Synthesis and Properties of Acrylic-Based Superabsorbent

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ABSTRACT: Acrylic-based superabsorbent polymers with partial-neutralized acrylic acid were synthesized by inverse suspension polymerization. The effects of reaction parameters, including the concentration of crosslinking agent and initiator, the neutralization degree of monomer, the monomer concentration, and phase ratio of a system, on the water absorption have been investigated. Furthermore, to improve the properties of salt-resistance and antielectrolyte for the polymer, acrylamide monomer containing non-ionic and hydrophilic groups was introduced into the system, which can suppress the salt effect and homoion effect. The water absorption $Q^{5/3}$ is proportional to the reciprocal of ionic strength, $1/S$, which follows Flory's elasticity gel theory. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 619–624, 2004

Key words: poly(sodium acrylate); inverse suspension polymerization; water absorption

INTRODUCTION

Because Fanta et al. succeeded in grafting acrylonitrile onto starch and other polysaccharides, superabsorbent polymers have been widely studied.[1–5] The most important feature for a superabsorbent polymer stems from this super absorption, especially the water absorption of from several hundred to a thousand times of its dry weight. It is widely used in daily life such as in sanitary accessories (disposable diapers, feminine napkins), soil for agriculture and horticulture, etc.[6,7] Most of these kinds of polymers are commonly synthesized on the basis of acrylic monomers, such as neutralized acrylic acid, by bulk polymerization, solution polymerization, and inverse suspension polymerization.[8,9] However, the heat transfer in the later stages of reaction and the posttreatment process are more complicated for the bulk and solution polymerization processes.[10,11]

As is well known, the chemical structure, morphology, and distribution of bead size of polymers are determined by the polymerization reaction conditions or reaction parameters, and the reaction parameters will affect the water absorption of the superabsorbent polymers. Some authors have studied these absorbent polymers to enhance the water absorption and the absorption rate.[12–14] However, based on practical requirements, we should focus more on the properties of salt resistance and antielectrolyte by introducing a second monomer-containing nonionic and hydrophilic group such as acrylamino, which can suppress the salt effect and homoion effect. Unfortunately, there is little work published on this aspect.

In the present work, a series of acrylic-based superabsorbent polymers with high water absorption and high salt resistance was synthesized by inverse suspension polymerization.

EXPERIMENTAL

Materials

Sodium acrylate (NaAA) was prepared from acrylic acid (AA) (Shanghai Chemical Reagent Co., Shanghai, China) which was distilled under reduced pressure. Acrylamide (AM), N,N'-methylene bisacrylamide (MBA), ethylene glycol dimethacrylate (EGDMA), Span-60, cyclohexane, potassium persulfate ($K_2S_2O_8$), and sodium chloride (NaCl) were also purchased from Shangai Chemical Reagent Co. AM was recrystallized twice in acetone solvent. MBA and EGEMA were used without further purification. $K_2S_2O_8$ was recrystallized from water. All reagents were of analytical grade.

Polymerization

A predetermined concentration of sodium hydroxide solution was carefully introduced (dropwise under cooling) into the acrylic acid to obtain a partial neutralized acrylate solution (see Fig. 3 for neutralization degrees). Then, accurately weighed water-soluble initiator ($K_2S_2O_8$) was added and dissolved into the dispersed phase solution under nitrogen bubbling (concentrations shown in Fig. 2).

The continuous phase was composed of cyclohexane containing an appropriate proportion of water

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TABLE I
Reaction Parameters of the Samples[a]

Sample No.	ND (%)	AM %	[M] (wt%)	[K$_2$S$_2$O$_8$] (wt %)	O/W	[MBA] (wt %)
1	75	0	36.7	0.0278	2	0.0223
2	70	0	36.7	0.0278	2	0.0223
3	75	13.39	36.7	0.0278	2	0.0223

* Here, ND denotes neutralization degree; AM% is based on AA; O/W is the phase ratio of oil to water; [□] denotes the concentration; and [M] represents the concentration of the monomer(s).

and suspending agent (Span 60). All of them were put into a 500-mL, five-necked, jacketed flask fitted with a stirrer, nitrogen inlet, condenser, drop funnel, and thermometer. It was heated up to the desired temperature with a thermostatic bath, while bubbling nitrogen into the liquid medium for 15 min. Then, a suitable amount of the oil-soluble crosslinking agent (MBA) was introduced into the continuous phase (concentrations shown in Fig. 1).

