

## High-Temperature Resistant Superabsorbent Based on Poly(acrylic acid) with Triallylammonium Chloride as Crosslinking Agent

Xiaoyun Zhang, Xiangpeng Wang, Sisi Zhang, Wei Wu

Department of Material Physics and Chemistry, College of Science, China University of Petroleum (East China), Qingdao 266580, China  
Correspondence to: W. Wu (E-mail: wuweipc@upc.edu.cn)

**ABSTRACT:** A novel high-temperature resistant superabsorbent was prepared by solution polymerization of partially neutralized acrylic acid (AA), using triallylammonium chloride as crosslinker, potassium persulfate as initiator. The factors that influence the water-absorbing capacity at 25 and 200°C such as mass concentration of monomer, mass ratio of crosslinker to AA, mass ratio of initiator to AA, and neutralization degree were investigated. The structure of the superabsorbent was characterized by Fourier transform infrared, thermogravimetric analysis, and scanning electron microscopy. The optimum conditions were obtained and the swelling ratios in distilled water and 1 wt % of NaCl solution could reach 841 and 74 g/g at 300°C, respectively. The superabsorbent also showed high swelling rate and good salt resistance. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41243.

**KEYWORDS:** crosslinking; gels; oil & gas; swelling; thermal properties

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### INTRODUCTION

Superabsorbent polymer (SAP) is a kind of important functional materials.<sup>1</sup> It can absorb and retain huge amounts of water or aqueous solutions even under certain pressure.<sup>2,3</sup> Owing to these unique properties, SAPs have been widely used in various fields such as medicine for drug delivery systems, artificial snow, agriculture and horticulture, healthcare products, profile control and water plugging, and so on.<sup>4–8</sup> However, most SAPs can only be used at room temperature. SAPs used at high temperature (>150°C) were rarely reported. This is because the traditional SAPs were prepared using *N,N*-methylenebisacrylamide (NMBA) as a crosslinking agent.<sup>9–13</sup> The crosslinked amide bonds are easily to hydrolyze at high temperature, and hence the SAPs become water soluble and lose their water retaining ability. This disadvantage restricts the further application of SAP at high temperature, such as being used as channel blocking agent for steam-stimulated oil well.<sup>14</sup> In a previous research, divinylbenzene (DVB) was used as a crosslinker to prepare an antihydrolyzing superabsorbent.<sup>15</sup> But the reported temperature is only 70°C. As DVB is volatile and insoluble in water, it cannot disperse well in water phase. This is detrimental to an effective polymerization. The crosslinking agent plays a key role in the preparation of a high-temperature resistant superabsorbent.

This article aims at preparing a novel high-temperature resistant superabsorbent based on partially neutralized acrylic acid (AA), using triallylammonium chloride (TAAC) as a crosslinking

agent. TAAC is a water-soluble polyfunctional crosslinker. It contains no chemical bonds that are easily to hydrolyze at a relative high temperature. The effects on water absorbency in distilled water at 25 and 200°C such as monomer concentration, crosslinker, and initiator concentration, neutralization degree were studied.

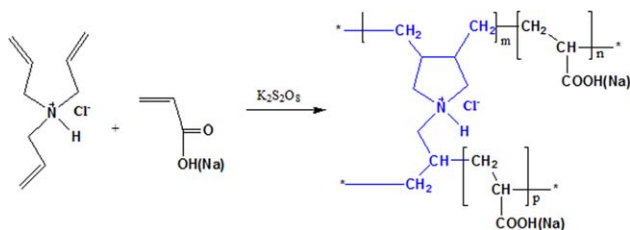
### EXPERIMENTAL

#### Materials

AA (chemically pure, Beijing Eastern Chemical Works, China) was used directly. Sodium hydroxide (NaOH), sodium chloride (NaCl), potassium persulfate (KPS), TAAC, NMBA, and DVB were of analytical grade and purchased from Sinopharm and used as received. All solutions were prepared with distilled water.

