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Change of Elastic Modulus of Strongly Charged Hydrogels at the Collapse Transition

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ABSTRACT: The swelling and mechanical behavior of polyelectrolyte gels with the degree of ionization varying from 7 to 100 mol % were studied in mixtures of a good solvent and a poor solvent. In a good solvent region for weakly charged gels the shear modulus decreases with the gel swelling, while for strongly charged gels swelling leads to the increase of the shear modulus. Also for strongly charged gels the elastic modulus can remain unchanged during the volume phase transition (for a weakly charged gel, a jump in the volume at the collapse transition is usually accompanied by a discontinuous upturn of the elastic modulus). Both of these features of strongly charged gels are attributed to a significant extension of the highly ionized subchains. At the same degree of swelling the modulus of the fully ionized gel was higher in the medium of lower polarity. This may be due to the formation of new effective cross-links between the subchains as a result of dipole−dipole attraction of ion pairs formed between charged groups of network and condensed counterions.

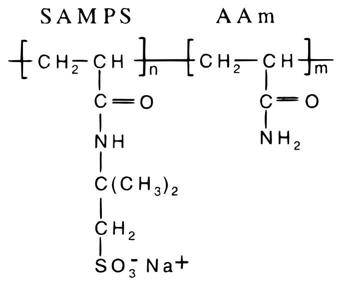
Introduction

The collapse of polymer gels is a phase transition at which the gel volume changes drastically in a narrow range of external parameters (concentration of a poor solvent, temperature, etc.). This phenomenon was under a thorough investigation since it was discovered in 1978.[1,2] For polyelectrolyte gels the collapse results from the interplay of two main forces: repulsive electrostatic interactions which make the gel swell and attractive interactions between polymer units in poor solvent conditions which tend to make the gel collapse. For weakly charged gels the osmotic pressure of mobile counterions dominates over other electrostatic factors. For strongly charged gels along with the osmotic pressure of counterions, direct electrostatic interactions become essential. The most important of them are the effect of condensation of counterions[3,4] and the chain stiffening due to the repulsion of similarly charged units along the chains (characterized by an electrostatic persistent length).[5,6]

A volume phase transition may be accompanied by a jumpwise change in some physical characteristics of the gel, such as the shear modulus.[7,8] For weakly charged gels a discrete change in the gel volume at the network collapse induces a discrete change in the modulus of elasticity G.[7] This is not surprising because for weakly charged gels the elastic modulus decreases monotonically with the gel swelling as a result of a decrease of the concentration of elastically effective subchains. This may not be the case for strongly charged gels, because for such gels the dependence of G on the degree of swelling Q becomes nonmonotonic. A Gaussian regime at low Q characterized by a decrease of G upon swelling is followed by an abrupt upturn of G associated with the strong stretching of the network subchains.[9,10]

The aim of this work is to study the change of the elastic modulus at the collapse of strongly charged gels when the effects of limited chain extensibility and of the condensation of counterions become important. The objects of the present investigation are anionic gels of poly(acrylamide-*co*-sodium 2-acrylamide-2-methylpropanesulfonate) (PAAm/SAMPS) with different contents of charged units (α from 7 to 100 mol %) and cationic gel of poly(diallyldimethylammonium chloride) (PDADMAC) with α = 100 mol % (Figure 1). These gels contain strong electrolyte groups, which fully dissociate in aqueous solutions, rendering the degree of gel swelling relatively insensitive to pH. The collapse was induced by a change in the composition of the mixed solvent: water−ethanol for anionic PAAm/SAMPS gels and water−acetonitrile for cationic PDADMAC gel.

(a) Anionic Gels



(b) Cationic Gel:

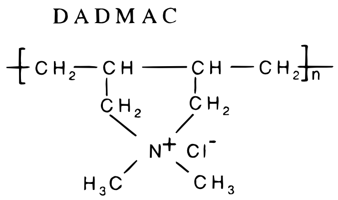


Figure 1. Chemical structures of anionic PAAm/SAMPS and cationic PDADMAC gels.

