Preparation and Characterization of Highly Swelling Smart Grafted Polymer Networks of Poly(vinyl alcohol) and Poly(acrylic acid–*co*–Acrylamide)

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Received 22 March 2005; accepted 1 September 2005
DOI 10.1002/app.23088
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Smart grafted polymer networks comprising random copolymer of poly(acrylic acid-*co*-acrylamide) and polyvinyl alcohol and exhibiting extraordinary water imbibition property were prepared by free radical polymerization method and characterized by Fourier Transform infrared spectroscopy, Ultra Violet spectroscopy, Environmental Scanning Electron Microscopy, Thermogravimetric Analysis, Differential Scanning Calorimetry, and X–ray Diffraction. The mesh size (ξ) and chain flexibility factor (α) of interpenetrating polymer networks were calculated for various grafted polymer network compositions and correlated with their water sorption capacity. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 84–95, 2006

Key words: graft copolymer; hydrogel; swelling

INTRODUCTION

Hydrogels are composed of hydrophillic natured three dimensional network chains entangled to one another by chemical or physical crosslinks. If enough interstitial space exists within the network, water molecules can become trapped and immobilized filling the available free volumes.[1,2] Hydrogels may absorb from 10 to 20% (an arbitrary lower limit) upto thousands of times their dry weight in water. Hydrogels may be chemically stable or they may degrade and eventually disintegrate and dissolve. They are called "reversible" or physical gels when the networks are held together by molecular entanglement, and/or secondary forces including ionic, H-bonding, or hydrophobic forces.[3,4] Hydrogels are called "permanent" or "chemical" gels when they are covalently-crosslinked networks. The chemical hydrogels may also be generated by crosslinking of water-soluble polymers or by conversion of hydrophobic polymers to hydrophilic polymers plus crosslinking to form a network. Sometimes in the later case, crosslinking is not necessary.[5]

There are many different macromolecular structures that are possible for physical and chemical hydrogels. They include the following: crosslinked or entangled networks of linear homopolymers, linear copolymers and block or graft copolymers; polyion–multivalent ion, polyion–polyion, or H-bonded complex; hydrophilic networks stabilized by hydrophobic domains; and IPNs or physical blends. Hydrogels may also have many different physical forms, including (a) solid molded forms (e.g., soft contact lenses), (b) pressed powder matrices (e.g., pill or as capsules for oral ingestion), (c) microparticles (e.g., as bioadhesives carriers or wound treatments), (d) coating (e.g., on implants or catheters; on pills or capsules; or coating on inside capillary wall in capillary electrophoresis), (e) membranes or sheets (e.g., as a reservoir in transdermal drug delivery path; or for 2D electrophoresis gels), (f) encapsulated solids (e.g., in osmotic pumps), and (g) liquids (e.g., that forms gels on heating or cooling). Hydrogels show sensitive response to external stimuli such as pH,[6–8] temperature,[9–11] ionic strength,[12] magnetic field,[13] ultrasonic stimuli,[14] electrical energy,[15] photoelectric stimuli,[16] and internal stimuli such as chemical architecture,[17] polymerization condition,[18] etc.

Poly(vinyl alcohol) is largest volume, synthetic, water-soluble polymer produced all over the world.[19] The main characteristics of PVA are (i) its semi-crystalline character despite its lack of stereoregularity,[20–21] and (ii) a strong tendency to exhibit both inter and intramolecular hydrogen bonds. Moreover, aqueous solution of PVA can transform into physically thermoreversible hydrogels under different condi-

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Contract grant sponsor: Department of Science and Technology, Government of India; contract grant number: SP/S1/G-11/2001.

tions.[22–23] The hydrogels of poly(vinyl alcohol) have good mechanical properties and higher water content; they are stable at room temperature and are able to retain their original shape. In addition, they are biocompatible. All these properties make PVA hydrogels suitable for different biomedical and pharmaceutical applications. Poly(acrylic acid) is a well-known ionic, hydrophilic, water permselective polymer having greater affinity for colonic mucosa than for mucosal tissue in the stomach or small intestine.[24,25] Poly(acrylic acid) and its copolymers have been widely used as carriers in controlled drug release technology because of their multifunctional nature, unique properties, and good biocompatibility. In addition, the pH responsive nature of acrylic acid polymers qualify them as a potential candidate in colon-specific drug delivery.[26]

In the present study, highly swelling random copolymer grafted hydrogel composed of poly(acrylic acid–*co*–acrylamide) and poly(vinyl alcohol) have been prepared. This study deals with their synthesis, characterization, and dependence of their swelling behavior on composition. The novelty of the present study lies in the fact that it offers a simple and cost-effective method of preparing hydrogels that demonstrate a water sorption potential more than hundred times their dry weights. Moreover, their swelling responsivity to external stimuli such as pH make them deserve as a candidate for targetted drug delivery applications.

EXPERIMENTAL

Materials

The poly(vinyl alcohol) (hot processed mol. wt. 72,000, degree of hydrolysis 98.6%) was obtained from the E.Merck, India and used as received. Acrylamide (AM) (E. Merck) was crystallized twice in methanol and dried in vacuum over anhydrous silica from a week. Acrylic acid (E. Merck) was freed from the inhibitor by distilling it under vacuum. *N*,*N*′-methylene-*bis*-acrylamide (MBA) (Central Drug House, Mumbai, India) was employed as a crosslinking agent and used as received. Potassium persulphate (KPS) (Loba Chemie, Mumbai, India) was employed as a free radical initiator. All other reagents used were of analytical grade and bi-distilled water was used throughout the experiments.

Preparation of grafted polymer network

The grafted polymer network was prepared by conventional free radical polymerization method as described in our previous work.[27] In brief, 10.5 m*M* of AM, 7.2 m*M* of AA, 0.5 g of PVA, 0.12 m*M* of MBA, and 0.073 m*M* of KPS were added into a petridish (2 in., Corning), and the mixture was homogenized. The total volume of the feed mixture was maintained to 15 mL. The petridish was then kept at 80°C for 30 min so that the entire mass was solidified, which indicate the formation of gel. The gel was placed at 60°C in oven for 2 h, where it changed into a thin semi-transparent film.

Purification

The dried gel (xerogel) was washed by equilibrating it in distilled water for 15 days and unreacted monomers or homopolymers were detected by UV spectrophotometer. A constant weight of the swollen grafted polymer network was noticed after 15 days, which implies that the grafted polymer network was insoluble. The swollen gels were dried at 60°C for 24 h and stored in air-tight containers.

