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Communications to the Editor

Phase Transition of Hydrogels by "Pinpoint-Variation" of Polymer Side Chains

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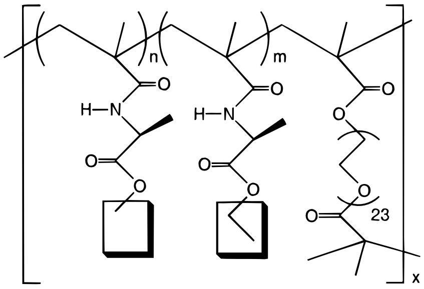
Synthetic polymer hydrogels consisting of hydrophobic polymer chain networks have been shown to represent a phase transition accompanying drastic discontinuous or continuous volume change with variation of surrounding conditions such as temperature or aqueous-organic solvent composition.[1−6] The change in volume of the hydrogels at an equilibrium state in the aqueous medium results from free energy changes of rubber elasticity of the polymer chain networks and in mixing those with water.[2] The latter reflecting the interaction of hydrophobic polymer chains with water molecules absorbed into the gel should vary not only with the change in the external circumstances but also with the variation of the nature of polymer chains. We found that a very small "pinpoint-variation" of the hydrophobic−hydrophilic character of the polymer chains containing L-alanine alkyl esters induced a phase transition with an abrupt volume change of the hydrogel at a consistent external temperature, and also that the degree of the hydrophobicity of the terminal alkyl groups of the side chains in the polymer chain determines the temperature at which the volume phase transition occurs. These novel facts suggest that the variation of the hydrophobic−hydrophilic character of polymer chains for the volume phase transition of hydrogels is equivalent to the variation of the external circumstance such as temperature.

The copolymers examined in this study consist of various portions of monomer units methacryloyl-L-alanine ethyl ester (MA-Ala-OEt) and methacryloyl-L-alanine methyl ester (MA-Ala-OMe),[7] so that they are characterized to have almost the same chemical structures with methacryloyl main chain and L-alanine ester side chains, except for the "pinpoint-difference" in the terminal small alkyl groups. The ethyl group enhances the hydrophobic character of the hydrogel, while the methyl group lowers it. Thus, we can study the hydrogels with a very small difference in hydrophobicity by changing the composition of pendant L-alanine ethyl and methyl esters.

Figure 1 represents the relationship between the composition of MA-Ala-OEt and MA-Ala-OMe in the copolymers and degree of swelling (S_w)[8] of the copolymer gels. The polymer gel consisting of 100% of MA-Ala-OEt showed a consistent S_w 4 with variation of temperature. In this polymer, the terminal ethyl groups with enhanced hydrophobic character associate with each other to prevent absorption of water molecules into the hydrogel.[9] Contrary to the homopolymer, the S_w values for the copolymers of MA-Ala-OEt and MA-Ala-OMe first decreased and increased dramatically with increasing portions of MA-Ala-OMe. For example, at the external temperature of 10 °C, the S_w of the copolymer hydrogel first decreased to 0.7 for a collapsed phase from the composition of MA-Ala-OEt/MA-Ala-OMe of 80/20 to that of 50/50 but abruptly increased to 13 at that of 40/60 and maintained at 15 for a swollen phase from those 30/70 to 0/100. This result shows that the terminal hydrophobicity on the pendant L-alanine ester group in the copolymer chains determines the swelling nature of the hydrogel and that there occurs a phase transition from a collapsed phase to a swollen one in the copolymers with the composition of MA-Ala-OEt/MA-Ala-OMe from 50/50 to 40/60 at 10 °C. It should be noted that the copolymer containing 10% MA-Ala-OMe showed only a slight variation in S_w depending on the change in temperature. This fact suggests that the development of both (a collapsed and swollen) phases characteristic of the copolymer systems needs introduction of some extent (over 10%) of comonomer.



