Novel Synthesis of Thermosensitive Porous Hydrogels

TAKEHIKO GOTOH, YUKO NAKATANI, SHUJI SAKOHARA

Department of Chemical Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739, Japan

ABSTRACT: The simplified method for the synthesis of thermosensitive porous hydrogels by a radical polymerization was presented and their swelling properties were examined experimentally. *N,N*-Diethylacrylamide (DEAAm) or *N*-isopropylacrylamide (NIPAm) as primary monomers and *N,N'*-methylenebisacrylamide (BIS) as a crosslinker were used. They were polymerized in water at various temperatures above the lower critical solution temperature (LCST) of poly-DEAAm (ca. 32°C) or poly-NIPAm (ca. 31°C) by using *N,N,N',N'*-,tetramethylethylenediamine (TEMED) and ammonium peroxsodisulfate (APS) as the polymerization accelerator and initiator, respectively. From the observation by a scanning electron microscope, it was found that these gels consisted of aggregated microgel particles, namely, a porous structure. The gels swelled below their LCSTs, and the swelling degree increased with lowering temperature. Furthermore, the gels swelled or shrank very fast in response to the change in temperature, and the shrinking rate was larger than the swelling rate. Such swelling properties and mechanical properties depended on the porous structure of the gels such as the size of the microgels and the pore volume, which largely changed with the synthesis temperature and the component of the primary monomer. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 895–906, 1998

Key words: thermosensitive gel; porous structure; lower critical solution temperature (LCST); *N*-isopropylacrylamide; *N,N*-diethylacrylamide

INTRODUCTION

Thermosensitive hydrogels have come to attract much attention from their reversible discontinuous large change in volume caused by a small change in temperature. This phenomenon, known as the volume phase transition, has been studied by many researchers experimentally and theoretically.[1-5] On the other hand, the studies on the applicable use of these gels to extraction,[6] adsorption,[7] actuator,[8] drug-delivery systems (DDS),[9] and so on have been also done actively.

In these applications, one of the important factors is swelling and shrinking. It is well known that the swelling rate is inversely proportional to the square of the characteristic length of the gel.[10,11] Hence, microgels or thin gel membranes have been synthesized to improve the swelling rate or shrinking rate. However, such small or thin gels have problems in their handling. On the other hand, it has been found that the gels composed of a porous (spongelike) structure swell or shrink very fast compared with nonporous gels of the same size.

Hirasa et al.[8,12,13] synthesized porous poly(vinyl methyl ether) (PVME) or poly-*N*-isopropylacrylamide (PNIPAm) gels by γ-ray irradiation to PVME or PNIPAm, which are thermosensitive polymers. Huang et al.[14] presented a new concept of the dewatering process of activated sludge by using porous PVME gel and suggested that the process is energy-conservative compared with the conventional mechanical dewatering processes. Furthermore, recently, Akehata et al.[15] put this idea into concrete use with a spiral feeder-type

dehydrator. However, the most serious problem of this process in industrial use is the employing of γ-ray irradiation to synthesize a porous gel. A simpler synthesis method available for industrial use must be developed.

Recently, Kabra and Gehrke[16] reported a "fast responsive" N-isopropylacrylamide gel synthesized by a radical polymerization. However, the relationship between the structure of the gels and the synthesis condition of the gels and the swelling or shrinking kinetics have not been much reported.

In this article, the simple synthesis method of thermosensitive porous hydrogels by a radical polymerization was presented, and their swelling properties and mechanical properties were examined experimentally. Some acrylamide derivatives such as N-isopropylacrylamide (NIPAm) and N,N-diethylacrylamide (DEAAm) have specific thermosensitive properties.[17] Although NIPAm and DEAAm are soluble in water, their polymers, poly-NIPAm and poly-DEAAm, are thermosensitive. In other words, these polymers dissolve in water below the lower critical solution temperature (LCST), while they have hydrophobic properties above their LCSTs. We paid attention to such properties of these acrylamide derivatives and tried to synthesize the thermosensitive porous hydrogels by utilizing the phenomenon of phase separation.

EXPERIMENTAL

Synthesis of Gels

DEAAm and NIPAm used as the primary monomers were commercial grade obtained from Kojin Co. Ltd. (Tokyo, Japan). Their polymers, poly-DEAAm and poly-NIPAm, have LCSTs of 32.0 and 30.9°C, respectively.[17]

In synthesizing the gel, N,N′-methylenebisacrylamide (BIS) was used as a crosslinking agent (crosslinker). N,N,N′,N′,-Tetramethylethylenediamine (TEMED) and ammonium peroxsodisulfate (APS) were used as the polymerization accelerator and initiator, respectively. They were all reagent grade purchased from Katayama Chemical (Osaka, Japan). All materials were used without further purification. Table I shows the concentrations of these materials used to synthesize the gels.

The concentrations of the primary monomer and crosslinker largely affected the mechanical

properties of the gels synthesized above the LCST. A relatively high concentration of the primary monomer was necessary to keep the cylindrical shape of the formed gel. In this work, the concentration of 2000 mol/m^3 was used to synthesize the DEAAm gels. On the other hand, 1500 mol/m^3 was used for NIPAm, because there is a limit in the solubility of NIPAm for water. The concentration of the crosslinker also affected the mechanical properties as well as the swelling properties. To make the gels hard enough for handling, the concentrations of the crosslinker of 40 and 60 mol/m^3 were used to synthesize the DEAAm gel and the NIPAm gel, respectively.

The desired amount of the primary monomer (DEAAm or NIPAm), BIS, and TEMED were dissolved in deionized water to make 50 mL. Another solution of 50 mL containing ammonium peroxisodisulfate as a polymerization initiator was prepared. Both solutions were heated to the desired temperature above the LCST of poly-DEAAm or poly-NIPAm under the bubbling of nitrogen gas for about 20 min. Then, they were put into a separable flask and agitated by a magnetic stirrer. Immediately, some glass tubes [length of 50 mm and internal diameter (i.d.) of 6, 10, 12, and 16 mm] were immersed in the mixed solution to form cylindrical gels. The gelation started soon and was completed within a few hours.

After the reaction was completed, the cylindrical gels were pushed out from the glass tubes and then cut off to the same length as the diameter. These gel samples were washed with deionized water to remove residual chemicals for 1 week. Then, some gel samples synthesized with the glass tube of 6-mm i.d. were dried at room temperature, and other gels were kept in deionized water.

