Inverse Suspension Polymerization of Sodium Acrylate

GUOJIE WANG, MIN LI, XINFANG CHEN

Institute of Materials Science, Jilin University, Changchun 130023, People's Republic of China

ABSTRACT: A superwater-absorbent sodium polyacrylate was synthesized by inverse suspension polymerization, using Span60 as the dispersant, cyclohexane as the organic phase, N,N'-methylene bisacrylamide as the crosslinking agent, and potassium persulfate as the initiator. The effect of reaction conditions such as reaction time, crosslinking agent, and dispersant on deionized-water and saline solution absorbability, average particle size, and distribution of the sol−gel of the resin is discussed. The deionized-water and saline solution absorbabilities of sodium polyacrylate prepared at proper conditions were 300−1200 and 50−120, respectively; the number-average particle size was 10−50 μm and the gel portion was 20−85% by weight. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 789−794, 1997

Key words: superwater-absorbent resin; sodium acrylate; inverse suspension polymerization; degree of absorption; gel

INTRODUCTION

Superwater-absorbent polymers can be classified into three kinds: starch system, cellulose system, and synthetic resin system. The capacity of superwater-absorbent resins to retain large amounts of water and a high rate of water absorption makes them very useful in a variety of applications in medicine, sanitary goods, the food industry, chemical engineering, and so on.[1−3] Superwater-absorbent resins can absorb several hundred or thousand times as much water as their own weight to an equilibrium value and are insoluble in water due to the presence of a three-dimensional network.[4] The hydrophilicity of water-absorbent resin is due to the presence of hydrophilic groups such as alcohols, carboxylic acids, amides, and sulfuric acids. The swollen equilibrium state results from a balance between the osmotic driving forces that cause water to en-

ter the hydrophilic polymer and the forces exerted by the polymer chains in resisting expansion. The fraction of the gel portion in water-absorbent resin is one of the most important factors that significantly influence its application, such as in producing a water-swellable elastomer. If a water-swellable elastomer is prepared by blending rubber and a superabsorbent polymer with a large amount of the sol portion, the degree of swelling of the water-swellable rubber is low and the sol portion will separate off upon being in contact with water for a long period of time; as a result, the strength of the thus-prepared elastomer is decreased remarkably and the water is polluted, similarly, the water swellability of water-swellable rubber prepared by blending rubber and a superabsorbent polymer with total gel mass is also inferior for its low swelling rate as well as its low swelling degree and no satisfactory effect can be expected. So, the distribution of sol−gel of a superabsorbent polymer should be quantified.

Inverse suspension polymerization of water-soluble monomers is an important method to synthesize superwater-absorbent resins. The advantage of inverse suspension polymerization over

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other methods is that a powder sample of a water-absorbent resin can result and the particle size can be easily controlled by controlling the reaction conditions. In recent years, the inverse suspension polymerization method to prepare water-absorbent resin has received much attention in fundamental and technological fields, but data on the inverse suspension polymerization are scarce and mainly confined to the patent literature.[5–8] This article deals with the synthesis of sodium polyacrylate by inverse suspension polymerization. Details of the effect of reaction conditions on the degree of absorption, particle size, and distribution of the sol–gel of the prepared sodium polyacrylate are given.

EXPERIMENTAL

Materials

All the reagents were used as received (chemical purity and special grade for analysis).

Preparation of Sodium Polyacrylate

In a 250 mL three-necked round-bottomed flask with a reflux and stirrer, cyclohexane (110 mL) and Span60 were added, which were heated into a solution in a water bath. An acrylic acid aqueous solution was neutralized by a sodium hydroxide aqueous solution; the neutralization was 75%. N,N'-Methylene bisacrylamide aqueous solution and a potassium persulfate aqueous solution were added into the sodium acrylate solution at room temperature, and the obtained mixture was added dropwise into the flask with vigorous stirring. The reaction was carried out under nitrogen with vigorous stirring for a period of time at 60°C first and then at 72°C for 1 h. Following the start of the reaction, there was a marked increase in the viscosity of the medium and the color changed from milky white to pink. The inversion of phases occurred (the aqueous phase, which formerly was the discontinuous phase, becomes the continuous phase) just like that of the polymerization of acrylamide.[9] After the prescribed time, precipitates (sodium polyacrylate) appeared when stirring was stopped. Water was separated as cyclohexane azeotrope from the polymer. Then, the precipitates were washed with large amounts of methanol and filtered. The resulted sodium poly-

acrylate, which was a white powder, was dried in a vacuum at 50°C.

