

Thermodynamics of Polydisperse Polymer Solutions I. Binary Mixtures

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ABSTRACT: The Lattice Fluid theory of polymer solutions, as reformulated recently, is now extended to polydisperse polymer-solvent systems. Analytical expressions are given for all basic thermodynamic quantities of the mixture as well as for the spinodals and the critical points. The theory is tested against experimental data on volumes of mixing, Flory-Huggins χ interaction parameters, spinodal curves and critical points for a number of mixtures of well characterized polydisperse polystyrene samples with cyclohexane. Comparison has also been made with experimental critical behavior of polydisperse polymer-monomodisperse polymer mixtures. The agreement between theory and experiment is satisfactory. Advantages and limitations of the theory are discussed.

KEY WORDS Polydispersity / Polymer Solutions / Thermodynamics /
Lattice-Fluid Theory /

The effect of polydispersity on the thermodynamic behavior of polymer solutions have long been the subject of extensive investigations.¹⁻⁴ In fact any complete thermodynamic theory of polymer systems cannot neglect the molecular weight heterogeneity of the polymer samples especially when applied to the phase behavior of these systems. In recent years the thermodynamic properties of polymer solutions are commonly interpreted with the so-called equation-of-state theories such as the new Flory theory⁵ and the Lattice-Fluid (LF) theory of Sanchez and Lacombe.⁶ Both of these theories have been proved quite successful in explaining many facets of the thermodynamic behavior of polymer solutions in terms of their "free-volume" properties or "equation-of-state" properties, and the facets of which the original well known Flory-Huggins theory¹ failed to explain. Although

the LF theory of Sanchez and Lacombe⁶ is less quantitative compared to the new Flory theory⁵ it has one significant advantage over the latter,⁵ namely, it can be applied to the vapor-liquid transition.

In a recent paper⁷ we reformulated the LF theory while maintaining essentially its original simplicity. The reformulated LF theory has been proved equally, if not more, successful than the new Flory theory. It became, thus, the frame for further extensions and applications to polymer-gas systems,⁸ random copolymer mixtures^{9,10}, glass transitions of polymer mixtures,¹¹ associated solutions¹² and to thermodynamics of contributions of functional groups.¹³

The present paper is the first in a series of paper in which the LF theory⁷ is extended to systems containing polydisperse polymers. It specifically deals with polydisperse polymer-

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solvent and polydisperse polymer–monodisperse polymer systems and presents the complete formalism for investigations of the thermodynamic behavior of these systems. It is subsequently applied to a typical polydisperse polymer–solvent system and a typical polydisperse polymer–monodisperse polymer system.

THEORY

In this section we will present the essentials of the Lattice–Fluid formalism pertinent to the case of polydisperse polymer–solvent systems. The development will follow closely the corresponding development of monodisperse polymer–solvent systems.⁷ Consider, then, a mixture of n_1 molecules of a solvent, each consisting of r_1 segments, with N_2 molecules of a polydisperse polymer at temperature T and external pressure P . The polydisperse polymer sample consists of n_2 molecules of a r_2 -mer, n_3 molecules of a r_3 -mer, \dots , n_c molecules of a r_c -mer such that

$$N_2 = n_2 + n_3 + \dots + n_c \quad (1)$$

All these molecules are arranged on a quasi-lattice of N_r sites, n_0 of which are empty. The LF partition function in the pressure ensemble and in its maximum term approximation may be written as

$$Z(T, P) = \left(\frac{1}{f_0}\right)^{n_0} \prod_{m=1}^c \left(\frac{w_m}{f_m}\right)^{n_m} \exp\left[\frac{-(E + PV)}{kT}\right] \quad (2)$$

where the site fractions f_i are defined by

$$f_0 = \frac{n_0}{N_r}; \quad f_i = \frac{r_i n_i}{N_r} \quad (3)$$

w_m in eq 2 is the number of configurations available to an r_m -mer in the close-packed pure state.

