Study of Poly(acrylamide-*co*-2-acrylamido-2-methylpropane sulfonic acid) Hydrogels Made Using Gamma Radiation Initiation

Chi Zhang, Allan J. Easteal

Department of Chemistry, University of Auckland, Auckland, New Zealand

ABSTRACT: Poly(acrylamide-*co*-2-acrylamido-2-methylpropane sulfonic acid) hydrogels were synthesized using gamma-radiation-initiated polymerization. The progress of copolymerization and crosslinking was observed by viscosity measurement on reaction mixtures subjected to varying radiation doses. The copolymer gels were characterized by differential scanning calorimetry, X-ray diffraction, scanning electron microscopy, infrared spectroscopy, and elemental analysis. The swelling behavior and other properties of the gels were found to be very similar to those of poly(acrylamide-*co*-2-acrylamido-2-methylpropane sulfonic acid) hydrogels synthesized using conventional free-radical initiation in the presence of crosslinkers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1322–1330, 2003

Key words: gamma radiation; copolymerization; hydrogel; acrylamide; 2-acrylamido-2-methylpropane sulfonic acid

INTRODUCTION

Copolymers of acrylamide (AAM) with sulfonated comonomers, especially 2-acrylamido-2-methylpropane sulfonic acid (AMPS), offer hydrogen-bonding capability and polyelectrolyte behavior in aqueous solutions.[1] The introduction of ionic groups into polymeric materials alters the polymer morphology and consequently the physical and chemical properties.[2] The presence of sulfonic acid groups results in a strong polyelectrolyte character.[3]

Hydrogels based on AMPS, synthesized using various methods, have been used in biochemistry,[1,4] for skin contact electrodes,[5] and to adhere medical devices to the skin or for drug delivery applications such as iontophoresis.[6]

Although the free-radical-initiated copolymerization of AMPS and the swelling behavior and volume phase transition together with other properties of poly(AAM–*co*–AMPS) gels have been investigated,[3,7–12] there have been few publications on gamma-radiation-initiated copolymerization of AMPS with AAM. It has been reported that poly(AAM–*co*–AMPS) synthesized using γ-radiation had a higher pure water absorbency but showed a large decrease in NaCl solution absorbency.[1] It was also found that a mixture of AAM and AMPS grafted onto starch using gamma irradiation had high water absorbency.[4]

Gamma-radiation-initiated synthesis of poly(AAM–*co*–AMPS) gels in the presence of a large amount of water and characterization of those gels are described in this work. To initiate polymerization in the AAM-AMPS comonomer–water system, the free radicals must be generated from an aqueous solution during the irradiation. Because the water content of the pregel solutions is high, the radiation chemistry of water is of particular importance, as the calculated electron fraction of water is more than 95%.

EXPERIMENTAL

Research-grade AAM (from Rhone-Poulenc, France), and AMPS (99%, Merck-Schuchardt, Germany) were used without further purification. For gel synthesis, 100 mL of an aqueous comonomer solution, 0.5 mol/L in AAM and 0.05 mol/L in AMPS, was purged with nitrogen for about 10 min at ambient temperature immediately before transferring 2-mL aliquots into soda glass vials. The vials were placed in the cavities of the three-layer aluminium reaction vessel shown in Figure 1. Each layer of the reaction vessel is a cylindrical block with five cavities drilled symmetrically about the axis of the block. The gamma radiation source provided a flux of radiation that varied along the axis of the reaction vessel, so that three sets of gels made with different radiation doses could be made in each experiment.

After assembly the reaction vessel was flushed with nitrogen for 10 min, evacuated and sealed, and then

Correspondence to: A. J. Easteal, Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand (aj.easteal@auckland.ac.nz).
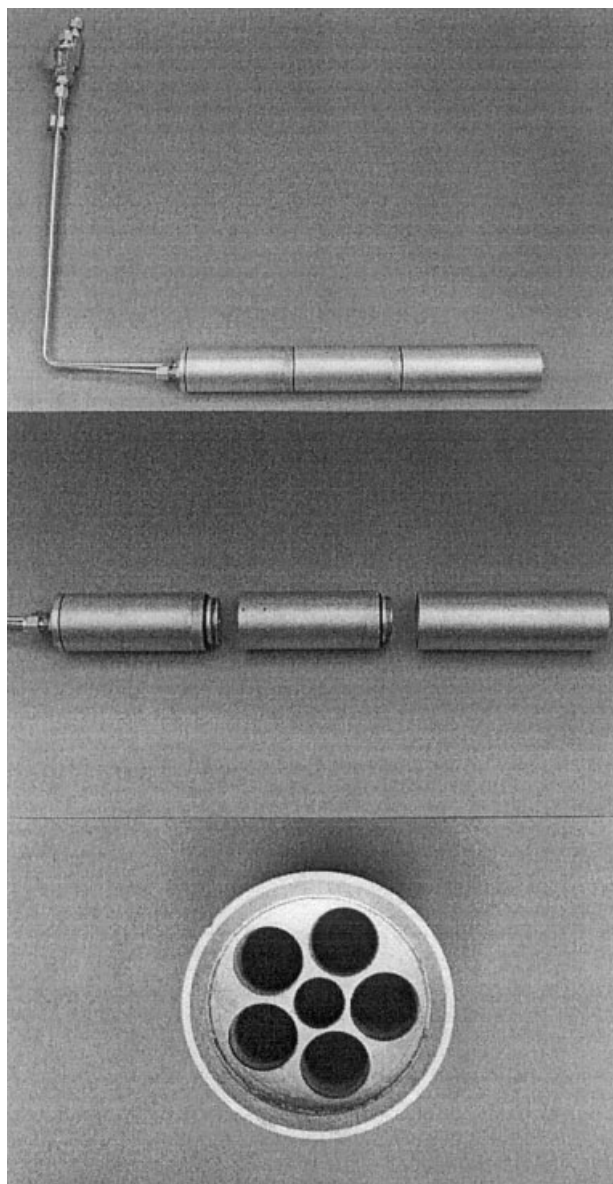
Figure 1 Aluminium irradiation vessel (top: Overview of the assembled vessel; middle: view of disassembled sections; bottom: cross section of one section). The central hole allows evacuation of the whole vessel.

