Synthesis and Swelling Properties of the Copolymer of Acrylamide with Anionic Monomers

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SYNOPSIS

A series of novel superabsorbent copolymers of acrylamide (AM), sodium allylsulfonate (SAS), sodium acrylate (AA), and *N,N'*-methylenebisacrylamide (BisA) were synthesized using potassium persulfate (KPS)/*N,N,N',N'*-tertramethylethylenediamine (TMEDA) as the initiator. The influences of synthetic variables (monomer concentration, temperature, initiator concentration, and pH) on the polymerization conversion ($y\%$) and swelling properties were studied in detail. These gels should have potential application as water superabsorbents. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Superabsorbents are crosslinked networks of hydrophilic polymers with a high capacity for water uptake[1] and have a variety of valuable applications.[2-5] Indeed, much attention has been directed to superabsorbent syntheses and applications over the past two decades.

Water-soluble monomers can produce hydrogels by free-radical copolymerization with suitable crosslinking agents. Recently, sodium allylsulfonate has been used to synthesize a number of water-soluble polymers[6-8] and superabsorbents.[9,10] In our previous studies,[10] we reported the synthsis of a novel superabsorbent based on the copolymerization of acrylamide, sodium allylsulfonate, sodium acrylate, and *N,N'*-methylenebisacrylamide, but the main point under discussion is the swelling kinetics and thermal stability of the absorbent. In the present work, we report the swelling properties of the title copolymer produced under variable reaction conditions to explore both quality-control issues and application.

EXPERIMENTAL

To establish the optimal conditions for copolymerization using KPS–TMEDA as the redox initiator, polymerization was carried out under various conditions as described earlier.[10] The variables studied included crosslinker concentration, monomer concentration, initiator concentration, temperature, and pH. Conversions ($y\%$) were calculated by the weight of the dried gel and swelling ratios were determined by dividing the wet weight by the dry weight of the sample. Also, the water-absorbencies of these samples in different pH solutions were studied using $0.1N$ NaOH and $0.1N$ HCl to adjust the pH. Nitrogen content of the copolymer was determined using the Kjeldahl method.

RESULTS AND DISCUSSION

Copolymerization of AM with SAS Crosslinked by BisA

Copolymerizations of AM, SAS, and BisA were carried out in the presence of KPS/TMEDA as the redox initiator in an aqueous solution for 2.5 h. When TMEDA was added to the reaction system, gelation occurred very rapidly. After standing for 2.5 h, the crosslinked polymer gels were cut into small pieces and immersed in ethanol, washed, and dried under reduced pressure. All hydrogels were transparent.

It is well known that hydrogel swelling is induced mainly by the electrostatic repulsion of ionic charges in the network, the content of which is determined

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Journal of Applied Polymer Science, Vol. 62, 911–915 (1996)
 CCC 0021-8995/96/060911-05

by the ratio of feed monomers. Table I illustrates the absorbability as a function of ionic units (i.e., —SO_3Na groups) within the copolymer network. Swelling increases with increasing anionic units, but an excess of ionic units leads to an increase in soluble material at a fixed crosslinker concentration. However, the conversion always decreases as the SAS concentration increases because of the chain-transfer reaction of SAS.[11] When the SAS concentration is over 0.12 mol/L, the gel is too soft to handle.

Figure 1 shows the conversion (y%) and the swelling ratio of the crosslinked poly(AM–SAS) as a function of crosslinker (BisA) concentration. As shown in Figure 1, conversion increases with increased crosslinker concentration until the BisA concentration is above 6.4×10^{-3} mol/L, at which point conversion increases become minute. The swelling ratio increases as the BisA concentration proceeds from 1.6×10^{-3} to 6.4×10^{-3} mol/L and decreases considerably with BisA concentrations higher than 6.4×10^{-3} mol/L. This is due to an increased crosslink density, e.g., the space between each crosslink decreases, thereby absorbency decreases.

