Macromolecules **1996,** *29,* 681−685

Weakly Charged Polyelectrolytes: Collapse Induced by Extra Ionization

Alexei R. Khokhlov* and Elena Yu. Kramarenko

Physics Department, Moscow State University, Moscow 117234, Russia

Received October 3, 1994; Revised Manuscript Received May 12, 1995[⊗]

ABSTRACT: Several experimental facts indicate that the collapse transition in weakly charged polyelectrolyte gels or single macromolecules can take place with an increase in the degree of ionization (e.g., during titration of a weak polyacid). This unusual behavior can be explained by the energy gain from the formation of ion pairs in the collapsed state of low polarity, which competes with the swollen state where most of the counterions are dissociated. An increasing degree of ionization increases the thermodynamic advantages of the collapsed state with an ionomeric multiplet structure over the swollen polyelectrolyte state. In some regimes, this effect can lead to reentrant phase transition behavior, i.e., to an initial decollapse of the gel upon charging with subsequent jumplike collapse at a higher fraction of charged monomer units.

1. Introduction

The phenomenon of the coil−globule phase transition or intramolecular chain collapse due to the attraction of monomer units is well-known in the physics of macromolecules.[1−3] Many interesting phenomena in polymer physics (from DNA compactization[4] to polymer gel collapse[5−8] are different manifestations of this transition.

Recently considerable attention has been paid to the coil−globule transitions in ion-containing polymer systems: single polyelectrolyte macromolecules and polyelectrolyte gels. In particular, a theory of the coil−globule transition in single polyelectrolytes was developed in ref 9, while a theory of the collapse of polyelectrolyte gels was formulated in refs 5 and 10−13. This latter theory is usually assumed to be in good agreement with experimental data (see, e.g., refs 8 and 14).

There are fewer experimental results for the coil−globule transition in dilute polyelectrolyte solutions (single macromolecules). One system (a solution of partially ionized poly(acrylic acid) (PAA) in methanol at room temperature) was investigated in detail in ref 15. In this paper the authors discovered the collapse of a weakly charged polyelectrolyte chain with an increase of the degree of ionization. Ionization was accomplished by titration with CH_3ONa. It was observed that the reduced viscosity at first grows and then decreases rapidly in a small interval of degree of dissociation of PAA. A thorough investigation of the titration behavior of PAA in methanol using different techniques (elastic light scattering, osmotic, potentiometric, conductance, and UV spectrophotometric measurements) has clearly demonstrated that after the initial swelling PAA molecules undergo a conformational transition which results in small compact particles where the macromolecular chain is collapsed. The same nonmonotonic conformational behavior has been found for poly(methacrylic acid) (PMAA) titrated in methanol and ethanol.[16,17] At first sight, this behavior is rather surprising: with an increase of the degree of ionization the chain first swells (which is natural) but then rapidly shrinks.

In the present paper we show that this behavior may be explained by considering counterion binding to the ions of the chains with formation of ion pairs.

The importance of this effect for the behavior of the systems containing weakly charged polyelectrolytes was pointed out in ref 16, while in ref 18 the detailed theory was formulated for the case of polyelectrolyte gels. In this paper we study theoretically the influence of the formation of ion pairs on the collapse behavior of the gels. The polymer volume fraction in the collapsed gel is relatively high; thus the effective dielectric constant of this gel is lower than that for pure water, leading to an increased probability of ion pairing with subsequent formation of ionomeric multiplet structure. As a result, several new effects were predicted in ref 18. In addition to the quantitative change of the parameters of the collapse transition (an increase of the region of stability of the collapsed state and an increase of the amplitude of the volume transition), it was found that two different collapsed phases (with and without essential ion pairing and multiplet structure) can exist, with possible phase transitions between all three states of the gel: swollen, collapsed, and supercollapsed (i.e., collapsed with multiplet structure).

