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On the Reasons for an Anomalous Demixing Behavior of Polymer Solutions

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ABSTRACT: Some extraordinary solutions of polymers in single solvents exhibit two liquid/liquid critical points, one within the usual composition range and a second one in the range of moderate to high polymer concentration. This particularity was studied theoretically by means of a recently established approach, which accounts explicitly for chain connectivity and for the ability of polymer molecules to respond to changes in their environment by conformational rearrangements. On the basis of model calculations, it is shown that the anomalous demixing behavior, i.e., the emergence of a second critical point, is bound to the necessary but not sufficient condition that a thermodynamically very unfavorable contact formation between polymer segments and solvent molecules (at fixed conformation of the components) is associated with an extraordinarily favorable conformational response. Possibilities to forecast whether certain systems behave normal or in an anomalous manner are discussed.

1. Introduction

Experimental evidence and model calculations have demonstrated the existence of certain polymer solutions and polymer mixtures that behave remarkably different from the big majority of such systems.[1−6] The most striking feature consists of the occurrence of two maxima or minima in the cloud point curves instead of one. For very high molecular weight polymers this feature implies the appearance of an off-zero critical concentration in addition to the normal critical point close to vanishing polymer content. Furthermore, a three phase line occurs at a certain characteristic temperature even for strictly binary mixtures.

The above-mentioned theoretical considerations rest either on a series expansion of the Flory−Huggins interaction parameter as a function of composition[2,3] or on an extended Flory−Huggins model accounting for nonpolar and polar interactions.[4] The present study was undertaken to find out whether a recently published approach,[7] which can describe the demixing of normal systems quantitatively,[8] is also capable to reproduce the reported irregularities.

2. Thermodynamic Background

For the simplest possible case of present interest (solutions of molecularly uniform macromolecules in a single low molecular weight liquid) the segment molar Gibbs energy of mixing, $\Delta\bar{\bar{G}}$, can be written as[9]

$$\frac{\Delta\bar{\bar{G}}}{RT} = (1-\varphi)\ln(1-\varphi) + \frac{\varphi}{N}\ln(\varphi) + g(1-\varphi)\varphi \qquad (1)$$

In this case a segment equals the molar volume of the solvent and N stands for the number of segments the polymer is made of; φ is the volume fraction of the polymer. The interaction parameter g relates to the segment molar residual Gibbs energy of mixing, $\Delta\bar{\bar{G}}^R$, as

$$g \equiv \frac{\Delta\bar{\bar{G}}^R}{RT\varphi(1-\varphi)} \qquad (2)$$

In the first instance g was introduced as a composition independent parameter.[9] For a realistic modeling g is nowadays usually treated as a function of φ such that it accounts for all deviations of an actual system from the first two combinatorial summands of eq 1.

Leaving the details of $\Delta\bar{\bar{G}}^R(\varphi,T,p)$ open, eq 1 yields the following critical conditions[10−12]

$$\frac{1}{1-\varphi} + \frac{1}{N\varphi} + \frac{1}{RT}\left(\frac{\partial^2\Delta\bar{\bar{G}}^R}{\partial\varphi^2}\right)_{p,T} = 0 \qquad (3)$$

and

$$\frac{1}{(1-\varphi)^2} - \frac{1}{N\varphi^2} + \frac{1}{RT}\left(\frac{\partial^3\Delta\bar{\bar{G}}^R}{\partial\varphi^3}\right)_{p,T} = 0 \qquad (4)$$

where eq 3 represents the spinodal condition. In addition to the above relations the following equation must also be fulfilled for the occurrence of double critical points (DCPs)

$$\frac{2}{(1-\varphi)^3} + \frac{2}{N\varphi^3} + \frac{1}{RT}\left(\frac{\partial^4\Delta\bar{\bar{G}}^R}{\partial\varphi^4}\right)_{p,T} = 0 \qquad (5)$$

The integral quantities $\Delta\bar{\bar{G}}^R$ and g are not directly accessible; usually one measures (e.g., via osmosis or vapor pressure) the differential Flory−Huggins interaction parameter χ, which is defined in terms of $\Delta\bar{\bar{G}}_1{}^R$, the segment molar residual chemical potential of the solvent as

$$\chi \equiv \frac{\Delta\bar{\bar{G}}_1{}^R}{RT\varphi^2} \qquad (6)$$

The two interaction parameters g and χ are interrelated by

$$\chi = g - (1-\varphi)\frac{\partial g}{\partial\varphi} \qquad (7)$$

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Ordinary polymer solutions phase separate (depending on the molar mass of the polymer) as the solvent quality falls below Θ conditions, where this characteristic state is defined by the condition that the second osmotic virial coefficient, A_2, be zero. According to phenomenological thermodynamics A_2 is related to χ_o, the limiting value of the differential interaction parameter for $\varphi \rightarrow 0$, by

