# An Efficient Preparation Method for Superabsorbent Polymers

### JUNWU CHEN, YAOMING ZHAO

Department of Polymer Materials Science and Engineering, South China University of Technology, Guangzhou, Guangdong 510641, People's Republic of China

Received 24 January 1998; accepted 23 October 1998

ABSTRACT: High water-absorbent polyacrylates could be prepared by concentrated aqueous solution polymerization within a short time period, heating the monomer mixture by water bath. The influences of initiator content, bath temperature, crosslinker content (*Cc*), and degree of neutralization on water absorbency (*Q*) were investigated. The temperature changing of the monomer mixture during polymerization was thoroughly analyzed. The increase of initiator content as well as the increase of bath temperature results in the increase of water absorbency and reduces the crosslinking efficiency. The results are in conformity with Flory's network theory and also illustrate that lower crosslinking efficiency occurs when the polymerization rate is faster. An empirical relation of  $Q = 1.40 \ Cc^{-0.665}$  is obtained and its exponent is very close to -0.6 in a derived relation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 119–124, 1999

**Key words:** superabsorbent; *in situ* aqueous solution polymerization; water absorbency; crosslinking; degree of neutralization

# INRODUCTION

Superabsorbents can absorb a large amount of water in a short time. The absorbed water can be retained even under pressure. Therefore, superabsorbents have great advantages over traditional water-absorbing materials such as cotton, pulp, sponge, etc. Superabsorbents are used widely in sanitary goods such as disposable diapers and hygienic napkins. They also are found to be valuable in artificial snow,<sup>1,2</sup> agriculture,<sup>3-6</sup> horticulture,<sup>3,6</sup> drilling fluid additives,<sup>7</sup> polymer concrete suited for use in repairing cracks,<sup>8</sup> dew-preventing coating,<sup>9</sup> fighting fire,<sup>10</sup> sealing composite in long distance cable,<sup>11,12</sup> and drug delivery.<sup>13,14</sup>

Journal of Applied Polymer Science, Vol. 74, 119-124 (1999)

Aqueous solution polymerization can be used to prepare superabsorbents. However, relatively low monomer concentration was used in the recent reports.<sup>15–18</sup> Finding a more efficient preparation method is interesting research and is especially valuable in industry. Data on aqueous solution polymerization at high monomer concentration are scarce and confined to patent literature.<sup>19–21</sup> A saturated concentration for acrylic monomer in water is 46.5% at ambient temperature when acrylic acid is 80% neutralized with sodium hydroxide. In our previous study,<sup>22</sup> a monomer concentration of 43.6% was used to prepare acrylic-based superabsorbents which were polymerized in a thermostatic oven. The monomer mixture was heated by hot air.

In this article, high water-absorbent polyacrylates were prepared by concentrated aqueous solution polymerization in which the monomer mixture was heated by water bath. The monomer concentration was 43.6% for all samples. It was found that heating by water bath had better heat

Correspondence to: J. Chen.

<sup>© 1999</sup> John Wiley & Sons, Inc. CCC 0021-8995/99/010119-06

transfer than that by hot air and the polymerization could be finished within 0.5 h. The temperature changing of the monomer mixture during polymerization was thoroughly analyzed. The effects of initiator content, bath temperature, crosslinker content, and degree of neutralization on water absorbency were investigated also.

# **EXPERIMENTAL**

## **Materials**

Sodium hydroxide (analytical grade, Shanghai Chemical Reagent Factory, China), potassium persulfate (KPS) (analytical grade, Shanghai Chemical Reagent Factory), triethylene glycol diacrylate (TEGDA) (Nakarai Chemical Ltd., Japan) were used as received. Acrylic acid (Shanghai Wulian Chemical Factory, China) was distilled under reduced pressure before use.

## **Preparation of Superabsorbent**

Typically, in a 250 ml beaker, cooled with 20°C recycled water bath, 15.5 g water was mixed with 36.7 g acrylic acid. The stirred acrylic acid aqueous solution was neutralized by dropwise adding sodium hydroxide aqueous solution (16.3 g sodium hydroxide and 36.1 g water). The neutralization was 80% and the monomer concentration was 43.6%. A weighed quantity of KPS and TEGDA was dissolved in the monomer mixture at ambient temperature while fully stirring. The aqueous monomer mixture was subjected in a flat-bottomed stainless steel dish (10 cm diameter). The dish was set on a water bath with a predetermined temperature and the bottom of the dish was heated by water. The monomer mixture was polymerized *in situ* and its temperature was determined with a thermometer. Each sample at experimental temperature could reach its highest temperature within nearly 0.5 h and a polymeric gel was formed. The product was cut into small pieces and then dried in a vacuum at 105°C for 8 h. The dried polymer was milled and screened through a 40-mesh sieve.

