

Hydrogels prepared by crosslinking copolymerization of N-allyl maleamic acid with acrylamide and acrylic acid

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Abstract—Copolymerization of N-allyl maleamic acid (AMA) with acrylamide and acrylic acid results in rapid crosslinking in water. Although AMA is slightly soluble in water, it forms clear solutions in 10% of aqueous acrylamide and 20% acrylic acid solutions. By radical initiation with potassium persulfate at 65°C or redox initiation at 0°C, these solutions undergo gelation in less than 10 min. The crosslinking efficiency of AMA was estimated based on equilibrium swellings of its acrylamide copolymer gels either by the Flory–Rehner theory or by correlation with swelling-crosslinking density plots of acrylamide–methylene bis-acrylamide (BIS) copolymer gels. These results showed that efficiency of AMA in crosslinking copolymerization with acrylamide at 0°C is less than 10%. On the other hand, its efficiency rises up to 40–60% and levels off at 65°C. Overall results indicate that AMA having maleate and allylic double bonds is an efficient crosslinker for preparing polyacrylamide and polyacrylic acid gels.

Keywords: Hydrogels; crosslinking copolymerization; N-allyl maleamic acid; polyacrylamide; polyacrylic acid.

1. INTRODUCTION

Hydrophilic polymer networks, the so-called hydrogels, have found wide application in chemical separation [1, 2], biomedical engineering, etc. [3–5]. Hydrogels derived from polyacrylic acid and polyacrylamide have received special interest due to their high swelling abilities. Those hydrogels are prepared mostly by crosslinking copolymerization with a water-soluble divinyl monomer. Acrylamide–methylene bis-acrylamide (BIS) is the most common crosslinker for preparing network structures of water-soluble polymers. However, the monomer (BIS) is not advisable as crosslinker for medical uses of the resulting hydrogels, owing to its slow hydrolysis in water, yielding a toxic chemical, formaldehyde [6]. Ethylene bis-acrylamide [7] and bisacryloyl piperazine [7] have been suggested as better reagents

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for the crosslinking. Trimethylolol propane trimethacrylate (TMPT) has been considered as an alternative crosslinker, although it becomes water miscible only in the presence of acrylic acid [8]. However, the hydrogels obtained from TMPT may have a higher crosslink density due to their trifunctional nature. A water soluble monomer, tetraallyl piperazinium dichloride, has also been demonstrated to be an efficient and non-hydrolysable crosslinker by our group [9].

In this work, we have investigated the use of N-allyl maleamic acid as comonomer for the preparation of polyacrylamide and polyacrylic acid hydrogels. N-allyl maleamic acid is prepared easily from maleic anhydride and allyl amine is an interesting crosslinker with maleate and allylic double bonds having different reactivities in copolymerization.

As will be shown below, processing conditions of water-insoluble AMA in crosslinking copolymerization with acrylic acid and acrylamide have been investigated and its crosslinking efficiency has been estimated either by the Flory–Rehner theory or by correlation of the equilibrium swelling values of the polyacrylamide gels with those obtained from BIS as the crosslinking agent.

2. EXPERIMENTAL

2.1. Materials

Acrylamide (Fluka), acrylic acid (Fluka), allyl amine (Fluka) and maleic anhydride (Acros) were used as supplied. Dimethoxy ethane (Aldrich) was distilled before use.

2.2. Preparation of N-allyl maleamic acid (AMA)

AMA was prepared in high yields (87–93%) by the reaction of maleic anhydride and allyl amine in dimethoxy ethane at 0°C (data not shown). It was re-crystallized from water to give a white crystalline product (mp 97–98°C).

2.3. Copolymerization of AMA with acrylamide

Copolymerization of acrylamide was carried out either by redox initiation in an ice bath or by thermal initiation at 65 or 80°C.

2.3.1. Thermal initiation method. Acrylamide (3.55 g, 50 mmol) and 0.194 g (1.25 mmol) AMA were placed in a flask attached to a reflux condenser and a nitrogen inlet. An appropriate amount of water was added to the flask, to obtain a total monomer concentration of 10%. Then 0.27 g (1 mmol) $K_2S_2O_8$ was added to the solution and nitrogen was flushed through the solution. The flask was mounted in a silicon-oil bath, the temperature of which was adjusted to 65°C. The mixture was stirred until gelation. The gel formed was left to stand at room temperature for 5 h. The gel was broken up, filtered and washed with an excess of water (1 : 200 ml).

