Macromolecules **1995,** *28,* 1103−1107

Phase Transitions in Swollen Networks[†]

R. Moerkerke, R. Koningsveld, and H. Berghmans*

Laboratory for Polymer Research, Katholieke Universiteit Leuven, Belgium

K. Dušek

Institute of Macromolecular Chemistry, Czech Academy Sciences, Prague, Czech Republic

K. Šolc

Michigan Molecular Institute, Midland, Michigan 48640-2696

Received August 23, 1994; Revised Manuscript Received November 10, 1994[®]

ABSTRACT: Equilibrium swelling of networks capable of separating into a highly swollen and a collapsed phase is discussed on the basis of a concentration-dependent pair interaction parameter. Classic rules, to be obeyed by the various binodals and their metastable and unstable extensions, rationalize the experimentally accessible portions of the phase diagram and are covered by a simple model yielding acceptable parameter values when fitted to swelling data on the system water/poly(*N*-isopropylacrylamide). The description of the solvent/network binodal is good, but the predicted location of the LCST miscibility gap for linear chains deviates considerably from the measured cloud points. It is probable that linear and branched chains do not differ much in enthalpic contributions to the interaction parameter but deviate appreciably in the entropic terms. This feature offers an acceptable explanation for the discrepancy.

Introduction

Several years ago Dušek, Patterson, and Prins presented a theoretical analysis of equilibrium swelling of a network in a single solvent.[1,2] The study led to the prediction that a swollen network phase in equilibrium with pure solvent may undergo a transition into two phases differing in degrees of swelling. Systems that are in equilibrium with liquid solvent or its vapor were considered, and the phenomenon should be expected to occur for certain values of the network structure parameters.

Later experimental work by Tanaka[3] and Ilavsky[4] has demonstrated the practical relevance of the theoretical considerations and produced phase diagrams that are in qualitative agreement with the diagrams presented by Dušek *et al.* Recently, a number of extensive reviews has been published in which the phenomenon is generally attributed to the polyelectrolytic nature of the networks studied in most cases.[5] However, nonpolar systems should also be expected to exhibit network demixing if the pair-interaction parameter depends on concentration in a suitable fashion. This possibility has been indicated earlier[1,2,6,7] and is worked out in some detail in this paper. The study aims at so-called χ-driven gel equilibria, and the role of the network is just that it prevents the system from becoming infinitely diluted.

The process of phase separation within a swollen gel is at the origin of the spectacular volume contractions or expansions that take place when these gels, submerged in an excess of solvent, are cooled or heated. The phase relationships, responsible for such behavior, are illustrated schematically in Figure 1, and the various transitions can be discussed considering three different cooling operations, each starting from a one-phase isotropic, not fully swollen gel, in the absence of free solvent. Figure 1 indicates these starting points by the polymer volume fractions ϕ_1, ϕ_2, and ϕ_3 at temperature T_1.

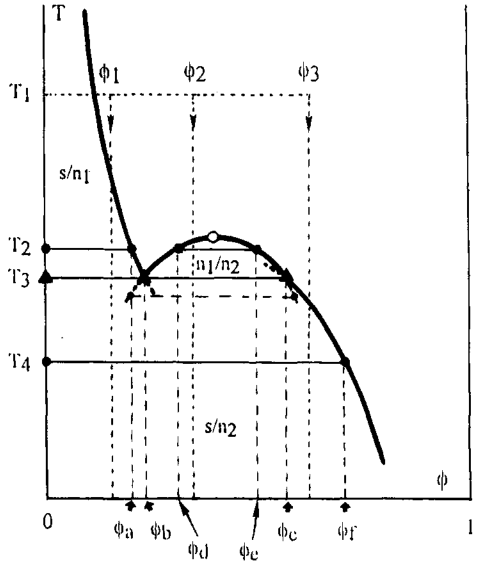

Figure 1. Schematic phase diagram for a binary system showing collapse of the network phase. Two-phase equilibria: solvent/swollen network, s/n$_1$; solvent/collapsed network, s/n$_2$; swollen network/collapsed network, n$_1$/n$_2$. Tie lines: ●—● or ●– – –●. Critical point: ○. Nonvariant three-phase equilibrium s/n$_1$/n$_2$: ▲—▲—▲.

