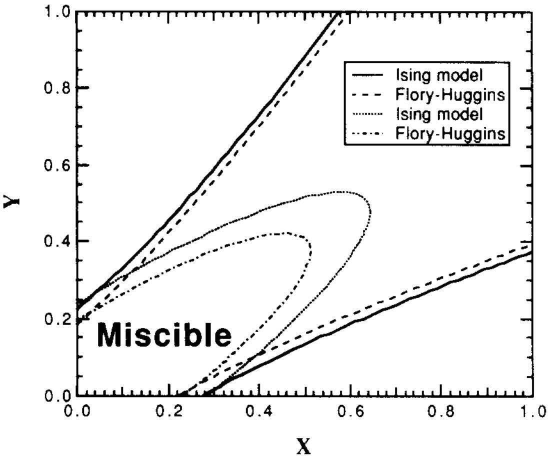

Figure 5 Miscibility map with specific interactions for a $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ mixture at two different absolute temperatures: $r_1=r_2=1000$, $\delta\varepsilon_{AC}/\omega_{AC}=-3.6$, $g_{AC}=10$. Outer curves (, - - -): $\chi_{AB}=0.04$, $\chi_{AC}=0.8$, $\chi_{BC}=0.06$. Inner curves (···, -·-): $\chi_{AB}=0.036$, $\chi_{AC}=0.73$, $\chi_{BC}=0.055$

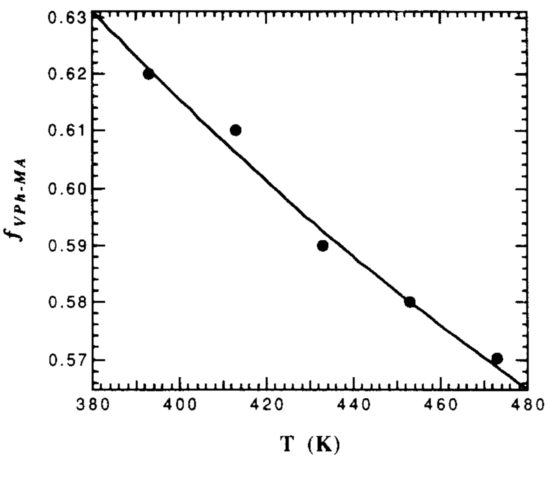

Figure 6 Fit of equation (17) to the fraction of hydrogen-bonded carbonyl groups of MA segments in the blend of PVPh homopolymer with E-MA copolymer. Blend composition of PVPh to PE-MA of 79 to 21 by volume. $\delta\varepsilon_{VPh\ MA}=-4.22\,\mathrm{kJ\,mol^{-1}}$ and $g_{VPh\ MA}=2.23$. Data are from Coleman *et al.*[17]

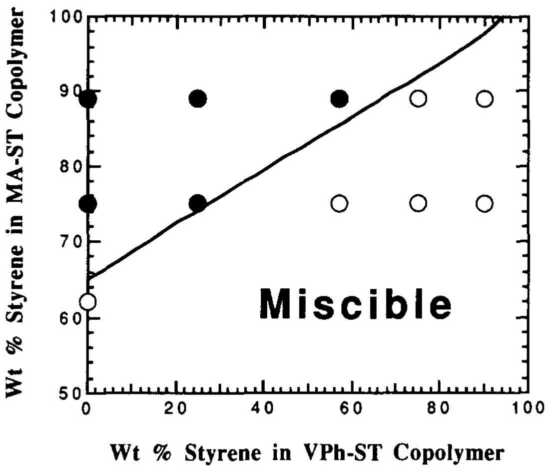

Figure 7 Comparison of theoretical miscibility map from the Ising-model approximation with experiment for the blend of poly(4-vinyl phenol-*co*-styrene) (VPh-ST) with poly(methyl acrylate-*co*-styrene) (MA-ST) at 150°C: $\delta\varepsilon_{\mathrm{VPh-MA}} = -4.22\ \mathrm{kJ\ mol^{-1}}$, $g_{\mathrm{VPh-MA}} = 2.23$, $\delta\varepsilon_{\mathrm{VPh-VPh}} = -3.39\ \mathrm{kJ\ mol^{-1}}$, $g_{\mathrm{VPh-VPh}} = 3.5$. The open and solid symbols represent, respectively, the experimentally determined miscible and immiscible points by Coleman *et al.*[1]. Theory predicts that immiscibility is caused by *LCST* behaviour

