

Miscibility behaviour of the system polystyrene/poly(*p*-methylstyrene)

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The miscibility behaviour of blends of polystyrene and poly(*p*-methylstyrene) was studied by differential scanning calorimetry and phase-contrast optical microscopy. Phase diagrams have been constructed for blends of different molar masses of the constituents. These blends exhibit upper critical solution temperature type of demixing, which is a rare phenomenon for high-molar-mass polymer blends. The Holes–Huggins theory, closely related to the Simha–Somcynsky hole theory, predicts this type of phase behaviour for this particular system in a semi-quantitative way. Theoretical predictions are made for the influence of pressure on the miscibility behaviour and for the excess volume and enthalpy for this blend.

(Keywords: miscibility; polystyrene/poly(*p*-methylstyrene) blends; Holes–Huggins theory; pressure influence; excess functions)

INTRODUCTION

It has been shown on many occasions that the Simha–Somcynsky (SS) cell model is a successful theory in describing equilibrium equation-of-state properties of homopolymers^{1–4}. In the early 1980s the theory was modified in order to deal with equation-of-state properties of single-phase multicomponent systems such as polymer solutions and polymer blends^{5–7}. This was performed basically by introducing appropriate mixing rules and by adapting the combinatorial term taking care of the mixing of different components. In a later stage the SS theory was extended in order to evaluate phase behaviour of polymer systems.

In the first instance, compositional derivatives of the free energy of mixing were determined from fourth-order composition polynomial approximations to the exact Gibbs free energy⁸. In this way Jain and Simha investigated lower critical solution temperature (*LCST*) phase behaviour of the polyethylene (PE)/*n*-hexane system. In further research explicit expressions were derived for the compositional derivatives of the free energy of mixing⁹. For the PE/*n*-hexane system the location and shape of the demixing region derived from the explicit expressions are quite different from the polynomial-derived results, indicating the inappropriateness of the approximations involved. The most important conclusion, however, was confirmed and extended in the exact work: *LCST* phase behaviour is governed by an iso-free-volume principle over a moderate pressure range.

A system that has been extensively studied is polystyrene/cyclohexane (PS/CH)^{10–12}. The SS theory is able to describe and predict the upper and lower critical solution temperature (*UCST* and *LCST*) phase behaviour at 1 bar in a quantitative way for this system, but fails to predict the subtle pressure influences on miscibility observed experimentally¹³.

Recently a modified hole theory was developed^{11,12}. In this theory, denoted by HH (Holes–Huggins) theory, the configurational partition function of the hole theory was refined theoretically. The HH theory predicts very accurately the pressure effects on miscibility behaviour. Thermodynamically, the complicated pressure dependence can be related to the curvature of excess volume and excess enthalpy. Furthermore the predicted compositional dependence of the excess volume is confirmed qualitatively by experiment¹³.

In this study the HH theory is used to evaluate the miscibility behaviour of the system polystyrene/poly(*p*-methylstyrene) (PS/PpMeS). This blend can be considered free of specific interactions, and the components with a rather narrow molar-mass distribution are easily synthesized so polydispersity effects are expected to be moderate. Unfortunately, PS and PpMeS are very similar from a physical and chemical point of view. This complicates the experimental detection of phase separation in this system.

THEORY

The basic ingredients of the HH theory for pure components and mixtures have been discussed extensively on previous occasions^{11,12}. It will suffice here to present the necessary equations for the calculation of miscibility behaviour.

The scaled equation of state of a pure homogeneous fluid is expressed by:

$$\tilde{p}\tilde{V}/\tilde{T} = (1-\eta)^{-1} + 2(1-\alpha)yQ^{-2}(AQ^{-2} - B)/[(1-\alpha y)\tilde{T}] \quad (1)$$

with

$$Q = y\tilde{V} \quad \alpha = \gamma(1-1/s) \quad \gamma = 2/z \quad (2)$$

$$\eta = 2^{-1/6}(1-\alpha)y/[(1-\alpha y)Q^{1/3}] \quad (3)$$

$$\tilde{V} = V/sv^* \quad (4)$$

$$\tilde{T} = Tc_sR/[z(1-\alpha)\epsilon^*] \quad (5)$$

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$$\tilde{p} = pv^*/[z(1-\alpha)\epsilon^*] \quad (6)$$

