Equation-of-State Analysis of Binary Copolymer Systems. 2. Homopolymer and Copolymer Mixtures

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ABSTRACT: The perturbed hard-sphere-chain (PHSC) equation of state for copolymer systems is applied to binary homopolymer blends and to mixtures of homopolymer and copolymer. Theoretical results for the effect of copolymer composition on lower critical solution temperature (LCST) are compared with experiment for homopolymer/copolymer mixtures containing poly(methyyl methacrylate-*co*-styrene) (MMA-*co*-S) and poly(acrylonitrile-*co*-styrene) (AN-*co*-S) random copolymers. The intersegmental parameters for the MMA−S and AN−S pairs are obtained from the miscibility maps containing MMA-*co*-S and AN-*co*-S random copolymers, respectively, differing in copolymer compositions. The homopolymer/copolymer systems studied in this work exhibit LCSTs in the experimentally accessible temperature range as the copolymer approaches 100% polystyrene. The PHSC equation of state predicts that the LCST of a homopolymer/copolymer system exhibits a maximum as the copolymer composition varies. Unique values are assigned to the intersegmental parameters for a given pair of segments.

Introduction

Phase behavior of copolymer mixtures at constant temperature and pressure depends primarily on copolymer composition and molecular weight. It is well-known that, without introducing favorable interactions such as hydrogen bonding between unlike molecules,[1,2] a mixture of a homopolymer and a copolymer or a pair of copolymers can be miscible over only a restricted copolymer composition range. Several authors have reported the so-called miscibility window in binary mixtures, where miscibility changes from immiscible → miscible → immiscible as the copolymer composition of one component varies.[3-6] The miscibility window occurs because intramolecular interactions become more unfavorable as the copolymer composition varies, leading to more favorable intermolecular interactions relative to intramolecular interactions. In addition to the miscibility window, some experimental evidence exists for the immiscibility window, where miscibility changes from miscible → immiscible → miscible as the copolymer composition of one component varies.[7,8]

Miscibility and immiscibility windows can be qualitatively explained by the well-known incompressible Flory−Huggins model[1,9-11] that represents only upper critical solution temperature (UCST) behavior associated with the phase separation upon cooling. Many miscible polymer blends, however, exhibit lower critical solution temperature (LCST) behavior at elevated temperature. In the absence of specific interactions, LCST behavior is caused by the free-volume effect arising from different compressibilities of components in the mixture. Equation-of-state theories are necessary to represent immiscibility caused by LCST behavior due to the free-volume effect. Equation-of-state theories are also able to represent immiscibility caused by UCST phase behavior.

Recently, several attempts have been made to generalize the existing equations of state for homopolymer systems to copolymer systems. In principle, equations of state for copolymer systems can be obtained by replacing the characteristic parameters of homopolymers with those of copolymers averaged over copolymer compositions. Among several equations of state applicable to homopolymer systems, the lattice-fluid model[12-14] was generalized for copolymer systems by Panayiotou[15] and by Kim et al.[16-18] Models based on the Prigogine−Flory−Patterson theory[19-21] were developed by Kammer et al.[22-24] and by Lee et al.[25,26] In addition to the free-volume effect, the model by Kammer et al.[23] also includes the effect of differences in segmental sizes. Generalization of Flory's equation of state for homopolymer systems[20,27] to copolymer systems was made by Shiomi et al.[28,29] Koningsveld et al.[30,31] also introduced the mean-field lattice-gas approach into their incompressible lattice-based theory for copolymer systems such that the model can predict LCST phase behavior arising from the free-volume effect. All of these equations of state are capable of representing the LCST caused by the free-volume effect. For copolymer systems, however, there has been little extensive comparison of equation-of-state theory with experiment.

Recently, Song et al.[32-35] and Hino et al.[36] presented a perturbed hard-sphere-chain (PHSC) equation of state applicable to mixtures of heteronuclear chain molecules. The PHSC equation of state for copolymer systems was *not* obtained by simply replacing the characteristic parameters of homopolymers with those of copolymers averaged over copolymer compositions. The PHSC equation of state for real copolymer mixtures[36] is based on a modified form of Chiew's equation of state[37] for athermal mixtures of heteronuclear hard-sphere chains by Song et al.[32] and a van der Waals perturbation whose parameters are related to the intermolecular potential as suggested by Song and Mason.[33] The screening effect, an effect of sequence distribution in the copolymer, was introduced into the PHSC equation of state in the first paper of this series.[38]

For copolymer systems, the most challenging task in the calculation of phase equilibria is to represent the phase behavior of various copolymer mixtures using only one consistent set of intersegmental parameters. For utility, the intersegmental parameters of a thermodynamic model for copolymer systems need to be independent of the type of mixtures. In this work, we

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Table 1. PHSC Equation-of-State Parameters for Homopolymers[33]

polymer	r/M (mol/g)	σ(Å)	ϵ/k_B (K)
polystyrene	0.011 17	5.534	724.7
poly(methyl methacrylate)	0.014 32	4.850	655.9
poly(vinyl methyl ether)[a]	0.018	4.659	489.5
polyacrylonitrile[a]	0.010 57	5.414	769.5
tetramethyl Bisphenol A polycarbonate[a]	0.012	5.249	631.6
poly(cyclohexyl methacrylate)	0.014 82	4.889	607.2

[a] This work.

compare the theoretical miscibility windows computed from the PHSC equation of state by Hino et al.[36] with experiment, using the same set of intersegmental parameters. The systems studied are homopolymer blends, homopolymer/copolymer mixtures, and a mixture of random copolymers containing two kinds of segments; these mixtures are denoted as A_{r_1}/B_{r_2}, $A_{r_1}/(C_YB_{1-Y})_{r_2}$, and $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$, respectively, where r_i is the number of effective hard spheres per molecule of component i and X and Y are segment number fractions for segments A and A or C in components 1 and 2, respectively. The systems $A_{r_1}/(C_YB_{1-Y})_{r_2}$ studied in this work exhibit LCSTs in the experimentally accessible temperature range as $Y \rightarrow 0$. The intersegmental parameters obtained here are used to analyze the more complicated copolymer systems in the third publication of this series.

Theory

Details of the PHSC equation of state for copolymer systems are given in refs 32 and 36.

