

Swelling Behaviors of Ionic Poly(*N,N*-dimethylacrylamide-*co*-acrylamide) Hydrogels in Various Media

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ABSTRACT: Polyelectrolyte hydrogels were synthesized from *N,N*-dimethylacrylamide, acrylamide, and itaconic acid with ammonium persulfate as a free-radical initiator in the presence of methylene(bis)acrylamide as a crosslinker. The swelling behavior of the ionic poly(*N,N*-dimethylacrylamide-*co*-acrylamide) hydrogels was investigated in pure water, in KSCN solutions with pHs 4 and 9, and in water–acetone mixtures according to the itaconic acid content in the hydrogel. The pulsatile swelling behavior of these hydrogels was stud-

ied both in water–acetone and in pH 2–9 buffer solutions. Although the equilibrium swelling ratio of the hydrogels with low concentrations of itaconic acid was almost not affected by changes in the temperature, the equilibrium swelling ratio of the hydrogels with high concentrations of itaconic acid increased in the temperature range of 20–50°C. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2140–2145, 2007

Key words: hydrogels; networks; swelling

INTRODUCTION

The most efficient water absorbers are polyelectrolyte hydrogels carrying dissociated, ionic-functional groups. These hydrogels can swell in water and hold a large amount of water while maintaining their physical dimensions.¹ Many structural factors (e.g., the charge, concentration, and pK_a of the ionizable group, degree of ionization, crosslinking density, and hydrophilicity) influence the degree of swelling of polyelectrolyte hydrogels.^{2–4} In addition, the properties of the swelling medium (e.g., the pH, ionic strength, counterion, and its valence) affect the swelling characteristics.^{5–7}

The swelling–shrinking kinetics of polyelectrolyte hydrogels is also one of the most important characteristics for the performance of devices. Most of the applications proposed for responsive gels depend on the kinetics of changes in the observed properties. By the incorporation of stimuli-responsive comonomers either into the backbone or as pendant groups, it is possible to prepare hydrogels with responsive properties. These polyelectrolyte hydrogels have become an important area of research and development in the fields of medicine, pharmacy, and biotechnology.^{8–10}

In this article, the effects of external stimuli such as the ionic strength, solvent composition, and temperature on the equilibrium swelling ratio (ESR) of ionic poly(*N,N*-dimethylacrylamide-*co*-acrylamide)

[P(DMAAm-*co*-AAM)] hydrogels are reported. The pulsatile swelling behavior of the hydrogels is also investigated both in water–acetone solutions and in pH 2–9 buffer solutions.

EXPERIMENTAL

Materials

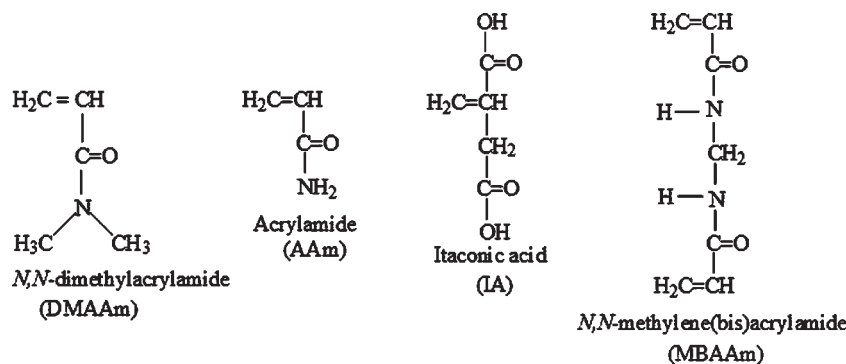
N,N-Dimethylacrylamide (DMAAm; Aldrich Chemical, Milwaukee, WI), acrylamide (AAM; Aldrich), itaconic acid (IA; Aldrich), *N,N*-methylene(bis)acrylamide (MBAAm; Aldrich), ammonium persulfate (APS; Aldrich), and *N,N,N',N'*-tetramethylethylenediamine (TEMED; Aldrich) were used as received. Glacial CH_3COOH , H_3PO_4 (85%), H_3BO_3 , and standardized NaOH were used to prepare Britton–Robinson (B–R) buffers. A B–R buffer solution was prepared in such a way that 2.3 mL of glacial acetic acid, 2.7 mL of phosphoric acid, and 2.47 g of boric acid were dissolved by the dilution of triple-distilled water to 1.0 L; 50-mL portions of this solution were taken, and the pH was adjusted to 4.0 or 9.0 by the addition of the appropriate amount of 2.0M NaOH.

