

Preparation of Glass-Fiber Membranes Grafted with Poly(NIPAAm containing triphenylmethane leucocyanide) and Permeation of Solutes Through the Membranes

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SYNOPSIS

Glass-fiber membranes (GF membranes) grafted with poly(*N*-isopropylacrylamide containing triphenylmethane leucocyanide) [poly(NIPAAm–LeCN)] were prepared. Ultraviolet irradiation of the GF membranes with poly(NIPAAm–LeCN) induced a change in the phase-transition temperature of the poly(NIPAAm) segments. The changes in both the phase-transition temperature of the poly(NIPAAm) segments and the permeation rate of solutes are discussed in relation to the dissociation of LeCN molecules. © 1995 John Wiley & Sons, Inc.

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 33°C in aqueous solutions, i.e., the poly(NIPAAm) hydrogels swell and shrink at temperatures below and above the LCST, respectively. The poly(NIPAAm) hydrogels have become of great interest from fundamental and practical points of view. In particular, many studies have focused on the field of controlled drug delivery,^{1,2} regulation of the activity of enzymes and cells,^{3,4} and thermocontrolled chromatography.⁵ In addition, several studies on the phase transitions of the hydrogels have been described in relation not only to temperature dependence, but also to solvent composition, pH, ionic composition, and small electric field dependencies.⁶ Irie et al. reported a synthesis of photosensitive gels by incorporating photosensitive triphenylmethane leuco derivatives into polyacrylamide gels and poly(NIPAAm) gels.^{7,8} For some applications, it would be desirable if such a phase transition could be controlled by irradiation of light, because the light can be used instantly. However,

there are few studies on switching of permeation of solutes through membranes, by means of photocontrol of the LCST of poly(NIPAAm), because of the difficulty to make strong membranes which consist of poly(NIPAAm) containing photochromic molecules such as triphenylmethane leuco derivatives, spiropyranes, and azobenzenes. In addition, the phase transition of poly(NIPAAm) gels is known to depend strongly on the addition of electrolytes in aqueous solutions.^{6,9} Consequently, the effect of electrolytes inhibits the use of the various inorganic salts as solutes for the photochemical control of permeation of solutes. In this article, we describe the preparation of glass-fiber membranes (GF membranes) grafted with the copolymer of NIPAAm and vinyl monomer bearing triphenylmethane leucocyanide (LeCN monomer) and discuss the photocontrol of permeation of solutes such as lithium chloride and poly(ethylene glycol)s in relation to the photodissociation of LeCN molecules.

EXPERIMENTAL

Materials

N-Isopropylacrylamide (NIPAAm) was kindly provided by Kohjin Co. and was purified by recrystallization using hexane and benzene. 3-Methacryl-

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oxypropyltrimethoxysilane was purchased from Shin-Etsu Co. Glass filter GF75 (thickness = 0.35 mm, diameter of filtration limit < 0.3 μm) was purchased from Advantec Co. Michler's ketone, 4-chlorostyrene, and other chemicals were of reagent grade. Bis[4-(dimethylamino)phenyl](4-vinylphenyl)methyl leucocyanide (LeCN monomer) was synthesized according to the method described previously.⁷

Preparation of GF Membrane Grafted with Poly(NIPAAm containing LeCN) and Linear Poly(NIPAAm containing LeCN)

GF membrane with methacrylate groups was prepared by treating the glass filter GF75 with 5 g of 3-methacryloxypropyltrimethoxysilane in a mixture of 20 mL of water, 5 mL of methanol, and 0.4 mL of concentrated hydrochloric acid at 30°C for 3 h. After the silane coupling reaction, the glass filter was washed several times with methanol and dried *in vacuo* to give the GF membrane with methacrylate groups.

