Synthesis and Properties of the Copolymer of Acrylamide with 2-Acrylamido-2-methylpropanesulfonic Acid

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ABSTRACT: A cross-linked copolymer of acrylamide (AM) with 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was prepared by solution polymerization. In this reaction, potassium persulfate (PPS) and *N,N*′-methylenebisacrylamide (NMBA) were used as initiator and cross-linker, respectively. This copolymer, poly(acrylamide-*co*-2-acrylamido-2-methylpropanesulfonic acid) (PAMA), can absorb up to 1749 g/g of dry polymer in distilled water and 87 g/g of dry polymer in 0.9 wt % NaCl aqueous solution at room temperature. The PAMA also has excellent performance in absorbing pure alcohols. Its absorbencies in methanol and glycol are about 310 g/g and 660 g/g, respectively. The effects of various salt solutions on the swelling properties were studied systematically, and the relationship between the absorbency and the concentrations of the different salt solutions can be expressed as $Q = kc^n$. Experimental results indicate that the absorbencies were stable at different water temperatures. The swelling rates of the copolymer in distilled water and a water/ethanol mixture (V_{water}:V_{alcohol} = 1:1) were also investigated, and the results showed that PAMA could absorb 992 g of distilled water per gram of dry polymer and 739 g of water/ethanol mixture per gram of dry polymer in five minutes. The PAMA has such good water retention at higher temperatures that the swollen gel can retain 71.6 and 49.5% of the maximum absorbency after being heated for 9 hours at 60 and 80 °C, respectively. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3481–3487, 2003

Key words: copolymerization; gels; swelling; cross-linking; networks

INTRODUCTION

Superabsorbents are cross-linked networks of hydrophilic polymers with a high capacity for water uptake, which are widely used in agriculture, horticulture, and private hygiene products.[1–5] Superabsorbents can absorb large amounts of water and retain water after being heated for several hours or being under pressure. Solution polymerization[6–10] and inverse suspension polymerization[11,12] are usually used for preparing superabsorbents, chemical reagents,[13,14] and plasma,[15] and a microwave[16] may be used to initiate these reactions. Many polymers, such as polyacrylonitrile, polyacrylate, and polyacrylamide, may be used as superabsorbents by cross-linking them. In this paper, we prepared poly(acrylamide-*co*-2-acrylamido-2-methylpropanesulfonic acid) (PAMA) in aqueous solution, using *N,N*′-methylenebisacrylamide (NMBA) as crosslinker and potassium persulfate (PPS) as initiator. We investigated not only the swelling properties of the PAMA in water and other solvents but also the effects of different salt solutions, pH, and the water temperature on the absorbency and the water retention of the PAMA at different temperatures.

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EXPERIMENTAL

Materials

NMBA was recrystallized in water twice. All reagents, including acrylamide (AM), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), PPS, and sodium hydroxide were used as received. Glycol, methanol, ethanol, acetone, and tetrahydrofuran (THF) were used as swelling media. All solutions were prepared in distilled water.

Preparation of PAMA

Firstly, AMPS was dissolved in water. Then, in an ice–water bath, the AMPS solution was neutralized to 65% with sodium hydroxide solution. Before polymerization, AM, NMBA, and PPS were added in the above partial-neutralized AMPS solution. Secondly, the reaction solution was heated and polymerized for 7 hours at 60–80 °C. The product was cut into small pieces by hand and vacuum-dried at 70 °C for 24 hours. Finally, the dry product, which was referred to as PAMA, was milled through a 40-mesh screen. The details of the basic compositions are presented here. The mole ratio of AM and AMPS is 1:2. The total

TABLE I
Absorbency of the PAMA in the Different Solvents

Solvent	Dielectric constant	Q (g/g)
water	78.54	1749
glycol	37.7	660
methanol	32.63	310
ethanol	24.3	0
acetone	20.7	18
THF	7.52	0

weight percent of both monomers is 20%. The weight percent of the cross-linker compared with the monomers is 0.02%. The weight percent of the initiator compared with the monomers is 0.02%.

Swelling measurement

Sample PAMA (0.5 g) was immersed in liquid at room temperature until equilibrium was reached. The swollen gel was then separated from unabsorbed water by screening through a weighted 100-mesh nylon bag and allowed to drain for one hour. Then, the swollen gel was weighted. The absorbency was calculated using the following equation:

$$Q = (W_2 - W_1)/W_1$$

Absorbency is expressed in grams of liquid retained in the gel per gram of dry copolymer. W_2 and W_1 are the weights of the swollen gel and the dry PAMA, respectively.

