Mixed Polyelectrolyte/Ionomer Behavior of Poly(methacrylic acid) Gel upon Titration

O. E. Philippova,* N. L. Sitnikova, G. B. Demidovich, and A. R. Khokhlov

Physics Department, Moscow State University, Moscow 117234, Russia

ABSTRACT: The titration of poly(methacrylic acid) gel with sodium methoxide was studied in water, methanol, dioxane, and their mixtures. There are three main regimes of the swelling behavior of the gels depending on the dielectric constant ϵ of the medium. In polar media with ϵ larger than a critical value ϵ_1, the gel swells monotonically with the increase of the degree of ionization, α, due to the osmotic pressure of counterions. In media with ϵ smaller than a critical value ϵ_2, the gel always shrinks with increasing α due to ion-pair formation with their aggregation to multiplets. In media with dielectric constants ranging from ϵ_1 to ϵ_2, the gel swells at α up to ca. 0.1 and then collapses. The collapse induced by ionization is in agreement with recent theoretical findings.

Introduction

Polyelectrolyte gels always contain a corresponding number of counterions which play an essential role in their swelling behavior.[1−3] In polar media, the charged links of a polyelectrolyte gel are dissociated, and the counterions are free to move in the overall volume of the gel (polyelectrolyte regime). In media of low polarity, the counterions condense on the corresponding co-ions, forming ion pairs (ionomer regime). Ion pairs can aggregate to multiplets due to dipole−dipole attraction.[4,5]

The influence of the formation of ion pairs on the collapse of polyelectrolyte gels in a mixture of good and poor solvents was studied experimentally in ref 6. It was shown that lowering the polarity of a solvent leads to a decrease of the concentration of a poor cosolvent required for network collapse and to a decrease of the volume gap at the collapse transition. These results were explained by an increasing tendency to form ion pairs in solvents with lower polarity.[6,7] The role of the nature of counterions in the formation of ion pairs in collapsed gels was studied in ref 8.

Experimental data are consistent with theoretical results.[6,7] Recently, the theory was generalized for the case when the solvent quality remains unchanged, while the degree of ionization of the gel, α, is varied.[9] It was shown that the collapse transition may be induced by extra ionization of the gel, because of the energy gain from the formation of ion pairs which increases with increasing α. The theoretical predictions can be demonstrated experimentally on a weak polyacid gel which can be gradually ionized by titration.

In the present paper, we describe results of an experimental study of the swelling behavior of poly-(methacrylic acid) (PMAA) gels with the increase of the degree of ionization in media of different polarity. Gel ionization was performed by titration with sodium methoxide. Water, methanol, dioxane, and their mixtures were used as solvents.

We here demonstrate that the swelling behavior of the polyelectrolyte gel with increasing α depends on the dielectric constant of the medium. The trend is a change from a polyelectrolyte to an ionomer regime with a lowering polarity of the medium; a mixed regime can also be found at intermediate polarities. In accord with theoretical predictions,[9] in the mixed regime switching from the polyelectrolyte to ionomer behavior can be induced by an increase in the degree of gel ionization.

Experimental Section

Gel Preparation. Poly(acrylic acid) (PAA) and PMAA gels were prepared by free-radical polymerization of the corresponding monomers in dimethylformamide at a monomer concentration of 3.06 mol/L with 2,2′-azobis(isobutyronitrile) $(1.53 \times 10^{-2}$ mol/L or 0.5 mol %) as initiator. N,N-Methylenebisacrylamide $(4.6 \times 10^{-2}$ mol/L or 1.5 mol %) was used as cross-linker. The gels were prepared in cylindrical glass tubes with an inner diameter of 0.40 cm under a nitrogen atmosphere at 63 °C for 3 h for acrylic acid and for 24 h for methacrylic acid and were washed with a large amount of methanol for 3 weeks to remove unreacted components and the sol fraction.

The weight fraction of the polymer in the swollen network is given by $\beta = m_0/m$, where m_0 is the mass of the dry gel and m is the mass of the swollen gel. In methanol, β is 0.024 for the PAA gel and 0.070 for the PMAA gel.

