

# Preparation of Poly(*N*-isopropylacrylamide)–SiO<sub>2</sub> Hybrid Gels and Their Thermosensitive Properties

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## SYNOPSIS

The swelling and adsorption behavior of poly(*N*-isopropylacrylamide)–SiO<sub>2</sub> hybrid gels, derived from copolymerization of *N*-isopropylacrylamide and 3-methacryloxypropyltrimethoxysilane (MPTMOS) and following hydrolysis and condensation, were investigated. The hybrid gels exhibited temperature dependence of both the swelling ratio and adsorption of solutes, and their temperature dependence was related to the MPTMOS content in the hybrid gels. In addition, the modification of thermosensitive properties of the hybrid gels could be achieved by treatment with other silane compounds. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Poly(*N*-isopropylacrylamide) [poly(NIPAAm)] hydrogels are well known to show thermally reversible swelling–shrinking behavior around 33°C in aqueous solutions with respect to a lower critical solution temperature. Many studies have been focused on the field of controlled drug delivery,<sup>1,2</sup> regulation of the activity of enzymes,<sup>3,4</sup> and thermocontrolled chromatography.<sup>5</sup> We have reported the preparation of the hydrogel membranes by graft copolymerization of NIPAAm on poly(vinyl alcohol) (PVA-*g*-NIPAAm) and their temperature dependence of the permeation through the PVA-*g*-NIPAAm membranes.<sup>6,7</sup> The hydrogel membranes were annealed prior to the permeation experiments, because the membranes without annealing were very soft and weak. On the other hand, as a new class of materials, inorganic–organic hybrid sol–gel glasses have recently attracted great attention in the field of material science. Incorporation of organic polymers into inorganic glass matrices via covalent bondings is particularly interesting because the new hybrid materials will have a controllable combination of properties of both organic polymers and inorganic glasses.<sup>8</sup> Therefore, it is expected that the hybrid-

ization of poly(NIPAAm) and inorganic glasses improves the physical and chemical properties of poly(NIPAAm) gels such as mechanical strength, thermal stability, and chemical stability. In this present work, we prepared hybrid gels composed of poly(NIPAAm) and polysiloxane and examined their thermosensitive behavior.

## EXPERIMENTAL

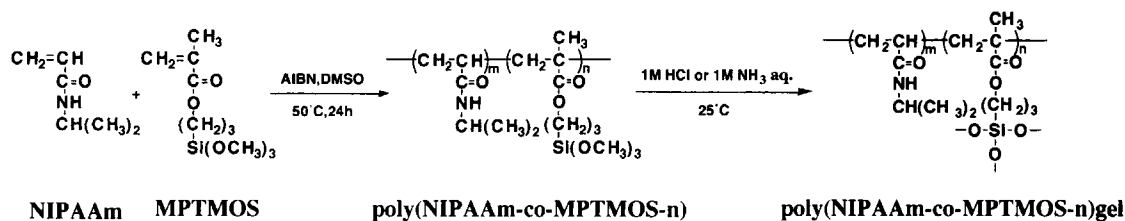
### Materials

NIPAAm was kindly provided by Kohjin Co. and purified by recrystallization using hexane and benzene. 3-Methacryloxypropyltrimethoxysilane (MPTMOS), 3-aminopropyltrimethoxysilane (APTEOS), and tetramethoxysilane (TMOS) were purchased from Shin-Etsu Co. Other chemical compounds were of reagent grade and were used as received.

### Synthesis of Copolymer Gels of NIPAAm and MPTMOS [Poly(NIPAAm-co-MPTMOS-*n*) Gels]

Mixtures of NIPAAm and MPTMOS (NIPAAm + MPTMOS = 2.0 g) were dissolved in 20 mL of dimethyl sulfoxide (DMSO), and then 0.02 g of 2,2'-azobisisobutyronitrile was added to the DMSO solutions as a radical initiator. Nitrogen was intro-

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Scheme 1

duced in the DMSO mixture solutions for about 1 h, and the polymerization was carried out at 50°C for 24 h with shaking. After polymerization, hydrolysis and condensation were carried out at 25°C for 1–7 days using 1M hydrochloric acid (HCl) or 1M ammonia aqueous solution (NH<sub>3</sub> aq) as the catalyst (Scheme 1).