Equation-of-State Parameters. The PHSC equation of state requires three parameters to describe homopolymers: number of effective hard spheres per molecular weight of polymer (M), r/M; segmental diameter, σ; and nonbonded segment pair-interaction energy, ϵ. These parameters were regressed from available pressure–volume–temperature (PVT) data for several homopolymers; they are tabulated in ref 33. The PHSC equation-of-state parameters of the homopolymers used in this work are given in Table 1.

The equation-of-state parameters for copolymer systems are computed as discussed in the first paper of this series. The weight-average molecular weight is used to compute the equation-of-state parameters.[38] In this work, M_i ($i = 1, 2$) is the weight-average molecular weight of component i used to compute equation-of-state parameters.

Equation-of-state parameters are not unique. Although the PHSC equation of state fits the pure-component PVT data of homopolymers very well, the set of equation-of-state parameters that gives the best fit of PVT data does not produce the phase diagrams consistent with experiment for the systems polystyrene/poly(vinyl methyl ether) (PS/PVME) and PS/tetramethyl Bisphenol A polycarbonate (TMPC) which show LCST phase behavior. The theoretical phase diagrams in these mixtures are sensitive to the ratios of equation-of-state parameters. It was therefore necessary to adjust the equation-of-state parameters of one component (PVME and TMPC) by first presetting r/M and then regressing for ϵ and σ. With the adjusted equation-of-state parameters, however, the PHSC equation of state still gives a better fit of the homopolymer PVT data than the lattice-fluid equation of state.[12-14]

Intersegmental Parameters. For a given pair of dissimilar segments α and β, the PHSC equation of state requires at least one adjustable intersegmental param-

eter, $\kappa_{\alpha\beta}$:[36,38]

$$\epsilon_{\alpha\beta} = \sqrt{\epsilon_\alpha \epsilon_\beta}(1 - \kappa_{\alpha\beta}) \quad (\alpha \neq \beta) \quad (1)$$

where ϵ_α is the minimum potential energy of the nonbonded segment–segment pair potential between similar segments α. Similarly, $\epsilon_{\alpha\beta}$ is the minimum potential energy between dissimilar segments α and β. An additional adjustable intersegmental parameter, $\zeta_{\alpha\beta}$, can also be introduced to relax the additivity of effective hard-sphere diameters of unlike segments α and β:[36,38]

$$b_{\alpha\beta}^{1/3} = \frac{(b_\alpha^{1/3} + b_\beta^{1/3})}{2}(1 - \zeta_{\alpha\beta}) \quad (\alpha \neq \beta) \quad (2)$$

where b_α and $b_{\alpha\beta}$ represent the van der Waals covolumes for effective hard spheres between similar and dissimilar segments, respectively; b_α and $b_{\alpha\beta}$ account for the excluded volume due to repulsive forces. The intersegmental parameters are obtained from experimental phase boundaries such as the critical point of the mixture and the boundary between miscible and immiscible regions on the miscibility map.

Calculation Procedure. The expressions for the spinodal and critical conditions as well as the chemical potential are required to perform phase equilibrium calculations; they are given in ref 36. Details of calculation procedures are given in the first paper of this series.[38]

Results and Discussion

System Poly(vinyl methyl ether)/Polystyrene. We first obtain the intersegmental parameters for the vinyl methyl ether–styrene (VME–S) pair from the phase diagrams of the system poly(vinyl methyl ether)/polystyrene (PVME/PS), which shows LCST type phase behavior. Using a fluorescence emission technique, Walsh et al.[39] reported a detailed analysis of molecular weight dependence of phase separation temperatures in the system PVME/PS. When the molecular weights of both PS and PVME are high, the system PVME/PS has a critical composition of about 80–90 wt % PVME.

The pure-component PVT data of PVME are reported in a figure in ref 40; they are, however, not tabulated. The PVT data of PVME were therefore simulated in the range 100–200 °C and 100–300 bar by the Simha and Somcynsky equation of state[41] using the parameters listed in ref 41. The PHSC equation-of-state parameters for PVME were then obtained by regressing the simulated PVT data. It was, however, necessary to preset one of three equation-of-state parameters because theory predicts an UCST in the system PVME/PS when the equation-of-state parameters for PVME obtained by three-parameter regression are used. With only one adjustable parameter κ, PHSC theory, using the equation-of-state parameters for PVME obtained by presetting r/M to 0.018, gives satisfactory agreement with experiment for the system PVME/PS. Additional intersegmental parameter ζ was later introduced such that the dependence of LCST on the molecular weight of PS is correctly predicted. Equation-of-state parameters for PVME are given in Table 1.

Figure 1a shows experimental phase diagrams and theoretical coexistence curves for the system PVME/PS with various molecular weights of PS reported by Walsh et al.[39] The intersegmental parameters for the VME–S pair are obtained such that the molecular weight dependence of LCSTs in Figure 1a is correctly repre-
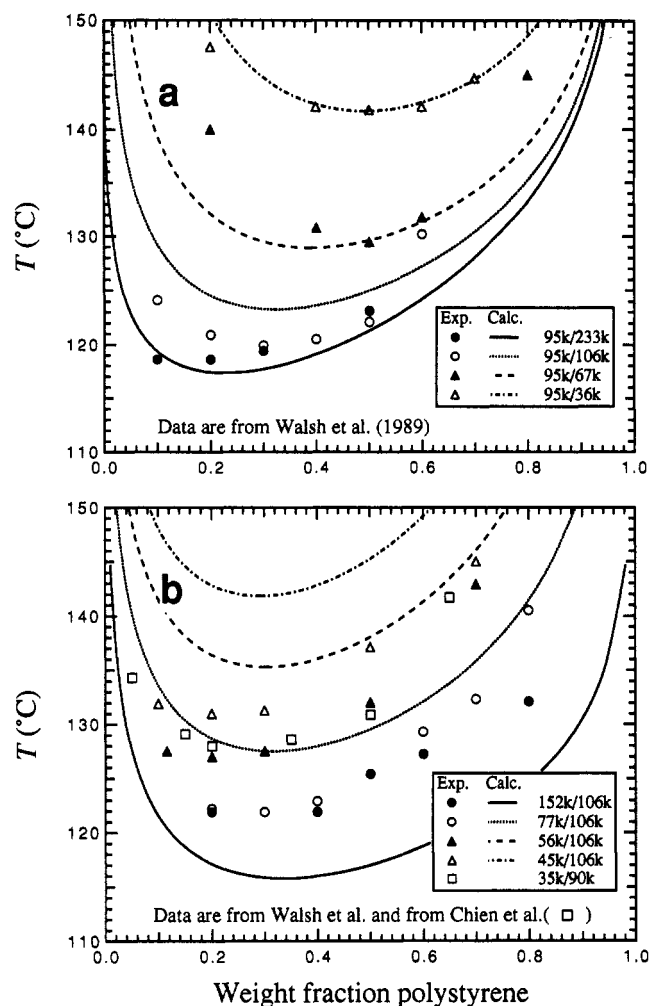
Figure 1. (a) Experimental phase diagrams and theoretical coexistence curves for the system PVME/PS with various molecular weights of PS.[39] (b) Experimental phase diagrams and theoretical coexistence curves for the system PVME/PS with various molecular weights of PVME.[39,42] In all calculations, $\kappa_{VME-S} = 0.010\ 93$ and $\zeta_{VME-S} = 0.0003$. M_w and M_w/M_n of polymers are given in Table 3.

