Self-assemblies in Ion-containing Polymers

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SUMMARY: Recent interest in ion-containing polymers is connected with the general shift of the main emphasis of polymer industry to functional polymer systems. The review of the main properties of ion-containing polymers making them suitable for the use for functional purposes is presented and illustrated by recent experimental and theoretical findings.

Introduction

The main cause lying behind the significant increase of interest to ion-containing polymers in the recent years is the general shift of the main emphasis of polymer industry from construction to functional polymers. From this viewpoint, it turned out that ion-containing polymers (polyelectrolytes, ionomers) are most appropriate for the use in functional polymer devices.

There are several reasons for this, and in this paper only some of those will be discussed. Namely, I will concentrate on the illustration of the following main points.

(i) Polyelectrolyte systems normally exhibit most pronounced sharp conformational transitions (in comparison with the systems containing only neutral polymer chains). In the regions of such transitions polyelectrolytes have extremely high susceptibility (response) to the changes in the external conditions (temperature, pH, ionic strength or composition of the solution etc.). Such systems are therefore often called responsive polymer systems, responsive polyelectrolyte gels being one of the most common examples (see below). This property is, of course, very useful for various functional polymer devices, such as sensors, actuators, soft manipulators etc.

(ii) Ion-containing polymer systems exhibit a rich variety of different microstructures on a nano-scale (nano-structures). The formation of such structures for these systems is a rule, not an exception. Moreover, these nanostructures can have different morphologies which can be easily changed by the variation of the external parameters. This property is very useful for the design of new functional polymer materials with regular, easily variable and controllable microstructure.

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(iii) The last, but not the least: let us ask ourselves the question: which of the known polymers perform most diverse and most complicated functions? The answer is clear: these are biopolymers functioning in the living systems, in particular, DNA and protein molecules. It should be emphasized that most of biopolymers are polyelectrolytes, and they are acting in aqueous media, the presence of ionic groups being most important factor allowing them to perform biological functions. Therefore, if we are looking for the most appropriate synthetic polymers to mimic some of the functions known for biopolymers, we should direct our attention mainly to ion-containing polymers.

The first two of the above points will be illustrated for the ionic gel systems, therefore we start the next section by the brief description of the main properties of these gels.

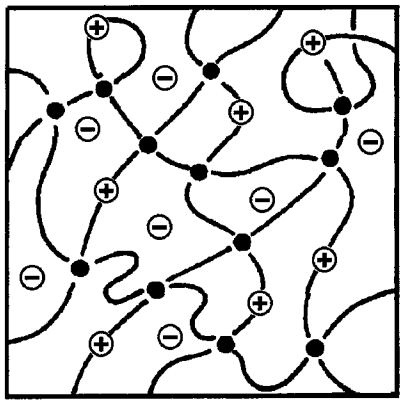

Fig. 1: Schematic representation of ionic gel.

Basic Properties of Responsive Ionic Gels. Gel Collapse Transition

The schematic picture of polyelectrolyte gel is presented in Figure 1. The gel contains charged monomer units and counter ions. Let us suppose that such a gel is immersed in a large volume of water. Then, in order to increase the entropy of translational motion the counter ions would like to leave the gel volume and to travel freely in the outside water medium. However, they cannot do this, because of the condition of macroscopic electroneutrality of the gel. They are forced to remain within the gel by this condition, and therefore they create a significant exerting osmotic pressure on the gel. This osmotic pressure is the origin of the most important physical effects for polyelectrolyte gel.

One of these effects is well known: all polyelectrolyte gels exhibit superabsorbing properties with respect to water. If the gels are not very tightly cross-linked, they can absorb up to several hundred parts of water per one part of the dry polymer. The physical origin of this effect is clear: to gain the translational entropy the counter ions try to occupy as much volume as possible, thus due to their osmotic pressure the gel swells in water medium like a balloon.

Another important effect with polyelectrolyte gels is the abrupt collapse transition of such gels occuring when the quality of solvent is becoming poorer. It is because of this transition these gels are called the responsive gels.