Effect of pH on absorbency

The method was the same as the swelling measurement in distilled water and in saline solutions. The pH values of the solution were adjusted with HCl or NaOH.

Water retention

The swollen gels that had reached equilibrium in water were drained in 100-mesh nylon bags for one hour; then the gels and the bags were put into an oven and heated at a constant temperature. They had been weighted at intervals of one hour in order to investigate the variation in their weights.

RESULTS AND DISCUSSION

Absorbency in different solvents

The PAMA prepared could absorb up to 1749 g/g of dry polymer in distilled water and 87 g/g of dry polymer in 0.9 wt % NaCl aqueous solution at room temperature. In this subsection, we investigate the absorbency of the PAMA in the different solvents.

Table I presents the absorbency of the PAMA in the different solvents. As shown in Table 1, the absorbency of the PAMA in the distilled water is far greater than that in other solvents. The dielectric constants of different solvents are also given in Table I. The results shown in Table I indicate that the absorbency of the PAMA is an increasing function of the rising dielectric constant of a solvent. The larger the polarity of the solvent, the stronger the affinity between polymer and solvent and the more the PAMA gel network swells.

Effect of salt solutions on absorbencies

Figure 1 shows the effect of the concentrations of the different univalent salt solutions on the absorbency of the PAMA. The results indicate that the absorbency is a decreasing function of the rising concentrations of the different univalent salt solutions, and in the different NaX (X stands for halogen) solutions with the same concentration, the absorbencies of the PAMA are in the order $I^- > Br^- > Cl^-$. The hydrations of the different X^- ions cause this order. Because it has the smallest ionic radius, the hydration of Cl^- is strongest among the three kinds of halogen ions, whereas that of I^- is weakest. The stronger the hydration of an ion, the larger the hydration number. Therefore, the hydration number of I^- is the smallest, and the influence of I^- on the polymer network is little shielded by water. Finally, the negative charge of I^- makes the network swell larger than that of Cl^-. For the same reason, the absorbency of the PAMA in NaCl solution is greater than that in KCl solution. In addition, the effects of the

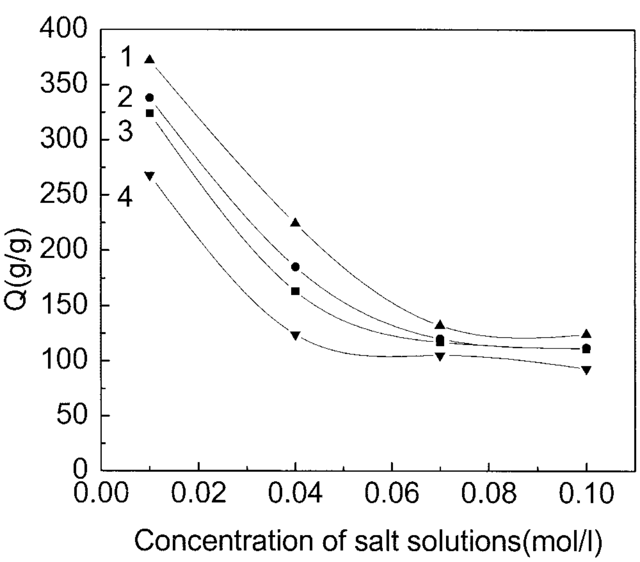

Figure 1 Effect of the concentrations of the different univalent salt solutions on the absorbencies of PAMA: (1) NaI; (2) NaBr; (3) NaCl; (4) KCl.

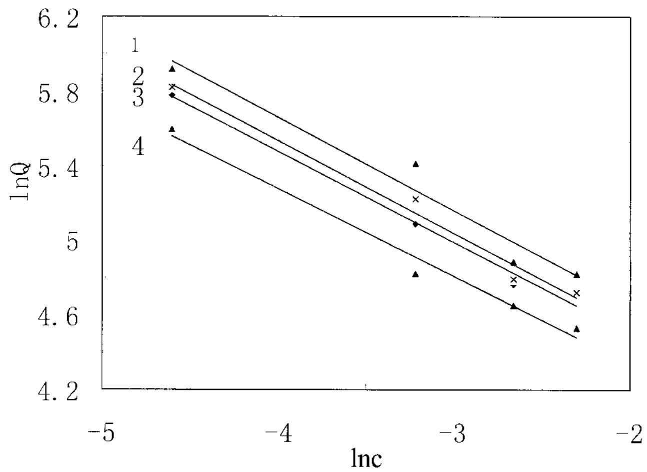

Figure 2 Logarithmic relationship between the absorbency and the concentrations of the different univalent salt solutions: (1) NaI; (2) NaBr; (3) NaCl; (4) KCl.