To calculate the pair interchange energy excluding specific interactions, ω_{ij}, we first calculate the Flory pair interaction parameter with:

$$\chi_{ij}=\frac{V_r}{RT}(\delta_i-\delta_j)^2 \qquad (23)$$

where V_r ($=100\ \mathrm{cm^3\ mol^{-1}}$ in this study) is the reference volume, R is the gas constant and δ_i is the solubility parameter of homopolymer consisting of segment of type i. δ_i can be estimated from group-contribution methods[1]. ω_{ij} is then obtained by equating equation (21) to equation (23):

$$\frac{\omega_{ij}}{k}=\frac{2}{z}\frac{V_r(\delta_i-\delta_j)^2}{R} \qquad (24)$$

The parameters for specific interactions between VPh and MA segments, $\delta\varepsilon_{\mathrm{VPh-MA}}$ and $g_{\mathrm{VPh-MA}}$, were obtained by assuming that in the mixture of poly(4-vinyl phenol) (PVPh) homopolymer and poly(ethylene-*co*-methyl acrylate) (E-MA, 74 wt% MA) copolymer reported by Coleman *et al.*[17], the fraction of hydrogen-bonded carbonyl groups of MA segments is equal to the fraction of VPh–MA interactions which are specific. We use the data of lowest E-MA volume fraction because at low E-MA fraction, MA segments interact primarily with PVPh. The choice of this assumption is not crucial (some other reasonable assumption could have been chosen) because we later adjust the parameters for the self-association of VPh segments such that the theoretical boundary between miscible and immiscible regions merges with the experimental boundary at a point on the miscibility map. *Figure 6* shows the fit of equation (17) with $\delta\varepsilon_{\mathrm{VPh-MA}} = -4.22\ \mathrm{kJ\ mol^{-1}}$ and $g_{\mathrm{VPh-MA}} = 2.23$ to the fraction of hydrogen-bonded carbonyl groups of MA segments (blend composition ratio of PVPh to E-MA is 79 to 21 by volume)[17].

Figure 7 compares the miscibility map calculated from the Ising-model approximation with experiment for the blend of poly(4-vinyl phenol-*co*-styrene) (VPh-ST) with poly(methyl acrylate-*co*-styrene) (MA-ST) at 150°C[1]. Since the molecular weight of polymer is not reported, the number of segments per molecule, r_1 and r_2, is set to 1000. By definition, r_i is the ratio of the molar volume of component i to the reference volume, V_r. For large values of r_1 and r_2, however, the theoretical miscibility map is insensitive to the values of r_1 and r_2. In this calculation, the surface fractions of segments (X and Y) are assumed to be equal to the volume fractions of segments. The solubility parameters and the segmental molar volumes were obtained from the literature[1,17].

In *Figure 7*, the parameters for specific interactions between VPh segments, $\delta\varepsilon_{\mathrm{VPh-VPh}}$, were obtained by assuming that the blend of PVPh homopolymer with MA-ST copolymer is immiscible above 65 wt% styrene content in MA-ST. The value of $g_{\mathrm{VPh-VPh}}$ was set to 3.5 so that the immiscibility of this blend is caused by *LCST* behaviour. If we use larger values for $g_{\mathrm{VPh-VPh}}$, the theory predicts that immiscibility is caused by *UCST*. With $\delta\varepsilon_{\mathrm{VPh-VPh}} = -3.39\ \mathrm{kJ\ mol^{-1}}$ and $g_{\mathrm{VPh-VPh}} = 3.5$, the theory predicts that immiscibility in the blends of VPh-ST with MA-ST is caused by *LCST* behaviour. We then use these parameters to predict the miscibility map of other systems containing VPh and MA segments.

