

Thermal and Swelling Studies of Hydrophobically Modified Polyacrylamide Hydrogels

Anu Anna Abraham, Akhil Kumar Sen

Department of Polymer Engineering, Birla Institute of Technology Mesra, Ranchi 835215, India

Received 17 July 2009; accepted 20 December 2009

DOI 10.1002/app.32036

Published online 27 April 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Hydrophobically modified polyacrylamide hydrogels were prepared by polymerizing acrylamide, using *n*-butyl acrylate and 2-ethyl hexyl acrylate as comonomers and dimethyl formamide as a solvent. We report here for the first time that the Alfred Q-e reactivity ratios are matching with the experimental value (elemental analysis result) for the terpolymer hydrogel systems. Differential scanning calorimetry (DSC) thermograms of the hydrogel samples revealed two endothermic transitions, one near 0°C, corresponding to the melting transition of ice and another above ambient temperature. This high temperature transition is due to the rearrangement of water molecules engaged in hydrophobic hydration surrounding the hydrophobic groups (alkyl side chains). This

depends on the type of hydrophobic groups and the gel compositions. Swelling and deswelling studies of the gels were performed using various solvents such as water and isopropyl alcohol. An abnormally high swelling and deswelling behavior was observed in the homopolymer gels and the gels with low amount of hydrophobic comonomers. This could be attributed to the more intramolecular cross-linked structure formed during synthesis in organic solvent. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2795–2802, 2010

Key words: hydrogels; swelling; DSC; TGA; copolymerization

INTRODUCTION

Hydrogels are three-dimensional hydrophilic polymer networks that absorb water but do not dissolve in it. They are widely used as sensors, separation membranes, adsorbents, drug delivery systems and in many other modern technologies.^{1–4} Stimuli sensitive hydrogels are an important class of hydrogels, which undergo large volume changes in response to small changes in external stimuli like pH, temperature, light, magnetic field, etc. Among many types of stimuli responsive polymers, temperature sensitive polymers are the most common.⁵ A classic example is poly(*N*-isopropylacrylamide) (PNIPAM) which has been widely studied for academic and industrial purposes due to its sharp volume phase transition (VPT) at an ambient temperature near (33°C).⁶ Other nonionic polymers like poly(vinyl methylether) also exhibit a VPT transition at a slightly higher temperature near (38°C).⁷ The aforementioned monomers have an inherent hydrophilic–hydrophobic balance, which makes them thermoresponsive i.e., above a certain temperature; the linear polymer precipitates out from solution. Thermoresponsive polymers can also be prepared from the mixture of hydrophilic

and hydrophobic monomers. This can be achieved by suitably maintaining a hydrophilic–hydrophobic balance between two different monomers, which do not have an inherent thermoresponsive property.^{8–11}

Acrylamide (AM) monomers are much more economical compared to the above two thermoresponsive monomers and their hydrogels are used in many biological and nonbiological applications.^{6,12} However these homopolymer gels do not have a thermoresponsive property, which limits its application in many areas. This can be overcome by a suitable hydrophobic modification of the polymer. These modifications can also significantly affect the mechanical and physical properties of a polymeric gel, apart from its thermal properties. The major aim of this study is to understand the effect of such modification on the properties of polyacrylamide hydrogels.

The hydrophobic modification of linear polyacrylamide and its applications have been reported in the literature.¹³ Previously, a polyacrylamide hydrogel was prepared by grafting linear polyacrylamide polymer with glycidyl methacrylate followed by free radical polymerization.¹⁴ The hydrophobic modifications of other hydrogels such as those based on poly(acrylic acid), poly(methacrylic acid) and poly(*N*-vinyl 2-pyrrolidone) have also been reported.^{15–18} But no studies have been done on the hydrophobic modification of polyacrylamide hydrogel with butyl acrylate or ethyl hexyl acrylate. The

Correspondence to: A. K. Sen (akhilsen@yahoo.co.in).

TABLE I
Sample Nomenclature, Composition, C/N Ratios and Enthalpy Changes

Sample code	Acrylamide (mol %)	Butyl acrylate (mol %)	2-Ethyl hexyl acrylate (mol %)	C/N ratio (Alfred Q-e reactivity ratio)	C/N ratio (elemental analysis)	Enthalpy change (J/g) (15–75°C)
AM	100	–	–	2.57	2.61	6
AB91	90	10	–	3.02	3.10	427
AB82	80	20	–	3.70	3.99	38
AE91	90	–	10	3.35	3.61	60
AE82	80	–	20	4.30	4.38	32
ABE9433	94	3	3	–	–	557
ABE955	90	5	5	3.20	3.28	1060
ABE8677	86	7	7	3.53	3.73	130
ABE811	80	10	10	4.04	4.34	64

advantage of this type of modification is the controlling of hydrophobic zone inside the gel structure. These hydrophobic zones can act as a selective material for adsorption of hydrophobic compounds (like pesticides or other organic material) from water.

