

A Comparative Study of Swelling Properties of Hydrogels Based on Poly(acrylamide-co-methyl methacrylate) Containing Physical and Chemical Crosslinks

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ABSTRACT: Poly (acrylamide-co-methyl methacrylate) hydrogels of different ratios were prepared by using chemical and physical crosslinks to study the effect of nature of crosslinks on swelling behavior of hydrogels. The chemically crosslinked gels were prepared by using *NN'*-methylene bis acrylamide, while physically crosslinked hydrogels were prepared by precipitation polymerization method, using dioxane as solvent. Detailed swelling kinetics such as swelling ratio, transport exponent n , diffusion coefficient D and the effect of pH on equilibrium swelling studies. The study revealed that the nature of crosslinks alter the swelling characteristics of the hydrogel. In chemically crosslinked

hydrogels the water transport is Fickian in nature, while in the case of the physically crosslinked hydrogels the water transport mechanism is anomalous indicating major change in relaxation mechanism due to nature of crosslinks. The results also indicate that with increasing acrylamide content the swelling ratio of the hydrogels were also increased, but the transport exponent n remains nearly constant. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 779–786, 2003

Key words: hydrogels; crosslinking; diffusion; swelling; relaxation

INTRODUCTION

Hydrogels are crosslinked polymeric network, hydrophilic in nature, which can absorb large amounts of water or biological fluids; but are insoluble. The hydrophilicity is due to the presence of hydrophilic groups such as alcohols, carboxyls, and sulphonic acid. Their low interfacial tension and higher permeability to small molecules, soft and rubbery nature make hydrogels well suited biomaterials, for applications such as contact lenses, artificial organs, tissue substitutes, bone in growth sponge, absorbent coating for blood perfusion, hemodialysis membranes, plastic surgery, and soft tissue replacements. To form a gel the monomer must be crosslinked with crosslinking agents such as ethylene glycol dimethacrylate (EGDMA), *NN'*-methylene bisacrylamide (*NN'*-MBA), 3-oxapentamethylene dimethacrylate, depending on monomer type.

Polyacrylamide (PAAm) based hydrogels are blood compatible biomaterials that find applications in coating of catheters and controlled release devices. PAAm hydrogels have sufficient hydrophilicity but are low in hydrolytic stability and tensile strength. Many attempts have been made to improve the mechanical

behavior of the hydrogels by modifying the method of synthesis,^{1–4} such as chemically crosslinking with crosslinking agents or the copolymerization with a second monomer, which is more hydrophobic than PAAm; such as sodium methacrylate¹ (SMA), butyl methacrylate² (BMA), ethyl methacrylate³ (EMA), and sodium acrylate⁴ (SA).

Knowledge relating to the transport of water in polymeric hydrogels is needed to improve the applications of these materials in implantable drug delivery systems. The complex water sorption kinetics of glassy polymers has attracted substantial theoretical and experimental interest over the decades due to its implications for understanding solvent transport and relaxation processes in the polymers.⁵ Work in this area has also been driven by the desire to use as glassy polymers as the rate-controlling agent in delivery systems for bioactive compounds.⁶ In monolithic delivery systems, the drug is initially dispersed or dissolved in the glassy polymer, and the solute release rate may be controlled by the polymer swelling rate and the velocity of the moving solvent front.^{7,8}

Sorption experiments are the simplest and commonest methods to investigate the diffusion characteristics. A glassy initially isotropic polymer sample becomes rubbery during solvent sorption and undergoes complex dimensional change for slab geometry. Shortly after exposure to the solvent, sharp penetration fronts develop that advance towards the center of the sample. These penetration fronts are typically assumed to

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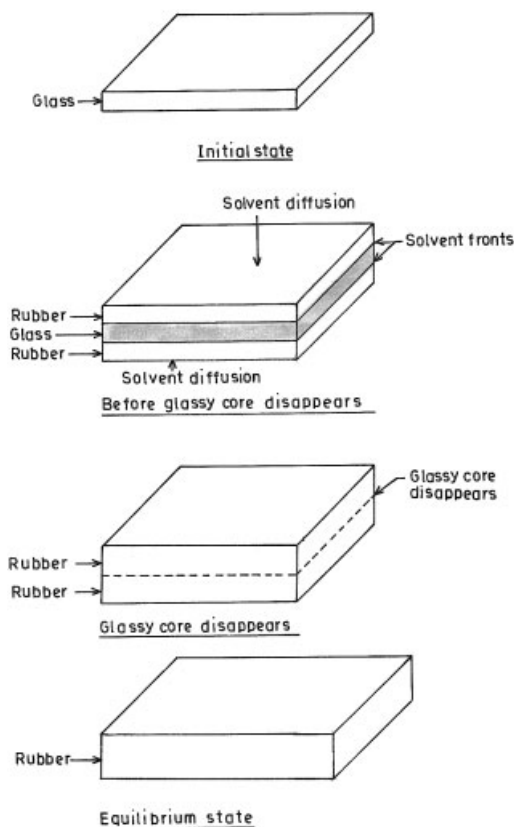