Table 2. Intersegmental Parameters

binary pair	κ	ζ
styrene−methyl methacrylate[a]	−0.021 25	−0.02
styrene−acrylonitrile	0.050 55	0
	(0.085)	(0)
vinyl methyl ether−styrene	0.010 93	0.000 3
vinyl methyl ether−methyl methacrylate	−0.025 3	−0.014 64
vinyl methyl ether−acrylonitrile	0.055 98	0.002 86
	(0.089 74)[c]	(0.004 25)[c]
TMPC−styrene[b]	−0.004 402	−0.003 166
TMPC−methyl methacrylate	−0.027 03	−0.018 10
TMPC−acrylonitrile	0.056 87	0.008 32
	(0.084 92)[c]	(0.007 47)[c]
cyclohexyl methacrylate−styrene	0.001 936	−0.001 718
cyclohexyl methacrylate−acrylonitrile	0.042 17	−0.003 17
	(0.063 27)[c]	(−0.007 70)[c]

[a] Reference 38. [b] Tetramethyl Bisphenol A polycarbonate. [c] For $\kappa_{S-AN} = 0.085$.

sented by the model; they are given in Table 2. Figure 1b shows experimental phase diagrams and theoretical coexistence curves for the system PVME/PS with various molecular weights of PVME by Walsh *et al.*[39] and Chien *et al.*[42] Theoretical coexistence curves are calculated using parameters identical to those used in Figure 1a. Theory slightly overestimates the molecular weight dependence of LCST for the systems in Figure 1b, perhaps because of polydispersity in PVME and of

Table 3. Characterization of Polymer Samples Used in Reference 39

sample	M_w	$M_w/M_n{}^a$
PS233	233000	1.06
PS106	106000	1.06
PS90[b]	90000	1.05
PS67	67000	1.08
PS36	35700	1.05
PVME152	152000	1.13
PVME95	95000	1.27
PVME77	77000	1.24
PVME56	56000	1.47
PVME45	45000	2.05
PVME35[b]	35200	1.91

[a] M_n, number-average molecular weight (g/mol); M_w, weight-average molecular weight (g/mol). [b] Reference 42.

uncertainty in the equation-of-state parameters for PVME. The characteristics of polymer samples used by Walsh *et al.*[39] and Chien *et al.*[42] are given in Table 3.

Systems Containing Vinyl Methyl Ether, Styrene, and Methyl Methacrylate. The copolymer-composition dependence of phase separation temperatures of the system PVME/poly(methyl methacrylate-*co*-styrene) (MMA-*co*-S) was first measured by Chien *et al.* by cloud-point measurement[42] and later by Halary *et al.* using a fluorescence-quenching technique.[43] The results of Chien *et al.* agree very well with those of Halary *et al.* The mixture of PVME and PS used by those authors is miscible up to about 120 °C. As the methyl methacrylate content rises, the LCST of the copolymer systems first increases and then decreases, going through the maximum LCST of about 150 °C when the copolymer contains about 20% MMA by weight.

To describe the phase behavior of the mixture of type $A_{r_1}/(C_Y B_{1-Y})_{r_2}$, three sets of intersegmental parameters are required. The parameters for the S−MMA pair, $\kappa_{S-MMA} = -0.02125$ and $\zeta_{S-MMA} = -0.02$, were obtained in the first paper of this series[38] from the miscibility map of the mixture of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ containing S-*co*-MMA random copolymers. Although the system $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ containing S-*co*-MMA random copolymers exhibits the screening effect, theoretical miscibility map and experiment show good agreement in the styrene-rich region without introducing the screening effect into the theory.[38] The intersegmental parameters for the VME−S pair were obtained in Figure 1a from experimental phase diagrams of the mixture of type A_{r_1}/B_{r_2} containing PVME and PS. With these two sets of intersegmental parameters, we use the phase diagram of the system PVME/(MMA-*co*-S) at a fixed copolymer composition reported by Chien *et al.*[42] to obtain the remaining intersegmental parameters for the VME−MMA pair. The polymer samples used by Chien *et al.*, however, are polydisperse; $M_w/M_n = 1.9$ for PVME and $M_w/M_n \cong 1.6$ for MMA-*co*-S copolymers where M_n is the number-average molecular weight. Therefore, it was first necessary to adjust slightly the κ_{VME-S} obtained in Figure 1a to 0.011 01 such that the theoretical LCST agrees with experiment in the system PVME/PS studied by Chien *et al.*[42]

