

Preparation and Swelling Properties of Crosslinked Sodium Polyacrylate

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ABSTRACT: Crosslinked sodium polyacrylate as a superabsorbent was prepared by inverse suspension polymerization with cyclohexane as the continuous phase and sorbite anhydride monostearic acid ester (span-80) as the dispersant. The crosslinking degree was regulated by NaOH. The distilled water absorbency (WA) of the polymer gel was about 700 times its own weight if the gel was allowed to swell at room temperature for 24 h. WA under various conditions, such as varying pH, temperature, reaction time, neutralization, and cyclohexane concentration, was investigated and optimized. Our results revealed that the optimal reaction conditions were 55°C, 25-min reaction time, 85% neutralization, and a 7:1 (v/v) cyclohexane/monomer ratio. Our results also showed that such synthesized polymer gels have a high WA and a good water-retention ability under different pressures. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1515–1520, 2001

Key words: superabsorbent; crosslinked sodium polyacrylate gel beads; inverse suspension polymerization

INTRODUCTION

A special kind of polymeric gel known as a *superabsorbent* can absorb water to several hundred times its own mass. This kind of polymer gel was first developed by a group of researchers at the Northern Regional Research Laboratory of the U.S. Department of Agriculture in the 1970s.¹ This superabsorbency makes such gels very useful for many applications, such as disposable pads, sheets, and towels for surgery, adult incontinence, and female hygiene products, even though they were originally developed for agricultural applications to improve the water-holding capacity of soils to promote the germination of seeds and plant growth.

Normally, a superabsorbent gel is a slightly crosslinked polymer network in which the polymer chains are often polyelectrolytes and contain carboxylate anions and sodium cations. The concentration of ionic groups inside the gel network results in an osmotic pressure difference. This is the driving force behind its superabsorbency.^{2,3} The swelling of the gel network is limited because the crosslinked chains are insoluble.⁴ Superabsorbent polymers can be prepared by grafting copolymerization, such as the grafting of acrylonitrile onto starch or cellulose with alkaline saponification, or more commonly by the modification of hydrophilic polymers, such as crosslinked sodium polyacrylate, which is abundant and cheap.^{5–7} In the preparation of polymers, suspension polymerization is a widely used method in which a monomer suspension is maintained by vigorous stirring during the reaction. Suspension polymerization has many attractive features because polymers thereby obtained are in the form of

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beads. In comparison with polymers obtained in emulsion or solution polymerization, they are purer and directly usable in some applications after a washing and drying process. The bead size can be controlled with variations in the stabilizer agent, the agitation, and the monomer/stabilizer ratio.

On the basis of our previous studies,^{8,9} in this study we developed a novel preparation of sodium polyacrylate gel beads as superabsorbents by inverse suspension polymerization, and we studied how various reaction conditions affected the water intake absorbency.

EXPERIMENTAL

Sample Preparation

Acrylic acid (Aa) was distilled at reduced pressure (boiling point = 20–21°C at 0.5 mmHg). Analytical-reagent-grade cyclohexane as the dispersion medium, sorbite anhydride monostearic acid ester as the stabilizer, potassium persulfate as an initiator, and sodium hydroxide were used without further purification. The suspension copolymerization was done under nitrogen at a constant temperature in a four-necked flask equipped with a stirrer, thermometer, reflux condenser, and gas

inlet tube. Cyclohexane (55 mL) and a proper amount of sorbite anhydride monostearic acid ester were added. The mixture was heated to a desired reaction temperature under vigorous stirring. A mixture of 5 mL of Aa, a proper amount of an 11M NaOH aqueous solution, and 0.02 g of potassium persulfate ($K_2S_2O_8$) as an initiator was added to start the reaction. The resultant polymer beads were isolated by filtration and then thoroughly washed with methanol. The purified polymer gel beads were dried with an infrared lamp at 40–50°C until a constant weight was reached. The reaction time was 3 h. The sample used for various tests had a neutralization degree of 85%.

