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Orhan Hazer^{ab}; Cengiz Soykan^a; Şenol Kartal^b

^a Faculty of Science and Arts, Department of Chemistry, University of Bozok, Yozgat, Turkey ^b Faculty of Science and Arts, Department of Chemistry, University of Erziyes, Kayseri, Turkey

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Synthesis and Swelling Behavior Analysis of Poly(acrylamidoxime-co-2-acrylamido-2-methylpropane Sulfonic Acid) Hydrogels

ORHAN HAZER,^{1,2} CENGİZ SOYKAN,¹ and ŞENOL KARTAL²

¹Faculty of Science and Arts, Department of Chemistry, University of Bozok, Yozgat, Turkey

²Faculty of Science and Arts, Department of Chemistry, University of Erciyes, Kayseri, Turkey

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An investigation of water uptake behavior of a novel poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid-co-N,N'-methylenebisacrylamide) hydrogel system was carried out with two major objectives. First, the study was initiated to understand the effect of various synthesis conditions, i.e., reaction temperature, initiator content, crosslinker content and pH, on the water absorbency of resulting hydrogels. The second reason was to evaluate these hydrogels after reaction with hydroxylamine hydrochloride to convert the C≡N (nitrile) groups to -C=N-OH (amidoxime) groups. The optimum amidoximation conditions were determined. The structure of the hydrogels, before and after amidoximation, was analyzed with FTIR and thermal methods. The optimum synthesis temperature, initiator concentration and crosslinker content were found to be 55°C, 1.5 (wt.%) and 1.5 (wt.%), respectively. The equilibrium water uptake increases with an increase in initiator (K₂S₂O₈) concentration and crosslinker (BAAm) content up to 1.5% and then it begins to decrease with a further increase in K₂S₂O₈ and BAAm content. The gel undergoes a drastic volume change in the pH range 5, thus indicating the dissociation of NH groups of acrylamidoxime. The pH increased at 7, and this pH shift may be attributed not only to the acidic region, but also the basic region. A drastic volume change is also observed at pH:10, which may be due to the dissociation of the AMPS SO₃H groups. The swelling ratio of the hydrogel sample in sea water, tap water and distilled water are collected. According to the results, the maximum swelling ratio was observed in the distilled water. Finally, the nitrile groups can be easily converted into amidoxime groups via treatment with a solution of hydroxylamine. The swelling behavior of hydrogels are in good agreement, before and after amidoximation.

Keywords poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid-co-N,N'-methylenebisacrylamide); amidoximation; hydrogels; swelling

1 Introduction

Hydrogel are three-dimensionally crosslinked hydrophilic polymer networks which have the capability to retain a large volume of water in the swollen state. Depending on the type of monomers (i.e., ionic or neutral) incorporated in the gels, they can be made to respond to a variety of external environmental changes such as pH, ionic strength, temperature or specific chemical compounds (1–4). These materials are of great importance due to their promising applications such as controlled drug-delivery systems (5–7), artificial muscles (8), sensor systems (9), tissue engineering (10), etc. These applications mainly depend upon the swelling

behavior of these polymeric hydrogels, which in turn, are controlled mainly by the crosslinking density. The degree of crosslinking in the polymer network structure is critical as it dictates the mechanical strength, swelling ratio and many other properties of the polymer gels by influencing molecular weight between crosslinks.

A number of papers have been published describing the synthesis of macroreticular resins containing amidoxime groups (11–14), due to their use in extracting heavy metals from wastewater. The synthesis of amidoxime resins in most papers involve the incorporation of nitrile groups in a polymer matrix, followed by the conversion of the nitrile groups into amidoxime groups via treatment with a solution of hydroxylamine.

Polymers carrying amidoxime groups are a class of materials with very interesting properties. On the one hand, polymeric amidoxime would be expected to have a polyampholytic character and, on the other, amidoxime groups, known as being very reactive, offer the possibility of

Address correspondence to: Cengiz Soykan, Faculty of Science and Arts, Department of Chemistry, University of Bozok, Yozgat, Turkey. Tel.: +90 354 242 1021/140; Fax: +90 354 242 1022; E-mail: soykan@erciyes.edu.tr

preparing new polymeric derivatives as well as of binding heavy metal ions. Amidoxime group containing polymers are very important in biological and environmental applications and can be obtained by conversion of hydrophobic nitrile groups to hydrophilic amidoxime groups (15). To increase the hydrophilicity of the nanomaterial and impart additional functionality for bioconjugation/attachment of some drugs/protein or active agent, the nitrile groups were converted to amidoxime groups with appropriate chemistry.

