

Preparation of Thermosensitive Cellophane-*Graft-N*-Isopropylacrylamide Copolymer Membranes and Permeation of Solutes Through the Membranes

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ABSTRACT: Thermosensitive membranes with high mechanical strength were prepared by heterogeneous graft copolymerization of *N*-isopropylacrylamide (NIPAAm) onto cellophane in a nitric acid solution using cerium ammonium nitrate as an initiator, and the permeation behavior of solutes such as lithium chloride and poly(ethylene glycol)s (PEGs) through the membranes at various temperatures was investigated. The degree of graft copolymerization of NIPAAm on cellophane depended on temperature, time, initiator concentration, and so on. The copolymer membranes having a high content of the NIPAAm moiety could be obtained at 25°C for 24 h. The permeation of Li⁺ through the membranes was affected by temperature, i.e., the permeation rate of Li⁺ increased with increasing temperature up to 32°C and then decreased rapidly above 35°C. The permeation rate of Li⁺ through the copolymer membranes at 40°C decreased considerably, but that at 20°C decreased slightly with an increasing amount of the NIPAAm moiety in the membranes. The permeation rate of PEGs with a molecular weight more than 1000 through the cellophane-*g*-NIPAAm copolymer membranes was considerably suppressed and only the permeation rate of PEG300 increased with increasing temperature up to 35°C and then decreased at 40°C. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 209–216, 1997

Key words: thermosensitive membrane; *N*-isopropylacrylamide; cellophane; permeation; lithium

INTRODUCTION

It is well known that poly(*N*-isopropylacrylamide) [poly(NIPAAm)] hydrogels are thermally reversible hydrogels and exhibit a lower critical solution temperature (LCST) around 32°C in an aqueous solution. The poly(NIPAAm) hydrogels have become of interest from fundamental and practical points of view.^{1–6}

A few studies on the permeation of solutes through poly(NIPAAm) hydrogel membranes

have been performed.^{7,8} Okano et al. reported the preparation of NIPAAm–butyl methacrylate (BMA)–methylenebisacrylamide (MBAAm) terpolymer membranes and the thermocontrolled permeation of glucose and insulin through poly(NIPAAm–BMA–MBAAm) membranes.⁸

In our previous article,⁹ we reported the preparation of the hydrogel membranes by the graft copolymerization of NIPAAm on poly(vinyl alcohol) (PVA) and the switching of the permeation of solutes such as lithium chloride and Methylene Blue through the PVA-*g*-NIPAAm membranes by changing temperature. The PVA-*g*-NIPAAm membranes have several advantages,⁹ but they do not have high mechanical strength. To prepare

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the thermosensitive membranes having high mechanical strength, we made the membranes by the grafting of poly(NIPAAm) onto cellophane, which are semipermeable membranes. In this article, the preparation of cellophane-*g*-NIPAAm copolymer membranes and the permeation behavior of LiCl or PEGs through the membranes at various temperatures are described.

EXPERIMENTAL

Materials

NIPAAm was kindly provided by Kohjin Co. and purified by recrystallization using hexane and benzene. Cellophane was a commercial one (Futamura Chemical Co.). Reagent-grade PEGs with various average molecular weights (MWs), PEG20000 (MW, 20000), PEG2000 (MW, 2000), PEG1000 (MW, 1000), and PEG300 (MW, 300), were purchased from Wako Pure Chemical Industry Co. Other chemical compounds were reagent grade and were used as received.

Graft Copolymerization of NIPAAm onto Cellophane

Commercial cellophane was soaked in deionized boiling water for 30 min to remove the plasticizer before copolymerization. Heterogeneous graft copolymerization of NIPAAm onto cellophane (60 mg) was carried out in a nitric acid solution using cerium ammonium nitrate as an initiator in a sealed test tube under a nitrogen atmosphere under shaking. After copolymerization, the products in the test tube were poured into propanone to remove the unreacted monomer and so on. After that, to remove the NIPAAm homopolymer, the grafted cellophane was soaked in deionized water and the temperature of the water was alternatively raised and lowered above and below the LCST and the grafted cellophane was washed until no turbidity in the water could be found at the temperature above the LCST. The weight increase of cellophane grafted was measured to determine the optimum conditions for graft copolymerization. The optimum conditions for the preparation of the graft copolymer membranes having a high content of the NIPAAm moiety were determined by varying the temperature, initiator concentration, NIPAAm concentration, and so on. The phase-transition temperature of the poly(NIPAAm) grafted onto cellophane was measured by

differential scanning calorimetry (Seiko Denshi Co., DSC/100).

