The Two Critical Concentrations in Polymer Science

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Several years ago Utracki and Simha reported a remarkable independence of molar mass of the ratio of the thermodynamic critical (consolute) concentration and the concentration of incipient coil overlap, also known as "critical" concentration. They investigated solutions of polystyrene in cyclohexane and also found the consolute concentration at the critical temperature to be approximately equal to the average segmental concentration within the coils. Here we supply an explanation for these indisputable experimental findings. To this end we examine three systems for which experimental information about the true consolute state and coil dimensions is available in the literature, viz. cyclohexane/polystyrene, methylcyclohexane/polystyrene, and diphenyl ether/polyethylene. The conclusion is that the two concentration ratios will usually vary with molar mass. The constancy observed by Utracki and Simha can be explained if it is assumed that their anionic polystyrene samples, though having narrow molar-mass distributions as expressed in M_w/M_n, were contaminated with small amounts of high molar-mass material responsible for considerable deviations between maximum-demixing and consolute concentrations. This conclusion is independent of whether the temperature- and concentration dependence of the coil dimensions are taken into account. For the concentration dependence we made use of an expression not published hitherto. Light-scattering data published earlier by Borchard and Rehage clearly demonstrate that the maximum in the 45/135 angular dissymmetry does not occur at the consolute concentration but close to, or at, the concentration at which the spinodal exhibits an extremum. Here we prove the latter point theoretically. The extremum of the spinodal is a consolute point in strictly binary systems only. Hence, the term "spinodal", rather than "critical", opalescence appears to be appropriate to indicate the phenomenon.

Introduction

In studies of polymer solutions, the term "critical concentration" has since long been used for two apparently unrelated phenomena. In the first place there is the consolute state in the Gibbsian sense in which the second and third derivatives of the Gibbs free energy with respect to concentration both equal zero.[1] On the other hand, the concentration at which incipient overlap of dissolved polymer coils occurs has also been called "critical", and usually been indicated by "c*". We shall distinguish the two concentrations here, naming them $c_{2,c}$ and c_2^*, respectively.

Several years ago, Utracki and Simha were investigating the viscosities of dilute and moderately concentrated polymer solutions and their scaling properties in respect to concentration and molar mass. In this connection the measurements were extended to sub-Θ temperatures and relations to the critical thermodyanmic coordinates of temperature and concentration were explored.[2] Analyzing Debye, Coll, and Woermann's[3] and their own data on the system cyclohexane/polystyrene, Utracki

and Simha concluded that c_2^* was proporional to the critical (consolute) concentration $c_{2,c}$, irrespective the polymer's molar mass. They also found that the polymer-segment concentration inside the coils, $c_{2,coil}$, was approximately equal to $c_{2,c}$. Both groups of authors[2,3] assumed $c_{2,c}$ to coincide with $c_{2,thr}$, at which the maximum occurs in the cloud-point curve (precipitation threshold after Tompa[4,5]). Such an assumption is valid only if the considered polymer samples are strictly monodisperse with respect to molar mass.[4−10] The samples used were characterized by M_n and ξ_n ($= M_w/M_n$) and, though having relatively small ξ_n values, were undefined with respect to ξ_w ($= M_z/M_w$). Since the latter ratio, rather than ξ_n, is determinative for the consolute state[7−10] it seemed worthwhile to reconsider the earlier analysis.[2]

Utracki and Simha[2] used polystyrene samples obtained from the same source as Debye et al.,[3] most of them having been prepared by anionic polymerization. Essential agreement exists between the two groups of authors with respect to threshold concentrations and temperatures, Table 1 (first four columns) lists their data.

