

# Water Absorbency of Poly(sodium acrylate) Superabsorbents Crosslinked with Modified Poly(ethylene glycol)s

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**ABSTRACT:** A series of novel crosslinkers, polyethylene glycol diacrylate (PEGDA) with different molecular weights, were prepared, consisting of acryloyl end groups and the PEG backbones. The corresponding poly(sodium acrylate) superabsorbents of 60 mol % neutralization degree were synthesized by using ammonium persulfate and dimethylaminoethyl methacrylate as redox initiators in aqueous solution. PEGDA was characterized by FTIR and  $^1\text{H-NMR}$ . The maximum of water absorbency ( $Q$ ) of superabsorbents occurred at a specific mole fraction of crosslinker;  $Q$ -values increased with increasing molecular weight of PEGDA at the

same mole fraction, whereas the water absorption rate was the opposite, in which  $Q$ -values decreased gradually with time ( $>24$  h). Compared with superabsorbents containing methylene bisacrylamide crosslinker with PEGDA, the  $Q$ -value of the former was significantly less than that of the latter, although levels of the residual monomer and the soluble polymer were opposite. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1851–1856, 2003

**Key words:** superabsorbents; water absorbency; crosslinking; molecular weight; FTIR

## INTRODUCTION

Superabsorbents can absorb a large amount of water within a short time, in which the absorbed water is then scarcely removable even under pressure. Thus superabsorbents have found extensive product applications such as disposable diapers, feminine napkins, artificial snows, agriculture, horticulture, food storage, gel actuators, water-blocking tapes, medicine for drug delivery systems, absorbent pads, drilling fluid additives, enhanced oil recovery, fighting fire, underground cable, and “smart” materials, used where environmental concerns are primary.<sup>1–13</sup> They have attracted the great attention of researchers and technologists in the past few decades.

At present the overwhelming majority of researchers have been focusing their interest on synthesis methods, influences of feeding ratio, types of raw materials, and additionally external factors on swelling behavior, network parameters, collapse of gels, gel complexes, theory of compression and expansion of hydrogels, and interpenetrating networks.<sup>14–20</sup> Nevertheless, there has been a paucity of research on

crosslinkers whose content is almost negligible compared with that of raw monomers, although they have played an important role up to now. Smith et al.<sup>21</sup> reported that superabsorbents, prepared by allyl-end-capped poly(ethylene glycol) crosslinkers (AEPEG) of 200, 400, and 600 molecular weight, contained low soluble polymer. AEPEG is less reactive than acrylate crosslinkers and it produced a network that has lower crosslinking density during the initial stage of polymerization and is apparently more uniform in crosslinking density as opposed to AEPEG of 3400 molecular weight; moreover, the mechanism of polymerization of allyl crosslinkers is normal vinyl polymerization. Arriola et al.<sup>22</sup> found that the relative rate of incorporation of trimethylol propane triacrylate (TMPTA) crosslinker into polyacrylic acid gels was exceedingly rapid; further, all of the double bonds of TMPTA were incorporated into the gel network, and superabsorbents prepared with TMPTA consisted of (1) a very heterogeneous network of highly crosslinked, high molecular weight polyacrylic acid formed during the early phase of the polymerization; (2) chains of low molecular weight that formed in the middle of the polymerization bridging through the pendant vinyl groups and containing a greater distance between crosslinking sites than chains formed initially; and (3) grafted polymer formed especially toward the end of the polymerization. However, the low efficiency ( $\sim 60$ – $70\%$ ) of TMPTA is postulated to be caused by a solubility problem in the monomer

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mixture at high neutralization, steric hindrance, and a lower percentage of solids. Accordingly, the reactivity of crosslinkers is very different in the various polymerization systems, whereas crosslinkers prominently affect the properties of superabsorbents.

In this study, a series of new crosslinkers of modified polyethylene glycol (PEGDA) with different molecular weights endcapped by acryloyloxy were synthesized. Because the polarity of acryloyloxy is superior to that of allyl, so is the reactivity of the acryloyloxy group. As a result, PEGDA with relatively high molecular weight is easily dissolved in water and acrylic acid, and is effectively incorporated into polymer networks. In the present work, the relationship between the molecular weight of PEGDA and the properties of the superabsorbents—water absorbency, water absorption rate, water retention, and levels of the residual monomer and the soluble polymer—were investigated.