#### Polymerization of Partially Neutralized AA

The polymerization was carried out under nitrogen atmosphere in a four-necked flask equipped with a thermometer and gas inlet at 60°C. Taken the sample with monomer concentration (weight percentage of AA in polymerization solution) of 30 wt %, AA neutralization degree of 80%, TAAC to AA ratio of 0.14 wt %, KPS to AA ratio of 0.17 wt % as a representative example, the detailed procedure is as follows: 10.8 g of AA was mixed with 8.2 g of distilled water. The stirred AA aqueous solution was neutralized by adding, dropwise, 16 g of 30% aqueous sodium hydroxide solution. After being purged with nitrogen for 30 min to remove the dissolved oxygen, the mixed solution



**Scheme 1.** Proposed crosslinking mechanism of poly(acrylic acid) using TAAC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

was heated in a water bath to 60°C, and then 30.2 mg of 50% TAAC solution and 18.4 mg of KPS (dissolved in 1 mL of water) were introduced into the monomer solution. The polymerization occurred normally within 5–10 min and was continued for 3 h. The resulting gel product was removed and cut into small pieces (thickness, 0.1–0.5 cm), and then dried in a vacuum oven at 80°C to constant weight. In a similar manner, a series SAPs with varied monomer, crosslinker and initiator ratios were prepared. All the samples used were milled through 20–50-mesh screen.

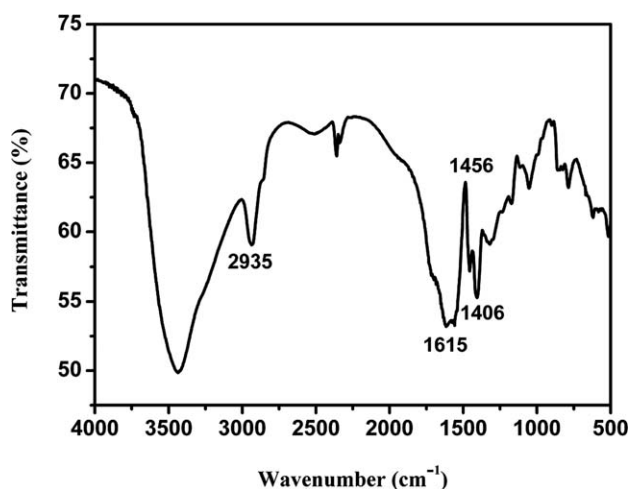
#### Water Absorbency Measurement

To determine water absorption capability, an accurately weighed sample (0.5 g) was immersed in 250 mL of distilled water for 24 h to reach swelling equilibrium at certain temperature. The measurement at high temperature was carried out in a JN-500B stainless steel pressure vessel (Qingdao Petroleum Instrument). Then, the completely swollen gel was separated from unabsorbed water by filtering through a 100-mesh screen. The remaining gel was collected and weighed. The water absorbency of the sample ( $Q_w$ ) was calculated based on the following equation:<sup>16</sup>

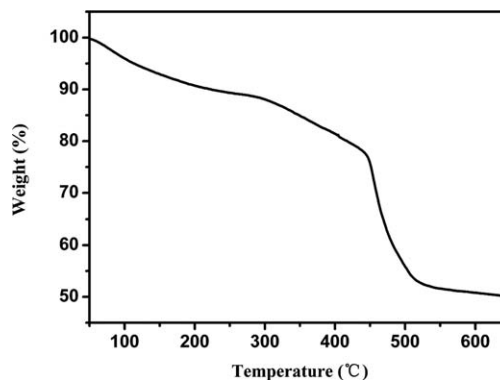
$$Q_w = (M_2 - M_1) / M_1 \quad (1)$$

where  $M_1$  and  $M_2$  represent the weights of the dried sample and the swollen gel (g), respectively.

To determine the swelling behavior of superabsorbent in different concentrations of saline solutions, water absorbencies in



**Figure 1.** FTIR spectrum of superabsorbent.



**Figure 2.** TGA curve of superabsorbent.

1–8% of NaCl solutions were measured similarly to that in distilled water.

#### Swelling Kinetics

For studying the rate of water absorbency of the superabsorbent, certain amount of samples (0.5 g) was added into a weighted tea bag and immersed in 500 mL of distilled water and 1 wt % of NaCl solution, respectively. At consecutive time intervals, the swelling ratios of the superabsorbent were measured according to the aforementioned method.

#### Characterization

Fourier transform infrared (FTIR) spectrum was recorded on a Thermo Nicolet NEXUS TM spectrophotometer in the range of 400–4000  $\text{cm}^{-1}$  (KBr disk). Thermal stability of samples was investigated using a Perkin-Elmer TGA 7 thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 10°C/min. Morphology of the samples was examined by a HITACHI S-4800 scanning electron microscope after coating with gold film.