with ϵ^* and v^* the energetic and volumetric scaling parameters in the Lennard-Jones potential that describes the intersegmental energetic interaction; z the lattice coordination number; s the number of segments per molecule; c_s the number of external degrees of freedom per segment; A and B geometrical constants equal to 1.011 and 1.2045 respectively; $(1-y)$ the fraction of vacant sites on the quasi-lattice; and R the gas constant, p the pressure, V the volume and T the temperature. This fraction $(1-y)$ satisfies the minimum condition of the free energy, viz.:

$$0 = (3\eta - 1 + \alpha y) / [(1-\eta)(1-\alpha y)] \\ + (1-\alpha)y[2BQ - 2 - 3AQ^{-4} + 4\alpha y(AQ^{-4} - BQ^{-2})] / [2\tilde{T}(1-\alpha y)^2] \\ - 1/c_s [\ln(1-y)/y + 1 - 1/s - \ln(1-\alpha y)/(\gamma y) - \alpha/\gamma] \quad (7)$$

The equation of state and minimization condition for a multicomponent and a single-component system are formally identical. For a multicomponent system the molecular parameters depend on composition. Following Prigogine *et al.*¹⁴ we obtain for a binary system:

$$\langle \epsilon^* \rangle \langle v^* \rangle^m = \epsilon_{aa}^* v_{aa}^{*m} q_a^2 + 2\epsilon_{ab}^* v_{ab}^{*m} q_a q_b + \epsilon_{bb}^* v_{bb}^{*m} q_b^2 \quad m = 2, 4 \quad (8)$$

where $\epsilon_{aa,bb}^*$ and $v_{aa,bb}^*$ correspond to the interactions of similar segments while ϵ_{ab}^* and v_{ab}^* belong to cross-interactions. The brackets $\langle X \rangle$ denote that the parameter X is averaged.

The external contact fraction q_a is defined by:

$$q_a = 1 - q_b = \phi_a [1 - \gamma(1 - 1/s_a)] / [1 - \gamma(1 - 1/\langle s \rangle)] \quad (9)$$

with the volume fraction of component a:

$$\phi_a = 1 - \phi_b = N_a s_a / (N_a s_a + N_b s_b) \quad (10)$$

with $N_{a(b)}$ the number of moles of component a (b).

The mixing parameters ϵ_{ab}^* and v_{ab}^* can be expressed relative to the pure component averages:

$$\epsilon_{ab}^* = X(\epsilon_{aa}^* \epsilon_{bb}^*)^{1/2} \quad (11)$$

$$v_{ab}^* = Y[(v_{aa}^{*1/3} + v_{bb}^{*1/3})/2]^3 \quad (12)$$

Writing the partition function for a binary system we obtain the following composition dependences for s and c_s :

$$\langle s \rangle = 1 / (\phi_a/s_a + \phi_b/s_b) \quad (13)$$

$$\langle c_s \rangle = \phi_a c_{s,a} + \phi_b c_{s,b} \quad (14)$$

The Helmholtz free energy A of mixing for a binary mixture in a volume V reads:

$$A/(N\langle s \rangle RT) = \phi_a \ln \phi_a/s_a + \phi_b \ln \phi_b/s_b + (1-y) \ln(1-y)/y \\ + \ln y/\langle s \rangle - (1-\langle \alpha \rangle y) \ln(1-\langle \alpha \rangle y)/\gamma y \\ - \langle c_s \rangle \ln[\langle v^* \rangle Q(1-\eta)^3] \\ + (1-\langle \alpha \rangle y) \langle c_s \rangle (AQ^{-4} - 2BQ^{-2}) / [2(1-\langle \alpha \rangle y)\tilde{T}] \quad (15)$$

Compositional derivatives of the Gibbs free energy G determine the miscibility behaviour of the mixture at constant T and p . The spinodal condition J_{sp} is defined by:

$$J_{sp} = (\partial^2 G / \partial \phi_b^2)_{p,T} = 0 \quad (16)$$

while at the consolute state the spinodal condition has to be fulfilled simultaneously with:

$$J_{cr} = (\partial^3 G / \partial \phi_b^3)_{p,T} = 0 \quad (17)$$

Because of the introduction of a Lennard-Jones interaction potential and the assumption of random mixing, in principle only mixtures with purely dispersive interactions can be handled. In this paper we report on the phase behaviour and related properties of the system PS/PpMeS in which only dispersive interactions are to be expected.

