Upper and lower critical solution temperature behaviour in polymer blends and its thermodynamic interpretation

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The simultaneous occurrence of upper (*UCST*) as well as lower critical solution temperatures (*LCST*) in polymer blends can be explained in terms of a refined version of the Prigogine–Flory–Patterson theory. A generalized interaction parameter is introduced which is ruled by three contributions: (i) the segmental interaction, (ii) the free-volume effect, and (iii) the size effect represented by a parameter ρ. The gap between *LCST* and *UCST* depends highly on the parameter ρ. With increasing size effect, the *UCST* and *LCST* approach and, finally, merge into an hourglass-shaped binodal.

(Keywords: *UCST*; *LCST*; blends; thermodynamics; miscibility)

INTRODUCTION

The phase behaviour of any mixture at constant pressure P and temperature T is directed by the Gibbs free energy of mixing, ΔG^{M}, which is given by:

$$\Delta G^{\mathrm{M}} = \Delta H^{\mathrm{M}} - T\Delta S^{\mathrm{M}} \qquad (1)$$

where ΔH^{M} and ΔS^{M} are the enthalpy and the entropy of mixing, respectively. According to the second law of thermodynamics, two components will only mix if the Gibbs free energy of mixing is negative:

$$\Delta G^{\mathrm{M}} < 0 \qquad (2)$$

Furthermore, the condition for phase stability in a binary mixture of composition ϕ (volume fraction) at fixed temperature and pressure is:

$$\left(\frac{\partial^2 \Delta G^{\mathrm{M}}}{\partial \phi^2}\right)_{P,T} > 0 \qquad (3)$$

To explain miscibility and lower critical solution temperature (*LCST*) behaviour in polymer blends, one has to consider three contributions to the Gibbs free energy of mixing[1,2]; the combinatorial entropy of mixing; the intermolecular interaction; and the free-volume effect arising from the different thermal expansion coefficients of the two components. In the context of the Flory–Huggins theory[3] it can be shown that the combinatorial entropy of mixing is proportional to $1/r$ of each component where r is the number of segments in a chain molecule. Hence, one may conclude that the combinatorial entropy of mixing becomes insignificant at high molar masses. The free-volume contribution is always positive and increases as a function of temperature. Therefore, $\Delta G^{\mathrm{M}} < 0$ required for mutual miscibility of polymers can only result from interactions between them leading to a negative contribution to the Gibbs free energy of mixing. In the case of homopolymers this is associated with specific interactions. The increase of the free-volume term with temperature results in a *LCST* which is typical for miscible polymers.

As shown recently[4–7] blends in which at least one of the components is a random copolymer exhibit miscibility and *LCST* behaviour in the absence of specific interactions. In that case misciblity may be enhanced by the repulsion of dissimilar segments in the random copolymer chain[4,5,8,9].

Some miscible polymer blends display not only *LCST* behaviour but also phase separation at low temperatures. The simultaneous occurrence of a *LCST* as well as an upper critical solution temperature (*UCST*) in blends of high-molar-mass polymers is expected to be rare. Nevertheless, it is a general phenomenon. However, in most of the cases the *UCST* shifts below the glass transition temperature and, therefore, is not accessible experimentally.

The existence of both an *UCST* and *LCST* has been found in some blends of high-molar-mass polymers: poly(butadiene)/poly(styrene-*co*-butadiene)[10], poly(acrylonitrile-*co*-styrene)/poly(acrylonitrile-*co*-butadiene)[11] and poly(methyl methacrylate)/poly(vinylidene fluoride)[12]; and also in blends of polystyrene and a random copolymer of carboxylated poly(2,6-dimethyl-1,4-phenylene oxide)[13].

The theory sketched above cannot explain satisfactorily the combined occurrence of an *UCST* and *LCST*. In this paper we present a refined version of the Prigogine–Flory–Patterson theory[2,14,15] which results in a straightforward interpretation of *UCST* and *LCST* behaviour.

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THE REFINED THEORY

In the usual version the theory explains the *LCST* behaviour of miscible polymers. The aim here is an adequate refinement of the theory to understand the fact that some blends exhibit additionally an *UCST*.

In the Prigogine theory[14] the basic quantities characterizing the thermodynamic state of a system are the reduced temperature ($\tilde{T}$), volume ($\tilde{V}$) and pressure ($\tilde{P}$) defined by:

$$\tilde{T} \equiv T/T^* \qquad \tilde{V} \equiv V/V^* \qquad \tilde{P} \equiv P/P^* \tag{4}$$

where the starred quantities are constant reference parameters. Expressing the potential energy $\varepsilon(r')$ of a pair of segments belonging to r-mers by the general function ζ with two scale factors ε^* and r^* characteristic of the molecular species:

$$\varepsilon(r') = -\varepsilon^* \zeta(r'/r^*) \tag{5}$$

then we can represent the starred quantities in (4) by the molecular parameters as follows

$$T^* = q\varepsilon^*/ck \qquad V^* = rr^{*3} \qquad P^* = q\varepsilon^*/rr^{*3} \tag{6}$$

The scale factors ε^* and r^* represent the coordinates of the minimum of the potential function $\varepsilon(r')$; r is the number of segments in a chain molecule; $3c$ is called the number of external degrees of freedom of an r-mer because it depends only on the environment of the chain. When z is the coordination number of the lattice then qz represents the number of the nearest neighbours of the r-mer or zq/r the nearest neighbours of a segment.

