Swelling and Collapse of Polymer Gel in Polymer Solutions and Melts

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ABSTRACT: Conformational changes in polymer networks swollen in solutions and melts of linear polymer chains are studied theoretically. The interaction of components is taken into account within the Flory–Huggins approximation, and the elastic free energy term is written in the Flory form. For the case of polyelectrolytic networks, the contribution of translation entropy of counterions is accounted for as well. It is shown that the variety of possible effects is not reduced to the contraction of the polymer network with the increase of concentration of linear chains. If the low molecular weight solvent is poor for the network chains, a jumpwise decollapse transition at high linear chain concentrations is possible. Discontinuous transitions can be realized even for networks composed of flexible and noncharged network chains if the length of linear polymer exceeds a certain critical value. For polyelectrolyte networks, conformational changes are mainly realized as discontinuous phase transitions; the amplitude of the jumps increases with the increase of the number of charges in network chains.

1. Introduction

Conformational changes in swollen gels immersed in solvents of different quality have became of great interest because of the phenomenon of the collapse of polymer networks first described by Tanaka.[1-5] This paper is devoted to the theoretical investigation of swelling and collapse of polymer gels in a solution of a linear polymer which is chemically different from the cross-linking polymer.

The problem of swelling of gels in a solution of a linear polymer was first analyzed by Boyer.[6] He performed the calculations using the Flory–Huggins theory and the assumption that linear polymers do not penetrate into the gel.

A somewhat more detailed theory was proposed in ref 7. In that paper, two simplifications were made: (i) the free chains are chemically identical to the chains of the network; (ii) the solvent is athermal; i.e., energetic interaction among all components is absent (all Flory–Huggins χ parameters are equal to zero). For this case it was shown that a swollen polymer gel immersed in a solution of a linear polymer shrinks as the concentration of linear polymer increases. As a rule, a large amount of the linear chains can penetrate the gel.

As to the case of linear polymer which is chemically different from the network polymer, in ref 7, as in ref 6, it was postulated (without explicit calculations) that, even if the incompatibility of these two polymers is very small, the free chains should not penetrate the gel. As a result, the contraction of gel with the increase of linear polymer concentration should be more pronounced. Experimental and theoretical examination of this conclusion confirmed its validity.[8-10]

In this paper we analyze the above-mentioned situation in more detail. We show that for the case of swelling of a gel in a chemically different polymer the variety of possible regimes is much greater than according to the predictions of refs 6 and 7. In particular, this is due to the fact that for some cases it is essential to take into account the possibility of penetration of linear polymer inside the gel.

We begin our analysis in the next section by considering the simplest case of swelling of a polymer gel in the melt of a linear polymer (binary system polymer + network). In section 3 the consideration is generalized for the most interesting case, network + polymer + solvent.

It is known that the presence of charged links on network chains strongly influences the character of polymer network swelling and collapse.[1-5] Therefore, in sections 4–6 we will study the swelling of polymer network in polymer solution in the presence of charged links. Swelling of weak polyelectrolyte networks in polymer solutions and melts is described in sections 4 and 5. Section 6 deals with the analysis of the complementary case when neutral network swells in a solution of a weak linear polyelectrolyte.

2. Network Immersed in a Polymer Melt

First, let us consider the simplest case when the network is immersed in a polymer melt with the degree of polymerization P. As usual[11] the free energy F_m can be written as a sum of two terms:

$$F_m = F_{int} + F_{el} \tag{1}$$

In the framework of Flory–Huggins lattice theory the free energy of interaction F_{int} per one lattice site divided by Boltzmann factor kT is given by[11]

$$F_{int} = \frac{\varphi_P}{P} \ln \varphi_P + \chi_{NP}\varphi_N\varphi_P \tag{2}$$

where φ_N and φ_P are volume fraction of the network links and polymer links within the network, respectively ($\varphi_N + \varphi_P = 1$); χ_{NP} is the polymer–network Flory–Huggins interaction parameter.

For the free energy of elastic deformation of network chains F_{el} we will use for simplicity the expression of the classical theory of rubber elasticity[11] (the qualitative results of this consideration do not depend on the expression of

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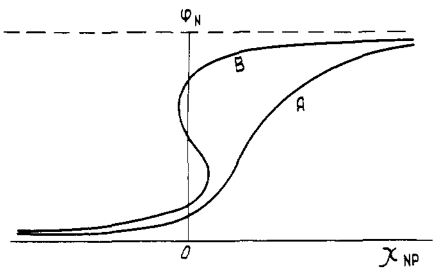

Figure 1. Dependences of φ_N on χ_{NP} for $P < P_{cr}$ (A) and $P > P_{cr}$ (B).

elastic free energy):

$$F_{el} = 3\frac{\varphi_N}{N}\left[\frac{\left(\frac{\varphi_o}{\varphi_N}\right)^{2/3} - 1}{2} - \frac{2}{f}\ln\left(\frac{\varphi_o}{\varphi_N}\right)^{1/3}\right] \qquad (3)$$

where N is the average degree of the polymerization of network chains, f is the functionality of cross-links, and φ_o is the volume fraction of network polymer in the so-called reference state where the conformation of network chains is most close to that of unpertubed Gaussian coils.

