Polymer Bulletin 35, 201–208 (1995)

Polymer Bulletin

Dependence of water sorption-desorption characteristics of *N,N′*-methylene-bis-acrylamide and tetraethyleneglycol diacrylate-crosslinked polyacrylamides on crosslinking

Mathew C. Chandy, V. N. Rajasekharan Pillai[*]

School of Chemical Sciences, Mahatma Gandhi University, Kottayam-686560, Kerala, India

Received: 30 January 1995/Revised version: 6 March 1995/Accepted: 14 March 1995

Summary

Hydrophilic monomers such as acrylamide (AA) when crosslinked with highly hydrophilic flexible tetraethyleneglycol diacrylate (TEGDA) and N,N'-methylene-bis-acrylamide (NNMBA) of intermediate polarity and hydrophilicity provides highly water swellable hydrogels. These water-swellable but water insoluble macromolecules possess a number of physicochemical properties useful for applications in biomedical and other technological fields. This paper describes the swelling/deswelling characteristics and the ability for water retention of these polymers in different compositions. Water sorption in these crosslinked polyacrylamides is dependent on a number of variables of polymer synthesis.

Introduction

Attempts have been made by various groups to delineate the sorption behaviour as well as the kinetics and mechanism of water sorption of synthetic hydrogels (1). Sorption behaviour of polyacrylamide gel spheres in water has been studied by Patel and coworkers (2). The hydrophilic-hydrophobic characteristics of gluteraldehyde-crosslinked gelatin grafted on acrylic monomers has been investigated (3). Kalachandra and Kusy compared the sorption behaviour of dimethacrylate monomers and their corresponding polymers (4). Kinetics and mechanism of water sorption in hydrophobic ionisable copolymer gels was investigated in great detail by Firestone and Siegel (1). ^{1}H NMR has been used by certain investigators to understand the properties of water in polymers (5). Depenedence of water sorption on the molecular weight and crosslinks as well as presence of plasticisers in poly(methyl methacrylate) was studied by Turner et al (6-8).

Acrylamide is polymerised by several means to produce a linear polymer, polyacrylamide (PAA), readily soluble in water and also in a few organic solvents. Because of its hydrophilic and water soluble nature, it is often

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[*] Corresponding author

copolymerised with fexible, hydrophilic and medium hydrophilic bifunctional crosslinking agents to produce water-swellable but water insoluble hydrogels. Thses copolymeric hydrogels can imbibe a large volume of water depending on the nature and extent of crosslinking, porosity and the method of polymerisation. Due to their high water sorption and water retention capabilities, they are put to a variety of uses such as molecular imprinting (9), metal-ion complexation (10,11) and other biomedical applications (12-14). The present investigations are aimed at understanding the dependence of water sorption on the variables of polymer synthesis, such as the chemical nature of monomers, nature and extent of crosslinking, hydrophilic-hydrophobic balance, porosity and pore dimensions as well as the specific morphology of the polymer.

Experimental

Materials and methods

Monomers and other chemicals are obtained from the following sources. Acrylamide (Astra IDL, Bangalore), N,N'- methylene-bis-acrylamide (BDH,England), tetraethyleneglycol diacrylate (Aldrich Chemical Company, U.S.A), Ammonium persulphate (Loba-chemie, Bombay) and tetramethyl ethylenediamine(TEMED) (Serva, Hiedelberg). Distilled water was used throughout for hydration and equilibration. Scanning elctron micrographs (SEM) were recorded on a Jeol JSM-35 scanning electron microscope.

Polymer synthesis

Polymer samples were prepared by radical polymerisation of the monomer mixture between two glass plates (15x10cm) silanised with a chloroform solution (5%) of trichloromethyl silane. Silanisation prevents the sticking of the polymer on the glass plates and ensures easy removal of the polymer membranes from surface of the glass plates. The glass plates were placed together with two polythene gaskets (2.25 mm thick) separating the glass plates. Spring clips were used to hold the glass plates together.

