Swelling of polyacrylamide gels in aqueous solutions of ethylene glycol oligomers

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ABSTRACT

Addition of a small amount of ethylene glycol oligomers (OEG), with the number of repeat units y = 2–4, in an aqueous solution leads to the contraction of both linear and cross-linked poly(acrylamide-co-acrylic acid) chains. The results present clear evidence for the screening effect of OEG on the ionic groups of the polymer chains. Measurements indicate that the pre-swollen poly(acrylamide-co-acrylic acid) gels immersed in aqueous OEG solutions are at equilibrium. However, as the molecular weight of OEG increases, these gels cannot attain their equilibrium swelling ratio due to the appearance of non-equilibrium structures. The stability of these structures increases as the initial swelling degree of the gels increases. © 1997 Elsevier Science Ltd

1 INTRODUCTION

Hydrophilic gels, called hydrogels, are important materials of both fundamental and technological interest. The swelling behavior of hydrogels in low molecular weight solvents has been investigated repeatedly in the last four decades. In recent years, attention has turned to the swelling and collapse phenomena that are observed when a hydrogel network is brought into contact with a solvent. The possibility of phase transition has been predicted theoretically 1–5 and proved experimentally on hydrolysed polyacrylamide (PAAm) gels swollen in acetone–water mixtures. 6–10 In a first-order phase transition, a change in a variable like pH, solvent composition or temperature can induce a discontinuous change in the

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volume of the swollen gel. Recently, we have shown that poly(acrylamide-co-acrylic acid) gels immersed in aqueous solutions of poly(ethylene glycol) (PEG) may also undergo a discontinuous volume change. The critical concentration of PEG required for a discontinuous volume collapse rises, as the proportion of ionizable groups increases or, as the molecular weight of PEG decreases. The distribution of PEG inside and outside the gel phase also changed discontinuously at the phase transition region. The experimental results were found to be in qualitative agreement with the calculation results based on the Flory–Huggins theory.

This study seeks to obtain further insight into the swelling behavior of PAAm gels in aqueous solutions of ethylene glycol oligomers and polymers. In the first part of this paper, we present our results of observations on poly(acrylamide-co-acrylic acid) gels immersed in aqueous oligo(ethylene glycol) (OEG) solutions. We report an unusual phenomenon in ionic PAAm gels; we observed a re-entrant swelling transition when the degree of polymerization of OEGs is continuously varied.

As first discussed by Dusek, an interesting feature of polymer gels is the possibility of the appearance of non-equilibrium states. These non-equilibrium states may be fixed if additional cross-links are introduced into the gel or if these states become kinetically frozen. The second part of this paper deals with the conditions for the appearance of non-equilibrium states in PAAm gels immersed in PEG solutions. We show that the non-equilibrium structures affect the conformation transition of network chains. No phase transition was observed when kinetically frozen structures appear. We also give a qualitative interpretation of the appearance of non-equilibrium states.

2 EXPERIMENTAL

2.1 Materials

PAAm gels were prepared by free-radical cross-linking copolymerization of acrylamide with a small amount of N,N'-methylenebis(acrylamide) (Bis) in aqueous solution. Acrylic acid (Ac) was used as the ionizable comonomer. Ammonium persulfate (APS) and N,N,N',N'-tetramethylmethylenediamine (TEMED) were, respectively, the initiator and the accelerator. The reactions were carried out at room temperature (21 ± 2°C). The gels were prepared according to the following scheme:

5 g acrylamide, 133 mg Bis, 40 mg APS and varying amounts of Ac
were dissolved in double distilled water to give a total volume of 100 mL. To eliminate oxygen from the polymerization system, nitrogen was bubbled through the solution for 10 min. After addition of 0.24 mL of TEMED, the solution was transferred to small tubes of 5.8 mm in diameter. The gelation took place within 5 min. After 3 h, the gels were cut into specimens of approximately 10 mm in length and used for further treatment.

Reagent-grade PEGs of different molecular weights (Fluka), ethylene glycol, diethylene glycol and tetraethylene glycol (Aldrich) were used without further purifications.