The gel collapse transition was first theoretically predicted by K.Dusek and D.Patterson in 1968[1)], and experimentally observed by T.Tanaka ten years later[2)]. Suppose that the quality of solvent for polyelectrolyte gel shown in Fig.1 is gradually decreasing. This can be achieved, for example, by the addition of poor organic solvent to water (in the initial Tanaka's experiments this was acetone).

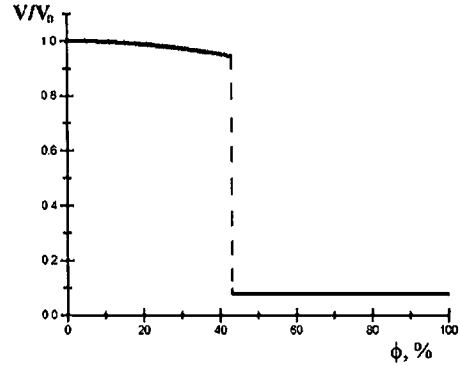

Fig. 2: Collapse of the gel induced by the increase of the fraction of organic poor solvent, phi. Vo is the volume of the gel swollen in pure water, V is the volume of the gel swollen in the mixture of water and organic solvent.

In Fig.2 one can see how the volume of the gel is changing with the change of the solvent quality (increase of the fraction, ϕ, of poor solvent in the solution). At a certain value of ϕ the jump-wise gel collapse is observed; the amplitude of this collapse can be indeed very large corresponding to the several hundred times volume change[3)]. The theory of this phenomenon[3-5)] shows that the large amplitude and the abrupt character of the collapse of ionic gels are due to the large difference between the two states of the gel:

(i) The swollen gel, which is actually superswollen due to the osmotic pressure of counter ions;

(ii) The collapsed gel which is stabilized by the attraction of uncharged monomer units.

There is a potential barrier between these two states, and therefore the corresponding phase transition is of the first order with the jump in volume which is considerably increasing with the increase of the osmotic pressure of counter ions (i.e. with the increase of the degree of charging of the gel chains)[3-5].

In the region of the transition the polyelectrolyte gel becomes a very responsive system: it is enough to change the external conditions (solvent quality, temperature, pH, ionic strength etc.) only a little bit, and the drastically large response of the system can be obtained (volume change in hundreds of times). This is the most simple illistration of the statement (i) in the Introduction.

We now move to a somewhat more complicated effects to illustrate other two points (ii) and (iii).

Microphase Separation for Polymer Gels and Solutions in Poor Solvents

The simplest polyelectrolyte system exhibiting the formation of regular nano-structures is an ionic gel (analogous to that shown in Fig.1) immersed in poor solvent. As it was shown in ref.[6] in this case the so-called microphase separation can occur due to the competition of the exerting osmotic pressure of counter ions and the attraction of monomer units in poor solvents.

This effect is illustrated in Fig.3. In moderately poor solvents the collapse of the gel sample as a whole may lead to the too significant increase of the exerting osmotic pressure of counter ions (and of the corresponding translational entropy contribution to the free energy). Instead, the regularly arranged aggregates of uncharged units can be formed (Fig.3) which are intercalated by the highly swollen regions containing most of chain charges and most of counter ions. As a result of this microphase separation transition the regular microstructure is formed in which the number of unfavorable polymer/solvent contacts is essentially diminished without significant overall volume change, i.e. without the change of exerting osmotic pressure of counter ions[6].

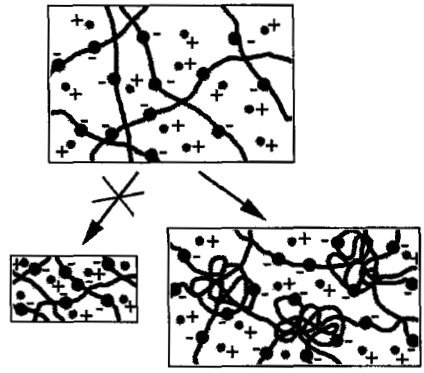

Fig. 3: Schematic illustration of the microphase separation for the ionic gel immersed in poor solvent.

