Self Assembled Hydrophobic Nanoclusters of Poly(methyl methacrylate) Embedded into Polyvinyl Alcohol Based Hydrophilic Matrix: Preparation and Water Sorption Study

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ABSTRACT: Hydrophilic matrices containing nanosized clusters of hydrophilic moieties have demonstrated potential applications in biomedical field. A novel hydrogel containing nanosized domains (20–35 nm) of hydrophobic moieties of poly(methyl methacrylate) (PMMA) was prepared by grafting crosslinked poly(acrylic acid-co-methyl methacrylate) chains onto polyvinyl alcohol (PVA) backbone using an efficient redox system. The graft copolymerization process was investigated to observe the influence of gel components on the kinetic parameters of grafting such as rate of grafting (R_g), grafting yield (G_y) and grafting efficiency (G_e). The prepared graft nanohydrogel was evaluated for its water sorption potential under varying chemical composition of the gel and changing pH, temperature, and ionic strength of the swelling bath. The swelling process was also examined mechanistically and diffusion constants (D) of water molecules through the swellable nanohydrogel were also evaluated. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1300–1310, 2009

Key words: hydrophilic polymers; nanocomposites; graft copolymers; swelling

INTRODUCTION

Discovery of water retaining materials with predesigned structures has formed the very foundation of advanced biomedical and pharmaceutical sciences.[1] Commonly coined as "nanohydrogels" or "smart materials," this unique class of macromolecular family owes a great number of applications such as controlled drug delivery systems,[2–4] soft contact lenses,[5] artificial implants,[6] actuators,[7] wound healing dressings,[8] agrochemical release carriers,[9] water purification devices,[10] etc. Their sensitive response to external stimuli such as pH,[11–13] temperature,[14–16] ionic strength,[17] magnetic field,[18,19] electric field,[20–22] ultraviolet light,[23] etc. and internal stimuli like chemical architecture,[24,25] initiators conditions,[26] etc. enable them to deserve as a potential candidate in biomaterial applications.

Recent past has witnessed continuing efforts to develop compatible materials with negatively charged surfaces for being used as artificial vessels with superior blood compatibility. Most of the studies were aimed at attempting to understand the blood compatibility of foreign materials from the view point of protein adsorption and cell adhesion[27] and it was shown that the blood compatibility is affected by various properties of the material surface, for example, surface charge, wettability, surface free energy, topography or roughness, and presence of specific chemical groups on the surface.[28] Moreover, it has been pointed out that the water structure on the surface of the material is one of the most important factors affecting blood compatibility.[29] In spite of the fact that a large number of investigations have been done to explore the possible factors responsible for blood compatibility of a material, a concrete conclusion has not yet emerged.

The fundamental property to which all such biomedical applications are credited lies in swelling of the nanohydrogels when they come in contact with an aqueous environment.[30] A study of the dynamics of water sorption by nanohydrogel, therefore, is of much importance as it not only monitors the progress of the swelling process, but also gives an insight into the mechanism of water transport,

which reflects the network structure of nanohydrogel framework.[31]

Thus, realizing the substantial contribution of nanohydrogels in biomedical fields, we, in the present article are reporting results on the preparation of a macromolecular matrix by grafting poly(acrylic acid-*co*-methyl methacrylate) chains onto poly(vinyl alcohol) and study of the effects of various factors on grafting parameter such as rate of grafting (R_g), grafting efficiency (G_e), and grafting yield (G_y). The selection of polyvinyl alcohol, acrylic acid, and methyl methacrylate as nanohydrogel components rest upon their well-known identity in biomedical and pharmaceutical fields.

EXPERIMENTAL

Materials

PVA (hot processed MW $\sim$ 72,000, degree of hydrolysis 98.6%), methyl methacrylate, acrylic acid were obtained from Merck Specialties Private Limited, Mumbai, India. N,N'-methylene bisacrylamide (MBA) (Central Drug House, Mumbai, India) employed as crosslinking agent, potassium persulphate (KPS) and potassium metabisulphite (MBS) (Merck Specialties Private, Mumbai, India) as polymerization initiator system were used as received. All other chemicals used were of analytical grade and double-distilled water was used throughout the experiments.

Polymerization

The nanohydrogel was prepared by free radical solution polymerization method using redox initiator.[32] Varying molar concentrations of AA (7.2–21.8 mM), MMA (4.6–18.6 mM) and PVA (0.75–1.50 g) were used. In a typical experiment, PVA (1.00 g), AA (21.8 mM), MMA (9.3 mM), and water (20 mL) were added into a round bottom flask and the mixture was homogenized by mechanical mixing. The temperature was raised to 35°C and oxygen-free nitrogen gas was purged for 30 min followed by addition of MBA (0.06 mM), KPS (0.36 mM), MBS (4.04 mM), and the mixture was poured into a petri dish (diameter 2 in.). The petri dish was covered and kept at 35°C for 72 h so that the whole mass solidified into a film type of gel.

Purification

The nanohydrogel prepared as earlier was equilibrated with double-distilled water minimum for 10 days so that the unreacted monomers and other reactants were leached out of the swollen gels. The swelling medium was analyzed for unreacted

methyl methacrylate/acrylic acid (monomer double bond estimation), to ensure their complete removal from nanohydrogel. The gel was dried at room temperature for a week and stored in airtight containers.

Grafting parameters

The percentage grafting yield (G_y), grafting efficiency (G_e) and rate of grafting (R_g)[33,34] were found by using the following equations, respectively.

$$\% \text{ grafting yield} = \frac{(W_g - W_o)}{W_o} \times 100 \qquad (1)$$

$$\% \text{ grating efficiency} = \frac{(W_g - W_o)}{m} \times 100 \qquad (2)$$

$$\text{Rate of grafting} = \frac{[(W_g - W_o) \times 1000]}{[M_w \times t \times V]} \qquad (3)$$

where, W_g, W_o, m, and M_w denote the weight of grafted PVA, ungrafted PVA, monomers (AA and MMA) used, and molecular weight of monomers, respectively, t is the polymerization time (h) and V is the total volume (mL) of the overall reaction mixture.