Swelling experiments

Pre-weighed dry samples were immersed in distilled water at room temperatures until they swelled till equilibrium. Two weeks was found to be enough for equilibrium swelling of the sample. The swelling ratio was calculated as a function of time as follows

$$\text{Swelling ratio} = \frac{(W_s - W_d)}{W_d} \tag{1}$$

where W_s and W_d are weights of swollen and dry gel, respectively.

Network studies

One of the important parameters characterizing crosslinks is M_c, the average molar mass between crosslinks, which is directly related to the crosslink density. The magnitude of M_c greatly affects the physical and mechanical properties of crosslinked polymers and its determination has great practical significance. Equilibrium swelling is widely used to determine M_c. Early research by Flory and Rehner laid the foundation for analysis of equilibrium swelling. According to the theory of Flory and Rehner, for a network

$$M_c = -V_1 d_p \frac{(V_s^{1/3} - V_s/2)}{\ln(1 - V_s) + V_s + \chi V_s^2} \tag{2}$$

where M_c is the number average molar mass of the chain between crosslinks; V_1 is the molar volume of water; d_p is the polymer density; V_s is the volume fraction polymer in the swollen gel; and χ is the Flory–

Huggins interaction parameter between solvent and polymer.[28]

The swelling ratio (Q) is equal to $1/V_s$. Here, the crosslink density, q, is defined as the mol fraction of crosslinked units.

$$q = \frac{M_o}{M_c} \tag{3}$$

where M_o is the molar mass of the repeating unit.

Since the hydrogel is a copolymeric structure, the molar mass of the polymer repeat unit, M_o, can be calculated using the following equation

$$M_o = \frac{n_{AM} \cdot M_{\mathrm{AM}} + n_{\mathrm{AA}} \cdot M_{\mathrm{AA}}}{n_{\mathrm{AM}} + n_{\mathrm{AA}}} \tag{4}$$

where n_{AM} and n_{AA} are the mol. Number of AM and AA (mol) and M_{AM} and M_{AA} being the molar masses of the two monomers, respectively.

Segmental flexibility

The network mesh size ξ can be calculated using the following expression[28]

$$\xi = V_s^{-1/3} \left[C_n \left(2M_c/M_r\right)\right]^{1/2} l \tag{5}$$

where V_s is the volume fraction of polymer in the swollen gel at equilibrium, C_n is the Flory characteristics ratio calculated as a weighed average value for PVA = 8.3, PAAm = 14.8, PAA = 6.7. M_c, the molecular weight between crosslinks was calculated using Flory–Rehner equation.[29] M_r is the molecular weight of the grafted polymer network repeating unit that was calculated as the weighed average of the repeating units of PVA (M_r = 44), PAAm (M_r = 71), PAA (M_r = 72) based on their molar ratios in the grafted hydrogel samples, l is the carbon–carbon bond length.

The studied samples of varying compositions have been graded relative to the sample with the highest ξ, equated to 100, i.e.,

$$\text{Chain flexibility factors } [\alpha] = \frac{\xi_i \times 100}{\xi_{\max}} \tag{6}$$

where ξ_i and $\xi_{\max}$ are the mesh size in the angstrom units of sample i and the sample with the maximum swelling, respectively.

Morphology

Environmental scanning electron microscopy (ESEM)

Morphological features of prepared dry and swollen hydrogels were studied by environmental scanning electron microscopy (Cameca–SU–SEM Probe) of dry and swollen films of the gel. It is notable here that no sample preparation is required by this technique for imaging the surface morphology of the gels.

Spectral analysis

FTIR spectra of grafted polymer network

The structural characterization of the grafted hydrogel was done by recording FTIR spectra of films of preformed polymers PVA, PAA, PAM, and prepared hydrogel on a Perkin–Elmer spectrophotometer (Paragon 1000 FTIR).

UV spectral analysis

UV spectra of native PVA, PAA, PAM, and grafted hydrogel films were recorded on a UV–vis double beam spectrophotometer (Systronics, No. 2201, India). For this purpose, the films of the above polymers were prepared of equal thickness (0.038 cm) by solution cast method and placed in cuvette to record their absorbance.

X–ray diffraction studies

X–ray diffraction (XRD) patterns of native PVA and prepared hydrogel were recorded on a Philips (Holland) automated X–ray powder diffractometer. For XRD study, the dried hydrogel sample was placed on the glass slide specimen holder and exposed to X–rays in vertical goniometer assembly. The scan was taken between 10° and 40° with a scanning speed of 2.48 min. The operating target voltage was 35 kV, tube current was 20 mA, and radiations used were Fe Kα 1 (1.54 nm).

Thermal analysis

Differential scanning calorimetry

DSC measurements were carried out on a TA instrument (V4–IC Dupont 2100) with nitrogen as purging gas. The experiments were performed from RT to 400°C at a heating rate of 10°C/min.

Thermogravimetric analysis

Thermal stability of preformed polymer PVA and prepared grafted hydrogels were evaluated on TGA instrument (TGA–7, Perkin–Elmer) within the temperature range RT to 660°C under N_2 atmosphere.

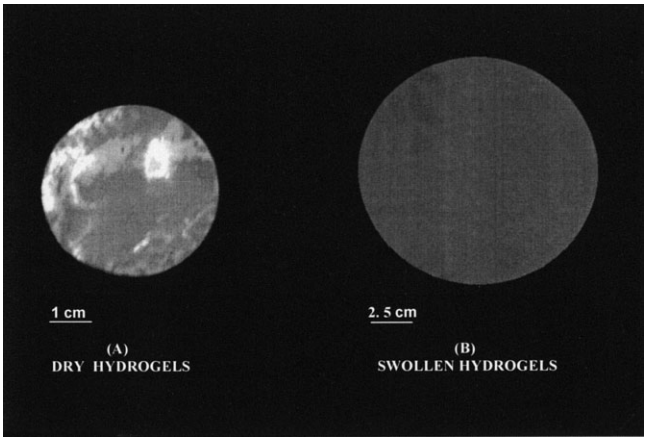

Figure 1 Photograph showing (a) dry grafted hydrogel film and (b) swollen grafted hydrogel film.