Swelling Experiments. The gel samples swollen in methanol (approximately 0.15 g) were placed into solutions of sodium methoxide of a definite concentration (3 mL of solution per 10^{-5} mol of network repeat units) at 25 °C until equilibrium was attained. The experiments were carried out in flasks filled with nitrogen. The neutralization was performed for the gels instead of the monomer mixture to provide the same network topology for the gel samples with different degrees of neutralization.

The degree of swelling of the gel samples equilibrated in sodium methoxide solution was characterized by the m/m_0 ratio, where m is the mass of the sample at the equilibrium state and m_0 is the mass of the dried gel sample.

Conductivity Measurements. The specific electrical conductivity Λ of PMAA gels was measured under an ac electric field (1 V, 1 kHz).

Results and Discussion

Typical swelling curves of PMAA gels as a function of α for methanol/water mixtures are shown in Figure 1 and for methanol/dioxane mixtures in Figure 2. It is seen that three general regimes of the swelling behavior of PMAA gel can be distinguished.

In the first regime, observed in sufficiently polar media, the gel swells with increasing α (Figure 1, curves 1−3). In the second regime, observed in less polar media, the gel swells at very low α and then collapses with increasing α (Figure 1, curves 4−7; Figure 2, curves 1 and 2; Figure 3). In the third regime, observed in media of sufficiently low polarity, increase of the
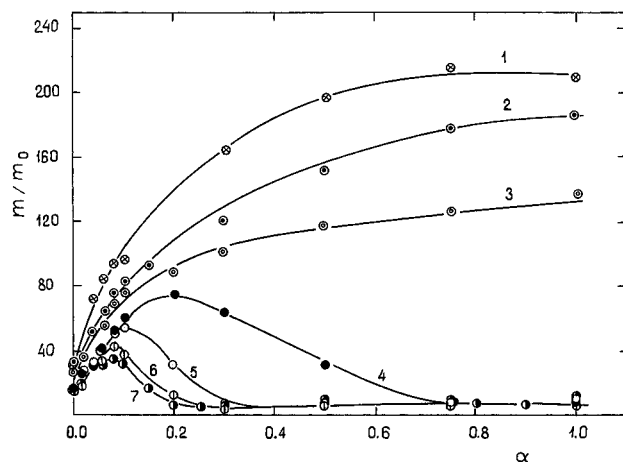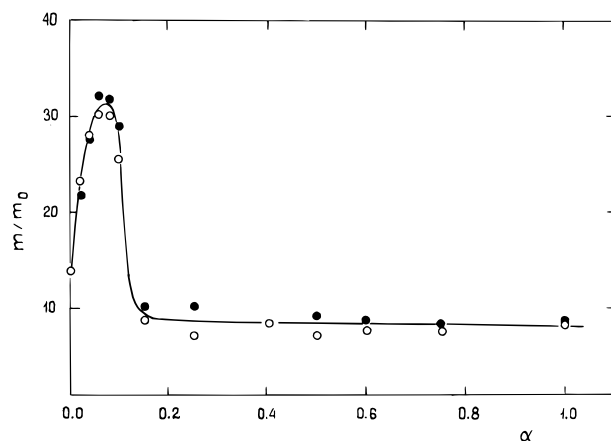
Figure 1. Degree of swelling m/m_0 of PMAA gels as a function of the degree of ionization α in water (1) and in methanol/water mixtures 20/80 vol % (2), 50/50 vol % (3), 65/35 vol % (4), 80/20 vol % (5), 90/10 vol % (6), and 95/5 vol % (7). m/m_0 is the ratio of the mass of the gel equilibrated in solution to the mass of the dried gel.
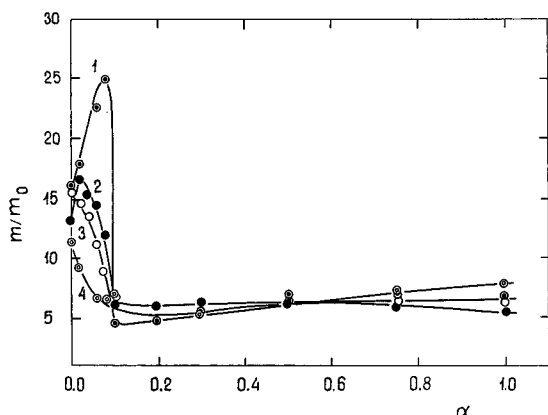
Figure 2. Degree of swelling m/m_0 of PMAA gels as a function of the degree of ionization α in methanol/dioxane mixtures 90/10 vol % (1), 75/25 vol % (2), 65/35 vol % (3), and 20/80 vol % (4). m/m_0 is the ratio of the mass of the gel equilibrated in solution to the mass of the dried gel.