The various samples prepared by taking different amounts of PVA, monomers, (AA and MMA) and crosslinker (MBA) in the feed mixture and G_y, G_e, and R_g are also presented in the Table I.

Swelling experiments

The progress of the swelling process was monitored gravimetrically as described elsewhere.[35,36] In a typical swelling experiment, a preweighed circular piece of dry nanohydrogel (0.04 g) was immersed into a definite volume (100 mL) of distilled water, taken out at different time intervals, soaked between two filter papers and finally weighed. The swelling ratio (SR) was calculated by the following equation:

$$\text{Swelling ratio (SR)} = \frac{\text{Weight of the swollen gel}}{\text{Weigh of the dry gel}} \qquad (4)$$

Dynamics of water sorption

Mostly the dynamics of water sorption process is investigated either by monitoring the change in physical dimensions of the swelling nanohydrogel or by knowing the amounts of water imbibed by the nanohydrogel at various time periods. In the present work also, the latter procedure was followed. For this purpose, the swelling nanohydrogel was taken out at different time intervals and its weight was

TABLE I
Data Showing the Variation in Grafting Parameters with Varying Concentration of the Nanohydrogel Components

PVA (g)	AA (mM)	MMA (mM)	MBA (mM)	Rate of grafting (%)	Grafting yield (%)	Grafting efficiency (%)
0.750	21.8	9.3	0.12	1.82	60.26	17.99
1.000	21.8	9.3	0.12	1.94	49.50	19.66
1.250	21.8	9.3	0.12	2.50	49.68	24.72
1.500	21.8	9.3	0.12	3.29	54.40	32.48
1.000	7.2	9.3	0.12	0.58	14.50	9.94
1.000	14.5	9.3	0.12	1.27	31.50	15.85
1.000	21.8	9.3	0.12	1.94	49.40	19.66
1.000	29.1	9.3	0.12	2.70	62.00	20.38
1.000	21.8	4.6	0.12	1.67	41.06	20.35
1.000	21.8	9.3	0.12	1.94	49.40	19.66
1.000	21.8	14.0	0.12	1.70	42.20	14.16
1.000	21.8	18.6	0.12	3.52	87.40	24.95
1.000	21.8	9.3	0.06	0.66	16.40	6.52
1.000	21.8	9.3	0.12	1.94	49.40	19.66
1.000	21.8	9.3	0.19	2.60	64.60	25.71
1.000	21.8	9.3	0.25	2.99	74.30	29.57

recorded. For the kinetic analysis of the results, the following equation was applied[37]

$$\frac{W_t}{W_\infty} = kt^n \quad (5)$$

where, k is the swelling rate front factor and n is the swelling exponent, and W_t and W_∞ are the water intakes at time t and equilibrium time, respectively. The value of n in the earlier equation provides an indication of the water transport mechanism. When $n = 0.5$, the swelling process is of Fickian nature and is diffusion controlled while the value of n between 0.5 and 1.0 suggests for nonFickian diffusion or more specifically anomalous diffusion. When n becomes exactly equal to unity, then the diffusion is termed as Case II diffusion. In some cases the value for n has been found to exceed unity and it has been termed as Super Case II transport. For ordinary diffusion, Fick's law is the appropriate constitutive equation for the mass transfer flux, and a mutual diffusion coefficient can be defined relative to the polymer-fixed frame of reference. For a plane sheet, the diffusion coefficient D can be calculated from the following equation:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \left\{ \exp \frac{-D(2n+1)^2 \pi^2 t}{l^2} \right\} \quad (6)$$

where t is time and l is the initial thickness of the dry sheet. Although this equation is readily evaluated using a spreadsheet program, it is instructive to examine the short-time limiting expression as well,[38]

$$\frac{M_t}{M_\infty} = 4 \left[\frac{Dt}{\pi l^2} \right]^{0.5} \quad (7)$$

The earlier equation clearly implies that a plot between M_t/M_∞ and $\sqrt{t}$ will yield a straight line

and with slope of the graph, the value of diffusion constant D can be calculated (Table II).

Penetration velocity measurement

The penetration velocity for each nanohydrogel composition was determined by the weight gain method as described by Peppas and Franson.[39] The penetration velocity was calculated from the slope of the initial portion of the penetrant uptake curve from the equation

$$v = \left[\frac{dW_g}{dt} \right] \left[\frac{1}{\rho} \right] \left[\frac{1}{2A} \right] \quad (8)$$

where, v denotes the penetration velocity, dW_g/dt denotes the slope of weight gain versus time curve, and ρ denotes the density of water. A denotes the area of one face of the slab and the Factor 2 accounts for the fact that penetration takes place through both the faces. The penetration velocities calculated for different nanohydrogels composition are listed in Table II.

pH effect

The influence of pH on the water sorption capacity of grafted nanohydrogel was investigated by swelling the preweighed nanohydrogel in an aqueous reservoir of known pH. The pH was adjusted by addition of 0.1N HCl and/or 0.1N NaOH to the swelling medium.