The graft copolymerization of NIPAAm and LeCN monomer on the GF membrane was performed as follows: The GF membrane with methacrylate groups was immersed in 20 mL of dimethylformamide (DMF) containing 1.8 g of NIPAAm, 0.2 g of LeCN monomer, and 0.06 g of 2,2'-azobisisobutyronitrile (AIBN). After nitrogen was introduced into the DMF solution for about 1 h, the polymerization was carried out at 50°C for 20 h. The obtained GF membrane was washed several times with acetone and water to give the GF membrane grafted with poly(NIPAAm–LeCN) (Scheme 1).

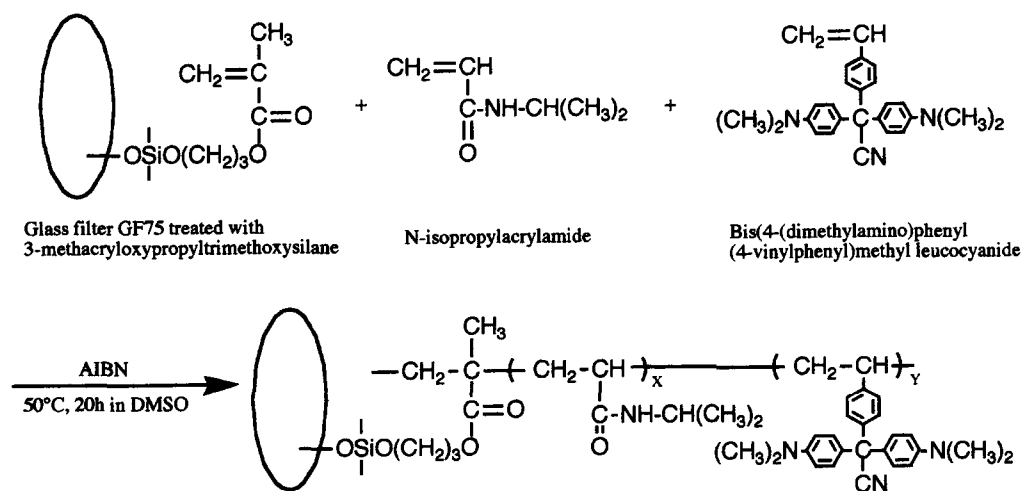
The linear copolymers of NIPAAm and LeCN were prepared as follows: 0.9 g of NIPAAm, 0.1 g of LeCN monomer (or 0.95 g of NIPAAm and 0.05 g of LeCN monomer), and 0.06 g of AIBN were dissolved in 20 mL of dimethyl sulfoxide (DMSO). After nitrogen was introduced into the DMSO solution for 1 h, the polymerization was carried out at 50°C for 20 h. The polymer was precipitated in water by heating and dried *in vacuo*. The polymer was purified by dissolving in water below 30°C and successive heating above 40°C to precipitate the linear poly(NIPAAm–LeCN). The content of LeCN in the linear poly(NIPAAm–LeCN) was determined by means of spectroscopy. A linear homopolymer of NIPAAm, poly(NIPAAm), was also prepared and purified in a similar manner to the linear poly(NIPAAm–LeCN).

Phase-Transition Behavior

The phase-transition behavior of the linear polymers was investigated by measuring transmittance of an aqueous solution containing poly(NIPAAm) or poly(NIPAAm–LeCN) at various temperatures.

Permeation Experiments

Permeation experiments were carried out at various temperatures with magnetic stirring, using a diaphragm glass cell consisting of two detachable parts (22 cm³ each) (Fig. 1). The glass filter membrane was set in the middle of the two parts of the cell, which were clamped and sealed tightly with silicon rubber packing. The effective membrane area in the



Scheme 1. S. Kurihara et al.