Figure 3. Degree of swelling m/m_0 of PMAA gels as a function of the degree of ionization α in methanol for the initially swollen (squares) and dried (circles) gels. m/m_0 is the ratio of the mass of the gel equilibrated in solution to the mass of the dried gel.

degree of ionization results in a shrinkage of the gel (Figure 2, curves 3 and 4).

Polyelectrolyte Regime. The first regime, which can be called the polyelectrolyte regime, is observed in polar media (ϵ larger than ~50), in particular, in water

and in methanol/water mixtures containing up to 60 vol % of methanol. In this regime, an increasing degree of ionization of PMAA gel results in gel swelling due to the osmotic pressure of counterions neutralizing the network charges. This behavior of polyelectrolyte gels in aqueous solutions has been extensively studied.[10–12]

Figure 1 shows that the ionization of PMAA gel in water ($\epsilon = 78.5$) leads to an increase of the degree of swelling of the gel by 2 orders of magnitude. In methanol/water mixtures containing up to 60 vol % methanol, the character of the swelling curve does not change. Methanol and water are nearly Θ solvents for the uncharged PMAA at room temperature. Thus, by varying the methanol content in the methanol/water mixture, we change the dielectric constant of the medium without a significant variation of the solvent quality. Figure 1 shows that lowering the polarity of the solvent (by an increase of the methanol content) results in a decrease of the equilibrium swelling. This can be explained by the decrease of the osmotic pressure of counterions as a result of their partial condensation on the network charges. An analogous effect was observed for linear PMAA in methanol/water mixtures containing 10, 20, 40, and 50% of methanol.[13]

Mixed Polyelectrolyte/Ionomer Regime. The second regime of swelling behavior of PMAA gels in the course of titration, which can be called the mixed polyelectrolyte/ionomer regime, was observed in a series of methanol/water and methanol/dioxane mixtures covering the range of dielectric constants from ~20 to ~50 (Figure 1, curves 4–7; Figure 2, curves 1 and 2). In this regime, the increase of the degree of ionization at first leads to the usual polyelectrolyte swelling of the gel due to the osmotic pressure of counterions. Then, at some critical value of the degree of ionization α^*, the gel collapses. Upon further increase of α, the swelling ratio of the collapsed gel remains constant.

The swelling curves are identical when obtained by shrinking swollen gel or by swelling dry gel (Figure 3). Thus, they correspond to the equilibrium state of the gel.

The gel collapse upon ionization can be assigned to the formation of ion pairs between network charges and counterions in the collapsed phase. Indeed, the formation of ion pairs in a polyelectrolyte gel should lead to two main effects: decrease of the osmotic pressure of mobile counterions in the network and additional effective cross-linking of the network due to aggregation of ion pairs into multiplets.[7,9] Both these effects render the formation of the collapsed gel phase with multiplet structure thermodynamically favorable at some critical ionization degree.[7,9] At this ionization degree, the electrostatic energy released in the ion-pair formation with their subsequent condensation to multiplets overcomes the entropy and elastic energy losses arising from the motional restrictions and the deformation of polymer chains caused by the aggregation. Since the charges in PMAA gels are not fixed and can migrate along the chain, this can help the gel to adopt a more favorable conformation with minimal losses of entropy and elastic energy.