## RESULTS AND DISCUSSION

### Crosslinking Mechanism of the Poly(acrylic acid)

#### Using TAAC

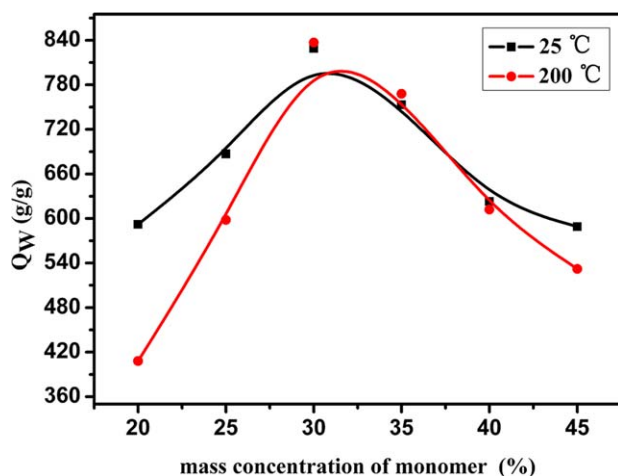
As previously reported, diallyldimethyl ammonium chloride forms a five-membered ring during polymerization.<sup>17,18</sup> Based on the facts, the mechanism using TAAC as crosslinking agent for the preparation of superabsorbent is shown in Scheme 1. Two allyl groups form five-membered ring structure in one macromolecular chain, whereas the third allyl group reacts with the other vinyl group to form the second chain. In this way, the crosslinked networks are capable of keeping water and stable at elevated temperature.

#### FTIR Spectrum Analysis

The FTIR spectrum of superabsorbent based on partially neutralized AA is shown in Figure 1. The absorption bands at 2935 and 1456  $\text{cm}^{-1}$  are attributed to the  $-\text{CH}_2-$  group on the polymeric chain. The absorption bands at 1615 and 1406  $\text{cm}^{-1}$  are ascribed to the appearance of  $-\text{C}=\text{O}$  from  $-\text{COO}^-$  groups. All the above information proves the successfully polymerization of partially neutralized AA.

#### Thermogravimetric Analysis

The thermogravimetric analysis (TGA) curve of the superabsorbent is shown in Figure 2. The high-temperature resistant



**Figure 3.** Effect of monomer mass concentration on water absorbency at 25 and 200°C. Neutralization degree was 80%; mass ratios of initiator, crosslinker (based on AA) were 0.17 and 0.14%, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

superabsorbent exhibits a two-stage weight loss profile. The weight loss about 20% below 450°C is ascribed to the moisture of water absorbed and bonded in sample. The main weight loss about 30% between 450 and 520°C was attributed to the decomposition of the superabsorbent. The decomposition temperature of SAP synthesized with TAAC was 450°C, indicating a good thermal stability for the superabsorbent capable being used at high temperature.

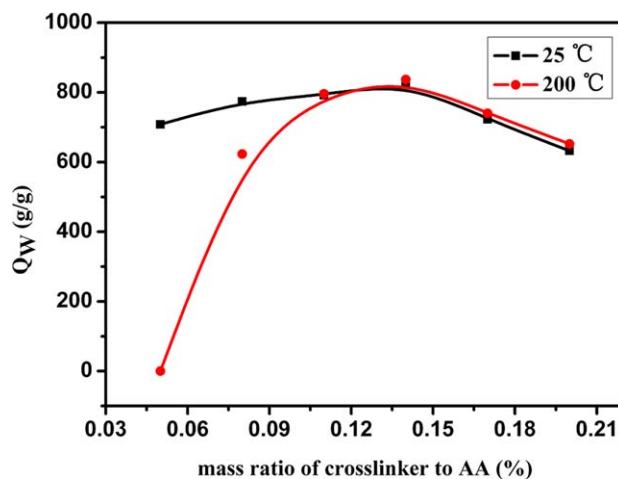
#### Effect of Monomer Mass Concentration on Water Absorbency

The influence of the total monomer concentration was studied by varying the AA amount from 20 to 45 wt % (Figure 3), whereas the other parameters were kept constant (neutralization degree: 80%; initiator: 0.17 wt % [based on AA], TAAC: 0.14 wt % [based on AA]).