The value of φ_o is defined by the conditions of network preparation (see ref 12). Usually φ_o is close to the volume fraction of polymer network at the preparation conditions: for example, for the dry networks prepared by cross-linking in the absence of diluent, $\varphi_o \sim 1$; while for diluted networks synthesized in the large amount of diluent, $\varphi_o \sim N^{-1/2} \ll 1$.

The equilibrium volume of the network is defined by the condition

$$\pi = {\varphi_N}^2 \frac{\partial(F(\varphi_N)/\varphi_N)}{\partial\varphi_N} = 0 \qquad (4)$$

where π is the osmotic pressure.

Substituting eqs 1–3 into eq 4, we obtain

$$\frac{1}{P}\ln(1 - \varphi_N) + \varphi_N\left(\frac{1}{P} - \beta\right) + \chi_{NP}{\varphi_N}^2 + \gamma{\varphi_N}^{1/3} = 0 \qquad (5)$$

where

$$\beta = 2/fN \qquad \gamma = {\varphi_o}^{2/3}/N$$

According to this equation, in athermal limit two different regimes can be distinguished, depending on the value of P:[7] the regime of a swollen network and the regime of an ideal network. If $P < N^{1/2}$ and the size R_N of network chains is $R_N \sim N^{3/5}/P^{1/5}$, then $\varphi_N \sim P^{3/5}/N^{4/5}$, which means that the network is swollen due to the effect of volume interaction. If $P > N^{1/2}$, then $R_N \sim N^{1/2}$ and $\varphi_N \sim N^{-1/2}$; i.e., the excluded-volume interactions of links of network chains are screened (see ref 12); this screening is completely analogous to the screening of volume interactions in a melt of sufficiently long chains.

As interaction parameter χ_{NP} increases (i.e., repulsion between network links and links of the linear polymer becomes stronger), the volume of the network decreases up to $\varphi_N \sim 1$ because of the practically full segregation of network from polymer melt. Typical dependences φ_N vs χ_{NP} are shown in Figure 1. One can see that as the parameter χ_{NP} increases two qualitatively different types of network behavior can be realized: either smooth contraction (Figure 1, curve A) or jumpwise transition (Figure 1, curve B).

The discrete first-order phase transition (Figure 1B) is realized only if $\varphi_o < 1$ (for diluted networks) and only if the values of P exceed a critical value: $P > P_{cr} \sim \gamma^{3/2}/\beta^{5/2} \sim N\varphi_o/(f/2)^{5/2} \sim N^{1/2}$. The discrete collapse takes place at a rather small value of χ_{NP}, $\chi_{NP} \sim N^{1/3}/P$, and as a result of this transition φ_N changes from $\varphi_N \sim \varphi_o$ to $\varphi_N \sim 1$. Note that the discrete transition is realized for the networks consisting of flexible and uncharged chains, while the collapse of such networks in low molecular weight (non-polymer) solvent is always smooth.

3. Network Swollen in Polymer Solution

Consider now a general case, when a network swells in a linear polymer solution. As before the free energy of the network F_S can be written as a sum:

$$F_S = F^{s}_{int} + F_{el} \qquad (6)$$

with expression 3 for the elastic free energy F_{el}. The free energy of interaction F^{s}_{int} (per lattice site and divided by kT) is now equal to[11]

$$F^{s}_{int} = \frac{\varphi_P}{P}\ln\varphi_P + \varphi_S\ln\varphi_S + \chi_{NP}\varphi_N\varphi_P + \chi_{NS}\varphi_N\varphi_S + \chi_{PS}\varphi_P\varphi_S \qquad (7)$$

where φ_P and φ_S are the volume fractions of linear polymer and solvent inside the network, respectively ($\varphi_P + \varphi_S + \varphi_N = 1$), and χ_{NP}, χ_{NS}, and χ_{PS} are the Flory–Huggins interaction parameters network–liner polymer, network–solvent, linear polymer–solvent, respectively.

The free energy F^{out} of external solution in the framework of Flory–Huggins theory is given by

$$F^{out} = \frac{{\varphi_P}^{out}}{P}\ln{\varphi_P}^{out} + {\varphi_S}^{out}\ln{\varphi_S}^{out} + \chi_{PS}{\varphi_P}^{out}{\varphi_S}^{out} \qquad (8)$$

Here ${\varphi_P}^{out}$ and ${\varphi_S}^{out}$ are volume fractions of linear polymer and solvent in the external solution, respectively (${\varphi_P}^{out} + {\varphi_S}^{out} = 1$).

Equilibrium volume of the network (which is defined by the value of φ_N) and the solvent composition inside the network (which is defined by the value of φ_P) can be found from the following equilibrium conditions: the equality of "chemical potential" inside and outside the network

$$\frac{\partial F_S(\varphi_N,\varphi_P)}{\partial\varphi_P} = \frac{\partial F^{out}({\varphi_P}^{out})}{\partial{\varphi_P}^{out}} \qquad (9)$$

and the equality of osmotic pressure inside and outside the network

$$-F_S + \frac{\partial F_S(\varphi_N,\varphi_P)}{\partial\varphi_N}\varphi_N + \frac{\partial F_S(\varphi_N,\varphi_P)}{\partial\varphi_P}\varphi_P = \frac{\partial F^{out}({\varphi_P}^{out})}{\partial{\varphi_P}^{out}} - F^{out} \qquad (10)$$