In generalization of (5) one may introduce the average interaction of a segment (say A) with the neighbour segments at a distance r' for the mixture in terms of the volume fraction ϕ:

$$\langle \varepsilon_{\mathrm{A}}^* \rangle \zeta(r'/\langle r_{\mathrm{A}}^* \rangle) = \phi_{\mathrm{A}} \langle \varepsilon_{\mathrm{AA}}^* \rangle \zeta(r'/\langle r_{\mathrm{AA}}^* \rangle) + \phi_{\mathrm{B}} \langle \varepsilon_{\mathrm{AB}}^* \rangle \zeta(r'/\langle r_{\mathrm{AB}}^* \rangle) \tag{7}$$

As can be seen the interaction energy $\langle \varepsilon_{\mathrm{A}}(r') \rangle$ is supposed to be of the same form as in (5). Henceforth, the quantities $\langle \varepsilon^* \rangle$ and $\langle r^* \rangle$ are average composition-dependent parameters. Using a (6–12) law for the potential function $\varepsilon(r')$ the parameters $\langle \varepsilon_{\mathrm{A}}^* \rangle$ and $\langle r_{\mathrm{A}}^* \rangle$ are given by:

$$\langle \varepsilon_{\mathrm{A}}^* \rangle = \frac{(\phi_{\mathrm{A}} \langle \varepsilon_{\mathrm{AA}}^* \rangle \langle r_{\mathrm{AA}}^* \rangle^6 + \phi_{\mathrm{B}} \langle \varepsilon_{\mathrm{AB}}^* \rangle \langle r_{\mathrm{AB}}^* \rangle^6)^2}{\phi_{\mathrm{A}} \langle \varepsilon_{\mathrm{AA}}^* \rangle \langle r_{\mathrm{AA}}^* \rangle^{12} + \phi_{\mathrm{B}} \langle \varepsilon_{\mathrm{AB}}^* \rangle \langle r_{\mathrm{AB}}^* \rangle^{12}} \tag{8}$$

$$\langle r_{\mathrm{A}}^* \rangle = \left(\frac{\phi_{\mathrm{A}} \langle r_{\mathrm{AA}}^* \rangle^{12} + \phi_{\mathrm{B}} \langle r_{\mathrm{AB}}^* \rangle^{12}}{\phi_{\mathrm{A}} \langle r_{\mathrm{AA}}^* \rangle^{6} + \phi_{\mathrm{B}} \langle r_{\mathrm{AB}}^* \rangle^{6}} \right)^{1/6}$$

Similar expressions exist for $\langle \varepsilon_{\mathrm{B}}^* \rangle$ and $\langle r_{\mathrm{B}}^* \rangle$. Assuming now that components A and B are random copolymers of monomers 1 and 2 and of 3 and 4, respectively, where α and β are the mole fractions of 1 in A and 3 in B, respectively, then it follows that:

$$\langle \varepsilon_{\mathrm{AA}}^* \rangle = \frac{[\alpha^2 \varepsilon_{11}^* r_{11}^{*6} + 2\alpha(1-\alpha)\varepsilon_{12}^* r_{12}^{*6} + (1-\alpha)^2 \varepsilon_{22}^* r_{22}^{*6}]^2}{\alpha^2 \varepsilon_{11}^* r_{11}^{*12} + 2\alpha(1-\alpha)\varepsilon_{12}^* r_{12}^{*12} + (1-\alpha)^2 \varepsilon_{22}^* r_{22}^{*12}} \tag{9}$$

$$\langle r_{\mathrm{AA}}^* \rangle = \left(\frac{\alpha^2 r_{11}^{*12} + 2\alpha(1-\alpha) r_{12}^{*12} + (1-\alpha)^2 r_{22}^{*12}}{\alpha^2 r_{11}^{*6} + 2\alpha(1-\alpha) r_{12}^{*6} + (1-\alpha)^2 r_{22}^{*6}} \right)^{1/6}$$

with analogous expressions for $\langle \varepsilon_{\mathrm{BB}}^* \rangle$ and $\langle r_{\mathrm{BB}}^* \rangle$. Furthermore, we have:

$$\langle \varepsilon_{\mathrm{AB}}^* \rangle = \alpha\beta\varepsilon_{13}^* + (1-\beta)\alpha\varepsilon_{14}^* + (1-\alpha)\beta\varepsilon_{23}^* + (1-\alpha)(1-\beta)\varepsilon_{24}^* \tag{10}$$

$$\langle r_{\mathrm{AB}}^* \rangle = \left(\frac{\alpha\beta r_{13}^{*12} + \cdots + (1-\alpha)(1-\beta) r_{24}^{*12}}{\alpha\beta r_{13}^{*6} + \cdots + (1-\alpha)(1-\beta) r_{24}^{*6}} \right)^{1/6}$$

Now we may express the average potential parameters in terms of the quantities δ_i, δ_i^r, χ_{ij} and R_{ij} as defined in the Appendix. Second-order terms are only taken into account for $\langle \varepsilon_{ii}^* \rangle$. After (9) and (10) it follows that:

$$\langle \varepsilon_{\mathrm{AA}}^* \rangle / \varepsilon_{11}^* = 1 + \varepsilon \qquad \langle r_{\mathrm{AA}}^* \rangle / r_{11}^* = 1 + \rho_{\mathrm{A}} \tag{11}$$

$$\langle \varepsilon_{\mathrm{BB}}^* \rangle / \varepsilon_{11}^* = 1 + \eta \qquad \langle r_{\mathrm{BB}}^* \rangle / r_{11}^* = 1 + \rho_{\mathrm{B}} \tag{12}$$