RESULTS AND DISCUSSION

Mechanism of swelling

The equilibrium swelling capacity of a hydrogel depends on both internal parameters, such as the macromolecular network, and external, like the environment contacting the material. In particular, for a polyelectrolyte network, characterized by fixed charges on macromolecular backbone, there are four polymer properties affecting polymer swelling: (1) the polymer chain hydrophilicity, which promotes polymer–solvent mixing and thus promotes material swelling, when in contact with water and water solution, (2) the presence of fixed ionic charges, which induces a "Donan–type" effect, an osmotic effect associated with the concentration of ionic charges in the hydrogel, which induces more water to penetrate the hydrogel to dilute this higher charges concentration, (3) the electrostatic repulsion between the charges of the same sign present on the polymer backbone, which tend to expand the macromolecular network and thus promotes polymer swelling; and (4) the elastic response, entropic in nature of the crosslink, which solubilize the polymer chains in the hydrogel network and counteracts polymer swelling.[30]

Environmental scanning electron microscopy

Morphology of a polymer surface is of extreme significance in biomaterial science as biocompatibility of a material is also determined by many surface parameters such as roughness, heterogeneity, clusters of hydrophobic or hydrophilic domains, microphase separation, etc. To examine the nature of the prepared grafted hydrogels surface, ESEM investigations have been done on both dry and swollen polymeric films (Fig. 1). For giving more insights into the grafted hydrogels morphology, the micrographs of PVA have been compared with that of the grafted hydrogel as shown in Figure 2 and Figure 3, respectively. In Figures 2(a) and 2(b) the images of native PVA and grafted hydrogel (dry state) are shown, Whereas in Figures 3(a) and 3(b), the two polymers have been depicted in swollen state.

A close examination of Figures 2(a) and 3(a) reveals that the PVA surface appears a little bit heterogeneous because of its semi-crystalline nature, which indicates the presence of both amorphous and crystalline regions in the polymer. However, the grafted hydrogel image shown in Figure 3(a) rather presents an even and homogeneous surface. This difference could be attributed to the presence of crosslinked copolymeric chains of poly(acrylamide–*co*–acrylic acid), which are also held with PVA chains via physical crosslinks and thus provide a compact arrangement that results in smooth surface.

In the swollen state, however, the two polymeric surfaces are shown in Figure 2(b) and Figure 3(b), respectively. It can be easily seen that in the swollen state the native PVA seems more heterogeneous than dry PVA because the swollen polymer contains relaxed macromolecular chains which, in turn, widens the interterestrial space within the polymer, thus enhancing its heterogeneity. On the other hand, the micrograph of the swollen hydrogel shown in Figure 3(b) clearly indicates the presence of significant cracks throughout the surface, which may be easily understood by the fact that because of large amount of imbibed water, the grafted polymer network experiences an internal stress that results in development of hair cracks on the polymer surface. It is also noticeable here that the surface lying between the cracks is still homogeneous and smooth.

FTIR spectra

The FTIR spectra of grafted hydrogel, PVA, PAM, and PAA shows (Fig. 4) the following peaks.

i. A broad peak near 3431 cm^{-1} suggests for the presence of hydrated —OH and —NH_2 groups of PVA and PAM because of O—H and N—H stretching, respectively.
ii. A minor peak at 2933 cm^{-1} implies for C—H stretching of methylene groups of constituent vinyl polymers.
iii. The presence of carboxylate ion is confirmed by the bands observed at 1631 cm^{-1} and 1353 cm^{-1} because of asymmetrical and symmetrical stretching of carboxylate anion. iv.

The unhydrolyzed acetate groups of PVA are indicated by stretching of C—O—C group at 1023 cm^{-1}.

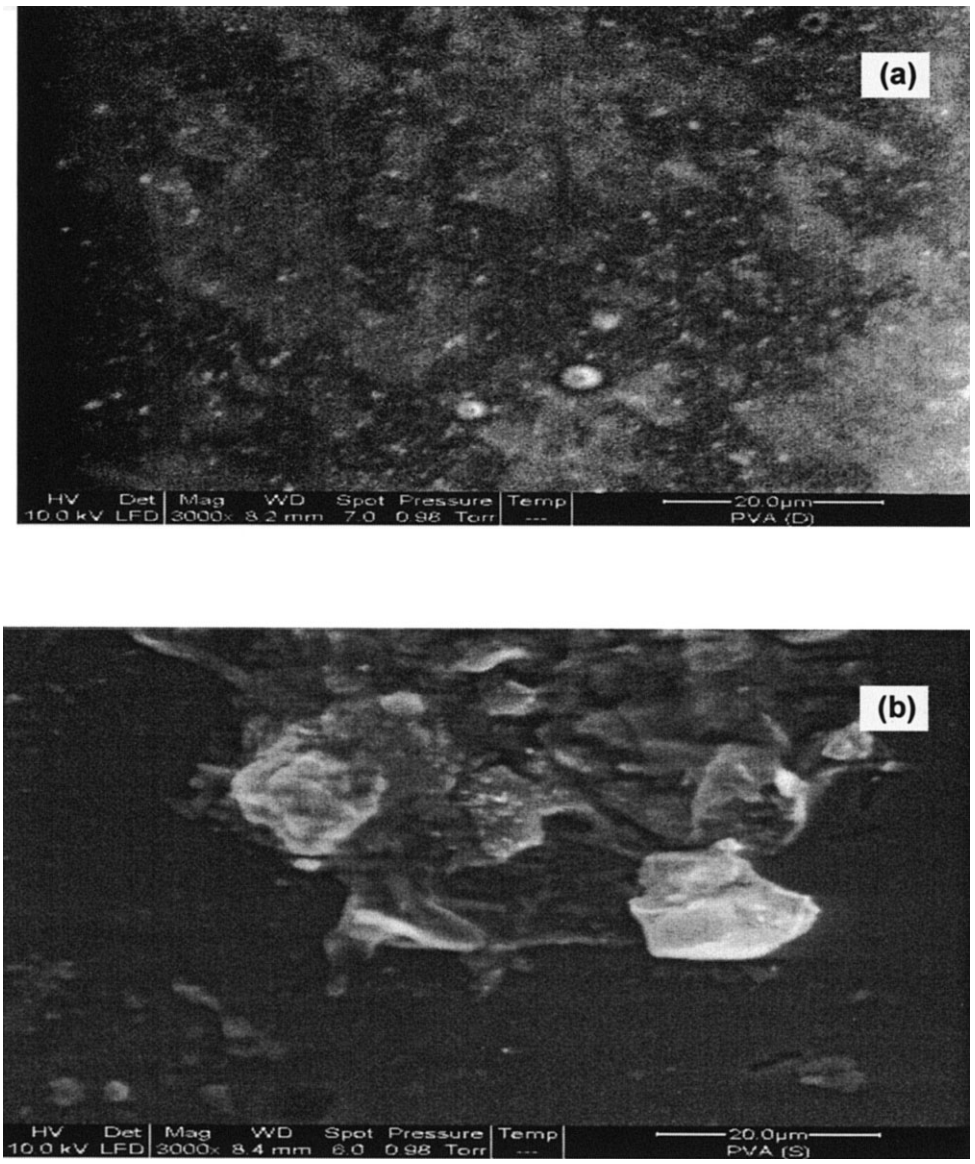

Figure 2 ESEM images of PVA film surface: (a) dry and (b) swollen.