Synthesis of the hydrogels

Polyelectrolyte hydrogels were prepared by the free-radical crosslinking copolymerization of DMAAm, AAM, and IA with a small amount of MBAAm as the crosslinker (Scheme 1). APS (0.06M) and TEMED (0.32M) were used as the redox initiator system. The crosslinker ratio (molar ratio of the crosslinker MBAAm to monomers DMAAm and AAM) was fixed at 3.5/100, whereas the IA concentration of the mono-

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Scheme 1 Molecular structures of the monomers.

mer mixture was varied from 0 to 14.8 mol %. Aqueous solutions containing DMAAm (0.7 mL), AAm (0.3 g), MBAAm (0.06 g), APS (1.5 mL), TEMED (2 mL), and IA (0.10, 0.15, 0.20, or 0.25 g) were prepared in 1 mL of pure water with the following DMAAm + AAm/IA molar ratios: 93.5/6.5, 90.6/9.4, 87.7/12.3, and 85.2/14.8. After nitrogen was bubbled for 15 min, these solutions were placed in poly(vinyl chloride) straws 4 mm in diameter and about 20 cm long. The poly(vinyl chloride) straws were sealed and immersed in a thermostated water bath at 20°C, and the polymerization was conducted for 24 h. After the reaction, the hydrogels were cut into specimens approximately 10 mm long, dried in a vacuum oven at 50°C to a constant weight, and subjected to Soxhlet extraction with water to remove the uncrosslinked polymer and unreacted IA from copolymers. The extracted gels were dried again in a vacuum oven at 50°C to a constant weight. When the aqueous extract was titrated with NaOH (0.05M), end-point detection was not observed just because there was no unreacted IA. The composition of the hydrogel was about the same as that of the mixture of monomers in the feed in accordance with yields of the reaction of polymerization close to 100%.

Measurement of the swelling and pulsatile kinetics

For the swelling dynamic studies, the hydrogels were immersed in deionized water. At a prescribed time interval, the hydrogels were taken from the water and weighed after the excess water was wiped off the surface of the hydrogels. The swelling ratio (SR) of the hydrogels was defined as follows:

$$\text{SR} = \frac{m_t m_d}{m_d} \quad (1)$$

where m_d and m_t are the masses of the dry hydrogel and the swollen hydrogel at time t , respectively.

The pulsatile swelling behavior was observed in buffer solutions with pH values between 2 and 9. Dur-

ing the pulsatile swelling process, the weight change of the hydrogels was measured at 5-min intervals, and the buffer solution was changed every 150 min.

Similarly, the pulsatile swelling behavior of the hydrogels was studied in water and in acetone. The hydrogels were first immersed in distilled water and kept at room temperature for 2 weeks to reach equilibrium. The equilibrated hydrogels were then quickly transferred into acetone. The weight change of the hydrogels was also measured at 5-min intervals. All the reported swelling and shrinking values were averages of at least three separate measurements.

Determination of the ESR

For the swelling measurements in aqueous KSCN solutions with pHs 4 and 9, the hydrogels were immersed in vials filled with aqueous KSCN solutions at concentrations ranging from 0.1 to 10⁷M. Aqueous KSCN solutions with pH 4 or 9 were prepared by the dilution of the 1.0M KSCN stock solutions (pH 4 or 9) with various volumes of B-R buffer solutions. The volume of the KSCN solutions in the vials was much larger than the hydrogel volume, so the concentration of the solution was practically unchanged. The mixtures were kept at room temperature for 2 weeks to allow the hydrogels to reach equilibrium. The hydrogels were removed from the solution and blotted with wet filter paper for the removal of excess water on the hydrogel surface; they were then weighed. ESR was calculated as follows:

$$\text{ESR} = \frac{m_s m_d}{m_d} \quad (2)$$

where m_s is the mass of the swollen hydrogel.