As shown in Figure 3, the water absorbency of the superabsorbent at 25 and 200°C exhibit similar tendency in distilled water. The swelling ratios increase with increasing the monomer concentration and reach the maximum at monomer concentration of 30 wt %. The initial increase in water absorbency can be explained by the fact that an increase in the monomer concentration leads to more effective crosslinking reaction, which decreases the amount of soluble macromolecules. The swelling ratios decrease after the maximum can be attributed to the branching and self-crosslinking reaction caused by chain transfer, as well documented in the literature.<sup>19,20</sup>

#### Effect of Crosslinker Concentration on Water Absorbency

The influence of TAAC contents on superabsorbent water absorbencies was investigated by varying the TAAC to AA ratio (Figure 4). When TAAC to AA ratio is <0.14 wt %, the swelling ratios ( $Q_w$ ) increase with the increase of TAAC concentration from 708 to 829 g/g at 25°C, and -1 to 837 g/g at 200°C. It should be noted that swelling ratio  $Q_w = -1$ , corresponding to  $M_2 = 0$ , means that the hydrogel is totally dissolved at this temperature. The water absorbency at 200°C is obviously lower than that at 25°C when the TAAC concentration is in the range

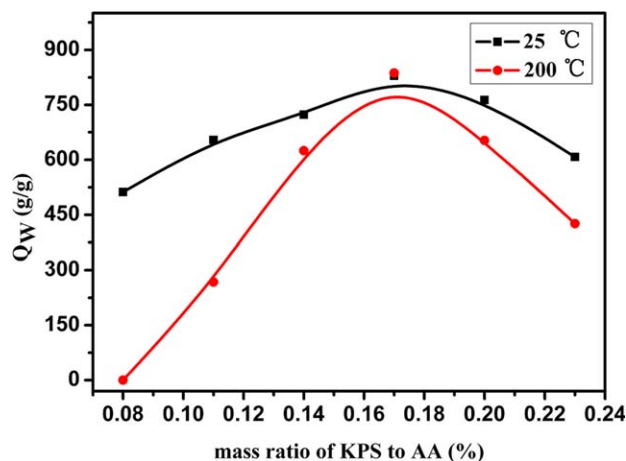


**Figure 4.** Effect of crosslinker concentration on water absorbency at 25 and 200°C. Neutralization degree was 80%; mass ratio of initiator (based on AA) was 0.17%; monomer mass concentration was 30%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

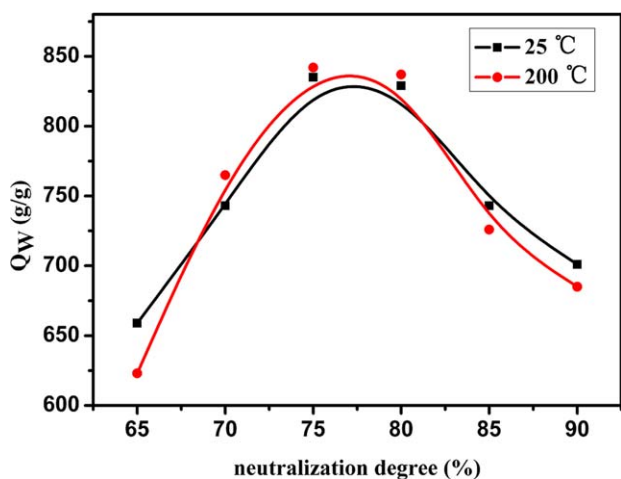
of 0.05–0.10%, indicating that part of the hydrogel became water soluble at 200°C owing to low crosslinking degree. The crosslinker content is a key factor on SAP absorbency, especially at high temperature. However, when an excessive amount of TAAC is added (>0.14 wt %), the crosslinking density of the superabsorbent also increases. This would result in a decrease in the space between the copolymer chains and lead to a decrease in water absorbency. Thus, superabsorbents with moderately crosslinked polymer networks can absorb and retain large quantities of aqueous fluids. The observation is similar to other SAP systems using NMBA as the crosslinker.<sup>21–23</sup>