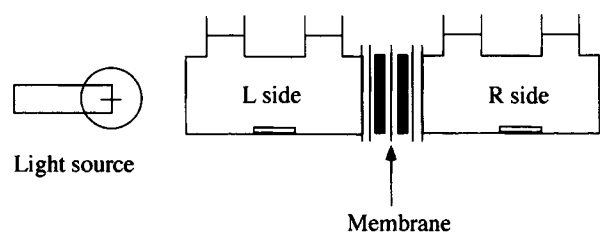


Figure 1 Experimental setup for measuring transport of LiCl or PEGs.

cell was 3.14 cm². The left (L) side was an aqueous solution containing a solute and the right (R) side was deionized water. The concentration of a solute permeated on the R side was measured when the membrane surface of the L side was exposing to ultraviolet (UV) light at various intervals. Lithium chloride (LiCl) and polyethylene glycols were used as permeation solutes. UV irradiation was performed with a 75 W high-pressure mercury lamp.

The concentration of the lithium ion (Li⁺) permeated on the R side was measured by a flame emission spectrophotometer (Shimadzu AA-640-13S). The concentration of polyethylene glycols (PEG600 with an average molecular weight of 600 and PEG2000 with the average molecular weight of 2000) permeated on the R side was measured on a Shodex refractometer SE-11.

RESULTS AND DISCUSSION

Synthesis of Poly(NIPAAm–LeCN) and GF Membrane Grafted with Poly(NIPAAm–LeCN)

The linear poly(NIPAAm–LeCN)s were prepared by copolymerization of NIPAAm and LeCN monomer. The contents of LeCN were 5.9 and 11.7 wt % determined by spectroscopy. The linear homopolymer of NIPAAm, poly(NIPAAm), was found to dissolve easily in water, while the linear

poly(NIPAAm–LeCN) exhibited less solubility in water. The incorporation of hydrophobic LeCN molecules resulted in less solubility of the linear poly(NIPAAm–LeCN) in water.

The grafting yield on the GF membranes is given in Table I. The grafting yield is defined by the following expression:

Grafting yield (%)

$$= \frac{\text{weight of polymer grafted}}{\text{weight of GF membrane}} \times 100$$

No graft polymerization was observed for the glass filter GF75 without any treatments. On the other hand, the grafting yields of the GF membrane treated with 3-methacryloxypropyltrimethoxysilane were 108 and 185% for poly(NIPAAm–LeCN) and poly(NIPAAm), respectively. Although the grafting yield of poly(NIPAAm–LeCN) was much lower than that of poly(NIPAAm), the scanning electron micrograph observation revealed that the graft polymerization of poly(NIPAAm–LeCN) took place at the surface as well as inside the GF membrane. The incorporation of LeCN molecules in the polymer segments grafted on the GF membrane was confirmed by the absorption band at 2200 cm⁻¹ due to cyano groups in the IR spectrum. Although the content of LeCN molecules in the grafted polymer segments could not be determined exactly, it can be expected that the content of LeCN molecules in the grafted polymer segments was about 10 wt % on the basis of the content of LeCN molecules in the linear poly(NIPAAm–LeCN) prepared in a similar condition without a GF substrate.

Photodissociation Behavior of LeCN

To investigate the photodissociation of LeCN molecules, the absorption spectra were measured as a function of UV irradiation time. Figure 2 shows the

Table I. Grafting Yield of GF Membranes

Substrate	Feed (g)		Weight (g)		Grafting Yield (%)
	NIPAAm	LeCN Monomer	Before	After ^a	
GF 75 ^b	2.0	—	0.13	0.13	—
GF membrane ^c	1.5	—	0.13	0.37	185
GF membrane ^c	1.8	0.2	0.13	0.27	108

^a Weight of GF membranes after graft polymerization.

^b Glass filter GF 75 without any treatment.

^c GF membrane with methacrylate groups obtained by treating GF 75 with 3-methacryloxypropyltrimethoxysilane.

