

# STUDY ON ACRYLAMIDE-SODIUM ACRYLATE COPOLYMER GELS

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## ABSTRACT

Acrylamide-sodium acrylate copolymer hydrogels have been obtained by radiation techniques. Two different methods have been used to introduce  $-\text{COONa}$  groups into polymer chains of the gels: (1) by partial hydrolysis of acrylamide homopolymer gel; (2) by direct copolymerization and crosslinking of acrylamide and sodium acrylate in aqueous solutions. It was found that the gels obtained in different ways had different properties, the swelling character of the gels obtained by partial hydrolysis were more sensitive to pH of swelling aqueous media. In order to explain these differences,  $^{13}\text{C}$ -NMR techniques were used to investigate the sequence distribution of monomer units of both gels.

## INTRODUCTION

In recent years, remarkable progress has been made in the field of high water-absorbing hydrogels<sup>[1,2]</sup>. However, most of the authors concentrated their attentions on the synthetic methods and applications of the gels, and only a few studied the structure and fundamental properties of the gels. In the present work, we obtained two series of acrylamide (AM)-sodium acrylate (AANa) copolymer gels by radiation techniques. The  $-\text{COONa}$  groups were introduced by partial hydrolysis of radiation polymerized and crosslinked AM homopolymer gels; or by direct radiation copolymerization and crosslinking of AM and AANa in an aqueous solution. The swelling character and microstructure of both gels were studied.

## EXPERIMENTAL

Technical-grade acrylamide was purified by sublimation under vacuum at  $80^\circ\text{C}$ . Technical-grade acrylic acid was freshly distilled under reduced pressure prior to use.

The radiation copolymerization and crosslinking of AM and AANa were performed in an aqueous solution of the corresponding monomers. AANa was prepared in situ by equivalently dropping NaOH solution into acrylic acid, then water and AM were added *pro rata*. The aqueous solution thus obtained was placed in a glass ampoule, and dissolved oxygen in the solution was removed by bubbling nitrogen gas for 15 minutes, then the ampoule was sealed and subjected to gamma ray radiation from  $^{60}\text{Co}$  in a thermostat. The dose rate was 22 rad/second, temperature  $31 \pm 1^\circ\text{C}$ , and the total monomer concentration 30 wt. %. The AM homopolymer gel was obtained in the same way. Soluble polymers were obtained before the dose reached the gelation dose ( $D_g$ ), and the gels were obtained after the dose reached the  $D_g$ <sup>[3]</sup>.

The partial hydrolysis of AM homopolymer was carried out in  $0.5\text{ M Na}_2\text{CO}_3$ .

aqueous solution at 60 °C. The degree of hydrolysis was estimated by pH titration: a given amount of gel or soluble polymer was swollen or dissolved in water, and was titrated with 0.1M HCl till pH=4.0, then a reverse titration by 0.1M NaOH solution was carried out until pH=7.0. All the titrations had to be performed very slowly. The water retention value (WRV) was determined by measuring the quantity of water retained by the gels at room temperature (g/g). Infrared (IR) spectra were obtained on a Perkin-Elmer 599B spectrometer.

The soluble samples used for  $^{13}\text{C}$ -NMR determination were purified by precipitation twice in a methanol-ethanol (50/50 by volume) mixture, then dried in a vacuum oven at 40 °C for at least 24 hours. Proton-decoupled  $^{13}\text{C}$ -NMR spectra were obtained with a 30% solution in  $\text{D}_2\text{O}$  at 50 °C using a JEOL FX-100 spectrometer operating at 25 MHz, in the presence of 1,4-dioxane as internal reference (67.4 ppm downfield from TMS). Flip angle and acquisition time were 90 °C and 1.5 second, respectively. The interval between the pulses was about 0.5 second.