Cooling of system ϕ_1 from T_1 to T_2 brings it into the two-phase region s/n$_1$ between the solvent axis and the swelling curve. The gel will deswell to volume fraction ϕ_a. At further cooling to T_3 deswelling will continue until the two-phase equilibrium solvent/gel ϕ_b has been reached. At T_3 there may also be equilibrium between the network phase ϕ_b and a collapsed swollen network ϕ_c. Since ϕ_b is in equilibrium with both pure solvent and phase ϕ_c, we have a three-phase-equilibrium situation which is nonvariant because the pressure has been fixed (1 bar). Hence, such equilibrium between solvent and either swollen or shrunken network phases can occur at a single temperature only, which is specific for the solvent/network system in hand. The removal of

---

[†] Dedicated to Prof. J. J. Hermans on the occasion of his 85th birthday.

[®] Abstract published in *Advance ACS Abstracts,* January 15, 1995.

0024-9297/95/2228-1103$09.00/0 © 1995 American Chemical Society

heat will not reduce the temperature but will result in the transformation of phase ϕ_b into pure solvent and phase ϕ_c. The temperature can be lowered only when phase ϕ_b has been transformed completely into ϕ_c, after which the temperature can decrease again and two-phase equilibrium reigns between pure solvent and the collapsed, deswollen network (for instance, ϕ_f at T_4). Thus, passing T_3 in a cooling experiments causes the polymer concentration in the gel phase to jump suddenly from ϕ_b to ϕ_c and, accordingly, forces the degree of swelling of that phase to change noticeably in an abrupt fashion.

Classic thermodynamics[8,9] ties such abrupt changes in concentration or other variables to the occurrence of nonvariant equilibrium, in the way described above. It also formulates rules for two-phase ranges bordering a nonvariant three-phase line in a binary system. For instance, if there is one two-phase range (solvent/collapsed network) below three-phase temperature T_3, there must be two two-phase ranges above T_3, one of which obviously is the solvent/swollen network equilibrium, s/n$_1$. The other two-phase region must be assigned to swollen network/collapsed network equilibrium, n$_1$/n$_2$, which may be expected to terminate in a critical point at $T > T_3$ where the two phases become identical.

Cooling a gel of concentration ϕ_2 from T_1 to T_2 will result in a phase separation into phases ϕ_d and ϕ_e. When T_3 is reached and any thermal exchange is stopped, two-phase equilibrium will be maintained between phases ϕ_b and ϕ_c. Further elimination of heat will, as above, establish the three-phase equilibrium and finally lead to two-phase equilibrium between the solvent and the shrinking gel. Cooling from T_1 to T_4 at ϕ_3 results in two-phase equilibrium solvent/network ϕ_f.

The various equilibria discussed above can also be established by isothermal swelling of the dry network. The phase diagram is then entered horizontally at the swelling temperature. The overwhelming majority of experiments has been concerned with swelling equilibria in the presence of free solvent, so that s/n$_1$ deswelling follows the curve down to ϕ_b at T_3 and the gel, after the transition n$_1$ → n$_2$, further deswells according to the s/n$_2$ mechanism. However, the possibility to induce s/n$_1$ or n$_1$/n$_2$ phase separations by changing the solvent concentration at constant T has, as far as we are aware, not been studied and appears to be a very interesting option.

In the previous studies[1,2] the presence of a diluent during the formation of a network was considered as a necessary condition for gel–gel equilibria to occur, at least when the polymer–solvent interaction parameter is independent of concentration. Dilution during network formation makes the network chains in the dry state supercoiled, so that the entropy change due to increase of chain dimensions can even be positive. The interplay of this change with attractive polymer–polymer interactions (moderately poor solvent) facilitates the development of gel–gel equilibria. It was recognized[1,2] that a concentration dependence of the interaction parameter would ease the transition, and it follows from the present analysis that, within a range of network parameters, this is a necessary condition.