hydration of the different ions are remarkable at the lower ionic concentration (i.e., 0.01 mol/L) and weak at the higher ionic concentration (i.e., 0.1 mol/L). The logarithmic relationship between the absorbency and the concentration of the univalent salt solution is linear (Fig. 2) and can be expressed as $Q = kc^n$. The values of the parameters in the equation for the different salt solutions are presented in Table II. It is found that the values of the parameters for the different NaX solutions approach each other.

Figure 3 shows the effect of the concentration of the bivalent salt solution on the absorbency of the PAMA. We can obtain both of the following conclusions from Figure 5: (1) The tendency of the absorbency for PAMA in the IIA group salt solutions is in the order $MgCl_{2(aq)} > CaCl_{2(aq)} > BaCl_{2(aq)}$. This phenomenon is caused by the same chemistry that caused the NaCl and KCl phenomenon. The hydration of an ion becomes weaker as the ionic radius increases; then, the ion with a weaker hydration may attach more easily to the sulfonic groups fixed on the polymer network. Thus, Ba^{2+} has a greater ability to complex with the sulfonic group than Mg^{2+} and Ca^{2+}, which can decrease the absorbency of the PAMA. (2) At the same concentration, the tendency for the PAMA to absorb is

TABLE II
Values of the Parameters of the Equation $Q = kc^n$ for Different Univalent Solutions

Salt solution	k	n	R^a
NaI	39.076	–0.4981	0.9786
NaBr	35.001	–0.4951	0.9917
NaCl	34.340	–0.4845	0.9946
KCl	30.238	–0.4662	0.9913

[a] R stands for Relative coefficient. The R in the below-mentioned tables is the same.

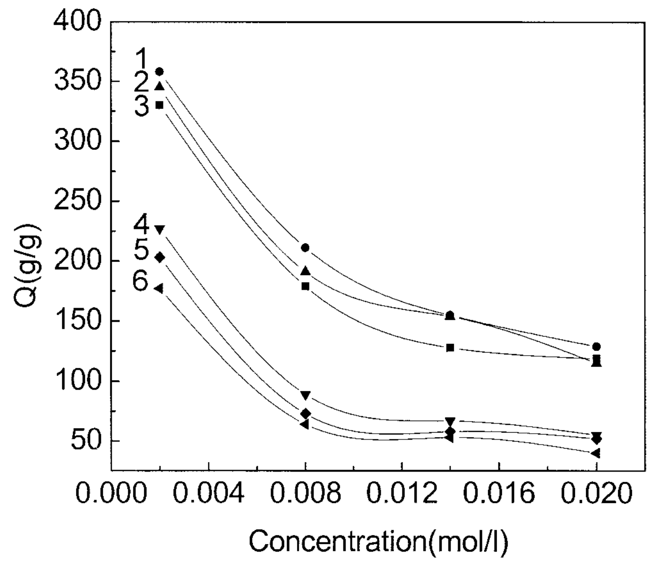

Figure 3 Effect of the concentrations of the different bivalent salt solutions on the absorbencies of PAMA: (1) Na_2SO_4; (2) $Na_2S_2O_3$; (3) Na_2HPO_4; (4) $MgCl_2$; (5) $CaCl_2$; (6) $BaCl_2$.

in the order $SO_4^{2-} > S_2O_3^{2-} > HPO_4^{2-}$. This result is related to both the hydration and the hydrolysis of the anionic group. However, the hydration of the complex anionic group is quite weak; hence, the absorbencies in the salt solutions containing different anionic groups are determined mainly by the hydrolysis of the anionic group. The degree of the hydrolysis of the bivalent anionic groups at the same concentration is in the order $HPO_4^{2-} > S_2O_3^{2-} > SO_4^{2-}$, and the same order exists for the alkalescence of the solutions; therefore,