Threshold concentrations are usually determined by cloud-point measurements that may involve visual observation or scattering techniques to detect incipient phase separation. Debye

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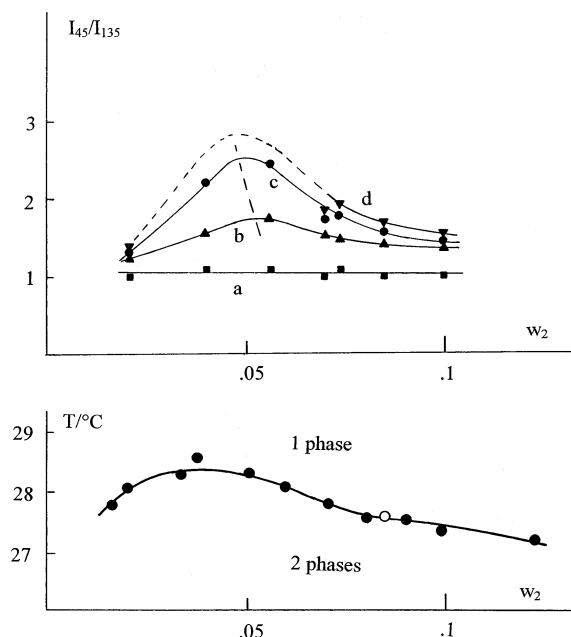*J. Phys. Chem. B, Vol. 108, No. 41, 2004* **16169**

Figure 1. Angular dissymmetry I_{45}/I_{135} as a function of polymer concentration and temperature (top) and cloud-point curve (bottom) for an anionic polystyrene in cyclohexane.[11–13] Molecular characteristics polymer: $M_w = 4.7 \times 10^3$ kg/mol, $\xi_n = M_w/M_n = 1.07$, $\xi_w = M_z/M_w = 1.4$. Dissymmetry measurements at cloud-point temperature $+ \Delta T$(in °C), a: $\Delta T = 8.6$, b: $\Delta T = 0.80$, c: $\Delta T = 0.20$, d: $\Delta T = 0.02$. Cloud points, filled circles; critical point (determined by measurements of phase volume ratios),[10,13] open circle. Concentration variable: weight fraction. Precipitation threshold at $w_2 \approx 0.04$.

TABLE 1: Experimental Data[2] on Cyclohexane/Polystyrene and Values of ξ_w, T_{thr}, and $\varphi_{2,c}$, Calculated to Match $\varphi_{2,thr,exp}$

	experimental			calculated		
M_w (kg/mol)	ξ_n	T_{thr} (°C)	$\varphi_{2,thr}$	ζ_w	T_{thr} (°C)	$\varphi_{2,c}$
82	1.05	19.8	0.072	1.165	20.0	0.0946
126	1.05	22.6	0.059	1.167	22.7	0.0807
153	1.04	22.9	0.053	1.152	23.7	0.0747
239	1.08	25.4	0.048	1.19	25.7	0.0637
360	1.16	25.9	0.038	1.28	27.2	0.0558
570	1.09	27.9	0.029	1.24	28.4	0.0459
884	1.68	27.9	0.028	1.27	29.3	0.0387
819	1.18	28.7	0.026	1.31	29.2	0.0405

et al.[3] used the angular dissymmetry, i.e., the ratio of the intensity of light scattered at 45° and 135°, measured at temperatures slightly above the cloud-point curve (CPC). They considered the concentration at which the maximum dissymmetry occurred to be identical to the maximum-demixing (threshold) concentration, in their view identical to the critical concentration.

Experimental evidence contradicting this view was later provided by Borchard and Rehage[11] who measured the dissymmetry in a system of which the CPC was known, as well as the location of the consolute point on the CPC.[12,13] Figure 1 summarizes their results. The cloud point curve was redrawn from the data in ref 13 and suggests the precipitation threshold to occur at about 4 wt %. This value is quite arbitrary because the curve is flat and the data scatter. Nevertheless, it is clear that a large disparity exists between threshold and critical concentrations, which is known to be due to the sample's relatively large ξ_w value.[7–10] The latter is caused by a long high-molar-mass tail in the molar-mass distribution (MMD) that could be detected by ultracentrifuge analysis but hardly showed up in a GPC scan.[14] The magnitude of the angular dissymmetry depends on ΔT, the temperature difference between scattering