Experimental Section

Gel Preparation. (a) Anionic Hydrogels. Anionic gels with different contents of charged units were obtained by free-radical copolymerization of uncharged and charged monomers (acrylamide (AAm) and sodium 2-(acrylamido)-2-methylpropanesulfonate (SAMPS), re-

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Table 1. Characteristic Data of the Prepared Gels

gel	C_m[a], wt %	α[b], %	C[c]	Q_0[d]	q[e], %
PAAm/SAMPS 1	10.4	7	0.005	230	100
PAAm/SAMPS 2	13.0	20	0.005	230	100
PAAm/SAMPS 3	19.0	50	0.005	180	100
PAAm/SAMPS 4	25.0	80	0.005	200	100
PAAm/SAMPS 5	29.0	100	0.005	180	97
PDADMAC	50.0	100	0.0033	190	40

[a] C_m is the total content of monomers in a pregel mixture. [b] α is the relative amount of charged gel units in a reaction. [c] C is the cross-linking density (mol of BIS per 1 mol of monomers in a reaction solution). [d] Q_0 is the equilibrium degree of swelling. [e] q is the degree of conversion.

spectively) in aqueous solution with *N,N′*-methylenebis(acrylamide) (BIS) (6.32 × 10^{-3} mol/L) as a cross-linker. Ammonium persulfate (APS) and *N,N,N′,N′*-tetramethylethylenediamine (TEMED) (2.0 × 10^{-3} mol/L) were used as initiator and accelerator, respectively. The total monomer concentration was fixed at 1.226 mol/L, the relative amounts of charged monomer (SAMPS) in polymerization mixture were 7, 20, 50, 80, and 100 mol %.

(b) Cationic Gel. To prepare a cationic PDADMAC gel, 63.6 mg BIS dissolved in 5.13 mL of water, 1.57 mL of 1 wt % APS solution, and 0.010 mL of TEMED were added to the 33.3 mL of 60 wt % aqueous solution of diallyldimethylammonium chloride.

When the polymerization was completed, both cationic and anionic gels were washed with deionized water. The equilibrium degree of swelling in water Q_0 and the degree of conversion of the prepared gels are compiled in Table 1. The equilibrium degree of swelling Q_0 is defined as the ratio of the mass of the gel swollen to equilibrium, m_{sw}, to that of the dry gel $Q_0 = m_{sw}/m_{dry}$. The degree of conversion q is defined as the ratio of the mass of the dry gel, m_{dry}, to the total mass of monomers and cross-linker in a pregel reaction mixture, m_0: $q = m_{dry}/m_0 \times 100\%$.

Swelling Studies. The gel samples were swollen to equilibrium in mixtures of good and poor solvents. As a poor solvent we used ethanol for anionic gels and acetonitrile for cationic gel. Water was a good solvent in both cases. The volume of solvent mixture was fixed at 9.16 × 10^5 and 1.8 × 10^3 mL per 1 mol of monomer units for anionic and cationic gels, respectively. While in the lower concentration range of poor solvent (<70 vol %) the gel samples swollen in water were immersed in the solvent mixtures, at higher poor solvent contents dried gel samples were used for this purpose. Equilibration took place for at least 4 weeks. The degree of swelling of equilibrated samples Q was defined as $Q = (D/D_0)^3 Q_0$, where D_0 is the diameter of sample swollen to equilibrium in water.

To present the results on the swelling behavior of the gels, we used a reduced degree of swelling $[Q] = QM/d_w$, where M is the mean molecular mass of the monomer unit of the network and d_w is the density of water. The value of $[Q]$ is nearly equal (with an accuracy of 1%) to the volume of solvent per 1 mol of monomer units of the network.

Stress−Strain Measurements. The elastic moduli of the gels were obtained from uniaxial compression measurements according to the procedure described elsewhere.[7] The elastic modulus G was determined from the slope of linear dependence

$$\sigma = f/S_0 = G(\lambda - \lambda^{-2})$$

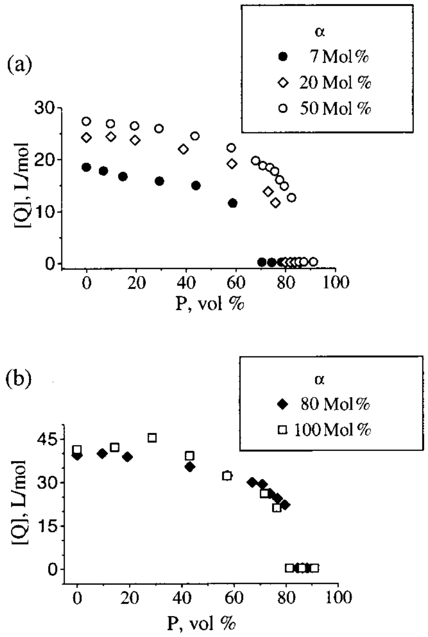

Figure 2. Equilibrium degree of swelling of the PAAm/SAMPS gels as a function of concentration of a poor solvent, ethanol, in a water−ethanol mixture for weakly charged anionic gels (a) (α = 7, 20, and 50 mol %) and for strongly charged anionic gels (b) (α = 80 and 100 mol %).