Preparation of Sample Specimens for Observation of Internal Structure of Gels by a Scanning Electron Microscope (SEM)

The internal structures of the gels were observed by SEM. The sample gel specimens were prepared by freeze-drying the swollen gel to avoid shrinkage in the drying process. tert-Butyl alcohol was selected as a solvent to make the sample gel swell, because the melting point of tert-butyl alcohol is relatively high, about 25°C, and amphiphilic NIPAm and DEAAm gels largely swell in tert-butyl alcohol. The preparation procedures of the sample specimens are as follows[18]: The dried gels were swollen in tert-butyl alcohol to equilibrium at

Table I Composition of the Gels

Use	Material	mol/m^3
Monomer	N,N-Diethylacrylamide (DEAAm)	2000
	N-Isopropylacrylamide (NIPAm)	1500
Linker	N,N′-Methylenebisacrylamide (BIS)	
	DEAAm	40
	NIPAm	60
Accelerator	N,N,N′,N′-Tetramethylethylenediamine (TEMED)	10
Initiator	Ammonium peroxsodisulfate (APS)	0.5

30°C. Then, the swollen gels were frozen in a refrigerator. The frozen gels were sliced to about 1-mm thick and dried under reduced pressure for several hours. The sample specimens scarcely shrank in the drying process.

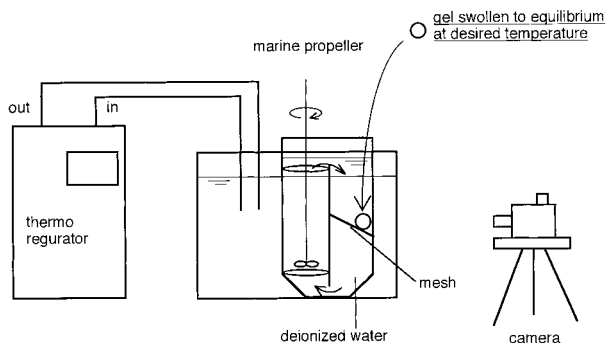### Measurement of Equilibrium Swelling Diameter and Swelling/Shrinking Rate of Gels

The equilibrium swelling degree of the gel at the desired temperature was measured as follows: A dried gel and deionized water were put into a rectangular cell, which was made of acrylic resin and immersed in a water bath of 10°C. After the gel swelled up to reach equilibrium, its swelling diameter was measured using a cathetometer. Then, the temperature of the water bath was increased to the desired temperature, and the equilibrium diameter was measured in the same manner as above. The procedures were repeated to 50°C. Then, to confirm the reversibility of swelling and shrinking, the temperature was decreased and the measurements of the equilibrium swelling diameter were repeated. The reversibility was almost complete.

Figure 1 shows an experimental apparatus for measurement of the swelling and shrinking rates. The apparatus was made of acrylic resin. A gel

swollen to equilibrium at the desired temperature was transferred to the apparatus placed in a water bath of the desired temperature, in which deionized water was circulated by a marine propeller to reduce the thickness of the thermal boundary layer. The gel was placed on the mesh in the apparatus, and a series of photographs of the gel was taken at desired time intervals until the gel reached the equilibrium swelling state.

Measurement of Elastic Modulus of Gels

The mechanical properties of the gels are also an important factor in applicable use. Especially, it is easily expected that the elastic moduli of porous gels are quite small compared with those of nonporous gels. From this point of view, measurements of the elastic moduli of the formed gels were performed. The large-size gels synthesized with a glass tube of 16-mm i.d. were used to measure the elastic modulus. A swollen gel sample was placed vertically in the rectangular vessel of the acrylic resin immersed in a water bath of the desired temperature. The vertical deformation caused by the loading weight on the gel was measured. The elastic modulus was evaluated from a linear relationship between the longitudinal strain and the stress assuming no volume change.[1]

RESULTS AND DISCUSSION

Outward Appearance of Formed Gels

DEAAm gels synthesized above the LCST, about 32°C, were opaque or milky white. With lowering of the synthesis temperature from the LCST, the degree of the opaqueness of the formed gel decreased, and the gel synthesized at 20°C was almost transparent. It is well known that the network of opaque gels is composed of dense and coarse parts, while that of transparent gels is ho-

