

Synthesis, Characterization, and Swelling Studies of Guar Gum-Based pH, Temperature, and Salt Responsive Hydrogels

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ABSTRACT: Stimuli-sensitive hydrogels constitute an important class of materials. In the present study, a simple method was used to induce temperature sensitivity and salt responsiveness in the guar gum (GG)-based hydrogel, which was synthesized by grafting GG with acrylic acid (AAc) using simultaneous gamma radiation technique. The carboxyl groups of poly(AAc) were partially modified to amide groups to generate a network that has pH-sensitive poly(AAc) and temperature-sensitive poly(*N*-isopropyl acrylamide). Swelling behavior of hydrogels was studied at various temperature, pH, and the salt sensitivity of the hydrogels was

studied by swelling the hydrogels in 0.9% NaCl solution. Characterization of these networks was carried out by X-ray diffraction, FTIR spectroscopy, and scanning electron microscopy to get evidence of the network formation and postreaction carried on the network. The hydrogel synthesized by the postreaction exhibited pH, temperature, and salt sensitivity, while the precursor hydrogel exhibited good salt tolerance. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: hydrogel; networks; swelling studies; stimuli sensitivity; salt tolerance

INTRODUCTION

Stimuli-responsive hydrogels are a special class of hydrogels those undergo large volume phase transitions on small variation in the environmental conditions such as temperature¹ and pH.² Stimuli-responsive hydrogels have a wide spectrum of applications in medicines, separation and enrichment technologies, chemical valves, actuators, and sensors.³ Polymers with tunable lower critical solution temperature (LCST) characteristics have been extensively investigated for biological applications such as cell patterning, smart drug release, and DNA sequencing.^{4,5} It has been reported that LCST is strongly dependent on many parameters including molecular weight, polydispersity index, and the monomer composition of copolymers that governs the hydrophilicity/hydrophobicity balance.^{6,7} The important characteristics of the thermosensitive hydrogels such as the LCST, rates of shrinking, and permeation rates of substances within the hydrogels can be controlled by suitable selection of the components with the defined hydrophilicity or hydrophobicity of the constituent monomer, variation of the cross-linking density, and/or nature of the medium. The influence of

temperature as an external stimulus on the swelling of poly(*N*-isopropylacrylamide) [poly(*N*-i-PAAM)] hydrogels is the most well-investigated study of the thermosensitive hydrogels.⁸ Stimuli-responsive hydrogels those exhibit good salt-tolerance have also been reported.⁹ Gemeinhart et al.,² have reported pH-sensitivity of poly(acrylamide-co-acrylic acid)-based hydrogels. Kabiri et al.,¹⁰ synthesized superabsorbent hydrogels having partially neutralized poly(acrylic acid) [poly(AAc)]. Synthesis of the temperature- and pH-sensitive xanthan-based hydrogels by incorporating poly(*N*-i-PAAM) or poly(methacrylic acid) [poly(MAAc)] has been recently reported.¹¹

Biopolymers are excellent starting materials to synthesize biocompatible and stimuli-responsive hydrogels. The cross-linking of a biopolymer in the presence of vinyl monomer and a cross-linking agent results in the network formation, which has qualities of both biopolymer and synthetic polymer. The stimuli-responsiveness of the synthesized hydrogel can be inherently induced by the proper selection of the monomer or can be induced by the postreaction. Such hydrogels are capable of interactions with their environment and at the same time the drawbacks of the biopolymer like ease of biodegradation are also improved.^{12,13}

Guar gum (GG), extracted from the ground endosperm of *Cyamopsis tetragonolobus*, is a high molecular weight hydrocolloidal heteropolysaccharide composed of galactan and mannan units, which are linked through glycosidic bonds. GG has a wide