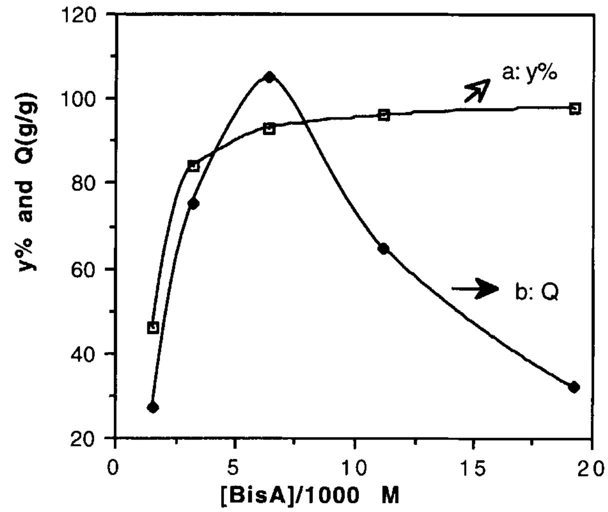

Figure 1 Influence of BisA concentration on conversion (y %) of poly(AM-*co*-SAS-*co*-BisA) and the water-absorbency (Q) in deionized water: [AM] = 0.97M; [SAS] = 0.04M; [KPS] = $2.67 \times 10^{-3}M$; [TMEDA] = $3.0 \times 10^{-3}M$; t = 35°C; 2.5 h. (a) conversion (y %); (b) water-absorbency (Q).

To study the effect of KPS concentration on conversion and swelling properties, the gelation time was recorded. As shown in Figure 2, the conversion increases and gelation time vigorously decreases with increasing KPS concentration. Obviously, higher KPS concentrations lead to an increase in the number of radicals, thereby to an increase in polymerization rate and decrease of gelation time. Absorbency tests showed that the swelling ratio decreases slightly as the KPS concentration increases.

Table I Influence of the Ionic Unit Content on the Swelling of Crosslinked Poly(AM–SAS)[a]

Entry	Monomer in the Feed (mol/L)		Element Content[b]	Repeating Units (mol %)[c]		Yield[d] (y%)	Water Absorbency (g/g) Q
	AM	SAS	N	-AM-	-SAS-		
S1	0.97	0.01	17.72	94.73	5.27	99.3	30
S2	0.97	0.02	17.23	93.35	6.65	99.1	72
S3	0.97	0.04	17.21	93.33	6.67	98.6	108
S4	0.97	0.10	15.89	89.38	10.62	98.0	172
S5	0.97	0.12	15.68	88.73	11.27	96.0	181
S6	0.97	0.16	14.71	85.62	14.38	93.0	190
S7	0.97	0.20	13.74	82.24	17.66	91.5	174
S8	0.97	0.24	13.43	81.24	18.76	90.0	166

[a] Reaction condition: [BisA] = 6.40×10^{-3} mol/L; [TMEDA] = 3.00×10^{-3} mol/L; [KPS] = 2.67×10^{-3} mol/L, at 35°C, 2.5 h.
[b] The nitrogen content of the copolymer was determined by using the Kjeldahl method. The repeating units were calculated from the nitrogen content.
[c] -AM-: —CH_2—CH— (with pendant $CONH_2$) ; -SAS-: —CH_2—CH— (with pendant CH_2—SO_3Na)
[d] It contains soluble (%).

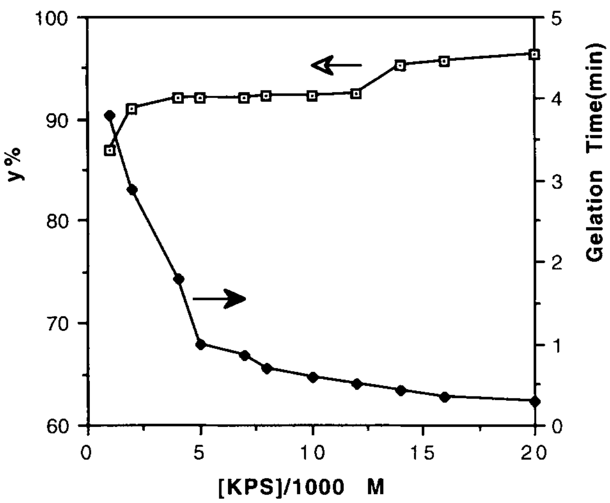

Figure 2 Influence of KPS concentration on conversion (y %) of poly(AM-*co*-SAS-*co*-BisA) and gel formation time (min): [AM] = 0.97M; [SAS] = 0.04M; [BisA] = 6.4 $\times$ $10^{-3}M$; [TMEDA] = 3.0 $\times$ $10^{-3}M$; t = 35°C; 2.5 h.