$$X_{\mathrm{AB}} = \lambda/(1+\varepsilon) \tag{13}$$

Again, the quantities ε, η, ρ_{A} and ρ_{B} are defined in the Appendix. According to (8) it follows for $\langle \varepsilon_{\mathrm{A}}^* \rangle$, $\langle r_{\mathrm{A}}^* \rangle$, $\langle \varepsilon_{\mathrm{B}}^* \rangle$ and $\langle r_{\mathrm{B}}^* \rangle$ that:

$$\langle \varepsilon_{\mathrm{A}}^* \rangle / \varepsilon_{11}^* = 1 + (\phi_{\mathrm{B}}/2)\Gamma - \phi_{\mathrm{B}} X_{\mathrm{AB}} - 9\rho^2 \phi_{\mathrm{A}} \phi_{\mathrm{B}} \tag{14}$$

$$\langle r_{\mathrm{A}}^* \rangle / r_{11}^* = 1 + (\rho_{\mathrm{A}}/2)(1+\phi_{\mathrm{A}}) + (\rho_{\mathrm{B}}/2)\phi_{\mathrm{B}} + K\phi_{\mathrm{B}} \tag{15}$$

$$\langle \varepsilon_{\mathrm{B}}^* \rangle / \varepsilon_{11}^* = 1 + (\phi_{\mathrm{B}} + \phi_{\mathrm{A}}/2)\Gamma - \phi_{\mathrm{A}} X_{\mathrm{AB}} - 9\rho^2 \phi_{\mathrm{A}} \phi_{\mathrm{B}} \tag{16}$$

$$\langle r_{\mathrm{B}}^* \rangle / r_{11}^* = 1 + (\rho_{\mathrm{A}}/2)\phi_{\mathrm{A}} + (\rho_{\mathrm{B}}/2)(1+\phi_{\mathrm{B}}) + K\phi_{\mathrm{A}} \tag{17}$$

with

$$\Gamma \equiv (\eta - \varepsilon)/(1+\varepsilon) \tag{14a}$$

$$\rho \equiv \rho_{\mathrm{B}} - \rho_{\mathrm{A}} + 2\beta(1-\beta)R_{34} - 2\alpha(1-\alpha)R_{12} \tag{14b}$$

$$K \equiv \alpha(1-\alpha)R_{12} + \beta(1-\beta)R_{34} - \alpha\beta R_{13} - \alpha(1-\beta)R_{14} - (1-\alpha)\beta R_{23} - (1-\alpha)(1-\beta)R_{24} \tag{15a}$$

In the context of the Prigogine theory and assuming random mixing, the configurational partition function of the mixture takes the form:

$$Q = \frac{(N_{\mathrm{A}} + N_{\mathrm{B}})!}{N_{\mathrm{A}}!\, N_{\mathrm{B}}!} [\langle r_{\mathrm{A}}^* \rangle^3 q(\langle \tilde{T}_{\mathrm{A}} \rangle, \langle \tilde{V}_{\mathrm{A}} \rangle)]^{c_{\mathrm{A}} r_{\mathrm{A}} N_{\mathrm{A}}} \times [\langle r_{\mathrm{B}}^* \rangle^3 q(\langle \tilde{T}_{\mathrm{B}} \rangle, \langle \tilde{V}_{\mathrm{B}} \rangle)]^{c_{\mathrm{B}} r_{\mathrm{B}} N_{\mathrm{B}}} \tag{18}$$

where N_{A}, N_{B} are the numbers of polymer molecules in the system and q represents the partition function for a segment. The Helmholtz free energy of mixing per mole of segments is:

$$\Delta F^{\mathrm{M}} = F - (\phi_{\mathrm{A}} F_{\mathrm{A}} + \phi_{\mathrm{B}} F_{\mathrm{B}}) \tag{19}$$

From (18) one can deduce the free energy of mixing. Omitting for a moment the combinatorial entropy of mixing, it follows that:

$$\Delta F^{\mathrm{M}}/RT = -\sum_{i=\mathrm{A,B}} \{3c_i\phi_i \ln(\langle r_i^* \rangle / \langle r_{ii}^* \rangle) + c_i\phi_i[\ln q(\langle \tilde{T}_i \rangle, \langle \tilde{V}_i \rangle) - \ln q(\langle \tilde{T}_{ii} \rangle, \langle \tilde{V}_{ii} \rangle)]\} \tag{20}$$

Now we may expand (20) in powers of $1/\langle \tilde{T} \rangle$ and $\langle \tilde{V} \rangle$ around $\ln q(\langle \tilde{T}_{\mathrm{AA}} \rangle, \langle \tilde{V}_{\mathrm{AA}} \rangle)$ at $\tilde{P} = 0$. In the following we neglect structural effects, i.e. $c_{\mathrm{A}} = c_{\mathrm{B}}$ and $q_{\mathrm{A}} = q_{\mathrm{B}}$. After some calculation we arrive at:

$$\begin{aligned}\frac{\Delta F^{\mathrm{M}}}{RT} = \frac{\Delta G^{\mathrm{M}}}{RT} = \frac{U_{\mathrm{A}}}{RT}\left[\phi_{\mathrm{A}}\theta_{\mathrm{A}} + \phi_{\mathrm{B}}\theta_{\mathrm{B}} - \phi_{\mathrm{B}}\left(\frac{\langle \varepsilon_{\mathrm{BB}}^* \rangle}{\langle \varepsilon_{\mathrm{AA}}^* \rangle} - 1\right)\right] \\ - \frac{C_{\mathrm{VA}}}{2R}\left[\phi_{\mathrm{A}}\theta_{\mathrm{A}}^2 + \phi_{\mathrm{B}}\theta_{\mathrm{B}}^2 - \phi_{\mathrm{B}}\left(\frac{\langle \varepsilon_{\mathrm{BB}}^* \rangle}{\langle \varepsilon_{\mathrm{AA}}^* \rangle} - 1\right)^2\right] \\ + c_{\mathrm{A}}\left(\frac{\partial \tilde{P}}{\partial \tilde{T}}\right)_{\mathrm{A}}\left[\phi_{\mathrm{A}}\theta_{\mathrm{A}}\Omega_{\mathrm{A}} + \phi_{\mathrm{B}}\theta_{\mathrm{B}}\Omega_{\mathrm{B}} - \phi_{\mathrm{B}}\left(\frac{\langle \varepsilon_{\mathrm{BB}}^* \rangle}{\langle \varepsilon_{\mathrm{AA}}^* \rangle} - 1\right) \right. \\ \left. \times (\langle \tilde{V}_{\mathrm{BB}} \rangle - \langle \tilde{V}_{\mathrm{AA}} \rangle)\right]\end{aligned}$$

$$-\frac{1}{2\langle\tilde{T}_{\mathrm{AA}}\rangle}c_{\mathrm{A}}\left(\frac{\partial\tilde{P}}{\partial\tilde{V}}\right)_{\mathrm{A}}[\phi_{\mathrm{A}}\Omega_{\mathrm{A}}^2+\phi_{\mathrm{B}}\Omega_{\mathrm{B}}^2$$
$$-\phi_{\mathrm{B}}(\langle\tilde{V}_{\mathrm{BB}}\rangle-\langle\tilde{V}_{\mathrm{AA}}\rangle)^2]$$
$$-3c_{\mathrm{A}}\left[\phi_{\mathrm{A}}\ln\left(\frac{\langle r_{\mathrm{A}}^*\rangle}{\langle r_{\mathrm{AA}}^*\rangle}\right)+\phi_{\mathrm{B}}\ln\left(\frac{\langle r_{\mathrm{B}}^*\rangle}{\langle r_{\mathrm{BB}}^*\rangle}\right)\right] \tag{21}$$

where

$$\theta_i\equiv\left(\frac{\langle\varepsilon_i^*\rangle}{\langle\varepsilon_{ii}^*\rangle}-1\right) \qquad \Omega_i\equiv(\langle\tilde{V}_i\rangle-\langle\tilde{V}_{ii}\rangle)$$

The molar configurational energy U_{A}, the heat capacity C_{VA} and the other quantities occurring in (21) can be replaced by the reduced volume and equation-of-state parameters using a suitable equation of state. According to Flory[15] the quantities $\tilde{V}$, $\tilde{T}$, $\tilde{P}$ are linked by the following equation of state:

$$\tilde{P}=\frac{\tilde{T}\tilde{V}^{-2/3}}{\tilde{V}^{1/3}-1}-\frac{1}{\tilde{V}^2} \tag{22}$$

At $\tilde{P}=0$, it follows that:

$$\tilde{T}=\frac{\tilde{V}^{1/3}-1}{\tilde{V}^{4/3}} \tag{22a}$$

Employing

$$c\frac{\partial\ln q}{\partial\tilde{V}}=\frac{PV^*}{RT} \quad\text{and}\quad c\tilde{T}\frac{\partial\ln q}{\partial\tilde{T}}=\frac{U}{RT}$$

one obtains

$$-\frac{U_{\mathrm{A}}}{RT}=c_{\mathrm{A}}\frac{1}{\tilde{T}_{\mathrm{A}}\tilde{V}_{\mathrm{A}}} \qquad \frac{C_{\mathrm{VA}}}{R}=c_{\mathrm{A}}\frac{\tilde{V}_{\mathrm{A}}^{1/3}}{\frac{4}{3}-\tilde{V}_{\mathrm{A}}^{1/3}} \tag{23}$$

The calculation of $\partial\tilde{P}/\partial\tilde{T}$ and $\partial\tilde{P}/\partial\tilde{V}$ is straightforward. From (20) an equation of state can be deduced. Expanding this equation of state in terms of pure component A at $\tilde{P}=0$ one can calculate the quantities Ω_i occurring in (21). It follows:

$$\Omega_{\mathrm{A}}=\frac{\tilde{V}_{\mathrm{A}}(\tilde{V}_{\mathrm{A}}^{1/3}-1)}{\frac{4}{3}-\tilde{V}_{\mathrm{A}}^{1/3}}\sum_{i=\mathrm{A,B}}\phi_i\theta_i+c_{\mathrm{B}}\phi_{\mathrm{B}}\tilde{V}_{\mathrm{A}}\left(\frac{\langle r_{\mathrm{B}}^*\rangle^3}{\langle r_{\mathrm{A}}^*\rangle^3}-1\right)$$

$$\Omega_{\mathrm{B}}=\frac{\tilde{V}_{\mathrm{A}}(\tilde{V}_{\mathrm{A}}^{1/3}-1)}{\frac{4}{3}-\tilde{V}_{\mathrm{A}}^{1/3}}\sum_{i=\mathrm{A,B}}\phi_i\theta_i-c_{\mathrm{A}}\phi_{\mathrm{A}}\tilde{V}_{\mathrm{A}}\left(\frac{\langle r_{\mathrm{B}}^*\rangle^3}{\langle r_{\mathrm{A}}^*\rangle^3}-1\right) \tag{24}$$

$$\langle\tilde{V}_{\mathrm{BB}}\rangle-\langle\tilde{V}_{\mathrm{AA}}\rangle=\frac{\tilde{V}_{\mathrm{A}}(\tilde{V}_{\mathrm{A}}^{1/3}-1)}{\frac{4}{3}-\tilde{V}_{\mathrm{A}}^{1/3}}\left(\frac{\langle\varepsilon_{\mathrm{BB}}^*\rangle}{\langle\varepsilon_{\mathrm{AA}}^*\rangle}-1\right)$$