Ultraviolet (UV) spectra

Molecular absorption in the ultraviolet region provides valuable information about the electronic structure of the absorbing molecule. In the present study, the UV spectra of prepared gel, PAA, PVA, and PAM have also been recorded and are shown in Figure 5 (a), (b), (c), and (d) respectively. It is clear from the spectra that the gel shows less transparency than pure PVA and PAA. This could be attributed to the phenomenon of microphase separation, which results in a loss of transparency of the hydrogel. The observed spectra (c) also reveals that λ_{max} of ungrafted PVA appears at 277 nm while it fully disappears in the spectra (a) of the gel, which may be due to the reason that as hydroxyls of PVA are used up in generating grafted site onto them and, therefore, the peak mentioned earlier disappears in the gel.

A close examination of the spectra (b) of pure PAA clearly indicate that a λ_{max} appears at 232 nm because of $n \rightarrow \pi^*$ transition in carboxyl groups of PAA, which is also seen in the spectra (a) of the gel, thus, confirming the presence of PAA in the hydrogel.

X–ray diffraction (XRD)

The XRD spectra of native PVA and hydrogel are depicted in Figure 6(a) and (b), respectively. The spectra (b) presents a sharp peak at 20.0 (2θ) and a larger peak area, which clearly suggest for an increased crystallinity of the hydrogel matrix.

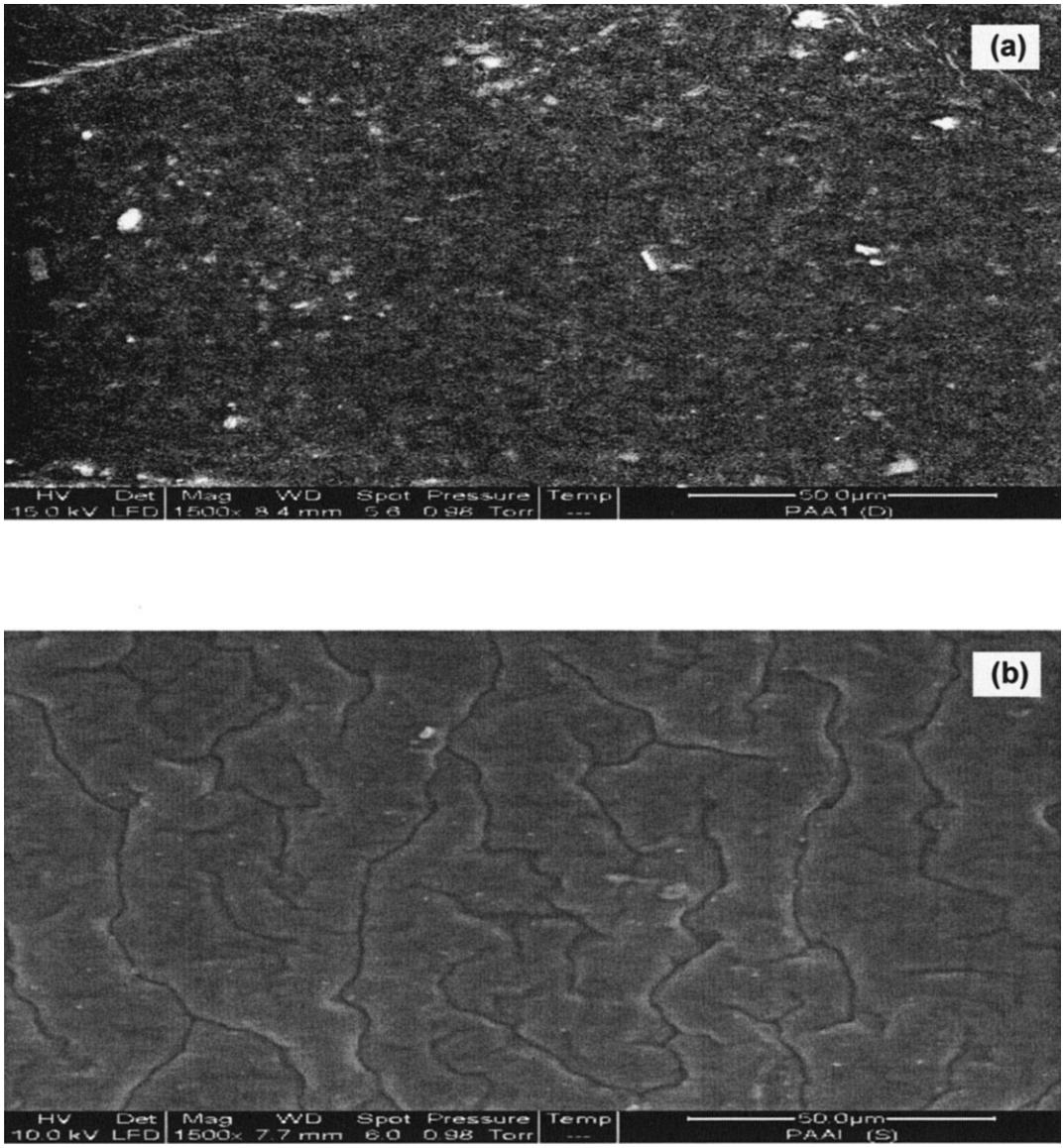

Figure 3 ESEM images of grafted hydrogel surface: (a) dry and (b) swollen.

Differential scanning calorimetry (DSC)

Thermal characterization of polymeric materials provide information not only about the thermal properties of the polymer but also gives insights into the structure of the resulting material. In the present study, therefore, DSC thermograms of constituents polymers (PAA, PAM, PVA), and prepared grafted hydrogel have been recorded and displayed in Figure 7 (a), (b), (c) and (d), respectively. The DSC thermogram (d) shows "semi–crystalline" nature of the gel. The glass transition temperature (T_g) appears at 71°C, which is slightly above the pure T_gs of PVA and PAM, which are 61.8 and 65.3°C, respectively. The observed increase in T_g implies for crosslinked nature of the vinyl polymers.

It is worth mentioning here that the DSC thermogram (c) of PAA contains a sharp melting endotherm at 260°C, which is indicative of highly crystalline nature of the polymer. This also suggests that the inclusion of copolymeric segments of PAA into the PVA matrix should bring about an enhancement in the crystallinity of the prepared polymer, which is also confirmed further by XRD studies as explained earlier. As far as T_g of PAA is concerned, it may have been suppressed because of strong prevailing interactions between various copolymeric segments within the hydrogel matrix. This suggests for marginal influence of T_g of PAA on the thermal properties of the hydrogel.

