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Saline solution absorbency and structure study of poly (AA-AM) water superabsorbent by inverse microemulsion polymerization

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Summary

A series of novel copolymer superabsorbents based on acrylamide (AM), acrylic acid(AA) were prepared by inverse microemulsion copolymerization using ammonium persulfate (APS) as the initiator and N,N-methylenebisacrylamide (MBA) as the crosslinking agent and OP-10 and SDS as complex surfactants. The synthetic variables (amount of crosslinking agent and initiator, water/oil ratio, monomer/ surfactant ratio and AA/ Am ratio) and their effects on the absorbencies of the synthesized superabsorbents were investigated. The experimental results of superabsorbent polymers (SAPs) showed the maximum saline solution absorbency of 130g/g within 75min, and the saline solution absorbency of 111g/g within 30min. FTIR indicated the structure of the acrylic acid and acrylamide copolymer. SEM indicated that the particles prepared with higher crosslinker content (0.03%) showed smaller pore sizes and less porous structures compared with those with less crosslinker content (0.01%) and the number of the micropores largely decreased with the water/oil ratio increasing from 8% to 14%.

Introduction

Superabsorbent polymers (SAPs) are lightly crosslinked networks of flexible polymer chains and can absorb a large amount of water compared with general water-absorbing materials in which the absorbed water is hardly removable even under some pressure. Because of their excellent characteristics, SAPs have raised considerable interests and researches, and have been used in agriculture and horticulture, sealing composites, artificial snow, drilling fluid additives, medicine for drug delivery system, etc [1–6].

The traditional method of synthesis of SAPs reported is solution [7-9], inverse suspension [10, 11] and inverse emulsion polymerization [12]. The extreme solution viscosity generated by solution polymerization leads to problems such as the difficulties in stirring and heat transfer, and the resin is obtained as a lump that has to be cut, dried, and pulverized before use. Although these problems may be overcome by inverse-suspension or -emulsion polymerization, the polymerization is unstable and coagulation and flocculation might occur during the inverse- suspension or -emulsion polymerization due to large particle size.

An important advantage of the inverse microemulsion polymerization of SAPs is the easier heat dissipation and lower viscosity. Moreover, the inverse microemulsion polymerization may occur at a higher rate to yield a high molecular weight polymer and keep stable due to smaller particle size. However, there is no report about the preparation of SAPs by inverse microemulsion polymerization. In this article, poly(AA-AM) superabsorbents were prepared by inverse- microemulsion polymerization technique using OP-10 and SDS as complex surfactants. The synthetic variables (amount of crosslinking agent and initiator, water/oil ratio, monomer/surfactant ratio and AA/ Am ratio) and their effects on the saline solution absorbencies of the synthesized superabsorbents were investigated. FTIR and SEM were used to characterize the structure of the synthesized superabsorbents.

Experimental

Materials

Acrylic acid(AA), analytical grade, purified by distillation under vacuum; acrylamide(Am), chemical grade ,purified by recrystallization ; N-methylene-bis-acrylamide(MBA), chemical grade, purified by recrystallization; sodium lauryl sulfate(SDS), Nonyl phenol polyoxyethylene ether (OP-10), chemical grade, ammonium persulfate (APS), analytical grade, used without further purification.

Preparation of superabsorbents by inverse microemulsion polymerization

A predetermined amount of 20% sodium hydroxide solution was added dropwise to the stirred aqueous AA solution in a 50 mL beaker cooled with an ice bath for partial neutralization. The crosslinking monomer, MBA and acrylamide, was dissolved in the above AA solution. The monomer solution was then added to the ammonium persulfate (APS) solution in a 50 mL vial until a clear mixture was obtained which was used as the disperse phase. Cyclohexane used as the continuous phase, in which a mixture of the complex surfactants SDS and OP-10(weight ratio 2:1) was dissolved, was poured into a four-necked flask fitted with a mechanical stirrer, thermometer, dropping funnel and a reflux condenser. The disperse phase containing the monomer and water soluble initiator was carefully added dropwise to the continuous phase under stir to form transparent inverse microemulsions. Temperature was increased slowly from room temperature to 70°C in a thermal water bath and the reaction systems were stirred for 2.5-4 h. After the reaction, the product was then poured into methanol to remove water. The dewatered product was washed by methanol several times to remove emulsifiers and initiator, and finally the product particles were filtered and dried at 70°C for 2 days.

