Ion Aggregation in Polymer Gels

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SUMMARY: This brief review deals with our early experimental studies of ion aggregation in polymer gels proceeding via the condensation of counterions on the oppositely charged monomer units of the network with the formation of ion pairs and their clustering into multiplets. The two particular cases of the emergence of ion aggregates are considered: (a) for monovalent counterions in media of low polarity and (b) for multivalent counterions in water.

Let us consider a gel with a small fraction of charged monomer units. Along with the charged units the gel contains small counterions neutralizing the network charges (Fig.1). When the counterions are free and can travel in the overall volume of the gel, the gel is in polyelectrolyte regime (Fig.1). An alternative regime can be observed, when counterions are condensed on oppositely charged monomer units with the formation of ion pairs. Different ion pairs can aggregate with each other to multiplets due to dipole-dipole attraction. In this case the gel is in ionomer regime.

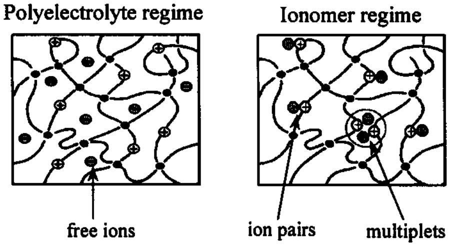

Fig. 1. Schematic representation of ion-containing gel in polyelectrolyte and ionomer regimes.

Let us consider the conditions for ion pair formation. Association of two opposite charges into an ion pair results in the gain in electrostatic energy. For the case of two monovalent ions the electrostatic energy E can be written in the following form:

$$E = \frac{e^2}{\varepsilon a}$$

where e is the elementary charge,

ε is the dielectric constant of the medium,

a is the intercharge distance in the ion pair.

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At the same time, the formation of an ion pair leads to a loss of the translational entropy of counterion. The loss of translational entropy is of the order of kT to the logarithmic factor accuracy.

When the gain in electrostatic energy overcomes the losses in entropy the ion pair formation is favorable. In this case we have the ionomer regime. As the electrostatic energy is directly proportional to the value of the charge of ions and inversely proportional to the dielectric constant of the medium, the ionomer regime can be realized in low polarity medium with small dielectric constant and in the case of multivalent counterions with a high value of charge. In its turn polyelectrolyte regime is realized, when the electrostatic interactions are weak and cannot overcome the losses in translational entropy. This regime is realized in polar medium with high dielectric constant and for monovalent counterions. Therefore, if we will take monovalent counterions, the transition from polyelectrolyte to ionomer regime can be induced just by decreasing the polarity of the medium.

The state of counterions determines many properties of the gels, in particular their swelling behavior. The swelling state of the gels in polyelectrolyte regime differs essentially from that in ionomer regime. In polyelectrolyte regime the gel is in a highly swollen state. To gain in the translational entropy the free counterions try to occupy as much volume as possible, but they cannot escape outside the gel because of the condition of macroscopic electroneutrality. As a result they create an exerting osmotic pressure leading to the gel swelling. By contrast, in ionomer regime the gel is in the collapsed state. This is due to two main reasons: the decrease of the intranetwork osmotic pressure because of the binding of mobile counterions and the additional cross-linking of the gel as a result of the aggregation of ion pairs to multiplets.

In addition to pure polyelectrolyte and pure ionomer regime a mixed polyelectrolyte/ionomer regime can be observed. In this regime some of counterions are free, while the others form ion pairs. A theoretical consideration performed by Prof.Khokhlov and Dr.Kramarenko(1) has shown that in this regime a very surprizing effect is possible, namely, the collapse induced by the gel ionization. This is indeed unexpected because one might think that when the degree of charging increases the gel should swell. But this is true only in polyelectrolyte regime when all the counterions are free. The situation is changed when along with free ions we have ion pairs. In this case with the increase of the gel ionization the number of both free ions and ion pairs increases. At small charge content the degree of swelling is determined by the contribution of free ions. But when the concentration of ion pairs becomes high enough so that the ion pairs can meet each other and form multiplets, the collapsed state with the multiplet structure becomes thermodynamically more favorable, and the gel shrinks.

In our work the gel collapse induced by ionization was for the first time observed experimentally. The experiment was performed as follows.(2) The poly(methacrylic acid) (PMAA) gel was immersed in a solvent mixture with a given value of dielectric constant and then the gel was gradually ionized by titration with sodium methoxide. Water, methanol, dioxane and their mixtures were used as solvents covering the range of dielectric constants from 78 to 2. It is to be noted that water and methanol are nearly θ-solvents for uncharged PMAA at room temperature. Therefore, by varying the content of water/methanol mixtures, we change the dielectric constant of the medium without a significant variation of the solvent quality.