A sharp melting endotherm is seen at 230°C, which is indicative of the developed crystallinity in the

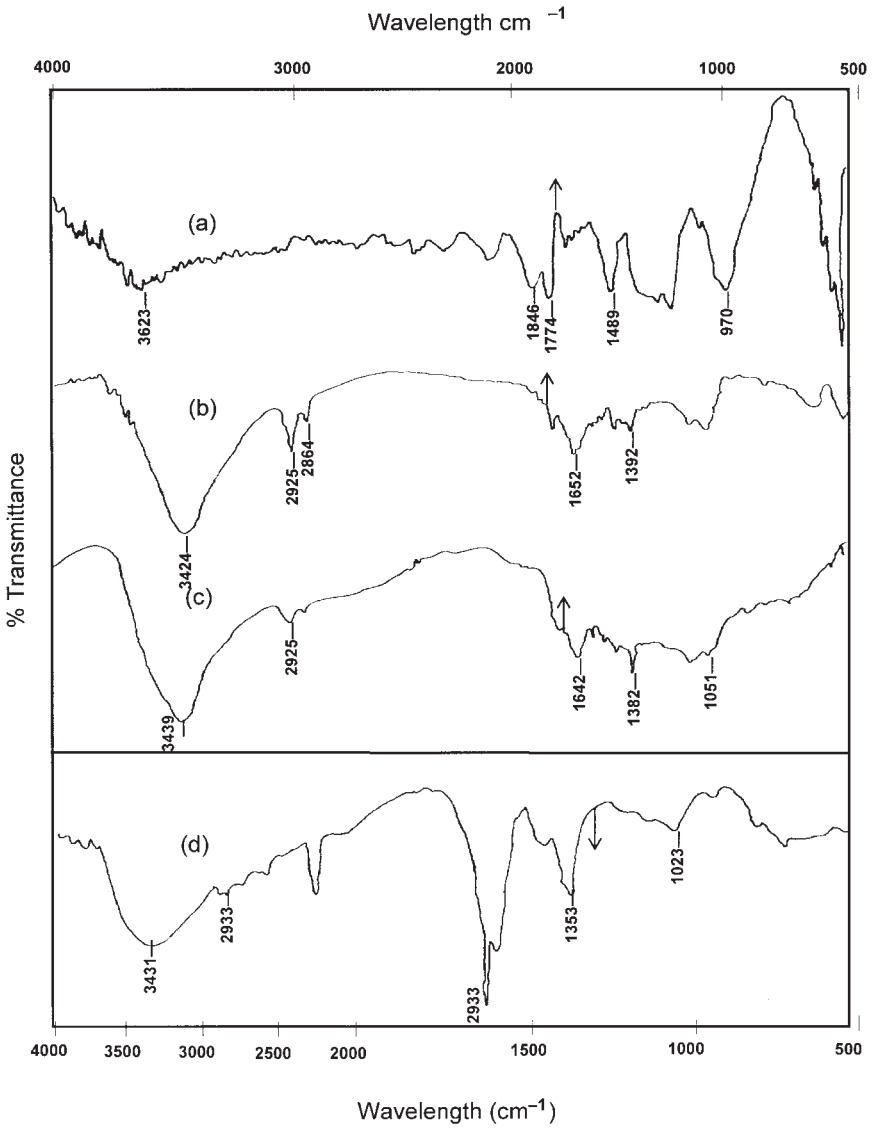

Figure 4 FTIR spectra of (a) PAA, (b) PAM, (c) PVA, and (d) grafted hydrogel.

grafted gel. It is also notable that the T_m of the gel is much lower than T_ms of PAM (270°C) and PAA (268°C), which could be due to the grafted nature of the gel, which, because of increased flexibility, results in lower T_m.

Thermogravimetric analysis (TGA)

A comparison between the TGA (Figures 8(a) and 8(b)) of ungrafted and grafted PVA clearly shows that:

i. In the native PVA major decompositions occur at 313, 410, and 480°C while in the grafted gel, it occurs at 361°C only.
ii. Several minor decompositions are observed in the grafted gel at 173, 284, 407, and 443°C while in the ungrafted PVA minor decomposition occurs at 218°C.
iii. Thus, a marginal fall in thermal stability of native PVA is observed, which could be attributed to the grafting of hydrophilic chains onto PVA.

On the basis of the observed finding, the scheme of graft copolymerization for the preparation of hydrogel may be suggested as given in Figure 9.

Dependence of swelling on structural parameters

Structural parameters of a hydrogel are of great significance in controlling the water sorption capacity of the network, which forms the basis of many diversified applications of hydrogels in pharmaceutical and

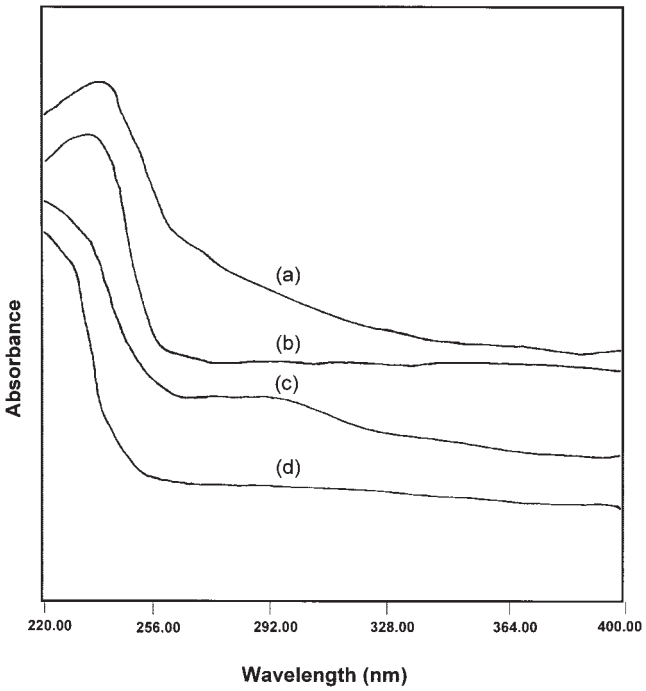

Figure 5 UV spectra of (a) grafted hydrogel, (b) PAA, (c) PVA, and (d) PAM.

biomedical science. Since the swelling of a hydrogel is intimately regulated by the elastic response of the constituent polymeric chains, it is worth to calculate structural parameters such as molecular weight between crosslinks (M_c), crosslink density (q), mesh size of the network (ξ), and chain flexibility factor (α). The swelling and structural parameters' data for various hydrogel compositions are depicted in Table I, which may be explained later.