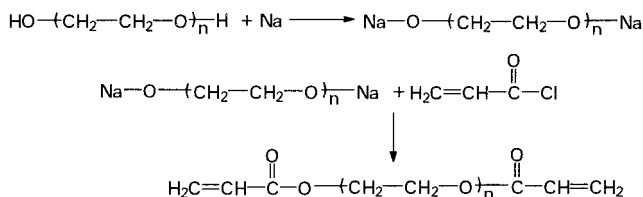
## EXPERIMENTAL

### Materials

Polyethylene glycol of 200 molecular weight (abbreviated 2PEG; other abbreviations follow the same pattern as that for 2PEG), 4PEG, 6PEG, 10PEG, and 15PEG (chemical purity) from Beijing Fine Chemical Co. Ltd. (China) were distilled under reduced pressure to remove water before use. Hydroquinone (analytical grade; Shanghai Biochemical Reagent Co., China), sodium powder in kerosene (Beijing Metal Product Co.), and sodium hydroxide (analytical grade) were directly used without further purification. Acryloyl chloride (AC) was prepared from acrylic acid according to Rehberg et al.<sup>23</sup> Acrylic acid (AA) (chemical grade; Oriental Chemical Plant, China) and dimethylaminoethyl methacrylate (DMAEMA, commercial grade; Shandong Qilu Chemical Plant, China) were purified by distillation under reduced pressure. Ammonium persulfate (APS, analytical grade) and methylene bisacrylamide (MBA, analytical grade), provided by Beijing Fine Chemical Co., were purified by recrystallization from water.

### Synthesis of PEGDA

The crosslinkers PEGDA were synthesized according to Scheme 1. Typically, a definite amount of the PEG was mixed with chloroform in a 250-mL four-neck round-bottom flask vessel equipped with a magnetic stirrer, a thermometer, inert-gas nitrogen (N<sub>2</sub>) inlet, and thermostat water bath, and then the equivalent sodium powder was added to the flask. The mixture was maintained for 6 h under N<sub>2</sub> flow, from which sodium polyethylene glycol (NaPEG) was produced. The AC and NaPEG in the feed mole ratio of 1.2 to 1.0



**Scheme 1** The synthesis route of PEGDA.

were reacted for 4 h, NaCl was removed by filtration, and then a small amount of hydroquinone was added into the filtrate, which was distilled in a rotary evaporator under reduced pressure to remove chloroform and the residual AC. Finally, the white viscous crosslinkers PEGDA were obtained. The yield was in the range of 83 to 92 wt %. 2PEG, 4PEG, 6PEG, 10PEG, and 15PEG endcapped by acryloyl group were denoted as 2PEGDA, 4PEGDA, 6PEGDA, 10PEGDA, and 15PEGDA, respectively, and the corresponding superabsorbents (see below) were denoted as PAAG2, PAAG4, PAAG6, PAAG10, and PAAG15, respectively.

### Preparation of superabsorbents

A 250-mL stainless steel beaker with a cap of three holes was used as the reaction vessel. The temperature was controlled by use of a thermostat water bath fixed with a temperature sensor. AA aqueous solution was neutralized into 60 mol % of the neutralization degree by dropwise addition of 50% NaOH aqueous solution in the ice-water bath on stirring and its concentration was about 35 wt %. After that, N<sub>2</sub> was slowly purged to drive off the remaining oxygen while fully stirring; a given quantity of the initiator APS was dissolved in the monomer solution at room temperature. After 15 min, the DMAEMA equivalent to APS was also added, after which crosslinkers PEGDA of different mole fractions and molecular weights were added to the neutralized AA solution, respectively. After 0.5 h stirring and flushing N<sub>2</sub> were stopped, and the polymerizations were carried out for 2 h at 40°C. The products were cut into small pieces after being immersed in an excess of deionized water for 20 days to remove the residual monomer and the soluble polymer; in the meantime, deionized water was changed once every 2 days. Finally, samples were dried in a vacuum for 1 day at 80°C. The dried superabsorbent polymers were ground and screened in the range of 60 to 80 mesh. For comparison, the poly(sodium acrylate) superabsorbent (PSAS) using MBA as crosslinking agent was also synthesized under the same conditions as described above for the other superabsorbents.