RESULTS AND DISCUSSION

Factors affecting grafting parameters

As shown in Table I, the percent G_y, G_e, and R_g vary with varying composition of the nanohydrogel. The obtained grafting data may be interpreted as below:

TABLE II
Data Showing the Variation of Penetration Velocity (v), Diffusion Constant (D), Diffusion Exponent (n) for Swelling of Nanohydrogel with Varying Composition

PVA (g)	AA (mM)	MMA (mM)	MBA (mM)	Thickness (cm)	n	$D \times 10^7$ (cm^2/s)	$v \times 10^4$ (cm/s)
0.750	21.8	9.3	0.12	0.068	0.55	0.24	1.98
1.000	21.8	9.3	0.12	0.068	0.58	1.77	2.80
1.250	21.8	9.3	0.12	0.068	0.50	2.32	9.62
1.500	21.8	9.3	0.12	0.068	0.47	3.27	0.57
1.000	7.2	9.3	0.12	0.068	0.66	6.60	1.44
1.000	14.5	9.3	0.12	0.068	0.60	6.61	2.46
1.000	21.8	9.3	0.12	0.068	0.58	1.77	2.80
1.000	29.1	9.3	0.12	0.068	0.50	3.90	4.38
1.000	21.8	4.6	0.12	0.068	0.30	1.37	4.94
1.000	21.8	9.3	0.12	0.068	0.58	1.77	2.80
1.000	21.8	14.0	0.12	0.068	0.61	3.99	1.44
1.000	21.8	18.6	0.12	0.068	0.65	4.19	2.78
1.000	21.8	9.3	0.06	0.068	0.50	8.16	1.37
1.000	21.8	9.3	0.12	0.068	0.58	1.77	2.80
1.000	21.8	9.3	0.19	0.068	0.64	0.52	1.79
1.000	21.8	9.3	0.25	0.068	0.70	0.48	0.89

When the amount of PVA increases from 0.75 to 1.5 g, both the G_y and G_e increase which may be attributed to the reason that increasing concentration of PVA results in increasing number of polymer radicals, i.e., PVA which obviously brings about an increase in grafting parameters.

In a similar way, when the concentration of AA and MMA are varied in the range 7.2–29.1 mM, and 4.6–18.6 mM, respectively. The grafting parameters constantly increase which can be again explained on the basis of proposed grafting mechanism. It is clear from the mechanism that increasing concentrations of monomers (AA and MMA) increase the availability of monomers molecules in the propagation step and, therefore, the extent of grafting increases.

It is also revealed by the data that increasing concentration of crosslinker from 0.06 to 0.25 mM show an increase in G_y, G_e, and R_g. These observed results may be explained on the basis of the fact that due to higher concentration of crosslinking agent in polymerization system, the monomer molecules come closer to the polymer chain due to increased crosslinked density and may get easily grafted on the polymer backbone.

Mechanism of water sorption

The nanohydrogel in the present study could be considered as a network in which specific interactions (ester groups) are operative between the macromolecular chains of PVA and the crosslinked copolymer P(AA-co-MMA). Between these network chains will be present free volume patches into which the penetrant water molecules may be accommodated. Now, for visualizing the nature of the dynamic swelling process let us consider the case when the nanohydrogel contacts a still aqueous medium (Fig. 1). As the penetrant invades the nanohydrogel surface, a moving front is observed that clearly separates the unsolvated glassy polymer region ahead of the front from the swollen and rubbery gel phase behind it.[40] Just ahead of the front, the presence of solvent plasticizes the polymer and causes it to undergo a glass to rubber transition.[41] Now the following possibilities arise:

i. If the glass transition temperature of the polymer (T_g) is well below the experimental temperature, the polymer will be in the rubbery state and polymer chains will have a higher mobility that allows an easier penetration of the solvent.[42] This clearly results in a Fickian diffusion (Case I) which is characterized by a solvent diffusion rate; R_{diff}, slower than the polymer relaxation rate, R_{relax} ($R_{\mathrm{diff}} \ll R_{\mathrm{relax}}$).

ii. If the experimental temperature is below T_g, the polymer chains are not sufficiently mobile to permit immediate penetration of the solvent in the polymer core. This gives rise to a nonFickian diffusion process which indcludes Case II diffusion and anamalous diffusion depending on the relative rates of diffusion and chain relaxation (for Case II, $R_{\mathrm{diff}} \gg R_{\mathrm{relax}}$ and for anamolous, $R_{\mathrm{diff}} \sim R_{\mathrm{relax}}$).

Different possibilities of diffusion processes are depicted in Figure 1(a–c), respectively.

Effect of nanohydrogel composition on swelling

Macromolecular hydrogels generally consist of hydrophilic (and/or hydrophobic) components
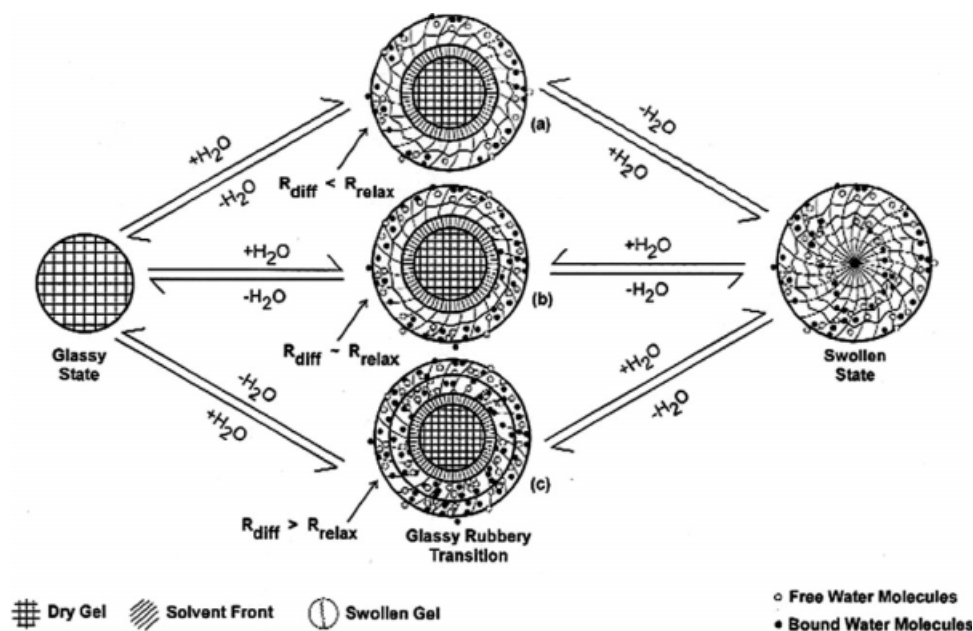
Figure 1 A hypothetical model depicting (a) Fickian, (b) Anomalous, and (c) nonFickian behavior.