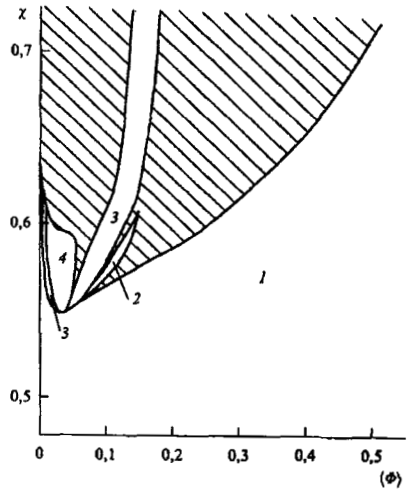

Fig. 4: Phase diagram for the solution of weakly charged polyelectrolytes in poor solvents. χ is the Flory-Huggins parameter for the polymer-solvent interaction, Φ is the polymer volume fraction in the solution. Shown are the regions of stability of disordered phase (1), of the phase of spherical micelles arranged in body-centered cubic lattice (2), of the phase of cylindrical micelles arranged in hexagonal lattice (3), of the lamellar phase (4), phase separation regions (5).

The first experimental observations in accordance with this theoretical prediction were made in refs.[7-8]. For example, in ref.[8] the small-angle neutron scattering experiments were performed for poly(isopropylacrylamide-co-sodium acrylate gels) swollen in heavy water. At

high enough temperatures the resulting scattering curves exhibited pronounced peak corresponding to the finite scattering wave vector, this peak becoming sharper with the increase of temperature. These results were explained by the effect shown in Fig.3: isopropylacrylamide is a temperature-sensitive monomer unit, and water is becoming a poorer solvent for this unit with the increase of temperature due to the enhancement of hydrophobic interactions. Therefore, for this polyelectrolyte gel system (charges are brought by sodium acrylate units) the microphase separation transition of the type shown in Fig.3 should occur with the increase of temperature, accompanied with the emerging of the SANS peak, as is indeed observed.

The arguments similar to that for the gels are valid also for weakly charged polyelectrolyte solutions immersed in poor solvents. The microphase separation should occur for this case as well, and initial paper[6] was in fact dedicated to polymer solutions, not gels. In Fig.4 one can see a phase diagram calculated in ref.[9] for the poor solvent solutions of weakly charged polyelectrolytes. With the decrease of the solvent quality, i.e. with the increase of the Flory-Huggins parameter χ, the microphase separation can occur; the formation of the regularly organised spherical, cylindrical or lamellar aggregates is possible. Shaded are the regions of macroscopic phase separation. One can see that the formation of the phase with microstructure is normally accompanied with the macroscopic phase separation: nanostructure is emerging in one of the coexisting phases.

In the application to the polelectrolyte gels immersed in poor solvents the microphase separation transition may result in the multistep collapse with the formation of ordered microstructures of different symmetry in the intermediate states, as it was shown in the recent paper[10].

Therefore, it is possible to conclude that a rich variety of nanostructures of different morphologies can be indeed observed in polyelectrolyte poor solvent systems. One more example along the same lines is given in the next section.

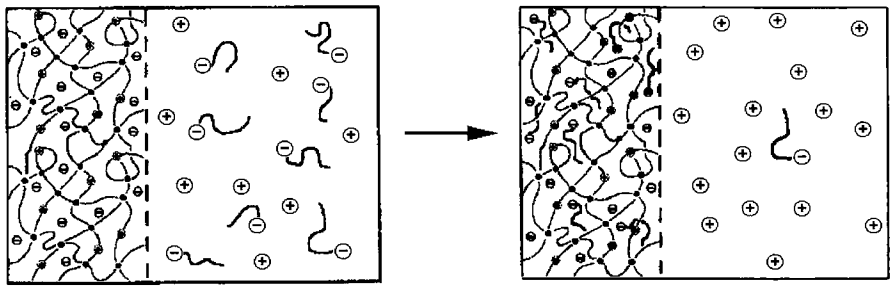

Fig. 5: Schematic representation of ionic gel interacting with the dilute solution of oppositely charged surfactants.