Absorption Power and Distribution of Sol–Gel Tests

The degree of absorption of the resin was measured by soaking 0.5 g resin in 1 L deioned water for 1 h and by soaking 1.0 g resin in 200 mL 0.9% NaCl aqueous solution for 1 h, filtered by a gauze filter, washed with large amounts of the solvents, then dried to a constant weight (gel portion). Q, the degree of absorption; and G, the fraction of the gel portion by weight extracted with deioned water, were calculated by the following equations:

$$Q = \frac{W_2 - W_1}{W_3} \quad G = \frac{W_3}{W_1}$$

where W_1 and W_2 are the weights of the resin before and after absorbing, respectively, and W_3 is the weight of the gel.

Measurement of Particle Size

A polarizing microscope Universal R Pol was used to measure the number-average particle size of sodium polyacrylate.

RESULTS AND DISCUSSION

The dispersant, organic phase, reaction temperature, stirring speed, and concentration of the initiator all can affect the particle size and degree of absorption of water-absorbent resin.[10] The effect of the concentration of the dispersant, amount of crosslinking agent, and reaction time on the characteristics, such as degree of absorption, particle size, and distribution of the sol–gel of the superwater-absorbent resin is discussed below.

Effect of Dispersant

Figure 1 shows photographs of sodium polyacrylate particles prepared using different amounts of Span60 as the dispersant. It can be seen that the number-average particle size of the resin decreased with increase of the Span60. The quantitative results of the effects of the dispersant on the average particle size, degree of absorption, and distribution of the sol–gel are given in Table I.
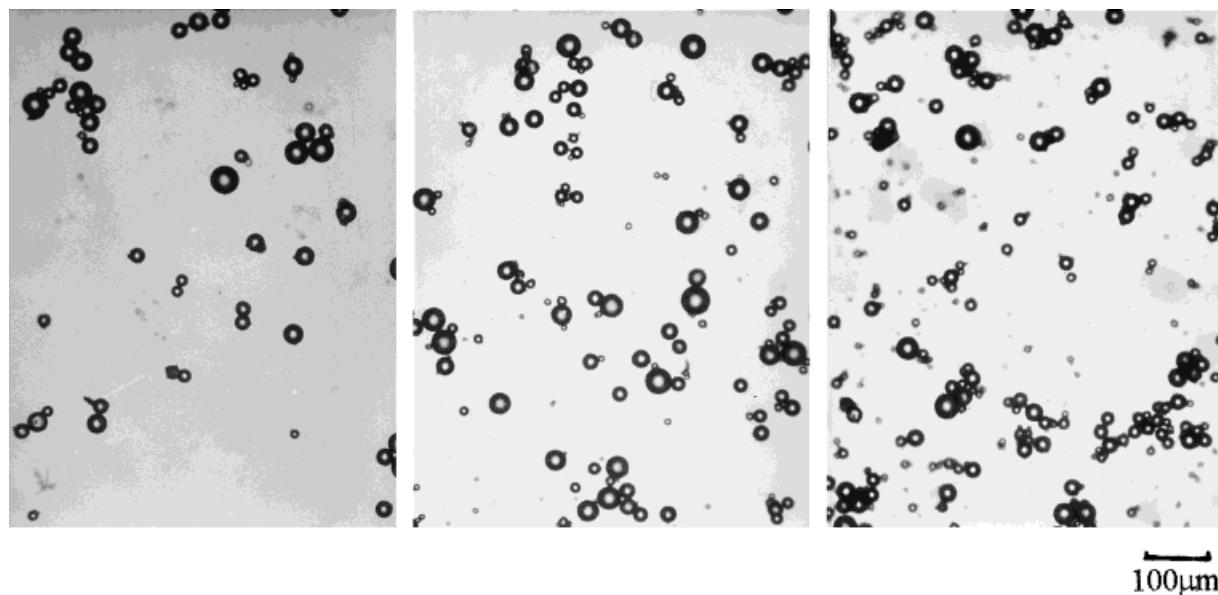
NO. 510   NO. 506   NO. 518

Figure 1   Polarizing microscope photographs of samples no. 510, no. 506, and no. 518.

