The effect of Crosslinking Agents on the Synthesis and Swelling of the Polymer Networks

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Summary: Polymer networks of 2-Hydroxyethyl methacrylate (HEMA) and N-Hydroxymethyl acrylamide (HMA) were prepared by varying the amount of the Ethylene dimethacrylate (EDMA) and N, N-Methylene diacrylamide (MDA) as crosslinking agents. These Polymer networks have the glassy behavior in dry state, with elasticity when they absorb certain amount of water. In both cases, the material behavior is influenced, to great extent, by the network prepared, i.e., by crosslinking reaction. It is known that the network characteristics (crosslink density, etc.) are influenced not only by the concentration of crosslinking agent, but also by its chemical structure. By varying the amount of crosslinking agents and equimolar ratio of the monomers, a wide range of networks were synthesized and the influence of the temperature and crosslinking on their swelling is discussed. A correlation between swelling data, derived from loosely crosslinked samples, led to the determination of the interaction parameters of strongly crosslinked polymer networks of series I and II has been described.

Introduction

The copolymerization is accompanied by a pronounced "gel effect". There occurs a stationary period before the formation of three-dimensional network where the ratio is independent of concentration of monomers. The rate in the region of gel effect depends upon the concentration of crosslinking agents, higher the concentration of the crosslinking agents, shorter will be the length of the stationary period. Crosslinking leads to a decrease in the mobility of growing radicals resulting in the formation of a three dimensional network [1].

A crosslinked polymer can not be dissolved completely but may swell to many times to its original volume by absorbing a liquid with which it is in contact [2]. Swelling occurs for the same reason that a linear polymer dissolves; the addition of solvent results in an increase in entropy. Swollen gel is infact an elastic rather than a viscous solution. The tendency toward swelling is opposed by an elastic refractive force arising as chains between network junctions are forced to assume elongated conformation. The equilibrium between two forces is analogous to an osmotic equilibrium, with network structure acting as solute, osmotic membrane and pressure generating devices. A gel previously swollen with pure solvent deswell to a smaller equilibrium volume when placed in contact with a polymer solution. The change in volume measures a change in activity of solution and thus the number average molecular weight [3]. The polar groups present within the network give it a hydroscopic character, so that when the gel is placed in the water or some other liquid used for swelling, there is a high concentration of polar groups within the gel as compared to that in water. Since the gel has a well kinetic network, so there is a tendency for water to diffuse to equalize the concentration. The osmotic forces which derives the water from exterior to the interior of the gel causes an internal pressure resulting in the swelling of the gel [4].

Some gels have limited swelling capacity whereas others have unlimited capacity. The rate of swelling differs widely in different systems. In thin film of gels with limited swelling capacity, the rate of swelling gradually approaches zero as maximum swelling approached. Swelling can take place upon contact not only with a liquid, but even with its vapours. The swollen gels are mechanically weak and can be dehydrated by evaporation of water at ordinary temperature, by heating or by removing of water with the aid of porous materials etc. [5,6]. Swelling of gels also depends upon the shape of gel. In case of films of hydrogels, the adsorption of water is normal for thinnest films. However as the film thickness is increased the adsorption turns out and the process starts at a very high rate followed by a

sigmoid shaped slowly approaching to sorption equilibrium [7-10]. Therefore the cylindrical type of polymer networks has been discussed in this paper.

Results and Discussion

The swelling phenomenon of polymer networks of series I and II are discussed in figure I and 2. Swelling of polymer may be described as the penetration of the liquid on to and through out the polymeric material. It is the distribution of the mobile component between two (or more) phases. Properties involving large deformation depend primarily on the long chain nature polymers and grass configuration of their chains [6]. The swelling take place at the free surface of the gel, so the swelling is higher at the initial stage. When the outer surface swells up, the swelling takes place at the inner surface of the gel. Swelling of gels depends upon the number and nature of substituents in the polymer chain. Presence of polar groups such as OH, $-NH_2$ esters and amide are of a considerable importance in the swelling of gels, usually swelling increases in their presence [7]. Swelling in gels also depends upon the amount of crosslinking it usually decreases with increase in crosslinking. Penetrate size and shape of the polymer is of considerable importance in swelling, in polymers depends upon their mutual compatibility. The swelling result indicates that with increase in the ratio of the crosslinking agents, the swellings are decreased. This can be explained on the basis of the fact that increasing the amount of crosslinking would increase compactness of gel, and therefore the absorption of water by the gel is decreased.