According to the LF theory each pure r_i -mer is characterized by three scaling constants T_i^* , P_i^* , ρ_i^* for the temperature, pressure and density respectively. If M_i is the molar mass, the

hard core volume per segment, v_i^* , and the specific hard core volume $v_{sp,i}^*$ are related by

$$r_i v_i^* = \frac{M_i}{\rho_i^*} = M_i v_{sp,i}^* \quad (4)$$

If s_i is the average number of external intermolecular contacts of each segment of the r_i -mer an interaction energy per segment, ε_i^* , can be defined as

$$\varepsilon_i^* = \frac{s_i}{2} \varepsilon_i = P_i^* v_i^* = k \cdot T_i^* \quad (5)$$

ε_i being the interaction energy for the i - i contact.

The average close-packed volume per segment in the mixture is assumed to be given by⁷

$$v^* = \sum_i \sum_j \varphi_i \varphi_j v_{ij}^* \quad (6)$$

where $v_{ii}^* = v_i^*$ and

$$v_{ij}^* = \xi_{ij} \left(\frac{v_i^{*1/3} + v_j^{*1/3}}{2} \right)^3 \quad (7)$$

ξ_{ij} being a binary volume parameter (equal to one for hard spheres). The segment fraction, φ_i , is defined by

$$\varphi_i = \frac{r_i n_i}{\sum_j r_j n_j} = \frac{r_i n_i}{rN} \quad (8)$$

N being the total number of molecules in the system ($N = \sum_j n_j$), while the surface fraction, ϑ_i , is given by

$$\vartheta_i = \frac{r_i n_i s_i}{\sum_j r_j n_j s_j} \quad (9)$$

The total volume, V , of the system is given by

$$V = N_r v^* = rN \bar{v} v^* \quad (10)$$

where \bar{v} is the reduced volume

$$\bar{v} = \frac{v}{v^*} = \frac{1}{\bar{\rho}} = \frac{\rho^*}{\rho} \quad (11)$$

v being the volume per segment and ρ the density of the system. The potential energy, E , of the system is given by⁷

$$-E = rN\tilde{\rho}\varepsilon^* \quad (12)$$

where

$$\varepsilon^* = \sum_i \varphi_i \varepsilon_i^* - \sum_i \sum_{j>i} \varphi_i \vartheta_j kT X_{ij} \quad (13)$$

and

$$X_{ij} = \frac{\varepsilon_i^* + \frac{s_i}{s_j} \varepsilon_j^* - 2 \sqrt{\frac{s_i}{s_j} \varepsilon_i^* \varepsilon_j^*}}{kT} \quad (14)$$

$$\varepsilon_{ij}^* = \zeta_{ij} \sqrt{\varepsilon_i^* \varepsilon_j^*} \quad (15)$$

ζ_{ij} being a binary interaction parameter (equal to one when Berthelot's rule holds).

Scaling constants for the mixture can be defined in an entirely analogous manner to that of pure components, or

$$\varepsilon^* = P^* v^* = kT^* \quad (5a)$$

and the reduced quantities by

$$\tilde{T} = \frac{T}{T^*}, \quad \tilde{P} = \frac{P}{P^*} \quad (16)$$

With the above definitions the LF equation of state is given by^{6,7}

$$r \frac{\tilde{P}\tilde{v}}{\tilde{T}} = 1 - r \left[1 + \frac{\ln(1-\tilde{\rho})}{\tilde{\rho}} + \frac{\tilde{\rho}}{\tilde{T}} \right] \quad (17)$$

and the chemical potential of component m in the mixture is given by

$$\begin{aligned} \frac{\mu_m}{kT} = & \ln \varphi_m + 1 - \frac{r_m}{r} + \ln \frac{\tilde{\rho}}{w_m} + r_m(\tilde{v}-1) \ln(1-\tilde{\rho}) \\ & + r_m \frac{\tilde{P}\tilde{v}}{\tilde{T}} \left(\frac{2 \sum_j \varphi_j v_{jm}^*}{v^*} - 1 \right) \\ & - \frac{r_m}{\tilde{v}\tilde{T}_m} - \frac{r_m}{\tilde{v}} \left[\sum_i \sum_{j>i} \vartheta_i \vartheta_j \frac{s_m}{s_i} X_{ij} \right. \\ & \left. - \sum_{i<m} \vartheta_i \frac{s_m}{s_i} X_{im} - \sum_{j>m} \vartheta_j X_{mj} \right] \quad (18) \end{aligned}$$