lowered into the central cavity of a Co^{60} source and irradiated for varying times at ambient temperature. Dose rates at each level of the reaction vessel were determined by Fricke dosimetry.[13]

Viscosity changes during irradiation were used to monitor the gel formation process. The viscosity of partially gelled samples was measured at 25°C using a Brookfield Model LVT Synchro-Lectric viscometer, calibrated using Brookfield viscosity standard fluids.

For thermal analysis by differential scanning calorimetry, gel samples (~10–15 mg) contained in aluminium crucibles were cooled to −30°C, then heated at 10°C/min to 300°C, using a Polymer Laboratories Model 12000 instrument, a differential scanning calo-

rimeter (DSC). The melting points of the ice formed by cooling the gels were determined as the onset temperatures of the corresponding endothermic transitions from at least two replicate determinations.

Powdered samples of vacuum-dried gels were heated in the DSC at 80°C for 20 min to vaporize residual water in the samples, cooled to −100°C at 20°C/min, held at −100°C for 2 min, and then heated to 400°C at 10°C/min.

Swelling/deswelling experiments were carried out on gel samples made in glass tubes 4.6–5 mm in diameter; the gel samples were sliced into cylinders about 10 mm in length. The gel cylinders were immersed in distilled water for 6 days, then in water–acetone mixtures of varying compositions for 6 days. Equilibrium swelling ratios were determined by measuring the diameter of the gel cylinders (to ±0.01 mm) using a digital micrometer. The swelling ratio was evaluated relative to the volume state at preparation, through the relationship

$$(V/V_0) = (d/d_0)^3 \qquad (1)$$

where d and d_0 are the diameters of the gel cylinder after swelling/deswelling and at preparation, respectively.

The crystallinity of the monomers and gels that had been dried under vacuum at 55°C and 30 mmHg to a constant weight was examined by X-ray powder diffraction using a Philips PW1130 diffractometer. A Philips XL30 scanning electron microscope was used to investigate the surface morphology of the dried gels.

For composition determination by elemental analysis, gel samples were divided into two portions. One portion was vacuum-dried but otherwise unpurified, whereas the other portion was purified by repeated cycles of swelling in water, deswelling in methanol, and centrifugation, prior to vacuum-drying. Elemental analysis for C, H, S, and N was carried out on gel samples that were heated to 100°C over silica gel immediately prior to analysis. Gel compositions were calculated from the sulfur and nitrogen contents of the gels, via the relationship

$$F_1 = 14.0.S\%/32.1.N\% \qquad (2)$$

where F_1 is the mole fraction of AMPS, and S% and N% are the weight percentages of S and N, respectively, in the copolymer.

FTIR spectra[14–17] of dried gels in the form of KBr discs containing 1%–2% polymer were obtained using a Bio-Rad model FTS-60 spectrometer.

RESULTS AND DISCUSSION

Gel formation

Other investigators have reported[18] that when an AAM aqueous solution at 77–393 K was initiated *in*
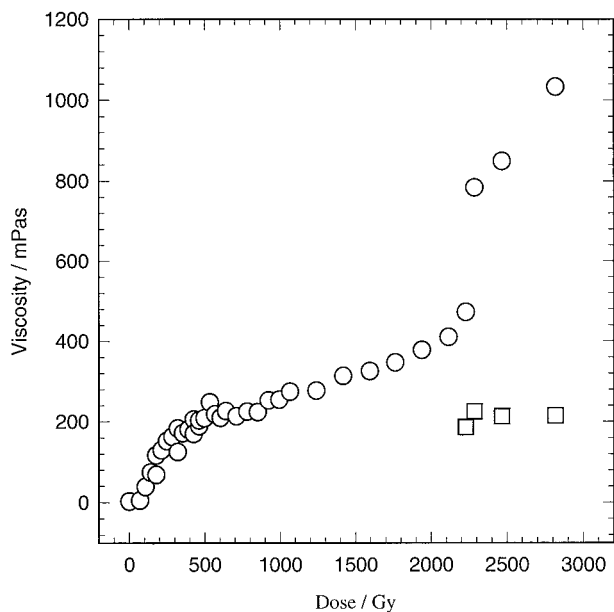
Figure 2 Dependence of shear viscosity of reaction mixture on radiation dose in the early stages of gel formation. (○) freshly irradiated solutions; (□) solutions aged for 50 days at ambient temperature.

