

# Relationship Between Water Absorbency and Reaction Conditions in Aqueous Solution Polymerization of Polyacrylate Superabsorbents

JUNWU CHEN, YAOMING ZHAO

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

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**ABSTRACT:** Polyacrylate superabsorbents were prepared by *in situ* aqueous solution polymerization in a polyethylene bag, which was submerged in a water bath. The influence of the initiator content, bath temperature, isopropanol content, initial monomer concentration, and crosslinker content ( $C_c$ ) on water absorbency ( $Q$ ) were investigated. The temperature change of the monomer mixture during polymerization was also analyzed. Increase of the chain ends in networks resulting from decrease of the molecular weight in free-radical polymerization causes an increase of the water absorbency of superabsorbents and also reduces the crosslinking efficiency. The results are in conformity with the classical network theory. An empirical relation of  $Q = 2.45 C_c^{-0.600}$  was obtained and the validity of Flory's swelling equation was confirmed indirectly. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 808–814, 2000

**Key words:** superabsorbent; ionic networks; *in situ* aqueous solution polymerization; free-radical polymerization; water absorbency; crosslinking

## INTRODUCTION

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, and sponge. Superabsorbents are widely used in sanitary goods such as in disposable diapers and hygienic napkins. They are also found to be valuable in artificial snow,<sup>1,2</sup> agriculture,<sup>3–5</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 coatings,<sup>9</sup> fire fighting,<sup>10</sup> sealing composites in long distance cable,<sup>11,12</sup> and drug delivery.<sup>13,14</sup>

In our previous studies,<sup>15,16</sup> polyacrylate superabsorbents were prepared by concentrated

aqueous solution polymerization in a stainless-steel dish, which was heated by hot air in a thermostatic oven<sup>15</sup> or heated from one side by a water bath.<sup>16</sup> Polymeric gel was formed at the end of the polymerization. However, air bubbles usually form in the polymeric gel because considerable polymerization heat was generated and could not be dissipated rapidly enough at the accelerated polymerization stage.

In this article, the monomer mixture was put into a sealed polyethylene bag which was clamped by two parallel stainless-steel plates and the item was submerged in water vertically in a predetermined temperature water bath.<sup>17</sup> The heat transfer was greatly improved because there were two sides to dissipate the polymerization heat and the temperature difference between the monomer mixture and the water bath was also greatly decreased. No air bubbles existed in the polymeric gels.

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Correspondence to: J. Chen.

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The temperature change of the monomer mixture during polymerization was analyzed. The effects of initiator content, bath temperature, isopropanol content, monomer concentration, and crosslinker content on water absorbency were also investigated.

## EXPERIMENTAL

### Materials

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

### Preparation of Polyacrylate Superabsorbent

Typically, in a 500-mL beaker, cooled in a 25°C recycled water bath, 31 g distilled water was mixed with 73.4 g acrylic acid. The stirred acrylic acid aqueous solution was neutralized by adding, dropwise, a sodium hydroxide aqueous solution (32.6 g sodium hydroxide and 72.2 g distilled water). The degree of neutralization was 80% and the monomer concentration was 43.6%. The monomer mixture was diluted with a certain weight of distilled water only when the effect of the initial monomer concentration on water absorbency was investigated. Isopropanol was added only when the effect of the isopropanol content on water absorbency was investigated. A weighed quantity of KPS and TEGDA were dissolved in the monomer mixture at ambient under full stirring. The aqueous monomer mixture was contained in a 30 × 30-cm polyethylene bag of which the film thickness was 13.1 μm. The mouth of the bag that contained the monomer mixture was sealed with a heat-welding machine, and then the bag was sandwiched vertically between a pair of stainless-steel plates (rectangular, 35 × 9 × 0.15 cm). The distance between the two parallel plates was 1 cm, obtained by setting four stainless-steel cubes, of which the side length was 1 cm, in four corners between the plates and clamping the plates with four clamps. From a small hole at the proper position, opened beforehand with a

punch on one side of the bag, a thermometer was inserted vertically in the monomer mixture to determine the temperature profile during polymerization. The moored reaction device was vertically submerged in a 70°C water bath and the shape of the monomer mixture was about 30 × 6 × 1 cm. The monomer mixture was polymerized *in situ* for 2 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 then screened through a 40-mesh sieve.

