Permeability Properties of Isometrically Temperature-Responsive Poly(acrylic acid)-*graft*-Oligo(*N*-isopropylacrylamide) Gel Membranes

NAOJI KUBOTA, TETSUYA MATSUBARA, YUKARI EGUCHI

Department of Applied Chemistry, Faculty of Engineering, Oita University, Dannoharu, Oita 870–11, Japan

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ABSTRACT: A series of temperature-responsive hydrogels were prepared by grafting oligo(*N*-isopropylacrylamide) (ONIPAAm) chains onto a crosslinked poly(acrylic acid) (PAAc) network, intending an application to drug delivery systems (DDS). Cloud points and swelling ratios of the obtained PAAc-*graft*-ONIPAAm gels were measured as a function of temperature under various pH conditions. At pH $>$ 4.5, the clear cloud points were observed at 31–33°C, which were almost the same values as that of poly(*N*-isopropylacrylamide) (PNIPAAm), whereas swelling/shrinkage phenomenon was not observed in the temperature range 25–45°C. It seemed that grafted ONIPAAm chains underwent the coil-to-globule transition, while the crosslinked PAAc network remained unchanged, due to the anionic charges on the main chains. In the presence of NaCl in the buffer solution, the phase transition temperature was slightly lowered. To assess the applicability of these temperature-responsive PAAc-*graft*-ONIPAAm gels to DDS, permeability of theophylline through the gel membranes was measured as a function of temperature. At a temperature below the cloud point, the permeability of theophylline was low, whereas it was high at an elevated temperature above the cloud point. J Appl Polym Sci 70: 1027–1034, 1998

Key words: *N*-isopropylacrylamide; acrylic acid; graft polymer; temperature-responsive hydrogel; permeability

INTRODUCTION

Poly(*N*-isopropylacrylamide) (PNIPAAm) gel is known to undergo a volume phase transition in water, in response to changes in temperature.[1,2] Thermal analysis of phase separation of PNIPAAm was first reported by Heskins and Guillet.[3] The linear PNIPAAm chain is soluble in cold water but separates from solution upon heating, with a lower critical solution temperature (LCST) of 31°C. The phase transition temperature of the PNIPAAm gel is controlled primarily by the same factors as those for linear PNIPAAm, and is close to that of the linear PNIPAAm solution. However, the transition temperature of the PNIPAAm gel is always slightly higher (1–2°C) than that of the linear PNIPAAm solution.[4] Furthermore, it decreases as the subchain length between two adjacent crosslinking points in the gel increases.[5] In general, the thermosensitivity of PNIPAAm is based on the specific hydrophilic/hydrophobic balance effects.[6] Therefore, the volume phase transition of the PNIPAAm gel is sensitive to comonomers incorporated into the network. Hirotsu et al. observed a systematic increase in the transition temperature with increasing the concentration of sodium acrylate (NaAAc) comonomer.[7] A simple interpretation of this result is that the hydrogel maintains its hydrated state at higher temperatures with addition of the hydrophilic group. In this case, however, microphase sep-

Correspondence to: N. Kubota.

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aration between polymer-rich and -poor domains occurs before the system undergoes the volume phase transition.[8] On the other hand, copolymerization of *N*-isopropylacrylamide (NIPAAm) with hydrophobic butylmethacrylate lowered the transition temperature of the hydrogel.[9]

Moreover, understanding how fast a gel swells or shrinks is important for practical applications of the gel undergoing volume phase transition. The response rate of a hydrogel is inversely proportional to the square of the gel's dimension.[10] However, it was reported that the temperature-responsive change of terminal-grafted PNIPAAm was more rapid than that of multi-grafted PNIPAAm.[11] Yoshida et al. prepared a temperature-responsive hydrogel with a comb-like structure of PNIPAAm chains grafted on the crosslinked PNIPAAm network.[12] In this case, the shrinking rate was fast, compared to the conventional PNIPAAm gel, due to the immediate dehydration of the grafted PNIPAAm chains in the gel matrix based on the large mobility of grafted chains. They also found that the attractive forces between dehydrated chains were enhanced for the gel with longer grafted chains, resulting in faster deswelling.[13]

Approaches such as stimuli-sensitive and swelling-controlled polymers have received much attention in current pharmaceutical research. Temperature-responsive polymers can change the release rate of incorporated drugs according to the temperature. Okano et al. prepared an intelligent drug delivery system (DDS) from PNIPAAm-*co*-butylmethacrylate,[9] and Lim et al. investigated interpenetrating polymer network of PNIPAAm/PAAc system for a DDS.[14] However, these systems are not suitable for a DDS that releases drugs in case of high body temperature, because drug release from them is essentially increased by swelling of the PNIPAAm hydrogel at a low temperature. An increase in body temperature induced by the presence of pathogens may be an important stimulus to the effective release of antihyperpyretic drugs.