vacuo or in air to form a polymer, the G values were: for generating free radicals, 0.88 per 100 eV; for crosslinking, 1.33 (*vacuo*)/0.62 (air) per 100 eV; and for main chain scission, 0.45 (*vacuo*)/0.52 (air) per 100 eV. Consequently, AAM should be easily crosslinked in an aqueous solution. The physical changes consequent on crosslinking include increased viscosity, lower solubility, and a higher melting point. It has been found that during irradiation polymers or copolymers containing units of the types —CH$_2$CH$_2$— and —CH$_2$CH(R)— generally crosslink, whereas polymers with units of the type —CH$_2$C(R'R")— degrade by chain scissions.[19,20] Consequently, AAM and AMPS tend to crosslink while longer polymer main chains are formed. Crosslinking probably occurs through the removal of a hydrogen atom from one of the chains by energetic free radicals. This leaves a radical site on the main chain, and the hydrogen atom produced will abstract another hydrogen atom from an adjacent chain. The two radical sites left on the adjacent chains can then recombine to form a crosslink.[19] A theoretical study[21] pointed out that H-shaped connections are required structurally for covalent gel formation on the basis of the heterochain branching theory. The X-shaped chain connections that are formed through crosslinking by high-energy radiation can be considered a special case of the H-shaped connection, in which the chain length of the bridge is zero. It was found that similar zero-bridge crosslinking can occur in curing of polyolefins such as polyethylene, or poly-(vinyl chloride) with high-energy electron beams.[22]

Figure 2, shows that in the present work the viscos-

ity of the irradiated solution increased with increasing dose in the early stages of gel formation. The initial rapid increase in viscosity at doses less than 2.2 kGy is most likely a result of the main chain propagation of comonomers. For doses between 2.2 and 3.2 kGy, the more rapid increase in viscosity probably arose from main chain entanglements and some interchain crosslinking. At doses above about 3.2 kGy the viscosity increased very rapidly, and the viscous liquid started to climb up the rotating spindle of the viscometer (the so-called Weissenberg effect[23]) because of an increasing proportion of covalently bonded crosslinks between chains. At doses around 6.6 kGy firm gels were formed, some shrinkage of the samples occurred with partial expulsion of water, and bubbles were formed at about 11 kGy. The viscosity data and experimental observations are summarized in Table I.

Aging of viscous liquids formed at low doses

The viscous liquids formed at doses below 2.9 kGy were unstable, in that the viscosity determined immediately after irradiation decreased after 50 days of aging at ambient temperature to a value in the range of 186–225 mPa s (see Fig. 2). This observation implies that in the early stage of gel formation the liquidlike system has sustained both irreversible and reversible changes. The irreversible changes are responsible for the threshold viscosity of about 200 mPa s, which is attributable primarily to linear chain growth. The re-

TABLE I
Dependence of Viscosity and Physical State of a 0.5 mol/L AAM + 0.05 mol/L AMPS Comonomer Solution on Absorbed Dose at Ambient Temperature

Dose/kGy	η/mPa s^{-1}	State
0	2.6	L
0.0712	4.6	L
0.533	248	L
1.065	275	L
2.230	472	L
2.287	783	L
2.467	849	L
2.819	1033	VL
3.173	WE	HVL
4.381	WE	HVL
4.492	WE	HVL
6.571	—	G
6.739	—	G
8.192	—	G*
8.794	—	G*
11.0	—	G*
11.2	—	G*
22.5	—	G*
50.8	—	G*

η = shear viscosity; WE signifies Weissenberg effect; L, VL, and HVL denote liquid, viscous liquid, and high-viscosity liquid; G and G* denote gel and gel-containing bubbles, respectively.