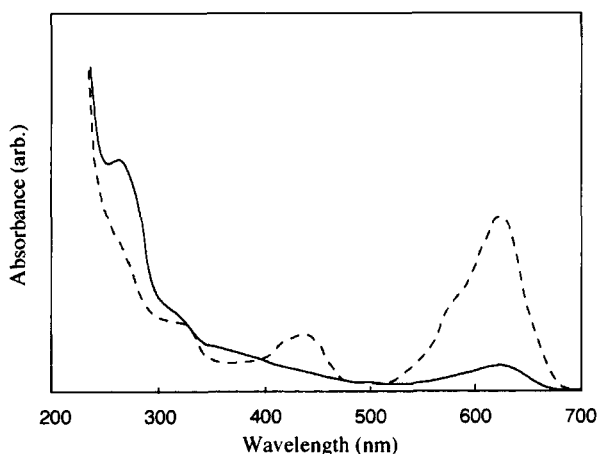


Figure 2 Absorption spectra of the linear poly(NIPAAm-LeCN) in water (—) before and (---) after UV irradiation at 25°C. The concentration of the linear poly(NIPAAm-LeCN) was 0.0125 wt %.

absorption spectra of the linear poly(NIPAAm-LeCN) in water before and after UV irradiation at 25°C. The increase of absorbances, at 420 nm corresponding to the triphenylmethane cation and at 620 nm corresponding to the quinoid ion, was observed by UV irradiation. The photodissociation and recombination reactions of LeCN molecules are expected to be influenced by adding various electrolytes.¹⁰ The time course of the photodissociation of the linear poly(NIPAAm-LeCN) in water, in the presence of LiCl or PEG600, is shown in Figure 3. The concentration of additives was 1.7 mM. The addition of LiCl reduced slightly the photodissociation reaction of LeCN molecules. However, a similar dissociation behavior was observed for the linear poly(NIPAAm-LeCN) even in the presence of LiCl.

Effect of Photodissociation of LeCN on Phase-separation Behavior

Poly(NIPAAm) is well known to exhibit the LCST around 33°C. Figure 4 shows the changes in transmittance of aqueous solutions containing poly(NIPAAm) or poly(NIPAAm-LeCN) as a function of temperature. The transmittance of the aqueous solution containing 0.4 wt % of poly(NIPAAm) decreased rapidly above 30°C and finally became 0 above 35°C, which is ascribed to the phase separation of the linear poly(NIPAAm) segments. The change in transmittance of the aqueous solution containing 0.0125 wt % of the linear poly(NIPAAm-LeCN) is also given in Figure 4, because of the low solubility of the linear poly(NIPAAm-LeCN) in water due to the hydro-

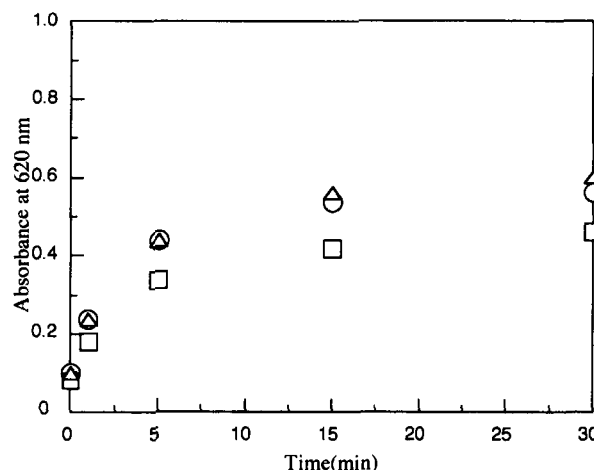


Figure 3 Photodissociation behavior of the linear poly(NIPAAm-LeCN) in water in the presence of additives at 25°C: (O) without additive; (Δ) in the presence of 1.7 mM of PEG600; (□) in the presence of 1.7 mM of LiCl.

phobicity of the LeCN molecule. The transmittance of the poly(NIPAAm-LeCN) aqueous solution decreased above 30°C, but it did not become 0 above 35°C. However, a similar change in transmittance of the aqueous solution containing 0.0125 wt % of the linear poly(NIPAAm) suggested that the phase separation of the linear poly(NIPAAm-LeCN) took place around 30°C.