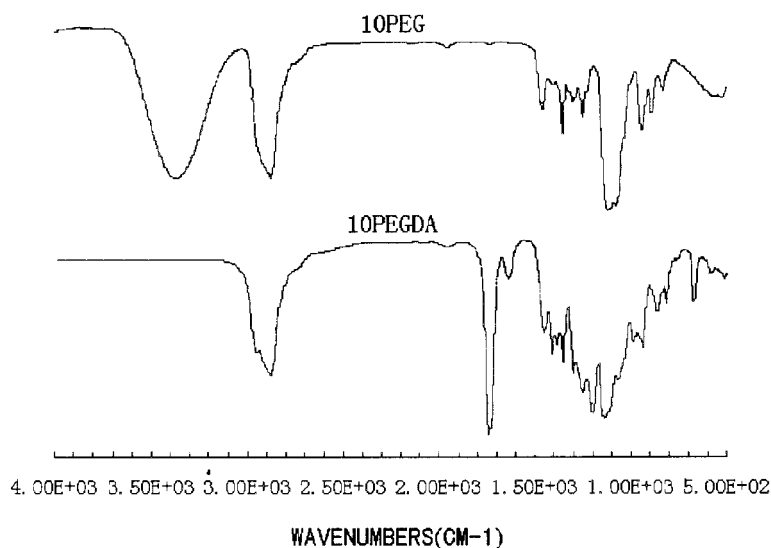


Figure 1 FTIR spectra of 10PEGDA and 10PEG.

### Analyses and measurements

#### Structure of PEGDA

The structure of PEGDA was characterized by a Nicolet-560 FTIR (Nicolet Analytical Instruments, Madison, WI) using KBr pellet and a Bruker DRX-300 (Bruker Instruments, Billerica, MA)  $^1\text{H-NMR}$  using  $\text{CD}_3\text{COCD}_3$  as solvent.

#### Water absorbency

Purified dry sample (100 mg) was weighed precisely and immersed in a large excess of deionized water until achieving swelling equilibrium for at least 6 h at room temperature, and then unabsorbed water was then filtrated through a 20-mesh sieve. The water absorbency ( $Q$ ) was determined by weighing the swollen superabsorbent and calculated according to the following relationship:

$$Q \text{ (g/g)} = (\text{weight of swelling superabsorbent} - 0.1) \times 10 \quad (1)$$

#### Residual monomer content

The residual monomer was easily dissolved in deionized water. Thus, tiny pieces of unpurified superabsorbents were directly put in the sieve before drying and washed with deionized water for 2 min so as to remove the residual monomer. The content of the residual monomer ( $C_r$ ) was calculated using the following formula:

$$C_r \text{ (%) } = \frac{(\text{weight of dry samples} - \text{weight of dry samples washed})}{\text{weight of the monomer}} \times 100 \quad (2)$$

#### Fraction of soluble polymer

The sample washed by deionized water in the preceding section was added to a small bag made of the 80-mesh stainless steel sieve, then the bag was put into a Soxhlet flask and extracted with methanol/deionized water (2 : 8 vol/vol) solution as solvent for 3 days at  $80^\circ\text{C}$ . The fraction of the soluble polymer ( $F_s$ ) can be written as

$$F_s \text{ (%) } = \frac{W_1 - W_2}{W_1} \times 100 \quad (3)$$

where  $W_1$  is the weight of the dry sample washed and  $W_2$  is the weight of the polymer superabsorbent after extraction.

## RESULTS AND DISCUSSION

### Structure of crosslinkers

The FTIR spectrum of 10PEGDA (Fig. 1) showed  $-\text{O}-\text{C}=\text{O}$ ,  $1730 \text{ cm}^{-1}$  (s), not  $\text{Cl}-\text{C}=\text{O}$ ,  $1760 \text{ cm}^{-1}$  (s);  $\text{C}=\text{C}$ ,  $1610 \text{ cm}^{-1}$  (w); and  $-\text{O}-$  (aliphatic ether),  $1110 \text{ cm}^{-1}$  (m). In particular, the disappearance of the hydroxy peak in 10PEGDA indicated that the hydroxy hydrogen for 10PEG was thoroughly substituted by the acryloyl group.