#### Effect of Initiator Concentration on Water Absorbency

Varying the amount of KPS initiator affected absorbency (Figure 5), especially at high temperature. As shown in Figure 5, the water absorbency increases with increasing KPS content and



**Figure 5.** Effect of initiator concentration on water absorbency at 25 and 200°C. Neutralization degree was 80%; mass ratio of crosslinker (based on AA) was 0.14%; monomer mass concentration was 30%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** Effect of neutralization degree on water absorbency at 25 and 200°C. Mass ratios of initiator, crosslinker (based on AA) were 0.17 and 0.14%, respectively; mass concentration was 30%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

then decreases with further increasing the initiator concentration. The maximum absorbencies were obtained at 0.17 wt % (based on AA) of KPS, both at 25 and at 200°C. This observation indicates that the initiator concentration is a key factor to the molecular weight of the polymer and the crosslinking degree. When the KPS concentration is lower than 0.17 wt %, the number of free radicals increases with the increase of the KPS concentration, which can improve the monomer conversion rate and the crosslinking reaction efficiency. Consequently, the swelling ratios increase. However, when the mass ratio of KPS to AA is higher than the optimum value, a great number of free radicals are generated, and this results in a short average chain length. The molecular weight of the polymer is low, and thus some hydrogels exhibit water solubility, may have contributed to the observed decreased water absorbency.<sup>24–27</sup>

#### Effect of Neutralization Degree on Water Absorbency

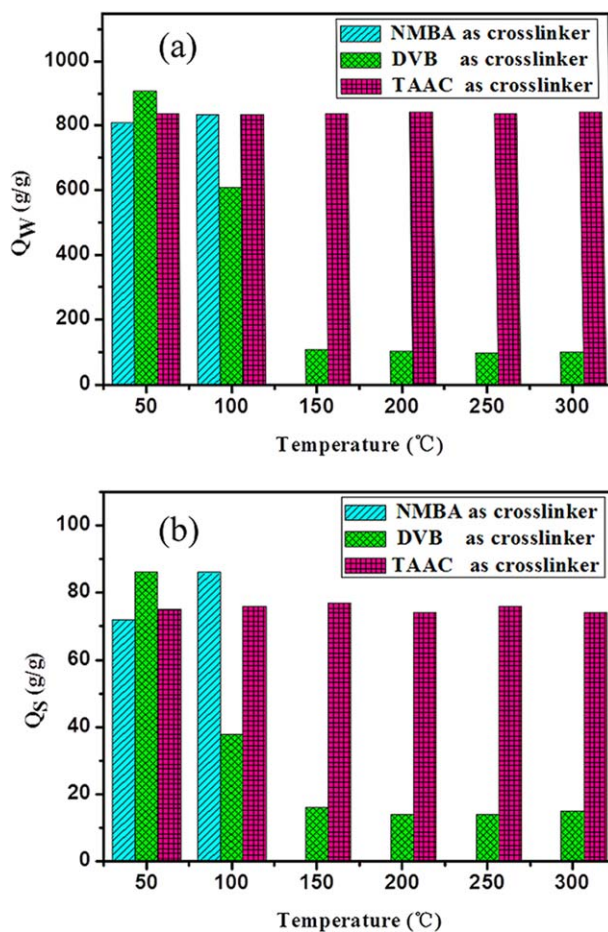
The effect of AA neutralization degree on water absorbency at 25 and 200°C is shown in Figure 6. There are little differences between absorbencies at 25 and at 200°C. This means that the neutralization degree is not a key factor to the network crosslinking. The water absorbency increases with increasing the neutralization degree, reached a maximum at 75% (835 g/g at 25°C and 842 g/g at 200°C) and then decreases. The tendency can be explained by the cooperative effect between  $-\text{COOH}$  and  $-\text{COO}^-$  groups. More  $-\text{COO}^-$  groups are grafted on the chain of superabsorbent with increasing the neutralization degree, which lead to a higher osmotic pressure between gel network and water. The water absorbency increases. However, a further increase of neutralization degree can introduce more sodium ions into the gel to react with  $-\text{COO}^-$  groups, and the electrostatic repulsion reduces. As a consequence, the free space in the gel reduces, and the water absorbency decreases accordingly.<sup>28–30</sup>

As discussed above, the optimum synthesis conditions thus obtained were as follows: the monomer concentration is 30%,