The hybrid gels were immersed in a large excess of acetone to remove monomers and polymers. After drying, the resulting hybrid gels were ground and sieved to obtain fine particles with diameters in the range of 0.8–1.2 mm. The molar ratio of MPTMOS to the total amount of monomer (MPTMOS + NIPAAm = 2.0 g) in the feed was varied as 1, 3, 5, 10, 30, 50, and 70 mol %. The hybrid gels obtained are abbreviated as poly(NIPAAm-co-MPTMOS-*n*) gel, where *n* refers to the mol % of MPTMOS fed in the polymerization. The structure of the hybrid gels was analyzed using elemental analysis and infrared spectroscopy.

#### Modification of Poly(NIPAAm-co-MPTMOS-1) Gel with Other Silane Compounds

To 1.5 mL of ethanol solution containing 10 vol % of APTEOS, 1.5 g of poly(NIPAAm-co-MPTMOS-1) gel was added, and then it was allowed to swell for at least several hours. Hydrolysis and condensation were carried out by adding 200 mL of 1M HCl to the alcoholic mixture and subsequently stirring for 72 h at 25°C (Scheme 2).

The resulting gel was immersed in water after washing with a large excess of acetone. APTEOS

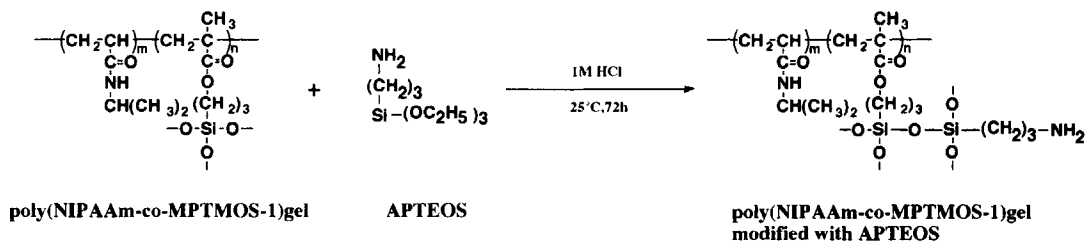
and other low molar mass chemicals in the modified hybrid gel were removed by heating above 32°C and cooling below 32°C. After treatment of the modified hybrid gels with 200 mL of 0.1M sodium hydroxide (NaOH) for 24 h with stirring, the gels were washed with water until the washing solution became neutral. After washing with acetone, the modified hybrid gels were dried at room temperature *in vacuo*. The modified hybrid gels with APTEOS were ground and sieved to obtain fine particles with diameters in the range of 0.8–1.2 mm. The poly(NIPAAm-co-MPTMOS-1) gel was treated with TMOS in a similar manner as above (Scheme 3).

#### Anion-exchange Capacity

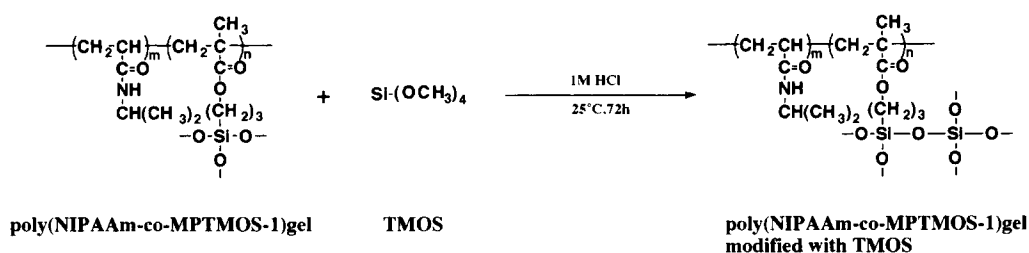
The anion-exchange capacity of the poly(NIPAAm-co-MPTMOS-1) gel modified with APTEOS was measured to estimate the amount of APTEOS incorporated. In 50 mL of 0.1M HCl, 0.250 g of the ground particle gel modified with APTEOS was placed. Next, 10 mL of 0.2M sodium bicarbonate and 5 mL of 2 wt/vol % soluble starch aqueous solution were added to 10 mL of the resulting acidic solution. The anion-exchange capacity was determined by titrating with 0.1M silver nitrate in the presence of 0.2 wt/vol % of fluorescein.