Saline solution absorbency using filtration method

Approximately 20–30 mg of dried superabsorbents with an average particle size of 215μm were dispersed in 60 ml of 0.9% NaCl solution for 30 min. Then, excess 0.1% NaCl solution was allowed to drain through a 300 mesh wire gauze. The weight of the superabsorbent containing absorbed 0.1% NaCl solution was measured after draining for 1 h, and the saline solution absorbency was calculated according to the following equation:

$$\text{Saline solution absorbency (g/g)} = (W2 - W1)/W1 \qquad \textbf{(1)}$$

where W1 and W2 are the weight of the dry and swollen superabsorbent, respectively.

Characterization of the water superabsorbent

The micrographs of superabsorbents were taken using SEM (JSM-5600LV, JEOL, Ltd). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold. FT-IR spectrum was carried out on a Perkin–Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station. The samples were prepared as KBr pellets or as liquid films interposed between KBr discs.

Results and discussions

Effects of crosslinker amount on the salt absorbency

Fig 1 plots the experimental data of the salt absorbency as a function of the crosslinker content. As shown in Fig 1, with an increase of crosslinker content, the salt absorbency increases initially and reaches a maximum when the crosslinker content is 0.01%. Beyond that, the salt absorbency decreases with a further increase of the crosslinker content. When the crosslinker content is below 0.01%, the salt absorbencies decrease with decrease in crosslinker content. Since little polymer units are held together by the cross-linking agent and soluble materials increase. However,

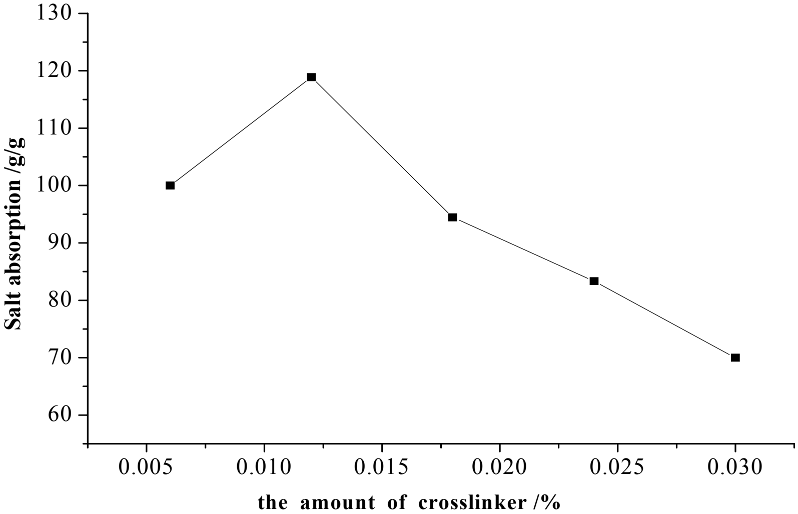


Fig 1. Effects of crosslinker content on the salt absorbency of the superabsorbents

higher crosslinker content results in more crosslink points and denser networks, which prevents the network from expanding to its fullest extent. The results are in conformity with Flory's network theory [13] and similar observations were previously reported by others [14,15].

Effects of water/oil ratio on salt absorbency of the superabsorbent

Effects of water/oil ratio on salt absorbency of the superabsorbent are shown in Fig 2. As shown in Fig 2, the salt absorbency decreases with the increase of water/oil ratio. Smaller particles can be formed when the water/oil ratio is low enough, and they can be stabilized by surfactant during inverse microemulsion polymerization, but as more water is added, the surface coverage ratio of surfactant decrease and the interdroplet attractive interactions lead to fusion and mass exchange. Therefore the resultant particles stuck together and the surface area of the particles decreased, resulting in a decrease in salt absorbency.