Substituting eqs 3 and 6–8 into eqs 9 and 10, we obtain the system of equations

$$\frac{1}{P}\ln\frac{\varphi_P}{{\varphi_P}^{out}} - \ln\frac{\varphi_S}{{\varphi_S}^{out}} + 2\chi_{PS}({\varphi_P}^{out} - \varphi_P) + (\chi_{NP} - \chi_{PS} - \chi_{NS})\varphi_N = 0 \qquad (11)$$

$$\gamma{\varphi_N}^{1/3} + \ln\frac{\varphi_S}{{\varphi_S}^{out}} + \varphi_N(1 - \beta) + (\varphi_P - {\varphi_P}^{out})\left(1 - \frac{1}{P}\right) + \chi_{NS}{\varphi_N}^2 + \chi_{PS}[{\varphi_P}^2 - ({\varphi_P}^{out})^2] + (\chi_{NS} + \chi_{PS} - \chi_{NP})\varphi_N\varphi_P = 0 \qquad (12)$$

which has been solved numerically for the values $\gamma = {\varphi_o}^{2/3}/\mathrm{N} \sim 7 \times 10^{-4}$, $\beta = 2/fN \sim 5 \times 10^{-3}$ (diluted network) and at different values of χ_{NS}, χ_{NP}, and χ_{PS}.

Results of these calculations for the athermal case $\chi_{NP} = \chi_{PS} = \chi_{NS} = 0$, which was already described in ref 7, are

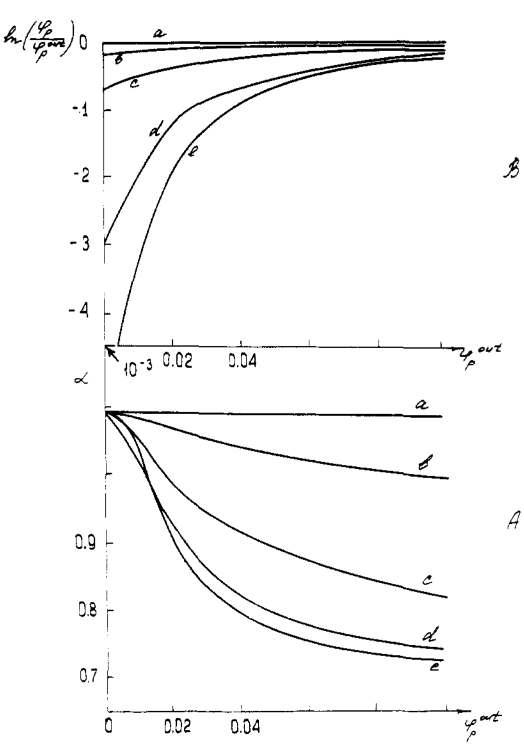

Figure 2. Dependences of α (A) and $\varphi_P/\varphi_P^{out}$ (B) on φ_P^{out} in the athermal case $\chi_{NP} = \chi_{NS} = \chi_{PS} = 0$ and at $P = 1$ (a), 10 (b), 100 (c), 500 (d), and 1000 (e).

presented in Figure 2. This figure shows the coefficient of network swelling with respect to the reference state, $\alpha = (\varphi_0/\varphi_N)^{1/3}$ (Figure 2A), and the ratio $\varphi_P/\varphi_P^{out}$ characterizing the change of polymer concentration within the network (Figure 2B) as functions of φ_P^{out} for different values of the degree of polymerization of linear polymer P. One can see that as φ_P^{out} increases the size of the polymer network decreases, which results from the well-known effect of screening of excluded-volume interactions in concentrated polymer solutions. At sufficiently large values of P this deswelling takes place in a narrow region of low concentration of the linear polymer, outside of which the size of the network practically does not change, and corresponds to the case of the absence of excluded-volume effects. In this region of low concentration, the polymer solution inside the network is essentially enriched by polymer component (Figure 2B): if φ_P^{out} is sufficiently low the linear polymer practically does not penetrate inside the network, whereas at $\varphi_P^{out} \sim 0.05$, $\varphi_P \sim \varphi_P^{out} - \varphi_N$; i.e., solution compositions inside and outside the network are practically identical.

In Figure 3, the plots of dependences of α and of $\varphi_P/\varphi_P^{out}$ on φ_P^{out} for $\chi_{NP} = \chi_{PS} = 0$ and for different values of χ_{NS} are shown. As the quality of the solvent for the network becomes worse, the dependences $\alpha(\varphi_P^{out})$ and $\varphi_P(\varphi_P^{out})$ change qualitatively. At low concentration of linear polymer, $\varphi_P/\varphi_P^{out}$ is always an increasing function of φ_P^{out}. For small values of χ_{NS}, the monotonous character of the function $\varphi_P/\varphi_P^{out}$ vs φ_P^{out} holds for high concentrations of the linear polymer as well. At $\chi_{NS} \geqslant 0.4$ and low values of φ_P^{out}, only small amounts of the linear polymer penetrate the network. This is physically due to the fact that the linear polymer loses conformational entropy within the network because of the excluded volume of the links of the network chains. Thus the concentration of linear polymer inside the network is much smaller than in the outer solution, which leads to an additional osmotic pressure compressing the network. With the increase of the value of χ_{NS} this effect becomes more pronounced. At sufficiently large values of χ_{NS}, this additional osmotic pressure induces the transition of the network to the globular state and practically complete elimination of linear chains from the network. In the case of $\chi_{NS} = 0.5$, this results in full segregation between linear polymer and the network at intermediate values of φ_P^{out}: $\varphi_P = 0$ at $\varphi_P^{out} \sim 0.2$–0.7.