where f is the value of exerted stress, S_0 is the cross-section of the undeformed swollen specimen, and λ is the relative deformation of the specimen.

Results and Discussion

Swelling Behavior. Figure 2 illustrates the dependences of the equilibrium degree of swelling of anionic PAAm/SAMPS gels on the concentration of poor solvent, ethanol, in the water−ethanol mixture. It is seen that all the gels under study undergo a discontinuous volume phase transition between swollen and collapsed states at a definite concentration of a poor solvent P_{crit}. For moderately charged polyelectrolyte gels (Figure 2a) the increasing ionization leads to two main effects: (a) to the increase of the degree of swelling in a good solvent and (b) to the shift of the collapse transition toward higher concentration of a poor solvent. Both of these effects are due to the increase of the osmotic pressure of free counterions.[7] Such swelling behavior of weakly charged gels was described in many papers (see, for example, ref 2).[11]

A somewhat different behavior is observed for strongly charged gels (Figure 2b). In this case (a) the degree of swelling in a good solvent is independent of α, while (b) at increasing content of charged units α in the gel the collapse transition shifts to the opposite direction in comparison with weakly charged gels, i.e., to the lower concentration of poor solvent. The first effect can be explained by the fact that the strongly charged chains are already fully extended and the additional charging does not influence their state. Also, at such a high charge density the introduction of additional charged units does not lead to the increase of the net charge of the chains in a result of the condensation of counterions. A slight shift of the collapse transition toward lower concentration of a poor solvent may be connected with an additional attractive interaction between extended chains of the same charge which arises when the chains

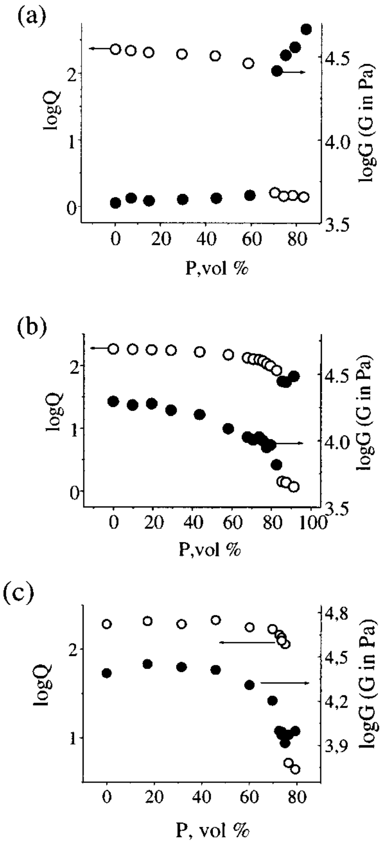

Figure 3. Shear modulus G (●) and equlibrium degree of swelling Q (○) for the anionic PAAm/SAMPS gels with $\alpha = 7$ mol % (a) and $\alpha = 50$ mol % (b) and for the cationic PDADMAC gel with $\alpha = 100$ mol % (c) as a function of concentration of a poor solvent in the external solution.

approach close enough to be able to share the counterion clouds.[3] One more possible reason for the shift of the collapse transition can be due to the dipole–dipole attraction of ion pairs formed by the counterions site bound to the network countercharges. With gel ionization the concentration of bound counterions becomes higher. This is favorable for the aggregation of the ion pairs to multiplets which effectively cross-link the gel chains promoting the collapse transition. Additional facts counting in favor of this hypothesis will be presented below.

Mechanical Behavior of Gels at Swelling Equilibrium. Figure 3 illustrates the dependence of the shear modulus, G, of anionic PAAm/SAMPS gels on the concentration of poor solvent, ethanol, in water–ethanol mixtures.