2-Acrylamido-2-methylpropane sulfonic acid (AMPS) has received attention in the last few years due to its strongly ionizable sulfonate group; AMPS dissociates completely in the overall pH range, and therefore, the hydrogels derived from AMPS exhibit pH independent swelling behavior. Liu et al. investigated the swelling properties of hydrogels derived from AMPS and N,N'-dimethylacrylamide (DMAA) (16). Tong and Liu observed a constant swelling capacity of AMPS/DMAA hydrogels in the entire pH range and concluded that the AMPS content of the hydrogel corresponds to its charge density (17). Okay et al. investigated the synthesis and characterization of hydrogels derived from acrylamide-co-2-acrylamido-2-methylpropane sulfonic acid sodium salt (18).

The present work focuses on the synthesis, characterization and the swelling behavior of acrylonitrile/2-acrylamido-2-methylpropane sulfonic acid (AN/AMPS) hydrogels and amidoximated acrylamidoxime-co-2-acrylamido-2-methylpropane sulfonic acid (AAmox/AMPS) hydrogels.

2 Experimental

2.1 Materials

The monomers 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and acrylonitrile (AN) were obtained from Merck Chemical and used without further purification. The crosslinker N,N'-methylene bisacrylamide (BAAm) and $K_2S_2O_8$ were also used as received from Merck. Ammonium acetate buffers (0.1 M) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in solutions of pH 4–6 and ammonium chloride buffer solutions (0.1 M) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to result in solutions of pH 8–10. Distilled and deionized water was used for the swelling experiments. For the preparation of the stock solutions and for the hydrogel synthesis, distilled and deionized water was distilled again prior to use and cooled under nitrogen bubbling.

2.2 Synthesis of Poly(acrylonitrile-co-2-acrylamido-2-methylpropane Sulfonic Acid)

In order to determine the chemical composition of the copolymer networks, a series of AN/AMPS copolymers was prepared under the same reaction condition. Appropriate

amounts of AN with AMPS having five different feed compositions (90/10; 70/30; 50/50; 30/70; 10/90) and, 5% N,N'-methylene bisacrylamide (total weight of monomers), 1% $K_2S_2O_8$ (total weight of monomers) and 10 ml deionized water were mixed in a round-bottomed flask equipped with mechanical stirrer and reflux condenser. The solution was purged with nitrogen for about 10 min, and the reaction mixtures were purged again for several minutes prior to heating. The reaction mixture was heated at 70°C with constant stirring. The mixtures were then cooled to room temperature and slowly poured. Solid polymers were purified by separated and finally dried under vacuum.

2.3 Swelling Studies

The swollen gels were taken out at regular time-intervals, wiped superficially with filter paper to remove the surface water, weighed and then put in the same bath. The mass measurements were continued until the gels attained constant weight. The percent mass swelling was determined using the following expression (19):

$$\%S_M = M_t - M_o / M_o \times 100 \quad (1)$$

where, M_t and M_o are the initial mass and mass at different time-intervals, respectively. All the experiments were carried out with five samples and the average values have been reported in the data.

2.4 Preparation of Amidoximated Copolymer Network

A solution of free hydroxylamine in methanol-water (5:1) was prepared from its hydrochloride salt. Accurately, 3 g of hydroxylamine hydrochloride was dissolved in 30 ml of methanol-water (5:1) mixture. The HCl of NH_2OH was neutralized by NaOH solution and the precipitate of NaCl was removed by filtration. The pH of the reaction was adjusted to pH 8–8.5 by controlling with NaOH solution (0.1 M). An appropriate amount of poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) was kept swelling in methanol (10 ml) overnight. The above-prepared free hydroxylamine solution was added to the swollen poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) in a flask fitted with condenser. The amidoximation reaction of the poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid)s with free hydroxylamine solution was carried out at refluxing temperature at 80°C for 12 h. The modified resin was filtered off, thoroughly washed with deionized water (five portions of 100 ml) and prepared (three portions of 100 ml) to remove the unreacted hydroxylamine and then dried at 50°C for 10 h.