In this article, we report PAAc-*graft*-oligo(*N*-isopropylacrylamide) (ONIPAAm) gels for a DDS that releases drugs at a high temperature. The temperature-responsiveness of ONIPAAm chains is used to control the mesh size in the network through changes in temperature. Due to the temperature-responsive coil-to-globule transition of PNIPAAm,[15] below the phase transition temperature, the pore size of macroporous glass beads modified with PNIPAAm was smaller than that above the phase transition temperature.[16] In addition, high molecular weight PAAc is a well-known bioadhesive polymer, which sticks to the hydrated mucosal cells. To prolong the residence time of a drug delivery vehicle in contact with such mucosal surface, PAAc is often incorporated into a delivery formulation.

EXPERIMENTAL

Materials

NIPAAm from Wako Pure Chemical Industries, Ltd., Osaka, Japan, was purified by recrystallization from a benzene–hexane mixture and dried *in vacuo*. NaAAc was purchased from Nacalai Tesque, Inc., Kyoto, Japan, and 2-aminoethanethiol hydrochloride (AET) from Tokyo Kasei Kogyo, Tokyo, Japan. Acryloyl chloride, 2,2′-azobisisobutylonitrile (AIBN), *N,N*-methylenebisacrylamide (BIS), ammonium persulfate (APS), *N,N,N′,N′*-tetramethylethylenediamine (TEMED), and theophylline were purchased from Wako Pure Chemical Industries. Ethanol, dichloromethane, and triethylamine were distilled just before use. All other chemicals were reagent grade and used without further purification.

Preparation of Amino-Terminated ONIPAAm

Referring the procedure by Chen et al.,[17] ONIPAAm with a terminal amino group was prepared by free radical polymerization of NIPAAm (10.0 g, 88.5 mmol) with AET (1.03 g, 8.85 mmol) in ethanol (60 cm^3) at 70°C for 7 h using AIBN (0.146 g) under nitrogen atmosphere. After evaporation of ethanol, the product was washed with diethyl ether and dried *in vacuo*. It was redissolved in a minimal amount of water and deionized with an anion-exchange resin (Amberlite IRA-900) column, and then lyophilized. The yield was 98.7%. The number-average molecular weight of amino-terminated ONIPAAm was determined by titration as follows: 0.5 g of sample was dissolved in 25 cm^3 of standard 0.1 mol/dm^3 HCl solution, followed by back-titration with 0.1 mol/dm^3 NaOH solution using a pH meter. The molecular weight was calculated by dividing the mass of sample by the difference in amounts of consumed NaOH in the presence and absence of sample.

Preparation of ONIPAAm Macromonomer

Amino-terminated ONIPAAm (5.95 g, 4.92 mmol) and triethylamine (1.4 cm^3, 9.84 mmol) were dis-

Table I Feed Compositions for Preparation of PAAc-*graft*-ONIPAAm Gels

Sample Number	NaAAc (mmol/dm^3)	ONIPAAm (mmol/dm^3)	BIS (mmol/dm^3)
1	732	5	40.5
2	732	10	40.5
3	732	20	40.5
4	732	30	40.5
5	1100	5	40.5
6	1100	10	40.5
7	1100	20	40.5
8	1100	30	40.5
9	1465	5	40.5
10	1465	10	40.5
11	1465	20	40.5
12	1465	30	40.5

Total volume was 4 cm^3.

solved in 30 cm^3 of CH_2Cl_2, and acryloyl chloride (0.40 cm^3, 4.92 mmol) was added to the solution very slowly, with stirring, at 0°C. The reaction mixture was stirred at 0°C for 1 h, then at room temperature overnight. After evaporation of CH_2Cl_2, the product was deionized with a mix-bed ion-exchange resin (Amberlite IRA-900 and Dowex HCR-W2) column, and then lyophilized. The yield was 97.4%.

