### **RESEARCH ARTICLE**

Revised: 24 June 2022



### Preparation, properties, self crosslinking mechanism, and characterization of UV initiated polyacrylic acid superabsorbent resins

Amatjan Sawut	L	Rena Simayi	Ι	Xiaohui Zhang	I	Menghao Jiang	L	Ziwen Zhu	I
Tongmeng Wu									

State Key Laboratory of Chemistry and Utilization of Carbon Based Energy Resources; College of Chemistry, Xinjiang University, Urumqi, People's Republic of China

#### Correspondence

Rena Simayi, State Key Laboratory of Chemistry and Utilization of Carbon Based Energy Resources; College of Chemistry, Xinjiang University, Urumqi, 830017, Xinjiang, People's Republic of China. Email: renasimayi@sina.com

#### **Funding information**

Doctoral Initiation Fund of Xinjiang University, Grant/Award Number: BS180218; General project of natural science of Xinjiang Autonomous Region, Grant/Award Number: 2022D01C22; Tianchi Doctors Project of Xinjiang Education Department of China, Grant/Award Number: 042312032

### Abstract

The self crosslinking polyacrylic acid (PAAsc) superabsorbent resins were prepared by UV irradiation without crosslinking agents and initiators. The effects of reaction factors on water absorbency and gel content of resins were investigated. The mechanism of self crosslinking polymerization was studied by means of <sup>1</sup>H NMR and ESR, while the structure and morphology of the resins were characterized by IR, NMR, and SEM. The results show that the polymerization mechanism and structure of PAAsc superabsorbent resins polymerized through light radiation is significantly different from those polymerized by initiators. The main chain of PAAsc contains double bonds and polar functional groups such as ether groups and ester groups, which improves the hydrophilicity of the main chain and significantly improves the liquid absorption ability of the superabsorbent material. Moreover, the swelling kinetics, salt-resistance, pH sensitivity, and water retention capacity of the PAAsc superabsorbents were studied. Owing to the remarkable water absorbency, salt resistance property and water retention capacity, this superabsorbent material has a broad application prospect in agriculture.

#### KEYWORDS

acrylic acid, mechanism of self crosslinking polymerization, superabsorbent resin, UV initiated polymerization

### 1 | INTRODUCTION

Superabsorbent resins are a kind of water swelling polymers containing strong hydrophilic groups and a certain degree of crosslinking. They are insoluble in both water and organic solvents, and can absorb water heavier than their own weight, enabling strong water absorption and water retention properties.<sup>1–3</sup> Polyacrylic acid (salt) superabsorbent resins have the advantages of simple synthetic process, high and fast water absorption, and good heat resistance, thus attracting extensive research and development interests, and having wide practical applications.<sup>4–8</sup> Therefore, this kind of superabsorbent resins have always occupied a leading position in the market.<sup>9</sup> At present, there are many methods to prepare polyacrylic acid (sodium) based superabsorbent hydrogels.<sup>10–17</sup> Among them, the synthesis by UV initiated polymerization has received considerable attention because of the short reaction time, low energy consumption., easy control of reaction process and the "5E" characteristics, that is, economical, efficient, energy saving, environment friendly of such light initiated reactions and the rapid curing, even at ambient temperatures, of the resultant materials.<sup>18–20</sup>

In recent years, there have been studies on the preparation of superabsorbent resins (or hydrogels) by UV light initiation, but most of them used initiators and cross-linking agents,<sup>14,21-23</sup> and the water absorption capacity of the prepared polymer has not been

significantly improved. There are few reports on the study of photoinitiated polymer superabsorbent materials without initiators and cross-linkers. Although there are several studies on photoinitiator-free reaction systems of acrylates,<sup>24–27</sup> little is known about self crosslinking polyacrylates obtained without any initiators and crosslinkers.

A series of super absorbent resins have been prepared by our research group via UV initiated polymerization using initiators and cross-linkers over the years.<sup>28–30</sup> In previous studies,<sup>31</sup> it was found that the super absorbent resins prepared by UV photo polymerization without any cross-linking agents and initiators had higher water absorption and salt resistance, however, the water absorption ability of each batch of resins fluctuated greatly. Therefore, the polymerization and crosslinking mechanisms and experimental conditions of this polymerization method needed to be further explored, which is of great significance to the future development of high-performance superabsorbent hydrogels.

In this study, the mechanism for the photolysis of monomers, acrylic acid, and sodium acrylate is described (high pressure mercury lamp was used for the irradiation), with the purpose of conducting comprehensive studies for the self-crosslinking mechanism of UV initiated polymerization of polyacrylic acid (sodium) superabsorbent resins prepared without any crosslinking agents and initiators, and the crosslinking mode of superabsorbent resins obtained was discussed. By optimizing the structure design and preparation conditions of water absorbent resins, the salt resistance, water absorption, and water retention properties of the material were improved. And the composition, structure and properties of these water absorbent resins were discussed.

### 2 | EXPERIMENTAL

### 2.1 | Materials and instrumentation

Acrylic acid: analytically pure, Tianjin Damao chemical reagent factory; Sodium hydroxide: analytically pure, Tianjin Fuchen chemical reagent factory; Irgacure-651(PI): Shanghai Aladdin Reagent Co., Ltd; Sodium chloride: analytically pure, Suzhou chemical reagent factory. Photochemical reactor: Xi'an Boyle (light source is high pressure mercury lamp, 500w, main wavelength 365 nm); Inova-400mhz nuclear magnetic resonance spectrometer of Varian company, USA; EQUINOX-55 Fourier transform infrared spectrometer of Bruker company, Germany; Leo 1450vp scanning electron microscope.