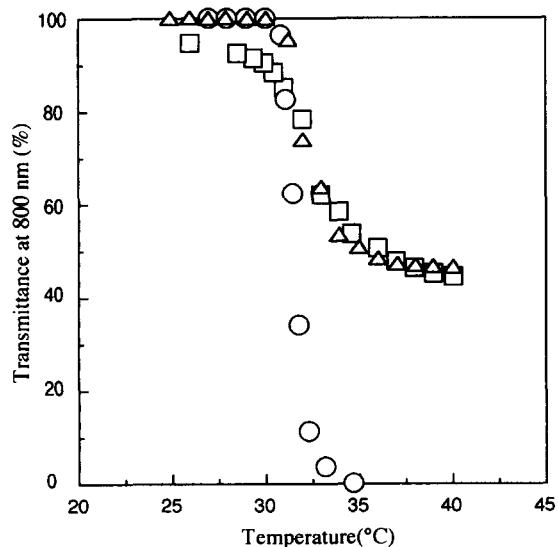


Figure 4 Temperature dependence of transmittance at 800 nm of the aqueous solution containing the linear poly(NIPAAm) or the linear poly(NIPAAm-LeCN): (O) 0.4 wt % of poly(NIPAAm); (Δ) 0.0125 wt % of poly(NIPAAm); (□) 0.0125 wt % of poly(NIPAAm-LeCN).

Figure 5 shows the effect of dissociation of LeCN molecules on the phase separation of the linear poly(NIPAAm-LeCN) in water. The phase-separation temperature of the linear poly(NIPAAm-LeCN) without UV irradiation was found to be around 30°C, showing a steep decrease of transmittance at 800 nm, while only a slight decrease of the transmittance was observed upon UV irradiation. The photodissociation of LeCN molecules in the poly(NIPAAm-LeCN) segments provides the fixed cations and free anions in the polymer segments. The increase of hydrophilicity of the whole polymer segments due to the formation of ionic species shifted the phase-separation temperature to higher temperature.¹¹

Figure 6 shows the influence of the photodissociation of LeCN molecules on the phase-separation behavior of the linear poly(NIPAAm-LeCN) in water with or without additives. UV irradiation in the presence of LiCl hardly influenced the phase separation of the linear poly(NIPAAm-LeCN). On the other hand, the suppression and broadening of the phase separation of the linear poly(NIPAAm-LeCN) even without UV irradiation was observed in the presence of PEG600. The broadened phase separation in the presence of PEG600 may be related to the adsorption of PEG600 on the poly(NIPAAm-LeCN) segments.¹² Contrary to the result in the presence of LiCl, however, the larger difference in the phase-separation behavior was observed by UV irradiation in the presence of PEG600. The results

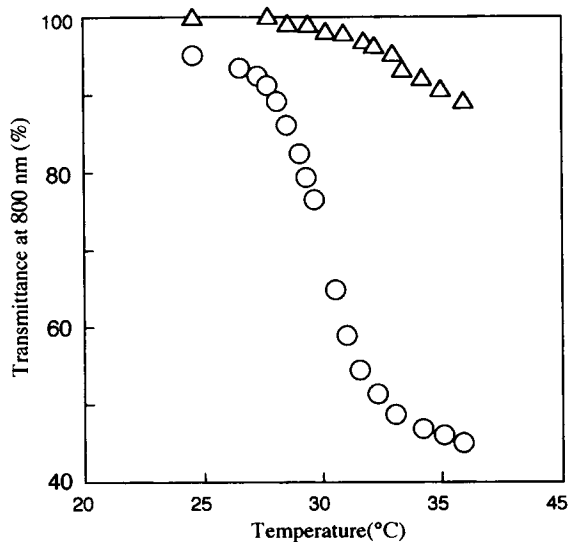


Figure 5 Temperature dependence of transmittance at 800 nm of the aqueous solution containing 0.0125 wt % of the linear poly(NIPAAm-LeCN): (○) in the dark; (△) UV irradiation.