The product was dried under vacuum at 45°C for 24 h. A similar procedure was followed for copolymerization with acrylic acid, except that the total monomer concentration was 20% by weight and polymerization temperature was 80°C.

2.3.2. Redox initiation method. Redox polymerization was carried out at 0°C in an ice-bath. $K_2S_2O_8$ (0.27 g) plus tetramethylethylene diamine (TMED) (0.2 ml) was used for the copolymerization of acrylamide.

2.4. Copolymerization of AMA with acrylic acid

Since the persulfate/*tert*-amine redox system works in basic or neutral conditions, redox copolymerization with acrylic acid was performed with the $KMnO_4$ /oxalic acid redox couple. First oxalic acid (0.09 g, 1 mmol) and 0.2 ml concentrated H_2SO_4 was added to the solution. Then a solution of 62 mg (0.4 mmol) $KMnO_4$ in 2 ml water was added all at once to the cold solution of the monomer mixtures. The hydrogels formed were isolated as described above.

2.5. Swelling of the gels

Dry gel samples about (0.2 g) were immersed in 100 ml of distilled water at room temperature until equilibrium swelling was reached. Then swollen gel samples were taken out and the excess water was removed quickly with blotting paper and samples were weighed.

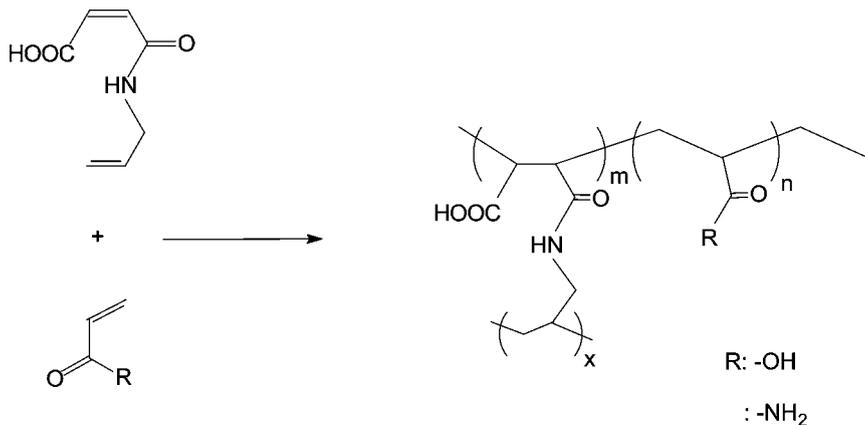
The percentage swelling was determined by calculating W/W_0 , where W and W_0 are the swollen and dry samples, respectively.

3. RESULTS AND DISCUSSION

Radical-initiated polymerization of N-allyl maleamic acid (AMA) itself gives rise to low-molecular-weight polymers with allyl pendant groups in each repeating unit (data not shown).

This result implies that reactivity ratios of maleate and allylic double bonds of AMA do not allow formation of crosslinked polymers and the allyl group is not involved in polymerization. However, copolymerization of AMA with acrylamide and acrylic acid results in rapid crosslinking (Scheme 1).

Although AMA is almost insoluble in cold water, its solubility in 10% acrylamide and 20% acrylic acid solutions is around 4%. This behavior facilitates copolymerization of AMA with these monomers in water even at 0°C. The crosslinking takes place either by thermally with $K_2S_2O_8$ (65°C) or by redox initiation at 0°C. This result indicates that the less reactive allyl groups also participate in copolymerization in either conditions. Since vinylic components of AMA are different, reactivities of these groups are expected to be different in the copolymerizations. As a result some part of allylic or maleate double bonds may remain unreacted. However, the



Scheme 1. Copolymerization of AMA with acrylamide and acrylic acid.

estimation of unreacted double bonds by IR spectra is almost impossible due to broadened bands at $1500\text{--}1680\text{ cm}^{-1}$ and $3050\text{--}3150\text{ cm}^{-1}$, corresponding to $\text{C}=\text{C}$ and $=\text{C}\text{--H}$ stretching vibrations, respectively.