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spectrum of uses, in the food, pharmaceutical, and cosmetics industries. Industrial application of GG includes in the field of textile industry, mining, water treatment, oil drilling, flotation, filtration aids, and other industrial applications. It is used as an effective binder, stabilizer, disintegrator, and thickener. It being cost-effective, nontoxic, noncorrosive, eco-friendly, and abundantly available biopolymer has attracted attention of researchers over the years. It finds applications as drug delivery devices as it degrades in the large intestine by the action of microbial enzymes.^{14,15} GG hydrates well in aqueous solutions, but concerns about its solution clarity, solubility in alcohol, and low thermal stability led to the development of a number of chemically modified forms of GG. Being nonionic, GG is not affected by the ionic strength or pH, but it degrades at a harsh pH and high temperature (for example, pH 3 and 50°C). Kumaresh et al.,¹⁶ have reported earlier GG-grafted (polyacrylamide)-based cross-linked anionic microgels as pH-sensitive drug delivery systems. Fujioka et al.¹⁷ have reported synthesis of superabsorbent hydrogels based on GG and succinic anhydride. Recently, the authors have reported the use of hydrogels based on the modified GG as the drug delivery device for release of tyrosine and L-DOPA¹⁸ and as adsorbents of Cu(II).¹⁹

From the perusal of the available published reports on the GG-based hydrogels, it is revealed that there is scanty information on the synthesis of a hydrogel that exhibits pH, temperature, and salt responsiveness. In view of the above, in the present study, the authors synthesized the cross-linked hydrogel by modifying GG with poly(AAc), and the later was partially converted to poly(*N-i*-PAAm). The stimuli responsiveness of the hydrogels with respect to pH, temperature, and the presence of salt were investigated. Characterization of these networks was carried out by X-ray diffraction (XRD), FTIR spectroscopy, and scanning electron microscopy (SEM) to get evidence of grafting and postreaction. The hydrogels exhibited large volume phase transitions on small change of stimulus. The hydrogels being stimuli sensitive, cost-effective, and biodegradable have potential applications in the specialty areas including drug release.

EXPERIMENTAL

Materials

Guar gum (GG), acrylic acid (AAc) (Merck, India), isopropyl amine, *N,N*-methylene bisacrylamide (*N,N*-MBAAm) (SISCO Research Laboratories, Mumbai, India), pH tablets (S.D Fine, Mumbai, India) were used as received.

Synthesis of networks

Graft copolymers were synthesized as follows. GG (1 g) was dissolved in water (40 mL) to obtain clear slurry. To it was added 1 g of AAc along with 5% *N,N*-MBAAm. The slurry was irradiated with γ -rays in gamma chamber for 24 h with the total resultant dose of 41.472 kGy. Distilled water was added to the reaction system, which was followed by stirring for 30 min. The networks were washed with acetone and dried at 40°C. The hydrogels obtained were designated as GG-*g*-poly(AAc)-*cl*-*N,N*-MBAAm (GG₁).

Functionalization of the networks by polymer analogous reaction

A known amount of GG₁ was taken and it was immersed in isopropylamine taken stoichiometrically equal to half the amount of poly(AAc) incorporated on GG₁. The amount of poly(AAc) in GG₁ was calculated gravimetrically by subtracting the weight of *N,N*-MBAAm and GG in GG₁ (taken before gamma irradiation) from the total weight of GG₁. The weight of poly(AAc) was converted to moles and isopropylamine equal to half the moles of poly(AAc) calculated was taken and GG₁ was dipped in it for 1 h to obtain GG-*g*-poly(AAc)-*co*-poly(*N-i*-PAAm)-*cl*-*N,N*-MBAAm (GG₂). The reaction was carried at room temperature. The sample was made free of unreacted isopropyl amine by giving it several washings with distilled water.