2.5 FT-IR Spectroscopy Studies

The FT-IR spectra of poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) and amidoximated poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) were

recorded on a Jasco 460 plus FR-IR spectrometer, in the spectral range 4000–400 cm^{-1} with a resolution of 4 cm^{-1} using the KBr disk technique.

2.6 Thermogravimetric Analysis

Thermal analysis of the polymer was carried out using a thermogravimetric analyzer (Setaram Labsys TG-DSC/DTA, France). About 10 mg of powdered sample was placed in aluminum crucibles and analyzed over the temperature range at 25–500°C at the rate of 10°C min^{-1} under the dry flow of N_2 at the rate of 30 ml min^{-1} .

3 Results and Discussion

The reaction mechanism for conversion of nitrile groups of poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) to amidoxime groups, via reaction with hydroxylamine hydrochloride in alkaline solution, is shown in Scheme 1.

3.1 FTIR Studies

Figure 1 shows the FT-IR spectra of poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid). It is clear from this spectra, the appearance of an adsorption peak at 2245 cm^{-1} may be attributed to the nitrile (-CN) groups. The FT-IR spectra of amidoximated poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) shows that the nitrile peak has been decreased, but not completely eliminated. It is also clear from Figure 2 that the appearance of two new adsorption peaks at about 1640 and 1660 cm^{-1} corresponds to the stretching vibration of -C=N bond. The other peaks were confirmed with an FT-IR atlas, which are consistent with the functional groups on both bare and amidoximated poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) functional groups. The results clearly show the conversion of the original nitrile groups to amidoxime groups through treatment with hydroxylamine.

3.2 Thermogravimetric Studies

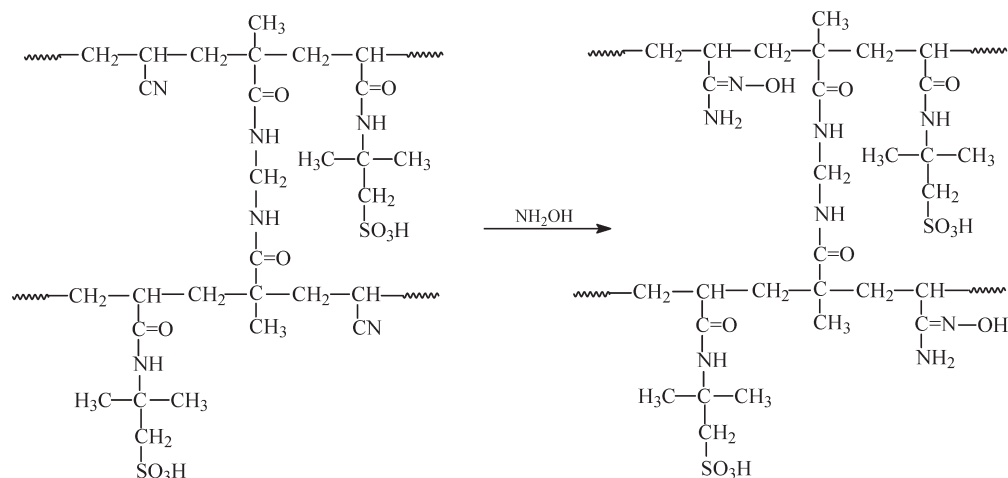
Figure 3 depicts the thermogram obtained for the copolymer and hydrogel sample 70/30. The values of initial decomposition temperature (T_{id}), temperature at a maximum rate of weight loss (T_{max}) and final decomposition temperature (T_{fd}) are 20, 250 and 460°C, respectively. It is clear that the polymer sample is quite stable. The interpretation of the thermogravimetric analysis results however, was complicated due to the bound water in the polymer samples. It was found that the copolymers always contained about 10 wt.% water, even after several months of drying at room temperature under vacuum (18). Figure 3 shows three degradation steps at 100, 150 and 250°C, which are due to the loss of associated water, anhydride formation, desulfonation and backbone degradation, respectively (18).