Figure 1 Experimental apparatus.
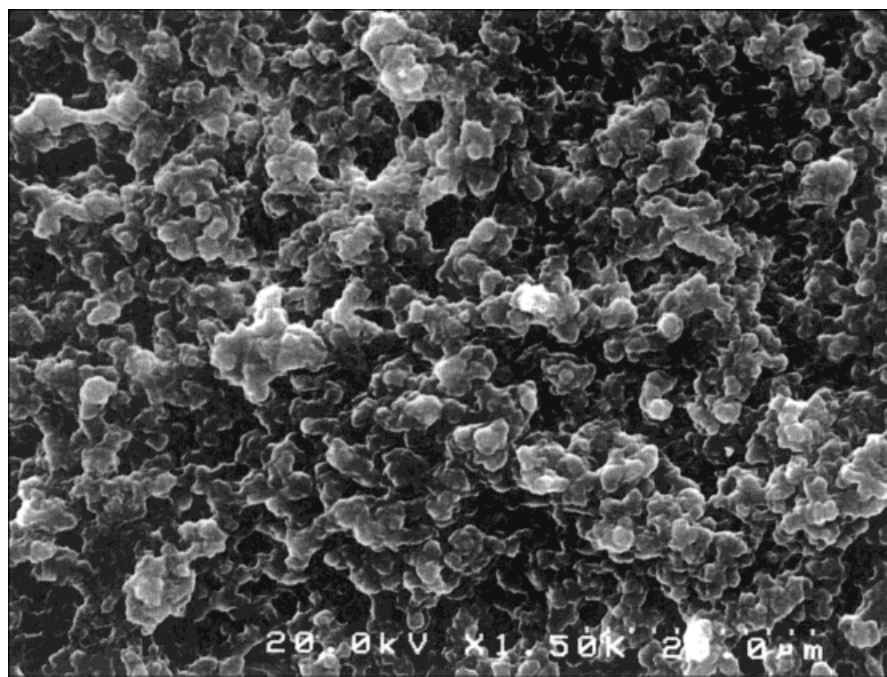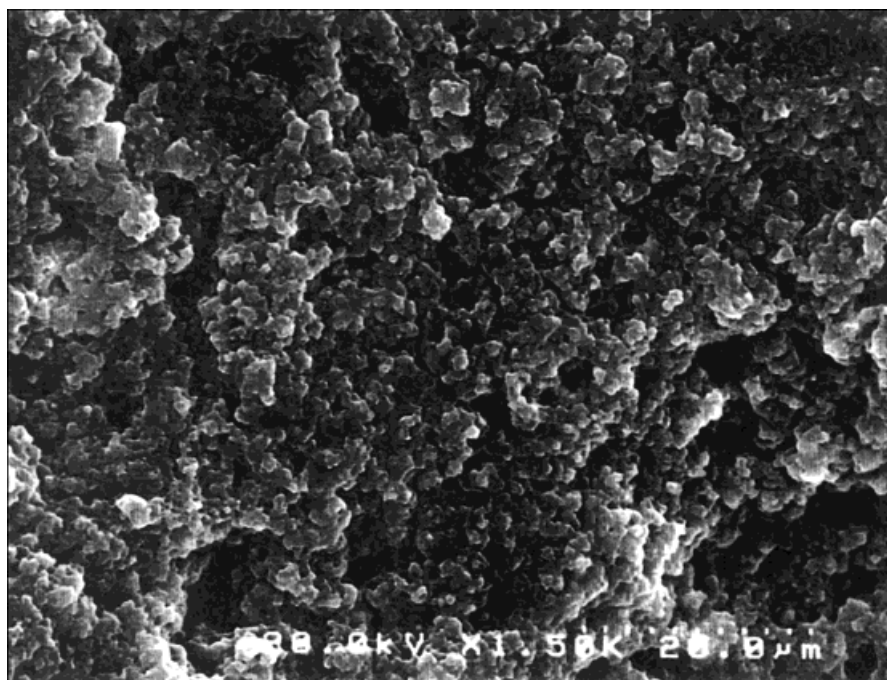
Figure 2   SEM photographs of porous gel synthesized at 50°C. The concentrations of primary monomer and crosslinker: (a) DEAAm: 2000 mol/m^3, BIS: 40 mol/m^3; (b) NIPAm: 1500 mol/m^3, BIS: 60 mol/m^3. Magnification 1500×.
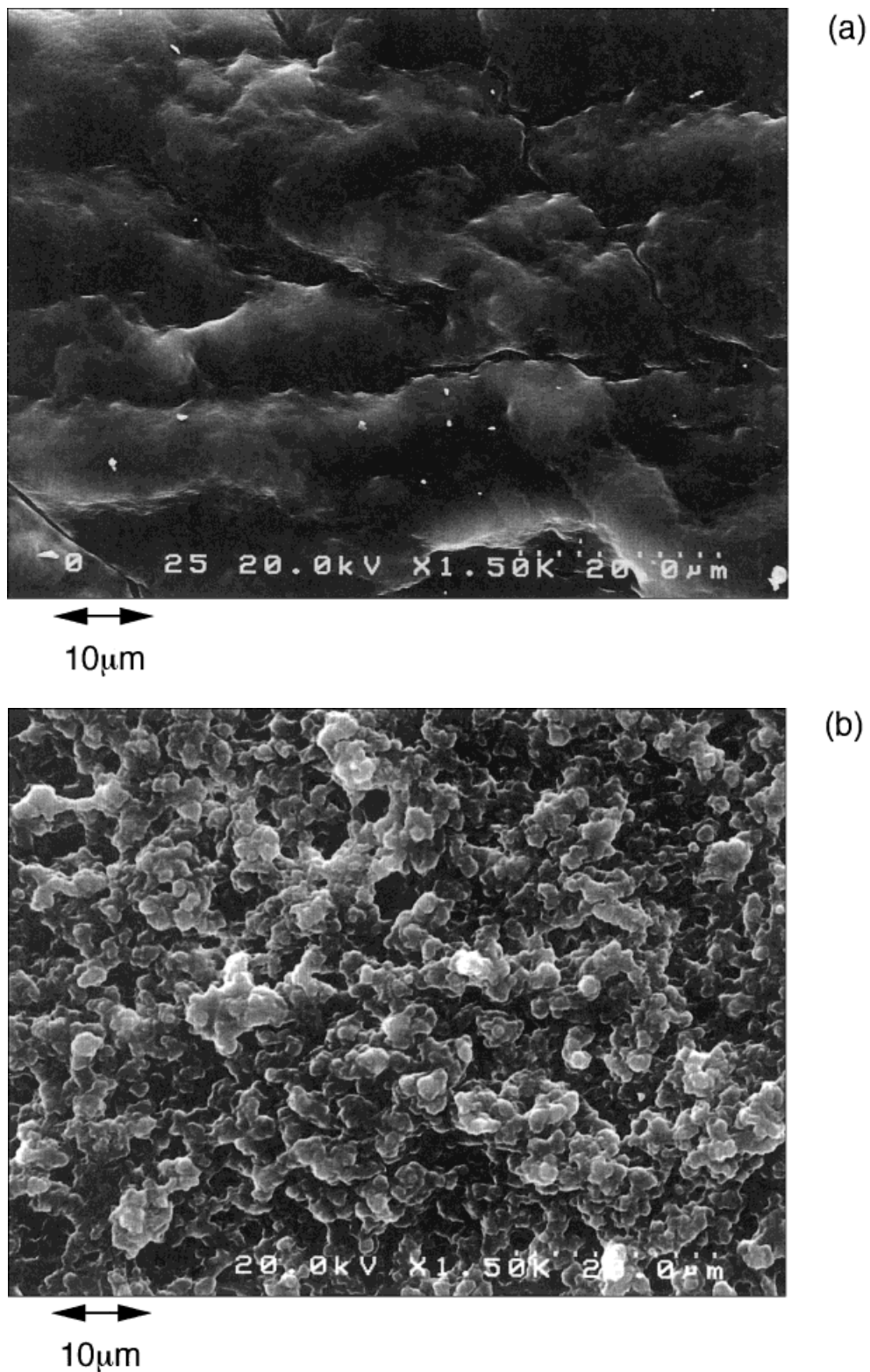
