New Type of Swelling Behavior upon Gel Ionization: Theory vs Experiment

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ABSTRACT: We report a combined experimental and theoretical study on the swelling behavior of polyelectrolyte gels with various types of counterions. Experimental research was focused on poly(methacrylic acid) and poly(acrylic acid) gels in methanol neutralized with different bases providing sodium, cesium, tetramethyl-, tetraethyl- or tetrabutylammonium counterions. The novelty of the theoretical treatment is that the counterion size is explicitly taken into account as well as the dependence of the ion association constant on the volume fraction of polymer within the gel. We demonstrate that, depending on the counterion size, three different regimes of the gel behavior are realized. In case of bulky tetrabutylammonium counterions the gel swells upon ionization. For small counterions (Na⁺, Cs⁺) the gel swelling at low ionization degrees is succeeded by its collapse. New type of behavior was observed and theoretically described for the gels with counterions of intermediate sizes (tetramethyl- and tetraethylammonium). In this case, the gel ionization causes first swelling, then collapse and finally reswelling of the gel. This distinction in gel behavior with counterions of different types is explained by decreasing tendency for ion pair and multiplet formation with growing counterion dimensions. Our finding of the counterion-controlled collapse/decollapse transition is significant for fundamental understanding of the role of ion association processes in polyelectrolyte gel behavior as well as for design of sensors and environmentally responsive containers for controlled delivery applications.

I. INTRODUCTION

Polyelectrolyte (PE) gels are of great interest due to their significant swelling in water and high responsiveness to external stimuli such as temperature, pH, salt concentration etc. Owing to these properties PE gels are widely used in various fields, in particular, as superabsorbents and sensors.

In the case of weakly charged gels both remarkable swelling and high responsiveness are mainly attributed to the presence of counterions. Counterions appear as a result of dissociation of ionic groups on gel subchains in polar media such as water and they are kept within the gel because of its total electric neutrality. Being confined in a limited volume of the gel the counterions strive to stretch the gel to increase the available volume and, hence, to increase their translational entropy, thus, providing an exerting osmotic pressure. It is due to this osmotic pressure that the swelling degree of PE gels increases with gel ionization and can be considerably higher than that of the neutral analogues. The water uptake by PE gels can reach 99.9% with respect to own mass of the dried gel.

Swelling of the gels with incorporation of ionic groups in their subchains can be considered as a standard PE behavior. It

has been observed in numerous experimental works, explained theoretically and reviewed in a number of publications.¹⁻³

More complex situations appear if a gel swells in media with not very high polarity. In this case some unusual effects originating from counterion association with ions on the gel subchains can take place. In particular, a new so-called supercollapsed state of the gel can exist.⁴ In this state practically all counterions form ion pairs associating into multiplets and the gel demonstrates ionomer-type behavior. The existence of the two distinct collapsed states of the gel was observed on an example of two-stage collapse of the poly-(diallyldimethylammonium chloride) hydrogels in an aqueous solution upon addition of sodium iodide.⁵ Multiplet formation in polyelectrolyte gels was proved experimentally by fluorescence spectroscopy for poly(methacrylic) gels with fluorescent europium counterions.^{6–8}

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Another interesting manifestation of counterion association is the gel collapse induced by its ionization. It was predicted theoretically⁹ and was first observed experimentally¹⁰ for poly(methacrylic acid) (PMAA) gels in methanol. Gel ionization was performed by titration with sodium methoxide. It has been found that incorporation of a small amount of charges into the gel subchains causes first gel swelling due to increasing osmotic pressure of mobile counterions. However, at some critical ionization degree the gel collapses. It has been found that the collapsed gel is more compact than initial uncharged one, this fact supports the theoretical conclusion of ion pair association into multiplets acting as additional physical cross-links. Ion pair aggregation in these gels was confirmed by dielectric spectroscopy.¹¹

