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Influence of Added Components on the Miscibility Behavior of the (Quasi-) Binary System Water/Poly(vinyl methyl ether) and on the Swelling Behavior of the Corresponding Hydrogels. 1. Tetrahydrofuran[†]

Bert Bergé, Ronald Koningsveld, and Hugo Berghmans*

Polymer Research Division, Department of Chemistry, Catholic University of Leuven,
Celestijnenlaan 200F, B-3001 Heverlee, Belgium

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ABSTRACT: Addition of an ether-group-containing second solvent (tetrahydrofuran, THF) to the binary system water/linear poly(vinyl methyl ether) proved to have a profound influence on liquid/liquid phase relations and to cause a sharp decrease in solvent power of the mixed solvent as compared to water alone. A classic thermodynamic analysis of the phase diagrams showed the ternary system to exhibit two mechanisms of three-liquid-phase separation, both passing through a critical end point and one of them involving a heterogeneous double critical point. The ternary miscibility gap vanishes in a homogeneous double critical point at about 18 °C. Replacement of the linear PVME by its cross-linked variety changed the phase behavior in a fashion resembling that of the binary system water/cross-linked PVME. A third mechanism of three-liquid-phase separation, not involving a critical end point, is now operative, experimental indications for which are presented. Below 30 °C, the ternary system water/THF/PVME is partially miscible and presents an example of co-nonsolvency, since both water and THF each mix in all proportions with the polymer in that temperature range. An explanation for the phenomenon given by Winnik et al. for the system water/methanol/poly(*N*-isopropylacrylamide) appears also to hold true for the present system.

Introduction

By now it is a well-established fact that not too tightly cross-linked networks, swollen in a single solvent, may exhibit a segregation into two gel phases differing markedly in degree of swelling, and both equilibrating with the pure solvent phase. The phenomenon, also known as gel collapse, was predicted theoretically in 1968 by Dušek and Patterson[1] and has since then found numerous experimental verifications.[2] Because of the chain connectivity throughout the network the two gel phases necessarily stay finely dispersed but their occurrence can be observed by the onset of turbidity. Classic thermodynamic implications of the phenomenon have been described elsewhere.[3,4]

Poly(vinyl methyl ether) (PVME) is a water-soluble polymer, aqueous solutions of which demix in a complex manner upon heating. The system water/linear PVME exhibits a peculiar type of lower critical-solution temperature (LCST) behavior that has recently been studied quite extensively by Schäfer-Soenen et al.[5] These authors demonstrated that the system represents an example of so-called type III demixing, as defined by Šolc et al.[6] Type III demixing is characterized by a bimodal miscibility gap with three critical points, two of which are stable (C_α and C_β). For the present system, they refer to temperature minima, one at about 5 wt % PVME (α-gap) and a second one at about 75 wt % of polymer (β-gap) (see Figure 1a). The third, unstable, critical point C_u is located between the two stable ones. Experimental evidence is provided by Figure 2a, top curve. The β-gap is insensitive to molar mass and its distribution.

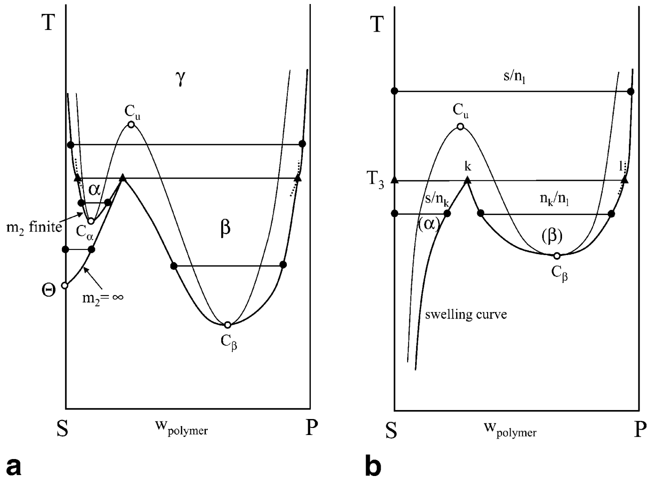

Figure 1. Schematic representation of type III demixing in a binary solvent/polymer system showing LCST behavior, for linear (a) and cross-linked polymer (b). Key: (●−●) two-liquid-phase equilibrium; (▲−▲) three-liquid-phase equilibrium; (thick lines) cloud-point or swelling curve; (thin lines) spinodal. C_u: unstable critical point. C_α, C_β: stable critical points; α, β, γ: regions of two-liquid-phase equilibria. s/n_k, s/n_l: solvent/swollen-network equilibrium; n_k/n_l: equilibrium between two swollen phases. Chain-length values for linear polymer (m_2) indicated. The critical point for $m_2 = \infty$ defines the Θ state.

Type II demixing refers to a miscibility gap with a single extremum, the location of which in temperature/concentration space is equally insensitive to molar mass and occurs at a polymer weight fraction around 0.5. The system water/poly(*N*-isopropylacrylamide) presents a case in point.[3,7] Type I demixing exhibits the usual Θ behavior, as does the α-gap of type III.[4]

Although the polymer used in this study has a wide molar-mass distribution, we still discuss the data obtained as if they refer to a strictly binary system. This

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* Corresponding author. E-mail: Hugo.Berghmans@chem.kuleuven.ac.be.

[†] Dedicated to Prof. Karel Šolc (Midland, MI) on the occasion of his 70th birthday.

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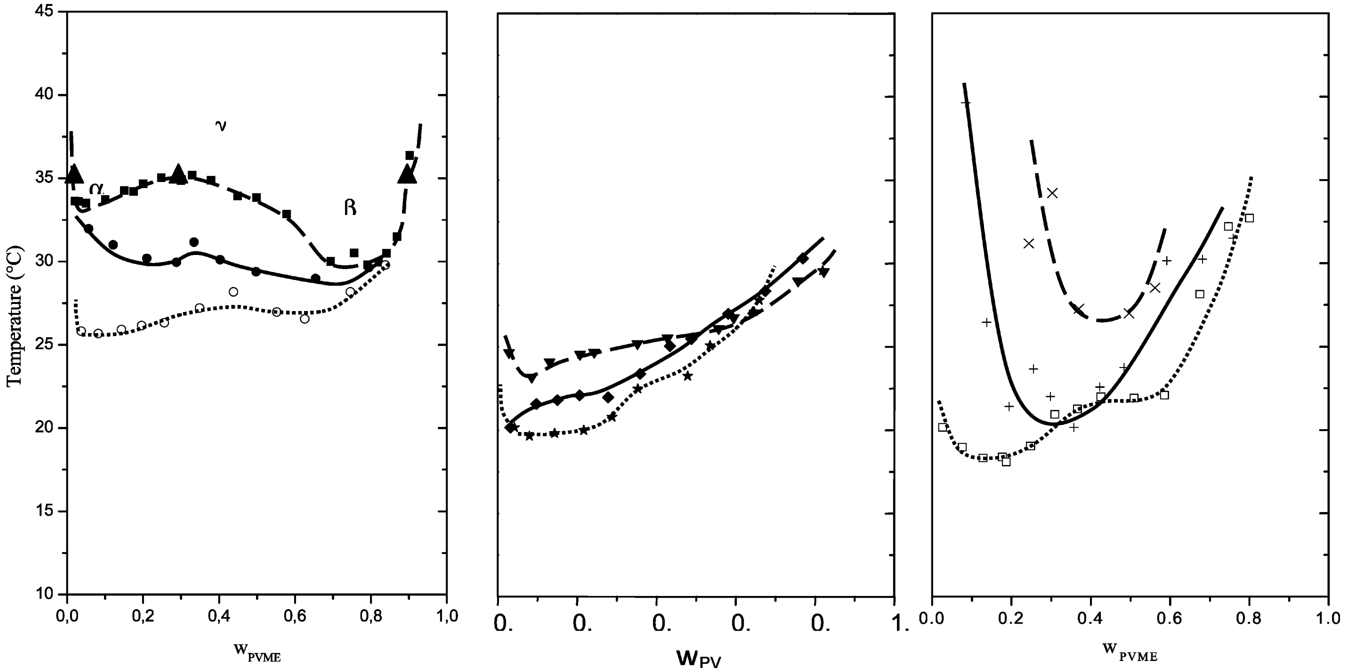