EXPERIMENTAL

Materials

PS was obtained from Pressure Chemical Company. PpMeS was synthesized by anionic polymerization under argon. The distilled and dried monomer was polymerized in toluene at 60°C using the initiator n-butyllithium. After 2 h the reaction was terminated by adding 2-propanol to the solution. The product was precipitated in 2-propanol and dried for 15 h under vacuum.

Blend preparation

PS and PpMeS were dissolved in toluene (0.5 wt%) at room temperature. After stirring the solutions for 15 h the solvent was evaporated to produce films with a typical thickness of 80 μm . The films were dried under vacuum for several days above T_g . The molar-mass characteristics of the blends are shown in Table 1.

Thermogravimetric analysis

The solvent content of the film was checked by thermogravimetric analysis (Perkin-Elmer TGA 7). A maximum weight reduction of 0.3% is observed before the blend reaches its degradation temperature.

Differential scanning calorimetry

All differential scanning calorimetry (d.s.c.) measurements were performed on a Perkin-Elmer DSC-7 system. Sample sizes were approximately 5 mg. After annealing at a certain temperature, the samples were quenched below T_g . Subsequently a temperature run was performed at a scan rate of 20 K min^{-1} and the blend was annealed at a different temperature. This cycle was repeated several times, varying the annealing temperature between T_g and the degradation temperature of the blend. This procedure was applied to PS/PpMeS blends with different compositions and different molar masses of the pure components. As a criterion of compatibility we used the appearance of one or two discontinuities in the d.s.c. thermogram after annealing for several hours at a certain temperature. Figures 1 and 2 illustrate examples of thermograms for a homogeneous and a heterogeneous system.

Phase-contrast light microscopy

The phase-contrast optical microscopy technique was used to detect phase separation. Standard optical microscopy was not applicable owing to the small difference

Table 1 Molar-mass characteristics of the blends expressed as M_w (kg mol^{-1}) measured by g.p.c. calibrated against PS standards

