Superabsorbent Polymer Solubilized Instantly by Decrosslinking with Sodium Hypochlorite

Running Head
Superabsorbent Polymer Solubilized Instantly

Abstract
A superabsorbent polymer crosslinked with diacylhydrazine was prepared. The swollen gel was instantly solubilized by treating with a small amount of sodium hypochlorite solution.

Keywords
Superabsorbent polymer, Diacylhydrazine, Oxidative decrosslinking

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Superabsorbent polymers (SAPs), which are typically crosslinked poly(sodium acrylate), absorb a large quantity of water, and retain the absorbed water even under the application of pressure to the swollen gel.[1,2] Owing to its high water-holding ability, SAP has been utilized in various fields, including the fabrication of sanitary products and desert greening. Because a typical SAP can absorb water up to several hundred times its own weight, swollen SAP is always heavy and requires a heavy social load for disposal. Some biodegradable SAPs have been reported.[3] However, degradation of such degradable SAPs proceeds slowly, and high degradability and high chemical stability have been incompatible.

In a previous study, we reported that some polymers crosslinked with diacylhydrazine can be rapidly decrosslinked by the action of sodium hypochlorite solution,[4,5] although diacylhydrazine exhibits appreciable stability under acidic and basic conditions, and is not adversely affected by heat or oxygen.[6-9] These results prompted the study of a novel SAP using a bifunctional diacylhydrazine monomer, **DAH**, as the crosslinker.[5] Since hypochlorite anion is highly hydrophilic, the oxidative degradation of diacylhydrazine occurs most rapidly in water. Thus, the decrosslinking of swollen hydrogel is one of the most effective applications of the oxidative degradation of diacylhydrazine. The

diacylhydrazine-crosslinked SAP (**DC-SAP)** was expected to exhibit stability during use and rapid decomposition after use after treating with sodium hypochlorite solution to make it soluble in water.

The copolymerization of sodium acrylate and **DAH** was carried out in a water initiated with V-501 as a water-soluble initiator (Scheme 1). The reactions were carried out at crosslinking ratios of 5% and 1%. The products were washed thoroughly with water, and the resulting soft hydrogel was poured into methanol little by little to precipitate the powder of **DC-SAP**, which was isolated by filtration, and washed thoroughly by methanol before drying in vacuo. The attenuated total reflection (ATR) IR spectrum of the **DC-SAP** exhibited strong absorption at 1557 cm^{-1}, and a weak absorption band at approximately 1650 cm^{-1} (Supporting Information). The former could be attributed to the $\nu_{C=O}$ of carboxylate, and the latter could be attributed to $\nu_{C=O}$ of the diacylhydrazine crosslinker.

[Scheme 1]

When water was added to the dry **DC-SAP**, it was rapidly absorbed, and the **DC-SAP** formed a swollen gel (see Supporting Information). The water-uptake of the **DC-SAP** was measured, and the results are summarized in Table 1. An very high water-uptake (*i.e.*, *ca*. 80,000%), was observed in the **DC-SAP** at a crosslinking ratio of 1%. The water-uptake of the **DC-SAP**, as well as conventional SAP decreased with increasing crosslinking ratio. It should be noted that the hydrophilic diacylhydrazine moiety did not inhibit the water-absorption of the **DC-SAP**.

Table 1. Water up-take of the **DC-SAP**.

crosslinking ratio	water up-take [a]
5%	10660%
1%	80520%

[a] Weight ratio of the absorbed water/dry SAP after immersion in deionized water for 24 h at 25 °C.

When the swollen polymers were treated with sodium hypochlorite solution, the **DC-SAP** became soluble immediately with the evolution of a small amount of nitrogen gas to obtain a clear solution. In a typical case, a hydrogel prepared from 40 mg of **DC-SAP** (1% crosslinking ratio) and 10 mL of water was treated with 1.0 mL of 5% sodium hypochlorite solution (ca. 150 equiv for diacylhydrazine). The hydrogel turned to a clear

solution within 5 sec (see Supporting Information). In addition to reagent-grade sodium hypochlorite solution, commercially available bleacher can also be used for the solubilization of the **DC-SAP** (see Supporting Information). As expected, the oxidative degradation of the diacylhydrazine moiety in the **DC-SAP** occurred rapidly to decrosslink the SAP.

Although it was difficult to estimate the rate of decrosslinking, the swelling state of **DC-SAP** largely affected the rate of decrosslinking. When dry **DC-SAP** powder was directly immersed in 5% sodium hypochlorite solution, no swelling was observed due to high ion-strength of the solution, and it took over 1 h to complete the dissolution.

The swollen hydrogel kept its shape for over one month. To demonstrate the chemical stability of the diacylhydrazine moiety in the **DC-SAP**, the hydrogel of **DC-SAP** swollen in 5% sodium hydroxide solution was heated at 100 °C for 36 h. Although the swollen gel remained unchanged, it immediately dissolved when a small amount of sodium hypochlorite solution was added. Thus, diacylhydrazine crosslinker did not decompose even in strong alkaline solution at high temperature, while it rapidly degraded via the oxidation with hypochlorite.

Because carboxylic acid is generated by the oxidation of diacylhydrazine by sodium hypochlorite, the degradation product of the **DC-SAP** was deduced to be pure poly(sodium acrylate). Thus, the solution was acidified after solubilization, and the precipitate was collected. Figure 1 shows the IR spectrum of the resulting polymer. The absorption peak of the $\nu_{C=O}$ of carboxylic acid was observed at 1720 cm^{-1}, and no shoulder was observed at approximately 1650 cm^{-1}, indicating that solubilization occurred via the oxidative degradation of the diacylhydrazine to carboxylic acid to decrosslink **DC-SAP**.

[Figure 1]

In this paper, the synthesis, water-uptake, and instant solubilization of diacylhydrazine-crosslinked SAP (**DC-SAP**) were described. It was demonstrated that the decomposition product was pure poly(sodium acrylate), and it should be noted that poly(sodium acrylate) and poly(acrylic acid) are the extremely safe substances. Because sodium hypochlorite is an inexpensive and readily available chemical, decrosslinking is fairly rapid, and the chemical oxidation of diacylhydrazine can proceed even in the presence of possible contaminations in SAP, the **DC-SAP** can be used as an alternative to the conventional SAP to reduce the load required for the disposal of SAP.

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Titles and legends to Figure

Scheme 1. Preparation of **DC-SAP**.

Figure 1. IR spectrum of the decrosslinking product isolated as the precipitate after the acidification of the reaction mixture.