(a) Good Solvent Region. From Figure 3 it is evident that at low concentrations of poor solvent the behavior of shear modulus is different for weakly and for strongly charged anionic gels. For weakly charged gels (Figure 3a) the modulus of elasticity decreases with decreasing P (i.e. with the gel swelling), while for strongly charged gels (Figure 3b) it increases with decreasing P. This distinction can be attributed to the limited extensibility of strongly charged subchains. Indeed, this becomes evident when the shear modulus, G, of the gels is plotted versus the degree of swelling (Figure 4). For a weakly charged gel (Figure 4a) the modulus of elasticity decreases with increasing Q, and hence with decreasing concentration of a poor solvent. For a strongly charged gel (Figure 4b) the dependence $G(Q)$ is nonmonotonic. At low degrees of swelling Q the modulus decreases with increasing Q, as expected on grounds of the Gaussian elasticity theory. At high degrees of swelling the modulus rises markedly. This behavior, which was observed for different ionic gels, is an indication of the limited extensibility of the chains.[9,10] Hence, the increase of the elastic modulus of strongly charged gels upon their swelling (i.e., with lowering P) is connected with the high stretching of the chains.

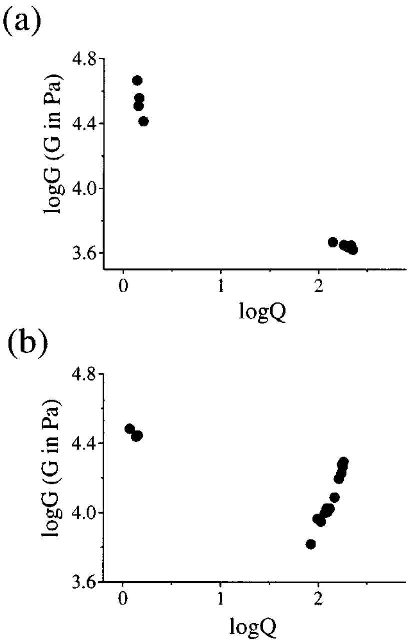

Figure 4. Shear modulus, G, as a function of the equilibrium degree of swelling of the anionic PAAm/SAMPS gels with $\alpha = 7\%$ (a) and $\alpha = 50\%$ (b).

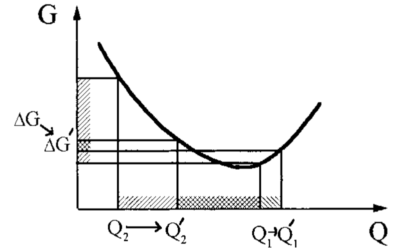

Figure 5. Schematic illustration of the variation of the elastic modulus of a strongly charged polyelectrolyte gel at collapse transition.

(b) Collapse Transition. For anionic PAAm/SAMPS gels independently on their degree of ionization (Figure 3a,b) the value of the modulus of elasticity rises sharply, simultaneously with volume phase transition. A similar effect was previously described for weakly charged gels.[7,8] In the present study it is demonstrated that this may be true for strongly charged gels as well.

A quite different behavior of the elastic modulus is observed at the collapse of fully ionized cationic PDADMAC gel (Figure 3c). For this gel the value of the modulus of elasticity remains almost unaffected by the volume phase transition. This effect seems to be quite unexpected; nevertheless it can be accounted for by the nonmonotonic character of the dependence $G(Q)$. Indeed, suppose that at the gel collapse the degree of swelling changes discontinuously from Q_1 to Q_2 (Figure 5). This shrinking should be accompanied by a change in the modulus of elasticity $\Delta G = G(Q_2) - G(Q_1)$. For a nonmonotonic dependence $G(Q)$ at certain values Q'_1

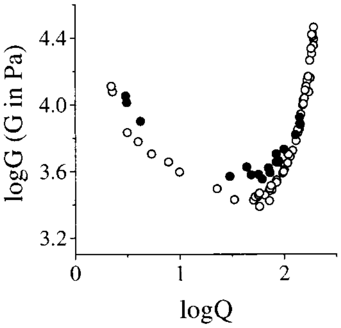

Figure 6. Shear modulus, G, of fully ionized PDADMAC gels as a function of the degree of swelling Q in water (○) and in ethanol (●).

and Q'_2 the variation of the modulus of elasticity $\Delta G'$ can be close to 0.