Figure 1 The schematic representation of the dimensional change that occurs upon swelling a glassy polymer sample in water.

be the point of the glass-to-rubber transitions. Schematic representation of the dimensional changes occurring in hydrogel at various stages of swelling are shown in Figure 1. Several research groups have noted that as long as a glassy core of polymer is present, the outer, solvent-swollen rubbery layer swells only in the direction of diffusion, as the glassy core resists stresses tending to cause isotropic expansion of the sample.⁹ Stresses in the glass have been postulated by several authors to significantly affect the sorption kinetics.^{10,11} Copolymerization reaction of poly (acrylamide-*co*-methyl methacrylate) (AAM-*co*-MMA) has been studied by various researchers.^{12,13} Parameters like reactivity ratios, effect of copolymer compositions on the molecular weight, dispersion stability, and the effect of solvent on copolymer composition were studied.

Most of the studies on hydrogels center on chemically crosslinked hydrogels. However, hydrogels can also be prepared by using physical crosslinks formed by incorporation of a hydrophobic monomer^{14,15} in a limited amount in the polymer chain. The difference in molecular structure of hydrogels prepared by chemical and physical crosslinks are illustrated in Figure 2. Physically crosslinked hydrogels were prepared based on AAm and MMA, which was further subjected to Hofmann degradation reaction to partially convert the

amide group into the vinyl amine group.¹⁴ But in the above work only water content of resulting hydrogel was determined, and no efforts were made to determine its swelling kinetics. Because two methods of AAm and MMA-based hydrogels are used by researchers; we thought it would be appropriated to investigate the difference in their swelling behavior from end use point of view.

The aim of present investigation was to compare the swelling kinetics of hydrogels with various monomer ratios prepared by using chemical and physical crosslinks because for hydrogels swelling characteristics are very important. The hydrogels of (AAM-*co*-MMA) were synthesized by two methods: (1) chemical crosslinked hydrogels were prepared by the chemically crosslinking of AAm with *NN'*-methylene bis acrylamide (*NN'*-MBA) as a crosslinking agent. (2) Physically crosslinked hydrogels were prepared by free radical precipitation polymerization reaction, using AAm and MMA in various ratios by the method used by Yamamoto and Sefton.¹⁴ The effect of the nature of crosslinks on dynamic swelling kinetics was studied. The transport exponent n , which indicates the mechanism of water transport and diffusion coefficient, were calculated. The rate to approach to equilibrium was also investigated.

EXPERIMENTAL

Raw materials

Methyl methacrylate from (CDH New Delhi) was purified by washing with 4% sodium hydroxide to remove the inhibitor. Acrylamide (SDS, Bombay) was

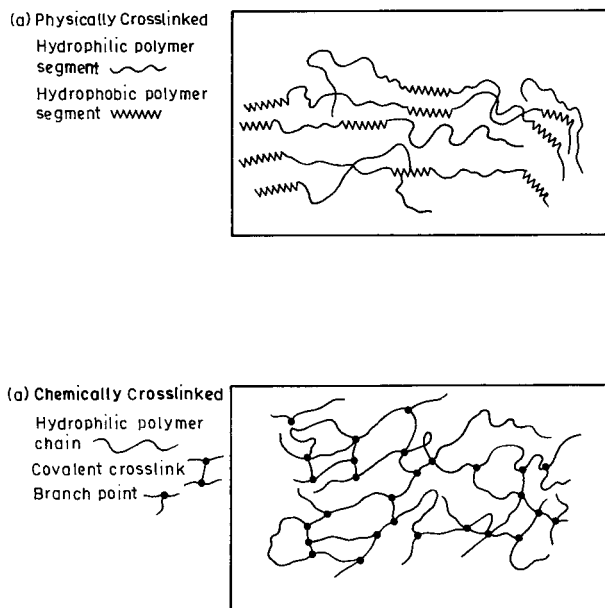


Figure 2 Systematic representation of molecular structure of (a) physically and (b) chemically crosslinked hydrogels.