This work deals with the synthesis of hydrophobically modified polyacrylamide hydrogels using *n*-butyl acrylate (BA) and 2-ethyl hexyl acrylate (EHA) as hydrophobic comonomers. Elemental analysis was used to determine the compositions. Theoretical compositions were calculated by Alfred Q-e reactivity ratio and are verified with the elemental analysis result. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used for the thermal characterization of gels. The swelling and deswelling behaviors of the hydrogels were also studied at various temperatures and different solvent conditions.

EXPERIMENTAL

Materials used

AM was used to prepare hydrogels and methylene bis acrylamide (MBA) was used as cross-linking agent. Butyl acrylate (BA) and EHA were used as hydrophobic comonomers and the reaction medium was dimethyl formamide (DMF). Ammonium per sulfate (AMPS) was used as initiator. All the chemicals were analytical grade and were obtained from reputed supplier. Double distilled water was used for this study.

Synthesis of gels

A series of hydrogels were prepared by a free radical polymerization of AM with BA and EHA. The concentration of the comonomers was varied from 0 to 20 mol % of the total monomer concentration. The polymerization was carried out in DMF solvent

using MBA as a cross-linker and AMPS as a free radical initiator. The sample nomenclature and its composition are shown in Table I.

The desired amounts of monomers and cross-linking agent (0.7 mol % in terms of total monomer) were dissolved in DMF solvent with constant stirring under nitrogen atmosphere. The initiator AMPS (0.44 mol % in terms of total monomer) was dissolved in DMF solvent separately and the solution were mixed with the above monomer solutions. The resultant mixture was poured immediately into a test tube (internal diameter 15 mm). Nitrogen gas was bubbled for five minutes inside the test tube and sealed. The total mols of the monomer (0.0225 mols) in the solvent were kept constant for all the compositions and the molar ratio were varied accordingly. The final volume was restricted to 5 mL in all the compositions.

The reaction was carried out in water bath at 45°C for 5 h and then heated to 65°C for 3 h to complete the reaction. The cylindrical gels were immersed in DMF and then in water separately, where the solvents and the water were replaced at intervals. The washed gels were dried in a vacuum oven at 65°C until a constant weight is achieved. Higher temperatures were avoided to minimize the side reactions like imidization.^{19,20} The synthesized gels with more hydrophobic contents appeared to be transparent, while those with less hydrophobic contents were opaque in DMF solvent; but the observations were reversed when the solvent was changed to water.

Characterization of gels

Elemental analysis

The elemental analysis of the vacuum dried hydrogels was carried out with an elemental analyzer (Elementar, Germany model: Vario EL111).

DSC

Differential scanning calorimeter (TA Instruments, model: DSCQ10) was used to study the thermal characteristics of the hydrogels. Equilibrium swollen hydrogels were taken for measurements after the removal of water on their surface by blotting with filter paper. Approximately 7–12 mg samples of hydrogel were weighed into aluminum pans, which were sealed hermetically. Empty closed aluminum pan was used as the reference cell. The thermal behavior was recorded for two temperature ranges, from -30°C to +20°C and from 15 to 75°C at heating rates of 1°C/min and 2°C/min, respectively. In both the cases, samples were equilibrated for 15 min at the starting temperature. The thermal analysis was carried out in nitrogen atmosphere.¹⁵

Thermogravimetric analysis

The thermal stability of the gels was studied using a thermogravimetric analyzer (Shimadzu Corporation, Japan, model: DTG 60). Thermograms were recorded from room temperature to 500°C at a heating rate of 10°C per minute and with nitrogen gas flow rate of 30 mL/min.

Swelling and Deswelling studies

The equilibrium swellings of gels were studied in excess quantity of distilled water at room temperature. Swelling studies at higher temperatures (30, 55, and 70°C) were done using a thermostatic water bath, whereas studies at low temperature (10°C) were carried out in a refrigerated bath. After reaching equilibrium swelling, the samples were removed and blotted dry. The % equilibrium swelling of the gels were determined gravimetrically²¹ for each temperature and calculated as

$$\% \text{ Swelling} = \frac{W_s - W_d}{W_d} \times 100$$

where W_s is the weight of equilibrium-swollen gel and W_d is the weight of the dry gel.

Isopropanol solvent was used for deswelling studies. Here, the water-swollen gels of known weight were kept in isopropyl alcohol and their shrinking was noted after it reached equilibrium. The % deswelling of the gels were noted as

$$\% \text{ Deswelling} = \frac{W_{sw} - W_{si}}{W_{sw}} \times 100$$

where W_{sw} is the weight of the equilibrium-swollen gel in water, W_{si} weight of equilibrium-swollen gel in isopropyl alcohol.