Finally, inserting the expressions (14)–(17) and (23), (24) into (21), neglecting higher than second-order terms in X_{AB}, Γ and ρ and adding the combinatorial entropy of mixing one gets for the Gibbs free energy of mixing:

$$\frac{\Delta G^{\mathrm{M}}}{RT}=2c_{\mathrm{A}}\phi_{\mathrm{A}}\phi_{\mathrm{B}}$$
$$\times\Bigg(\frac{\tilde{V}_{\mathrm{A}}^{1/3}}{\tilde{V}^{1/3}-1}\{X_{\mathrm{AB}}+\tfrac{9}{2}\rho^2-\tfrac{1}{2}[\Gamma/2+X_{\mathrm{AB}}(\phi_{\mathrm{B}}-\phi_{\mathrm{A}})]$$
$$\times[\tfrac{3}{2}(\rho_{\mathrm{B}}-\rho_{\mathrm{A}})-3K(\phi_{\mathrm{B}}-\phi_{\mathrm{A}})]\}$$
$$+\frac{\tilde{V}_{\mathrm{A}}^{1/3}(\frac{4}{3}-\tilde{V}_{\mathrm{A}}^{1/3})}{(\tilde{V}_{\mathrm{A}}^{1/3}-1)^2}\tfrac{9}{16}[(\rho_{\mathrm{B}}-\rho_{\mathrm{A}})-2K(\phi_{\mathrm{B}}-\phi_{\mathrm{A}})]^2$$
$$+\frac{\tilde{V}_{\mathrm{A}}^{1/3}}{4(\frac{4}{3}-\tilde{V}_{\mathrm{A}}^{1/3})}[\tfrac{7}{4}\Gamma^2+\Gamma X_{\mathrm{AB}}(1+6\phi_{\mathrm{B}})$$
$$-X_{\mathrm{AB}}^2(1+4\phi_{\mathrm{A}}\phi_{\mathrm{B}})]$$
$$-3[K-\tfrac{1}{16}(\rho_{\mathrm{B}}-\rho_{\mathrm{A}})^2-\tfrac{1}{4}K(\rho_{\mathrm{B}}-\rho_{\mathrm{A}})$$
$$\times(\phi_{\mathrm{B}}-\phi_{\mathrm{A}})-K^2/4]\Bigg)$$
$$+(\phi_{\mathrm{A}}/r_{\mathrm{A}})\ln\phi_{\mathrm{A}}+(\phi_{\mathrm{B}}/r_{\mathrm{B}})\ln\phi_{\mathrm{B}} \tag{25}$$

To a good approximation one can assume that the quantities R_{ij} vanish. Furthermore, with an inaccuracy of less than 1% one can neglect the second-order terms in $X_{\mathrm{AB}}\rho$, $X_{\mathrm{AB}}\Gamma$ and X_{AB}^2. As a result (25) simplifies to:

$$\frac{\Delta G^{\mathrm{M}}}{RT}=2c_{\mathrm{A}}\phi_{\mathrm{A}}\phi_{\mathrm{B}}\left[\frac{\tilde{V}_{\mathrm{A}}^{1/3}}{\tilde{V}_{\mathrm{A}}^{1/3}-1}\left(X_{\mathrm{AB}}^{\mathrm{T}}+\frac{\frac{4}{3}-\tilde{V}_{\mathrm{A}}^{1/3}}{\tilde{V}_{\mathrm{A}}^{1/3}-1}\tfrac{9}{16}\rho^2\right)\right.$$
$$\left.+\frac{\tilde{V}_{\mathrm{A}}^{1/3}}{\frac{4}{3}-\tilde{V}_{\mathrm{A}}^{1/3}}\tfrac{7}{16}\Gamma^2\right]$$
$$+(\phi_{\mathrm{A}}/r_{\mathrm{A}})\ln\phi_{\mathrm{A}}+(\phi_{\mathrm{B}}/r_{\mathrm{B}})\ln\phi_{\mathrm{B}} \tag{26}$$

where

$$X_{\mathrm{AB}}^{\mathrm{T}}\equiv X_{\mathrm{AB}}+\tfrac{9}{2}\rho^2-\tfrac{3}{8}\Gamma\rho \tag{26a}$$