The dispersed phase was added dropwise, at a predetermined flow rate for isothermal polymerization, into the flask containing the continuous phase, while the agitation speed was maintained at about 500 rpm. The polymerization reaction was run at 333 K for 3 h and then dehydrated by azeotropism. The reaction was stopped and the suspension solution was introduced into 1000 mL methanol to precipitate the polymer and the polymer was filtered and washed with distilled methanol several times. The product was dried under vacuum for 24 h before being weighed.

By using the method above, we developed some samples for tests. Table I shows the reaction parameters of the samples.

Properties measurements

In water absorption, 0.5 g of the dry sample (the sizes of samples were all between 80 and 100 mesh) was immersed in 500 g distilled water for at least 12 h to reach the swelling equilibrium at room temperature. The completely swollen gel was filtered through a 100-mesh nylon pocket, and the remaining swollen gel was weighed. The water absorption Q (g/g) was calculated as

$$Q = (W_s - W_d)/W_d \qquad (1)$$

where W_s and W_d represent the swollen and dried weight of sample (g).

The liquid absorption Q_L was carried out in various electrolytes such as NaCl, H$_2$SO$_4$, and methanol, etc. The calculation of liquid absorption was the same as eq. (1).

The absorption rate was characterized by a vortex test, which was performed and specified as follows[15]: 100 g distilled water was introduced into a beaker and was stirred with a magnetic stirrer at a constant rate. Then, the predetermined amount of dried sample was added into the beaker. The hydrogel subdued the fluidity and precluded the agitation from inducing a swirl. The absorption rate was expressed in terms of the time from the addition of sample to the cessation of swirl.

RESULTS AND DISCUSSION

The absorption mechanism of crosslinking polymer can be elucidated in terms of the swelling behavior, which is caused by diffusion because of the affinity between polymer network and external solution. Thus, in moderately crosslinked acrylic-based polymer, the water absorption relates to the polymer network nature, involving the crosslinking density, strength of the hydrophilic group, and elasticity of the polymer network. It also depends on the type of solvent and the characteristics of the external solution. The type of solvent has an extensive effect on the dissolved ions. The controlling characteristics of the external solution are primarily the charge number and ionic strength.

The balance of the following three main forces determines the swelling equilibrium of hydrophilic hydrogel[16,17]:

(1) The free energy between the network chains of polymer and the external solvent;
(2) The electrostatic repulsion resulting from the presence of these fixed charges on the polymer chains, which is known as the Donnan effect;
(3) The elastic retractile response of the network (elastic swelling).

Forces (1) and (2) promote hydrogel swelling, whereas force (3) suppresses it.

For a crosslinked polymer, the water absorption, Q, can be expressed as a function of the crosslinking density through Flory's elasticity gel theory,[18] which, in the dilute polymer solution approximation, takes the form

$$Q^{5/3} = [(i/2V_u S^{1/2})^2 + (1/2 - X_1)/V_1]/V_e/V_0 \quad (2)$$

where Q, V_e/V_0, $([1-2] - X_1)/V_1$, V_u, i/V_u, and S are the water absorption, the crosslinking density of polymer, the affinity between polymer and external solution, the volume of structural unit, the fixed charge per unit volume of polymer, and the ionic strength of external solution, respectively.

TABLE II
Water Absorption of Polymers Using Different
Crosslinking Agents (T = 293 K)[a]

Crosslinking agent	Q (g/g)	Absorption rate (s)
Self-crosslinking	182.7	300.0
EGDMA	283.4	78.4
MBA	281.9	19.0

[a] Here, the absorption rate is characterized by time, which is measured by the aforesaid vortex test. The crosslinking agent concentration was 0.025 wt %.