2.2 Post-treatment of the gel samples

The prepared gels were divided into two parts. The first part of the gel samples, which we shall call hereafter “gels after synthesis”, was subjected to swelling experiments without further treatment. The second part was immersed in a large excess of distilled water to remove the unreacted species. It was found that the sol fraction in the gels is less than 0.1% after extraction with water. Then, the equilibrium swollen gels in water, called “pre-swollen gels”, were used for swelling experiments.

It is to be noted that the impurities in the gel samples after synthesis may influence their swelling behavior. In order to check this point, part of the pre-swollen gels was successively washed with acetone–water mixtures containing increasing amounts of acetone and, finally, with pure acetone. The gels were then dried in vacuum at room temperature. Using this solvent exchange procedure, the good solvent water in the pre-swollen gels was gradually replaced by the non-solvent acetone. Thus, the gel was transferred from a rubbery to the glassy state without the appearance of heterogeneities due to microsyrneresis. It was found that the equilibrium swelling ratio of these “dry” gels is the same as that of the corresponding “gels after synthesis”. Therefore, we conclude that the impurities in the gel samples after synthesis do not affect their swelling behavior. This comparison also shows that the gels after synthesis attain their equilibrium volume in aqueous OEG or PEG solutions.

2.3 Methods

For the swelling measurements, PAAm gel samples of different initial states (pre-swollen gels, dry gels, or gels after synthesis) were immersed in vials (100 mL) filled with an OEG (or PEG)–water solution. The volume of solution in the vial was much larger than the gel volume, so that the concentration of the solution was practically unchanged. The vials were
placed in a temperature-controlled bath at 25 ± 0.1°C. In order to reach
the equilibrium degree of swelling, the gels were immersed in solutions for
at least one week. The diameter of the gels was measured by a calibrated
digital compass and the equilibrium swelling ratio of the gels related to the
network formation state, $V/V_0$ (where $V$ and $V_0$ are the volumes of gel at
equilibrium and reference conditions, respectively), was calculated as:

$$V/V_0 = (D/D_0)^3$$

(1)

where $D$ and $D_0$ are the diameter of the gels after equilibrium swelling
and after synthesis, respectively. Each swelling ratio reported in this paper
is an average of at least two separate measurements; standard deviations
of the measured swelling ratios were less than 10 and 5% of the mean for
swollen and collapsed gels, respectively.

The PEG concentration inside the gel samples was measured by
refractometry using an Abbe refractometer at 20°C, as described in Ref.
14. All measurements were performed in duplicate; standard deviations of
the measured PEG distributions were generally less than 5% of the mean.

2.4 Calculations

2.4.1 Characteristics of the networks

An ionic polymer network can be best characterized by the mean number
of segments, $N$, and the mean number of ionic units, $f$, between successive
junctions. The value of $N$ of a network can be estimated from either the
swelling ratio or the elastic modulus. When the network is swollen to
equilibrium with pure solvent, the chemical potential of the solvent in the
network, $\Delta \mu_1$, equals that of the surrounding pure solvent, i.e. zero. The
thermodynamic equilibrium condition for such an ionic PAAm network
swollen in pure water may be written as:15

$$\frac{\Delta \mu_1}{RT} = \ln(1 - \nu_2) + \nu_2 + \chi_{12} \nu_2^2 + N^{-1} \left( \nu_2^{(2/3)} \nu_1^{1/3} - \frac{\nu_2}{2} \right) - N^{-1} \nu_2 f = 0$$

(2)

where $\nu_2$ is the volume fraction of network in the equilibrium swollen gel,
which can be calculated from $\nu_2 = \nu_2^0 \left( \frac{V_1}{V_0} \right)^{-1}$, $\nu_2^0$ is the volume fraction of
the network after preparation, $\chi_{12}$ is the interaction parameter between
PAAm and water, $R$ is the gas constant and $T$ is temperature. Note that
the subscripts 1 and 2 denote water and PAAm network, respectively.