#### Phase-transition Temperature

The phase-transition temperature of the hybrid gels was examined using differential scanning calorimetry (Seiko DSC100).



Scheme 2



Scheme 3

### Swelling Ratio

In a bag made of nonwoven textile fabric, 1.0 g of the dried hybrid gel ( $W_d$ ) was placed, and the bag was immersed in water for 6 h. An empty bag was also immersed in water. Both bags were wiped with a filter paper to remove water on their surface. The swelling ratio was determined by measuring the weights of the bag containing gel ( $W_s$ ) and the empty bag ( $W_e$ ):

$$\text{Swelling ratio} = (W_s - W_e)/W_d$$

### Adsorption Experiments

In 50 mL of a 1.5 mM sodium benzenesulfonate (SBS) or sodium dodecylbenzenesulfonate (SDBS) aqueous solution, 0.100 g of the hybrid gel was placed. After shaking for 24 h at various temperatures, the amount of SBS (or SDBS) adsorbed on the hybrid gel was determined by measuring absorbance at 260 nm of the supernatant.

## RESULTS AND DISCUSSION

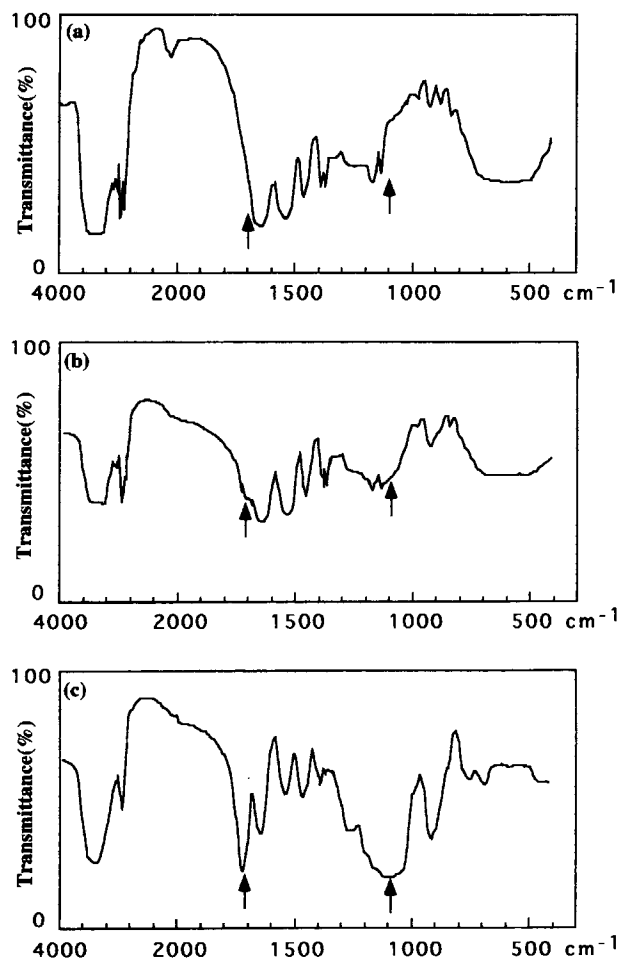
A result of elemental analysis of the poly(NIPAAm-co-MPTMOS- $n$ ) gels is given in Table I. The amount of MPTMOS fed in the polymerization was

varied as 1, 3, 5, 10, 30, 50 and 70 mol %. It is clearly seen that the content of MPTMOS in the hybrid gels increases linearly with increasing the amount of MPTMOS fed in the polymerization. Although the hybrid gels obtained were fragile, the increase in the content of MPTMOS improved qualitatively the strength of the hybrid gels. Figure 1 shows IR spectra of three hybrid gels ( $n = 1, 10,$  and  $70$ ) prepared by hydrolysis and condensation with 1 M HCl as the catalyst. In the IR spectra, the absorption bands at  $1650\text{ cm}^{-1}$  due to amide I and  $1550\text{ cm}^{-1}$  due to amide II were observed for all the hybrid gels. Absorbance at  $1730\text{ cm}^{-1}$  due to the carbonyl moiety increased with increasing the content of MPTMOS. In addition, the broadening of the band at  $1080\text{ cm}^{-1}$  due to  $\text{—Si—O—Si—}$  linkage was recognized with respect to an increase in the MPTMOS content. The treatment with 1 M NH<sub>3</sub> aq. as the catalyst provided almost similar results to those with 1 M HCl.