Observation of Cellophane Grafted with Poly(NIPAAm) by Scanning Electron Microscopy

After drying the grafted cellophane, it was covered with a gold vapor and then pictures of the surface and cross section of the grafted cellophane were taken by scanning electron microscopy.

Permeation of Solutes Through the Cellophane-*g*-NIPAAm Membranes

Permeation experiments were carried out at various temperatures with magnetic stirring, using a diaphragm glass cell consisting of two detachable parts (22 cm³). The membrane that had been soaked in water at the desired temperature prior to use was set in the middle of the two parts of the cell, clamped, and sealed with silicon rubber packing. The effective membrane area in the cell was 3.14 cm². The left side was deionized water and the right side was a solution containing solutes. Both solutions were adjusted to the desired temperature prior to the transport experiments. The concentration of Li⁺ or PEG was measured by a flame emission spectrophotometer or a refractometer, respectively.

RESULTS AND DISCUSSION

Synthesis of Cellophane-*g*-NIPAAm

The graft copolymerization of vinyl monomers on cellulose using Ce(IV) salt as an initiator in an aqueous solution was studied many researchers.¹⁰⁻¹² In this study, the graft copolymerization of NIPAAm onto cellophane was carried out by changing the copolymerization conditions. Grafting (%), polymerization (%), and grafting efficiency (%) of the graft copolymerization of NIPAAm onto cellophane are defined as follows:

Grafting (%)

$$= \frac{\text{copolymer (g)} - \text{cellophane (g)}}{\text{cellophane (g)}} \times 100 \quad (1)$$

Polymerization (%)

$$= \frac{\text{product (g)} - \text{cellophane (g)}}{\text{NIPAAm monomer (g)}} \times 100 \quad (2)$$

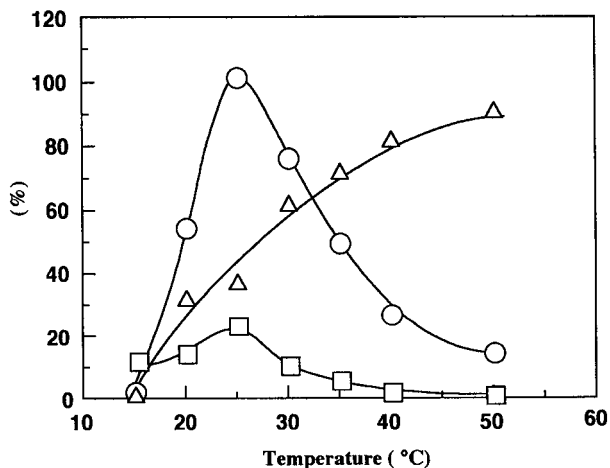


Figure 1 Effect of polymerization temperature on grafting of NIPAAm. [Ce(IV)] = 4.2 mmol dm⁻³, [NIPAAm] = 0.5 mol dm⁻³, [HNO₃] = 0.17N, 24 h. (○) Grafting (%); (△) polymerization (%); (□) grafting efficiency (%). Grafting (%) = {[copolymer (mg) - cellophane (mg)]/[cellophane (mg)]} × 100. Polymerization (%) = {[product (mg) - cellophane (mg)]/[NIPAAm monomer (mg)]} × 100. Grafting efficiency (%) = {[copolymer (mg) - cellophane (mg)]/[product (mg) - cellophane (mg)]} × 100.

Grafting efficiency (%)

$$= \frac{\text{copolymer (g)} - \text{cellophane (g)}}{\text{products (g)} - \text{cellophane (g)}} \times 100 \quad (3)$$

First, the graft copolymerization of NIPAAm onto cellophane was carried out by changing the temperature (Fig. 1). Other conditions except the