Blend	$M_{w,PS}$	$M_{w,PpMeS}$
1	37	133
2	50	133
3	50	44
4	110	44

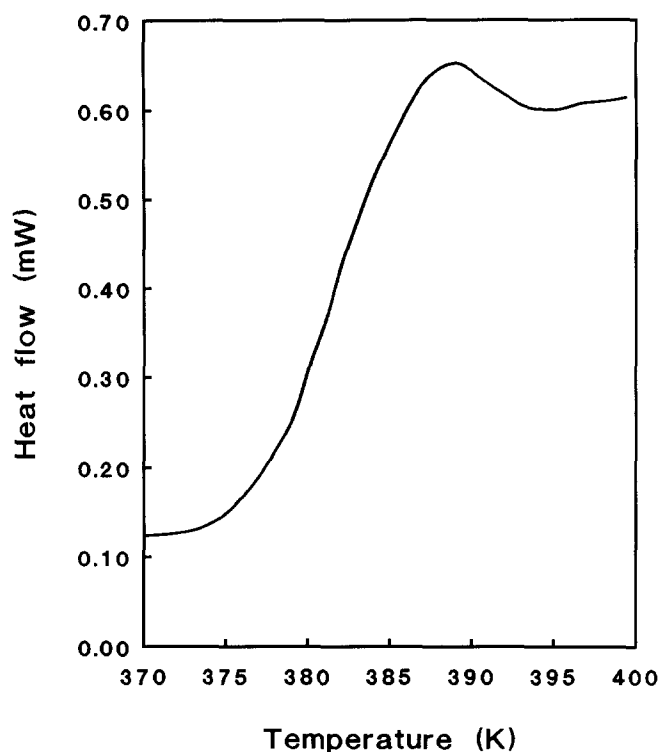


Figure 1 Thermogram of a homogeneous system PS 37/PpMeS 133

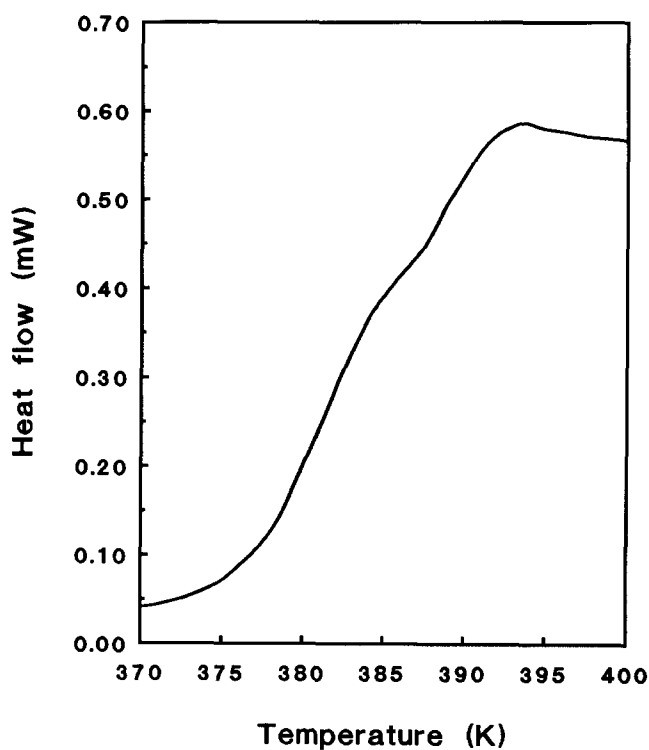


Figure 2 Thermogram of a heterogeneous system PS 37/PpMeS 133

in refractive index of the two homopolymers. The temperature programme used in the d.s.c. experiments was used in the microscopy experiments as well.

RESULTS AND DISCUSSION

Experimental

D.s.c. and phase-contrast microscopy techniques were used to determine the state of miscibility of the blends mentioned in Table 1. For three blends differing in molar

mass we clearly observed a transition from a heterogeneous to a homogeneous phase region with increasing temperature and vice versa. In Figures 3–6 the results of the d.s.c. and microscopy experiments are shown graphically. The two techniques give consistent results. The results indicate UCST phase behaviour, which is quite exceptional for high-molar-mass blends. This kind of phase behaviour is observed frequently for polymer/solvent or oligomer/oligomer systems but it is rather extraordinary for polymer/polymer systems. In fact, this is one of the very few polymer/polymer blends known to exhibit this kind of phase behaviour^{15–19}.

Theoretical

Estimation of molecular parameters. For the theoretical evaluation of miscibility behaviour, pure component parameters are required. These parameters, shown in Table 2, are extracted from equation-of-state data using a multiparameter estimation program developed at DSM, The Netherlands²⁰.

In the description of PS we take the monomer unit as one segment. For PpMeS we choose a segmental molar mass so that v_{PS}^* and v_{PpMeS}^* only differ by a few per cent. This is a quite arbitrary manoeuvre but Prigogine²¹ pointed out that in order for the mixing rules (equation (8)) to be valid the segmental reducing volumes should not differ by more than 5%.

Predictions. For values of the mixing parameters X and Y extremely close to one (see Table 2), the miscibility gap for the system PS 37/PpMeS 133 is predicted in a quantitative way as shown in Figure 3. Here the computed spinodal is compared with the experimental information. The values of the mixing parameters indicate that the intermolecular interactions are indeed dispersive. Therefore the blend obeys the restrictions inherent in the derivation of the theory.

In order to predict the phase behaviour of blends with different molar mass, we assume all model parameters to be constant except s_a and s_b . The predicted spinodals are presented in Figures 4–6. The temperature shift of the UCST with changing molar mass is slightly underestimated by theory. The discrepancy is most pronounced for the PS 110/PpMeS 44 blend.