and cloud point measurements. The smaller ΔT, the larger the dissymmetry, the maximum of which is seen in Figure 1 (top) to shift and increase with decreasing polymer concentration. Similar observations were made by Debye et al. (see Figure 1 of ref 3, sample C), who pointed out that this phenomenon poses a principal difficulty if the dissymmetry is used for the determination of the consolute point in a binary system. The critical concentration being known in Borchard and Rehage's case, we note that the angular dissymmetry does not relate to the consolute state in this example. We show below that it does relate to the extremum in the spinodal, which is only a critical point in strictly binary systems.[10]

Liquid−Liquid Critical State. The liquid/liquid critical state (φ_{2c}, T_c) can be calculated with Gibbs' equations for spinodal $(J_s = 0)$ and critical point $(J_c = 0)$.[1] For a *strictly*-binary system we have

$$J_s = [\partial^2(\Delta G/NRT)/\partial\varphi_2{}^2]_{p,T}; \; J_c = [\partial^3(\Delta G/NRT)/\partial\varphi_2{}^3]_{p,T} \quad (1)$$

For a *quasi*-binary solution containing $\sum n_{2i}$ moles of a molecularly polydisperse polymer we may write for ΔG, the free enthalpy of mixing,

$$\Delta G/NRT = \varphi_1\ln\varphi_1 + \sum(\varphi_{2i}/m_{2i})\ln\varphi_{2i} + g\varphi_1\varphi_2 \quad (2)$$

The total volume is considered to be built up of N volume units, each equaling the volume of a solvent molecule of which there are n_1 moles in the system. The polymer chains i each occupy m_{2i} volume units; $N = n_1 + \sum n_{2i}m_{2i}$. The volume fractions of solvent and polymer are φ_1 and φ_2, respectively, and g is the interaction function. We have: $\varphi_1 = n_1/N$, $\varphi_{2i} = n_{2i}m_{2i}/N$, $\varphi_2 = \sum\varphi_{2i}$. The "relative chain length" m_{2i} is given by

$$m_{2i} = (v_2 M_{2i})/(v_1 M_1) \quad (3)$$

where M_1 and M_{2i} are the molar masses of solvent and polymer species i, and v_2 and v_1 are the specific volumes of polymer and solvent. As a more convenient alternative to volume fractions, weight fractions may be used for φ_1 and φ_2, m_{2i} is then given by the molar-mass ratio M_{2i}/M_1.[10]

Equation 2 is the FHS expression for ΔG derived independently by Staverman and Van Santen,[15,16] Huggins,[17,18] and Flory.[19,20] An earlier discussion by Staverman on heats of mixing in nonpolymeric systems[21,22] suggests a useful temperature and concentration dependence of g for polymer solutions:[23]

$$g = a + b/(1 - c\varphi_2); \; b = b_s + b_h/T \quad (4)$$

where a, b_s, b_h, and c are constants, to be determined experimentally on the system of interest.

Application of the multicomponent version of eqs 1 to 2 and 3 yields[1,7–10]

$$\{1/\varphi_1 + 1/(m_{w2}\varphi_2)\}/2 = a + b(1 - c)/(1 - c\varphi_2)^3$$

$$\text{(spinodal)} \quad (5)$$

$$\{1/\varphi_1{}^2 - \xi_w/(m_{w2}\varphi_2{}^2)\}/6 = bc(1 - c)/(1 - c\varphi_2)^4$$

$$\text{(consolute state)} \quad (6)$$

where $\xi_w = m_{z2}/m_{w2}$, and m_{w2} and m_{z2} are the weight- and z-average relative chain lengths of the polymer. Experimental spinodal and critical data can be used to determine values of the parameters in eqs 5 and 6 for a given system.[10,23] Such data are available for the systems diphenyl ether/polyethylene,[8,24,25] cyclohexane/polystyrene,[26] and methylcyclohexane/ polysty-