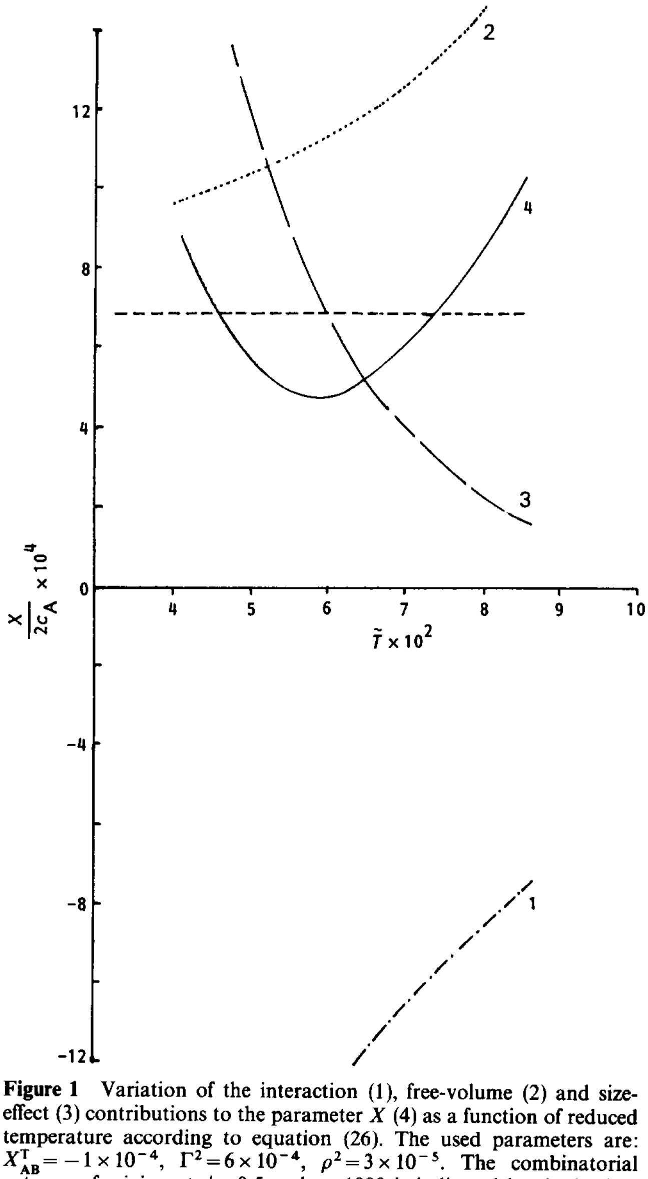

Figure 1 Variation of the interaction (1), free-volume (2) and size-effect (3) contributions to the parameter X (4) as a function of reduced temperature according to equation (26). The used parameters are: $X_{\mathrm{AB}}^{\mathrm{T}}=-1\times10^{-4}$, $\Gamma^2=6\times10^{-4}$, $\rho^2=3\times10^{-5}$. The combinatorial entropy of mixing at $\phi=0.5$ and $r=1000$ is indicated by the broken straight line

DISCUSSION

In equation (26) a generalized interaction parameter X is defined via

$$\Delta G^{\mathrm{M}}/RT = \phi_{\mathrm{A}}\phi_{\mathrm{B}}X + (\phi_{\mathrm{A}}/r_{\mathrm{A}})\ln\phi_{\mathrm{A}} + (\phi_{\mathrm{B}}/r_{\mathrm{B}})\ln\phi_{\mathrm{B}}$$

As can be seen, three effects contribute to the interaction parameter X: (i) the segmental interaction represented by the parameter X_{AB}; (ii) the free-volume effect arising from the different free volumes of the components and represented by the parameter Γ; (iii) the size effect resulting from the differences in the sizes of the segments and represented by the parameter ρ. We should notice here that the volume of mixing calculated in the same approximation as the Gibbs free energy of equation (26) also depends on the parameters X_{AB}, Γ and ρ. When there is no size effect, i.e. $\rho=0$, and $X_{\mathrm{AB}}<0$, $\Gamma>0$, then the volume of mixing ΔV^{M} is negative. With increasing ρ the sign of ΔV^{M} will change whereas ΔG^{M} keeps the same sign. The three contributions as a function of reduced temperature are shown in *Figure 1*. Since X_{AB} is negative the interaction term is also negative and favours mixing. However, it dominates the unfavourable free-volume and size-effect terms only within a certain range of temperatures. Therefore, *LCST* as well as *UCST* occur.

From equation (26) it follows that the parameter X is a free-energy parameter containing an enthalpic part X_H and an entropic part X_S:

$$X = X_H + X_S \qquad X_H = -T\,\partial X/\partial T \tag{27}$$

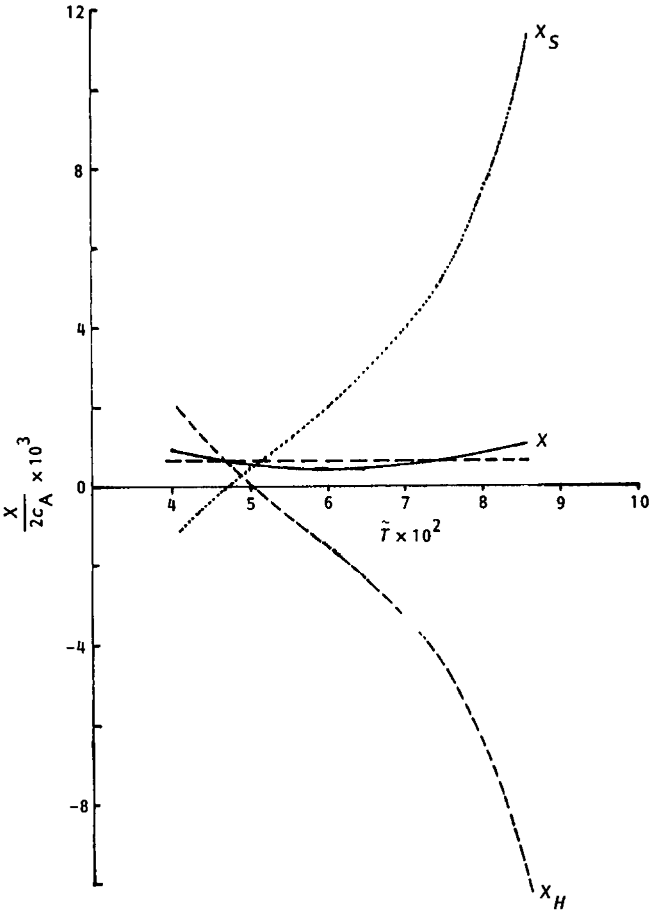

Figure 2 Representation of the parameter X and its enthalpic and entropic parts, X_H and X_S, respectively, *versus* reduced temperature as calculated from equations (27) and (28). The parameters are chosen as in *Figure 1*