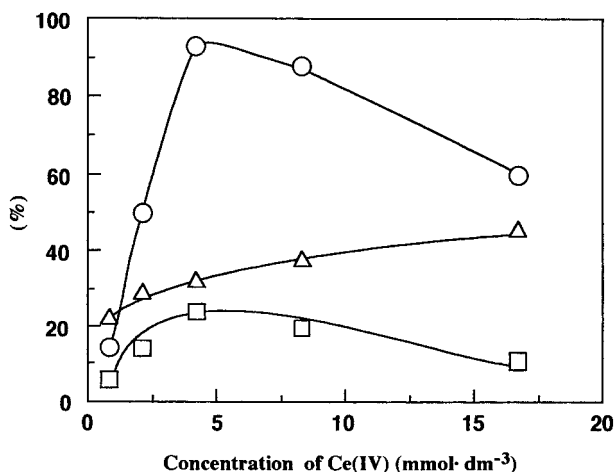


Figure 2 Effect of initiator concentration on grafting of NIPAAm. Polymerization: [NIPAAm] = 0.5 mol dm⁻³, [HNO₃] = 0.17N, 24 h, 25°C. (○) Grafting (%); (△) polymerization (%); (□) grafting efficiency (%).

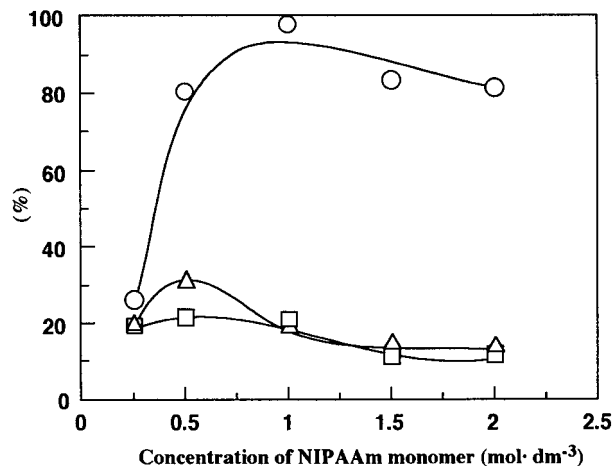


Figure 3 Effect of monomer concentration on grafting of NIPAAm. Polymerization: [Ce(IV)] = 4.2 mol dm⁻³, [HNO₃] = 0.17N, 24 h, 25°C. (○) Grafting (%); (△) polymerization (%); (□) grafting efficiency (%).

temperature were the same. The polymerization (%) increased with increasing temperature. This means that the polymerization of NIPAAm proceeded with increasing temperature. On the other hand, grafting (%) and grafting efficiency (%) increased with increasing temperature up to 25°C and then decreased at temperatures above 30°C. It is known that poly(NIPAAm) dissolves in water at temperatures below the LCST (about 32°C) and does not dissolve above the LCST. The decrease in the grafting (%) at temperatures above 30°C is attributed to the fact that the poly(NI-

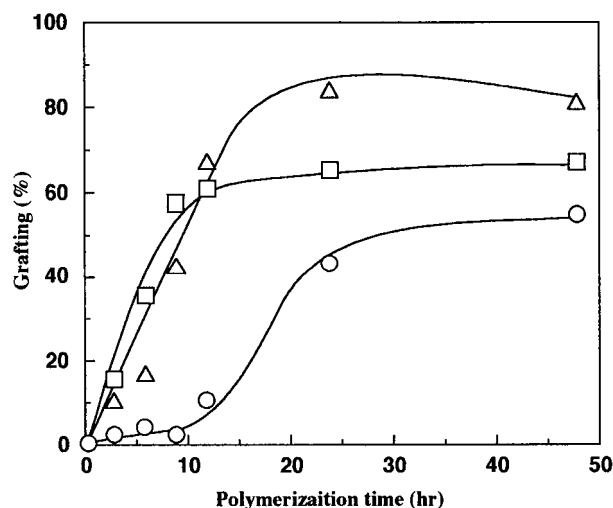


Figure 4 Time dependence of grafting of NIPAAm onto cellophane at different temperatures. [Ce(IV)] = 4.2 mmol dm⁻³, [NIPAAm] = 0.5 mol dm⁻³, [HNO₃] = 0.17N. (○) 20°C; (△) 25°C; (□) 30°C.

Table I Elemental Analysis of Cellophane, Poly(NIPAAm), and Cellophane-*g*-NIPAAm Copolymer Membranes with Various NIPAAm Contents

Samples	Grafting (%) ^a	Elemental Analysis			Grafting (%) ^b
		H (%)	C (%)	N (%)	
Cellophane	—	6.6	40.8	0.0	—
Poly(NIPAAm)	—	10.3	59.1	11.5	—
CN-1	5.2	6.9	42.7	1.6	14.7
CN-2	31.3	7.4	45.7	3.6	40.1
CN-3	89.6	8.1	49.2	5.8	87.3

Polymerization: cellophane 60 mg, [Ce(IV)] = 4.2 mmol dm⁻³, [HNO₃] = 0.17N, 25°C, 24 h. [NIPAAm] (mol dm⁻³): CN-1, 0.25; CN-2, 0.5; CN-3, 1.0.