For the swelling measurements in water–acetone mixtures, the hydrogels were immersed in water–acetone mixtures with various compositions. The hydrogels were kept at room temperature for 2 weeks to reach equilibrium. The hydrogels were removed from the solution and blotted with wet filter paper for the

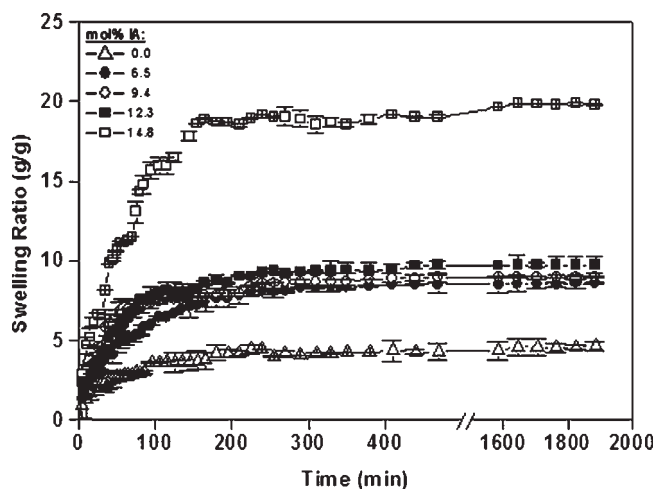


Figure 1 SR as a function of time for the ionic P(DMAAm-co-AAm) hydrogels in water at 25°C.

removal of excess solvent on the hydrogel surface; they were then weighted.

Similarly, for the temperature-response studies, hydrogels were equilibrated in distilled water at temperatures ranging from 10 to 60°C. The hydrogels were allowed to swell in distilled water for at least 24 h at each predetermined temperature, which was controlled up to $\pm 0.1^\circ\text{C}$ in a Thermo Haake K10 constant-temperature water bath. After immersion in distilled water at a predetermined temperature, the hydrogels were removed from the water and blotted with wet filter paper for the removal of excess water on the hydrogel surface; they were then weighed. After this weight measurement, the hydrogels were re-equilibrated in distilled water at another predetermined temperature, and their swollen weight was determined.

RESULTS AND DISCUSSION

Swelling kinetics

When a dry hydrogel is brought into contact with water, water diffuses into the hydrogel, and the hydrogel swells. Diffusion involves the migration of water into preexisting or dynamically formed spaces among hydrogel chains. Swelling of the hydrogel involves a larger scale segmental motion, resulting ultimately in an increase in the separation distance among the hydrogel chains.¹¹

The swelling kinetics of the ionic P(DMAAm-co-AAm) hydrogels in water are shown in Figure 1. The data show that the swelling rate increased with the IA concentration increasing from 0.0 to 14.8 mol %. The nonionic P(DMAAm-co-AAm) hydrogel had an SR of about 3.0 within 50 min or 4.0 within 150 min, whereas the ionic P(DMAAm-co-AAm) hydrogel with 14.8 mol % IA had SRs of about 11.0 and 19.0, respectively, within the same time frames.

To determine the diffusion mechanism, the initial swelling data were fitted to the following exponential equation:¹²

$$F = \frac{M_t}{M} = kt^n \quad (3)$$

where F is the fractional uptake, M_t is the amount of absorbed water at time t , M is the maximum amount of absorbed water, k is a characteristic constant of the hydrogel, and n is a characteristic exponent of the mode of transport of the penetrant. The constants n and k were calculated from the slopes and intercepts of the graph of $\log F$ against $\log t$ for the series of ionic P(DMAAm-co-AAm) hydrogels in water. In eq. (3), n provides information about the mechanism of swelling kinetics. For the first case, $n = 0.5$, corresponding to Fickian diffusion, the rate of diffusion is much lower than the rate of relaxation, and for the second, $n = 1$, the diffusion is very fast, contrary to the rate of relaxation; the third case corresponds to anomalous diffusion, with n values lying between 0.5 and 1.