Figure 2. Cloud points as a function of the weight fraction of linear PVME for various weight fractions of THF in the mixed solvent water/THF. Left: (■) 0; (●) 0.1; (○) 0.2; (▲−▲) three-liquid-phase equilibrium. Middle: (▼) 0.3; (◆) 0.4; (★) 0.5. Right: (□) 0.6; (+) 0.7; (×) 0.8.

is permitted as long as we restrict the discussion to qualitative features that usually do not differ significantly between strictly and quasi-binary and ternary systems.[4] If the solvent consists of a single component we have a binary system and the phase rule prescribes a unique temperature for three phases to coexist in nonvariant equilibrium. It has been demonstrated that a system containing one or two swollen network phases obeys the phase rule so that the network can obviously be considered to behave as a single component.[3] A sudden jump in the degree of swelling occurs if the temperature of a network, swollen to equilibrium, is changed and the system passes through a nonvariant state. If the network shrinks in the process the phenomenon is known as "gel collapse" (Figure 1b, collapse from k to l at T_3). Upon reversal of the temperature change the network shows a sudden increase of its degree of swelling.

The examples used in the early experimental verifications of the phenomenon did not refer to binary systems but to swelling in a binary solvent, or to aqueous systems with added electrolytes.[2] Yet the observed collapses occurred so suddenly upon small changes of external variables, such as solvent composition or ionic strength, that they have sometimes been mistaken for nonvariant states. It has been demonstrated that such an invariance is only apparent because the three-phase *regions*, now involved, are usually very shallow. Hence, they are being passed within narrow ranges of solvent composition or ionic strength and thus escape experimental observation.[4,8,9]

The collapse phenomenon has been suggested to present an interesting tool in practically important situations because of its appearance as a "molecular switch" mechanism. Controlled-drug release has been mentioned,[2] and other biological applications might be envisaged. However, it has been found that the conditions may already change drastically if a third component is added to the simple binary system showing gel collapse.[8,9] As a consequence, it should not be overlooked that practical systems will not easily be moldable into a required switching behavior on the basis of binary or ternary predictions alone. It was found also that a comparison with the analogous linear system is helpful in understanding phase relations in the cross-linked case. Three-phase equilibrium and β-gap are observed in both varieties and are shifted only marginally in temperature with respect to one another.[3,4,9,10]

It is the purpose of this and subsequent papers in this series to increase the insight into the complexities involved and to do so by an investigation of the first step toward the practically relevant multicomponent situation. In particular, we study the influence of the addition of a second solvent to the binary system water/PVME, which was studied quantitatively in recent work.[5,8,9,11] Here the influence of the addition of an ether-group-containing solvent to the system water/PVME was investigated. In this context, we selected tetrahydrofuran (THF), which is a good solvent for PVME and mixes in the temperature range 12.5−71.8 °C in all proportions with water. Addition of THF introduces a competition for hydrogen bonds between the VME units and THF, to the extent that co-nonsolvency occurs which has a profound influence on phase relations in the linear as well as in the cross-linked system.

Experimental Section

1. Materials. PVME was purchased from Aldrich. The molar-mass distribution was determined by GPC with THF as the solvent and polystyrene as the calibration standard. This yielded a weight-average molar-mass value of $M_w = 20$ kg/mol and a polydispersity index $M_w/M_n = 2$. Deionized water was used as one of the solvents. The other solvent, THF, was purchased from Aldrich and used as received. It contained less than 0.025% of butylated hydroxytoluene as inhibitor. Concentrations of the constituents of binary and ternary systems are specified as weight fractions, w_i. We denote water by subscript 1, THF by 2, and PVME by 3.

