# Liquid-liquid phase behavior of mixtures according to the Simha-Somcynsky theory

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# Liquid-Liquid Phase Behavior of Mixtures According to the Simha-Somcynsky Theory

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It is well known that equilibrium thermodynamic properties are governed by different functional derivatives of the thermodynamic functions of state. For example, the phase behavior of mixtures of low and/or high molar mass components is determined by the compositional derivatives of the free energy. In this contribution, the merits of the Simha-Somcynsky theory in describing and predicting the phase behavior of mixtures are considered. The influence of temperature and composition on the miscibility behavior for practically binary polymer solutions are studied. Furthermore, the important aspect of polydispersity, inherent to synthetic polymer systems will be addressed.

## INTRODUCTION

Polymer properties are often combined by mixing two or more polymers. The morphology required to obtain the desired property may range from a completely (miscible) homogeneous to a two or multiphase (immiscible) structure. Often, polymer blends are subjected to elevated pressures and temperatures during processing. These factors influence the miscibility and consequently the ultimate morphology obtained. Moderate pressures of a few hundred bar may already have a marked influence on the location of the miscibility gap in the phase diagram.

The miscibility of polymer systems is determined by the thermodynamic functions of state. Although true equilibrium is not always obtained, the equilibrium state presents the driving force to the formation of multiphase materials. Therefore, knowledge of this equilibrium situation is valuable because it defines the final state of kinetically determined processes. In order to relate miscibility behavior of polymer systems to thermodynamic and molecular variables, a reliable and accurate description of the thermodynamic functions of state is a prerequisite. The Simha-Somcynsky (S-S) hole theory proved to be quantitatively successful in the description and prediction of equation of state properties of polymer systems (1, 2).

In the past few years, the S-S theory has been adapted to deal with compositional derivatives of the free energy, e.g. phase behavior (3-5). So

far, a systematic evaluation of miscibility behavior according to the S-S theory and comparison with experimental data have not been presented. Such a systematic study requires detailed and accurate experimental information. Such information on phase behavior for polymer blends is not readily available yet. For polymer solutions, a wealth of accurate and detailed information is at hand. Therefore, the present discussion will be based on polymer solution data. The influence of some molecular variables, e.g. molar mass, molar mass distribution, and flexibility will be discussed. The influence of pressure on the phase diagram has already been documented to some extent (3-6).

### The Simha-Somcynsky Theory: Some Thermodynamic Equations

The underlying assumptions of the Simha-Somcynsky (S-S) theory have been discussed on several occasions (7, 8). Therefore, we will only summarize the equations which are necessary in the present discussion, for both single components and mixtures.

#### Pure Component

In the S-S theory, a molecular liquid is modeled on a quasi cell lattice of which the cells can either be vacant or occupied by one and only one segment of a molecule. For a pure, monodisperse component $i$, the molar Helmholtz free energy $F_i$ at a temperature $T$ and molar volume

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$V$ reads (3, 4):

$$F_i/(RT) = ln(y_i/s_i)$$

$$+ s_i(1 - y_i)/(y_i) \, ln(1 - y_i)$$

$$+ (s_i - 1)(1 - ln(z - 1)) \qquad (1)$$

$$- c_i[ln(v_{ii}^*(1 - \eta_i)^3/Q_i)$$

$$+ 3/2 \, ln(2\pi M_{oi}RT/(N_a h)^2)$$

$$- y_i Q_i^2(AQ_i^2 - 2B)/(2\tilde{T}_i)]$$

with $y_i$ the fraction of occupied lattice cells; $s_i$ the number of lattice sites occupied by a molecule of a component of molar mass $M_i$ possessing $3c_i$ external degrees of freedom; $\epsilon_{ii}^*$ and $v_{ii}^*$, the maximum attraction energy and segmental hard core volume characterizing the Lennard-Jones pair interaction potential; $z$ the number of nearest neighbours of a lattice cell; $Q_i = (y_i \tilde{V}_i)^{-1}$; $\eta_i = 2^{-1/6} y_i Q_i^{1/3}$; $M_{oi}$ $(= M_i/s_i)$ is the segmental molar mass; $A$ $(= 1.011)$ and $B$ $(= 1.2045)$ are constants. $R$, $N_a$, and $h$ are the gas, Avogadro's and Planck's constants.

In $Eq$ $1$ and in the equations to follow, the thermodynamic variables, $T$, $V$, and $P$ often enter the equations in reduced form, expressed by tildes, i.e., $\tilde{T}$ $(= T/T^*)$, $\tilde{V}$ $(= V/V^*)$ and $\tilde{P}$ $(= P/P^*)$. The reducing parameters are defined as:

$$T_i^* = q_i z \epsilon_{ii}^*/(c_i R) \qquad (2.a)$$

$$P_i^* = q_i z \epsilon_{ii}^*/(s_i v_{ii}^*) \qquad (2.b)$$

$$V_i^* = v_{ii}^*/M_{oi} \qquad (2.c)$$

where $q_i z$ $(= s_i(z - 2) + 2)$, the number of intermolecular nearest neighbors of the s-mer.

