Kinetically Frozen Structures in Polymer Gels Immersed in a Poor Solvent

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SUMMARY: Non-equilibrium kinetically frozen structures were observed in weakly charged polyacrylamide gels immersed in a poor-solvent. These structures are due to the vitrification of polymer-rich regions inside the gel which appear during the gel collapse. The paper presents the main results of the study of these structures by electron microscopy, SAXS and mechanical measurements.

The microphase separation is a very common phenomenon for polymer systems and it is well studied for weak polyelectrolytes (PE) [1, 2, 3)]. The main reason for microphase separation in PE systems is a competition of PE swelling due to osmotic pressure of counter ions of charged network and hydrophobic attraction of uncharged polymer parts which tend to segregate from a solvent (so called polyelectrolyte effect). The formation of microdomain structures in PE systems caused by the polyelectrolyte effect was well studied for PE gels swollen in a polar media by means of small-angle neutron scattering (SANS) [4, 5, 6)].

There are also other reasons for microphase separations in PE, e.g. (a) ionomer effect or formation of ion pairs and multiplets and (b) effect of vitrification or formation of glassy kinetically frozen structures (Fig. 1). These effects will be considered in details in the present work for weakly charged PE gels in a poor solvent.

The objects of the present study were weakly charged polyacrylamide gels containing small amount of cationic (diallyldimethylammonium bromide) and anionic (sodium and cesium methacrylate) groups. To induce the formation of microheterogeneities the external parameter – quality of solvent – was varied by changing the fraction of poor solvent – ethanol in water/ethanol mixture.

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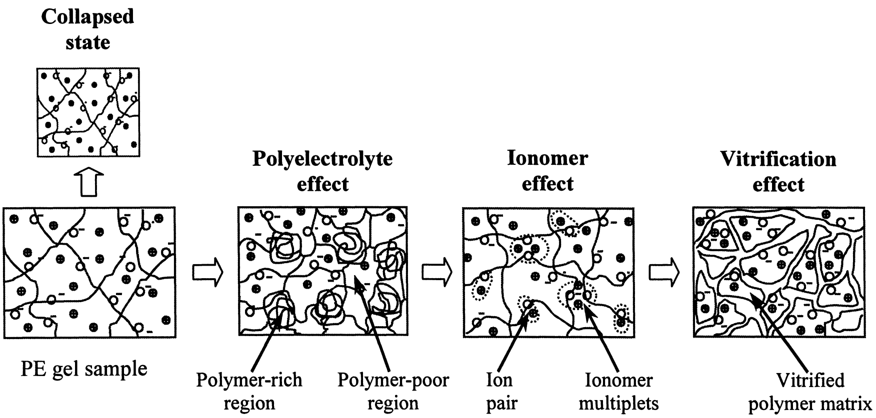

Fig.1. A schematic illustration of the three types of the possible microstructures for PE gels in a poor solvent.

To distinguish the region corresponding to non-equilibrium kinetically frozen structures two sets of experiments were made. In the first set (A) the dried samples of the gel were immersed in the water/ethanol mixtures, while in the second set (B) – the water-swollen in water gels were put in the water/ethanol mixtures. In other words in the set (A) the equilibrium was reached by swelling of the dried samples, while in the set (B) the equilibrium was reached by contraction of the swollen samples. If the final state of the gel samples does not depend on the way of achieving the state the results of both sets of experiments will coincide, e.g. the final state of the gel will correspond to the equilibrium state.

Fig.2 demonstrates that at the concentration of ethanol below 60% the swelling curves for the gels in the both sets of experiments are almost identical. But at further increase of ethanol content in the mixture in the set B a rather high the degree of swelling of the gel is observed, thus the equilibrium swelling of the gel is not reached.

The reason of this phenomenon is the following: when the gel sample swollen in water is immersed in a poor solvent the system becomes unstable, spinodal decomposition sets in and the polymer within the gel tends to segregate from the solvent. This results in a strong fluctuation of polymer concentrations and in the appearance of polymer-rich and polymer-poor regions in the gel. However, pure polyacrylamide at room temperature is in the glassy state. Therefore, the glass transition in the polymer-rich regions takes place. This leads to the stabilization of non-equilibrium structure of the gel in which the glassy regions surround the regions with a large amount of solvent (Fig.1). The vitrification prevents further removal of the solvent from the gel as a result the gel does not reach the collapsed state.