For the PAAm gel–water system, the $\chi_{12}$ parameter was reported to be
0.48, $\chi_{12}$ was held constant at this value in the calculations described here. For unchanged PAAm gels, the last term on the right-hand side of eqn (2), i.e. the ionic contribution equals zero. Thus, substituting $\chi_{12} = 0.48$, $f = 0$, $v_2^2 = 0.035$ and the experimentally determined equilibrium $v_2$ value into eqn (2) leads to the average number of segments in a network chain $N$. The value $v_2 = 0.0216$, found by experiments for the non-ionic PAAm gels swollen in pure water, yielded $N = 1487$. Assuming that the value of $N$ does not change with the addition of acrylic acid (Ac) comonomer in the monomer mixture during synthesis, the mean number of ionic units in a network chain, $f$, can also be estimated from eqn (2). For example, using $\chi_{12} = 0.48$, $N = 1487$, $v_2^2 = 0.035$ and the equilibrium value $v_2 = 0.00223$, found by experiments for PAAm gels with 13 w/w% Ac content (with respect to dry copolymer), yielded $f = 5.71$, indicating that, on average, 5.71 charges exist in a network chain composed of 1487 segments.

2.5 Interaction parameter between PAAm and ethylene glycol oligomers ($\chi_{23}$)

The thermodynamic equilibrium condition for an ionic PAAm gel swollen in a polymer melt may be written as:

$$\frac{\Delta \mu_3}{yRT} = \ln(1 - v_2) + \frac{1}{y} v_2 + \chi_{23} v_2^2 + N^{-1} \left( v_2^{\text{H},v} - \frac{v_2}{2} \right) - \frac{1}{N} N^{-1} v_2 f = 0$$

(3)

where $y$ is the number of segments in the linear polymer and $\chi_{23}$ is the interaction parameter between the PAAm network and the linear polymer (component 3). Assuming that $y$ is equal to the degree of polymerization of ethylene glycol oligomers (OEG), eqn (3) can be applied to PAAm gels swollen in pure OEG. Thus, using the values $N = 1487$, $v_2^2 = 0.035$, $f = 0$ and the equilibrium swelling ratios of non-ionic PAAm gels in pure ethylene glycol (MEG), diethylene glycol (DEG) and tetraethylene glycol (TEG) with $y = 1$, 2 and 4, respectively, eqn (3) can be solved for the corresponding unknown $\chi_{23}$ parameters. The equilibrium values $v_2 = 0.0303$, 0.0923 and 0.1598 yielded $\chi_{23} = 0.50$, 0.27 and 0.14 for the systems PAAm–MEG, PAAm–DEG and PAAm–TEG, respectively.

2.5.1 The ternary system PAAm gel/water/OEG

For this system, the state of equilibrium swelling of the PAAm network is obtained when the water and the OEG inside the network are in
thermodynamic equilibrium with those outside. This equilibrium state is described by the equality of the chemical potential of these components in both phases. The set of equations derived for this system was given in Ref. 14. In order to solve these equations, in addition to the parameters \( \gamma_{12} \) and \( \gamma_{23} \) calculated above, the interaction parameter between water and OEG, \( \gamma_{13} \), must be known. In the present study, \( \gamma_{13} \) was estimated by fitting the equilibrium swelling data of non-ionic PAAm gels in aqueous OEG solutions. The \( \gamma_{13} \) parameters found were 0.013, 0.066 and 0.136 for water–MEG, water–DEG and water–TEG systems, respectively.

3 RESULTS AND DISCUSSION

3.1 Influence of the chain length of ethylene glycol oligomers (OEG)

Previously, we have observed a discontinuous volume collapse of poly(acrylamide-co-acrylic acid) gels immersed in aqueous solutions of PEG, \( \text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_y-\text{H} \), with a number of repeat units, \( y \), of 6–450.\(^{14}\) In this section we focus on the swelling behavior of the same gels in aqueous solutions of ethylene glycol oligomers with \( y < 6 \). Preliminary experiments showed that the initial state of the gels does not affect their swelling behavior in OEG solutions. Thus, the equilibrium volume of the gels in OEG solutions is independent of whether the gel is in a swollen or in a dried state prior to the swelling experiments.