Preparation of PAAc-*graft*-ONIPAAm Gel

ONIPAAm macromonomer (25–148 mg, 5–30 mmol/dm^3), BIS (25 mg, 40.5 mmol/dm^3), and TEMED (20 mm^3) were dissolved in 2 cm^3 of deionized water. NaAAc (275–550 mg, 732–1465 mmol/dm^3) was dissolved in 2 cm^3 of deionized water. Both solutions were mixed, and nitrogen gas was bubbled under cooling for 20 min to remove residual oxygen. To the solution, 40 mg of APS was added, and the mixture was immediately poured onto a glass dish of 6-cm diameter. The radical polymerization was carried out at room temperature under nitrogen atmosphere. After standing overnight, the obtained gels were extensively washed with a 1/15 mol/dm^3 phosphate-buffered solution (PBS) of pH 7.4. The feed compositions of monomers are listed in Table I, and the synthetic route is illustrated in Figure 1. IR spectra of the gels were recoded on a Hitachi 270–50 IR spectrophotometer.

Measurement of Cloud Point

Cloud points of the gels were measured by reading the transmittance at 600 nm on a Shimadzu UV-120–02 spectrophotometer. The PAAc-*graft*-ONIPAAm gel equilibrated in a PBS of predetermined pH (pH 4.5–7.4) overnight was cut into pieces and placed in a cuvette. A cuvette holder in the spectrophotometer was thermally controlled by using a heating circular. A thermocouple was inserted into the gel in the cuvette to obtain an accurate temperature reading. The temperature was raised from 25 to 45°C, and the transmittance value was read every 1°C increment of sample in the cuvette. The time duration between each temperature increment was 10 min.

Determination of Swelling Ratio

Each gel punctured by a cork borer, which has a diameter of 20 mm and a thickness of 2 mm, was immersed in a PBS of pH 7.4 containing 0.9% NaCl for at least 24 h at 40°C. The swollen gel membranes were taken out of the PBS and tapped with filter paper to remove excess solution on the surface, and then weighed. In the same manner, they were reequilibrated at 30°C and weighed. Finally, the gels were vacuum dried at 50°C. The swelling ratio was calculated by dividing the swollen gel weight by the dried polymer weight.

Measurement of Permeability

Permeation experiments were conducted using a diaphragm-type cell consisting of two chambers.

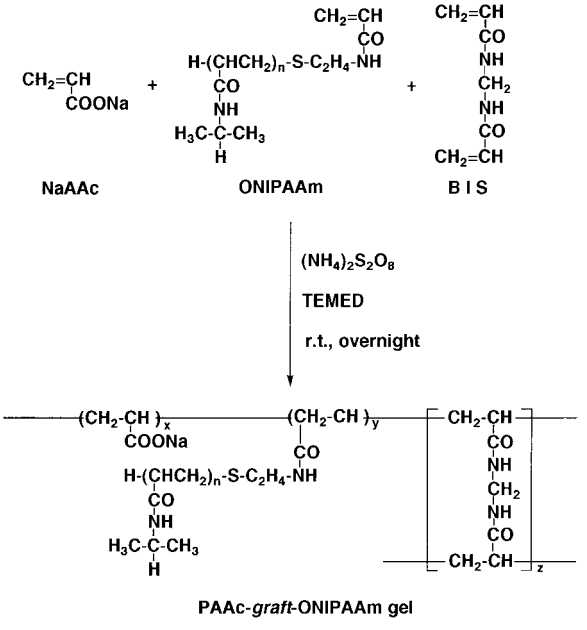

Figure 1 Synthetic route for PAAc-*graft*-ONIPAAm gels.

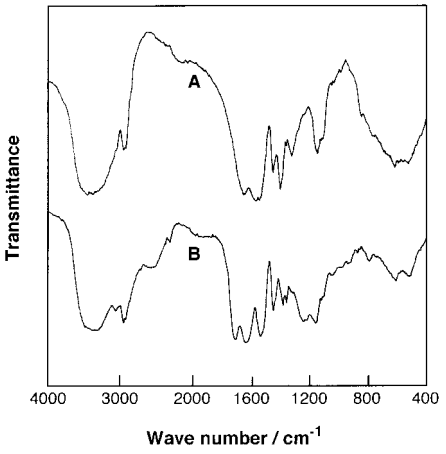

Figure 2 IR spectra of PAAc-*graft*-ONIPAAm gels: (A) PAAc-*graft*-ONIPAAm gel neutralized; (B) PAAc-*graft*-ONIPAAm gel treated with HCl solution of pH 1.6 for 1 h.