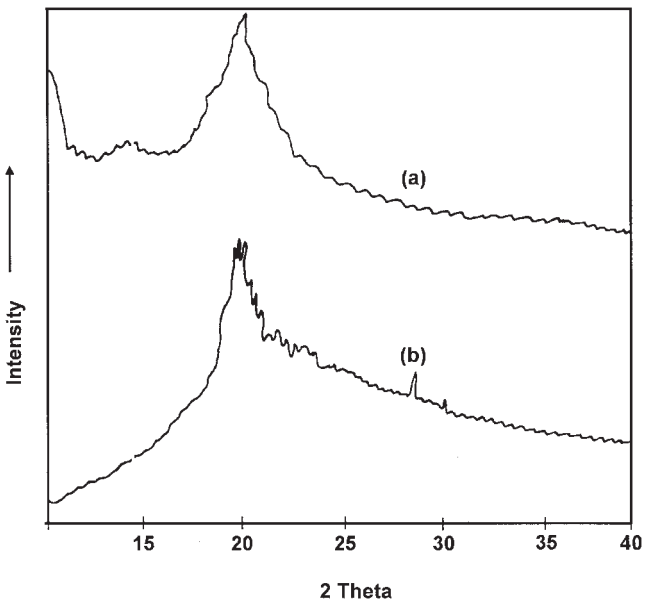

Figure 6 XRD spectra of (a) PVA, (b) grafted hydrogel.

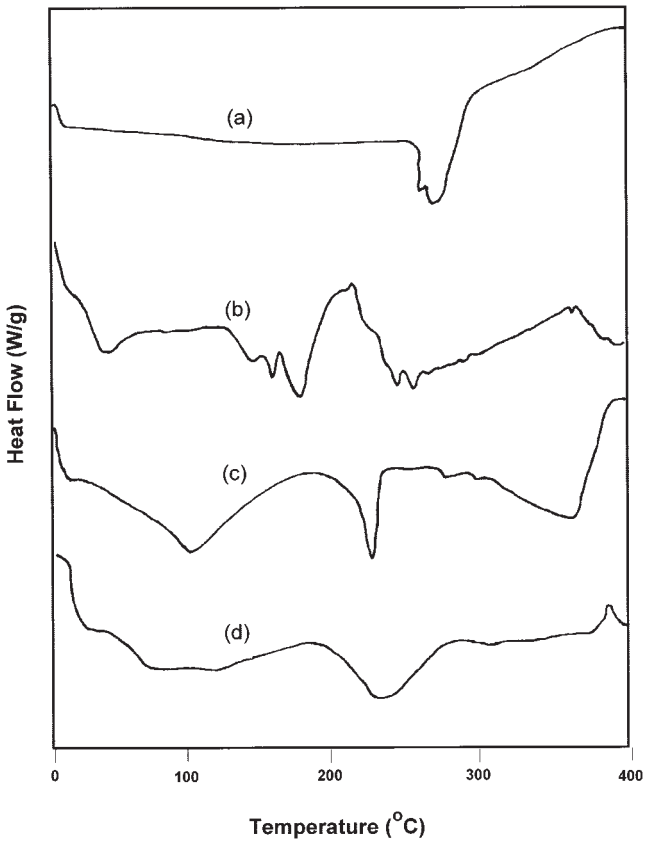

Figure 7 DSC thermograms of (a) PAA, (b) PAM, (c) PVA, and (d) grafted hydrogel.

Effect of polyvinyl alcohol (PVA)

When the concentration of PVA increases in range from Nil to 1.0 g, the swelling of the gel decreases constantly (Fig. 10). The observed decrease can be explained by the fact that PVA is a hydrophilic polymer and will produce strong interaction with the copolymer chains when present in increasing amounts in the feed mixture of the gel. This consequently increases the compactness of the gel, and thus less number of penetrant water molecules will be allowed to enter and swell the gel. Obviously, a fall in the swelling ratio is noticed. A similar type of decrease in the swelling ratio has been reported by Gravier et al.,[31] who synthesized hydrogels of PVA and sodium acrylate and noticed a fall in the swelling ratio with increasing number of molar ratios of PVA.

The observed findings are also supported by data shown in Table I, which clearly show that mesh size, chain flexibility factor, and molecular weight between crosslinks also decrease with increasing concentration of polyvinyl alcohol in feed mixture.

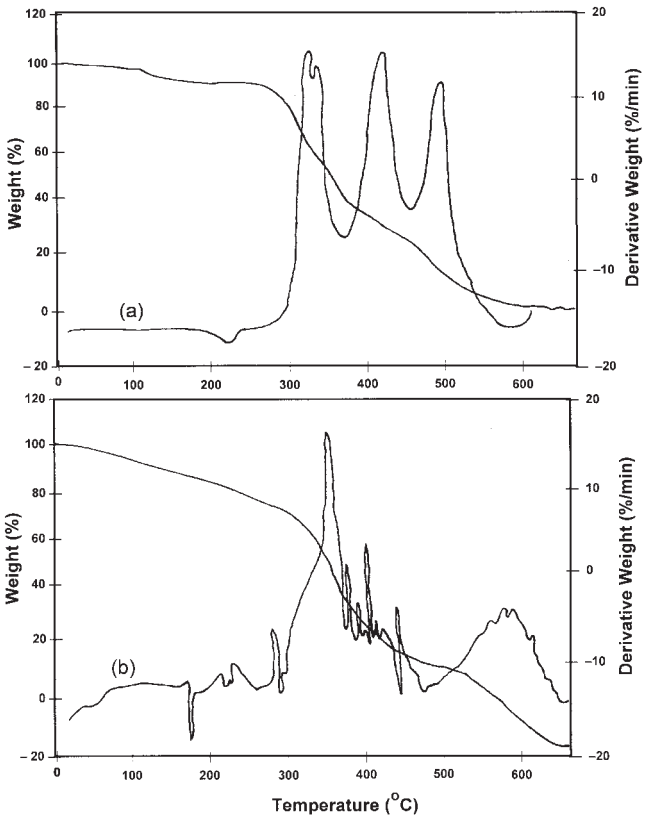

Figure 8 TGA curves (with DTA) of (a) PVA and (b) grafted hydrogel.

Effect of monomer

The influence of non-ionic monomer (acrylamide) on the structural parameters has been examined by varying the concentration of the monomer in the range of 7.04–21.1 m*M* in the feed mixture of the gel. The results depicted in Figure 11 clearly reveal that the swelling ratio decrease with increasing acrylamide concentration. The results may be explained by the fact that enhanced acrylamide content in the hydrogel results in longer polyacrylamide blocks in the copolymer, which, because of greater hydrogen bonding forces between the —$CONH_2$ groups of polyacrylamide, results in a dense network with narrow mesh sizes. Moreover, larger segments of polyacrylamide molecules inhibit the free rotation of network chains due to increased cohesion forces. The mesh size, chain flexibility factors, and molecular mass between crosslinks decreases with increasing concentration of acrylamide (Table I).