Figure 2 shows a DSC thermogram of the poly(NIPAAm-co-MPTMOS-1) gel in water. A clear endothermic point was observed due to the phase transition of poly(NIPAAm) in the copolymers,<sup>6,7</sup> and the maximum endothermic point at  $32.6^\circ\text{C}$  was taken as the phase-transition temperature. In Figure 3, the swelling ratio of the poly(NIPAAm-co-MPTMOS-1) gel treated with 1 M HCl was plotted as a function of temperature.

**Table I** Preparation of Poly(NIPAAm-co-MPTMOS- $n$ ) Gels

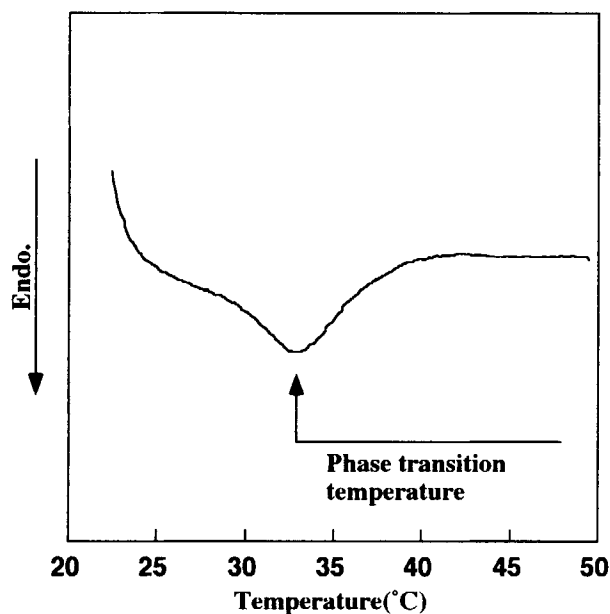
$n$	Feed (g)		Elemental Analysis			MPTMOS Content (Mol %)	Phase-transition Temperature ( $^\circ\text{C}$ )
	NIPAAm	MPTMOS	H (%)	C (%)	N (%)		
1	1.957	0.043	9.9	55.6	10.7	0.9	32.6
3	1.873	0.127	9.8	53.8	10.1	3.0	31.4
5	1.793	0.207	10.0	53.9	9.7	6.5	30.9
10	1.608	0.392	9.7	52.7	9.0	10.7	30.1
30	1.031	0.969	8.8	48.2	6.4	28.6	—
50	0.626	1.374	7.4	41.3	3.5	52.7	—
70	0.327	1.673	6.9	39.0	1.9	72.0	—



**Figure 1** IR spectra of the (a) poly(NIPAAm-co-MPTMOS-1) gel, (b) poly(NIPAAm-co-MPTMOS-10) gel, and (c) poly(NIPAAm-co-MPTMOS-70) gel.

