Conformational Transitions in Polyelectrolyte Networks in Binary Solvents: Microheterogeneities in the Collapsed State

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ABSTRACT: Microheterogeneities in positively charged gels of diallyldimethylammonium bromide copolymerized with acrylamide and negatively charged gels of sodium and cesium methacrylate copolymerized with acrylamide appear as a result of the collapse of these gels in poor solvents (water–ethanol mixtures). Three possible reasons for microheterogeneities are analyzed: the polyelectrolyte effect (i.e., competition between the attraction of the uncharged parts of the chains in poor solvent and electrostatic repulsion coupled with osmotic pressure of counterions), the ionomer effect (i.e., the formation of ionomer multiplet structure), and vitrification (i.e., partial formation of glassy kinetically frozen polyacrylamide-rich regions). Both macroscopic observations and SAXS experiments were made. The dry and water-swollen gels immersed in the water–ethanol mixtures show different final states at high ethanol contents, which proves the existence of kinetically frozen structures for these cases. For highly charged cationic gels we observed an increase of the scattering exponent which correlates with the volume phase transition while for smaller charge density this increase occurs at higher ethanol contents with the appearance of kinetically frozen structures. These results suggest that in the former case the microdomain structure appears mainly as a result of the ionomer effect while in the latter case the main factor is partial vitrification. In contrast to recent results in purely aqueous systems, no SAXS scattering maxima were observed, apparently due to the high irregularity of the microstructures.

Introduction

The conformational transitions of weakly charged polyelectrolyte (PE) networks in a poor solvent have been extensively studied both experimentally[1-7] and theoretically.[7-12] It was shown that the PE networks undergo a volume phase transition from a swollen to a collapsed state when the quality of solvent becomes poorer. However, the details of structural changes in the gels in the course of the volume phase transition were not clearly understood.

Recently, this problem has attracted more attention. On the basis of theoretical considerations, it was predicted that weakly charged PE networks in a poor solvent should also undergo a microphase separation transition. There are three possible reasons for microphase separation in weakly charged PE networks in a poor solvent: a polyelectrolyte effect,[10-12] an ionomer effect,[13,14] and formation of kinetically frozen structures.[15]

The polyelectrolyte effect can be observed in weakly charged PE solutions and gels if the attractive hydrophobic forces are nearly compensated by repulsive electrostatic interactions. In this case, the uncharged hydrophobic parts of the chains tend to segregate from the solvent, but macroscopic phase separation (or gel collapse) results in a too high loss of translational entropy of counterions; thus a microphase-separated modulated structure is favored from the viewpoint of the free energy.[10-12]

The ionomer effect can be observed if the medium inside the PE network has a low enough dielectric constant. In this case the counterions lose their mobility and form ions pairs with charged network units. These ion pairs attract each other via dipole–dipole interactions and form multiplets.[13,16,17] The formation of multiplet structure can be regarded as a sort of microphase separation transition.[14] The ionomer effect as well as the polyelectrolyte effect results in the appearance of thermodynamically equilibrium microdomain structures.

In PE networks in a poor solvent one can also expect kinetically frozen structures due to the spinodal decomposition intercepted by vitrification.[15] This effect leads to the formation of nonequilibrium microdomain structures in the network.

At present there exist only a few experimental data describing microdomain structures in weakly charged PE gels in poor solvents. In particular, the formation of microdomain structures in PE networks due to the polyelectrolyte effect was observed recently for weakly charged poly(*N*-isopropylacrylamide-*co*-acrylic acid) (NIPA/AA) gels[18] and for poly(acrylic acid) (PAA) gels[19,20] in deuterium oxide by means of small-angle neutron scattering (SANS).

The aqueous solvent can be made poorer by variation of temperature or by the addition of a poor organic solvent. In this way gel collapse was induced in most of the experimental studies.[1-7] The aim of the present paper is to study possible microheterogeneities in the weakly charged cationic and anionic gels immersed in good solvent/poor solvent mixtures. The investigation of such microheterogeneities should help clarify the phenomenon of the collapse of PE gels in poor solvents and suggest new ways of obtaining polymer materials with a controllable and readily variable microstructure.