Ion aggregation processes should be strongly influenced by the dielectric constant of the solvent and by the size and valency of counterions. A detailed study of the effect of the solvent and counterion type on the gel collapse has been performed by Satoh and co-workers.^{12-17¹} They have investigated counterion- and solvent-specific behaviors for weak polyacid (alkali-metal polyacrylate),12,13 weak polybase (poly(allyl amine) salts),¹⁴ strong polybase (partially quater-nized poly(4-vinyl pyridine) gels)^{15,16} and strong polyacid (alkali-metal poly(styrene sulfonate))¹⁷ gels. The swelling occurred in aqueous organic solvent mixtures. Organic solvents used were methanol, ethanol, 2-propanol, tert-butanol, dimethyl sulfoxide, acetone, acetonitrile, tetrahydrofuran, dioxane. The authors conclude that the solvent specificity is mainly defined by the dielectric constant, the higher is the dielectric constant of the organic solvent, the higher is the critical value of the organic solvent fraction at which the transition into the collapsed phase took place. However, it also depends on gel subchain hydrophobicity which causes some solvent redistribution as a result of preferential sorption of one of the solvent components by the gel^{1,18} and gives rise to different accessibility of the organic solvent to the charged groups. Satoh and co-workers examined also the influence of the counterion nature on the collapse behavior. For alkali counterions (Na⁺, K⁺, Li⁺, and Cs⁺) no common tendency was found. To explain it the authors have proposed a size-fitting idea that there exists some optimum counterion size in the ion-cluster formation and that a size-fitting effect essentially contributes to the gel collapse. One could suggest that the variation of the size of counterions in a larger range could clarify the situation. Also, the preferential sorption which can take place in mixed solvents used in papers¹²⁻¹⁷ can conceal the role of the size of counterions.

A theory of the gel collapse taking into account the counterion size as well as counterion nonelectrostatic interactions with each other and with the gel monomer units was proposed in ref 19. It has been shown that indeed the counterion size influences considerably the gel swelling and the character of the collapse transition. Besides, an increase in the counterions size leads to a decrease of the fraction of ion pairs. However, the theory does not consider the supercollapsed state of the gel with multiplet structure, although it is in this dense state the influence of the counterion size should be the most crucial.

Here, in a combined experimental and theoretical study we focus on the effects of counterion nature and size in PE gel collapse. Experimentally we study collapse transition induced by gel ionization on the example of polyacrylate and polymethacrylate gels in methanol. In contrast to papers,^{12–17} we use one-component solvent, this allows us to avoid all

complications connected with the possible redistribution of components of a mixed solvent in the process of the collapse transition. As to the counterions, we study the effect of not only relatively small conterions like Na⁺ and Cs⁺, but also counterions whose size is comparable with the size of the gel monomer units, in particular, tetramethylammonium (TMA), tetraethylammonium (TEA), and tetrabutylammonium (TBA) ions (see Figure 1).



Figure 1. Schematic representation of various types of counterions used in this study and their sizes.

In the theoretical description, we explicitly take into account not only the own size of counterions but also the dependence of the dielectric constant on the volume fraction of low-polar polymer within the gel as well as ion association processes with the formation of ion pairs and multiplets and explain experimental results on the collapse/decollapse transitions in PE gels induced by counterions of different types. We have shown both experimentally and theoretically that a new type of transition between collapsed and swollen states of the gel can be realized in case of rather bulky counterions not capable to form a stable supercollapsed state at high ionization degrees.

II. EXPERIMENTAL PART

Gel Preparation. Gels were prepared by free-radical polymerization of acrylic acid (AA) or methacrylic acid (MAA) in dimethylformamide at a monomer concentration of 3.06 mol/L. 2,2'-Azobis(isobutyronitrile) $(1.53 \times 10^{-2} \text{ mol/L or } 0.5 \text{ mol }\%)$ and $N_{,N'}$ -methylene(bisacrylamide) (4.6 × 10⁻² mol/L or 1.5 mol %) were used as initiator and cross-linker, respectively. The polymerization was performed in cylindrical glass tubes with inner diameter of 0.40 cm under a nitrogen atmosphere at 63 °C for 24 h. The prepared gels were washed with a large amount of methanol for 3 weeks to remove unreacted components and sol fraction. Gels with grafted noctyl chains were prepared by free-radical copolymerization of AA and n-octyl acrylate at the same conditions as PAA gels. By ¹³C NMR spectroscopy it was shown that *n*-octyl acrylate units are randomly distributed along the polymer chains.²⁰⁻²³ The gels are denoted in terms of type and molar content of hydrophobic comonomer units. For example, C8-20% PAA indicates a gel containing 20 mol % of noctyl acrylate (C8) and 80 mol % of AA repeat units. Details of preparation and characterization of the polymer gels are described elsewhere.^{6,7,10,20–23}