^a These values were calculated from weight increase of the cellophane grafted.

^b These values were calculated by using the contents of nitrogen in the membranes.

PAAm)s grafted onto cellophane cover the surface of the cellophane due to their low solubility at temperatures above 30°C and prevent the following graft polymerization of NIPAAm onto the cellophane. Next, the effect of the concentration of Ce(IV) on the grafting of NIPAAm was studied at 25°C (Fig. 2). The maximum grafting (%) was obtained at the concentration of 5 mmol dm⁻³ of Ce(IV). The decrease in the grafting (%) above the concentration is due to the increase in the homopolymerization of NIPAAm and the oxidation of cellophane by the excess presence of cerium ammonium nitrate.^{12,13} The graft copolymerization was also carried out by changing the concen-

tration of NIPAAm at 25°C and the polymerization time at different temperatures (Figs. 3 and 4). The maximum grafting (%) was obtained at the concentration of 1 mol dm⁻³ of NIPAAm and after 24 h at various temperatures.

Consequently, the cellophane-*g*-NIPAAm membranes having about 100 grafting (%) of poly(NIPAAm) could be obtained by the graft copolymerization of NIPAAm (1 mol dm⁻³) onto cellophane (60 mg) at 25°C for 24 h in the presence of Ce(IV) (5 mmol dm⁻³) as an initiator in a 0.17 mol dm⁻³ HNO₃ aqueous solution.

The elemental analyses of the cellophane-*g*-NIPAAm membranes obtained by changing the concentration of NIPAAm are shown in Table I. The grafting (%) obtained from elemental analysis did not exactly coincide with that obtained from the weight increase of cellophane. In this study, we

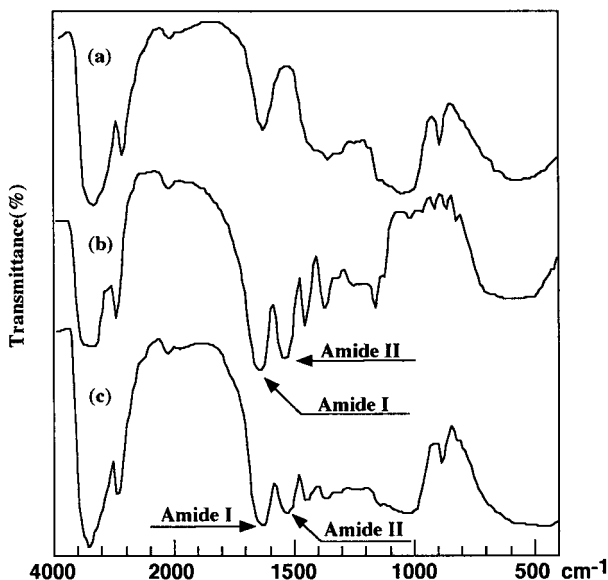


Figure 5 IR spectra of (a) cellophane, (b) poly(NIPAAm), and (c) cellophane-*g*-NIPAAm copolymer membrane.

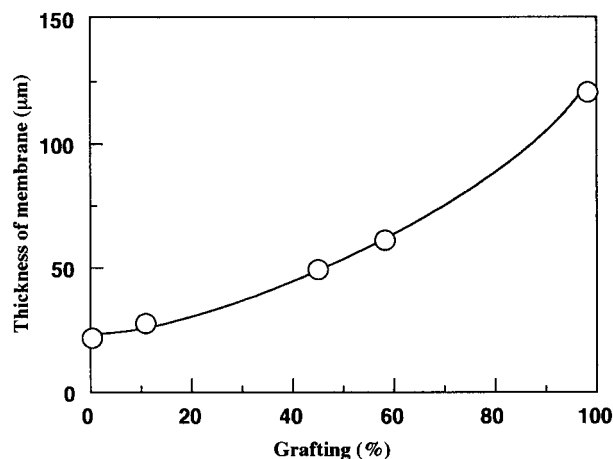


Figure 6 The relationship between grafting (%) and thickness of dry cellophane-*g*-NIPAAm copolymer membranes.