The effect of ionic monomer, i.e., acrylic acid has also been investigated on the structural parameters of the hydrogel by varying the concentration in the range of 7.2–29.1 m*M*. The results (Fig. 12) clearly indicate that the swelling ratio increases up to 14.5 m*M* while a fall is noticed beyond this optimum concentration.

The SR (Q) of a hydrogel can be best described by Flory's swelling theory as given below

$$Q^{5/3} = \frac{[(i/2\ Vu\ S^{1/2}) + (1/2 - X_1)/V_1]^{1/2}}{(V_e/V_\sigma)} \quad (7)$$

where i/Vu is the concentration of fixed charge referred to the unswollen network; S, the ionic concentration of external solution; $(1/2 - X_1)/V_1$, the affinity of the hydrogel with water; and V_e/V_σ, the crosslinked density of hydrogels. Q has a relation to the ionic osmotic pressure, crosslinked density, and affinity of the hydrogels with water from the equation.

It is also notable that structural parameters also modulate in respective way with water sorption ca-

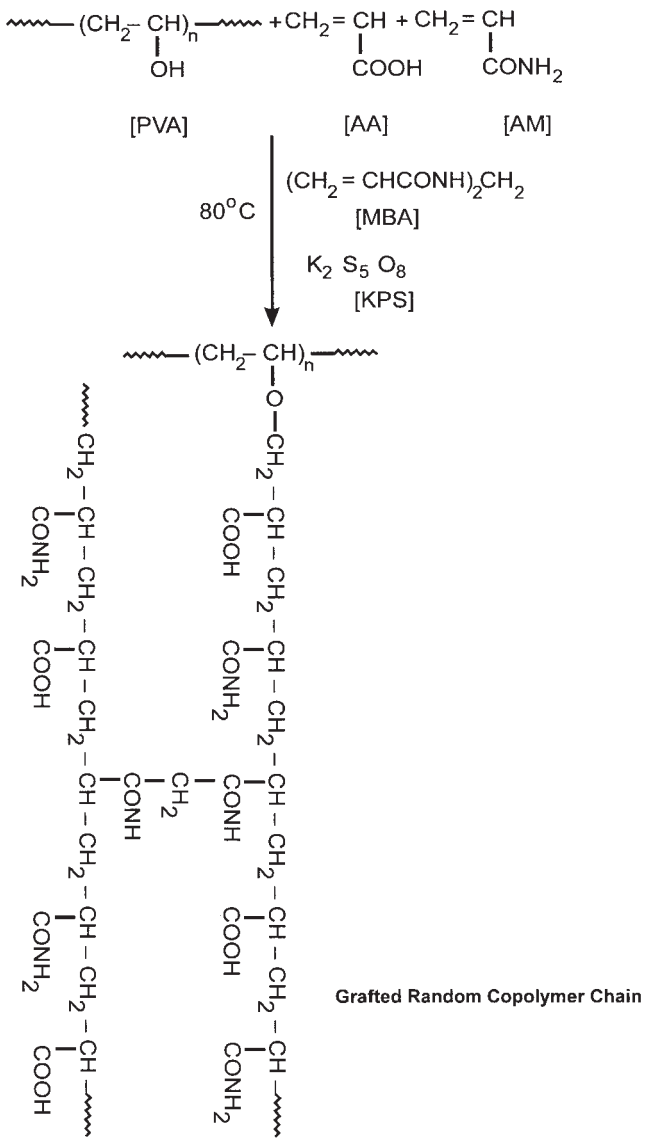

Figure 9 Reaction scheme for the preparation of grafted hydrogel.

TABLE I
Data Showing the Variation of Average Molecular Weight between Crosslinks (M_c), Crosslink Density (q), Mesh Size (ξ), and Chain Flexibility Factor (α) with Various Compositions of the IPN

PVA (g)	AM (m*M*)	AA (m*M*)	MBA (m*M*)	M_c	q (10^3)	ξ (Å)	α
0.50	10.5	7.2	0.13	13,088	5.45	352	48.15
0.75	10.5	7.2	0.13	5568	12.0	201	27.4
1.00	10.5	7.2	0.13	1893	37.0	105	14.3
0.50	7.04	7.2	0.13	37,700	1.89	731	100.0
0.50	10.5	7.2	0.13	13,088	5.45	352	48.1
0.50	14.0	7.2	0.13	10,980	6.49	305	41.7
0.50	21.1	7.2	01.3	8299	8.58	267	36.5
0.50	10.5	7.2	0.13	13,088	5.45	352	98.1
0.50	10.5	14.5	0.13	24,144	2.96	508	69.4
0.50	10.5	21.8	0.13	15,231	4.70	386	48.7
0.50	10.5	29.1	0.13	10,530	5.88	240	40.6
0.50	10.5	7.2	0.06	14,135	5.04	665	51.1
0.50	10.5	7.2	0.13	13,088	5.45	352	48.1
0.50	10.5	7.2	0.19	1614	0.44	82	11.2
0.50	10.5	7.2	0.25	1048	0.68	59	8.07

pacity of the hydrogel. The results obtained may be explained by the fact that in the initial range of added acrylic acid concentration, the added monomer produces greater number of —COOH and —COO^{-} groups, which, because of mutual repulsion, expands the network mesh size, allowing large number of water molecules to diffuse into the gel. This clearly results in a larger swelling, greater mesh size, and chain flexibility. However, upon further increasing the acrylic acid content, the observed decrease in swelling ratio could be attributed to greater intermolecular association between —COOH of polyacrylic acid segments and —$CONH_2$ of polyacrylamide blocks, which, because of reduction in mesh size and chain flexibility factor, tend to decrease the gel (Table I).