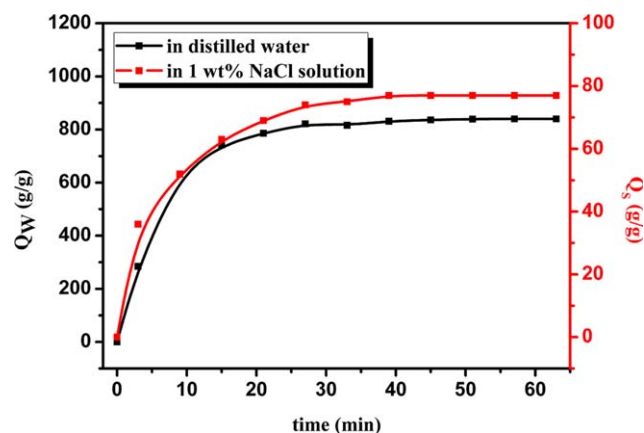
the mass ratios of crosslinker to AA and initiator to AA are 0.14 and 0.17%, respectively, and the neutralization degree is 75%. Therefore, superabsorbent polymers prepared under this optimized conditions were used for the following studies.

#### Swelling Behaviors of Superabsorbents Prepared with Different Crosslinkers in Distilled Water and 1 wt % of NaCl Solution at Different Temperatures

Swelling behaviors of superabsorbents prepared under optimized conditions were investigated in distilled water and 1 wt % of NaCl solution at different temperatures (Figure 7). SAPs prepared under the same condition but using different crosslinking agents (DVB and NMBA) are also present for comparison. As shown in Figure 7, it is obvious that superabsorbent synthesized from NMBA becomes water soluble at 150°C. Superabsorbent synthesized using DVB as crosslinker begins to dissolve at 100°C and a little water is retained at higher temperature. However, superabsorbent synthesized from TAAC does not dissolve even at 300°C and shows good water absorption capability. Its swelling ratios reach 841 and 74 g/g in distilled water and 1 wt % of NaCl solution, respectively. The results indicate that the structure of crosslinker plays a critical role in the thermal



**Figure 7.** Swelling ratios of superabsorbents with different crosslinkers at different temperatures. (a) In distilled water, (b) in 1 wt % of NaCl solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** Swelling rates in distilled water and 1 wt % of NaCl solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

stability of hydrogel. When NMBA was used as crosslinker, the hydrolysis process of amide bonds might be completed at 150°C, and thus the hydrogel became water soluble. When DVB was used as crosslinker, it could not be uniformly dispersed in the monomer system because it is not soluble in water phase. This would lead to an ineffective crosslinking. The hydrogel thus formed would dissolve at high temperature. When TAAC was used as crosslinker, more stable crosslinking structure was formed. With increasing the temperature, the three-dimensional structure of the hydrogel could still maintain well.

#### Swelling Kinetics

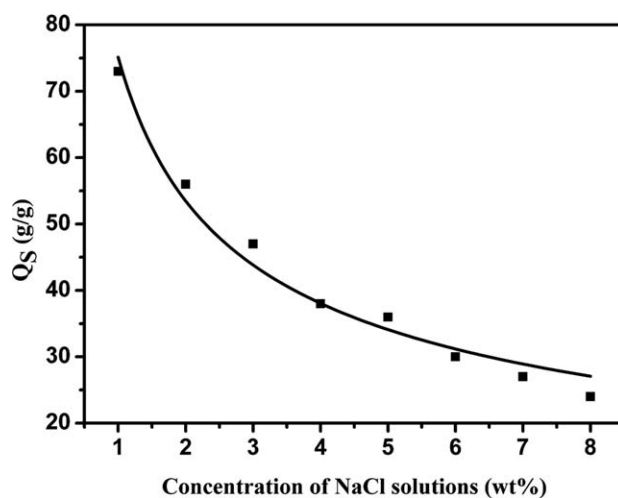
Figure 8 shows the dynamic swelling behavior of superabsorbent samples with certain particle sizes (20–50 mesh) in distilled water and in 1 wt % of NaCl solution. As shown in Figure 8, the water uptake is relatively fast, and the superabsorbent could achieve absorption equilibrium within 30 min. The swelling ratios of the superabsorbent could reach nearly 80 and 90 g/g in distilled water and in 1 wt % of NaCl solution in 20 min. Hence, the superabsorbent prepared with TAAC shows high swelling rates both in distilled water and in 1 wt % of NaCl solution.