Figure 1(A)–(C) shows the equilibrium degree of swelling, \( V/V_0 \), of poly(acrylamide-co-acrylic acid) gels with different acrylic acid (Ac) content plotted as a function of the concentration of ethylene glycol oligomers (OEG) in the external solution. The number of repeat units of OEG, \( y \), is 1, 2 and 4 in Fig. 1(A), (B) and (C), respectively. The filled circles represent the results of measurements for non-ionic PAAm gels, whereas the filled and empty triangles represent the measurements for ionic gels with 13 and 22 w/w\% Ac contents (in the dry copolymer), respectively. The empty circles represent the results of measurements for ionic gels with 13 w/w\% Ac carried out in OEG/water mixtures of pH = 6.5–6.7. The solid curves show the trend of data obtained for the ionic gels. The dashed and dotted curves were calculated using the Flory–Huggins theory for non-ionic and ionic gels, respectively, as described in the previous section. In aqueous solutions of monoethylene glycol [Fig. 1(A)], the volume of the non-ionic gel remains almost constant over the entire range of the solvent composition. Non-ionic gels start to de-swell in di- and tetraethylene glycol solutions when their concentrations
Fig. 1. Variation of the equilibrium swelling ratio $V/V_o$ of poly(acrylamide-co-acrylic acid) gels with the concentration of OEG in the outer solution (v/v%). The number of repeat units ($y$) in OEG is (A) 1, (B) 2 and (C) 4. Acrylic acid (Ac) content in the dry copolymer = 0 (●), 13 (▲) and 22 w/w% (△). The symbol (○) represents the $V/V_o$ values of gels with 13 w/w% Ac content, swollen in aqueous OEG solutions of pH = 6.5–6.7. The solid curves show the trend of data obtained for ionic gels. The dashed and dotted curves were calculated using the Flory–Huggins theory for non-ionic and ionic gels ($f = 5.71$), respectively.
exceed about 50%. The calculation results (dashed curves) are in good agreement with the experimental data.

As expected, the gel with ionic constituent swells in water much more than the corresponding neutral gel due to the electrostatic repulsion between charged groups on the network chains, as well as due to the osmotic pressure of mobile ions within the gel phase. However, as can be seen in Fig. 1(A)–(C), the ionic gel decreases its volume sharply when a relatively small amount of OEG was added to water. At about 50% OEG concentration, the volume of the ionic gel approaches that of the corresponding non-ionic gel. Then, further increase of OEG concentration changes the gel volume only slightly. However, calculations using the Flory–Huggins theory for ionic gels (dotted curves) predict that the volume of the gels does not change much over the whole concentration range of OEG–water mixtures. Thus, experimental data shown in Fig. 1 for ionic gels do not support this prediction. It must be noted that the aqueous solutions of OEG exhibit pH values in the range 6.2–6.7, 4.2–4.9 and 3.5–4.8 for \( y = 1, 2 \) and 4, respectively, whereas those of PEG (\( y \geq 6.4 \)) have pH values between 6.5 and 7.5. Since pH is an important parameter determining the ionization degree of gels, we also repeated the swelling experiments at a fixed pH value, namely at pH = 6.5–6.7, using titration of OEG/water mixtures with a dilute NaOH solution. The results of these measurements are also shown in Fig. 1(A)–(C) as empty circles. Although the extent of de-swelling of ionic PAAm gels decreases after adjusting the pH of aqueous OEG solutions, the experimental data also indicate a large decrease in the equilibrium gel volume on raising the OEG concentration in the external solution. The decrease in the gel volume is significant in tetracethylene glycol solutions of concentrations as high as 80%.

This interesting swelling behavior of ionic PAAm gels in aqueous solution of ethylene glycol oligomers (OEG) may be due to the action of OEG as an organic solvent rather than a linear chain. The experimental results can be explained by the formation of an increasing number of ion pairs between the charges of the network and the mobile counter-ions, in the presence of water/OEG mixtures. The importance of ion pairing for the collapse behavior of ionic gels has been demonstrated both experimentally\textsuperscript{19} and theoretically.\textsuperscript{20,21} The formation of ion pairs is known to be more pronounced for solutions with a lower solvent dielectric constant \( \varepsilon \). Since the dielectric constants, \( \varepsilon \), of ethylene glycol (MEG), diethylene glycol (DEG) and tetaethylene glycol (TEG) are 40, 32 and 20, respectively,\textsuperscript{22} compared to the value \( \varepsilon = 80 \) for water, increasing the content of OEG in the aqueous solution decreases the solvent dielectric constant inside the gel and, therefore, increases the number of ion pairs.
The mixtures of water with TEG have the lowest $\varepsilon$ and, therefore, form more ion pairs than those with DEG or MEG. Thus, the osmotic pressure in the gels was lower in water/TEG mixtures and the degree of swelling was smaller. It was also shown that the number of ion pairs is controlled by $\varepsilon$ of the gel medium and, therefore, it is much larger for the collapsed gels.\textsuperscript{21} As the TEG content of aqueous solutions increases, the ionic gel de-swells and $\varepsilon$ of the gel medium decreases. Thus, the number of ion pairs increases as the TEG content increases and, in mixtures with 80% TEG, the number of ion pairs can be so large that an abrupt transition to the collapsed state becomes possible [Fig. 1(C)]. In these solvent mixtures, the formation of ionomer multiplets is also possible, which would lead to further contraction of the gel.\textsuperscript{20,21}