Microstructures Formed by Charged Surfactants Interacting with Oppositely Charged Gels

Let us consider ionic gel swollen in a large volume of very dilute solution of oppositely charged surfactants (well below the critical micelle concentration, CMC; see Fig.5). Then the counter ions can actually leave the volume of the gel, and be replaced by the surfactant molecules. If the volume charge density of charges on the gel chains is much higher than that of the surfactant molecules in the outside solution, practically all of the counter ions will leave the gel and will be replaced by the surfactant molecules[11]. In other words, surfactant molecules will be effectively absorbed by the gel. Their concentration can therefore easily exceed CMC, and the micelles should be formed inside the gel.

This micelle formation is further enhanced by the following effect first predicted theoretically in ref.[11] and then confirmed experimentally[12-13]. The formation of the charged micelle in the aqueous medium (without the gel) requires the partial immobilization of some counter ions compensating the large micellar charge (Fig.6a), therefore the translational entropy of these counter ions is lost. On the other hand, in the gel the micellar charge is compensated by the charges on the network chains which are initially immobilized. Thus, there is no loss of translational entropy for this case, and the formation of the micelle inside the gel turns out to be thermodynamically more favorable than in simple aqueous solution. In particular, the CMC in the gel should be much lower than in the outside solution, and this effect was directly experimentally proven in ref.[13].

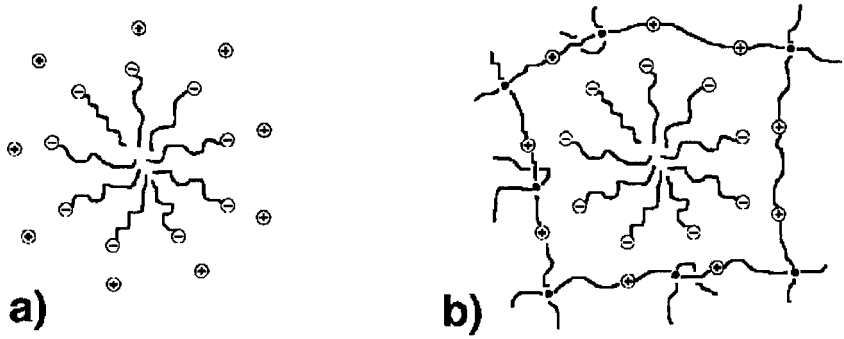

Fig. 6: Schematic representation of surfactant micelle formed in water (a), and within the oppositely charged gel (b).

Anyway, by one reason or another, micelles are easily formed within the oppositely charged gel. The surfactants are playing the role of counter ions, but after they are organised in the micelles, they can no longer exhibit exerting osmotic pressure. Therefore the gel collapses. This picture of the possible effects predicted theoretically in ref.[11] was confirmed for numerous gel-surfactant systems[12-15].

When we turned to the studies of the microstructures of the collapsed gel/surfactant complexes, we did not expect to see much order because of the statistical character of the gel formation. To our surprise, this was not the case: for example in Fig.7 one can see the results of small-angle X-ray scattering (SAXS) experiments for the cationic gel of poly(diallyldimethyl-ammonium bromide) interacting with oppositely charged surfactant sodium dodecyl sulfate[16]. The SAXS data have shown pronounced sharp peaks manifesting high ordering in the system. Therefore, in spite of the fact that polyelectrolyte gel is statistically disordered, it is an appropriate medium for surfactant self-assemblies[16-18].

From the width of the main peak in Fig.7 one can estimate the distance over which the surfactant aggregates within the gel are practically perfectly ordered. It turns out to be around 80 nm which is much larger than the mesh size of the gel (of order 15 nm)[16]. Therefore, the gel chains do not impose significant disturbances in the surfactant self-assemblies.

Moreover, another important result comes from the comparison of the ordering of surfactants in the gel and in pure water (at the same surfactant concentration)[19]. It appears that the surfactants in the gel are much more ordered, therefore statistically disordered gel medium not only does not disturb, but actually promotes the formation of perfect surfactant self-assemblies. This result may have interesting consequences for the general problem of

formation of perfect supramolecular structures in the volume. Up to now the best tool for the supramolecular self-assembly was a surface. If the structure formation in the volume is needed, surface is not appropriate and gel medium may be its replacement. Actually, the above results show that one needs a very small fraction of space to be occupied by the gel chains to induce perfect volume self-assemblies.