crosslinked with a suitable crosslinking agent. Apart from the chemical functional of the hydrogel, the swelling of hydrogel network is also regulated by the physical forces and subsequent elastic responses of the constituent macromolecular chains of the matrix. According to Flory's swelling theory, the following equation can be given:

$$Q^{5/3} = \left[\frac{\left\{ (i/2V_N . S^{1/2}) + (1/2 - X_1)/V_1 \right\}}{(V_e/V_\sigma)} \right] \quad (9)$$

where, i/V_N is the concentration of the fixed charge referred to unswollen network, S is ionic concentration in the external solution, $(1/2 - X_1)/V_1$ is the affinity of hydrogel for water, and V_e/V_σ is the crosslinked density of the hydrogel. The earlier equation reveals that swelling ratio has direct relations to ionic osmotic pressure, crosslinked density and the affinity of hydrogel for water. Therefore, the swelling of the hydrogel can be controlled by varying its chemical composition.

Effect of polyvinyl alcohol

When nanohydrogel film was made with native PVA, it was thin, transparent, low in water sorption capacity, weak in mechanical strength, and the film reached the equilibrium swelling within half an hour. Thus, the film did not show gradual swelling with time (Fig. 2) which is an essential prerequisite for drug delivery application.

When the concentration of PVA varies in the range 0.75–1.50 g, the swelling ratio also changes appreciably. It is observed that, initially, the swelling

ratio increases while in the later course, it constantly decreases. The results (Fig. 2) also reveal that at higher content of PVA, the equilibrium swelling is attained earlier in comparison to the nanohydrogel with low PVA contents. The results can be explained by the fact that an increasing proportion of PVA results in a greater hydration of its chain because of the hydrophilic nature of PVA. However, beyond an optimum concentration (1.0 g), the decrease
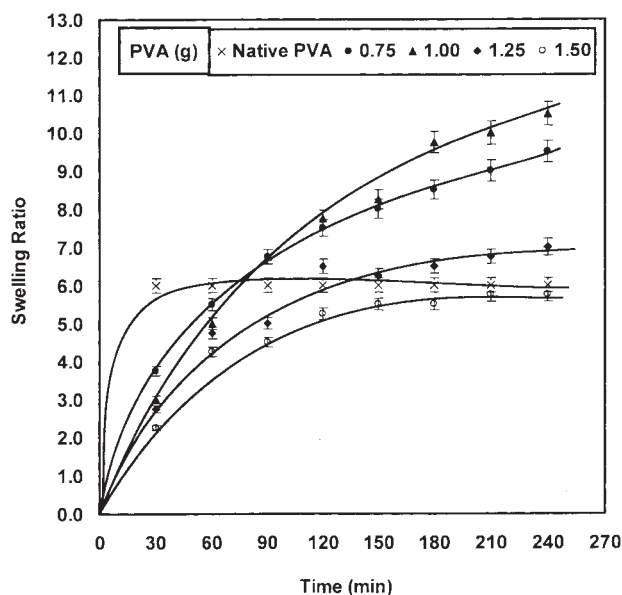

Figure 2 Effect of PVA content of the network on its swelling at fixed composition of the nanohydrogels [AA] = 21.87 mM, [MMA] = 9.30 mM, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, pH = 7.0, Temp. = 27 ± 0.2°C, Thickness = 0.068 cm.
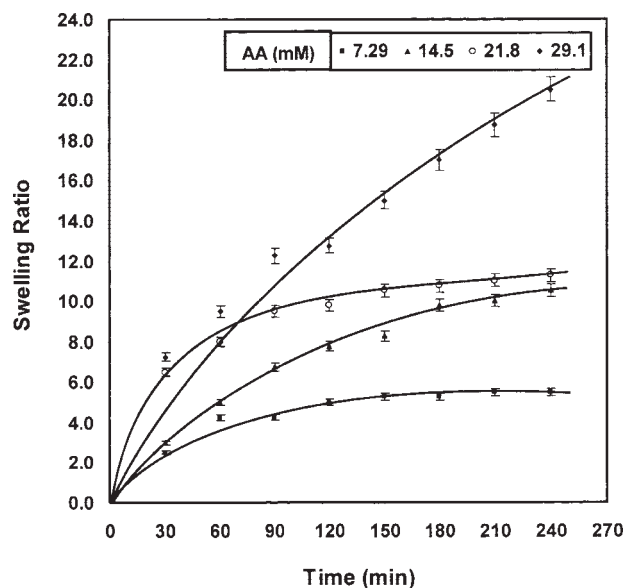
Figure 3 Effect of AA content of the network on its swelling at fixed composition of the nanohydrogels [AA] = 1.00 g, [MMA] = 9.30 mM, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, pH = 7.0, Temp. = 27°C ± 0.2°C, Thickness = 0.068 cm.

observed in the swelling ratio is due to much greater compactness of the gel, which inhibits diffusion of penetrant water molecules into the gel matrix. The arrival of equilibrium swelling of nanohydrogel at earlier times at higher PVA concentration may be due to a slow relaxation of PVA chains with obviously leads to a restricted penetration of water molecules. This clearly brings about in an early arrival of equilibrium swelling of the nanohydrogel. It was also observed that below 0.75 g of PVA, no nanohydrogel formation occurred.