Each chamber had a volume of 25 cm^3 and an effective diffusion area of 4.0 cm^2. The gel membrane equilibrated in the PBS of pH 7.4 containing 0.9% NaCl at the desired temperature was placed in the cell whose temperature was controlled by a circulating thermostat (30 and 40°C). To the left-hand chamber, 25 cm^3 of the PBS containing theophylline (3.0 g/dm^3) was introduced, and 25 cm^3 of the PBS was added to the right-hand chamber. The solutions in the chambers were stirred. From both solutions, 0.1 cm^3 of samples were withdrawn at proper intervals and diluted to 10 cm^3. The concentration of theophylline was determined from the absorbance at 271 nm using a Hitachi U-2000 spectrophotometer.

RESULTS AND DISCUSSION

Preparation of PAAc-*graft*-ONIPAAm gel

The number-average molecular weight of amino-terminated ONIPAAm was estimated as 1230 (n = 10.2) by titration. This value is fully consistent with the initial monomer ratio of NIPAAm to AET. For the second step, a polymerizable end group was introduced into amino-terminated ONIPAAm to form a macromonomer. Finally, ONIPAAm macromonomer was polymerized with NaAAc (Fig. 1). Figure 2 shows the IR spectra of the PAAc-*graft*-ONIPAAm gel obtained and the PAAc-*graft*-ONIPAAm gel treated with HCl solution of pH 1.6. The spectrum of the former has the absorption peaks at 1580 cm^{-1} and 1400 cm^{-1} assigned to carboxylate groups of NaPAAc, and that of the latter shows the absorption at 1720 cm^{-1} assigned to carboxyl groups of PAAc. Further, both spectra have the absorption bands at 1650 cm^{-1} and 1540 cm^{-1} assigned to amide I and II of ONIPAAm, respectively.

Phase Transition of PAAc-*graft*-ONIPAAm gel

Hydrophobic interaction is peculiar in the phase transition of hydrogels containing hydrophobic polymers. We measured cloud points as phase transition temperature for the PAAc-*graft*-ONIPAAm gels. Figures 3–6 exhibit the temperature dependence of the transmittance at 600 nm for the gels having various contents of NaAAc and NIPAAm monomers in the systems under pH conditions of 4.5, 5.0, 6.0, and 7.0, respectively. The cloud point was determined from the intersection of the baseline and the tangent to the decreasing transmittance. Because the pK_a of AAc is 4.25, the cloud point could not be observed at pH < 4.0; the PAAc-*graft*-ONIPAAm gels were always tur-

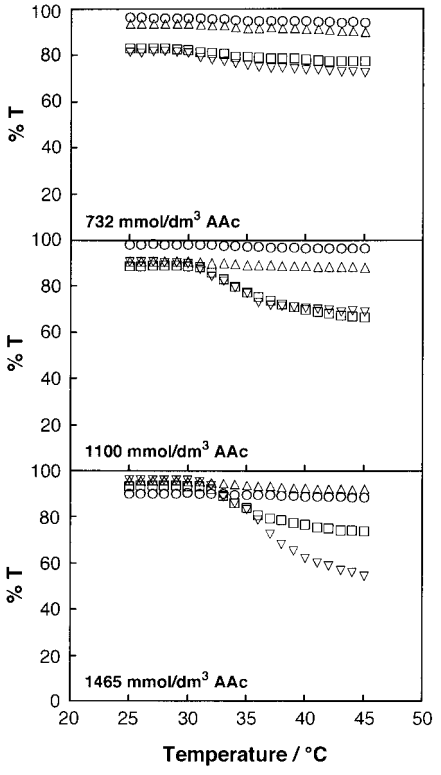

Figure 3 Temperature dependence of optical transmittance of PAAc-*graft*-ONIPAAm gels at pH 4.5: (○) 5 $mmol/dm^3$ ONIPAAm; (△) 10 $mmol/dm^3$ ONIPAAm; (□) 20 $mmol/dm^3$ ONIPAAm; (▽) 30 $mmol/dm^3$ ONIPAAm.