$$\chi_0 = \frac{1}{2} - \rho_2^{\,2} V_1 A_2 \tag{8}$$

V_1 is the molar volume of the solvent and ρ_2 the density of the polymer. In the composition range within which only contacts between two polymer molecules must be considered (pair interaction) the Flory–Huggins interaction parameter for Θ conditions thus reads

$$\chi_{o,\Theta} = \frac{1}{2} \tag{9}$$

2.1. Series Expansion of *g*. Schäfer-Soenen[3] et al. used a three membered series to describe the composition dependence of the integral interaction parameter g for their modeling

$$g = g_{os} + \frac{g_{oh}}{T} + g_1\varphi + g_2\varphi^2 \tag{10}$$

and confined the temperature influences to the composition independent term. From eq 10 we obtain by means of eq 7 the following expression for χ (φ)

$$\chi = \left(g_{os} + \frac{g_{oh}}{T} - g_1\right) + 2(g_1 - g_2)\varphi + 3g_2\varphi^2 \tag{11}$$

The limit $\varphi \rightarrow 0$ yields χ_o and because of eq 9 the Θ temperature is given as

$$\Theta = \frac{g_{oh}}{1/2 + g_1 - g_{os}} \tag{12}$$

2.2. The New Approach. In view of the numerous difficulties of existing theories with the quantitative description of experimental observations, we have begun our theoretical considerations from a starting point that is fundamentally different from the usual procedure, namely from the dilute side of the solutions, and account explicitly for two features that were obviously overlooked in the past.[7,13] These are the fact that the segments of a given macromolecule cannot be evenly distributed over the entire volume of the system (due to chain connectivity) and the ability of chain molecules to change their conformation in response to changes in their environment (conformational response).

This procedure yields the following expression[7] for g

$$g = \frac{\alpha}{(1-\nu)(1-\nu\varphi)} - \zeta(1 + (1-\lambda)\varphi) \tag{13}$$

The parameter α quantifies the thermodynamic changes resulting form the opening of 1 mol of contacts between polymer segments (by inserting solvent molecules) at infinite dilution ($\varphi \rightarrow 0$) *without changing the conformation of the polymer chain*. This first step of the mixing process does in the general case not yet comprise the total effect. To reach the minimum of the Gibbs energy of the total system the polymer chain undergoes a *conformational relaxation*, quantified by the parameter ζ. With normal systems this rearrangement in response to changes in the environment is absent under Θ conditions. Under these special circumstances ($T = \Theta$) the conformational response ζ becomes zero and α assumes the value of 0.5. The parameter ν was introduced to quantify the changes in g associated with an increase of the polymer concentration beyond the range of pair interaction; it accounts primarily for the changes in the deviation of the entropy of mixing from combinatorial behavior. The parameter λ allows for the specific influences of the molecular weight of the polymer (effects of chain connectivity); it can be obtained from the Kuhn–Mark–Houwink constants K and a (relating the intrinsic viscosity of a given polymer in a certain solvent at specified T and p to its molar mass) according to

$$\lambda = \left(\frac{1}{2} + \kappa N^{-(1-a)}\right) \tag{14}$$

where the factor κ is given by

$$\kappa = K\rho_2\left(\frac{\rho_2}{\rho_1}M_1\right)^a \tag{15}$$

ρ_i are the densities of the components and M_1 is the molar mass of the solvent. For sufficiently high molecular weight polymers, λ turns out to be so close to 0.5 that this parameter can in most cases be set equal to 0.5 without noteworthy loss of accuracy.

If one wants to reduce the number of parameters of eq 13 and to retain the influences of molar mass implicitly, one can eliminate one of them by introducing the combined parameter $\zeta\lambda$ and setting the isolated remaining λ equal to 0.5, its limiting value for infinite molar mass of the polymer. In this manner one remains with three adjustable parameters for isothermal conditions (by analogy with the parameters for the isothermal series expansion of eq 10).

$$g = \frac{\alpha}{(1-\nu)(1-\nu\varphi)} - \zeta\lambda(2 + \varphi) \tag{16}$$

As stated earlier, the determination of the system specific parameters of the above relation is normally carried out in terms of the Flory–Huggins interaction parameter χ by measuring the chemical potentials of the components (mostly that of the solvent). By means of eq 7 we obtain the following expression χ (φ)

$$\chi = \frac{\alpha}{(1-\nu\varphi)^2} - \zeta\lambda(1 + 2\varphi) \tag{17}$$

From eqs 16 and 17 it is obvious that there exist two clearly separable reasons for the composition dependence of g and χ. One is related to the parameter α, where ν quantifies the composition dependence of the effects associated with the opening of intersegmental contacts at fixed conformation. The other contribution originates from ζ and also becomes larger at high φ. According to experimental evidence[7,8,13] α and $\zeta\lambda$ are normally not independent of each other (as is conceivable in view of the physical meaning of these parameters). If knowledge on this interrelation is available for a certain class of polymer/solvent systems, a quantitative thermodynamic description of ordinary polymer solutions requires only two adjustable parameters.