The use of the reducing parameters makes it possible to define an effective principle of corresponding state for the equation of state (7):

$$\tilde{P}_i \tilde{V}_i/\tilde{T}_i - 1/(1 - \eta_i) \qquad (3)$$

$$- 2y_i Q_i^2(AQ_i^2 - B)/\tilde{T}_i = 0$$

The fraction of occupied sites $y_i$ is determined by the minimization of the free energy (7), viz.

$$3c_i((\eta_i - 1/3)/(1 - \eta_i)$$

$$+ y_i Q_i^2(2B - 3AQ_i^2)/(6\tilde{T}_i)) \qquad (4)$$

$$- s_i + 1 - s_i ln(1 - y_i)/y_i = 0$$

In practice an extra relation between the number of external degrees of freedom $3c_i$ and the relative linear polymer chain length $s_i$ is postulated:

$$3c_i = s_i + 3 \qquad (5)$$

*Multicomponent Systems*

The hole theory has been extended to multicomponent systems (3, 4). A polydisperse polymer $A$ is presented as a mixture of homologues differing in chain length $s_{ai}$ and, eventually, other molecular parameters. For a binary mixture of two polydisperse polymers $A$ and $B$ having $n_a$ and $n_b$ homologues respectively, the molar Helmholtz free energy of the mixture reads:

$$F_m/(RT) = \sum_{}^{n_a} x_{ai} \, lnx_{ai}$$

$$+ \sum_{}^{n_b} x_{bi} \, lnx_{bi} + ln(y/\langle s \rangle)$$

$$+ \langle s \rangle(1 - y)ln(1 - y)/y$$

$$+ (\langle s \rangle - 1)(1 - ln(z - 1)) \qquad (6)$$

$$- \langle c \rangle[ln(\langle v^* \rangle(1 - \eta)^3/Q)$$

$$+ 3/2 \, ln(2\pi \langle M_0 \rangle RT/(N_a h)^2)$$

$$- yQ^2(AQ^2 - 2B)/(2\tilde{T})]$$

where the different parameters depend on composition. The definitions of these parameters are summarized in Appendix A. In short, the mixture is characterized by the molecular parameters of the pure components and by the parameters dealing with the cross pair interactions between segments of different components and different homologues. For the mixture the minimization condition, $Eq$ $4$, and the equation of state, $Eq$ $3$, determining $y$ and $\tilde{V}$, remain identical in form, provided the parameters become composition dependent according to $Eqs$ $A.1$–$A.9$. The molar Gibbs free energy $G_m$ can be computed from $Eqs$ $3$, $4$ and $6$:

$$G_m/RT = F_m/RT + \langle c \rangle \tilde{P}\tilde{V}/\tilde{T} \qquad (7)$$

For mixtures, the possibility exists that the heterogeneous state becomes the equilibrium state in a certain temperature and pressure region of the phase diagram. The spinodal condition, defining the boundary between the stable and unstable regions of the phase diagram, is given by the first Gibbs determinant, $J_{sp}$, viz. (9):

$$J_{sp} = \left| \frac{\partial^2 \Delta G}{\partial x_i \partial x_j} \right|_{P,T} \qquad (8)$$

The critical conditions satisfy $Eq$ $8$ simultaneously with the second Gibbs determinant $J_c$, obtained by substituting any row from $Eq$ $8$ by the row vector (9):

$$[\partial J_{sp}/\partial x_i]_{P,T} \qquad (9)$$

## RESULTS AND DISCUSSION

In order to evaluate the predictive and descriptive quality of the hole theory for thermodynamic properties related to compositional derivatives of the free energy, accurate experimental data for well characterized polymer samples are necessary. For polymer mixtures these data are not readily available. On the other hand, for polymer solutions a wealth of literature data is at hand. The system polystyrene (PS)/cyclohexane (CH) is selected for the present discussion. For this system miscibility data are available for solutions of polymer samples with very narrow molar mass distributions. In the following, these solutions will be approx-

imated as binary mixtures of monodisperse polystyrene fractions in cyclohexane. Furthermore, miscibility data are available for solutions of polydisperse polymer fractions for which the molar mass distribution is characterized as accurately as possible.

## Practically Binary Polymer Solutions

For six polystyrene fractions with a narrow molar mass distribution critical (10) conditions in cyclohexane are known. The molar mass distribution characteristics for the PS-samples are summarized in *Table 1*. For details concerning the materials and the experimental techniques, the interested reader is refered to the original literature (10–12). In the computations the polystyrene samples will be approximated to be monodisperse. The molecular parameters characterizing the pure components in the S-S theory, computed from equation of state data (13, 14), are summarized in *Table 2*. For this purpose a multiparameter estimation program was used. To compute the molecular parameters from equation of state data for cyclohexane, the chain length and the flexibility parameter $c$ are fixed. For the considered polymer samples, no experimental PVT data are available. The scaling parameters $P^*$, $V^*$ and $T^*$ are determined from experimental data of Quach and Simha (14).

Assuming that the PVT surface does not change in the molar mass region considered, the molecular parameters were computed from Eqs 2 and 5. The cross parameters, $\epsilon_{12}^*$ and $v_{12}^*$, were adjusted to give quantitative agreement between the computed and experimental critical conditions. These parameter values are summarized in *Table 2* also. The parameters

become dependent on chain length as shown in *Figs. 1* and *2*.