Effect of acrylic acid

Acrylic acid, being an ionic monomer is expected to exert a great influence on the swelling profiles of gel as an increase in its concentration in the feed mixture could result in a significant enhancement in ionic nature of the end-polymer. In this study the concentration of acrylic acid has been varied in the range 7.29–29.1 mM and the results are shown in Figure 3 which clearly reveal that the swelling ratio constantly increases with increasing concentration of acrylic acid. The observed increasing swelling with increasing polyacrylic acid content may be attributed to the fact that with increasing number of carboxyl anions in the PAA segments, repulsion forces become more and more pronounced, thus causing a rapid and larger relaxation of network chains. This, in turn, widens the mesh sizes of the gel and, therefore, the swelling ratio increases.

Effect of methyl methacrylate

An effective route to bring about the desired modification in the sorption as well as mechanical properties of a polymer is by introduction of a hydrophobic monomer into the hydrophilic system. This normally results in a change in the maximum hydration and diffusion of the swelling agent into the matrix as well as the organization of water molecules depending on the chemical composition and the distribution of the hydrophobic monomeric units along the macromolecular chains.[43] For instance, the water gain property of a polymer of 2-hydroxyethyl methacrylate was affected by means of the introduction of a hydrophobic monomer such as furfurylacrylate.[44] Similarly, inclusion of a hydrophobic crosslinker into the polymer matrix has also been attempted for altering physical properties of the polymer.[45] The effect of increasing concentration of MMA on the swelling behavior of nanohydrogel has been examined by varying concentration in range 4.6–18.6 mM in the feed mixture of the nanohydrogel. The results (Fig. 4) show that when the amount of MMA increases in feed mixture, the swelling of the nanohydrogel constantly decreases. The results can be explained by the fact that MMA is hydrophobic monomer and when the amount of MMA increases in the nanohydrogel, hydrophobicity of nanohydrogel increases, which reduces the diffusion of water molecules in the gel.
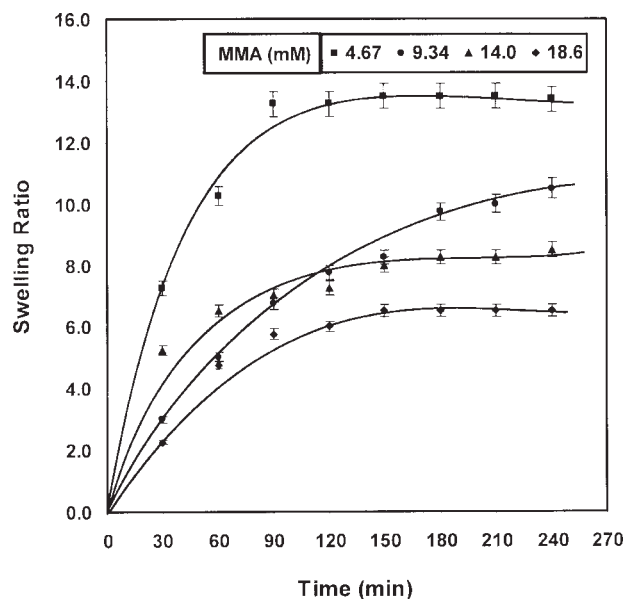

Figure 4 Effect of MMA content of the network on its swelling at fixed composition of the nanohydrogels [PVA] = 1.0 g, [AA] = 21.87 mM, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, pH = 7.0, Temp. = 27°C ± 0.2°C, Thickness = 0.068 cm.
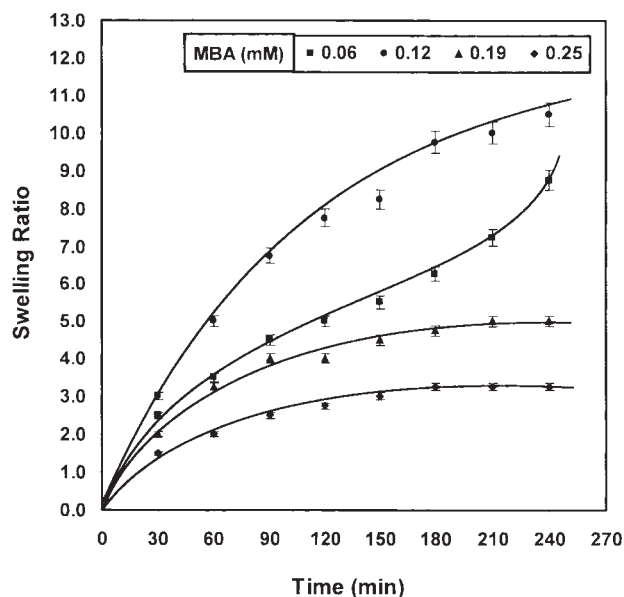
Figure 5 Effect of MBA content of the network on its swelling at fixed composition of nanohydrogels [PVA] = 1.00 g, [AA] = 21.87 mM, [MMA] = 9.30 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, pH = 7.0, Temp. = 27°C ± 0.2°C, Thickness = 0.068 cm.

Effect of crosslinker

The influence of increasing crosslinker content in the nanohydrogel on the swelling behavior was investigated by employing different amounts of crosslinking agent (MBA) while in network preparation. When MBA is varied in the concentration range 0.06–0.25 mM (Fig. 5) in the feed mixture of the gel, it is observed that from 0.06 to 0.12 mM, the swelling ratio increases while after 0.12 mM, the swelling ratio constantly decreases. The reasons for the observed initial increase may be explained by the fact that in the initial but small range of MBA, crosslinks are developed in the matrix which results in an increasing water storage capacity of the gel. This obviously gives rise to an increasing swollen gel with increasing swelling ratio. However, the decreased swelling beyond 0.12 mM is quite expected as much increased number of crosslinks makes nanohydrogel denser and as a consequence, the water permeation becomes increasingly difficult through reduced mesh sizes. The authors have noticed similar type of results earlier also.[46]

Some workers[47] reported an increase in glass transition temperature (T_g) of the polymer with increasing crosslink density, and thus, a glassy nature of the matrix does not permit loosening of the macromolecular chains, which results in lower water sorption.