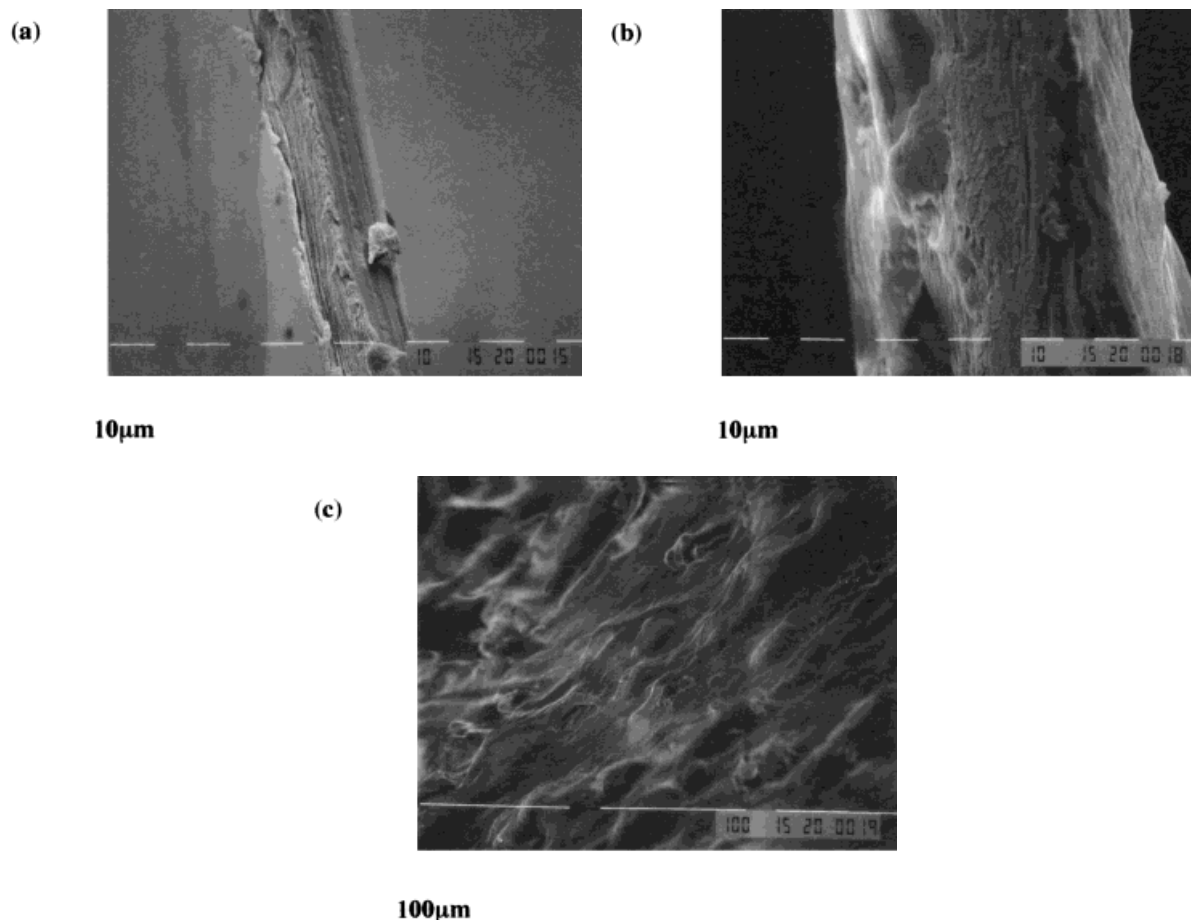


Figure 7 Scanning electron micrograph (SEM) of (a) cellophane and (b) cellophane-*g*-NIPAAm copolymer membrane; (c) ($\times 1500$).

determined the grafting (%) from the weight increase of the grafted cellophane.

Figure 5 shows the IR spectra of (a) cellophane, (b) poly(NIPAAm), and (c) the cellophane-*g*-NIPAAm membrane. Absorption bands at $1500\text{--}1700\text{ cm}^{-1}$ due to amide I and II were observed in the IR spectra of the cellophane-*g*-NIPAAm membrane. This result indicates that NIPAAm was introduced into the cellophane.

