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APPLICATION OF THE SANCHEZ-LACOMBE LATTICE FLUID THEORY TO THE SYSTEM PVME/PS AND MODEL CALCULATIONS

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ABSTRACT

Cloud point curves reported in the literature for five representatives of the system poly(vinyl methyl ether)/polystyrene were evaluated theoretically by means of the Sanchez-Lacombe lattice fluid theory. The measured phase separation behavior can be described within experimental error using only one adjustable parameter (quantifying the interaction between the unlike mers). The Flory-Huggins interaction parameters calculated from this theoretical description depend in good approximation linearly on composition (volume fractions) and on the inverse temperature. An evaluation of these data yields a maximum heat effect which is almost one order of magnitude less (ca. - 0.25 J/cm^3) than obtained via Hess's cycle (dissolution of the components and of the blend) from calorimetric measurements. Model calculations on the basis of the present theory demonstrate that the critical points shift to a different extent upon a certain relative change in the molar mass of the blend components. The sensitivity of the calculated phase diagrams against changes in the scaling parameter decreases in the following order: interaction energies between unlike mers, differences in the scaling temperatures, pressures and densities.

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INTRODUCTION

The phase separation behavior of flowing polymer-containing fluids (solutions and blends) has attracted much experimental and theoretical attention during the past years [1-25]. Starting point of all attempts to forecast the effects of mechanical fields is an accurate theoretical description of the equilibrium mixing the phase separation of the system poly(vinyl methyl ether)/polystyrene, to which extent the Sanchez-Lacombe lattice fluid theory (SLLFT) is helpful for that purpose. In this context it is also investigated to which concentration and temperature dependent Flory-Huggins interaction parameters the results of the SLLFT translate. Furthermore, we study the sensitivity of this theory towards variations of the characteristic parameters of the pure components and of the mixture, a feature which is important for realistic predictions.

Theoretical Background

In the lattice fluid theory, as formulated by Sanchez-Lacombe [10, 11] the following relations hold true for the thermal equation of state and for $\overline{\overline{G}}$, the Gibbs energy per one mol of mers, in the case of the pure components *i*

$$\tilde{\rho}_i^2 + \tilde{P}_i + \tilde{T}_i[\ln(1-\tilde{\rho}_i) + (1-\frac{1}{r_i^0})\tilde{\rho}_i] = 0 \tag{1}$$

$$\overline{\overline{G}}_i = \frac{G_i}{r_i^0 N_i} = \varepsilon_{ii}^* \left\{ -\tilde{\rho}_i + \tilde{P}_i\tilde{\upsilon}_i + \tilde{T}_i\left[(\tilde{\upsilon}_i - 1)\ln(1-\tilde{\rho}_i) + \frac{1}{r_i^0}\ln\left(\frac{\tilde{\rho}_i}{\omega_i^0}\right)\right]\right\} \tag{2}$$

For mixtures these relations read:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + 1 - \frac{1}{r})\tilde{\rho} \right] = 0 \tag{3}$$

$$\overline{\overline{\mathrm{G}}}_{\mathrm{M}} = \frac{\mathrm{G_M}}{r\mathrm{N}} = \varepsilon^* \left\{ -\tilde{\rho} + \tilde{P}\tilde{\mathrm{v}} + \tilde{T}\left[\tilde{\upsilon} - 1)\ln(1-\tilde{\rho}) + \frac{1}{r}\ln\tilde{\rho} + \frac{\phi_1}{r_1}\ln\frac{\phi_1}{\omega_1} + \frac{\phi_2}{r_2}\ln\frac{\phi_2}{\omega_2} \right]\right\} \tag{4}$$

where the ϕ_i stands for volume fractions and the Gibbs energy is formulated for a binary polymer blend.

The different symbols have the following meaning: $\tilde{\rho}_i\ \tilde{P}_i\ \tilde{\upsilon}_i\ \tilde{T}_i$ and $\tilde{\rho}, \tilde{P}, \tilde{\upsilon}, \tilde{T}$ are the reduced densities, pressures, volumes, and temperatures for the

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pure components and for the mixture, respectively, obtained from the unreduced variables of state and the scaling parameters (denoted with asterisks and accessible from measured P, υ, T data) by

$$\tilde{P}_i = P/P^*_i \qquad \tilde{P} = P/P^* \tag{5}$$

$$\tilde{T}_i = T/\tilde{T}_i \qquad \tilde{T} = T/\tilde{T} \tag{6}$$

$$\tilde{\upsilon}_i = V_i/V_i^* \qquad \tilde{\upsilon} = V/V^* \tag{7}$$

$$\tilde{\rho}_i = 1/\tilde{\upsilon}_i \qquad \tilde{\rho} = 1/\tilde{\upsilon} \tag{8}$$

$$V_i^* = r_i^0 N_i \upsilon_i^* \qquad V^* = (r_1 N_1 + r_2 N_2)\,\upsilon^* \tag{9}$$

r_i^0 and r_i give the number of lattice sites occupied by a molecule of component i in the pure fluid and in the fluid mixture, respectively. The former parameter is accessible from

$$r_i^0 = M_i P_i^* / k T_i^* \ \rho_i^* \tag{10}$$

where M_i is the molecular mass and ρ_i^* is the close-packed density.