TABLE II
Dependence of Thermal Properties of Water in Poly(AMPS) Gels on Monomer Concentration in Pregel Solution

dose/kGy	C mol L^{-1}	T_m/°C	ΔH_m/J g^{-1}	State
8.1	0.5	−1.8 ± 0.7	160 ± 24	gel
8.5	1.0	−5.8 ± 1.3	117 ± 24	gel
8.0	1.5	−9.9 ± 4.0	55 ± 23	gel

Uncertainties based on standard deviations of five or more determinations.

versible changes that caused the viscosity to be substantially larger immediately after gel formation are likely to be associated with physical crosslinks such as chain entanglements and interchain hydrogen bonds, which are eliminated by deentanglement or reorientation of the polymer main chain coils and the breaking and relaxation of hydrogen bonds.[24]

This behavior is similar to that reported by Sabharwal and coworkers[25] on the irradiation of linear polyPVME aqueous solutions. They found that the half-life for decay of macroradicals was a function of radiation dose and polymer concentration. At high doses and high polymer concentrations, the concentration of radicals per polymer chain was high, and radical recombination occurred primarily by intramolecular recombination. On the other hand, when polymer concentration or radiation dose was low, as in the present case, the concentration of radicals per polymer chain was low, and the recombination of radicals could occur via an intermolecular process, leading to an increase in molecular weight and gel formation. Consequently, crosslinking can take place at relatively low doses.

Melting point of water in hydrogels

For the poly(AAM–*co*–AMPS) hydrogels it was difficult to obtain freezing points even at small (0.5°C/min) cooling rates because of supercooling, but it was relatively straightforward to determine the melting point and enthalpy of fusion of water in the gels. A previous study[26] using Raman spectroscopy and DSC showed two different water structures existing within poly(AAM–*co*–AMPS) gels made by free-radical-initiated polymerization: bound (hydration, destructured) water and free (bulk, structured) water. A higher concentration of AAM-AMPS copolymer chains in the gel led to pronounced occurrence of defects in the hydrogen-bonded water structure and increased the fraction of bound water relative to free water.

The concentration effect for gels made in the present study is shown by the data in Table II: at approximately constant radiation dose, increasing AMPS concentration in the pregel solution decreased both the melting point and the enthalpy of fusion of water in

AMPS homopolymer hydrogels. The concentration effect can be explained as follows. AMPS is a moderately strong acid; hence, the sulfonic acid side groups on the backbone chains are highly ionised and water molecules will strongly interact with the sulfonic acid groups. As the AMPS concentration of the ionized groups increases, the ionized groups have a structure-breaking effect on water, hence increasing the ratio of destructured to structured water.

Figure 3 shows that in the 0.5*M* AAM/0.05*M* AMPS system, the melting point of the viscous liquid or gel after irradiation is virtually independent of radiation dose, following an initial increase of about 3°C for a 1 kGy dose. The same trend was exhibited by a solution of AAM.
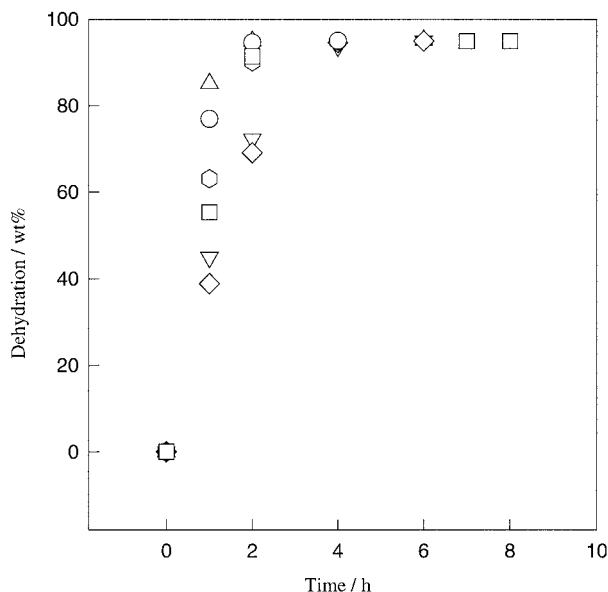
Dehydration

The rate of dehydration of poly(AAM–*co*–AMPS) gels with varying irradiation dose was determined gravimetrically on samples maintained in a vacuum oven at 55°C and 33 mmHg for varying times. The extent of dehydration defined by

$$\% \text{ dehydration} = 100 \times (W_o - W_t)/W_o \quad (3)$$

where W_o and W_t are the gel sample weights at preparation and after drying for time t, respectively, is shown as a function of dehydration time in Figure 4. The extent of dehydration of all gels became virtually constant at 95% after about 6 h, corresponding to complete dehydration.
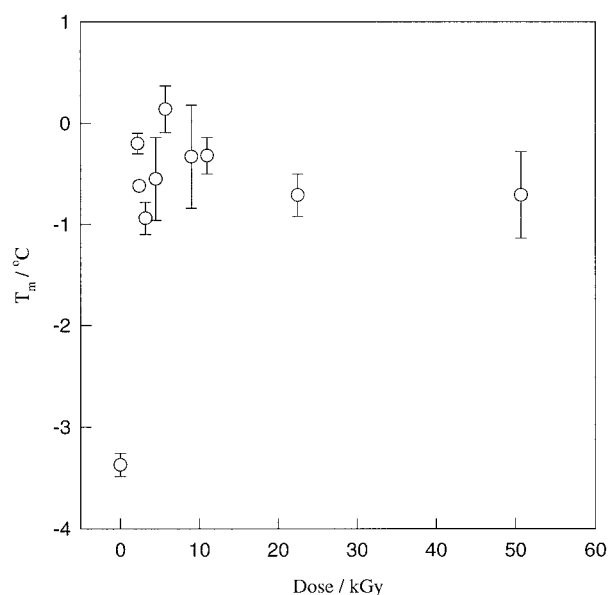
Figure 3 Dependence of melting point of water in poly(AAM–*co*–AMPS) hydrogel on dose. Error bars represent standard deviations of at least five determinations.