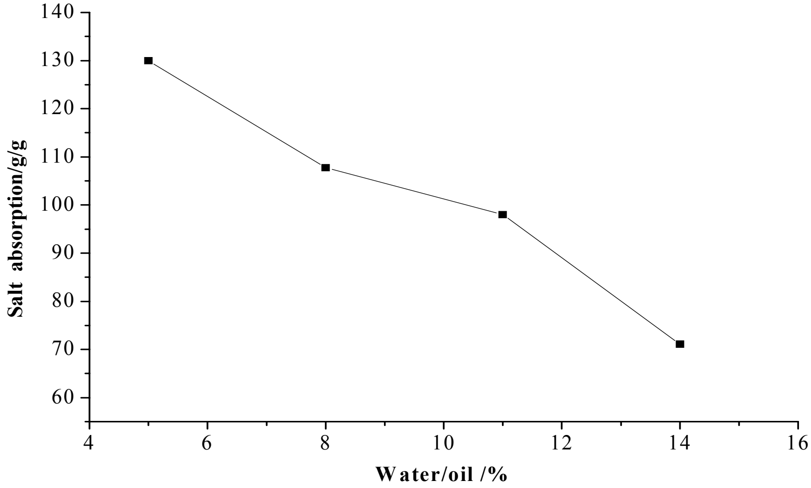


Fig 2. Effects of water/oil ratio on salt absorbency of the superabsorbent

Effects of monomer/ surfactant ratio on salt absorbency of the superabsorbent

Fig. 3 plots the experimental data of the salt absorbency as a function of the monomer/ surfactant ratio. When the monomer/surfactant ratio is beyond 50%, the water absorbencies decrease with increase in monomer/surfactant ratio. However, the water absorbency decreases with the decrease of monomer/surfactant ratio from 20 to 50%.

The strong increase in salt absorbency may be attributed to the increase in particle concentration with increase in monomer/surfactant ratio. As a result, the probability of capture of perfect polymer gel network can be formed which will increases the salt absorbency. However as more monomer is added, the surface coverage ratio of surfactant decrease and the interdroplet attractive interactions lead to fusion and mass exchange. Therefore the resultant particles stuck together and the surface area of the particles decreased, resulting in a decrease in salt absorbency.

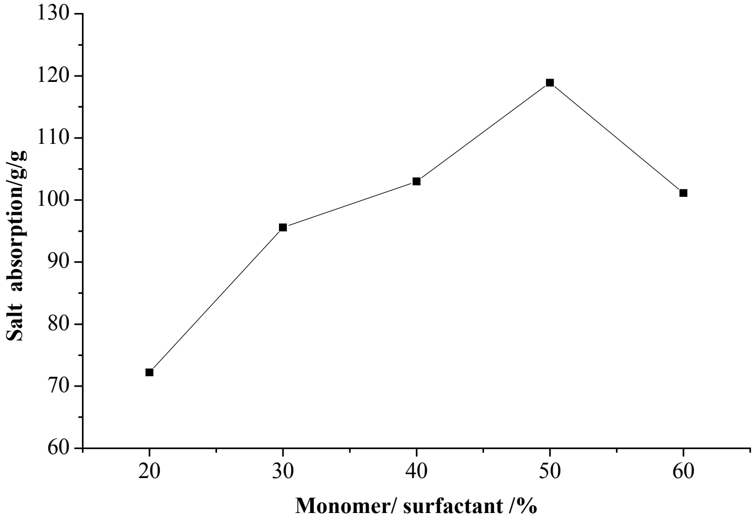


Fig 3. Effect of monomer/surfactant ratio on salt absorbency of the superabsorbent(AA/Am=7/3)

Effects of AA/ Am ratio on salt absorbency of the superabsorbent

According to Flory's network theory [13], the fixed charges on polymeric network of superabsorbent play an important part in the swelling of the superabsorbents. They are related to electrostatic repulsion between charges on the polymeric backbone and to osmotic pressure difference between polymeric network and external solutions. Therefore, the amount and type of hydrophilic groups on polymeric network play important roles in influencing salt absorbency of the superabsorbent.

As can be seen from Fig. 4, equilibrium salt absorbencies increase with increasing the mass ratio of AA to AM from 40/60 to 70/30, and then decrease with further increasing the ratio to 80/20. When more AA is added, the electrostatic