RESULTS AND DISCUSSION

Elemental analysis (CHNO)

The composition of the hydrogels can be determined by measuring the C/N ratio obtained from elemental analysis, taking into consideration the presence of a nitrogen atom in AM monomer unlike in a BA or EHA monomer. Initially the reactivity ratios were calculated using the Alfred Q-e values of the monomers. Theoretical C/N ratios were then calculated from copolymer and terpolymer equations using the above reactivity ratio. The theoretical compositions were then compared with the experimental C/N results.

The Q and e values of the monomers AM, BA, and EHA are 0.23, 0.38, 0.41, and 0.54, 0.85, and 0.39, respectively.²² The reactivity ratios r_1 (AM to BA) and r_2 (AM to EHA) were calculated with the help of eqs. (1) and (2). The reactivity ratios of dimers in various combinations calculated, are shown in Table II.

The copolymer compositions were then calculated based on the eq. (3), where r_1 and r_2 are the above reactivity ratios and f_1 and f_2 are the monomer mol fractions in the feed. F_1 is the monomer mol fraction of AM in the copolymer formed.

$$r_1 = \frac{Q_1}{Q_2} \exp(-e_1(e_1 - e_2)) \tag{1}$$

$$r_2 = \frac{Q_2}{Q_1} \exp(-e_2(e_2 - e_1)) \tag{2}$$

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{(r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2)} \tag{3}$$

For the determination of terpolymer composition, the Alfred Goldfinger eq. (4) was used.²³ F_1 , F_2 , and F_3 denote the monomer mol fraction in the polymers whereas f_1 , f_2 , and f_3 are the monomer mol fraction in the feed, for monomers AM, BA, and EHA respectively.

$$\begin{aligned} F_1 : F_2 : F_3 &= f_1 \left[\frac{f_1}{r_{31}r_{21}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{31}r_{23}} \right] \left[f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}} \right] \\ &: f_2 \left[\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{12}r_{32}} + \frac{f_3}{r_{32}r_{13}} \right] \left[\frac{f_1}{r_{21}} + f_2 + \frac{f_3}{r_{23}} \right] \\ &: f_3 \left[\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}} \right] \left[\frac{f_1}{r_{31}} + \frac{f_2}{r_{32}} + f_3 \right] \end{aligned} \tag{4}$$

TABLE II
Reactivity Ratios of Monomers

Monomer composition	Reactivity ratio	
AM- BA	r_{12}	0.715
	r_{21}	1.26
AM-EHA	r_{13}	0.517
	r_{31}	1.89
BA-EHA	r_{23}	0.626
	r_{32}	1.29

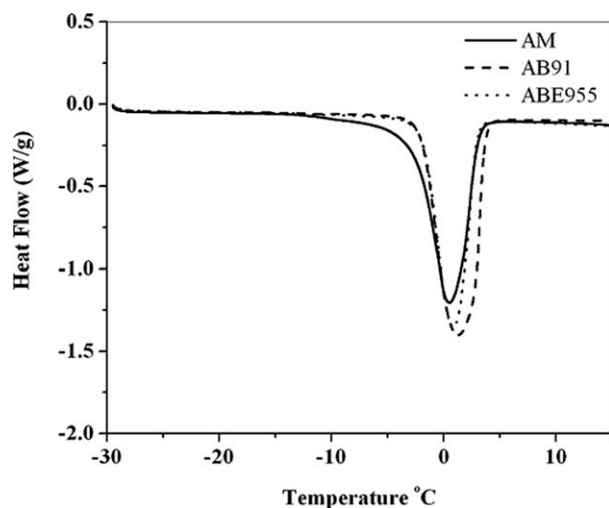


Figure 1 DSC thermograms denoting melting of water in the hydrogel.

The theoretical and experimental C/N ratios for the different polyacrylamide gel compositions are included in Table I, which shows that the experimental C/N ratios were found to be similar with the theoretical C/N ratio. All the experimental values are slightly higher than theoretical value. This may be due to the hydrolysis of amide group during the synthesis and purification.¹⁹ The overall increase in C/N ratio in the copolymer indicates that the incorporation of the comonomers into the polyacrylamide hydrogel. This is expected, as the comonomer does not contain any nitrogen in the monomer unit.

DSC

The DSC study of the gels were carried out from -30°C to 75°C . Two endothermic peaks were observed, one at low temperature near 0°C and another above ambient temperature.