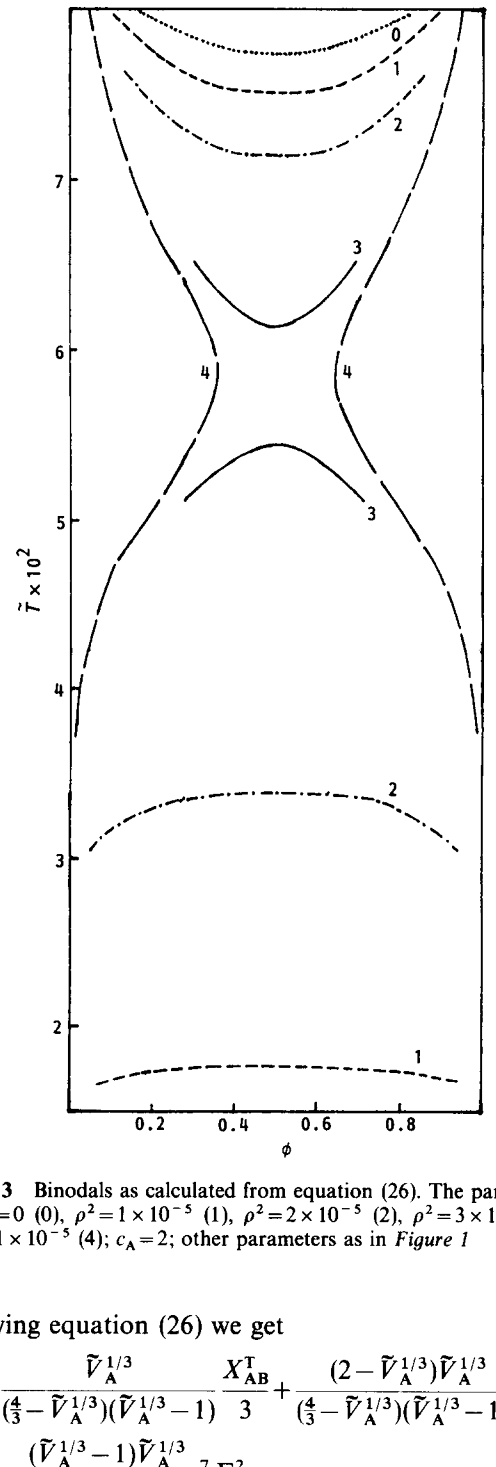

Figure 3 Binodals as calculated from equation (26). The parameters are: $\rho=0$ (0), $\rho^2=1\times10^{-5}$ (1), $\rho^2=2\times10^{-5}$ (2), $\rho^2=3\times10^{-5}$ (3), $\rho^2=3.1\times10^{-5}$ (4); $c_{\mathrm{A}}=2$; other parameters as in *Figure 1*

Applying equation (26) we get

$$\frac{X_H}{2c_{\mathrm{A}}} = \frac{\tilde{V}_{\mathrm{A}}^{1/3}}{(\frac{4}{3}-\tilde{V}_{\mathrm{A}}^{1/3})(\tilde{V}_{\mathrm{A}}^{1/3}-1)}\frac{X_{\mathrm{AB}}^{\mathrm{T}}}{3} + \frac{(2-\tilde{V}_{\mathrm{A}}^{1/3})\tilde{V}_{\mathrm{A}}^{1/3}}{(\frac{4}{3}-\tilde{V}_{\mathrm{A}}^{1/3})(\tilde{V}_{\mathrm{A}}^{1/3}-1)^2}\frac{\rho^2}{8} - \frac{(\tilde{V}_{\mathrm{A}}^{1/3}-1)\tilde{V}_{\mathrm{A}}^{1/3}}{(\frac{4}{3}-\tilde{V}_{\mathrm{A}}^{1/3})^3}\tfrac{7}{12}\Gamma^2 \tag{28}$$

Notice that $X_H \sim \Delta H^{\mathrm{M}}$ and $X_S \sim -\Delta S^{\mathrm{M}}$. The variation of the different terms with respect to reduced temperature is depicted in *Figure 2*. At high temperatures the temperature dependence of X_H and X_S is approximately the same as at $\rho=0^9$. At low temperatures, however, a completely different behaviour occurs for $\rho\neq0$. At $\rho=0$, X_H decreases with decreasing temperature and approaches X whereas X_S levels off to a small positive value. Here, X_H increases because the term is proportional to ρ^2, which acts as an additional repulsion at low temperatures, leading to an increase of the parameter X. As a result, the *LCST* behaviour is an entropy-driven process whereas the *UCST* is caused by the enthalpic contribution associated with the size effect.