TABLE I
Feed Composition of Chemically Crosslinked Poly(acrylamide-co-methylmethacrylate) Hydrogels

Sample designation	Monomer feed ratio AAm/MMA	Weight of AAm (g)	Weight of MMA (g)	Benzoyl peroxide (g)	NN'-MBA (g)	Solvent 50% aq dioxane
C ₁	40/60	3.408	7.200	0.068	0.034	20 mL
C ₂	50/50	4.260	6.000	0.085	0.043	20 mL
C ₃	60/40	5.112	4.800	0.102	0.051	20 mL
C ₄	80/20	6.816	2.547	0.136	0.068	20 mL

recrystallized from methanol. Benzoyl peroxide (CDH, New Delhi) was recrystallized from a chloroform/methanol mixture. Dioxane (Qualikems, New Delhi), Petroleum ether (S.D. Fine, Mumbai) and NN'-methylene bis acrylamide (BDH, England) were used as received. Distilled water was used for all the experiments.

Synthesis of hydrogels

The chemically and physically crosslinked hydrogels were prepared by using different ratios of AAm and MMA, along with other chemicals that are shown in Tables I and II, respectively. The chemically crosslinked hydrogels containing 40, 50, 60, and 80% AAm ratios were designated by C₁, C₂, C₃, and C₄, respectively (Table I). They were synthesized by using different monomer compositions, NN'-MBA and Benzoyl peroxide (BPO). NN'-MBA and BPO were used as a crosslinker and initiator, respectively. AAm, MMA, NN'-MBA, and BPO were dissolved in 50% aqueous dioxane and the solution was heated at 80°C for 8 h. After curing, the hydrogels were initially immersed in 50% aqueous dioxane for 2 days to remove unreacted monomer.

Table II gives the details of synthesis of physically crosslinked hydrogels of 40, 50, 60, and 80% AAm ratios that are designated by P₁, P₂, P₃, and P₄, respectively. Physically crosslinked hydrogels were synthesized by radical precipitation polymerization using a method similar to that of Yamamoto and Sefton.¹⁴ Various ratios of AAm and MMA (0.12 mol in total) were dissolved in 80 mL of dioxane. Polymerization was initiated by 0.3 g (1.8 mol % of the total monomer feed) of benzoyl peroxide. The reaction was carried

out in a controlled temperature bath, with continuous stirring by a mechanical stirrer in a sealed three-neck flask under nitrogen atmosphere at 70°C. After some time turbidity develops and white precipitate starts collecting in the flask, and the reaction was carried for 4 h. The resulting hydrogel was precipitated with petroleum ether. The hydrogel was continuously stirred for 6 h in toluene and water to separate the homopolymer of PMMA and PAAm, respectively, and dried in an oven at 45°C.

Sample preparation

The chemically crosslinked hydrogels matrix were cut into smaller rectangular matrices, and the aspect ratio (length: thickness) was kept greater than 10. The thickness of the matrix was varied approximately, ranging from 0.60–4.00 mm, and finally dried under vacuum to a constant weight. The thickness of each matrix was measured at 10 points by a thickness gauge, and the mean is taken for calculation. Physically crosslinked hydrogel matrices were made by the solvent-casting method using the polymer solution in 50% aqueous dioxane. For obtaining uniform thickness of a cast film a perfectly horizontal surface was used so the casting solution does not flow under gravity after casting. This was achieved by using a wooden table fixed with one stationary and two adjustable levelling screws that was leveled by spirit level. A glass plate uniformly clamped with aluminium strips on both sides was used as a mold for casting. This mold was placed on a leveled wooden plate and the casting solution was poured at one end of the plate. The solution was then uniformly spread over the entire plate by drawing it with a smaller glass plate towards the other end.

TABLE II
Feed Composition of Physically Crosslinked Poly(acrylamide-co-methylmethacrylate) Hydrogels

Sample designation	Monomer feed ratio AAm/MMA	Weight of AAm (g)	Weight of MMA (g)	Benzoyl peroxide (g)	Dioxane (mL)
P ₁	40/60	3.408	7.200	0.3	80 mL
P ₂	50/50	4.260	6.000	0.3	80 mL
P ₃	60/40	5.112	4.800	0.3	80 mL
P ₄	80/20	6.816	2.547	0.3	80 mL

The number and thickness of strips decide the thickness of resulting matrix.