3. Criteria for the Occurrence of Multiple Critical Points

From earlier publications[2-4,14] it is evident that the demixing behavior of anomalous systems is bound to an uncommonly pronounced concentration dependence of the interaction parameters. In the following we investigate which values, α, ν, and $\zeta\lambda$, must be assumed to yield more than one critical point.

Equation 16 and the first critical condition eq 3 yield[8]

$$\frac{1}{(1-\varphi_c)} + \frac{1}{N\varphi_c} - \frac{2\alpha}{(1-\nu\varphi_c)^3} + 2\zeta\lambda(1+3\varphi_c) = 0 \qquad (18)$$

The second critical condition eq 4 reads[8]

$$\frac{1}{(1-\varphi_c)^2} - \frac{1}{N{\varphi_c}^2} - \frac{6\alpha\nu}{(1-\nu\varphi_c)^4} + 6\zeta\lambda = 0 \qquad (19)$$

which can be rewritten as

$$\zeta\lambda = \frac{1}{6}\left(\frac{1}{N{\varphi_c}^2} + \frac{6\alpha\nu}{(1-\nu\varphi_c)^4} - \frac{1}{(1-\varphi_c)^2}\right) \qquad (20)$$

Inserting $\zeta\lambda$ from eq 20 into eq 18 yields the following relation

$$\alpha = \frac{[6{\varphi_c}^3(N-1) + {\varphi_c}^2(11-2N) - 4\varphi_c - 1][1-\nu\varphi_c]^4}{6{\varphi_c}^2N(1-\varphi_c)^2(4\nu\varphi_c + \nu - 1)} \qquad (21)$$

Equation 21 must hold true for all critical points of a given system. However, insertion of the different φ_c into this relation needs not yield identical α values. The reason is that the corresponding critical temperatures are in the general case dissimilar so that the resultant α (and possibly also ν) are at variance. Nonetheless eq 21 is beneficial to perceive combinations of α and ν values that yield more than one solution for the critical composition φ_c.

Another interesting question related to the critical state concerns the occurrence of double critical points; eq 5 in combination with eqs 2 and 16 yields

$$\frac{2}{(1-\varphi_{DCP})^3} + \frac{2}{N{\varphi_{DCP}}^3} - \frac{24\alpha\nu^2}{(1-\nu\varphi_{DCP})^5} = 0 \qquad (22)$$

Eliminating α in the above expression by means of eq 21 results in the following condition, which enables the calculation of the composition of the mixture at the DCP as a function of the parameter ν

$$8\nu^2{\varphi_{DCP}}^5(N-1) - \nu{\varphi_{DCP}}^4[N(17\nu-5) - 23\nu + 5] + {\varphi_{DCP}}^3[N(4\nu^2+\nu-1) - 21\nu^2 + 14\nu + 1] + {\varphi_{DCP}}^2 \times (5\nu^2 - 12\nu - 3) + \varphi_{DCP}(\nu^2 + 2\nu + 3) + \nu - 1 = 0 \qquad (23)$$

We are now coming to the calculation of critical lines. To that end we treat the critical composition of eq 21 as the independent variable and plot α as a function of φ_c, keeping the parameter ν constant within a physically realistic range (0 to 0.7). For combinations of α and ν leading to the emergence of further critical points we must obtain the same α at least twice. The condition for the occurrence of double critical points (eq 5) is fulfilled at the minima of the different critical lines. For $\alpha > \alpha_{DCP}$ there exist three solutions for eq 21, where only the lowest and the highest φ_c correspond to stable critical points, in contrast to the middle φ_c, which represent unstable critical points. Figure 1 demonstrates this situation for two ν values.

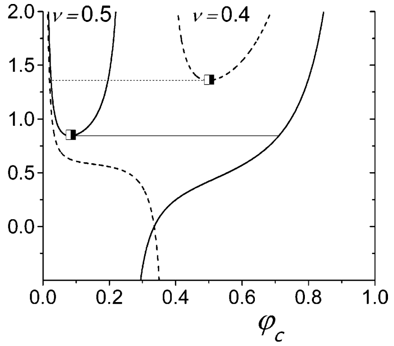

Figure 1. Example for plots of α as a function of φ_c according to eq 21 at the constant ν values indicated in the graph. The horizontal lines mark the minimum value α must exceed for a given ν to generate an additional critical point. (◨) anomalous double critical points.