The importance of ion pairing for the collapse behavior of polyelectrolyte gels was experimentally demonstrated in ref 19 where the interaction of slightly cross-linked charged gels of poly(diallyldimethylammonium chloride) with sodium salts of chloride, bromide, iodide, and acetate in aqueous media was studied. It was found that the addition of sodium iodide leads to a sharp discontinuous collapse of the gel while an increase in the concentration of other salts causes a continuous shrinking. The peculiar feature of this salt-induced collapse is that the region of stability of the collapsed phase increases with the increase of the degree of charging of the gel chains. It was assumed that the reason for this is ion pairing between the cations of the gel and counterions in the collapsed gel with subsequent formation of an ionomeric multiplet structure. This makes the collapsed phase competitive with the swollen one, and this phase becomes increasingly energetically favored with an increase of the degree of charging of the gel chains. The strong influence of the nature of anionic species on the gel behavior has been explained by different association constants for different ions. Similar phenomena which were observed in ref 20 can be explained analogously.

The similarity of the just-described results for polyelectrolyte gels and the results of refs 15−17 for the

---

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

0024-9297/96/2229-0681$12.00/0

solutions of weakly charged polyelectrolytes is obvious. In both cases the collapsed phase is formed when the fraction of charged links increases. Therefore, it is natural to assume that in the experiments of Klooster et al.[15] the collapse of the polyelectrolyte coils at a sufficiently high degree of charging is also due to a kind of “supercollapsed” phase with ionomer-type multiplet structure being thermodynamically favored.

Thus, experimental data, both on polymer gels and single macromolecules, indicates the importance of accounting for mixed polyelectrolyte/ionomer behavior, i.e., for the partial formation of ion pairs and multiplets in weakly charged polyelectrolyte systems. The aim of this paper is to apply the theory developed in ref 18 for the experimental situation of refs 15−17 and 19−20, i.e., for the case when the polymer is a weak polyacid which is subsequently gradually ionized by titration and where the accompanying increase of the fraction of charged links causes the collapsed ionomeric state to become relatively more favorable.

In ref 18 we discussed the behavior of polyelectrolyte gels with a constant degree of ionization which may collapse when the solvent quality is varied. Now we examine the theory for the case when the solvent quality remains unchanged, while the degree of ionization of the polyacid gel is changed by titration. We then explain the experimental results of refs 15−16 on the nonmonotonic conformational behavior of PAA and PMAA upon titration and of refs 19−20 invoking a similar effect for cationic gels in sodium iodide solutions.

Below we consider specifically polyelectrolyte gels but recognize that similar calculations can be carried out for dilute solutions of weakly charged polyelectrolytes.

In the next section we recall the model of ref 18 and the expression for the free energy of the system. Results and discussion are presented in section 3.

2. Free Energy of a Polyelectrolyte Gel with Mixed Polyelectrolyte/Ionomer Behavior

Let us consider a sample of a weakly charged polymer gel swollen in a large amount of salt-free solvent.

As in ref 18 we use the following notation: T is the temperature, k is Boltzmann constant, a is the characteristic size of a monomeric unit, N is the total number of monomeric units in the gel, and m is the average number of monomeric units in the chain between two nearest-neighbor branch points.

As to the state of ionization of the gel, we will assume that polymer chains are polycarboxylic acids. In salt-free aqueous solutions most of the COOH groups are un-ionized. On addition of a base (e.g., NaOH), Na^+ ions substitute H^+ in carboxylic groups, and the equilibrium

$$COO^-Na^+ \rightleftarrows COO^- + Na^+ \qquad (1)$$

in pure water is shifted to complete dissociation. Thus, the gel becomes ionized. Let us assume that this results in one charged monomer unit per σ uncharged links, $\sigma \gg 1$ since we consider a weakly charged gel.