3.3 Determination of Optimum Swelling Parameters for AN/AMPS Hydrogel

In order to evaluate these parameters, five copolymer samples with varying crosslinking ratios (i.e., number of moles of crosslinker/number of moles of monomers) were prepared. The results, of dynamic water uptake as depicted in Figure 4, clearly indicate that the copolymer network 70/30 (feed composition) have the best swelling ratio.

The temperature of the external solution influences the swelling behavior of hydrogels in many ways. If the polymer present in the hydrogel possesses a lower critical solution temperature, then a sharp volume phase transition is expected across the LCST, otherwise, the chemical nature of monomer units within the polymer network decides the swelling trend. However, the increase in temperature is usually accompanied by the enhancement of solvent diffusion into the gel matrix. The results, as depicted in Figure 5, clearly suggest that the value of diffusion coefficients increases with the temperature which is a simple consequence of the increased rate of solvent penetration into the gel matrices. According to Figure 5, the water absorbency increases with reaction temperature up to 55°C, and then it begins to decrease with a further rise of temperature. It is clear that 55°C seems to be the optimum reaction temperature at which the resulting hydrogels demonstrate maximum water uptake. When the temperature is decreased below 55°C, the rate of polymerization decreases which results in enhancement of crosslink density (20). This causes the equilibrium water uptake to decrease. However, when the reaction temperature is increased beyond 55°C, the rate of polymerization increases, thus resulting in the formation of macromolecular chains of low molecular weight. This causes the equilibrium water uptake value to decrease. Similar results have also been reported elsewhere (21). In this way, the reaction temperature plays an important role in influencing the water absorbing capacity of hydrogels.

The amount of initiator used in the reaction mixture plays a significant role in governing the water uptake properties of resulting hydrogels. In order to investigate this, we synthesized hydrogels with varying amounts of initiator $\text{K}_2\text{S}_2\text{O}_8$ in the range 0.25–2.5 (% total weight of monomers), and their equilibrium water uptake was measured in the 25°C. Figure 6 displays some interesting findings. It is clear that the equilibrium water uptake increases with an increase in initiator concentration up to 1.5 (% total weight of monomers) and then it begins to decrease with a further increase in $\text{K}_2\text{S}_2\text{O}_8$ content. Initially, when the concentration of initiator is 0.25 (% weight of total monomers), the minimum water uptake of resulting hydrogel may be due to the fact that the network does not form efficiently with a small number of free radicals. However, with the increase in $\text{K}_2\text{S}_2\text{O}_8$ content, the number of primary free radicals increases and the polymeric chains with relatively higher molecular weight are produced. This results in an increase in equilibrium water uptake. However, when the



Sch. 1. Reaction mechanism for conversion of nitrile groups in poly(acrylonitrile-co-2-acrylamido-2-methylpropane sulfonic acid) to amidoxime groups to produce poly(acrylamidoxime-co-2-acrylamido-2-methylpropane sulfonic acid).

$\text{K}_2\text{S}_2\text{O}_8$ concentration is increased beyond 1.5%, the equilibrium swelling again begins to decrease. This may be attributed to the fact that the concentration of free radicals becomes so high that the growing macromolecular chains are

terminated at a faster rate. This results in the formation of low molecular weight polymeric segments within the hydrogel network. Consequently, the resulting hydrogels demonstrate a decrease in the water uptake.

