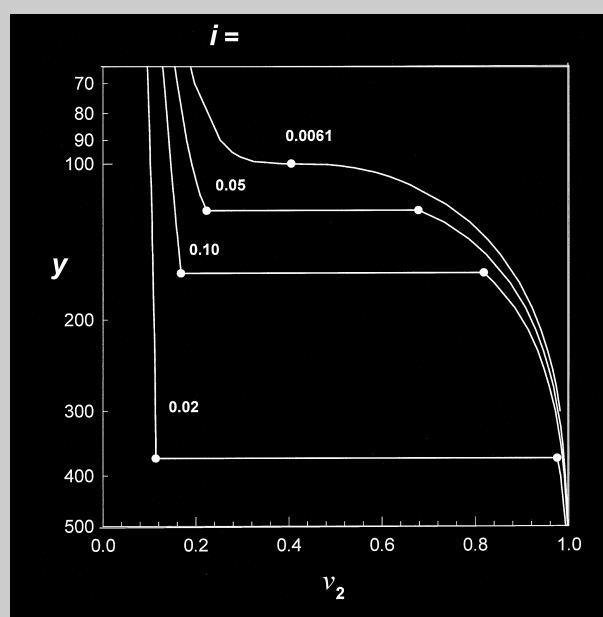


Full Paper: A strong concentration dependence of the solvent–polymer interaction parameter χ is known to be a requirement for the first-order volume phase transition in uncharged polymer networks in solvents. Another possibility for the observation of phase transition in nonpolar networks is to increase the number of lattice sites occupied by a solvent molecule. This possibility has been indicated earlier and is worked out in detail in this paper. Using the theory of swelling equilibrium, we examine the polymer network systems immersed in a polymer melt. The critical conditions for the phase transition in both uncharged and ionic networks are described.

Variation of the crosslinked polymer volume fraction v_2 with the number of segments of linear polymer y . Calculations were for networks with various charge densities i indicated in the Figure and using $N = 79.5$, $\chi = 0.014979$, and $v_2^0 = 0.05$. The network with $i = 0.0061$ is in the critical state in polymer melt of $y = 100$.



Volume Phase Transition of Polymer Networks in Polymeric Solvents

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Introduction

Polymer gels are important materials of both fundamental and technological interest. Investigations of the swelling behavior of hydrophilic gels called hydrogels have been reported repeatedly in the last four decades. In recent years attention has turned to the swelling and collapse phenomena that are observed when a hydrogel network is brought into contact with a solvent. The possibility of a first-order phase transition in polymer networks has been predicted theoretically and verified experimentally on ionic acrylamide-based hydrogels swollen in solvents.^[1–3] In such a transition, a change in a variable such as pH, solvent composition or temperature can induce a discontinuous change in the volume of the swollen gel.^[4]

As Tanaka and others have shown, a small proportion of ionizable units on the polymer chains seems to be essential

for a discontinuous shrinkage of the gel.^[4] Thus, the phenomenon of phase transition in gels has been attributed to the polyelectrolyte nature of the network chains. More detailed calculations indicated that a strong concentration dependence of the polymer–solvent interaction parameter χ may also induce a discontinuous shrinkage of the swollen gel, even in nonpolar matrices.^[5–7] However, experimental verification of this prediction is difficult to achieve due to the fact that the indicated requirement for the polymer collapse is rare for real polymer–solvent systems.^[8,9] Another possibility for the observation of phase transition in nonpolar networks is to increase the number of lattice sites occupied by a solvent molecule. This possibility has been indicated earlier by Vasilevskaya and Khokhlov.^[10] It was shown that even uncharged networks immersed in polymer solutions or melts may undergo first-order phase transitions.

Here, we examine the system consisting of a polymer network and linear polymer chains using the theory of equilibrium swelling. Although the main emphasis is placed on uncharged networks, we also discuss the case of ionic networks. As was observed by Vasilevskaya and Khokhlov, the uncharged networks undergo first-order volume phase transition in a melt of linear polymer chains if the network parameters and the chain length of linear polymer are suitably adjusted.^[10] The critical conditions for the phase transition of both uncharged and ionic networks are calculated.