Water Absorbency (WA) and Water Retention (WR)

Polymer beads (0.1 g) were immersed in distilled water, tap water, and a 0.9% aqueous solution for a sufficiently long time. The swollen beads were filtered through a silk sieve (~20 mesh) to remove the nonabsorbed liquid and were weighed. WA was expressed as the absorbed liquid per gram of dried beads. Swollen polymer gel beads were placed in a bag of gauze that was supported by a funnel and loaded with a weight for 20 min. The WR after different pressures was determined in

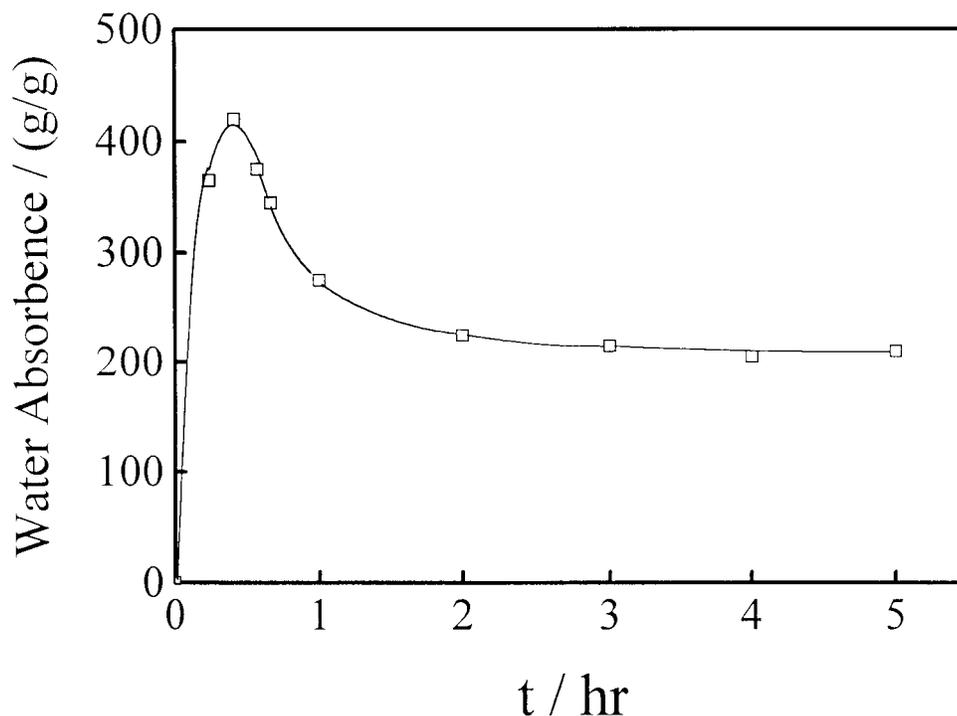


Figure 1 Reaction time dependence of WA of gel beads in distilled water.