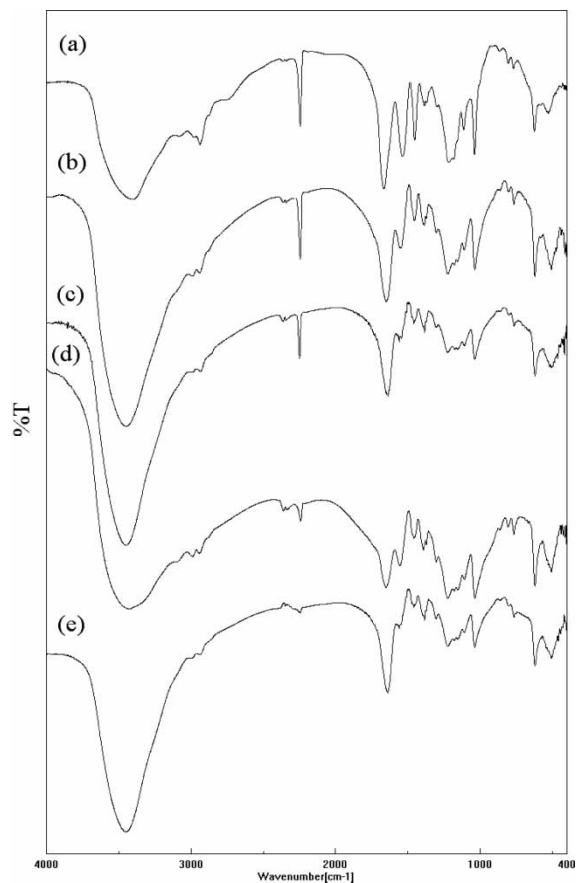


Fig. 1. FTIR spectra of AAmox/AMPS hydrogels; AAmox: AMPS (feed composition) = (a) 90:10; (b) 70:30; (c) 50:50; (d) 30:70; and (e) 10:90.

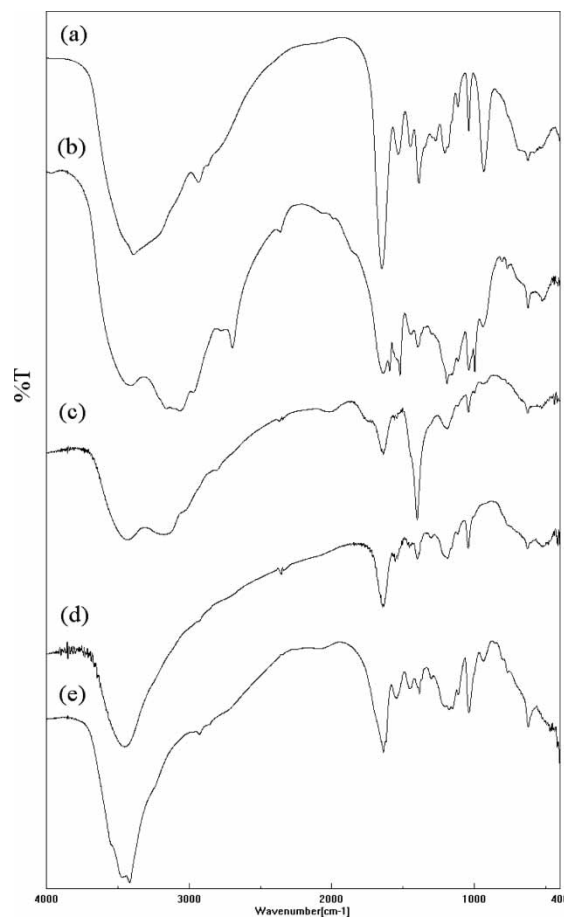


Fig. 2. FTIR spectra of AAmox/AMPS hydrogels; AAmox: AMPS (feed composition) = (a) 90:10; (b) 70:30; (c) 50:50; (d) 30:70; and (e) 10:90.

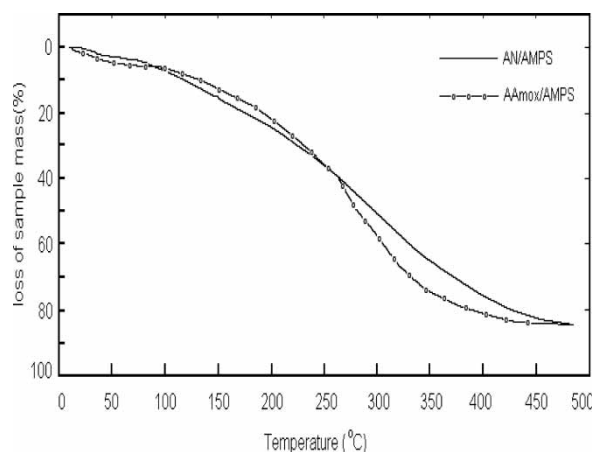


Fig. 3. Thermogram of hydrogel samples of 70/30 AN:AMPS and 70/30 AAmox:AMPS feed composition.