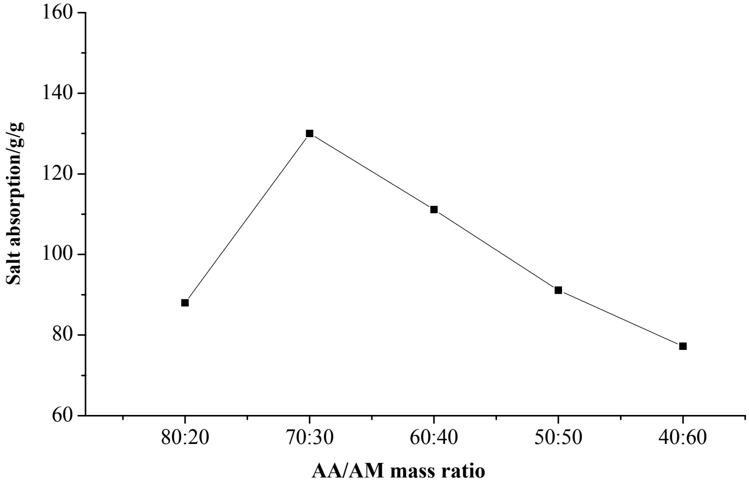


Fig 4. Effects of AA/ Am mass ratio on salt absorbency of the superabsorbent

repulsion, ionic hydrophilic property and osmotic pressure difference increase, and the network can be expanded more easily and the equilibrium salt absorbency increase[16]. However, further increasing the AA/Am mass ratio to a certain extent generate more sodium ions in the polymeric network, which reduce the electrostatic repulsion by screening the negative charges of –COO– groups, and thus decrease the equilibrium salt absorbency. Besides, introducing some acrylamide into an acrylic acid polymer can speed up absorption by lowering resistance to permeation. The increase in permeability resulting from the introduction of acrylamide into the polymer is attributable to higher chain mobility or more free volume.

Effects of initiator content on the salt absorbency

Figure 5 shows the effect of the initiator content on salt absorbency. The salt absorbency increases as APS content increases from 0.5 to 1.0 wt % and decreases with further increases in the content of APS. With increase of the initiator concentration, the molecular weight of the macromolecules decrease, and the relative amount of polymer chain ends increase. As mentioned in previous study [17,18], the polymer chain ends do not contribute to the salt absorbency. Therefore, the salt absorbency decreases with increase of the initiator content. However, when the content of photoinitiator is below 1%, the swelling capacity of superabsorbent composite also decreases. This may due to a decrease in the number of radicals produced by initiator and small amount of radicals can not guarantee the rapid crosslinking reaction by inverse microemulsion polymerization. Therefore the network cannot be formed efficiently during inverse microemulsion polymerization, and the salt absorbency decreases.

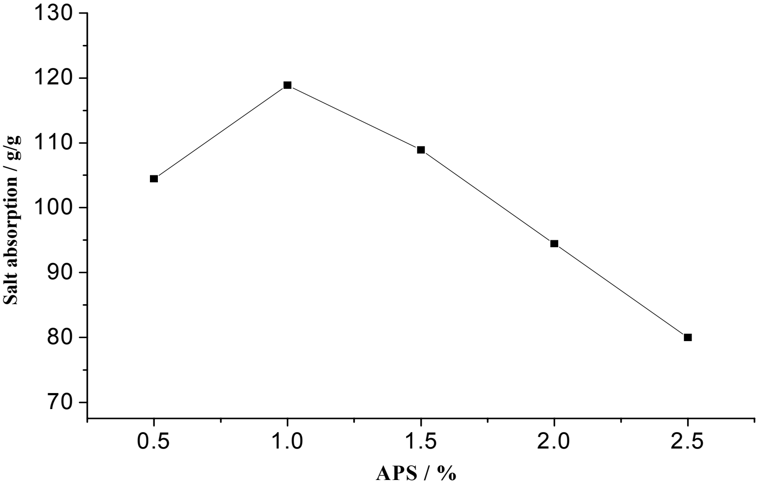


Fig 5. Effects of initiator content on salt absorbency of the superabsorbents

Salt absorbency rate of the superabsorbent

Relationship between salt absorbency and absorption time was shown in Fig 6. As indicated by Fig 6, salt absorption was rapid, requiring 30min to reach 111g/g and 75 min to reach maximum uptake (130g/g). An increase in rate of absorption would be