Thus, for each set of critical conditions we have a different set of molecular parameters. The number of adjustable parameters can be reduced considerably, if we define two parameters; i.e. $\Theta$ and $\Omega$:

$$\Omega = \epsilon_{12}^*/(\epsilon_{11}^*\epsilon_{22}^*)^{1/2} \tag{10}$$

and

$$\Theta = v_{12}^*/((v_{11}^{*\,1/3} + v_{22}^{*\,1/3})/2)^3 \tag{11}$$

For purely dispersive interactions $\Omega$ equals one. If the segmental volume $v_{12}^*$ would be equal to the hard sphere average of the pure components segmental volumes, $\Theta$ equals one also. In *Figs. 3* and *4* it can be observed that both parameters are very close to one. More important however, is the observation that both parameters are chain length independent within
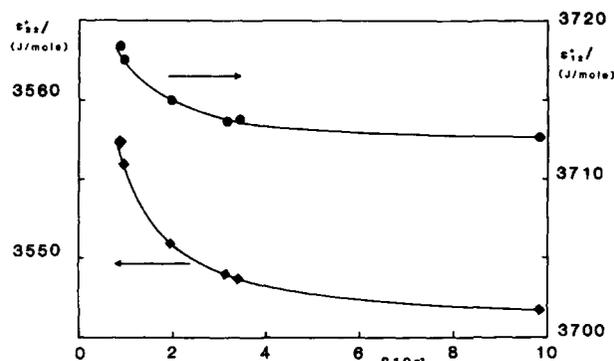


*Fig. 1. Chain length dependence of molecular parameters $\epsilon_{22}^*$ and $\epsilon_{12}^*$ for PS fractions with a narrow molar mass distribution.*
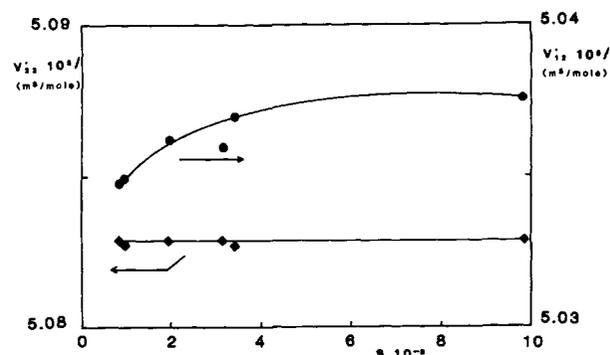


*Fig. 2. Chain length dependence of molecular parameters $v_{22}^*$ and $v_{12}^*$ for PS fractions with a narrow molar mass distribution.*

**Table 1. Molecular Distribution Characteristics of PS Fractions and Critical Conditions ($T_{cr}$, $w_{cr}$) in CH.**

| Sample code | $M_n$ [kg/mole] | $M_w$ [kg/mole] | $M_z$ [kg/mole] | $T_{cr}$ [K] | $w_{cr}$ mass fraction |
|---|---|---|---|---|---|
| M1 | 45.0 | 45.3 | 45.6 | 287.29 | 0.149 |
| M2 | 49.0 | 51.0 | 55.0 | 288.85 | 0.146 |
| M3 | 102.0 | 103.0 | 104.0 | 296.85 | 0.092 |
| M4 | 154.0 | 166.0 | 181.0 | 296.60 | 0.099 |
| M5 | 174.0 | 180.0 | 185.0 | 296.95 | 0.095 |
| M6 | 436.0 | 520.0 | 593.0 | 301.15 | 0.064 |
| M7 | 450.0 | 498.0 | 590.0 | — | — |
| M8 | 211.0 | 522.0 | 790.0 | — | — |
| M9 | 154.0 | 672.0 | 1800.0 | — | — |

**Table 2. Molecular Parameters for CH and PS Samples According to the S-S Theory. Also the Cross Parameters $\epsilon_{12}^*$ and $v_{12}^*$ are Listed.**

| Component | $\epsilon^*$ [J/mole] | $v^* 10^5$ [m$^3$/mole] | $c$ | $s$ | $M_0 10^2$ [kg/mole] | $\epsilon_{12}^*$ [J/mole] | $v_{12}^*$ [m$^3$/mole] |
|---|---|---|---|---|---|---|---|
| M1 | 3557.3 | 5.0828 | 287.0 | 858.1 | 5.279 | 3718.4 | 5.0347 |
| M2 | 3555.9 | 5.0827 | 323.0 | 966.1 | 5.279 | 3717.5 | 5.0349 |
| M3 | 3550.7 | 5.0829 | 651.4 | 1951.1 | 5.279 | 3714.9 | 5.0361 |
| M4 | 3549.0 | 5.0828 | 1049.2 | 3144.5 | 5.279 | 3713.6 | 5.0359 |
| M5 | 3548.7 | 5.0827 | 1137.6 | 3409.8 | 5.279 | 3713.7 | 5.0369 |
| M6 | 3546.7 | 5.0829 | 3284.4 | 9850.2 | 5.279 | 3712.6 | 5.0376 |
| CH | 3926.9 | 4.9985 | 1.8 | 1.9 | 4.421 | — | — |

save bounds of experimental uncertainty derived from equation of state data.

Thus, for the system PS/CH the cross parameters can be computed from the pure component parameters and the parameters $\Theta$ and $\Omega$. Hereby, all the theoretical parameters for the binary system are defined. We are now in a position to predict other thermodynamic properties for binary systems. Here, we will concentrate on the spinodal conditions, shown in *Fig. 5*. Details concerning the computational methods have been presented elsewhere (6).