The amount of crosslinker used in the reaction mixture plays a significant role in governing the water uptake properties of resulting hydrogels. In order to investigate this, we synthesized hydrogels with varying amounts of crosslinker *N,N'*-methylene bisacrylamide (BAAm) in the range 1.5–10.0 (% total weight of monomers), and their equilibrium water uptake was measured at 25°C. The results, as depicted in Figure 7, displays some interesting findings. It is clear that the maximum water uptake was observed at 1.5% crosslinker ratio (% total weight of monomers) and then it begins to decrease with further increase in crosslinker content. The concentration of the crosslinker BAAm was fixed at 1.5%. In Figure 7, the swelling ratio was decreased with increasing crosslinker ratio. This is probably due to the reduction in the mesh size of the gel on raising the crosslinker content, which slows down the diffusion rate of water molecules out of the gel phase.

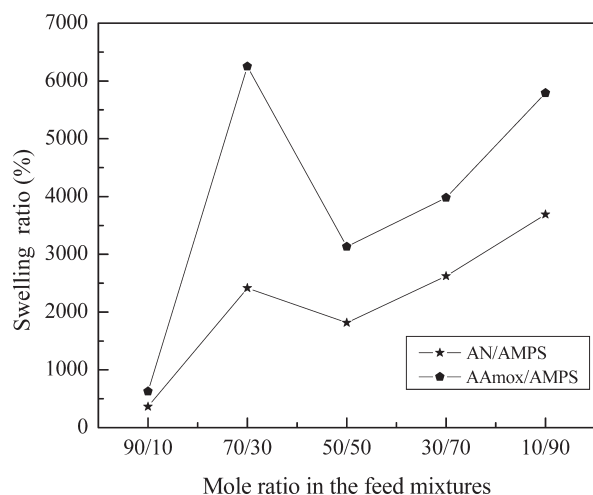


Fig. 4. The relationship between the swelling ratio vs. mole ratio in the field.

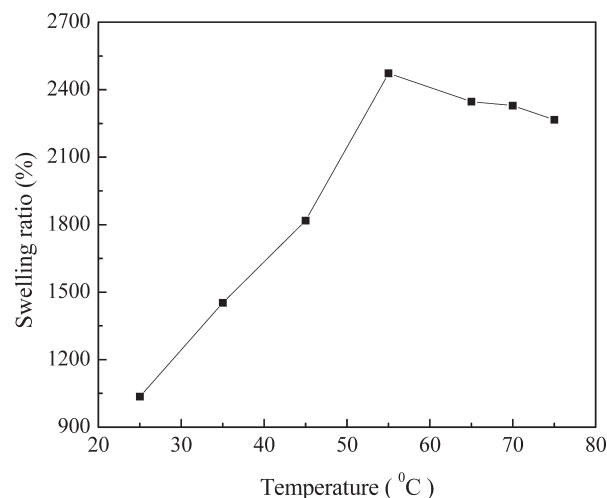


Fig. 5. Equilibrium water uptake of hydrogel samples prepared at different reaction temperature.

3.4 Swelling Kinetics of AAmox/AMPS Hydrogel

The kinetics of polymerization and hence, it may also influence the swelling behavior of the resulting hydrogels. To investigate this, we synthesized hydrogel sample (70/30 feed composition) at different times, ranging from 0 to 400 min. Dynamic water uptake, as depicted in Figure 8, clearly indicates that with an increase in crosslinking ratio, the water uptake at different time-intervals decreases. This is simply due to the fact that with an increase in crosslinking ratio, the number of crosslinks per unit volume increases, causing a decrease in the free space available between crosslinks for accommodation of a water molecule. Moreover, the increased rigidity of the network also restrict the movement or relaxation of macromolecular chains in the matrix, thus contributing towards a lower degree of swelling.

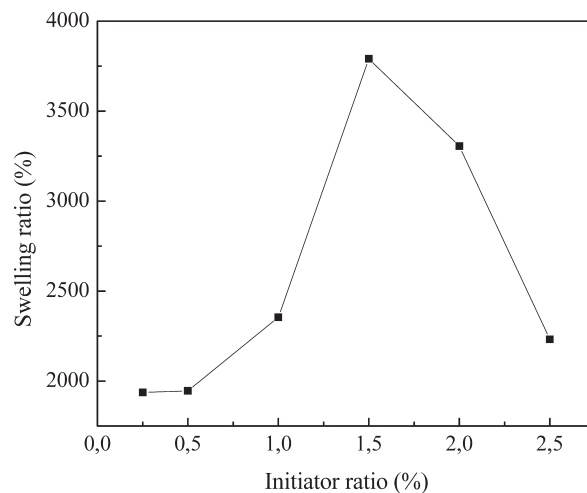


Fig. 6. The relationship between the swelling ratio with the initiator ratio.