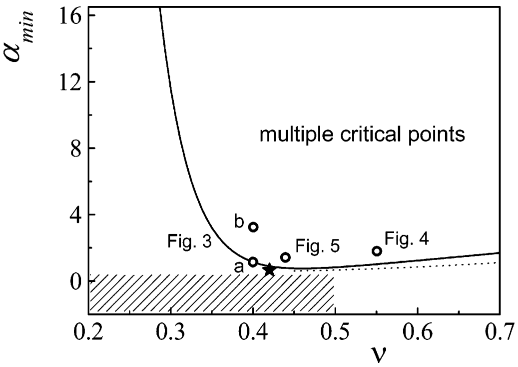

Figure 2. Borderline between normal and anomalous demixing calculated for $N = 1000$ (full) and for $N \to \infty$ (dotted, indistinguishable from the full line left to the minimum). The lowest value of α_{min} required for the emergence of a second critical point is indicated by the full asterisk. Typical α and ν values of normal systems[7] are located within the hatched area. Also indicated are the parameter combinations used to calculate the phase diagrams presented in the next section.

By means of the procedure visualized in Figure 1, it is possible to make out combinations of α and ν causing the first occurrence of a second critical point. In this manner one acquires a borderline α_{min} as a function of ν that separates the region of normal demixing behavior from the region of multiple critical points. Because of the fact that this curve represents the combinations of parameters leading to the occurrence of double critical points, we might also call it the double critical line. Figure 2 shows the results for $N = 1000$ and for infinitely long chains.

To effectuate more than one critical point, the parameters α and ν must be chosen adequately (i.e., on the borderline of Figure 2 or above it). The third parameter $\zeta\lambda$ required for a complete description of a given system at constant temperature can be calculated from eq 20. Figure 2 also demonstrates the existence of a minimum value of α_{min} (α*, asterisk in Figure 2). As long as α remains below this characteristic figure, the calculated phase behavior remains normal, irrespective of the value of the ν parameter. This decisive α^* can be obtained by differentiating twice: α (eq 21) with respect to φ_c, yielding α_{min} and the resulting α_{min} with respect to ν. Unfortunately the corresponding equations become rather unhandy. For that reason α^* was determined numerically. For $N \geq 1000$, $\alpha^* = 0.426$ and the corresponding composition of the anomalous critical composition becomes $\varphi_{DCP} = 0.237$.

4. Modeling of Phase Diagrams

To model spinodal lines and binodal lines, we must treat at least one of the three parameters of the present approach as temperature dependent. For simplicity and in agreement with the usual procedure[3] we incorporate all temperature effects into one parameter, namely α as formulated in eq 24

$$g = \frac{\alpha_1 + \alpha_2(T - T_s)}{(1 - \nu)(1 - \nu\varphi)} - \zeta\lambda(2 + \varphi) \qquad (24)$$

T_s represents a reference temperature within the interval of interest. Despite this unrealistic assumption (α and ζ are in reality closely interrelated,[7,8,13] which means that both parameters must vary with T) some first insight into the general features of anomalous systems should become accessible. For the Θ temperature of the systems, eq 24 in combination with eqs 17 and 9 yields the following expression:

$$\Theta = T_s + \frac{0.5 + \zeta\lambda - \alpha_1}{\alpha_2} \qquad (25)$$

Spinodal and binodal lines were calculated by means of a direct minimization of the Gibbs energy of the system as described in the literature.[15,16] To gain a first overview concerning the shape of the miscibility gaps for different combinations of the parameters α and ν, we show the extension of the unstable regimes for an exothermal system (LCST, Figure 3) and for an endothermal system (UCST, Figure 4).

Figure 3 demonstrates how the behavior of a polymer solutions becomes anomalous as α increases. For these calculations the parameters ν and α_2 (quantifying the temperature dependence of α) were kept constant. The absolute magnitude of α (i.e., α_1) on the other hand was chosen such that the parameter combination leading to an anomalous critical point either lies on the boarder line of Figure 2 (part a) or within the area of multiple critical points (part b).

In agreement with the parameters selected for Figure 3a, the anomalous stable and the anomalous unstable critical point turn up jointly in form of a double critical point. In this case, the three phase line (cf. Figure 5) runs through the DCP. With increasing deviation of a system from the normal behavior (larger α at given ν) the two types of anomalous critical points separate as demonstrated in Figure 3b. So far we have investigated the effects of uncommonly large α values in combination with nearly normal ν values. To complete the picture we have also calculated phase diagrams for nearly normal α along with uncommonly large ν values, this time for LCST behavior. The result is shown in Figure 4.

