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On immiscibility-loop phase behaviour of polymer blends

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Abstract

A generalized Flory–Huggins parameter χ is utilized to study immiscibility-loop phase behaviour of binary polymer blends. Special emphasis is placed on the temperature dependence of the χ parameter. It turns out that specific interactions, that gradually become weaker with ascending temperature, lead to miscibility at low temperatures and, eventually, to phase separation at sufficiently high temperatures (lower critical solution temperature behaviour). In addition, if a favourable noncombinatorial entropy contribution to parameter χ becomes more and more dominant with increasing temperature then it leads again to a homogeneous system (upper lower critical solution temperature behaviour). From a molecular point of view, this stabilization of the mixture at high temperatures might be attributed to nonrandom packing effects caused by structural disparities of the constituents. It is also demonstrated that immiscibility-loop phase behaviour can only be observed in blends of constituents having sufficient asymmetry in the polymerization indices. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blends; Immiscibility-loop; Phase stability

1. Introduction

Usually, miscible polymer–polymer blends tend to phase separate at elevated temperatures, i.e., an entropy-driven lower critical solution temperature (LCST) occurs where the mixture phase separates upon heating [1–6]. For miscibility of polymers, favourable interactions between the constituents are necessary owing to the small combinatorial entropy of mixing in polymer mixtures. Phase separation at sufficiently high temperatures is then caused by noncombinatorial entropy contributions to the free energy of mixing. Polymer blends displaying an upper critical solution temperature (UCST) are also known. Phase separation at low temperatures and miscibility at sufficiently high temperatures was reported, e.g. for blends of polystyrene (PS) and its deuterated analogue [7] and also for PS blended with differently substituted polystyrenes [8]. There are also blends exhibiting both LCST and UCST with the LCST situated above the UCST [9–11].

Recently, it was reported that polymer–oligomer blends also display immiscibility-loop phase behaviour where the UCST occurs at higher temperatures than the LCST. Such phase behaviour was found when isotactic polypropylene was blended either with hydrogenated oligo-(cyclopentadiene) [12] or hydrogenated oligo(styrene-co-indene) [13,14]. In Ref. [15], it was inferred from measurements of interfacial tensions that blends of poly(isobutylene), having a relatively low molecular mass of 1500 g/mol, and poly(dimethyl siloxane) of high molecular mass may exhibit also a closed immiscibility gap. Although, the LCST is expected to shift to very low temperatures. Also for polymer solutions, e.g. aqueous solutions of poly(ethylene glycol) [16] or poly(propylene glycol) [17], immiscibility-loop phase behaviour was observed.

The phase behaviour of polymer mixtures is controlled by two thermodynamic quantities, the entropy of mixing, comprising combinatorial and noncombinatorial contributions, and the energy of mixing which is related to interactions between the segments. The noncombinatorial entropy of mixing and the energy of mixing represent the excess free energy of mixing, ΔF^{E}. Then, the Helmholtz free energy of mixing per total number of monomers, ΔF^{M}, might be expressed by

$$\Delta F^{\mathrm{M}} = \Delta F^{\mathrm{E}} - T\Delta S_{\mathrm{comb}}. \tag{1a}$$

The combinatorial entropy of mixing, ΔS_{comb}, is given in the context of the Flory–Huggins theory by the well-known expression [18] while the excess free energy of mixing is represented by

$$\frac{\Delta F^{\mathrm{E}}}{RT} = \chi \Phi_{\mathrm{A}} \Phi_{\mathrm{B}} \tag{1b}$$

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where Φ_i is the monomer volume fraction of component i and χ is a dimensionless free-energy parameter. In the following, parameter χ is considered as a function of temperature and volume only; a potential concentration dependence of χ is neglected. The phase stability of polymer blends is crucially governed by the temperature dependence of parameter χ. In the limit of very high degrees of polymerization, the parameter χ has to be negative for miscibility of the blend constituents. LCST behaviour will occur if parameter χ turns from negative to positive values at a certain temperature. For an immiscibility loop, the parameter χ has to be negative at low and high temperatures and positive in a temperature range in between. It becomes obvious, owing to the small combinatorial entropy of mixing in polymer mixtures, noncombinatorial entropy as well as energy contributions to the free energy of mixing assume a major role.

This paper focuses on a temperature dependence of parameter χ that allows to describe immiscibility-loop phase behaviour.

