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Phase Transition of N-Substituted Acrylamide Gels

In hydrogels there sometimes occurs a reversible, discontinuous large volume change in response to a continuous change in environmental conditions such as solvent composition, pH, ionic composition, and temperature.[1–3] This kind of phase transition is observed universally in various natural and synthetic gels. Recently, poly(*N*-isopropylacrylamide) gels (abbreviated as NIPA gel) in water have been shown to exhibit a thermoshrinking type of transition,[4] in which the collapse of the gels occurs in response to an increase in temperature. These temperature-sensitive gels have been attracting much attention because of their technical importance and scientific interest. The temperature-induced collapse transition of the gels is analogous to the phase separation of polymer solutions with a lower critical solution temperature (LCST),[5] which cannot be explained by conventional polymer–solution theories such as the Flory–Huggins model.[6] This means that the thermoshrinking type phase transition of gels cannot be explained by Tanaka's theory, based on the Flory–Huggins model, and may depend largely on the affinity between the polymer chain and the solvent, water.

In previous papers, we focused on the molecular structure of *N*-isopropylacrylamide, which has not only hydrophilic groups (NH, C═O) but also a hydrophobic group (isopropyl), and suggested from differential scanning calorimetry (DSC) analyses that hydrophobic interaction as well as hydrophilic interaction may play an important role in the thermoshrinking type transition.[7] Furthermore, we proposed a theory that considered hydrophobic interactions and demonstrated the applicability of the model to the expression of thermoshrinking phase transitions.[8] Judging from these results, gels whose monomers are composed of both hydrophobic and hydrophilic groups have the possibility of undergoing a thermoshrinking type phase transition in water.

Recently, Ito[9] examined the solubility of a series of poly(*N*-alkylacrylamides) in water. According to his results, the solubility depended on the side-chain length of the alkyl group, and some poly(*N*-alkylacrylamides) showed phase separation at higher temperatures in water. In the present paper, we synthesized gels of *N*-*n*-propylacrylamide and *N*-cyclopropylacrylamide whose polymers showed LCST type phase behavior in water and compared their phase transitions in water with that of NIPA gel.

Preparation of Samples. Monomers of *N*-*n*-propylacrylamide (NNPA) and *N*-cyclopropylacrylamide (NCPA) were prepared from the corresponding alkylamines and acryloyl chlorides via the following reaction:[9]

$$\mathrm{CH_2{=}CHCOCl + NH_2R + (C_2H_5)_3N \xrightarrow[\text{benzene}]{0\text{–}10\ ^\circ\mathrm{C}} CH_2{=}CHCONHR + (C_2H_5)_3NHCl}$$

The synthesized monomers were purified by vacuum distillation under a nitrogen atmosphere. NIPA monomer, provided by Eastman Kodak Co., was purified by recrystallization from a benzene/*n*-hexane mixture.

Gel samples were prepared by free-radical polymerization in water at room temperature according to a method reported by Hirotsu et al.[10] Reagents, *N*,*N*′-methylenebisacrylamide (BIS; cross-linker), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED; accelerator) were special grade products of Tokyo Kasei Kogyo Co., Ltd., and were used without further purification. Potassium persulfate (KPS) was used as an initiator after recrystallization from a water solution. Monomers of the main constituent of the gels (NIPA/NNPA/NCPA), BIS, and TEMED were dissolved in distilled, degassed water. To the solution was added 30 mM of the initiator, and the concentrations of the monomer, BIS, and TEMED were adjusted to ca. 700, 25, and 0.012 mM, respectively. This pregel solution was then transferred into a vial containing glass tubes of 1.65-mm inner diameter. After gelation was complete (1 h), the 1.65-mm-diameter gels were taken out of the tubes and immersed in water for 1 day to wash away any residual chemicals. Then these gels were cut into 1.6–1.7-mm-length rods.

Polymer solutions of NIPA, NNPA, and NCPA were prepared by the following method. Monomers were dissolved in benzene that had been degassed by bubbling nitrogen gas and polymerized in a sealed tube with azobis(isobutyronitrile) (AIBN) as the initiator at 60–70 °C. The polymers were separated by the precipitation technique from the reaction solution using *n*-hexane and fractionated in an acetone/*n*-hexane mixture at room temperature.

Measurement of Swelling Equilibria and Transition Temperatures. The gel rods were immersed in an excess of pure water until equilibrium was attained. The diameter of the gels, *d*, was measured by calibrated scale photography. The swelling ratio of the gels was calculated from the ratio of the equilibrium gel diameter to the original diameter d_0 as follows:

$$\text{swelling ratio } V/V_0 = (d/d_0)^3$$

where d_0 is 1.65 mm. The experimental uncertainty of swelling ratio measurements was estimated to be 15%.

Phase transition temperatures of the gels and the cloud points of the polymer solutions were measured by thermal analysis with a differential scanning calorimeter (Seiko I. Inc., Ltd., DSC-100). For the DSC measurements, 15 mg of sample was used, and pure water was adopted as reference. The scanning rate was set at 0.5 °C/min for the gels and 1.0 °C/min for the polymer solutions to obtain clear DSC thermograms. The transition temperatures were determined from the intersection point of the base line and the leading edge of the endotherm. The details of the determination technique were described in our previous paper.[7]

Results and Discussion. Figure 1 shows the temperature dependence of the equilibrium swelling ratio of NNPA and NCPA gels together with that of NIPA gel. The swelling of the gels in water is strongly dependent on the structure of the monomer composing the gels. NCPA gel underwent a continuous volume change in a higher temperature region (40–50 °C). NNPA gel, on the other hand, showed a discontinuous volume transition around 25 °C, 10 °C lower than NIPA.