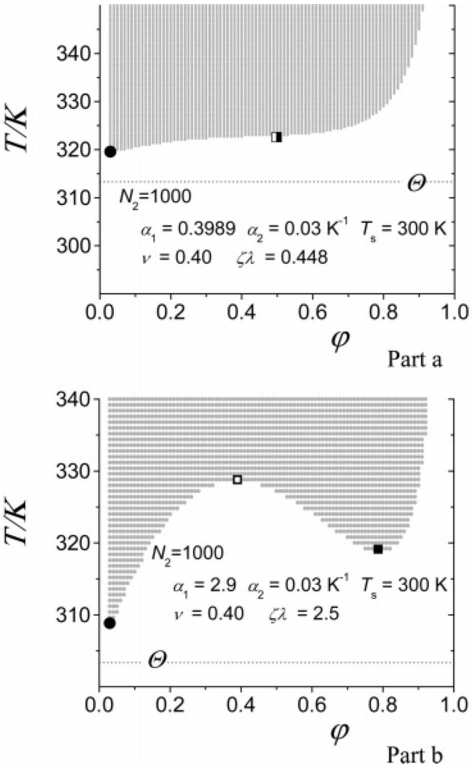

Figure 3. Unstable areas calculated for two exothermal model systems (ν values left of the minimum in Figure 2) by means of the parameters listed in the graphs. The dotted lines indicate the Θ temperature: (●) normal critical points; (■) stable anomalous critical point; (□) unstable anomalous critical point; (◧) anomalous double critical point.

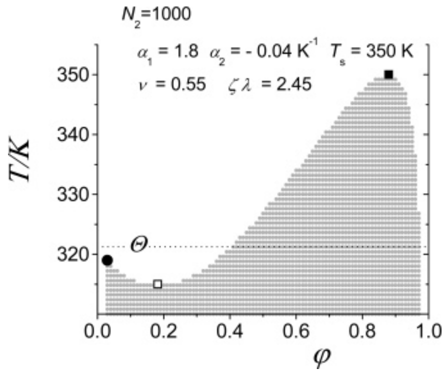

Figure 4. Like Figure 3, but for an UCST system and a ν value right of the minimum in Figure 2.

The shape of the unstable area shown in Figure 4 resembles strongly that observed and calculated for flowing polymer solutions at high shear rates (Figure 2 of ref 17). In both cases, the polymer becomes least soluble at high polymer concentrations, well beyond the normal critical point. Despite these similarities the physical reasons of the like phenomena are fundamentally different. With stagnant solutions the anomalous behavior depicted in Figure 4 results from large α and $\zeta\ \lambda$ values in combination with an uncommonly pronounced increase of the Flory–Huggins interaction parameter with rising polymer concentration. With the sheared solutions, on the other hand, the reason lies in the concentration dependence of the stored energy, which must be added to the Gibbs energy of mixing under near equilibrium conditions. More precisely, at a given shear rate the system can store considerably more energy at higher polymer concentrations due to the larger viscosities of these solutions.

The comparison of Figures 3 and 4 demonstrates that the relative positions of the normal critical temperature

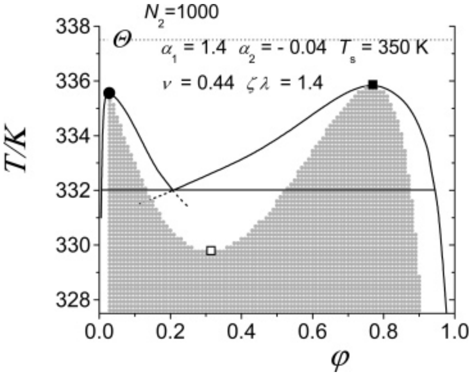

Figure 5. Like Figure 3 but for a combination of ν and α values close to the minimum of the borderline (cf. Figure 2). Stable binodals are drawn in full, their continuations below the three phase temperature (intersection of the binodals) are shown as broken lines.