On the other hand, the equilibrium of reaction 1 is shifted to complete dissociation only if a given monomer unit is surrounded by water. This is essentially the case for the gels strongly swollen in water. For collapsed gels the volume fraction of polymer (nonpolar component) is high; therefore the conditions for reaction 1 are changed and one may suppose that some fraction, β, of Na^+ ions forms ions pairs. Then the total number of ion pairs in the gel is $(N/\sigma)\beta$, while the number of charged monomer units and counterions is $(N/\sigma)(1 - \beta)$. The same situation takes place if the gel is swollen in some solvent of lower polarity (e.g., methanol, cf. the Introduction): for this case the fraction of Na^+ ions forming ion pairs can be substantial even for the highly swollen gels.

Formulating this in a slightly more general form, one can say that β depends strongly on the dielectric constant ϵ of the gel medium which in turn is different for different gel conformations: in the swollen state the value of ϵ is close to that of the solvent, ϵ_0, while in the collapsed state it is close to that of the dry polymer (ϵ_1 is of order 1). Following the method used in ref 18 we adopt a linear interpolation of the dielectric constant of the partially swollen gel

$$\epsilon = \epsilon_0 - (\epsilon_0 - \epsilon_1)\Phi \qquad (2)$$

where Φ is the volume fraction of polymer inside the gel. The fact that ϵ depends on Φ is central to the theory of polymer gel collapse.[18]

We write the free energy of the network as a sum of four terms:

$$F = F_{el} + F_{int} + F_0 + F_d \qquad (3)$$

where F_{el} is the free energy of elastic deformation of the network, F_{int} is the free energy of non-Coulomb volume interactions of monomeric links, F_0 is the free energy connected with entropy of mobile ions, and F_d is the free energy connected with ion pair formation.

The first term, F_{el}, can be written in Flory's form[21] modified by Birshtein and Pryamitsyn to account for supercoiled conformations in the collapsed state:[22]

$$F_{el} = \frac{3}{2}kT\left[\left(\frac{V}{V_0}\right)^{2/3} + \left(\frac{V_0}{V}\right)^{2/3}\right] \qquad (4)$$

where V is the equilibrium volume of the network and V_0 is the volume of the network in the reference state in which the network chains are the closest to Gaussian coils.[12]

The free energy of volume interaction of monomeric links, F_{int}, can be written within the framework of the Flory−Huggins approximation:[21]

$$F_{int} = kT\frac{V}{a^3}[(1 - \Phi)\ln(1 - \Phi) + \Phi - \chi\Phi^2] \qquad (5)$$

where χ is the Flory−Huggins polymer−solvent interaction parameter. Here we assume χ = constant, although it is known[23] that the effective value of this parameter can vary upon titration. The volume fraction of monomeric units inside the gel, Φ, is connected with the concentration of these units, $n = N/V$, through

$$\Phi = na^3$$

The next term, F_0, is connected with the translational entropy of mobile counterions. Their number inside the network is equal to $(N/\sigma)(1 - \beta)$, so that (ref 18)

$$F_0 = \frac{N}{\sigma}(1 - \beta)kT\ln\left[\frac{n}{\sigma}(1 - \beta)\right] \qquad (6)$$

Finally, we need to take into account the free energy of $(N/\sigma)\beta$ counterions that are in the bound state and form ion pairs.

$$F_{\rm d} = -A_1 kT\frac{N}{\sigma}\beta\frac{u_0}{1-\dfrac{\epsilon_0-\epsilon_1}{\epsilon_0}\Phi} + kT\frac{N}{\sigma}(1-\beta)\ln[(1-\beta)] + kT\frac{N}{\sigma}\beta\ln[\beta] \quad (7)$$

where A_1 is a numerical constant of order 1 and $u_0 = e^2/(\epsilon_0 akT)$. The first term is the energy gain due to ion pair formation. Here we take into account the dependence (2) of the dielectric constant ϵ on volume fraction Φ. The last two terms are connected with the combinatorial entropy of bound counterions (see ref 18 and note 28). We shall neglect the energy gain due to the association of ion pairs into multiplets. This contribution was analyzed in detail in ref 18 and it was shown that it is less important than the contribution (7) due to the ion pairing, and taking this contribution into account does not lead to qualitatively new results.