The first and second terms in the numerator are related to force (1) and (2) that favor the water absorption Q.

Crosslinking agent type and concentration

The crosslinking agent is one of the most sensitive factors that affects the superabsorbent water absorption. Highly concentrated solutions of acrylic acid may cause self-crosslinking through hydrogen bonds on the polymer backbone without crosslinking agent.

In general, the molecular structure of the crosslinking agent contains two or more double bonds, which will take part in the radical copolymerization with acrylate and form the crosslinking network in the polymerization process.

Table II shows the water absorption Q and absorption rate of the polymer synthesized by inverse suspension polymerization with different crosslinking agents. It was observed that the water absorption of polymer by self-crosslinking was lower than that of the polymer with the participation of the crosslinking agent. Furthermore, the product synthesized by self-crosslinking did not have granular structure and separated from the solvent with difficulty. When the self-crosslinking polymer was swollen, its gel became paste-like with lower intensity. This might be due to the more noncrosslinked portion dissolving in water.

In addition, the water absorption of polymer using crosslinking agent MBA was almost identical with that of crosslinking agent EGDMA, while the absorption rate was faster for the nonionic group on MBA.

On the other hand, Figure 1 shows that the water absorption varies with the increase of crosslinking agent concentration. The results suggest that the water absorption had an optimal value: the water absorption would increase with increasing crosslinking agent concentration and then would decrease. In general, the crosslinking agent concentration was directly related to the crosslinking density, which greatly influenced the water absorption. Lower crosslinking density provided unfavorable percentages of soluble polymers; for example, when the amount of the crosslinking agent decreases from 0.0223 wt % to 0,
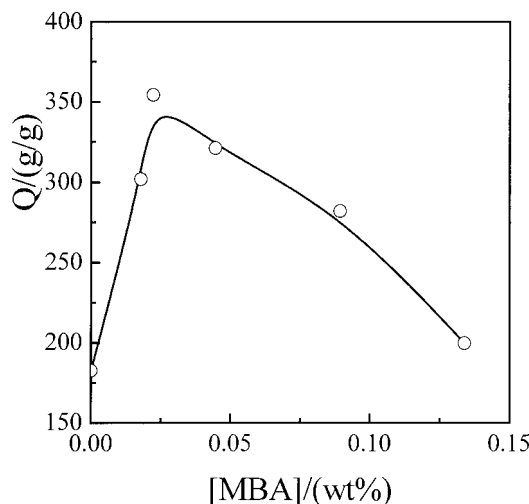

Figure 1 Effect of crosslinking agent (MBA) concentration on water absorption (Q).

the sol fraction increases from 8.1 to 34.4%, which resulted in the decrease of water absorption.

Concentration of initiator

In free-radical polymerization, the initiator has an effect on both the polymerization rate and the molecular weight of polymer. In the process for crosslinking polymerization, the initiator also affects the crosslinking degree and molecular weight between two crosslinking points. The lower initiator concentration results in the decrease of the crosslinking degree and the conversion, whereas, based on the principle of kinetic chain length, the polymer molecular weight will increase with decreasing initiator concentration.

The effect of initiator concentration on water absorption is shown in Figure 2: the polymer water absorption varied with the initiator concentration.
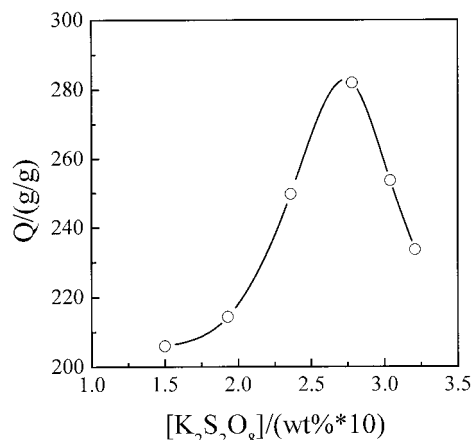
Figure 2 Effect of initiator ($K_2S_2O_8$) concentration on water absorption (Q).
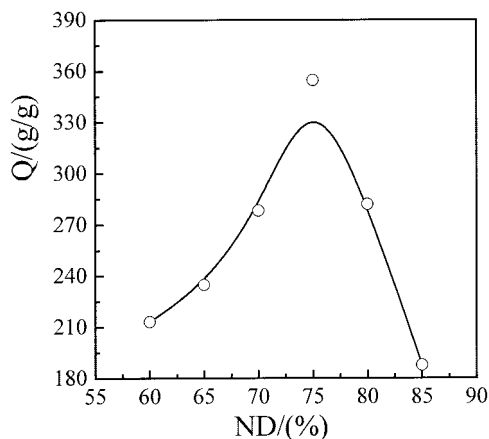
Figure 3 Effect of neutralization degree (ND) of AA on water absorption (Q).