#### Swelling Behavior in Different Concentrations of NaCl Solutions

The equilibrium swelling ratios of superabsorbent in different concentrations of NaCl solutions are shown in Figure 9. The water absorbency decreases with increasing the salt concentration. Based on the Flory theory, ion strength is an important factor on water absorbency. When the salt concentration increases, the ion strength will increase correspondingly, and the water absorbency decreases. However, the SAP still demonstrates excellent water absorption of nearly 50 g/g in 3 wt % of NaCl solution, indicating a good salt resistance.

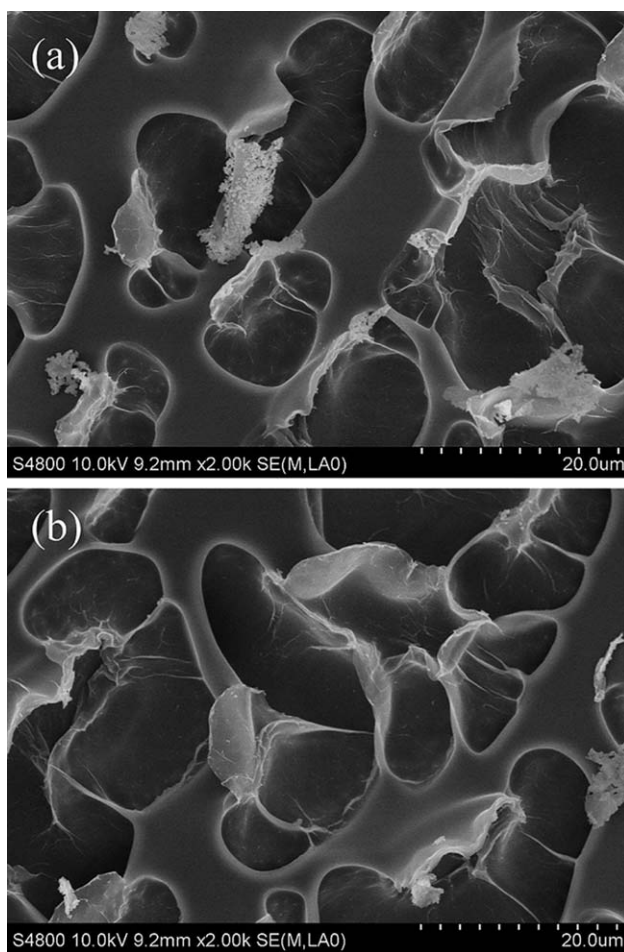
#### Scanning Electron Microscopy Analysis

The surface structures of the hydrogels formed from the SAP were studied using scanning electron microscopy (SEM). Figure 10 shows the SEM micrographs of superabsorbent after absorption at 25 and 300°C. It can be clearly observed that the two



**Figure 9.** Swelling behavior in different concentrations of NaCl solutions.

samples had similar well-spaced network structures. The surface morphologies of superabsorbent after absorption at 25 and 300°C had little difference. The observation verifies the result that the superabsorbent has good high-temperature resistant property.