Swelling Equilibrium in a Single Solvent

We employ the usual expression for ΔG, the change in Gibbs free energy of a network due to isotropic deformation in swelling, and write

$$\Delta G = \Delta G_{\mathrm{el}} + \Delta G_{\mathrm{mix}} \tag{1}$$

The elastic contribution to ΔG is defined by

$$\Delta G_{\mathrm{el}} = kT[(3A\nu_e/2)\Phi_0^{2/3}(\phi^{-2/3} - 1) - B\nu_e \ln(\phi^{-1})] \tag{2}$$

where kT has its usual meaning, Φ_0 is the polymer volume fraction at network formation, and ϕ is the polymer volume fraction in the swollen network.[1,2] The number of elastically active chains is denoted by ν_e. When the phase transition is driven by the state of the network chains after network preparation, the values of the factors A and B in eq 2 become very important. Hermans[10] was one of the first authors who discussed these aspects in relation to network structure. This discussion resulted in the formulation of modern theories of network swelling.

We use a maneuver suggested earlier[11] to avoid to some extent the dissention in the literature about appropriate values for A and B, allowing them to vary linearly with ϕ. Thus we do not introduce new parameters and have

$$A = (f-2)/f + 2\phi/f; \quad B = 2\phi/f \tag{3}$$

where f is the functionality of the cross-links. Equation 3 corresponds to Flory and Erman's junction fluctuation theory.[12] The lower limit at $\phi \to 0$ relates to the "phantom network" limit which is universal. The upper limit (at $\phi \to 1$) is not universal, since A might exceed unity (*cf.*, *e.g.*, ref 13).

The contribution to ΔG arising from the mixing of solvent and network is written as[14]

$$\Delta G_{\mathrm{mix}}/RT = n_0 \ln \phi_0 + g n_0 m_0 \phi \tag{4}$$

where R is the gas constant, n_0 and ϕ_0 are the amount in moles and the volume fraction of the solvent, respectively, and m_0 is the number of lattice sites occupied by a solvent molecule. The interaction function g is assumed to depend on ϕ which, judged by the results of the earlier analysis,[1,2] may underlie phase separation within the swollen network. We write

$$g = g_0 + g_1\phi + g_2\phi^2 \tag{5}$$

It is convenient to define equilibrium between phases with the aid of a function Z which represents $\Delta G/RT$ per mole of lattice sites. If the system contains N moles of lattice sites, we have $\nu_e/N = \phi/m_c$, where m_c is the number of lattice sites occupied by an average network chain. The network is assumed to be perfect. Thus,

$$Z = \Delta G/NRT = G_{AB} + (\phi_0/m_0)\ln \phi_0 + g\phi_0\phi \tag{6}$$

where

$$G_{AB} = (3A/2m_c)\Phi_0^{2/3}(\phi^{1/3} - \phi) + (B/m_c)\phi \ln \phi$$

Equilibrium between a pure solvent and a swollen network is determined by the equality of the chemical potential μ_0 of the solvent in the two phases:

$$\Delta\mu_0/RT = Z - \phi Z_\phi = 0 \tag{7}$$

where $Z_\phi = \partial Z/\partial\phi$. If the network phase itself separates into a swollen (a) and a collapsed phase (b), we have the conditions

$$[Z - \phi Z_\phi]_a = [Z - \phi Z_\phi]_b \quad (8a)$$

$$[Z_\phi]_a = [Z_\phi]_b \quad (8b)$$

in which the equality of the chemical potential of the polymer segments in the two phases is also ensured. In the nonvariant three-phase situation mentioned in the Introduction we have the additional condition that the left- and right-hand sides of eq 8a both equal zero.