Figure 4 Effect of monomer NaAA (M) concentration on water absorption (Q).

When the initiator concentration was lower, the polymerization rate was relatively slow. This might be attributed to the smaller crosslinking degree that resulted in an increase in the content of soluble polymer. However, when the initiator concentration was too high, a decrease of water absorption resulted.
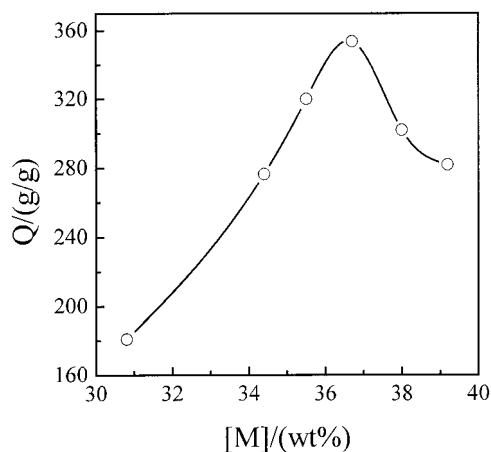
Neutralization degree (ND)

Owing to the high activity of acrylic acid monomer, acrylic acid is usually neutralized by alkali before polymerization instead of its direct polymerization. In this system, sodium hydroxide (NaOH) was selected as the neutralizing agent.

Figure 3 shows the effect of neutralization degree of AA on the water absorption: the lower the neutralization degree, the fewer are the neutralized carboxylic functionalities, which would decrease the ionic concentration and the osmotic pressure between the polymer network and the external solution and resulted in the decrease of water absorption. A higher neutralization degree would increase the salt formation from acrylic acid in the aqueous phase, thereby enhancing osmotic pressure. However, when the neutralization degree exceeded a definite value, the polymer suffered from the alkaline environment, which affected the dissociation of the sodium acrylate. Consequently, the chain segment would freeze and not stretch.

Concentration of monomer

The monomer concentration is one of the most significant factors affecting polymer stability. In general, the monomer concentration is too low to bring about crosslinking polymerization, and an agglomeration phenomenon takes place. On the contrary, when the monomer concentration exceeds a critical value, the

polymerization will be very fast even to a runaway level.

As shown in Figure 4, the monomer concentration had also an optimal value for the water absorption. The monomer concentration in the water phase would directly affect the polymer crosslinking degree. A suitable range for the monomer concentration was between 35 and 40%.
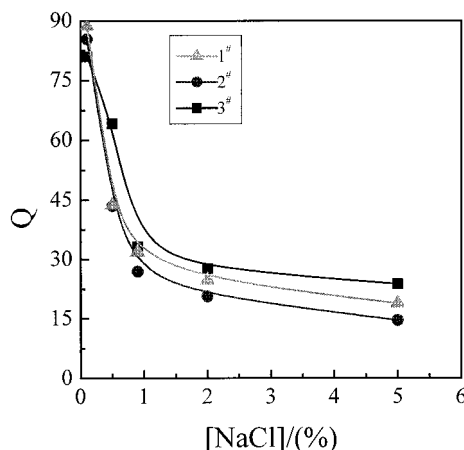
Phase ratio (O/W)