### 2.2 | Synthesis of resins

# 2.2.1 | Synthesis of self crosslinking sodium polyacrylate (PAAsc) superabsorbent Resins

The quartz tube was placed into the UV polymerization device. A certain amount of acrylic acid was absorbed using a pipette and placed into the quartz tube. Under the electromagnetic stirring, a certain advanced \_\_WILEY 3667

amount of distilled water was added to adjust the concentration of acrylic acid. The solution was neutralized with 5 mol/L sodium hydroxide solution (75% neutralization degree). After the solution was fully and evenly mixed, it was cooled by circulating water at constant temperature (reaction temperature was  $9^{\circ}C-11^{\circ}C$ ). The irradiation with ultraviolet lamp for 35 min (with nitrogen protection or no protection conditions) developed the original liquid into a gel, that is, the desired product. The diagram of reaction device is shown in Figure 1.

### 2.2.2 | Post treatment of super absorbent resins

The post-treatment of the superabsorbent resins was carried out in two steps: first, without any treatment, the resins were directly vacuum dried until the mass is constant, then the mass  $m_1$  of the resin before treatment was recorded, followed by crushing into powder, and the water absorption ability was measured; Second, a certain amount of water absorbent resin sample was immersed in 15% acetone/water mixture at room temperature. After the full swelling, the acetone was added to the white swelling substance, the resulting mixture filtered and washed with acetone to remove the soluble parts. The solid sample was then dried in vacuum until the mass was constant. The mass of the absorbent resin was recorded as  $m_2$ , and the water absorption and gel content values were measured.

# 2.3 | The property test and structure characterization of the resins

### 2.3.1 | Determination of water absorbency

Sample (0.1000 g) with a particle size of 60–80 mesh was accurately weighed, and placed in a beaker filled with excess amount of water (1000 ml) or different concentrations of sodium chloride solutions (300 ml), standing until the swelling equilibrium of the sample was reached (about 240 min) before filtering with 100 mesh nylon screen for 10 min. After the mass of the resin after water absorption was weighed, the liquid absorption rate was calculated according to the following formula:

$$Q_{eq}(g \cdot g^{-1}) = \frac{W_t - W_0}{W_0},$$
 (1)

where  $W_t$ ,  $W_0$  are the weights of swollen and dried samples, respectively.

### 2.3.2 | Determination of gel content

According to the relationship between the mass and the gel content of the product: the ratio of  $m_1$  and  $m_2$  (mass of products obtained



before and after the post-treatment step) is equal to the gel content of the product, the calculation formula is expressed as follows

$$Gel \operatorname{content}(\%) = m_2/m_1, \tag{2}$$

where  $m_1$ ,  $m_2$  are the weights of samples before and after acetone treatment, respectively.

### 2.3.3 | Absorbency in different salt solutions

Absorbency of the superabsorbent was evaluated in different concentrations of NaCl, CaCl<sub>2</sub>, and FeCl<sub>3</sub> salt solutions according to the above-described method (measurement of water absorbency), except that salt solutions were used instead of distilled water.

### 2.3.4 | Absorbency at various pH values

Absorbency of sample in solutions with different pH was measured according to the above-mentioned method (Section 5.0.3.). Test solutions with various acidic and basic pH values were adjusted to the desired pH value by addition of diluted HCI (pH 2.0) or NaOH (pH 12.0).

### 2.3.5 | Measurement of water retention in soil

Different amounts (0.2, 0.5, and 0.8 g) of the superabsorbent were well-mixed with 200 g of dry soil and kept in 500 ml glass beakers, then 80 g of tap water was slowly added into the beaker and the

beaker was weighed ( $W_0$ ). A control experiment without the superabsorbent was also carried out. The beakers were maintained at room temperature and weighed every day ( $W_i$ ) for 30 days. The water retention in the soil ( $W_r$ %) was calculated by the following equation:

$$W_{\rm r}\% = \frac{W_{\rm i}}{W_0} \times 100\% \tag{3}$$

### 2.3.6 | Characterization by <sup>1</sup>H NMR

Liquid nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy was used for the determination of polymerization mechanism and structure characterization of product.

- Mechanism analysis: the aqueous solution of NaOD was used to partially neutralize the acrylic acid, before placed into the quartz NMR tube under the ultraviolet light, and the NMR tube was taken for nuclear magnetic resonance analysis at different time intervals.
- Structural characterization: a small amount of dried and smashed resins was passed through a 100 mesh sieve before placed into the NMR tube filled with heavy water and left for swelling for 1 h. The NMR spectra were then obtained by nuclear magnetic resonance instrument (Varian inova-400).

### 2.3.7 | Characterization by IR

The sample was smashed into powder and mixed with potassium bromide to prepare tablets. The infrared spectrum was then taken by Bruker equinox infrared spectrometer (FTIR).



FIGURE 2 Effects of (A) monomer concentration, (B) exposure time, (C) temperature, and (D) neutralization degree on the water absorbency of superabsorbent and the gel content

# 2.3.8 | Characterization by scanning electron microscope

After fully swelled in distilled water and frozen using liquid nitrogen, the resins were placed in a freeze dryer for vacuum drying for 48 h. The morphology of the outer layer was observed by electron microscope scanner, with the acceleration voltage of 20 kV.

### 2.3.9 | Characterization by TGA

The thermogravimetric (TGA) measurement was carried out using the STA449F3GA simultaneous thermal analyzer (NETZSCH Corporation, Hanau, Germany) with the temperature ranging from  $30^{\circ}$ C to  $800^{\circ}$ C under a nitrogen atmosphere. The nitrogen flow was 30 ml/min and heating rate was  $5^{\circ}$ C/min.

### 3 | RESULTS AND DISCUSSION

### 3.1 | Optimization of PAAsc synthesis conditions

The influences of the preparation conditions on the water absorption capacities and gel content of the superabsorbent polymer were investigated.