For this reason, the residual double bonds of AMA in the copolymerization with acrylamide were estimated by correlation of the values obtained with the Flory–Rehner theory with the crosslinking densities of the gels with equilibrium swellings:

$$\ln(1 - v_2) + v_2 + \chi \cdot v_2^2 = \rho \cdot V/M_c(v_2^{1/3} \cdot v_2^{02/3} - v_2/2),$$

where v_2 is the volume fraction of the polymer in swollen state, v_2^0 is the volume fraction of the polymer after preparation, V is the molar value of the solvent (water), ρ is the density of polymer in dry state and M_c is the molecular weight of the polymer segments between two crosslinks.

By using the polyacrylamide/water interaction parameter $\chi = 0.48$ and density of polyacrylamide $\rho = 1.35$, the M_c values of AMA–acrylamide gels were calculated using the Flory–Rehner equation. The corresponding average number of the repeating units between crosslinked points on one chain can be obtained by $n = M_c/2M$, where M is the molecular weight of the monomer, acrylamide. The results are listed in column f of Table 1.

In order to determine the crosslinking efficiency of AMA, the n values must be compared with the inverse of the crosslinker ratio of the feed composition. For instance, in the copolymerization of acrylamide with 5% AMA at 0°C , the M_c value calculated from the Flory–Rehner equation is 29.4×10^3 . Dividing this value by molecular weight of acrylamide, 71 g/mol , this leads to about 414 repeating units. This corresponds to 207 repeating acrylamide units per polymer chain. The theoretical value can be predicted from the feed composition. 5%, of crosslinker ratio which corresponds to $1/2 \times 0.05 = 10$ repeating units per chain. The crosslinking efficiency was obtained by the ratio of the two values $(10/207) \times 100\% = 4.83\%$. Similar estimations yield low efficiencies (less than

Table 1.

Gelation characteristics and crosslinking efficiency of AMA in copolymerization with acrylamide

Temperature (°C)	r_0^a (%)	Gelation time (s)	Gelation time for BIS crosslinker (s)	W/W_0^b	W'/W_0^c	f^d (%)	r^e	r/r_0^f (%)
0	2.5	570	270	37.5	9.1	3.0	<0.1	4.0
0	5.0	210	168	15.3	6.5	4.8	0.2	4.0
0	10.0	93	60	10.8	4.6	9.7	0.85	8.5
65	2.5	225	145	11.2	7.3	57.2	0.90	36.0
65	5.0	192	110	8.9	5.6	50.0	1.7	34.0
65	10.0	160	85	5.7	4.6	41.6	4.3	43.0

^a r_0 is crosslinker ratio (crosslinker/co-monomer (moles/moles)) in the feed composition (total monomer concentration 10% (w/w₀)).

^b W/W_0 is the swelling ratio (weight to weight of the gel).

^c W'/W_0 swelling ratio of the gel prepared with BIS as crosslinker.

^d f is crosslinking efficiency of AMA which is defined as $f = M_c/M_0$, where M_c is molecular weight of the segments between two crosslink points.

^e r is crosslinker ratio obtained from Fig. 1.

^f r/r_0 is crosslinking efficiency estimated from Fig. 1.

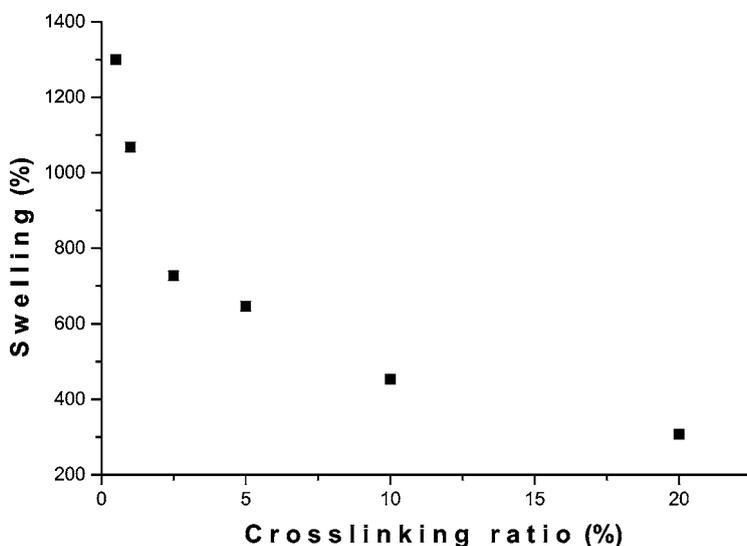


Figure 1. Swelling *versus* molar ratio of BIS to monomer for polyacrylamide hydrogels prepared at 0°C.