Swelling Experiments. The gels of PAA or PMAA salts were obtained by neutralization of PAA or PMAA gels swollen in methanol with the corresponding base: tetramethyl-, tetraethyl- or tetrabuty-lammonium hydroxide, sodium methoxide, and cesium hydroxide. To perform the neutralization the gel samples swollen in methanol (approximately 0.15 g) were placed into solutions of base of a definite concentration (3 mL of solution per 10^{-5} mol of network repeat units) at 25 °C. The experiments were performed under nitrogen atmosphere. The base was added to the gel (not to the monomer) in order to provide the same network topology of the gel samples with different degrees of neutralization. When calculating the degrees of ionization we neglected the self-dissociation of AA and MA units (in acid form) as it is negligibly small. The gels were allowed to swell at room temperature for at least two weeks before the measurements.

Comparison of the data from the gels stored for different periods of time shows that two weeks is enough time to get equilibrated samples. The degree of swelling of the gel samples was characterized by the $(m - m_{dry}) / m_{dry}$ ratio, where *m* is the mass of the gel at equilibrium and m_{dry} is the mass of the dried gel.

III. THEORETICAL MODEL

Our theoretical model considers a sample of a charged polymer gel swollen in a large amount of a salt-free solvent. The gel consists of ν_0 flexible subchains, N is the average number of monomeric units of the size a in the subchain, i.e. the chain between two nearest-neighbor branching points. Let in the reference state all subchains are unperturbed Gaussian coils,²⁴ polymer volume fraction inside the gel is of the order of $\Phi_0 \sim N^{(-1/2)}$ and the gel volume can be estimated as $V_0 \sim N\nu_0 a^3/\Phi_0$. The equilibrium state of the gel in a solvent is characterized by the swelling ratio with respect to the reference state defined as

$$\alpha = \left(\frac{V}{V_0}\right)^{1/3} = \left(\frac{\Phi_0}{\Phi}\right)^{1/3} \tag{1}$$

where V and Φ are network equilibrium volume and polymer volume fraction, respectively.

Concerning the gel ionization, we consider polymer chains to be polycarboxylic acids. In water solutions most of the COOH groups are not ionized. When a base (e.g., X^+OH) is added to the solution, monovalent X^+ ions substitute H^+ ions in carboxylic groups, and the resulting salt easily dissociates into ions:

$$-COO^{-}X^{+} \rightleftarrows -COO^{-} + X^{+}$$
⁽²⁾

and the gel acquires charges. Let us assume that in average the gel subchains contain Nf ions, $f \ll 1$.

Complete dissociation 2 takes place in aqueous solutions, however, in media of lower polarity some fraction p of X^+ ions will form ion pairs with carboxylic groups of the gel. Moreover, due to dipole-dipole attraction the ion pairs are capable of joining into multiplets acting as additional physical cross-links of the gel. Let us denote as q the fraction of ion pairs forming multiplet structure. Thus, Nfq and Nfp are the numbers of ionizable groups per gel subchain involved in multiplets and ion pairs, respectively. The number of mobile X^+ counterions per subchain is equal to the number of subchain charged groups, i.e., to Nf(1 - p - q).

The gel free energy in k_BT units per gel subchain has the following form:

$$F_{tot} = F_{el} + F_{vol} + F_c + F_{agg} \tag{3}$$

The first F_{el} term is the free energy of elastic deformation of the network subchain:

$$F_{el} = \frac{3}{2} \left(1 + \frac{\nu}{\nu_0} \right) \left[\left(1 + \frac{\nu}{\nu_0} \right)^{1/3} \alpha^2 + \left(1 + \frac{\nu}{\nu_0} \right)^{-1/3} \alpha^{-2} \right]$$
(4)

This expression takes into account both the formation of ν new network cross-links owing to multiplet formation and consequent shortening of mean subchain contour length.⁴ Each charged group associated into multiplet results in one additional gel subchain, thus $\nu/\nu_0 = Nfq$. The more the total number of cross-links is, the less the average length \tilde{N} of subchains is: $\tilde{N} = N\nu_0/(\nu_0 + \nu)$.