TABLE 2: Parameter Values for Cyclohexane/Polystyrene (CH/PS), Methylcyclohexane/Polystyrene (MCH/PS), and Diphenylether/Polyethylene (DPE/PE)

	CH/PS	MCH/PS	DPE/PE
a^a	−0.1597	0.131	0
$b_s{}^a$	0.4987	0.469	−0.6086
b_h (in K)^a	111.74	65.3	482.2
c^a	0.2365	0.442	0
β^2 (in 10^{-18} cm^2)	7.6	7.1	19
C^* (in K^{-1})	3.4×10^{-4}		
v_1 (in cm^3/g)^b	1.285	1.300	1.03
v_2 (in cm^3/g)^b	0.973	0.973	1.27

^{a} Values based on volume fractions for CH/PS and DPE/PE, on weight fractions for MCH/PS. ^{b} Average value for the temperature range of critical data[26] (later values than Debye et al.[2] used so that the experimental $\varphi_{2,\text{thr}}$ values in Table 1 differ somewhat from those reported by Debye et al.).

rene[27,28] (see Table 2). These values can be used to calculate critical states for solutions with a polymeric solute of any MMD, including the hypothetical case of strictly binary solutions in which the polymer is a single-component substance.

Overlap and Inside-Coil Concentrations. Overlap and inside-coil concentrations usually being quoted in g/100 mL (c_2), we shall also use this quantity which is related to the volume fraction φ_2 by

$$c_2 = 100\varphi_2\rho_2 = 100\varphi_2/v_2 \tag{7}$$

where ρ_2 is the density of the polymer in solution.

The concepts of overlap and inside-coil concentration are necessarily quite approximate, since the mean polymer concentration within a coil is not a fixed quantity but a monotonically decreasing function of distance from the center of mass. The inside-coil concentration is most nearly constant and relates to a definite radius in the case of dendrimers,[29] but such constancy is a poor approximation for random coils. If we ignore these limitations, we may define the polymer concentration of incipient coil overlap by V, the total volume of the system, being filled with closely packed spheres of radius $\langle r^2 \rangle^{1/2}$:

$$N_2V_2 \equiv (4\pi N_A/3)n_2\langle r^2 \rangle^{1.5} = \epsilon V \tag{8}$$

where N_2 and n_2 are the number of molecules and moles of polymer, each occupying a volume V_2, N_A is Avogadro's constant, $\langle r^2 \rangle$ is the mean-square radius of gyration of the polymer coils, and ϵ is a geometric factor of order unity, accounting for interstitial volume, distribution of repeat units between ranges inside and outside the radius of gyration, and other effects.[2,30] The overlap concentration c_2^* follows from

$$c_2^* = 100n_2M_2/V = 100\epsilon M_2/(4\pi N_A/3)(\langle r^2 \rangle)^{1.5} \tag{9}$$

which equation we may assume also to provide a good approximation of the average polymer concentration inside the coils, $c_{2,\text{coil}}$, if ϵ is set equal to 1. For a single-component polymer the molar-mass dependence of $\langle r^2 \rangle$ is defined by

$$\langle r^2 \rangle = \beta^2\alpha^2 M_2 \tag{10}$$

At zero polymer concentration, we shall assume the temperature dependence of the expansion factor α to be given by[31]

$$\alpha^3(0) = C(1 - \Theta/T)m_2^{1/2} + 1 \tag{11}$$

where C is a constant and Θ is the Flory temperature. This expression is far from exact,[32] but gives a fairly good repre-

TABLE 3: Critical Concentration $c_{2,c}$, Overlap Concentration c_2^*, and Concentration within Coils $c_{2,c}c_{\text{coil}}$ (all in g/100 mL) Calculated for Binary Mixtures of Cyclohexane and Polystyrene