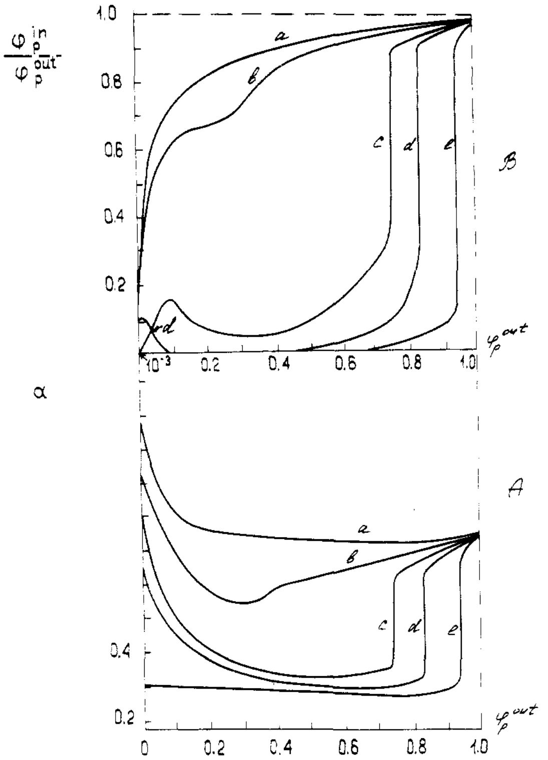

Figure 3. Dependences of α (A) and $\varphi_P/\varphi_P^{out}$ (B) on φ_P^{out} at $P = 100$, $\chi_{NP} = \chi_{PS} = 0$ and $\chi_{NS} = 0$ (a), 0.3 (b), 0.4 (c), 0.5 (d), and 1 (e).

Another very remarkable change in the character of the swelling behavior of the polymer network takes place at high values of φ_P^{out} for $\chi_{NS} \geqslant 0.4$. It can be seen from Figure 3 that for this case the linear polymer again penetrates the network. The reason is the gain in energy due to the contacts between network and linear polymer as well as the gain in translational entropy of the linear chains, which exceeds the loss in conformational entropy of the linear chains penetrating the gel. As a result, the volume of the network increases. This increase is realized as a first-order phase transition with the jump of the network volume and of the volume fraction of the linear polymer within the network.

The conformational changes in the polymer network plotted in Figure 3 for $\chi_{NS} = 0.4$–0.5 can be related to the effects of reentrant conformational transitions in polymer networks already described in the literature.[14,15] However, unlike what has been described before about reentrant transitions, in our case the collapse of polymer network is realized smoothly and the decollapse is a jumpwise first-order phase transition.

If the low molecular weight solvent is poor for the polymer gel ($\chi_{NS} > 0.5$), the network is in the globular state in pure solvent. The gel remains in a contracted state up to some critical value of φ_P^{out}, when a jumpwise decollapse of the network happens as a result of the penetration of the linear polymer into the sample (see Figure 3, $\chi_{NS} = 1$). The jump of the network size at the high concentration of a linear polymer in external solution depends on the degree of polymerization P of a linear

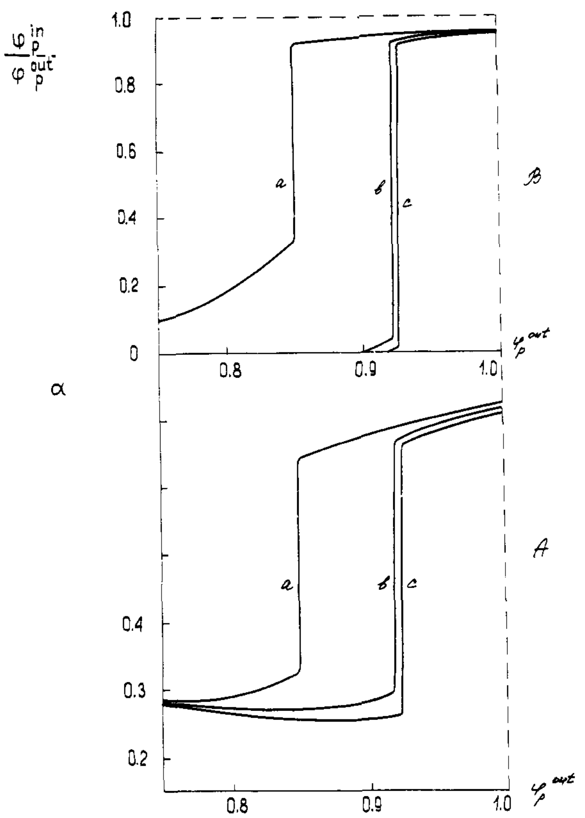

Figure 4. Dependences of α (A) and $\varphi_P/\varphi_P^{out}$ (B) on φ_P^{out} at $\chi_{NS} = 0.5$, $\chi_{PS} = \chi_{NS} = 0$, and $P = 100$ (a), 500 (b), and 1000 (c).

polymer. With increase of P the critical value of φ_P^{out} at which transition takes place, as well as the amplitude of the jump, increases. This is illustrated by the plots shown in Figure 4. It should be noted that such reentrant transitions occur only for long linear polymers.