Swelling measurement

Dynamic swelling measurements were made by gravimetric measurements. The hydrogel sample was placed in a beaker and was suspended in 500 mL water at 25°C. The hydrogel sample was removed at different time intervals, quickly blotted free of surface water using filter paper, weighed on an analytical balance (accuracy ± 0.0002), and returned to the swelling medium. The swelling ratio was calculated from the equation.

$$\text{Swelling ratio} = \frac{\text{Swollen weight of the sample}}{\text{Dry weight of the sample}} \quad (1)$$

The water absorbed by the hydrated network is quantitatively represented by the equilibrium water content (EWC), the ratio of weight of water in the hydrogel to the weight of the hydrogel at equilibrium hydration, expressed as a percentage.

$$\text{EWC} = \frac{\text{Weight of water in the gel}}{\text{Total weight of the hydrated gel}} \times 100 \quad (2)$$

Data analysis

The dynamic swelling properties of a hydrogel includes the solvent sorption rate, the rate of approach to equilibrium swelling, the solvent front velocity, and the transport mechanism controlling solvent sorption. The solvent sorption rate indicates the solvent uptake per unit time, and is directly related to the equilibrium swelling degree of the hydrogel. The transport mechanism, which indicates the relative importance of diffusion and relaxation, is typically determined by fitting sorption data (for short time or $M_t/M_\infty \leq 0.6$) to the empirical expression.¹⁶⁻¹⁸

$$M_t/M_\infty = Kt^n/L_0 \quad (3)$$

where M_t is the mass of solvent absorbed at time t , M_∞ is the mass of solvent absorbed at equilibrium, K is a rate constant, n is the transport exponent, and L_0 is the initial thickness. For a slab geometry when $n = 0.50$, the process is diffusion controlled and is termed Fickian or Case I transport. Transport is assumed to be relaxation controlled (Case II) when $n = 1.0$. When the exponent n is between 0.50 and 1.0, or if the dimensional dependence deviates from the expressed by eq.

(1), the transport is termed anomalous. An observation of $n > 1$ is termed super case II.

For cases of Fickian transport, the rate to approach to equilibrium can be characterized by diffusion coefficient value D , which can be calculated for planar geometry from the equation.^{8,19}

$$M_t/M_\infty = (4/\pi^{0.5})(Dt/L_0^2)^{0.5} \quad (4)$$

The appearance of the dimensionless time group (Dt/L_0^2) in these equations indicates that the plot of M_t/M_∞ vs. \sqrt{t}/L_0 will yield a single master curve (referred to as a "diffusion plot") that is independent of sample dimension and initially linear. The thickness dependence is a valuable means of identifying the transport mechanism. Because case II transport will scale with t/L_0 and anomalous transport may have a complex dimensional dependence.

RESULTS AND DISCUSSION

The dynamic swelling behavior of PAAm hydrogels are important in biomedical and pharmaceutical applications. Control of these properties is particularly important for polymer drug delivery systems and a hydrogel absorbent. The swelling kinetics depend upon the chemical composition and the method of preparation of the hydrogels. The dynamic swelling behavior of the PHEMA-based hydrogel have been widely studied.^{20,21} However, limited work has been on PAAm-based hydrogels,^{3,4} and swelling kinetics of AAm-co-MMA-based hydrogels has not been reported yet to the author's knowledge.

In the present study the dynamic swelling behavior of chemically and physically crosslinked poly(AAm-co-MMA) hydrogel has been investigated. The effect of copolymer composition and sample thickness on the swelling kinetics has also been examined.

Effect of hydrogel composition

Table III shows the swelling characteristics of the chemically crosslinked C_1 , C_2 , C_3 , C_4 and physically crosslinked P_1 , P_2 hydrogels. All the hydrogel samples were prepared of same thickness, approximately 1.60–1.64 mm, by the method described in the previous section. Figure 3 shows a plot between swelling ratio and \sqrt{t} for poly(AAm-co-MMA) hydrogels at 25°C, to study the effect of AAm content on swelling. The equilibrium swelling ratio of chemically crosslinked hydrogels from 3.10 to 3.50 as the AAm content increases from 40 to 50%, which is marginal, but when the AAm content was raised from 50 to 80%, the swelling ratio increased considerably from 5.46 to 14.10. This clearly indicates that swelling ratio increases substantially for higher AAm content hydrogels. The swelling ratio of physically crosslinked hy-

TABLE III
Swelling Characteristics of Chemically and Physically Crosslinked Poly(AAm-co-MMA) Hydrogels