2. Determination of Cloud Points and Coexisting-Phase Compositions. The cloud point for a given binary or

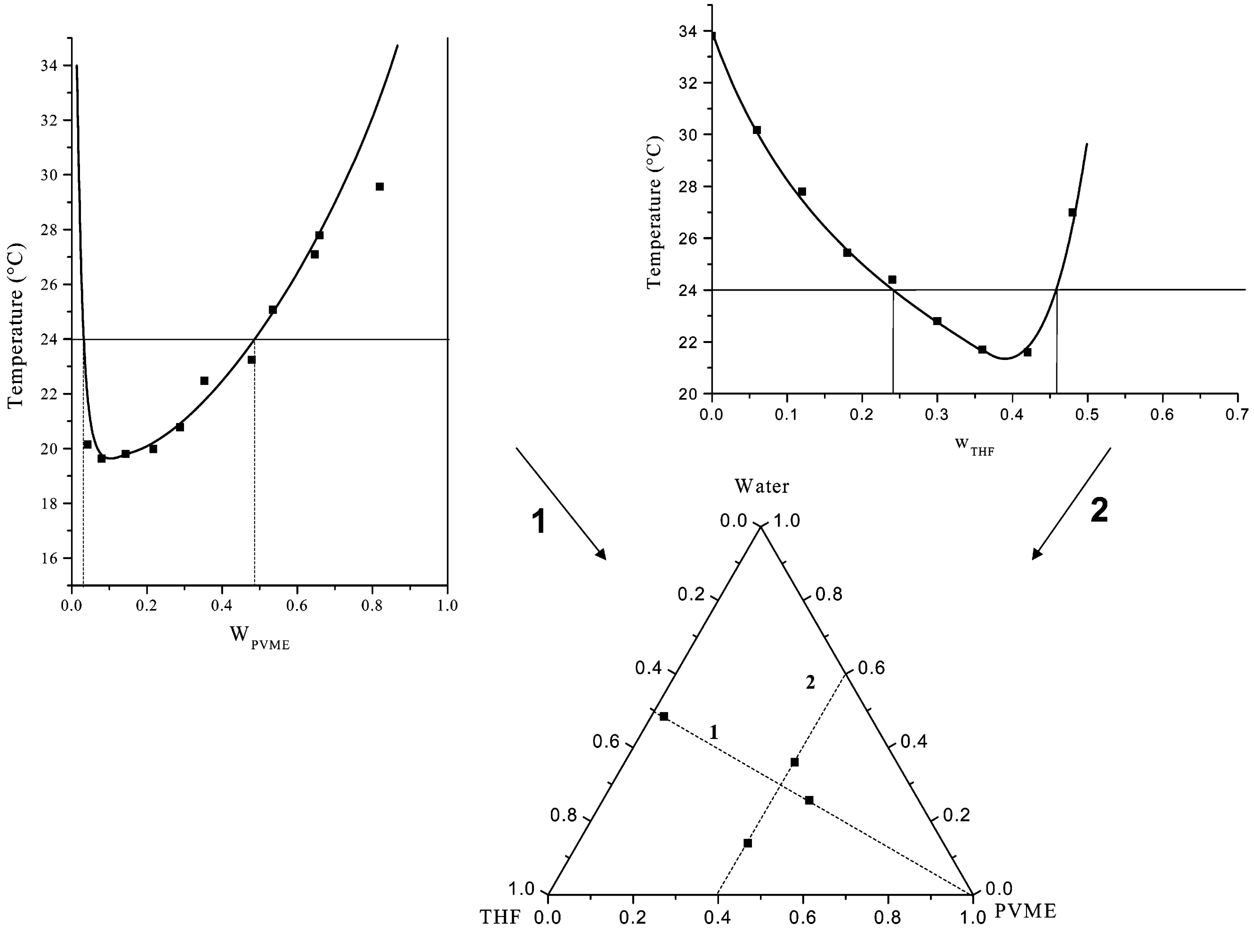

Figure 3. Construction of ternary isotherms from the curves in Figure 2.

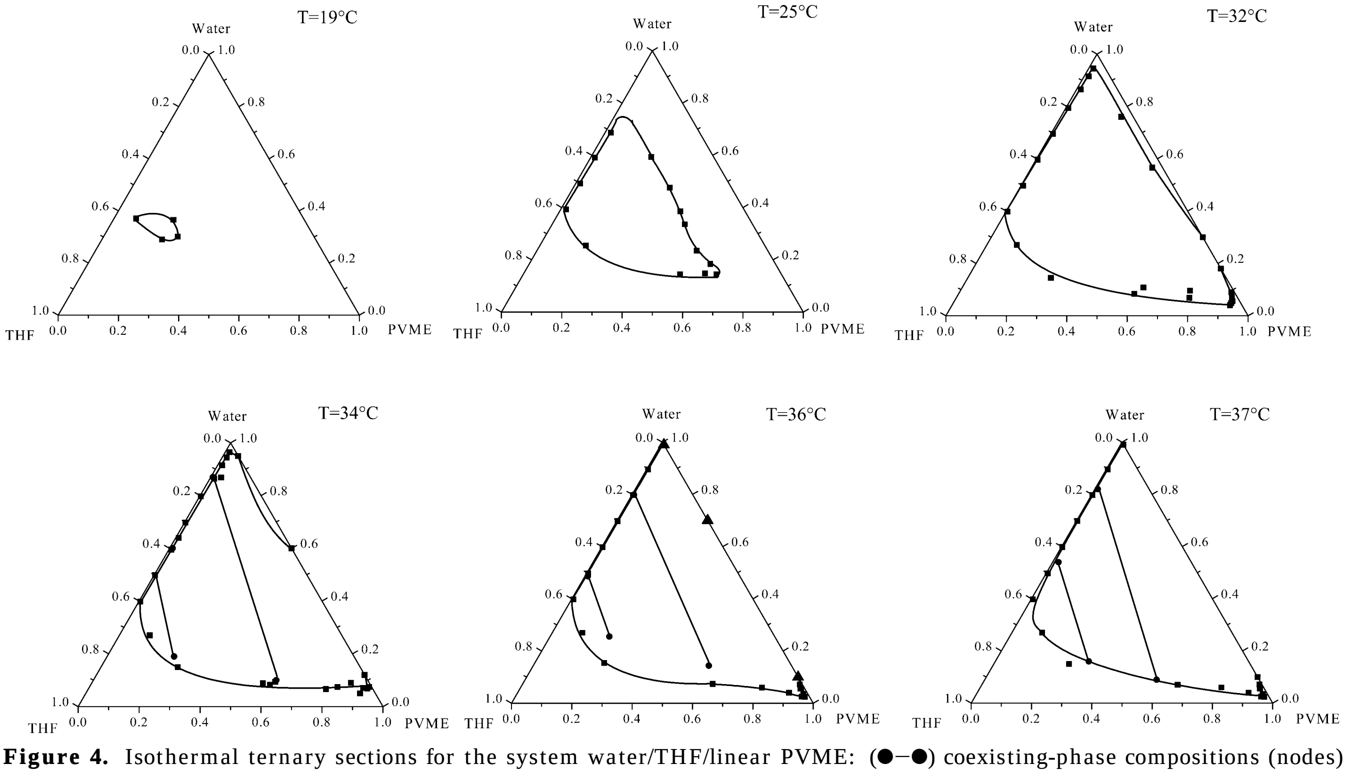

Figure 4. Isothermal ternary sections for the system water/THF/linear PVME: (●–●) coexisting-phase compositions (nodes) and tie lines, (■) cloud points (see Figure 3); (▲–▲) binary three-liquid-phase equilibrium at 36 °C.

ternary composition is the temperature at which a homogeneous system becomes turbid upon a change in temperature, which indicates the onset of liquid/liquid-phase separation.[4] The latter phenomenon is accompanied by an either exothermal or endothermal heat effect, which we detected with a Perkin-Elmer-7 differential scanning calorimeter at a scanning rate of 5 °C/min.[12] Homogeneous samples were prepared by adding the appropriate amount of a water/THF mixture to the dry polymer in a DSC sample pan. The time needed for complete dissolution was determined separately by following the process in test tubes. An alternative method consists of adding THF to water/PVME solutions of various concentrations.

Compositions of coexisting phases in demixed systems were determined by heating a homogeneous solution while stirring. When the required temperature was reached the system was kept at that temperature for several days to allow the phases to settle. After their isolation the solvent was distilled off and analyzed for its composition by gas chromatography. Because of the fact that water could not be detected directly, a known amount of acetone was added. Since the calibration curve for mixtures of THF and acetone appeared not to depend on the presence of water, we could calculate the water/THF ratios in the samples of distilled mixed solvent from such GC measurements. The GC used here was a Varian 3300.

