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Phase Transition Behavior of Poly(N-isopropylacrylamide-co-N,N-dimethylaminopropylacrylamide) Hydrogels

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Abstract

The copolymer hydrogel of N-isopropylacrylamide (NIPAAm) and N,N-dimethylaminopropylacrylamide (DMAPAA) was synthesized by free radical copolymerization. The phase transition behavior of p(NIPAAm-co-DMAPAA) hydrogels as a function of temperature and SDS concentration was studied. The p(NIPAAm-co-DMAPAA) hydrogels exhibited larger swelling capacity than the homo p(NIPAAm) hydrogel. The phase transition temperature of p(NIPAAm-co-DMAPAA) hydrogels increased with an increase of DMAPAA content. In aqueous SDS solution, the swelling capacity of p(NIPAAm-co-DMAPAA) hydrogel decreased with an increase of SDS concentration. The phase transition temperature of p(NIPAAm-co-DMAPAA) hydrogels was found to be almost independent of the SDS concentration.

Introduction

Hydrogels are hydrophilic polymer of both natural and synthetic origin that can absorb large amounts of water while being insoluble in water due to the presence of the three-dimensional network [1]. Their phase transition behavior is generally known to depend on the changes of external conditions such as temperature[2-4], pH [5], solvent composition [5-8], and so forth. Hydrogels have been extensively utilized in the biomedical [9-11], pharmaceutical [12-14], and related fields. In the previous report, we studied the effects of crosslinking density and introduction of acidic monomers such as acrylic acid or methacrylic acid on the phase transition of N-isopropylacrylamide hydrogel [15]. Through this study, we have found that the water content of N-isopropylacrylamide hydrogel decreased with an increase of crosslinking density and the thermosensitivity of N-isopropylacrylamide hydrogel with acidic monomers was affected by the pH change. In this paper, we have investigated the effects of gel composition and the anionic surfactant (sodium dodecyl sulfate, SDS) on the swelling properties and phase transition temperature of positively ionized, N-isopropylacrylamide copolymer hydrogel with N,N-dimethylaminopropyl acrylamide.

Experimental

Materials

N,N-dimethylaminopropylacrylamide(DMAPAA, in 75% aqueous solution) and N-isopropylacryamide(NIPAAm) were purchased from Kohjin Co.(Tokyo Japan), NIPAAm was purified by recrystallization in benzene by adding hexane. N,N'-methylenebis(acrylamide)(MBAAm) and N,N,N',N'-tetramethylenediamine(TEMED) were purchased from Aldrich Chem. Co.(Milwaukee, Wisconsin, USA). MBAAm was purified by recrystallization from methanol. Potassium persulfate was purchased from Junsei Co.(Tokyo, Japan) and was purified by recrystallization from ethanol. SDS was purchased from TCI Co.(Tokyo, Japan) and were used without further purification. In all the experiments below triply distilled water was used.

Hydrogel synthesis

Homo DMAPAA hydrogels were prepared by free radical polymerization. MBAAm (0.3 g, crosslinker).

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TEMPED (50 μg, accelerator) and potassium persulfate (50 mg, initiator) were mixed with DMAPAA (7.7 g)in aqueous solution and polymerization was carried out at 70°C for 2h under dry nitrogen atmosphere. Degree of crosslinking of hydrogel was controlled by the amount of MBAAm to find the maximum water absorption point. After the reaction was completed, hydrogels prepared were thoroughly washed over the sufficiently long period so as to ensure the complete removal of any residual chemicals and stored in aqueous solution to reach the swelling equilbrilium. NIPAAm-co-DMAPAA hydrogels were prepared by free radical copolymerization of DMAPAA and NIPAAm, using MBAAm as the crosslinker. DMAPAA was added at concentrations from 1.0 to 4.0 mol % with respect to NIPAAm (7.7 g) in ethanol/water (3:2 by volume), and then the reaction was carried out in micropipettes (Φ = 1.7 mm) under dry nitrogen atmosphere at 70°C for 2h. [It needs to be noted that the above mol % of DMAPAA for copolymer hydrogels corresponds to the feed composition adopted just for the qualitative comparison in this study.] After the gelation was completed, the products were also thoroughly washed to remove any residual chemicals, and cut into suitable lengths.