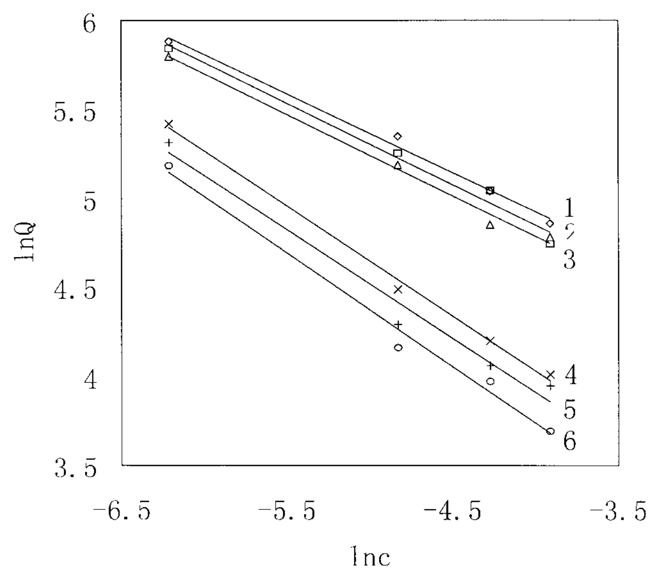

Figure 4 Logarithmic relationship between the absorbency and the concentrations of the different bivalent salt solutions: (1) Na_2SO_4; (2) $Na_2S_2O_3$; (3) Na_2HPO_4; (4) $MgCl_2$; (5) $CaCl_2$; (6) $BaCl_2$.

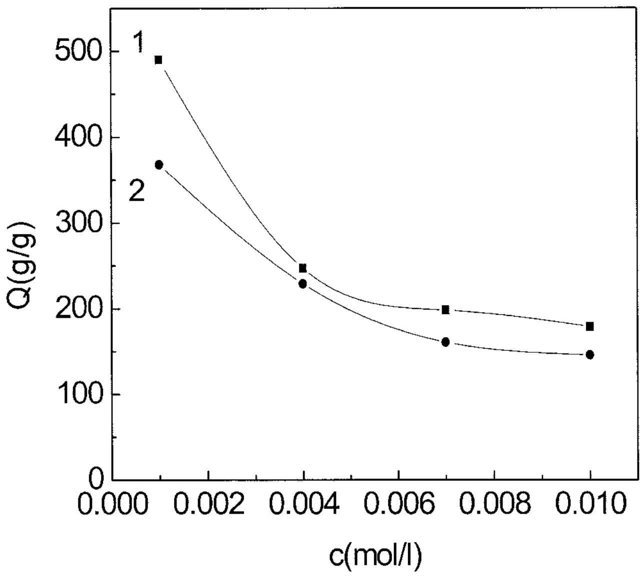

Figure 5 Effect of the concentrations of the different trivalent salt solutions on the absorbencies of PAMA: (1) Na_3PO_4; (2) $Na_3C_6H_8O_7$.

the absorbencies of the PAMA in these solutions are in the inverse order. In addition, Figures 1 and 3 show that the absorbency of the PAMA in the bivalent cationic salt solution is much lower than that in the univalent cationic salt solution at the same concentration. It is well known that the multivalent cation can chelate with the sulfonic group, hence causing the loose cross-linked polymer network to become so tight by the ionic cross-linking that the solution has difficulty penetrating. The relationship between ln*Q* and ln*t* is given in Figure 4. As shown in Figure 4, we can conclude that *Q* is a decreasing function of the increasing solution concentration, which may be expressed as $Q = kc^n$. The values of the parameters in the equation are presented in Table III. It is found that the values of the same parameters for the different MCl_2 solutions (M stands for alkaline earth metals) approach each other as do the values of the same parameters for the different NaY solutions (Y stands for the different salt anionic group).

TABLE III
Values of the Parameters in the Equation $Q = kc^n$ for different Bivalent Solutions

Bivalent salt solutions	*k*	*n*	*R*
Na_2SO_4	24.386	–0.4397	0.9960
$Na_2S_2O_3$	20.660	–0.4555	0.9920
Na_2HPO_4	19.184	–0.4578	0.9962
$MgCl_2$	4.789	–0.6167	0.9981
$CaCl_2$	4.403	–0.6078	0.9881
$BaCl_2$	3.274	–0.6375	0.9937