3. Cross-Linking of PVME: Preparation of the Hydrogels. We used radiation-induced cross-linking of PVME in solutions of 10 wt % PVME in deionized water. The solutions were flushed with nitrogen and then sealed. The sample tubes had a free space above the solution to allow room for expansion of the sample during irradiation. The samples were irradiated at 16 °C by high-energy X-rays with a dose of 80 kGy. The radiation was generated by an electron accellerator. After irradiation, the gels were removed from the sample holder and non-cross-linked polymer was extracted with acetone in a Soxhlet apparatus during several days. After the extraction the samples were dried in a vacuum. A more extensive description of the cross-linking method has been given by Moerkerke et al.[10]

Swelling equilibrium at a given temperature was determined by allowing the dry network to imbibe the equilibrium amount of the two solvent components from a large excess of mixed solvent. The gel was surface-dried and weighed. The solvent was distilled out of the swollen gel and analyzed for its composition by GC.

Results

1. Water/THF/Linear PVME. Cloud points as a function of the PVME concentration are plotted in Figure 2 for various water/THF compositions of the mixed solvent, the THF content of which varied from 0 to 0.8 in weight fraction w_2 (mole fraction range of 0−0.5). We observe that the addition of THF first shifts the α-side of the miscibility gap toward lower temperatures. This downward shift is changed into a sharp increase when the THF content of the mixed solvent exceeds a weight fraction of $w_2 = 0.6$. At $w_2 > 0.85$ complete ternary miscibility pertains. At $w_2 = 0$, we note a marked bimodality which disappears gradually when the THF concentration in the mixed solvent is increased. This process occurs via two less marked mimima at $w_2 = 0.1$ and 0.2 and a minimum plus shoulder at $w_2 = 0.3-0.6$.

Despite possible inaccuracies in the individual cloud points, the general pattern conveyed by the data in Figure 2 is a that of a transition from bimodal to unimodal LCST curves, passing though a temperature minimum at about 18 °C. This is all we need for the qualitative classic thermodynamic explanation presented below.

It is helpful to consider ternary isotherms. Smooth curves were drawn through the data in Figure 2 and w_3 readings were taken at constant w_1/w_2 ratio or w_2 readings at constant w_3, as illustrated in Figure 3 (routes 1 and 2, respectively). Some characteristic ternary isotherms so obtained are shown in Figure 4. At 19 °C we notice a small closed miscibility loop. It must have developed out of a ternary LCST below 19 °C, located aproximately at $w_2 \approx 0.55$ and $w_3 \approx 0.2$; the system was found to be homogeneous at 18 °C. Increasing temperature causes the closed loop to become larger, and touch the water/PVME axis slightly below 32 °C in the minimum of the β-gap in water/PVME. (see Figure 2a, top curve). At 34 °C the ternary loop touches the binary water/PVME axis in the minimum of the binary α-gap. The binary three-phase line is virtually nonvariant and exists at 36 °C only. This three-phase equilibrium does not disappear upon addition of THF but moves into the composition triangle, as discussed below.

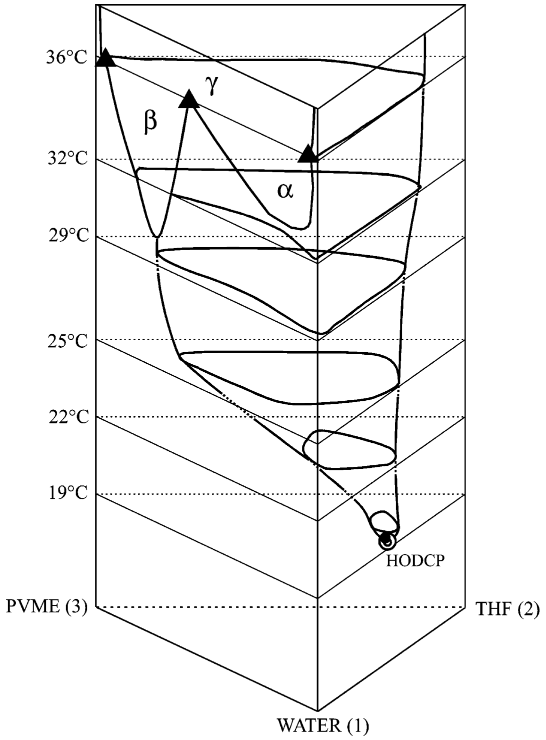

Figure 5. Three-dimensional representation of partial miscibility relations in the system water/THF/linear PVME: (▲−▲) three-liquid-phase equilibrium; (⊙) HODCP, homogeneous double critical point.

At higher temperatures the ternary gap extends still further, leaving only a very narrow range of miscibility along the water/THF axis. The fact that THF/PVME is miscible in all proportions (at any of the temperatures considered here) forces the ternary gap away from the THF/PVME axis. On the water/THF side, also a completely miscible system at the considered temperatures, the ternary gap comes remarkably close to the water/THF axis. A possible consequence of this behavior will be advanced in the discussion.

We have indicated some experimental data points on coexisting-phase compositions at 34, 36, and 37 °C. It is seen in Figure 4 that such concentrations do not always coincide with cloud-point compositions. Although the molar-mass distribution in the polymer might make itself noted here,[4] we rather think that the way in which the ternaries have been constructed is responsible for the not-too-large deviations. The orientation of the tie lines is a significant indicator (see below).

Figure 5 collects the information gained for the linear system in a three-dimensional diagram demonstrating the peculiar pattern of ternary phase relations in the present system.

2. Water/THF/Cross-Linked PVME. Figure 6 shows the swelling data we collected on the system water/THF/cross-linked PVME at 20, 25, and 29 °C. A curve