Thermal changes at lower temperature

Water behaves differently in constrained nanoscopic structures and at least three different forms of water have been detected.^{24–26} These are bulk (free) water,

which has similar properties as that of normal water. Second is interfacial water, which is weakly bound and exhibits a melting transition near 0°C . Third is bound water, which is strongly associated and whose melting transition cannot be detected even at temperatures as low as -100°C .¹⁵ Of the three types, only bulk and interfacial water could be detected using DSC.^{16,27,28}

Figure 1 shows the DSC thermogram of homopolymer polyacrylamide hydrogel, copolymer gel with butyl acrylate (AB91) and terpolymer gel with butyl acrylate and 2-ethyl hexyl acrylate (ABE955) from -30°C to $+20^{\circ}\text{C}$. The endothermic transition starts from around -10°C and ends at $+5^{\circ}\text{C}$, with the peak value observed near 0°C . This corresponds to the melting point of bulk (free) and interfacial water and the shift in melting point is due to the change in environment of water molecules, which is observed in many hydrogel systems.^{15,27}

The physicochemical properties of a hydrogel depend not only on the molecular structure, gel structure, degree of cross linking and water content, but also on the relative amount of free and interfacial water. The total amount of free and interfacial water can be obtained from the enthalpy of melting, where ΔH_m is the total enthalpy in J/g of swollen gel. ΔH is the latent heat in J/g of pure water and is 321.17 J/g .¹⁵ The ratio $\frac{\Delta H_m}{\Delta H}$ represents the total amount of free and interfacial water present per unit mass of gel. The bound water can be calculated as the difference between the total water content of the sample, obtained from swelling studies and the free and interfacial water in the gel.

From the DSC graphs the free and interfacial water were calculated and are shown in Table III. The calculated bound water and total water content (from swelling studies) in the gels are also presented in Table III. It is seen that the free and interfacial water content as well as total water content decreases with the hydrophobicity of monomers, whereas the bound water and bound water to total water ratio increases with hydrophobicity. This is due to the increase in number of water molecules surrounding the hydrophobic units (hydrophobic hydration effect), which increases with the addition of hydrophobic units in the hydrogel. Similar observations are also reported in the literature.^{15,28,29}

TABLE III
Free and Interfacial Water, Bound Water and Total Water Contents of the Gels

Sample	Free and interfacial water (g/g of gel)	Bound water (g/g of gel)	Total water (g/g of gel)	Bound water/total water
AM	0.736	0.165	0.901	0.183
AB91	0.675	0.176	0.851	0.206
ABE955	0.506	0.307	0.813	0.377

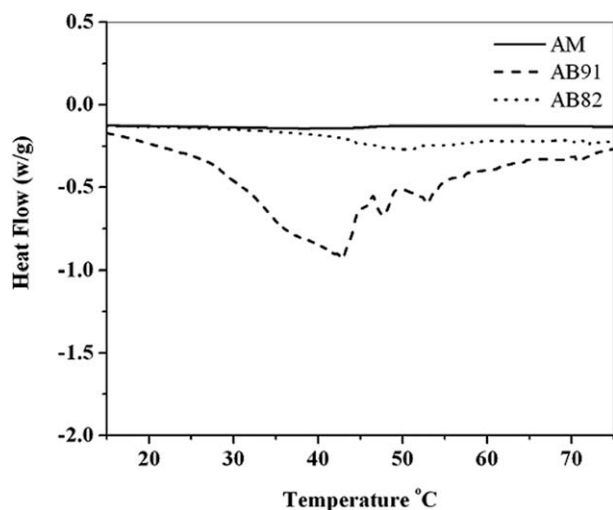


Figure 2 DSC thermograms of AM and AM-BA copolymer gels.

Thermal changes above ambient temperature

The DSC thermogram of polyacrylamide hydrogel and its copolymers with butyl acrylate from 15 to 75°C are shown in Figure 2. Homopolymer of polyacrylamide hydrogel does not show any peak in this region but the copolymers show endothermic changes. A similar type of endothermic transition is reported in case of thermosensitive hydrogel like PNIPAM.⁵ But this is due to the phase separation of PNIPAM at 33°C, which is the lower critical solution temperature of linear polymer.⁶ In this case a large endothermic peak is observed in case of hydrogels with 10 mol % butyl acrylate content (AB91) but the effect was seen to decrease and the thermal changes were lowered in hydrogels with 20 mol % comonomer (AB82). This is explained as follows.

When a hydrophobic compound is placed inside the water, the water molecules tend to form a cage like structure around the hydrophobe with a minimum breaking of the hydrogen bonds. This is known as hydrophobic effect³⁰ and the water forming the hydrophobic effect is interfacial water. The large thermal changes, which are observed in case of butyl acrylate copolymer is due to the change in water structure around the hydrophobe. In case of gels with low hydrophobic (10 mol % butyl acrylate) content the hydrophobic groups remain in many small domains inside the network structure due to which many endothermic peaks are observed [Fig. 3(a)]. But with the increase in butyl acrylate concentration there is a decrease in the small hydrophobic zones, arising from their merging into larger zones, which consequently decreases the interfacial water [Fig. 3(b)]. Hence small thermal changes were observed in case of 20 mol % butyl acrylate composition.

