EFFECT OF pH ON THE PHASE TRANSITION OF N-ISOPROPYLACRYLAMIDE-SODIUM ACRYLATE COPOLYMER GEL

YOSHIMI SEIDA*1) AND YOSHIO NAKANO*2)
Dept. of Chemical Engineering, Shizuoka University, Johoku 3-5-1, Hamamatsu, Shizuoka 432

Key Words: Polymer Gel, N-isopropylacrylamide, Sodium Acrylate, pH, Hydrogen Bonding, Phase Transition, Thermosensitive Swelling

Introduction

Volume phase transition of gels is induced by intermolecular forces such as ionic7,10), hydrophobic2,3,9), van der Waals6) and hydrogen bonding5) forces. The phase behavior of gel induced by these forces has been classified into four types by IImain et al4). It is possible to control the phase behavior of a gel by means of molecular design. For example, the thermosensitive swelling of N-substituted acrylamide gel, which shrinks at high temperature in water due to hydrophobic interaction of its network, depends on its molecular structure5). The hydrophobicity of N-substituent plays an essential role in the thermosensitive swelling of the gel. The temperature at which the gel collapses (phase transition temperature, $T_p$) decreases with the hydrophobicity of N-substituent. In the case of copolymer gel prepared with two kinds of N-substituted acrylamide monomers having different hydrophobicities, the thermosensitive swelling depends on the hydrophobicity as well as the composition of the two monomers3,8,12).

In the present study, N-isopropylacrylamide-sodium acrylate copolymer gel was synthesized to study the dependency of thermosensitive swelling on solution pH. In low-pH solution the gel showed a decrease of $T_p$ with ionic group content. Such phase behavior of the thermosensitive gel is different from those of hydro-
philic-monomer copolymerized gels reported so far\(^ {3,8,12}\). The force acting between the polymer networks which affects the decrease of \( T_p \) was examined.

1. Experimental

1.1 Sample preparation

\( N \)-isopropylacrylamide-sodium acrylate copolymer gel (NIPA-SA copolymer gel) was prepared by a free radical copolymerization as follows. 70 mmol mixture of \( N \)-isopropylacrylamide: NIPA (Eastman Kodak Co. Ltd.) and sodium acrylate: SA (prepared in our laboratory) monomer was dissolved in 100 ml distilled water to prepare a 700 mM solution of NIPA + SA. 0.7 mmol of \( N, N' \)-methylenbisacrylamide (crosslinker), and 6 mmol of ammonium persulfate (initiator) was added. This solution was polymerized after \( N_2 \)-purge and the addition of 400\( \mu \)l of tetramethylethylenediamine (accelerator) at 273K. After the polymerization, the gel was crushed into pieces and immersed in a large amount of distilled water to wash away the residual chemicals. The gel was sieved to collect the sizes of 355\( \mu \)m to 425 \( \mu \)m in diameter after drying at room temperature.

1.2 Equilibrium swelling volume of gel

0.02 g of sample gel was placed in a testing glass tube filled with 10 ml of pH-controlled solution and kept in a temperature-controlled water bath for 24 hr. The equilibrium swelling volume of the gel was determined by the packing height of the gel. The pH of the solution was controlled by HCl or NaOH and the pH value after equilibrium was employed because the pH changed during the experiment due to ion exchange with the gel.

1.3 Measurement of phase transition temperature \( (T_p) \)

The phase transition temperature of the gel in each pH solution was measured by DSC: differential scanning calorimeter (Seiko Instr. Inc., DSC220). The scanning range was set from 293K to 333K and the scanning rate was 2K/min.

Figure 1 shows the pH dependency of the equilibrium thermosensitive swelling volume of the gel with 50 mM SA (ionic group). In the low-pH (<4) solution, the thermosensitive swelling was similar to that of pure NIPA gel reported elsewhere\(^ {3,12}\). In the high-pH (>5) solution, the thermosensitive swelling became more moderate than that observed in the low-pH solution, depending on the solution pH. Similar behavior was observed with increase of SA content. The gel did not collapse in its close-packed state at even a higher temperature. This means that the thermosensitive swelling depends on the amount of dissociated ionic groups. The increase of SA content raised the \( T_p \) in the high-pH solution and reduced the \( T_p \) in the low-pH solution. These phenomena were explained clearly by the following results of DSC analysis.

Figure 2 shows the relationship between \( T_p \) and solution pH in equilibrium for a series of gels. The dissociation curve of acrylic acid (\( et \)) is shown by the dotted line in the figure. No dependence of \( T_p \) on solution pH appeared over the range of pH of 2 to 11 in pure NIPA gel. \( T_p \) of NIPA-SA copolymer gels decreased with ionic group content in the low-pH (<3) solution, in which a considerable number of ionic groups were undissociated (proton type) due to ion exchange with the outer solution\(^ {7,11}\). To the contrary, \( T_p \) increased in the high-pH solution, in which a considerable number of ionic groups were dissociated (sodium type)\(^ {7,11}\). \( T_p \) of the gel with 10 mM SA no longer increased under the complete dissociation of the all ionic groups (pH>7). \( T_p \) disappeared when the content of SA in the gel was still higher, 50 and 100 mM in the region of pH higher than 6 due to excess increase of hydrophilicity. The increase of copolymerized hydrophilic content in NIPA copolymer gels generally increases the \( T_p \) of the gel as well as its swelling volume\(^ {3,8,12}\). Therefore, the hydrophobicity of the gels is weakened and \( T_p \) increases with SA content.
results in the low-pH solution as shown in Fig.2, however, are not consistent with this tendency. It is well known that polycarboxylic acids such as poly (acrylic acid) or poly (methacrylic acid) form polymer-polymer complexes with poly (acrylamide), poly (ethylene glycol), poly (vinyl pyrrolidone) and so on. These polymer-polymer complexes are induced by hydrogen bonding under appropriate conditions of pH. In the NIPA-SA copolymer system it may be possible to form a hydrogen bonding complex between NIPA and neighboring acrylic acid in low-pH solution. The electrostatic interaction of the network disappears, reducing the polymer-polymer distance in the undissociated ionic group. NIPA forms complex with acrylic acid not only through hydrogen bonding but also through ion-dipole interaction between the partially protonated amide group of NIPA and the dipole of C = O of the carboxylic group of acrylic acid, as shown in Fig.3. The hydrogen bonding complex enhanced the decrease of \( T_p \) of the gel in the low-pH solution. The effect of the hydrogen bonding complex on \( T_p \) is made clearer by the following discussion. Fig. 4 shows the thermosensitive swelling of NIPA gel in the aqueous solution of acrylic acid AA (pH = 2) and sodium acrylate SA (pH = 7.8). The free molecules of AA interact with NIPA through hydrogen bonding in this system. \( T_p \) of the gel decreased drastically with the addition of AA (proton type), while it decreased a little by the addition of SA. We also confirmed the state of water in these solutions by the DSC analysis and found that SA bonded the water more strongly than AA. As the hydrophobic interaction is the entropic phenomenon caused by the structural rearrangement of water molecules, the additive which bonds water strongly may result in lower \( T_p \) due to the decrease of entropy. Regardless to this understanding, the gel in the solution with AA resulted in lower \( T_p \) (Fig.4). From these results, the potential force that decreases \( T_p \) drastically in the solution AA is hydrogen bonding. Therefore, we concluded that the decrease of \( T_p \) in the NIPA-SA copolymer gel was induced by hydrogen bonding.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 6555705) from the Ministry of Education, Science and Culture of Japan.

Literature cited