Effect of pH

The role of pH in affecting the swelling characteristics of nanohydrogels is of great practical signifi-

cance, particularly when the nanohydrogel incorporates ionic polymer segments.[48] In the present study, since the nanohydrogel contains copolymeric chains of AA and MMA, the nanohydrogel is expected to exhibit a high pH dependent swelling. The effect of pH on the swelling ratio of the nanohydrogels has been investigated by varying the pH of the swelling medium in the range 2.0–11.0. The results are depicted in Figure 6, which clearly reveal that the degree of water sorption constantly increases with increasing pH of the swelling medium. One more notable point is that the increase in swelling ratio becomes more prominent only after pH 9.0.

The results can be explained by the fact that pK_a value of PAA is 4.7[49] and, therefore, above pH 4.7, the carboxylic group (unesterified and produced by hydrolysis of ester) of the polymer will be present as carboxylate ion (COO⁻), thus, producing repulsive forces among the ionic polymer segments. Because of this repulsion, the macromolecular chains of nanohydrogels will stretch and the free volumes available within the nanohydrogel widen. This clearly results in a larger swelling ratio. Similar larger water sorption at higher pH has also been reported by other workers.[50]

It has also been found that at pH 2.0, the swelling is substantially reduced. This may be due to the compact arrangement of nanohydrogel chains, resulting from the strong interaction between PVA and poly(AA-*co*-MMA) polymeric segments because of formation of hydrogen bonds between carboxylic
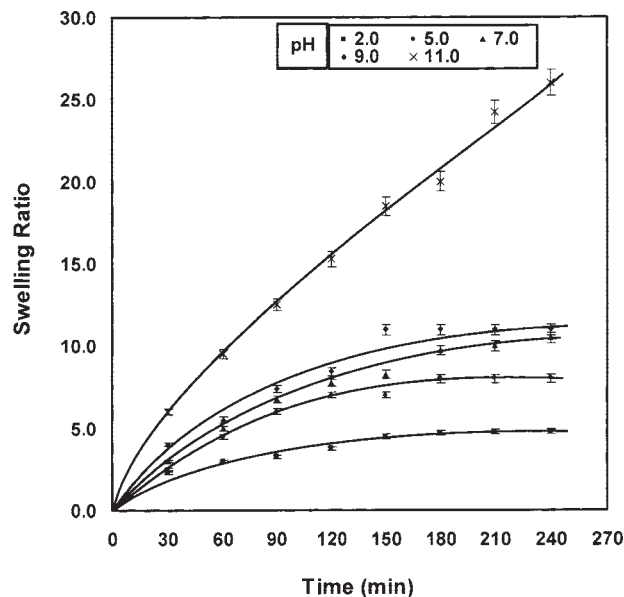

Figure 6 Effect of pH on swelling medium on equilibrium swelling at fixed composition of nanohydrogels [PVA] = 1.00 g, [AA] = 21.87 mM, [MMA] = 9.30 mM, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, Temp. = 27°C ± 0.2°C, Thickness = 0.068 cm.
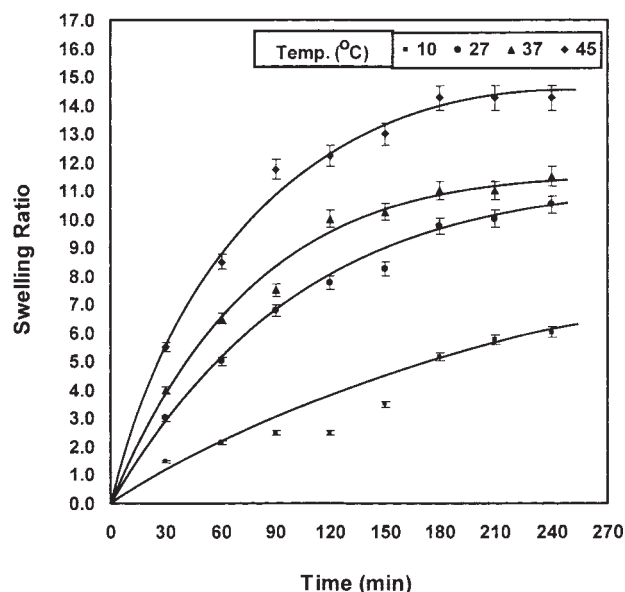
Figure 7 Effect of temperature on swelling medium at fixed composition of nanohydrogels [PVA] = 1.00 g, [AA] = 21.87 mM, [MMA] = 9.30 mM, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, pH = 7.0, Thickness = 0.068 cm.

groups (COOH) of PAA. This compactness of network also results in reluctance of the matrix chains towards relaxation and, therefore, an equilibrium swelling is attained at much earlier time. On the other hand, at pH 11.0, where the swelling is much greater, an equilibrium swelling is also noticed at later times which are due to the reason that at later times, the nanohydrogel chains might have relaxed so much that there is no further scope for more relaxation and as a consequence, an equilibrium swelling is attained.

Effect of temperature

The temperature of the swelling medium is an important parameter that also affects the swelling pattern of nanohydrogel. In the present work, the effect of temperature on the swelling ratio of the nanohydrogel has been investigated by varying in the range 10–45°C. The results are depicted in Figure 7, which clearly indicates that both the swelling rate and swelling ratio increase with an increase in temperature. The results are quite expected and may be attributed to the fact that with rising temperature, the segmental mobility of the nanohydrogel network also increases which consequently widens free volumes in the nanohydrogel accessible to penetrant water molecules. This clearly explains the increased swelling of the nanohydrogels.