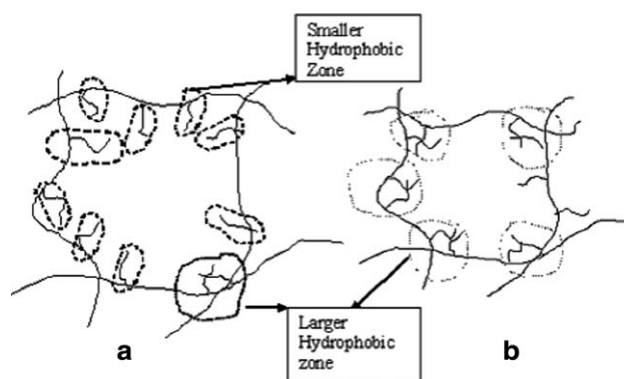


Figure 3 Hydrophobic association of branched chains in network structure.

Figure 4 represents the DSC thermogram of AM and its copolymer with EHA from 15 to 75°C. In all the cases very low thermal changes are observed. This is due to the longer side chain of 2-ethyl hexyl group compared to butyl group. The longer side chains will associate themselves due to hydrophobic effect and minimum amount of water molecules will form interfacial water around the alkyl chain. Hence, the thermal changes are low even in case of 10 mol % EHA concentration. Since the thermal changes are high in case of butyl acrylate copolymers and very low in case of ethyl hexyl acrylate copolymers, it is expected that intermediate composition may give a corresponding thermal change. So we have checked the DSC curve for mixed compositions.

The thermal behavior of AM terpolymers with butyl acrylate and EHA are represented in Figure 5. The thermal changes were found to increase initially with hydrophobic content (ABE9433) and are maximum at some intermediate compositions (ABE955). Further increase in the hydrophobic content

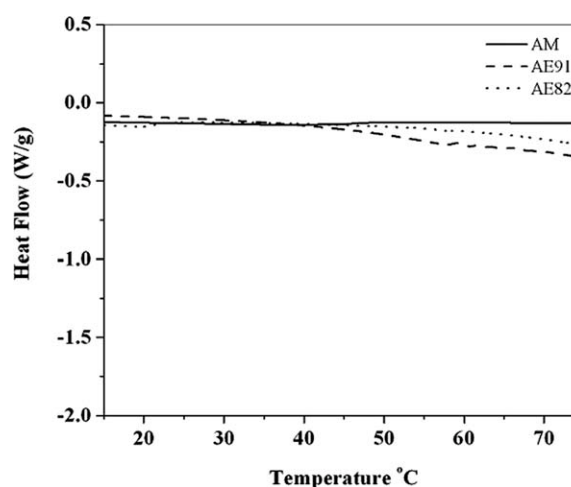


Figure 4 DSC thermograms of AM and AM-EHA copolymer gels.

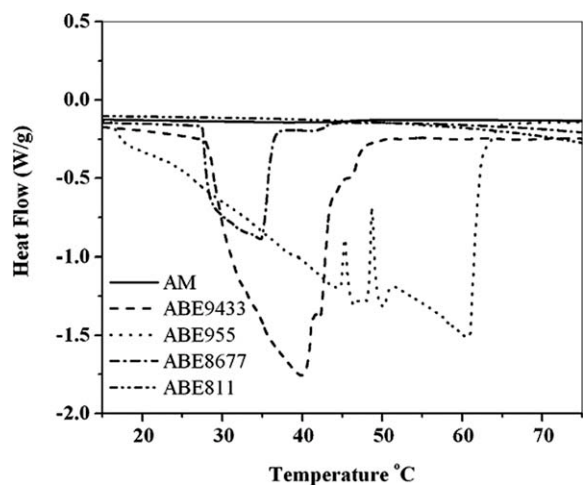


Figure 5 DSC thermograms of AM and AM-BA-EHA terpolymer gels.

decreases the thermal changes associated (ABE8677). The large thermal change is related to interfacial water around the hydrophobic side chains (butyl and or ethyl hexyl group) inside the gel. Many investigators^{29,31,32} have assumed that the interfacial water present in the polymer networks may behave differently than normal water. It is expected that the transient hydrophobic zones, which have associated at lower temperature, are easy to break at high temperature. This reversible thermoresponsive property of the gel may be explored for the regeneration process of used gel under certain conditions.

The enthalpy values are calculated from 15 to 75°C for DSC curve and are shown in Table I. The highest enthalpy change takes place in case of ABE955 terpolymers. So it is expected that the maximum numbers of hydrophobic zones are present in this composition at a particular cross-link density.