Experimental Section

The gels were prepared by free-radical copolymerization of acrylamide (0.7 mol/L) and *N,N'*-methylenebisacrylamide (7×10^{-3} mol/L) with the corresponding amount of diallyldimethylammonium bromide (DADMAB) or sodium methacrylate (SMA) in aqueous solution. Ammonium persulfate (9.5×10^{-4} mol/L) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) (9.5×10^{-4} mol/L) were respectively the initiator and accelera-

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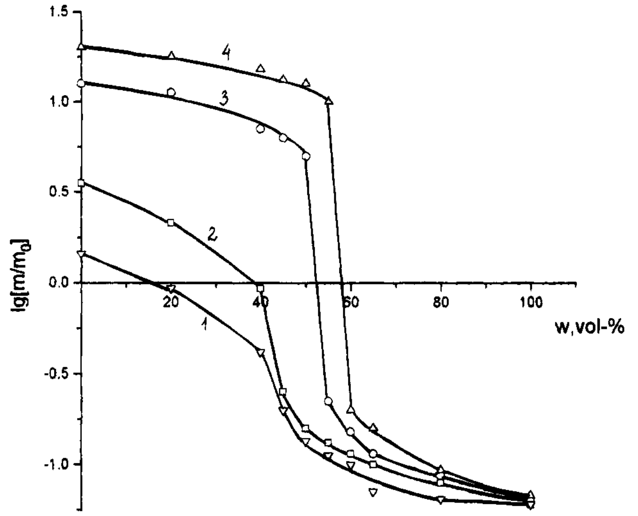

Figure 1. Swelling ratio as a function of ethanol concentration in water–ethanol mixtures for polyacrylamide gel (1) and poly(acrylamide-*co*-diallyldimethylammonium bromide) gels containing 2 (2), 5 (3), and 10 mol % (4) of cationic chain units (the set A of experiments, swelling of dry gels).

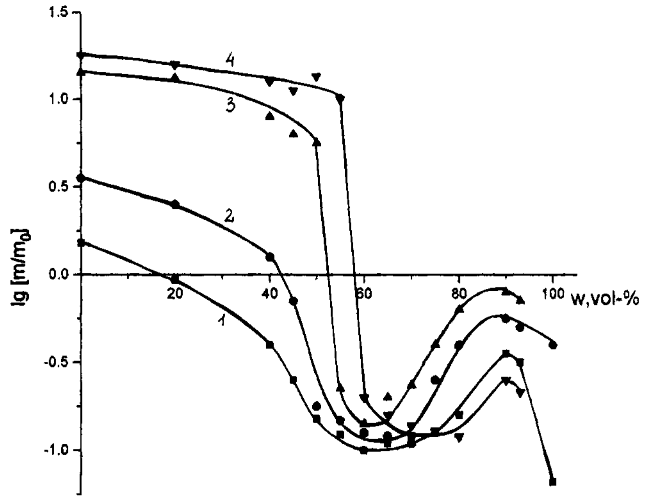

Figure 2. Swelling ratio as a function of ethanol concentration in water–ethanol mixtures for polyacrylamide gel (1) and poly(acrylamide-*co*-diallyldimethylammonium bromide) gels containing 2 (2), 5 (3), and 10 mol % (4) of cationic chain units (the set B of experiments, collapse of swollen gels).

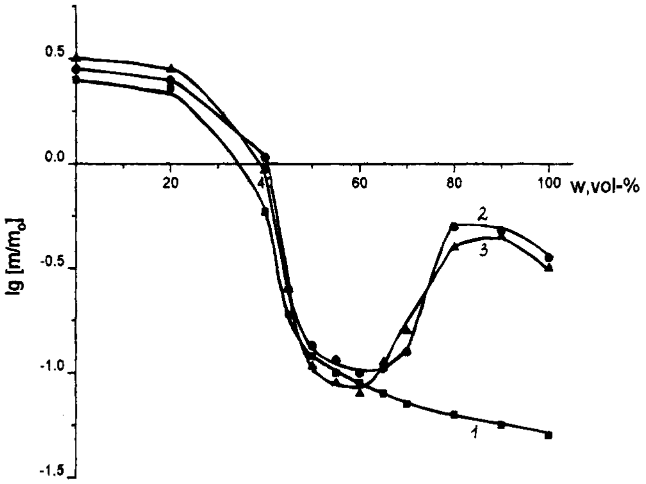

Figure 3. Swelling ratio as a function of ethanol concentration in water–ethanol mixtures for poly(acrylamide-*co*-sodium methacrylate) gel containing 2 mol % of anionic chain units for the sets A (1) and B (2) of experiments and for poly(acrylamide-*co*-cesium methacrylate) gel containing 2 mol % of anionic chain units for the set B of experiments (3).