Since a polyelectrolyte gel contains charged monomer units and counterions, one can expect that we should take into account also normal Coulomb interactions within the gel (e.g., calculated in the Debye–Huckel approximation). However, the corresponding term is missing in eq 3. This is, as shown in refs 8 and 13, because this contribution is much smaller than the translational entropy term. Therefore, in eq 3 of all the electrostatic contributions, we take into account only the ion pairing which influences the translational entropy of counterions.

To obtain the equilibrium values of the network volume and the concentration of bound counterions, we should minimize the expression for the free energy defined by eqs 3–7 with respect to the parameters V and β.

In ref 18 we have shown that at low values of the ratio ϵ_1/ϵ_0 the free energy expressed by eqs 3–7 has three minima which correspond to the swollen, collapsed, and "supercollapsed" states. This new third state is close to a densely packed dry gel and in this state practically all counterions are associated into ion pairs. The occurrence of such a "supercollapsed" state is a manifestation of an avalanche-type process, but its nature is quite different from that described in ref 9. It results from the following loop of positive feedback: the decrease of gel volume leads to the decrease of dielectric constant of the gel medium which favors ion pairing and therefore the number of mobile counterions decreases, which causes the further shrinking of the gel, etc. It should be mentioned that by changing the external parameters it is possible to induce the conformational transitions between all three states of the network (swollen, ordinary collapsed, and "supercollapsed"). In particular, the collapse of the network can be realized as the sequence of two first-order phase transitions.

3. Results and Discussion

In ref 18 we studied the collapse of a gel induced by change of the solvent quality, i.e., of the parameter χ. In the context of the experimental results of refs 15–17 and 19–20, we now assume parameter χ fixed, while the collapse is induced by titration. We plot all the dependences as functions of the parameter $1/\sigma$ which is monotonously increasing upon titration.

In Figure 1 we plot the dependence of the swelling ratio $\alpha = (V/V_0)^{1/3}$ (Figure 1a) and the fraction of ion pairs β (Figure 1b) on $1/\sigma$ for $A_1 = 1$, $u_0 = 1$ (which corresponds to polar solvents) and for different solvent quality. The parameters of the network are the same as in ref 18: $m = 500$, $\Phi_0 = 0.01$. The chosen values of χ parameters correspond to the case of the solution near the Θ condition ($\chi = 0.5$) or somewhat below the Θ point ($\chi = 0.7$–0.9). It can be seen that incorporation of a small amount of charges in the network chains during titration at first leads to the swelling of the network. In a Θ solvent this swelling is continuous, while in poor solvents, where the neutral gel is in a globular state, it is accompanied by a discontinuous first-order phase transition. With the increase of χ the transition point shifts to a higher value of the ionization degree, in accordance with general expectations. In the swollen state practically all counterions are mobile (β is close to zero, see Figure 1b); it is the osmotic pressure of mobile counterions that defines the volume of the network in this state. Thus, the value of α depends little on χ for highly swollen gels but grows with the increase of $1/\sigma$.