Fig.2 demonstrates the dependencies of the degree of swelling of PMAA gel on its degree of ionization. Different curves correspond to media of different polarities. It is seen that the character of the swelling behavior of the gel upon ionization depends significantly on the dielectric constant of the medium. In polar media the gel shows a pure polyelectrolyte behavior - it swells with increasing degree of ionization. In low polarity media the gel shows a pure ionomer behavior - it shrinks with increasing degree of ionization.

In media of intermediate polarities we first observed experimentally(2) the mixed polyelectrolyte / ionomer behavior, which was predicted theoretically.(1) At low degrees of ionization the gel shows polyelectrolyte behavior and swells, but then with further increase of the degree of ionization the gel behavior is switched from polyelectrolyte to ionomer regime and the gel shrinks. To demonstrate the fact that the collapse is induced by the formation of ion pairs, the conductivity measurements were performed. It was shown that the gel collapse is accompanied by a significant drop of the reduced conductivity (Fig.3). This proves that the gel collapse proceeds with the binding of free counterions to ion pairs. Thus, we observed the transition from polyelectrolyte to ionomer regime for monovalent counterions upon decreasing the polarity of the medium.

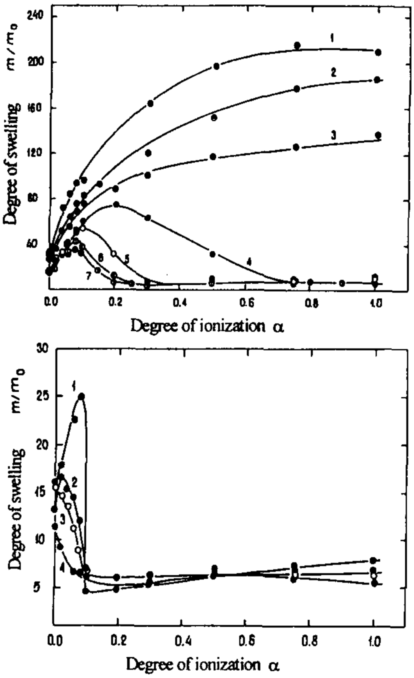

Fig.2.:Degree of swelling of PMAA gels as a function of the degree of ionization α
top: in water (1) and in methanol/water mixtures 20/80 vol% (2), 50/50 vol% (3), 65/35 vol% (4), 80/20 vol% (5), 90/10 vol% (6), and 95/5 vol% (7);
bottom: in methanol/dioxane mixtures 90/10 vol% (1), 75/25 vol% (2), 65/35 vol% (3), and 20/80 vol% (4) at 25^0 C.

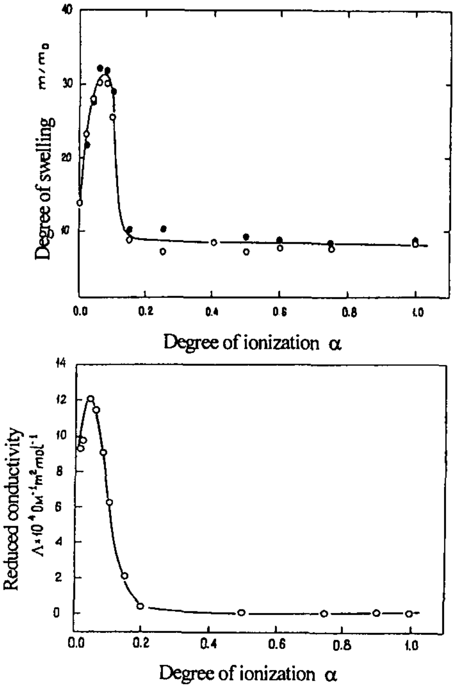

Fig.3.: Degree of swelling (*top*) and the reduced conductivity (*bottom*) as a function of the degree of ionization α for PMAA gel in methanol at 25^{0}C.

m/m$_0$ is the ratio of the mass of the gel equilibrated in solution to the mass of the dried gel.

Another possibility to realize the ionomer regime consists in the use of multivalent counterions. In this case the electrostatic interactions are so strong that we can expect the ion aggregation even in rather polar media. To be able to study the ion aggregates on a molecular level, we used fluorescent counterions, namely the trivalent europium ions.

Eu^{3+} ions are widely used as fluorescent probes, because their luminescence is very sensitive to their microenvironment.[3)] The most sensitive are fluorescence bands corresponding to the forbidden f-f transitions. Usually these bands are very weak, but strong and asymmetric electric field around Eu^{3+} ions leads to a significant enhancement of these bands. In particular, the enhancement of forbidden bands can be due to the binding of Eu^{3+} ions to oppositely charged ligands.

In our study the Eu^{3+} ions were incorporated in the gel of poly(sodium acrylate) by ion exchange reaction. Fig.4 shows the fluorescence spectrum of Eu^{3+} in the gel swollen in water and in aqueous solution of low molecular weight salt of Eu^{3+}. It is known that at these conditions the low molecular weight salt is completely dissociated and we observe the fluorescence of free ions. It is seen that in the gel the relative intensity of the forbidden band increases significantly. This indicates that in the gel Eu^{3+} ions are bound to oppositely charged groups of the network. Therefore, Eu^{3+} ions are not bound to small ligands, but they are bound to polymer ligands. The reason is that in the case of polymer ligand the formation of ion aggregates leads to much smaller losses of entropy, because the anions are initially immobilized on the polymer chains.