Obviously, the fraction of the gel portion was nearly stable in the samples prepared by using different amounts of the dispersant within the studied range; the degree of absorption increased with increase of the dispersant and decrease of the particle size. The mechanism of hydration of polymers and interaction between polymers and water was studied by Carlsson et al.[11] and Takahashi[12] who suggested that water absorbed by the water-absorbent polymer included bound water and large amounts of free water in a three-dimensional network, and the more the bound water, the more the free water and the higher the degree of absorption. According to the above mechanism, the same weight resins with a small particle size absorbed more bound water because of its higher surface-to-volume ratio, so its degree of absorption was high.
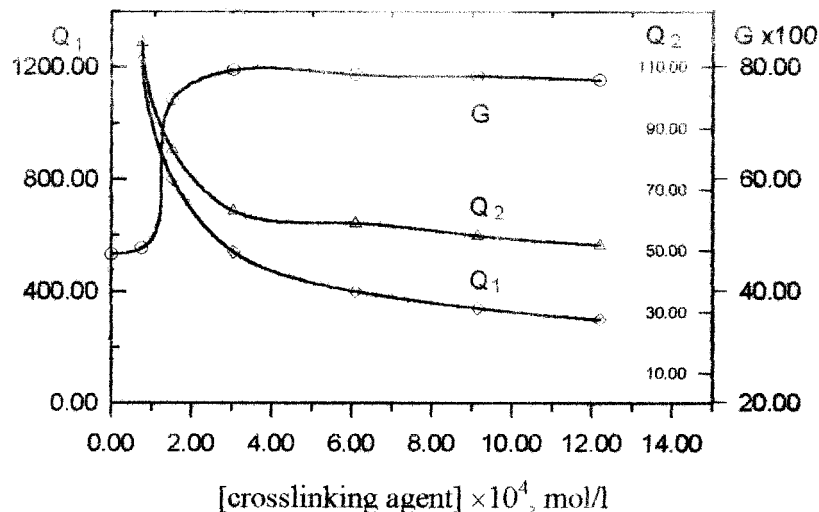
Effect of Crosslinking Agent

The effect of the amount of crosslinking agent on the degree of deionized-water absorption, saline solution absorption, and the fraction of gel is shown in Figure 2. Clearly, it can be seen that the degree of absorption decreased with increase of the amount of crosslinking agent within the studied range. As we know, the mechanism of water absorption of sodium polyacrylate is based on its three-dimensional network. The more crosslinking agent, the greater the crosslinking density, the smaller the three-dimensional network, and the lower the degree of absorption. From the curve of the fraction of the gel versus the concentration of the crosslinking agent, it can be seen that the gel mass increased much with the increase of the crosslinking agent when the concen-

Table I   Effect of Amount of Dispersant on Average Particle Size, Degree of Absorption, and Fraction of Gel

Sample No.	Span60 (mol/L)	D (μm)	Q_1	Q_2	$G \times 100$
510	4.68×10^{-3}	25.8	520	59	76.6
506	9.37×10^{-3}	21.8	540	63	79.3
518	1.87×10^{-2}	17.0	620	68	75.8

[Crosslinking agent], 3.05×10^{-4} mol/L; reaction time, 3 h; D, the average particle size; Q_1, the degree of deionized-water absorption; Q_2, the degree of saline solution absorption; G, the fraction of the gel.

Figure 2 Plots of the degree of absorption in deioned water (Q_1) in 0.9% NaCl aqueous solution (Q_2) and the fraction of gel (G) versus the concentration of crosslinking agent. [Dispersant], 9.37×10^{-3} mol/L; reaction time, 3 h.

tration of the crosslinking agent was low; after that, the fraction of the gel reached its maximum value and maintained a constant one when the concentration of the crosslinking agent reached 3.05×10^{-4} mol/L. The fraction of the gel should increase with increasing the amount of the crosslinking agent, but it did not increase to 100% and reached a constant value, which resulted from the two-stage reaction procedure: At the earlier stage, most of the resulted polymer was sol, as will be also discussed later.