Figure 2 compares theoretical coexistence and spinodal curves with cloud points for the system PVME/(MMA-*co*-S) containing 29.2% methyl methacrylate by weight in the copolymer. The intersegmental parameters for the VME−MMA pair were obtained by assuming that the critical temperature and mixture composition are 127 °C and 79 wt % PVME, respectively; they are given in Table 2. Agreement between the theoreti-
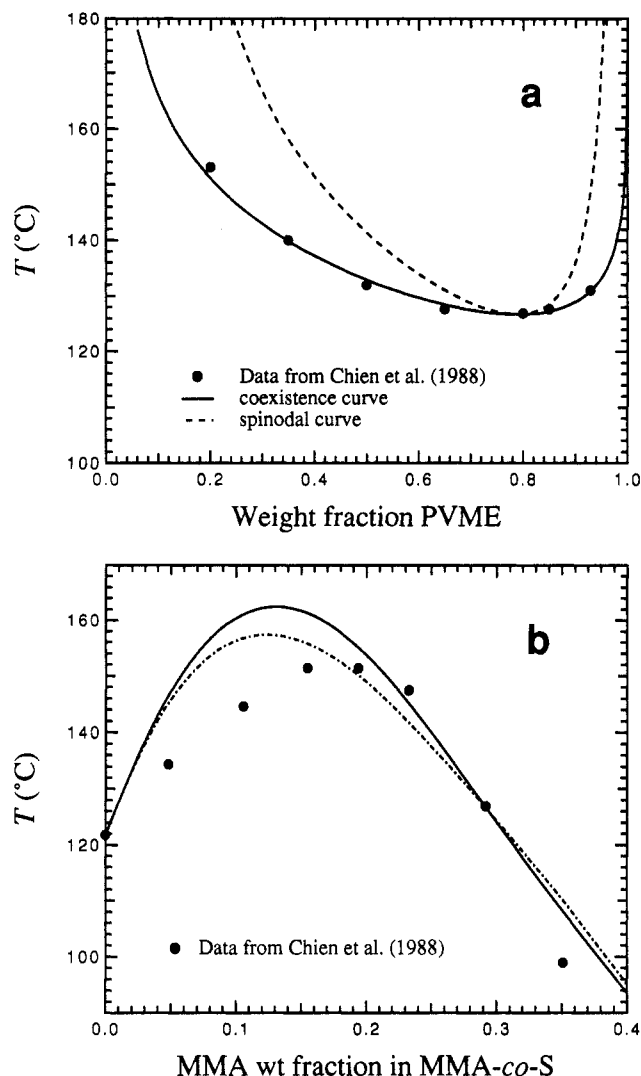
Figure 2. (a) Comparison of theoretical coexistence and spinodal curves with cloud points for the system PVME/(MMA-co-S) containing 29.2% MMA by weight in the copolymer.[42] Theoretical curves are for $M_1 = 35\ 200$ and $M_2 = 130\ 000$: $\kappa_{VME-S} = 0.011\ 01$, $\zeta_{VME-S} = 0.0003$, $\kappa_{VME-MMA} = -0.0253$, $\zeta_{VME-MMA} = -0.01464$, $\kappa_{S-MMA} = -0.02125$, and $\zeta_{S-MMA} = -0.02$. (b) Copolymer-composition dependence of LCST for the system PVME/(MMA-co-S):[42] $M_1 = 35\ 200$ and $M_2 = 130\ 000$, (—) Theory with the parameters used in Figure 6a; (— · —) Theory with $\kappa_{VME-MMA} = -0.02879$ and $\zeta_{VME-MMA} = -0.01685$.

cal coexistence curve and experimental cloud points is good. To examine how the choice of critical composition affects the prediction of LCST at different copolymer compositions, we also obtain the second set of intersegmental parameters for the VME−MMA pair ($\kappa_{VME-MMA} = -0.02879$, $\zeta_{VME-MMA} = -0.01685$) by assuming that the critical composition is 60 wt % PVME.

Figure 2b compares the calculated copolymer composition dependence of LCST for the system PVME/(MMA-co-S) with experiment determined by cloud-point measurements.[42] Theoretical LCSTs are for $M_1 = 35\ 200$ and $M_2 = 130\ 000$, respectively. The model underestimates the methyl methacrylate composition at which the LCST is the maximum. Because our calculations neglect the possible screening effect in MMA-co-S copolymers,[38] theory and experiment are in surprisingly good agreement. The maximum LCST is slightly lower for the second set of intersegmental parameters for the VME−MMA. However, it is clear that the choice of critical composition in Figure 2a does not have a significant effect on the prediction of LCST.

In the system PVME/(MMA-co-S), LCST increases as the methyl methacrylate content rises because intramolecular interactions of copolymers become more unfavorable, leading to more favorable intermolecular interactions relative to intramolecular interactions. The maximum LCST therefore depends primarily on the magnitude of interaction energies between methyl methacrylate and styrene segments. Figure 2b shows that the previously determined intersegmental parameters for the S−MMA pair can be used as the parameters for the S−MMA pair in the system PVME/(MMA-co-S). These intersegmental parameters were obtained from the mixture containing S-co-MMA random copolymers differing in copolymer compositions, Figure 3 of ref 38.

Systems Containing Vinyl Methyl Ether, Styrene, and Acrylonitrile. The LCST in the system PVME/(MMA-co-S) increases as much as about 30 °C relative to that in the system PVME/PS. An interesting question is how much the LCST increases if methyl methacrylate in the MMA-co-S copolymer is replaced by acrylonitrile, which has more unfavorable interactions with styrene. For the mixture of PVME with poly-(acrylonitrile-co-styrene) (AN-co-S) random copolymer, the copolymer-composition dependence of cloud-point temperatures at a fixed mixture composition was measured by Min and Paul.[44] The mixture composition was chosen to be 80% PVME by weight because the minimum in the cloud points occurs near this composition. The data by Min and Paul may be taken as the LCST of the system PVME/(AN-co-S).

Pure-component *PVT* data of polyacrylonitrile (PAN) are not available. The PHSC equation-of-state parameters for PAN were obtained as follows. We first regress the equation-of-state parameters (ϵ, σ, and r/M) of AN-co-S random copolymers[18] at various acrylonitrile contents using the PHSC equation of state for homopolymers.[33] A plot of equation-of-state parameters obtained in this manner against the mole fraction of acrylonitrile in the copolymer roughly follows straight lines. Equation-of-state parameters for PAN were then obtained by linear extrapolation to zero styrene content in the copolymer; they are given in Table 2.

Only limited information is available for the phase behavior of the mixture containing acrylonitrile and styrene segments from which the intersegmental parameters for the S−AN pair can be obtained. An experimental miscibility map of a mixture of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ containing AN-co-S random copolymers in the styrene-rich region was obtained by Molau.[45] Schmitt *et al.*[46] also reported the molecular weight dependence of the partial miscibility map at a fixed acrylonitrile composition of one component. Unfortunately, refs 45 and 46 do not report the temperatures at which those miscibility maps represent the phase behavior of the mixture. Molau,[45,47] however, implied that the experiment was carried out at temperatures above the glass transition temperature of the mixture.