Characterization of hydrogels

Synthesized hydrogels were characterized by FTIR spectroscopy, SEM, and XRD to get evidence of network formation and postreactions. FTIR spectra were recorded on Perkin Elmer in transmittance mode in KBr. X-ray diffraction patterns of samples were recorded on PANalytic XRD with XPERT-PRO Diffractometer system using a typical wavelength of 1.54060 Å (Cu-K α radiation). The diffraction angle 2θ was varied from 10 to 70°. The SEM analysis of the hydrogels was carried out on Scanning electron Microscope (Leo 435 VP) after coating with Au/Pd at 15 kV using the same magnification to get a comparative result. Swelling studies were studied as a function of pH, temperature, and 0.9% NaCl concentration by an earlier reported method.²⁰ Solution of the desirable pH was prepared from the pH tablets (of 4.0, 5.6, 7.2, and 8.2 and 9.0 pH) available commercially. pH solution of 1.2 pH was prepared by a known method using HCl and KCl molar solutions. In all the cases, the final pH was confirmed with a Cyberscan pH meter (Eutech Instruments).

A known weight (0.1 g) of the dried hydrogel was used for all the swelling studies. The effect of pH on swelling was observed with respect to time in buffer solutions of 1.2, 4.0, 5.6, 7.2, 8.2, and 9.0 pH at 37°C. Effect of 0.9% NaCl solution on swelling at various pH was observed with respect to time by swelling the hydrogels in 0.9% NaCl solution prepared in solutions of different pH (1.2, 4.0, 5.6, 7.2, 8.2, and 9.0 pH) at 37°C. The temperature sensitivity of the hydrogels was determined by swelling them at different temperature (22, 27, 32, 37, and 42°C) for 8 h in the above-mentioned pH range. The swollen polymers were taken out from the solution, wiped-off gently with the soft-tissue paper and weighed immediately to calculate % swelling (P_s) from the following relationship:

$$P_s = \left(\frac{\text{Weight of swollen hydrogel} - \text{Weight of dry hydrogel}}{\text{Weight of dry hydrogel}} \right) \times 100$$

RESULTS AND DISCUSSION

Synthesis and characterization of hydrogels by XRD, FTIR, and SEM

The hydrogels were synthesized by the γ -ray simultaneous initiation method, where all the components were irradiated at the same time. γ -Ray initiation generates free radicals on guar gum (preferably at position 6) and monomer and cross-linker. Cross-linking takes place instantaneously to generate three-dimensional network. The synthesized hydrogels were characterized by XRD, FTIR, and SEM. In the case of GG₁ peaks of intensity 436.44, 400.03, 484.06, 342.61, and 331.40 appear at 2θ values of 18.22, 23.281, 29.607, 37.198, and 40.361, respectively, whereas for GG₂ peaks at the above reported 2θ appeared at the lower intensity of 297.24, 352.70, 345.00, 309.57, and 304.94, respectively. These results indicate that on reaction of GG₁ with isopropyl amine the resultant hydrogel obtained, i.e., GG₂, is less crystalline than the precursor. Poly(AAc) is reported to form inter-chain complexes or transient network by the way of hydrogen-bond formation.²⁰ On postreaction with isopropyl amine, the inter-chain association is broken and that results in some loss of crystallinity. The differences in the XRD patterns of two hydrogels and the variation in the peaks intensity provide evidence of postreaction on GG₁ to yield GG₂ (Fig. 1).

Characterization of the synthesized hydrogels was also carried with FTIR spectroscopy to obtain evidence of grafting and postreactions. In the spectrum of pure GG, the characteristic peaks are in the range of 3500–3200 cm^{-1} (for O–H stretching, polymeric association) and 1200–800 cm^{-1} (C–C and C–O