The second F_{int} term is the free energy of interactions of uncharged monomeric units written in the framework of Flory–Huggins lattice theory:^{24–26}

$$F_{vol} = \frac{N}{\Phi} [(1 - \Phi - f\Phi) \ln(1 - \Phi - f\Phi) - \chi \Phi^2]$$
(5)

Here χ is the polymer–solvent interaction parameter.

This expression explicitly takes into account the nonzero volume of counterions (the term $f\Phi$). In case of point-like counterions this term is absent in the interaction free energy (see previous publications^{4,9}). It should be noted that in the framework of the lattice theory the counterion and monomer unit volumes are set to be equal to each other. The presence of bulky counterions causes some additional steric effects and plays a crucial role in the system behavior. Interactions between counterions and other components (solvent molecules and monomer units) are neglected or corresponding χ parameters are set to zero.

The next term in 3, F_{c} describes the free energy of translational motion of the counterions. All counterions are held within the gel because of its electroneutrality. The counterion concentration inside the network is equal to $f\Phi/a^3$, thus, the entropy of their translational motion is given by

$$F_c = Nf \ln(f\Phi) \tag{6}$$

Finally, the last F_{agg} term in 3 accounts for the aggregation free energy due to ion pair and multiplet formation. For the sake of simplicity one multiplet is assumed to consist of two ion pairs. Ion pairing and multiplet formation are described as thermoreversible reactions, the free energy F_{agg} for this case was calculated in ref 27, and it reads

$$F_{agg} = Nf \left[p + \frac{3}{2}q + 2\ln(1 - p - q) \right]$$
(7)

Here the fractions p of ion pairs and q of multiplets in the system are connected with the volume fraction of ions in polymer chains $f\Phi$ through the mass action laws:

$$\frac{p}{(1-p-q)^2} = k_p f \Phi \qquad \frac{q}{p^2} = 2k_m f \Phi \tag{8}$$

The value of p depends strongly on the ion association constant $k_p = \exp(-E/k_{\rm B}T)$, where E is the binding energy of ions in an ion pair, $E = -e^2/\varepsilon b$, ε is the dielectric constant of the gel medium and b is the distance between ions in an ion pair. It is natural to expect that counterion dimensions could affect the ion pair size. Indeed, small counterions can more easily approach charges in polymer chains forming contact ion pairs with $b \sim a$ while for bulky counterions b > a due to stronger effect of excluded volume interactions. Thus, the association energy would be different for different types of counterions.

As in refs 4 and 9, we suppose that the dielectric constant of the gel medium depends on the polymer volume fraction within the gel and adopt linear interpolation dependence of ε on Φ :

$$\varepsilon = \varepsilon_0 (1 - \delta \varepsilon \Phi) \tag{9}$$

where $\delta \varepsilon = (\varepsilon_0 - \varepsilon_p)/\varepsilon_0$, ε_0 and ε_p being the dielectric constants of the pure solvent and pure polymer, respectively. The ion pair association constant then equals

$$k_p = \exp\left(\frac{e^2}{\varepsilon b k_B T}\right) = \exp\left(\frac{u_0}{(1 - \delta \varepsilon \Phi)b/a}\right)$$
(10)

where $u_0 = e^2/\varepsilon_0 a k_B T$. The parameter b/a is of the order of unity and characterizes the relative size of an ion pair depending on the type of counterion.

Finally, the multiplet association constant is defined as $k_m = mk_p$, since the energy gain of multiplet formation from two ion pairs is of the order of *E*. In the calculations below we put the numerical constant m = 1. The case of no multiplet formation corresponds to m = 0 (see eq 8).

Theoretical dependencies were obtained via minimization of the total free energy F_{tot} with respect to the swelling ratio α . Parameters N = 100 and $\delta \varepsilon = 0.8$ were fixed in all subsequent calculations. We also set $u_0 = 3.5$, keeping in mind that in the experiments gels were immersed in methanol. For aqueous solutions u_0 is of the order of unity.