2. The temperature dependence of parameter χ

From thermodynamic standard relations, it follows that

$$-\frac{\partial}{\partial T}\left(T^2 \frac{\partial}{\partial T}\frac{\Delta F^{\mathrm{E}}}{RT}\right) = \frac{\Delta C_V^{\mathrm{E}}}{R} \tag{2}$$

where ΔC_V^{E} is the molar excess heat capacity of the mixture. If one neglects the concentration dependence of parameter χ, it is justified to approximate ΔC_V^{E} by $C_{V\mathrm{A}}\Phi_{\mathrm{A}}\Phi_{\mathrm{B}}$, i.e., the variation of ΔC_V^{E} with temperature is ruled by that of $C_{V\mathrm{A}}$. Eq. (2) leads then with Eq. (1b) to the following relationship for the temperature dependence of parameter χ

$$-\left[\frac{\partial}{\partial \tilde{T}}\left(\tilde{T}^2 \frac{\partial \chi}{\partial \tilde{T}}\right)\right]_{\tilde{T}=\tilde{T}_{\mathrm{A}}} = \frac{C_{V\mathrm{A}}}{R}. \tag{3}$$

In Eq. (3), the temperature is replaced by the reduced temperature $\tilde{T}$. This allows easily to apply Flory's equation-of-state. The reduced quantities for pure substance A are defined by $\tilde{X}_{\mathrm{A}} \equiv X/X_{\mathrm{A}}{*}$ with $X_{\mathrm{A}}{*}$ being the respective reference parameter of substance A. Quantity $V_{\mathrm{A}}{*}$ is the specific hard-core volume at 0 K.

Application of Flory's equation-of-state in the limit $\tilde{P} \longrightarrow 0$ [19]

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

implies for the temperature dependence of the heat capacity [5]

$$\frac{C_V}{R} = \frac{\tilde{V}^{1/3}}{4/3 - \tilde{V}^{1/3}}. \tag{5}$$

Parameter χ becomes solely a function of reduced volume in the limit of Eq. (4), $\chi = \chi(\tilde{V})$. After inserting Eq. (5) into Eq. (3) and integrating twice, one arrives at

$$\chi(\tilde{V}_{\mathrm{A}}) = B + \frac{\left[A\tilde{V}_{\mathrm{A}}^{4/3} - 1\right]}{\tilde{T}_{\mathrm{A}}\tilde{V}_{\mathrm{A}}^{4/3}} - 3\ln\left(\tilde{T}_{\mathrm{A}}\tilde{V}_{\mathrm{A}}^{4/3}\right) \tag{6}$$

where the integration constants A and B are adjustable constants. Eq. (6) gives in combination with Eq. (4) the temperature dependence of quantity χ or, vice versa, Eq. (4) can be used to formulate parameter χ as a function of reduced volume only.

3. Results and discussion

As mentioned before, parameter χ is a free-energy parameter comprising an energetic part, χ_U and an entropic part, χ_S

$$\chi = \chi_U + \chi_S$$

with

$$\chi_S = \frac{\partial}{\partial \tilde{T}}(\tilde{T}\chi).$$

Note, $\chi_U \propto \Delta U^{\mathrm{M}}$ and $\chi_S \propto -\Delta S^{\mathrm{E}}$ where ΔU^{M} is the energy of mixing and ΔS^{E} the noncombinatorial entropy of mixing. With Eq. (6), it follows that

$$\chi_U = \frac{1}{\tilde{T}_{\mathrm{A}}\tilde{V}_{\mathrm{A}}}\left[A\tilde{V}_{\mathrm{A}} - 1\right] \tag{7a}$$

and

$$\chi_S = B + 1 - 3\ln\left(\tilde{T}_{\mathrm{A}}\tilde{V}_{\mathrm{A}}^{4/3}\right). \tag{7b}$$

In this approximation, the coefficients A and B rule the energetic and noncombinatorial entropic contribution, respectively, to parameter χ. Eq. (6) shows that $(\chi - B)$ is for $A < -0.0312$ a negative and monotonously increasing function of $\tilde{V}^{1/3}$. For sufficiently high positive values of B, parameter χ may turn to positive values which corresponds to occurrence of an LCST that shifts to lower temperatures with increasing B. If constant A is in the range $-0.0312 \leq A \leq 0.422$, the function $(\chi - B)$ displays the same curvature, however, it passes to positive values above a certain value of $\tilde{V}^{1/3}$. This change shifts to lower temperatures with ascending A (from $\tilde{V}^{1/3} \approx 1.33$ to ≈ 1.055 in the indicated range). For $A \geq 1$, $(\chi - B)$ is positive and a monotonously descending function of $\tilde{V}^{1/3}$. Hence, parameter χ may turn to negative values if $B < 0$. This corresponds to occurrence of a UCST. In the range $0.422 < A < 1$, the function $(\chi - B)$ is negative at sufficiently low temperatures and displays a maximum at $A\tilde{V} = 1$ where $\chi_U(A\tilde{V} = 1) = 0$ and $[\chi(A\tilde{V} = 1) - B]_{\max} = (\chi_S - B) > 0$. Moreover, the slope of $\chi = \chi(\tilde{V}^{1/3})$ is given by