Swelling measurements

To measure the swelling characteristics of new synthetic gels, pDMAPAA and p(DMAPAA-co-NIPAAm) hydorgels were cut into small pieces. The cylindrical gels were equilibrated in water and SDS solutions with different concentrations: 0.1, 0.5, 1.0, 3.0, 5.0, and 10 mM, respectively, for 12 h at 10 ~ 70°C. Temperature was controlled within ±0.1°C by circulating water around the gels during the measurement. The weight of gel before and after equilibrium swelling was measured in a specially designed sieve. Water content (%) was calculated according to Eq.(1):

$$Water\ content\ (\%) = (M_s - M_d) / M_s \times 100 \qquad (1)$$

where M_s and M_d indicate the weights of swollen and dry gels, respectively. The swelling capacity was determined as the weight ratio of swollen gel to dry gel.

Results and discussion

The kinetics of water adsorption for p(DMAPAA) and p(NIPAAm) hydrogels at 25°C is shown in Fig. 1. The water adsorption of the hydrogels drastically increased within 5 min and then gradually leveled off with increasing time. The water contents of p(NIPAAm) and p(DMAPAA) hydrogels are 82% and 95%, respectively, for early 5 min. The first abrupt change of the water content indicates that the absorption of water on the hydrogels occurs at a fast process. The absorbed water content of p(DMAPAA) hydrogel was larger than that of p(NIPAAm) hydrogel. This is considered to arise from the fact that the tertiary amine groups of p(DMAPAA) provide the site for hydrogen bonding between polymer and water molecules.

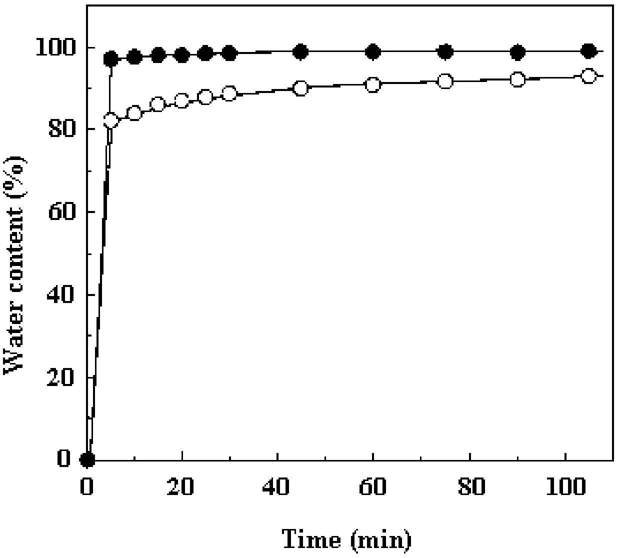

Fig. 1. The kinetics of water adsorption for p(DMAPAA) (●) and p(NIPAAm) (○) hydrogels as a function of time at 25°C.

The change of water content of homo p(DMAPAA) hydrogel as a function of time at different temperatures is shown in Fig. 2. The water content of p(DMAPAA) hydrogel was kept constant at 30°C. The water content of p(DMAPAA) hydrogel decreased with an increase of temperatures. To be dehydrated, sufficient energies to break hydrogen bonding has to be supplied to the hydrogels. At lower temperatures, it is difficult for the hydrogels to expel the water molecules, which may bind with hydrogel via hydrogen bonding. At 60°C, however, the hydrogel starts to expel the water molecules around 12 h, and after 18 h the hydrogel was equilibrated. At 70°C the hydrogel starts to expel the water around 8 h, and after 12 h the hydrogel was equilibrated. It is thought that this effect results from the dehydration of p(DMAPAA) hydrogel by an increase of temperature.

As can be seen from Fig. 2, the p(DMAPAA) exhibited a high phase transition temperature compared to that of p(NIPAAm), 32°C.

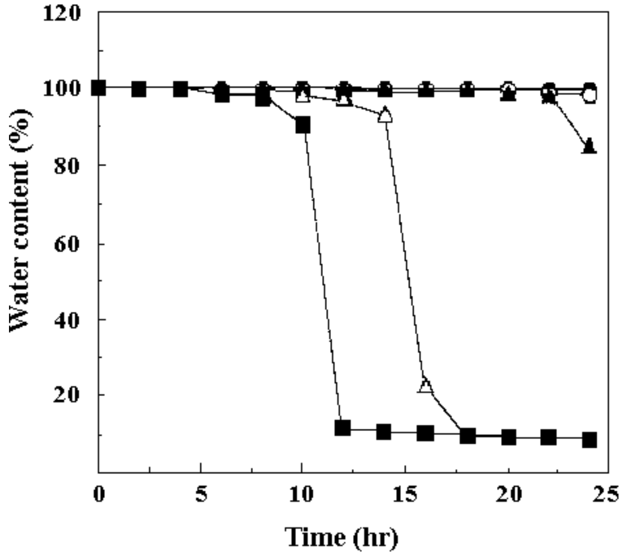

Fig. 2. The change of water content of p(DMAPAA) hydrogel as a function of time at different temperatures. The temperatures were 30°C (●), 40°C (○), 50°C (▲), 60°C (△) and 70°C (■), respectively.