It follows from eq 6 that

$$Z_\phi = C_{AB} - (\ln \phi_0 + 1)/m_0 + g_0(1 - 2\phi) + g_1\phi(2 - 3\phi) + g_2\phi^2(3 - 4\phi) \quad (8c)$$

with

$$C_{AB} = \phi_0^{2/3}[(A/2m_c)(\phi^{-2/3} - 3) + (3/fm_c)(\phi^{1/3} - \phi)] + (B/m_c)(\ln \phi + 1) + (2\phi/fm_c) \ln \phi$$

If nonvariant three-phase equilibrium occurs in systems obeying eq 6, the system must have two critical points, one being stable and the other one unstable.[15,16] It has been shown that such a situation cannot arise in a binary system unless the interaction parameter g is at least a quadratic function of concentration.[15] Two conditions must be obeyed at a critical point: they are given by a zero value of the second and third derivatives of Z with respect to ϕ, the former being known as the spinodal condition. Thus we have

Spinodal: $$X_{AB} + 1/(m_0\phi_0) = 2g_0 + 2g_1(3\phi - 1) + 6g_2\phi(2\phi - 1) \quad (9a)$$

Critical Point: $$Y_{AB} + 1/(m_0\phi_0^2) = 6g_1 + 6g_2(4\phi - 1) \quad (9b)$$

where

$$X_{AB} = \Phi_0^{2/3}[-(A/3m_c)\phi^{-5/3} + (2/fm_c)(\phi^{-2/3} - 3)] + B/(m_c\phi) + (4/fm_c)(\ln \phi + 1)$$

$$Y_{AB} = \Phi_0^{2/3}[(5A/9m_c)\phi^{-8/3} - (2/fm_c)\phi^{-5/3}] - B/(m_c\phi^2) + 6/(fm_c\phi)$$

The calculation of equilibria involving swollen and collapsed phases may proceed as follows. It is assumed that the network formation took place in the dry state ($\Phi_0 = 1$). Values of f, m_0, and m_c are fixed and two critical concentrations are chosen, which allows calculation of g_1 and g_2 with eq 9b and the two critical g_0 values with eq 9a. (We assume the temperature dependence of g to be limited to g_0.) Fixing m_c to 1000, m_0 to 1, f to 3, and the two critical concentrations to 0.05 and 0.25, we find $g_1 = 0.297\,931\,8$ and $g_2 = 0.031\,410\,6$ and obtain the full phase diagram shown in Figure 2a. Three-phase equilibrium occurs at $g_0 = 0.759\,873$.

For the interaction function thus defined we may let the two-phase state of the swollen network vanish by a decrease of m_c. The two critical points then approach each other, to coalesce in a double critical point at which the fourth derivative of Z with respect to ϕ vanishes. This condition leads to

$$Z_{AB} + 2/(m_0\phi_0^3) - 24g_2 = 0 \quad (9c)$$

with

$$Z_{AB} = 4[10(2 + \phi - f)/(27\phi^{5/3}) - 1]/(fm_c\phi^2)$$

Using eqs 9c and 9b and the present g_1 and g_2 values, we find the double critical point to occur at $m_{c(dcp)} = 81.2527$, $\phi_{dcp} = 0.18426$ (Figure 2b). In Figure 2c we show an intermediate case at $m_c = 300$ in which the stable critical point in Figure 2a has just become metastable and is located just below the stable solvent/one-phase swollen network curve.

Though this treatment includes the assumptions embodied in eq 3, it does not depend on them. Employing the original Flory–Rehner expression for ΔG_{el},[14] with A and B independent of concentration and equalling unity and zero, respectively, we obtain a very similar phase diagram.[9] Obviously, the values of the coefficients in eq 5 then differ somewhat from those of Figure 2. An analogous result is obtained when the more rigorously derived expression of James and Guth[17] is used for ΔG_{el} with $B = 0$ and $A = (f - 2)/f$, which now corresponds to phantom-network elasticity. Hence, phase behavior of swollen networks, as indicated by Figure 1, is likely to be found in practice in systems for which the pair-interaction parameter depends markedly on concentration, if other reasons like ionic interactions are absent, or otherwise in addition to those.

