Superabsorbent Polymeric Materials X: Effect of Degree of Neutralization on Swelling Behavior of Crosslinked Poly(Sodium Acrylate) in Aqueous Salt Solutions

Wen-Fu Lee* and Yu-Lin Huang

Department of Chemical Engineering, Tatung University, Taipei 104, Taiwan, ROC

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Abstract: A series of xerogels based on different degrees of neutralizations (DN) of acrylic acid (AA) and N,N-methylene-bis-acrylamide (N MBA) were prepared by inverse suspension polymerization. The influence of the DN values of AA on water absorbency and swelling behavior for these highly absorbent polymers in deionized water and various saline solutions were investigated. Results indicate that the equilibrium-water absorbency (Qeq) increases with an increase in the DN of AA until the DN value reaches 95% and then decreases at 100% of the DN value. However, the initial absorption rate for these gels decreases with an increase in the DN value of AA in both deionized water and 0.9 wt% NaCl solution. The adsorption of copper ions by these gels was also investigated.

Keywords: Superabsorbent, Water absorbency, Swelling behavior, Xerogel, Sodium acrylate, Inverse suspension polymerization.

Introduction

Superabsorbent polymers, which do not dissolve in water, can absorb and hold a large amount of water under pressure compared with the traditional water-absorbing materials such as cotton, paper, and sponge. Because of their excellent characteristics, these polymers are widely used in many products, such as disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, medicine for drug delivery systems, and absorbent pads. In such applications, water absorbency or water retention is essential [1-8]. Hence, some researches have attempted to modify these absorbent polymers to enhance their absorbency, gel strength, and absorption rate [9-23].

Flory presented the swelling theory for hydrophilic polymers with nonionic network or ionic network structure [24]. Ogawa et al. studied the kinetics of the swelling of poly(sodium acrylate) [poly(SA)] by picture analysis with a microscope-VTR system, calorimetry, and gravimetry techniques [25].

A series of superabsorbent polymers for swelling behavior in deionized water and various saline solutions were reported in our previous reports [26-31]. These polymers included poly(SA) containing nonionic comonomer 2-hydroxyethyl methacrylate (HEMA) [26], zwitterion monoclonomer 3,3-dimethylmethacryloyloxyethyl ammonium propane sulfonate (DMAPS) [27], 3,3-dimethyl acrylamidopropyl ammonium propane sulfonate (DMAAPS) [28], anionic monomer sodium 2-acrylamido-2-methyl propane sulfonate (NaAMPS) [29], and poly(SA) with various initial total monomer concentrations [30].

According to our previous studies, the SA gels containing the nonionic comonomer HEMA reduced the water absorbency but improved initial absorption rate and gel strength. However, contrary results were obtained for an SA gel containing the zwitterion comonomers, DMAPS and DMAAPS, and anionic comonomer NaAMPS. Moreover, the water absorbency increased when the initial total

*To whom all correspondence should be addressed. Tel: 886-2-25925252 ext. 3451; Fax: 886-2-25861939 E-mail: wfllee@ttu.edu.tw

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monomer concentration of poly(SA) increased, but the opposite result was observed for initial absorption rate.

The water absorbency for a water absorbent polymer containing 50-100 mol% of degree of neutralization (DN) of acrylic acid has been reported in many patents, but the water absorbency and swelling behavior for these superabsorbent polymers containing various DNs in deionized water and saline solutions were not investigated in detail. Hence, the main purpose of this article is to investigate the influence of the DN values of AA on the water absorbency and swelling behavior in aqueous solutions.

**Experimental**

1. **Materials**
   
The materials used were purchased from Tokyo Kasei Industries Ltd. including acrylic acid (AA), N,N'-methylene-bis-acrylamide (N MBA). Sodium hydroxide and NMBA were used directly. 4,4'-Azobis(4-cyanovaleric acid) (ACVA) as an initiator and sorbitan monostearate (Span 60) as an inverse suspension stabilizer were also purchased from Tokyo Kasei Industries Ltd. Methanol and cyclohexane were of reagent analytical grade.

2. **Preparation of SA monomer with different DN values**
   
Sodium acrylate (SA) solutions with different DN values were prepared by adding AA to a predetermined amount of aqueous caustic solution in order to obtain a theoretically complete neutralization (sodium hydroxide and AA in equal moles of 0.0075, 0.0085 and 0.0095). Then, 75, 85, and 95 mol% neutralized acrylic acid was obtained by adding 0.0025, 0.0015 and 0.0005 mole of AA to the SA solution. These solutions are hereafter referred to as SA75, SA85, and SA95 [32].

3. **Inverse suspension polymerization**
   
A 300 mL four-neck separable flask equipped with a reflux condenser, a stirring rod and a thermometer was charged into 60 mL cyclohexane and 0.15 g sorbitan monostearate. The mixture was stirred until the sorbitan monostearate was dissolved (continuous phase).

The crosslinking agent, NMBA, was introduced into SA monomer solution and the mixture was stirred until the NMBA was dissolved completely. The monomer solution and 0.15 g initiator, ACVA (dispersion phase), were introduced into the reactor. Air was flushed from the reactor by introducing nitrogen until the entire process was completed. The stirrer speed was maintained at 250 rpm. The polymerization was set at 70 °C for 4 h. After the reaction, the suspension solution was cooled and then precipitated by 800 mL cold methanol under stirring. The product was filtered and washed several times with a mixture of water and methanol (1/9 in volume). The product was then dried in a vacuum oven at 120 °C for 1 day. A white powdered polymer was obtained, and the yield was over 98 %. The compositions of samples are listed in Table I.

4. **Measurement of saturated water absorbency**
   
The samples were dried in a vacuum oven at 70 °C before any tests were conducted. All of the samples were used had a particle sizes in the range of 60-100 mesh.

4.1 **Suction filtration method**
   
The sample (50 mg) was immersed in an excess of deionized water or various NaCl solutions with different concentrations for at least 8 h to reach swelling equilibrium at room temperature. When the sample reached the swelling equilibrium, the residual water was removed by suction filtration with an aspirator (250 mmHg) for 5 min. The gel was weighed and the equilibrium absorbency $Q_{eq}$ was calculated using the following equation:

$$Q_{eq} = \frac{W_{wet} - W_{dry}}{W_{dry}}$$  \hspace{1cm} (1)

where $W_{dry}$ is the weight of the dried sample and