$$\chi' = -3\frac{\left(4/3 - \tilde{V}^{1/3}\right)\left(A\tilde{V} - 1\right)}{\left(\tilde{V}^{1/3} - 1\right)^2}.$$

For $A\tilde{V} > 1$ the slope is negative and its magnitude

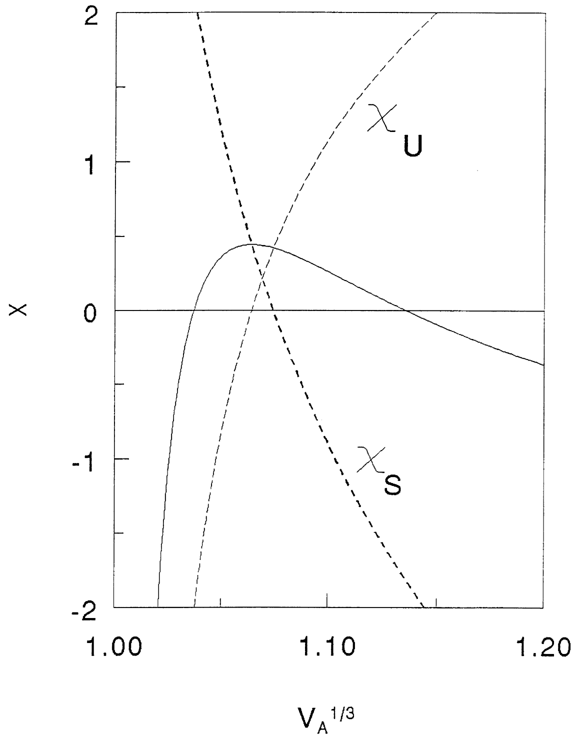

Fig. 1. Parameter χ and its constituents χ_U and χ_S as a function of $\tilde{V}_A^{1/3}$. Parameters $A = 0.83$, $B = -8.8$.

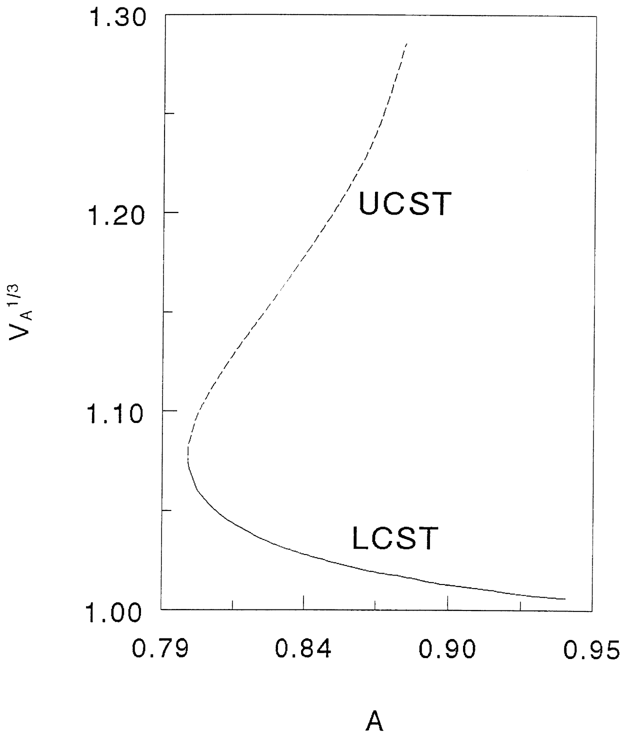

Fig. 2. Critical temperatures as a function of parameter A. Parameters $B = -8.66$, $r_A = 1000$, $r_B = 50$.