As seen in Table I, Fickian behavior was observed in water for all P(DMAAm-co-AAm) hydrogels. The results in Table I also indicate that the swelling exponent increased with increasing IA content in the hydrogel. The results appear justified because with increasing IA content, the compact arrangement of macromolecular chains was increased in the ionic P(DMAAm-co-AAm) hydrogels. Thus, because of the increasing compactness of the ionic P(DMAAm-co-AAm) hydrogels, the relaxation of macromolecular chains slowed down, and this resulted approximately in a non-Fickian process, that is, a chain-relaxation-controlled process.

For calculating the diffusion coefficient of water moving through the ionic P(DMAAm-co-AAm) hydrogels, the following equation was employed:¹²

$$D = \pi r^2 \left(\frac{k}{4} \right)^{1/n} \quad (4)$$

where D is the diffusion coefficient of water (cm^2/s) and r is the radius of the dry gel.

TABLE I
Variation of the Diffusion Parameters with the Molar Percentage of IA in the Ionic P(DMAAm-co-AAm) Hydrogels

IA (mol %)	n	$k \times 10^2$	$D \times 10^5$ (cm^2/s)
0.0	0.34	11.2	6.5
6.5	0.51	6.8	10.8
9.4	0.53	9.2	12.3
12.2	0.54	9.0	20.8
14.8	0.55	6.5	21.2

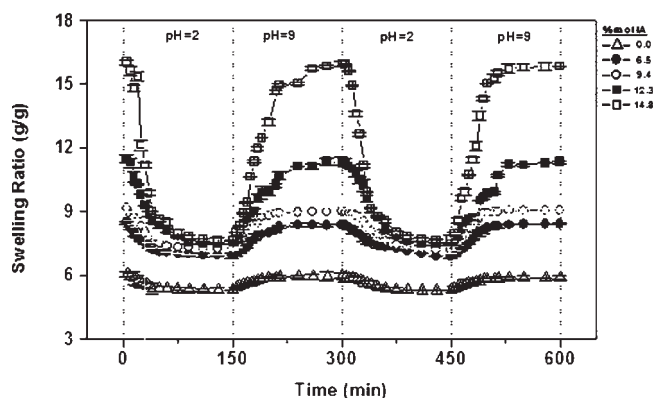


Figure 2 Pulsatile pH-dependent swelling behavior of ionic P(DMAAm-co-AAm) hydrogels.

The D values are also presented in Table I. The extensive SR is not constant through the entire process, and neither is D . Therefore, eq. (3) was applied to the initial stages of swelling, and plots of $\ln F$ versus $\ln t$ yielded straight lines to almost a 60% increase in the mass of the hydrogel. In this case, the D values calculated by eq. (4) are apparent values for the initial swelling behavior of these hydrogels. With an increase in the content of IA in the hydrogel, the values of the diffusion coefficient increased because of a greater penetration of water into the hydrogel. This result was caused by their hydrophilic property and proved that the IA unit was mainly more hydrophilic than the DMAAm and AAm units of the hydrogel.

Pulsatile pH-dependent swelling behavior

Figure 2 shows the pulsatile swelling behaviors of the ionic P(DMAAm-co-AAm) hydrogels at 25°C with solution pH values alternating between 2 and 9. The SR was measured in 5-min steps, and the buffer solution was switched every 150 min. As shown in this figure, the SRs of these hydrogels were smallest in the pH 2 solution because of the presence of strong hydrogen bonds between the carboxylic acid groups. At pH 9, the carboxylic acid groups transformed into the ionized form (COO^-). The electrostatic repulsion between the ionized groups caused the hydrogels to swell.¹³ On the other hand, the SR of the ionic hydrogels very much also depended on the number of ionizable groups in the hydrogel. This was due to the fact that, as the IA content in the P(DMAAm-co-AAm) hydrogel increased, the charges on the polymeric chains also increased. This led to the expansion of the hydrogels because of the high electrostatic repulsion, so the swelling capacities of the hydrogels increased. As a result, the swelling process proved to be repeatable and rapidly responded to changes in pH.