Hydrogel type	Equilibrium water content (EWC)	Swelling ratio	Transport Exponent (<i>n</i>)	Log <i>K</i>	Diffusion coefficient (cm ² min ⁻¹)
C ₁	67.96	3.10	0.50	-0.56	1.06 × 10 ⁻⁵
C ₂	71.77	3.50	0.51	-0.61	1.03 × 10 ⁻⁵
C ₃	89.90	5.46	0.51	-0.58	1.07 × 10 ⁻⁵
C ₄	91.20	14.10	0.53	-0.62	1.04 × 10 ⁻⁵
P ₁	50.87	2.30	0.83	-1.40	^a —
P ₂	81.70	5.24	0.65	-1.12	^a —

Samples thickness were approximately 1.60–1.64 mm.
^a *D* value were determined only for Fickian case using eq. (4)

drogels is also shown in Table III, which increases from 2.30 to 5.24 as the AAm content in hydrogel increases from 40 to 50%. The hydrogels having more than 50% AAm content were not used in swelling studies because of they were water soluble. From Table III it can be concluded that swelling ratio increases with increase in AAm content, which is mainly due to increased proportion of more effective binding sites in the polymer chain. The equilibrium water content of these hydrogels was calculated by eq. (2). The results are given in Table III. The water content of the hydrogel prepared by Yamamoto and Sefton was 44 for 40% AAm content hydrogel, while in the present study the swelling ratio of the same composition P₁ hydrogel is found to be 50.87, which is quite close. The transport mechanism of the same C₁, C₂, C₃, C₄, and P₁, P₂ hydrogels were also studied; by fitting swelling data to empirical eq. (3) to calculate the transport exponent *n* and log *k*. As described earlier, the value of *n* gives

the indication of the nature of transport mechanism operating in the system. The transport exponent *n* and log *K* were calculated by plotting data log *M_t* / *M_∞* vs. log *t* using linear regression. *K* is the rate constant characteristics of the polymer solvent system. The value of *n* for C₁, C₂, C₃, and C₄ hydrogels was found at approximately 0.50, as shown in Table III. It shows the diffusion is Fickian in nature. The value of *n* and log *K* are also listed in Table III. The same swelling data of C₁, C₂, C₃, and C₄ hydrogels are plotted on the diffusion plot, as shown in Figure 4. The diffusion plot is between *M_t* / *M_∞* and *t*^{0.50} / *L*₀. All the samples initially followed the same common curve, called the diffusion curve. This portion of the curve can be characterized by diffusion coefficient. Diffusion coefficient *D* was calculated by eq. (5). The diffusion coefficient value for all hydrogel samples are given in Table III. The diffusion coefficient of water in PAAm hydrogel crosslinked by NN'-MBA were determined by Candau et al.²² and Tanaka et al.²³ by two different methods using Quasi-Elastic-Light-Scattering and laser light scattering spectroscopy. They observed the *D* value in the range of 3–4 × 10⁻⁷ cm² min⁻¹.

Similarly, eq. (3) was also applied to the swelling data for physically crosslinked hydrogels P₁ and P₂.

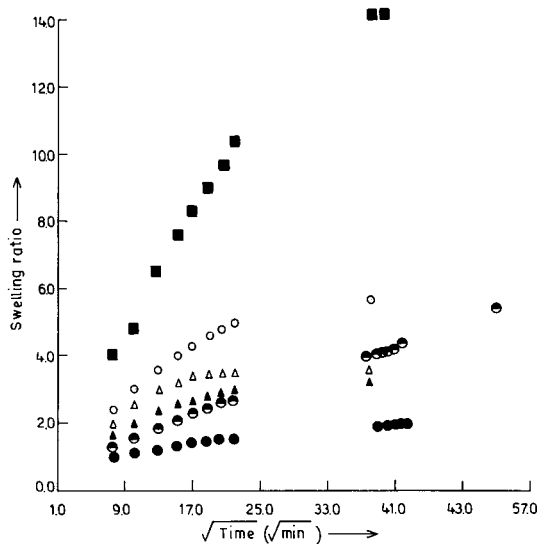


Figure 3 Water sorption rate of chemically and physically crosslinked poly(AAm-co-MMA) gels with different amounts of AAm given as a swelling ratio against the root of time (▲), C₁; (△) C₂; (○) C₃; (■) C₄; (●) P₁; (half filled, half open circles) P₂.