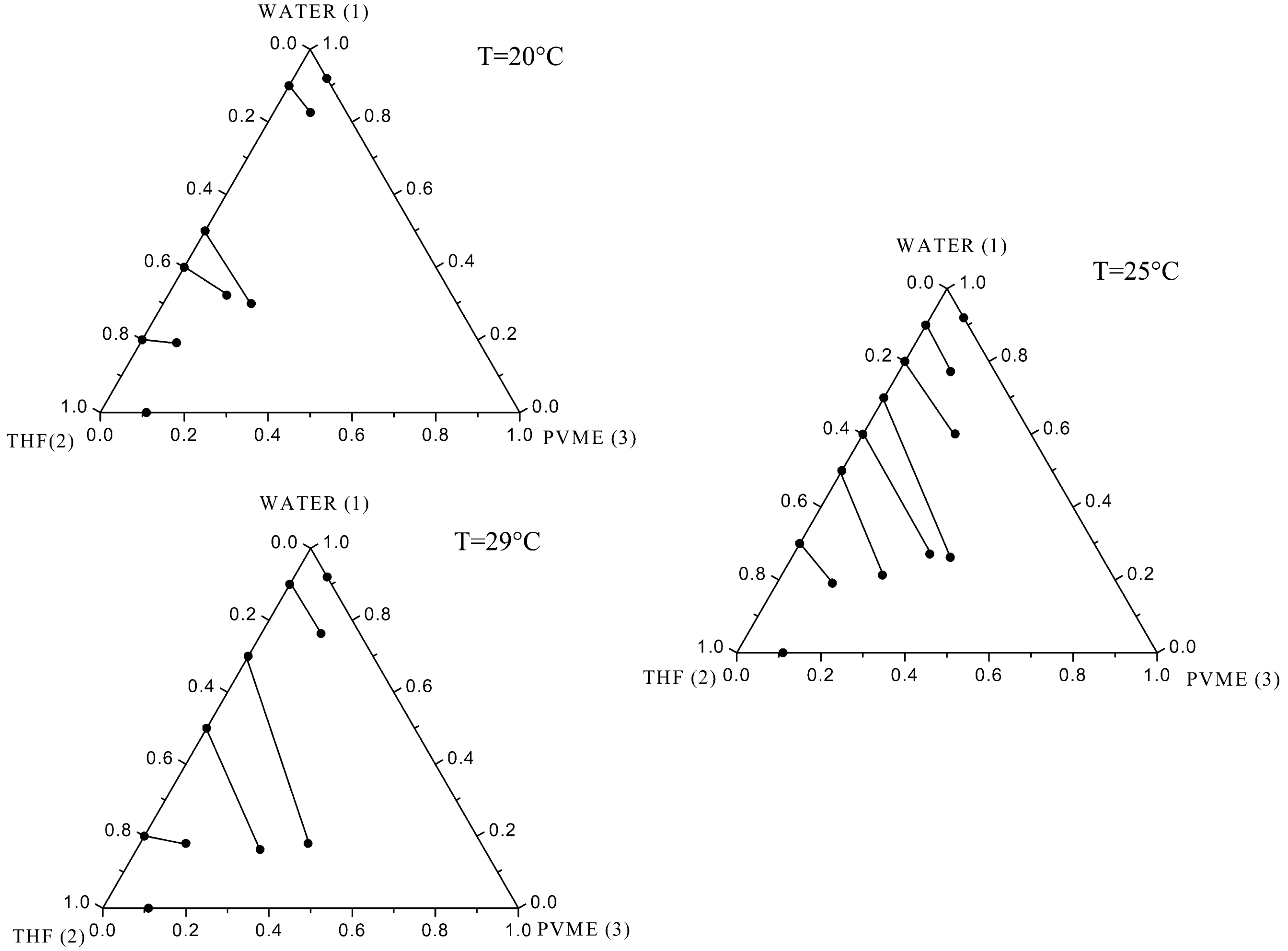

Figure 6. Swelling data for the ternary system water/THF/cross-linked PVME at 20, 25, and 29 °C: (●−●) coexisting-phase compositions and tie lines.

connecting the compositions of gels, swollen to equilibrium, is called the swelling curve and usually connects the two binary swelling equilibria on the THF/PVME and water/PVME sides by an only slightly curved line.[4] (Swelling curves have not been drawn in Figure 6.) The data points indicate a distortion of the swelling curve, which becomes more pronounced upon an increase of temperature. Note that the two swollen networks at 20 °C, equilibrating with the solvent mixtures at $w_2^0 = 0.5$ and 0.6, do not differ much in composition. However, the two equilibria are significantly different, as is indicated by the disparity between the w_2^0 values. A similar instance can be seen at 25 °C ($w_2^0 = 0.3$ and 0.4). Therefore, we feel assured that the observed distortions are real.

Discussion

1. Linear Polymer. Many years ago Korteweg and Schreinemakers discussed the various consequences an interference of two miscibility gaps in a ternary system will have.[13−15] These considerations supply a useful rationale for the development of phase relations in the system water/THF/PVME, as collected in Figure 4.

It should be noted that the subsequent analysis is based on the following indisputable facts. First, we have the system water−PVME the bimodal LCST behavior of which has been established as far as the β-gap is concerned. The α-gap shows its usual dependence on these parameters, but this effect is negligible in present context. Further, the system exhibits three critical points.[4−6,10] Second, the data of Figure 2 demonstrate that addition of THF causes the bimodality to vanish gradually and a ternary minimum to occur in the ternary miscibility gap at about 18 °C. The latter state represents a so-called homogeneous double critical point (HODCP)[13] below which the system is completely miscible.

Figure 7 reveals implications that must be involved. Starting with the completely miscible system at 18 °C and heating, we first encounter the HODCP at 18 °C < T < 19 °C (I). Upon a change in temperature, it forms two ternary critical points, C_β and C_t, identical in stability. In this case both are stable and demarcate the closed miscibility loop (II).

We postulate that, at a unique temperature between 19 and 29 °C (III), the ternary loop develops a so-called heterogeneous double critical point (HEDCP[13]) on its spinodal curve. If the temperature is raised to about 29 °C, the HEDCP splits up into a metastable critical point C_α and an unstable one, C_u, demarcating a secondary binodal, which is initially confined to the area within the ternary miscibility loop.

Korteweg and Schreinemakers' elegant considerations[13−15] are full of fine details, such as the crescent shape of the secondary binodal and the location of the tie lines (see Figure 7, detail at $T \sim 29$ °C). Such binodals refer to metastable equilibria m/m if both nodes