# 3.1.1 | Effect of the monomer concentration on water absorbency and gel content of PAAsc

The effects of monomer concentration on the monomer conversion in grafts and the water absorption capacities of PAAsc superabsorbent were shown in Figure 2A.

As can be seen, with the increase of monomer concentration, the water absorption and gel content of PAAsc resins initially increase and then decrease. When the monomer concentration is low, there is less opportunity for the collision of monomer molecules, thus the reaction is incomplete, meaning there is more unreacted acrylic acid, leading to low gel content and water absorption of the treated resin, resulting in low crosslinking density of the material; With the increase of monomer concentration, the water absorption and gel content of the resins will increase. Evidently, the increase of monomer concentration promotes the chain growth reaction and monomer conversion, resulting in the increase of water absorption and gel content. While the monomer concentration continues to increase, the opportunity for the transfer of chain free radicals to monomer molecules is enhanced, resulting in the dominance of linear polymerization.

As a result, the amount of soluble polymer increases, leading to the decrease of gel content and the water absorption of the treated resin, indicating that the crosslinking density of the resulted resin is

3669

<u>3670</u> WILEY advanced technologi

unreasonable and the degree of crosslinking is uneven. On the other hand, the viscosity of the reaction medium increases not only with the raise of monomer concentration, but also during the polymerization process. The increase of viscosity hinders the movement of free radicals and monomers, leading to the premature termination of chain growth reaction, affecting the grafting reaction, thus resulting in the decrease of liquid absorption rate and gel content. When the monomer concentration is 20%, the water absorption of the gel of PAAsc is the largest. Therefore, 20% is selected as the optimal monomer concentration.

# 3.1.2 | Effect of exposure time on water absorbency and gel content of PAAsc

The effects of exposure time on water absorbency and gel content of PAAsc superabsorbent were shown in Figure 2B. As can be seen, before 35 min, with the extension of reaction time, the liquid absorption rate and gel content of PAAsc resins both increased. After 35 min, the water absorption rate of the resin decreased rapidly, but the gel content continued to increase. Short reaction time leads to insufficient active sites in the reaction system to initiate complete polymerization, resulting in poor water absorption and low gel content of the resin. With the increase of exposure time, reactive free radicals are continuously generated in the reaction system, and the conversion and grafting rate of monomers are also increased, resulting in the increase of water absorption and gel content. However, the prolonged exposure time causes a crowded crosslinking and the chain termination and chain transfer reactions occur more frequently, leading to uneven polymerization, thus resulting in the failure to form an effective three-dimensional network structure. As a consequence, the water absorption decreases and the gel content continues to increase. Therefore, the exposure time of 35 min is regarded as the optimal reaction time.

# 3.1.3 | Influences of temperature on water absorbency and gel content of PAAsc

The effects of temperature on water absorbency and gel content of PAAsc superabsorbent were shown in Figure 2C. When the reaction temperature is above 9°C, the temperature has influence on the water absorption of the resin, but with the increase of the reaction temperature, the gel content decreases continuously. This is because increasing the temperature can accelerate the free radical chain transfer rate and reduce the degree of polymerization. When the temperature is relatively low (2°C-5°C), the gel content is the lowest. At low temperature, the slow generation of free radicals decelerates the conversion of monomers and the grafting reaction, thus the crosslinking density of the polymer is low, resulting in the decrease of the water absorption and the gel content of the resin. Therefore, the optimal reaction temperature range is 9°C-11°C.

# 3.1.4 | Effect of neutralization degree on water absorbency and gel content of PAAsc

The effects of neutralization degree on the monomer conversion in grafts and the water absorption capacities of PAAsc superabsorbent were shown in Figure 2D. As can be seen, with the increase of monomer neutralization degree, the gel content of PAAsc resin continuously decreases, while the water absorption of the resin first increases and then decreases. The change of neutralization degree is actually reflected by the variation in the ratio of –COOH and –COONa groups in the reaction system.

The increase of neutralization degree means the increase of —COONa, thus the increase of ionic groups leads to the limitation of self-crosslinking reaction, and the increase of water-soluble homopolymer units. Therefore, when the neutralization degree is low, the resultant resin has a high crosslinking density and gel content, and a low absorption capacity. As the number of COONa, the main water absorbent group, increases the polymer network formed constantly expands to accommodate a large amount of water. When the neutralization rate is too high, the crosslinking density of the resin decreases, resulting in the loose network structure which is unable to hold much water, together with the increasing amount of water-soluble homopolymer, leads to the decrease of water absorption and gel content of the resin. Therefore, the neutralization degree of 75% is considered as the suitable value.

### 3.2 | Optimization of post-treatment conditions

According to the literature and the previous research, unreacted monomers and water-soluble polymers in superabsorbent resins can both affect the water absorption of the resin, but there are few studies on the post-treatment of superabsorbent resins. When analyzing the structure of PAAsc superabsorbent resin by NMR (Figure 3B), it was evident from the spectra that the residual monomers and watersoluble polymers could not be removed by simple water washing and vacuum drying. Therefore, the post-treatment of superabsorbent resin was systematically studied. These super absorbent resins have poor swelling in organic solvents; hence the monomers and water-soluble homopolymer units surrounded by reticular macromolecules cannot be removed by organic solvents because of the unbreakable hydrogen bonds between them.

As shown in Figure 3A, with the increase of acetone content in the aqueous solution, the water absorption of the superabsorbent resin decreases rapidly. Therefore, the swelling degree of the superabsorbent resin is controlled by using a mixture solvent of water and acetone. Initially, the resin is dissolved in low concentration acetone aqueous solution (5%), then filtered, washed and concentrated with higher concentration acetone aqueous solution (10%–20%), and then washed and concentrated with 20%–30% concentration acetone aqueous solution. Monomers and water-soluble homopolymers can be separated via the described method to improve the purity and water absorption of the resin.