It can be observed in *Fig. 5* that the agreement between experimental and predicted spinodals deteriorates with decreasing molar mass for both spinodal branches. However, quantitative agreement between computed and experimental concentrated spinodal branches can be achieved, if for the polymer *Eq 5* is abandoned and separate values for the number of external degrees of freedom is allowed for each PS fraction. Consequently, the other pure PS molecular parameters, as well as the values for the cross parameters, need to be recomputed, in order to get a consistent and quantitative description of PVT and critical data. The new parameter values are summarized in *Table 3*. The computed
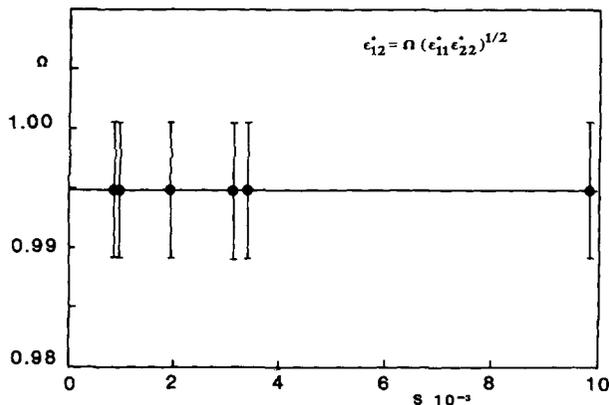
*Fig. 5. Experimental spinodal (●) and critical (■) conditions for three different PS fractions in CH (10–12). Computed spinodals and critical conditions for molecular parameters in Table 2 (—, ■).*

*Fig. 3. Parameter $\Omega$ versus chain length. The error bars shown are due to the uncertainties in the pure component parameters derived from equation of state data.*

*Fig. 4. Parameter $\Theta$ versus chain length. The error bars shown are due to the uncertainties in the pure component parameters derived from equation of state data.*

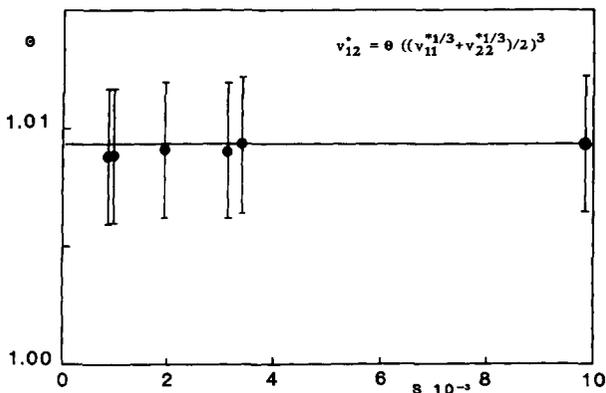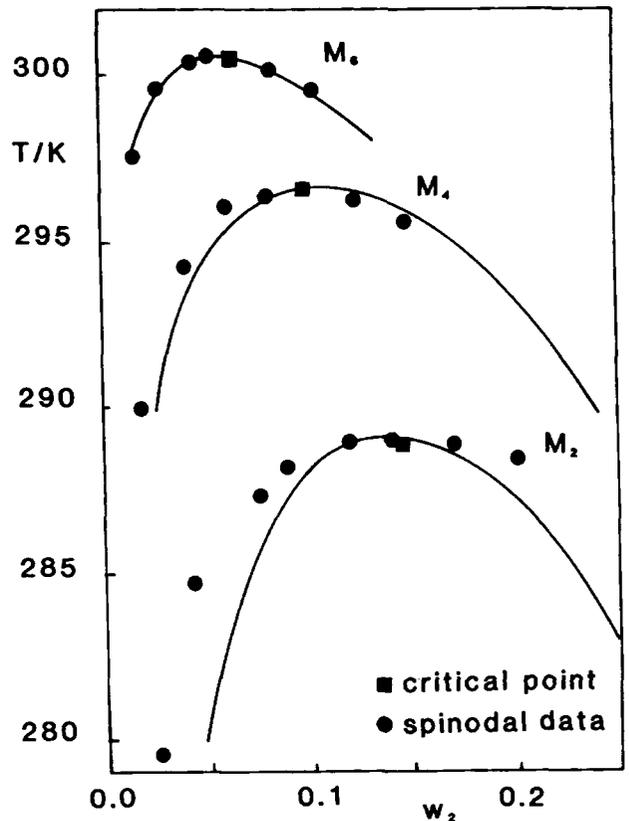spinodal and critical conditions are shown in *Fig. 6*. The values of the flexibility parameter $c$ adapted for the different PS fractions are shown in *Fig. 7*. For comparison, the chain length dependence according to *Eq 5* is shown also.

Remaining deviations for the dilute branches of the spinodals can be attributed to dilute solution effects. These deviations can be eliminated elegantly by the bridging function concept introduced by Koningsveld, *et al.* (15, 16), and Irvine and Gordon (17).

The almost quantitative success of the S-S theory for the UCST region of the phase diagram is very gratifying. One is now in the position to predict the LCST region of the phase diagram with the parameters determined from the UCST phase behavior. The results are shown in *Fig. 8*. A direct comparison with experimental data is not possible because only cloud point data for a polystyrene fraction with an ill defined molar mass distribution are available (22). A qualitative comparison shows that the shape and location of the LCST miscibility gap are very similar to the experimental situation. So far, it is clear that the hole theory offers a successful description and prediction of polymer solution phase behavior.