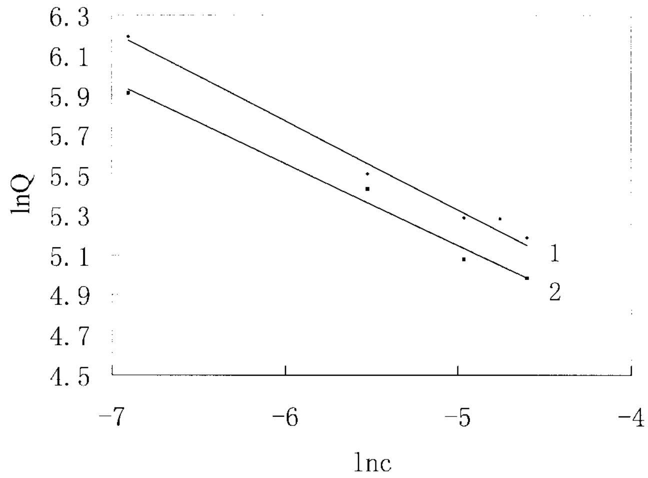

Figure 6 Logarithmic relationships between the absorbency and the concentrations of the different trivalent salt solutions: (1) Na_3PO_4; (2) $Na_3C_6H_8O_7$.

The effect of the concentrations of the different trivalent salt solutions on the absorbency is given in Figure 5. As shown in Figure 5, the absorbency of the PAMA in the different trivalent salt solutions decreases with an increase of the concentrations of the different trivalent salt solutions. The absorbency of the PAMA in Na_3PO_4 solution is larger than that in $Na_3C_6H_8O_7$ solution at the same concentration. This phenomenon cannot be explained by the above reasons. The hydrations of both PO_4^{3-} and $C_6H_8O_7^{3-}$ are weak, and the hydrolysis of the Na_3PO_4 solution is stronger than that of the $Na_3C_6H_8O_7$ solution at the same concentration. The behavior may be caused by the hydrogen bonds among the 2-hydoxy-1,2,3-propanetricarboxylic acid molecules in the $Na_3C_6H_8O_7$ solution. The hydrogen bonds make several molecules form a multimolecular structure, which then makes the movement of the molecules more difficult. Therefore, the absorbency of the PAMA in $Na_3C_6H_8O_7$ solution becomes smaller. The logarithmic relationship between the absorbency and the concentrations of the different trivalent salt solutions is also linear (Fig. 6), so the relations between *Q* and *c* could be expressed as $Q = kc^n$, and the values of the parameters in the equations are presented in Table IV.

Effect of pH on absorbency

Figure 7 gives the effects of pH values of a solution on the swelling behavior of the PAMA. As shown in

TABLE IV
Values of the Parameters in the Equation $Q = kc^n$ for different Trivalent Salt Solutions

Absorbency	*k*	*n*	*R*
Na_3PO_4	21.981	–0.4463	0.9963
$Na_3C_6H_8O_7$	22.149	–0.4099	0.9920

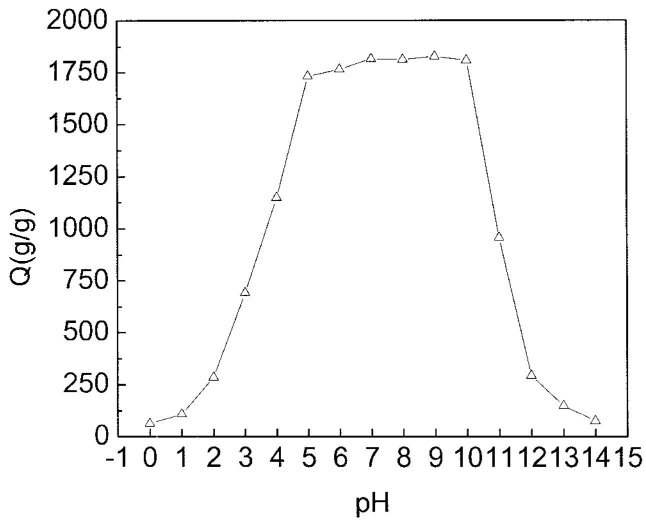

Figure 7 Effect of pH on absorbency.