Theory

Swelling of a polymer network is governed by at least three free energy terms; the changes in the free energy of mixing ΔG_m , in the free energy of elastic deformation ΔG_{el} , and in the free energy of electrostatic interactions ΔG_i :

$$\Delta G = \Delta G_m + \Delta G_{el} + \Delta G_i \quad (1)$$

The Flory–Huggins expression for the free energy of mixing ΔG_m for a system of a polymer network and linear polymer chains is:^[11]

$$\Delta G_m = RT(n_1 \ln v_1 + n_2 \ln v_2 + y n_1 v_2 \chi) \quad (2)$$

where R is the gas constant, T is temperature, n_j and v_j are the number of moles and the volume fraction, respectively, of the component j ($j = 1$ and 2 for linear polymer and polymer network, respectively, and from the material balance $v_1 = 1 - v_2$), χ is the interaction parameter between linear and crosslinked polymer, and y is the number of lattice sites occupied by a linear polymer chain, i.e., the number of segments in the linear polymer. (We assume monodisperse linear polymers). According to the affine network theory, the free energy of elastic deformation ΔG_{el} is given by:^[11]

$$\Delta G_{el} = \frac{3}{2} RT \left(\frac{V}{NV_1} \right) (a^2 - 1 - \ln a) \quad (3)$$

where V is the volume of crosslinked polymer, N is the average number of segments in the network chains, V_1 is the molar volume of segment, a is the linear swelling ratio with respect to the after-synthesis stage of the gel, i.e.,

$$a = \left(\frac{v_2^0}{v_2} \right)^{1/3} \quad (3a)$$

where v_2^0 is the volume fraction of polymer network at the preparation conditions. The existence of fixed ions on the network chains results in nonequal distribution of mobile counterions between the inside and outside the gel. For

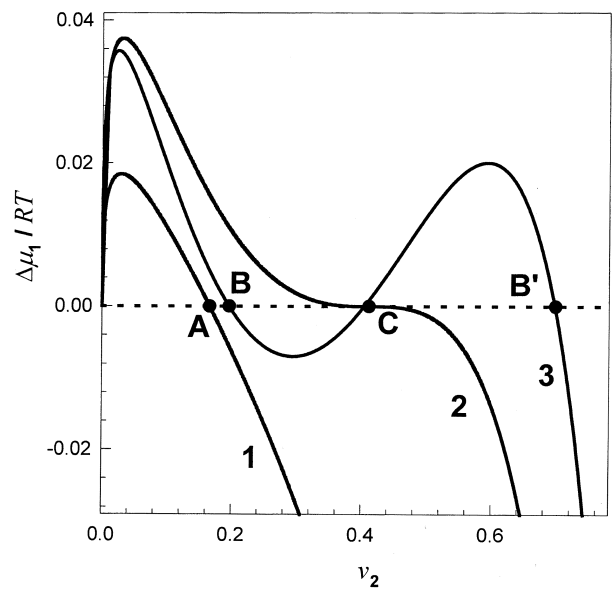


Figure 1. Reduced chemical potential of linear polymer in the gel $\Delta\mu_1$ calculated for $i = 0$, $N = 74.43$, $\chi = 0.015323$ shown as a function of the crosslinked polymer volume fraction v_2 . Curve 1: $v_2^0 = 0.05$, $y = 50$. Curve 2: $v_2^0 = 0.05$, $y = 100$. Curve 3: $v_2^0 = 0.04$, $y = 119.63$.

weakly charged ionic gels, the electrostatic interactions can be neglected and the ionic contribution (ΔG_i) may be written as follows:^[11]

$$\Delta G_i = RT \left(\frac{i}{N} \frac{v_2}{v_1} n_1 \right) \ln \left(\frac{i}{N} v_2 \right) \quad (4)$$

where i is the number of ionic segments in the network chain. Note that the first and second terms in parenthesis are the total number of mobile counter ions inside the gel and their concentration, respectively. Substitution of Equation (2)–(4) into Equation (1) and differentiating with respect to the number of moles of linear polymer n_1 yield the following equation for the reduced chemical potential of linear polymer $\Delta\mu_1$:

$$\frac{\Delta\mu_1}{RT} = \ln(1 - v_2) + v_2 + y\chi v_2^2 + yN^{-1}v_2(a^2 - 0.5 - i) \quad (5)$$