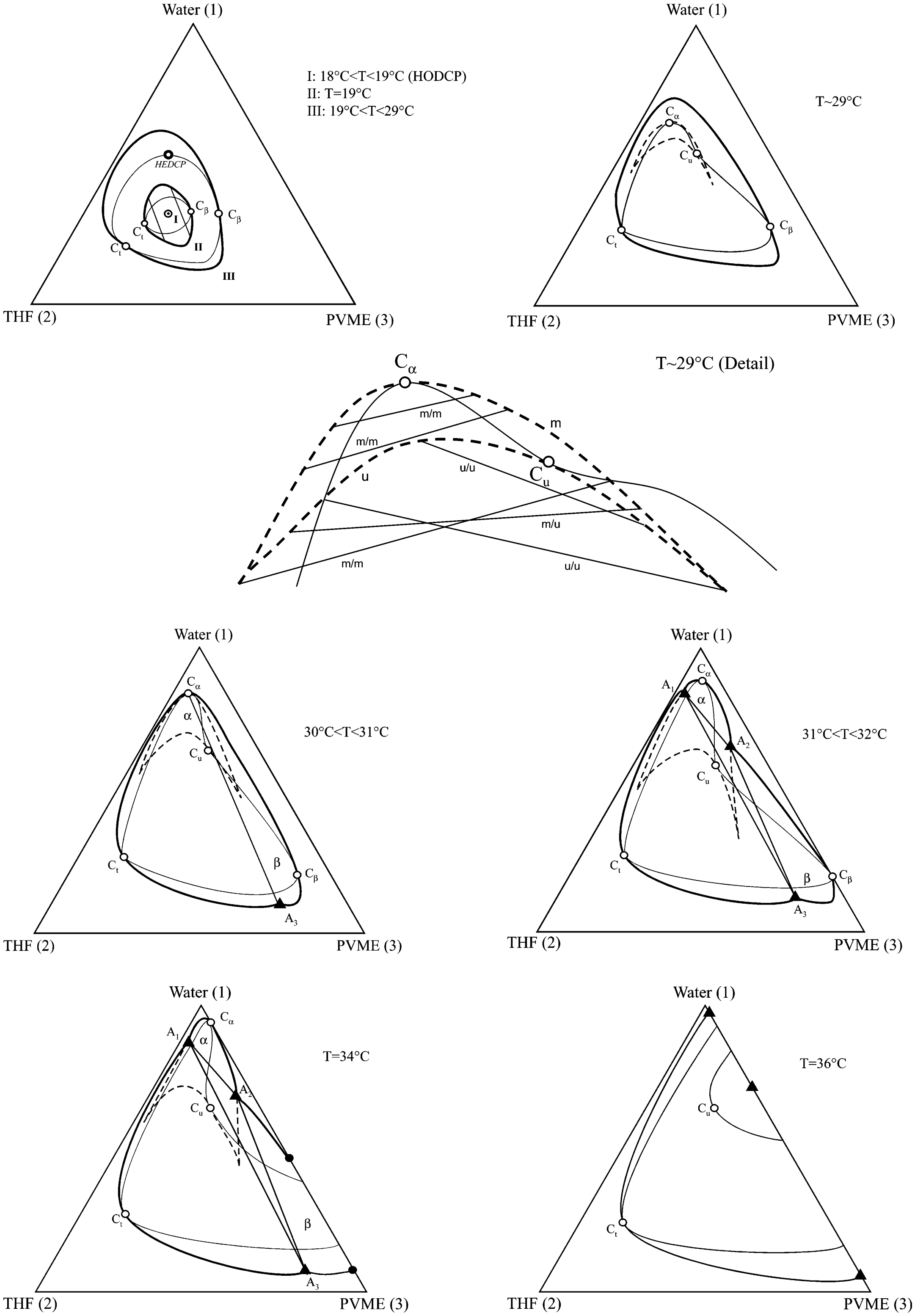

Figure 7. Partial miscibility patterns for water/THF/linear PVME according to classic rules (schematic). Key: thick curves, cloud-point curves; thin curves, spinodals; (○) C_α, C_β, C_t, C_u = critical points; (▲) A_1, A_2, A_3 = three-phase equilibrium (see text); (⊙) homogeneous and (thick ring) heterogeneous double critical points (HODCP and HEDCP, respectively); light straight lines, tie lines; dashed curves, metastable or unstable secondary binodals.

(coexisting-phase compositions) lie outside the spinodal curve on positively curved parts of the Gibbs free-energy surface for the considered temperature. Within the spinodal domain this curvature is negative in at least one direction and nodes, both lying within that domain, refer to unstable equilibria (u/u) that will spontaneously convert to a more stable state by spinodal decomposition. The m/m and u/u equilibria are separated by sections of the crescent curves extending beyond their intersections with the spinodal, where m/u equilibria pertain that are also susceptible to spinodal decomposition. Korteweg and Schreinemakers proved that the two cusps occurring on the crescent represent nodes in equilibrium with the compositions at which the spinodal

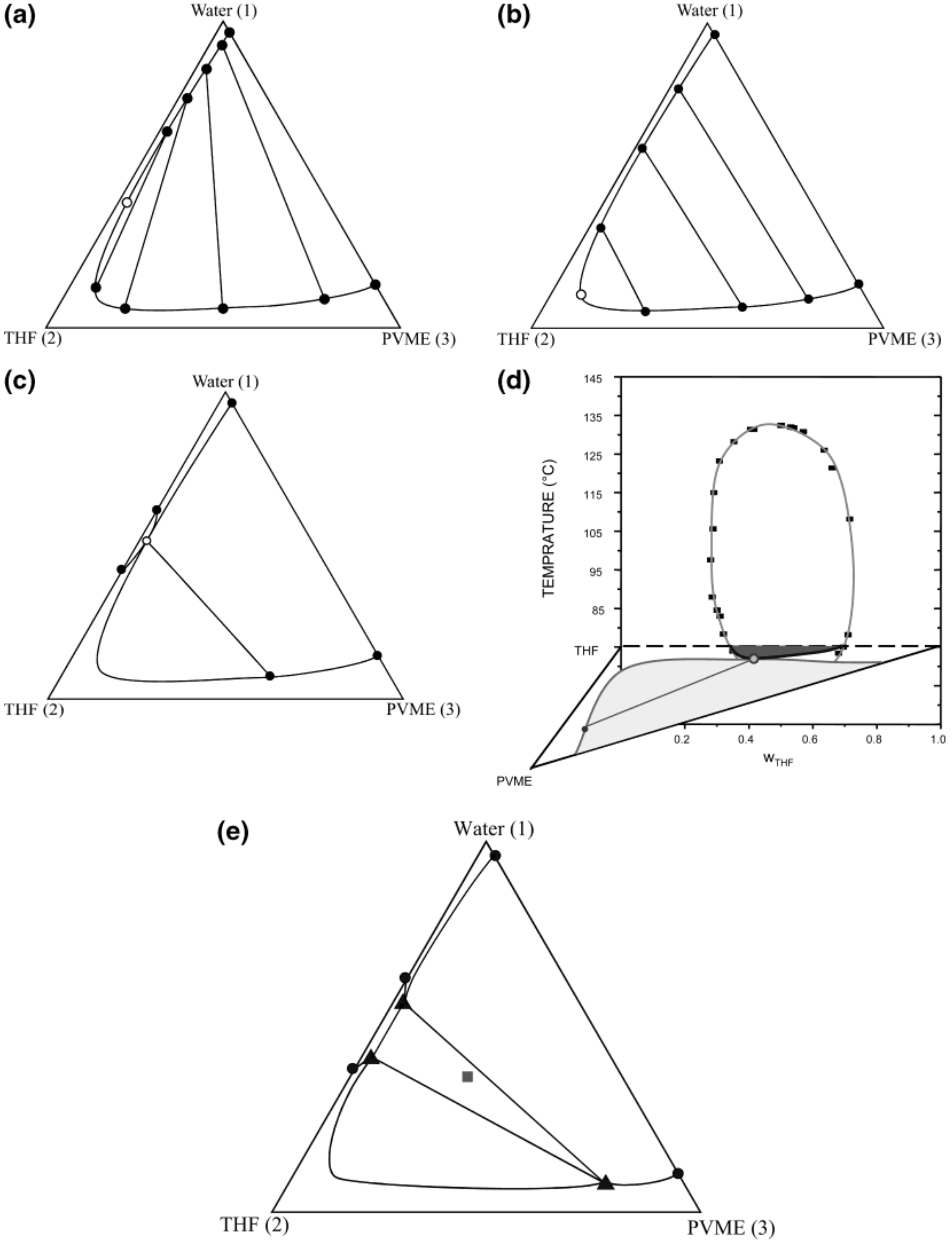

Figure 8. (a, b) Conceivable patterns of tie lines for the ternary system water/THF/linear PVME at about 70 °C: (○) critical points; (●–●) tie lines. (c) Interference of the water/THF miscibility loop with the ternary miscibility gap for tie-line pattern b at about 75 °C: (○) critical point. The shallow range of miscibility on the water/THF side was exaggerated for the sake of clarity. (d) Three-dimensional illustration of phase relations at about 75 °C. (e) Three-phase separation according to pattern b at $T \approx 80$ °C: (■) system investigated experimentally. $w_1 = 0.35$, $w_2 = 0.35$, and $w_3 = 0.30$.

intersects the crescent-shaped binodal (see also ref 16).