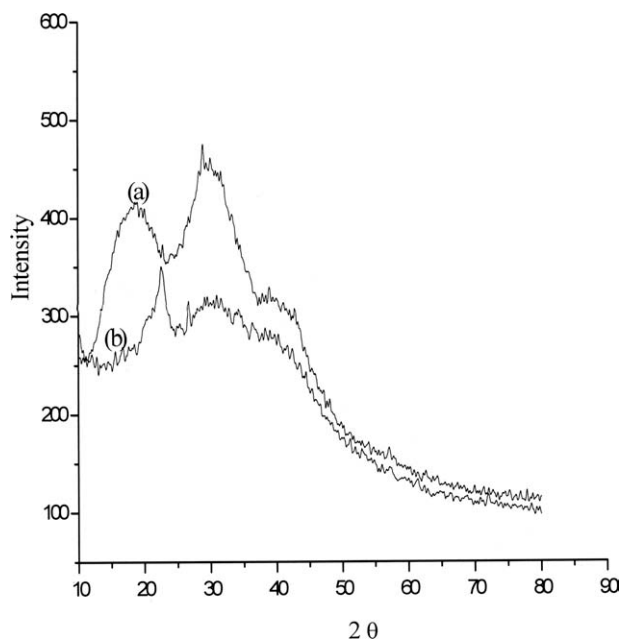


Figure 1 XRD data of (a) GG-g-poly(AAc)-cl-N,N-MBAAm and (b) GG-g-poly(AAc)-co-poly(N-i-PAAm)-cl-N,N-MBAAm.

stretching vibration of hexapyranosyl moiety).²¹ In the present case, the FTIR spectrum of GG₁ has a peak at 3403 cm^{-1} ascribed to the O–H stretching, and another peak appears at 1719 cm^{-1} due to the C=O stretching of carboxylic acid group of the grafted poly(AAc) along with the other peaks characteristic to GG indicates grafting of poly(AAc) onto the GG backbone. FTIR spectrum of the hydrogel containing poly(N-i-PAAm), GG₂, synthesized *in situ* by the partial conversion of poly(AAc) by reaction with isopropylamine, has peaks at 3444 cm^{-1} (for O–H stretching), 1637 cm^{-1} (for amide C=O stretching) and at 1167 cm^{-1} and 1127 cm^{-1} due to the skeletal vibrations of isopropyl gem-dimethyl group.

Hydrogels were also characterized by SEM (Fig. 2). SEM images of the hydrogels GG₁ and GG₂ are compared taking the images recorded at the same magnification ($\times 3.20$ K). The continuous morphology of GG₁ is resultant of the inter-chain-hydrogen bonding formed by the carboxylic groups of the poly(AAc) chains that results in the transient network formation. Such smooth and homogeneous morphology for the cationic GG grafted with poly(AAc) occurring due to the strong interfacial interaction between CGG and poly(AAc) has been reported et al.²² Since such network is broken on the postreaction, the surface morphology of GG₂ is different and it has particles of regular shape (more like octahedral-type). SEM depicting change in morphology of GG on grafting has also been reported.²³ The contrast in the surface morphology is also the testimony