Illustrative calculations of the reduced chemical potential $\Delta\mu_1$ according to Equation (5) for uncharged networks ($i = 0$) are shown in Figure 1 as a function of the crosslinked polymer volume fraction v_2 . Calculations were for $N = 74.43$ and $\chi = 0.015323$. Curves 1 and 2 were calculated for $v_2^0 = 0.05$. For short linear chains, i.e., for $y = 50$, (Curve 1), the network immersed in polymer melt is in a swollen state and has an equilibrium concentration $v_2 = 0.166$ (A in Figure 1). Curve 2 was calculated for $y = 100$, which yields a critical behavior at $\Delta\mu_1 = 0$

(C). Curve 3 was calculated using $v_2^0 = 0.04$ and $y = 119.63$, yielding a three phase equilibrium, i.e., one swollen network phase with $v_2 = 0.196$, the other collapsed network phase with $v_2 = 0.697$ (B and B', respectively), in coexistence with pure linear polymer ($v_2 = 0$).

At critical interaction, in this case at point C in Figure 1, both the first and second derivatives of the chemical potential $\Delta\mu_1$ with respect to v_2 become zero. Assuming that χ parameter is concentration independent, one obtains from Equation (5) the following two equations for the critical state of the network:

$$\frac{1}{yRT} \frac{\partial \Delta\mu_1}{\partial v_2} = -v_2[y(1 - v_2)]^{-1} + 2\chi v_2 + N^{-1} \left(\frac{1}{3} \alpha^2 - \frac{1}{2} - i \right) = 0 \quad (6)$$

$$\frac{1}{yRT} \frac{\partial^2 \Delta\mu_1}{\partial v_2^2} = -[y(1 - v_2)^2]^{-1} + 2\chi + \frac{2}{9} N^{-1} \alpha^2 / v_2 = 0 \quad (7)$$

Solutions of Equation (6) and (7) yield the crosslink density N_{cr} and the interaction parameter χ_{cr} at the critical point as:

$$N_{cr} = \frac{y(1 - v_2)^2 [9(1 + 2i) - 10\alpha^2]}{18v_2^2} \quad (8)$$

$$\chi_{cr} = \frac{1}{y(1 - v_2)^2} \left(\frac{1}{2} + \frac{2v_2\alpha^2}{9(1 + 2i) - 10\alpha^2} \right) \quad (9)$$

If the polymer network is in thermodynamic equilibrium with the linear chains, the reduced chemical potential of linear polymer $\Delta\mu_1$ will vanish. Thus, equating $\Delta\mu_1$ to zero, Equation (5), (8), and (9) can be solved to yield N_{cr}/y , $y\chi_{cr}$, and v_2 at the critical point, with i and v_2^0 as independent parameters.

The passage from the critical to the triphasic region, in which two gel phases coexist with a pure linear polymer phase is manifested by the appearance of van der Waals loop in the dependence of the excess chemical potential of linear polymer $\Delta\mu_1$ on the crosslinked polymer concentration v_2 , as illustrated in Figure 1 (Curve 3). When the loop appears in this dependence, the stability conditions of the coexisting phases and their concentrations can be calculated by using the Maxwell construction. A triphasic equilibrium requires the conditions:

$$\Delta\mu_1(v_2') = \Delta\mu_1(v_2'') = 0 \quad (10a)$$

and

$$\Delta\mu_2(v_2') = \Delta\mu_2(v_2'') \quad (10b)$$

where v_2' and v_2'' are the volume fractions of crosslinked polymer in the coexisting phases and $\Delta\mu_2$ is the reduced chemical potential of a polymer network segment. Equation (10b) can be replaced with the equivalent condition:^[12]

$$\int_{v_2'}^{v_2''} \Delta\mu_1 v_2^{-2} dv_2 = 0 \quad (10c)$$

Equation (10c) shows that Maxwell's construction can be performed on the dependence of $\Delta\mu_1 v_2^{-2}$ on v_2 . For instance, the points B and B' on Curve 3 in Figure 1 were calculated by use of Equation (10a) and (10c) and they represent the volume fractions of crosslinked polymer in the coexisting phases (v_2' and v_2''), in equilibrium with pure linear polymer phase.