Thermogravimetric analysis

Figure 6 shows the thermal behavior of polyacrylamide gels and its copolymers starting from room temperature to 500°C. In case of polyacrylamide homopolymer the small amount of weight loss takes place up to 180°C. This is due to the moisture present in the sample. At higher temperature the significant weight loss occurred in two stages one at 180 to 360°C and another is above 360°C. Van Dyke et al.³³ have also made similar observations for polyacrylamide homopolymer. They have also observed that water, ammonia and small quantities of carbon dioxide are released in the 180–360°C range of temperature where the polymer chain remains intact and the reaction occurs on the pendant amide groups. In the last stage of decomposition the main chain break down takes place, releasing carbon dioxide, water, nitrile compounds and imides. Like homopolymers,

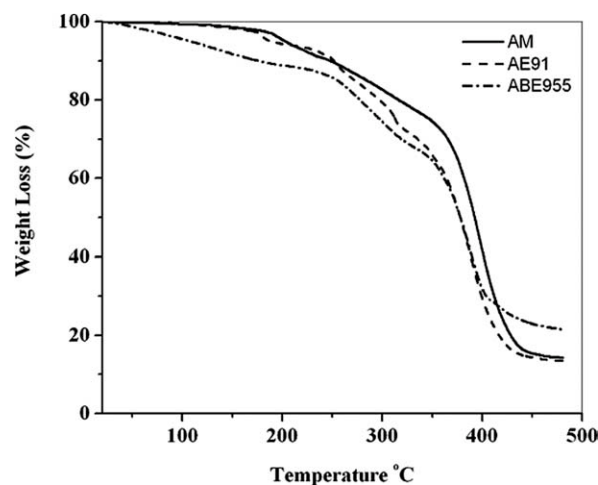


Figure 6 TGA of AM and its copolymer gels.

copolymers also show three stages of weight loss but the amounts are slightly different. In general the incorporation of hydrophobic group, does make a significant change in the overall thermal stability of the hydrogel system.

Swelling and deswelling measurements

Figure 7 depicts the percentage equilibrium swelling of hydrogels vs total comonomer concentrations, where equal amounts of comonomers (x% BA and x% EHA) are present in the terpolymer composition. polyacrylamide homopolymer hydrogel shows the highest percentage equilibrium swelling, which decrease with increasing comonomer content in the gel. These highly swollen gels were found to be soft in nature and easily broken into fragments. The important factor in swelling is the microstructure of

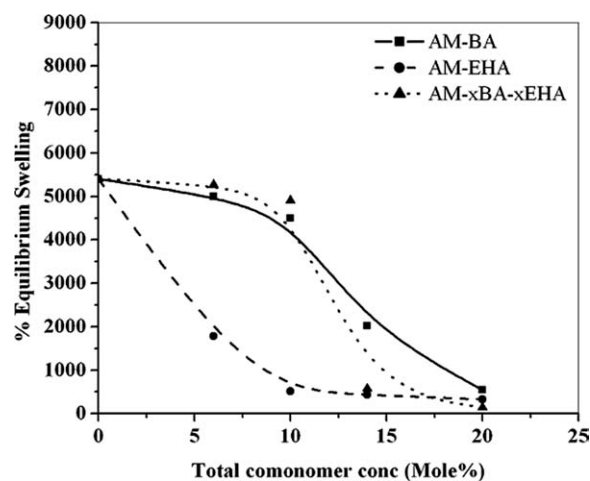


Figure 7 % Equilibrium swelling of gels vs total comonomer concentration [For terpolymers, comonomer conc. = (x moles of BA + x moles of EHA)].

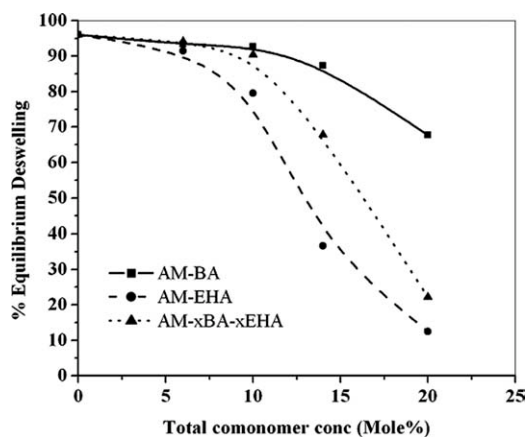


Figure 8 % Equilibrium deswelling of gels in isopropyl alcohol vs total comonomer concentration [For terpolymer, comonomer conc. = (x moles of BA + x moles of EHA)].

the gel network, which depends on the type of solvent (organic or aqueous) used during the synthesis of hydrogel.³⁴

Kwok et al.³⁵ has shown that the polyacrylamide hydrogel synthesized in a mixture of organic solvent and water have looser and heterogeneous network structures than those formed in water. As the gels are synthesized in DMF solvent more open structures are expected which show high swelling. A similar high swelling behavior was observed in hydrophobically modified poly(acrylic acid) gels synthesized in DMF solvent.³⁴ On the other hand polyacrylamide hydrogels synthesized in aqueous medium show three times lower swelling behavior.³⁶ As explained earlier this is due to the solvent effect in hydrogel preparations.

The gels with more hydrophobic content (10 mol % and above comonomers) appeared to be transparent in DMF solvent, while those with less hydrophobic content (below 10 mol % comonomers) were opaque. The above observations were reversed when the gels are swollen in water. This is due to the phase separation of the hydrophobic group in different solvent conditions.