Figure 2a contains some tie lines (connecting coexisting-phase compositions) to demonstrate how the two-phase equilibria around the three-phase line develop.[8,9,16] It is seen that the solvent/swollen network binodal (s/n_1, s/n_2) has to assume a sigmoidal shape in order to pass continuously through two of the three-phase points. Its two extrema 1 and 2 occur on the spinodal curve but do not represent critical phases; they coexist with pure solvent phases 1′ and 2′, respectively. The sigmoidal binodal for n_1/n_2 equilibrium has four extrema, two of which are critical points (o) where the spinodal also shows an extreme. The other two (3 and 4) are not critical, though lying on the spinodal, but coexist with the cusp phases 3′ and 4′, respectively. The conjugation between cusps and points of intersection between spinodal and binodal (or shadow curve in the case of linear polymolecular polymers) is a general phenomenon, well documented for non-cross-linked systems.[8,9,16,18,19]

Swelling Equilibrium in the System Water–Poly(*N*-isopropylacrylamide)

Swelling in the system water/poly(*N*-isopropylacrylamide) has been investigated in some detail by various authors.[20-23] Figure 3a shows equilibrium data obtained by Inomata *et al.*[22] on the cross-linked polymer in water without added salt. The temperature coefficient of swelling is negative in this system which corresponds to lower critical solution (LCST) behavior in aqueous solutions of the linear polymer. Deferring a comparative study of the various sets of data to a later paper, we here use the swelling data merely to discuss the concentration dependence of the interaction parameter as a possible cause of phase separation within the swollen gel.

The average number of segments in the network chains not having been reported by Inomata *et al.*, we use m_c as a parameter to obtain the best fit of the swelling data to eq 7 ($m_c = 60$). The authors prepared the network in aqueous solution at $\Phi_0 = 0.08$, at a weight ratio of monomer to cross-linker (CL) of about 17. Since we use the water molecule as the lattice site (on a weight basis), the average molar mass of the