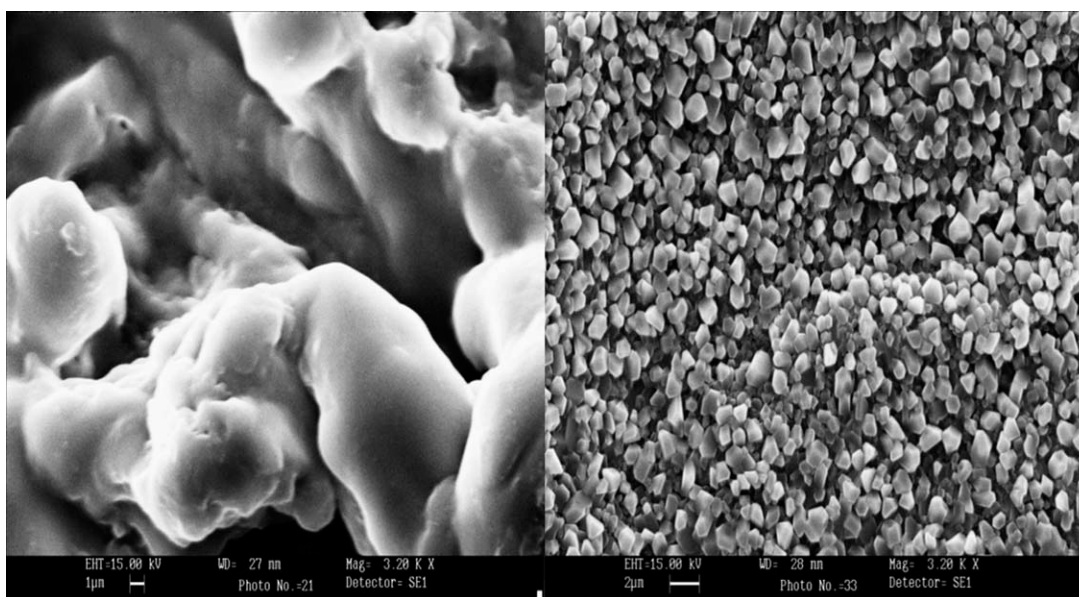


Figure 2 SEM of (left) GG-g-poly(AAc)-*cl*-N,N-MBAAm and (right) GG-g-poly(AAc)-*co*-poly(*N*-*i*-PAAm)-*cl*-N,N-MBAAm.

of the polymer analogous reaction that was carried on the GG₁.

Swelling behavior of hydrogels

Swelling behavior of hydrogel is the most important aspect that defines their end-uses. The swelling behavior of a hydrogel is dependent on the structural and environmental factors. In fact, the former dictates the later. Taking cognizance of the same, and in view of the potential applications of the synthesized hydrogels, the hydrogel structure was suitably tailored to make it responsive to the external stimuli. Swelling studies of the hydrogels were carried as a function of swelling time, pH, temperature, and salinity.

Effect of time and pH of the swelling medium on the swelling behavior of hydrogels

The swelling of both the hydrogels was studied at 37°C with respect to time at different pH (1.2, 4.0, 5.6, 7.2, 8.2, or 9.0; Fig. 3). The hydrogels exhibited large volume phase transitions with time and pH change. GG₁ attained equilibrium swelling within 90 min. An increase in the water uptake with an increase in time is the manifestation of the time-dependent stretching of cross-link chains of hydrogels that allow more water in the interior of the hydrogel. It was also observed that it exhibited higher P_s in the alkaline pH than in the acidic pH. While in the acidic media, the hydrogel shrank as the ionization of the carboxylic groups of the poly(AAc) did not take place, whereas in the alkaline medium the carboxylic groups ionized and interacted more with

water resulting in the higher P_s values. Postreaction has positive effect on the swelling of hydrogels as GG₂ did not only swell faster than the GG₁ it also exhibited larger water uptake. It also attained the equilibrium swelling within 30 min in the media of 1.2 or 5.6 pH, whereas in the medium of 4.0, 7.2, 8.2, or 9.0 pH, it attained the equilibrium swelling after 120 min. The rapid and larger swelling in this case is manifestation of the open structure of this hydrogel than that of the precursor hydrogel. As foresaid GG₁ has transient network due to the inter-chain