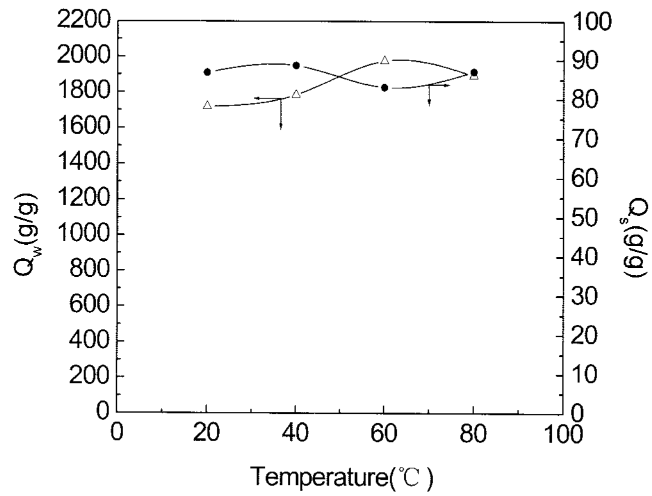

Figure 8 Effect of the water temperature on the absorbencies of PAMA.

Figure 7, the absorbency of the PAMA roughly maintains a constant from pH 5 to pH 10. This behavior can be explained by the buffer action of the sodium sulfonic group with an acid or base. The absorbency decreases rapidly from pH 5 to pH 2 and from pH 10 to pH 12, which implies that the buffer action has been destroyed. However, the absorbency changes slowly with the variation of pH below 2 or above 12, and the absorbencies of the PAMA at pH 0 and at pH 14 are still up to 63 g/g and 76 g/g, respectively. This fact indicates that the PAMA still has a high absorption capacity in the solution with a high concentration of acid or base.

Effect of water temperature

The effect of the water temperature on the absorbency of the PAMA is given in Figure 8. This figure shows

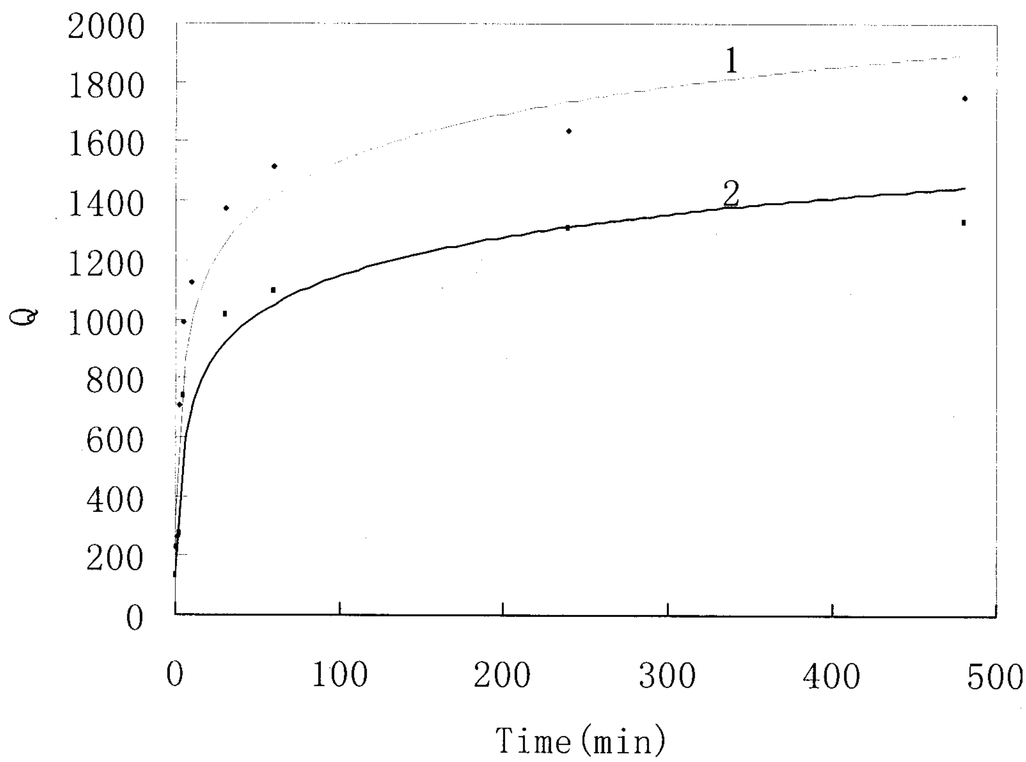

Figure 9 Swelling rates of the PAMA in different solvents: (1) distilled water; (2) the water/ethanol mixture (V_{water}:$V_{ethanol}$ = 1:1).