To obtain the intersegmental parameters for the S−AN pair, we use the data by Molau[45] assuming that the miscibility map was obtained at 170 °C. Figure 3 compares the theoretical miscibility map with experiment for the mixture of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ containing AN-co-S random copolymers ($M_w = 140\ 000−170\ 000$ g/mol, $M_w/M_n = 1.3−2.0$). Theoretical miscibility maps were computed at 170 °C for $M_1 = M_2 = 150\ 000$ using only one intersegmental parameter, κ_{S-AN} (ζ_{S-AN}
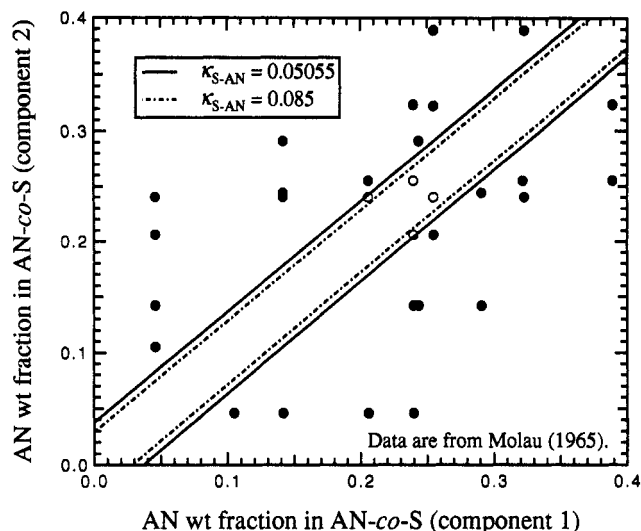
Figure 3. Comparison of theoretical miscibility maps with experiment for mixtures of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ containing AN-*co*-S random copolymers:[45] (O) miscible; (●) immiscible. Theoretical miscibility maps are at 170 °C for $M_1 = M_2 =$ 150 000; (—) $\kappa_{S-AN} = 0.050\ 55$, $\zeta_{S-AN} = 0$; (-··-) $\kappa_{S-AN} = 0.085$, $\zeta_{S-AN} = 0$. Theory predicts that immiscibility is caused by UCST behavior. For this system, however, the origin of immiscibility is not reported.

Figure 4. Copolymer-composition dependence of cloud points for the system PVME/(AN-*co*-S) containing 80 wt % PVME.[44] Curves are calculated LCSTs for $M_1 = 99\ 000$ and $M_2 = 200\ 000$: $\kappa_{VME-S} = 0.010\ 96$, $\zeta_{VME-S} = 0.0003$; (—) $\kappa_{S-AN} = 0.085$, $\zeta_{S-AN} = 0$, $\kappa_{VME-AN} = 0.089\ 74$, $\zeta_{VME-AN} = 0.004\ 25$; (-··-) $\kappa_{S-AN} = 0.050\ 55$, $\zeta_{S-AN} = 0$, $\kappa_{VME-AN} = 0.055\ 98$, and $\zeta_{VME-AN} = 0.002\ 86$.

$= 0$). Because it is difficult to identify the boundary between miscible and immiscible regions and because the temperature is not known precisely, we obtain two intersegmental parameters; $\kappa_{S-AN} = 0.050\ 55$ and 0.085. The theoretical miscibility map with $\kappa_{S-AN} = 0.050\ 55$ gives a slightly wider miscible area than that with $\kappa_{S-AN} = 0.085$. The theory with $\kappa_{S-AN} = 0.085$ also seems to underestimate slightly the miscible area. With these parameters, theory predicts that immiscibility is caused by UCST behavior.

It is possible to estimate the intersegmental parameters that predict immiscibility due to LCST behavior. To obtain LCST behavior in the system shown in Figure 3, it is necessary to use an unreasonably large ζ_{S-AN} (e.g., -0.1). Such a large ζ_{S-AN}, however, is physically unrealistic because with this value the second virial cross coefficient for acrylonitrile and styrene segments deviates more than 30% from that obtained with the assumption of additivity of effective hard-sphere diameters. The measured densities of AN-*co*-S random copolymers indicate that the AN-*co*-S random copolymer essentially exhibits volume additivity.[4]

The remaining intersegmental parameters for the VME−AN pair are obtained using the LCST of the system PVME/(AN-*co*-S) at a fixed copolymer composition reported by Min and Paul.[44] Although Min and Paul did not report the polydispersity indexes of the polymers, these polymers may be polydisperse. It was therefore necessary to adjust slightly the κ_{VME-S} obtained in Figure 1a to 0.010 96 such that the theoretical LCST agrees with experiment in the system PVME/PS studied by these authors. Experiment shows that, for the system PVME/(AN-*co*-S) containing 80% PVME by weight, the cloud-point temperature is approximately 128 °C when the copolymer contains 11.5% acrylonitrile by weight. We take this point as the LCST of the mixture and obtain the intersegmental parameters for the VME−AN pair from the LCST. Intersegmental parameters for the VME−AN pair are given in Table 2.

Figure 4 compares the copolymer-composition dependence of theoretical LCST for the system PVME/(AN-
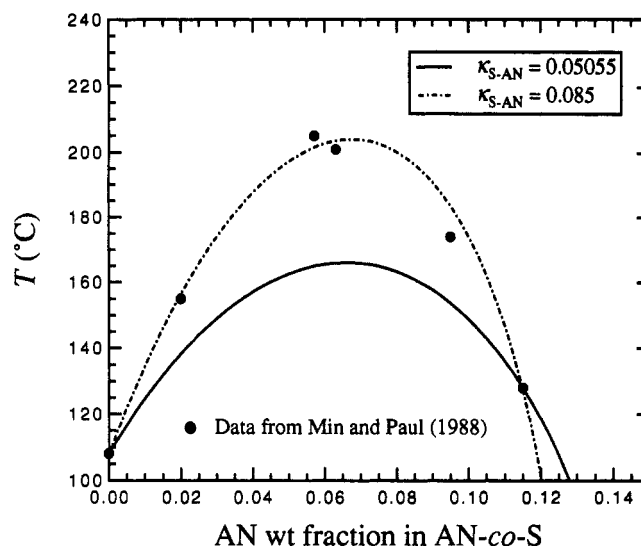
co-S) with the cloud points of the mixtures containing 80 wt % PVME. Theoretical LCSTs are for $M_1 = 99\ 000$ and $M_2 = 200\ 000$. Although the copolymer composition at which the LCST is the maximum is smaller for the system PVME/(AN-*co*-S) (7% AN by weight) than that for the system PVME/(MMA-*co*-S) (20% MMA by weight), the increase in the LCST for the system PVME/(AN-*co*-S) is higher than that for the system PVME/(MMA-*co*-S). This observation follows because the interactions between acrylonitrile and styrene segments are more unfavorable than those between methyl methacrylate and styrene.