Figure 3 Effects of synthesis temperature on porous structure of DEAAm gel. Synthesis temperature: (a) 30°C; (b) 50°C. Magnification 1500×.
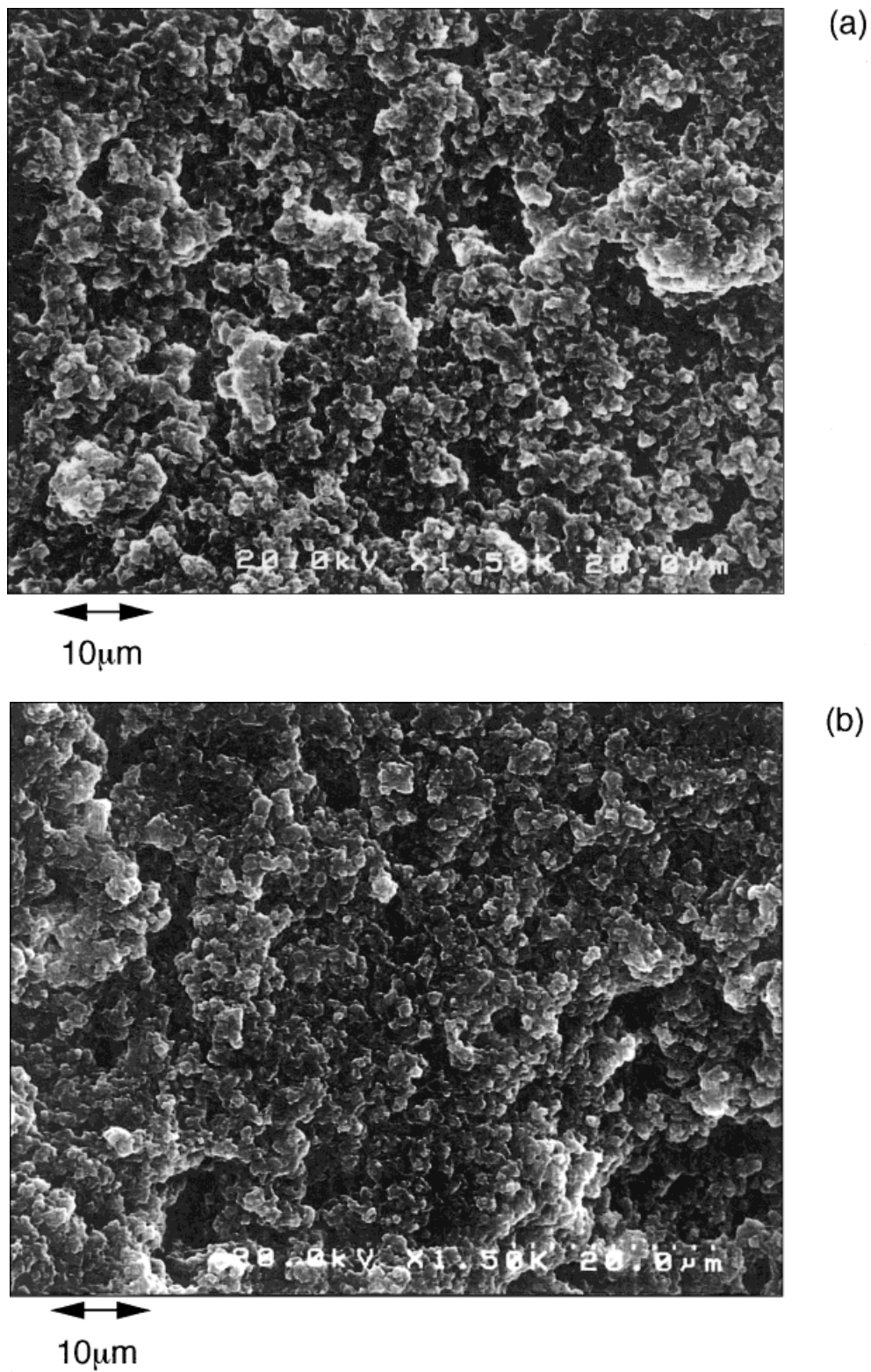
Figure 4   Effects of synthesis temperature on porous structure of NIPAm gel. Synthesis temperature: (a) 30°C; (b) 50°C. Magnification 1500×.
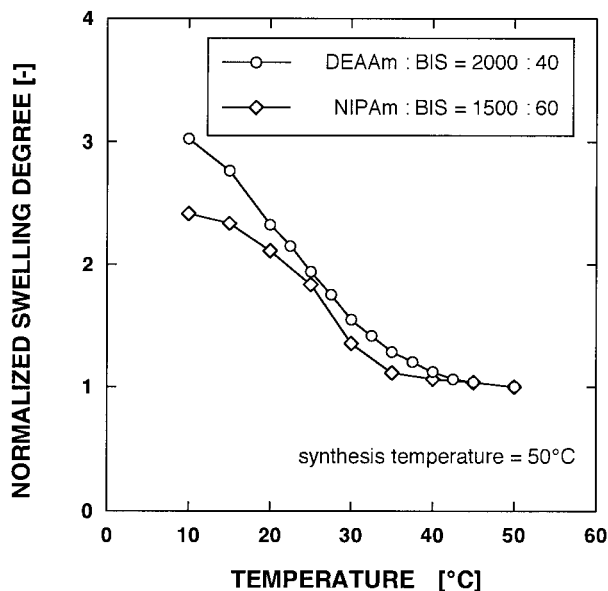
Figure 5 Change in swelling degree with temperature.