In order to investigate the effect of positive charge introduced on the swelling equilibrium of nonionic p(NIPAAm) hydrogel, the random copolymer of NIPAAm and DMAPAA was synthesized. Equilibrium swelling curves of homo p(NIPAAm) hydrogel and p(NIPAAm-co-DMAPAA) hydrogels with different DMAPAA concentrations were measured as a function of temperature. Figure 3 shows the change of swelling capacity of p(NIPAAm-co-DMAPAA) hydrogels as a function of temperature in water. The swelling capacity of homo p(NIPAAm) hydrogel was smaller than that of p(NIPAAm-co-DMAPAA) hydrogels. The swelling capacity of p(NIPAAm-co-DMAPAA) hydrogels and volume change at the phase transition increased with an increase of DMAPAA content. As the DMAPAA parts of p(NIPAAm-co-DMAPAA) hydrogel are ionized in aqueous solution, the copolymer hydrogels become more hydrophilic than homo p(NIPAAm) hydrogel, and hence the hydrophilicity increased may contribute to the stronger hydrogen bonding and result in the increased swelling capacity. The thermo-reversible phase transition of p(NIPAAm) hydrogel occurred at approximately 32°C. On the other hand, the p(NIPAAm-co-DMAPAA) hydrogels had relatively higher phase transition temperatures than the p(NIPAAm) hydrogel. The phase transition temperature of p(NIPAAm-co-DMAPAA) hydrogels increased with an increase of DMAPAA content. All the swelling curves of p(NIPAAm-co-DMAPAA) hydrogels with lower DMAPAA content merged into a single line at the shrunken state of p(NIPAAm) gel at 80°C. However, the p(NIPAAm-co-DMAPAA) hydrogel having 4 mol % DMAPAA does not entirely shrink up to 80°C due to the presence of high ionic osmotic pressure. The swelling capacity of hydrogels decreased with an increase of temperature. This phenomena could be ascribed to the dehydration of hydrogels caused by an increase of temperature.

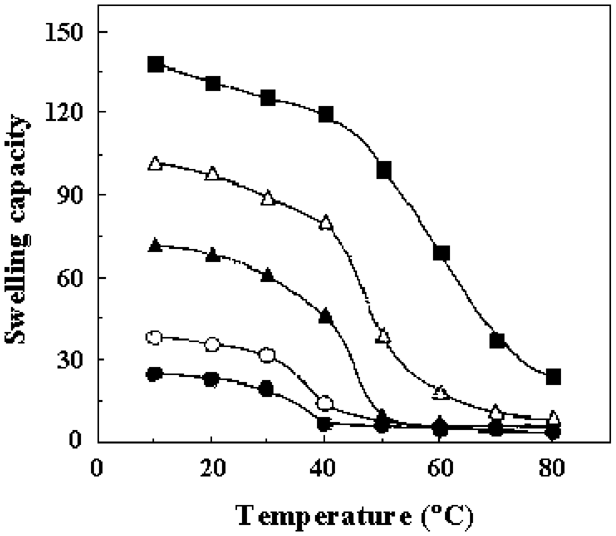

Fig. 3. Change of swelling capacity of p(NIPAAm-co-DMAPAA) hydrogel as a function of temperature in water. The concentrations of DMAPAA in p(NIPAAm-co-DMAPAA) copolymer were 0 mol % (●), 1.0 mol % (○), 2.0 mol % (▲), 3.0 mol % (△) and 4.0 mol % (■), respectively.

In Figure 4, the effect of anionic surfactant (SDS) on the thermo-reversible swelling process of the p(NIPAAm-co-DMAPAA) hydrogel was studied as a function of temperature and surfactant concentration. Figure 4 shows the SDS concentration dependence for the change of swelling capacity of p(NIPAAm-co-DMAPAA) hydrogels at 20°C. The swelling capacity of p(NIPAAm-co-DMAPAA) hydrogels in aqueous SDS solutions decreased with an increase of SDS concentration. This may suggest that SDS binds to the polymer network within the gel phase through both electrostatic and hydrophobic interaction, subsequently converting the p(NIPAAm-co-DMAPAA) gel into a neutral gel.