M_2 (kg/mol)	m_2	T_c (°C)	$c_{2,c}$ (eq 2−4)	c_2^*				$c_{2,\text{coil}}$		
				I^a	II^b	III^c	I^a		II^b	III^c
10	90	−7.8	19.19	14.02	16.18	14.49	18.92		21.83	19.31
25	225	8.0	14.11	8.87	10.19	9.36	11.97		13.71	12.45
50	451	15.9	11.05	6.27	7.19	6.53	8.46		9.70	8.94
100	901	21.2	8.57	4.43	5.07	4.81	5.98		6.84	6.24
500	4507	28.0	4.57	1.98	2.27	2.21	2.68		3.06	2.95
1000	9014	29.5	3.43	1.40	1.61	1.58	1.81		2.18	2.12

^{a} Chain dimensions at $T = \Theta$, $\varphi_2 = 0$ ($\alpha = 1$). ^{b} Chain dimensions at T_c, for $\varphi_2 = 0$ (eq 12). ^{c} Chain dimensions at T_c and $\varphi_{2,c}$ (eq 13).

sentation of $\alpha(0)$ over a large range of molar masses.[33,34] Onclin et al.,[35,36] comparing values of α for the system cyclohexane/polystyrene by different authors, found that their disagreement about the value of Θ impeded a meaningful analysis of the joint data. It was demonstrated that a plot according to

$$\alpha^3(0) - 1 = C^*(T - \Theta)m_2^{1/2} \tag{12}$$

in which each author's own Θ value was used, considerably improved the comparison at temperatures both above and below Θ and allowed a value for C^* to be determined.

Since $c_{2,c}$ is generally significantly different from zero, we need to know how α depends on concentration. There are several experimental and theoretical studies in the literature showing that α is a rapidly decreasing function of concentration down to the unperturbed value of unity.[31,37−39] Onclin et al. found that a good approximation for temperatures above Θ is given by

$$\alpha^3(\varphi_2) = \{\alpha^3(0) - 1\} \exp(-\zeta\varphi_2) + 1 \tag{13}$$

where ζ is an empirical constant, equal to about 10 for polystyrene in CS_2, toluene, and cyclohexane. The data for cyclohexane below Θ are less definite, but the form of eq 13 is for such conditions supported by the calculations of Okamoto.[37]

Obviously, knowledge of the mean-square radius of gyration is required to obtain the overlap concentration c_2^*. For this purpose, the previous authors[2] made use of their measured intrinsic viscosities. Here we employ more recent theoretical and empirical representations of the temperature and concentration-dependent expansion factor.

Analysis of Experimental Data. We apply the above equations to three systems: cyclohexane/polystyrene, methylcyclohexane/polystyrene, and diphenylether/polyethylene. Values for the various parameters are listed in Table 2. The packing factor ϵ was assumed to equal 0.741, the value for close hexagonal packing of spheres.[40]

1. Cyclohexane/polystyrene. Utracki and Simha[2] found the ratio between $c_{2,\text{thr}}$ and c_2^* at the threshold temperature to be independent of molar mass,

$$c_{2,\text{thr}} = 1.51c_2^* \tag{14}$$

Note that the precise meaning of c_2^*, discussed in the preceding section, is not relevant. Utracki and Simha used the quantity defined by eq 9 and found the indisputable experimental result of eq 14.

Table 3 collects values calculated for a range of molecular masses, corresponding to that used in the determination of parameters a, b, and c;[26] Figure 2 summarizes the results. It is

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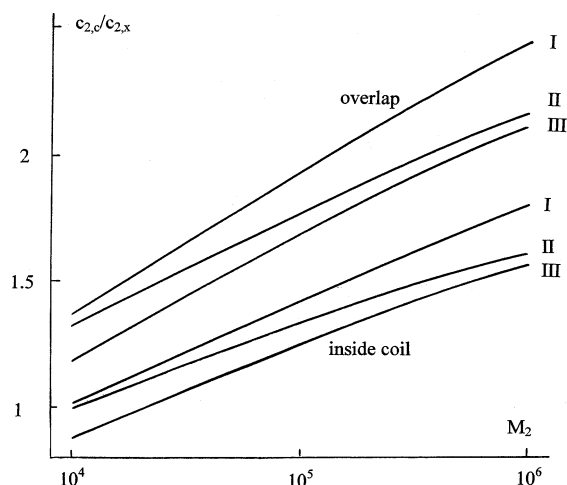*J. Phys. Chem. B, Vol. 108, No. 41, 2004* **16171**