mogeneous macroscopically.[19] Such a outward appearance of the gel suggests that the internal structure of the DEAAm gel largely changes by the synthesis temperature around the LCST of poly-DEAAm.

On the other hand, the outward appearance of the NIPAm gels was scarcely changed by the synthesis temperature, and the gel was opaque or milky white even if it was synthesized at 20°C, which is much lower than the LCST of poly-NI-

PAm, about 31°C. Similar observation results were reported in the literature.[20] The effects of the component of the primary monomer on the network structure must be investigated further.

Internal Structure of Gels Observed by SEM

Figure 2 shows SEM photographs of the inside of the DEAAm gel [Fig. 2(a)] and the NIPAm gel [Fig. 2(b)] synthesized at 50°C. Many small particles of several microns are observed in these gels. In other words, these gels are porous as expected. These small particles are considered to be small gels produced by the phase separation, because the synthesis temperature of these gels, 50°C, is much higher than the LCSTs of their polymers. Therefore, it can be said that the porous gel can be easily synthesized by copolymerizing DEAAm or NIPAm with an adequate amount of a crosslinker above the LCST of poly-DEAAm or poly-NIPAm. However, the particle size and the pore diameter largely depended on the synthesis temperature of the gel and the component of the primary monomer.

Figure 3 shows an example of the effect of the synthesis temperature on the internal structure of the DEAAm gels. The gels were synthesized at 30°C [Fig. 3(a)] and 50°C [Fig. 3(b), same as Fig. 2(a)], respectively. In the DEAAm gel synthesized at 30°C, which is close to the LCST of poly-DEAAm, the microgel particles and the pores are not observed. From these photographs, it can be
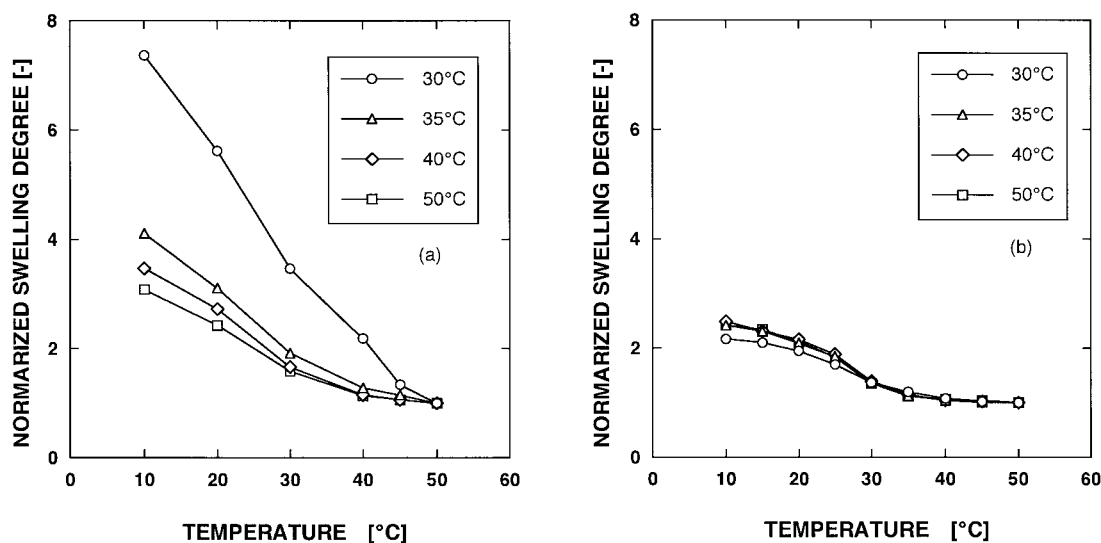

Figure 6 Effect of synthesis temperature on swelling degree: (a) DEAAm gel; (b) NIPAm gel.

said that temperature much higher than the LCST of poly-DEAAm is necessary to form the microgel particles by phase separation, that is, the porous structure.

On the other hand, the difference of the internal structure of NIPAm gels synthesized at 30 and 50°C is not clear, as shown in Figure 4. The NIPAm gel synthesized at 30°C is also composed of similar aggregated microgel particles as of that synthesized at 50°C. The outward appearance of these NIPAm gels were also almost the same as mentioned above. From these results, it can be said that the effects of the synthesis temperature on the internal structure of the NIPAm gels are largely different from those of the DEAAm gels.

Change in Swelling Degree of Gels with Temperature

Figure 5 shows an example of the change in the swelling degree with temperature for the DEAAm gel and the NIPAm gel. These gels were synthesized at 50°C. The swelling degree is shown by normalizing it with that of 50°C. The swelling degrees of both gels decrease with increasing temperature, as expected. However, the manner of the decrease of the swelling degree differs with each primary monomer component. The swelling degree of the NIPAm gel decreases remarkably around the LCST of poly-NIPAm, while that of the DEAAm gel decreases monotonously with increasing temperature.

Effects of Synthesis Temperature on Swelling Degree

Figure 6 shows the swelling degree of the DEAAm gel [Fig. 6(a)] and the NIPAm gel [Fig. 6(b)] synthesized at various temperatures of 30–50°C. The DEAAm gel synthesized at 30°C, which is close to the LCST, swelled remarkably compared with those synthesized at higher temperature, although the swelling degree of DEAAm increased with decreasing synthesis temperature. On the other hand, the swelling degree of the NIPAm gel scarcely depended on the synthesis temperature. These phenomena are considered to be closely related to the internal structures of the gels. In the case of the DEAAm gel synthesized at 30°C, the microgel particles were not observed, as shown in Figure 3, and the porous structure was developed with increasing synthesis temperature. The internal structure of the NIPAm gel, however, was almost independent of these synthesis tempera-
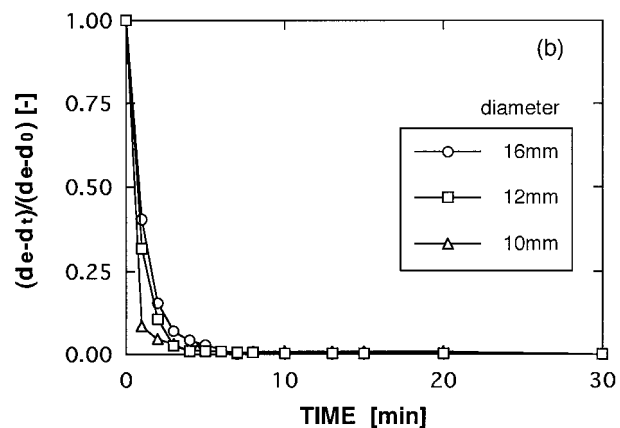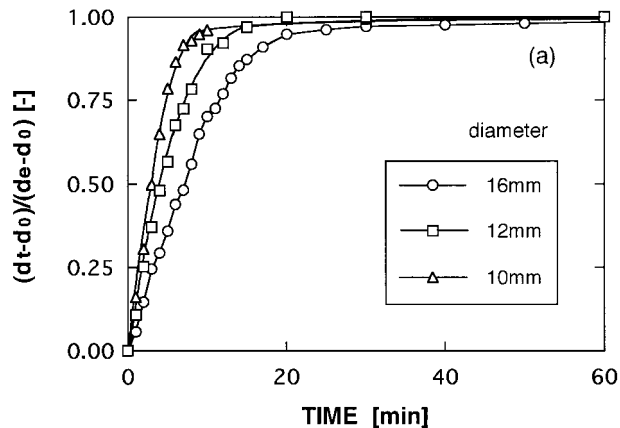

Figure 7 Swelling rate and shrinking rate of DEAAm gels of different size: (a) swelling rate; (b) shrinking rate.

tures, as shown in Figure 4. These results suggest that the microgel particles consisted of a tightly entangled polymer network and that the flexibility of such a network for swelling is small.