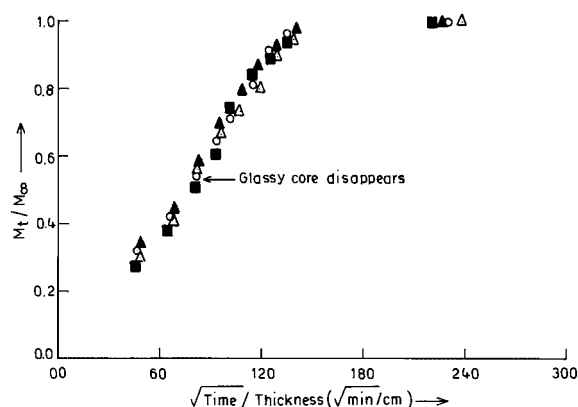


Figure 4 Diffusion plot of chemically crosslinked hydrogels. Sample thickness 1.60–1.64 (mm) (▲) C₁; (△) C₂; (○) C₃; (■) C₄.

TABLE IV
Sorption Data from Figures 5 and 6 Water Transport in Glassy Chemically Crosslinked C₂ and C₃ Hydrogels Are Diffusion Controlled

Hydrogel type	Initial thickness (mm)	Swelling ratio	Transport exponent (<i>n</i>)	Log <i>K</i>	Diffusion coefficient (cm ² min ⁻¹)
C ₂	3.04	3.67	0.50	-0.76	1.55 × 10 ⁻⁵
	2.20	3.54	0.52	-0.66	1.51 × 10 ⁻⁵
	1.54	3.68	0.50	-0.47	1.13 × 10 ⁻⁵
C ₃	2.20	6.91	0.52	-0.83	6.25 × 10 ⁻⁶
	1.58	5.71	0.50	-0.64	6.01 × 10 ⁻⁶
	1.20	5.48	0.50	-0.48	6.18 × 10 ⁻⁶

The values for *n* were 0.83 and 0.65, respectively. These values clearly indicate that the diffusion was anomalous in nature. The log *K* values were -1.40 and -1.12 for P₁ and P₂ hydrogels, respectively. Only for the Fickian transport has it been suggested that the rate of approach to equilibrium can be characterized by diffusion coefficient value *D*.¹⁰ The study revealed a considerable difference in the mechanism of transport for the AAm-co-MMA hydrogels, which is probably due to the difference in the molecular structure of hydrogels (Fig. 2). Physically crosslinked hydrogels have approximately linear structure, while chemically crosslinked hydrogels have a network-type structure, giving rise to the difference in approach to the equilibrium. The equilibrium swelling for the approximately same thickness of matrix was obtained in 25 h for chemically crosslinked hydrogel, while it took 48 h for the physically crosslinked hydrogel. The above difference in behavior is of considerable importance in controlled release applications.

Effect of thickness

To study the effect of thickness, three thicknesses for C₂ hydrogels were subjected to sorption studies and

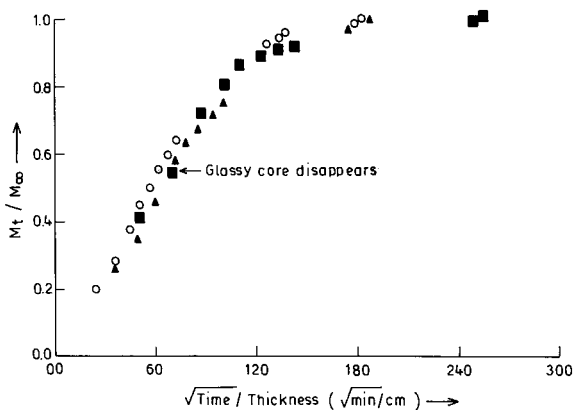


Figure 5 Water sorption kinetics of the C₂ sample as a function of thickness. A single, initially linear master curve when sorption is plotted against the square root of time indicates a Fickian transport mechanism. Initial thickness (mm): (○) 3.04; (▲) 2.2; (■) 1.54.

the results are given in Table IV. The transport exponent *n* values were 0.50, 0.52, and 0.50 for the C₂ hydrogel sample, respectively (which can be approximately taken as 0.50). For C₃ hydrogel three sample thicknesses were also used, as given in Table IV. The *n* and log *K* values were calculated from eq. (3) and results are given in Table IV. It was clear from the table that the values of all samples prepared by C₂ and C₃ hydrogels were approximately 0.50. Thus, the diffusion through the chemically crosslinked hydrogels was Fickian in nature.