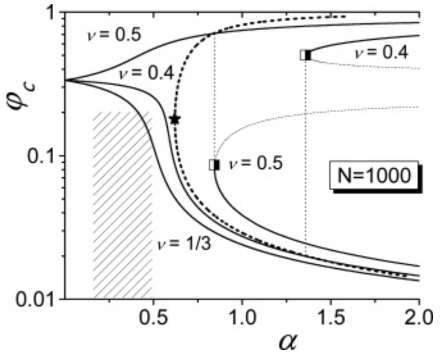

Figure 6. Critical compositions as a function of α for N = 1000 and for the different constant ν values indicated in the graph. The borderline (broken) separates normal from anomalous demixing behavior of polymer solutions (cf. Figure 2); its apex (full asterisk) marks the minimum α value a system must exceed to exhibit a second critical point (◨, DCPs). The hatched area represents the range of φ_c and α values that are typical for normal systems. Anomalous behavior sets in as the individual lines for constant ν intersect the borderline. The middle critical compositions (dotted lines, unstable critical points) correspond to the third extremum of the spinodal line and are located inside the miscibility gap.[3,4]

and of the stable anomalous critical temperature may vary considerably as a function of the value of parameter ν. This result is conceivable in view of the role of ν for the composition dependence of g. With normal polymer solutions the increase of g with rising φ does not change the characteristic features of the demixing curves. For $\nu = 0.4$ the dissolution power of the solvent is still lowest at the normal critical point (Figure 3). For $\nu = 0.55$, on the other hand, the contribution of the first term of eq 17 to the interaction parameter at larger φ values has become so dominant that the polymer-rich mixtures phase separate first upon cooling (cf. Figure 4); according to the present results, the demixing of concentrated solutions already sets in before Θ conditions are reached. Such a behavior has actually been observed (see Figure 4 of ref 3).

To obtain a more detailed picture of the phase diagrams of anomalous polymer solutions, the parameters were chosen such (cf. Figure 2) that the modeling yields two comparable critical temperatures as shown in Figure 5. In this case, the binodal curves were calculated in addition to the unstable area; their intersection yields the three phase line indicated in this graph.

5. Discussion

From the model calculation of the last section it becomes obvious that the present approach yields, depending on the particular combination of parameters, either one or two stable critical points per system, where the critical compositions vary considerably. A third critical point that can also be calculated corresponds to a third extremum of the spinodal line. It represents an unstable anomalous critical point and is located inside the miscibility gap.[3,4] To visualize this features, we plot φ_c as a function of α in Figure 6. Because of the fact that the normal critical composition is located at very low polymer concentrations, the abscissa requires a logarithmic scale to enable a discrimination of the individual curves.

From to the evaluation of experimental data[7,8,13,18] for normal polymer solutions it is obvious that α for worse than Θ conditions (i.e., for incipient phase separation) is always less than 0.5. This observation, which is in Figure 6 indicated by the hatched area, demonstrates that the α values for such systems remain well below the minimum value required for the appearance of a second critical point (asterisk). To produce such a phenomenon the parameter ν must be considerably higher than the usual $^1/_3$ and α must also be larger than normal.

With the intention to learn more on the differences between normal and anomalous polymer solution, we discuss their particularities in terms of the Θ conditions, which must exist for both types of systems if the components mix completely at some temperature. From eq 17, we obtain the following generally valid expression for χ within the composition range of pair interaction

$$\chi_o = \alpha - \zeta\lambda \tag{26}$$

In the vast majority of cases, i.e., for normal systems, the conformational relaxation vanishes at the Θ conditions (i.e., $\zeta_\Theta = 0$) and eq 26 becomes

$$\chi_{o,\Theta} = \alpha_\Theta \tag{27}$$

Because of eq 9 this implies

$$\alpha_\Theta^{\text{normal}} = \frac{1}{2} \tag{28}$$

With exceptional systems, like with H_2O/PVME[3], there obviously exists another possibility to realize the pseudo-ideal conditions prevailing in the Θ state ($A_2 = 0$), namely via a compensation of the α and $\zeta\lambda$ contributions such that $\chi_{o,\Theta} = {}^1/_2$. Under this premise, eq 26 yields the following Θ condition for anomalous systems

$$\chi_{o,\Theta} = \frac{1}{2} = \alpha_\Theta^{\text{anomalous}} - (\zeta\lambda)_\Theta^{\text{anomalous}} \tag{29}$$

where $\alpha_\Theta^{\text{anomalous}} \neq 0.5$ and $(\zeta\lambda)_\Theta^{\text{anomalous}} \neq 0$. For such exceptional systems the unperturbed state results from an exact compensation of an uncommonly unfavorable contact formation between the components ($\alpha > 0.5$) by an extraordinarily advantageous conformational response ($\zeta\lambda \gg 0$). In the case of H_2O/PVME large α values have to be expected because of the pronounced differences in the chemical nature of the components. From reports[19] on the formation of a complex between water and PVME and the fact that the system exhibits LCST