Swelling and Shrinking Rates of Gels

Swelling and shrinking rates depend on the size of the gel or the swelling degree of the gel as a matter of course. In the case of a nonporous gel, it is well known that the swelling rate is inversely proportional to the square of the characteristic length in an equilibrium state.[11] In this work, first, we tried to correct the swelling rate and the shrinking rate of the porous gel in the same manner as with the nonporous gel.

Figure 7(a,b) shows the swelling rate and shrinking rate of DEAAm gels of different size, respectively. These gels were synthesized with
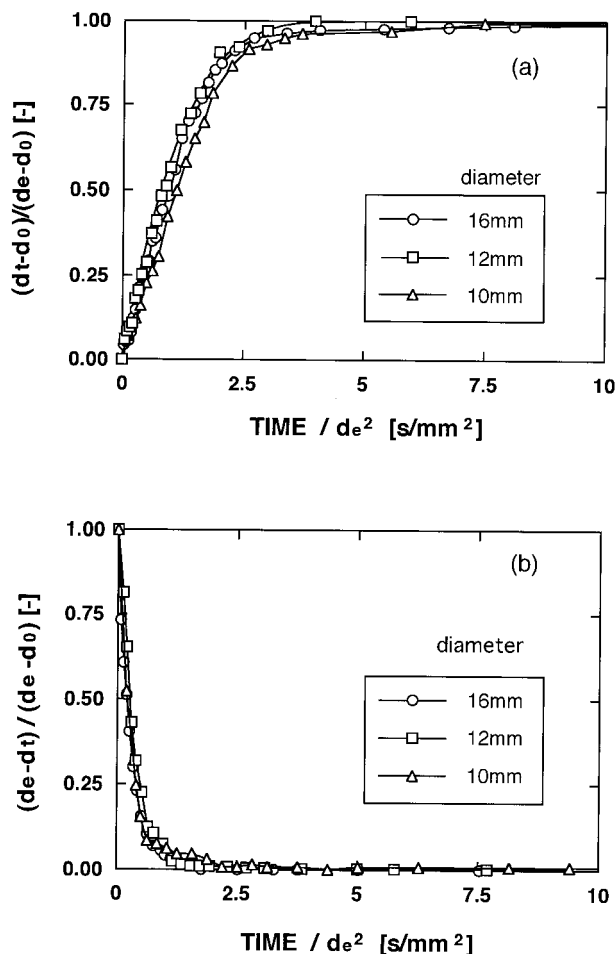
Figure 8   Swelling rate and shrinking rate normalized by equilibrium swelling diameter: (a) swelling rate; (b) shrinking rate.

glass tubes of 16-, 12-, and 10-mm i.d. at 50°C. The longitudinal axis shows the normalized gel diameter: $(d_t - d_0)/(d_e - d_0)$, where d_t is the gel diameter at $t = t$; d_0, the diameter at $t = 0$; and d_e, the equilibrium diameter. The small-size gel swelled or shrank faster as a matter of course. In Figure 8, the time was normalized with d_e^2. The swelling curves and shrinking curves of the three gels of different size overlapped one another. From these results, it can be said that the effects of the swelling degree of gels on the swelling rate and shrinking rate of a porous gel can be also corrected by the square of the equilibrium diameter, although further investigations are necessary.

The swelling rates of these porous gels are quite large as expected. Furthermore, the shrinking rate is greater than the swelling rate, because the gels swell from the shrunken state in the

swelling process and the shrunken gel has a larger resistance against the diffusion of water into the gel. On the other hand, in the shrinking process, the gel shrinks from the swollen state through which the diffusion resistance of water is considered to be small. In such a case, it is expected that the rate of heat transfer into the gel controls the shrinking rate.

In Figure 9(a,b), the swelling rate and the shrinking rate are compared with the heat-transfer rate, respectively. The heat-transfer rate was measured with a thermocouple inserted into the center of the gel. In the swelling process, the swelling rate is small compared with the heat-transfer rate, while the shrinking rate is comparable to the heat-transfer rate. From these facts, it can be said that the shrinking rate is controlled by the heat transfer, as expected.

Standing on these results, the effects of the synthesis temperature of the DEAAm gel and the NIPAm gel on the swelling and shrinking rates were examined. Figure 10 shows the results for DEAAm gels synthesized at various temperatures of 30–50°C. The swelling rate increased with in-
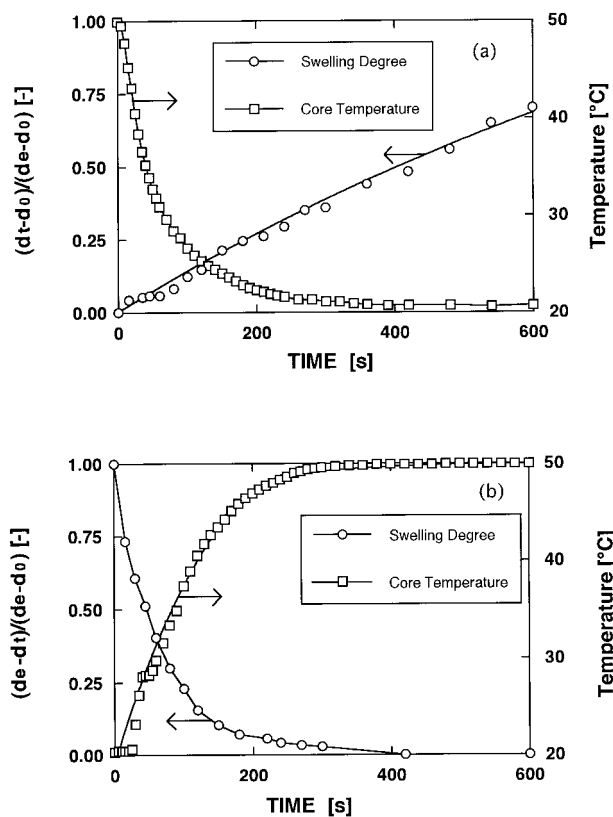