When the critical ionization degree α^* is reached, the equilibrium between free ions and ion pairs is displaced toward the formation of ion pairs which aggregate to multiplets. To demonstrate ion-pair formation, conductivity measurements were performed. The typical dependence of the reduced conductivity of PMAA gel (i.e., the conductivity per carrier ion) on the degree of
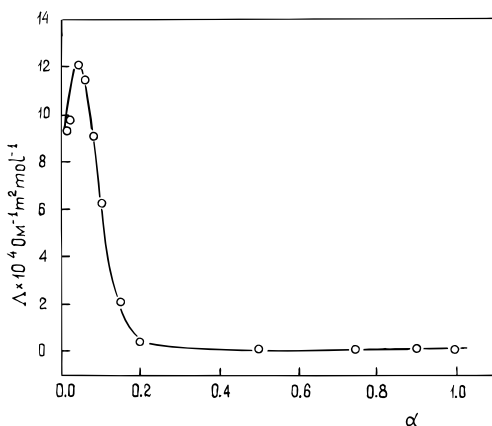
Figure 4. Reduced conductivity (the conductivity per carrier ion) Λ vs degree of ionization α for PMAA gel in methanol.
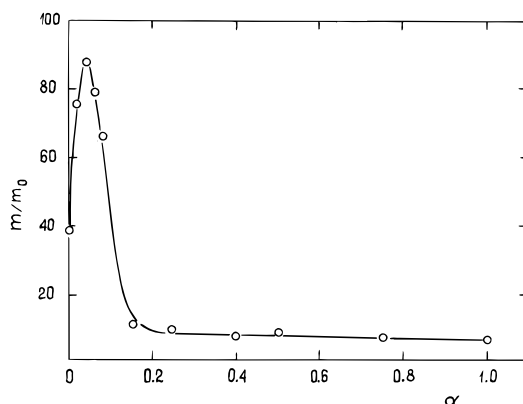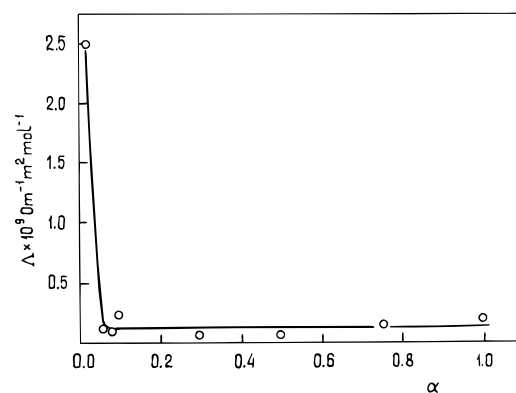

Figure 5. Degree of swelling m/m_0 of PAA gel as a function of the degree of ionization α in methanol. m/m_0 is the ratio of the mass of the gel equilibrated in solution to the mass of the dried gel.

Figure 6. Reduced conductivity (the conductivity per carrier ion) Λ vs degree of ionization α for PMAA gel in 20/80 vol % methanol/dioxane mixture.

ionization is presented in Figure 4. In spite of the increase of the concentration of the charged network units upon titration, the reduced conductivity increases only at low α and then falls, reaching a constant value unaffected by further increase of α. The decrease of the reduced conductivity with ionization of the gel confirms the formation of ion pairs. A comparison of Figure 4 with the corresponding swelling curve (Figure 3) shows that the gel swelling at low α correlates well with the increase of the reduced conductivity, while the gel collapse is accompanied by a significant drop of the reduced conductivity. Thus, gel collapse can be associated with formation of ion pairs. The collapse induced by ionization was also found for linear PAA and PMAA in methanol solutions. It was investigated by osmotic pressure, elastic light scattering, forced Rayleigh scattering, and UV spectrophotometric, viscometric, conductometric, and potentiometric measurements.[14−17]

The critical value α^* for the PMAA gel in methanol is 0.08 (Figure 3). The conformational transition of linear PMAA when titrated with sodium methoxide in methanol is also observed at $\alpha^* = 0.08$.[17] Experiments for the PAA gel in methanol lead to a similar α^* value (Figure 5).

The critical value α^* at which the gel collapses depends on the dielectric constant of the medium. The addition of water to methanol, increasing the dielectric constant, shifts the point of collapse to a higher α (Figure 1, curves 4−7; Figure 2, curves 1 and 2). This result is consistent with theoretical predictions.[9] At the same time, the degree of swelling of the gel at α^* decreases markedly when lowering the polarity of the

medium (Figures 1 and 2) because of the increasing tendency for partial condensation of counterions, which results in a decrease of the intranetwork osmotic pressure.