The equilibrium deswelling of gels in isopropyl alcohol vs comonomer concentration are shown in Figure 8. Here the equilibrium water swollen gels were kept in isopropyl alcohol and the decrease in swelling was measured. The shrinking was maximum for polyacrylamide hydrogels and the effect is reduced with the increase in hydrophobic content. This is expected, as the outside environment (isopropanol) is hydrophobic in nature. The water molecules inside the polyacrylamide hydrogels will diffuse out and mix with the outside isopropanol solvent due to the entropy and osmotic reasons. However the situation will be reversed with the incorporation of hydrophobic comonomers in the gel. This is due to

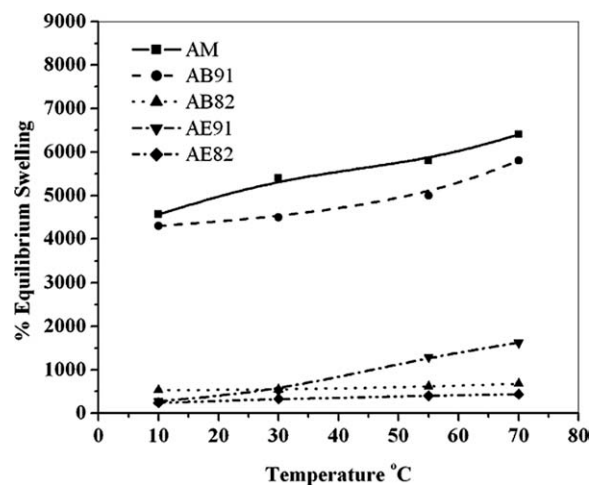


Figure 9 % Equilibrium swelling vs temperature for AM and its copolymer gels.

more accommodation of isopropanol inside the gel structure. The deswelling pattern of the terpolymer gels falls in between these of the two copolymers.

Swelling and deswelling with respect to temperature

The swelling of polyacrylamide and its copolymer with BA and EHA from 10 to 70°C are shown in Figure 9. The high swelling for polyacrylamide and 10% butyl acrylate copolymer may be due to the more open structures formed during the synthesis in organic solvent. The swelling of the other hydrogel increases with rise in temperature but the increase is comparatively small. The later observations are reported in case of poly(acrylic acid) hydrogel copolymerised with methyl methacrylate monomers.¹⁵

Figure 10 is the swelling behavior of terpolymer gels. As in copolymers two distinct types of swelling

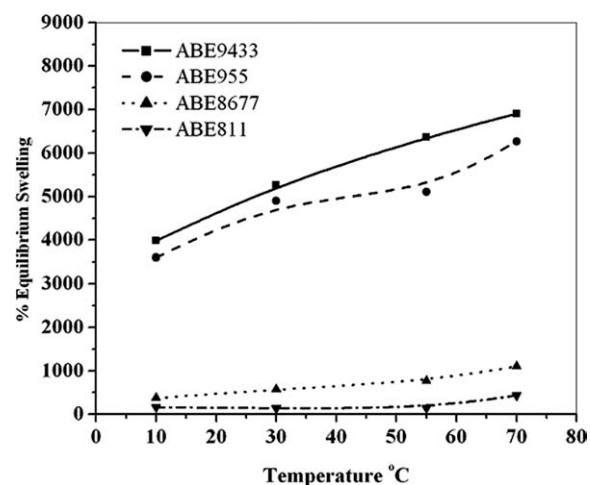


Figure 10 % Equilibrium swelling vs temperature for terpolymer gels.

were observed here. Higher swelling is observed in case of gels with lower hydrophobic content (below 10 mol %), the reasons for which are similar as that for copolymer gels of lower hydrophobic content.

All the above-prepared hydrogels show an increase in swelling with temperature. The observed increase may be attributed to the fact that on increasing temperature, both the segmental mobility and diffusion of water molecules increase, which leads to an enhanced swelling of the hydrogel.

CONCLUSIONS

polyacrylamide hydrogels with different hydrophobic contents were prepared by free radical polymerization of AM with BA and EHA. The copolymer compositions are almost similar to feed composition as shown by elemental analysis result and supported by Alfred Q-e reactivity ratio. DSC curves of the modified hydrogels show a new type of endothermic peak above ambient temperature. This new peak is due to the presence of hydrophobic content inside the hydrogel and strongly depends on the type of side chain and its concentration within the gel. The terpolymer of AM with equal amounts of BA and EHA (5 mol % each) shows the highest endothermic change. This is due to the large number of hydrophobic zones inside the gel structure. The thermal stability of the copolymer is almost unchanged in comparison to polyacrylamide homopolymer.

Swelling and deswelling behavior is high in case of gels with low amount (below 10 mol %) of hydrophobic content. Also these types of hydrogels show high increase in swelling with rise in temperature. This unusual behavior of gels with low hydrophobic content is attributed to the more intramolecular linkage formed leading to more open structure during the synthesis in organic medium.