Thus, the data indicate a significant influence of the chain stretching on the elastic modulus of strongly charged gels when the quality of solvent is varied. Also in highly ionized polymers, the condensation of counterions produces an important effect which should become more pronounced in low polar media.[12]

Effect of the Polarity of Medium. To reveal the effect of the counterion condensation on the elastic properties of gels, the elastic modulus G of fully ionized PDADMAC gel was studied as a function of the degree of swelling Q in two solvents of different polarity: water ($\epsilon \sim 81$) and ethanol ($\epsilon \sim 24$). In contrast to previous data (Figure 4), the values of Q in Figure 6 do not correspond to equilibrium swelling, but they are obtained by partial drying of the gel samples swollen to equilibrium in the above-mentioned solvents. Figure 6 shows that the main distinction between the gels swollen in water and in ethanol is observed for shrunken gels. At low Q the elastic modulus of the gel in ethanol is higher than in water (at the same Q values). Probably, this deviation is connected with the increase of the condensation of counterions with the formation of ion pairs in a solvent of lower polarity. At the gel shrinking the concentration of polymer inside the gel becomes high enough to make the aggregation of ion pairs to multiplets more favorable. The aggregation of ion pairs belonging to different gel chains contributes to the elastic modulus by acting as additional cross-linking which increases the density of elastically effective chains.

A possible effect of such a cross-linking on the elastic modulus of the network was estimated theoretically for fully ionized polymer network in media of different polarity. The free energy of the network was minimized with respect to the number of additional cross-links n per one monomer unit at given values of the degree of swelling Q and the dielectric constant of the medium ϵ. The equilibrium values of n were used for calculation of elasticity modulus of the network G.

To take into account both the process of ion condensation, which is specific for strongly charged polyelectrolytes, and the process of ion pair formation, the following simplifying assumption was made. All of the counterions of the network were considered to be distributed between three different states characterized by the constant value of the electrostatic potential.

The first state is that of the mobile counterions which are able to move freely throughout the whole network. The fraction of the counterions in this phase will be denoted as β_1. The remaining part of the counterions is assumed to be in one of two possible condensed states. One type of condensed counterions (state 2) has only a restricted mobility in the molecular vicinity of network subchains. The second type of condensed counterions (state 3) associate closely with the opposite charges on the gel chains forming the ion pairs. We denote the fraction of the condensed ions which are not included in ionic pairs as β_2. If the total number of monomer units (ionic groups) in the network is N and the volume of the network is V, one could easily express the concentration of the counterions in each of these three states (c_1, c_2, and c_3, respectively):

$$c_1 = \frac{N_1}{V_1} = \frac{\beta_1 N}{V} = \frac{\beta_1 \phi}{al^2}$$

$$c_2 = \frac{N_2}{V_2} = \frac{\beta_2(1-\beta_1)}{al^2}$$

$$c_3 = \frac{N_3}{V_3} = \frac{1}{(4/3)\pi {r_0}^3}$$

where ϕ is the volume fraction of the polymer in the network, a is the length of the monomer unit, l^2 is the cross-section of the subchain, and r_0 is the distance between the two ions forming the ion pair. In writing these expressions for c_1, c_2, and c_3, we assume that the volume per counterion in the state 2 is al^2 and $(4/3)\pi r_0^3$ in the state 3. The volume fraction of polymer in the network ϕ is inversaly proportional to the degree of swelling Q:

$$\phi \sim 1/Q \tag{1}$$

In the theoretical consideration we will use ϕ instead of Q for convenience.

To find equilibrium values of the parameters of the counterion distribution β_1 and β_2 between states 1 and 2, 2 and 3, we use a Boltzmann equation:[13]

$$c_i = c_j \exp\left\{-\frac{(-e)\delta\psi_{ij}}{k_B T}\right\}$$

where indicies i and j denote the number of state ($i, j = 1, 2$ for β_1, and $i, j = 2, 3$ for β_2); $\delta\psi_{ij}$ is a difference of the electrostatic potential between states i and j and $(-e)$ is a counterion charge.