Polarizing microscope photographs of sodium polyacrylate prepared using different amounts of the crosslinking agent are shown in Figure 3. It can be seen that the amount of the crosslinking agent had little effect on the number-average particle size.

Effect of Reaction Time

Figure 4 shows polarizing microscope photographs of the sodium polyacrylate particles prepared at different reaction times. As can be seen, the number-average particle size and the fraction of the gel decreased with a prolonged reaction time, yet the degree of absorption increased, which is shown in Table II. The reaction was carried out in stages which avoided the following problems: If the reaction temperature was kept at 60°C, the content of the gel was very low and no satisfactory result could be obtained; if at the beginning of the reaction it was then increased

to 72°C, autoacceleration occurred strongly and particle size could not be controlled. The decrease of the particle size with increase of the reaction time was due to autoacceleration, which was observed at the later stage (1 h, 72°C) and was much moderated with the earlier stage (60°C) prolonged. According to the mechanism of radical

NO. 508   NO. 525
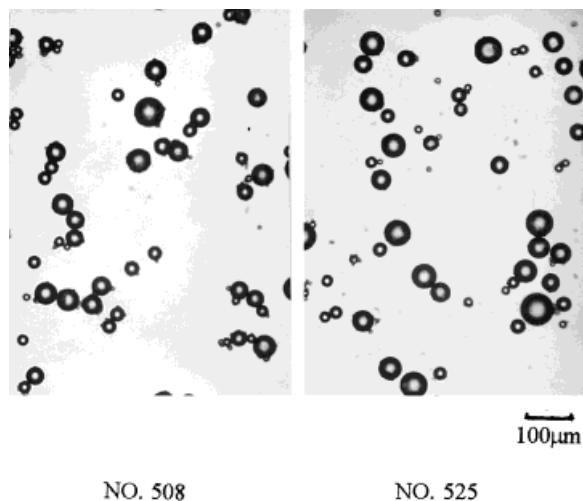
Figure 3 Polarizing microscope photographs of samples no. 508 and no. 525. No. 508: [crosslinking agent], 1.52×10^{-4} mol/L; [dispersant], 9.37×10^{-3} mol/L; reaction time, 2.5 h; average particle size, 33.0 μm. No. 525: [crosslinking agent], 1.22×10^{-3} mol/L; [dispersant], 9.37×10^{-3} mol/L; reaction time, 2.5 h; average particle size, 33.4 μm.