tor. Three samples of cationic gel and three samples of anionic gel with 2, 5, and 10 mol % of charged groups (DADMAB and SMA, respectively) were prepared. Gelation was carried out in cylindrical tubes at room temperature for 24 h. The prepared gels were washed in a large amount of distilled water for 3 weeks.

To obtain the poly(acrylamide-*co*-cesium methacrylate) (PACMA) gels from the corresponding poly(acrylamide-*co*-sodium methacrylate) (PASMA) gels, the gels were immersed for 7 days in an aqueous solution of CsCl containing a 6-fold excess of cesium ions with respect to sodium ions in the gel. The gel samples were then washed in a large amount of distilled water for 2 days.

Water–ethanol mixtures prepared from redistilled water and denatured ethanol (Aldrich) were used for swelling of the gels.

The swelling ratio, related to the state of network formation, was determined from m/m_0, where m is the mass of the gel after swelling in water–ethanol mixtures and m_0 is the mass of the gel after preparation.

For the small-angle X-ray scattering (SAXS) experiments we used a commercial Kratky camera (Paar, Austria) equipped with a position-sensitive detector system (OED-50-M, Braun, Germany). Measurements were carried out with Ni-filtered Cu Kα radiation. The distance from sample to detector was 220 mm. The scattering patterns were collected by a multichannel analyzer with 4096 channels. The measuring time was 1000 s for each sample in most cases. The raw data were transformed to scattering vector units ($2\pi \times 2 \sin \theta/\lambda$) and desmeared using standard desmearing techniques.[21] Background scattering from the camera could be neglected. Normalization to absolute units was not performed; i.e., the scattering intensity depends on the relative amount of material in the sample holder slit.

Results and Discussion

We used acrylamide gels containing small amounts of cationic (DADMAB) or anionic (sodium or cesium methacrylate) groups. Water–ethanol mixtures with different fractions of ethanol were used as solvent.

The swelling curves of the gels in water–ethanol mixtures are presented in Figures 1–5. To determine the regions corresponding to nonequilibrium kinetically frozen structures, we performed two sets of experiments. In set A we placed the dried gel samples in water–ethanol mixtures (Figures 1 and 3–5). In set B we placed the gels swollen in water into water–ethanol mixtures (Figures 2–5).

As seen from Figures 1–5, at low concentrations of ethanol in the mixture the swelling ratio of the gel decreases continuously. Then in a narrow region of solvent composition, a sharp decrease of the relative mass of the gel is observed.

For both cationic and anionic gels an increase of the charge density of the network leads to an increase of the volume gap at the transition and to the rise of the ethanol content in the mixture at which the gel collapses. These results, which are in good agreement with those obtained earlier,[6] can be explained by the osmotic pressure of the counterions which tend to swell the network. This osmotic pressure increases with increasing number of charged monomer units in the network.

At ethanol concentrations less than 60 vol %, the curves for the A and B sets of experiments are almost identical for all the gel samples (Figures 1–5). This indicates that in this range of ethanol concentrations all the samples are at equilibrium.