In inverse suspension polymerization, organic solvents, such as aliphatic and alicyclic hydrocarbons, are used as the continuous phase instead of the water that is generally used for classical suspension polymerization. The phase ratio O/W is defined as the volume ratio of cyclohexane to water. Partially neutralized poly(acrylic acid) could dissolve in the cyclohexane and became granular, but could expand sufficiently in water phase. The phase ratio O/W will greatly influ-
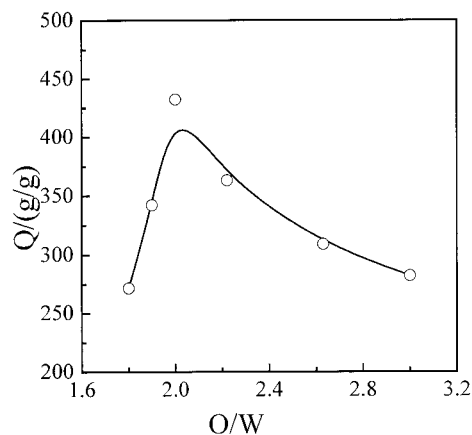
Figure 5 Effect of phase ratio (O/W) of cyclohexane to water on water absorption (Q).
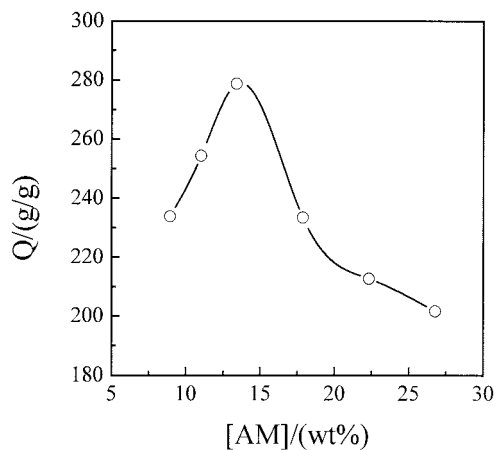
Figure 6 Effect of acrylamide (AM) concentration on water absorption (Q) of poly (AA-*co*-AM).

Figure 7 Effect of NaCl concentration on liquid absorption (Q_L).

ence the expansion of the polymer particles, the process of crosslinking polymerization, and the crosslinking degree.

The phase ratio O/W also affects the water absorption, as shown in Figure 5. Lower phase ratio will be advantageous to enhance crosslinking degree. However, at an extremely low phase ratio, the crosslinking polymerization will take place both on the surface and inside of the particle, which results in a decrease of water absorption.

Properties of antielectrolyte

In some properties for superabsorbent polymer, the property of antielectrolyte plays a very important role. To enhance the absorption rate and the antielectrolyte properties for poly(acrylic acid), which is an anionic polymer, a nonionic monomer, such as AM, is introduced into and copolymerized with acrylic acid and its neutralized derivative.

Taking poly(acrylic acid) as an example, once the hydrophilic group interacts with the water, the water will gradually permeate into the polymer interior and the bonds of COO^- and Na^+ will dissociate from the hydrophilic NaCOO; the carboxyl on the chain will diffuse into the water phase. In addition, the partial ion divorced from the chain will diffuse into solvent and result in a negative charge on the chain. The swelling force resulting from the presence of these fixed charges on the polymer chains may be identified with the osmotic pressure.[18] The equilibrium between the swollen ionic gel and its surroundings resembles the Donnan equilibrium. In fact, there are two forces which promote hydrogel swelling as said above. In general, the electrostatic repulsion in an ionic gel is much stronger than the force resulting from the mixing free energy. Thus, the latter force could be neglected and in this case the electrostatic repulsion

determines the swelling equilibrium. If the external solution contains ions, the electric potential difference between the interior of the gel and its surroundings will decrease rapidly, which result in a smaller swelling ratio. When the gel continues to swell, owing to the exchange of ions between gel interior and outer solution, the osmotic pressure reduces, which is just the opposite of the elasticity shrinkage of the network. When these two reactions reach equilibrium, the liquid absorption degree of the absorbent polymer will be determined.