Results and Discussion

Uncharged Networks

In this section, critical conditions required for a first-order volume phase transition in uncharged polymer networks ($i = 0$) immersed in a polymer melt were calculated. The critical parameters evaluated were N_{cr}/y , $y\chi_{cr}$, and $v_{2,cr}$, where N_{cr}/y is the normalized chain length of the network chains, that is, the number of segments in the network chain divided by that in the linear polymer and $y\chi_{cr}$ is the interaction energy per linear chain.

Figure 2A shows the critical concentration $v_{2,cr}$ plotted as a function of the volume fraction of polymer network after its preparation v_2^0 . $v_{2,cr}$ increases with increasing v_2^0 , i.e., with a decreasing degree of dilution of the network at preparation, and, it becomes unity at $v_2^0 = 0.165$. This indicates that the uncharged network can collapse in polymer melt if $v_2^0 < 0.165$, i.e., if the network at preparation is diluted at least six-fold with a good solvent. The higher the degree of dilution of the network ($1/v_2^0$), the lower is the critical polymer concentration. In Figure 2B, the values of N_{cr}/y and $y\chi_{cr}$ are shown as functions of v_2^0 . For practical network crosslink densities ($N = 10^2$) and for linear polymer chains, that are in a liquid state at usual temperatures ($y \leq 10^1$), the normalized chain length of the network chains N/y is in the order of 10^1 . According to Figure 2, this value yields $v_2^0 < 0.02$ and $\chi < 0.07$ for the observation of critical phenomena in uncharged network-linear polymer systems. The hatched area in Figure 2 shows this region. Thus, the presence of a large amount of a diluent during the network preparation is necessary for the observation of phase transitions in uncharged networks immersed in polymer melt. An additional condition is that the interaction parameter χ between linear polymer and crosslinked polymer must have non zero but close to zero values, i.e., a phase separation could be observed if the linear polymer is slightly incompatible with the crosslinked polymer.

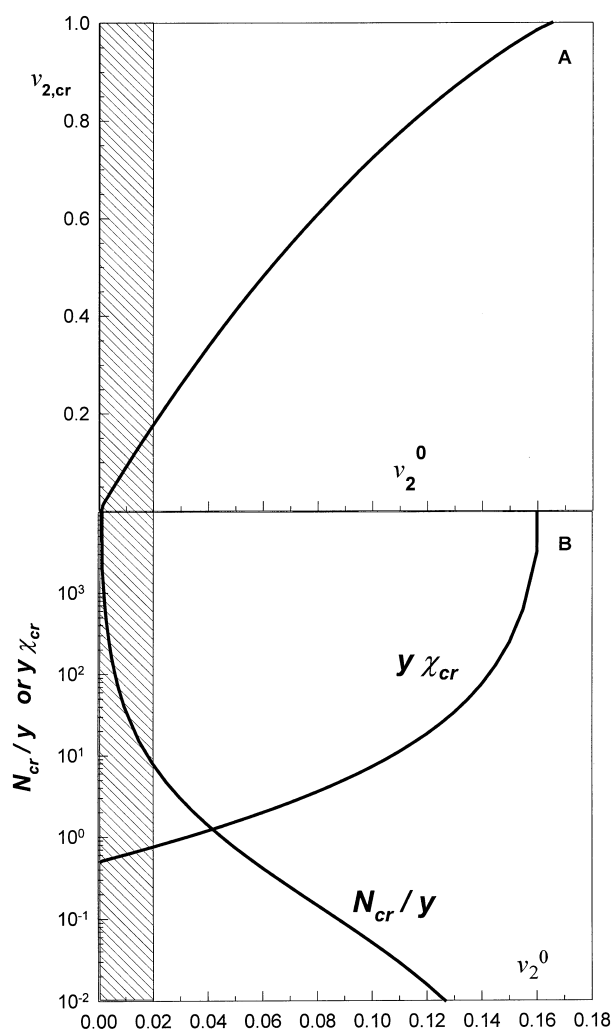


Figure 2. Critical parameters $v_{2,cr}$ (A), N_{cr}/y and $y\chi_{cr}$ (B) required for critical behavior shown as a function of the volume fraction of polymer network after its preparation v_2^0 .