At a further increase of the ethanol content in the mixture, the behavior of the gel in the two sets of experiments is quite different. In set A the relative

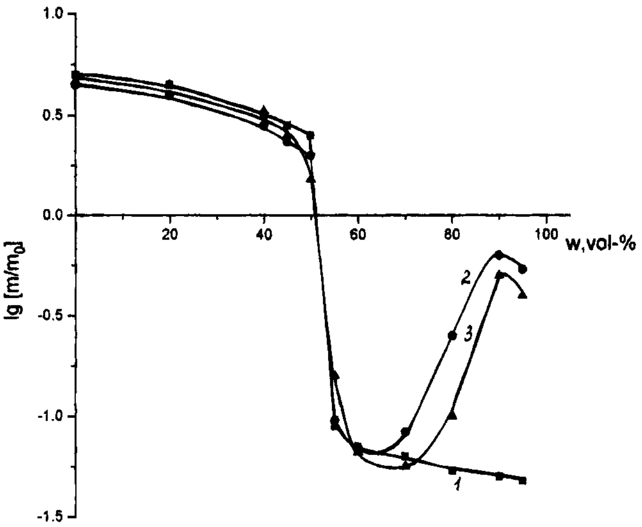

Figure 4. Swelling ratio as a function of ethanol concentration in water–ethanol mixtures for poly(acrylamide-*co*-sodium methacrylate) gel containing 5 mol % of anionic chain units for the sets A (1) and B (2) of experiments and for poly(acrylamide-*co*-cesium methacrylate) gel containing 5 mol % of anionic chain units for the set B of experiments (3).

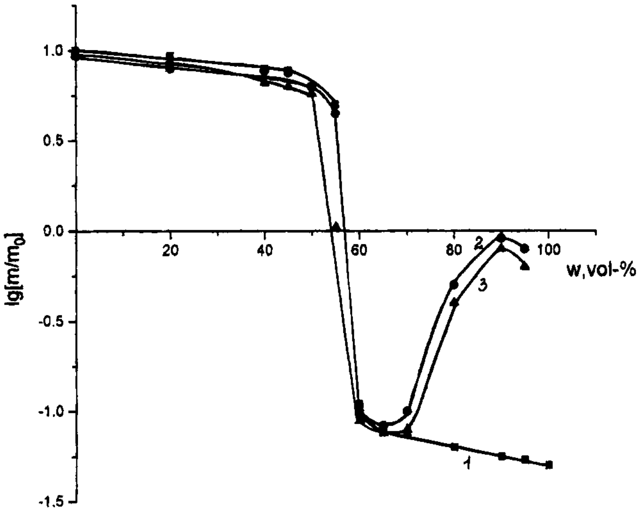

Figure 5. Swelling ratio as a function of ethanol concentration in water–ethanol mixtures for poly(acrylamide-*co*-sodium methacrylate) gel containing 10 mol % of anionic chain units for the sets A (1) and B (2) of experiments and for poly(acrylamide-*co*-cesium methacrylate) gel containing 10 mol % of anionic chain units for the set B of experiments (3).

mass of the gel slightly decreases when the quality of the solvent becomes poorer (Figures 1 and 3–5). In set B a significant increase of the relative mass of the gel is observed (Figures 2–5). These data indicate that in set B the equilibrium swelling of the gel is not reached. The wide scatter of the swelling ratio data for all the gel samples in set B at a high content of ethanol in the mixture (Figures 2–5) is additional evidence for the formation of nonequilibrium structures.

When the gel sample swollen in water is immersed in a poor solvent, the system becomes unstable, spinodal decomposition sets in[22] and the polymer within the gel tends to separate into polymer-rich and polymer-poor regions. However, pure polyacrylamide at room temperature is glassy. The glass transition in the polymer-rich regions leads to the stabilization of a nonequilibrium structure of the gel, in which the glassy regions surround regions containing a large amount of solvent. The vitrification prevents further removal of the solvent from the gel. As a result we observe the formation of kinetically frozen structures. Earlier this phenomenon was described for polymer solutions.[15] In ref 6 it was noted that immersion of a swollen gel in mixtures with a high content of poor solvent leads to heterogeneities due to microsyneresis and the samples remain inhomogeneous even after 2 months of observation.

From Figures 2–5 it can be seen that the kinetically frozen glassy structures for the charged gels contain more solvent than the corresponding structures of the uncharged gel. Apparently, in the course of the spinodal decomposition of a weakly charged gel, the neutral parts of the gel form polymer-rich regions, while solvent-rich regions are formed near the charged groups. The removal of water from the area around the charged groups is unfavorable because of a too large loss of entropy of counterions. Thus in Figures 2–5 it is observed that the greater the charge density of the gel, the larger the relative mass of the gel in the kinetically frozen state. The sole exception is the poly(acrylamide-*co*-diallyldimethylammonium bromide) gel containing 10 mol % of charged units (PADADMAB-10). The reason for this behavior of PADADMAB-10 gel will be discussed below.