**Figure 10.** SEM micrographs of superabsorbent after absorption at different temperatures. (a) 25°C and (b) 300°C.

## CONCLUSIONS

A novel high-temperature resistant superabsorbent was synthesized through solution polymerization based on partially neutralized AA, using TAAC as crosslinker, KPS as initiator. The optimum synthesis conditions obtained were as follows: the mass concentration was 30%, the mass ratios of crosslinker to AA, initiator to AA were 0.14 and 0.17%, and the neutralization degree was 75%. The superabsorbent showed good high-temperature resistance and salt resistance. The swelling ratios of SAP could reach 841 and 74 g/g in distilled water and 1 wt % of NaCl solution at 300°C, respectively. Besides, the SAP performed a high swelling rate, which could get absorption equilibrium within 30 min. Based on these properties, this kind of superabsorbent could be used as steam channel-blocking agents in the steam-stimulated heavy oil reservoirs.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Suo, A.; Qian, J.; Yao, Y.; Zhang, W. *J. Appl. Polym. Sci.* **2007**, *103*, 1382.
2. Wang, W.; Zhang, Y.; Wang, A. *Polym. Adv. Technol.* **2008**, *19*, 1852.
3. Chen, Z.; Liu, M.; Ma, S. *React. Funct. Polym.* **2005**, *62*, 85.
4. Ma, S.; Liu, M.; Chen, Z. *J. Appl. Polym. Sci.* **2004**, *93*, 2532.
5. Chen, X.; Shan, G.; Huang, J.; Huang, Z.; Weng, Z. *J. Appl. Polym. Sci.* **2004**, *92*, 619.
6. Zhang, J.; Li, A.; Wang, A. *React. Funct. Polym.* **2006**, *66*, 747.
7. Cheng, Z.; Li, J.; Yan, J.; Kang, L.; Ru, X.; Liu, M. *J. Appl. Polym. Sci.* **2013**, *130*, 3674.
8. Ferfera-Harrar, H.; Aiouaz, N.; Dairi, N.; Hadj-Hamou, A. S. *J. Appl. Polym. Sci.* **2014**, *131*, 1.
9. Li, Y.; Ke, A.; Lin, S.; Ouyang, N. *Int. J. Polym. Mater.* **2011**, *60*, 1164.
10. Zhu, Z.; Sun, H.; Qin, X.; Jiang, L.; Pei, C.; Wang, L.; Zeng, Y.; Wen, S.; La, P.; Li, A.; Deng, W. *J. Mater. Chem.* **2012**, *22*, 4811.
11. Bardajee, G. R.; Pourjavadi, A.; Soleyman, R.; Ghavami, S. *Adv. Polym. Technol.* **2012**, *31*, 41.
12. Tian, D.; Li, S.; Liu, X.; Wang, J.; Hu, S.; Liu, C.; Xie, H. *J. Appl. Polym. Sci.* **2012**, *125*, 2748.
13. Singh, T.; Singhal, R. *J. Appl. Polym. Sci.* **2012**, *125*, 1267.
14. Dong, X.; Liu, H. *Open Petrol. Eng. J.* **2012**, *5*, 1.
15. Xie, J.; Zhang, X.; Dai, H.; Dong, H.; Jiang, X. *Chem. Res. Appl.* **2010**, *22*, 934.
16. Chen, Z.; Dong, F.; Liu, M.; Qi, X. *Polym. Eng. Sci.* **2011**, *51*, 2453.
17. Lu, J.; Xiao, C. *J. Wuhan Univ. Nat. Sci. Ed.* **2007**, *53*, 397.
18. Zhao, Q.; Sun, J.; Chen, S.; Zhou, Q. *J. Appl. Polym. Sci.* **2010**, *115*, 2940.
19. Bardajee, G. R.; Pourjavadi, A.; Soleyman, R.; Ghavami, S. *Adv. Polym. Technol.* **2012**, *31*, 41.
20. Chen, J.; Zhao, Y. *J. Appl. Polym. Sci.* **2000**, *75*, 808.
21. Liu, J.; Wang, Q.; Wang, A. *Carbohydr. Polym.* **2007**, *70*, 166.
22. Liu, J.; Wang, W.; Wang, A. *Polym. Adv. Technol.* **2011**, *22*, 627.
23. Zhang, J.; Wang, Q.; Wang, A. *Carbohydr. Polym.* **2007**, *68*, 367.
24. Ma, Z.; Li, Q.; Yue, Q.; Gao, B.; Xu, X.; Zhong, Q. *Biore-source Technol.* **2011**, *102*, 2853.
25. Wang, W.; Wang, A. *J. Appl. Polym. Sci.* **2010**, *115*, 1814.
26. Liu, C.; Zhang, M.; Zhu, J.; Ma, S. *J. Appl. Polym. Sci.* **2008**, *110*, 2440.
27. Raju, K. M.; Raju, M. P.; Mohan Y. M. *J. Appl. Polym. Sci.* **2002**, *85*, 1795.
28. Tang, Q.; Lin, J.; Wu, J.; Xu, Y.; Zhang, C. *J. Appl. Polym. Sci.* **2007**, *104*, 735.
29. Wu, L.; Liu, M.; Liang, R. *Bioresource Technol.* **2008**, *99*, 547.
30. Wu, L.; Liu, M. *Carbohydr. Polym.* **2008**, *72*, 240.