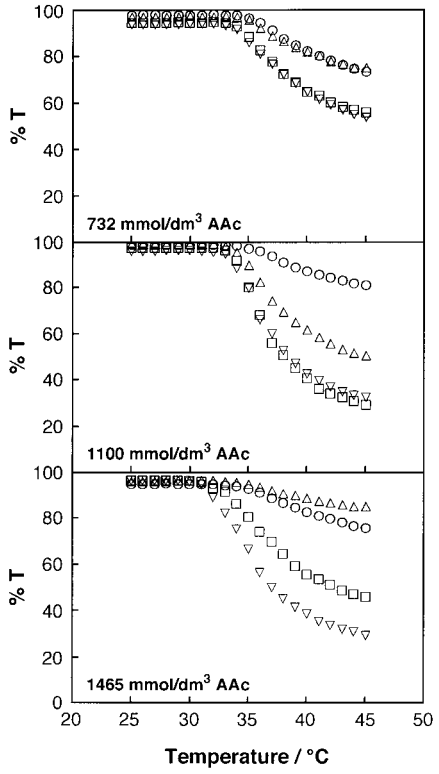

Figure 4 Temperature dependence of optical transmittance of PAAc-*graft*-ONIPAAm gels at pH 5.0: (○) 5 mmol/dm^3 ONIPAAm; (△) 10 mmol/dm^3 ONIPAAm; (□) 20 mmol/dm^3 ONIPAAm; (▽) 30 mmol/dm^3 ONIPAAm.

bid at pH < 4.0. At higher pH, carboxyl groups of PAAc are ionized, and the gels become opaque at 31–33°C after a step-wise increase in temperature. Additionally, the higher the ONIPAAm content, the larger the change in the transmittance. This is due to the increase of hydrophobic interaction at the higher ONIPAAm content. Appearance of these cloud points indicates that the PAAc-*graft*-ONIPAAm gels became heterogeneous when the temperature reached the phase transition temperature of ONIPAAm. At the molecular level, ONIPAAm chains are phase-separated from water molecules.

It was reported that the volume phase transition temperature and the volume change at the transition increased with increasing the amount of ionizable groups in the network.[7] However, the PAAc-*graft*-ONIPAAm gels in this study show an almost constant cloud point, regardless of the content of hydrophilic AAc over a wide range of compositions. It seems that only the grafted ONIPAAm chains caused the phase transition, unlike the random copolymer system of NIPAAm and AAc, considering that the comb-like ONIPAAm chains grafted on the PAAc gel have the same phase transition temperature as the linear PNIPAAm homopolymer.[17] Because linear PNIPAAm dehydrates and aggregates freely above its LCST, terminally grafted ONIPAAm also dehydrates and aggregates freely above its phase transition temperature.

To apply these graft polymers to biomaterials, it should be considered whether the polymers retain their temperature-response at physiological conditions of pH 7.4 in a saline solution. Figure 7 shows the temperature dependence of the transmittance at 600 nm in the PBS of pH 7.4 containing 0.9% NaCl. In this case, the phase transition temperature is slightly lower than that in the case without NaCl, but the extent is not as large. This result is probably due to the high osmotic pressure of external NaCl solution. The phase transition temperature of linear PNIPAAm is independent of molecular weight,[4] and the linear PNIPAAm chains have a sharper transition temperature than the microgel.[5] Accordingly, the

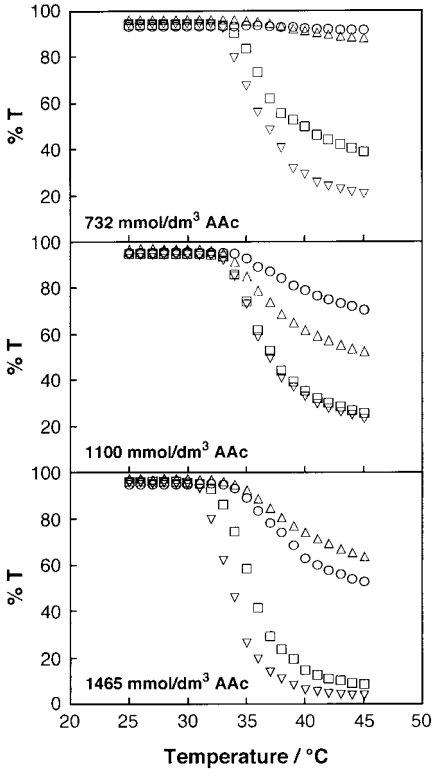

Figure 5 Temperature dependence of optical transmittance of PAAc-*graft*-ONIPAAm gels at pH 6.0: (○) 5 mmol/dm^3 ONIPAAm; (△) 10 mmol/dm^3 ONIPAAm; (□) 20 mmol/dm^3 ONIPAAm; (▽) 30 mmol/dm^3 ONIPAAm.