The corresponding expression for the chemical potential of pure component m is

$$\begin{aligned} \frac{\mu_m^0}{kT} = & \ln \frac{\tilde{\rho}_m}{w_m} + r_m(\tilde{v}_m-1) \ln(1-\tilde{\rho}_m) \\ & + r_m \frac{\tilde{P}_m \tilde{v}_m}{\tilde{T}_m} - \frac{r_m}{\tilde{v}_m \tilde{T}_m} \quad (19) \end{aligned}$$

On the basis of eq 10 the volume of mixing, ΔV^M , is given by

$$\Delta V^M = V - \sum_i V_i^0 = rNv^* \left(\tilde{v} - \sum_i \varphi_i \tilde{v}_i \frac{v_i^*}{v^*} \right) \quad (20)$$

Using eq 12 the heat of mixing is given by

$$\begin{aligned} \Delta H^M = & E + PV - \sum_i (E_i^0 + PV_i^0) \\ = & rN \left[\sum_i \varphi_i \tilde{\rho}_i \varepsilon_i^* - \tilde{\rho} \varepsilon^* \right] + P \Delta V^M \quad (21) \end{aligned}$$

All the above equations are quite general and are applicable to any multicomponent mixture. They will now be applied to the special case of our polydisperse polymer-solvent system. A number of simplifications are possible in this case. Let us, first, define two overall fractions for the polydisperse polymer, the overall segment fraction, Φ_2 , and the overall surface fraction, Θ_2 , given by

$$\Phi_2 = \sum_{i>1} \varphi_i; \quad \Theta_2 = \sum_{i>1} \vartheta_i \quad (22)$$

In order to keep manageable the complexity of the formalism we further assume that all polymer molecules, regardless of their size, are characterized by the same scaling constants $v_2^*, \varepsilon_2^*, T_2^*, P_2^*, \rho_2^*, v_{sp,2}^*$ and the same number of external contacts per segment, s_2 . In the polymer sample we may define a number average, a weight-average and a z -average number of segments given respectively by

$$\bar{r}_{2N} = \frac{\sum_{j>1} n_j r_j}{N_2} = \frac{\bar{M}_{2N}}{\rho_2^* v_2^*} \quad (23)$$

$$\bar{r}_{2w} = \frac{\sum_{j>1} n_j r_j^2}{\sum_{j>1} n_j r_j} = \frac{\sum_{j>1} \varphi_j r_j}{\Phi_2} = \frac{\bar{M}_{2w}}{\rho_2^* v_2^*} \quad (24)$$

$$\bar{r}_{2Z} = \frac{\sum_{j>1} n_j r_j^3}{\sum_{j>1} n_j r_j^2} = \frac{\sum_{j>1} \varphi_j r_j^2}{\sum_{j>1} \varphi_j r_j} = \frac{\bar{M}_{2Z}}{\rho_2^* v_2^*} \quad (25)$$

The Flory-Huggins χ interaction parameter^{1,2,5} can be defined in our case by

$$\frac{\mu_1 - \mu_1^0}{kT} = \ln \sigma_1 + \left(1 - \frac{r_1 v_1^*}{\bar{r}_{2N} v_2^*}\right) \sigma_2 + \chi \sigma_2^2 \quad (26)$$

where the volume fractions σ_i are given by

$$\sigma_1 = \frac{\varphi_1 v_1^*}{\varphi_1 v_1^* + \Phi_2 v_2^*}; \quad \sigma_2 = 1 - \sigma_1 \quad (27)$$

Using eq 18 and 19 and the above simplifications we obtain

$$\begin{aligned} \chi = & \left\{ \ln \frac{\varphi_1}{\sigma_1} + \Phi_2 \left(1 - \frac{r_1}{\bar{r}_{2N}}\right) \right. \\ & - \sigma_2 \left(1 - \frac{r_1 v_1^*}{\bar{r}_{2N} v_2^*}\right) + r_1 \tilde{\rho} X_{12} \Theta_2^2 + \ln \frac{\tilde{\rho}}{\rho_1} \\ & + r_1 (\tilde{v} - 1) \ln(1 - \tilde{\rho}) - r_1 (\tilde{v}_1 - 1) \ln(1 - \tilde{\rho}_1) \\ & + r_1 \frac{\tilde{P}\tilde{v}}{\tilde{T}} \left[\frac{2(\varphi_1 v_1^* + \Phi_2 v_{12}^*)}{v^*} - 1 \right] \\ & \left. - r_1 \frac{\tilde{P}_1 \tilde{v}_1}{\tilde{T}_1} - \frac{r_1}{\tilde{T}_1} (\tilde{\rho} - \tilde{\rho}_1) \right\} / \sigma_2^2 \quad (28) \end{aligned}$$