# Measurement of Water Absorbency

The accurately weighed resin (about 1 g) was immersed in 800 g of distilled water or 250 g 0.9%sodium chloride aqueous solution (0.9% saline solution) and allowed to soak for 2 h. The swollen gel was then separated from unabsorbed water by screening through an 80-mesh sieve and the sieve was then weighed to determine the weight of the water-swollen gel. The water absorbency (Q) was calculated using the following equation:

$$Q = (W_2 - W_1)/W_1 \tag{1}$$

where  $W_2$  and  $W_1$  are the weights of the waterswollen gel and the dry resin, respectively. Q was calculated as grams of water per gram of resin.

## **RESULTS AND DISCUSSION**

## Temperature Changing of Monomer Mixture During Polymerization

The temperature changing of the monomer mixture is shown in Figure 1. The temperature of the monomer mixture rises steadily when it is heated by the water bath. The temperature difference between the water bath and the monomer mixture as well as polymerization heat contributes to the temperature elevation of the monomer mixture. Curves in Figure 1 can be divided into four sections according to the different rates of temperature changing; however, the transition point between two successive sections is hard to divide exactly. The beginning 2 min can be regarded as the first section, fast temperature elevation occurring due to the big temperature difference between the water bath and the monomer mixture. The average rates of temperature elevation of the first section are 15°C/min and 19.5°C/min for curve a and curve b, respectively. The results show that the water bath has better heat transfer to the monomer mixture than hot air in a thermostatic oven.<sup>20</sup> The successively slight temperature elevation can be regarded as the second section. The periods during the section are 16 min and 8 min for curve a and curve b, respectively, and the average rates of temperature rising is 0.75°C/min and 1.13°C/min for curve a and curve b, respectively. The third section corresponds to an accelerated polymerization process. The polymerization rate increases during the process because of the temperature elevation of the monomer mixture and the increase of viscosity of the monomer mixture. Fast temperature elevation arises again because a large quantity of polymerization heat generates during the process. The monomer mixture can reach its maximum temperature at the end of the accelerated polymerization process. The average rates of temperature



**Figure 1** Temperature changing of the monomer mixture during polymerization. *Dn*, degree of neutralization, 80%; *Ci*, molar ratio of KPS to monomer, 1.37  $\times 10^{-3}$ ; *Cc*, molar ratio of TEGDA to monomer, 1.26  $\times 10^{-3}$ ; temperature of water bath: (a) 70°C, (b) 80°C.

elevation are 8°C/min and 11°C/min for curve a and curve b, respectively. The polymerization is nearly over when the temperature of the monomer mixture reaches a maximum. In this article, reaction time is defined as the time at the maximum temperature. The reaction time is 22 min and 13 min for curve a and curve b, respectively. Therefore, the preparation of the superabsorbent in this work is efficient because of high monomer concentration and short reaction time. So heating of monomer mixture by water bath has better heat transfer than that by hot air in a thermostatic oven in our previous study.<sup>22</sup> Due to the cooling of water bath, the fourth section corresponds to the temperature dropping after the accelerated polymerization.

#### **Effect of Initiator Content**

The effect of the initiator content (Ci, molar ratio of KPS to monomer) on reaction time is listed in Table I. Reaction time decreases with the increase of Ci because the polymerization rate increases with the increase of Ci. The reaction time at 80°C is shorter than that at 70°C when the initiator content is the same. The highest temperature of the monomer mixture during the polymerization at different Ci is also listed in Table I. The highest temperature of the monomer mixture

Table IThe Effect of Ci on Reaction Time andHighest Temperature at Two Temperatures ofWater Bath

	Reaction Time (min)		Highest Temperature (°C)	
$Ci imes 10^3$	70°C	80°C	70°C	80°C
0.55	32	20	87	98
0.95	28	17	94	106
1.37	22	13	102	109
1.84	18	11	105	112
2.46	15	9	108	115

Reaction condition:  $Cc = 1.26 \times 10^{-3}$  (*Cc*, molar ratio of TEGDA to monomer), Dn = 80% (*Dn*, degree of neutralization).

increases with the increase of Ci. At the same Ci, the highest temperature at 80°C is higher than that at 70°C.