For the equilibrium between states 1 and 2 we take $\delta\psi_{ij}$ in the form of the electrostatic potential of the positively charged cylinder[13]

$$\delta\psi_{12} = 2\frac{\rho}{\epsilon}\ln\left(\frac{r_2}{r_1}\right)$$

where ρ is a charge density on the cylinder:

$$\rho = e\beta_1/a$$

Here we have taken into account the partial neutralization of the charges on the cylinder by the condensed counterions. The value r_1 is approximately equal to the distance between two neighbor subchains ($r_1 \sim (l/\phi)^{1/2}$), while r_2 is of the order of the subchain diameter ($r_2 \sim l$). Hence, for the equilibrium between states 1 and 2 one can write

$$\ln\left(\frac{1-\beta_1}{\beta_1}\right) = \left(1 - \frac{u_0\beta_1}{a}\right)\ln\phi \qquad (2)$$

where u_0 is the electrostatic constant

$$u_0 = e^2/\epsilon k_B T$$

To determine the fraction β_2, we will use the Debye–Huckel potential for state 2 and the spherical Coulomb potential for state 3. In this case the value of the $\delta\psi_{23}$ can be expressed as follows:

$$\delta\psi_{23} = \frac{e}{\epsilon a'}\exp\left\{-\frac{a'}{r_d}\right\} - \frac{e}{\epsilon r_0}$$

where r_d is a Debye–Huckel radius[13]

$$r_d = \left(\frac{al^2}{4u_0(1-\beta_1)\beta_2}\right)^{1/2} \qquad (3)$$

and a' is an average distance between the mobile counterion in the state 2 and its nearest counterpart on the network chain, which is not included in the ionic pair, and, hence, can participate in efficient Coulomb interactions:

$$a' = \frac{a}{2(1-(1-\beta_1)(1-\beta_2))}$$

Finally, for the fraction β_2 one can obtain the following:

$$\ln\left\{(1-\beta_1)\beta_2\frac{(4/3)\pi r_0^{\,3}}{al^2}\right\} = \frac{u_0}{r_0} - (1-(1-\beta_1)(1-\beta_2))\frac{2u_0}{a}\exp\left\{-\frac{1}{(1-(1-\beta_1)(1-\beta_2))}\frac{a}{2r_d}\right\} \qquad (4)$$

The numerical solution of the eqs 2 and 4 gives us the equilibrium values of the parameters β_1 and β_2 at a given volume fraction of the polymer ϕ (or at a given degree of swelling of the network Q, see (1)) and the dielectric constant of the solvent ϵ.

To obtain an equilibrium number of the physical cross-links n, we will minimize the part of the free energy of the network, which is dependent on the ion pair aggregation. This part of the free energy can be written as a sum of three terms:

$$F_n = F_{el.st.} + F_{ent} + F_{elast}$$

where $F_{el.st.}$ is the gain of the electrostatic energy from the pairs aggregation, F_{ent} is the loss of the entropy accompanying the aggregate formation, and F_{elast} is the energy of the elastic deformation of the network.

For calculations $F_{el.st.}$ was used as[14]

$$F_{el.st.} = -Nk_BT\frac{Au_0 n}{r_0}$$

where A is the numerical constant smaller than unity which was (somewhat arbitrarily) taken to be equal to 0.3 (for more details see ref 14).

The loss of the entropy F_{ent} in the process of ion pairs aggregation is connected to the restriction of the motion of the ion pairs included in the aggregate:

$$F_{ent} = -Nk_BTn\ln\left(\frac{c'}{c''}\right)$$

where c' and c'' are the concentrations of the ionic pairs in the network and in the aggregates, respectively. They were taken as

$$c' = (1-\beta_1)(1-\beta_2)\frac{\phi}{al^2}$$

$$c'' = \frac{1}{al^2}$$

The elastic contribution to the free energy F_{ent} was written in a form that accounts for limited extensibility of the network chains:[15]

$$F_{elast} = -\frac{dNk_BT}{2}\frac{a}{b}\left[xL^*(x) + \ln\left\{\frac{L^*(x)}{\mathrm{sh}(L^*(x))}\right\} - \gamma xL^*(\gamma x) - \ln\left\{\frac{L^*(\gamma x)}{sh(L^*(\gamma x))}\right\}\right]$$