gradually decreases with increasing $\tilde{V}^{1/3}$. Therefore, $(\chi - B)$ remains positive. If $B < 0$, however, parameter χ might turn after the maximum again to negative values. In other words, we have an LCST at low temperatures while a UCST turns up at high temperatures. This is illustrated for one example in Fig. 1. We use in Fig. 1 and, similarly, in the following figures, the quantity $\tilde{V}_A^{1/3}$ as an equivalent of temperature according to Eq. (4); increasing $\tilde{V}_A^{1/3}$ means increasing temperature. Here, miscibility originates from favourable interactions at low temperatures while at high temperatures a positive noncombinatorial entropy contribution becomes dominant. Obviously, the negative value of parameter B reflects here in a phenomenological way the structural disparities of the constituents at the monomeric and chain level, i.e., differences in monomer size and chain stiffness, that give rise to a positive noncombinatorial entropy as discussed in Refs. [20,21]. Fig. 2 shows the variation of the critical points with parameter A for a given set of values for parameter B and the degrees of polymerization, r_A and r_B. With increasing value of A, the LCST shifts to lower temperatures while the UCST shifts to very high temperatures. In other words, the immiscibility loop becomes more and more extended when A or the value of χ_U increases.

Fig. 3 gives a phase diagram for an oligomer–polymer blend with an immiscibility loop, calculated with parameter χ after Eq. (6) and using Eq. (1a). Relevant equations for spinodal, binodal and the critical points are given in the appendix. Only for blends with pronounced asymmetry in the polymerization indices, one can observe asymmetrical immiscibility loops. When the degrees of polymerization for the constituents approach each other more and more, the LCST and UCST shift to lower and higher temperatures, respectively, and the phase diagram becomes more symmetric. This is indicated in Fig. 4 where the concentrations of the coexisting concentrated and diluted phases with highest and lowest concentration, respectively, are depicted versus polymerization index r_B at $\tilde{V}_A^{1/3} = \text{const}$. The selected value of $\tilde{V}_A^{1/3}$ represents the horizontal symmetry axis of the corresponding phase diagram. Fig. 4 demonstrates that with increasing polymerization index r_B the coexisting phases rapidly approach highly diluted regimes. For a completely symmetrical blend, with polymerization indices $r_A = r_B$, the phase diagram is also symmetrical. This is shown for one example in Fig. 5.

In conclusion, occurrence of an immiscibility loop in polymer blends requires both favourable interactions between the constituents and structural dissimilarities of the constituents that lead to a positive noncombinatorial entropy contribution. With increasing temperature, the interactions are weakened, causing LCST behaviour, while the noncombinatorial entropy contribution becomes more and more dominant, leading eventually again to phase stability of the blend or UCST behaviour. This phase behaviour is experimentally easily accessible only for blends with asymmetrical polymerization indices.

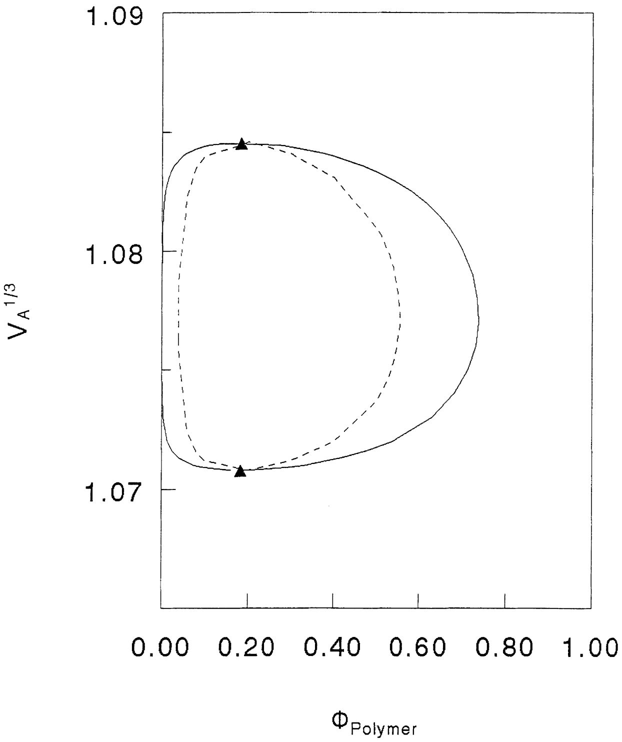

Fig. 3. Binodal and spinodal (--) calculated with parameter χ, Eq. (6). Markers indicate the critical points. Parameters $A = 0.8$, $B = -8.66$, $r_A = 1000$, $r_B = 50$.