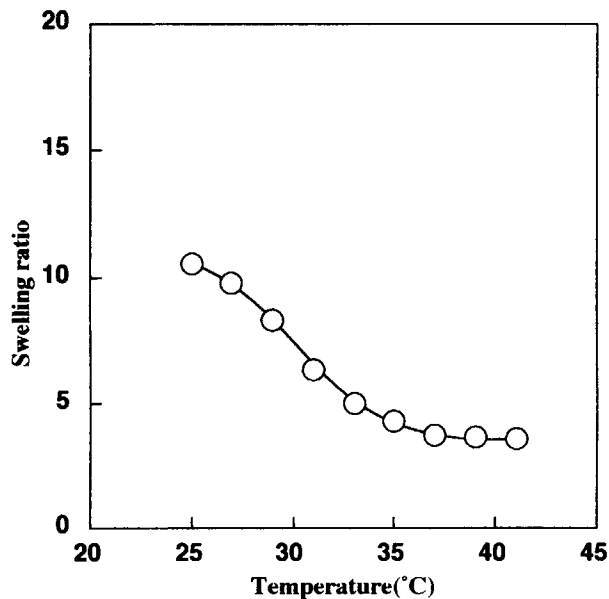
The swelling ratio was measured after immersing the hybrid gels in water for 24 h at various temperatures. The swelling ratio decreased with increasing temperature up to around 35°C and became almost constant above the temperature, namely, the shrinking of the hybrid gels took place around 35°C. This temperature agreed approximately with the phase-transition temperature determined by DSC. Therefore, the temperature dependence of the swelling ratio is closely related to the dehydration of the hybrid gels due to the phase transition of poly(NIPAAm) segments.

The catalyst dependence of a structure of networks as well as the rate of hydrolysis and condensation have been reported.<sup>9</sup> Figure 4 shows the hydrolysis and condensation time dependence of the swelling ratio of the poly(NIPAAm-co-MPTMOS-*n*) gels. No significant reaction time dependence of the swelling ratio was observed for the poly-

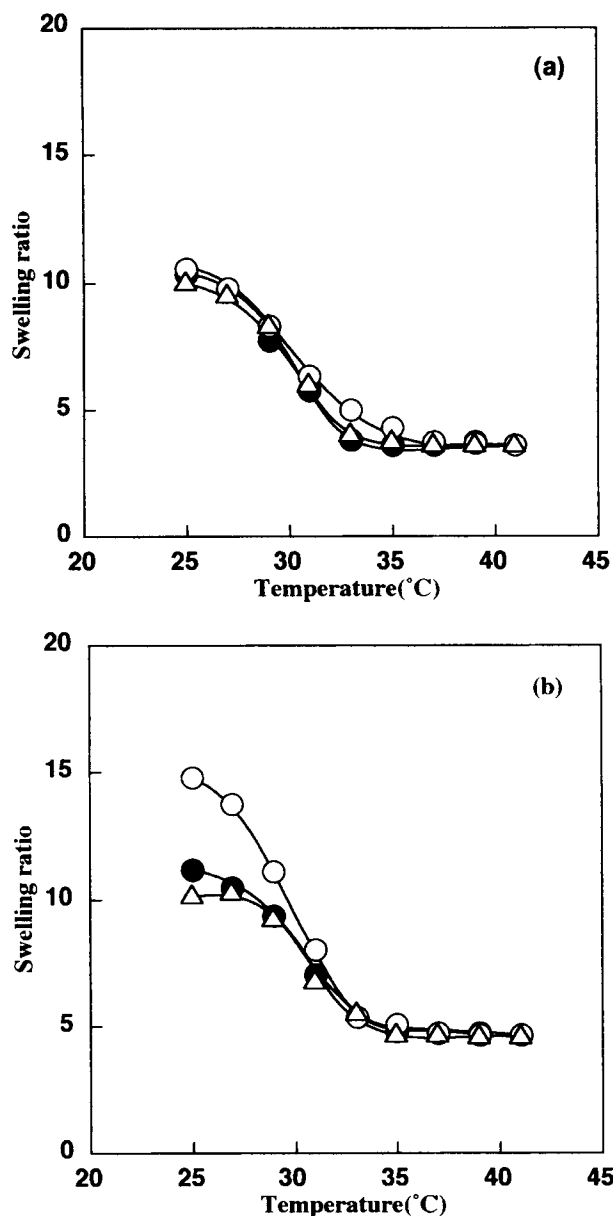


**Figure 2** DSC thermogram of the poly(NIPAAm-co-MPTMOS-1) gel in water obtained by heating at a rate of 1.0°C/min.

(NIPAAm-co-MPTMOS-1) gel with 1M HCl, while a little influence was recognized for the hybrid gel treated with 1M NH<sub>3</sub> aq. for 24 h. However, the swelling behavior of the hybrid gels treated with 1M NH<sub>3</sub> aq. for 72 and 168 h is almost similar to those of gels with 1M HCl. Although the effect of the kind



**Figure 3** Temperature dependence of the swelling ratio of the poly(NIPAAm-co-MPTMOS-1) gel treated with 1M HCl for 24 h.