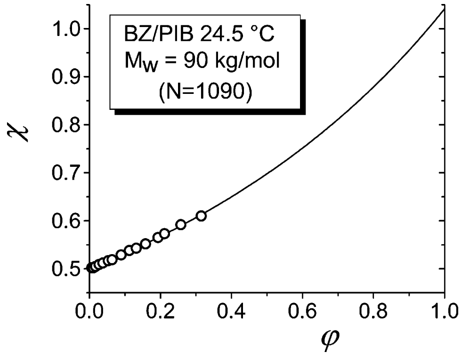

Figure 7. Representation of the composition dependence of the Flory–Huggins interaction parameter obtained from osmometry[20] for the system benzene/polyisobutylene at the Θ temperature of 24.5 °C by means of eq 17.

behavior, we can infer that the large ζ values are caused by the very favorable heat effects associated with that process.

A compensation of the individual contributions to χ_o, analogous to that discussed above, by negative α values and equivalent negative conformational responses should in principle also be possible. However, so far the evaluation of experimental data has never led to α < 0. For the present discussion, such a combination would be irrelevant anyway, because it does according to the present approach not yield multiple critical points.

We are now going to apply the just discussed criteria of anomalous behavior to the system benzene/polyisobutylenes (BZ/PIB), which is believed to exhibit two off-zero critical concentrations.[3] That conjecture rests on the pronounced composition dependence of the interaction parameter χ observed in osmotic measurements over a large range of compositions.[20] In the present nomenclature the series expansion of the Flory–Huggins interaction parameter can be written as

$$\chi = \chi_o + \chi_1\varphi + \chi_2\varphi^2 + \dots \tag{30}$$

If χ does not depend on φ, the critical volume fraction for infinite molecular weight of the polymer, φ_c^∞, is always zero. In the general case its value can be calculated[20] as

$$\varphi_c^\infty = 1 - \frac{1}{\sqrt{3\chi_1 + 8\chi_2\varphi + \dots}} \tag{31}$$

The neglect of higher terms than χ_1 leads to the condition of $\chi_1 > {}^1/_3$ for the realization of off-zero critical values. However, according to the present approach a sufficiently large χ_1 does not necessarily indicate the existence of two critical points. For that reason, we evaluate the reported osmotic data[20] according to eq 17 as shown in Figure 7.

The quantitative description of the published data requires only one single parameter, namely $\nu = 0.3070 \pm 0.0018$, if we assume normal behavior (i.e., $\alpha_\Theta = 0.5$ and $\zeta_\Theta = 0$). Even in case we adjust all three parameters of eq 17 the resulting α and ζ deviate only negligibly from the above values. We can therefore conclude that multiple critical points are absent for the system BZ/PIB despite the fact that φ_c^∞ may be different from zero. The characteristic data of all polymer solutions of interest are for a more detailed discussion collected in Table 1.

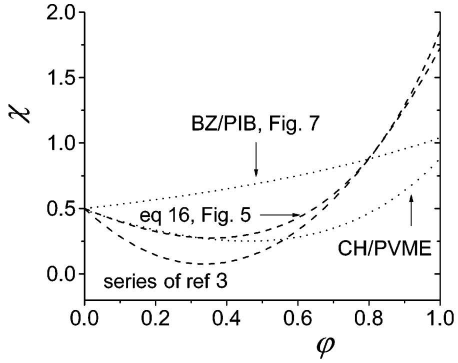

Figure 8. Composition dependence of χ at the Θ temperature for the modeling of more than one critical point by series expansion[3] and by the present approach (eq 16). For comparison this graph also shows experimental results for the systems benzene/polyisobutylene[20] (cf. Figure 7) and for cyclohexane/poly(vinyl methyl ether).[7,21]

Table 1. Systems, Parameters and Θ Temperatures: Θ_+ (Endothermal Mixing) and Θ_- (Exothermal Mixing)

Two Critical Points: Series Expansion Eq 10

	g_{os}	g_{oh}/K	g_1	g_2	Θ, K
Figure 2, part III of ref 1	6.3	−1700	−0.0125	1.25	$\Theta_- = 292.47$, eq 12

Two Critical Points: New Approach Eq 24

	α_1	$\alpha_2 K$	ν	ζλ	Θ, K
Figure 3	2.9	0.03	0.40	2.50	$\Theta_- = 303.33$
Figure 4	1.8	−0.04	0.55	2.45	$\Theta_+ = 321.25$
Figure 5	1.4	−0.04	0.44	1.40	$\Theta_+ = 337.50$

Experimental Examples for Uncommon $\chi(\varphi)$ at $T = \Theta$

	α	ν	ζλ	Θ, °C
CH/PVME from refs 7 and 21	1.54	0.382	1.05	$\Theta_+ = 51$
BZ/PIB ref 20 and Figure 7	0.50	0.307	0.00	$\Theta_+ = 24.5$

Figure 8 portrays the functions χ (φ) required for the modeling of anomalous behavior in terms of a series expansion[3] of g and on the basis of the new approach (eq 17) as shown in Figure 5. For comparison it also includes experimental data for two systems of uncommon composition dependence of χ, which should—according to the present approach—nevertheless behave normal because the deviation from the usual behavior does not suffice to produce a second critical point.