If an entropic correction q_{12} term⁷ need be used, the fourth term in the previous equation should read $r_1 (\tilde{\rho} X_{12} + q_{12}) \Theta_2^2$. If we further assume that the reduced densities $\tilde{\rho}_j$ for the pure constituents of the polymer sample are the same (or, equivalently $r_j \rightarrow \infty$ for all $j > 1$), eq 20 and 21 as well as the equation for the heat of mixing at infinite dilution, ΔH^∞ , reduce to the corresponding expressions for the case of solvent-monodisperse polymer system.⁷

Phase Stability

The condition for the spinodal⁴ in our system may be written as

$$D = \begin{vmatrix} g_{22} & g_{23} & \cdots & g_{2c} \\ g_{32} & g_{33} & \cdots & g_{3c} \\ \cdot & \cdot & \cdots & \cdot \\ g_{c2} & g_{c3} & \cdots & g_{cc} \end{vmatrix} = 0 \quad (29)$$

where

$$g_{ji} = \left[\frac{\partial}{\partial \varphi_j} \left(\frac{\partial g}{\partial \varphi_i} \right)_{T,P,\varphi_k \neq i,j} \right]_{T,P,\varphi_m \neq i,j} \quad (30)$$

and

$$g = \frac{G}{rNkT} \quad (31)$$

G being the Gibbs free energy of the system ($G = -kT \ln Z$). By using the simplifying assumptions reported previously eq 29 reduces to

$$\begin{aligned} \frac{1}{\varphi_1 r_1} + \frac{1}{\Phi_2 \bar{r}_{2w}} - 2 \frac{\vartheta_1}{\varphi_1} \frac{\Theta_2^2}{\Phi_2^2} (\tilde{\rho} X_{12} + q_{12}) \\ + 2 \frac{\tilde{P}\tilde{v}}{kT} (v_1^* + v_2^* - 2v_{12}^*) - \tilde{\rho} Q_2 \psi_2 = 0 \quad (32) \end{aligned}$$

where

$$Q_2 = \beta P^* \tilde{T} \psi_2 \quad (33)$$

$$\psi_2 = \tilde{\rho} \lambda_2 + \frac{P\tilde{v}}{kT} D_2 + \frac{1}{r_1} \quad (34)$$

$$\lambda_2 = \frac{1}{\tilde{T}_2} - \frac{1}{\tilde{T}_1} + \left(\Theta_2^2 - \vartheta_1^2 \frac{s_2}{s_1} \right) X_{12} \quad (35)$$

$$D_2 = 2[\varphi_1 (v_{12}^* - v_1^*) + \Phi_2 (v_2^* - v_{12}^*)] \quad (36)$$

and

$$\beta P^* = \frac{\tilde{v}^2}{\tilde{T}\tilde{v} \left(\frac{1}{\tilde{v}-1} + \frac{1}{r} \right) - 2} \quad (37)$$

At the critical point the following condition should be satisfied in addition to eq 29

$$Y = \begin{vmatrix} \frac{\partial D}{\partial \varphi_2} & \frac{\partial D}{\partial \varphi_3} & \cdots & \frac{\partial D}{\partial \varphi_c} \\ g_{32} & g_{33} & \cdots & g_{3c} \\ \cdot & \cdot & \cdots & \cdot \\ g_{c2} & g_{c3} & \cdots & g_{cc} \end{vmatrix} = 0 \quad (38)$$