The results shown in figure 1 and 2 can be explained on the basis that the gel has a well defined three dimensional network, and when the swelling takes place, water becomes bound between these networks. At the point of the maximum swelling, the gel can no longer retain its three dimensional network structure and water retained by these networks starts releasing. It is generally accepted that where well defined crystallites are formed, these are in accessible to water, nevertheless, a significant portion of the total water uptake may be associated with polar group in the surface of these crystallites. As their surface area is a function of their size, it follows that there is no unique relation between sorptive capacity and degree of crystallinity [11]. If the inter-chain

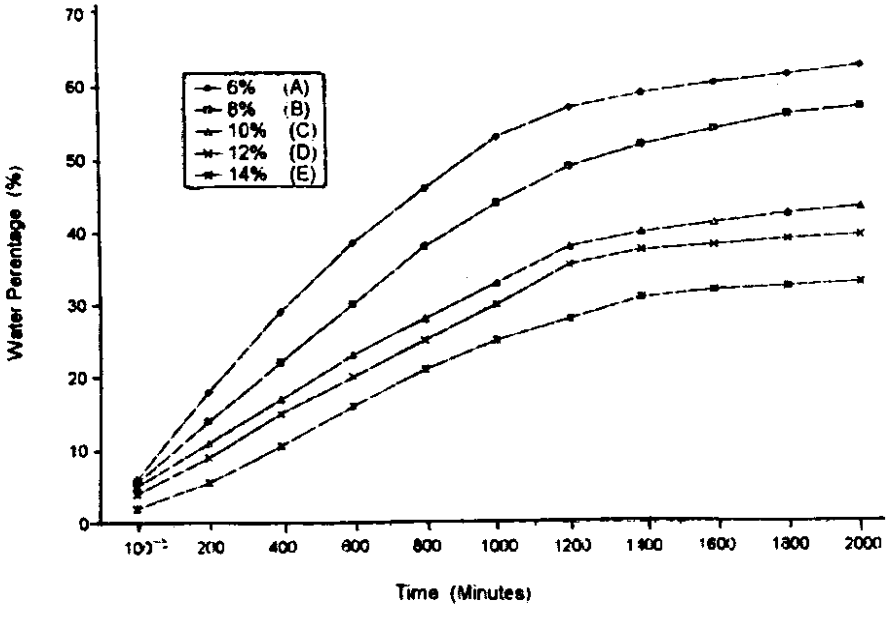

Fig. 1: Swelling of polymer networks in water at about 37 °C (series 1)
EGDA 6% (A).
EGDA 8 % (B).
EGDA 10 % (C).
X EGDA 12 % (D).
Ж EGDA 14 % (E).