IV. RESULTS AND DISCUSSION

Typical experimental swelling curves for PMAA gels neutralized with different bases are shown in Figure 2. The corresponding theoretical dependences of the swelling ratio α on the degree of ionization *f* are presented in Figure 3. In this figure, we also plot the estimated values of the fraction of multiplets *q* at different *f*. The calculations were performed for $\chi = 0.5$, i.e., for Θ solvent conditions corresponding to the present experimental system



Figure 2. Effect of the fraction of ion-containing units f on the degree of swelling of gels of N-alkylammonium and alkali salts of PMAA with counterions of different size.

because methanol is a Θ solvent for PMAA gel in acid form.¹⁰ The volume fraction of gel monomer units in the initial state was taken equal to $\Phi_0 = 0.1$. Different counterions were characterized by different values of the dimensionless parameter b/a.

From Figures 2 and 3, it is seen that depending on the type of the counterions three general scenarios of the gel swelling behavior can be distinguished.

Regimes of Gel Swelling. A. Polyelectrolyte Regime. The first scenario is realized when neutralization is performed by TBA hydroxide which gives the salt with the largest counterion among the used ones. Increase of the ionization degree leads to the swelling of the gel which is typical for polyelectrolyte regime (Figures 2a and 3a). In this regime, ion association is not favorable because of a low energy gain from counterion binding in large ion pairs (the theoretically calculated values of *p* and *q* are close to zero, see Figure 3a). The growth of the gel volume with *f* is due to increasing osmotic pressure of mobile counterions. This regime is usually observed in polar solvents such as water or in water/organic mixtures at small fractions of nonpolar cosolvent and is described by classical theories.¹ In the highly swollen state of the gel the volume fraction of the counterions is small and the own volume of the counterions is negligible. In accordance with classical results^{1,24} the equilibrium state of the gel is set by a balance between osmotic pressure of mobile counterions and elastic stretching of the gel subchains. The swelling ratio is then defined just by the number of counterions per gel subchain $\alpha \sim (Nf)^{1/2}$ monotonically increasing with f. This theoretical result is valid for rather low ionization degrees of the gel. At high f counterions cannot be treated as an ideal gas due to enhanced contribution from electrostatic interactions and a possible Onsager-Manning condensation of counterions on the strongly charged gel subchains.²⁸ Experimentally observed slight decrease of the swelling degree at f > 0.5 (Figure 2a) can be attributed to these effects neglected in the theoretical model.

B. Polyelectrolyte/lonomer Switching. The second opposite scenario is experimentally observed for small sodium and cesium counterions (Figure 2b) and theoretically described for a high value of the association constant when strong contact ion pairs with short distances between ions are formed (Figure 3b).

In this case initial swelling of the gel in a narrow range of f is followed by an abrupt gel collapse. In the course of the collapse the gel becomes even more compact—supercollapsed—than it was when uncharged at f = 0. As soon as the supercollapsed state is reached the gel stays in this state with further increase of f up to unity. This type of behavior was predicted theoretically in ref 9 and was first observed experimentally in ref 10. It is attributed to the ever-growing ion pair formation when the system switches to an ionomer regime.

The occurrence of the supercollapsed state is shown to be a manifestation of an avalanche-type process of consequent gel shrinking and counterion binding. The medium within the gel becomes less polar with a decrease of the gel volume and the growth of association constant results in an additional counterion binding. The osmotic pressure exerted by the counterions decreases, which in turn leads to further shrinking of the gel and so on. Thus, the gel adopts a dense ionomeric conformation additionally stabilized by multiplet formation, $q \sim 1$ (see Figure 3b).

Experimentally the ion association is confirmed by conductivity experiments.¹⁰ It was shown that despite of the increasing amount of ion-containing network units appearing

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Figure 3. Dependence of the swelling ratio α (left column) and of the fraction of multiplets q (right column) on the fraction of charged groups f for $\chi = 0.5$, $\Phi_0 = 0.1$ and various ion pair dimensions b/a = 0.80, 0.95, 1.00, and 1.20.

during neutralization, the reduced conductivity increases only at low f and then falls, reaching a constant value unaffected by further increase of f. As to the multiplets their formation was evidenced by us^{29,30} for the same system by dielectric spectroscopy studies.

The relative effect of ion pair and multiplet formation for sodium and cesium counterions in this regime will be discussed in more details below.