In Fig. 2, the OEG distribution inside and outside the gel, $v_3/\phi$, is shown as a function of the OEG concentration in the solution. Here, $v_3/\phi$ represents the ratio of the volume fraction of OEG in the gel phase ($v_3$) to that in the solution phase ($\phi$); thus $v_3/\phi = 1$ means that the OEG concentration inside the gel is equal to that in the solution, whereas $v_3/\phi = 0$ means that the gel excludes all the OEG molecules. The experiments were carried out using PAAm gels with different Ac content immersed in aqueous solutions of OEG with $y = 1$, 2 and 4. Figure 2 indicates that a large amount of OEG can penetrate into the gel phase. For ionic gels, the $v_3/\phi$ ratio is about 0.8 and is essentially independent of the concentration and chain length of OEG within the limits of experimental error. For non-ionic gels, the $v_3/\phi$ ratio decreases with increasing OEG concentration in the outer solution.
Fig. 3. Variation of the swelling ratio, $V/V_{o}$, of poly(acrylamide-co-acrylic acid) gel with the number of repeat units in ethylene glycol polymers, $y$. The PEG concentration in the outer solution = 10 (●), 20 (○), 30 (▲), 40 (△) and 60 v/v% (▼). Acrylic acid (Ac) content in the dry copolymer is 0 and 13 w/w% in (A) and (B), respectively. The dashed curves in (B) represent the swelling behavior of gels at pH 6.5–6.7. The lower dotted curves in (B) represent the swelling behavior of the non-ionic gels in polymer solutions of concentrations 10 (1), 20 (2) and 30% (3).

In Fig. 3(A) and (B), the equilibrium swelling ratio of the gels is shown as a function of $y$ (degree of polymerization of ethylene glycol polymers) for a fixed PEG concentration in the external solution. The experimental data points for PEG having molecular weights higher than 300, which correspond to $y > 6.4$, were taken from Ref. 14. For the non-ionic gels [Fig. 3(A)], an increase in $y$ decreases the volume of the gel phase. This was expected due to the effect of the mixing entropy of the linear polymers. An increase in $y$ decreases the osmotic pressure of the solution phase, so that the gel shrinks. Contrary to the non-ionic gels, the volume of the ionic gel first decreases as $y$ increases from 1 to 4, but then it increases again rapidly up to $y = 6$ [Fig. 3(B)]. Further increase in $y$ decreases the gel volume only slightly. A re-entrant swelling behavior is shown in Fig. 3(B) for ionic PAAm gels in aqueous OEG solutions. The
lower dotted curves in the region $y = 1–6$, shown in Fig. 3(B), represent the swelling behavior of non-ionic gels for comparison. It can be seen that the volume of the ionic gel approaches that of the non-ionic gel at $y = 2–4$. The results of experiments carried out at pH $= 6.5–6.7$ are also shown in Fig. 3(B) as dashed curves. The gel volume first moves to smaller values as $y$ increases from 1 to 4 and then goes up again. These results also indicate that the addition of a small amount of OEG into water results in the destruction of the solvation structure of water molecules around carboxyl groups of the network chains due to the formation of ion pairs and so, the association of the dehydrated chains in water/OEG mixtures results in smaller gel volumes than those in polymer solutions of higher molecular weight.