Figure 4 Dependence of dehydration from poly(AAM–*co*–AMPS) gels on dehydration time at 55°C and 33 mmHg pressure. The symbols correspond to different radiation doses (kGy) as follows: (△) 2.2; (▽) 6.7; (◇) 9.0; 11.2; (○) 22.5; (□) 50.8.

The extent of dehydration of the gels at short dehydration times depended on the dose at preparation (Fig. 5). For a 1- or 2-h dehydration, the extent of dehydration initially decreased for doses up to about 10 kGy, then subsequently increased, passing through a maximum at about 20 kGy for a 1-h dehydration. The growing polymer chains initially reduced the lability of water through the interaction of water with sulfonic acid groups that became less mobile as the chain length increased. With further increases in dose, increasing crosslink density generated a higher network pressure, which tended to expel water from the network, increasing the extent of water loss. At very high doses the rigidity of the gel inhibited diffusion of water molecules—hence, loss of water from the gel.

Gel swelling behavior

Ilmain and coworkers[24] have discussed the types of interactions that are operative in gels. Many gels undergo reversible, discontinuous volume changes in response to changes in, for example, temperature, gel composition, or light irradiation.[27] These transitions result from the competition between repulsive intermolecular forces, usually electrostatic in nature, that act to expand the polymer network, and attractive forces that act to shrink it. The van der Waals interaction causes phase transitions in hydrophilic gels in a mixed solvent, such as an AAM gel in an acetone–water mixture.

Because AMPS is a moderately strong acid (pK = 1.9), the sulfonic acid groups on the AAM–AMPS

backbone chains in poly(AAM–*co*–AMPS) gels are highly dissociated, and the swelling ratios of gels prepared by free-radical initiation is independent of pH, from pH 2 to pH 10, at a constant ionic strength.[8] For poly(AAM–*co*–AMPS) gel produced by 8.19 kGy of gamma irradiation, after swelling for 6 days in water, the average value of V/V_0 was 35.4 (see Fig. 6). The swelling was reversible, and the gel showed volume phase transition that is characteristic of this system in water–acetone mixtures.[8]

Gel morphology

SEM micrographs of the surfaces of dried poly(AAM–*co*–AMPS) gels with doses in the range of 2.2–50.8 kGy showed a homogeneous surface morphology at all doses, which can be attributed to the low concentration of the comonomers in the pregel solution and to short-range X-shaped crosslinks with zero-bridge chain length.[21,22]

Wide-angle X-ray diffraction patterns of dried poly(AAM–*co*–AMPS) gels formed at doses of 9.0 and 50.8 kGy showed no reflections, implying absence of crystalline domains, which is consistent with random copolymerization and crosslinking.

Thermal properties of dried gels

Aggour[28] determined the thermal stability of polyAMPS, polyAAM, and poly(AAM–*co*–AMPS) using thermogravimetry. He reported that polyAAM and polyAMPS showed appreciable degradation at about 245°C and 182°C, respectively, and that a second stage
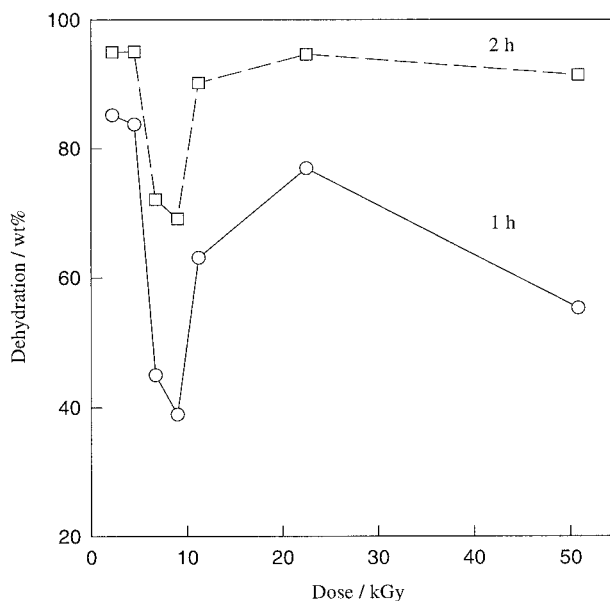
Figure 5 Short time dependence of dehydration of poly(AAM–*co*–AMPS) gels. (○) 1-h dehydration and (□) 2-h dehydration at 55°C and 33 mmHg pressure.
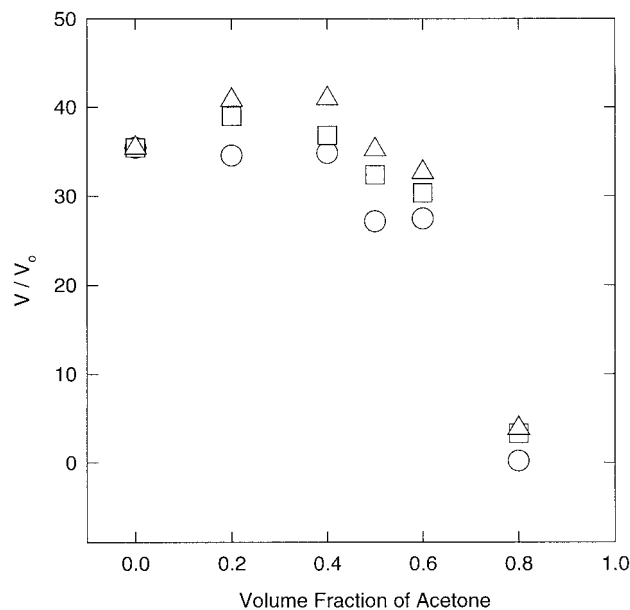
Figure 6 Swelling ratios (V/V_0) of irradiated poly(AAM–*co*–AMPS) gels (corresponding to 8.19 kGy irradiation) in acetone–water mixtures: (◯) volume state after deswelling; (□) volume state after reswelling in water for 6 days, (◇) volume state after reswelling in water for 12 days.