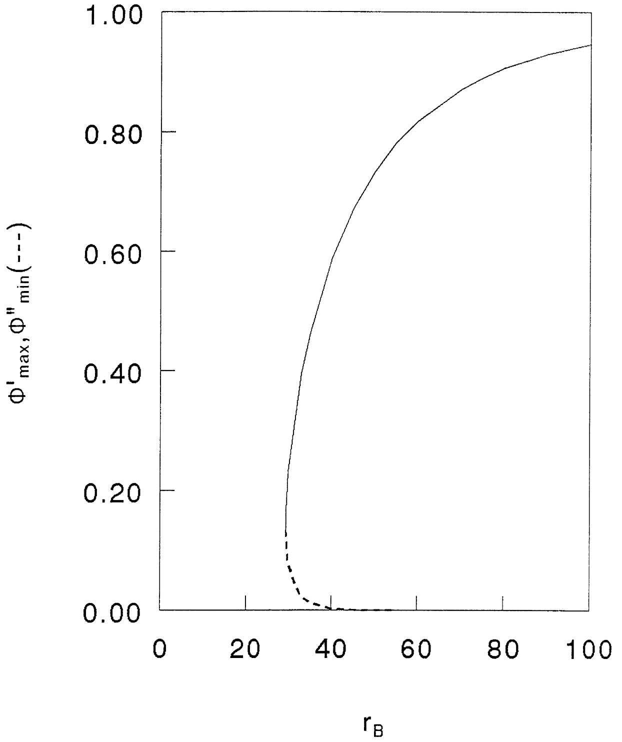

Fig. 4. Highest and lowest concentration (--) of the coexisting phases versus polymerization index r_B. Parameters: $\tilde{V}_A^{1/3} = 1.078$, $A = 0.8$, $B = -8.66$, $r_A = 1000$.

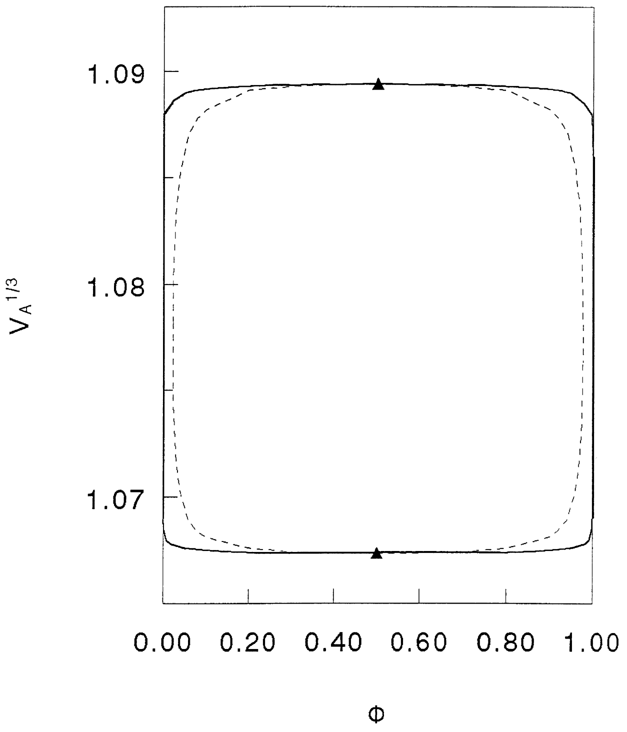

Fig. 5. Binodal and spinodal (--) for a symmetrical blend. Markers indicate the critical points. Parameters: $A = 0.8$, $B = -8.66$, $r_A = r_B = 1000$.

Appendix

The spinodals were calculated from

$$\frac{1}{r_A \Phi_A} + \frac{1}{r_B \Phi_B} - 2\chi = 0 \tag{A.1}$$

with parameter χ from Eq. (6).

The binodals are obtained by simultaneously solving the two equations:

$$\frac{1}{r_A} \ln\left(\frac{\Phi'}{\Phi''}\right) = (\Phi' - \Phi'') \times \left[\left(\frac{1}{r_A} - \frac{1}{r_B}\right) - \chi(\Phi' + \Phi'') + 2\chi\right], \tag{A.2}$$

$$\frac{1}{r_B} \ln\left(\frac{1 - \Phi'}{1 - \Phi''}\right) = (\Phi' - \Phi'') \times \left[\left(\frac{1}{r_A} - \frac{1}{r_B}\right) - \chi(\Phi' + \Phi'')\right]. \tag{A.3}$$

Critical points are given by the solution of

$$\frac{1}{\Phi_{A_{cr}}} = 1 + \sqrt{\frac{r_A}{r_B}} \quad \text{and} \quad \chi_{cr} = \frac{1}{2}\left(\frac{1}{\sqrt{r_A}} + \frac{1}{\sqrt{r_B}}\right)^2. \tag{A.4}$$

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