Effect of the ionic strength

It is well known that a balance between the osmotic pressure (π) and the polymer elasticity sets the physical dimensions of the swelling hydrogels.¹⁴ π of an ionic hydrogel during swelling is given as the sum of the pressures due to polymer-solvent mixing (π_{mix}), due to deformation of network chains to a more elongated state (π_{el}), and due to the nonuniform distribution of mobile counterions between the hydrogel and the external solution (π_{ion}):¹⁴

$$\pi = \pi_{\text{mix}} + \pi_{\text{el}} + \pi_{\text{ion}} \quad (5)$$

π of the hydrogel determines whether the hydrogel will expand or shrink; when nonzero, π provides a driving force for hydrogel volume change. In the case of an ionic system, π is mainly contributed by π_{ion} , which is caused by the concentration difference

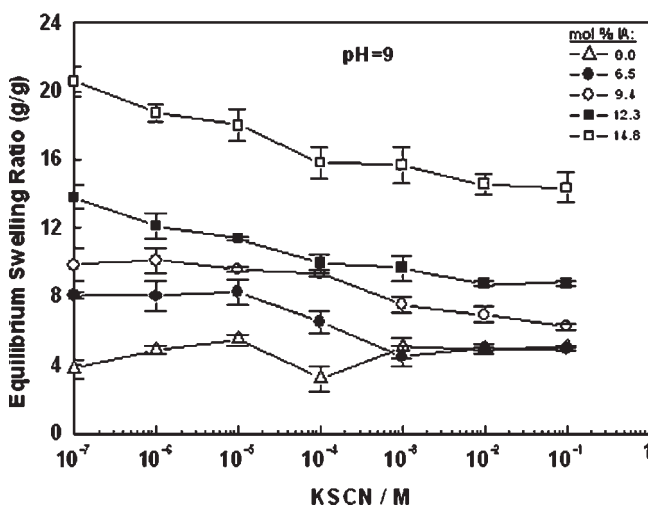
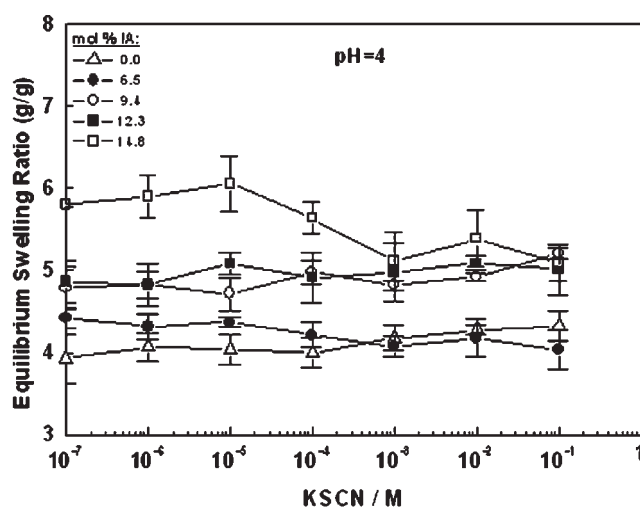


Figure 3 Variation of ESR of ionic P(DMAAm-co-AAm) hydrogels with the KSCN concentration in the external solution (pHs 4 and 9) at 25°C.

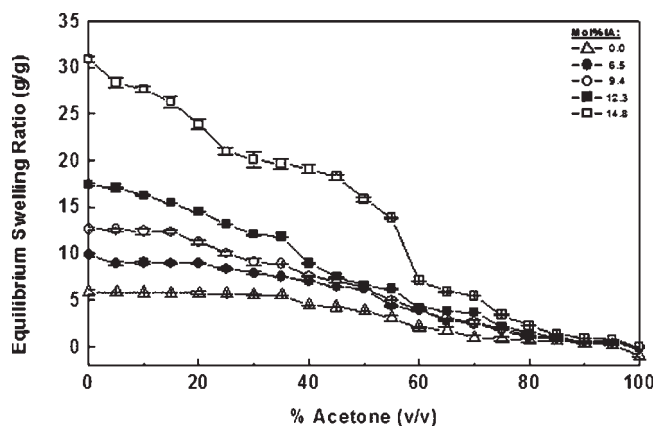


Figure 4 Variation of ESR of ionic P(DMAAm-co-AAm) hydrogels in water–acetone mixtures.