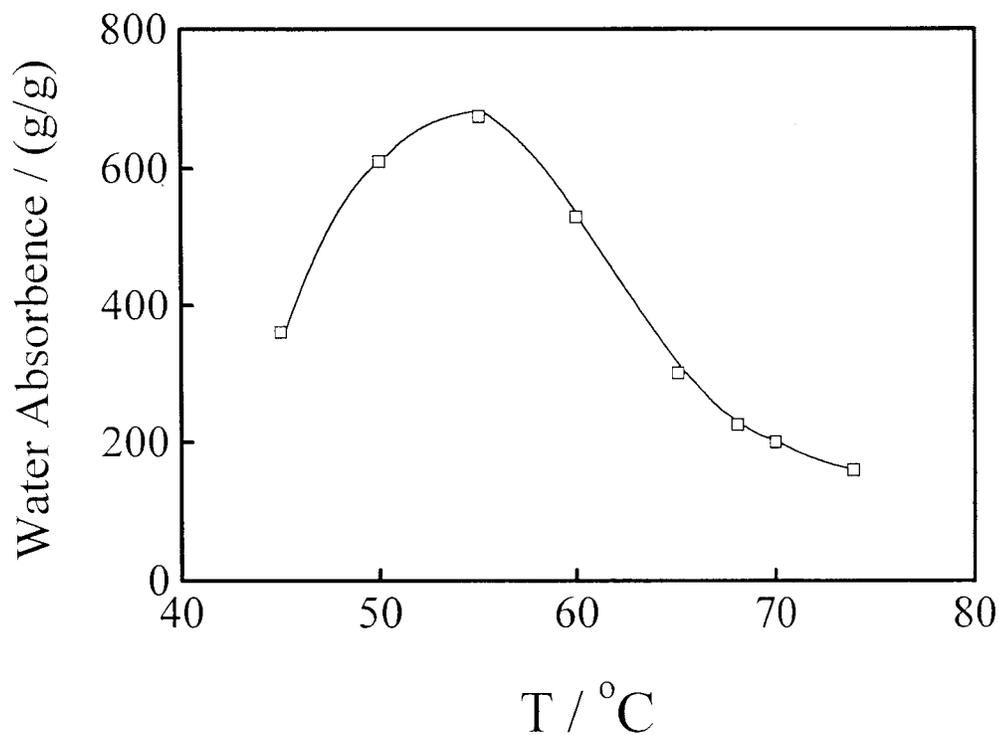


Figure 2 Reaction temperature dependence of WA of gel beads in distilled water.

terms of the weight change of the swollen polymer gel beads before and after the pressure was applied. As for the determination of WR under an

ordinary pressure (atmospheric pressure), the swollen gel beads were placed into a sieve with a known mesh size and weighed at different times.

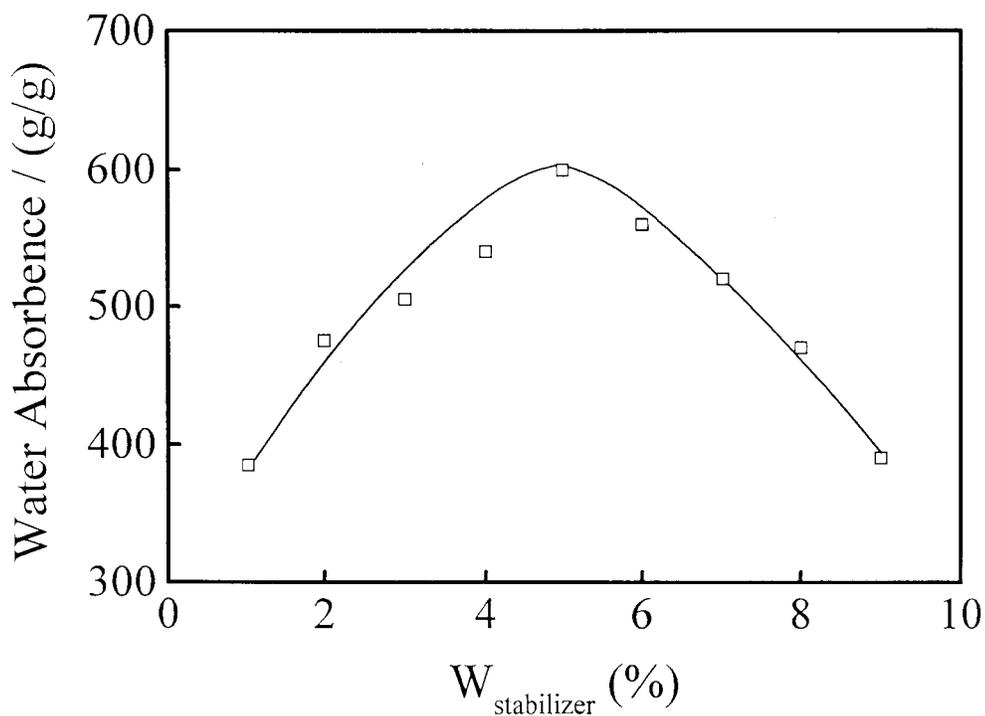


Figure 3 Stabilizer composition dependence of WA of gel beads in distilled water.