According to the above experimental data, di- and tetraethylene glycols seem to be the most efficient de-swelling agents for the ionic PAAm gels. To confirm this assumption, experiments have also been conducted using linear poly(acrylamide-co-acrylic acid) chains dissolved in OEG–water mixtures. For this purpose, linear poly(acrylamide-co-acrylic acid) of molecular weight $2 \times 10^5$ daltons, having 10% acrylic acid units, purchased from Polyscience was used. 10% aqueous solutions of OEG of various chain lengths were selected as solvents. The viscosities of the polymer solutions were measured in an Ubbelohde viscometer at 25°C. In Fig. 4, reduced viscosities, $\eta_{\text{red}}$, defined as:

$$\eta_{\text{red}} = \frac{(t - t_0)}{t_0}$$

(4)

![Graph](image)

**Fig. 4.** Variation of the reduced viscosity of linear poly(acrylamide-co-acrylic acid) chains in OEG–water mixtures with the number of repeat units in OEG, $y$. OEG concentration = 1.0 (●), 1.4 (○), 2.0 (▲), 3.0 (△) and 4.0 (◇) g/L.
where $t_0$ and $t$ are the flow times of solvent and polymer solution of concentration $c$ (in g/mL) through the capillary of the viscometer, respectively, are shown as a function of the number of repeat units of OEG, $y$, in the solution. The viscosity of the polymer solutions shows a minimum at $y = 4$, i.e. in tetraethylene glycol (TEG)–water mixture. In Fig. 5, reduced viscosity values for the above polymer were plotted against its concentration. With the exception of the TEG–water mixtures, a decrease in the reduced viscosity with increasing polymer concentration can be seen from the figure, indicating typical polyelectrolyte behavior of poly(acrylamide-co-acrylic acid) solutions. This is expected. Using a second order polynomial fit of the data points shown in Fig. 5, the initial slopes of $\eta_{\text{red}}$ vs $c$ dependences were calculated as $-370, -276, -159, +23$ and $-190$, respectively, for $y = 0, 1, 2, 4$ and 6.4. Thus, the decrease in $\eta_{\text{red}}$ with dilution becomes weaker as $y$ increases for $y < 4$, and, in the TEG–water mixture, the reduced viscosity vs concentration curve exhibits a positive slope. The initial slope of the curves decreases again with a further increase in $y$. By extrapolating the plot of $\eta_{\text{red}}$ vs $c$ to zero concentration, the intrinsic viscosity of the polymer sample in the TEG–water mixture was calculated as 119.5 mL/g. Using this value and for $K = 6.31 \times 10^{-3}$, $a = 0.8^{23}$ the weight-average molecular weight of the poly(acrylamide-co-acrylic acid) sample was calculated as $2.2 \times 10^6$ daltons, which is close to the value reported by the manufacturer. Thus, the chains dissolved in TEG–water mixtures behave as a non-ionic polymer. The above results, obtained with both cross-linked and linear ionic PAAm chains, clearly show that the addition of a small amount of tetraethylene glycol in water screens the excess expansion of ionic polymer coils due to the ionization of the polymer chains.
3.2 Appearance of non-equilibrium structures

If a swollen gel is placed in a poor solvent, the gel de-swells due to the increase of the polymer–solvent interaction parameter $\chi$. This de-swelling process usually leads to the formation of two continuous phases, namely gel and liquid phases, as illustrated in Fig. 6(A), and the network chains in the gel attain an equilibrium state. The term macrosyneresis is used to describe the de-swelling process in gels. However, as first pointed out by Dusek, a de-swelling process may also end in a non-equilibrium state. In this case, the de-swelling may occur in the form of microsyneresis, in which the gel and separated liquid phases form a dispersion [Fig. 6(B)]. Dusek pointed out that microsyneresis will take preference over macrosyneresis when the relaxation of the network chains is slower than the separation of water in the micro-domains of the gel. Recently, Khokhlov et al. reported the appearance of kinetically frozen structures within the ionic gels due to microsyneresis.

Experiments carried out using OEG–water mixtures showed that both ionic and non-ionic PAAm gels attain their equilibrium volume in these solutions, independent of the initial state of the gel. However, in PEG solutions, different final states of the gel were detected. In the following, we studied the de-swelling processes of swollen poly(acrylamide-co-acrylic acid) gels in PEG–water mixtures. Prior to the immersion of the gels in aqueous PEG solutions, they were swollen in water to different degrees.
The decrease of the volume of ionic PAAm gels is shown in Fig. 7 as a function of the contact time with pure PEG 300. Here, the gel A was directly immersed into PEG 300 after its synthesis. The gel B was partially swollen and gel C was swollen to equilibrium in water prior to the de-swelling experiments in PEG 300. The dotted horizontal line represents the equilibrium volume of the gel in PEG 300. It seems that the pre-swollen gels de-swelling only slightly in PEG 300 and they cannot reach their equilibrium volume. However, the gel used after synthesis reaches its equilibrium volume after about 1.5 h.