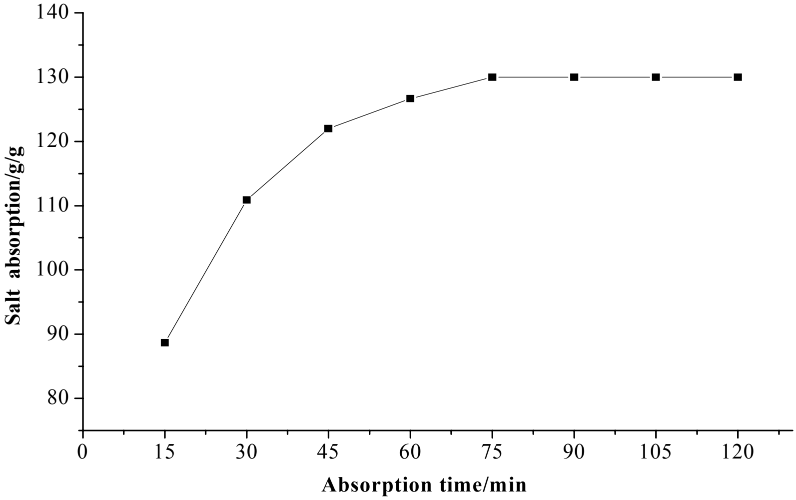


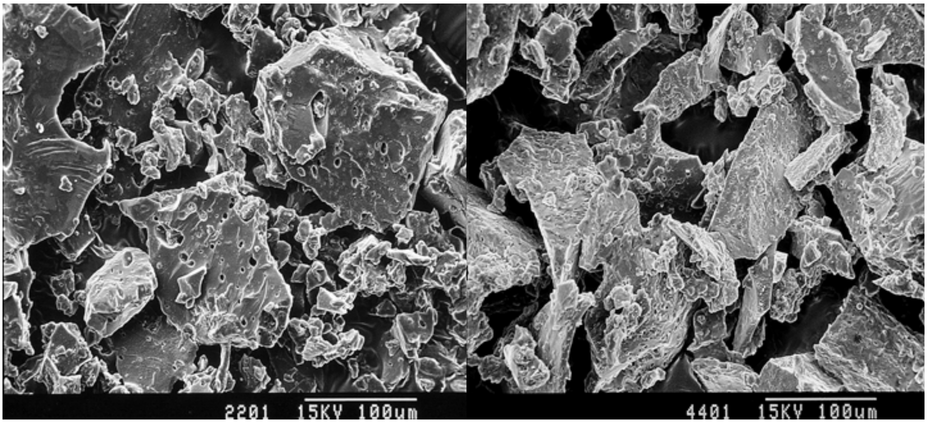
Fig 6. Relationship between salt absorbency and absorption time

expected from the increase in surface area with decreasing particle size prepared by inverse microemulsion polymerization. Besides, the inverse microemulsion keep stable and relatively perfect polymer network might be formed, which will increase the initial salt absorbency and equilibrium salt absorbency.

SEM observations of the superabsorbent

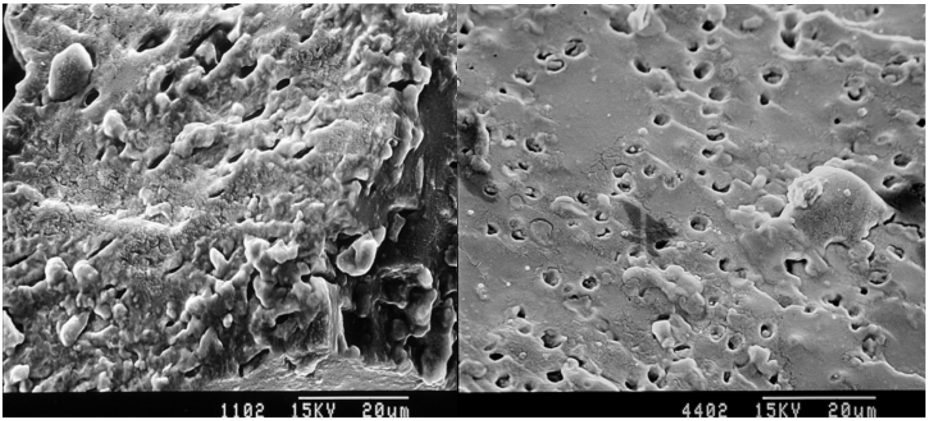
The microphotographs of the particles for two series of superabsorbents with different crosslinker content observed from SEM are shown in Figure 7. As shown in these figures, the particles obtained from inverse suspension polymerization approach an irregular, undulant and microporous surface and some aggregates occur, an indicative of particle conglomeration after remove of surfactant and water by washing and drying. Although this undulant and microporous surface is convenient for the penetration of water into the polymeric network, the particles prepared with more crosslinker content (0.03%) showed a smaller pore size and a less porous structure compared with those with less crosslinker content (0.01%) . This different shape will affect their salt absorption behavior and these observations are in good agreement with our salt-absorbency observations. As indicated in Fig 1, the salt absorbency of the superabsorbents prepared with more crosslinker content (0.03%) was lower than those with less crosslinker content (0.01%) because these pores make an increased surface area and thus increase the salt absorbency.