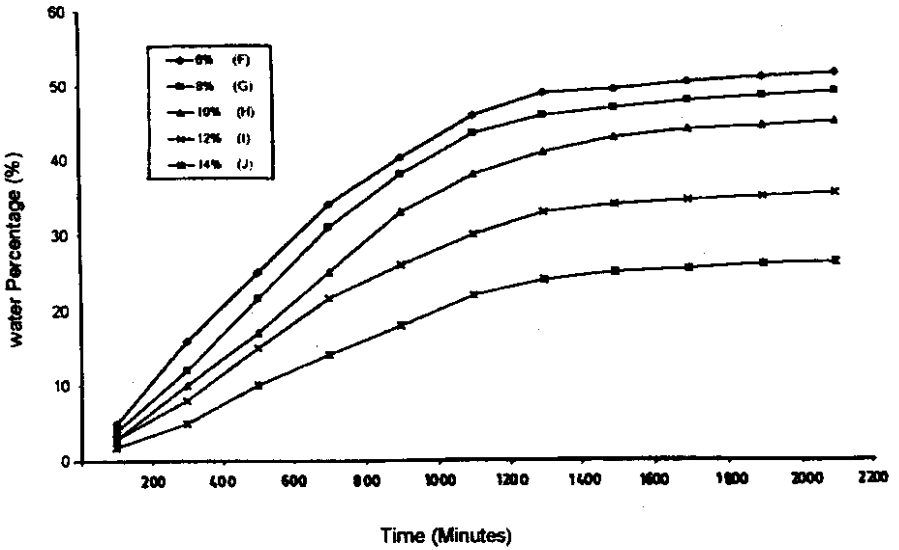

Fig. 2. Swelling of polymer networks in water at 37 °C (series II).

MDA 6% (F).
MDA 8 % (G).
MDA 10 % (H).
X MDA 12 % (I).
Ж MDA 14 % (J).

hydrogen bonds are weak or the degree of order in the crystallites is relatively low, the swelling and eventual disruption of polymer matrix may occur [12,13]. So a limit of crosslinking is essential, as in the present work it was restricted to 14%.

The swelling of gel depends greatly on the temperature. The swelling results of hydrogels indicate that with increase of temperature from 25-50°C, there is a decrease in the maximum swelling (fig. 3 and 4). This can be explained as inter molecular H-bonding between the polar groups. and the water molecules start disappearing with increase in temperature and therefore decrease in swelling of gel is observed. It seems interesting to note that the temperature change in swelling experiments result in reduced amount of water uptake (fig. 3 and 4) which indicates that the water imbibed by the polymer networks may have various forms. Thus at higher temperature one form of water is released and rest of the water remains in the matrix. The thermodynamic analysis of the temperature variation of the sorption isotherm is helpful investigation of the physical states of the sorbed water. From the results it seems that there might be at least two types of water one which is firmally bound, which could with stand the temperature upto 50°C while other is expelled from the polmer matrix. The results suggest that more firmally bonded water is many times greater than the loosely bonded bulk water. The difference of equilibrium uptake of systems at 25°C and 50°C is not very high, which is in fact indicative of bulk water.

Thin film of the polymer network was observed under the polarized light microscopes indicating its semicrystalline nature (fig. 5a). As structure of polymer network is not a single crystal but it depends upon the number, size and fine structure depend on the temperature of crystallization which determine the critical size of the nucleating center. Fig. (5b) indicates the morphology observed from thin section of polymer network widely separated spherical shaped discrete particles are microdomains. It seems to propose that formation of microdomains perhaps occur once the-OH double bond stoichiometric reaction was almost completed.

Experimental

Materials HMA, EDMA and MDA were supplied by E-Merck and were used without further purification. A standard of Azo iso butryonitrile