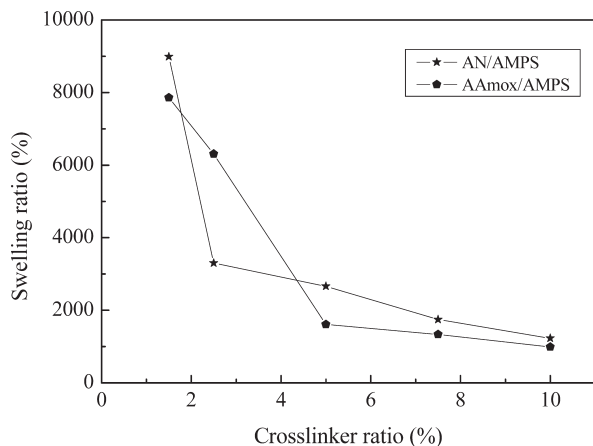


Fig. 7. The relationship between the swelling ratio with the crosslinker ratio.

3.5 Effect of pH on the Swelling Ratio of AAmox/AMPS Hydrogel

If the polymer matrix contains some ionizable groups, which can dissociate or become protonated at some suitable pH values of the external medium, then the swelling capacity of the hydrogel is affected by the variation in pH. The effect of pH of the swelling medium on the equilibrium water uptake of the sample (70/30 feed composition) was determined in buffer media of varying pH, ranging from 3 to 10, with ionic strength maintained at 0.1 M at the physiological temperature 25°C. The results, as depicted in Figure 9, clearly reveal that the gel undergoes drastic volume change in the pH range 3 to 5, indicating the dissociation of NH groups of acrylamidoxime. It is clear from Figure 9 that the increase in the equilibrium water uptake is much more pronounced near the 6 and 10, which may be attributed to the dissociation of the SO₃H groups of AMPS around these pH values. When the pH of the external medium increases beyond 2, the ionization of SO₃H groups in the gel matrix causes a sudden increase in the swelling

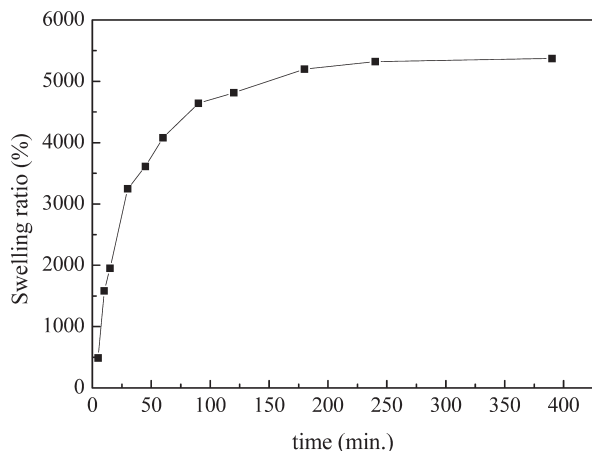


Fig. 8. Dynamic uptake of water as a function of time of hydrogel sample (70/30 feed composition of AAmox/AMPS).

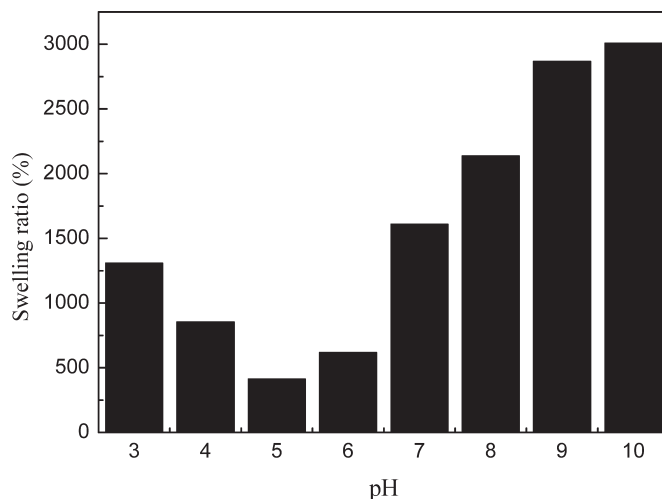


Fig. 9. Effect of change in pH of the swelling media on the water uptake.