Figure 5 shows the dependence of the discovered effect of reentrant transition on the compatibility of a linear polymer and a network. We have chosen for the calculations the following values: $\chi_{NS} = 0.5$, $\chi_{NP} = 0$, at which the effects described above are most pronounced (see Figure 3, curve d).

As the value of χ_{NP} increases (i.e., the degree of compatibility of network and linear polymer decreases) the jump of the dependence $\alpha(\varphi_P^{out})$ moves to higher concentrations of linear polymer, and when $\chi_{NP} \sim 0.4$ the jump vanishes, because at large values of χ_{NP} the network does not mix with polymer melt.

On the contrary, if we pass to the region of the negative values of χ_{NP} (attraction between the links of the network and linear polymer), the jump at first moves to the region of smaller concentrations of φ_P^{out} and finally disappears altogether. At $\chi_{NP} < -0.5$ the dependence $\alpha(\varphi_P^{out})$ is monotonous because the linear polymer, having high compatibility with the network polymer, strongly penetrates the gel from the very beginning. Thus the quality of the mixture in which polymer network swells is effectively improved.

4. Polyelectrolyte Network in Polymer Melt

Now let us consider the following system: polymer network swells in a polymer solution, and the chains of the network carry charged links. The total charge of the network is compensated by oppositely charged counterions, which move freely within the network.

The swelling of polyelectrolyte networks is usually studied in aqueous solutions. However, for the sake of simplicity we begin with the consideration of swelling of a polyelectrolyte network in a melt of a linear polymer. The analysis of this particular case is necessary for the study of the general situation.

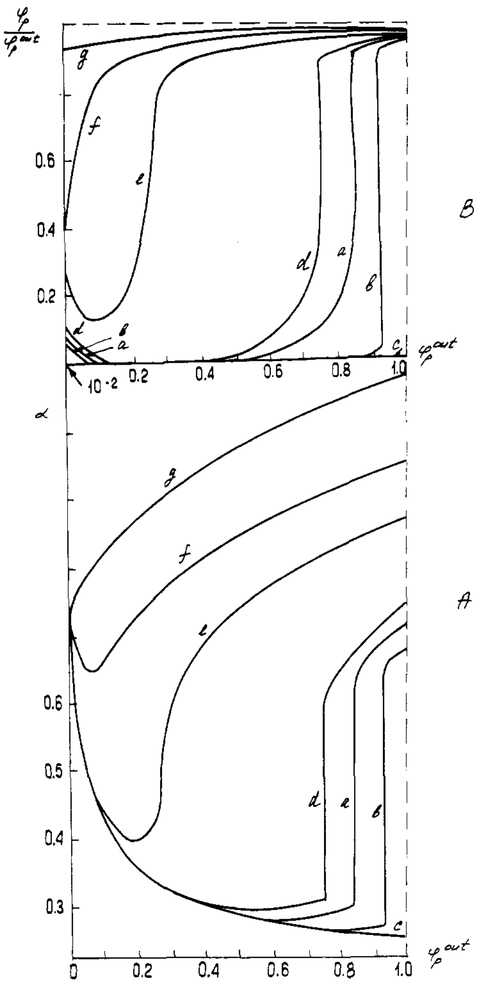

Figure 5. Dependences of α (A) and $\varphi_P/\varphi_P^{out}$ (B) on φ_P^{out} at $\chi_{PS} = 0$, $\chi_{NS} = 0.5$, $P = 100$, and $\chi_{NP} = 0$ (a), 0.01 (b), 0.04 (c), -0.01 (d), -0.1 (e), -0.2 (f), and -0.5 (g).

In this case free energy of the network (per lattice site and divided by kT) is a sum of three terms: the free energy of interaction F_{int} (eq 2), the elastic free energy F_{el} (eq 3), and the contribution of the charged links $F_{o,N}$.

$$F_m = F_{int} + F_{el} + F_{o,N} \tag{13}$$

It was shown in refs 2 and 3 that, in the case of a weakly charged polyelectrolyte network, in order to describe the effect of charges it is sufficient to take into account only the translational entropy of counterions, because the direct electrostatic interactions themselves are negligible. If m_N is the average number of charged links in a network chain, $F_{o,N}$ should be written as

$$F_{o,N} = \frac{m_N\varphi_N}{N}\ln\left(\frac{m_N\varphi_N}{N}\right) \tag{14}$$

Substituting free energy eq 12 with eqs 2, 3, and 13 into equilibrium conditions (eq 4) we obtain

$$\frac{1}{P}\ln(1-\varphi_N) + \varphi_N\left(\frac{1}{P} - \beta - \frac{m_N}{N}\right) + \chi_{NP}\varphi_N^{2} + \gamma\varphi_N^{1/3} = 0 \tag{15}$$

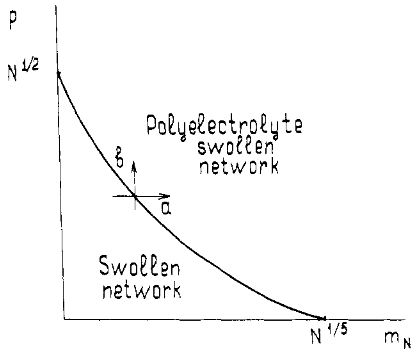

Figure 6. Diagram of states of polyelectrolyte network in polymer melt (athermal case).

where

$$\beta = 2/fN \qquad \gamma = \varphi_0^{2/3}/N$$

Equation 15 gives the equilibrium size of the polymer network as a function of m_N, N, and χ_{NP}.