Figure 2 shows the effect of initiator content on water absorbency. The water absorbency increases linearly with the increase of initiator content. At the same Ci, the water absorbency at 80°C is higher than that at 70°C.

The relation between the swelling ratio and network structure parameter for the swelling of ionic networks was given by Flory,<sup>23</sup> usually used as the following two equivalent equations:



**Figure 2** Effect of initiator content (*Ci*, molar ratio of KPS to monomer). Dn = 80%;  $Cc = 1.26 \times 10^{-3}$ ; temperature of water bath: (a) 70°C, (b) 80°C.

$$q_m^{5/3} \cong \left[ (i/2v_u S^{*1/2})^2 + (\frac{1}{2} - \chi_1)/v_1 \right] / (\nu_e/V_0) \quad (2)$$

$$q_m^{5/3} \approx [(i/2v_u S^{*1/2})^2 + (\frac{1}{2} - \chi_1)/v_1](Mc/\rho_p)(1 - 2Mc/Mn)^{-1}$$
(3)

where  $q_m$  is swelling ratio,  $i/v_u$  is the concentration of fixed charge referred to the unswollen networks,  $S^*$  is the ionic strength of the swollen solution,  $\chi_1$  is the polymer-solvent thermodynamic interaction parameter,  $v_1$  is the molar volume of water,  $v_e/V_0$  is crosslinking density which refers to the number of effectively crosslinked chains in unit volume, Mc is the average molecular weight of network chains,  $\rho_p$  is the density of polymer, and Mn is the average molecular weight of the polymer before crosslinking.

(1 - 2 Mc/Mn) in eq. (3) expresses the correction for network imperfection resulting from chain ends.<sup>23</sup> The network imperfection is higher when Mn is smaller and this also means there are more chain ends in the networks. It is predicted from eq. (3) that networks with more chain ends have higher swelling ratio  $q_m$  when Mc is the same.

KPS is a thermal initiator in free-radical chain polymerization. The degree of polymerization decreases with the increase of KPS content.<sup>24</sup> On the other hand, as polymerization temperature is increased, the rate of polymerization is strongly enhanced, and the degree of polymerization is reduced because of the increase of the termination rate and the temperature dependence of chain transfer reaction.<sup>25</sup> So the molecular weight decreases when initiator content or polymerization temperature is increased. This results in the increase of the relative amount of the polymer chain ends in networks. Therefore, the experimental results in Figure 2 conform with eq. (3) and directly support the Flory's network theory.

At the same crosslinker content, the water absorbency increases when the crosslinking efficiency decreases according to eq. (2). As shown in the experimental results in Figure 2, water absorbency increases with the increase of Ci or with the increase of the temperature of water bath. So the crosslinking efficiency decreases with the increase of Ci or bath temperature. The increase of Ci as well as the increase of temperature of water bath will result in a faster polymerization rate.<sup>25</sup> Therefore, the reduction of crosslinking efficiency may be attributed to higher polymerization rate.



**Figure 3** Effect of crosslinker content (*Cc*, molar ratio of TEGDA to monomer). The dashed line is best-fit curve according to a relation of  $Q = 1.40 \ Cc^{-0.665}$ . Dn 80%; *Ci* 1.37 × 10<sup>-3</sup>, at 70°C.

#### Effect of Crosslinker Content

The effect of crosslinker content (Cc, molar ratio of TEGDA to monomer) on water absorbency is shown in Figure 3. The water absorbency decreases with the increase of Cc. This conforms with Flory's water absorbency eq. (2).

The relation between  $q_m$  and Q is eq. (4) when water is the swelling agent:

$$q_m = Q\rho_p / \rho_s + 1 \tag{4}$$

where  $\rho_p$  and  $\rho_s$  are the density of polymer and swelling solvent, respectively.