In Figure 4, the curve with $\kappa_{S-AN} = 0.050\ 55$ gives lower LCST than that with $\kappa_{S-AN} = 0.085$, which represents more unfavorable interactions between acrylonitrile and styrene segments. The maximum LCST appears to be sensitive to the choice of intersegmental parameter κ_{S-AN}.

Systems Containing Tetramethyl Bisphenol A Polycarbonate, Styrene, and Methyl Methacrylate. The copolymer-composition dependences of LCST in the system $A_{r_1}/(C_Y B_{1-Y})_{r_2}$ are also reported for mixtures of tetramethyl Bisphenol A polycarbonate (TMPC) and MMA-*co*-S and for the system TMPC/(AN-*co*-S) studied by Kim and Paul.[18] The phase separation temperatures in these systems are about 120 °C higher than those in the systems PVME/(MMA-*co*-S) and PVME/(AN-*co*-S). TMPC and polystyrene (PS) are miscible up to about 240 °C.[18]

Pure-component *PVT* data for TMPC are reported by Kim and Paul in ref 17 together with the phase diagram of the system TMPC/PS. These authors determined the phase separation temperatures by the dsc method. In this technique, the polymer blends of known proportions were first annealed for 5 min at temperatures near the expected phase separation temperature. The breadth of the glass transition region in the dsc scans was then determined as a function of annealing temperature; the onset of a large change in this plot was identified as the phase separation temperature.

The PHSC equation-of-state parameters ϵ and σ of TMPC were regressed by presetting r/M to 0.012. To
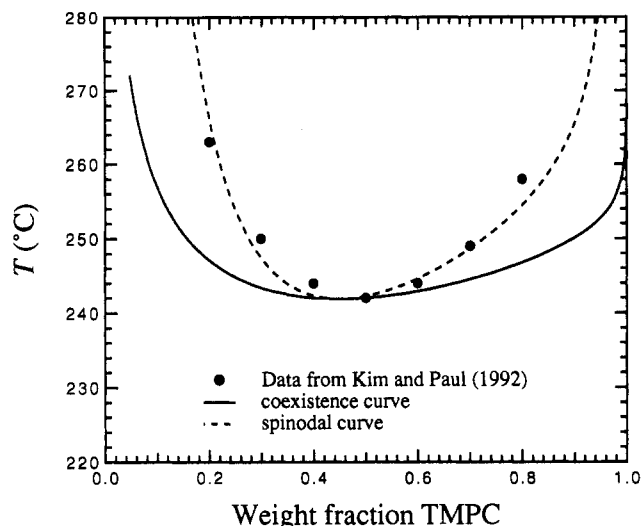
Figure 5. Comparison of theory with experimental phase diagram determined by the dsc method for the system TMPC/PS.[18] Theory is for $M_1 = 33\,000$ and $M_2 = 330\,000$ with $\kappa_{TMPC-S} = -0.004\,402$ and $\zeta_{TMPC-S} = -0.003\,166$.

Figure 6. Copolymer-composition dependence of LCST for the system TMPC/(MMA-*co*-S).[18] Solid curve is the calculated LCST for $M_1 = 33\,000$ and $M_2 = 200\,000$: $\kappa_{TMPC-S} = -0.004\,402$. $\zeta_{TMPC-S} = -0.003\,166$, $\kappa_{TMPC-MMA} = -0.027\,03$, $\zeta_{TMPC-MMA} = -0.018\,10$, $\kappa_{S-MMA} = -0.021\,25$, and $\zeta_{S-MMA} = -0.02$.

obtain good agreement of theory with the experimental phase diagram in the system TMPC/PS, it was necessary to use the equation-of-state parameters obtained by presetting r/M to this value. The equation-of-state parameters ϵ and σ for TMPC that give the best fit of pure-component *PVT* data are about 30% smaller than those of PS. When the optimum equation-of-state parameters of TMPC are used, theory predicts an UCST in the system TMPC/PS where experiment shows a LCST, probably because the difference in equation-of-state parameters is large. By presetting r/M to 0.012, the equation-of-state parameters of TMPC are comparable to those of PS. The adjusted PHSC equation-of-state parameters for TMPC are given in Table 2.

Figure 5 compares theoretical coexistence and spinodal curves with the phase separation temperatures determined by the dsc method for the system TMPC/PS.[17] The weight-average molecular weight determined by light scattering measurements and the polydispersity index determined by gel permeation chromatography (GPC) measurements of TMPC are reported to be $M_w = 33\,000$ g/mol and $M_w/M_n = 2.1$, respectively. For polystyrene, $M_w = 330\,000$ g/mol and $M_w/M_n = 3.3$, determined by GPC measurements. Theoretical curves are for $M_1 = 33\,000$ and $M_2 = 330\,000$. The intersegmental parameters for the TMPC–S pair were obtained by assuming that the critical temperature and mixture composition are 242 °C and 55 wt % PS, respectively; they are given in Table 3. With these parameters, the calculated spinodal curve agrees very well with experiment. In addition, theory predicts that the LCST in the system TMPC/PS is insensitive to the molecular weight of PS. For example, the theoretical LCST increases only 2.2 °C when the molecular weight of PS decreases from 330 000 to 100 000. The analysis by Guo and Higgins,[48] who determined the cloud points of the system TMPC/PS with various molecular weights of polydisperse PS, also shows that the LCST in the system TMPC/PS is insensitive to the molecular weight of PS. It is, however, not clear that the phase separation temperatures determined by the dsc method represent the spinodal curve.