Figure 2. Ratios $c_{2,c}/c_{2,x}$ ($c_{2,c}/c_2^*$, or $c_{2,c}/c_{2,coil}$) as a function of molar mass M, calculated for strictly binary solutions of polystyrene in cyclohexane. Upper set of three curves, $c_{2,c}/c_2^*$; lower set, $c_{2,c}/c_{2,coil}$. *I*, unperturbed dimensions (eq 10); II, temperature-dependent $\langle r^2 \rangle$ (eq 11); III, temperature and concentration dependent $\langle r^2 \rangle$ (eq 13).
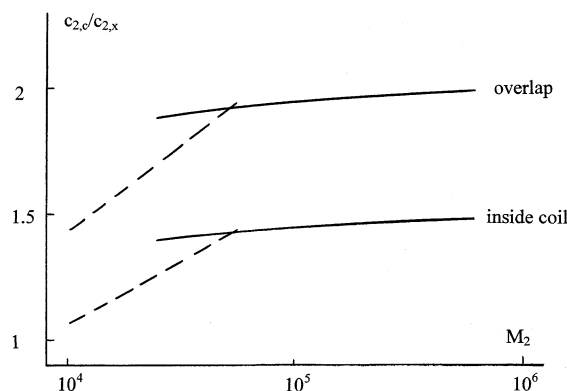

Figure 3. Ratios $c_{2,c}/c_2^*$, and $c_{2,c}/c_{2,coil}$ as a function of molar mass M_2, calculated for strictly binary polymer solutions. Full curves, diphenylether/polyethylene; dashed curves, methylcyclohexane/polystyrene. Case I (unperturbed dimensions; eq 10).

TABLE 4: Critical Concentration $c_{2,c}$, Overlap Concentration c_2^*, and Concentration within Coils $c_{2,coil}$ (all in g/100 mL) Calculated for Binary Methylcyclohexane/Polystyrene Mixtures (chain dimensions at $T = \Theta$, $\varphi_2 = 0$)'

M_2 (kg/mol)	m_2	T_c (°C)	$c_{2,c}$	$c_{2,over}$	$c_{2,c}/c_{2,over}$	$c_{2,coil}$	$c_{2,c}/c_{2,coil}$
10	102	9.2	21.66	15.11	1.43	20.38	1.06
25	255	30.6	16.26	9.55	1.70	12.89	1.26
50	509	41.6	12.92	6.76	1.91	9.12	1.42

seen that there is no chain-length-independent proportionality between $c_{2,c}$ and c_2^*, and neither can the concentration inside the coils, though closer to $c_{2,c}$, be identified with the latter. Correction for the temperature (column II) and concentration dependence of α (column III) does not affect this conclusion. The trends are similar, and we see in Figure 2 that the use of the unperturbed value of $\langle r^2 \rangle$ (zero concentration, $T = \Theta$) does not lead to incorrect results, the ratios so obtained merely being somewhat too large. The experimental $\varphi_{2,thresh}$ values of Debye et al.[2] were adapted to conform to the density values for solvent and polymer used in this paper.

2. Methylcyclohexane/polystyrene. As far as we are aware, no information on the temperature and concentration dependence of $\langle r^2 \rangle$ exists in the literature, and we have to be content with a comparison of the critical concentration with c_2^* and $c_{2,coil}$,

calculated for $T = \theta$, $\varphi_2 = 0$ (series I). Critical data for the molar-mass range $10-50$ kg/mol have been reported,[28] as well as data on unperturbed dimensions.[41] The latter data, together with the interaction parameter data of Table 2, yield the c_2 values listed in Table 4. The two c_2 ratios are plotted in Figure 3. The chain-length dependences of $c_{2,c}/c_2^*$ and $c_{2,c}/c_{2,coil}$ are comparable to those in the system cyclohexane/polystyrene (Figure 2).