Scaling pressures and temperatures can also be expressed in terms of the interaction energies ε^* and of υ^*, the close-packed volume of a mer

$$P_i^* = \varepsilon_{ii}^*/\upsilon_i^* \qquad P^* = \varepsilon^*/\upsilon^* \tag{11}$$

$$T_i^* = \varepsilon_{ii}^*/k \qquad T^* = \varepsilon^*/k \tag{12}$$

where ε_{ii}^* is the total interaction energy of a mer of the pure component i. The following relation is used to calculate ε^* for a binary mixture

$$\varepsilon^* = \phi_1^2\, \varepsilon_{11}^* + 2\,\phi_1\, \phi_2\, \varepsilon_{12}^* + \phi_2^2\, \varepsilon_{22}^* \tag{13}$$

ε_{12}^* is the interaction energy of a mer belonging to component i when it is surrounded by z mers belonging to component j. In terms of the deviation of ε_{12}^*

from the arithmetic mean

$$\Delta\varepsilon^{*} = \varepsilon_{12}^{*} - \frac{\varepsilon_{11}^{*} + \varepsilon_{22}^{*}}{2} \tag{14}$$

Equation (13) can be rewritten as

$$\varepsilon^{*} = \phi_1\varepsilon_{11}^{*} + \phi_2\varepsilon_{22}^{*} + 2\phi_1\phi_2\Delta\varepsilon^{*} \tag{15}$$

The closed-packed volume of a mer in the mixture υ^{*} and r, the average number of mers, are calculated according to

$$\frac{1}{\upsilon^{*}} = \frac{\phi_1}{\upsilon_1^{*}} + \frac{\phi_2}{\upsilon_2^{*}} \tag{16}$$

$$\frac{1}{r} = \frac{\phi_1}{r_1} + \frac{\phi_2}{r_2} \tag{17}$$

The parameters ω_i^0 and ω_i signify the number of configurations available to a r_i^0 mer and to a r_i mer in the close-packed state [10, 26]; they are calculated according to

$$\omega_i^0 = \delta_i^0 r_i^0/\sigma_i^0\, e^{r_i^0-1} \qquad\qquad \omega_i = \delta_i r_i/\sigma_i\, e^{r_i-1} \tag{18}$$

where δ_i^0 and δ_i represent the flexibility parameters; σ_i^0 and σ_i are the symmetry numbers of the r_i^0 mers and r_i, -mers. For the present computations, the values of parameters of Equation 18 are $\sigma_i = \sigma_i^0, = 1$, $\delta_i^0 = \delta_{i,\mathrm{max}}^0 = z\,(z - 1)\, r_i^{0-2}$, and $\delta_i, = \delta_{i,\mathrm{max}}^0 = z\,(z - 1)\, r_i^{-2}$ (Reference 10), where z, the coordination number of the lattice, was taken to be 8.

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Phase Diagrams of the System Polyvinyl Methyl Ether)/Polystyrene (PVME/PS)

By means of the relations of the previous section, it is possible to calculate phase diagrams starting from the Gibbs energy of mixing per mer, $\Delta\overline{\overline{G}}_M$, defined as

$$\Delta\overline{\overline{G}}_M = \overline{\overline{G}}_M - \left(\phi_1\overline{\overline{G}}_1 + \phi_2\overline{\overline{G}}_2\right) \tag{19}$$

The spinodal and binodal curves were computed using a new method [27] not requiring the derivatives of the Gibbs energy. For the theoretical description of the phase separation behavior of the present blend a generalization of the theory [13]