The influence of counterions on the swelling curve for set B was examined for PASMA and PACMA gels, containing 2, 5, and 10% of charged units. The results obtained are presented in Figures 3–5. It is seen that the change of the type of counterions from sodium to cesium does not influence noticeably the swelling curves of the gels of different charge density.

The mechanical properties of the gel samples also change. The swollen gels before the volume-phase transition are predominantly liquid-containing soft, "wobbly" objects. The collapsed gels near the phase transition (at ethanol contents of 60–75 vol %) are rubbery, whereas the gels at higher ethanol concentration are glassy. The mechanical measurements, confirming the consistency tests, will be published in a following paper.

In weakly charged polyacrylamide gels in a binary solvent one can also expect the appearance of the microdomains caused by the polyelectrolyte and/or the ionomer effects. The polyelectrolyte effect should be more important in the swollen state of the gel at high water content, whereas the ionomer effect must dominate in the collapsed state in a medium with a relatively low dielectric constant.

To characterize the microscopic structure of the gel samples under investigation, the SAXS technique was employed. For the SAXS measurements we used only gel samples of set B, in which the water-swollen gels were placed in water–ethanol mixtures. For these samples we can a priori expect the existence of microdomains caused by polyelectrolyte and/or ionomer effects and also the kinetically frozen structures.

We found that all the SAXS intensity profiles of slightly charged polyacrylamide gels were monotonically decreasing functions. Figure 6 shows double-logarithmic plots for SAXS intensity functions $I(q)$ for some gel samples. It is seen that these plots are mainly linear. The slopes of these plots allow us to obtain the scattering exponents μ, whose analysis permits us to gain valuable information about the microstructure of the gels.

For polymer solutions in a good solvent in the semidilute regime, μ is expected to be 5/3 (self-avoiding walk). In Θ-solvent μ becomes equal to 2 (random

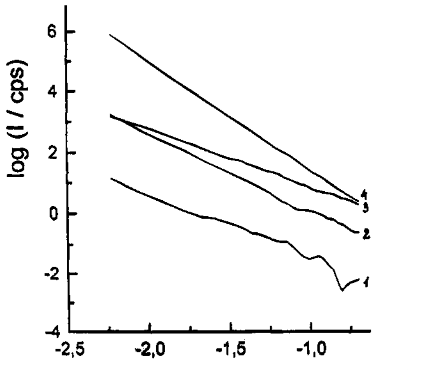

Figure 6. Double-logarithmic plots for SAXS intensity functions $I(q)$ for poly(acrylamide-*co*-diallyldimethylammonium bromide) gel containing 10 mol % of charged units in water (1) and in water–ethanol mixtures containing 80 vol % (2), 60 vol % (3), and 86 vol % (4) of ethanol.

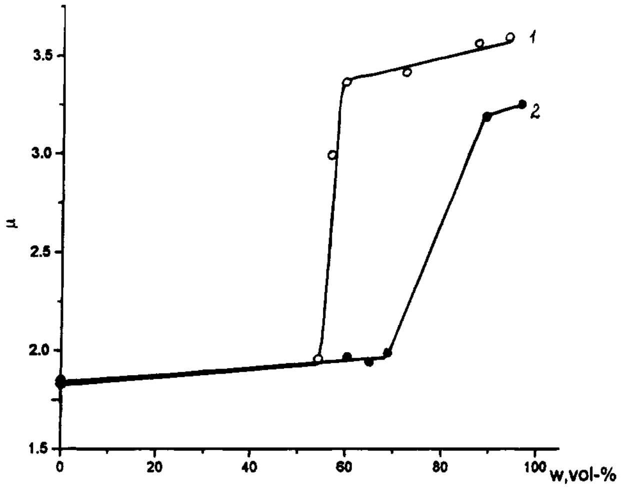

Figure 7. Scattering exponent μ as a function of ethanol concentration in water–ethanol mixture for poly(acrylamide-*co*-diallyldimethylammonium bromide) gel containing 10 mol % (1) and 5 mol % (2) of charged units.