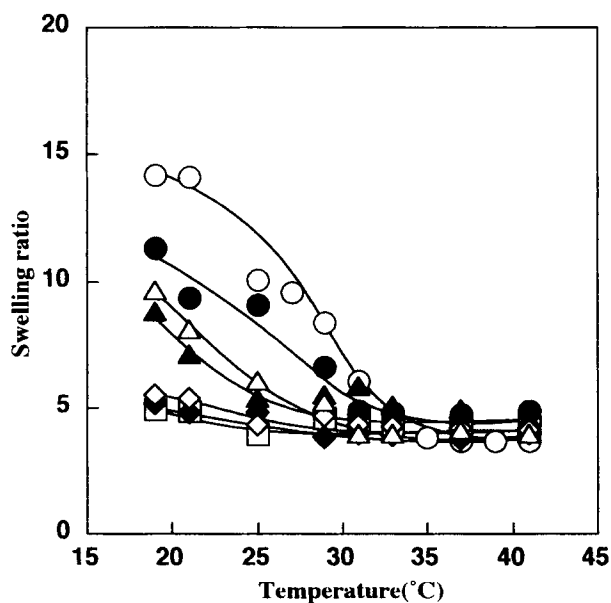
**Figure 4** Temperature dependence of the swelling ratio of the poly(NIPAAm-co-MPTMOS-1) gel treated with (a) 1M HCl or (b) 1M NH<sub>3</sub> aq for (○) 24 h, (●) 72 h, and (△) 168 h.

of catalyst on the structure of the resulting gels could not be concluded from the results, the catalyst was clearly found to influence the rate of hydrolysis and condensation.

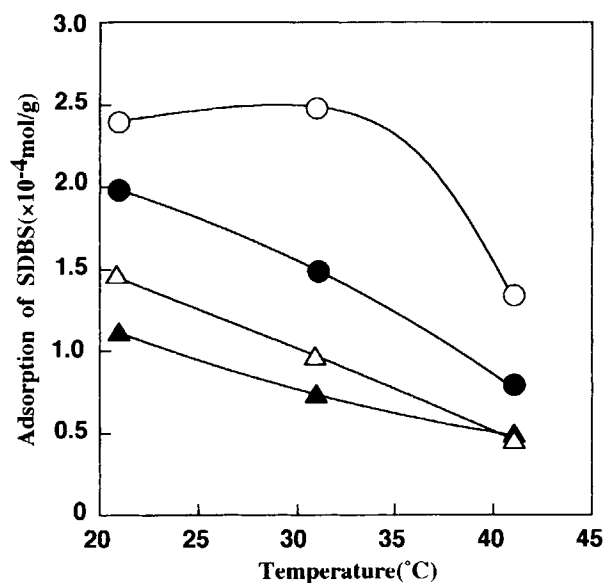
The phase-transition temperatures determined by DSC are also listed in Table I. It is clearly seen that the phase-transition temperature decreases with an increase in the MPTMOS content up to 10 mol %. Figure 5 shows the effect of MPTMOS content on the swelling ratio of the poly(NIPAAm-co-

MPTMOS-*n*) gels. The decrease of the swelling ratio was observed for all the poly(NIPAAm-co-MPTMOS-*n*) gels with increasing temperature. In addition, the swelling ratio below 30°C decreased with increasing the MPTMOS content; particularly, the swelling ratio of the poly(NIPAAm-co-MPTMOS-*n*) gels (*n* = 30, 50, 70) below 30°C was depressed. Actually, no endothermic peak was observed for the poly(NIPAAm-co-MPTMOS-*n*) gels (*n* = 30, 50, 70). On the other hand, the swelling ratio of the poly(NIPAAm-co-MPTMOS-1) gel was smaller than those of others above 35°C, i.e., the MPTMOS influenced the static properties of the hybrid gels such as the spread of the network in water. Therefore, the increase in hydrophobicity as well as rigidity due to formation of —Si—O—Si— linkages resulted in the effect of the MPTMOS content on the swelling ratio.