The PS/PpMeS system shows no LCST type of demixing behaviour experimentally and a LCST is not predicted with the HH theory, not even at extremely high and physically unrealistic temperatures. For systems without specific interactions LCST phase behaviour is governed by equation-of-state properties of the constituents²². In terms of the HH theory LCST demixing will occur only when the free-volume difference of the pure components exceeds a certain value. This has been

Table 2 Molecular parameters and cross-interaction parameters according to the HH theory

	Pure component parameters:			
	c^* (J mol ⁻¹)	v^* (m ³ mol ⁻¹)	c_s	M_w/s (kg mol ⁻¹) ^a
PS	6691.6	9.8462×10^{-5}	0.85322	0.1040
PpMeS	7114.7	9.8422×10^{-5}	0.89964	0.1005
Cross-interaction parameters: $X = 1.0001731$ $Y = 1.0005239$				

^a M_w/s expresses the molar mass per segment

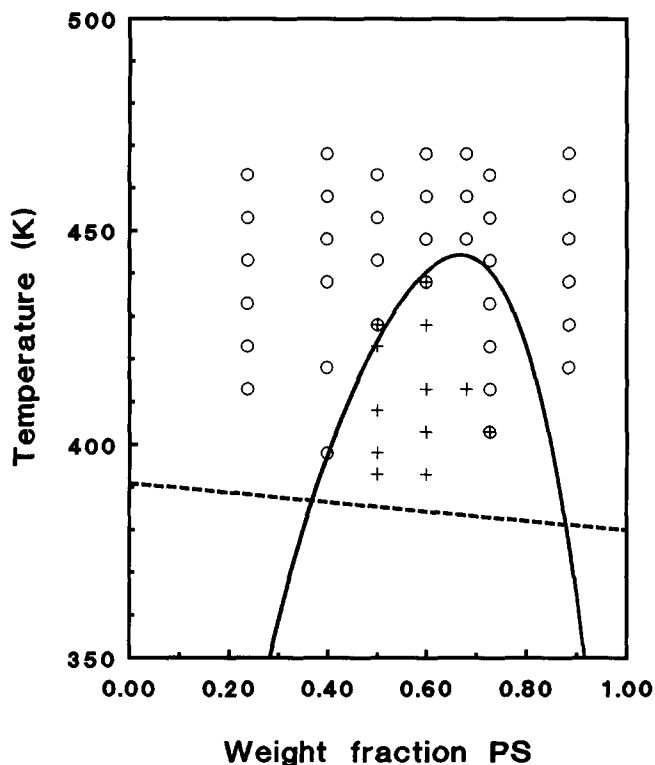


Figure 3 Experimental phase diagram and theoretical spinodal (—) for the system PS 37/PpMeS 133: (---) T_g line; (+) heterogeneous; (O) homogeneous; (⊕) homo/heterogeneous

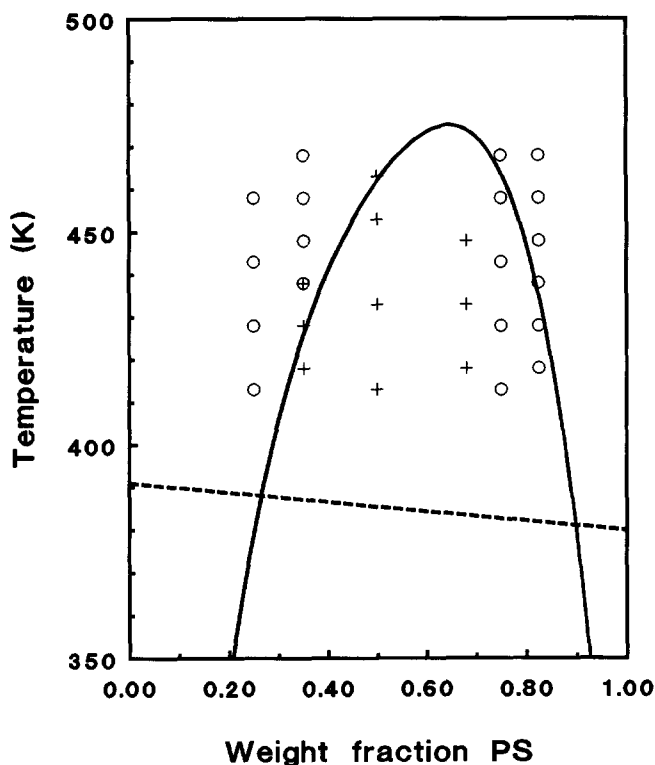


Figure 4 Experimental phase diagram and theoretical spinodal for the system PS 50/PpMeS 133: see Figure 3 for details

shown before for the Simha-Somcynsky theory^{8,9} and is also valid for the HH theory.