Table 1. Values of Scattering Exponents μ for Poly(acrylamide-*co*-cesium methacrylate) Gel Containing 5 mol % of Anionic Chain Units in Water–Ethanol Mixtures with Different Contents Ethanol *W*

N	*W*, vol %	state of the gel	μ
1	0	swollen	1.75
2	60	collapsed	1.78
3	80	glassy	2.68
4	95	glassy	2.70

walk). The same exponents are also expected for polymer gels at scattering vectors $q \gg 1/\xi$, where ξ is the correlation length (the so-called Edwards screening length).[18] The scattering exponent 4 indicates the presence of a microphase-separated two-phase structure with smooth phase boundaries according to the Porod law.[23]

For all the gels under investigation the values of the scattering exponents in water (good solvent) are equal to 1.70–1.74 (Figure 7, Table 1). Let us consider the changes in the values of μ when the quality of the solvent becomes poorer for positively charged PADADMAB-10 gel. Curve 1 in Figure 7 shows the scattering exponents, μ, evaluated at $0.1 < q < 0.47$ nm^{-1}, as a function of ethanol concentration in the solvent mixture. From Figure 7 it can be seen that at a low ethanol fraction the exponent μ is 1.7. Then, in the narrow range of ethanol content the scattering exponent increases and approaches 3.3. A jumpwise change of the scattering exponent adequately correlates to a volume change in the network collapse. Therefore, the PADADMAB-10 gel seems to undergo some kind of microphase separation together with the formation of the collapsed state. A further increase of the ethanol fraction results in a slight increase of μ (Figure 7). This demonstrates that for this gel sample the formation of kinetically frozen structures (which according to Figure 2 takes place for this sample only at an ethanol content exceeding 80 vol %) does not influence significantly the value of the scattering exponent. Here it is also worthwhile to note that the increase of the relative mass of the gel with the increase of the ethanol content due to the formation of the kinetically frozen structures (for set B) for PADADMAB-10 is much less pronounced than for the other gel samples under investigation (Figures 2–5).

The dependence of the scattering exponent μ on the quality of the solvent was also studied in ref 18 for NIPA/AA gel by means of SANS. The quality of the solvent (D_2O) decreases on heating, and at 50.8 °C the gel collapses discontinuously. It was shown that at 40–50 °C (before the collapse of the gel) μ increases and approaches 3.5–4.0, which indicates the presence of a microphase-separated structure. The existence of the microphase separation was also proved by the observation of a distinct scattering maximum, which starts to appear at 35 °C.[18] It is to be emphasized that the increase of the scattering exponent and the appearance of the scattering maximum were detected before the collapse transition of the gel, i.e., in the swollen state.

In ref 18 the formation of the microdomains has been attributed to the polyelectrolyte effect. There is enough evidence that this is indeed the case since all the experiments in ref 18 were performed in D_2O with a relatively high dielectric constant, where ionic groups have to dissociate. The microphase separation was obtained already in the swollen state where the formation of ion pairs or kinetically frozen structures is highly unlikely.

The microphase separation in the gel due to the polyelectrolyte effect can be explained as follows. As the quality of solvent becomes poorer, the polymer–polymer attractive interactions become stronger, which leads to the gel shrinking. However, a shrinking process results in a decrease of the translational entropy of the counterions. To avoid this, the solvent molecules are repelled from the neutral parts of the network and tend to locate near the charged groups. The neutral parts of the gel shrink and the regions around the charged groups swell locally so as to maintain the volume of the network, thus generating spatial concentration fluctuations in the system.[18] When the hydrophobic interaction overcomes the electrostatic repulsive interaction, a macroscopic shrinking transition takes place. Therefore, the microdomains caused by the polyelectrolyte effect can be observed for gels swollen in polar solvents before the macroscopic phase transition.