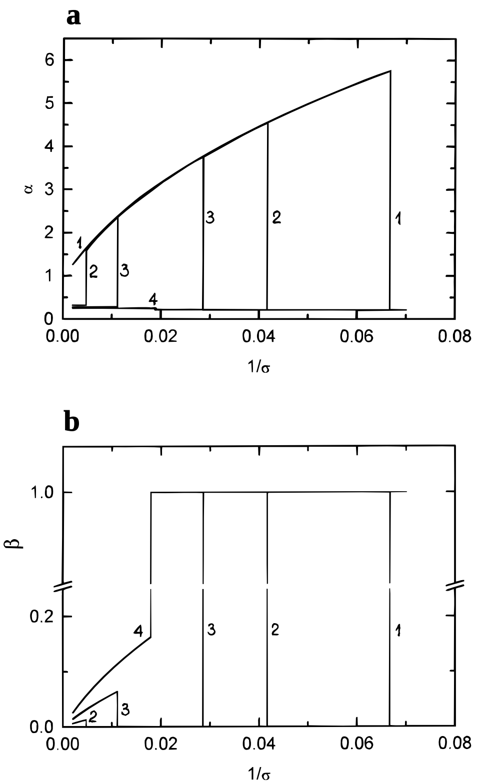

Figure 1. Dependence of the swelling ratio α (a) and of the fraction of ion pairs β (b) on the parameter $1/\sigma$ for $u_0 = 1$, $\epsilon_1/\epsilon_0 = 0.05$, and $\chi = 0.5$ (1), 0.7 (2), 0.8 (3), 0.9 (4).

The swelling of the gel continues until $1/\sigma$ reaches the critical value

$$1/\sigma = (1/\sigma)_{\rm cr} \sim A_1 u_0 \epsilon_0/\epsilon_1$$

At this degree of ionization the gel suddenly shrinks and the value of β becomes close to unity (i.e., all counterions form ion pairs). The reason for this is clear: the minimum of the free energy corresponding to the "supercollapsed" state (see ref 18) becomes more favorable than the minimum corresponding to the swollen state, and the system switches from the swollen polyelectrolyte to the "supercollapsed" ionomeric behavior. The transition is accompanied by the avalanche-type process described at the end of section 2. It is interesting to note that in the "supercollapsed" state the network is more compact than the initial neutral gel. The reason for this is the tendency to form a denser gel

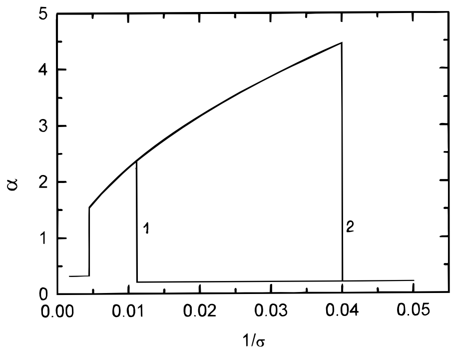

Figure 2. Dependence of the swelling ratio α on the parameter $1/\sigma$ for $\chi = 0.7$, $u_0 = 2$, and $\epsilon_1/\epsilon_0 = 0.05$ (1) and $\epsilon_1/\epsilon_0 = 0.1$ (2).

to minimize the dielectric constant and maximize the energy gain from ion pairing.

Thus, in agreement with the observations of refs 15–17 and 19–26, the change of the gel volume during the titration is nonmonotonous: initial swelling is followed by sudden collapse and switch from polyelectrolyte to ionomer behavior. It is even possible to have a reentrant collapse transition (curves 2 and 3 in Figure 1). Thus, this is a new way to induce reentrant collapse (other possibilities are described in refs 24–27) and it will be interesting to see if this possibility can be experimentally realized.

With the increase of χ (i.e., when the solvent becomes poorer) the initial decollapse occurs at higher ionization degrees of the network chains, while the reverse transition to a “supercollapsed” state takes place at lower values of $1/\sigma$ (cf. curves 2 and 3 in Figure 1a). Thus, the poorer the solvent, the smaller the region of stability of the swollen state. At $\chi = 0.9$ the gel is never swollen; with the increase of $1/\sigma$ the transition from a normal collapsed state (where only a small fraction of counterions form ion pairs) to the “supercollapsed” ionomeric state takes place. This transition cannot be clearly seen in Figure 1a (curve 4) because both states of the gel are very contracted; however it is very pronounced in Figure 1b: at the transition point the value of β changes in a jumplike fashion from a value less that 0.2 for the collapsed gel to 1 for the “supercollapsed” gel.