3. Diphenylether/polyethylene. A different situation is encountered in the system diphenylether/polyethylene (Figure 3). The c_2 ratios show much less dependence on chain length. An explanation is not obvious, we merely note that the sizes of solvent molecule and polymer segment, comparable in the first two systems, are quite different here. The β value in Table 2 is due to Chiang.[42] Critical and inside-coil concentrations are significantly different.

Discussion

For the three systems considered, we may safely conclude that the molar mass independence of the ratio of threshold and overlap concentrations in a polymer solution, reported earlier by Simha and Utracki,[2] does not pertain to the ratio of consolute and overlap concentrations. Neither can the critical and the average segment concentrations within the coils be considered equal.

The obvious explanation for the discrepancy may be sought in the fact that threshold and critical concentrations do not coincide in a nonbinary polymer solution. Three nonpolar systems were studied, two of which (solutions of polystyrene) are characterized by a marked dependence of the thermodynamic interaction parameter on concentration. The available data on the third system, diphenylether/polyethylene, point to the interaction parameter being independent of polymer concentration.[8,9,24,25] Yet, the present analysis contradicts Simha and Utracki's findings for all three systems, and an explanation is called for.

Critical point and precipitation threshold are identical in the strictly binary case but show a deviation increasing with the width of the MMD. The last three columns in Table 1 show calculated values for ξ_w needed to let $c_{2,thr}/c_2^* = 1.51$ for all samples. In the calculation, the MMDs of the samples were represented by binary mixtures of two monodisperse polymers, differing in chain length.[10] It is seen that the polystyrene samples used in the earlier work,[2,3] though having narrow distributions with respect to ξ_n, in line with their preparation by anionic polymerization, probably had slightly larger ξ_w values than is usually thought. The extensive investigation by Borchard and Rehage[11] (Figure 1) lends credibility to this view. Whether the possible occurrence of high-molar-mass contaminations had to do with the early stage of development of the anionic polymerization technique in the 1960s is difficult to say. Over the years, determinations of CPCs in solutions of anionic samples have been reported, as well as their characterization by GPC, but they are very rarely accompanied by a check on the location of the critical point. One such study[43] revealed a significant discrepancy between threshold and consolute concentrations, comparable to that indicated by the data in Table 1.

We may check the influence of the MMD on the two concentration ratios. Assuming the β^2 values of Table 2 still to be relevant, we only need to replace M_2 in eqs 10 and 11 by M_z, which quantity can be calculated with the ξ_w values in Table 1 which force the $c_{2,thr}/c_2^*$ ratios to equal 1.51 for all samples. We have done the calculation for case I only (eq 10, $\alpha = 1$) and find that the ratio $c_{2,thr}/c_2^*$ varies from 1.6 to 2.2 in the

molar-mass range of the samples in Table 1, quite comparable to the situation of Figure 2.

The independence of chain length of the two c_2 ratios reported by Utracki and Simha thus appears to be an accidental though perfectly valid result, very probably caused by a small but not negligible polymolecularity of the samples, in combination with the particular interaction function of the system in hand. Whether such an independence could be expected to exist for the other two systems is questionable. However, the possibility does exist that MMDs can be found that are accompanied by threshold concentrations leading to a chain-length independence of the two c_2 ratios. The system methylcyclohexane might hold better prospects than diphenylether/polyethylene because of the much wider MMDs usually occurring in the latter case.

The present analysis also reveals a contradiction between Debye's interpretation of the angular dissymmetry and Borchard and Rehage's data. The latter indicate that the maximum in angular dissymmetry in a polymer solution does not occur at the critical concentration, but at a lower concentration shifted toward the precipitation threshold. In fact, in one of Debye's own figures one notices a shift to lower concentration similar to that shown in Figure 1.