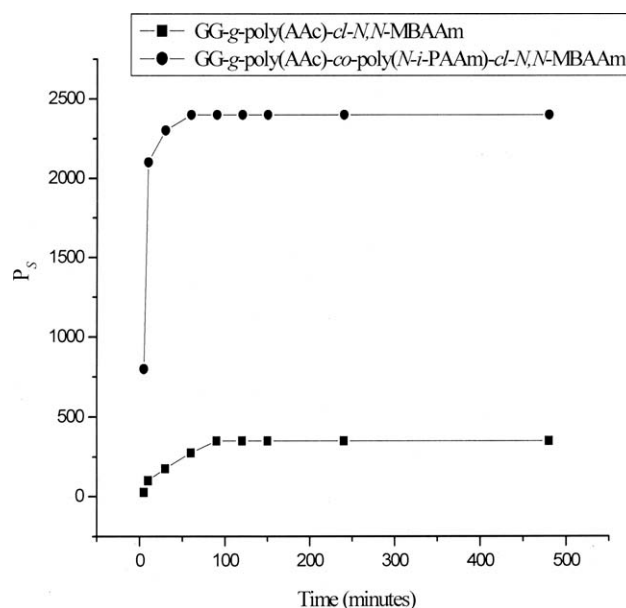


Figure 3 P_s of GG-g-poly(AAc)-*cl*-N,N-MBAAm and GG-g-poly(AAc)-*co*-poly(*N*-*i*-PAAm)-*cl*-N,N-MBAAm in 5.6 pH with respect to time 37°C.

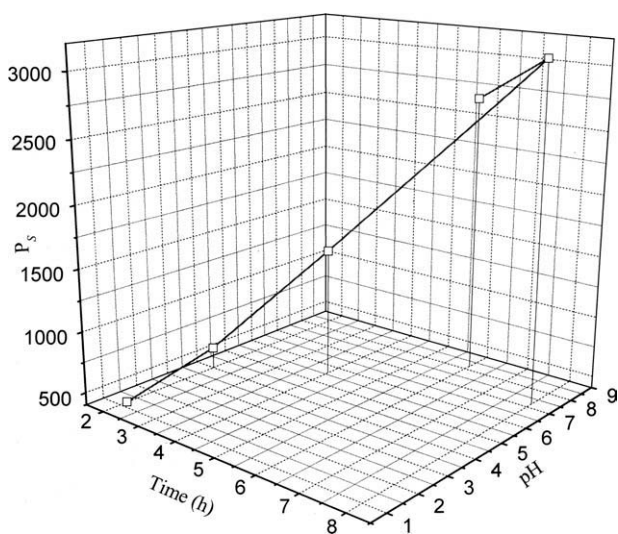


Figure 4 P_s of GG-g-poly(AAc)-co-poly(*N-i*-PAAM)-*cl*-*N,N*-MBAAm, GG₂, on cumulative swelling in 1.2, 4.0, 5.6, 7.2, and 8.2 pH for 2, 2, 4, 8, and 6 h, respectively, at 37 °C.

interactions and hydrogen bond formation. The same is broken after the postreaction and hydrogel structure opens up that is manifested in larger water uptake by GG₂ than its precursor. Two types of interactions are expected in GG₂ those include hydrophobic association between the poly(*N-i*-PAAM) chains and other hydrophilic interactions between the poly(AAc) segments. Such divergent associations result in the opening of the hydrogel matrix and greater influx of swelling medium into it. On cumulative swelling study, i.e., on swelling the same hydrogel in 1.2, 4.0, 5.6, 7.2, or 8.2 pH for 2, 2, 4, 8, or 6 h, respectively (compatible with the pH of gastro intestinal tract), it was observed that P_s

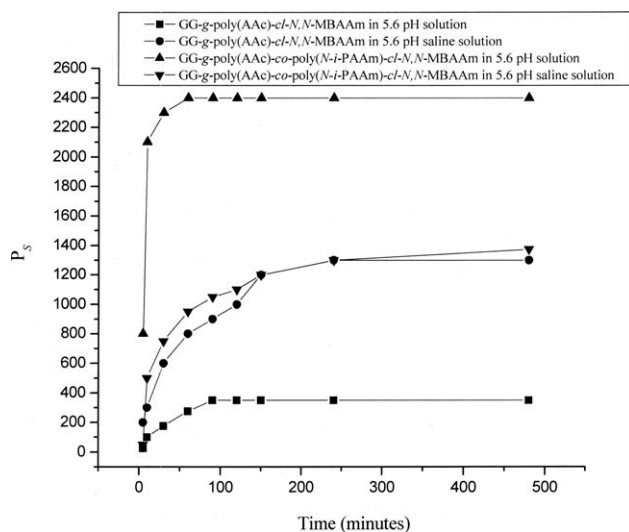


Figure 5 P_s of GG-g-poly(AAc)-*cl*-*N,N*-MBAAm and GG-g-poly(AAc)-co-poly(PAAm)-*cl*-*N,N*-MBAAm in 5.6 pH solution and 5.6 pH saline solution.