In a typical polymerisation recipe, acrylamide (1.7g, 95mmol) and NNMBA (19mg, 5mmol) were dissolved in distilled water (25ml), purged with nitrogen gas to remove dissolved gases and ammonium persulphate (25mg) was added as initiator followed by tetramethyl ethylenediamine (TEMED) (10 μl) as redox initiator. The mixture of solutions was immediately injected into the annular space in the glass mould and allowed to polymerise at room temperature. Polymerisation is complete in about 30 min but kept undisturbed overnight for post curing. The polymer sample was carefully separated from the glass plates after loosening the spring clips and dipping the glass mould in a dish of distilled water. The hydrophilic polymer film was shaken at slow speed in a gyratory shaker for equilibrium hydration with frequent changes of water. This change of water ensures complete leaching of soluble monomers, linear polymers and other salts and ions from the polymer. Acrylamide copolymers containing 10, 15 and 20 mole percentage of the crosslinking agent A (1-4) were prepared as described. TEGDA-crosslinked polyacrylamides (AA-TEGDA) with 5,10,15 and 20 mole percentages B (1-4) were also prepared similarly.

Equilibrium water content (EWC)

Equilibrium water contents of the copolymers A (1-4) and B (1-4) were determined by measuring the weight differences in equilibrium hydrated and dry samples. Samples of 2 cm diameter were cut from the preswollen polymer, surfaces carefully wiped with a blotting paper and the swollen weight determined. Samples were then dehydrated in vacuum at 50°C overnight to constant weight. EWC was calculated as the ratio of the weight of water in the gel to the total weight of hydrated gel expressed as percentage. The final value reported is an average of the results from at least three measurements.

Water sorption/desorption measurements

The swollen weights of the hydrated samples were determined after wiping off the surface water carefully. They were allowed to dehydrate completely in vacuum at room temperature, 40°C and 50°C. Weight loss of the samples at regular intervals of time was noted till they assumed constant weights. The percentage desorption was plotted against time. Similar experiments were performed with samples A (1-4) and B (1-4).

Scanning electron microscopy

Vacuum-dried polymer samples were sputtered with gold and scanned at 15 KV using a scanning electron microscope provided with a tungsten elctron gun and micrographed at various magnifications.

Results and discussion

Preparation of crosslinked copolymers

Acrylamides crosslinked with NNMBA and TEGDA in 5, 10, 15 and 20 mole percentages were prepared by varying the relative amounts of the monomers (Table 1).

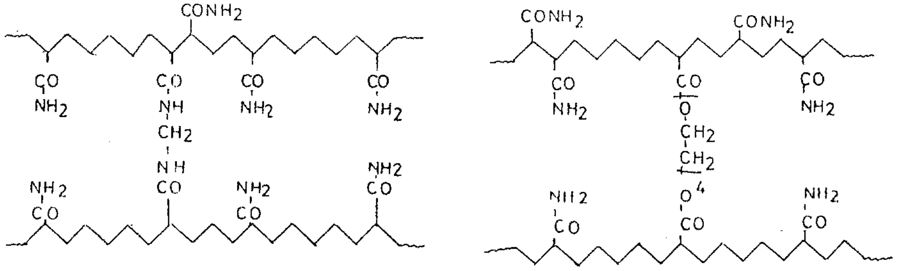
Table 1. Preparation of crosslinked acrylamides[a, b]

Polymer designation	crosslink density (mole%)	amount of AA (mg)	NNMBA (mg)	Polymer designation	crosslink density (mole%)	amount of AA (mg)	TEGDA (mg)
A1	5	170	19	B1	5	134	30
A2	10	159	39	B2	10	127	60
A3	15	150	58	B3	15	120	90
A4	20	142	78	B4	20	113	121

a. Amounts of ammonium persulphate and TEMED were kept constant at 25mg and 10 μl respectively

b. Volume of water in each experiment was 25ml

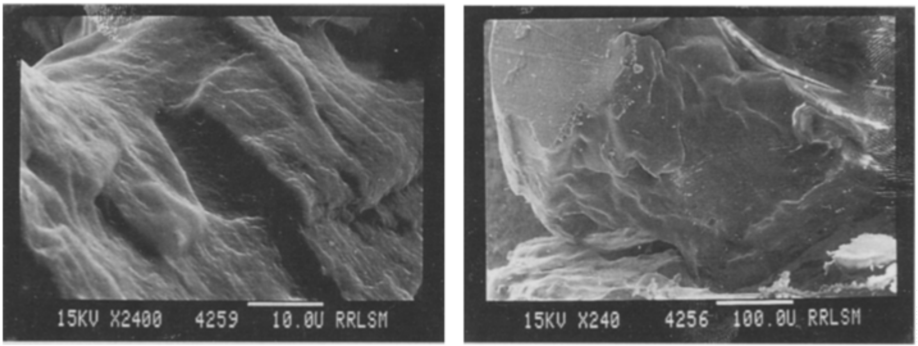
The chemical structures of the copolymers are depicted in Scheme 1.