### Influence of Polydispersity

Every synthetic polymer has a molar mass distribution that can have a profound influence

**Table 3. Molecular Parameters for PS Fractions, Adapting an Adjusted Value for the Flexibility Parameter c and Cross Parameters $\epsilon^*_{12}$, $v^*_{12}$ According to the S-S Theory.**

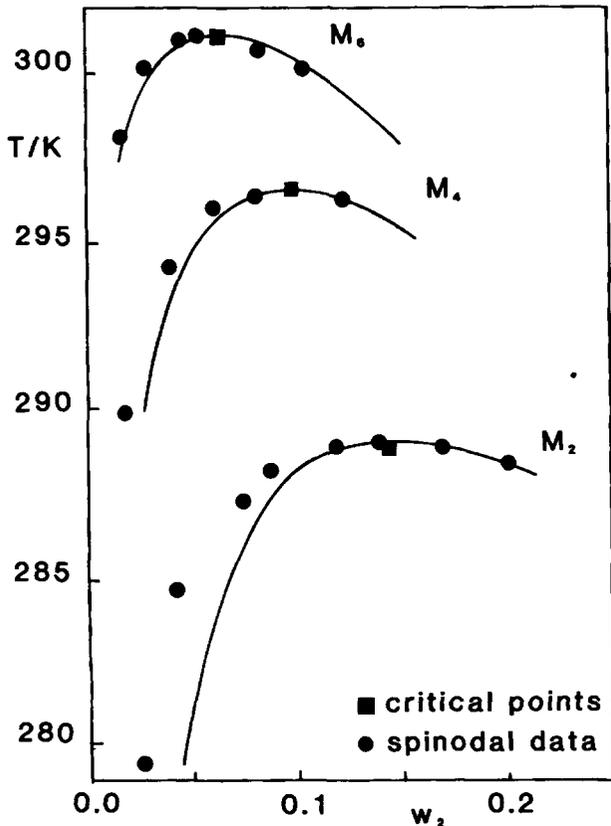| Component | $\epsilon^*$ [J/mole] | $v^* 10^5$ [m³/mole] | c | s | $M_0 10^2$ [kg/mole] | $\epsilon^*_{12}$ [J/mole] | $v^*_{12}$ [m³/mole] |
|---|---|---|---|---|---|---|---|
| M2 | 3440.7 | 4.844 | 323.6 | 1014.6 | 5.027 | 3653.2 | 5.0289 |
| M4 | 3527.0 | 4.968 | 1062.2 | 3218.9 | 5.157 | 3701.9 | 5.0496 |
| M6 | 3605.5 | 5.082 | 3350.6 | 9854.7 | 5.277 | 3744.9 | 5.0851 |



Fig. 6. Experimental spinodal (●) and critical (■) conditions for three different PS fractions in CH (10-12). Computed spinodals and critical conditions for molecular parameters in Table 3 (—, ■).



Fig. 7. Flexibility parameter c per segment versus critical composition. Values shown in Table 3 (—, ●). According to Eq 5 (---).

on the phase diagram. The evaluation of thermodynamic properties is certainly complicated by polydispersity. For example, one is confronted with the problem of representing the molar mass distribution. In the past, continuous distribution functions were used. However, this might not be the best solution, particularly if one wants to compute thermodynamic properties efficiently. A useful representation of molar mass distributions was discussed by Irvine and Kennedy (18). Any molecular mass distribution, even if it is formally unbounded in terms of the number of components, can be approximated by its r-equivalent analogue, comprising approximately $\gamma/2$ $\delta$-function components. This approximation allows the matching of r moments of the $\delta$-distribution to those of the original distribution. In general, the other moments of the distributions will not match.

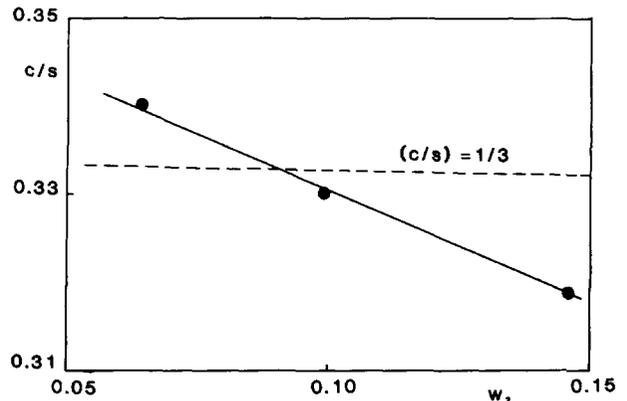To exemplify the influence of polydispersity, spinodals and critical conditions were com-

puted for three polydisperse PS samples having comparable mass average molar masses $M_w$. For these systems experimental spinodal data are available (12). The computational results together with the experimental data are shown in *Fig. 9*. The molecular characteristics and the r-equivalent representations are summarized in *Table 1* and *4* respectively.

Upon inspecting *Fig. 9*, it becomes clear that in the hole theory the spinodal is not solely determined by the mass average molar mass $M_w$. This statement is in qualitative agreement with experimental facts. The observed temperature shift with increasing polydispersity, shown by the experimental spinodals, is reproduced in the computations quite well. However, a quantitative agreement with experimental spinodal data has not been achieved yet. Especially, the crossing of the spinodals at certain compositions isn't predicted.