Figure 6 compares the theoretical copolymer-composition dependence of LCST with experiment for the systems TMPC/(MMA-*co*-S).[18] Theory is for $M_1 =$
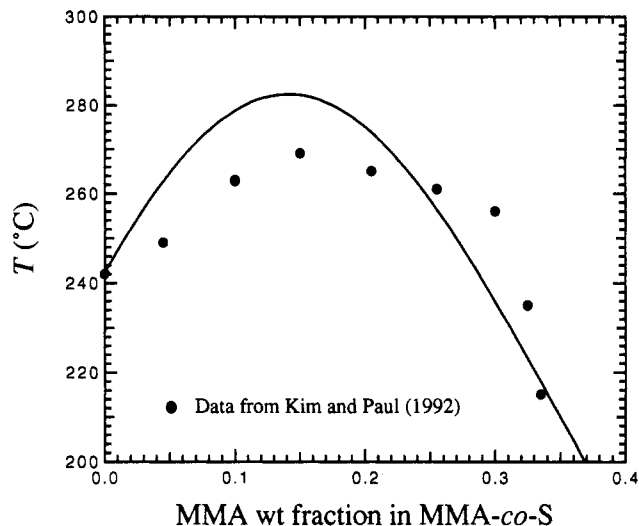
$33\,000$ and $M_2 = 200\,000$. The intersegmental parameters for the S–MMA pair are the same as those used in the systems PVME/(MMA-*co*-S). The critical compositions in the system TMPC/(MMA-*co*-S) do not vary significantly with the copolymer composition.[18] The intersegmental parameters for the TMPC–MMA pair were obtained by assuming that, in the system TMPC/(MMA-*co*-S) containing 35% methyl methacrylate by weight in the copolymer, the critical temperature and mixture composition are 210 °C and 45 wt % TMPC, respectively. The copolymer-composition dependence of LCST in the system TMPC/(MMA-*co*-S) is similar to that in the system PVME/(MMA-*co*-S) shown in Figure 2. The phase separation temperatures for the former system, however, are above 120 °C higher than those in the latter system. Using the same set of intersegmental parameters for the S–MMA pair, theory gives fair agreement with experiment over a wide temperature range.

Systems Containing Tetramethyl Bisphenol A Polycarbonate, Styrene, and Acrylonitrile. Figure 7a compares theoretical coexistence and spinodal curves with cloud points for the system TMPC/(AN-*co*-S) containing 18% acrylonitrile by weight in the copolymer. In Figure 7a, the intersegmental parameter for the S–AN pair is $\kappa_{S-AN} = 0.085$. The critical mixture composition in the system TMPC/(AN-*co*-S) shifts toward the copolymer-rich composition as the acrylonitrile content in the copolymer rises.[18] The intersegmental parameters for the TMPC–AN pair were obtained by assuming that, in the system shown in Figure 7a, the critical temperature and mixture composition are 180 °C and 60 wt % TMPC, respectively; they are given in Table 2. Theoretical curves are for $M_1 = 33\,000$ and $M_2 = 200\,000$. The second set of intersegmental parameters is also obtained using $\kappa_{S-AN} = 0.050\,55$ and $\zeta_{S-AN} = 0$ for the S–AN pair.

Figure 7b compares the theoretical copolymer-composition dependence of LCST with experiment for the system TMPC/(AN-*co*-S).[18] Theoretical curves are for $M_1 = 33\,000$ and $M_2 = 200\,000$. Similar to the system PVME/(AN-*co*-S) in Figure 4, the theory with $\kappa_{S-AN} = 0.050\,55$ underestimates the LCST. Theoretical LCST with $\kappa_{S-AN} = 0.085$ and experiment show good agreement.
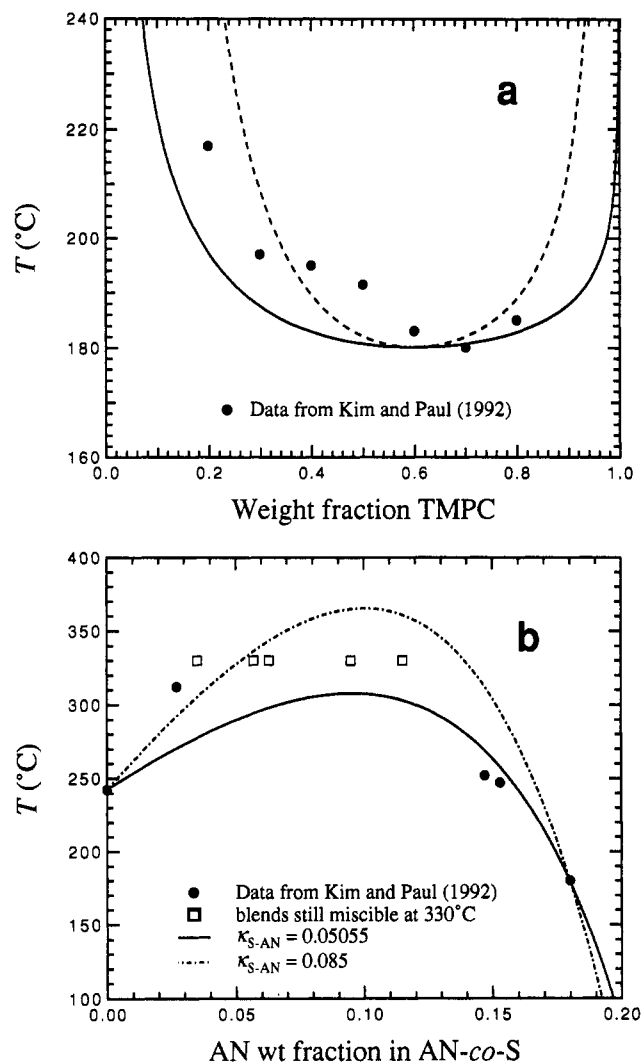
Figure 7. (a) Comparison of theoretical coexistence and spinodal curves with the phase separation temperatures determined by the dsc method for the system TMPC/(AN-*co*-S) containing 18% AN by weight in the copolymer.[18] Theoretical curves are for $M_1 = 33\,000$ and $M_2 = 200\,000$: $\kappa_{TMPC-S} = -0.004\,402$, $\zeta_{TMPC-S} = -0.003\,166$, $\kappa_{TMPC-AN} = 0.084\,92$, $\zeta_{TMPC-AN} = 0.007\,47$, $\kappa_{S-AN} = 0.085$, and $\zeta_{S-AN} = 0.0$. (b) Copolymer-composition dependence of LCST for the system TMPC/(AN-*co*-S):[18] $M_1 = 33\,000$, $M_2 = 200\,000$, (—) Theory with the parameters used in Figure 7a; (- · -) $\kappa_{S-AN} = 0.050\,55$, $\zeta_{S-AN} = 0$, $\kappa_{TMPC-AN} = 0.056\,87$, and $\zeta_{TMPC-AN} = 0.008\,32$.