At 30 °C < T < 31 °C, C_α reaches the stable loop and becomes a stable critical point, at which the crescent−shaped binodal touches the ternary loop. By virtue of the latter, critical phase C_α now coexists with phase A_3. Such unique states are by no means rare and were called the "critical end point" by van der Waals[17] because lowering of the temperature (in the present case) will cause the critical point to vanish. An increase of the temperature (31 °C < T < 32 °C) will lead to C_α to extend outside the stable ternary loop, so that a triangular three−phase region must come into existence, demarcated by its corners A_1, A_2, and A_3. In the meantime C_β has moved over to the water−PVME axis, merging at 31 °C < T < 32 °C with the critical point C_β of the binary β-gap (see also Figure 2a, top curve). Raising the temperature to 34 °C will bring C_β outside the composition triangle and, on further heating, also C_α and, finally, C_u. At 36 °C the three-phase triangle has reached the water-PVME axis (nonvariant binary three−phase equilibrium; Figures 1a and 2a, top curve).

Note that the phenomena described above are dictated by the number of ternary critical points that must be

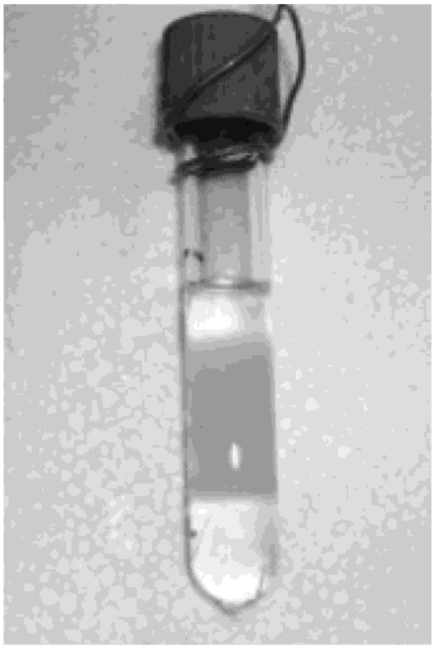

Figure 9. Three-liquid-phase equilibrium in the system water/THF/linear PVME with overall composition, after 48 h of equilibrating at 80 °C.

present on account of the three that have to accompany the type III behavior in the binary system water/PVME (Figures 1a and 2a),[18] as well as the two that have to accompany a ternary miscibility gap.

The location of the tie lines in Figure 4 at 34, 36, and 37 °C not only offered evidence that we may expect the two critical points on the closed gaps to occur approximately at the locations indicated in Figure 7 but also give us a clue as to what must be expected to happen at temperatures above those considered so far. The binary system water/THF contains a closed miscibility gap with critical (T/w_{2c}) coordinates at (71.8/0.53) and (137.1/0.48).[19] The course of the data in Figure 4 indicates that the narrow range of miscibility adjoining the water/THF axis at higher temperatures may be reasonably expected to continue up to the miscibility gap of water/THF. Assuming that the orientation of the ternary tie lines remains essentially unaltered, we must expect a critical end−point situation to arise at the LCST of water/THF. Figure 8 illustrates this schematically. A straightforward coincidence of C_t with the lower critical point of the water/THF loop would require the tie lines in the ternary gap to fan out as indicated in Figure 8a. We have seen, however, that the pattern sketched in Figure 8b is more probable. If we are right, a critical end-point mechanism should be operative, and show up in a well-noticeable three−phase separation at $T > 71.8$ °C (Figure 8, parts c and d). We checked this at 80 °C (situation depicted schematically by Figure 8e) and found our prediction, based on purely classical arguments, to be verified by the experiment. This is illustrated in Figure 9 which shows the three liquid phases formed at 80 °C in the water/THF/PVME mixture indicated by the square symbol in Figure 8e.

Homogeneous and heterogeneous double critical points in polymeric systems have been discussed in detail by Šolc and Yang.[20,21]

2. Cross-Linked Polymer. Type II and type III behaviors have both been found to have their analogues in the cross-linked variety of the polymer.[3,4,8−10] For the type III system water/PVME, the analogue of the β-gap consists of the occurrence of an equilibrium among two network phases, differing in degree of swelling, located close to but not exactly in the temperature−concentration range where the linear system exhibits its β-gap (see Figure 1).

We assume that the ternary system water/THF/PVME behaves in a similar fashion. This would imply that the deformation of the swelling curves in Figure 6 is related to a ternary closed miscibility gap, penetrating down to about 18 °C.

It is seen in Figure 1b that the swelling curve and the left-hand part of the curve demarcating the β-gap (equilibrium between two network phases, n_k and n_l, differing in degree of swelling) approach one another if the temperature is raised from $T < T_3$ to T_3, where the two curves intersect and equilibrium pertains between pure solvent and n_k, pure solvent and n_l, and n_k and n_l. We might expect the temperature and concentration location of the HODCP not to differ much from that in the linear system, and to lead to the development of a closed n_k/n_l loop upon an increase in temperature. This loop will then approach the ternary swelling curve until it touches the latter sideways. In this situation the two tie lines involved must be aligned.[14] Sideways merging of miscibility gaps without direct involvement of critical points has been described elsewhere.[16,22−24]

It is illustrated in Figure 10 that further heating will cause the closed loop to penetrate the swelling curve which gives rise to two three-phase triangles, separated by a two-phase domain s/n_l of equilibrium between mixed solvent and shrunken network phases. These two three−phase triangles have so far escaped direct experimental observation. However, we note that, if they do appear, they will force the tie lines related to the swelling curve to fan out. The data in Figure 6 show that such behavior was actually observed in the lower parts of the diagrams and offers support to the mechanism advanced here.

3. Co-Nonsolvency. With co-solvency, a mixture of two poor solvents is found to act as a good solvent, provided their cohesive energy densities are larger and smaller than that of the polymer. The effect can thus be attributed to the energy of mixing being an average value that does not affect the ternary Gibbs free energy as unfavorably as it does in the two binary cases where it leads to demixing.

If the addition of a good solvent to a solution of a polymer in another good solvent causes a marked decrease of the miscibility, one speaks of co-nonsolvency.[25−28] Apparently, the present system is a case in point.

An explanation of co-nonsolvency is less obvious. Winnik et al.[26−27] reported the system water/methanol/poly(*N*-isopropylacrylamide) (PNIPA) to show such behavior and suggested that a solvation layer of highly organized water molecules causes the PNIPA chains in water to be stiffer than in methanol where coil conformations pertain. With water, the entropy is then smaller than with methanol, but the energy will probably be smaller too, because the contacts between free water molecules and the chains are mainly free water/solvated water contacts. Upon addition of methanol, the solvation layer is gradually destroyed and the poor-solvent character that water has for the “dry” polymer chains becomes predominant, to disappear with the further addition of good solvent methanol.