## RESULTS AND DISCUSSION

AM homopolymer gels had quite small WRVs. However, when they were partially hydrolyzed in basic solutions and part of the  $-\text{CONH}_2$  groups in the polymer chains were converted to  $-\text{COONa}$  groups, the WRVs could increase by hundreds folds<sup>[3]</sup> due to the formation of the  $-\text{COONa}$  groups which were much more hydrophilic than the  $-\text{CONH}_2$  groups. The  $-\text{COONa}$  group produced by partial hydrolysis could be verified by its characteristic infrared absorption at  $1460\text{ cm}^{-1}$  which was attributed to the asymmetric stretch resonance of the carbonyl in the  $-\text{COONa}$  group (see Fig. 1).

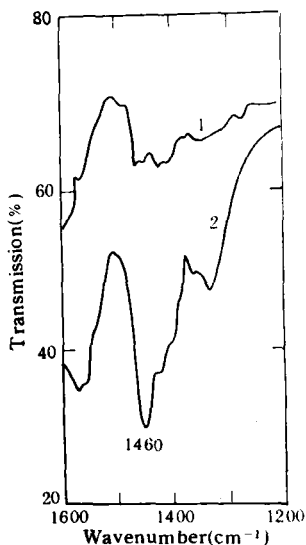


Fig. 1 IR spectra of AM polymer gels  
1. Before hydrolysis; 2. After 24 hr. hydrolysis

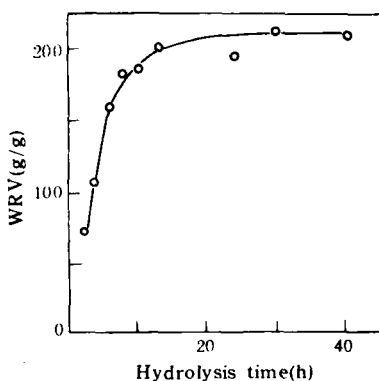
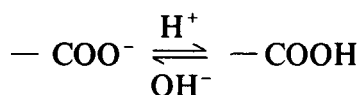


Fig. 2 The dependence of WRV on hydrolysis time  
Medium: 0.5M  $\text{Na}_2\text{CO}_3$  aq. solution  
Temperature: 60 °C

Fig. 2 shows the dependence of WRV of AM polymer gels on hydrolysis time. One could conclude that the WRV of the polymer gels increased with increasing hydrolysis time, after 12 hours' hydrolysis, an equilibrium was

reached, and about 20% of the  $-\text{CONH}_2$  groups were converted into  $-\text{COONa}$  groups in the polymer chains. By improving the hydrolysis conditions (both media and temperature), much less time was required of reaching hydrolysis equilibrium 12 hours versus 60 days in the literature<sup>[4]</sup>, where the gels were hydrolyzed in 0.1 M NaOH aqueous solutions at room temperature.

Fig. 3 shows the pH dependence of WRVs of the polymer gels. The WRVs of the AM homopolymer gels before hydrolysis were almost independent of pH of swelling aqueous media (open circles curve), but for gels after 24 hours' hydrolysis, the swelling curve (solid circles) was quite different from the former. When the pH of the swelling aqueous media was below 2.0, the WRVs of the latter were very small, and increased slightly with increasing pH. But when the pH attained about 2.5, the WRVs became highly sensitive to the change of pH, in other words, a small change in pH could result in a large change in WRV. For example, the WRV increased about 20 times with an increase in pH from 2.5 to 3.5. Further increase in pH caused only a slight change in WRV. All the above change was reversible, i.e., when acid solution was added to a swollen gel, due to the decreasing of pH, the gel began to shrink and release the absorbed water; on the other hand, if we added basic solution to a shrunk gel, it would swell again by absorbing water. All these phenomena could be explained by the electrostatic interaction of  $-\text{COO}^-$  groups in the polymer chains resulting from ionization of the  $-\text{COONa}$  groups:



Recognizing the essential role in swelling played by the  $-\text{COONa}$  groups in the polymer chains, we tried to introduce the  $-\text{COONa}$  groups by direct radiation copolymerization and crosslinking of AM and AANA aqueous solution. The swelling curve of the gel thus obtained was similar to the solid circle curve of