a b

Scheme 1. Polyacrylamides with a) NNMBA and b) TEGDA cross-links

Preparation of polymer films using the monomers and crosslinking agents in appropriate mole ratio provides optimum hydrophilic-hydrophobic balance to the resulting copolymer. The morphological features of the 10% crosslinked acrylamides (A2 and B2) are shown in Figure 1. Both the polymers contain large pores of varying dimensions which account for their high water sorption.



a b

Fig.1. Scanning electron micrographs of 10% crosslinked polyacrylamides: crosslinks (a) NNMBA and (b) TEGDA

Equilibrium water content (EWC)

Both copolymers exhibit very high EWCs at room temperature. EWC values were found to decrease with increasing crosslink density (Figure 2). It was observed that in AA-TEGDA, increase in TEGDA concentration does not appreciably alter the equilibrium water content. This is due to the extreme hydrophilicity and flexibility of TEGDA. Incorporation of higher proportions of TEGDA only increases the hydrophilicity of the copolymer. NNMBA being a mid-range hydrophilic crosslinker does not induce hydrophilicity of a high order. This is reflected in the curve which slightly falls as crosslink density increases. However the drop is not very sharp. Both the copolymers can retain their hydrophilic character even at high crosslink densities.

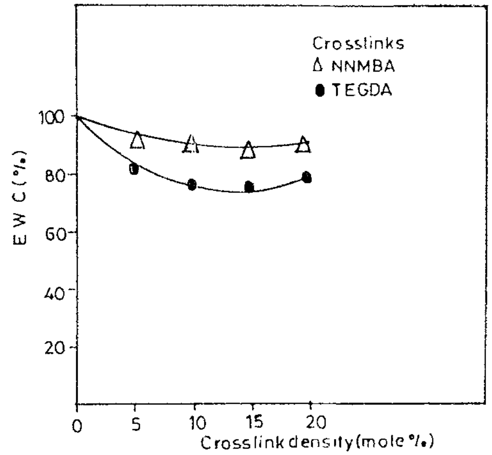
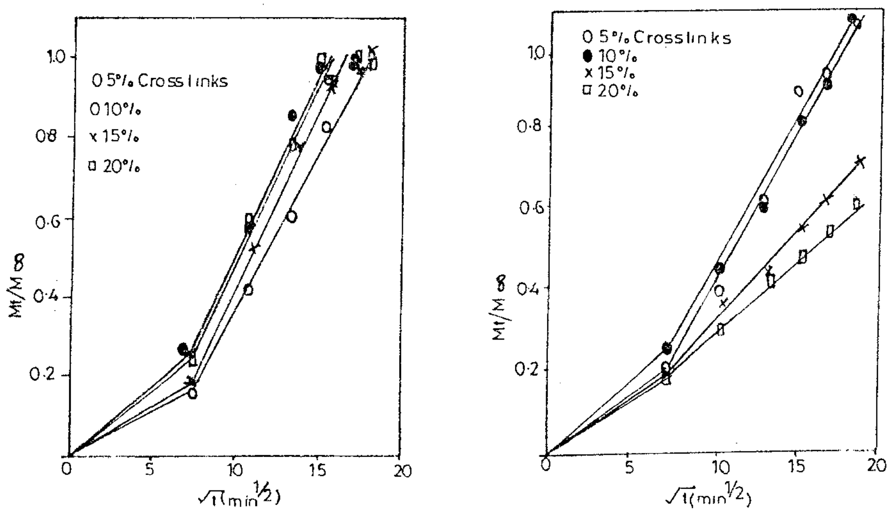


Fig.2 Variation in EWC with crosslink density

Sorption-desorption

The desorption curves for samples A (1-4) and B (1-4) are shown in Figure 3 a and b. Desorption is expressed as $Mt/M\infty$, where Mt is the weight loss at time t and $M\infty$ is the total weight loss. Time abscissa is expressed as $(time)^{1/2}$. This method of plotting allows one to find out whether the desorption is Fickian or not (15). A linear relationship between $Mt/M\infty$ and $t^{1/2}$ denotes that the water transport in the polymer films is diffusion-controlled (Fig.3).



a b

Fig.3. Desorption curves of a) AA-NNMBA and b) AA-TEGDA copolymers in distilled water at 50°C

Figure 4 shows the dependence of temperature on desorption curves of 5% AA-NNMBA.