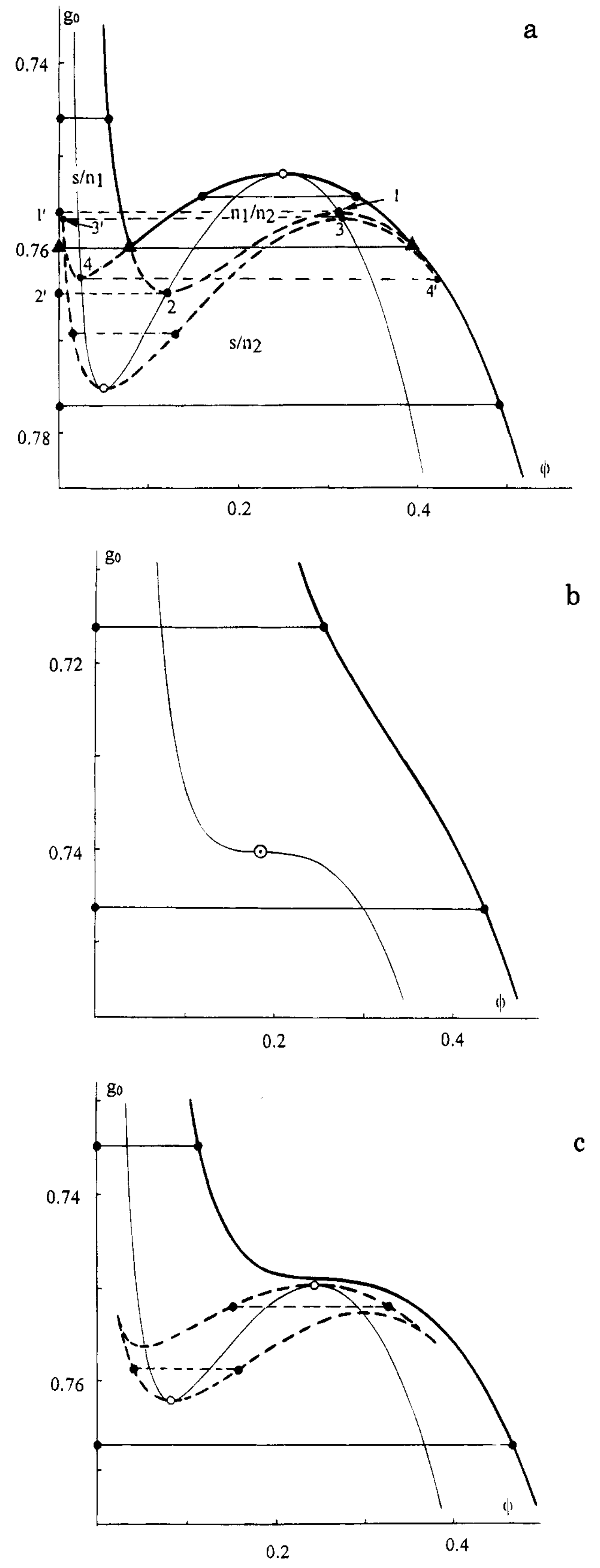

Figure 2. Phase diagram in terms of g_0 against polymer volume fraction ϕ, calculated with eqs 5–8 for $f = 3$, $m_0 = 1$, $g_1 = 0.297\,931\,8$, $g_2 = 0.031\,410\,6$. (a) $m_c = 1000$. (b) $m_c = 81.2527$. (c) $m_c = 300$. Symbols as in Figure 1. Spinodal: light drawn curve. Double critical point: (⊙).

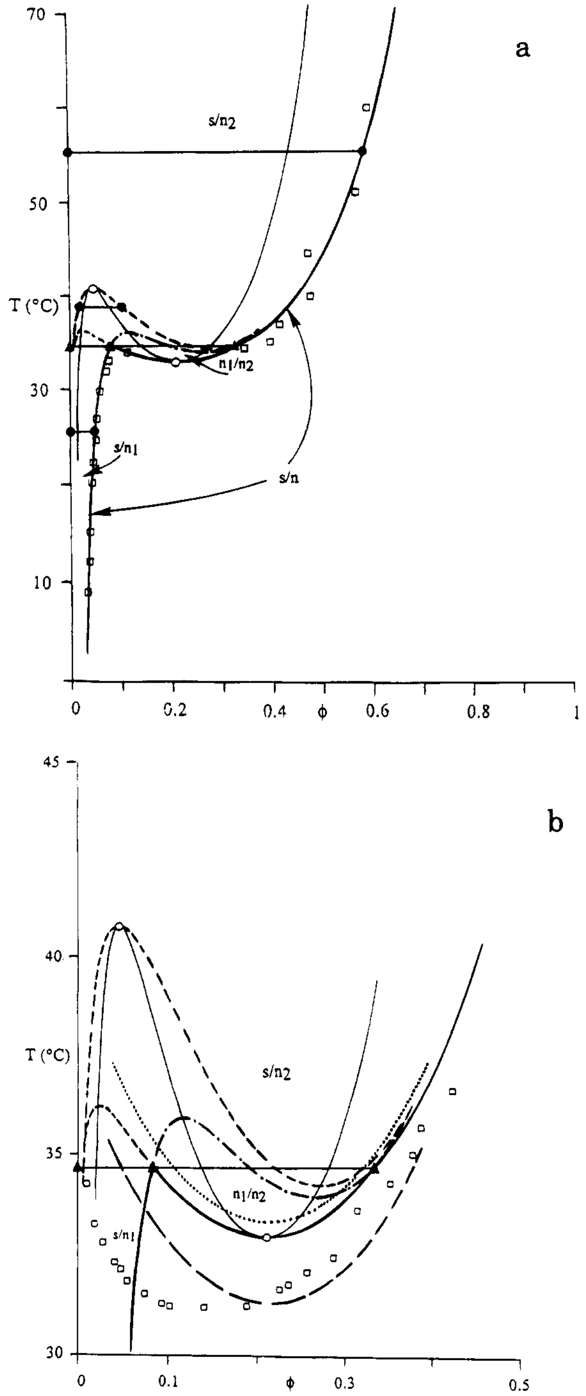

Figure 3. Swelling of a poly(*N*-isopropylacrylamide) network in water. (a) Data:[22] □. Description with eqs 5–8: heavy curves (connected by a dash–dotted curve) demarcate the two-phase ranges s/n_1 and s/n_2. Spinodal: light curve. Further symbols as in Figure 1. (b) Enlargement of the central part of Figure 3a. Added are cloud-point data for linear chains in water (□)[24] and their description with the network g-parameters in Table (···) and with a slightly adapted value of g_0, (– –).