The assignment of hydrogens in the  $^1\text{H-NMR}$  spectrum of 10PEGDA is exhibited in Figure 2.

The FTIR and  $^1\text{H-NMR}$  spectra of the other crosslinkers were nearly identical to that of 10PEGDA.

### Water absorbency

The absorbency ( $Q$ ) increases dramatically in deionized water with the increasing mole fraction of

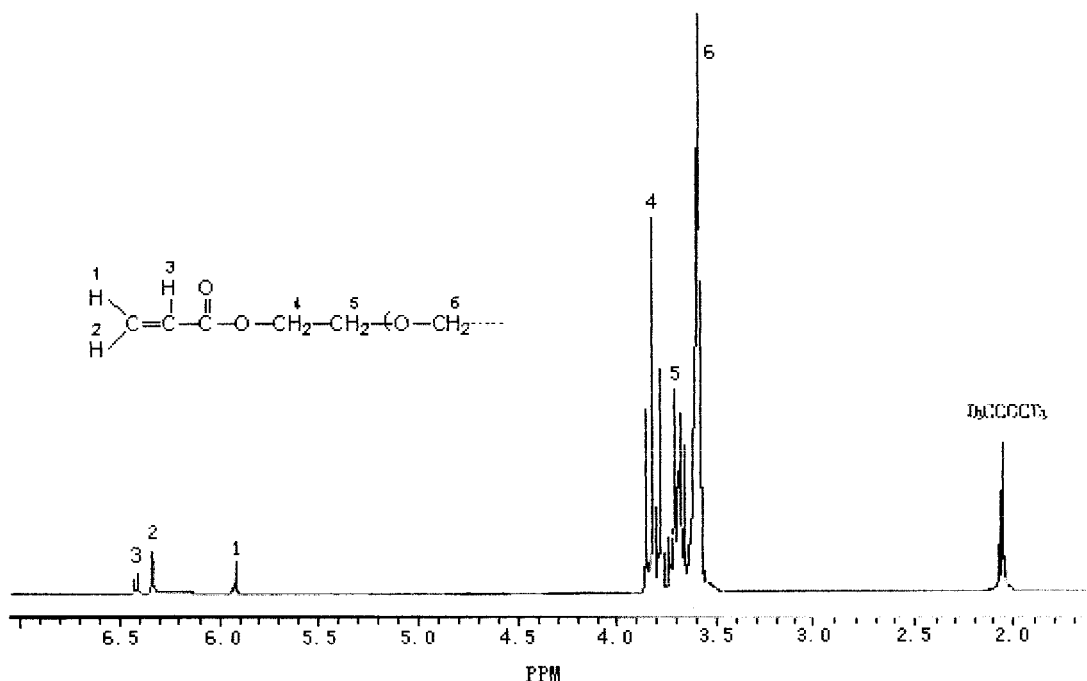


Figure 2  $^1\text{H-NMR}$  spectrum of 10PEGDA.

crosslinking agent ( $M_c$ ) at low  $M_c$  but then decreases significantly with the continuous addition of crosslinking agent at high  $M_c$ ; and there is a maximum of  $Q$  ( $Q_{\max}$ ) at the optimal  $M_c$ , which is defined as the optimum mole fraction of crosslinkers (Fig. 3). For instance,  $Q_{\max}$  values of PAAG2, PAAG4, PAAG6, PAAG10, and PAAG15 are 1600, 2400, 3200, 3460, and 4030 g/g, respectively. Polymers cannot be effectively crosslinked at low  $M_c$ , which leads to poor water absorbency, and the crosslinking density is too high at high  $M_c$ ; that is, the mesh size of the networks is very small, thus causing significantly less water absorbency. Thus, only at the optimum  $M_c$ , networks formed effectively and reasonably distributed are of the appropriate mesh size, and thus may absorb the most water; in other words,  $Q_{\max}$  occurs at the optimum  $M_c$ .