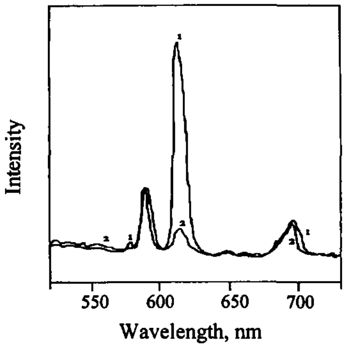

Fig. 4.: Fluorescence emission spectra of the gel of poly(europium acrylate) (PA-Eu) (1), equilibrated in water, and of aqueous solution of $Eu(NO_3)_3$ (2), obtained under excitation at 395 nm (in both cases the concentration of Eu^{3+} was 0.011 mol/L). The spectra are normalized to the intensity of the allowed 591-nm band.

In water a free Eu^{3+} ion is surrounded by a hydration shell consisting of 9 water molecules. At binding, the ligand can expel some of these water molecules. This process should lead to the increase of the lifetime of the excited state of Eu^{3+}, because water molecules are effective quenchers of the luminescence of Eu^{3+}. The rate of deexcitation via this process is directly proportional to the number of water molecules in the first coordination sphere and does not depend appreciably on the other ligands coordinated around Eu^{3+} ion. This makes the basis of a method of determination of the number of water molecules surrounding rare earth ions from the fluorescence relaxation data.[4] The treatment of the experimental data by means of this method has shown that the binding to polymer chains leads to the release of 4-5 water molecules from the hydration shell of Eu^{3+} ion.5)

Thus, Eu^{3+} ions form ion aggregates with the network countercharges. These ion aggregates are characterized by (1) the immediate contact of oppositely charges ions which is evident from fluorescence relaxation data and (2) by very asymmetric arrangement of network countercharges around Eu^{3+} ions which is evident from the enhancement of forbidden bands. Due to this asymmetric distribution of charges the aggregate can be considered as a dipole. Such dipoles can further aggregate with each other to multiplets due to dipole-dipole attraction. The multiplet formation can be studied by means of energy transfer $Eu^{3+} \rightarrow Nd^{3+}$ between different kinds of counterions simultaneously present in the gel.

Fig.5 shows the decay curves of the excited state of Eu^{3+} in the gel. It is seen that in the presence of acceptor (Nd^{3+}) the decay rate increases. This is obviously due to the energy transfer $Eu^{3+} \rightarrow Nd^{3+}$.

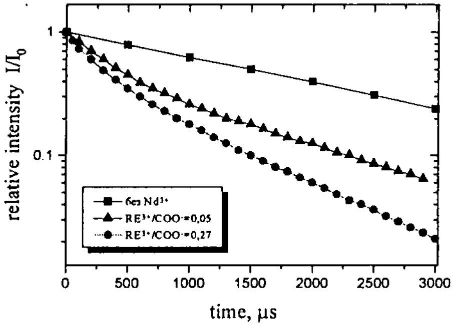

Fig. 5.:Decay curves of fluorescence from Eu^{3+} ($^5D_0$) level in PA-Eu gel at θ=0.27 (1) and in PA-Eu,Nd gels at θ=0.05 (2) and 0.27 (3) at a constant Eu/Nd ratio equal to 9 (λ_{ex} = 530 nm, λ_{em} = 614 nm).

If we assume a random distribution of counterions in the system (i.e. the absence of multiplets), the decay rate should be proportional to the overall concentration of acceptors. At the same time, in our experiments it was shown that the 60-fold increase of the concentration of acceptors is accompanied by a rather slight increase of the rate of energy transfer (by a factor of ca.2). Such behavior is possible if ions aggregate with each other to multiplets. In this case even at low average concentration of acceptors the decay rate is high enough, because of the close contact between donors and acceptors inside the multiplets.

The treatment of the relaxation data gave the value of the aggregation number of multiplets. It was shown that the multiplets consist of 7 rare earth ions together with the corresponding network countercharges. The aggregation number remains constant upon variation of the overall concentration of rare earth ions in a wide range (from 0,2 to 2 mol/L).

Conclusions

It was shown that collapse of polymer gels can be induced by the gel ionization, if the polarity of medium is rather low. The reason for the collapse transition in this case is the formation of ion pairs and multiplets. The formation of ion pairs and multiplets was studied on a molecular level by fluorescence probe method for the case of trivalent rare earth counterions. The fluorescence data obtained provide strong evidence of the site binding of multivalent cations to the gel countercharges with their subsequent aggregation to multiplets consisting of ca.7 rare earth ions.

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