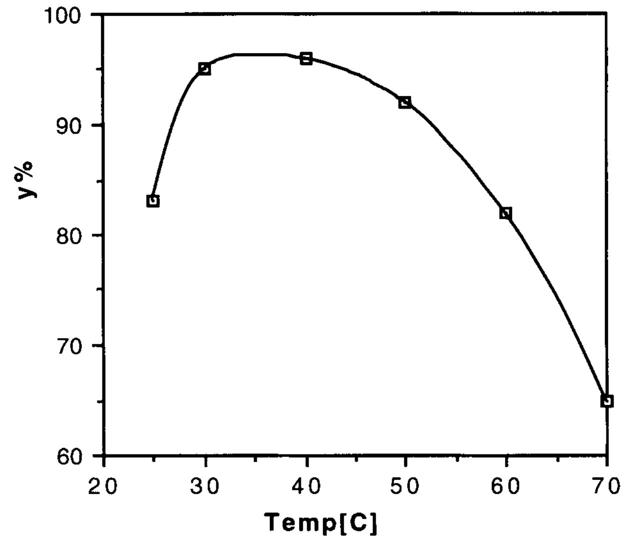

Figure 3 Influence of reaction temperature on conversion (y %) of poly(AM-*co*-SAS-*co*-BisA): [AM] = 0.97M; [SAS] = 0.04M; [BisA] = 6.4 $\times$ $10^{-3}M$; [KPS] = 2.67 $\times$ $10^{-3}M$; [TMEDA] = 3.0 $\times$ $10^{-3}M$; 2.5 h.

Figure 3 shows the influence of temperature on the conversion. The polymerization was carried out at 25, 30, 40, 50, 60, and 70°C, keeping all other variables constant. Raising the temperature causes the conversion to pass through a maximum at 35°C. At further low temperature, the initiation is ineffective and there is poor conversion. On the other hand, high temperatures lead to a short-chain polymer network which increases soluble materials.

To obtain greater insight into the effects of TMEDA, polymerizations were studied at various TMEDA concentrations. In Figure 4, the conversion is presented as a function of TMEDA concentration. As the TMEDA concentration increases, the conversion increases and reaches a maximum at a TMEDA concentration of 3.0 $\times$ 10^{-3} mol/L. When the TMEDA concentration is over 3.0 $\times$ 10^{-3} mol/L, conversion slowly decreases.

The effect of pH on conversion is shown in Figure 5. Since TMEDA is a base, it was added to the reaction system first and KPS was added after adjusting the pH. High yields are obtained when the pH is between 9 and 12. When the TMEDA concentration is 3.0 $\times$ 10^{-3} mol/L, the pH of the reaction solution is ~ 9 and no pH adjustment is required for high yield. The effect of pH on water absorbency was also tested. The results show that at high pH (>12) the swelling ratio is dramatically increased due to hydrolysis of amide groups to carboxylate groups (— CO_2Na; increased ionic content).

Copolymerization of AM and SAS with AA Crosslinked by BisA

Ionic content, which greatly influences water absorbency, can be raised by increasing the monomer ratio of SAS (— SO_3Na groups) or by raising the pH (>12) of the reaction mixture (lead to — CO_2Na groups). To study how acrylate content affects the swelling ratio, sodium acrylate was added to the po-