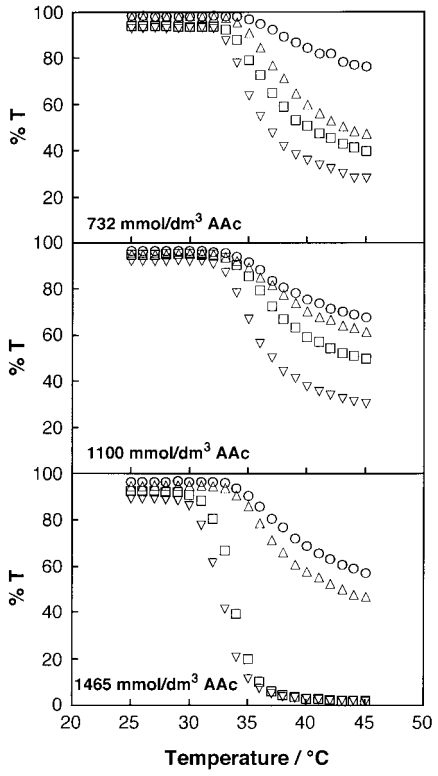

Figure 6 Temperature dependence of optical transmittance of PAAc-*graft*-ONIPAAm gels at pH 7.0: (○) 5 mmol/dm^3 ONIPAAm; (△) 10 mmol/dm^3 ONIPAAm; (□) 20 mmol/dm^3 ONIPAAm; (▽) 30 mmol/dm^3 ONIPAAm.

PAAc-*graft*-ONIPAAm gel system also shows the sharp response to the change in temperature.

Table II lists the swelling ratios of the PAAc-*graft*-ONIPAAm gel at 30 and 40°C, along with those of the PAAc gel for comparison. The swelling ratio of the former gel is lower than that of the latter gel. However, clear changes in swelling ratio cannot be detected between 30 and 40°C for either system. This result supports the concept mentioned above that swelling is independent of temperature, and the grafted ONIPAAm chains bring about the coil-to-globule transition according to the temperature. The cloud point indicates microscopic inhomogeneity without volume phase transition. These phenomena allow us to expect that the PAAc-*graft*-ONIPAAm gel membranes will show an isometric phase transition in response to the change in temperature.

Permeability Properties of PAAc-*graft*-ONIPAAm Gel Membranes

The permeability of theophylline through the PAAc-*graft*-ONIPAAm gel membrane, consisting of 1100 mmol/dm^3 PAAc and 30 mmol/dm^3 ONIPAAm, in response to a change in temperature between 30 and 40°C, was studied. This temperature change was designed to cross the transition temperature, which was determined by the cloud point measurement. Permeability of theophylline was calculated from the following equation derived from the Fick's law of diffusion, as previously reported:[18,19]

$$\frac{P}{\delta} = -\frac{V}{2At} \ln \frac{\Delta C_t}{C_0},$$

Table II Swelling Ratios of PAAc-*graft*-ONIPAAm and PAAc Gels

Temperature	PAAc-*graft*-ONIPAAm[a]	PAAc
30°C	40.4	48.4
40°C	40.1	45.4

[a] Prepared from 1100 mmol/dm^3 NaAAc, 30 mmol/dm^3 ONIPAAm, and 40.5 mmol/dm^3 BIS.

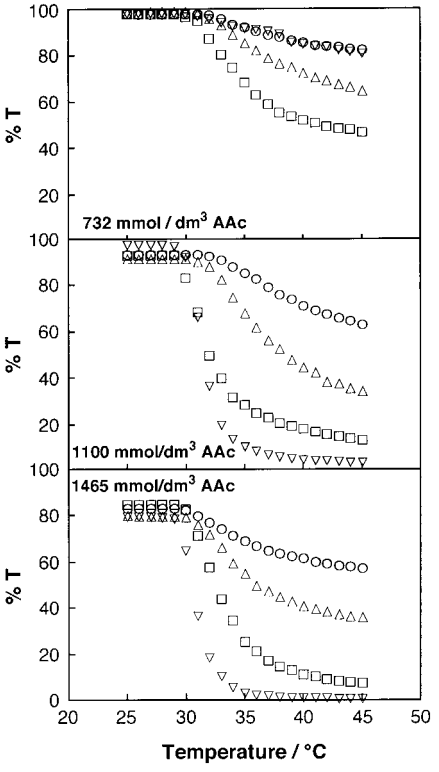

Figure 7 Temperature dependence of optical transmittance of PAAc-*graft*-ONIPAAm gels at pH 7.4 containing 0.9% NaCl: (○) 5 mmol/dm^3 ONIPAAm; (△) 10 mmol/dm^3 ONIPAAm; (□) 20 mmol/dm^3 ONIPAAm; (▽) 30 mmol/dm^3 ONIPAAm.