In Figure 7 experimental site fraction y (free-volume fraction = $(1 - y)$) for both components as a function of temperature is plotted at atmospheric pressure. The free-volume difference for both components is extremely

small and increases only slightly with temperature. Consequently the blend will not phase-separate in the indicated temperature range.

UCST type of demixing is controlled by the energetic contributions to the free energy. In Figures 8 and 9 excess volume and excess enthalpy at indicated pressure at the

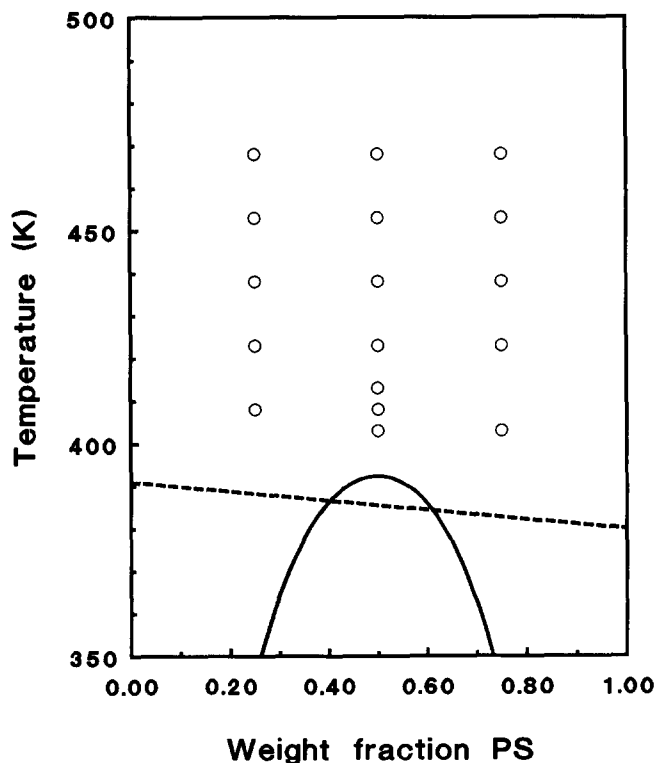


Figure 5 Experimental phase diagram and theoretical spinodal for the system PS 50/PpMeS 44: see Figure 3 for details

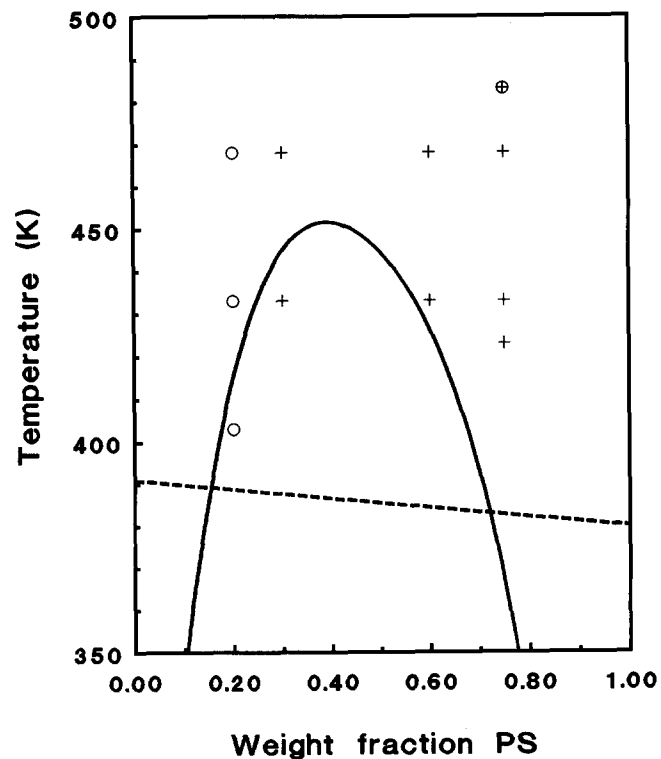


Figure 6 Experimental phase diagram and theoretical spinodal for the system PS 110/PpMeS 44: see Figure 3 for details