**FIGURE 3** (A) Absorbance capacity of the superabsorbent resin in acetone solution, (B)<sup>1</sup>H NMR spectrum of before and after treatment of PAAsc superabsorbent

Sample no	Water absorption(g.g $^{-1}$ ) treatment before & after	Salt absorption(g.g $^{-1}$ ) treatment before & after	Gel content (%) (or yield)
1	4800 & 6900	220 & 290	69.3
2	3700 & 6800	180 & 270	54.6
3	5600 & 7200	240 & 320	78.1
4	5200 & 6400	230 & 280	81.3
5	4600 & 7100	210 & 290	65.2

 TABLE 1
 The absorbency of superabsorbent before & after the treatment and gel content

It can be seen from Figure 3B that, on the NMR spectrum of crude PAAsc resin,  $\delta$  1.31–2.68 ppm is the proton peak of polypropylene chain. The peak at 5.63–6.21 ppm is assigned as the proton peak of residual monomer acrylic acid. After treatment, the characteristic peak of acrylic acid here basically disappeared, indicating that this method is very effective in treating and purifying superabsorbent resin.

It can be seen from Table 1 that, the liquid absorption rate of the resin is improved after treatment, especially in deionized water, which shows that the post-treatment method adopted is effective in removing the residual monomers and soluble polymers in the super absorbent resin.

# 3.3 | The influence of crosslinking agent and initiator on the water absorbency and gel content of resins

Under the same polymerization conditions, the water absorbency and gel content of the super absorbent polymers obtained without crosslinking agent and initiator were compared with those of the resins prepared by solely adding crosslinking agent or initiator (at different amounts), and adding both crosslinking agent (MBA) and initiator (APS) (at different mounts), respectively. The results were illustrated in Figure 4. Under the conditions of adding only crosslinking agent, the water absorbency of the resins decreases and the gel content increases with the amount of crosslinking agent increases. This is due to the selfcrosslinking effect of the system during UV initiated polymerization. According to Flory–Rehner theory,<sup>32,33</sup> the self-crosslinking polymer showed excellent swelling in water and the degree of swelling was inversely proportional to the cross-linking density. Therefore, the use of excess crosslinking agent will increase the crosslinking density of the resin and reduce the water absorption.

In the case of adding only initiator (Figure 4A (b, c, d origins) and Figure 4B (b, c, d origins)), the water absorbency and gel content of the resins decrease with the increase of the initiator dose. This is because the low decomposition activation energy of the initiator in the system leads to the early breaking of some molecular double bonds and the formation of non-crosslinked linear polymers, which in turn increase the water solubility of the material thus reducing the crosslinking density. With the appropriate amount of crosslinking agent and initiator, the chain growth reaction can be promoted by initiator while the crosslinking density of polymer can be adjusted by the crosslinking agent, leading to the increase in the water absorption and gel content of resins. However, water absorption ratio of these resins is significantly lower than that of super absorbent resins prepared without initiator and crosslinking agent. This shows that the mechanism of photo-initiated reaction is different from self-initiating and self-crosslinking reaction.



**FIGURE 4** (A) Effect of crosslinker and initiator on absorbency. (B) Effect of crosslinker and initiator on gel content. As can be seen from (A, B), the water absorption is the highest without crosslinking agent and initiator.

## 3.4 | Analysis of self crosslinking mechanism of UV initiated PAAsc superabsorbent

# 3.4.1 | Analysis of initial free radicals in reaction system by electron spin resonance

The free radicals produced in the process of photo-polymerization combined with free radical trapping agents to form relatively stable spin adducts, the electron spin resonance (ESR) was then measured (the trapping agent used is 5,5-dimethylpyrroline-1-pyrroline N-oxide [DMPO]). The free radicals produced in the reaction can be captured by DMPO.

At the initial stage of UV initiation reaction, the signal of spin adducts of hydroxyl radical trapped and bound by DMPO was mainly detected due to the good selectivity of DMPO for the hydroxyl radical. With the progress of polymerization, the signal for the carbon radical of monomer and polymer appeared, while the signal of hydroxyl radical weakened. This shows that hydroxyl radical and its related radicals are produced in the initial stage of UV initiated polymerization of acrylic acid (Figure 5).

# 3.4.2 | NMR analysis of the photopolymerization process

The reaction system was monitored by NMR during the UV initiated polymerization of acrylic acid: the reactant acrylic acid was placed in an NMR tube, and a certain amount of sodium hydroxide solution prepared with heavy water was added for partial neutralization (75%). The NMR tube was then exposed to direct UV irradiation and NMR spectrum taken every 5 min. The results were depicted in Figure 6.

It can be seen from the NMR spectra that in the first 10 min weak characteristic peaks related to oxygen atom ( $-O-CH_2-$ , -O-CH-, or O=C-CH-, ester, ether, alcohol or ketone) appeared at about 2.51, 3.67, and 4.31 ppm. But there are no characteristic peaks for hydrogen atom on carbon-carbon single bonds (1.2-2.4 ppm) at this point, indicating that the double bond has not yet split or changed in position, but the carboxylic moiety has changed. The characteristic



**FIGURE 5** ESR spectra of free radicals generated in the process of the acrylic acid UV polymerization

peak of hydrogen atom on carbon-carbon single bonds appeared after 15 min of light radiation. According to the <sup>1</sup>H NMR results and the characteristic peaks of hydroxyl radicals in ESR spectra, the initially generated radicals and intermediates were speculated as follows:



After UV irradiation of acrylic acid, radical A and hydroxyl radical are first produced. Due to the permeability effect, the electron density of radical A changes thus turning into radical B. The concentration of free radicals generated in the initial stage is low. Hence, radicals A, B, the hydroxyl radical and monomers combine with each other in different ways to produce intermediates C, D, E, F, J, and hydrogen peroxide. The chemical shift values of the hydrogen atoms in these intermediates basically agree with their structure. The appearance of the characteristic peaks for hydrogens on the carbon–carbon single bonds indicates the beginning of the chain growth reaction.