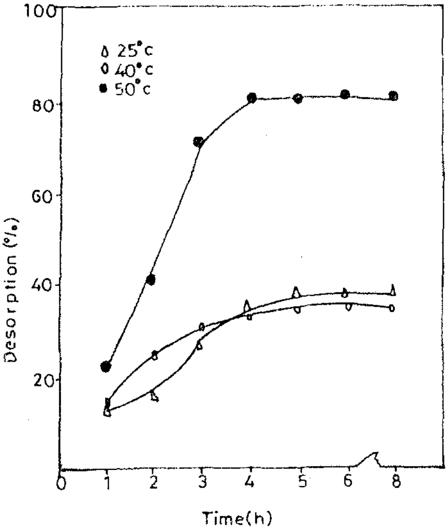


Fig.4 Dependence of temperature on the desorption curves

The desorption process is quicker at higher temperatures. At 50°C, within 4h, 80% desorption was complete while at 25°C only 35% desorption took place in 4h. At 40°C also, desorption is a slow process. This increased water retention capacity of the polymer at room temperature over a time lag of 4-6h, suggests the applicability of these hydrogels in dressing wounds and burns. In 5% TEGDA-crosslinked acrylamide (B1) desorption is a slow process compared to that of 5% AA-NNMBA. At 50°C within the first 4h, 80% water of equilibrium hydrated AA-NNMBA was desorbed while AA-TEGDA desorbed only 30% (Figure 5).

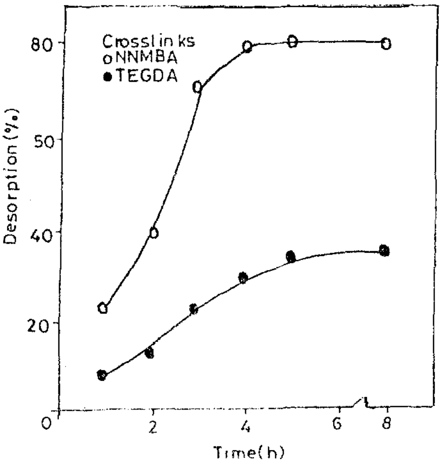


Fig.5. Variation in desorption profiles with copolymer composition

Sorption Kinetics

Figure 6 represents sorption kinetics of NNMBA-crosslinked polyacrylamides A (1-4). In distilled water, the sorption is complete in 6-7 hours. There is not much difference in the sorption kinetics of the copolymers with varying proportions of the monomers.

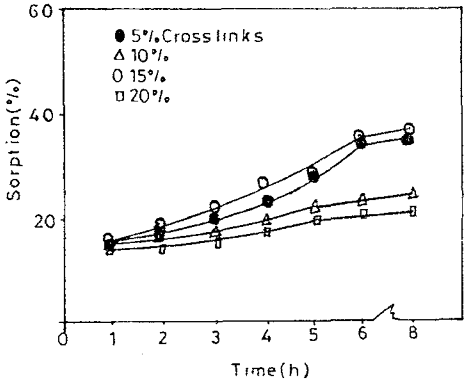


Fig.6. Sorption kinetics of AA-NNMBA (10%) at 25^{o}C

Effect of crosslinking agent and polymerisation conditions on morphology

The surface features of 10% NNMBA-crosslinked polyacrylamide are different from those of 10% TEGDA-crosslinked polyacrylamide (Fig. 1). This is obviously due to the nature of the crosslinking agent which induces distinct surface features such as pores and channels. However there is some difference in the surface characteristics of 10% NNMBA-crosslinked polyacrylamide prepared by solution polymerisation and that prepared in the film form in presence of TEMED. The polymerisation conditions definitely influences the morphology of the polymer.

Conclusions

1. Acrylamide crosslinked with hydrophilic crosslinking agents in 5-10 mole proportions provide hydrogels capable of sorbing large quantities of water.
2. The water transport in these polymers is approximately diffusion controlled or near Fickian.
3. TEGDA-crosslinked acrylamide posses a higher water retention capability at room temperature, compared to NNMBA-crosslinked polyacrylamide.

Acknowledgements

The authors are grateful to the University Grants Commission, New Delhi for the financial support in the form of Teacher Fellowship (Faculty Improvement Programme) to MCC.

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