The most striking feature of Figure 8 consists of the fact that the existence of more than one critical point is obviously bound to the occurrence of minima in χ (φ) in combination with large limiting values for vanishing solvent content of the mixtures. The particular combination of α and ν inside the area of multiple critical points in Figure 2 decides on the details of χ (φ). Lower ν values than that underlying Figure 8 (e.g., that used for Figure 3) lead to much deeper minima at higher polymer concentrations. Higher ν values (e.g., that of Figure 4) result in shallower minima at lower φ in combination with extremely high limiting values of χ for vanishing solvent content of the mixture.

The minima in χ (φ) postulated by the present modeling appear strange at the first sight, they have, however, actually been observed experimentally[21] for the system cyclohexane/poly(vinyl methyl ether) (CH/PVME) and can be explained in terms of the present approach.[7] This is also a Θ system, which differs from that modeled in ref [3] only by the exchange of water by cyclohexane. One might speculate that the minima in

$\chi(\varphi)$ for these systems are caused by the flexibility of the polymer, enabling a very favorable conformational response even under Θ condition (cf. Table 1). For CH/PVME $\alpha_\Theta = 1.54$, which implies that it may, like H_2O/PVME, behave anomalous according to the criteria formulated above, subject to the condition that ν leads to a position of the system above the borderline of Figure 2 ($\nu > 0.385$). Vapor pressure measurements[21] with CH/PVME have resulted[7] in an average ν value of 0.372. According to this result the system should behave normal, i.e., exhibit only one critical point. However, because of unavoidable experimental uncertainties, this inference is not compelling.

In conclusion it appears worthwhile to speculate on whether tabulated information on the thermodynamic properties of the components may yield indications for anomalous demixing. The most extensive collection of data is probably offered by the solubility parameters, δ, of solvents and polymers. Within the scope of that approach the interaction parameters are often written as[22]

$$\chi = g = \frac{(\Delta\delta)^2 V_s}{RT} + \text{const} \qquad (32)$$

where $\Delta\delta$ is the difference between the solubility parameters of the components and the constant assumes typically values on the order of $^1/_3$; the molar volume of the solvent is usually taken for V_s, the molar volume of the segment. The choice of δ for the present purposes can to some extent be justified by the fact that it is based on the properties of the pure components only and does consequently, like α, not account for any conformational response.

From the data listed in the Polymer Handbook[22] the first term of eq 32 assumes the following values for the systems of present interest: H_2O/PVME: 5.98, CH/PVME: 0.37, and BZ/PIB: 0.59. This means that the constant of eq 32 would have to assume values on the order of -5 for H_2O/PVME to yield reasonable interaction parameters (in agreement with the ζ term of eq 29), whereas this constant remains small for the other two systems. Despite the well-known deficiencies of the rather simplistic solubility parameter theory it looks as if the fact that a given polymer is within a certain temperature range totally miscible with a solvent of an exceptionally dissimilar solubility parameter may constitute a clue for anomalous demixing behavior. In terms of eq 29 of the present approach such an unexpected miscibility is attributed to a very favorable conformational response, which compensates the rather adverse effects of contact formation.

6. Outlook

The model calculations of the last section have shown that the emergence of a second critical point, i.e., anomalous demixing behavior, is bound to a very special composition dependence of the Flory–Huggins interaction parameter. As demonstrated in Figure 8 it requires pronounced minima in that function. Within the scope of the approach accounting explicitly for chain connectivity and conformational variability of polymer molecules this feature requires a particular, unusual compensation of the two terms of eq 17 at the Θ conditions as formulated in eq 29. In contrast to normal systems the α_Θ values are no longer equal to 0.5 but considerably larger and the conformational response ζ_Θ is no longer zero but positive and sizable, comparable to that of thermodynamically good solvents. Furthermore, the parameter ν must exceed a characteristic minimum value.

The determination of the system specific parameters of the present approach unfortunately constitutes a rather time-consuming task because it requires the measurement of chemical potentials over a sufficiently large range of compositions. For this reason it would be very helpful to dispose of quicker means to assess the probability of a particular system to behave in a normal or in an anomalous manner. It looks as if the solubility parameter theory could be of some help for that purpose.

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