The critical value $(1/\sigma)_{\mathrm{cr}}$ depends strongly on the dielectric constant ϵ_1 of the bulk polymer. This is illustrated in Figure 2. With an increase of the polarity of the bulk polymer the point of collapse to ionomeric state shifts to higher values of ionization degree while the point of initial decollapse remains unchanged, i.e., the region of stability of supercollapsed state decreases significantly. The reason for this is lower energy gain from the formation of ion pairs in the dense gel phase of higher polarity.

On the other hand, the dependence of the collapse behavior on the polarity of the solvent, ϵ_0, is rather weak. This can be seen from Figure 3a: one notices only a very slight shift of the transition point for the solvent of lower polarity which is due to the greater tendency to form ion pairs. From Figure 3b one can see that the amount of counterions forming ion pairs in the swollen gel depends strongly on the dielectric constant of the solvent (although it remains much smaller than unity).

Finally, the results obtained above for the case of polyelectrolyte gels are equally valid for single weakly charged polyelectrolyte macromolecules. In rough approximation we may consider the interior of the coil as a kind of gel which is swollen in the excess of solvent; usually this type of approximation gives qualitatively correct results.

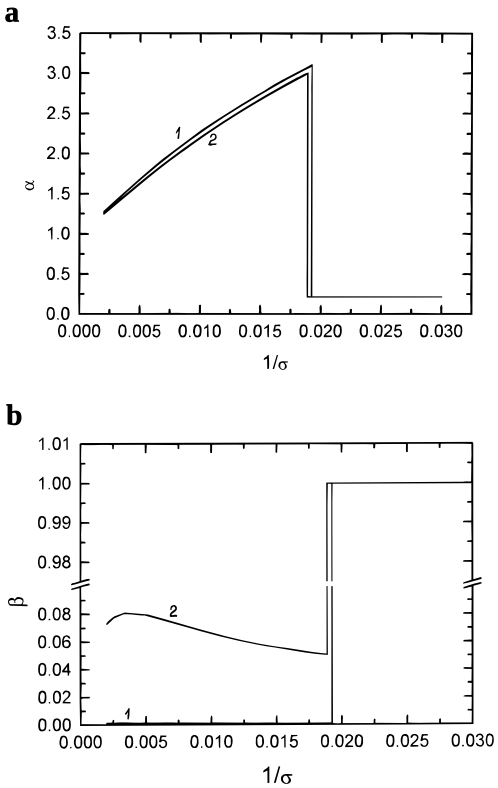

Figure 3. Dependence of the swelling ratio α (a) and of the fraction of ion pairs β (b) on the parameter σ for $\chi = 0.5$; $u_0 = 4$, $\epsilon_1/\epsilon_0 = 0.1$ (1) and $u_0 = 8$, $\epsilon_1/\epsilon_0 = 0.2$ (2).

4. Conclusions

We have shown that the experimentally observed nonmonotonous swelling of weakly charged polyelectrolyte gels and macromolecules upon titration may be explained by the partial formation of ion pairs, especially in the collapsed phase. When the degree of ionization is initially increased the macromolecule (or gel) swells mainly because of the increased osmotic pressure of the counterions. But simultaneously the collapsed phase with counterions condensed on polymer chains and forming ion pairs becomes relatively more favorable thermodynamically. At some critical value of the degree of ionization, the “supercollapsed” ionomeric phase starts to correspond to the absolute minimum of the free energy and an abrupt collapse takes place.

This collapse induced by ionization has been observed experimentally both for single macromolecules and for gels. Thus, this effect is of general significance in the physics of ion-containing polymers.

Acknowledgment. The authors are grateful to the Russian Foundation for Fundamental Research and to the International Science Foundation for financial support. E.Yu.K. is grateful also to the Royal Swedish Academy of Sciences and the International Center for Fundamental Physics in Moscow.

References and Notes

(1) Lifshitz, I. M.; Grosberg, A. Yu.; Khokhlov, A. R. *Rev. Mod. Phys.* **1978**, *50*, 683.