Chemical structure of polymer hydrogel

The same phase transition of the copolymer hydrogels was observed at a temperature lower than 30 °C, and the composition of L-alanine ethyl and methyl esters in the copolymer at the midpoint of the phase transition varies with external temperature: 14/86 at 20 °C, 46/54 at 10 °C, 66/34 at 5 °C, and 83/12 at 0 °C. Interest-

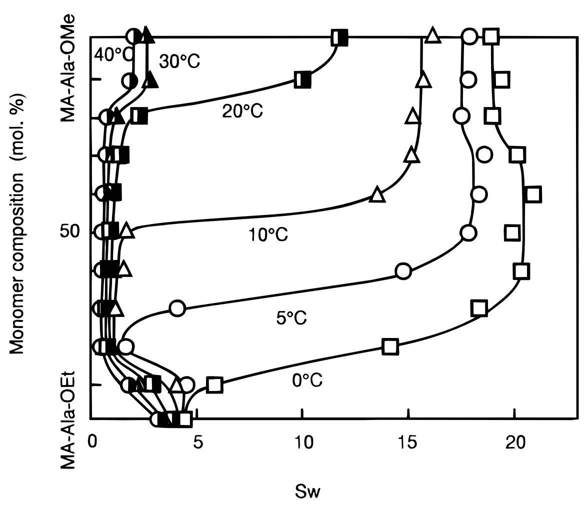


Figure 1. Dependence of the degree of swelling (S_w) of hydrogels on the composition of L-alanine methyl and ethyl ester side chains in copolymers.

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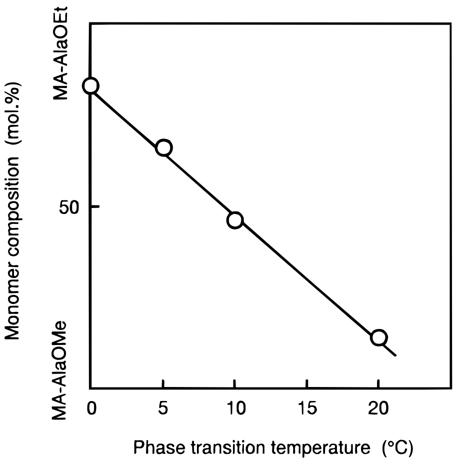

Figure 2. Monomer compositions in the copolymer gel at specific phase transition temperatures.

ingly, these monomer compositions in the copolymer gels at the phase transition are linearly related with the temperatures of the aqueous medium where the gels are allowed to stand, as shown in Figure 2.

It is a surprising fact that the dramatic volume phase transition from the swollen state to the collapsed one is caused by the change in only 10–20% of the terminal alkyl groups as a minor structural part in the MA-Ala copolymers from methyl to ethyl. This fact suggests that the equilibrium between a polymer–polymer interaction and a polymer–solvent one established in the hydrogels is much more sensitive to the hydrophobic–hydrophilic character of the polymer chains than one can expect.

The swelling nature of the hydrophobic polymer gels in the aqueous medium has been explained by the formation of an ice-like structure of water molecules around hydrophobic groups which is familiar in proteins. The formation of the ice-like structure around the hydrophobic groups makes it thermodynamically possible for the polymer chains to assume an extended conformation.[10,11] Thus the gels expand to form the swollen state. With increasing hydrophobicity of the polymer chains, however, the polymer–polymer interaction becomes predominant over the polymer–solvent interaction stabilized by the ice-like structures. Then the hydrogels form a collapsed state by aggregation of the hydrophobic polymer chains. In our copolymer system, the stability of the ice-like structures is so large at 0 °C that the swollen state is maintained until the polymer chains get a highest hydrophobicity at a highest composition of the ethyl group. The stability of the ice-like structures is reduced at elevated temperatures so that the polymer chains can aggregate even at a reduced polymer–polymer interaction in the copolymers with an increasing portion of the terminal methyl group. The results obtained in this study, therefore, strongly suggest that the variation of the internal hydrophobic–hydrophilic character of the copolymer chains is equivalent to the variation of the external temperature for the phase transition of the hydrogel, and the transition temperature is surprisingly sensitive to the hydrophobic–hydrophilic character of polymers.

References and Notes

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(7) The monomers Ma-Ala-OR were prepared by the reaction of L-alanine alkyl esters with methacryloyl chloride followed by purification by column chromatography. The monomers thus obtained and 0.2 mol % of tricosaethylene glycol dimethacrylate as a cross-linking agent were polymerized in ethanol by irradiation of 30 kGy of γ-rays from a ^{60}Co source at 25 °C. The unconverted monomers were extracted with ethanol from the gel, which was allowed to stand in fresh water several times to give a hydrogel.
(8) The S_w values were obtained by the following equation: $S_w = (W - W_0)/W_0$, where W is the weight of the hydrogel at an equilibrium state in water at a specific temperature and W_0 is the weight of lyophilized hydrogel. The S_w change is consistent with the volume change of the hydrogel.
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