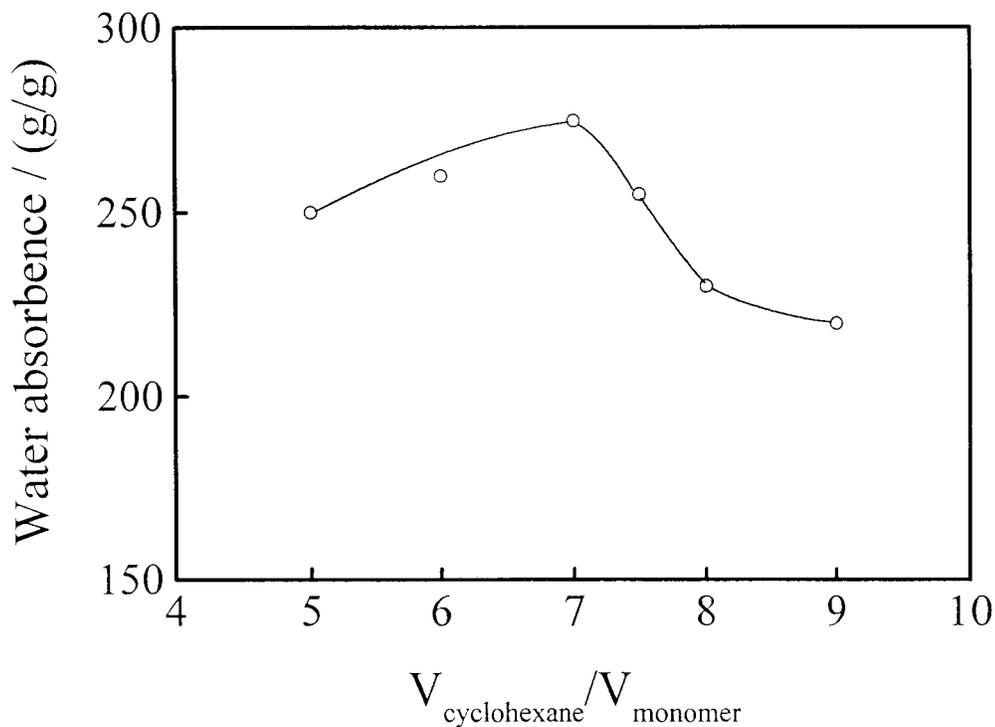


Figure 4 Dispersant concentration dependence of WA of gel beads in distilled water.

RESULTS AND DISCUSSION

Figure 1 shows that the WA increased as the polymerization time increased for up to half an

hour. The decrease of WA after the maximum could be attributed to an overcrosslinking of the polymer gel network, which hindered the stretching of the polymer chains in the network and

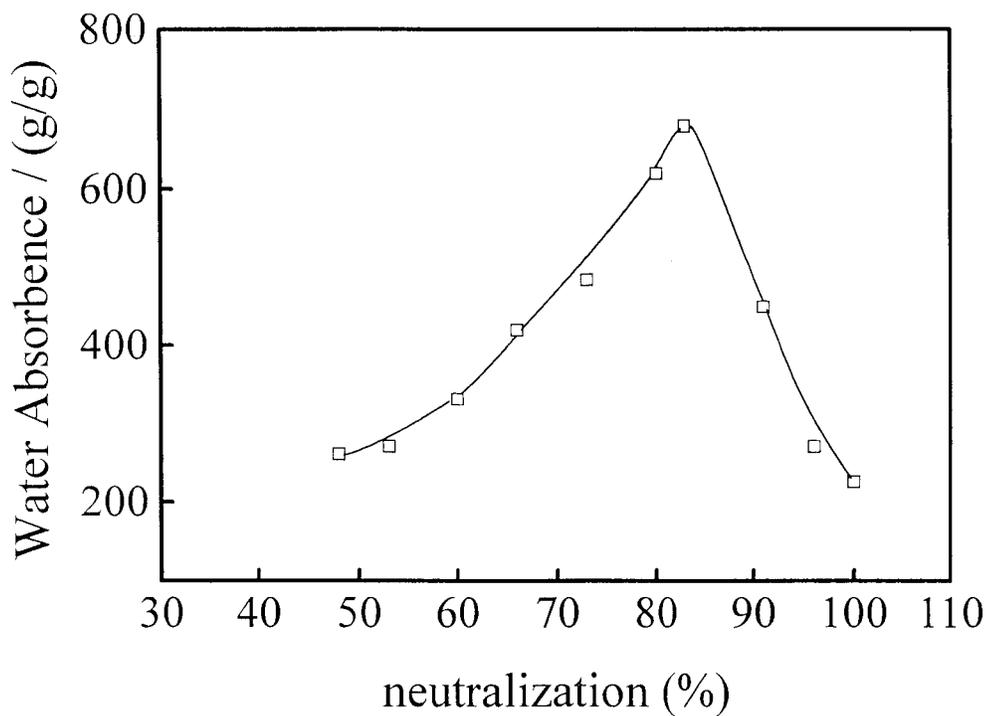


Figure 5 Neutralization degree dependence of WA of gel beads in distilled water.