Systems Containing Cyclohexyl Methacrylate, Styrene, and Acrylonitrile. Copolymer-composition dependence of LCST, similar to that in the systems PVME/(AN-*co*-S) and TMPC/(AN-*co*-S), is also available for mixtures of poly(cyclohexyl methacrylate) (PCHMA) and AN-*co*-S random copolymers.[49] PCHMA and PS are reported to be miscible to about 240 °C. Unfortunately, ref 49 does not report the detailed characteristics of polymer samples and the complete phase diagram of the system TMPC/PS. The intersegmental parameters for the CHMA–S pair were obtained by assuming that the critical temperature and mixture composition in the system PCHMA/PS are 240 °C and 70 wt % PS, respectively, for $M_1 = M_2 = 200\,000$.

Figure 8 compares the theoretical LCST with the phase separation temperature for the system PCHMA/(AN-*co*-S). The open and solid circles are for blends that are clear and cloudy, respectively, after annealing for 15 min at the indicated temperature. The open squares represent the blends that are clear to the thermal
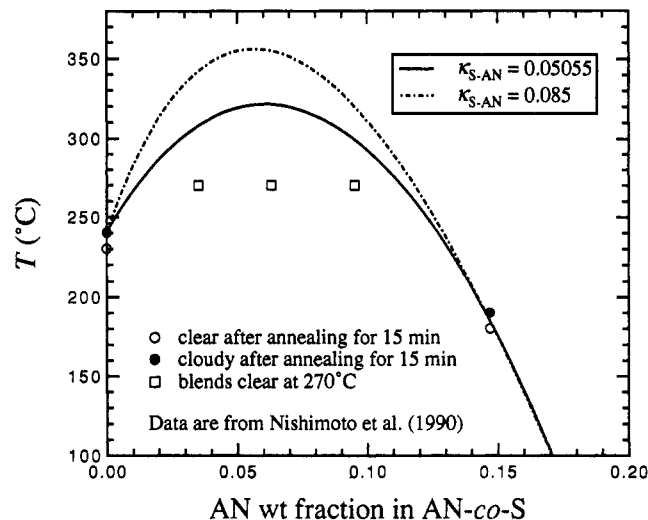

Figure 8. Copolymer-composition dependence of LCST for the system PCHMA/(AN-*co*-S):[49] $M_1 = M_2 = 200\,000$, $\kappa_{CHMA-S} = 0.001\,936$, $\zeta_{CHMA-S} = -0.001\,718$, (—) $\kappa_{S-AN} = 0.085$, $\zeta_{S-AN} = 0$, $\kappa_{CHMA-AN} = 0.063\,27$, and $\zeta_{CHMA-AN} = -0.007\,70$; (- · -) $\kappa_{S-AN} = 0.050\,55$, $\zeta_{S-AN} = 0$, $\kappa_{CHMA-AN} = 0.042\,17$, and $\zeta_{CHMA-AN} = -0.003\,17$.

decomposition temperature (270 °C). The mixture composition is 50 wt % PS for all measurements. Theory is for $M_1 = M_2 = 200\,000$.

The solid curve is calculated using the intersegmental parameter $\kappa_{S-AN} = 0.050\,55$ for the S–AN pair. The semibroken curve is for the theory with $\kappa_{S-AN} = 0.085$. The intersegmental parameters for the CHMA–AN pair were obtained by assuming that the critical temperature and mixture composition are 185 °C and 70 wt % PS for the AN-*co*-S copolymer containing 14.7% acrylonitrile by weight. The predicted maximum LCST with $\kappa_{S-AN} = 0.085$ is about 30 °C higher than that predicted with $\kappa_{S-AN} = 0.050\,55$. Theory and experiment are in good agreement. In the subsequent paper of this series, the intersegmental parameters obtained here are used to analyze the miscibility map of the system poly-(cyclohexyl methacrylate-*co*-methyl methacrylate)/poly-(acrylonitrile-*co*-styrene), a system containing four kinds of segments which requires six sets of intersegmental parameters.

Intersegmental Parameters for the Styrene–Acrylonitrile Pair. For mixtures of type $A_{r_1}/(C_Y B_{1-Y})_{r_2}$ containing AN-*co*-S random copolymers shown in Figures 4 and 7b, the measured copolymer-composition dependences of LCST agree better with the theoretical LCSTs with $\kappa_{S-AN} = 0.085$ than those with $\kappa_{S-AN} = 0.050\,55$. The theory with $\kappa_{S-AN} = 0.085$, however, seems to underestimate the miscible area in the miscibility map of the mixture of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ containing AN-*co*-S random copolymers shown in Figure 3.

These observations may be explained by the effect of nonrandom mixing. Since the interactions between acrylonitrile and styrene segments are highly unfavorable, the number of contacts between AN-*co*-S copolymers in the real mixture is likely to be smaller than that predicted by random mixing. Consequently, the number of contacts between homopolymer and AN-*co*-S copolymer in the real mixture can be larger than that in the random mixture, leading to enhanced solubility of AN-*co*-S copolymers. If the same intersegmental parameters are used for the S–AN pair, the theory which takes nonrandom mixing into account may give a higher LCST than that given by a theory which

assumes random mixing. In the present theory, the perturbation term for attractive interactions assumes the random mixing of molecules.

As a first approximation, however, a value between 0.050 55 and 0.085 can be used as the intersegmental parameter for the S–AN pair, κ_{S-AN}, with $\zeta_{S-AN} = 0$. In the subsequent paper of this series, we use $\kappa_{S-AN} = 0.50\ 55$ to analyze miscibility maps of systems containing styrene and acrylonitrile segments.

Conclusions

The perturbed hard-sphere-chain equation of state is able to represent immiscibility caused by lower critical solution temperature phase behavior in copolymer systems. The PHSC equation of state is applied to homopolymer/copolymer mixtures containing poly(methyl methacrylate-co-styrene) and poly(acrylonitrile-co-styrene) random copolymers, where the mixture of homopolymer and polystyrene exhibits a LCST. The intersegmental parameters for the S–MMA and S–AN pairs were obtained from experimental miscibility maps for mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing S-co-MMA and S-co-AN random copolymers, respectively. Using these intersegmental parameters for the S–MMA and S–AN pairs, the theoretical copolymer-composition dependence of LCST shows fair agreement with experiment.

Intersegmental parameters are obtained for 10 pairs of segments. In the systems studied in this work, unique values are assigned to the intersegmental parameters for a given pair of segments.

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