Debye's scattering function[44] can be written as

$$1/I(\vartheta) \propto \varphi_2^2 J_s + A \sin^2(\vartheta/2) \qquad (15)$$

where $I(\vartheta)$ is the intensity of light scattered at angle ϑ, and A is a factor depending on the wavelength of the light but not on φ_2 or ϑ. This equation differs only trivially from that derived many years later by Higgins and Benoit.[45]

It follows from eq 15 that Δ, the angular dissymmetry, is

$$\Delta \{\equiv I(45)/I(135)\} = \{\varphi_2^2 J_s + B(67.5)\}/\{\varphi_2^2 J_s + B(22.5)\} \qquad (16)$$

where $B(\vartheta/2) \equiv A \sin^2(\vartheta/2)$.

From eq 5 we have

$$J_s = 1/\varphi_1 + 1/(m_{w2}\varphi_2) - 2a - 2b(1 - c)/Q^3 \qquad (17)$$

where $Q = 1 - c\varphi_2$.

Further,

$$(\partial J_s/\partial T)(\varphi_2, m_{w2} \text{ constant}) = -2(1 - c)Q^{-3}\partial b/\partial T =$$
$$2(1 - c)Q^{-3}b_h/T^2 \qquad (18)$$

The latter quantity is positive for cyclohexane/polystyrene because $c < 1$ and $b_h > 0$. Also, since J_s increases, Δ will decrease with increasing T (see eq 16), as is found experimentally.

To calculate the concentration at which Δ is maximum at constant T we need to analyze eq 16:

$$\Delta_2 \equiv (\partial\Delta/\partial\varphi_2)(T, m_{w2} \text{ constant}) =$$
$$(2\varphi_2 J_s + \varphi_2^2 J_{s2})\{B(22.5) - B(67.5)\}/\{\varphi_2^2 J_s + B(22.5)\}^2 \qquad (19)$$

where

$$J_{s2} \equiv (\partial J_s/\partial\varphi_2)(T, m_{w2} \text{ constant}) =$$
$$1/\varphi_1^2 - 1/(m_{w2}\varphi_2^2) - 6b(1 - c)/Q^4 \qquad (20)$$

Hence, eq 20 not only defines the critical state in a *strictly-binary* system ($m_2 = m_{w2}$) but also the extremum in the spinodal

in a *quasi*-binary one. Note that Δ_2 is zero in this state since both J_s and J_{s2} are zero (see eqs 5 and 6).

To ascertain that the extremum in Δ is indeed a maximum we need to determine the sign of $\Delta_{22} \equiv (\partial\Delta_2/\partial\varphi_2)(T, m_{w2}$ constant)

$$\Delta_{22} = \{B(22.5) - B(67.5)\}B(22.5)^{-2}\varphi_2^2 J_{s22} \qquad (21)$$

in which expression terms with J_s and J_{s2} have been left out since they equal zero. The first term on the rhs being negative, $J_{s22} \{\equiv(\partial^2 J_s/\partial\varphi_2^2)(T, m_{w2}$ constant)$\}$ should be positive for all m_{w2}.

$$J_{s22} = 2/\varphi_1^3 + 2/(m_{w2}\varphi_2^3) - 24bc^2(1 - c)/Q^5 \qquad (22)$$

An analytical solution does not seem obvious, but it can be shown numerically that J_{s22} is positive for all m_{w2} in the system cyclohexane/polystyrene. Hence, the maximum of the angular dissymmetry will occur at the concentration φ_{2sp}, at which the spinodal exhibits an extremum. In a strictly binary system this extremum is a critical point; in a quasi-binary system the critical concentration is larger and the threshold concentration is smaller than the extremum of the spinodal.[46] Hence, "spinodal" opalescence would be a more exact term for the phenomenon than the familiar "critical" opalescence.

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