Figure 6 shows the relationship between grafting (%) and the thickness of dry cellophane-*g*-NIPAAm membranes. The thickness of the cellophane-*g*-NIPAAm membranes increased with increased grafting (%). This result suggests that the graft copolymerization of NIPAAm occurred on the surface of cellophane or in the cellophane.

To confirm this phenomenon, scanning electron micrographs of cellophane and cellophane-*g*-NIPAAm membrane were taken (Fig. 7). Figure 7(a), (b), and (c) represents the pictures of cross section of cellophane and the cellophane-*g*-NI-

PAAm membrane and the surface of the cellophane-*g*-NIPAAm membrane, respectively. The size of the cross section of the cellophane-*g*-NIPAAm copolymer membrane became above twice that of cellophane. These figures indicate that the graft copolymerization of NIPAAm occurred not only on the surface of cellophane but also in the cellophane.

Figure 8 shows the DSC curve of the wet cellophane-*g*-NIPAAm membrane. The phase-transition temperature of poly(NIPAAm) in the cellophane-*g*-NIPAAm membranes was 32.7°C . The temperature was almost the same as that of the NIPAAm homopolymer.

The transmittance of light of 660 nm through the cellophane-*g*-NIPAAm membrane in water was measured at various temperatures. The results are shown in Figure 9. In this case, the transmittance of light through the membrane at 20°C was referred to as 100%. The transmittance began to decrease at temperatures above 25°C and

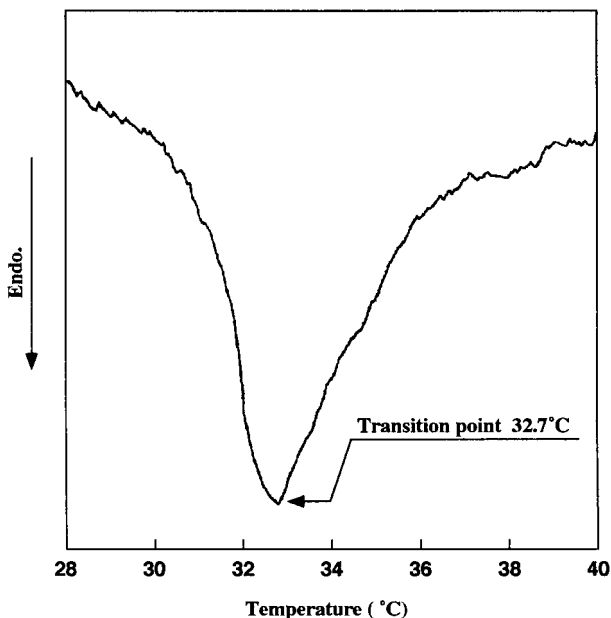


Figure 8 DSC curve of cellophane-*g*-NIPAAm copolymer membrane.

decreased significantly at temperatures above 30°C. Also, a slight transmittance of light was observed even at temperatures above 34°C.

Permeation of Solutes Through Cellophane-*g*-NIPAAm Membranes

The permeation of Li^+ through the cellophane-*g*-NIPAAm membrane was carried out at various

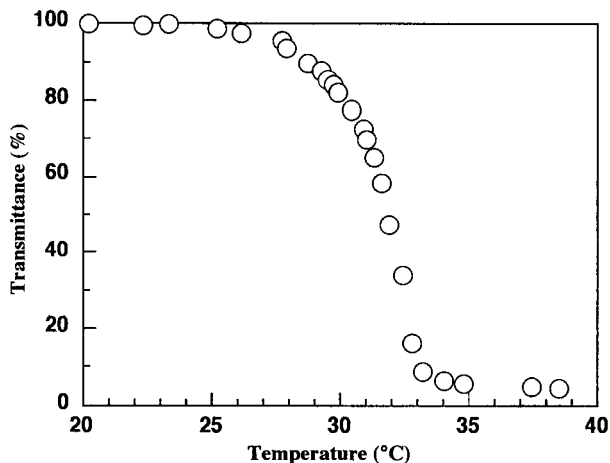


Figure 9 Transmittance of light through cellophane-*g*-NIPAAm copolymer membrane at various temperatures.