To have a more quantitative insight into the temperature effects, the Gibbs-Helmholtz equation[51] can be applied, according to which

$$\frac{d\ln(W_\infty)}{d(1/T)} = \frac{-\Delta H_m}{R} \quad (10)$$

where, R is a gas constant and ΔH_m is the enthalpy of mixing between the dry polymer and an infinite amount of water. When W_∞ is plotted against equal swelling temperature ($1/T$), a straight line with a negative slope is obtained (Fig. 8) which means an endothermic process. The value of ΔH_m has been calculated to be 6.33 kJ/mol.

Effect of electrolyte

Theoretical[52] as well as experimental[53] considerations have established that a balance between the osmotic pressure and the polymer elasticity sets the physical dimensions of nanohydrogels. The osmotic pressure results from a net difference in concentrations of mobile ions between the interior of the gel and the exterior solution. Increasing the ionic concentration in bathing medium reduces the mobile ion concentration difference between the polymer gel and the external solutions (osmotic swelling pressure) and hence the gel volume is reduced, i.e., the gel shrinks. Although there are various theories and models, which can predict the equilibrium swelling response of nanohydrogels to change in ionic strength, however, Donnan membrane equilibrium theory can well interpret the results. According to this theory, when a gel is placed in contact of a liquid the solvent chemical potential μ, in both the gel and the solution phase, must be equal at equilibrium.
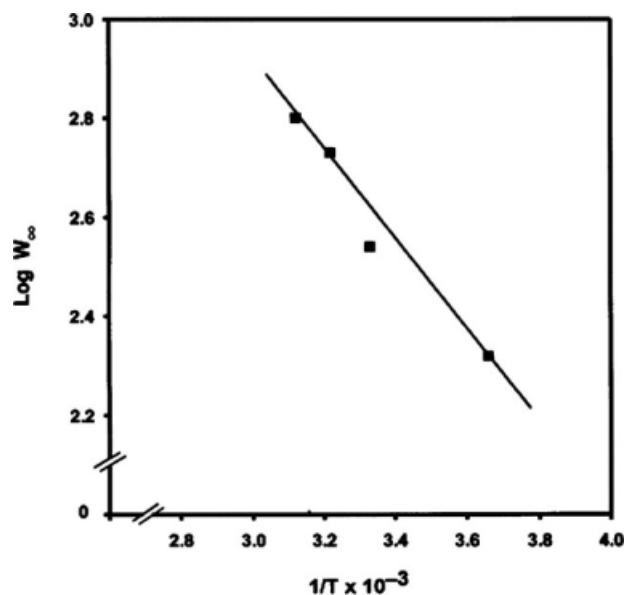

Figure 8 A plot drawn between $1/T$ and ln W_∞ for evaluating enthalpy of mixture ΔH_m.
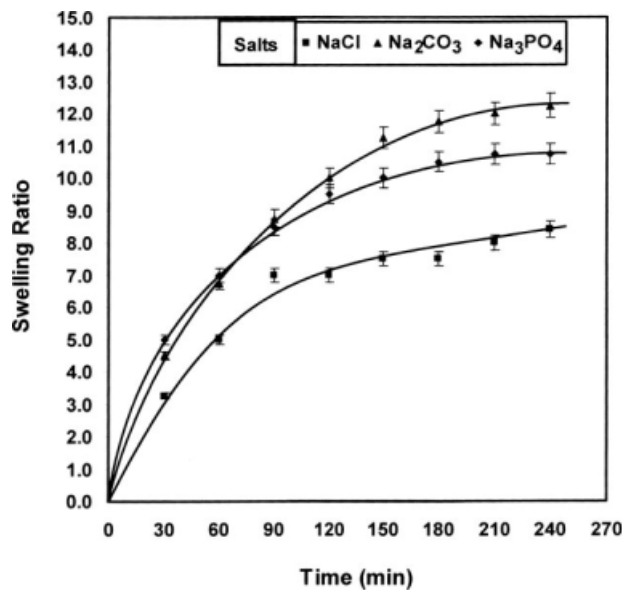
Figure 9 Effect of Ionic concentration on swelling medium at fixed composition of nanohydrogels [PVA] = 1.00 g, [AA] = 21.87 mM, [MMA] = 9.30 mM, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, pH = 7.0, Temp. = 27°C ± 0.2°C, Thickness = 0.068 cm.

$$\Delta\mu_1^g = \Delta\mu_1^s \tag{11}$$

where, the superscripts g and s represent the gel and the solution phase, respectively.

In terms of osmotic pressure, π, eq. (11) can be written as

$$\pi = \frac{\left(\Delta\mu_1^g - \Delta\mu_1^s\right)}{V_1} = 0 \tag{12}$$

where, V_1 is the molar volume of the solvent. Osmotic pressure π of the gel determines whether the gel will expand or shrink. In the case of an ionic system, the osmotic pressure is mainly contributed by π ions, which are caused by the counter ion difference between the gel and the outer solution. Now, avoiding ion-ion, ion-solvent and ion-polymer interaction, the above eq. (12) may be written as

$$\pi_{ion} = RT \sum_i \left(C_i^g - C_j^s\right) \tag{13}$$

where, C_i is the mobile ion concentration of species i and the superscripts "g" and "s" represent gel and solution phases, respectively. The earlier equation implies clearly that the greater the difference between the concentration of mobile ions inside and outside the gel, the greater would be the osmotic pressure and larger would be the swelling of nanohydrogel.

In the present investigation, the relative effects of added anions on the degree of water sorption by

nanohydrogel have been investigated by adding sodium salts of Cl^-, CO_3^{2-}, and PO_4^{3-} ions into the nanohydrogel system at equimolar concentration (0.1M). The results are shown in Figure 9 which indicates that equilibrium swelling of the nanohydrogel increases up to CO_3^{2-} ion after that a fall in swelling is noticed. This can be explained by the fact that when number of charges increases from Cl^- to CO_3^{2-} ion, more repulsion is produced within the gel due to penetration of added anions into the gel. However, in the case of PO_4^{3-} ion, the observed lower swelling is due to the reason that being largest in size, the PO_4^{3-} ions may not diffuse into the gel, thus, reducing the osmotic pressure (π_{ion}) which consequently causes a fall in the swelling ratio.