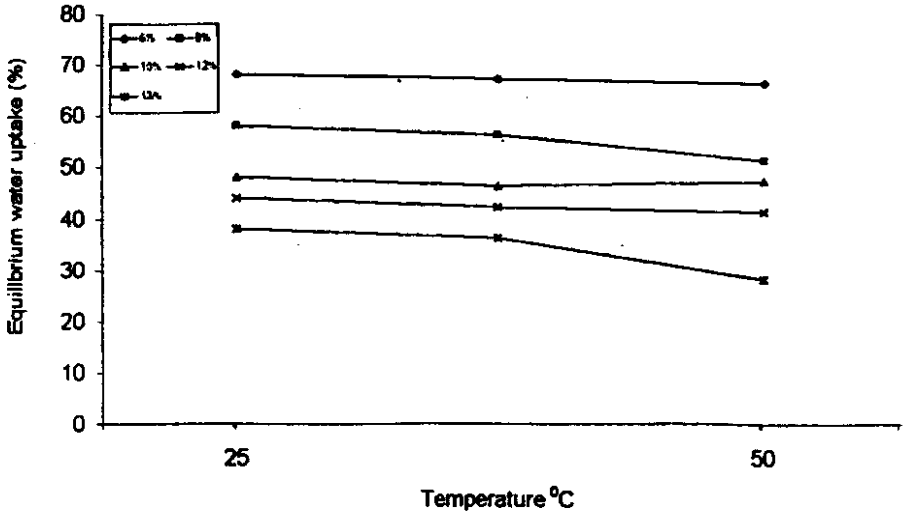

Fig. 3: Effect of temperature on equilibrium swelling (series I).

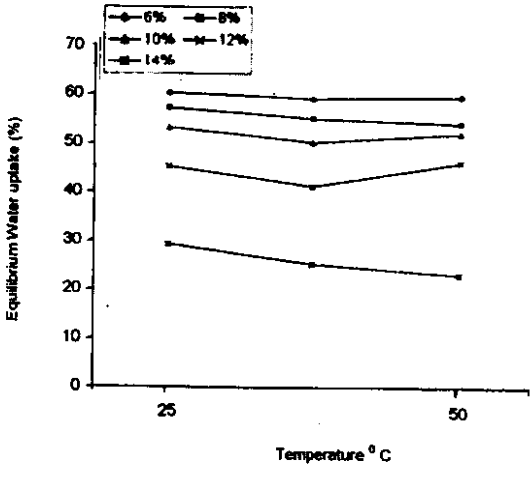

Fig. 4: Effect of temperature on equilibrium swelling (series II).

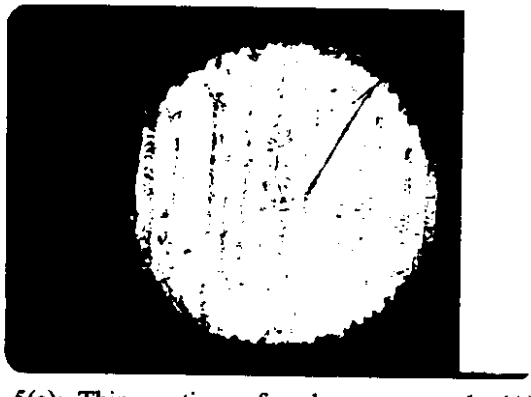

Fig. 5(a): Thin section of polymer network (A) under the microscope before swelling.

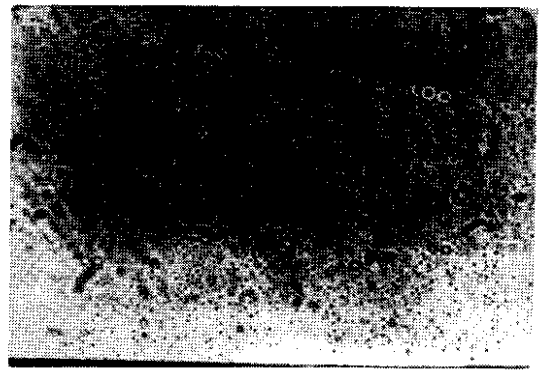

Fig. 5(b): Thin section of polymer network (B) under the microscope after swelling.

(AIBN) from E-Merck was prepared with distilled methanol and filtered on suction. The filtrate was allowed to stand in ice bath and crystals formed were separated by suction and dried to get recrystalized AIBN. HEMA. from E-Merck was made moisture free by allowing to flow through a 40 cm. long column packed with anhydrous aluminium oxide.