In Fig. 8(A), the swelling ratio of poly(acrylamide-co-acrylic acid) gels is plotted as a function of the PEG 300 concentration in the external solution. The filled symbols belong to the gels after synthesis and the empty symbols to pre-swollen gel samples. For gel samples after synthesis, a first order phase transition is observed at about 70% PEG concentration. However, if the same gel samples are swollen to equilibrium in water prior to the measurements, they remain in the swollen state over the entire PEG 300 concentration and no collapse transition was observed. Similar swelling curves were also observed using PEG solutions of different molecular weights. Figure 8(B) illustrates the swelling curves of ionic PAAm gels in aqueous solutions of PEG 5000 (y = 113). The pre-swollen PAAm gel with 13% Ac content remains in the swollen state over the entire range of PEG concentration, while the same gel after synthesis undergoes a collapse transition at 18% PEG 5000 concentration. Here, the swelling experiments could not be carried out at PEG concentrations higher than 50% because PEG 5000 was not dissoluble.

In Fig. 9, the swelling ratio of poly(acrylamide-co-acrylic acid) gels in
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Fig. 8. Variation of the swelling ratio $V/V_o$ of poly(acrylamide-co-acrylic acid) gels with the concentration of PEG in the outer solution. Swelling measurements were carried out using gels after synthesis (filled symbols) and using pre-swollen gels (empty symbols). Acrylic acid (Ac) content in the dry copolymer = 13 (●, ○) and 22 w/w% (▲, △). $y = 6.4$ (A) and 113 (B).

80% aqueous solution of PEG 300 is shown as a function of their pre-swelling time in water. The solid curve illustrates the trend of the experimental data shown as empty circles. For pre-swelling times less than 60 min, the gel attains its equilibrium volume in PEG solutions. However, as the pre-swelling time increases, the gel cannot attain its equilibrium volume in PEG solutions. The filled circles in Fig. 9 represent the swelling ratio of the gel in water as a function of time. It seems that as the initial volume of the gel increases, the gel fails to de-swell in the PEG solution to its equilibrium volume, as is observed when de-swelling is from the initial state after synthesis.

When a gel sample swollen in water is immersed in a poor solvent, the system becomes unstable and spinodal decomposition sets in. As a result,
Fig. 9. Variation of the swelling ratio $V/V_0$ of poly(acrylamide-co-acrylic acid) gels in PEG 300-water mixture (80/20 v/v) with the pre-swelling time in water. The right axis represents the swelling ratio of the gels in water at given contact times. Acrylic acid (Ac) content of the gels was 13%.

the gel separates into polymer-rich and polymer-poor regions. One may think that the polymer-rich regions of the gel will pass into the glassy state earlier than those with low polymer concentration. Thus, during the de-swelling process, micro-domains in a glassy state will appear, which are embedded in polymer-poor regions in a rubbery state. Under favorable conditions, removal of water from polymer-poor regions results in the transition of the whole network region in the glassy state. This leads to the formation of homogeneous collapsed gels in an equilibrium state. According to our results, PAAm gels attain their equilibrium volumes in PEG solutions if they are used directly after the network formation process. However, highly swollen gels cannot attain their equilibrium volume in PEG solutions, even after 2 months of observation. This is probably due to the slow relaxation of the network chains in the polymer-poor regions compared to the rate of removal of water molecules from the gel. Thus, under such conditions the inhomogeneities within the gel remain fixed.

4 CONCLUSIONS

1. The addition of a small amount of OEG with a number of repeat units $y = 2–4$ in the aqueous solution leads to the contraction of both linear and cross-linked poly(acrylamide-co-acrylic acid) chains. These results present clear evidence for the screening effect of OEG on the ionic groups of the polymer chains. Linear and network chains of ionic PAAm in 10% TEG–water mixtures behave like non-ionic polymers.
2. The immersion of swollen ionic PAAm gels in PEG solutions leads to the formation of non-equilibrium structures. These structures become more stable as the initial swelling degree of the gels increases.

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