From Figures 1−3 it is evident that the polarity of the solvent influences significantly the abruptness of the collapse transition. In methanol, the gel collapse proceeds over a relatively small range of α, while in more polar media, e.g., in a 65/35 methanol/water mixture, the gel shrinks gradually over a very large range of α. This can be explained by a decrease of the tendency for ion-pair formation.

Because methanol is a Θ solvent for PMAA at room temperature, the un-ionized PMAA gel is in its unperturbed state. Figure 3 shows that in the collapsed state, the network is more compact than the initial neutral gel. This supports the assumption that ion pairs aggregate to multiplets which act as additional cross-linkers of the gel.

It should also be remarked that in contrast to the collapse of highly ionized gels, the collapse of slightly ionized gels (near the critical α^*) is generally accompanied by a macroscopic disruption of a gel sample. One conceivable reason for this is a significant stress of gel chains in the region of the abrupt transition between the highly swollen and the collapsed gel with a multiplet structure.

Figures 1−3 show that the collapsed gel contains ~85% of solvent. Thus, the multiplet formation does not result in a nearly complete release of solvent from the collapsed gel, as predicted.[9] Also, the degree of swelling of the collapsed gels does not depend on the polarity of the medium and on the degree of ionization (Figures 1−3). This is contrary to the expectation of a tighter cross-linking of the collapsed gel when more ion pairs are involved in the multiplet structure.

Ionomer Regime. The third regime of the swelling behavior of PMAA gels upon titration, denoted as the ionomer regime, was observed in nonpolar media at ϵ lower than ~20, in particular, in dioxane and methanol/dioxane mixtures containing more than 35 vol % dioxane (Figure 2, curves 3 and 4). In this regime, the increase of the degree of ionization of the gel leads to gel shrinking. The contraction is more pronounced at low α and reaches a limiting value at α higher than ca. 0.1. Further increase of α does not influence appreciably the degree of swelling. Conductivity measurements show that gel shrinking is accompanied by a decrease of the reduced conductivity (Figure 6).

At such low dielectric constants of the medium, most of the counterions are in the form of ion pairs. With an

increasing degree of ionization of the gel, the concentration of ion pairs increases, which favors the aggregation of ion pairs to multiplets. The latter effect causes additional cross-linking of the gel. A more detailed study of the formation of multiplets in the collapsed gels is in progress.

Thus, in polar solvents, the change of the swelling ratio of polyelectrolyte gel with ionization is determined by mobile counterions, while in low polar media, it is the formation of ion pairs and their clustering to multiplets that govern the swelling behavior of the gel.

The values of ϵ corresponding to the transition from one regime of the gel swelling behavior to another should be considered as rough estimates of the dielectric constant of the solution in which the gel sample is immersed. In fact, the solvent composition inside the gel may differ from the solvent composition of the exterior solution.[1,18] This is one of the most essential features of the swelling behavior of gels in mixed solvents. In ref 18 it was demonstrated that the effect of preferential absorption of one of the cosolvents by the network is more pronounced for the collapsed gel, because the probability of contacts of solvent molecules with polymer links in the collapsed gel is higher. In the swollen state, the composition of the solvent within the gel is nearly the same as in the surrounding solution. In addition to the redistribution of the components of the mixed solvent between the gel and the surrounding solution, we can suggest the partitioning of mixed solvent inside the network; e.g., we can assume that a very polar environment around the charged groups might favor water molecules more than methanol ones. The analogous effect was observed for ionomers put in an organic solvent containing traces of water.[19] Nevertheless, we believe that a nonrandom distribution of solvent in the gel will not considerably affect the main conclusions of the present paper, because the data obtained for different solvents are consistent with each other and are satisfactorily explained within the framework of our theoretical concept.

Conclusion

The swelling behavior of a polyelectrolyte gel upon ionization depends on the dielectric constant of the medium. This dependence is determined by the state of network counterions. In polar media, we observe the polyelectrolyte regime of swelling behavior, where most of the charged network units dissociate, and a significant fraction of counterions are mobile. In nonpolar media, we observe the "ionomer regime", where practically all counterions form ion pairs with the corresponding co-ions. In media of intermediate polarity, part of the counterions are free, while others form ion pairs. Increasing ionization of the gel favors ion-pair formation, which results in a changeover from the polyelectrolyte to the ionomer regime.

References and Notes

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MA951697P