of counterions between the hydrogel and the outer solution. π_{ion} is given by¹⁴

$$\pi_{\text{ion}} = RT \sum_i (C_i^g - C_i^s) \quad (6)$$

where R is the gas constant; T is the temperature; and C_i^g and C_i^s are the mobile ion concentrations of the hydrogel and solution phases, respectively. Equation (6) clearly implies that the larger the difference is in the ionic concentration between the hydrogel and solution, the greater the swelling will be.

The effect of the external ionic strength on the ESR of the ionic P(DMAAm-co-AAm) hydrogels at 25°C is shown in Figure 3. The pHs of the solutions were fixed at 4.0 and 9.0 to obtain minimum and maximum swelling for each hydrogel. The effect of the ionic strength on the ESR was clearly observed at these pHs. An increase in the ionic strength generally caused a decrease in the SR, as the difference in the concentration of mobile ions between the hydrogel and solution was reduced, causing a decrease in the osmotic swelling pressure of these mobile ions inside the hydrogel. However, as shown in Figure 3, the KSCN solutions with pH 4 had no appreciable influence on the ESRs of the hydrogels. However, in KSCN solutions with pH 9, the ESR of the hydrogels decreased slightly with increasing concentration. On the other hand, the effect of the amount of IA in the hydrogel can be clearly seen by a comparison of the ionic strength dependence of the ESR of the hydrogels with 6.5 or 14.8 mol % IA. The changes in the ESR of the hydrogels were observed most clearly in the fully swollen state (pH 9.0). When the ionic strength of the solution was increased from 10^{-7} to $10^{-1}M$, the ESR was 12% at pH 4.0 and 30% at pH 9 for the hydrogel with 14.8 mol % IA. In this case of the hydrogel with 6.5 mol % IA, the ESR was observed to decrease by 9 and 39% at pHs 4 and 9, respectively.

Effect of the solvent composition

ESRs of the ionic P(DMAAm-co-AAm) hydrogels are shown in Figure 4 as a function of the acetone concentration in the outer water–acetone mixtures. The ionic P(DMAAm-co-AAm) hydrogels had high equilibrium swelling values in pure water. This behavior indicates that attractive interactions between the polymer chain and water molecule dominate the attraction between polymer chains. When acetone and water are mixed, the two solvents have an attractive interaction resulting in an increase in the free energy for polymer–polymer contact. The increase in the affinity among polymer segments induces the collapse of the polymer network. The nonionic P(DMAAm-co-AAm) hydrogels exhibited a small change in the SR over the entire range of acetone concentrations, whereas the ionic P(DMAAm-co-AAm) hydrogels, especially the hydrogels with high IA contents, underwent two discontinuous phase transitions at about 10–20 and 40–60% acetone concentrations. This difference can be explained by the dependence of the ionization degree of the carboxylic acid groups of the ionic P(DMAAm-co-AAm) hydrogels in water–acetone mixtures.

Pulsatile swelling behavior in acetone and in water

The pulsatile swelling behavior of the ionic P(DMAAm-co-AAm) hydrogels at 25°C in water and in acetone was investigated to confirm the repeatability of the swelling process (Fig. 5). The hydrogels underwent a number of swelling–deswelling cycles without undergoing any deformation in their shapes. When a completely swollen hydrogel was placed in acetone, the deswelling process started with the formation of weak hydrogen bonds between the acetone and network chains. This facilitated the movement of individual water and acetone molecules through the network and resulted in the observed rapid deswelling of the ionic P(DMAAm-co-AAm) hydrogels in acetone.