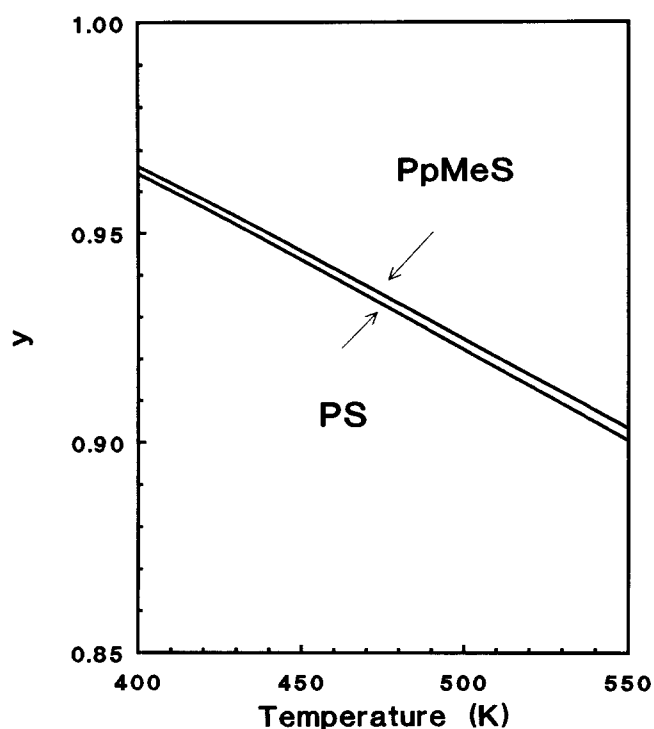


Figure 7 Occupied site fraction for PS and PpMeS as a function of temperature

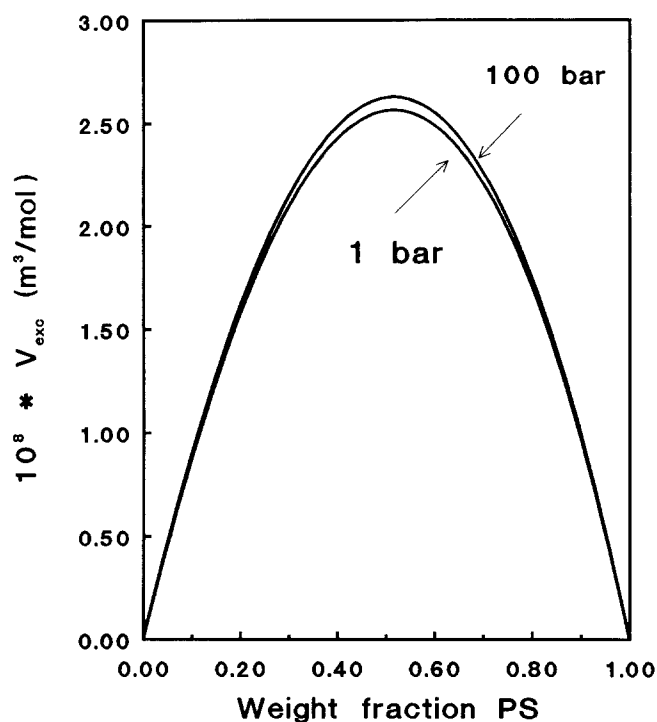


Figure 8 Predicted excess volume for the system PS 37/PpMeS 133 at atmospheric and elevated pressure

corresponding critical temperature are presented. The positive excess enthalpy indicates unfavourable dispersive interactions and leads to phase separation at sufficient low temperatures.