In the athermal case ($\chi_{NP} = 0$) eq 15 leads to two different regimes, as in case of a neutral network. For the first one, the equilibrium size of the network is determined by a balance of the elastic free energy and the free energy of interaction of the links due to their excluded volume. For this regime, the presence of charges is not important and all the results coincide with those obtained in section 2. This regime was referred to as the regime of swollen network. For this regime $\varphi_N^{I} \sim P^{3/5}/N^{4/5}$ and $R_N^{I} \sim N^{3/5}/P^{1/5}$.

For the second regime, the size of the network is due to the balance of the elastic free energy and the contribution from the translational entropy of counterions: $\varphi_N^{II} \sim (Nm_N^3)^{-1/2}$ and $R_N^{II} \sim (Nm_N)^{1/2}$. The latter regime will be referred to as the regime of swollen polyelectrolyte network.

The regions of validity of these two regimes are presented in Figure 6. From Figure 6 one can see that the larger is P, the narrower is the region of the regime of swollen network, and if $P > N^{1/2}$, the network is always in the regime of a swollen polyelectrolyte network. This fact can be explained again by the partial screening of the excluded-volume interaction in the polymer solution; when $P > N^{1/2}$ this interaction is screened completely. It should be recalled that the neutral network in the melt of a polymer with the degree of polymerization $P > N^{1/2}$ is in the regime of an ideal network as a result of the full screening of the excluded-volume interaction. In the case of polyelectrolyte networks, this regime is not realized because of the relatively large entropic contribution of the "gas" of counterions.

Generally speaking, φ_N^{I} may be both larger and smaller than φ_N^{II}. In Figure 7 we present the dependences of φ_N on m_N at constant P (a) and the dependences of φ_N on m at constant P (b) (the crossover line is traversed in different directions, which are shown in Figure 6). Figure 7a shows that with the increase of m_N at constant P the network swells additionally, whereas in (b) the network shrinks with the increase of P. But this contraction is much less than that of the neutral network (cf. $\varphi_N \sim N^{-1/2}$ in the case of a neutral network and $\varphi_N \sim (Nm_N^3)^{-1/2}$ for a polyelectrolyte network). When $m_N > N^{1/5}$ this contraction is completely absent.

As for the case of neutral networks, with the increase of χ_{NP} the polyelectrolyte network either deswells monotonously or undergoes the jumpwise transition. However, for the polyelectrolyte network the jumpwise transition can be observed for wider ranges of parameters, because the critical value P_{cr}, above which the collapse is realized as a first-order phase transition, decreases with increase of the number of charges on the network chains: $P_{cr} \sim (N/m_N^5)^{1/2}$. If $m_N > N^{1/5}$, the polyelectrolyte network undergoes a jumpwise collapse even in low molecular solvent. This conclusion is in agreement with the results of numerous papers, where the swelling of a polymer network in a nonpolymer solvent has been studied (see, for example, refs 1–6).

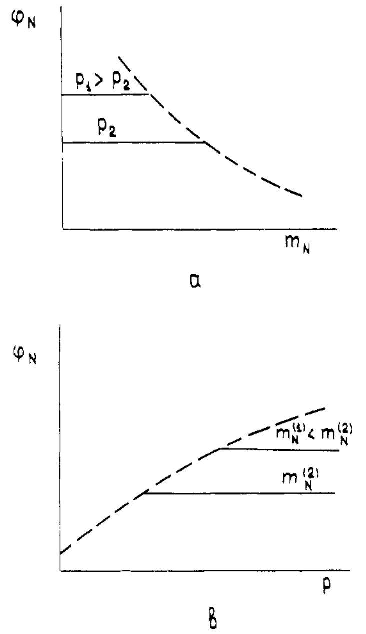

Figure 7. Dependences $\varphi_N(m_N)$ at constant P (a) and $\varphi_N(P)$ at constant m_N (b).

5. Polyelectrolyte Network in Polymer Solution

Now we will consider a polyelectrolyte network which swells in a polymer solution.