The DSC thermograms upon heating of these gels are shown in Figure 2. While clear endothermic peaks corresponding to the phase transition were observed for NNPA and NIPA gels, no indication of transition for NCPA gel was detected even in the thermal analyses. The transition temperatures determined from the DSC thermograms for NNPA and NIPA gels were close to the temperatures at which the gel volumes changed discontinuously as shown in Figure 1. The transition heats for NNPA and NIPA gels were 3.4 and 2.4 kJ/mol, respectively.

Figure 3 shows the cloud points for the polymer aqueous solutions of NNPA ($M_w = 2 \times 10^5$) and NIPA ($M_w = 3 \times 10^6$). The cloud temperatures measured in this work agreed with the values reported by Ito for these systems within experimental error and were only slightly lower than the corresponding temperatures of the volume transition of

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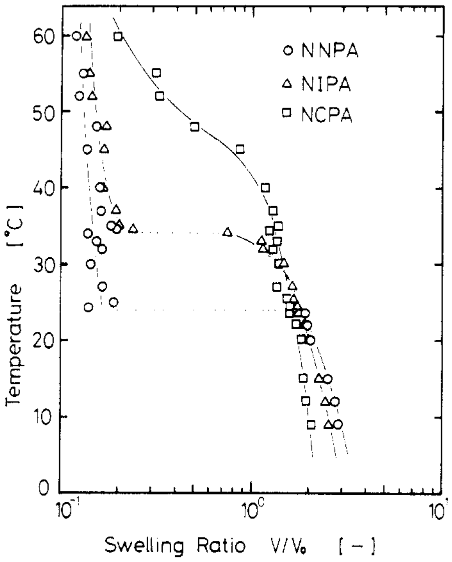

Figure 1. Swelling equilibria for gels of *N*-isopropylacrylamide (NIPA), *N*-*n*-propylacrylamide (NNPA), and *N*-cyclopropylacrylamide (NCPA).

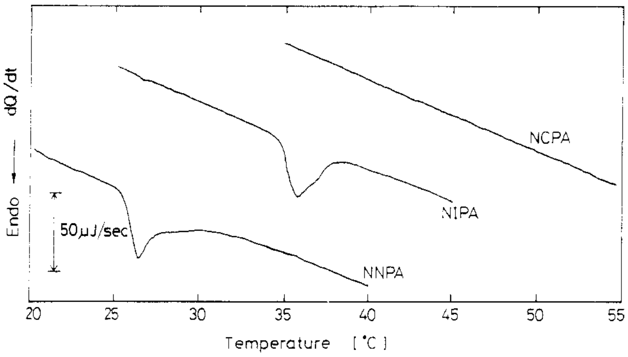

Figure 2. DSC thermograms of NIPA, NNPA, and NCPA gels.

the gels. The cloud temperatures for both samples gradually decreased with concentration, which confirmed that the phase separation of both samples was LCST behavior.

In previous papers,[7,8] we pointed out that the thermoshrinking type of volume phase transition of hydrogels in water and the LCST type phase separation of polymer aqueous solutions might both be induced through an aggregation of polymer segments due to the hydrophobic interaction. Generally, the strength of the hydrophobic interaction is proportional to the number of water molecules that form the hydrophobic hydration and increases with temperature. It can therefore be presumed that the gel whose hydrophobic group has a larger surface (contact) area undergoes a discontinuous volume phase transition in water at lower temperatures due to the strength of the hydrophobic interaction. Among the alkyl substitutes of the acrylamide used in this study, the surface area of the cyclopropyl group of NCPA is the smallest and that of the *n*-propyl group of NNPA is larger than that of the isopropyl group of NIPA. Our experimental results for these gels and polymer solutions, shown in Figures 1–3, substantiate the presumptions mentioned above and confirm the theoretical model proposed in a previous paper. As for NCPA, the strain of the bond angles of the cyclopropyl group as well as its surface area can be considered to weaken the hydrophobic interaction between cyclopropyl groups at higher temperatures, because the strain reduces the overlap of electron clouds and makes the cyclopropyl group more hydrophilic compared with the isopropyl group.[11]

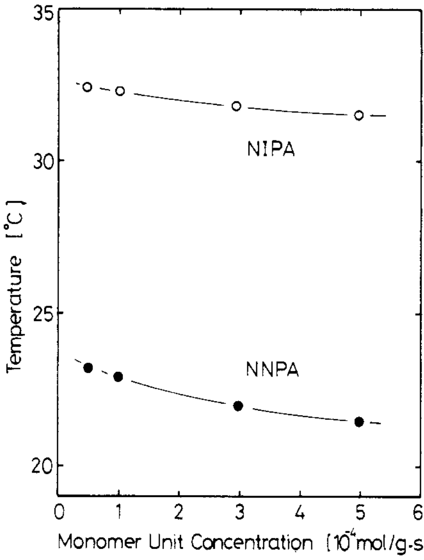

Figure 3. Cloud points determined from DSC analyses for polymer aqueous solutions of NIPA and NNPA. It was demonstrated in a previous paper[7] that the transition points from DSC thermograms could be regarded as the cloud points. The polymer concentration is described by that of monomer units in a unit weight of the solution.

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