With the previous simplifying assumptions eq 38 reduces to

$$\begin{aligned} & \frac{1}{\varphi_1^2 r_1} - \frac{\bar{r}_{2z}}{\Phi_2^2 \bar{r}_{2w}^2} + 6 \frac{g_1}{\varphi_1} \frac{\Theta_2^2}{\Phi_2^2} \left\{ \left(\frac{\Theta_2}{\Phi_2} - \frac{g_1}{\varphi_1} \right) \right. \\ & \quad \times (\bar{\rho} X_{12} + q_{12}) - \bar{\rho}^2 Q_2 X_{12} \left. \right\} \\ & \quad + \bar{\rho}^2 Q_2^2 \left\{ \left(\frac{1}{\bar{r}_{2N}} - \frac{1}{r_1} \right) - 4\bar{\rho} \lambda_2 \right. \\ & \quad \left. - Q_2 \left(\frac{2\bar{\rho}^2}{\bar{T}} - \frac{1}{(\bar{v}-1)^2} \right) \right\} \\ & \quad - 2 \frac{PQ_2}{kT} \{ 3(v_1^* + v_2^* - 2v_{12}^*) - \bar{\rho} Q_2 D_2 \} = 0 \end{aligned} \quad (39)$$

APPLICATIONS

In this section we will apply the above formalism, first, to a typical example of a polydisperse polymer-solvent system, namely, the polystyrene-cyclohexane mixture. This particular system became the subject of numerous intensive investigations over many years^{3,14-21} resulting in abundantly confirmed extensive experimental data. Scholte²⁰ has reported spinodal data for polystyrene in cyclohexane from light scattering measurements and for three well characterized polydisperse polymer samples. Koningsveld *et al.*¹⁹ on the other hand have reported experimental data on critical temperatures and critical compositions for a number of mixtures of cyclohexane with polystyrene samples of a wide variety of molecular weight distributions all produced by mixing proprietary sharp fractions of polystyrene. In what follows the present theory will be applied to these two sets of data.

In order to apply the theory to the system of Cyclohexane (1)-Polystyrene (2) we need first the LF scaling constants for the pure components. The LF constants have been obtained from the volumetric properties of pure compounds at 25°C reported by Höcker *et al.*^{18,22} and are: $T_1^* = 502$ K, $P_1^* = 417$ MPa, $\rho_1^* = 886$ kg m⁻³; $T_2^* = 632$ K, $P_2^* = 466$ MPa and $\rho_2^* = 1139$ kg m⁻³. Following Saeki *et al.*²¹ the value 1.68 was assigned to the ratio s_1/s_2 . The two adjustable binary parameters ζ_{12} and q_{12} of the theory have been determined from a least-square fit of the above two sets of data.^{19,20} The values of the binary parameters so obtained are: $\zeta_{12} = 1.0349$ and $q_{12} = -0.058$ both dimensionless. In Table I are shown the experimental¹⁹ and the calculated critical temperatures and critical compositions with both the present theory and the five-parameter theory of Kennedy *et al.*³ As observed the performance of the present theory is gratifying. In Figure 1 are shown experimental²⁰ and calculated spinodals for three systems of different molecular weight and molecular weight distribution polystyrenes. Again the performance of the theory is quite satisfactory. In the same Figure are shown experimental²⁷ and calculated spinodals (dashed curves a and b) for two heterodisperse Polystyrene-Cyclohexane systems. Molecular weight averages of the two Polystyrene samples are as following: curve a: $\bar{M}_n = 54000$, $\bar{M}_w = 110000$, $\bar{M}_z = 173000$; curve b: $\bar{M}_n = 45000$, $\bar{M}_w = 165000$, $\bar{M}_z = 432000$. The experimental data are reproduced rather satisfactorily with the above set of binary parameters.

Using the above binary parameters (ζ_{12} and q_{12}) we have calculated the predictions of the theory for the χ interaction parameter at 25°C. In Figure 2 are shown the experimental and predicted χ interaction parameters. As observed experiment and theory are in very good agreement. Volumes of mixing over extended ranges of composition can be reproduced easily by the LF model⁷ by slightly adjusting the volume parameter ξ_{12} . In the present case the

Table I. Critical temperatures and critical compositions for the system cyclohexane(1)–polystyrene(2)