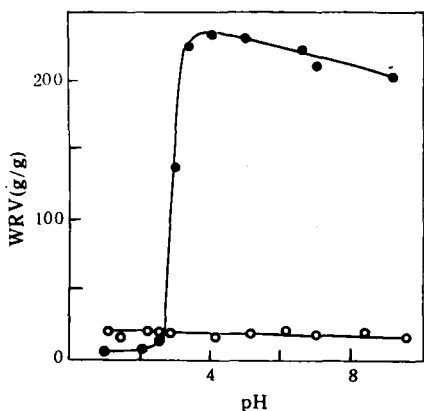


Fig. 3 The dependence of WRVs on pH of swelling aq. media

- : Gels after 24 h. hydrolysis;
- : Gels before hydrolysis

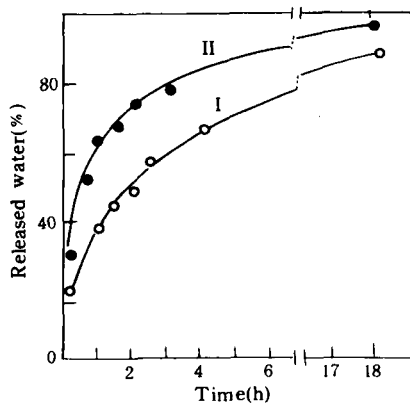


Fig. 4 The time dependence of the percentage of released water

- : gel (II) by hydrolysis;
- : gel (I) by direct copolymerization

Fig. 3, but some differences between the two gels existed. In order to study these differences, the following experiment was carried out. Gel (I) was obtained by direct radiation copolymerization and crosslinking of AM with 20 mol. % AANa, and gel (II) was obtained by 24 hours' partial hydrolysis of AM homopolymer gel. According to the literature<sup>[4]</sup>, about 20 mol. % of its  $-\text{CONH}_2$  groups were converted to  $-\text{COONa}$  groups. Both gels were first swollen to equilibrium, then acid solution was dropped in, so they began to shrink and release the absorbed water at once. The released water was measured as a function of time. Fig. 4 shows the time dependence of the percentage of released water. One could find from Figure 4 that gel (II) obtained by partial hydrolysis was more sensitive to acid than gel (I), in other words, gel (II) released the absorbed water faster than gel (I) did. We supposed that this difference between the two gels might be related to differences in the sequence distribution of the monomer units.

Caudau and Zekhnimi had applied  $^{13}\text{C}$ -NMR techniques to study microstructure of linear AM-AANa copolymers prepared by inverse microemulsions<sup>[5]</sup>. Since gels were insoluble, we could not use directly  $^{13}\text{C}$ -NMR techniques to study their microstructure, so we carried out radiation (Co) polymerization and partial hydrolysis of both soluble polymers and gels in parallel, the only difference between soluble polymers and gels prepared was radiation dose which had little influence on sequence distribution of the monomer units, then we used  $^{13}\text{C}$ -NMR techniques to study sequence distribution of the monomer units of the soluble polymers. Because the gels were obtained under the same conditions, it could be expected that the knowledge of the microstructure of the soluble polymers would make a possible quantitative comparison between the two corresponding gels.

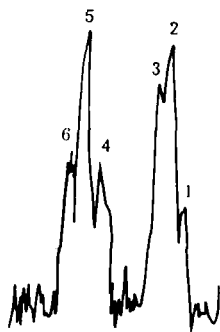


Fig. 5  $^{13}\text{C}$ -NMR spectrum of carbonyl resonances for copolymer obtained by direct copolymerization, with 40 mol. % of AANa

Fig. 5 is  $^{13}\text{C}$ -NMR spectra of carbonyl resonances for the copolymer obtained by direct copolymerization, the resonance area of acrylamide (M) at higher field, and acrylate units (A) at lower field were well separated and further split into two sets of three broad lines. The polymers obtained by partial hydrolysis of AM homopolymers gave similar spectra. By following the evolution of these peaks with copolymer composition, these resonances were assigned to acrylamide-centered (MMM, MM A,  $\overline{\text{M}}\text{A}$ ) and acrylate-centered triads ( $\overline{\text{M}}\text{A}\text{M}$ ,

M $\overline{A}\overline{A}$ , A $\overline{A}\overline{A}$ ) from high to low field. The different chemical triad assignments and the relative intensities of each triad are listed in Tables 1 & 2.