As illustrated in Figure 7A,B, as the reaction proceeds, the peak area of the hydrogens on the carbon–carbon double bonds decreases while the peak area of the hydrogens on the C—C single bonds increases. In addition, the peak areas of hydrogen atoms at different positions on the

double bond constantly change (initially 2:1, 15 min later 1.92:1, and 1.81:1 after the reaction) during the reaction. This shows that the double bond moves from the end to the middle of the chain. The intermediates speculated above also contain "the middle double bond" structure, in consistency with this observation. However, the total peak area of hydrogen atoms on the double bonds is still considerable, indicating that there are still a large number of unreacted monomers.

# 3.4.3 | Reaction mechanism for the synthesis of PAAsc by UV initiation

According to the above ESR and <sup>1</sup>H NMR spectra, the possible mechanism of free radical polymerization is speculated as follows. ogies

### 1. Chain initiation

WILEY

3674

Chain initiation consists of two steps, first forming preliminary free radicals, featured by endothermic reaction, high activation energy and slow reaction speed.



The second step is to form free radical active centers of monomer in addition to intermediate products such as C, D, E, F, J, and hydrogen peroxide, and addition of primary radicals to monomers and other intermediates. The characteristics of this process includes exothermic reaction, low activation energy and fast reaction speed.

2. Chain growth reaction



The monomer radicals rapidly initiate the addition of monomers and intermediates to form macromolecular chain radicals.



3. Chain termination reaction





Free radicals, chain radicals and intermediates containing two double bonds are chain polymerized into a network structure. The main chain of the resin contains polar groups such as ether, carbonyl, and ester groups. Therefore, the hydrophilicity of the main chain is increased and the water absorption capacity is greatly improved.

# 3.5 | Characterization of PAAsc superabsorbent resins

In order to further confirm the structure, the structural characteristics of water-soluble polyacrylic acid (PAA) and PAAsc superabsorbent resin were compared by <sup>1</sup>H NMR, IR, and TG analysis.



**FIGURE 6** <sup>1</sup>H NMR spectra of reaction system in the process of UV polymerization

# 3.5.1 | <sup>1</sup>H NMR analysis of PAAsc superabsorbent resin and PAA

The resulted product was analyzed by NMR after passing through the acetone aqueous solution. The results are shown in Figure 8A. According to the chemical shift of hydrogens on the <sup>1</sup>H NMR spectrum of the product, the structural fragments of self-crosslinked acrylic super absorbent resins were preliminarily speculated. As illustrated in the figure, the peak at 1.18-2.45 ppm (a, b) correspond to the protons on the polypropylene chain, and the characteristic peak of carbonyl ortho carbon proton appears at 2.56 ppm (c, d), while the signal at 3.67 ppm (h) is assigned to the hydroxyl linked methylene hydrogens, and the signal for the methylene hydrogens connected to ester chain or ether chain was found at 4.26 ppm (e). The characteristic peaks of hydrogens on carbon-carbon double bonds are appeared at 5.64 (f) and 6.03 ppm (j). The fact that the peak area ratio of the two hydrogens (f and j) is different (2:1-1.68:1) indicates that the position of some double bonds has changed, meaning the double bonds now exist at both end and middle positions of the chain.

In order to further clarify the crosslinking position, <sup>1</sup>H NMR analysis of PAA was carried out and compared with PAAsc super absorbent resins. The results are displayed in Figure 8B. It can be seen from Figure 6 that there are no characteristic peaks related to crosslinking (2.5-4.3 ppm) on the spectrum of water-soluble polyacrylic acid while crosslinking related peaks are present on the spectrum of PAAsc, indicating that the functional groups and structural points correspond to these characteristic peaks play an important role in cross-linking and the unique water absorption ability of the resins.

### 3.5.2 | IR analysis of PAAsc superabsorbent resin

The infrared spectra of PAA and PAAsc are compared, and the results are presented in Figure 8C.



FIGURE 7 <sup>1</sup>H NMR spectra of product (A) after 15 min, (B) after 35 min reaction



FIGURE 8 <sup>1</sup>H NMR spectra of (A) PAAsc and its estimated structure, (B) PAA and PAAsc, (C) IR spectra of PAA and PAAsc, (D) TGA curves of PAAsc and PAAsc an

The IR spectra of PAAsc and PAA indicate the presence of absorption bands at 3411 and 3393  $\text{cm}^{-1}$  corresponding to the stretching of OH group of PAAsc and PAA, respectively. The band at 1562  $\text{cm}^{-1}$  is assigned to the COO<sup>-</sup> stretching, and 1406  $\text{cm}^{-1}$ comes from the symmetric stretching of COO<sup>-</sup> in the structure. The absorption peaks at 1712 and 1716  $cm^{-1}$  belong to the stretching vibration of C=O of PAAsc and PAA, respectively. The characteristic signal at 1052 cm<sup>-1</sup> on the infrared spectrum of PAAsc superabsorbent resin is the stretching vibration of C-O-C system containing ether or ester, but there is no such peak in the infrared spectrum of water-soluble polyacrylic acid. Furthermore, the infrared characteristic vibration of carbon-carbon double bond appears at 992 and 898 cm<sup>-1</sup> on the IR spectrum of PAAsc, while the characteristic peaks of carbon-carbon double bonds are not detected on the IR of PAA. In other words, the IR spectrum of polyacrylic acid polymer, which needs an initiator during the synthesis, does not have the characteristic absorption peaks of double bond, ester or ether moieties, while the resins initiated by UV light showed clear absorption peaks related to double bond and ether functionality.