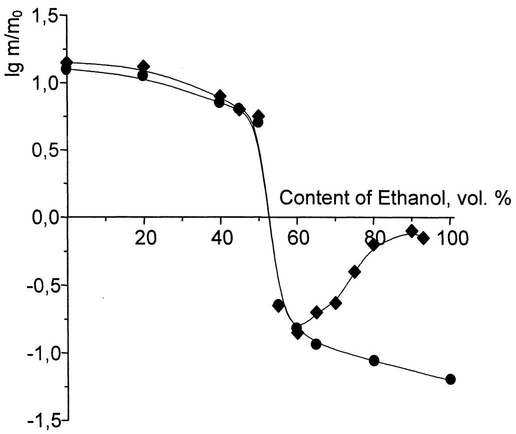

Fig. 2. The degree of swelling as a function of ethanol content in water/ethanol mixtures for PAA-DADMA*Br* gel, containing 5 mol % of cationic units for the sets A (●) and B (♦) of experiments

Non-equilibrium structures due to vitrification effect were found for both cationic and anionic gels in water/ethanol mixtures containing more than 70% of ethanol, when the gel samples swollen in water were immersed in poor solvent. It was shown that the charged gels are vitrified in a highly swollen state in comparison with the uncharged gels.

Scanning electron microscopy.

Morphological studies of the gels were performed with electron microscope JSM-5300LV (JEOL, Japan). The gel samples for microscopic measurements were prepared by freeze-drying of initially solvent-containing gel samples according to the procedure described in ref. $^{7)}$. Scanning electron microscopy data for the PAA-DADMA*Br* gel samples containing 10mol. % of charged units are presented in the Fig. 3.

It is clearly seen that the morphology of the samples is different at different content of a poor solvent in the water/ethanol mixture.

From Fig. 3 (a) we can see that the collapsed gel sample represents a fibrous matrix containing fragile polymer walls and big holes inside. Apparently, these holes correspond to the gel space, which is mainly occupied by a solvent, while matrix walls correspond to the polymer-rich regions. At high content of the ethanol in the solvent (87 vol. %) Fig. 3 (b) reveals the formation of continuous vitrified shell, which contains more or less circular lumps. From Fig. 2 it is evident that at such concentration of poor solvent the gel sample is in non-equilibrium state. We can assume that these lumps correspond to close pores filled with the solvent, where the walls are composed of the vitrified polymer component. Such structure changes can be attributed to the appearance of kinetically frozen regions in the gel samples. Therefore, electron microscopy data confirmed the appearance of glassy kinetically frozen structures in PE gels on the microscopic scale at high ethanol content in the mixture.

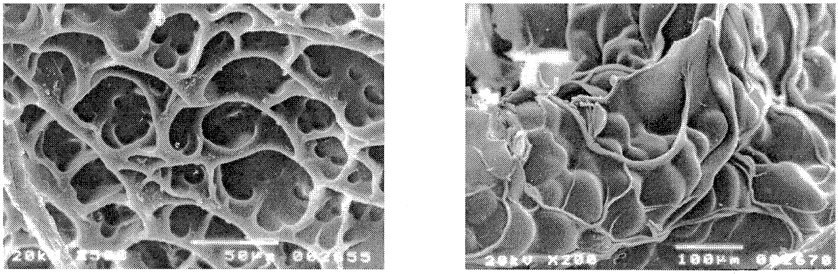
a b

Fig. 3. Scanning electron microphotographs of PAA-DADMA*Br* – 10 mol. % gel swollen in water/ethanol mixture in ratio 40/60 vol. % (a) and 13/87 vol. % (b), correspondingly.

Mechanical measurements.

The formation of kinetically frozen structures is also reflected in the mechanical properties of the gel samples. Fig. 4 illustrates the dependence of the modulus of elasticity, G, of the PAA gel and PAA-DADMA*Br* gels with different content of charged units on the concentration of poor solvent, ethanol, in the water-ethanol mixtures.

The elastic moduli, G, of the gels were obtained by the penetration tensile method according to the procedure described in ref. 8). The elastic modulus was determined from the slope of linear dependence:

$$G = \frac{3F}{16h^{3/2}R^{1/2}}$$

where F – the value of the acting force, h – is the indentation depth into the sample and R – is the radius of the penetrating spherical indentor .