$$x = (2(n_0+n)b/a)^{1/2}$$

$$\gamma = (\phi_0/d\phi)^{1/3}$$

$$b = 2(l_0 + l_e)$$

$$l_e = \frac{u_0}{16}\left(\frac{r_d}{a'}\right)^2 \qquad (5)$$

where L^* is the inverse Langevin function, b is the length of the statistical segment, and d is the factor which accounts for imperfection of the network. The adjustable parameter d was set to be equal to 0.15 to provide qualitative agreement between the theoretical and experimental dependencies of the elastic modulus on the degree of swelling of the network. n_0 is the number of the chemical cross-links in the network per one monomer unit, l_0 and l_e are the persistence length and the electrostatic persistence length[13] of the network subchains, and ϕ_0 is the polymer volume fraction in the reference state:

$$\phi_0 = l^2\left(\frac{2(n_0+n)}{ab^3}\right)^{1/2}$$

in which all network subchains are assumed to be Gaussian coils.

The elastic modulus of the network G was calculated as[16]

$$G = G_0\left(\frac{1}{6}\left(\frac{L^*(\gamma x)}{\gamma x} + \frac{dL^*(\gamma x)}{d(\gamma x)}\right) + \gamma^{-4}\right),$$

where

$$G_0 = 2\frac{k_BT(n_0+n)\phi_0\gamma}{al^2}$$

The results of calculations are shown in Figure 7. One can see that the values of the elastic moduli of the network at $\epsilon = 81$ and $\epsilon = 24$ are different in all ranges of Q values (Figure 7a). In the region of high degree of swelling this difference is due to the different values of

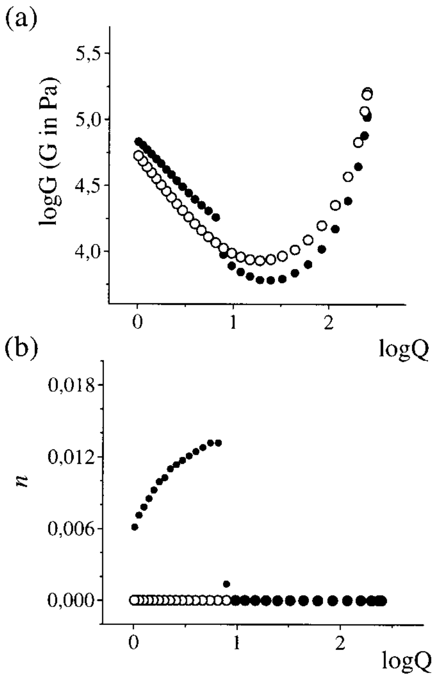

Figure 7. Theoretically predicted dependence of the elastic modulus G and the number of the physical cross-links n on the degree of swelling Q in water (○) and in ethanol (●).

the electrostatic persistence length l_e in solvents of different polarity (see eqs 3 and 5). The number of physical cross-links n in this region is equal to zero for both solvents (Figure 7b).

A decrease of the degree of swelling up to the certain value Q_{crit} leads to the jumpwise increase of the number of physical cross-links n in the solvent of lower polarity (Figure 7b). Thus, from this model it is evident that the low value of dielectric constant is more preferable for the formation of aggregates of ion pairs.

The comparison of the theoretical and experimental curves (Figures 6 and 7) shows a rather good agreement at the low values of the degree of swelling, which could be evidence of the assumption of the availability of aggregation of the associated ionic pairs in a medium of low polarity. Meanwhile, one can see some discrepancies between theoretical and experimental results in the region of high values of Q. The origin of these discrepancies is probably connected with the inhomogeneity of the investigated network. Due to the inhomogeneous distribution of the polymer, density in the network leads some domains in the network to reach the conditions for the ion pairs aggregation earlier than it happens for the entire network. Thus, the additional cross-linking of these domains induces the slight increase of the elastic modulus.

Conclusions. The behavior of the elastic modulus and the degree of swelling of polyelectrolyte gels with different degrees of ionization was investigated at the collapse transition induced by addition of a poor solvent. It was observed that the mechanical and swelling behavior are qualitatively different for weakly and strongly charged polyelectrolyte gels. This difference is determined by the two main factors:

(a) The subchains of the strongly charged gels in a swollen state are highly stretched. It leads to the nonmonotonic dependence of the elastic modulus on the degree of swelling of the gels.

(b) The behavior of strongly charged polyelectrolyte gels is significantly affected by the process of counterions condensation.

The influence of the counterion condensation on the mechanical properties of the fully ionized polyelectrolyte gel was also discussed for the media of different polarity.

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