### 3.5.3 | TGA analysis

The TGA of PAA and PAAsc superabsorbent were shown in Figure 8D.

The TGA curves demonstrated the difference between the two polymers. The initial mass loss (80°C-258°C) of the two is mainly due to the loss of the adsorbed water by resin, which is 4.9% (PAAsc) and 5.1% (PAA), respectively. For PAA, the weight loss of 10.8% from 258°C to 406°C was attributed to the elimination of water molecules from two adjacent carboxyl groups in the polymer chain. For PAAsc, the weight loss was 6.7% from 258°C to 392°C due to elimination of water molecules from two adjacent carboxyl groups of paasc polymer chain. The weight loss from 406°C to 527°C is 37.3% for PAA and from 392°C to 518°C is 38.7% in the case of PAAsc, these stages can be considered as the destruction of PAA and PAAsc structures, respectively. It can be concluded from the data that the weight loss of PAA polymer is higher than that of PAAsc, indicating that the thermal stability of PAA is lower than that of PAAsc superabsorbent resin.

**FIGURE 9** (A, B) SEM images of PAAsc superabsorbent, (C, D) the pictures of PAAsc superabsorbent before and after swelling



# 3.5.4 | Morphology analysis of PAAsc superabsorbent resin by SEM

Figure 9A,B displays the scanning electron microscope results of PAAsc super absorbent resins after freeze-drying.

The surface layer of super absorbent resins easily loses water during freeze-drying, showing a network structure on the scanning electron microscope (SEM) image. The water inside the resin is difficult to remove and remains inside through hydrogen bonding with the resin skeleton, but the free water in the center of the resin matrix is easy to evaporate to form a highly porous morphology, indicating that the polyacrylic acid has formed self-crosslinked network structure. It can be seen from the figure that basically uniform sized interconnected pores are distributed on the resin surface, resulting in the high water absorption and great swelling rate of the material. The pictures of PAAsc superabsorbent before and after swelling are provided. The volume of the PAAsc superabsorbent greatly increases without dissolution, demonstrating the superabsobency of the cross linking polymer.

### 3.6 | Properties of PAAsc superabsorbent polymer

# 3.6.1 | Swelling kinetics of PAAsc superabsorbent resins

The absorption kinetics in distilled water and 0.9% NaCl solution for PAAsc superabsorbent resins are shown in Figure 10A. It can be seen from Figure 10A that the water absorption rate of PAAsc

superabsorbent resins in deionized water is faster than that of in brine. The water absorbed within 60 min is the 66% of the maximum amount, while the brine absorbed by the resin within 60 min can reach 64% of the maximum value. This is mainly because of the physical adsorption process through capillary action on the porous polymer surface, thus the liquid absorption rate is considerably fast.

At 120 min, the water absorption reaches 96% of the maximum value. The salt water absorption rate reaches 93% of the maximum within 120 min, and the maximum absorption amount of salt water can be reached within 160 min. During this process, water molecules interact with the hydrophilic groups of the resin through hydrogen bonds, the hydrophilic groups continue to dissociate, and the electrostatic repulsion force between ions increases, resulting in the expansion of the network, thus slowing down the liquid absorption speed.

With the increase of water absorption, the osmotic pressure difference inside and outside the molecular network constantly decreases, and finally reaches the water absorption equilibrium. The rate of resin absorbing deionized water is faster than that of absorbing brine; this is originated from the fact that the osmotic pressure difference of resin in deionized water is greater than that of in brine. These data show that the material prepared has good water absorption capacity.

# 3.6.2 | Water absorbency of PAAsc in different salt solutions

In the application of superabsorbent resins, most of the contact system is a solution containing a variety of electrolytes, emphasizing the



FIGURE 10 Properties of the superabsorbent polymer (A) swelling kinetics in distilled water and 0.9% NaCl solution, (B) water absorbency in different salt solutions, (C) water absorbency in different pH solutions, (D) water retention capacity in soil

importance of investigating the absorption capacity of superabsorbent resin in electrolyte solution. In this study, electrolyte solutions of different concentrations were prepared, and the absorption of electrolyte solution by resin was tested. The effects of salt solution concentration and cation type (cations with different charges) on swelling behavior of PAAsc were shown in Figure 10B.

With the increase of ionic strength (S =  $1/2 \sum Z_i^2 C_i$ ), the water absorption of superabsorbent resin is significantly decreased. This result is attributed to the decrease of ionic concentration/strength difference inside and outside the molecular network, leading to the decrease of osmotic pressure, resulting in the decrease of liquid absorption capacity of the resin. In the same concentration of cationic salt solution with different valence, the difference in the water absorption capacity of polymer increases with the increase of ionic charge number. The reason for this change is that in addition to the reduction of osmotic pressure caused by ionic strength, the divalent and trivalent ions cross-linked with carboxylic groups on the polymer chain to form complexes (NaCl > CaCl<sub>2</sub> > FeCl<sub>3</sub>).