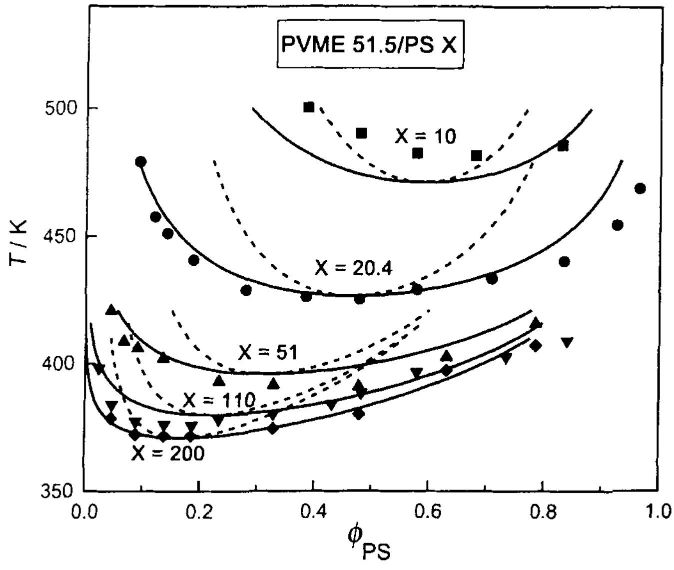

Figure 1. Cloud points [9] measured for the system PVME 51.5/PS X (the molar mass of PS in kg/mol is indicated at the curves) plus binodals (full lines) and spinodals (dotted lines) calculated according to the SLLFT one adjustable parameter, namely $\Delta\varepsilon^*/k = 0.444$ *K*, was used for all theoretical calculations, irrespective of the molar masses of the components.

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considering specific interactions turned out to be unnecessary, in contrast to blends of PVME with deuterated PS where these special effects can obviously not be neglected as demonstrated in Reference 13.

Figure 1 shows the measured cloud point curves [9] for blends of PVME 51.5 (the numbers giving the molar mass in kg/mol) with various PS samples differing in molar mass, together with the corresponding calculated binodal and spinodal lines. The theoretical curves were obtained as described in the previous section using the scaling parameters collected in Table 1. In view of the considerable experimental uncertainties (difficulties in the assignment of cloud points to binodal or spinodal conditions particularly at larger distances from the critical point, in the exact determination of the molar masses of the components and remaining polydispersity effects) only one adjustable parameter, namely $\Delta\varepsilon^*$, identical for all different blends, was used to describe the actual behavior- its numerical value is the arithmetic mean of the best fits for each individual curve. The precision of the mathematical description of the cloud point curve measured for a given blend is

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TABLE 1: Characteristic Parameters of Poly(Vinyl Methyl Ether) and of Polystyrene

	T_i^*, K	P_i^*, *bar*	ρ_i^*, g/cm^3
P VME[13]	657	3580	1.10
PS[32]	735	3530	1.105

	$10^{-3} M_w$[9]	M_w/M_n[9]	$10^{-3} r_i^0$
PVME 51.5	51.5	---	3.11
PS 10	10.0	1.06	0.53
PS 20.4	20.4	1.06	1.08
PS 51	51.0	1.06	2.70
PS 110	110.0	1.06	5.83
PS 200	200.0	1.06	10.59

naturally considerably better than that shown in Figure 1, and should constitute a good starting point for the theoretical discussion of shear influences.

In Reference 12, Sanchez and Lacombe applied the SLLFT [10, 11] to polymer solutions, but the ω_i in Equation 4 were omitted because it was assumed that they do not depend on composition [11]. In fact, however, they should vary with concentration according to the combining rules of Sanchez-Lacombe [11, 12]. Phase diagrams calculated with ω_i give indeed a much better fit than those neglecting ω_i.

For an easier comparison of the present theoretical calculations with other thermodynamic data published in the literature, the Gibbs energy of mixing of the system PVME/PS, required to describe the observed phase separation behavior theoretically, is also formulated in terms of g, the (integral) Flory-Huggins interaction parameter [1].

This transformation starts from the definition of g in terms *of* $\Delta\overline{\overline{G}}^R$, the residual free energy of mixing per mer

$$\frac{\Delta\overline{\overline{G}}^R}{kT} = \phi_1 \phi_2 g \tag{20}$$

obtained from the total Gibbs energy of mixing by

$$\overline{\overline{\Delta G}}^{R} = \overline{\overline{\Delta G}}_{M} - \overline{\overline{\Delta G}}_{M}^{Comb} \tag{21}$$

where $\overline{\overline{\Delta G}}_{M}^{Comb}$, the combinatorial Gibbs energy is given as

$$\overline{\overline{\Delta G}}_{M}^{Comb} = kT\left(\frac{\phi_1}{r_1}\ln\frac{\phi_1}{\omega_1} + \frac{\phi_2}{r_2}\ln\frac{\phi_2}{\omega_2}\right) - kT\left(\frac{\phi_1}{r_1^0}\ln\frac{1}{\omega_1^0} + \frac{\phi_2}{r_2^0}\ln\frac{1}{\omega_2^0}\right) \tag{22}$$