For Flory-Huggins type of free energy expressions, it can be proven that spinodal conditions are determined only by the mass average molar mass $M_w$ (19-21). In the hole theory it isn't resolved yet which moments of the molar mass distribution determine the spinodal conditions. It is hoped that taking into account the proper moments of the molar mass distribution, the crossing of the spinodal curves can be understood theoretically as well. This is a matter of current research. A general conclusion, concerning the influence of polydispersity on spinodal conditions, that can be obtained from the present results is that the hole theory behaves quite differently from the aforementioned Flory-Huggins type of models.
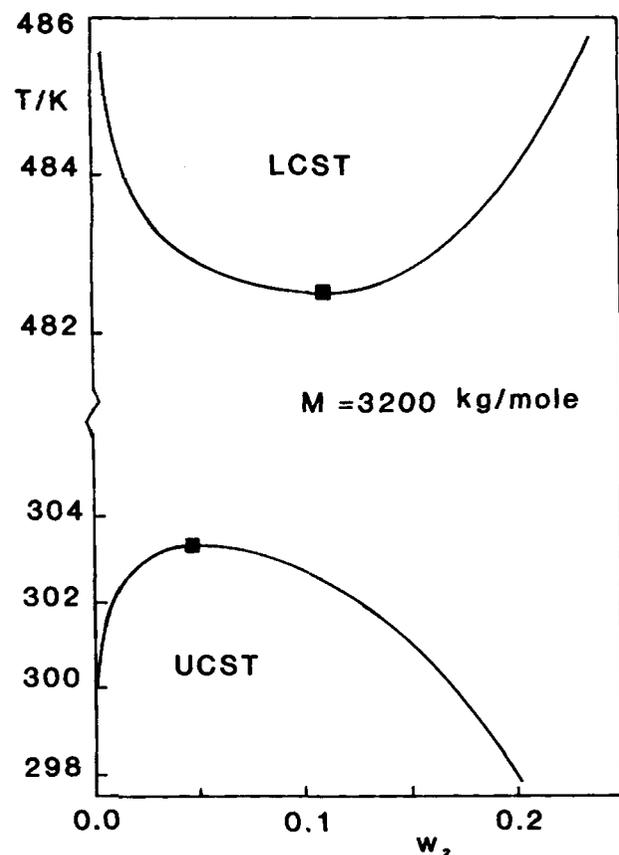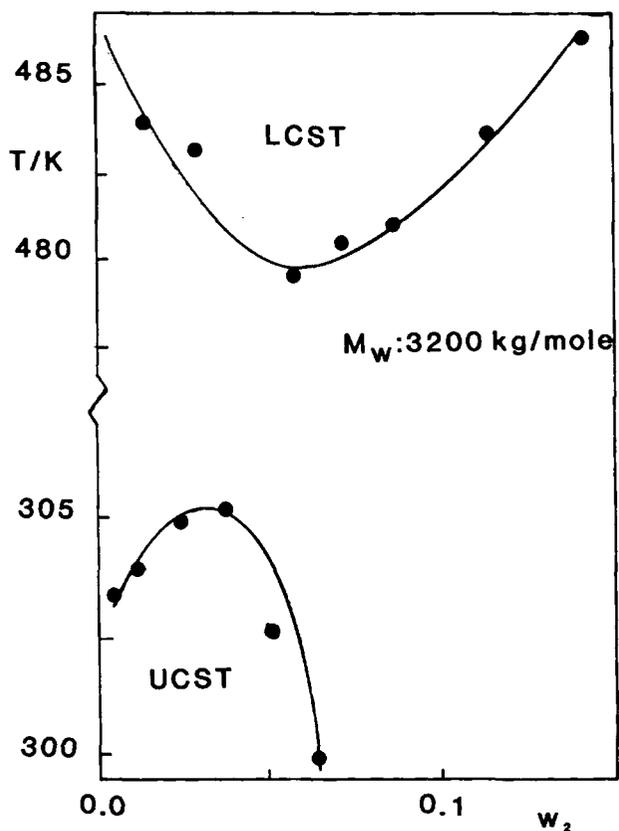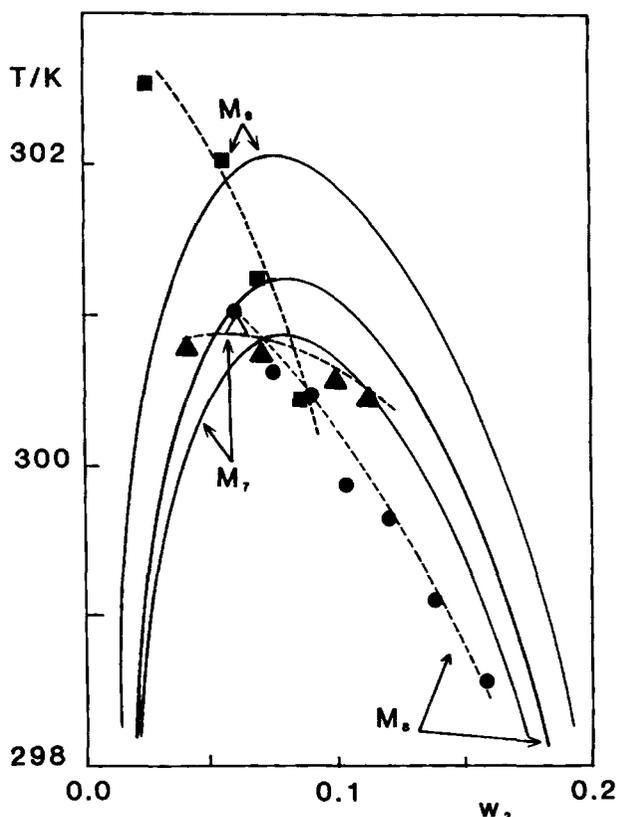
Fig. 9. Experimental spinodal data for polydisperse PS fractions with similar mass average molar masses (■, ●, ▲, ---) (10, 12). Computed spinodal conditions for the r-equivalent polymer solutions listed in Table 4 (—).