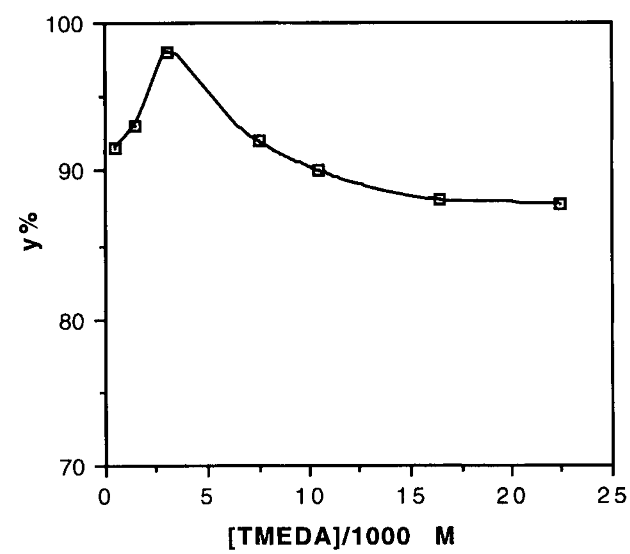

Figure 4 Influence of TMEDA concentration on conversion (y %) of poly(AM-*co*-SAS-*co*-BisA): [AM] = 0.97M; [SAS] = 0.04M; [BisA] = 6.4 $\times$ $10^{-3}M$; [KPS] = 2.67 $\times$ $10^{-3}M$; t = 35°C; 2.5 h.

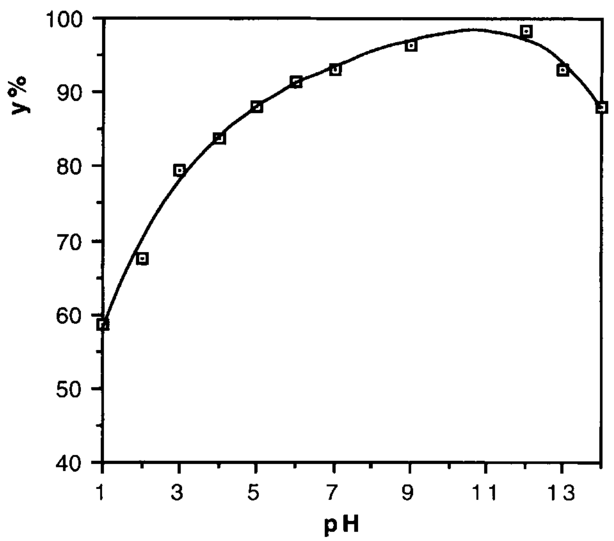

Figure 5 Influence of pH on conversion (*y* %) of poly(AM-*co*-SAS-*co*-BisA): [AM] = 0.97*M*; [SAS] = 0.04*M*; [BisA] = 6.4 × 10^{-3}*M;* [KPS] = 2.67 × 10^{-3}*M;* [TMEDA] = 3.0 × 10^{-3}*M; t* = 35°C; 2.5 h.

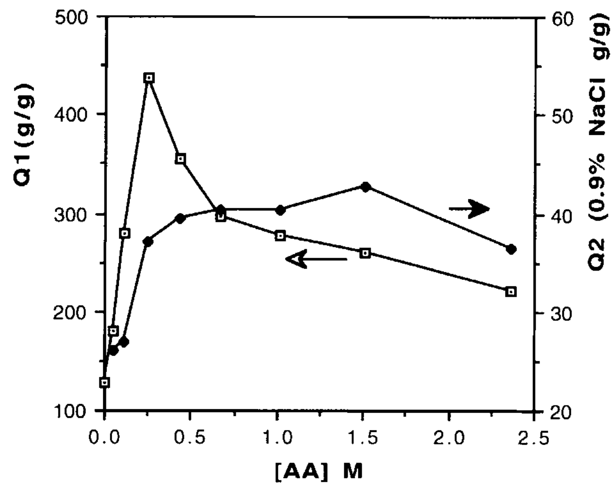

Figure 6 Influence of AA concentration on the water-absorbency of poly(AM-*co*-SAS-*co*-AA-*co*-BisA) in deionized water (Q1) and in 0.9% NaCl H_2O (Q2): [AM] = 0.97*M*; [SAS] = 0.04*M*; [BisA] = 6.4 × 10^{-3}*M;* [KPS] = 2.67 × 10^{-3}*M;* [TMEDA] = 3.0 × 10^{-3}*M; t* = 35°C; 2.5 h.

lymerization system. The resulting conversion was high (>98%) and the swelling ratio was notably enhanced (see Fig. 6). At fixed AM (0.97 mol/L), SAS (0.04 mol/L), and BisA (6.4 × 10^{-3} mol/L) concentrations, the swelling ratio increases and reaches a maximum (437 g/g in deionized water) at an AA concentration of 0.40 mol/L. Swelling decreases gradually when the AA concentration is over 0.40 mol/L.