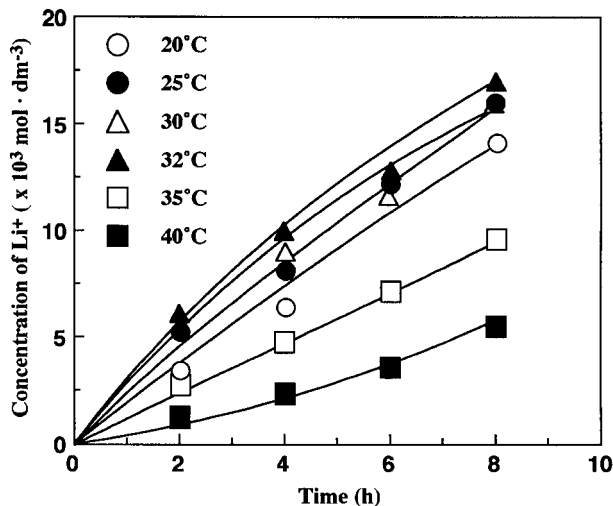


Figure 10 Changes in concentration of Li^+ on the left side of the membrane at various temperatures. Cellophane-*g*-NIPAAm membrane (grafting = 90%).

L	R
Water	0.045M LiCl

temperatures (20–40°C) (Fig. 10). The temperature dependence of the permeation rate of Li^+ through the cellophane-*g*-NIPAAm membrane is shown in Figure 11. In this figure, the temperature dependence of the permeation rate of Li^+ through the cellophane is also shown for compari-

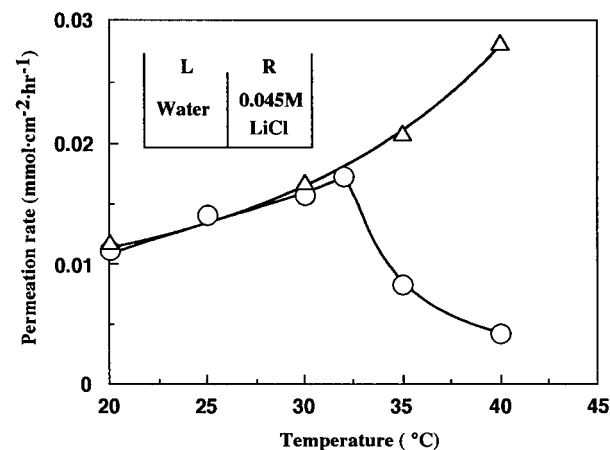


Figure 11 Temperature dependence of the permeation of Li^+ through cellophane and cellophane-*g*-NIPAAm copolymer membrane. (Δ) Cellophane; (\circ) cellophane-*g*-NIPAAm copolymer membrane (grafting 90%). Permeation rate ($\text{mmol cm}^{-2} \text{h}^{-1}$) = $(C_t \times v)/(S \times t)$. C_t : Concentration of solution after t h (mmol dm^{-3}); v : volume of solution (dm^3); S : surface area of membrane (cm^2); t : time (h).

son. The permeation rate of Li^+ through the cellophane-*g*-NIPAAm membrane increased with increasing temperature up to 32°C and decreased rapidly at temperatures above 35°C, while the permeation rate of Li^+ through the cellophane increased with increasing temperature in the temperature range studied.

This is due to the deswelling of the moieties of poly(NIPAAm) in the cellophane-*g*-NIPAAm membranes at temperatures above the LCST. Thus, we could control the permeation rate of Li^+ through the cellophane-*g*-NIPAAm membranes by varying the temperature slightly. However, the permeation of Li^+ could not be suppressed completely even at 40°C.

The permeation of PEGs with different molecular weights through the cellophane-*g*-NIPAAm copolymer membranes was also carried out by changing the temperature (Fig. 12). The PEG20000 did not permeate at all through the cellophane because of its high molecular weight. The permeation rate of PEGs with molecular weight of more than 1000 through the cellophane-*g*-NIPAAm copolymer membrane was considerably suppressed. The permeation rate of PEG1000 and PEG2000 through the membrane increased gradually with increasing temperature in the temperature range studied. However, only the permeation rate of PEG300