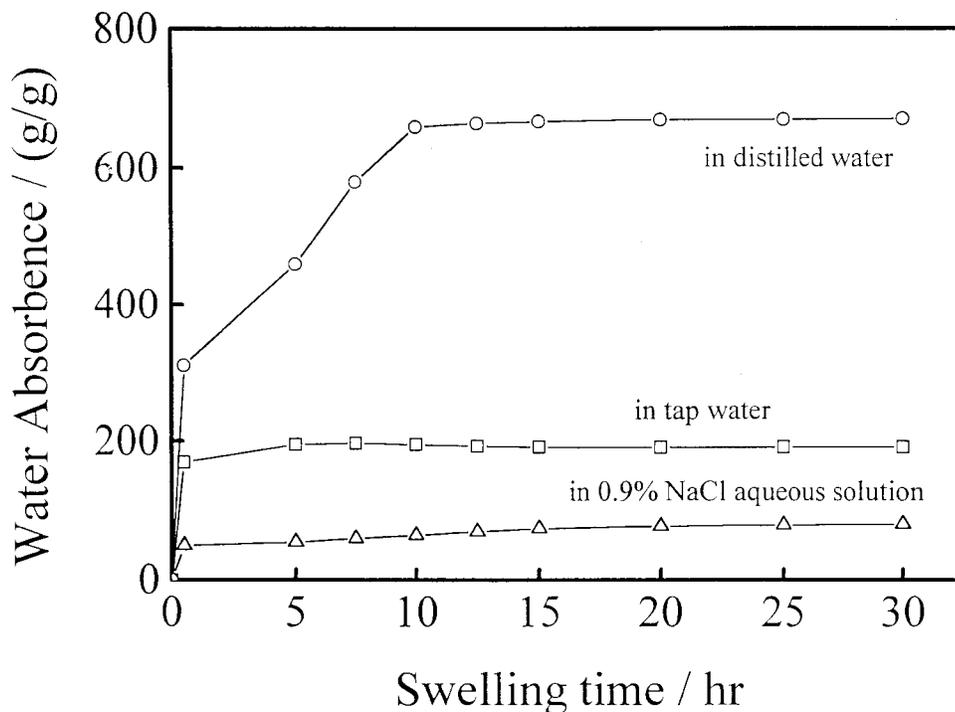


Figure 6 Swelling kinetics in different fluids: (○) distilled water, (□) tap water, and (△) 0.9% aqueous NaCl.

reduced the value of WA. WA approached a constant value after about 2 h, indicating that the reaction was completed by this time.

Figure 2 shows that WA reached a maximum if the reaction was done at 55°C. Generally, it is known that to reach a higher WA, one needs to make the average length of the subchains between two neighboring crosslinking points longer (i.e., fewer crosslinking points) and reduce dangling chain ends. The existence of a maximum in the temperature dependence of WA could be attributed to a balance among chain growth, the crosslinking reaction, and termination. Before the maximum was reached (i.e., from 45 to 55°C), the increase in temperature led to a dominant chain-length growth, so that WA increased with the temperature. A further increase in the temperature gradually made the crosslinking and chain termination dominant, so that WA started to decrease in from 55 to 70°C.

Figure 3 shows that as the stabilizer concentration increased, WA increased in the concentration range 1–5% but decreased when the stabilizer concentration was higher than 5%. There existed an optimal stabilizer concentration of about 5%, at which WA reached its maximum. It is known that the size of the polymer gel beads

decreases as the stabilizer concentration increases, and water can only be contained inside a three-dimensional polymer network. As the bead becomes smaller, the surface layer constitutes relatively more volume so that WA decreases in the stabilizer concentration range 5–9%. The increase of WA from 1 to 5% could be attributed to the imperfect formation of the polymer gel network because there was an insufficient amount of stabilizers.