Each sample prepared was also evaluated for swelling in 0.9% NaCl solution (Fig. 6, Q2). These gels only swelled 25–40 times their own weight in 0.9% NaCl solution, which is 10 times less than the swelling in deionized water.

Effect of pH on Swelling Behavior

The influence of solution pH on water absorbency for crosslinked poly(AM–SAS) (sample S3) and crosslinked poly(AM–SAS–AA) (sample A1) at room temperature is shown in Figure 7. The solution pH was adjusted with 0.1*N* HCl and 0.1*N* NaOH and the resulting water absorbency of each sample (S3 and A1) was markedly affected by pH with maximum water absorbency at pH 6. Since the pK_a of poly(acrylic acid) is ~ 4.7, the carboxyl groups of these hydrogels are not ionized at pH < 4.7. The swelling ratio of sample A1 (containing —CO_2Na groups) varied greatly between pH 4 and 5. On the other hand, the swelling ratio of sample S1 (containing stronger acid —SO_3Na groups) was less affected between pH 4 and 5.

CONCLUSION

1. The novel water-absorbent copolymers crosslinked poly(AM–SAS) and poly(AM–SAS–AA) were prepared in an aqueous solution by copolymerization of their respective monomers with *N,N'*-methylenebisacrylamide. Potassium persulfate with *N,N,N',N'*-tetramethylethylenediamine initiated polymerization under various conditions.

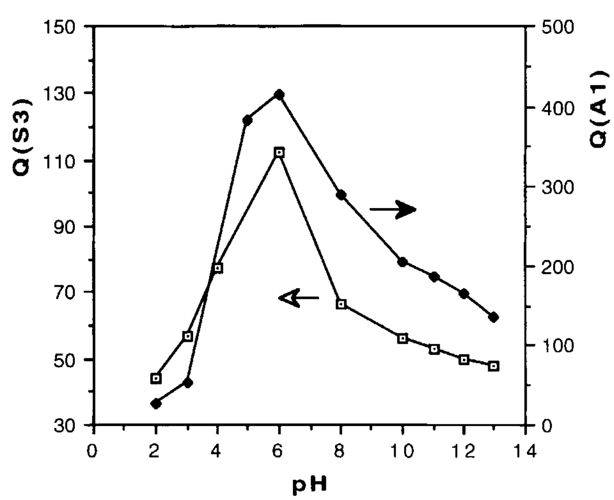

Figure 7 Influence of pH on the water-absorbency of the S3 and A1 samples, Q(S3) for S3; Q(A1) for A1. A1 sample: [AM] = 0.97*M*; [SAS] = 0.04*M*; [AA] = 0.25*M*; [BisA] = 6.4 × 10^{-3}*M;* [KPS] = 2.67 × 10^{-3}*M;* [TMEDA] = 3.0 × 10^{-3}*M; t* = 35°C; 2.5 h.

2. The absorbency of these copolymers increases to a maximum as the crosslinking increases. Excess crosslinking leads to a swelling decrease. The absorbency of crosslinked poly(AM–SAS–AA) is much higher than that of crosslinked poly(AM–SAS).
3. The swelling ratio of the absorbents decreases at high or low pH and the swelling change between pH 4 and 8 is dramatic. The properties of these pH-sensitive materials show promise in a variety of applications, particularly in systems which undergo only minute changes in pH, triggering the hydrogel to expand or shrink to change its diffusional characteristics rapidly. These materials should have applications in controlled drug-delivery systems.

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Received May 25, 1996
Accepted May 30, 1996