Effect of crosslinker

The presence of crosslinks in a hydrogel is a key parameter to affect the overall properties of polymer and determine its final applications. In the present study, the crosslinker has been varied in the range of 0.06–0.25 m*M* in the feed mixture and its impact on the swelling ratio and structural parameters have been investigated. The results summarized in Figure 13 clearly indicate for a suppressed swelling due to increased number of crosslinks. The results also reveal a decrease in mesh sizes and chain flexibility factor as evident from the Table I. The observed results are quite expected and are attributable to the reason that greaterly crosslinked network should

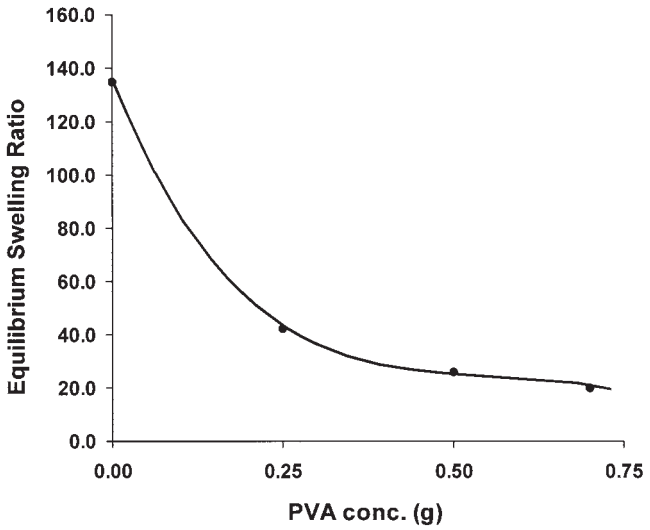

Figure 10 Variation in the equilibrium swelling ratio (SR) of grafted hydrogel with various amounts of PVA.

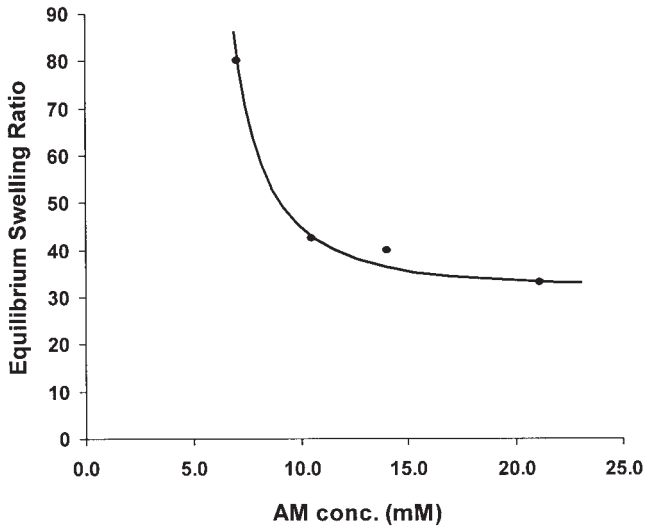

Figure 11 Variation in the equilibrium swelling ratio (SR) of grafted hydrogel with various amounts of AM.

possess narrow mesh sizes and restrained flexibility of macromolecular chains. Naturally, both these factors decrease the water sorption capacity.

CONCLUSIONS

Inclusion of random copolymer of acrylic acid and acrylamide into the PVA matrix results in a hydrophilic grafted polymer network displaying significant water sorption property. A close examination of the ESEM images of native PVA and grafted polymer network indicate that in the dry state the surface appears heterogeneous, while in the swollen state the native PVA becomes more heterogeneous and the grafted polymer network exhibits minor cracks on its surface.

The structural characterization of the grafted polyvinyl alcohol by FTIR spectroscopy clearly marks the presence of hydroxyls, carboxylics, and amides, due to the constituent polymers.

The UV spectra of the prepared hydrogel clearly suggests for reduced transparency of the gel due to microphase separation during graft coplymerization. The spectra also confirms the presence of constitutent polymers in the hydrogel. The absence of λ_{max} of PVA (at 277 nm) in the spectra of the hydrogel indicates for utilization of hydroxyls of PVA as grafting sites.

Differential scanning calorimetry (DSC) of the prepared grafted polyvinyl alcohol clearly suggests for an enhanced crystallinity in the network, which is further reflected by changed glass transition temperature and crystalline melting point. The prepared grafted polyvinyl alcohol shows a marginal change in thermal stability while number of minor decompositions are substantially reduced in the grafted polymer network.

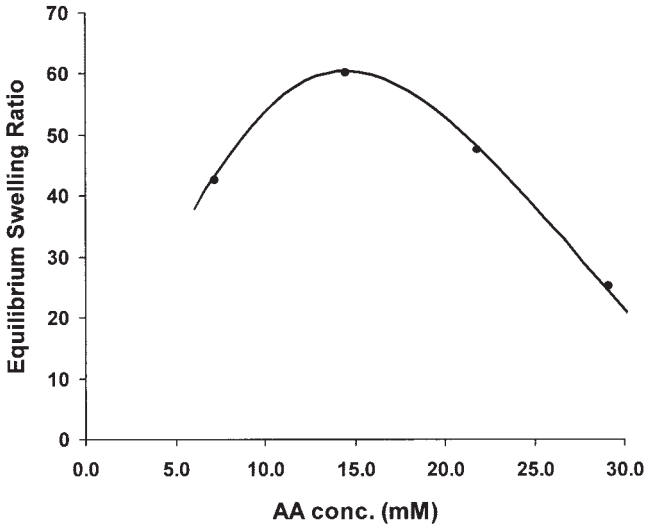

Figure 12 Variation in the equilibrium swelling ratio (SR) of grafted hydrogel with various amounts of AA.

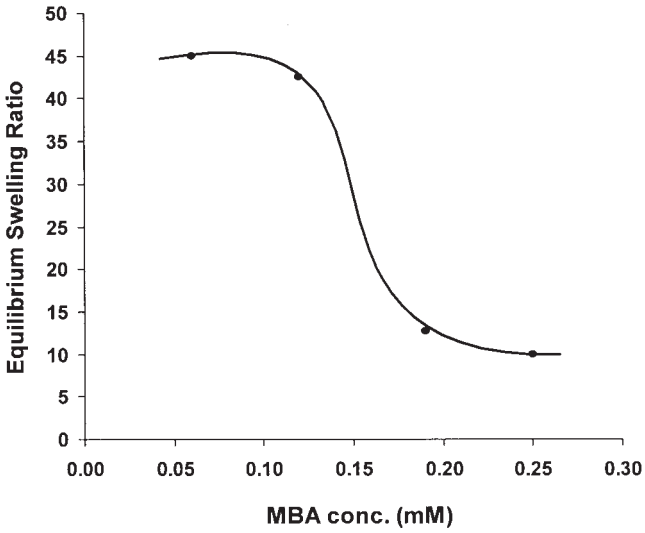

Figure 13 Variation in the equilibrium swelling ratio (SR) of grafted hydrogel with various amounts of MBA.

The grafted polyvinyl alcohol shows a regular variation in its swelling ratio with changing concentrations of the constituent polymers and crosslinking agent. It is found that with increasing contents of PVA, AM, and MBA (crosslinker) the swelling ratio, mesh size, and chain flexibility decrease while in the case of acryilc acid the swelling and structural parameters increase initially, and thereafter exhibit a fall with increase in acrylic acid concentration.

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