The sorption data of C₂ and C₃ hydrogels were plotted on diffusion plots (*M_t/M_∞* vs. *t*^{0.50}/*L*₀), as shown in Figures 5 and 6. All samples follow a initially linear same common curve while the glassy core was present, and the value of *M_t/M_∞* was approximately up to 0.50. It shows that initially the hydrogels were of different thickness swells at the same rate. This portion of the curve can be characterized with a diffusion coefficient, which was calculated by eq. (5). The various values for diffusion coefficient for C₂ and C₃ hydrogels are given in Table IV. This same common curve can be considered to be independent of the initial thickness of the sample. After the disappearance of the glassy core, the experimental data lie above the Fickian curve due to dimensional rearrangements

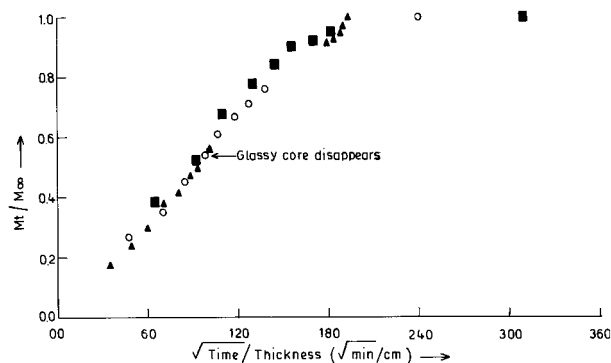


Figure 6 Water sorption kinetics of the C₃ sample as a function of thickness. A single, initially linear master curve when sorption is plotted against the square root of time indicates a Fickian transport mechanism. Initial thickness (mm): (▲) 2.20; (○) 1.58; (■) 1.20.

TABLE V
Sorption Data from Figures 7 and 8

Hydrogel type	Initial thickness (mm)	Swelling ratio	Transport exponent (n)	Log K
P ₁	1.72	2.04	0.83	-1.29
	1.24	2.14	0.83	-1.39
	0.68	2.02	0.84	-0.84
P ₂	3.80	5.03	0.62	-1.31
	1.83	5.49	0.64	-1.07
	1.07	5.19	0.63	-0.88

Anomalous water transport in glassy physically crosslinked P₁, P₂ hydrogels is observed.

(Fig. 1), and curve separately. Brien et al.²⁰ have recently shown that, after disappearance of the glassy core, the dimensional rearrangements decrease the thickness of the polymer, but increase the diffusional area of the sample. The velocity of the swelling front that separates the inner unswollen glassy regions from the outer swelling rubbery regions is important in characterizing the transport mechanism. The sorption data from Figures 5 and 6 are given in Table IV. The results show that different sample thicknesses do not affect the transport mechanism, diffusion coefficient, and equilibrium swelling ratio. The swelling results also show that the sorption rate of these hydrogels is proportional to the degree of swelling and inversely proportional to the square of the thickness. The results also show that differences in time required to swell these samples to equilibrium. The thickest sample takes the longest time to swell (approximately 49 h) and diffusion time increases with increasing thickness.

These phenomena were also examined for non-Fickian systems, so the previously described experiments were repeated for poly (AAm-co-MMA) hydrogels prepared by physical crosslinks. Three thicknesses for both P₁ and P₂ hydrogels were used as given in Table V. The transport exponent value were 0.83, 0.83, and 0.84, respectively, which can be approximately 0.83 for the P₁ hydrogel. The transport exponent n value were 0.63, 0.64, and 0.63, respectively, for P₂ hydrogels, which can be taken as approximately 0.63. The values of n for P₁ and P₂ hydrogels were between 0.50 to 1.0, which indicate that the diffusion of physically crosslinked hydrogels is anomalous in nature. The value of n is put in terms of t^n/L_0 , which now became $t^{0.83}/L_0$ and $t^{0.63}/L_0$. Graphs were plotted of M_t/M_∞ vs. $t^{0.83}/L_0$ and M_t/M_∞ vs. $t^{0.63}/L_0$ for P₁ and P₂ hydrogels, respectively, as shown in Figures 7 and 8. No significant variation with thickness was observed for transport exponent n and equilibrium swelling ratio, but the time required to swell for it is clear to reach equilibrium swelling as we increase the thickness. This is also verified by Figure 8, where the thickest matrix of thickness (3.80 mm) took 49 h to reach equilibrium swelling, which is considerably higher than

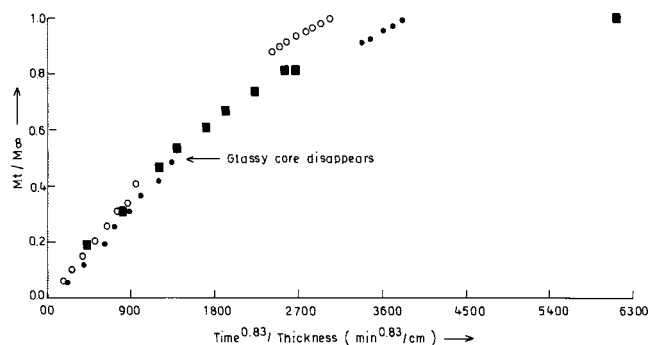


Figure 7 Water sorption kinetics of the P₁ hydrogel as a function of thickness. The transport mechanism is anomalous. Initial thickness (mm). (○) 1.72; (●) 1.24; (■) 0.68.

rest of the matrices. The sorption data from Figures 7 and 8 are listed in Table V.