network chains is $18m_c$. The doubly unsaturated CL has a molar mass of 154, and, with $f = 4$, half of this weight must be assigned to a chain. Then, the weight ratio of monomer to CL in the network is $(18m_c)/(154/2) = 14$, a value close enough to the above number to be acceptable.

The data fit is improved by letting g_1 and g_2, in addition to g_0, depend on temperature: $g_1 = g_{1s} + g_{1h}/T$. In order to let this procedure yield physically acceptable parameter values, we had to take the highly-associated water structure into account, which was done in a first approximation by assigning a value of 10 to m_0. This led to the data description indicated in Figure 3a by the heavy drawn curve marked s/n (solvent/network). We

Table 1. Interaction Parameters from Fits of the Data[22] to Eqs 5–8 ($m_c = 60$; $m_0 = 10$; $\Phi_0 = 0.08$; $f = 4$)

	Network	
$g_{0_s} = 2.9655$	$g_{1_s} = -0.079\,164$	$g_{2_s} = -2.9549$
$g_{0_h} = -986.24$ K	$g_{1_h} = -0.061\,307$ K	$g_{2_h} = 664.66$ K
	Linear Chains	
$g_{0_s} = 2.995$		

may now complete the phase diagram by calculating the two critical points with eqs 9a,b and the n_1/n_2 binodal (network/network) with eqs 8a,b. Finally, the spinodal curve is computed with eq 9a. We pinpoint the nonvariant three-phase situation with eqs 7 and 8a,b and find it, within the present description, to occur at about 35 °C.

Figure 3b gives an enlargement of the central part of Figure 3a and once more demonstrates the details of phase behavior in swollen systems that, on the basis of classic considerations as applied here, can be deduced from the swelling data of Inomata *et al.*[22]

Discussion

The description of the swelling data is quite acceptable and supplies a meaningful pattern for the extensions of the two equilibrium curves, s/n and n/n, according to classic rules.[8,9,16] The actual parameter values used for Figure 3a are listed in Table 1 and should not be given too much weight. Though giving an acceptable description, they are correlated so that their absolute magnitude does not have much significance. In fact, the present analysis only had the objective of demonstrating the possible importance of a strong concentration dependence of the pair-interaction parameter for network collapse and has shown that this may be the case.

A mere description of data gains in credibility if the parameters allow prediction of other measured data, not used in their assessment. Marchetti *et al.*[24] reported LCST cloud-point data for the linear, non-cross-linked polymer, that might be employed for the purpose. The model, used to calculate Figure 2a, predicts such cloud-point curves to occur at g_0 values larger than those pertinent to the swollen-network equilibria.[25,26] In the present LCST example this would involve higher temperatures. The fact that Marchetti *et al.*'s cloud points are located at lower temperatures already demonstrates that the prediction is not going to work satisfactorily, as shown by the dotted curve in Figure 3b.

It is probable that the main cause of the latter disagreement must be sought in the architecture of the polymer chains which are branched in the swelling experiment and linear in the determination of the cloud points. An earlier comparison of the swelling of unimodal and bimodal networks of identical m_c[11] yielded identical enthalpic parameter values but different entropy contributions to the interaction parameter. It would therefore seem to be reasonable to assume the enthalpic terms in Table 1 to be valid also for the linear case and to check whether small variations in the entropic terms might lead to a better agreement. Figure 3b demonstrates that such is the case, at the cost of a small change in g_{0_s} alone (Table 1).