Figure 5 shows the temperature dependence for

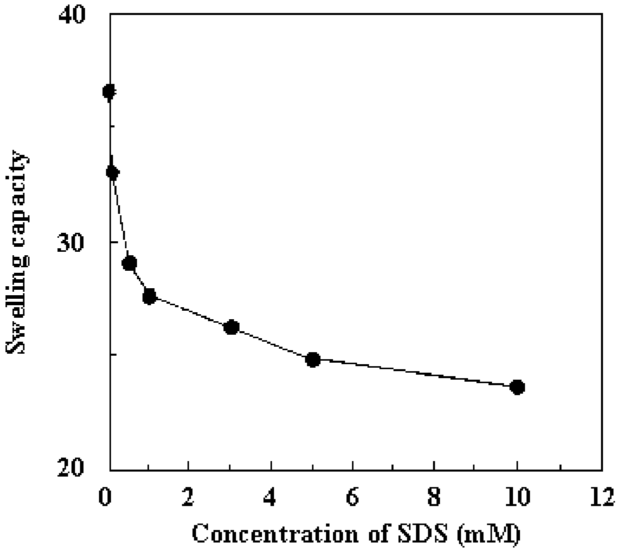

Fig. 4. Change of swelling capacity of p(NIPAAm-co-DMAPAA) hydrogel as a function of SDS concentration at 20°C. The concentration of DMAPAA in p(NIPAAm-co-DMAPAA) copolymer was 1.0 mol %.

the change of swelling capacity of p(NIPAAm-co-DMAPAA) hydrogels in various SDS solutions. The swelling capacity of p(NIPAAm-co-DMAPAA) hydrogel with 1.0 mol % DMAPAA in all SDS solutions decreased with an increase of temperature. The phase transition temperature of p(NIPAAm-co-DMAPAA) hydrogels was almost independent of the concentration of SDS solutions employed. In surfactant solution, the swelling capacity of p(NIPAAm-co-DMAPAA) hydrogels was affected by the association of hydrogels and surfactant. As the surfactant dissociated and becomes electrolytic character in aqueous solution, there will arise an interaction between hydrogel and surfactant. This electrolytic interaction may reduce the amount of hydrogen bonding between hydrogels and water molecules. Accordingly, as the concentration of SDS is increased, there will be more association between hydrogel and surfactant. Thus, the swelling capacity of copolymer hydrogels decreased with increasing SDS concentration at temperature below the phase transition. Finally, the hydrogels of p(NIPAAm-co-DMAPAA) discussed above are expected to posess not only thermo- but also pH-sensitivity owing to the cationic character of DMAPAA, the pH-sensitivity of copolymer hydrogels will be investigated in a forthcoming study.

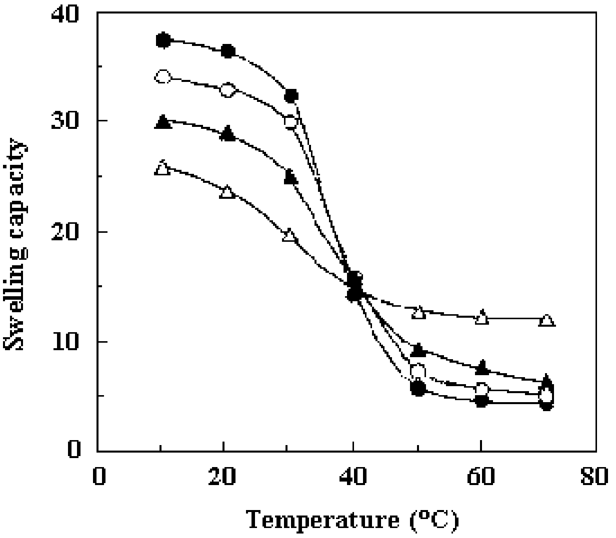

Fig. 5. Change of swelling capacity of p(NIPAAm-co-DMAPAA) hydrogel as a function of temperature in various SDS solutions. The concentrations of SDS were 0 mM (●), 0.1 mM (○), 0.5 mM (▲) and 10.0 mM (△), respectively. The concentration of DMAPAA in p(NIPAAm-co-DMAPAA) copolymer was 1.0 mol %.

Conclusion

The introduction of positively charged group (DMAPAA) into the nonionic p(NIPAAm) hydrogels caused both the swelling capacity and the phase transition temperature of the hydrogels to increase. The swelling capacity of p(NIPAAm-co-DMAPAA) hydrogels was found to be strongly affected by the concentration of anionic surfactant (SDS). However, the concentration of anionic surfactant had little effect on the phase transition temperature of p(NIPAAM-co-DMAPAA) hydrogels.

Acknowledgments

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