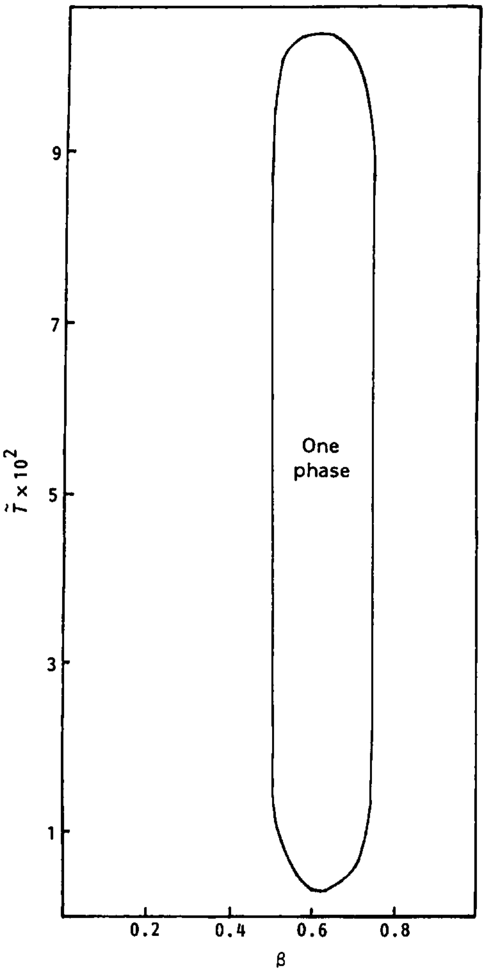

Figure 4 Miscibility map of a homopolymer/copolymer blend ($\alpha=1$) as calculated by employing equation (26). The used parameters are: $\chi_{13}=9.6\times10^{-3}$, $\chi_{14}=0.03$, $\chi_{34}=0.08$; $\delta_3=\delta_4=0.065$; $\delta_3^r=\delta_4^r=5.5\times10^{-3}$; $c_A=2$; $r=1000$; $\phi=0.5$. Miscibility occurs only inside the curve

Now, phase diagrams can be deduced from the Gibbs free energy of mixing (equation (26)). Results are shown in *Figure 3*. As can be seen the phase behaviour varies dramatically with the size parameter ρ. At $\rho=0$ only *LCST* behaviour occurs. With increasing ρ the gap between *LCST* and *UCST* diminishes more and more; finally, an hourglass-shaped phase diagram results. Remarkably, extremely small changes in the parameter ρ alter the phase behaviour from *UCST/LCST* behaviour to immiscibility, as is demonstrated by curves 3 and 4 in *Figure 3*. Furthermore, one may establish that simultaneously experimentally accessible *LCST* and *UCST* in one system are rare because the position of the binodals is very sensitive to the ratios ρ^2/X_{AB}, ρ/Γ and X_{AB}/Γ^2 and, as indicated above, small changes in the ratios can shift the *UCST* far below the glass transition temperature.

The same treatment may also be used to account for miscibility and *LCST/UCST* behaviour in blends containing random copolymers. As a matter of fact, the positions of *LCST* and *UCST* depend highly on the copolymer composition. Therefore, for blends containing copolymers of varying composition, one observes different binodals. The binodals may be employed to map the miscibility in copolymer/homopolymer blends at constant blend composition as a function of copolymer composition. An example for a *T*–β plot as calculated on the basis of equation (26) is shown in *Figure 4*. Miscibility is confined to a certain region of copolymer composition. We should notice here that the experimental observation of miscibility–immiscibility boundaries as a function of copolymer composition permits the quantitative determination of the individual segmental parameters occurring in equations (A6)–(A10).

In conclusion, the simultaneous occurrence of a *LCST* and an *UCST* is associated with positive contributions to the Gibbs free energy of mixing due to the free-volume effect and the differences in segmental sizes, respectively, whereby the latter effect is most striking at low temperatures. When the size effect is negligible only *LCST* behaviour is experimentally observable. The complex phase behaviour of polymer blends can be explained satisfactorily in terms of a refined equation-of-state theory.

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APPENDIX

It is useful to introduce the following notations:

$$\delta_i=\varepsilon_{ii}^*/\varepsilon_{11}^*-1 \qquad i=2,3,4 \tag{A1}$$

$$\delta_i^r=r_{ii}^*/r_{11}^*-1 \qquad i=2,3,4 \tag{A2}$$

$$\chi_{ij}=(1/\varepsilon_{11}^*)[\tfrac{1}{2}(\varepsilon_{ii}^*+\varepsilon_{jj}^*)-\varepsilon_{ij}^*] \qquad i\neq j;\ \begin{matrix} i=1,2,3 \\ j=2,3,4\end{matrix} \tag{A3}$$

$$R_{ij}=(1/r_{11}^*)[\tfrac{1}{2}(r_{ii}^*+r_{jj}^*)-r_{ij}^*] \tag{A4}$$

$$X_{AB}=(1/\langle\varepsilon_{AA}^*\rangle)[\tfrac{1}{2}(\langle\varepsilon_{AA}^*\rangle+\langle\varepsilon_{BB}^*\rangle)-\langle\varepsilon_{AB}^*\rangle] \tag{A5}$$

Furthermore:

$$\varepsilon=(1-\alpha)\delta_2-2\alpha(1-\alpha)\chi_{12}-18\alpha(1-\alpha)(\delta_2^r)^2 \tag{A6}$$

$$\rho_A=(1-\alpha)\delta_2^r-2\alpha(1-\alpha)R_{12} \tag{A7}$$

$$\eta=\beta\delta_3+(1-\beta)\delta_4-2\beta(1-\beta)\chi_{34}-18\beta(1-\beta)(\delta_3^r+\delta_4^r)^2 \tag{A8}$$

$$\rho_B=\beta\delta_3^r+(1-\beta)\delta_4^r-2\beta(1-\beta)R_{34} \tag{A9}$$

$$\lambda=\alpha\beta\chi_{13}+\alpha(1-\beta)\chi_{14}+(1-\alpha)\beta\chi_{23}+(1-\alpha)(1-\beta)\chi_{24}-\alpha(1-\alpha)\chi_{12}-\beta(1-\beta)\chi_{34} \tag{A10}$$