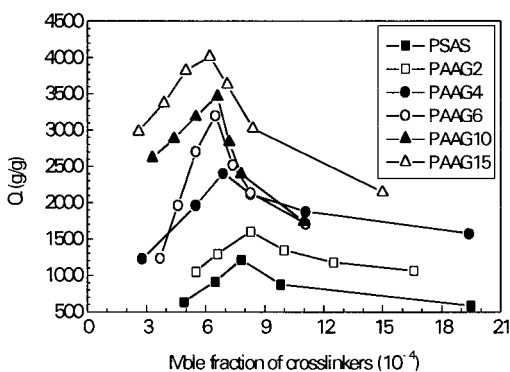
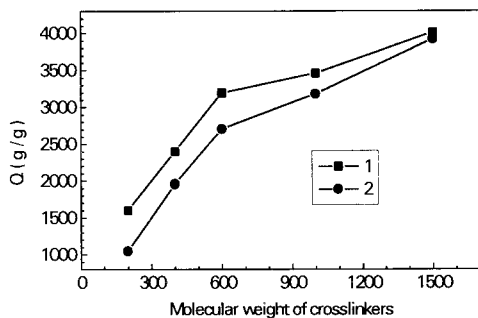


Figure 3 Effect of mole fraction of crosslinkers on absorbency in deionized water.

Polymer superabsorbents crosslinked by PEGDA have much greater capacity for water absorbency than PSAS whose  $Q_{\max}$  is 1210 g/g. Herein, on the one hand, reactivity of MBA is far greater than that of AA and the degree of crosslinking is extremely heterogeneous because of the faster reaction of MBA than that of AA during the polymerization process; thus it is inevitable that AA is not completely crosslinked but polymerized into a lot of linearly soluble long-chain polymers, whose superabsorbent particles it may encapsulate, thus preventing free water from penetrating to the inside of networks at the late stage of polymerization. On the other hand, the longer molecular chain of PEGDA than that of MBA causes the polymer networks crosslinked by PEGDA to possess a larger mesh size than that of PSAS, so that the former networks have a greater capacity for water than the latter networks.<sup>24</sup>

Figure 4 shows that the greater the molecular weight ( $M_w$ ) of PEGDA, the higher the water absorbency of the corresponding polymer superabsorbent at the same  $M_c$ . The result is attributed to variations of reactivity and chain length of PEGDA. First, the reactivity of PEGDA is weaker than that of MBA and the distribution of PEGDA in the polymer networks is more uniform; second, the reactivity of PEGDA decreases gradually with the  $M_w$  increment, thus ensuring that PEGDA of high  $M_w$  may incorporate into polymer networks from the beginning to the end of polymerization; finally, the high  $M_w$  of PEGDA implies long molecular chains. Of course, the space dimension of meshes of networks bearing PEGDA with



**Figure 4** Variation of absorbency with molecular weight of crosslinkers in deionized water: (1) variation of  $Q_{max}$ ; (2) variation of  $Q$  at  $M_c = 5.5 \times 10^{-4}$ .

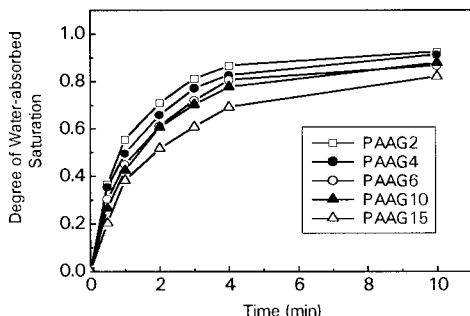
high  $M_w$  grows much larger than that in the case of PEGDA with low  $M_w$ . As mentioned above, these are beneficial to improving the water absorbency of superabsorbents.