Dilution during the network formation is known to produce supercoiled polymer chains in the dry state so that the increase of their dimensions during swelling does not require much loss of their conformational entropy. The entropy change during swelling of supercoiled chains can even be positive. In addition, a low χ -parameter value promotes the swelling process of the network. Opposing this, the penetration of linear chains into the network, that is, the gel swelling, is accompanied by a large loss of entropy of single chains due to the fact that the conformational entropy of linear chains in the polymer melt is much higher than that in the polymer network. The interplay of these two opposing effects provides the development of first-order volume phase transitions in uncharged networks immersed in polymer melt. Note that the contraction of such networks in low-molecular-weight solvents or solvent mixtures are always smooth.

The relationship between $y\chi_{cr}$ and N_{cr}/y required for the volume phase transition is given in Figure 3 by the

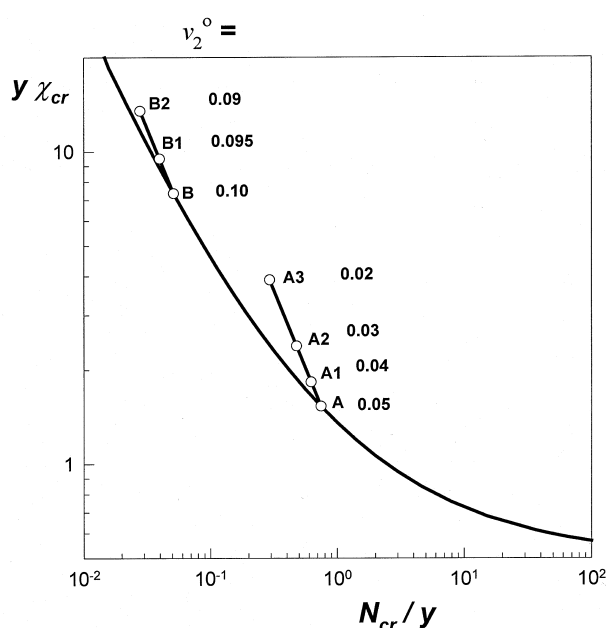


Figure 3. Relationship between $y\chi_{cr}$ and N_{cr}/y required for critical behavior in uncharged polymer networks immersed in polymer melt. Each point on the solid curve corresponds to a specific value of v_2^0 , two of which are indicated in the Figure. The network passes from the critical state to the triphasic region by decreasing the v_2^0 value, i.e., by moving from the solid curve upward along the open symbols.

solid curve. Calculations were for various values of v_2^0 . Each point on the curve corresponds to a specific value of v_2^0 . For example, points A and B were calculated for $v_2^0 = 0.05$, and 0.10, respectively. The coordinates of these points specify the parameters required for the critical state in the network, which is in equilibrium with linear chains. At point A for example, for which $v_2^0 = 0.05$, the critical parameters are $y\chi_{cr} = 1.5323$ and $N_{cr}/y = 0.7443$. Thus, a polymer network with $v_2^0 = 0.05$ is in the critical state in the melt of polymer chains of chain length $y = 100$, if $\chi_{cr} = 1.5323 \times 10^{-2}$ and $N_{cr} = 74.43$. As the degree of dilution after the gel preparation v_2^0 decreases, i.e., as one moves downward along the curve in Figure 3, the critical value of N/y increases and that of $y\chi_{cr}$ decreases. Extrapolation to $N = \infty$ yields $\chi_{cr} = (2y)^{-1}$, indicating that $\chi_{cr} > (2y)^{-1}$ is required for a phase separation of an uncharged network immersed in polymer melt.