### Measurement of Water Absorbency

The accurately weighed resin (about 1 g) was immersed in 800 g distilled water and allowed to soak at 25°C for 2 h. The swollen gel was then separated from the 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:

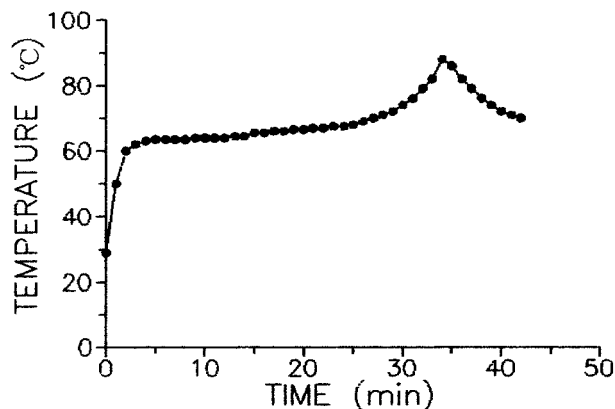
$$Q = (W_2 - W_1)/W_1 \quad (1)$$

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

## RESULTS AND DISCUSSION

### Temperature Change of Monomer Mixture During Polymerization

The temperature change of the monomer mixture is shown in Figure 1. The temperature of the monomer mixture increases steadily when the monomer mixture is heated by the water bath. The temperature difference between the water bath and the monomer mixture as well as the polymerization heat contributes to the temperature elevation of the monomer mixture. The curve in Figure 1 can be divided into four sections according to the different rates of the temperature change; however, the transition point between two successive sections is hard to divide exactly. The beginning 2 min can be regarded as the first section, with a rapid temperature increase occurring due to the big temperature difference between the water bath and the monomer mixture. The successively slight temperature elevation can be regarded as the second section for which the



**Figure 1** Temperature change of monomer mixture during polymerization. Temperature of water bath, 70°C;  $C_i$ , molar ratio of KPS to monomer,  $9.50 \times 10^{-4}$ ;  $C_c$ , molar ratio of TEGDA to monomer,  $8.40 \times 10^{-4}$ ;  $C_m$ , initial monomer concentration, 43.6%.

period is about 23 min. The third section corresponds to an accelerated polymerization process for which the period is about 9 min. The polymerization rate increases continuously during the process because of both the temperature increase and the increase of the viscosity of the monomer mixture. A rapid temperature increase occurs again because a large quantity of polymerization heat is generated during the process. The monomer mixture can reach its maximum temperature at the end of the accelerated polymerization process. The polymerization is nearly over when the temperature of the monomer mixture reaches a maximum. Due to the cooling of the water bath, the fourth section corresponds to the temperature decreased after the accelerated polymerization.

### Effect of Initiator Content

Figure 2 shows the effect of the initiator content ( $C_i$ , molar ratio of KPS to monomer) on the water absorbency. The water absorbency increases linearly with increase of the initiator content. The same results were also presented in a previous study in which only one side of the monomer mixture was heated by a water bath.<sup>16</sup>

The relation between the average kinetic chain length ( $\nu$ ) and concentration of the initiator in free-radical polymerization is given by the following equation<sup>18</sup>:

$$\nu = 1/2k_p(fk_i k_t)^{-1/2}[I]^{-1/2}[M] \quad (2)$$

where  $k_p$ ,  $k_i$ , and  $k_t$  are the rate constants for propagation, initiation, and termination, respectively;  $f$ , the efficiency of initiation by the initiator; and  $[I]$  and  $[M]$ , the initial concentration of the initiator and monomer, respectively. The molecular weight in free-radical polymerization will decrease with increase of the initiator concentration according to eq. (2).

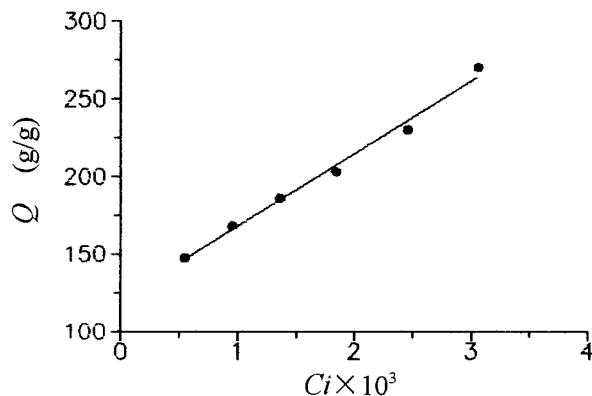
The relation between the swelling ratio and network structure parameter for the swelling of ionic networks was given by Flory,<sup>19</sup> usually used as the following two equivalent equations:

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

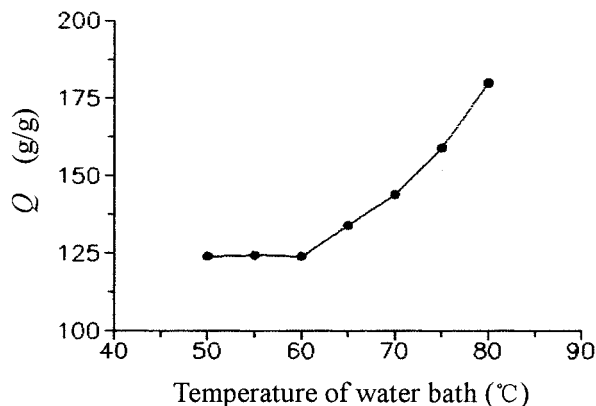
$$q_m^{5/3} \cong [(i/2v_u S^*)^{1/2}]^2 + (1/2 - \chi_1)/v_1] \times (M_c/\rho_p)(1 - 2M_c/M_n)^{-1} \quad (4)$$

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

$(1 - 2M_c/M_n)$  in eq. (4) expresses the correction for network imperfection resulting from the chain ends.<sup>19</sup> The network imperfection is higher when  $M_n$  is smaller and this also means the there are more chain ends in the networks. From eq. (4), it is predicted that networks with more chain ends



**Figure 2** Effect of initiator content ( $C_i$ , molar ratio of KPS to monomer) on absorbency  $Q$ . Temperature of water bath, 70°C.  $C_c = 8.40 \times 10^{-4}$ ;  $C_m = 43.6\%$ .



**Figure 3** Effect of temperature of water bath on water absorbency  $Q$ .  $C_i = 5.50 \times 10^{-4}$ ;  $C_c = 8.40 \times 10^{-4}$ ;  $C_m = 43.6\%$ .

have higher swelling ratios,  $q_m$ , when  $M_c$  is the same.

The reduction of molecular weight in free-radical polymerization with increased initiator content will result in increase of the relative amount of the polymer chain ends in the networks. Therefore, the experimental results in Figure 2 are in conformity with eq. (4) and directly support the Flory network theory.

### Effect of Bath Temperature

The effect of bath temperature on water absorbency was investigated between 50 and 80°C. The results are shown in Figure 3. The water absorbency changes little when the bath temperature is between 50 and 60°C and the water absorbency increases continuously when the bath temperature is between 60 and 80°C.

KPS is a thermal initiator in free-radical polymerization. The half-life of the decomposition of KPS decreases with increase of the bath temperature. The number of the resulting free radicals in unit time increases along with increase of the decomposition rate of KPS. The degree of polymerization is reduced because of the increase of the termination rate as well as the temperature dependence of the chain-transfer reaction.<sup>18,20</sup> So, the molecular weight decreases when the polymerization temperature is increased.

At the same crosslinker content, the water absorbency increases when the crosslinking efficiency decreases according to eq. (3). From the experimental results in Figures 2 and 3, water absorbency increases with increase of  $C_i$  as well as with increase of the bath temperature between

and 80°C. So, the crosslinking efficiency decreases with increase of  $C_i$  or with the bath temperature between 60 and 80°C. It should be pointed out that the effect of the bath temperature on water absorbency is rather limited when the bath temperature is between 50 and 60°C, so the variation of the number of chain ends in the networks is rather small within that temperature range.

Sometimes, water absorbency does not increase with increase of  $C_i$  or the reaction temperature<sup>15,21-24</sup>; the reason could be attributed to the different extents of self-crosslinking in the polymerization. Aoki and Yamasaki reported on self-crosslinking in the preparation of a polyacrylate superabsorbent by inverse suspension polymerization and that no crosslinker was needed in the preparation.<sup>25</sup> Water absorbency decreases with increase of  $C_i$  or the reaction temperature when self-crosslinking is dominant.<sup>21,22</sup> Water absorbency changes little with increase of  $C_i$  or the reaction temperature when the effect of self-crosslinking is close to that of the increase of the chain ends in the networks.<sup>23,24</sup> From the above results, the effect of self-crosslinking is much smaller in this preparation.