(2) Lifshitz, I. M. *Zh. Eksp. Teor. Fiz.* **1968**, *55*, 2408 (*Sov. Phys.—JETP* **1969**, *28*, 1280).

(3) Grosberg, A. Yu.; Khokhlov, A. R. *Statistical Physics of Macromolecules*; Nauka Publishers: Moscow, 1989; English translation, AIP Press; New York, 1994.

(4) Lerman, L. S. In *Physico−Chemical Properties of the Nucleic Acids*; Duchesme, J., Ed.; Academic Press: New York, 1973; p 61.

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

(6) Tanaka, T.; Fillmore, D.; Sun, S.-T.; Nishio, J.; Swislow, G.; Shah, A. *Phys. Rev. Lett.* **1980**, *45*(20), 1636.

(7) Nicoli, D.; Young, C.; Tanaka, T.; Pollak, A.; Whitesides, G. *Macromolecules* **1982**, *16*, 887.

(8) Khokhlov, A. R.; Starodubtzev, S. G.; Vasilevskaya, V. V. *Adv. Polym. Sci.* **1993**, *109*, 123.

(9) Khokhlov, A. R. *J. Phys. A.: Math. Gen.* **1980**, *13*, 979.

(10) Dusek, K.; Patterson, D. *J. Polym. Sci.* **1968**, *2*, 1209.

(11) Ilavsky, M. *Polymer* **1981**, *22*, 1687.

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

(13) Vasilevskaya, V. V.; Khokhlov, A. R. In *Mathematical Methods for Polymer Studies*; Lifshitz, I. M., Molchanov, A. M., Eds.; Pushino: 1982; p 45.

(14) Shibayama, M.; Tanaka, T. *Adv. Polym. Sci.* **1993**, 109.

(15) Klooster, N. Th. M.; van der Touw, F.; Mandel, M. *Macromolecules* **1984**, *17*, 2070, 2078, 2087.

(16) Morawetz, H.; Wang, Y. *Macromolecules* **1987**, *20*, 194.

(17) Austin, M. Ph.D. Thesis, California Polytechnic State University, 1993.

(18) Khokhlov, A. R.; Kramarenko, E. Yu. *Macromol. Theory Simul.* **1994**, *3*, 45.

(19) Starodoubtsev, S. G.; Khokhlov, A. R.; Sokolov, E. L.; Chu, B. *Macromolecules* **1995**, *28*, 3930.

(20) Kudo, S.; Kosaka, N.; Konno, M.; Saito, S. *Polymer* **1992**, *33*, 5040; **1993**, *34*, 2370.

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

(22) Birshtein, T. M.; Pryamitsyn, V. A. *Vysokomol. Soed. A* **1987**, *29*, 9, 1858.

(23) Hill, T. L. *An Introduction to Statistical Thermodynamics*; Addison-Wesley Publishing Co. Inc.: Massachusetts, 1960.

(24) Katayama, S.; Hirokawa, Y.; Tanaka, T. *Macromolecules* **1984**, *17*, 2641.

(25) Katayama, S.; Ohata, A. *Macromolecules* **1985**, *18*, 2781.

(26) Amiya, T.; Hirokawa, Y.; Hirose, Y.; Li, Y.; Tanaka, T. *J. Chem. Phys.* **1987**, *86*, 2375.

(27) Vasilevskaya, V. V.; Ryabina, V. R.; Starodubtzev, S. G.; Khokhlov, A. R. *Vysokomolek. Soed. (Polym. Sci. USSR)* **1991**, *33A*, 885.

(28) Strictly speaking, we should take into account also the combinatorial entropy

$$kT\frac{N}{\sigma}\ln\frac{1}{\sigma} + kTN\left(1-\frac{1}{\sigma}\right)\ln\left(1-\frac{1}{\sigma}\right)$$

connected with the migration of H^+ ions along the chains. However, this contribution is independent both of Φ and β and does not play any role in the subsequent analysis.

MA946426D