The hydrophobic associations present at low swelling state (low temperature), are expected to break at high swelling state (at high temperature) and the process to be reversible in nature. This hydrophobic association at low swelling state may show different types of adsorption behavior towards hydrophobic compound like organic pollutants in water. This reversible thermoresponsive property can be exploited for possible application in separation of organic impurities from water.

References

- Lee, K. Y.; Kong, H. J.; Larson, R. G.; Mooney, D. J. *Adv Mater* 2003, 15, 1828.
- Peppas, N. A.; Bures, P.; Leobandung, W.; Ichikawa, H. *Eur J Pharm Biopharm* 2000, 50, 27.
- Yoshida, R.; Uchida, K.; Kaneko, Y.; Sakai, K.; Kikuchi, A.; Sakurai, Y.; Okano, T. *Nature* 1995, 374, 240.
- Cai, W.; Anderson, E. C.; Gupta, R. B. *Ind Eng Chem Res* 2001, 40, 2283.
- Zhang, J. T.; Huang, S. W.; Xue, Y. N.; Zhao, R. *Macromol Rapid Commun* 2005, 26, 1346.
- Pelton, R. *Adv Coll Inter Sci* 2000, 85, 1.
- Ichijo, H.; Kishi, R.; Hirasa, O.; Takiguchi, Y. *Polym Gels Networks* 1994, 2, 315.
- Badiger, M. V.; Lele, A. K.; Bhalariao, V. S.; Varghese, S.; Mashelkar, R. A. *J Chem Phys* 1998, 109, 1175.
- Inamata, H.; Wada, N.; Yagi, Y.; Goto, S.; Satio, S. *Polymer* 1995, 36, 875.
- Kotakai, K.; Yoshida, M.; Hasegawa, S.; Iijima, Y.; Yonerawa, S. *Macromolecules* 1996, 29, 1065.
- Varghese, S. Ph.D. Thesis, University of Pune, India, 2001.
- Peppas, N. A.; Huang, Y.; Lugo, M. T.; Ward, J. H.; Zhang, J. *Ann Rev Biomed Eng* 2000, 2, 9.
- Peer, W. J. *Polymers in Aqueous Media*; Glass, J. E., Ed. ACS: Washington, DC, 1989; 223, 381.
- Song, P.; Zhang, Y.; Kuang, J. *J Mater Sci* 2007, 42, 2775.
- Katime, I.; Apodaca, E. D.; Mendizabal, E.; Puig, J. E. *J Mac Sci Part A* 2000, 37, 307.
- Huglin, M. B.; Rehab, M. M.; Zakaria, M. B. *Macromolecules* 1986, 19, 2986.
- Liu, Y. Y.; Liu, W. O.; Chen, W. X.; Sun, L.; Zhang, G. B. *Polymer* 2007, 48, 2665.
- Matsuda, A.; Gong, J. P.; Osada, Y. *Polym Gels Networks* 1998, 6, 307.
- Thomas, W. W. *Encyclopedia of Polymer Science and Technology*, Bikales, N., Ed. Wiley Interscience: NY, 1964; 1, 177.
- Candau, F.; Zekhnini, Z.; Heatley, F.; Franta, E. *Colloid Polym Sci* 1986, 264, 676.
- Bajpai, S. K.; Singh, S. *React Functional Polym* 2006, 66, 431.
- Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; Wiley Interscience: UK, 1988.
- Zhou, X. Ph. D. Thesis, University of Waterloo, Canada, 2004.
- Drost-Hansen, W. *Ind Eng Chem* 1969, 61, 10.
- Etzler, F. M. *Croat Chem Acta* 1983, 56, 563.
- Casillas, N.; Puig, J. E.; Olayo, R.; Hart, T. J.; Franses, E. I. *Langmuir* 1989, 5, 384.
- Li, W.; Xue, F.; Cheng, R. *Polymer* 2005, 46, 12026.
- Davis, T. P.; Huglin, M. B.; Yip, D. C. F. *Polymer* 1988, 29, 701.
- Higuchi, A.; Iijima, T. *Polymer* 1985, 26, 1833.
- Tanford, C. *The Hydrophobic Effect: Formation, Micelles and Biological Membranes*, 2nd ed.; John Wiley and Sons: USA, 1980, 30.
- Nakamura, K.; Hatakeyama, T.; Hatakeyama, H. *Polymer* 1983, 24, 8713.
- Lowman, A. M.; Peppas, N. A.; Mathiowitz, E., Eds. *Encyclopedia of Controlled Drug Delivery*; Wiley: New York, 1999, 397.
- Van Dyke, J. D.; Kasperski, K. L. *J Polym Sci Part A: Polym Chem* 1993, 31, 1807.
- Patras, G.; Qiao, G. G.; Solomon, D. H. *Macromolecules* 2001, 34, 6396.
- Kwok, A. Y.; Qiao, G. G.; Solomon, D. H. *Polymer* 2003, 44, 6195.
- Karadag, E.; Saraydin, D. *Turk J Chem* 2002, 26, 863.