A marked dependence of g on ϕ has the interesting consequence that the critical concentration for liquid–liquid equilibrium at infinite linear chain length m may become two-valued.[6,26–29] Using the present symbols, we have for limit $1/m \rightarrow 0$:

$$\phi^2[6g_1 + 6g_2(4\phi - 1) - (m_0\phi_0)^{-2}] = 0 \qquad (10)$$

which has one root at $\phi = 0$, the usual critical concentration for infinite chain length. The expression between square brackets supplies another root, also called the limiting critical concentration, ϕ_L, at $m = \infty$.[29] We find this root at $\phi_L \simeq 0.25$. This feature is a subject of current research.

Acknowledgment. The authors thank Prof. A. R. Khokhlov (Moscow) for a helpful discussion. R.M., R.K., and H.B. are indebted to National Fund for Scientific Research (NFWO), IWONL, and Ministry of Scientific Programmation through IUAP-16 for financial support. K.D. thanks the Grant Agency of ASCR.

References and Notes

(1) Dušek, K.; Patterson, D. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 1209.
(2) Dušek, K.; Prins, W. *Adv. Polym. Sci.* **1969**, *6*, 1.
(3) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820.
(4) Ilavsky, M. *Macromolecules* **1982**, *15*, 782.
(5) Dušek, K., Ed. Responsive Gels. Volume Phase Transition. *Adv. Polym. Sci.* **1993**, *109* and *110*.
(6) Erman, B.; Flory, P. J. *Macromolecules* **1986**, *19*, 2342.
(7) Hirotsu, S. Reference 5, Vol. *110*, p 1.
(8) Bakhuis Roozeboom, H. W. *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre*; Vieweg: Wiesbaden, FRG, 1901–1913.
(9) Koningsveld, R.; Stockmayer, W. H.; Nies, E. *Polymer Phase Diagrams*; Oxford University Press: Oxford, U.K., in preparation.
(10) Hermans, J. J. *J. Polym. Sci.* **1962**, *59*, 191.
(11) Petrović, Z.; MacKnight, W. J.; Koningsveld, R.; Dušek, K. *Macromolecules* **1987**, *20*, 1088.
(12) Flory, P. J.; Erman, B. *Macromolecules* **1982**, *15*, 800.
(13) Erman, B.; Monnerie, L. *Macromolecules* **1989**, *22*, 3342.
(14) Flory, P. J.; Rehner, J., Jr. *J. Chem. Phys.* **1943**, *11*, 521.
(15) Šolc, K.; Kleintjens, L. A.; Koningsveld, R. *Macromolecules* **1984**, *17*, 573.
(16) Šolc, K.; Koningsveld, R. *J. Phys. Chem.* **1992**, *96*, 4056.
(17) James, H. M.; Guth, E. *J. Chem. Phys.* **1953**, *21*, 1039.
(18) Tompa, H. *Trans. Faraday Soc.* **1949**, *45*, 1142.
(19) Šolc, K. *Macromolecules* **1977**, *10*, 1101.
(20) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984**, *81*, 6379.
(21) Hirotsu, S.; Hirokawa, Y.; Tanaka, T. **1987**, *87*, 1392.
(22) Inomata, H.; Goto, S.; Saito, S. *Macromolecules* **1990**, *23*, 4887.
(23) Hirotsu, S. *J. Chem. Phys.* **1991**, *94*, 3949.
(24) Marchetti, M.; Prager, S.; Cussier, E. L. *Macromolecules* **1990**, *23*, 3445.
(25) Borchard, W. *Prog. Colloid Polym. Sci.* **1975**, *57*, 39.
(26) Borchard, W. *Eur. Polym. J.* **1978**, *14*, 661.
(27) Dušek, K. *Collect. Czech. Chem. Commun.* **1969**, *34*, 3309.
(28) Koningsveld, R.; Kleintjens, L. A. *Pure Appl. Chem., Macromol. Chem.* **1973**, *8*, 197.
(29) Kennedy, J. W.; Gordon, M.; Koningsveld, R. *J. Polym. Sci., Part C* **1972**, *No. 39*, 43.

MA941162G