Figure 6 shows that the curve of the water absorption has a peak value with increasing acrylamide concentration. When a small amount of acrylamide was copolymerized with the acrylic acid, it not only weakened the hydrogen bond between water and carboxyl group, which would reduce the swelling ratio of the polymer, but also exerted an influence on absorbency, due to the synergistic effect of different hydrophilic groups. However, because of acrylamide being a non-
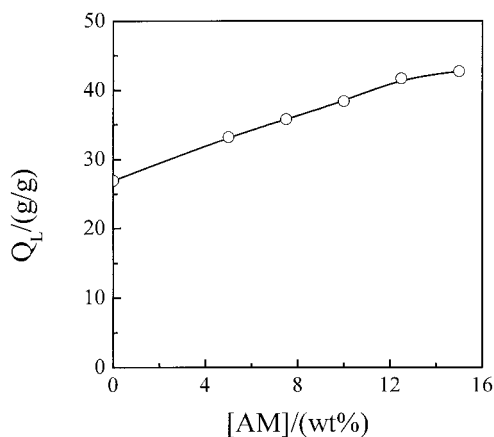
Figure 8 Effect of AM concentration on liquid absorption (Q_L).
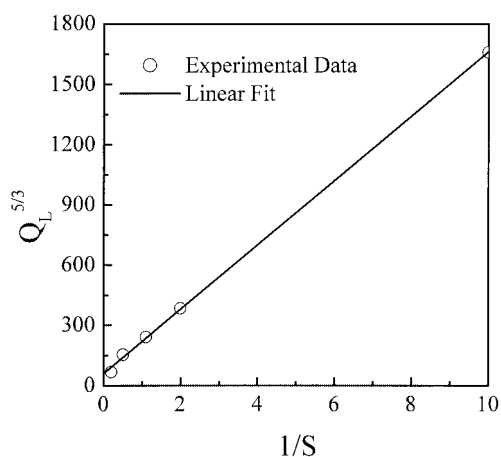
Figure 9 Effect of reciprocal of ionic strength (S) of NaCl on liquid absorption (Q_L).

ionic monomer, its dissociation degree in water was lower than an ionic monomer such as acrylic acid. As a result, the water absorption would decrease.

On the basis of the different liquid absorption curves shown in Figure 7, the saline resistance of polymer containing AM was better than that of polymer without AM. Therefore, to enhance the saline resistance of polymer, nonionic and hydrophilic groups should be introduced into the polymer chain by copolymerization with AM. Of course, the acrylamide concentration also affects the properties of saline resistance (see Fig. 8). The more AM that was introduced into the reaction system, the better was the saline resistance affected. This effect can be explained as follows: when the amount of AM increases, the gel fixed charge content decreases, so the nonion reaction between the polymer and surroundings plays a more important role, resulting in improvement of its saline resistance.

According to Flory's elasticity gel theory,[18] and its simplification,

$$Q^{5/3} = A + B/S \qquad (3)$$

where Q and S are the liquid absorption and the ionic strength of absorption medium, respectively.

Figure 9 shows that good linear relationships between $Q^{5/3}$ and $1/S$ were achieved for low ionic strength and the correlation coefficient of the data was 0.99974 for sample no. 1. Both A and B are empirical parameters. For this system, A equaled 59.45, which was related to the affinity with medium and crosslinking density, B equaled 160.10, which was influenced by the fixed charge density of the polymer.

CONCLUSION

In summary, the results of this article provide a theoretical basis and experimental data to optimize compounding formulae and design polymer structures. Through investigating the effects of reaction parameters, including the concentrations of crosslinking agent and initiator, the neutralization degree of monomer, the monomer concentration, and phase ratio of a system, on the absorption properties for superabsorbent, optimal values for these parameters were gained. Furthermore, we also investigated the properties of antielectrolyte. For acrylic-based superabsorbent, when nonionic and hydrophilic groups were introduced into the polymer chain by copolymerization, the salt resistance and the rate absorption would greatly increase because of a decrease of the salt effect and homoion effect. The water absorption $Q^{5/3}$ is proportional to the reciprocal of ionic strength $1/S$, which follows Flory's elasticity gel theory.

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