of degradation started at about 303°C. He concluded that the thermal stability of AAM–AMPS copolymers lies between the stabilities of the corresponding homopolymers. He further suggested that thermal degradation of poly(AAM–*co*–AMPS) occurs in three stages: decomposition of amide groups, degradation of sulfonic groups, and breakdown of the polymer backbone.

In the differential scanning calorimeter scans, shown in Figure 7, peak melting points of 87.4 and 193.4°C for AAM and AMPS, respectively, can be seen. Thermally induced polymerization of AAM occured at 133.6°C and was followed by decomposition at around 236°C. For AMPS, melting was followed immediately by decomposition at about 207°C. The PolyAAM gel with a dose of 8.1 kGy showed a glass-transition temperature of approximately 146°C; endotherms associated with several stages of decomposition at around 227°C, 252°C, and 290°C; and a final decomposition peak at around 393°C, which is consistent with the decomposition temperature range (326°C–410°C) recently reported by Silva and coworkers.[29]

The polyAMPS gel with a dose of 8.1 kGy showed a weak transition, probably the glass-transition temperature[30] (T_g), at about 125°C. The first stage of decomposition appeared to begin at around 170°C, the second stage at about 220°C, and the final stage at approximately 300°C. These observations are consistent with previously reported thermal decomposition temperatures for polyAMPS.[28] Dried poly(AAM–*co*–

AMPS) gels showed similar thermal behavior that was essentially independent of dose. The three principal features were a very broad, weak endothermic baseline shift corresponding to a T_g on the order of 150°C, a strong, less broad endotherm with an onset temperature of about 220°C, and a strong, sharp endotherm with a peak temperature of about 298°C. The endotherm at 220°C is attributed to the cleavage of weak crosslinks and the decomposition of amide groups, and the signal at 298°C is probably a result of degradation of sulfonic groups and breakdown of the polymer backbone. The thermal stability of dried poly(AAM–*co*–AMPS) gels was intermediate between the stabilities of dried polyAAM and polyAMPS gels, as expected for random copolymerization. The DSC data are summarized in Table III.

Composition of dried copolymer gels

Both copolymer composition and monomer sequence distribution in copolymers are controlled by monomer reactivity ratios as well as comonomer mixture composition. In a gamma-radiation-initiated copolymerization system, it is difficult to determine reactivity
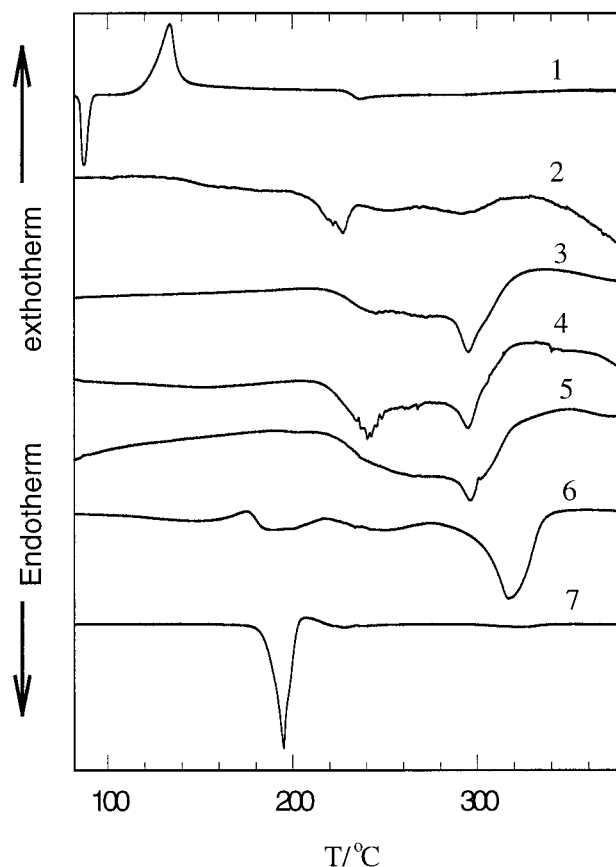
Figure 7 DSC scans of: 1, AAM monomer; 2, polyAAM (8.1 kGy dose); 3, 4, and 5, poly(AAM–*co*–AMPS) gel after 2.2, 9.0, and 50.8 kGy, respectively, of irradiation; 6, polyAMPS (8.1 kGy dose); and 7, AMPS monomer.