Usually, Q is very large and  $\rho_p$  is higher than  $\rho_s$  for acrylic-based superabsorbent. Then unit one in eq. (4) can be omitted and then we have

$$q_m \cong Q\rho_p / \rho_s \tag{5}$$

For a given chemical structure of superabsorbent and a given swollen solution,  $[(i/2v_u S^{*1/2})^2 + (1/2 - \chi_1)/v_1]$  in eq. (2) can be regarded as a constant (assumption 1). From eqs. (2) and (5), eq. (6) can be obtained.

$$Q \cong k_1 (\nu_e / V_0)^{-0.6} \tag{6}$$

where  $k_1$  is a constant.

Here, we suppose that samples at different Cc have the same crosslinking efficiency (assumption 2), so  $\nu_e/V_0$  is proportional to Cc, then we have

$$\nu_e/V_0 = k_2 C c \tag{7}$$

where  $k_2$  is a constant relevant to crosslinking efficiency.

From eqs. (6) and (7), we can obtain

$$Q \cong k_3 C c^{-0.6} \tag{8}$$

where  $k_3 = k_1 k_2^{-0.6}$ .

Equation (8) gives the relation between water absorbency Q and crosslinker content Cc.

Grapher 1.50 (Golden Software, Inc.) is used to obtain the best fit relation between Q and Cc. The following relation  $Q = 1.40Cc^{-0.665}$  is generated. The relation is drawn in a dashed line in Figure 3. The empirical relation fits the experimental results well. The exponent -0.665 in the empirical relation is very close to -0.6 in eq. (8) and the two assumptions in the derivation of eq. (8) are also proved to be reasonable.

#### Effect of the Degree of Neutralization

Figure 4 shows the effect of the degree of neutralization (Dn) on water absorbency. The water absorbency increases with the increase of Dn when Dn is less than 75%. The water absorbency decreases with the increase of *Dn* when *Dn* is higher than 75%. There exists a maximum water absorbency at a Dn of 75%. Flory described the mechanism of the swelling of ionic networks.<sup>23</sup> If the polymer chains making up the network contain ionizable groups, the swelling forces may be greatly increased as a result of the localization of charges on the polymer chains. When crosslinked poly(acrylic acid) is neutralized with sodium hydroxide, the negatively charged carboxyl groups attached to the polymer chains set up an electrostatic repulsion which tends to expand the network. In a certain range of Dn, the electrostatic repulsion increases with the increase of Dn, resulting in the increase of water absorbency. However, the concentration of sodium ions also increases with the increase of Dn. Sodium ions, by screening the negative charges of carboxyl groups, reduce the electrostatic repulsion tremendously. Therefore, there exists an optimum proportion of acrylic acid to sodium acrylate in the



**Figure 4** Effect of degree of neutralization;  $Cc = 8.40 \times 10^{-4}$ ,  $Ci = 1.37 \times 10^{-3}$ , at 70°C.

preparation of acrylic-based superabsorbent. A Dn of 75% is recommended according to the experimental results. The same result was reported by Song et al.<sup>26</sup>

### Water Absorbency in a Saline Solution

For many applications, it is more important to know the behaviors of superabsorbents in physiological solutions. Water absorbency in the distilled water  $(Q_1)$  and 0.9% saline solution  $(Q_2)$  is listed in Table II.  $Q_2$  is much smaller than  $Q_1$  for each sample because the ionic strength  $(S^*)$  in 0.9% saline solution is bigger than that in the distilled water. According to eq. (2), the bigger the  $S^*$  is, the smaller the Q is. The ratio of  $Q_2$  to  $Q_1$  is also listed in Table II. For the five samples,  $Q_2/Q_1$ decreases with the increase of water absorbency. This means denser network has better salt resistance.