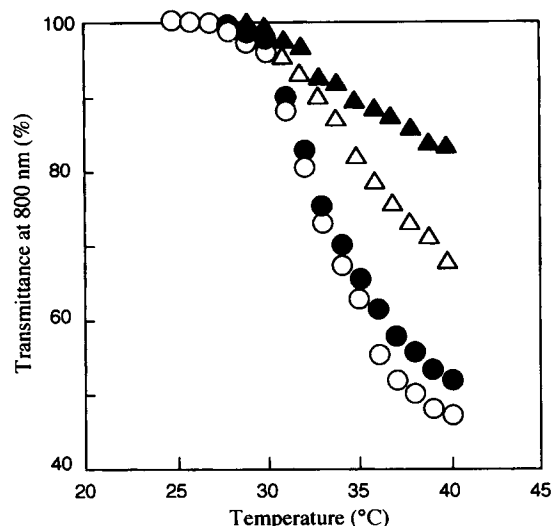


Figure 6 Temperature dependence of transmittance at 800 nm of the aqueous solution containing 0.0125 wt % of the linear poly(NIPAAm-LeCN) in the presence of (○, ●) LiCl or (△, ▲) PEG600. (○, △) in the dark; (●, ▲) UV irradiation.

suggest that the change in the phase-separation temperature is ascribed not only to change in the hydrophilicity of the polymer segments, but also to the osmotic pressure between a polymer-rich phase and an external aqueous phase, namely, the increase of osmotic pressure by UV irradiation providing ionic species in the polymer segments raised the phase-separation temperature of the linear poly(NIPAAm-LeCN) in water.^{7,8} Therefore, the different effect on the phase-separation behavior between LiCl and PEG600 is interpreted in terms of the ionic property of additives. The larger change in the phase-separation temperature by UV irradiation in the presence of PEG600 is closely related to the nonionic property of PEG600.

Effect of Photodissociation of LeCN on Permeation of Solutes

Figure 7 shows the permeation behavior of solutes through the GF membrane grafted with poly(NIPAAm) or poly(NIPAAm-LeCN) at 25°C. The permeation rates decreased with increase of the molecular size in the order of LiCl < PEG600 < PEG2000. In addition, the permeation rate through the GF membrane grafted with poly(NIPAAm-LeCN) was lower than that through the GF membrane grafted with poly(NIPAAm). The grafting yield of the poly(NIPAAm-LeCN) segments on the GF membrane with methacryloyl groups was lower than that of poly(NIPAAm) seg-

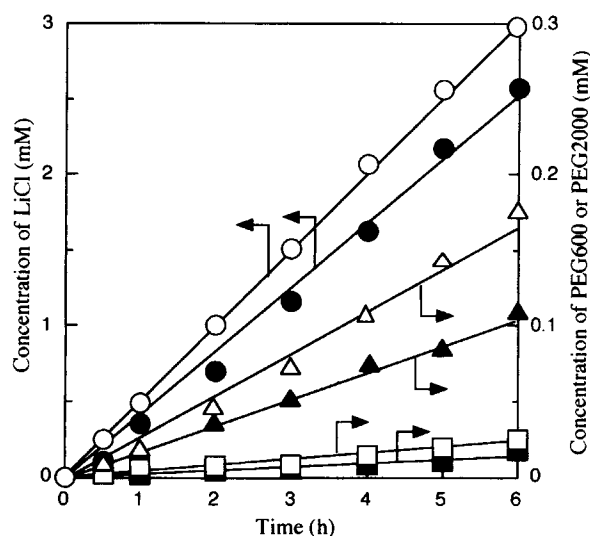


Figure 7 Changes in concentration of a solute permeated on R side at 25°C. Open symbols exhibit data for the GF membrane grafted with poly(NIPAAm) and solid symbols exhibit data for the GF membrane grafted with poly(NIPAAm-LeCN): (○, ●) LiCl; (△, ▲) PEG600; (□, ■) PEG2000.

ments on the GF membrane with methacryloyl groups. Therefore, the increase of the hydrophobicity of the membrane due to incorporation of the LeCN molecules resulted in a lower permeation rate through the GF membrane grafted with poly(NIPAAm-LeCN).