# 3.6.3 | Water absorbency of PAAsc in solutions with different pH values

liquid absorption performance of PAAsc was measured. The results are shown in Figure 10C. As shown in the figure, the liquid absorption rate of PAAsc superabsorbent resin initially increases and then decreases with the increase of pH value of the solution. The PAAsc superabsorbent polymer has a high liquid absorption capacity in the pH range of 5–9. Under acidic conditions, the dissociation of carboxyl sodium groups in the polymer network structure is limited, and it is easy to form intramolecular hydrogen bonds, thus reducing the network volume. When the pH value of the solution is around 7, the maximum liquid absorption rate is reached. Due to the ionization and outward movement of sodium ions in the polymer, large amount of anionic carboxyl groups are formed in the polymer, resulting in the increase of electrostatic repulsion between the main chains, exaggerating the volume of the polymer molecules to contain a larger amount of water.

With the increase of pH value (9–11), the metal ions in the alkali solution diffuse into the polymer, so that the anionic electric field on the main chain is balanced, resulting in the reduction of the electrostatic repulsion between the main chains and the curling of the molecular chains, leads to the decrease of the liquid absorption rate of the resin.

# Dilute sodium hydroxide and hydrochloric acid were used to prepare

### 3.6.4 | Water retention property of PAAsc in soil

The water retention capacity of the PAAsc superabsorbent in soil at different dosages was shown in Figure 10D. As indicated in the figure,

Dilute sodium hydroxide and hydrochloric acid were used to prepare solutions with different pH values, and the effect of pH value on the



the rate of water loss for the soil mixed with the PAAsc superabsorbent is obviously slower compared with that of without the superabsorbent.

As shown in the figure, the soil without superabsorbent resin is dried after 11 days under the natural state, while the soil with 0.2 g superabsorbent resin still maintains 21% water retention after 11 days under the same conditions, and the water retention rates of the soil mixed with 0.5 and 0.8 g superabsorbent resin are even higher. After 30 days, the soil with 0.8 g superabsorbent resin still has a water retention rate of 18%, indicating that the water retention capacity of the soil is greatly improved and the water retention time is greatly prolonged. Evidently, the addition of super absorbent resin increases the water absorption capacity of the mixed soil, significantly reduces the evaporation rate of water in the soil, and slows down the drying rate.

### 4 | CONCLUSIONS

PAAsc superabsorbent resins were prepared by UV initiation method with acrylic acid as the raw material without crosslinking agent and initiators. The UV initiated polymerization process and crosslinking mechanism were studied by <sup>1</sup>H NMR tracking analysis and ESR free radical analysis. The structure, morphology, and thermal stability of PAAsc resins were studied by NMR, IR, SEM, and thermogravimetric analysis. The results of <sup>1</sup>H NMR and IR indicated that PAAsc resins are cross-linked polymers while SEM results revealed that the resins have a highly porous morphology. The selfcrosslinking reaction mechanism and the structure of the resin show that PAAsc hydrogel is not only a polymer with threedimensional network structure crosslinked by chemical bond, but also has carbon-carbon double bonds, ether groups, ester moieties, and other polar functionalities on the main chain, thus improving the hydrophilicity of the main chain and significantly enhancing the liquid absorption capacity of the material. The maximum water absorbency of PAAsc after treatment was 7200 g/g in distilled water and 275 g/g in 0.9 wt% aqueous NaCl solution. Owing to the considerable water absorbency, salt resistance and water retention capacity of the synthesized PAAsc superabsorbent, it can be considered as an excellent candidate for application in the agricultural field.

### ACKNOWLEDGMENTS

This study is financially supported by General project of natural science of Xinjiang Autonomous Region (No. 2022D01C22); Doctoral Initiation Fund of Xinjiang University (No.BS180218) and Tianchi Doctors Project of Xinjiang Education Department of China (No. 042312032).We sincerely appreciate the support.

### CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

### DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### REFERENCES

- Zhang W, Wang P, Liu S, et al. Factors affecting the properties of superabsorbent polymer hydrogels and methods to improve their performance: a review. J Mater Sci. 2021;56:16223-16242.
- Behera S, Mahanwar PA. Superabsorbent polymers in agriculture and other applications: a review. *Polym Plast Technol Mater.* 2019;59: 341-356.
- 3. Wei P, Chen W, Song Q, Wu Y, Xu Y. Superabsorbent hydrogels enhanced by quaternized tunicate cellulose nanocrystals with adjustable strength and swelling ratio. *Cellulose*. 2021;28:3723-3732.
- Guilherme MR, Aouada FA, Fajardo AR, et al. Superabsorbent hydrogels based on polysaccharides for application in agriculture as soil conditioner and nutrient carrier: a review. *Eur Polym J.* 2015;72:365-385.
- Santos RVA, Costa GMN, Pontes KV. Development of tailor-made superabsorbent polymers: review of key aspects from raw material to kinetic model. J Polym Environ. 2019;27:1861-1877.
- Myint KTT, Liu Y, Niu H, Chen J, Jiao Z. Photodegradation of organic pollutants via carbon nitride/graphene-oxide nanocomposite loaded on Polyacrylic acid hydrogel with free separation. *Catal Surv from Asia*. 2021;25:159-167.
- Ma J, Wang T. Preparation and characterization of water-absorbing polyurethane foam composites with microsized sodium polyacrylate particles. J Appl Polym Sci. 2018;135:46702-46709.
- 8. Bai M, Wilske B, Buegger F, et al. Relevance of nonfunctional linear polyacrylic acid for the biodegradation of superabsorbent polymer in soils. *Environ Sci Pollut ResInt*. 2015;22:5444-5452.
- 9. Zohuriaan J, Kabiri K. Superabsorbent polymer materials: a review. *Iran Polym J.* 2008;17(6):451-477.
- Guo X, Pfeifer C, Wilhelm M, Luy B, Guthausen G. Structure of superabsorbent Polyacrylate hydrogels and dynamics of Counterions by nuclear magnetic resonance. *Macromol Chem Phys.* 2019;220:1800525.
- Choi S, Kim HR, Kim HS. Fabrication of superabsorbent nanofibers based on sodium polyacrylate/poly(vinyl alcohol) and their water absorption characteristics. *Polym Int*. 2019;68:764-771.
- Yu Y, Peng R, Yang C, Tang Y. Eco-friendly and cost-effective superabsorbent sodium polyacrylate composites for environmental remediation. J Mater Sci. 2015;50:5799-5808.
- Sun G, Huang Y, Li D, et al. Blue light initiated Photopolymerization: kinetics and synthesis of superabsorbent and robust poly(N,N'dimethylacrylamide/sodium acrylate) hydrogels. *Ind Eng Chem Res.* 2019;58:9266-9275.
- McLaughlin JR, Abbott NL, Guymon CA. Responsive superabsorbent hydrogels via photopolymerization in lyotropic liquid crystal templates. *Polymer.* 2018;142:119-126.
- Demeter M, Meltzer V, Călina I, Scărişoreanu A, Micutz M, Albu Kaya MG. Highly elastic superabsorbent collagen/PVP/PAA/PEO hydrogels crosslinked via e-beam radiation. *Radiat Phys Chem.* 2020; 174:108898.
- 16. Tally M, Atassi Y. Optimized synthesis and swelling properties of a pH-sensitive semi-IPN superabsorbent polymer based on sodium alginate-g-poly(acrylic acid-co-acrylamide) and polyvinylpyrrolidone and obtained via microwave irradiation. *J Polym Res.* 2015;22:181.
- Mohammad N, Atassi Y, Tally M. Synthesis and swelling behavior of metal-chelating superabsorbent hydrogels based on sodium alginateg-poly(AMPS-co-AA-co-AM) obtained under microwave irradiation. *Polym Bull.* 2017;74:4453-4481.
- Kim H-J, Czech Z, Bartkowiak M, Shim G-S, Kabatc J, Licbarski A. Study of UV-initiated polymerization and UV crosslinking of acrylic monomers mixture for the production of solvent-free pressuresensitive adhesive films. *Polym Test*. 2022;105:107424.