Equations (2), (4), (15), (20), and (21) yield

$$\begin{aligned} g = \frac{1}{kT\phi_1\phi_2}\Bigg\{ & \left[\varepsilon^*\left(-\tilde{\rho} + \tilde{P}\tilde{\upsilon}\right) - \phi_1\varepsilon_{11}^*\left(-\tilde{\rho}_1 + \tilde{P}_1\tilde{\upsilon}_1\right) - \phi_2\varepsilon_{22}^*\left(-\tilde{\rho}_2 + \tilde{P}_2\tilde{\upsilon}_2\right)\right] \\ & + kT\Bigg\{\left[\left(\tilde{\upsilon} - 1\right)\ln\left(1 - \tilde{\rho}\right) + \frac{1}{r}\ln\tilde{\rho}\right] - \phi_1\left[\left(\tilde{\upsilon}_1 - 1\right)\ln\left(1 - \tilde{\rho}_1\right) + \frac{1}{r_1^0}\ln\tilde{\rho}_1\right] \\ & - \phi_2\left[\left(\tilde{\upsilon}_2 - 1\right)\ln\left(1 - \tilde{\rho}_2\right) + \frac{1}{r_2^0}\ln\tilde{\rho}_2\right]\Bigg\}\Bigg\} \end{aligned} \tag{23}$$

which reduces for large values of r and r_i^0 to

$$\begin{aligned} g = \frac{1}{kT\phi_1\phi_2}\Big\{ & \left[\varepsilon^*\left(-\tilde{\rho} + \tilde{P}\tilde{\upsilon}\right) - \phi_1\varepsilon_{11}^*\left(-\tilde{\rho}_1 + \tilde{P}_1\tilde{\upsilon}_1\right) - \phi_2\varepsilon_{22}^*\left(-\tilde{\rho}_2 + \tilde{P}_2\tilde{\upsilon}_2\right)\right] \\ & + kT\left[\left(\tilde{\upsilon} - 1\right)\ln\left(1 - \tilde{\rho}\right) - \phi_1\left(\tilde{\upsilon}_1 - 1\right)\ln\left(1 - \tilde{\rho}_1\right) - \phi_2\left(\tilde{\upsilon}_2 - 1\right)\ln\left(1 - \tilde{\rho}_2\right)\right]\Big\} \end{aligned} \tag{24}$$

The evaluation of the theoretical Gibbs energy of mixing adjusted to the actual behavior with respect to g demonstrates that the Flory-Huggins interaction parameter depends on composition and to some extent on the molar mass of PS. From Figure 2 it can be seen that g varies almost linearly with composition under isothermal conditions, and Figure 3 displays the temperature dependence of g for constant composition in terms of an Arrhenius diagram.

Mathematically, $g(\phi_{PS}, T)$ can be represented by the following, intuitively formulated relation

$$g = \frac{A\phi_{PS} + B}{T} + \left(C\phi_{PS} + D\right)10^{-3} \tag{25}$$

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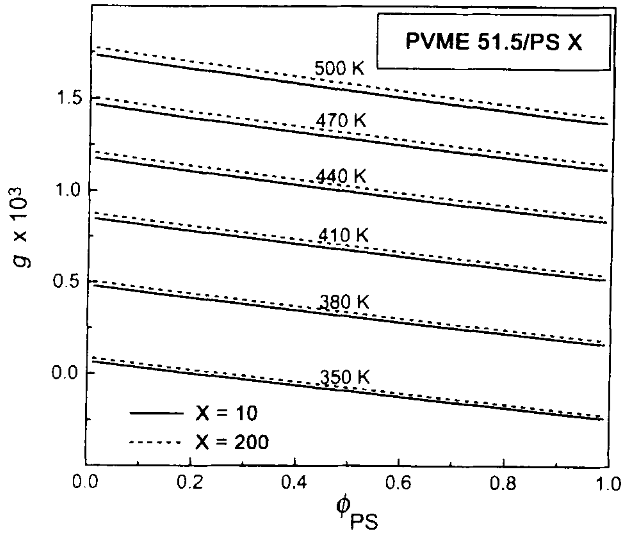

Figure 2. Composition dependence of Flory-Huggins interaction parameter *g* at the different indicated temperatures for blends of PVME 51.1 with PS 10 and PS 200, respectively.