due to increased ion osmotic swelling pressure, as well as chain relaxation resulting from the electrostatic repulsion among the SO₃H group along the macromolecular chain. This causes some hinderance offered in the ionization of SO₃H group in the polymer matrix due to the crosslinked structure of the polymer matrix. To sum up, the observed increase in equilibrium water uptake with a rise in pH of the external medium arises from the ionization of SO₃H group of AMPS which ultimately causes an increase not only in the ion osmotic swelling pressure, but also in the extent of the chain relaxation process. Similar results have also been previously obtained (22).

3.6 Effect of Temperature on the Swelling Ratio of AAmox/AMPS Hydrogel

Temperature affects the kinetics of polymerization and hence, it may also influence the swelling behavior of the resulting hydrogel. To investigate this, we synthesized a 70/30 (feed composition) hydrogel at different temperatures, ranging from 25 to 45°C. It is clear from Figure 10 that the water

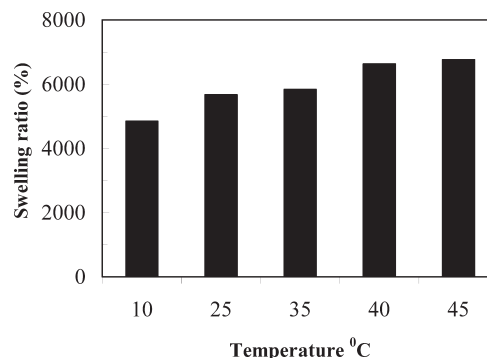


Fig. 10. Effect of temperature of the swelling media on the water uptake.

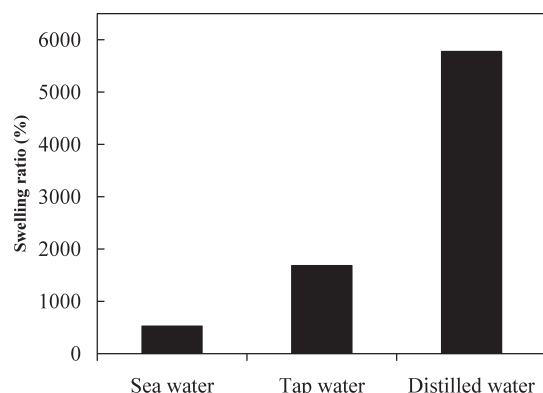


Fig. 11. Effect of electrolyte content of the swelling media on the water uptake.

absorbency increases with temperature up to 40°C and then it begins to plateau with further rise of temperature. It is clear that 40°C seems to be the optimum temperature at which the resulting hydrogels demonstrate maximum water uptake. In this way, the temperature plays an important role in influencing the water absorbing capacity of hydrogels.

3.7 Effect of Electrolyte Content on the Swelling Ratio of AAmox/AMPS Hydrogel

In Figure 11, the swelling ratio of the 70/30 hydrogel sample in sea water, tap water and distilled water are collected. The maximum swelling ratio was observed in the distilled water. This may be attributed to the fact that the concentration of free cation and anions are controlling the swelling ratio.

4 Conclusions

In this study, the relation between the formation mechanism and swelling behavior of AN/AMPS and AAmox/AMPS-based hydrogels was studied. The hydrogels were prepared by using N,N'-methylenebis(acrylamide)(BAAM) as a crosslinker and potassium persulfate ($K_2S_2O_8$) as an initiator. Polymerization temperature, initiator ratio and crosslinker ratio were fixed for the AN/AMPS hydrogel. After obtaining the optimum conditions for synthesis of the AN/AMPS hydrogels, the amidoximated hydrogels were synthesized. Moreover, the synthesis conditions, i.e., synthesis temperature, concentration of initiator and crosslinker, exhibit great

influence on the water absorbency of the resulting hydrogels. Finally, a sharp change in pH, temperature and electrolyte content, under different media for the swelling hydrogel was observed.

5 Acknowledgments

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