Table 4. r-equivalent δ-distributions for PS fractions M4, M5 and M6 listed in Table 1.

|     | $w_1$ | $s_1$ | $w_2$ | $s_2$ |
| --- | --- | --- | --- | --- |
| M4 | 0.86472 | 7829.9 | 0.13528 | 19685.0 |
| M5 | 0.45198 | 2086.6 | 0.54802 | 16322.9 |
| M6 | 0.70687 | 2109.2 | 0.29313 | 38341.1 |

## CONCLUSIONS

The present results show that the hole theory offers a basis to evaluate the phase behavior of polymer systems. The number of external degrees of freedom has an important influence on the shape of the miscibility gap. Adjusting the value of the flexibility parameter, the computed spinodals can be made to agree with experimental data. In the S-S theory the non-combinatorial entropy contributions to the free energy, derived from the cell partition function, play an important role. In many other theoretical studies, this extra contribution to the free energy is not taken into account. It can be appreciated that for polymer mixtures this extra free volume term becomes even more important. In this case the Flory-Huggins combinatorial entropy is very small and other entropy contributions will dictate the shape and location of the miscibility gap. The influence of polydispersity on the miscibility behavior in the Simha-Somcynsky theory is shown to be more complex than that



Fig. 8. (a) Experimental cloud point data (—, ●) for PS fraction with mass average molar mass $M_w$ = 3200 kg/mole (22). (b) Computed UCST and LCST miscibility gaps for a monodisperse polystyrene fraction with molar mass equal to $M_w$ of the experimental system (spinodals (—) and critical conditions (■)).

expected for Flory-Huggins like models. For such an approach it can be shown that the weight average molar mass determines the shape and position of the miscibility gap. For the hole theory other moments of the molar mass distribution become important as well. The exact influence of the molar mass distribution on the complete phase diagram of polymer solutions is a topic of current research. Also the effect of double polydispersity, present in a mixture of two polydisperse polymers $A$ and $B$, will be considered in future research.

Strictly, the hole theory is only applicable to concentrated systems. In order to be able to model the dilute region of the phase diagram, dilute solution effects have to be considered. This can be accomplished according to the bridging function concept. Once more, for polymer blends, dilute solution effects would be noticeable on both ends of the composition range.

## NOTATION

| | |
|---|---|
| $A, B$ | constants in segmental pair potential |
| $c_i$ | flexibility parameter of component $i$ |
| $\langle c \rangle$ | average flexibility parameter for mixture |
| $F_i$ | molar Helmholtz free energy of component $i$ |
| $F_m$ | molar Helmholtz free energy of mixture |
| $G_m$ | molar Gibbs free energy of mixture |
| $h$ | Planck's constant |
| $J_{sp}$ | spinodal determinant |
| $M_{oi}$ | segmental molar mass of component $i$ |
| $\langle M_o \rangle$ | average segmental molar mass of mixture |
| $N_a$ | Avogadro's number |
| $n_a(n_b)$ | number of homologues of component $a(b)$ |
| $P$ | absolute pressure |
| $\tilde{P}$ | reduced pressure of mixture |
| $P^*$ | scaling pressure of mixture |
| $\tilde{P}_i$ | reduced pressure of component $i$ |
| $P_i^*$ | scaling pressure of component $i$ |
| $q_i z$ | number of external nearest neighbours of s mer |
| $Q$ | $(y\tilde{V})^{-1}$ |
| $Q_i$ | $(y_i \tilde{V}_i)^{-1}$ |
| $R$ | gas constant |
| $s_i$ | chain length of component $i$ |
| $\langle s \rangle$ | average chain length in mixture |
| $T$ | absolute temperature |
| $\tilde{T}$ | reduced temperature of mixture |
| $T^*$ | scaling temperature of mixture |
| $\tilde{T}_i$ | reduced temperature of component $i$ |
| $T_i^*$ | scaling temperature of component $i$ |
| $V$ | molar volume |
| $\tilde{V}$ | reduced volume of mixture |
| $V^*$ | scaling molar volume of mixture |
| $\tilde{V}_i$ | reduced volume of component $i$ |
| $V_i^*$ | scaling molar volume of component $i$ |
| $v_{ij}^*$ | characteristic segmental volume of contact $i$–$j$ |
| $\langle v^* \rangle$ | average segmental volume in mixture |
| $x_i$ | mole fraction of component $i$ |
| $x_{ai} (x_{bj})$ | mole fraction of homologue $i(j)$ of component $a(b)$ |
| $y_i$ | fraction of occupied lattice sites for component $i$ |
| $y$ | fraction of occupied lattice sites in mixture |
| $z$ | lattice coordination number |
| $\epsilon_{ij}^*$ | characteristic segmental energy of contact $i$–$j$ |
| $\langle \epsilon^* \rangle$ | average characteristic segmental energy in mixture |
| $\eta$ | $(2^{-1/6} y Q^{1/3})$ |
| $\eta_i$ | $(2^{-1/6} y_i Q_i^{1/3})$ |
| $\Omega$ | $(\epsilon_{12}^* / (\epsilon_{11}^* \epsilon_{22}^*)^{1/2})$ |
| $\Theta$ | $v_{12}^* / ((v_{11}^{*1/3} + v_{22}^{*1/3})/2)^3$ |

## APPENDIX A: COMPOSITION DEPENDENCE OF MOLECULAR PARAMETERS IN THE S-S THEORY

For a binary mixture of components $A$ and $B$ with no specific interactions, comprising $n_a$ and $n_b$ homologues, respectively, the molecular parameters become composition dependent according to:

$$\langle s \rangle = \sum x_{ai} s_{ai} + \sum x_{bi} s_{bi} \tag{A1}$$

$$\langle qz \rangle = \sum x_{ai}(s_{ai}(z-2)+2) + \sum x_{bi}(s_{bi}(z-2)+2) \tag{A2}$$

$$\langle M_o \rangle = (\sum x_{ai} s_{ai} M_{oai} + \sum x_{bi} s_{bi} M_{obi})/\langle s \rangle \tag{A3}$$