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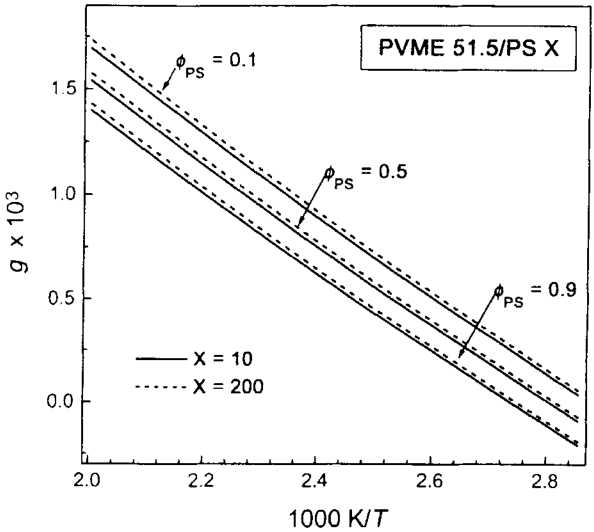

Figure 3. Temperature dependence of Flory-Huggins interaction parameter *g* for blends of PVME 51.5 with PS 10 and PS 200, respectively, at the different constant volume fractions of PS indicated in the graph.

TABLE 2. Parameters Describing the Integral Flory-Huggins Interaction Parameter of the System PVME-/Ps as a Function of Composition and Temperature as Formulated in

	A	*B*	*C*	*D*
PVME 51.51/*PS* 10	0.07416	-1.95265	-0.51739	5.61823
PVME 51.1/*PS* 20.4	0.07708	-1.96457	-0.52771	-5.66290
PVME 51.5/*PS* 51	0.07878	-1.97155	-0.53369	5.68899
PVME 51.5/PS 110	0.07939	-1.97406	-0.53583	5.69838
PVME 51.5/PS 200	0.07963	-1.97504	-0.53666	5.70203
average-values	0.07781	-1.96757	0.53026	5.67411

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g was calculated according to Equation 23 and the values of A, B, C, and D are determined by fitting Equation 25 to the calculated g values. The values of A, B, C, and D are listed in Table 2; it should be noted that the number of parameters required for the individual description of the temperature or the composition dependence reduces to two.

By means of the above relation and the definition of g (Equation 20), it is possible to split the Gibbs residual energy of mixing into its enthalpy and its entropy part. The enthalpy of mixing is given by

$$\Delta\bar{\bar{H}}_M = - kT^2 \left(\frac{\partial g}{\partial T}\right) \phi_1 \; \phi_2 \qquad (26)$$

In the evaluation of the present data the different thermal expansivity of the components need not be taken into consideration.

Figure 4 shows the result of this evaluation in terms of the concentration dependence of ΔH_M for various temperatures. The exothermicity (ca. - 19 J/mol at 50°C) as calculated from the temperature and molecular weight dependence of the phase separation behavior, is approximately one order of magnitude less pronounced than that obtained from caloric measurements (ca.- 240 J/mol at PVME/PS = 50/50) [25] (application of Hess' law, dissolution of the components and their blends). The reasons for this discrepancy, which appears to be beyond the admittedly considerable experimental errors of both methods, are presently unknown. An

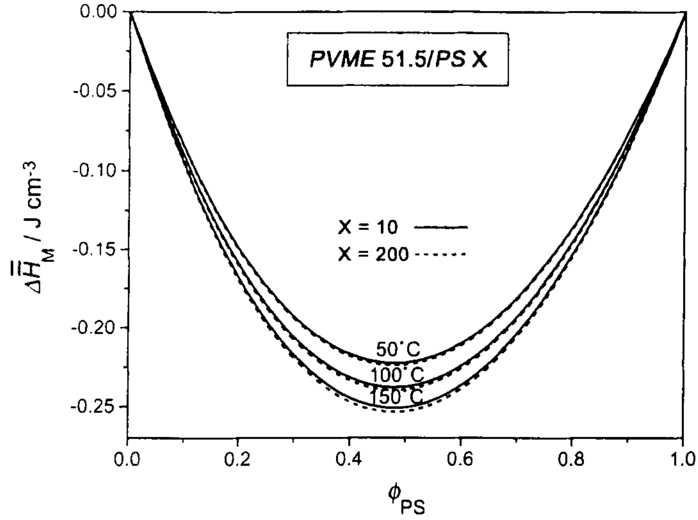

Figure 4. $\Delta \overline{\overline{H}}_M$, the heat of mixing for blends of PVMS 51.5 with PS 10 or PS 200, as a function of (φ_{PS}, the volume fraction of PS, as calculated from the temperature dependence of g at the different indicated temperatures.