By moving upward from the point A in Figure 3 along the open symbols denoted by A1, A2, and A3, the network passes to the triphasic region, in which two gel phases coexist with a pure linear polymer phase. Calculations using Equation (10a) and (10c) indicated that the passage from the critical to the triphasic region occurs by increasing the degree of dilution of the network at preparation, i.e., by decreasing the v_2^0 value. This is illustrated in Figure 4 as the dependence of the equilibrium volume fraction of crosslinked polymer in the gel v_2 on the chain length of linear polymer y for various values of

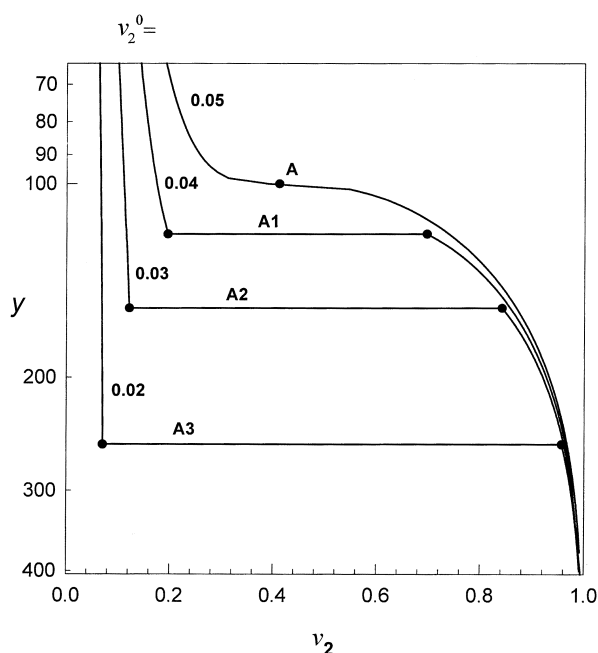


Figure 4. Variation of the crosslinked polymer volume fraction v_2 with the number of segments of linear polymer y . Calculations were for uncharged networks ($i = 0$) with $N = 74.43$, $\chi = 0.015323$, and using v_2^0 values indicated in the Figure. The network with $v_2^0 = 0.05$ is in critical state in polymer melt of $y = 100$. The symbols A, A1, A2, and A3 correspond to those in Figure 3.

v_2^0 . The symbols A, A1, A2, and A3 in this Figure correspond to those in Figure 3. It is seen that the magnitude of polymer collapse increases, as v_2^0 decreases, i.e., as the distance from the critical curve in Figure 3 increases. Simultaneously, the value of chain length y required for a phase transition shifts to higher values as v_2^0 decreases.

Ionic Networks

The effect of the number of charged units on the network chains i on the critical polymer concentration $v_{2,cr}$ is shown in Figure 5 for various values of v_2^0 . The critical polymer concentration rapidly decreases as the ionic group content of the network increases. Even bulk cross-linked networks ($v_2^0 = 1$) can collapse in the melt of polymer chains, if charged groups are present in the gel. Figure 6 shows the relationship between the critical parameters $y\chi_{cr}$ and N_{cr}/y required for the critical state in the networks. The curves were calculated by keeping v_2^0 constant and by changing the number of charged units per network chain i . Each point on the curves corresponds to a specific value of i . For example, the positions A, B, and C correspond to $i = 1.7$, 2.7, and 4.4, respectively. It is seen that, N_{cr} increases and χ_{cr} decreases as the charge density of the network increases, i.e., the collapse transition occurs easier as the number of charged units on the network chain increases. Illustrative calculations of the

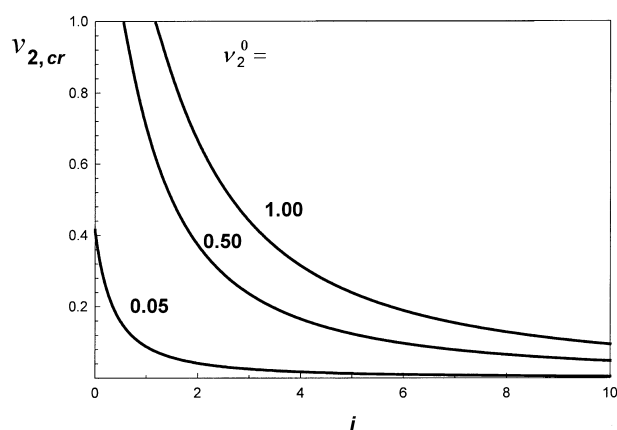


Figure 5. Critical volume fraction $v_{2,cr}$ required for critical behavior shown as a function of the number of charged units in the network chains i . Calculations were for three different values of v_2^0 .