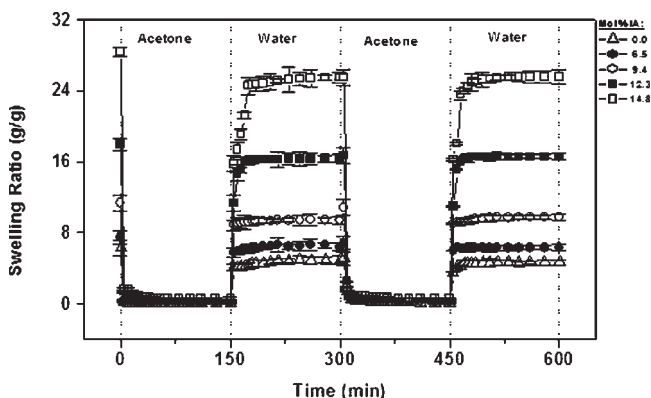


Figure 5 Pulsatile swelling behavior of ionic P(DMAAm-co-AAm) hydrogels in response to solvent changes (water and acetone) at 25°C.

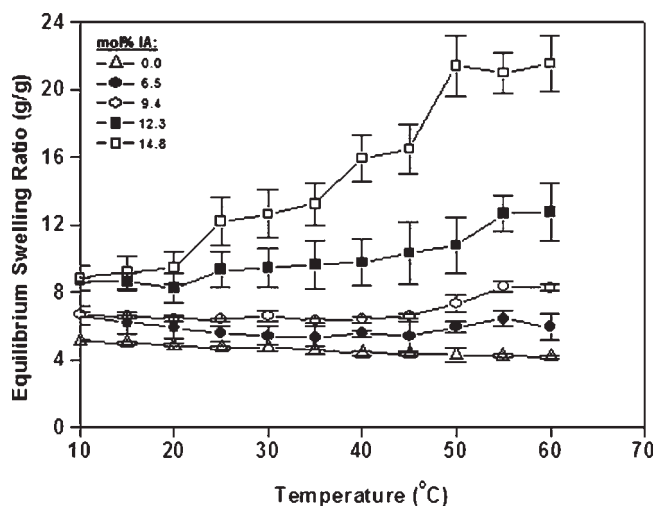


Figure 6 Variation of ESR of ionic P(DMAAm-co-AAm) hydrogels as a function of temperature in water.

Effect of the temperature

Figure 6 illustrates the temperature dependence of the ESR of the ionic P(DMAAm-co-AAm) hydrogels in water when the temperature increased from 10 to 60 °C. The ionic P(DMAAm-co-AAm) hydrogels with less than 12.2% IA showed a small change in the SR over the entire range of temperatures, whereas the hydrogels with 12.2 or 14.8 mol % IA exhibited a positive temperature coefficient, which indicated swelling at higher temperatures and shrinking at lower temperatures. When the external temperature was increased from 10 to 60 °C, the volume or water content inside the P(DMAAm-co-AAm) hydrogels with 14.8 mol % IA first increased drastically between 10 and 50 °C and finally remained almost constant. At low temperatures, the ESR was low because the carboxylic acid groups in the side chains were not ionized and intermolecular complexation via hydrogen bonds occurred (physical crosslinking). As the degree of ionization increased at high temperatures (especially for the hydrogels with high IA contents), the increased hydrophilicity resulted in greater degrees of swelling.

CONCLUSIONS

In this study, ionic P(DMAAm-co-AAm) hydrogels were prepared at a fixed crosslinker ratio and monomer concentration, but at various charge densities, that is, IA concentrations between 6.5 and 14.8 mol %. The ESR of the hydrogels was measured in pure water and in KSCN solutions with pHs 4 and 9 and in water-acetone mixtures. The swelling studies showed that the swelling media and ionic content were basic parameters affecting the ESR of the hydrogels. Also notable is the fact that the incorporation of only a few percent of the IA ionic monomer radically changed the swelling behavior of the hydrogels. The ESR of the hydrogels with low IA concentrations was almost not affected by the change in the temperature. However, the ESR of the hydrogels with high IA concentrations gradually increased with increasing temperature.

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