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explanation by the fact that the former information refers to temperatures ranging from 100 to 220°C, whereas the latter stems from measurements at 50°C is rather unlikely in view of only the little curvature of the lines in Figure 3. It appears worthwhile to note in this context that theoretical calculations using the lattice cluster theory (ca.- 27 J/mol at 50°C) [28] and the refined version of the Prigogine-Flory-Patterson theory (ca. - 85 J/mol at ·100°C) [29] also yield much smaller heat effects than that measured calorimetrically. The results of calculations concerning $\Delta \overline{\overline{H}}$ of the system PVME/PS-d (ca. - 85J/mol at 100°C) [30]and of the system PVME/PS (ca. - 522 J/mol at 90°C), [31], are also greatly different from the experimental data of Shiomi *et al.* [25].

Model Calculations

After having demonstrated that the SLLFT is well suited to describe the actual phase separation behavior of the system PVME/PS, it is now discussed how sensitive the position and extension of the regions of incomplete miscibility of a polymer pair are against a variation of the different theoretical parameters. To that end, we first calculate spinodal curves for further representatives of the system PVME/PS, altering the molar masses of the components. Then, it is studied for

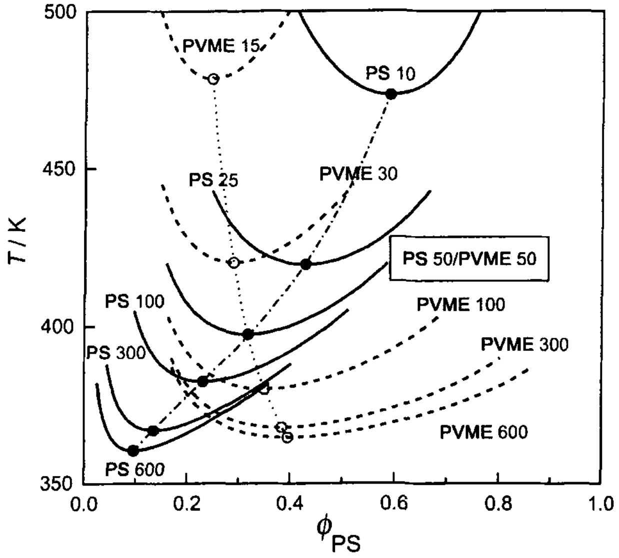

Figure 5. Spinodals curves and critical points calculated for different representatives of the systems *PVME/PS* calculated by means of the SLLFT, using the scaling parameters of Table 1 and $\Delta\varepsilon^*/k = 0.444\ K$ (the value obtained from measured phase diagrams). Full lines and full circles refer to blends of PVME 50 with PS of different molar mass indicated in the graph. Broken lines and open circles stand for mixtures of PS 50 with PVMEof different molar mass.

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model blends exhibiting LCSTs how a variation of the interaction energies between two types of mers and differences in the scaling parameters of the pure components modify the phase separation behavior.

The effects of a systematic variation of molar masses of PVME and PS are shown in Figure 5, where the spinodal curve of the system PVME 50/PS 50 serves as the reference. It is investigated how a change in the molar mass of PVME, keeping that of PS constant at 50 kg/mol, alters the critical temperatures T_c, and the critical composition $\phi_{PS,c}$ (minima of the spinodals); furthermore, keeping the molar mass of PVME constant at 50 kg/mol, it is checked what molar mass of PS is required to yield approximately the same critical temperature as for the corresponding combination of PVME 50 and PS.

Upon reduction of the molar mass of one component, the critical temperature increases and the critical mixture becomes richer in this constituent. These shifts in T_c and $\phi_{PS,c}$ are in qualitative accord with the results of the original Flory-

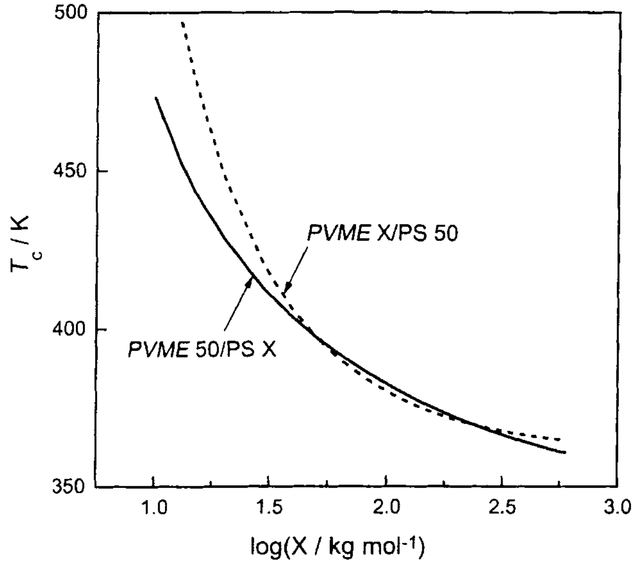

Figure 6. Critical temperature of the systems PVME 50/PS X and PVME X/PS 50 as a function of the molar mass X from SLLFT with $\Delta\varepsilon^*/k = 0.444\,K$.