General thermodynamics correlates the shift of the critical temperature with pressure to the curvature of excess volume (v_{exc}) and enthalpy (h_{exc}) with respect to the weight fraction PS (w_{PS}):

$$(\partial T/\partial p)_c = T(\partial^2 v_{exc}/\partial w_{PS}^2)_{p,T}/(\partial^2 h_{exc}/\partial w_{PS}^2)_{p,T} \quad (18)$$

As shown in Figures 8 and 9 the predicted excess volume and enthalpy have a negative curvature over the entire composition regime. Therefore the critical temperature will increase with pressure. In Figure 10 the predicted critical temperature as a function of pressure is shown. We do not have any experimental information about the pressure influence on the demixing behaviour of the PS/PpMeS system.

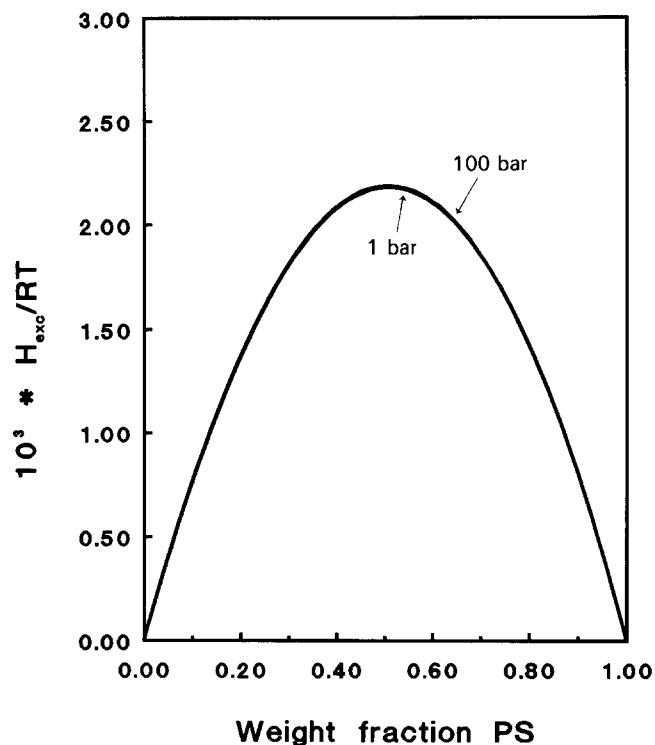


Figure 9 Predicted excess enthalpy for the system PS 37/PpMeS 133 at atmospheric and elevated pressure. Note the excess enthalpy is hardly pressure-sensitive

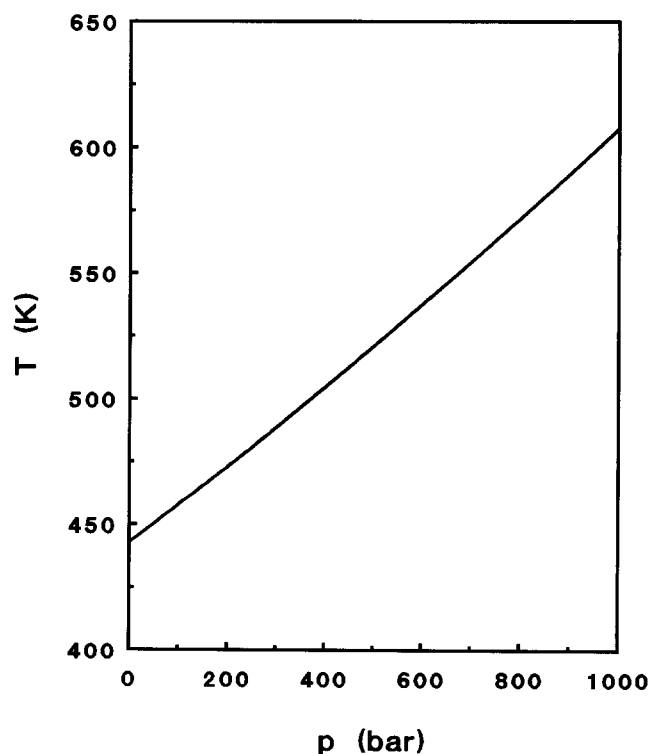


Figure 10 Prediction for the pressure dependence of the UCST for the blend PS 37/PpMeS 133

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