**Water absorption rate**

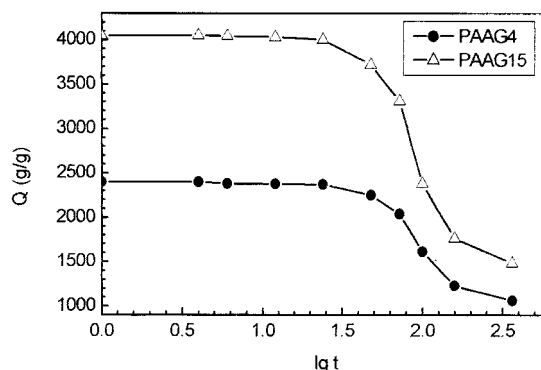
The degree of water-absorbing saturation was defined as the ratio of  $Q$  at any time to  $Q_{eq}$  at the swelling equilibrium. Figure 5 indicates that the water absorption rate for polymer superabsorbents in deionized water is in the order of PAAG2 > PAAG4 > PAAG6 > PAAG10 > PAAG15. The initial absorption rate is sharply increased in deionized water within 4 min after the slower rate of achieving swelling equilibrium.

**Retention of water absorbency**

The sample at swelling equilibrium was put in a beaker at 30°C and weighed every 2 h; its water absorbency was calculated according to eq. (1). The  $Q$  value of PAAG4 was almost constant within 48 h, but slowly decreased after 48 h;  $Q$  of PAAG15 was similar to that of PAAG4 in 24 h, but decreased significantly after 24 h;  $Q$  of PAAG4 and PAAG15 decreased to 1060 and 1480 g/g, respectively, at 360 h (Fig. 6), although  $Q$  of



**Figure 5** Swelling kinetics curves of superabsorbents containing crosslinkers with different molecular weights in deionized water.



**Figure 6** Plot of water absorbency against logarithm of time (h) (30°C).

PAAG4 was still less than that of PAAG15. It is well known that there is a large quantity of free water inside the swelling superabsorbent whose interaction with polymers is extremely weak<sup>24</sup>; furthermore, the larger the mesh size of networks, the more free water, so some water is easily deflected. As a result, the water absorbency decreases.

**Comparison of reactivity of PEGDA with MBA**

Both the content of the residual monomer and the level of soluble polymers decrease with an increase of the mole fraction of PEGDA, and they are lower than that of MBA at a similar mole fraction (Table I). The greater density of the electronic cloud of acrylamido causes its the double bond to be more active than acryloyloxy. Therefore, MBA is mainly depleted in the early stage of polymerization. For PEGDA, the reactivity of the double bond is poorer than that of acrylamido and its molecular chains are longer than those of MBA; hence the reactive difference between PEGDA and AA is far less than that between MBA and AA, and polymerization with MBA produces more soluble polymers. In addition, it is shown that water absorbency is enhanced with a decrease in residual monomer content and level of soluble polymer, thus further verifying the validity of the former inference.

**TABLE I**  
Effect of Type of Crosslinkers on Polymerizations<sup>a</sup>

Crosslinker	$M_c (10^{-4})$	$C_r$ (wt %)	$F_s$ (wt %)	$Q_{eq}$ (g/g)
4PEGDA	3.5	4.3	7.8	1380
4PEGDA	5.1	2.9	4.1	1860
15PEGDA	3.3	3.8	6.9	3160
15PEGDA	5.5	2.1	3.9	3920
MBA	3.0	5.2	12.6	430
MBA	4.7	3.7	8.7	610

<sup>a</sup>  $M_c$ , mole fraction of crosslinking agent;  $C_r$ , content of the residual monomer;  $F_s$ , fraction of the soluble polymer;  $Q_{eq}$ , water absorbency at swelling equilibrium.

## CONCLUSIONS

Poly(ethylene glycol) crosslinker endcapped by an acryloyl group is easily prepared. The larger the molecular weight of the crosslinkers, the higher the water absorbency of the superabsorbents; and the water absorbency of superabsorbents crosslinked by PEGDA is much greater than that of superabsorbents crosslinked by MBA. There is an optimum mole fraction of crosslinkers in polymer gels. The water absorption rate decreases with an increase of molecular weight of the crosslinkers. Even for half a month at 30°C, the water-absorbing retention of superabsorbents is not less than the  $Q_{\max}$  of PSAS. The results are primarily attributed to the more uniform incorporation into polymer superabsorbents for PEGDA and the much larger space dimension of the network meshes.

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