# CONCLUSION

Superabsorbent can be prepared efficiently by concentrated aqueous solution polymerization in a short time. The temperature of the monomer mixture changes during the polymerization process. The water absorbency increases linearly with the increase of initiator content, and the higher the temperature of water bath, the higher the water

~ 1		Water Absorbency (g/g)		
Sample No.	Cc	Distilled Water $(Q_1)$	0.9% Saline Solution $(Q_2)$	$Q_2/Q_1$
S1	$1.68 imes10^{-3}$	104	28	0.27
S2	$8.40 imes10^{-4}$	162	36	0.22
S3	$6.30 imes10^{-4}$	188	40	0.21
S4	$4.20 imes10^{-4}$	250	48	0.19
S5	$2.10 imes10^{-4}$	401	63	0.16

Table II Water Absorbency in the Distilled Water and 0.9% Saline Solution

Reaction condition: Dn is 80%; Ci is  $1.37 \times 10^{-3}$ ; bath temperature is 70°C.

absorbency is. Lower crosslinking efficiency occurs when the polymerization rate is faster. The results conform with Flory's network theory that higher network imperfection or more chain ends cause higher swelling ratio of the networks. A relation of  $Q = K Cc^{-0.6}$  (K is a constant) is derived from Flory's water-absorbing equation for the swelling of ionic networks. The water absorbency decreases with the increase of crosslinker content and an empirical relation of  $Q = 1.40Cc^{-0.665}$  is obtained. The optimum degree of neutralization is 75%. Denser network has better salt resistance.

# REFERENCES

- Tanaka, H.; Kambayashi, T.; Sugiyama, Y.; Nagai, T.; Nagata, K.; Kubota, K.; Hirano, K. Eur. Pat. 501,482, 1992.
- Miura, Y.; Hirano, K.; Nate, T.; Kambayashi, T.; Ohtsuka, M.; Nagai, T. Eur. Pat. 440,256, 1991.
- Shimomura, T.; Namba, T. In Superabsorbent Polymers; Buchholz, F. L.; Peppas, N. A., Eds.; ACS Symposium Series 573; American Chemical Society: Washington, DC, 1994.
- 4. Honda, N.; Wakumoto, H.; Nakano, T.; Ueki, H.; Hiratsuka, J. Eur. Pat. 122,797, 1984.
- 5. Clarke, J. B. Eur. Pat. 101,253, 1984.
- Tsuji, S.; Musika, H.; Itoh, M.; Saga, J.; Fujiwara, T.; Hatsuda, T. Eur. Pat. 356,161, 1990.
- 7. Walker, C. O. U. S. Pat. 4,664,816, 1987.
- Hefner, R. E.; Haynes, D. I. U.S. Pat. 4,611,015, 1986.
- Hosoya, Y.; Watanabe, N.; Takagi, I.; Miyoshi, A. Eur. Pat. 342,996, 1989.

- 10. Katzer, M. F. U.S. Pat. 3,354,084, 1967.
- 11. Tsubakimoto, T.; Shimomura, T.; Kobayashi, H. Jpn. Pat. 62,149,335, 1987.
- 12. Tanaka, K. Kogyo Zairyo 1994, 42, 18.
- Ende, M. T.; Hariharan, D.; Peppas, N. A. React Polym 1995, 25, 127.
- Conte, U.; LaManna, A.; Giunchedi, P. Eur. Pat. 468,392, 1992.
- Smith, P. B.; Cutie, S. S.; Henton, D. E.; Powell, C.; Kosman, J.; Howell, B. A. J Polym Sci, Polym Chem Ed 1997, 35, 799.
- Zhou, W. J.; Yao, K. J.; Kurth, M. J. J Appl Polym Sci 1997, 64, 1001.
- Zhou, W. J.; Yao, K. J.; Kurth, M. J. J Appl Polym Sci 1997, 64, 1009.
- Liu, Z. S.; Rempel, G. L. J Appl Polym Sci 1997, 64, 1345.
- Takeda, H.; Taniguchi, Y. U.S. Pat. 4,525,527, 1985.
- Alexander, W.; Anderson, M.; Teppo, M. Eur. Pat. 206,808, 1986.
- Makita, M.; Tanioku, S.; Touda, T. U.S. Pat. 4,703,067, 1987.
- 22. Chen, J.; Zhao, Y. J Appl Polym Sci, to appear.
- Flory, P. J. Principles of Polymer Chemistry; Cornell University Press, Ithaca, NY, 1953.
- Seymour, R. B.; Carraher, C. E. Polymer Chemistry, An Introduction; Marcel Dekker, New York, 1981.
- Allcock, H. R.; Frederick, W. L. Contemporary Polymer Chemistry; Prentice-Hall, Englewood, Cliffs, NJ, 1981.
- Song, Y.; Cui, Z.; Chen, X. Yingyong Huaxue 1995, 12,117.