TABLE III
Thermal Properties of AAM and AMPS Monomers and Dried Homopolymer Gels
and Dried Poly(AAM-*co*-AMPS) Gels

Sample	dose/kGy	$T_m/°C$	$T_g/°C$	$T_{pp}/°C$[a]	$T_d/°C$[b]
AAM	N/A	87.4 (peak)	—	133 (peak)	236 (peak)
AMPS	N/A	193.4 (peak)	—	—	207
polyAAM	8.1	—	146	—	227–393 (peaks)
polyAMPS	8.1	—	125	—	189–317 (peaks)
copolymer	2.2, 9.0, 50.8	—	≈150	—	220–298 (peaks)

[a] Thermally induced polymerization temperature.
[b] Decomposition temperature.

ratios because crosslinking occurs even at low conversion. However, the copolymer gel compositions can be determined using elemental analysis.

Poly(AAM–*co*–AMPS) gel samples were analysed for C, H, N, and S in order to understand the effects of radiation dose on the chemistry of the gels. The element loss (wt %) defined by

$$E_L = 100(E_0 - E_i)/E_0 \qquad (4)$$

where E_0 is the weight percentage of a specific element in the comonomer mixture, and E_i is the weight percentage of that element in the dried copolymer gel, is shown as a function of radiation dose in Figure 8. The element loss was systematically larger for sulfur than for nitrogen and carbon and was roughly independent of dose except at the highest dose. Because sulfur was present only in AMPS units, the higher sulfur loss relative to nitrogen and carbon suggests that AMPS monomer may suffer radiation-induced degradation

to form gaseous products such as SO_2 or that fewer AMPS units were incorporated in the copolymer gel network because AMPS is less reactive than AAM in radiation-induced copolymerization.

For free-radical-initiated copolymerization of (1) AAM and (2) AMPS, the monomer reactivity ratios r_1 = 1.21, r_2 = 0.62,[9] and r_1 = 1.05, r_2 = 0.42[3] have been reported. Both sets of reactivity ratios indicate that in a free-radical-initiated reaction, the copolymer first formed contains an excess of AAM units relative to the proportion of AAM in the pregel solution. The data in Figure 9 show, likewise, that in gamma-radiation-initiated copolymerization AAM was the more reactive monomer because the mole fraction, F(AAM), of AAM in the copolymer gels was always larger than its mole fraction, f(AAM), (0.909) in the pregel solution. Figure 9 also shows that at very large doses F(AAM) approached f(AAM), so that almost all the unreacted AMPS initially present in the pregel solution was eventually incorporated into copolymer chains. This
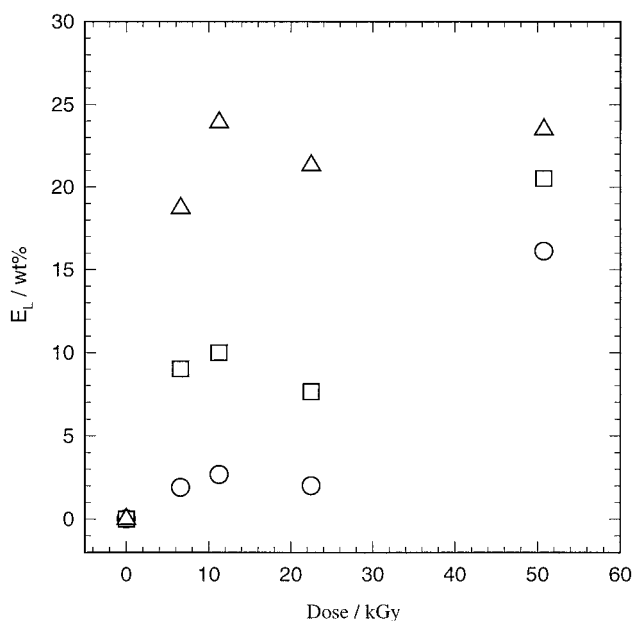