Besides, the SEM microphotographs of the particles for two series of superabsorbents with different water/oil ratio are shown in Fig 8. As shown in Fig 8, there exist many micropores with the water/oil ratio of 8%.However, the number of the micropores largely decreased with the water/oil ratio increasing from 8% to 14%.This indicated that when more water is added, the surface coverage ratio of surfactant decrease and the interdroplet attractive interactions lead to fusion and mass exchange during inverse microemulsion polymerization. Therefore the resultant particles stuck together, resulting in a decrease in surface areas and salt absorbency, as indicated in Fig 2.



(a) (b)

Fig 7. SEM images of the inverse microemulsion superabsorbent, (a) crosslinking agent content = 0.03%; (b) crosslinking agent content = 0.01%



(a) (b)

Fig 8. SEM images of the inverse microemulsion superabsorbent, (a) water/oil ratio =14%; (b) water/oil ratio = 8%

FTIR spectrum of the superabsorbent

The FTIR spectrum in the range 4000–400 cm^{-1} of superabsorbent is shown in Fig 9. The absorption peaks at 3430cm^{-1} contribute to the OH and NH stretching frequencies. and the bands at 2860 cm^{-1} and 2927cm^{-1} correspond to the symmetrical and asymmetrical of methene, respectively. Further, the spectrum also shows peaks at 1730cm^{-1} corresponding to the carbonyl group of acid moiety of the AA unit, and 1564 and 1402cm^{-1} corresponding to the COO- and 1659 cm^{-1} corresponding to the amide moiety of the AM unit, and the peaks at 1118cm^{-1} corresponding to C-O-C group. This FTIR analysis indicates that all of the monomeric units- acrylamide, sodium acrylate, and acrylic acid are incorporated in the copolymer backbone.

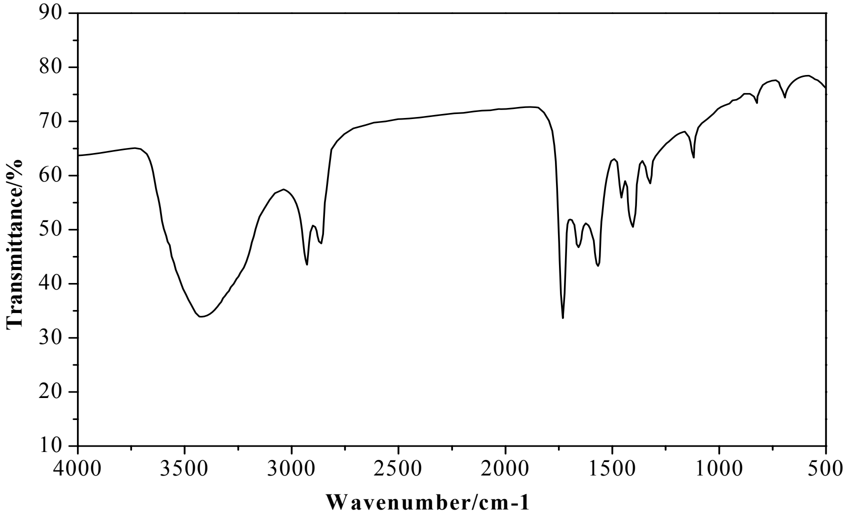


Fig 9. FTIR spectrum of the water superabsorbent

Conclusions

A novel superabsorbent poly acrylic acid -co-acrylamide was prepared by inverse microemulsion copolymerization. The saline absorbency was affected by polymerization conditions such as concentrations of crosslinker and initiator, water/oil, monomer/surfactant and AA/ Am ratio. Superabsorbent has the maximum saline solution absorbency of 130g/g within 75min, and the saline solution absorbency of 111g/g within 30min under an optimum condition. SEM indicated an unequal, fluctuant and porous surface of the superabsorbent, and the particles prepared with higher crosslinker content showed smaller pore sizes and less porous structures and the number of the micropores largely decreased with the water/oil ratio.

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