Synthesis, Purification and Composition of Polymer networks

A dried two-neck 250ml quickfit flask, preheated at 60°C was evacuated by the help of a vacuum pump for one hour in order to remove the traces of solvent and moisture. After releasing the vacuum accurately the weighed quantity of monomer along with crosslinking agent was introduced in the flask which was again attached to vacuum system

Table-1:Composition of Polymer Networks (Series-1)

Composition of Polymer Networks	HEMA (ml)	HMA (g)	AIBN (g)	EDMA (g)
A	13	10	0.002	0.5431
B	13	10	0.002	0.7235
C	13	10	0.002	0.9036
D	13	10	0.002	1.0842
E	13	10	0.002	1.2652

Table-2:Composition of Polymer Networks (Series II).

Composition of Polymer Networks	HEMA (ml)	HMA (g)	AIBN (g)	MDA (g)
F	13	10	0.002	0.328
G	13	10	0.002	0.4389
H	13	10	0.002	0.5486
I	13	10	0.002	0.6559
J	13	10	0.002	0.7652

with constant shaking to ensure a homogenous mixture. After the complete dissolution, vacuum was released and the AIBN (initiator) was added to the flask. The system was again subjected to vacuum quickly. Shaking the components vigorously, the flask was warmed at 60°C till the contents of the flask became a big viscous, indicating the start of polymerization. The vacuum was released and the contents were poured into preheated (at 60°C) polypropylene tube tied in stand, for molding and curing and placed in an oven at 90 to 100 °C for two hours. A transparent polymer was formed within three to four hours. All the compositions as indicated in table 1 and 2 were prepared in the same way by varying the ratio of crosslinking agents of series I and II. Setting time varies with the amount of crosslinking agents. The polymer networks were stored in a desicator. Polymer networks of accurately known weight in the cylindrical form were used in these experiments.

Each polymer was cut into equal pieces, which were placed in distilled water for 24 hours to extract any unreacted monomers. The removal was monitored by I.R. The swollen network was left to dry to constant weight under vacuum at 40 °C and stored in a desicator.

The composition of polymer networks were varied by altering the amount of crosslinking agents while the ratio of monomers remained constant. The feed of the crosslinking agents were varied from 6% to 14% w/w of the two monomers in order to obtain a polymer of desired mechanical strength and swellability. Various compositions employed are summarized in table 1 and 2. EDMA was used as crosslinking agent, the system A,B,C,D and E denotes the concentration of EDMA as 6%, 8%, 10%, 12% and 14% respectively in series I, whereas MDA was used as crosslinking, the system F, G, H, I and J denotes the concentration of MDA as 6%, 8%, 10%, 12% and 14% respectively in series II.

The Composition of Polymer networks

Swelling experiments were carried out both to estimate the water uptake in hydrogels and their study of swelling isotherm. The hydrogels of all the composition were taken out from the desicator, allowed to an ambient temperature and accurately weighed. These were placed in the sample bottles containing a large excess of distilled water at a desired temperatures 25°C, 37°C and 50°C, in a thermomex and allowed to swell to equilibrium. After this time the samples, one after other, were removed with tissue and immediately reweighed in a stopered weighing bottle. The water uptake in times of parts per hundred (pph) of the initial derived polymer was evaluated from the following relationship.

Swelling or water uptake (pph)=(Ws-Wd)/ Wd)x100 Where Ws is weight (g) of swollen sample and Wd is weight (g) of the initial dried hydrogel sample.

Morphology and Microscopy

One of the compositions (A) was chosen as representative from a number of polymer networks and examined under a microscope equipped with camera and exposmeter. The samples, as thin film was used in slides for microscopy.

Conclusions

The data obtained appear to be very reasonable and correlate with similar data in the literature, particularly considering most of the tabulated literature data for such polymers are based on the hydrophilic character of the surface interface of the networks.

For the polymer series used in this study, variation in the crosslinking agents is inversely proportional to the sorption capacity. The polymer networks produce a series of hydrogels with a controllable and wide range of water contents. Water

residues in the polymer networks have at least two forms, the bonded water and the bulk water. The water imbibed in initial stages is added as bonded water, and which is imbibed later adds to bulk water only.

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