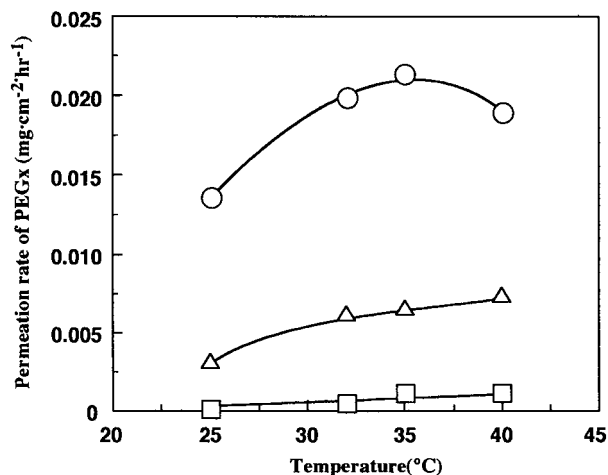


Figure 12 Permeation rate of PEGs from the mixed PEGx (×: 300, 1000, 2000) solution at various temperatures. Membrane: cellophane-*g*-NIPAAm copolymer membrane (grafting = 58 wt %). (○) PEG300; (△) PEG1000; (□) PEG2000.

L	R
Water	mixed PEG solution

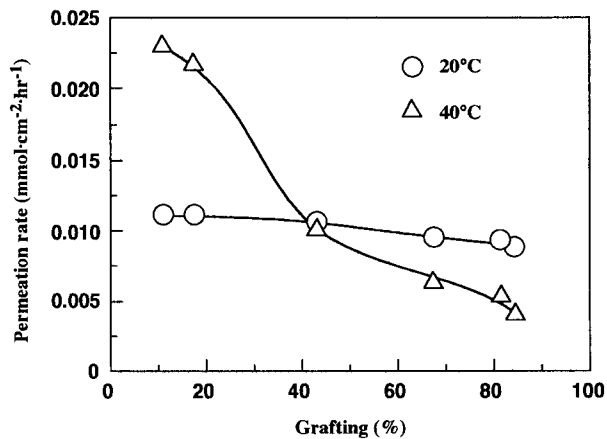


Figure 13 Relationship between grafting (%) and permeation rate of Li^+ at 20 and 40°C. Membrane: cellophane-*g*-NIPAAm copolymer membrane.

L	R
Water	0.045M LiCl

increased with increasing temperature up to 35°C and then decreased at 40°C.

The permeation of Li^+ through the cellophane-*g*-NIPAAm membranes with different grafting (%) was investigated at 20 and 40°C (Fig. 13). The permeation rate of Li^+ through the cellophane-*g*-NIPAAm membranes at 40°C decreased rapidly with increasing content of the NIPAAm moiety in the membrane. This is due to the deswelling of the moiety of poly(NIPAAm) in the cellophane-*g*-NIPAAm membranes at 40°C.

On the other hand, the permeation rate of Li^+ at 20°C decreased slightly with an increasing content of the NIPAAm moiety. This is due to the high swelling of the moiety of poly(NIPAAm) in the membranes. However, the permeation rate of Li^+ at 20°C through the cellophane-*g*-NIPAAm membranes containing the NIPAAm moiety of less than 40% was lower than that at 40°C. It is considered that the poly(NIPAAm) moiety deswollen in the cellophane-*g*-NIPAAm membranes having a low content of the poly(NIPAAm) moiety could not cover all the surface of the membrane or the channel in the membrane. Therefore, Li^+ can easily permeate through noncovered parts of the cellophane membranes with the hydrophobic poly(NIPAAm) moiety deswollen. This is why the higher transport rate of Li^+ at 40°C than at 20°C through the cellophane-*g*-NIPAAm membranes with a low content of NIPAAm moiety was observed.

CONCLUSION

1. Thermosensitive membranes having high mechanical strength could be prepared by graft copolymerization of NIPAAm onto cellophane using Ce(IV) salt as an initiator in a HNO₃ aqueous solution.
2. The cellophane-*g*-NIPAAm copolymer membranes having the desired amount of poly(NIPAAm) could be obtained by changing the conditions for graft copolymerization of NIPAAm onto the cellophane.
3. The permeation rate of Li⁺ through the cellophane-*g*-NIPAAm copolymer membranes could be controlled by changing the temperature from 32 to 40°C.
4. The permeation rate of Li⁺ through the copolymer membranes at 40°C decreased considerably, but that at 20°C decreased slightly with an increasing amount of the NIPAAm moiety in the membranes.
5. The permeation rate of PEGs with a molecular weight more than 1000 through the cellophane-*g*-NIPAAm copolymer membrane was considerably suppressed, and only the permeation rate of PEG300 had

the same temperature dependence as that of Li⁺.

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