Figure 8 compares the miscibility map predicted by the Ising-model approximation with experiment for the blend of VPh-ST with E-MA at 25°C[1,17]. The surface fractions of segments are assumed to be equal to the volume fractions of segments. The parameters for specific interactions are identical to those used in *Figure 7*. The model predicts that immiscibility is caused by *LCST* behaviour. Agreement with experiment is good.

CONCLUSIONS

A simple lattice theory, based on an Ising-model approximation, has been developed for calculating phase equilibria in copolymer systems. Specific interactions (hydrogen bonding) were also included based on the incompressible lattice-gas model by ten Brinke and Karasz[10]. The resulting expression for the Helmholtz energy of mixing is able to predict immiscibility caused

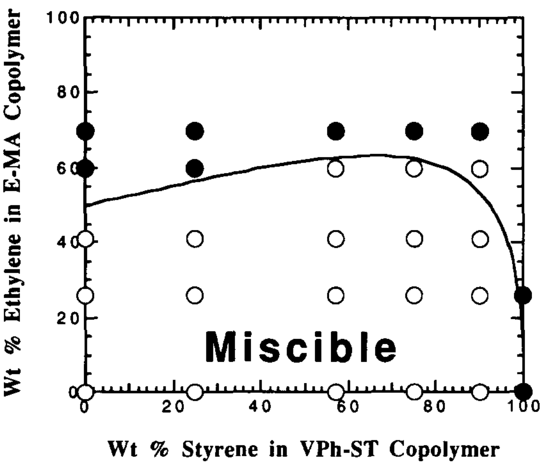

Figure 8 Comparison of predicted miscibility map from the Ising-model approximation with experiment for the blend of poly(4-vinyl phenol-*co*-styrene) (VPh-ST) with poly(ethylene-*co*-methyl acrylate) (E-MA) at 25°C. The parameters for specific interactions are identical to those used in *Figure 7*. The open and solid symbols, respectively, represent the experimentally determined miscible and immiscible points by Coleman *et al.*[1,17]. Theory predicts that immiscibility is caused by *LCST* behaviour

by *LCST* behaviour. The miscible area predicted by the Ising-model approximation is larger than that obtained from the Flory–Huggins theory. For systems containing vinyl phenol and methyl acrylate segments, predicted miscibility maps are in good agreement with experiment.

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NOMENCLATURE

$\Delta_{\text{mix}}A$	Helmholtz energy of mixing
A	Segment of type A
B	Segment of type B
C	Segment of type C
D	Segment of type D
f_{ij}	Fraction of *i–j* interactions which are specific
g_{ij}	Degeneracy parameter for *i–j* contact
k	Boltzmann constant
N_{12}	Number of 1–2 contacts for a real (non-random) mixture
N_{12}^{*}	Number of 1–2 contacts for a random mixture
N_r	Total number of lattice sites
q_i	Surface parameter for component *i*
R	Gas constant
r_i	Size parameter for component *i*
T	Absolute temperature
$\tilde{T}$	Reduced temperature
$\tilde{T}_c$	Reduced critical temperature
$\tilde{T}_{ij}$	Pair reduced temperature
$\Delta_{\text{mix}}U$	Internal energy of mixing
V_r	Reference volume, a constant here set at $100\,\text{cm}^3\,\text{mol}^{-1}$
X	Surface fraction of segment A in component 1
x_i	Mole fraction of component *i*
Y	Surface fraction of segment A or C in component 2
z	Lattice coordination number, a constant here set equal to 6

Greek letters

Γ_{12}	Non-randomness factor for 1–2 contact
δ_i	Solubility parameter of homopolymer consisting of segment of type *i*
$\delta\varepsilon_{ij}$	Difference between specific interaction energy and non-specific interaction energy of *i–j* contact
ε_{ij}	Non-specific interaction energy of *i–j* contact
θ_i	Surface fraction of component *i*
τ_{12}	Copolymer interchange energy excluding specific interactions
ϕ_c	Critical volume fraction
ϕ_i	Volume fraction of component *i*
χ_{ij}	Flory pair interaction parameter
Ψ_{12}	Copolymer interchange energy including specific interactions
ω_{ij}	Pair interchange energy excluding specific interactions