C. Reentrant Polyelectrolyte/lonomer/Polyelectrolyte Switching. Finally, completely new scenario was first observed for PMAA gels with the counterions of intermediate size tetramethyl- and tetraethylammonium ones (Figure 2c). One can see that the charging of the gel causes its collapse at small fas in the case of small sodium and cesium ions. However, the supercollapsed state for these counterions is stable only in a limited range of f whereas at high ionization degree the gel swells again. This is the first observation of the reentrant swelling of the gels upon ionization.

Similar behavior was recently observed by us at the titration of linear PAA with tetramethylammonium hydroxide in methanol solutions.^{31,32} In this case, the specific viscosity first increases, then drops and finally recovers its maximum value

with increasing degree of ionization. The initial drop of viscosity is accompanied by the decrease of the specific conductivity indicating the binding of some counterions with the formation of ion pairs.^{31,32} Simultaneously, the ¹H NMR shows the disappearance of the signals assigned to the protons of macromolecular chains,³¹ which is due to the collapse of macromolecules resulting in the hindering of their internal motion. The latter leads to a drastic decrease of the spin-spin relaxation times of polymer protons, as a result, their signals widen to infinity and are not observed in the spectrum. $^{31, 53}\ At$ the reswelling at higher degree of ionization the NMR signals reappear. Simultaneously, the specific conductivity increases indicating the dissociation of ion pairs with the release of counterions.^{31,32} Therefore, for counterions of intermediate size the transition from polyelectrolyte to ionomer regime is followed by a reentrant transition from ionomer to polyelectrolyte regime, when the degree of ionization increases. In the present study such double transition is first observed in polymer gels.

The developed theory accounting for the counterion own volume also predicts for the first time a possibility of consequent collapse and reentrant swelling of the gel upon charging. The reentrant ionomer/polyelectrolyte switching is shown to occur with ion pairs of intermediate size, the corresponding curves calculated for b/a = 1.00 and b/a = 0.95 are shown in Figure 3c. Similar effect has recently been found by us theoretically in the case of polymer micelles. Ionic coronae of micelles resembling PE gel medium undergo successive collapse and reswelling unduced by extra ionization in the solvent of low polarity.³⁴

The physical reason of the first collapse transition at small fwas discussed in the previous section. The second transition from ionomer to polyelectrolyte state is only possible for rather bulky counterions. Neglecting the counterion size in this case we could not have predicted the gel reswelling. Indeed, in the dense ionomer state the energy gain from an ion pair formation $E = -e^2/\varepsilon_n b$ is purely defined by the dielectric constant of the dry polymer, it does not depend on the fraction of charged groups in the gel and as soon as the energy gain from ion association exceeds the entropy loss of counterions translational motion the ionomer structure is formed and stays unchanged with further increase of ionization degree. This result is valid for point-like counterions. In reality incorporation of more ionic groups into the polymer gel in the ionomer state should enhance the polymer media polarity. Ion pairs formed by bulky counterions possess significant dipole moments and the dielectric properties of the ionomer state should differ from those of low-polar uncharged polymer. Thus, ionization of the gel in ionomer state could result in a decrease of the ion association constant and further ion pairing could become unfavorable leading to reswelling of the gel. Our theory accounts for this effect implicitly. By substitution the inequality for uncharged polymer volume fraction $\Phi < 1/(1 + f)$ into eq 9 we obtain the following estimation of the energy gain from ion binding E(f)

$$E(f) \ge -\frac{e^2}{b\varepsilon_p} \frac{(1+f)}{(1+f\varepsilon_0/\varepsilon_p)} > -\frac{e^2}{\varepsilon_p b}$$
(11)

for $\varepsilon_0 > \varepsilon_p$ and any *f*.

According to the theoretical calculations the region of ionomer state stability becomes narrower with an increase of the counterion size (see Figure 3c). This result has rather lucid explanation. The energy gain from ion association decreases with an increase of the size of ion pairs, b/a, and the supercollapsed ionomer state becomes less favorable. Thus, with growing counterion size the collapse transition shifts to higher ionization degrees while the reswelling occurs at smaller f.

This conclusion is in agreement with the experimental observations. Indeed, from Figure 2c, it is seen that the gel with larger TEA counterions remains in the collapsed state in a narrower range of f in comparison with the corresponding gel with TMA counterions. This is evidently because of the fact that more bulky TEA ions form weaker ion pairs with the network charges.