$$\langle c \rangle = \sum x_{ai} c_{ai} + \sum x_{bi} c_{bi} \tag{A4}$$

$$\langle \epsilon^* \rangle \langle v^* \rangle^2 = \sum_{}^{n_a} X_{ai}(\sum_{}^{n_b} X_{bi} \epsilon_{aibj}^* v_{aibj}^{*2}) \tag{A5}$$

$$\langle \epsilon^* \rangle \langle v^* \rangle^4 = \sum_{}^{n_a} X_{ai}(\sum_{}^{n_b} X_{bi} \epsilon_{aibj}^* v_{aibj}^{*4}) \tag{A6}$$

with $X_{ai} = x_{ai}(s_{ai}(z-2)+2)/\langle qz \rangle$

$$T^* = \langle qz \rangle \langle \epsilon^* \rangle / (\langle c \rangle R) \tag{A7}$$

$$P^* = \langle qz \rangle \langle \epsilon^* \rangle / (\langle s \rangle \langle v^* \rangle) \tag{A8}$$

$$V^* = \langle v^* \rangle / \langle M_o \rangle \tag{A9}$$

## REFERENCES

1. R. Simha and R. K. Jain, *Colloid Polym. Sci.*, **263**, 905 (1985).
2. R. K. Jain, R. Simha, and C. M. Balik, *Indian J. Pure Appl. Phys.*, **22**, 651 (1984).
3. R. K. Jain and R. Simha, *Macromolecules*, **17**, 2663 (1984).
4. R. Simha and R. K. Jain, *Polym. Eng. Sci.*, **24**, 1284 (1984).
5. E. Nies and A. Stroeks, "Integration of Polymer Science and Technology", p. 231, Eds. P. J. Lemstra and L. A. Kleintjens, Elseviers Appl. Sci. Publ., London (1987).
6. E. Nies, A. Stroeks, R. Simha, and R. K. Jain, to be published.
7. R. Simha and T. Somcynsky, *Macromolecules*, **2**, 342 (1969).
8. R. Simha, *Macromolecules*, **10**, 905 (1977).
9. J. W. Gibbs, "Collected Works", p. 132, Vol. 1, Yale University Press (1984).
10. R. Koningsveld, L. A. Kleintjens, and A. R. Schultz, *J. Polym. Sci. A2*, **8**, 1261 (1970).
11. J. Goldsbrough, *Sci. Progress* (Oxford), **60**, 281 (1970).

12. K. W. Derham, J. Goldsbrough, and M. Gordon, *Pure Appl. Chem.*, **38**, 97 (1974).
13. J. Jonas, D. Hasha, and S. G. Huang, *J. Phys. Chem.*, **84**, 109 (1974).
14. A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971).
15. R. Koningsveld, W. H. Stockmayer, J. W. Kennedy, and L. A. Kleintjens, *Macromolecules*, **7**, 73 (1974).
16. P. Irvine and M. Gordon, *Macromolecules*, **13**, 761 (1980).
17. E. Nies, R. Koningsveld, and L. A. Kleintjens, *Progress in Coll. Polym. Sci.*, **71**, 1 (1985).
18. P. Irvine and J. W. Kennedy, *Macromolecules*, **13**, 772 (1980).
19. W. H. Stockmayer, *J. Chem. Phys.*, **17**, 588 (1949).
20. R. Koningsveld, H. A. G. Chermin, and M. Gordon, *Proc. R. Soc.*, **A319**, 331 (1970).
21. P. Irvine, Ph.D. Thesis, University of Essex (1979).
22. A. A. Tager, A. A. Anikeyeva, V. M. Andreyeva, T. Ya. Gumarova, and L. A. Chernoskutova, *Vysokomol. Soyed.*, **A10**, 1661 (1968).

## DISCUSSION: E. NIES

*L. A. Utracki:* You introduced the $\Omega$ and $\Theta$ interaction parameters. Jain and Simha studied n-paraffin mixtures and assumed there are no excess intermolecular interactions. On this basis they calculated $\epsilon_{12}^*$ and $v_{12}^*$. Would the values of $\Omega$ and $\Theta$ be equal to one?

*E. Nies:* The parameters $\Omega$ and $\Theta$ define deviations of the cross parameters $\epsilon_{12}^*$ and $v_{12}^*$ with respect to the pure component parameters $\epsilon_{11}^*$, $v_{11}^*$, $\epsilon_{22}^*$ and $v_{22}^*$. For the mixture the complete set of the molecular parameters define average values for $\epsilon^*$ and $v^*$. The equations to compute these averages, used presently, are identical to the equations used by Jain and Simha. In our computations $\epsilon_{12}^*$ and $v_{12}^*$ are assumed to be constant and independent of composition. Jain and Simha adapted different $\epsilon_{12}^*$ and $v_{12}^*$ values for each mixture composition. So, for the calculations of Jain and Simha $\Omega$ and $\Theta$ will not be equal to one and depend on composition.

*L. A. Utracki:* You have also fairly good data on phase equilibria in oligostyrene/oligobutadiene mixtures from the centrifugal homogenizer and pulsed induced critical scattering at DSM, published by Koningsveld, *et al.* Did you check if the theory describes these dependencies?

*E. Nies:* These data show a double peak on the phase separation curves, which at this stage we were not able to generate with the theory. Furthermore, the systems were fairly polydisperse.

*L. A. Utracki:* How certain you are of the crossing of spinodals show on one of your figures? There are only three data points per curve.

*E. Nies:* We have more data from Manfred Gordon and Ron Koningsveld laboratories supporting these results. Manfred, Gordon, *et al.*, were able to ascribe these results to the dilute solution effect.