100μm
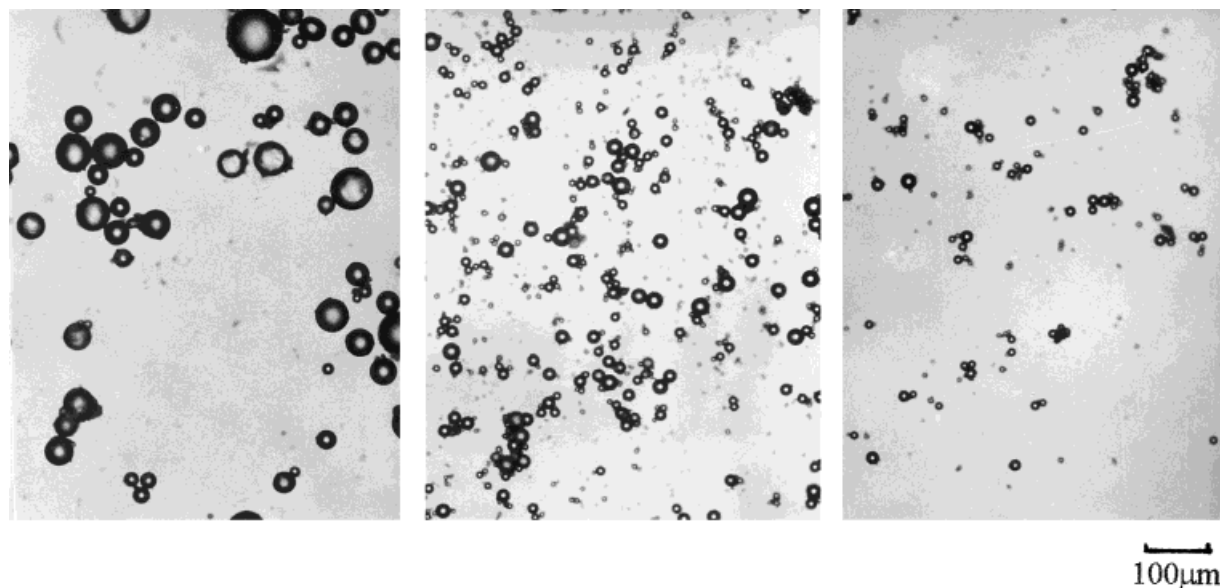
NO. 429   NO. 526   NO. 426

Figure 4   Polarizing microscope photographs of samples no. 429, no. 526, and no. 426.

polymerization,[13,14] the conversion from monomer to polymer increases with increasing reaction time; then, the viscosity increases and autoacceleration occurs due to the increased viscosity, and in autoacceleration, a great change of conversion occurs. At the earlier stage (60°C), the aqueous phase of the monomer became the continuous phase, and the conversion increased gradually with the reaction time prolonged without autoacceleration. The longer the earlier stage, the higher the conversion, so the reaction with a longer earlier stage possessed a higher conversion when it entered the later stage and increase of the conversion would not be high in its later stage and autoacceleration was weakened. In the lighter au-

toacceleration, the change of conversion was less, the effect of viscosity on particle size was lower, and the polymer particles could not be easily stuck together and the particle size became smaller. So, the particle size of sample no. 429 was the largest and that of sample no. 426 was the smallest. In the earlier stage, the sol portion was dominant, as can be seen from the relation between the fraction of the gel and reaction time: The longer the reaction time, the less the gel portion. That the degree of absorption increased with increase of the reaction time was due to that the particle size decreased with increase of the reaction time: The longer the reaction time, the smaller the particle size and the higher the degree of absorption.

Table II   Effect of Reaction Time on Average Particle Size, Degree of Absorption, and Fraction of the Gel

Sample No.	Time (h)	D (μm)	Q_1	Q_2	$G \times 100$
429	2	38.0	400	53	82.9
526	5	16.6	460	96	35.4
426	10	10.2	570	114	24.9

[Crosslinking agent], 6.10×10^{-4} mol/L; [dispersant], 9.37×10^{-3} mol/L; D, the average particle size; Q_1, the degree of deionized-water absorption; Q_2, the degree of saline solution absorption; G, the fraction of the gel.
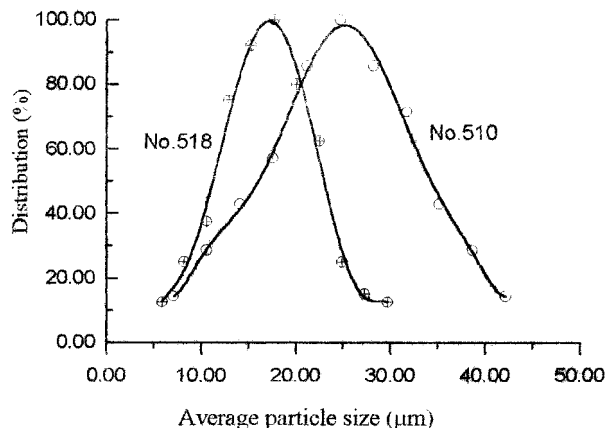
Figure 5 The distribution of the particle size of samples no. 510 and no. 518. No. 510: [crosslinking agent], 3.05×10^{-4} mol/L; [dispersant], 4.68×10^{-3} mol/L; reaction time: 3 h; average particle size, 25.8 μm. No. 518: [crosslinking agent], 3.05×10^{-4} mol/L; [dispersant], 1.87×10^{-2} mol/L, reaction time, 3 h; average particle size, 17.0 μm.

Distribution of Particle Size

The distributions of the particle size of samples no. 510 and No. 518 are given in Figure 5, from which it can be seen that the distribution of particle size belongs to normal distribution.

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