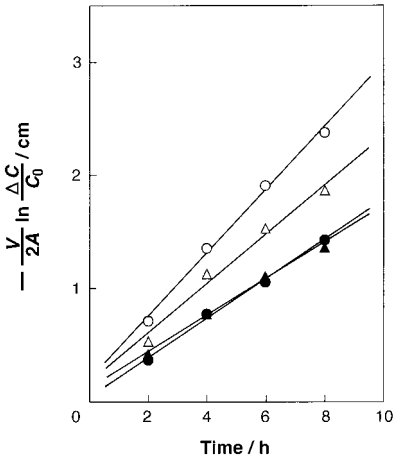

Figure 8 Permeabilities of PAAc-*graft*-ONIPAAm and PAAc gel membranes for theophylline: (○) PAAc-*graft*-ONIPAAm membrane at 40°C; (△) PAAc membrane at 40°C; (●) PAAc-*graft*-ONIPAAm membrane at 30°C; (▲) PAAc membrane at 30°C.

where P is the permeability coefficient, δ is the membrane thickness, V is the volume of each chamber, A is the membrane area, t is the time, ΔC_t is the concentration difference between both solutions, and C_0 is the initial concentration of theophylline. Figure 8 depicts the results of the permeation experiment using pH 7.4 PBS containing 0.9% NaCl. The slopes of the curves indicate the permeabilities, P/δ. As can be seen, a lower permeability was observed at 30°C, and when the temperature was raised to 40°C, the permeability increased.

Table III compiles the permeabilities and permeability coefficients of theophylline through the PAAc-*graft*-ONIPAAm and PAAc gel membranes. The change in permeability at higher temperature for the PAAc gel membrane can be explained by an increase in diffusivity with temperature. The change in permeability for the PAAc-*graft*-ONIPAAm gel membrane is higher than that for the PAAc gel membrane. The grafted ONIPAAm chains maintain high mobility as opposed to PAAc networks crosslinked each other, because they are free-end polymers. When external temperature is elevated above the phase transition temperature, the grafted ONIPAAm chains rapidly dehydrates to form tightly packed globule chains.[20] For low molecular weight chains, the intramolecular collapse is prior to intermolecular aggregation, because it involves no cooperative chain movement.[21] As a result, the polymer network seems to open the channels for solutes. Therefore, the conformations of the ONIPAAm chains grafted on the PAAc network are responsible for the increase and decrease of permeation rate. At the higher temperature, the ONIPAAm chains shrink, leaving the PAAc network open and facilitating increased drug permeation. At the lower temperature, however, the ONIPAAm chains extend to fill in the PAAc network and reduce the permeation rate of drug. This is schematically represented in Figure 9. This phenomenon is useful for a DDS that releases incorporated drugs at high temperature.

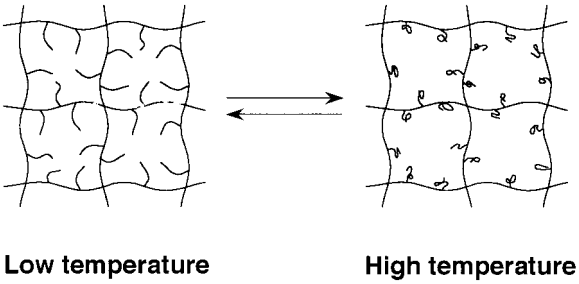

Figure 9 Schematic representation of phase transition corresponding to temperature for PAAc-*graft*-ONIPAAm gel.