The adsorption of sodium benzenesulfonate (SBS) or sodium dodecylbenzenesulfonate (SDBS) on the poly(NIPAAm-co-MPTMOS-*n*) gels was measured to clarify the effect of MPTMOS content on properties of the hybrid gels. No adsorption of SBS was observed for all the poly(NIPAAm-co-MPTMOS-*n*) gels. On the other hand, SDBS was found to be adsorbed on the poly(NIPAAm-co-MPTMOS-*n*) gels (*n* = 1, 3, 5, 10) as shown in Figure 6. The amount of SDBS adsorbed decreased with increase in the MPTMOS content. Comparison



**Figure 5** Temperature dependence of the swelling ratio of poly(NIPAAm-co-MPTMOS-*n*) gels: (○) *n* = 1; (●) *n* = 3; (△) *n* = 5; (▲) *n* = 10; (◇) *n* = 30; (◆) *n* = 50; (□) *n* = 70.



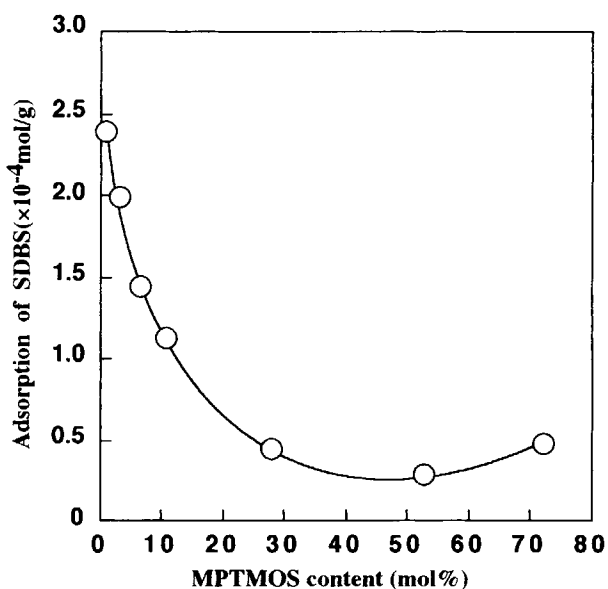
**Figure 6** Temperature dependence of the amount of SDBS adsorbed on the poly(NIPAAm-co-MPTMOS-*n*) gels: (○) *n* = 1; (●) *n* = 3; (△) *n* = 5; (▲) *n* = 10.

of the result of SBS with that of SDBS reveals that the hydrophobic interaction between dodecyl groups of SDBS and the poly(NIPAAm-co-MPTMOS-*n*) gels contributes to the adsorption of SDBS on the hybrid gels. Except for adsorption on the poly(NIPAAm-co-MPTMOS-1) gel, the amounts of adsorption decreased with increasing temperature. Consequently, the amounts of adsorption is closely related to the volume of the poly(NIPAAm-co-MPTMOS-*n*) gels in water, i.e., the penetration rate of SDBS into the hybrid gels relating to the pore size of the gel networks results in the temperature dependence of adsorption. On the other hand, a small increase in the amount of SDBS adsorbed on the poly(NIPAAm-co-MPTMOS-1) gel at 30°C may be interpreted in terms of hydrophobicity. The hydrophobicity is known to increase with respect to aggregation of poly(NIPAAm) segments in water.<sup>10</sup> The swelling ratio of the poly(NIPAAm-co-MPTMOS-1) gel at 30°C is larger than those of other hybrid gels, namely, SDBS can penetrate into the poly(NIPAAm-co-MPTMOS-1) easily compared to others. Therefore, the higher mobility of the SDBS at higher temperature and higher hydrophobicity caused the difference between the poly(NIPAAm-co-MPTMOS-1) gel and others.