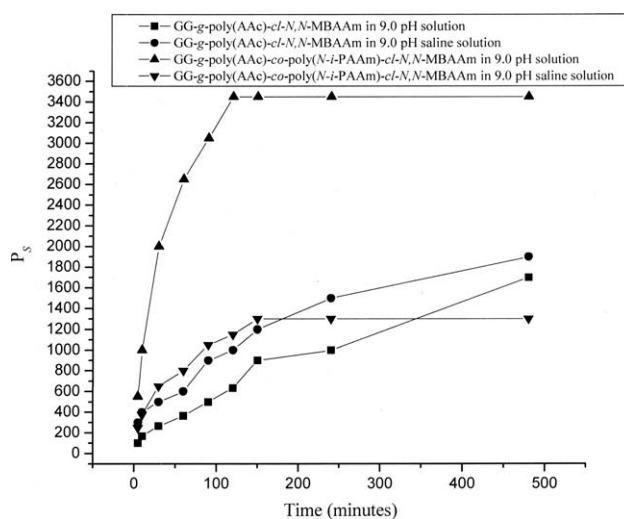


Figure 6 P_s of GG-g-poly(AAc)-*cl*-*N,N*-MBAAm and GG-g-poly(AAc)-co-poly(*N-i*-PAAM)-*cl*-*N,N*-MBAAm in 9.0 pH solution and 9.0 pH saline solution.

increased continuously for both the hydrogels with an increase of time and pH until pH 8.2. These results indicate that these hydrogels have potential use as colon specific drug delivery devices (Fig. 4).

Effect of 0.9% NaCl on swelling behavior of hydrogels at different pH

The effect of 0.9% NaCl solution as a swelling medium (prepared in 1.2, 4.0, 5.6, 7.2, 8.2, or 9.0 pH) is presented in Figures 5 and 6 for 5.6 and 9.0 pH, respectively. P_s of GG₂ was observed to be lower than in the corresponding solutions of pH prepared

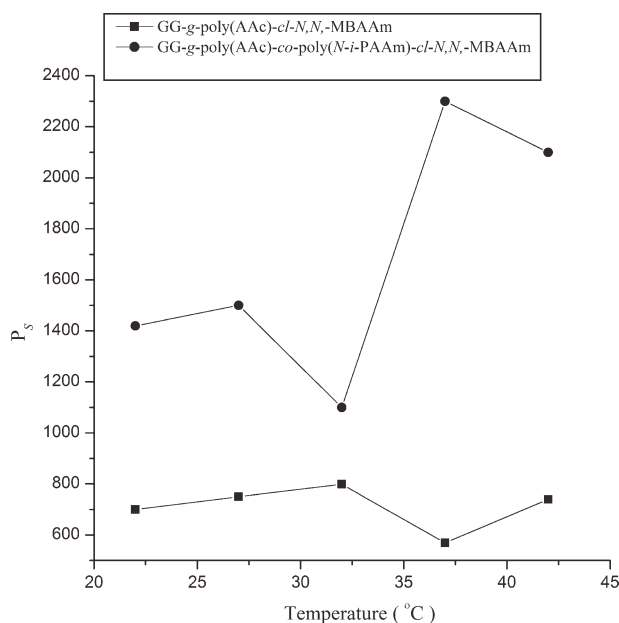


Figure 7 P_s of GG-g-poly(AAc)-*cl*-*N,N*-MBAAm and GG-g-poly(AAc)-co-poly(*N-i*-PAAM)-*cl*-*N,N*-MBAAm at 22, 27, 32, 37, and 42 °C in 5.6 pH solution after 8 h.