Hindered Multiplet Formation. One more important observation comes from the comparison of parts b and c of Figure 2. It is seen that for the series of tetraalkylammonium ions the degree of swelling of the gel decreases with decreasing radius of counterions (Figure 2c). This is in contrast to the behavior of the gels with alkali counterions, which swell more in the case of smaller counterions (Figure 2b). This difference can be attributed to the fact that the ion pairs with bulky tetraalkylammonium ions cannot form multiplets so efficiently

as alkali ions do. As a result the decrease of the degree of swelling with decreasing size of tetraalkylammonium counterions reflects primarily more pronounced tendency of smaller TMA ions for the formation of ion pairs. At the same time, for alkali ions the contribution of ion aggregation to multiplets becomes predominant. In this case, the most important fact is that bigger cesium ions give ion pairs with larger dipole moments, and such ion pairs demonstrate a more marked ability to further aggregate into multiplets. As a result, the degree of swelling for the gels with cesium ions becomes smaller than for the corresponding gels with sodium ions.

To demonstrate the importance of the multiplet formation in the collapse of the gels with alkali counterions we introduced in polymer chains some amount of short *n*-octyl grafts sterically hindering the aggregation of ion pairs with each other. Figure 4



Figure 4. Effect of the content of ion-containing units on the degree of swelling of gels of sodium salts of HM PAA with different content of *n*-octyl side chains.

shows that the incorporation of *n*-octyl side groups affects significantly the collapse transition. The higher is the amount of grafted groups the larger is the content of ion-containing units, at which the collapse is observed. For the C8–50 gel with 50% of grafted units the collapse disappears completely despite the fact that methanol is somewhat poorer solvent for this gel in comparison with other less hydrophobic counterparts. The later fact is particularly evidenced from a lower initial degree of swelling for this gel in the uncharged state (see Figure 4). The observed swelling of C8–50 gel may be due to the fact that the side groups hinder the aggregation of ion pairs to multiplets thus decreasing the gain in energy due to the formation of ionomer structures.

Trying to describe this observed phenomenon theoretically we take into account that incorporation of *n*-octyl side groups affects (i) effective solvent quality for network subchains, (ii) polymer volume fraction inside the gel in the reference state in which the network subchains are Gaussian coils, and (iii) multiplet formation process. In the framework of the present theory these factors are governed by the parameters χ , Φ_0 and m, respectively. Let us assume for the sake of simplicity that there are no multiplet formation in the hydrophobically modified (HM) PAA gel at all. In Figure 5, we plot two curves, corresponding to PAA ($\chi = 0.35, \Phi_0 = 0.1, m = 1$) and HM PAA ($\chi = 0.5, \Phi_0 = 0.175, m = 0$) gels. It should be stressed that ratios V/V_{dry} instead of α are depicted in Figure 5 because reference states for these gels are rather distinct. Here V_{drv} is the volume of the uncharged polymer gel without any solvent. Moreover, we assume only half of HM PAA gel units is capable of ionization, and the value of f on horizontal axis denotes the fraction of ionized AA units.



Figure 5. Effect of the side chains on the degree of swelling of gels. Curves correspond to m = 1, $\chi = 0.35$, $\Phi_0 = 0.1$ (1) and m = 0, $\chi = 0.5$, $\Phi_0 = 0.175$ (2).

One can see, first, that at f = 0 the PAA gel swells more than the HM one because incorporation of *n*-octyl side chains reduces effective solvent quality of methanol. Second, hindering of multiplet formation in HM PAA gel (m = 0) shifts the point of the gel collapse to a higher values of \tilde{f} because there are no additional energy gain from multiplet formation in ionomer regime, though ion pairing is still favorable.

Comparison of PAA and PMAA Gels. Now let us compare the behavior of two different gels: PAA and PMAA gels. From Figures 2 and 6 it is seen that in the both gels the



Figure 6. Effect of the content of ion-containing units on the degree of swelling of gels of *N*-alkylammonium salts of PAA with counterions of different size.