Figure 9   Swelling rate and shrinking rate with heat-transfer rate: (a) swelling rate; (b) shrinking rate.
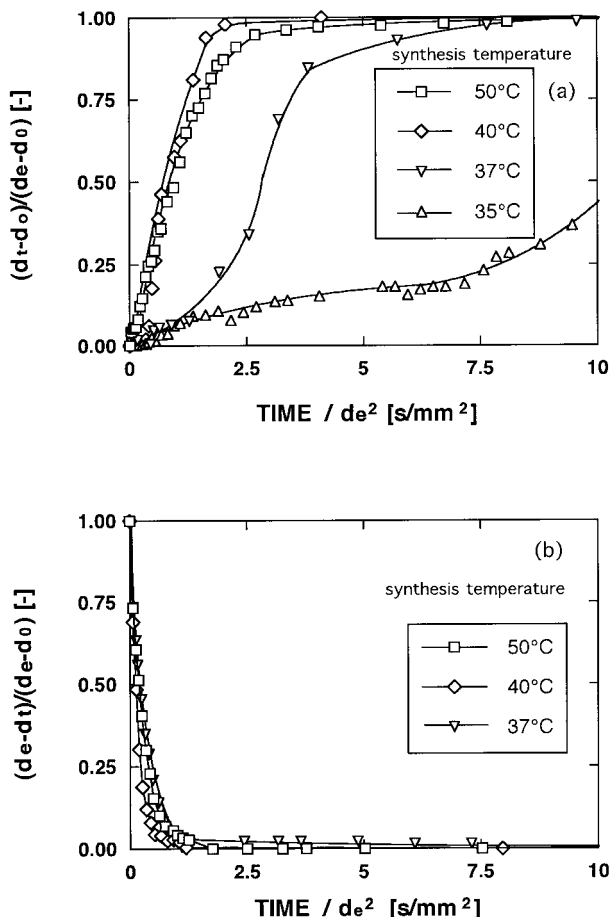
Figure 10 Effect of synthesis temperature on swelling rate and shrinking rate of DEAAm gel: (a) swelling rate; (b) shrinking rate.

creasing synthesis temperature of the gels. On the other hand, the shrinking rate scarcely changed with the synthesis temperature. These results are also considered closely related to the internal structures of the DEAAm gels. The size of the microgel particles in the DEAAm gels decreased with increasing synthesis temperature; in other words, the pore structure in the DEAAm gel was developed with increasing synthesis temperature as mentioned above. Upon comparing the swelling rate with the internal structure, it can be said that the swelling rate is controlled by the degree of development of the porous structure. On the other hand, the shrinking rate is not dependent on the internal structure of the gels but controlled by the heat-transfer rate. In fact, the heat-transfer rate is almost independent of the synthesis temperature of the gels.

Figure 11(a,b) shows the swelling and shrinking rates of NIPAm gels synthesized at various

temperatures of 30–50°C, respectively. The swelling rate increased with increasing synthesis temperature, similar to that with the DEAAm gels. But the effects of the synthesis temperature are not as large as compared with those of the DEAAm gels shown in Figure 10, because the synthesis temperature scarcely affects the pore structure of the NIPAm gels in the experimental range as mentioned above. From these results, it can be said that the swelling rate depends on the pore structure of the gel which is determined by the synthesis temperature and the component of primary monomer and that the shrinking rate is limited by the heat-transfer rate.

Elastic Modulus of Formed Gels

Figure 12 shows the elastic moduli of the DEAAm gel [Fig. 12(a)] and the NIPAm gel [Fig. 12(b)] synthesized at various temperatures of 30–50°C.
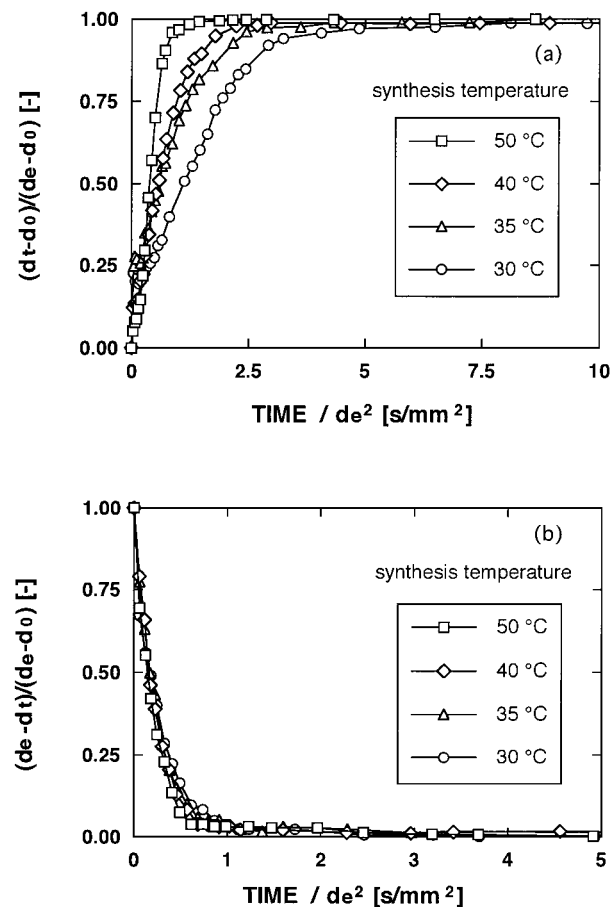