The penetration measurements were carried out in such a way that the penetrating steel-sphere (with various radii R = 0,125÷0.35 cm) was gradually intended (step 0,2 mm) into the test gel samples down to the maximum indentation depth of 2 mm. Each time after 5 minutes of relaxation the force F_i corresponding to the indentation h_i was read off. Samples in the cylindrical shape were placed in supports, which exactly fitted with the lower half of the sample. The dependence of F on the depth of indentation, $h^{3/2}$, was linear for all the samples used in this study.

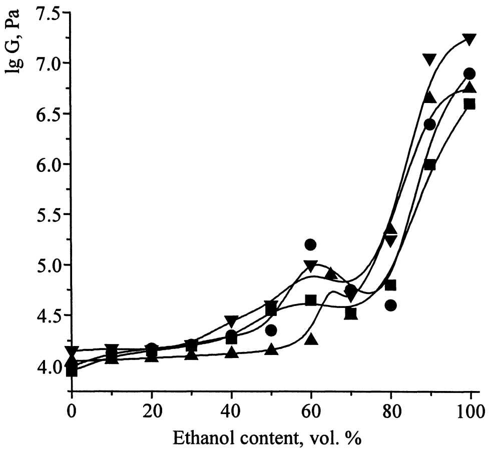

Fig. 4. Dependencies of the elasticity modulus G on the ethanol concentration for PAA gel (■) and for the PAA-DADMA*Br* gels, containing 2 (▼), 5 (●) and 10 (▲) mol.% of charged units.

As it is seen from Fig.4 the value of the modulus of elasticity rises sharply, simultaneously with volume phase transition. A similar effect was previously described for weakly-charged polyacrylamide gels in references[9, 10)]. The considerable increase of the modulus of elasticity, G, of the gels by two orders of magnitude was observed in the region of formation of kinetically frozen structures in comparison with the collapsed state. So high values of elasticity modulus ($G = 10^6\text{-}10^7\ Pa$) are inherent for the glassy state.

Small-angle X-ray Scattering

To characterize the microscopic structure of the gel samples under investigation, the SAXS technique was also employed (only for set B of experiment). Fig. 5 demonstrates the behavior of scattering exponent μ as a function of ethanol content. The values of scattering exponent μ, whose analysis permits to gain important information about the microstructure of the gel, were calculated from asymptotic equation of the scattered intensity:

$$I(q) \approx q^{-\mu}$$

We found that for the gel with relatively low charge density (cationic gel containing – 5% of charged groups) a jumpwise increase of μ from 1,7 to 3.5 correlates well with a formation of kinetically frozen structures or increasing of the relative mass of the gel samples. So high values of μ indicate the formation of the microstructures with smooth phase boundaries[4)].

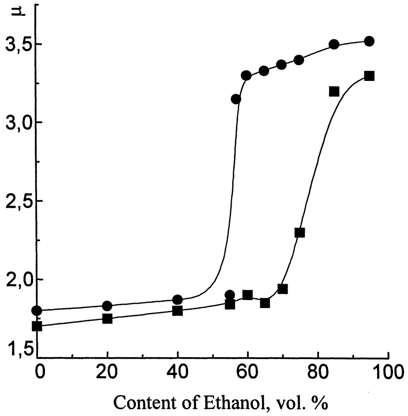

Fig. 5. Scattering exponent μ as a function of ethanol content in water/ethanol mixtures for PAA-DADMA*Br* gel, containing 5 mol % (■) and 10 mol % (●) of charged units

Alternatively, for the gel with high content of charged groups (DADMABr-10%) an increase of scattering exponent correlates with volume change in the gel, namely, it occurs together with collapse transition (that is before the formation of glassy regions). This means that for the highly charged samples the formation of frozen structures does not influence significantly the value of the scattering exponent. Therefore, in this case the microsegregation can be caused by another effect, most probably, by an ionomer effect.

The ionomer effect manifests itself only at sufficiently high concentration of charged groups and in the medium with low polarity when ion pairs easily form multiplets. The probability of this process enhances at the gel collapse when the polarity of the gel medium is additionally decreased due to high concentration of relatively low polar polymer chains. As a result the dipole-dipole attraction between ion pairs can emerge that in its turn leads to the formation of ionic aggregates - multiplets. These multiplets can act as additional cross-links in the PE gel.

Thus, the ionomer effect seems to be the main reason for the appearance of the microstructures for the highly charged gels while for the gel with relatively low ionic content the sharp interphase boundaries are observed only when the kinetically frozen structures start to be formed.

Acknowledgements

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