10%) for other compositions when copolymerization is carried out at 0°C. Whereas the crosslinking efficiency of AMA lies in the 40–60% range for the hydrogels prepared at 65°C, accordingly the swelling percentages are somewhat low.

This result implies that crosslinking efficiency of AMA is substantially higher than those of the gels prepared at 0°C. But high crosslinking density at elevated temperatures might be due to self-crosslinking of polyacrylamide by imide forma-

Table 2.

Gelation characteristics and crosslinking efficiency of AMA in copolymerization with acrylic acid

Temperature (°C)	r_0^a (%)	Gelation time (s)	W/W_0 (%)	M_c	F^b (%)
0	2.5	720	4343	24907	11.4
0	5.0	300	1936	8670	16.3
0	10.0	120	1292	5580	12.7
0	20	90	701	1862	19.0
80	2.5	300	3526	9020	31.5
80	5.0	120	1780	3690	38.5
80	10.0	90	806	913	77.7
80	20.0	50	391	440	80.6

^a Total monomer concentration 20% (w/w).

^b Crosslinking efficiency estimated from the Flory–Rehner equation.

tion between neighboring amide units. In order to eliminate the self-crosslinking effect, polyacrylamide gels were also prepared by using methylene bis-acrylamide (BIS) of which acryloyl groups are quantitatively involved in crosslinking [10].

The gels with different crosslinking densities were prepared at 0 and 65°C. Then, equilibrium gel swellings were plotted as a function of molar ratio of BIS to acrylamide (Fig. 1). The swelling curves of the gels obtained at 0 and 65°C are almost identical, which reveals efficiency of BIS does not change within the 0–65°C range. This result also indicates that no additional crosslinking comes from imidization of polyacrylamide at 65°C.

As a result, the high crosslinking efficiency of AMA at 65°C is due to higher reactivity of AMA at this temperature. Since the allyl group is less reactive in copolymerization, low crosslinking density at 0°C must be due to the lower reactivity of this group at low temperatures.

In the last part of this study, crosslinking efficiencies of AMA were also estimated by using swelling-crosslinker ratio curve in Fig. 1.

Since the double bonds of BIS are quantitatively involved in crosslinking, Fig. 1 represents correlation of swelling with the crosslinking density. The molecular masses of AMA and BIS are almost equal (155 and 154 Da, respectively). By using swelling ratios of AMA–polyacrylamide gels the corresponding crosslinker ratios were obtained by direct reading from abscissa of Fig. 1 and are also given in Table 1.

Hence, the crosslinking ratio of 0.2% found for the gel with 5% of AMA at 0°C indicates an efficiency of $0.2/5 = 0.04$. This is comparable with the value (4.83%) that, obtained from the Flory–Rehner equation. This behavior is also observed for the other gels with AMA. Moreover, longer gelation times in copolymerization of AMA than those of BIS are in consistent with the above assumption. Similar correlation is valid also for AMA–polyacrylic acid hydrogels (Table 2).

In copolymerization with acrylic acid, crosslinking efficiencies of AMA (by Flory–Rehner theory) are higher at 20% of total monomer concentrations, compared with those for the polyacrylamide gels.

In conclusion, a new crosslinker, AMA with maleate and allyl double bonds, shows low crosslinking efficiencies at 0°C. Most probably the less reactive double bond is the allyl group of AMA. Crosslinking efficiency can be enhanced by increasing temperature and rises up to 40–60% at 65°C. It is clear that AMA can successfully be employed as a crosslinker for the preparation of polyacrylamide and polyacrylic acid hydrogels.

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