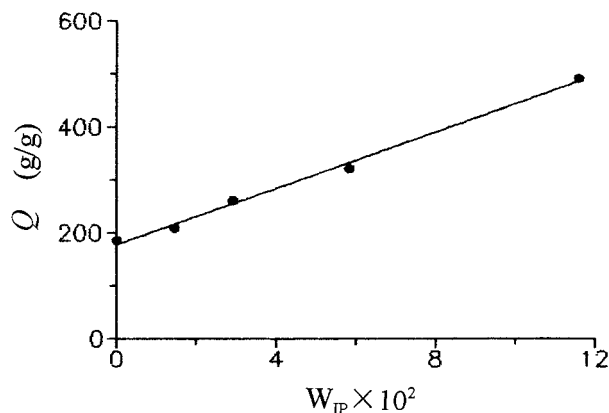
### Effect of Isopropanol

Isopropanol has a moderate chain-transfer constant in radical polymerization,<sup>26</sup> and it is usually used as a chain-transfer agent in the polymerization of acrylonitrile for wet spinning of acrylic fiber or Orlon.<sup>27</sup> The effect of the content of isopropanol ( $W_{IP}$ , weight ratio of isopropanol to monomer) on water absorbency is shown in Figure 4. Water absorbency increases linearly with increase of the content of isopropanol.

The effect of chain transfer on the degree of polymerization ( $X_n$ ) is given by the following equation when termination is by disproportionation<sup>18</sup>:

$$(X_n)^{-1} = 2k_t R_p k_p^{-2} [M]^{-2} + C_M + C_I [I] [M]^{-1} + C_S [S] [M]^{-1} + C_P [P] [M]^{-1} + C_Y [Y] [M]^{-1} \quad (5)$$

where  $R_p$  is the rate of propagation;  $[S]$ ,  $[P]$ , and  $[Y]$ , the concentration of the solvent, polymer, and chain-transfer agent, respectively; and  $C_M$ ,  $C_P$ ,  $C_S$ ,  $C_P$ , and  $C_Y$ , the chain-transfer constants for the polymer radicals to the monomer, initiator, solvent, polymer, and chain-transfer agent, respectively.



**Figure 4** Effect of isopropanol content ( $W_{IP}$ , weight ratio of isopropanol to monomer) on water absorbency  $Q$ .  $C_i = 1.37 \times 10^{-3}$ ,  $C_c = 8.40 \times 10^{-4}$ , and  $C_m = 43.6\%$ , at  $70^\circ\text{C}$ .

From eq. (5), eq. (6) could be obtained:

$$(X_n)^{-1} = (X_n)_0^{-1} + C_Y[Y][M]^{-1} \quad (6)$$

where  $(X_n)_0^{-1} = 2k_t R_p k_p^{-2} [M]^{-2} + C_M + C_I [I][M]^{-1} + C_S [S][M]^{-1} + C_p [P][M]^{-1}$ . From eq. (6), the degree of polymerization or molecular weight will decrease with increase of the concentration of the chain-transfer agent in free-radical polymerization. The number of chain ends in the networks will increase and water absorbency will increase according to eq. (4). The crosslinking efficiency decreases with increase of the chain-transfer agents. The experimental results in Figure 4 are also in conformity with Flory's network theory.

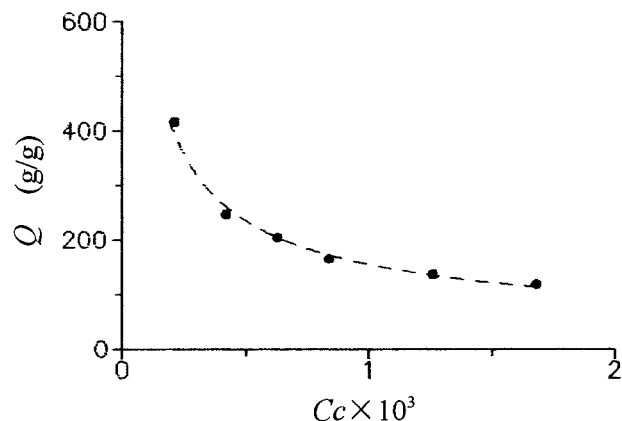
#### Effect of Initial Monomer Concentration

The effect of initial monomer concentration ( $C_m$ , wt %) on water absorbency is shown in Table I. Water absorbency decreases with increase of  $C_m$ . It is hard to obtain a polymeric gel in the prepa-

**Table I** Effect of Initial Monomer Concentration on Water Absorbency

$C_m$ (wt %)	$Q$ (g/g)
25	281
30	279
35	205
43.6	165

$C_i = 9.50 \times 10^{-4}$ ;  $C_c = 8.40 \times 10^{-4}$ , at  $70^\circ\text{C}$ .



**Figure 5** Effect of crosslinker content ( $C_c$ , molar ratio of TEGDA to monomer). Dashed line is the best-fit curve according to the reaction  $Q = 2.45C_c^{-0.600}$ .  $C_i = 9.50 \times 10^{-4}$  and  $C_m = 43.6\%$ , at  $70^\circ\text{C}$ .

ration when  $C_m$  is lower than 25% and water absorbency is hard to measure exactly because of the excessive water-soluble material.