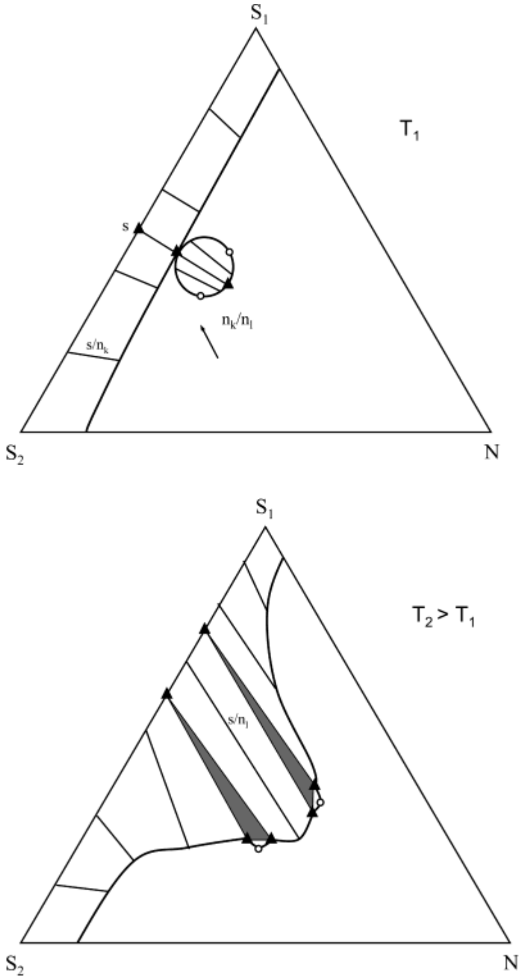

Figure 10. Schematic illustration of sideways merging without direct involvement of critical states, for a cross-linked polymer P swollen in a mixed solvent s (components S_1 and S_2): thin lines, tie lines; n_a/n_l, s/n_k, and s/n_l, two-phase-equilibrium domain; shaded areas demarcated by ▲, three−phase equilibrium; (○) critical point.

This explanation may also be valid for the present system. Recent experimental evidence suggests a strong attractive interaction between water and PVME.[29] THF may be expected to have a destructive influence on this interaction, which leads to a decreased solubility of the polymer.

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References and Notes

(1) Dušek, K.; Patterson, D. *J. Polym. Sci.* **1968**, *6*, 1209.
(2) Dušek, K., Ed. Responsive Gels. *Adv. Polym. Sci.* **1993**, *109*; **1993**, *110*.
(3) Moerkerke, R.; Koningsveld, R.; Berghmans, H.; Dušek, K.; Šolc, K.; *Macromolecules* **1995**, *28*, 1103.
(4) Koningsveld, R.; Stockmayer, W. H.; Nies, E. *Polymer Phase Diagrams*; Oxford University Press: Oxford, England, 2001.
(5) Schäfer-Soenen, H.; Moerkerke, R.; Berghmans, H.; Koningsveld, R.; Dušek, K.; Šolc, K. *Macromolecules* **1997**, *30*, 410.
(6) Šolc, K.; Dušek, K.; Koningsveld, R.; Berghmans, H. *Collect. Czech. Chem. Commun.* **1995**, *60*, 1661.
(7) Afroze, F.; Nies, E.; Berghmans, H. *J. Mol. Struct.* **2000**, *554*, 55.
(8) Meeussen, F. Ph.D. Thesis, Catholic University of Leuven, 2002.
(9) Moerkerke, R. Ph.D. Thesis, Catholic University of Leuven, 1998.
(10) Moerkerke, R.; Meeussen, F.; Koningsveld, R.; Berghmans, H.; Mondelaers, W.; Schacht, E.; Dušek, K.; Šolc, K. *Macromolecules* **1998**, *31*, 2223.
(11) Moerkerke, R.; Koningsveld, R.; Nies, E.; Berghmans, H.; Dušek, K.; Šolc, K. In *Chemical and Physical Networks*; Te Nijenhuis, K.; Mijs, W. J., Eds.; Wiley: New York, 1998; Vol. 1, p 463.
(12) Arnauts, J.; De Cooman, R.; Vandeweerdt, P.; Koningsveld, R.; Berghmans, H. *Thermochim. Acta*, **1994**, *335*, 1.
(13) Korteweg, D. J. *Sitzungsber. Kais. Akad. Wissensch. Wien, Math.-Naturwiss. Kl., Abt. A*, **1889**, *98*, 1154.
(14) Schreinemakers, F. A. H. In *Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre, Vol. III, Die ternären Gleichgewichte, Part* 2, *Systeme mit zwei und mehr Flüssigkeiten ohne Mischkristalle und ohne Dampf*; Bakhuis Roozeboom, H. W., Ed.; Vieweg: Braunschweig, Germany, 1913.
(15) Korteweg, D. J.; Schreinemakers, F. A. H. *Verh. Kon. Acad. Wetensch. Amsterdam* **1911**, *20*, 476, 490.
(16) Šolc, K.; Koningsveld, R. *J. Phys. Chem.* **1992**, *96*, 4056.
(17) See: van der Waals, J. D.; Kohnstamm, Ph. D. *Lehrbuch der Thermodynamik*; Barth: Leipzig, Germany, 1912; Vol. II.
(18) Ref 4, p 149.
(19) Matouš, J.; Novák, J. P.; Šobr, J.; Pick, J. *Collect. Czech Chem. Commun.* **1972**, *37*, 2653.
(20) Šolc, K. *Macromolecules* **1986**, *19*, 1166; **1987**, *20*, 2506.
(21) Šolc, K.; Yang, Y. C. *Macromolecules* **1988**, *21*, 829.
(22) Šolc, K.; Stockmayer, W. H.; Lipson, Koningsveld, R. *Mulitiphase Macromolecular Systems*; Culbertson, B. M., Ed.; Plenum: NewYork, 1989, p 5.
(23) Vanhee, S. Ph.D. Thesis, Catholic University of Leuven, 1994.
(24) Vanhee, S.; Koningsveld, R.; Berghmans, H.; Šolc, K.; Stockmayer, W. H. *Macromolecules* **2000**, *33*, 3924.
(25) Wolf, B. A.; Wilms, M. M. *Makromol. Chem.* **1978**, *179*, 2265.
(26) Winnik, F. M.; Ringsdorf, H.; Venzmer, J. *Macromolecules* **1990**, *23*, 2415.
(27) Winnik, F. M.; Ottaviani, M. F.; Bossmann, S. H.; Pan, W.; Garcia-Garibay, M.; Turo, N. J. *Macromolecules* **1993**, *26*, 4577.
(28) Schild, H. G.; Muthukumar, M.; Tirrell, D. A. *Macromolecules* **1991**, *24*, 948.
(29) Zang, J.; Bergé, B.; Meeussen, F.; Nies, E.; Berghmans, H.; Shen, D. *Macromolecules* **2003**, *36*, 9145.

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