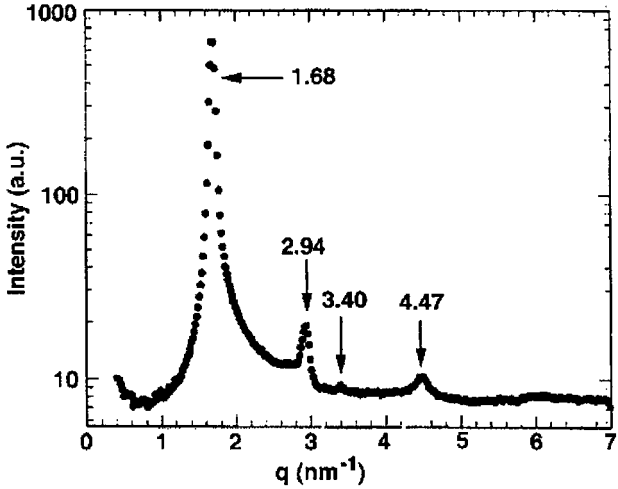

Fig. 7: Small-angle X-ray scattering curve for the complex of cationic poly(diallyldimethylammonium chloride) gel and oppositely charged surfactant sodium dodecyl sulfate.

Important parallels with the functioning of macromolecules in biological systems are immediately arising here, since in many cases the biological medium can be characterized as a gel. Here we are coming to the point (iii) mentioned in the Introduction. Another illustration of the same statement is given in the next section. We will deal below with amphiphilic rather than charged polymers, but the underlining ideology will be the same.

Conformation-Dependent Sequence Design (Engineering) of AB-copolymers. Protein-like copolymers

It is known that globular proteins-enzymes perform one of the most complicated functions in the living systems: they are responsible for the catalysis of many biochemical reactions. Very schematic representation of a protein molecule is given in Fig.8: macromolecule exists in the compact globular form and all monomer units can be roughly subdivided into two classes: hydrophobic and hydrophilic, hydrophobic units primarily constituting the globular core, while hydrophilic units form the envelope for this core. (Charged monomer units are considered within this representation as hydrophilic.)

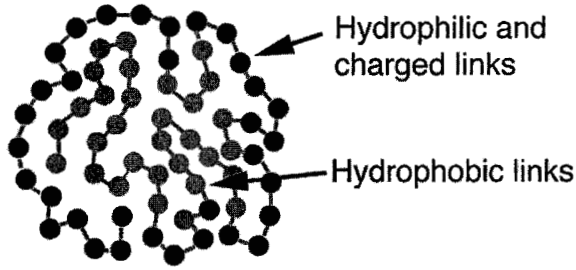

Fig. 8: Schematic representation of the structure of globular protein molecule. Hydrophobic units are shown by dark circles, hydrophilic by light ones.

The unique feature of globular proteins which permits them to perform all the biological functions is that they stay in solution without precipitation in the globular form shown in Fig.8. The physical reason for this is a stabilizing hydrophilic envelope around the hydrophobic core.

The problem which can be raised in this context within the framework of the point (iii) mentioned in the Introduction is the following. Whether it is possible to have a synthetic AB-copolymer with the AB-sequence such that in the most dense globular conformation all the A-units form a dense core, while all the B-units are on the surface? In ref.[20] we called those copolymers "protein-like" ones. It should be emphasized that the above requirement is very restrictive, i.e. only a negligibly minor fraction of all possible copolymers can form in the globular form the conformation shown in Fig.8.

Protein-like copolymers are expected to have interesting properties, in particular, unlike usual copolymers they will remain in the solution in the compact globular conformation without the precipitation.

The simplest way to prepare protein-like copolymers is by computer simulations[20-22]. The idea is the following. At first the homopolymer chain is considered and the strong attraction of monomer units is introduced. The homopolymer globule is formed and one of its instant conformations is considered. The monomer units which appear to be in the core in this conformation (called in ref.[20] a "parent" conformation) are attributed to A-"color" and called hydrophobic. The monomer units on the surface are attributed to B-"color" and called hydrophilic. After this "coloring" procedure the primary structure is fixed, uniform strong attraction between the monomer units is removed and different interaction potentials are introduced for A- and B-links. The protein-like copolymer is then ready.