Figure 8 Dependence of element loss on dose for purified poly(AAM–*co*–AMPS) gels. The symbols denote the elements as follows: (△) sulfur; (□) nitrogen; (○) carbon.
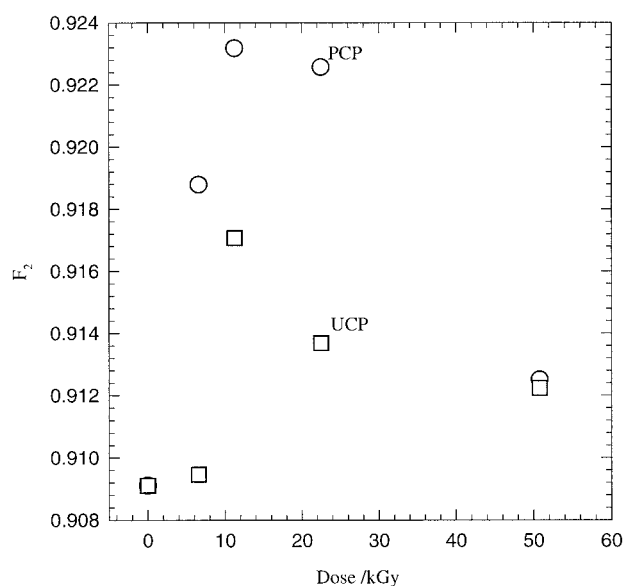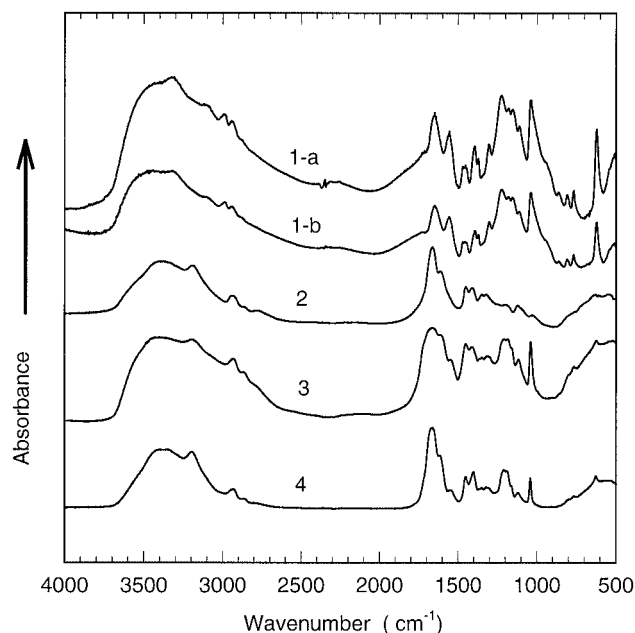

Figure 9 Dependence of AAM mole fraction (F_2) in copolymer gels on dose: (PCP) purified copolymer gels; (UCP) unpurified copolymer gels. The mole fraction of AAm in the copolymer, F(AAm) = F_2 = 1 − F_1.

Figure 10 FTIR spectra of (1-a) polyAMPS synthesized using free-radical initiation; (1-b) polyAMPS gel synthesized by gamma irradiation (8.5 kGy); (2) polyAAM synthesized by gamma irradiation (8.1 kGy); (3) and (4) poly(AAM–*co*–AMPS) gel synthesized by gamma irradiation at 2.3 and 50.8 kGy, respectively. Spectra have been offset for clarity.

tendency is analogous to the copolymer composition drift that is observed in conventional free-radical-initiated reactions.[3]

FTIR spectra

The IR spectra of the dried poly(AAM–*co*–AMPS) gels were very similar to those of the AAM–AMPS copolymers prepared by free-radical-initiated polymerization[9,31] and by initiation with a high-frequency discharge.[12] The FTIR spectrum of the gamma-initiated polyAMPS gel is shown in Figure 10, together with the spectra of free-radical-initiated polyAMPS, gamma-initiated polyAAM gel, and poly(AAM–*co*–AMPS) gels at low- and high-radiation doses. Comparison of the spectrum of polyAMPS in this work with reported spectra[26,32–34] of polyAMPS synthesized using various types of chain initiation indicates that the homopolymer structure is independent of the mode of initiation.

CONCLUSIONS

Gamma radiation initiation was successfully used to synthesize AAM–AMPS copolymer gels. Radiation dose greatly increased the viscosity of the reaction mixture, as expected. The aging effect, in which the viscosity of the reaction mixture decreases on standing, is attributed to the disappear-

ance of temporary interactions such as entanglements between chains.

Gamma-initiated poly(AAM–*co*–AMPS) gels respond to external stimuli in the same way as do the corresponding gels synthesized by free-radical or photochemical initiation in the presence of methylene bisacrylamide crosslinker. They swell in water, collapse in a acetone–water solution with a high proportion of acetone, and recover their shape and volume in water after collapse, implying microreversible properties of the network.

The absence of Bragg reflections from the dried gels indicates insignificant crystallinity and suggests that gamma-radiation-initiated copolymerization of AAM with AMPS yields random copolymers. The homogeneous surface morphology is consistent with short-range (zero-bridge) crosslinking.

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