In our study the quality of the solvent was varied by changing the fraction of the poor solvent (ethanol) in the water–ethanol mixture. Collapse is observed in water–ethanol mixtures containing more than 50 vol % of ethanol. This medium has a relatively low dielectric constant in comparison with that of water. Therefore, some of the links which can potentially dissociate should form ion pairs with the corresponding counterions. Hence, one can expect the emergence of the ionomer effect (cf. ref 16). This effect is further enhanced in the collapsed state, where the fraction of polar solvent is lowered because a significant fraction of space is occupied by the polymer chains (this effect was studied theoretically in ref 17). Thus one can expect the formation of a pronounced multiplet structure together with the gel collapse. A jumpwise change of the scattering exponent adequately correlated to a volume change at the network collapse supports this hypothesis.

Thus, the ionomer effect seems to be the main reason for the appearance of the microstructure for the highly charged PADADMAB-10 gel.

One can suppose that the ionomer effect can manifest itself only at sufficiently large concentrations of charged groups when the ion pairs easily form multiplets. Thus, it is of interest to consider the effect of the charge density of the PE network on the formation of the microstructure in the gel. Let us compare the values of the scattering exponents for PADADMAB gels containing 5 (PADADMAB-5) and 10 mol % of charged units (curves 1 and 2 in Figure 7). For PADADMAB-5 gel the value of μ increases only slightly (from 1.74 to 1.9) when the content of ethanol increases from 0 to 70 vol %. In contrast to PADADMAB-10 gel, the phase transition of the PADADMAB-5 gel in the collapsed state (at 52 vol % of ethanol; see Figure 2) has no effect on the value of μ. Therefore, the decrease of the charge density seems to destroy the microstructure due to the ionomer effect in the collapsed state. The rise of the scattering exponent for PADADMAB-5 gels was observed only at a relatively high content of ethanol in the mixture, which correlates with the increase of the relative mass of the gel in the swelling curves due to the formation of kinetically frozen structures. At a high ethanol content the value of μ for PADADMAB-5 gel becomes equal to 3.5, which indicates the formation of the microstructure with smooth phase boundaries.

The analogous behavior of the scattering exponent was observed for PACMA gel containing 5 mol % of charged units (PACMA-5) (Table 1). The phase transition of the PACMA-5 gel in the collapsed state at 52 vol % of ethanol (see Figure 4) has no effect on μ. The large values of the scattering exponent for PACMA-5 gel were obtained only at 80−90 vol % of ethanol in the mixture where the kinetically frozen structures are formed. Note that the maximum μ for the PACMA-5 gel ($\mu = 2.7$) is smaller than for the PADADMAB-5 gel.

Thus, for PACMA-5 and PADADMAB-5 gels the microheterogeneities seem to be mainly due to the kinetically frozen structures.

Among the PADADMAB gel samples under investigation, only PADADMAB-10 gel has the ionomer-type microstructure in the collapsed state before the kinetically frozen microstructure emerges. The ionomer multiplets act as additional cross-links in the gel. The last fact can be responsible for a smaller relative mass of PADADMAB-10 gel in the kinetically frozen state in comparison with that of the PADADMAB-2 or PADADMAB-5 gel samples (Figure 2).

For the case of sufficiently regular microdomain structures, the structure factor $I(q)$ should have a peak at a finite scattering vector q which characterizes the period of the structure. Such a peak was indeed observed in the SANS spectra obtained for NIPA/AA gels[18] and for partially neutralized PAA gels.[19,20]

Despite the high values of the scattering exponents which suggest the existence of the microdomains, we have not detected any scattering maxima. This indicates probably that the microdomains are quite irregular. One can assume three possible reasons for the irregularity of the size and the distribution of the microdomains. The first may be connected with the vitrification effects. These effects lead to kinetically frozen structures which are much less regular than microdomains at the usual microphase separation transition. The second reason for the irregularity of the microdomains is the inhomogeneity of the gel structure itself (inhomogeneous cross-linking or tendency to microgel formation characteristic for networks obtained by free-radical copolymerization, particularly in the presence of a diluent). Finally, there is the possible superposition of three effects (polyelectrolyte, ionomer, and vitrification) which induce the appearance of the microstructure. Probably, these effects lead to microstructures with quite different characteristic dimensions. It is obvious that in the present work the bromide counterions serve as contrast for SAXS measurements and the obtained SAXS data reflect the distribution of the bromide ions in the gel. Clearly, the superposition of the three above-mentioned effects on the behavior of bromide ions can be quite complicated.

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