The free energy of the polymer network F_N can be written as a sum of the free energy of a neutral network immersed in polymer solution F_S (eq 6) and the contribution from the translational entropy of counterions (eq 14):

$$F_N = F_S + F_{o,N} \tag{16}$$

Repeating the calculations made in section 3 and using expression 16 for the free energy of a polymer network, we obtain the following system of equations describing equilibrium values of φ_N and φ_P:

$$\frac{1}{P}\ln\frac{\varphi_P}{\varphi_P^{out}} - \ln\frac{\varphi_S}{\varphi_S^{out}} + 2\chi_{PS}(\varphi_P^{out} - \varphi_P) + (\chi_{NP} - \chi_{PS} - \chi_{NS})\varphi_N = 0 \tag{17}$$

$$\gamma\varphi_N^{1/3} + \ln\frac{\varphi_S}{\varphi_S^{out}} + \varphi_N(1-\beta) + (\varphi_P - \varphi_P^{out})\left(1 - \frac{1}{P}\right) + \chi_{NS}\varphi_N^2 + \chi_{PS}[\varphi_P^2 - (\varphi_P^{out})^2] + (\chi_{NS} + \chi_{PS} - \chi_{NP})\varphi_N\varphi_P - \varphi_N\frac{m_N}{N} = 0 \tag{18}$$

This system of equations was solved for the same values of the parameters γ, β, and φ_0 as in section 3.

First let us consider the influence of the charge of the network chains on the effects which have been described in section 3.

Consider the case when the network swells in a mixture of poor solvent and linear polymer compatible with the

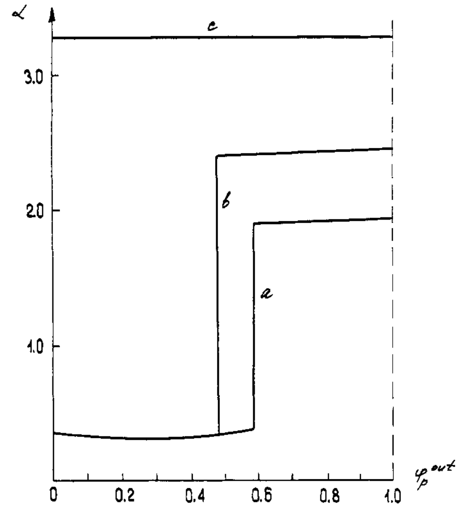

Figure 8. Dependences of α on φ_P^{out} for polyelectrolyte network at $\chi_{NP} = \chi_{PS} = 0$, $\chi_{NS} = 1$, $P = 100$, and $m_N = 3$ (a), 5 (b), and 10 (c).

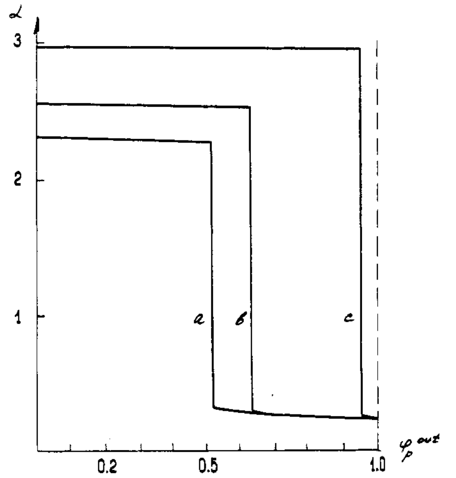

Figure 9. Dependences of α on φ_P^{out} for polyelectrolyte network at $\chi_{PS} = \chi_{NS} = 0$, $\chi_{NP} = 0.5$, $P = 100$, and $m_N = 5$ (a), 6 (b), and 8 (c).

network chains. In this case a neutral network undergoes a phase transition upon increase of polymer concentration φ_P^{out} (see Figure 3, curve e). Because of the charges on the network chains the transition point moves to smaller values of φ_P^{out} and the amplitude of the jump increases (Figure 8). At values of m_N higher than a certain value, the jump in the dependence $\alpha(\varphi_P^{out})$ vanishes because the size of network is defined by the contribution $F_{o,N}$ even in pure solvent and energetic non-Coulombic interactions are unimportant for all values of φ_P^{out}.

Let us suppose now that the solvent is good for the network and that the linear polymer is compatible with the network polymer. The question is the following: whether it is possible to observe a reentrant transition in polymer networks upon increasing φ_P^{out} similarly to the effect observed for the case of neutral network. To answer this question it is necessary to take into account that the spatial size of a polyelectrolyte network chain is much larger than that of a neutral network, because of the additional swelling due to the osmotic pressure of counterions. Therefore, even sufficiently long macromolecules can penetrate the network in dilute polymer solution without essential loss in conformational entropy.

Besides that, the deswelling of polyelectrolyte networks leads to additional loss in entropy (in comparison with the case of a neutral network) owing to the decrease of translational entropy of the counterions. That is why for the case of polyelectrolyte networks the reentrant transition can be realized hypothetically only if the degree of polymerization of linear polymer is very high. However, in practice, for realistic values of the parameters it is never observed.

Figure 9 shows the dependences α on φ_P^{out} for polyelectrolyte networks swollen in solutions of incompatible linear polymer ($\chi_{NP} > 0$). The availability of charges on the network chains causes the collapse to be realized as a first-order phase transition with a jump of the size of the polymer network. As the number of charged links m_N increases, the critical value of φ_P^{out} at which the phase transition occurs shifts to higher values of φ_P^{out} up to $\varphi_P^{out} \sim 1$.

It should be emphasized that the discrete network collapse in polymer solution can be realized only for polyelectrolyte networks. For neutral networks, deswelling with the increase of concentration of a linear polymer is always continuous, in agreement with the results of refs 8 and 9.