Effect of pH on swelling ratio

To see the effect of pH on equilibrium swelling ratio of C₂, C₃, C₄, P₁, and P₂ hydrogels, swelling studies were conducted using different pH solutions. Swelling characteristics of these hydrogels at different pHs are shown in Figure 9. It was observed that as the pH of swelling medium increases, the equilibrium swelling ratio increased gradually for all types of hydrogels. As the AAm content in hydrogel increased the equilibrium swelling ratios also increased, at higher pH. In chemically crosslinked hydrogels not much difference was observed in the swelling ratio at the acidic medium, but at basic medium when the pH was raised to 9 the swelling ratio increased from 5.9 to 22. When the pH of the swelling medium was 12, the swelling ratio increased from 15.11 to 31.30, and at 14 pH, the swelling ratio increased from 26.76 to 36.20, respectively, with the AAm content were raised from 50 to 80%, as shown in Figure 9.

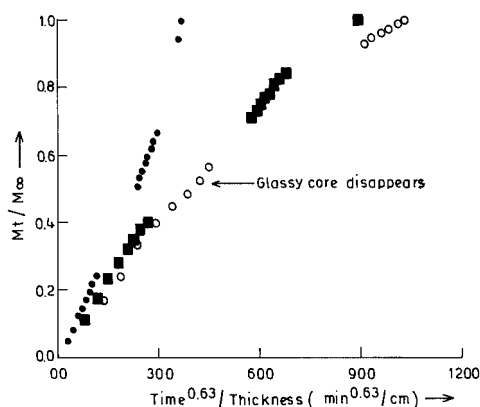


Figure 8 Water sorption kinetics of the P₂ hydrogel as a function of thickness. The transport mechanism is anomalous. Initial thickness (mm). (●) 3.80; (■) 1.83; (○) 1.07.

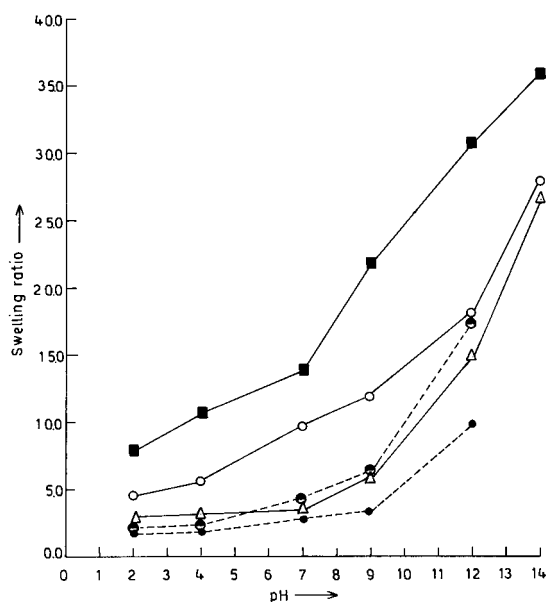


Figure 9 Swelling isotherm for hydrogels measured as a function of pH at 25°C. (Δ) C₂; (\circ) C₃; (\blacksquare) C₄; (\bullet) P₁; (half filled, half open circles) P₂.

The swelling ratio of physically crosslinked P₁, P₂ hydrogels were increased from pH 2 to pH 12, but at pH 14, the hydrogels tend to solubilize in the swelling medium. In the basic medium the swelling ratio of the hydrogel increased substantially because the amide group become more prone to hydrolysis and the acrylamide change to acrylic acid under basic conditions. The carboxylate group of acrylic acid ionized and the mutual ionic repulsion between these groups caused the molecule to adopt a greatly expanded configuration, which opened up the polymer matrix leading to higher swelling of the matrix.

CONCLUSION

From the above study the following conclusions may be drawn:

1. With an increase in the AAm content of the (AAm-co-MMA) hydrogel, the swelling ratio was increased.

2. The transport of water through chemically crosslinked hydrogels was Fickian, while for physically crosslinked hydrogels it was anomalous in nature, which indicate that the transport mechanism of the hydrogels depends upon the nature of the crosslinks.
3. It can also be concluded that the equilibrium swelling ratio of hydrogels was increased with an increase in pH of the swelling medium.

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