Effect of pH and acrylic acid on swelling

The dependence of equilibrium swelling on pH at different acrylic acid concentration is illustrated in Figure 10. The equilibrium swelling of the nanohydrogels increased with increasing pH of swelling medium and increasing amount of acrylic acid content in the gel. The difference in swelling degree in various pH media may be attributed to the extent of hydrogen bonding established between PVA and PAA chains in the polymer networks. At low pH, the nanohydrogels form compact structure composed of hydroxyl groups of PVA and carboxyl of PAA, resulting in decrease in equilibrium swelling. At high pH, increase in the concentration of PAA content, increases equilibrium swelling of gel due to
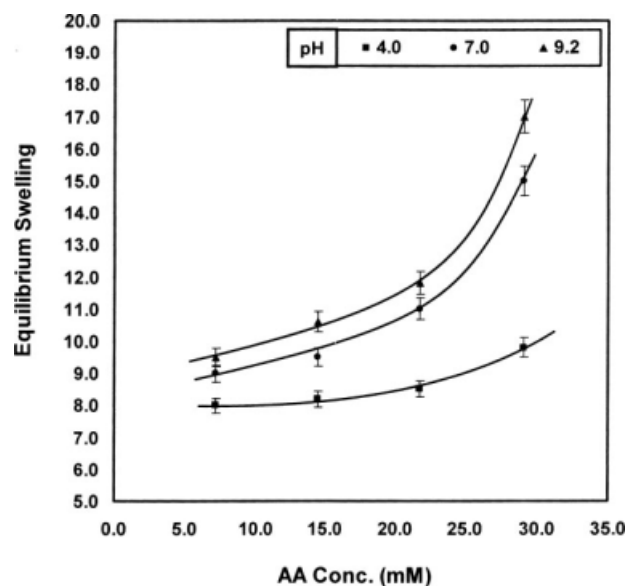

Figure 10 Effect of pH on equilibrium swelling in different concentrations of AA at fixed composition of nanohydrogels [PVA] = 1.00 g, [MMA] = 9.30 mM, [MBA] = 0.12 mM, [KPS] = 0.36 mM, [MBS] = 4.04 mM, Temp. = 27°C ± 0.2°C, Thickness = 0.068 cm.

enhanced repulsion between the carboxylate ions of PAA chains generated due to greater dissociation of COOH groups at higher pH. Similar type of observation was found in case of polyacrylic acid-chitosan hydrogel.[54]

Analysis of kinetic data

Dynamics of water uptake process is dependent on the chemical architecture of the gel which overall influences mechanism of water transport within the swelling network. In the present study also, the values of swelling exponent "n" and diffusion constant "D" have been determined from Ficks equations described earlier in the text and the calculated values at varying chemical composition of the gel are summarized in Table II.

The results clearly reveal that in most of the cases, the value of "n" lies between 0.50 and 1.0, which indicates for an anomalous type of swelling behavior. As mentioned earlier, the anomalous (or non-Fickian) mechanism is obtained when the rate of diffusion of water molecules and that of chain relaxation becomes almost equal. In the present work because of grafted nature of the nanohydrogel and presence of hydrophobic segments in the copolymer chains, the rate of relaxation of network chains may slow down and come to the level of diffusion of water molecules into the gel and, thus, results in an anomalous type of swelling.

It is interesting to note that a Fickian (i.e., $n = 0.50$) sorption mechanism is also achieved at the highest employed concentrations of PVA and AA, and minimum of MBA. At these concentrations, the water intake becomes diffusion controlled, i.e., of Fickian nature. The reason for the observed Fickian diffusion at these specified concentrations may be that at higher PVA and PAA contents, the network chains are held with greater hydrogen bonding and, therefore, the mesh size of the gel becomes too small to slow down the diffusion of water molecules into the matrix. This obviously makes the water-sorption process as diffusion controlled. Similarly, at low crosslinker content, the crosslink density may be so small that the network chains relax fast and frequently in comparison to diffusion rate of water molecules. This also explains diffusion controlled (i.e., Fickian) nature of water sorption process.

CONCLUSIONS

When macromolecular chains of poly(methyl methacrylate-co-acrylic acid) are grafted onto polyvinyl alcohol using a redox system, a grafted nanohydrogel is produced which structurally contains hydrophobic nanodomains of polymethyl methacrylate and display interesting water sorption properties.

The grafting parameters such as % grafting yield, % grafting efficiency and rate of grafting increase with increasing feed concentrations of polymer, monomers and crosslinking agent.

The water intake capacity of prepared grafted nanohydrogel varies significantly with chemical composition of the gel. In the case of PVA and crosslinking agent (MBA) the swelling ratio initially increases with increasing concentrations in the early range while at higher concentration, a fall in swelling ratio is noticed. The increase in concentration of ionic monomer (acrylic acid) brings about a constant increase in swelling ratio of the gel while with increasing concentration of the hydrophobic monomer (MMA), just reverse trend is observed.

The water imbibitions capacity of the grafted nanohydrogel increases when pH of the swelling media varies in the range 2.0–11.0. However, a significant rise in swelling is seen only beyond pH 9.0. The swelling is also favored by increasing temperature of the swelling media thus indicating an endothermic nature of the water sorption process.

The presence of salts in the swelling bath also influences water sorption capacity of the nanohydrogel. In the case of Cl^- and CO_3^{2-} ions an increase in swelling is observed while a fall in water sorption is noticed when trivalent phosphate ions are present in the swelling bath.

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