Figure 4 shows that WA increased with the cyclohexane volume ($V_{\text{cyclohexane}}$) until a maximum was reached at $V_{\text{cyclohexane}}/V_{\text{monomer}} = 7:1$, where V_{monomer} was kept to 5 mL. If $V_{\text{cyclohexane}}/V_{\text{monomer}}$ was too low, the resultant particles easily formed a lump, leading to the decrease in WA. However, if $V_{\text{cyclohexane}}/V_{\text{monomer}}$ was beyond a critical value, the resultant particles stuck together, resulting in a decrease in WA.

Figure 5 shows that there also existed a maximum in the dependence of WA on the degree of neutralization. From 50 to 85%, the swollen gel beads had good strength if WA was not too high. However, in the high neutralization range (>85%), the gel strength was rather poor, and part of the polymer gel network became soluble. It is easy to understand the increase of WA as the neutraliza-

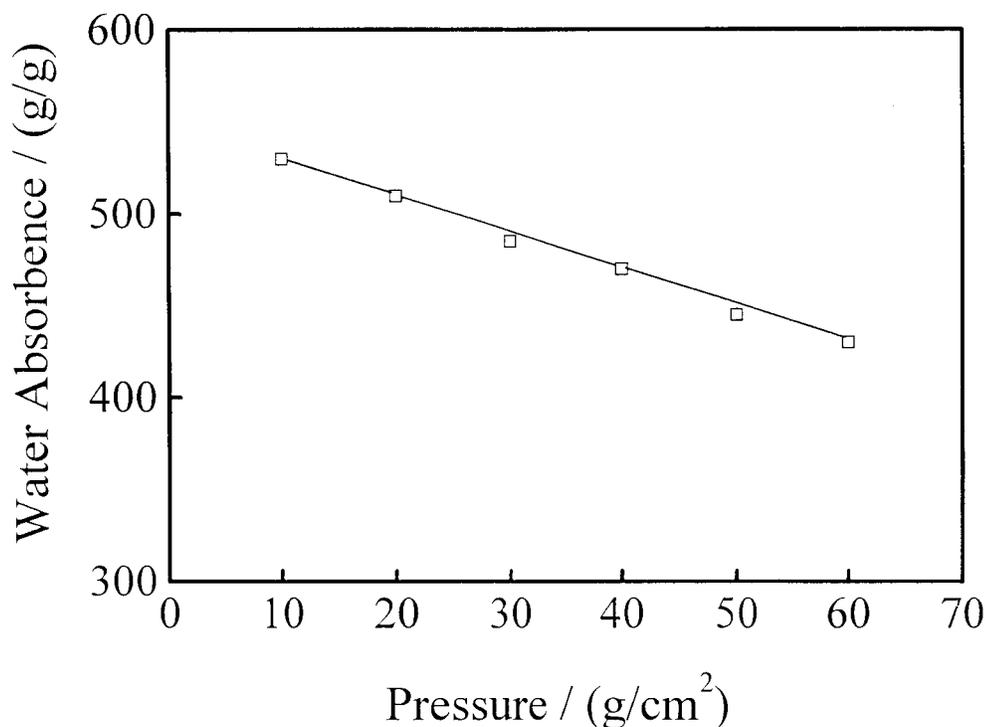


Figure 7 Applied pressure dependence of WA of gel beads in distilled water.

tion increased in from 50 to 85%. As for the decrease of WA from 85 to 100%, we could attribute it to the monomer acidity; namely, the polymerization rate of Aa and the crosslinking degree depended on the pH.¹⁰

Figure 6 shows that the gel beads swelled most in distilled water, less in tap water, and considerably less in the 0.9% NaCl aqueous solution. This could be attributed to the ionic strength of the swelling solution. As the ionic strength increased, the electrostatic repulsion between the carboxylic groups decreased so that the gel swelling decreased.^{9,11}

Figure 7 shows that WA decreased only slightly as the applied pressure increased. Under an applied pressure of 50 g/cm², WA was still as high as 445 g/g, indicating excellent WR. For most applications of superabsorbent polymers, such as those in agriculture, forestry, and gardening, the pressure is 1 atm. Our results showed that WA of the beads used was 390 g/g even after 96 h at 30°C, indicating that the hydrogel developed in this study had excellent WR.

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