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Huggins lattice theory: The different extent to which ($\phi_{PS,c}$ changes in the case a variation in the molar mass of PVME or PS is, however, not; it results from free volume effects in the present theory taken account of. Another interesting feature can be seen from Figure 6. This graph demonstrates that the critical temperatures become less sensitive towards a reduction in the molar mass of PS than of PVME as M falls below 50 kg/mol. The reason for this behavior lies again in the different thermal expansivities (free volumes) of the two polymers which become particularly influential at high temperatures (i.e. in the region of the critical temperatures of lower molar mass components).

We now investigate how differences in the scaling parameters change the phase behavior. To that end ε^*, T^*, P^* *and* ρ^* of a model blend A 50/B 50 are varied symmetrically to the arithmetic mean of the corresponding data for the system PVME/PS. Figure 7 shows the effects of a change in the interaction between unlike mers quantified by $\Delta\varepsilon^*$ (Equation 14). As expected, the components become more compatible as they interact more favorably, i.e. as ε_{12}^* and consequently, $\Delta\varepsilon^*$ increase. Less anticipated, is a shift of the critical point towards the A side of the phase diagram as the compatibility rises.

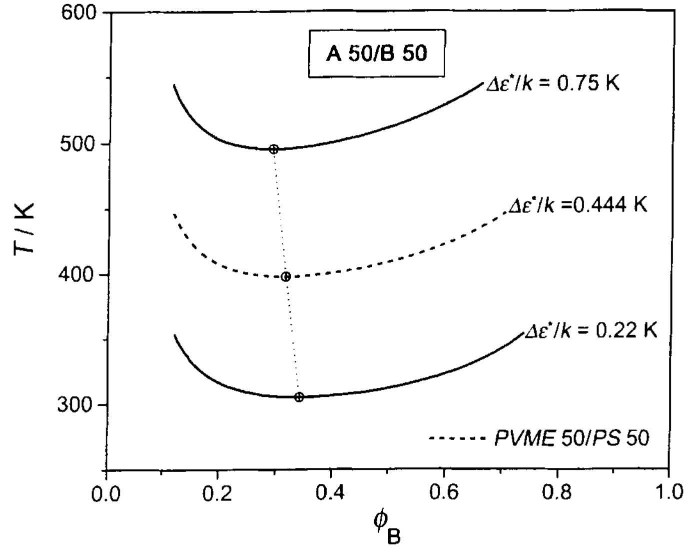

Figure 7. Spinodal curves calculated for a model blend A 50/B 50 using the experimentally determined parameters of the system PVME/PS (broken line), except for $\Delta\varepsilon^*/k$, which is varied (full lines); also shown is the shift of the critical point associated with a variation of the interaction between unlike mers (dotted line).