Experimental					Calculated			
$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_z \times 10^{-3}$	T_c/K	M_{c_2}	Kennedy <i>et al.</i> ³		This work	
					T_c/K	W_{c_2}	T_c/K	W_{c_2}
27	35.4	45.5	284.6	0.179	—	—	287.9	0.196
49	51	55	288.9	0.146	286.5	0.216	290.3	0.153
55	61.5	70.5	290.5	0.143	289.0	0.159	291.4	0.143
91	93	96	293.7	0.117	290.3	0.169	293.8	0.110
154	166	181	296.6	0.099	293.1	0.125	296.5	0.083
200	286	438	298.7	0.095	296.4	0.119	298.5	0.073
210	346	550	300.2	0.092	297.8	0.174	299.2	0.068
375	394	423	300.7	0.070	299.6	0.090	299.8	0.052
490	527	593	301.2	0.064	300.3	0.089	300.7	0.046
1250	1500	1700	303.2	0.042	302.0	0.065	303.2	0.027

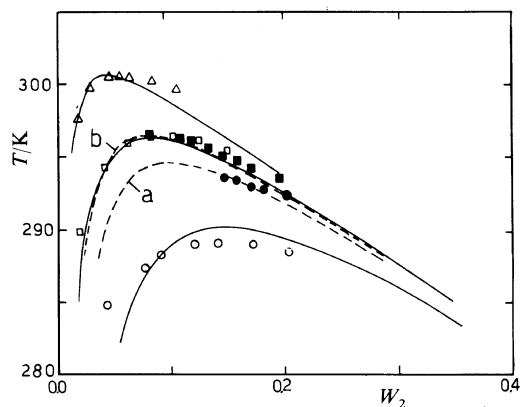


Figure 1. Experimental²⁰ and calculated spinodals (solid curves) for the system cyclohexane(1)–polystyrene(2) vs. the weight fraction of polystyrene. Circles are for $\bar{M}_n = 49000$; squares for $\bar{M}_n = 154000$ and triangles for $\bar{M}_n = 435000$. Filled circles and rectangles are experimental data of Derham *et al.*²⁷ Corresponding dashed curves a and b are calculated as explained in the text.

volumes of mixing reported by Höcker *et al.*¹⁸ are reproduced to within experimental error by setting $\zeta_{12} = 1.0049$.

The critical points reported by Koningsveld *et al.*¹⁹ and used in this work are of the UCST type (upper critical solution temperature). In addition to UCST behavior the cyclohexane–polystyrene system exhibits also the common LCST behavior (lower critical solution temperature). Critical temperatures of this latter

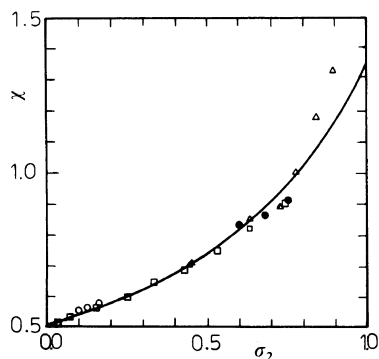


Figure 2. The reduced residual chemical potential χ for the system cyclohexane(1)–polystyrene(2). The solid curve is predicted by the present theory. Open circles are from osmotic pressure measurements of Palmen²³ at 26°C. Filled circles represent vapor pressure measurements of Schmoll and Jenckel²⁴ at 25°C. Triangles show vapor pressure results of Krigbaum and Geymer²⁵ at 24°C and squares indicate values of Scholte²⁶ obtained by equilibrium ultracentrifugation at 30°C. σ_2 is the hard core volume fraction of polystyrene.⁷

type ranging from 180°C to 220°C have been reported in the literature.^{14–17,28} The present model does predict a LCST for our system. It is not, however, expected that the pure component parameters and the binary parameters which have been determined at about 300 K to be appropriate at 500 K. On the basis of the volumetric properties reported by Höcker *et al.*¹⁸ the following pure component LF pa-

Table II. LCST's for the system cyclohexane(1)–polystyrene(2)

Experimental 17, 28		Calculated
$\bar{M}_w \times 10^{-4}$	T_{cr}/K	T_{cr}/K
3.70	510.9	508.3
9.72	502.1	500.5
20.0	496.9	496.6
40.0	494.7	493.9
67.0	491.7	492.4
270	488.6	489.9
333	488.2	489.7