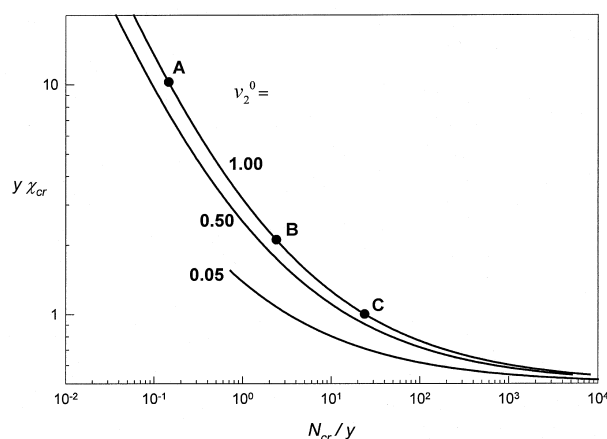


Figure 6. Relationship between $y\chi_{cr}$ and N_{cr}/y required for critical behavior in polymer networks immersed in polymer melt. The curves were calculated by keeping v_2^0 constant and by changing the number of charged units per network chain i . Each point on the curves corresponds to a specific value of i . For example, the positions A, B, and C correspond to $i = 1.7$, 2.7, and 4.4, respectively.

effect of the charge density of the network on the volume phase transition are shown in Figure 7 as the dependence of v_2 on the size of the linear polymer y . Even small amounts of charged units in the network induce first-order volume phase transitions in polymer melt.

Conclusion

In concluding, using the theory of swelling equilibrium, we have calculated the critical parameters required for a first-order volume phase transition in polymer gels immersed in polymer melt. The requirements for the critical state are a high degree of dilution of the network at preparation ($v_2^0 < 0.165$) and a slight incompatibility of the network chains with the linear polymer. Introduction of ionic units into the network facilitates the attaining of

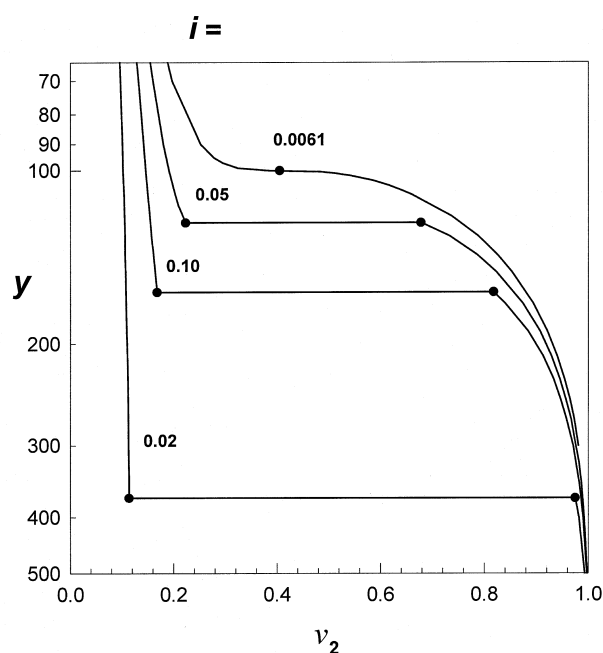


Figure 7. Variation of the crosslinked polymer volume fraction v_2 with the number of segments of linear polymer y . Calculations were for networks with various charge densities i indicated in the Figure and using $N = 79.5$, $\chi = 0.014979$, and $v_2^0 = 0.05$. The network with $i = 0.0061$ is in the critical state in polymer melt of $y = 100$.

the critical state of the network immersed in polymer melt.

It is to be noted that the phase transition described here has not been observed experimentally as yet. The system poly(*N*-isopropylacrylamide) (PNIPA)–poly(ethylene glycol) (PEG) seems to be a suitable candidate for this observation.^[13] The isopropyl groups on the network chains create attractive interactions between PNIPA and PEG segments so that PEG of molecular weight 200 $\text{g} \cdot \text{mol}^{-1}$ is a good polymeric solvent for PNIPA.^[13]

According to the present calculations, increasing the molecular weight of PEG may induce a first-order volume phase transition in the PNIPA network. Other suitable candidates for this observation would to be systems of hydrophobic networks immersed in a series of paraffin hydrocarbons of various chain lengths. Increasing number of carbon atoms in the linear molecule may induce collapse transition in the hydrophobic network.

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