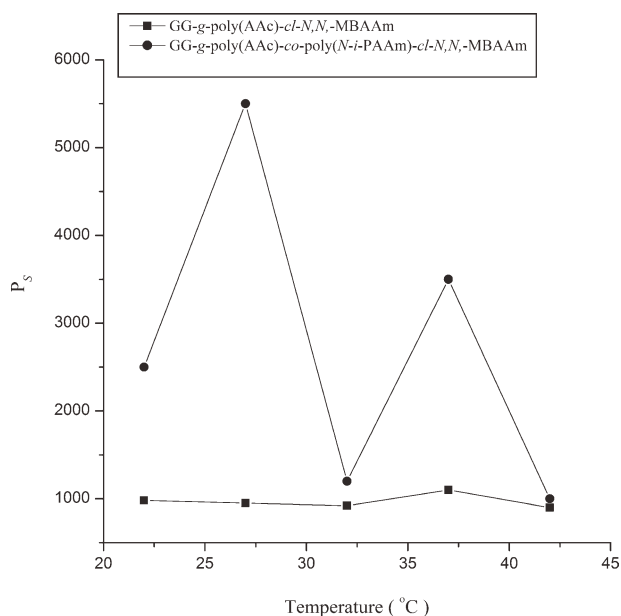


Figure 8 P_s of GG-g-poly(AAc)-cl-N,N-MBAAm and GG-g-poly(AAc)-co-poly(N-i-PAAm)-cl-N,N-MBAAm at 22, 27, 32, 37, and 42 °C in 9.0 pH solution after 8 h.

without NaCl at 37 °C. This indicated that this hydrogel exhibited salt sensitivity. This behavior can be attributed to the fact that the presence of NaCl in the external environment increased the osmotic pressure of the solutions, hence ex-osmosis sets in, and the result is the lower swelling or lesser amount of water in the hydrogel phase. The balance between the osmotic pressure and polymer elasticity sets the physical dimensions of the hydrogel. The presence of salt in the surrounding medium affects swelling. In the present case, GG₁ exhibited some salt-tolerance, i.e., low de-swelling, in 0.9% NaCl solution prepared in media of different pH. The salt tolerance exhibited by this hydrogel can be explained by the fact that ion exchange between the Na⁺ of the swelling medium and H⁺ of the poly(AAc) at the higher or alkaline pH, where the later ionizes with a great ease.

Effect of temperature on the swelling behavior of hydrogels at different pH

The swelling behavior of the hydrogels was studied for 8 h in 1.2, 4.0, 5.6, 7.2, 8.2, and 9.0 pH at temperature 22, 27, 32, 37, or 42 °C. It is well-documented in the published reports that at the higher temperature, swelling decreases due to the elastic retractile nature of hydrogels and also due to an increase in the thermal mobility of water. In the present case, GG₁ exhibited both temperature and pH-dependent swelling behavior with the maximum P_s , for example, at 22 °C in 5.6 pH and at 37 °C in 9.0 pH solution. These results indicate that both the hydrogels

exhibited both temperature and pH sensitivity. In the case of GG₂, it was observed that it attained maximum P_s at 37 °C for 1.2, 4.0, and 5.6 pH, a technologically significant temperature that is higher than LCST (32.5 °C) of poly(N-i-PAAm) as presented in Figs. 7 and 8, for 5.6 and 9.0 pH, respectively.

CONCLUSION

In the present study, guar gum was successfully used as backbone to synthesize stimuli responsive hydrogels by following a simple and clean protocol involving grafting, cross-linking, and polymer analogous reaction, which affects the structural attributes of the hydrogel. The hydrogels exhibited fast swelling and stimuli-responsiveness at the technologically significant pH or temperature. These stimuli-responsive hydrogels being cost-effective, biocompatible, and biodegradable are easy to synthesize. The hydrogels are technologically important and have potential applications in drug delivery and separation processes.

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