As mentioned above, many researchers found an increased release rate of drugs through the

Table III Permeabilities and Permeability Coefficients of Theophylline through PAAc-*graft*-ONIPAAm and PAAc Gel Membranes

Membrane[a]	Permeability ($\times 10^{-5}$ cm/s)		Permeability Coefficient ($\times 10^{-6}$ cm/s)		Permeability Ratio (40°C/30°C)
	30°C	40°C	30°C	40°C	
PAAc-*graft*-ONIPAAm	4.8	7.7	5.9	9.5	1.6
PAAc	4.4	5.7	5.4	7.0	1.3

[a] Membrane thickness was about 1.2 mm.

swollen PNIPAAm hydrogels at the lower temperature, and lower release rate of drugs through the collapsed PNIPAAm hydrogels at higher temperature. In contrast, our system shows an increased permeation rate of drug at the higher temperature, and lower permeation rate of drug at the lower temperature. Mesh size of the PAAc network is changed between the opened and filled states. Such a system would be highly useful to increase the release of drugs at higher body temperature, not at lower body temperature. However, it should be necessary to further optimize graft chains, comonomer, and crosslinker concentrations, to obtain an ON–OFF drug delivery system.

In conclusion, the phase transition behavior of the PAAc-*graft*-ONIPAAm gels became significant with increasing ONIPAAm content, whereas the phase transition temperature was not changed by increasing the PAAc content at pH range 4.5–7.4. These hydrogels showed the cloud point, but did not show the swelling/shrinkage phenomenon. Consequently, the PAAc-*graft*-ONIPAAm gel is thought an isometrically temperature-responsive gel. Controlled release and permeation of drugs through the PAAc-*graft*-ONIPAAm gel membrane were regulated to some extent by the coil-to-globule transition of ONIPAAm chains grafted on the PAAc network.

REFERENCES

1. T. Tanaka, *Phys. Rev. Lett.,* **40,** 820 (1978).
2. Y. Horikawa, T. Tanaka, and E. S. Matsuo, *J. Chem. Phys.,* **81,** 6379 (1984).
3. M. Heskins and J. E. Guillet, *J. Macromol. Sci. Chem.,* **A2,** 1441 (1968).
4. K. Otake, H. Inomata, M. Konno, and S. Saito, *Macromolecules,* **23,** 283 (1990).
5. C. Wu and S. Zhou, *Macromolecules,* **30,** 574 (1997).
6. L. D. Taylor and L. D. Cerankowski, *J. Polym. Sci., Polym. Chem.,* **13,** 2551 (1975).
7. S. Hirotsu, Y. Hirokawa, and T. Tanaka, *J. Chem. Phys.,* **87,** 1392 (1987).
8. M. Shibayama, Y. Fujikawa, and S. Nomura, *Macromolecules,* **29,** 6535 (1996).
9. T. Okano, Y. H. Bae, H. Jacobs, and S. W. Kim, *J. Controlled Release,* **11,** 255 (1990).
10. E. S. Matsuo and T. Tanaka, *J. Chem. Phys.,* **89,** 1695 (1988).
11. Y. G.Takei, T. Aoki, K. Sanui, N. Ogata, Y. Sakurai, and T. Okano, *Macromolecules,* **27,** 6163 (1994).
12. R. Yoshida, K. Uchida, Y. Kaneko, K. Sakai, A. Kikuchi, Y. Sakurai, and T. Okano, *Nature,* **374,** 240 (1995).
13. Y. Kaneko, K. Sakai, A. Kikuchi, R. Yoshida, Y. Sakurai, and T. Okano, *Macromolecules,* **28,** 7717 (1995).
14. Y. H. Lim, D. Kim, and D. S. Lee, *J. Appl. Polym. Sci.,* **64,** 2647 (1997).
15. M. Meewes, J. Ricka, M. de Silva, R. Nyffenegger, and Th. Binkert, *Macromolecules,* **24,** 5811 (1991).
16. M. Gewehr, K. Nakamura, N. Ise, and H. Kitano, *Makromol. Chem.,* **193,** 249 (1992).
17. G. Chen and A. S. Hoffman, *Nature,* **373,** 49 (1995).
18. N. Kubota, K. Ohga, M. Moriguchi, *J. Appl. Polym. Sci.,* **42,** 495 (1991).
19. N. Kubota, Y. Kikuchi, Y. Mizuhara, T. Ishihara, and Y. Takita, *J. Appl. Polym. Sci.,* **50,** 1665 (1993).
20. K. Kubota, S. Fujishige, and I. Ando, *J. Phys. Chem.,* **94,** 5154 (1990).
21. X.Qiu, C. M. S. Kwan, and C. Wu, *Macromolecules,* **30,** 6090 (1997).