**Table 1** Relative intensities and chemical triad assignments of acrylamide and acrylate carbonyl resonances for copolymer obtained by direct copolymerization

| Shift (pm)         | 180.61                           | 181.24                           | 181.63                           | 183.93                           | 184.56                           | 185.10                           |
|--------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| Assignment         | M $\overline{M}\overline{M}$ (1) | M $\overline{M}\overline{A}$ (2) | A $\overline{M}\overline{A}$ (3) | M $\overline{A}\overline{M}$ (4) | A $\overline{A}\overline{M}$ (5) | A $\overline{A}\overline{A}$ (6) |
| Relative intensity |                                  |                                  |                                  |                                  |                                  |                                  |
| Z* = 0.12          | 0.67                             | 0.21                             | 0                                | 0.12                             | 0                                | 0                                |
| Z = 0.25           | 0.39                             | 0.34                             | 0.03                             | 0.15                             | 0.10                             | 0                                |
| Z = 0.50           | 0.11                             | 0.24                             | 0.15                             | 0.13                             | 0.24                             | 0.15                             |

\* Z represents the molar fraction of AANa unit

**Table 2** Relative intensities and chemical triad assignments of acrylamide and acrylate carbonyl resonances for copolymer obtained by hydrolysis

| Shift (pm)         | 180.61                           | 181.24                           | 181.63                           | 183.93                           | 184.56                           | 185.10                           |
|--------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| Assignment         | M $\overline{M}\overline{M}$ (1) | M $\overline{M}\overline{A}$ (2) | A $\overline{M}\overline{A}$ (3) | M $\overline{A}\overline{M}$ (4) | A $\overline{A}\overline{M}$ (5) | A $\overline{A}\overline{A}$ (6) |
| Relative intensity |                                  |                                  |                                  |                                  |                                  |                                  |
| Z = 0.13           | 0.63                             | 0.24                             | 0                                | 0.13                             | 0                                | 0                                |
| Z = 0.27           | 0.27                             | 0.33                             | 0.12                             | 0.21                             | 0.07                             | 0                                |
| Z = 0.40           | 0.04                             | 0.31                             | 0.25                             | 0.20                             | 0.18                             | 0.02                             |
| Z = 0.50           | 0                                | 0.20                             | 0.30                             | 0.21                             | 0.26                             | 0.03                             |

It was noteworthy that the differences in the acrylamide unit distribution between AM-AANa copolymers obtained by partial hydrolysis and by direct copolymerization were quite obvious. Due to the neighbouring group effects, that is, the electrostatic repulsion between the anionic reagents and the polymer substrate resulted in a mechanism of autoretarded reaction<sup>[6]</sup>, the copolymer obtained by partial hydrolysis led to a little probability of finding long sequences of acrylate groups along the polymer chain. On the other hand, because the reactivity parameters ( $r_{AM} = 0.90$ ,  $r_{AANa} = 0.34$ )<sup>[3]</sup> of the AM-AANa radiation copolymerization favoured longer blocks of monomer units, the copolymer obtained by direct copolymerization of the two corresponding monomers showed a less alternating monomer unit distribution than that obtained by partial hydrolysis. From the above discussions, we could conclude that there are differences in sequence distribution of the monomer units of the two gels, which could well explain their different swelling properties.

#### Keywords :

Acrylamide; Sodium acrylate; Radiation; Hydrogel; Water Retention Value; <sup>13</sup>C-NMR

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