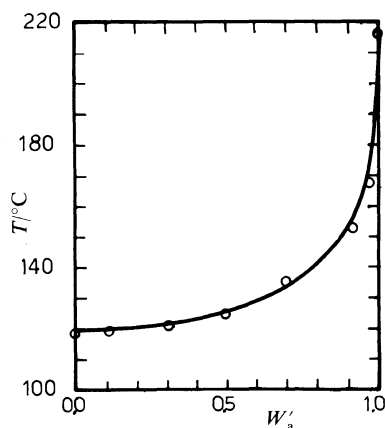


Figure 3. Influence of polydispersity on the phase behavior in the system PVME(1)–polydisperse polystyrene(2). Circles are experimental cloud points²⁹ of a mixture 50 wt% in polystyrene. Solid curve is the corresponding calculated spinodal. W'_a is the weight fraction of constituent a in the polydisperse polystyrene sample.

rameters have been obtained at 200°C: $T_1^* = 592$ K, $P_1^* = 384$ MPa, $\rho_1^* = 815$ kg m⁻³; $T_2^* = 806$ K, $P_2^* = 412$ MPa, $\rho_2^* = 1081$ kg m⁻³. With these pure component parameters and the same set of binary parameters we calculated the LCST's for our system. Comparison with experiment^{17,28} is made in Table II. As observed the performance of the model is again quite satisfactory.

The formalism presented in this work is equally valid to the case of monodisperse polymer(1)–polydisperse polymer(2) systems. It is worth comparing, then, our model with

experimental data pertinent to this type of systems. Nishi and Kwei²⁹ have reported experimental cloudpoints for mixtures of monodisperse Poly(vinyl methyl ether) (PVME) (1)–polydisperse Polystyrene (2) 50% wt. in Polystyrene. Polystyrene samples were obtained by mixing two monodisperse samples a ($M = 10000$) and b ($M = 110000$). In Figure 3 are compared the experimental data with the calculated spinodals for mixtures 50%wt in Polystyrene. Pure component parameters and binary parameters for this system have been obtained from our previous work.⁷ The trend of LCST with the polydispersity of the Polystyrene sample is well reproduced by the present model.

DISCUSSION AND CONCLUSIONS

In spite of the satisfactory performances reported in the previous section the LF model has inherent limitations as any other similar free-volume model for polymer solutions. The oversimplistic approach of the present work (\tilde{p}_j the same for all pure constituents of the polydisperse polymer or $r_j \rightarrow \infty$ for all $j > 1$) is not expected to hold for highly polydisperse polymer-solvent systems. Derham *et al.*²⁷ and Scholte³⁰ have conducted a series of careful experimental pulse induced critical scattering measurements for highly polydisperse Polystyrene–Cyclohexane systems. Scholte's Polystyrene samples were characterized by the same \bar{M}_w (100000) but with an \bar{M}_n ranging from 21600 to 70000. In a temperature vs. composition diagram the experimental spinodal curves are departing from each other. In the studied composition range the spinodals for the two extreme \bar{M}_n values have shown a maximum deviation of ca. 1.7 degrees centigrade. The present model, when using the pure component and binary parameters of the previous section, calculates a maximum deviation of only 0.3 degrees centigrade in the same composition range. Agreement between theory and experiment can be reached by slightly

changing the binary parameter ζ_{12} as following: For the samples with \bar{M}_n equal to 70000, 38000 and 21600, ζ_{12} must be equal to 1.03487, 1.03500 and 1.03505 respectively. These changes in ζ_{12} correspond to small changes in X_{12} which can easily be obtained by changes in T_2^* of pure polymer by a few degrees centigrade or equivalently by a small change in the thermal expansion coefficient of the polymer.³¹ Unfortunately the volumetric properties of the different polydisperse Polystyrene samples, from which one could get their characteristic LF constants, are not available.

The change of ζ_{12} (or X_{12}) with \bar{M}_n , although successful, is essentially a rather empirical approach. Other more fundamental approaches such as the group-contribution approach¹³ may be applied to polydisperse systems and may lead to a formalism with manageable complexity. Such an approach, however, can be useful only after the establishment of a rich database with the characteristic group and intergroup parameters.

In any case, and because of its simplicity, the present model may form the basis for more refined treatments of the phase behavior (UCST, LCST, liquid-vapor transition) of polymer solutions.

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