TABLE V
Values of the Parameters in the equation $Q = a\ln t + b$

Absorbency	a	b	R
Q_w (distilled water)	229.06	479.19	0.9423
Q_m (water/alcohol mixture)	189.23	276.92	0.9609

TABLE VI
Values of the Parameters in the Equation $W = at + b$

Water retention (%)	a	b	R
W_{60}	–2.8255	95.936	0.9821
W_{80}	–5.3788	95.555	0.9915

that the absorbency of the PAMA in distilled water and in 0.9 wt % NaCl aqueous solution is stable over a range of temperatures. The differences between the maximum absorbencies and the minimum absorbencies are 257 g/g in distilled water (14% of the mean absorbency) and 5 g/g in 0.9 wt % NaCl solution (5.8% of the mean absorbency). Therefore, the PAMA may be used in a wide range of temperatures.

The swelling rates of the PAMA in distilled water and in the mixture of water and ethanol (V_{water}:$V_{ethanol}$ = 1:1) are given in Figure 9. It is found that PAMA is characterized by high swelling rates. One gram of the PAMA may absorb about 992 g of water (57% of the maximum absorbency in distilled water) and 739 g of the water/ethanol mixture (55% of the maximum absorbency in this solution) in five minutes. The curves of the swelling rates could be fitted as the logarithmic functions, which may be expressed as $Q = a\ln t + b$. The values of the parameters in the equation are presented in Table V.

Water retention at constant temperature

Figure 10 shows the water retention of the PAMA at both constant temperatures. It is found that the water retention of the PAMA is excellent. The copolymer can retain 71.6% and 49.5% of the absorbency after being heated for 9 hours at 60 and 80 °C, respectively. The relationship between the absorbency and the heating time is linear and can be expressed by the equation $W = at + b$, where W stands for water retention and t stands for time. The values of the parameters in this equation are presented in Table VI.

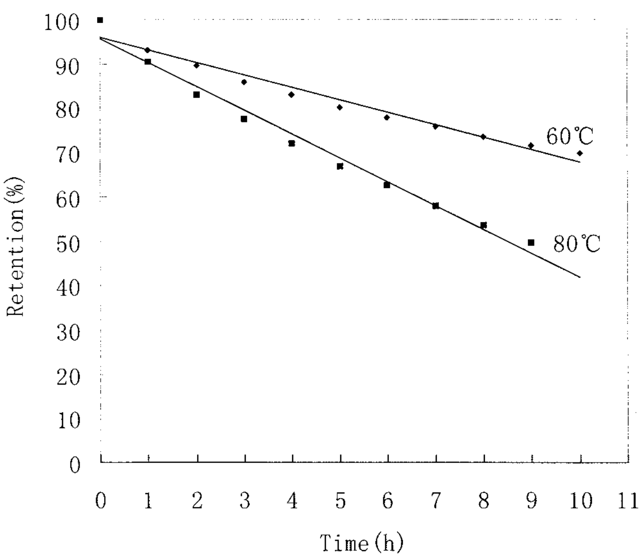

Figure 10 Retention of the swollen gel at temperatures of 60 and 80 °C: (1) 60 °C; (2) 80 °C.

CONCLUSION

A novel superabsorbent polymer, PAMA, was prepared in aqueous solution using AM and AMPS as monomers, and the swelling properties of the PAMA were studied. The experimental results show that the PAMA has high absorbency not only in water but also in some pure alcohols. The absorbency of the PAMA decreases as the polarity of the solvent increases.

The influences of various salt solutions on absorbency were investigated systematically. The results indicate that the absorbency is a decreasing function of the rising salt concentration, which can be expressed as $Q = kc^n$. The values of the parameters in the equation for several salt solutions were presented in this article.

The effects of pH on the absorbency were studied. It was found that the absorbencies of the PAMA roughly maintain a constant from pH 5 to pH 10, increase from pH 0 to pH 5, and decrease from pH 10 to pH 14. The absorbencies are still up to 63 g/g and 76 g/g at pH 0 and pH 14, respectively.

The absorbencies at different water temperatures are stable, which implies that the PAMA can be used in a wide range of temperatures. The PAMA has high swelling rates in distilled water and in a water/alcohol mixture, and the swelling rates may be expressed as $Q = a\ln t + b$.

The retentions of the copolymer at constant temperature are also excellent. After being heated for 9 hours at 60 and 80 °C, the retentions are still 71.6 and 49.5% of the absorbency, respectively. The retention at the constant temperature may be expressed as a function of time: $W = at + b$.

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