- Tsupphayakorn-aek P, Suwan A, Tulyapitak T, Saetung N, Saetung A. A novel UV-curable waterborne polyurethane-acrylate coating based on green polyol from hydroxyl telechelic natural rubber. *Prog Org Coat*. 2021;163:106585.
- Guo XD, Zhou HY, Wang JX. A novel thioxanthonehydroxyalkylphenone bifunctional photoinitiator: synthesis, characterization and mechanism of photopolymerization. *Prog. Org. Coat.* 2021;154:106214.
- Wan T, Liao L, Huang R, et al. Synthesis and swelling behaviors of microcrystal muscovite composite superabsorbent by photopolymerization. J Wuhan Univ Technol-Mater Sci Ed. 2016;31:151-156.
- 22. Jockusch S, Turro NJ, Mitsukami Y, et al. Photoinduced surface crosslinking of superabsorbent polymer particles. *J Appl Polym Sci.* 2009; 111:2163-2170.
- Qin X, Zhao F, Liu Y, Feng S. Frontal photopolymerization synthesis of multilayer hydrogels with high mechanical strength. *Eur Polym J*. 2011;47:1903-1911.
- Jagtap A, More A. A review on self-initiated and photoinitiator-free system for photopolymerization. *Polym Bull.* 2021:1-35. doi:10.1007/ s00289-021-03887-4
- Bauer F, Decker U, Naumov S, Riedel C. Photoinitiator-free UV curing and matting of acrylate-based nanocomposite coatings: part 3. *Prog Org Coat*. 2014;77:1085-1094.
- Elsner C, Boulares-Pender A, Hähnel M, Konieczny R, Kühnel C, Buchmeiser MR. Photoinitiator-free plasma-induced polymerization and microstructuring of acrylate-based coatings on 3D substrates. *Macromol Mater Eng.* 2009;294:422-431.
- Tehfe M-A, Mondal S, Nechab M, et al. New thiols for Photoinitiatorfree thiol-acrylate polymerization. *Macromol Chem Phys.* 2013;214: 1302-1308.

- Sawut A, Yimit M, Sun W, Nurulla I. Photopolymerisation and characterization of maleylatedcellulose-g-poly(acrylic acid) superabsorbent polymer. *Carbohyd Polym.* 2014;101:231-239.
- 29. Liu L, Sawut A, Abliz S, Nurulla I, Dolat B, Yimit M. Ultravioletinduced polymerization of superabsorbent composites based on sodium humate and its urea release behavior. *RSC Adv.* 2016;6: 101123-101132.
- Li Y, Sawut A, Hou G, He M, Yimit M. UV polymerization and property analysis of maleacylated methyl cellulose acrylic acid absorbent resin. *Pol J Chem Technol.* 2020;22:34-41.
- Dolat B, Sawut A, Yimit M, Nurulla I. Ultraviolet photopolymerization and performances of fast-water absorbing sodium polyacrylate. J Appl Polym Sci. 2015;132:42787-42793.
- Flory PJ, Rehner J. Statistical mechanics of cross-linked polymer networks I. rubberlike elasticity. J Chem Phys. 1943;11:512-520.
- Borges FTP, Papavasiliou G, Teymour F. Characterizing the molecular architecture of hydrogels and Crosslinked polymer networks beyond Flory-Rehner–I. Theory. *Biomacromolecules*. 2020;21: 5104-5118.

How to cite this article: Sawut A, Simayi R, Zhang X, Jiang M, Zhu Z, Wu T. Preparation, properties, self crosslinking mechanism, and characterization of UV initiated polyacrylic acid superabsorbent resins. *Polym Adv Technol*. 2022;33(10): 3666-3680. doi:10.1002/pat.5819