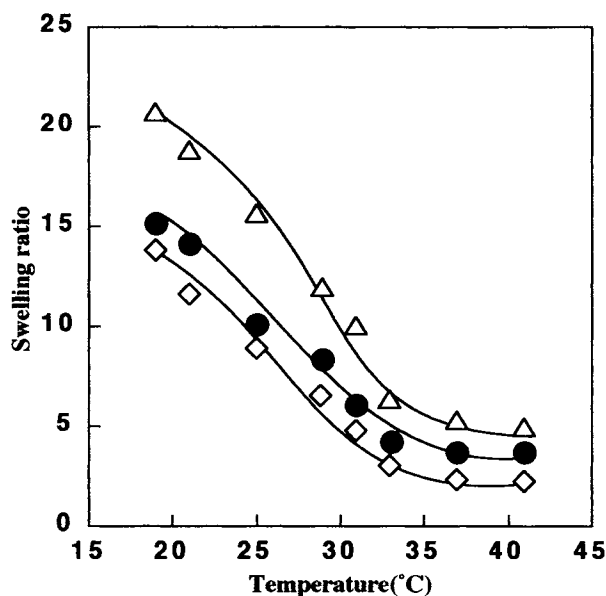
Figure 7 shows the amount of SDBS adsorbed on the poly(NIPAAm-co-MPTMOS-*n*) at 21°C. Although the amount of SDBS adsorbed decreased with increasing the MPTMOS content up to 50 mol %, a significant increase in the amount of

adsorption was recognized for the poly(NIPAAm-co-MPTMOS-70). The swelling ratio of the hybrid gels at 21°C decreased with increasing the MPTMOS content as shown in Figure 5. Therefore, the increase in the amount of adsorption for the poly(NIPAAm-co-MPTMOS-70) gels is interpreted in terms of an increase in hydrophobicity. Incorporation of MPTMOS in the hybrid gels and consequent formation of —Si—O—Si— linkages increased the hydrophobicity and rigidity of the poly(NIPAAm-co-MPTMOS-*n*) gels.

Figure 8 shows the swelling ratio of poly(NIPAAm-co-MPTMOS-1), poly(NIPAAm-co-MPTMOS-1) modified with TMOS, and poly(NIPAAm-co-MPTMOS-1) modified with APTEOS. The swelling ratio was decreased by modification with TMOS. The decrease of swelling ratio of the modified hybrid gels with TMOS may be closely related to the increase in hydrophobicity and rigidity due to condensation and formation of —Si—O—Si— gel networks. Although the elemental analysis indicated the incorporation of TMOS in the hybrid gels, it was difficult to estimate the amounts of TMOS incorporated into the hybrid gels. Contrary to the treatment with TMOS, the modification of the hybrid gels with APTEOS brought about the increase in the swelling ratio. The increase in the swelling ratio is due to incorporation of hydrophilic amino groups in the poly(NIPAAm-co-MPTMOS-1) gel. The anion-exchange capacity of the poly(NIPAAm-co-



**Figure 7** Amounts of SDBS adsorbed on the poly(NIPAAm-co-MPTMOS-*n*) gels at 21°C.



**Figure 8** Change in the swelling ratio of three hybrid gels: (●) poly(NIPAAm-co-MPTMOS-1) gel; (Δ) poly(NIPAAm-co-MPTMOS-1) gel modified with APTEOS; (◇) poly(NIPAAm-co-MPTMOS-1) gel modified with TMOS.

MPTMOS-1) gel was 0.13 meq/g. On the basis of the value of the anion-exchange capacity, the amount of APTEOS incorporated in the hybrid gels was about 3 mol %, which was more than three times of the MPTMOS content in the hybrid gel. Therefore, the hybrid gels may be promising for reacting hybrid gels, i.e., the modification of the hybrid gels is easily achieved by treatment with other silane compounds bearing various functional groups.

## CONCLUSION

Poly (*N*-isopropylacrylamide)-SiO<sub>2</sub> hybrid gels were prepared by copolymerization of *N*-isopropylacrylamide and 3-methacryloxypropyltrimethoxysilane (MPTMOS) and following hydrolysis and condensation. The hybrid gels exhibited temperature dependence of both the swelling ratio and adsorption of solutes due to the phase transition of poly-(NIPAAm), and their temperature dependence was related to the MPTMOS content in the hybrid gels. In addition, the modification of thermosensitive properties of the hybrid gels could be achieved by treatment with other silane compounds.

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