Figure 11 Effect of synthesis temperature on swelling rate and shrinking rate of NIPAm gel: (a) swelling rate; (b) shrinking rate.
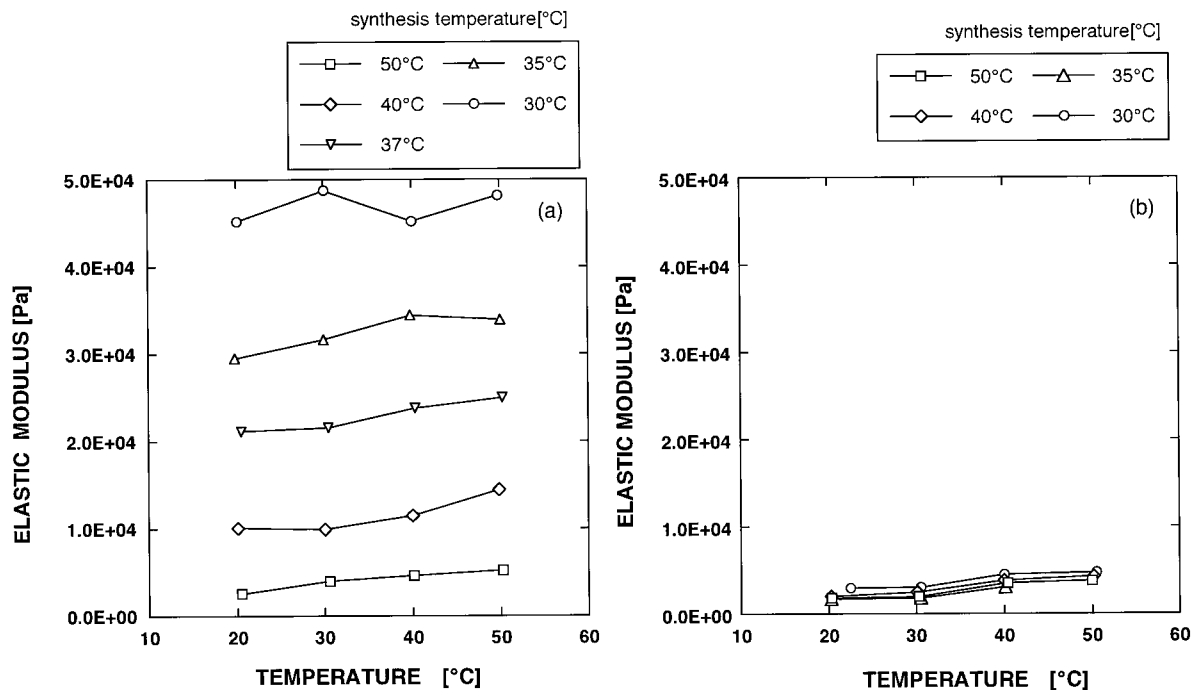
Figure 12   Effect of synthesis temperature on elastic modulus of the gel: (a) DEAAm gel; (b) NIPAm gel.

The modulus of the DEAAm gel decreased remarkably with increasing synthesis temperature. On the other hand, the moduli of the NIPAm gels are very small and almost independent of the synthesis temperature. These results are also considered closely related to the internal structures of these gels. The porous structure of the DEAAm gels is developed with increasing synthesis temperature, while the NIPAm gels developed a pore structure in the experimental range, as mentioned above. Therefore, it can be said that the elastic modulus decreased according to the development of the porous structure.

CONCLUSION

Thermosensitive porous gels were synthesized simply by a radical polymerization. *N,N*-Diethylacrylamide (DEAAm) and *N*-isopropylacrylamide (NIPAm) which have specific thermosensitive properties were used as primary monomers, and the synthesis was performed at the temperatures above the lower critical solution temperatures (LCSTs) of poly-DEAAm and poly-NIPAm. From the observation by SEM, it was confirmed that the formed gels consisted of aggregated gel particles of several microns, that is, the porous gels.

These gels were thermosensitive and swelled below their LCSTs, although the swelling degree depended on the synthesis temperature and the component of the primary monomer. These gels swelled or shrank very fast in response to the change in temperature. Especially, the shrinking rate was larger than the swelling rate, and it was suggested that the rate was controlled by the heat-transfer rate. Furthermore, it was found that the swelling rate was closely related to the internal structure of gel, that is, the size of the microgel particles and the pore volume. Consequently, it can be concluded that the fast responsible porous gels can be synthesized simply by a novel method proposed by the authors, although the effects of the composition of the monomer or crosslinker on their swelling properties and the mechanical properties must be investigated further.

REFERENCES

1. T. Tanaka, L. O. Hocker, and G. B. Benedek, *J. Chem. Phys.,* **59,** 5151 (1973).

2. T. Tanaka, *Phys. Rev. Lett.,* **40,** 820 (1978).

3. S. Hirotsu, Y. Hirokawa, and T. Tanaka, *J. Chem. Phys.,* **87,** 1393 (1987).

4. S. Katayama and A. Ohta, *Macromolecules,* **18,** 2782 (1985).

5. H. Inomata, S. Goto, and S. Saito, *Macromolecules,* **23,** 4887 (1987).

6. R. F. S. Freitas and E. L. Cussler, *Sep. Sci. Technol.,* **22,** 911 (1987).

7. Y. Seida and Y. Nakano, *J. Chem. Eng. Jpn.,* **29,** 767 (1996).

8. O. Hirasa, *Kobunshi Ronbunshu,* **46,** 661 (1989).

9. H. Katono, K. Sanui, N. Ogata, T. Okano, and Y. Sakurai, *Polym. J.,* **23,** 1179 (1991).

10. T. Tanaka and D. J. Fillmore, *J. Chem. Phys.,* **70,** 1214 (1979).

11. Y. Li and T. Tanaka, *J. Chem. Phys.,* **92,** 1365 (1990).

12. O. Hirasa, *Kobunshi,* **35,** 1100 (1986).

13. R. Kishi, O. Hirasa, and H. Ichijo, *Polym. Gels Networks,* **5,** 145 (1997).

14. X. Huang, H. Unno, T. Akehata, and O. Hirasa, *J. Chem. Eng. Jpn.,* **20,** 123 (1987).

15. T. Akehata, M. Mochizuki, T. Kawakami, and A. Hayashi, in *Proceedings of the 29th Autumn Meetings of the Society of Chemical Engineers,* Japan, Vol. 2, 1996, p. 165.

16. B. G. Kabra and S. H. Gehrke, *Polym. Commun.,* **32,** 322 (1991).

17. S. Ito, *Kobunshi Ronbunshu,* **46,** 437 (1989).

18. T. Inoue, *Denshikenbikyou,* **24,** 226 (1989).

19. T. Tanaka, *Sci. Am.,* **Jan.,** 110 (1981).

20. C. M. Rathejen, C.-H. Park, and P. R. Goodrich, *Polym. Gels Networks,* **3,** 101 (1995).