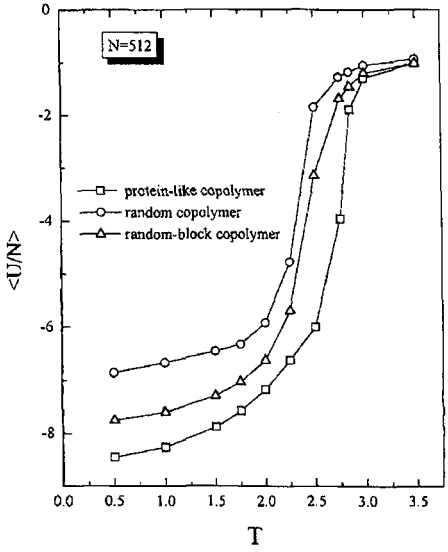

Fig. 9: Energy of attraction of hydrophobic B-units in the globule of AB-copolymer (per one unit) vs temperature for three types of AB-copolymers discussed in the text.

We have studied the coil-globule transition for the protein-like AB-copolymers (with 1:1 A/B composition) occuring upon the increase of attraction of hydrophobic A-units (for hydrophilic B-units the solvent was chosen to be always good, i.e. only excluded volume repulsion exists between these units). The obtained results were compared with those for random AB-copolymers with the same A/B composition and for "random-block" copolymers with the same A/B composition and the same length of A- and B-blocks as in "protein-like" copolymers.

The computer experiment was performed by Monte-Carlo method with the use of the bond-fluctuation model[23-24].

In Fig.9 one can see the energy of attraction of hydrophobic B-units as a function of temperature. For all three types of AB-copolymer chains the coil-globule transition is occuring upon the decrease of temperature (or effective increase of the attraction of B-units). However, for protein-like copolymers the transition occurs at higher temperatures and is more abrupt. Also, it is possible to show that it has much faster kinetics than in the other two cases[20].

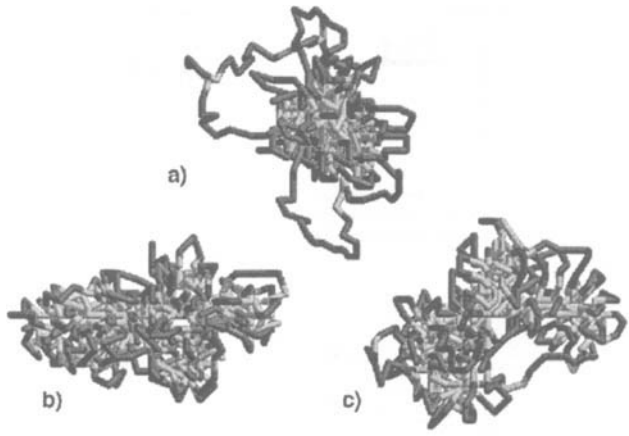

Fig. 10: Typical snapshot pictures for globules formed by protein-like (a), random (b) and random-block (c) AB-copolymers.

The reason for this difference is clear from the inspection of the typical conformations of the globule for three types of copolymers (Fig.10). In the case of protein-like copolymers we have a much better formed compact globular core which actually coincides with the core in the "parent" conditions. This core is stabilized by the long loops of hydrophilic chains, therefore globules from protein-like copolymers will most probably remain in the solution, while two other globules will most likely precipitate.

To conclude, "protein-like" copolymer has "inherited" (or "memorized") some of the properties of the parent conformation, and this information became apparent when the attraction between the A-units is introduced.

This procedure was called in ref.[22] the conformation-dependent sequence design (engineering) of AB-copolymers. Some other examples of the realization of the same idea can be found in refs.[22,25]. The studies in this direction may not only lead to the synthesis of new types of synthetic AB-copolymers, but also may help in the understanding of the early stages of prebiological molecular evolution.

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