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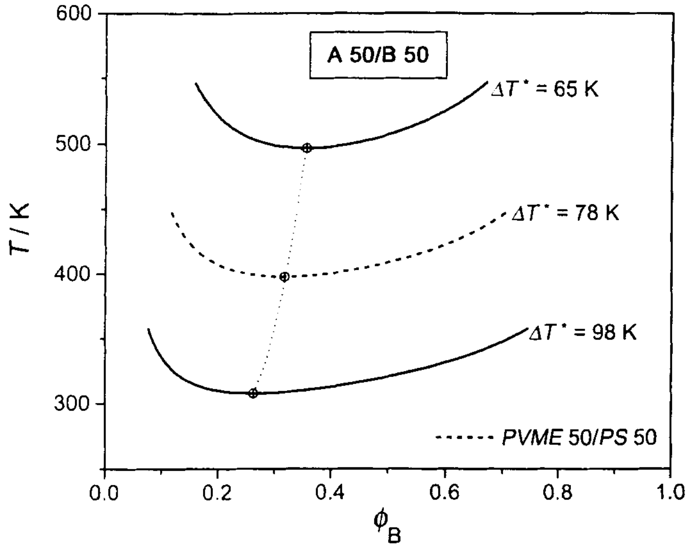
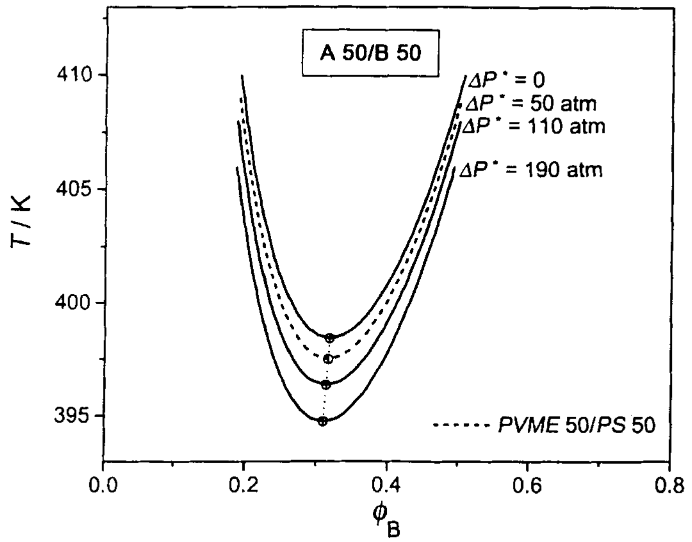
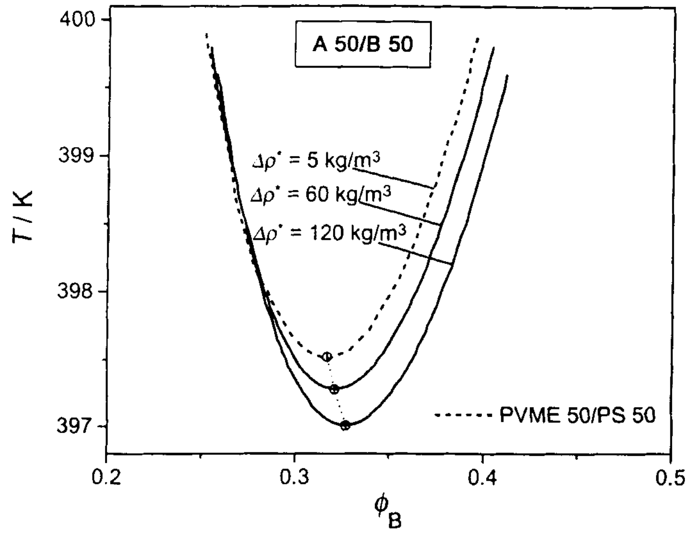
The effects of differences in the scaling parameters of the pure components are demonstrated by the next three graphs, where ε_{12}^*/k is kept constant at a value of 696.444 K. As T^*, P^* or ρ^* of the two polymers become increasingly more similar, the miscibility gap withdraws to higher temperatures, i. e. the compatibility rises. The magnitude of the effect is largest for T^* and least for ρ^*, as can be seen from the Figures 8 a-c. As T_A^*, 4 and T_B^*, or P_A^* and P_B^* move towards each other, the critical composition shifts towards component B, whereas a reduction of $\Delta\rho^*$ has the opposite effect.

CONCLUSIONS

The present results demonstrate that the SLLFT constitutes a sound basis for the theoretical description of phase separation behavior of the system PVME/PS. Only one adjustable parameter is required which, upon transformation, yields







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practically linear dependencies of the integral Flory-Huggins interaction parameter g on composition (volume fractions) and on inverse temperature. This approach is therefore well suited for the modeling of shear influences on the phase separation of polymer blends exhibiting LCSTS. The information concerning the sensitivity of the results towards changes in the scaling parameters is very helpful for such calculations. According the present findings the susceptibility of the critical temperature decrease rapidly in the following order: $\Delta\varepsilon^*$, ΔT^*, ΔP^* *and* $\Delta\rho^*$.

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Figure 8 a-c. Spinodal curves calculated for a model blend A 50/B 50 using the experimentally determined parameters of the system PVME/S (broken lines) and varying the scaling temperatures

(part a: $T_A^*/K = 696.0 - \Delta T^*/2$ and $T_B^*/K = 696.0 + \Delta T^*/2$)

or the scaling pressures

(part b: $P_A^*/bar = 3555.0 + \Delta P^*/2$ and $P_B^*/bar = 3555.0 - \Delta P^*/2$

or the scaling densities

(part c: $\rho_A^*/kg\ m^{-3} = 1102.5 - \Delta\rho^*/2$ and $\rho_B^*/kg\ m^{-3} = 1102.5 + \Delta\rho^*/2$

Full lines demonstrate the effects of these partial variations of the scaling parameters of the pure components; dotted lines combine the corresponding critical points.

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