The average kinetic chain length will increase with increase of the monomer concentration according to eq. (2); then, water absorbency will decrease according to eq. (4) and crosslinking efficiency increases. The experimental results also support Flory's network theory. Baker et al.<sup>28</sup> obtained the same results in the preparation of a polyacrylamide hydrogel. The same results were also reported by Lee and Wu in the preparation of a polyacrylate superabsorbent by inverse suspension polymerization.<sup>29</sup>

#### Effect of Crosslinker Content

The effect of crosslinker content ( $C_c$ , molar ratio of TEGDA to monomer) on water absorbency is shown in Figure 5. The water absorbency decreases with increase of  $C_c$ . This is in conformity with Flory's water absorbency eq. (3).

The relation between  $q_m$  and  $Q$  is shown in eq. (7) when water is the swelling agent:

$$q_m = Q\rho_p/\rho_s + 1 \quad (7)$$

where  $\rho_p$  and  $\rho_s$  are the density of the polymer and swelling solvent, respectively. Usually,  $Q$  is very large and  $\rho_p$  is higher than  $\rho_s$  for an acrylic-based superabsorbent. Then, the unit 1 in eq. (7) can be omitted and we have

$$q_m \cong Q\rho_p/\rho_s \quad (8)$$



For a given chemical structure of a superabsorbent and a given swollen solution,  $[(i/2v_u S^{*1/2})^2 + (1/2 - \chi_1)/v_1]$  in eq. (3) could be regarded as a constant (assumption 1). From eqs. (3) and (8), eq. (9) can be obtained:

$$Q \cong k_1(\nu_e/V_0)^{-0.6} \quad (9)$$

where  $k_1$  is a constant.

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

$$\nu_e/V_0 = k_2 Cc \quad (10)$$

where  $k_2$  is a constant relevant to crosslinking efficiency. From eqs. (9) and (10), we can obtain

$$Q \cong k_3 Cc^{-0.6} \quad (11)$$

where  $k_3 = k_1 k_2^{-0.6}$ . Equation (11) gives the relation between water absorbency  $Q$  and crosslinker content  $Cc$ .

Grapher 1.50 (Golden Software Inc.) was used to obtain the best-fit relation between  $Q$  and  $Cc$ . The following relation  $Q = 2.45Cc^{-0.600}$  was generated. The relation is drawn by a dashed line in Figure 5. The empirical relation fits the experimental results well. The exponent  $-0.600$  in the empirical relation is equal to that in eq. (11) and the two assumptions in the derivation of eq. (11) are also proved to be reasonable. Flory's swelling equation is usually used as a qualitative interpretation of the relation between the swelling ratio and network parameters; however, the relationship between  $Q$  and  $Cc$  in the study testifies to the validity of Flory's swelling equation indirectly.

Different extents of deviation of the exponent from that in eq. (11) were found in inverse suspension polymerization and other kinds of concentrated aqueous solution polymerizations of polyacrylate superabsorbents in our previous studies<sup>15,16,30</sup> and the reason could be attributed to the extent of self-crosslinking and the nonuniformity of the crosslinking. Assumption 2 in the deduction of eq. (11) may not be fully satisfied in those preparations.

## CONCLUSIONS

High water-absorbent polyacrylates were prepared by *in situ* concentrated aqueous solution

polymerization in a polyethylene bag, which was submerged in a water bath with a predetermined temperature. The temperature of the monomer mixture changes during the polymerization process. The water absorbency increases linearly with increase of the initiator content. The water absorbency is little changed when the bath temperature is between 50 and 60°C and water absorbency increases continuously when the bath temperature is between 60 and 80°C. Water absorbency increases linearly with increase of the isopropanol content. Water absorbency decreases with increase of the initial monomer concentration. The increase of end chains in networks resulting from the decrease of molecular weights in free-radical polymerization causes the increase of the water absorbency of superabsorbents and also reduces the crosslinking efficiency. The results are in conformity with Flory's network theory that higher network imperfection or more chain ends in networks causes the 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 increase of the crosslinker content and an empirical relation of  $Q = 2.45Cc^{-0.600}$  is obtained and its exponent is equal to that of the derived equation. The validity of Flory's swelling equation is confirmed indirectly in this study when two assumptions in the deduction of the relation between  $Q$  and  $Cc$  are fully satisfied.

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