6. Neutral Network in Solution of Linear Polyelectrolyte

Consider now a neutral network swollen in a polyelectrolyte solution. Let m_P be an average number of charged links per macromolecule. The counterions which are necessary for the total electroneutrality are also present in the system. As before we start with the case of a melt. The free energy of the network should also be written as a sum:

$$F = F_m + F_{o,P} \tag{19}$$

where F_m is the free energy of the neutral network described in section 1, eq 1. $F_{o,P}$ corresponds to the contribution of the translational entropy of counterions and is given by

$$F_{o,P} = \frac{m_P\varphi_P}{P}\ln\left(\frac{m_P\varphi_P}{P}\right) \tag{20}$$

It can be shown that if $m_P/P \to 0$ (weak polyelectrolyte) the free energy eq 19 with eqs 1–3 and eq 19 may be rewritten as

$$F = \varphi_P\frac{m_P + 1}{P}\ln\varphi_P + \chi_{NP}\varphi_N\varphi_P + F_{el} \tag{21}$$

Comparing eq 21 and eqs 1–3 we conclude that the present case corresponds exactly to the case of a neutral polymer network swollen in a solution of linear polymer of renormalized length P^*: $P^* = P/(1 + m_P)$.

Thus we can distinguish the same two regimes at $\chi_{NP} = 0$ as for the electroneutral case: the regime of a swollen network and the regime of an ideal network. But the transition from the former regime to the latter one occurs at larger value of P. The collapse of the network upon decrease of the quality of the polymer solvent becomes discrete in the melt of longer macromolecules: $P > P_{cr} \sim (m_P + 1)N^{1/2}$. The jump manifests itself at larger values of χ_{NP}. Thus the polyelectrolyte can mix with a network polymer which is absolutely incompatible with the same neutral linear polymer. This conclusion is in agreement with the conclusion of ref 15, where it was found that mutual compatibility of two different linear polymers is improved if the one of them carries charged links.

Accordingly one can show that the network swells in a solution of linear polyelectrolyte in the same manner as for swelling in a solution of a linear polymer with the degree of polymerization equal to $P^* = P/(m_P + 1)$.

7. Conclusions

We have studied the swelling of polymer networks in polymer solutions and melts. We have found that in this system many interesting regimes can be realized which were not reported before:

(1) A new phase transition is found for a network immersed in long polymer melts, which occurs when the degree of polymerization exceeds a critical threshold. As a result of this transition, the network swollen in a polymer melt discontinuously separates from the melt.

(2) For gels immersed in a solution of long polymer compatible with the network chains, the realization of jumpwise decollapse is possible if the low molecular weight solvent is poor for the cross-linked polymer. The so-called reentrant transition can take place as well, if the low molecular weight solvent is good enough for the gel chains.

(3) In polymer melts and solutions the jumpwise transition is realized for the networks which consist of flexible and noncharged chains, while in low molecular weight (nonpolymer) solution the collapse of such gels is always smooth.

(4) If network chains carry charged links, the transition becomes sharper: the amplitude of the jump increases, and the critical value P_{cr} decreases. The collapse of charged networks in a solution of a polymer that is incompatible with the network becomes discontinuous, while in case of electroneutral networks, a first-order phase transition cannot be observed.

(5) Polymer networks swell in a solution of a weakly charged polyelectrolyte analogously to the swelling in solution of polymer with a renormalized length of polymer chain: $P^* = P/(m_P + 1)$. Thus, with increase of the charge of the linear polymer the collapse phase transition becomes less sharp.

References and Notes

(1) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820.

(2) Tanaka, T. *Polymer* **1978**, *20*, 1404.

(3) Vasilevskaya, V. V.; Khokhlov, A. R. In *Mathemematical Methods for Polymer Studies*; Lifshitz, I. M., Molchanov, A. M., Eds; SCBR: Puschino, 1982; p 45.

(4) Tanaka, T.; Sun, S.-T.; Nishio I. In *Scattering Techniques in the Application to Supramolecular and Nonequilibrium System*; *Proc. NATO Adv. Study Inst.* **1981**, *73*, 321.

(5) Vasilevskaya, V. V.; Ryabina, V. R.; Starodybtzev, S. G.; Khokhlov, A. R. *Vysokomol. Soedin.* **1989**, *31A*, 713.

(6) Boyer, R. F. *J. Chem. Phys.* **1945**, *13*, 363.

(7) Brochard, F. *J. Phys.* **1981**, *42*, 505.

(8) Momii, J.; Nose, T. *Macromolecules* **1989**, *22*, 1384.

(9) Adachi, K.; Nakamoto, T.; Kotaka, T. *Macromolecules* **1989**, *22*, 3106.

(10) Mironchenko, Yu. V.; Shilov, V. V.; Khokhlov, A. R.; Lipatov, Yu. S. *Vysokomol. Soedin.* **1988**, *30A*, 307.

(11) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.

(12) Khokhlov, A. R. *Polymer* **1980**, *21*, 376.

(13) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(14) Katayma, S.; Hirokawa, J.; Tanaka, T. *Macromolecules* **1984**, *17*, 2641.

(15) Katayama, S.; Ohata, A. *Macromolecules* **1984**, *18*, 2781.

(16) Vasilevskaya, V. V.; Starodybtzev, S. G.; Khokhlov, A. R. *Vysokomol. Soedin.* **1987**, *29B*, 930.