pure swelling at ionization (polyelectrolyte regime) is observed for TBA counterions, whereas the double transition swellingcollapse-swelling (mixed polyelectrolyte-ionomer regime) is observed for TMA ions. At the same time, for the ions of intermediate size-TEA ions-the type of behavior is quite different for these two gels: a pure polyelectrolyte swelling is observed in the case of PAA gel, whereas the double transition swelling-collapse-swelling occurs in PMAA gel. This may be explained by stronger polymer-solvent interactions in PAA gel favoring its swelling. Indeed, methanol is a Θ solvent for uncharged PMAA gel at room temperature,¹⁰ while it is a good solvent for PAA gel. This is reflected, for example, in the fact that the degrees of swelling of the uncharged PMAA and PAA gels in methanol are equal to ca. 12 and 28, respectively. Higher swelling of PAA gel resulting in a more pronounced expansion of its chains prevents the transition of the gel to the collapsed state. Figure 6 shows that although in the case of TEA counterions PAA gel does not exhibit a collapse upon neutralization, its degree of swelling remains lower than for larger TBA ions, especially in the range of f corresponding to the collapsed state of PMAA gel with TMA counterions (0.1-0.2). This may indicate that some amount of ion pairs is still

formed, but they cannot compete effectively with osmotic pressure of mobile counterions inducing the gel swelling.

These explanations are fully supported by theoretical findings. In Figure 7, we plot swelling curves for gels in a



Figure 7. Dependence of the swelling ratio α (a) and of the fraction of multiplets *q* (b) on the fraction of charged groups *f* for $\chi = 0.35$, $\Phi_0 = 0.1$ and various ion pair dimensions b/a = 0.80 (4), 0.95 (3), 1.00 (2), and 1.20 (1).

good solvent (the value of Flory–Huggins interaction parameter is equal to $\chi = 0.35$). It is quite natural that repulsive volume interactions in a good solvent make the swollen state more favorable in comparison with Θ solvent conditions. The curves of Figures 3 and 7 calculated for b/a = 1resemble the experimental curves obtained for gels with TEA counterions. These gels undergo collapse and reentrant swelling in Θ solvent (Figure 2c), while in good solvent their behavior is purely polyelectrolyte (Figure 6). Gel with slightly smaller counterions (b/a = 0.95) collapses even in good solvent (Figure 7), but the region of ionomer state stability is narrower than under Θ conditions (Figure 3c). These curves resemble behavior of the PMAA and PAA gels with TMA counterions.

It is worth noting that in accordance with experimental observations the swelling ratio of the uncharged gel at $\chi = 0.35$ is higher than the one in Θ solvent (compare Figures 3 and 7). It is due to short-range repulsion of monomer units in a good solvent.

Interesting effect was found theoretically in the case of a poor solvent (Figure 8). At very low degrees of ionization network stays in a usual collapsed state due to volume interactions, the fraction of bound counterions is quite low (Figure 8b). Gel charging results in three consequent abrupt transitions. The first transition is the gel swelling due to osmotic pressure of counterions. Under further charging the gel shrinks into the supercollapsed ionomer state ($q \approx 1$) because of the avalanche-



Figure 8. Dependence of the swelling ratio α (a) and of the fraction of ion pairs *p* and multiplets *q* (b) on the fraction of charged groups *f* for $\chi = 0.75$, b/a = 1, $\Phi_0 = 0.1$.

type process of ion condensation. The possibility of this couple of transitions has already been demonstrated in ref 9. Taking into account the counterion own volume the present theory predicts the second gel decollapse, i.e., the third first order transition.

V. CONCLUSION

When the polarity of solvent allows an effective competition between polyelectrolyte and ionomer behavior, the size of counterions is of crucial importance as it determines the gel swelling. Depending on the size of counterions three different types of swelling behavior upon gel ionization can be observed. (1) For bulky counterions (TBA) PMAA gel swells at ionization (pure polyelectrolyte behavior). (2) For small counterions (Na⁺, Cs⁺) the initial gel swelling at low f is followed by its collapse, after which the gel stays in the collapsed state up to f = 1 (polyelectrolyte/ionomer switching). (3) For counterions of intermediate size (TMA, TEA) charging of the gel causes first its swelling, then collapse and finally reswelling, when some degree of ionization is reached (polyelectrolyte/ionomer/polyelectrolyte switching). The last type of behavior in the gels was first observed in the present paper. The theoretical analysis shows that it is due to weakness of ionic associations (ion pairs and multiplets) for rather big counterions, which results in their disruption upon some increase of the local polarity of the medium taking place at gel ionization.

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Notes

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