The permeation of solutes through polymer membranes is expected to depend on the micropore size and hydrophobicity of polymer membranes. To reveal the temperature dependence of the micropore size of the GF membrane grafted with poly(NIPAAm-LeCN) on the permeation of solutes, the relative amounts permeated to the amounts permeated at 30°C for 3 h was plotted as a function of permeation temperature in Figure 8. The relative permeation rate of LiCl was almost independent of the permeation temperature. The permeation rate of LiCl was very rapid compared to that of PEGs, as can be seen in Figure 7. The micropore size of the GF membrane grafted with poly(NIPAAm-LeCN) is probably larger than the molecular size of LiCl (Li^+ and Cl^-) even in the shrunken membrane. The relative permeation rate of PEG2000 increased with temperature. The result shown in Figure 7 suggests that the permeation of PEG2000 is strongly depressed even when the GF membrane is in a swollen state. Therefore, the temperature dependence of the relative permeation rate is ascribed not to the change in the micropore size but to the increase of diffusion mobility with increasing temperature. On

the other hand, the relative permeation rate of PEG600 showed a typical temperature dependence of permeation through polymer membranes which consisted of poly(NIPAAm), i.e., an increase of permeation rate up to the LCST and a successive decrease of permeation rate above the LCST.¹³ The phenomenon is closely related to the decrease of the micropore size of the membrane owing to the phase transition of poly(NIPAAm-LeCN) segments to the shrunken state above the LCST. The increase of permeation rate above 35°C is also due to the increase of diffusion mobility with temperature.

On the basis of the results shown in Figure 8, it is expected that one could control the permeation of PEG600 photochemically through the GF membrane grafted with poly(NIPAAm-LeCN). Figure 9 shows the changes in the permeation rate of PEG600 by UV irradiation at 25 and 35°C. Although the absorption spectrum of the GF membrane grafted with poly(NIPAAm-LeCN) could not be measured, the photodissociation of the LeCN molecules was observed with the naked eye as the change of the membrane color. Upon UV irradiation, the color of the membrane changed rapidly from pale green to deep green. No change in the permeation rate was observed by UV irradiation at 25°C. The permeation rate at 35°C in the dark was almost the same as that at 25°C, as shown in Figure 9, while the permeation rate was enhanced by UV irradiation at 35°C. The amounts of PEG600 permeated increased as much as 2.3 times by UV irradiation. The pho-

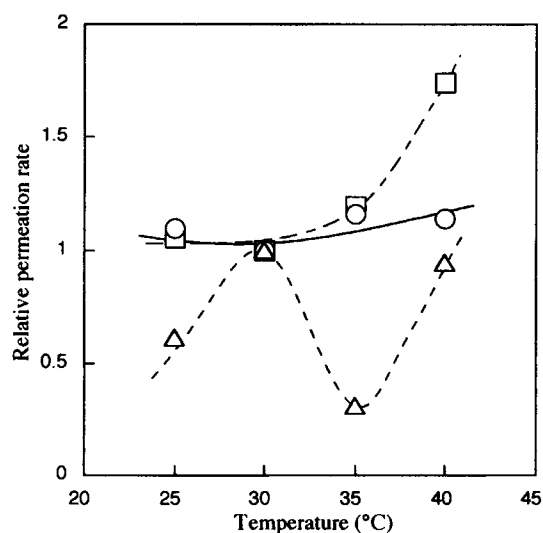


Figure 8 Temperature dependence of relative amounts permeated of solutes to that at 30°C for 3 h through the GF membrane grafted with poly(NIPAAm-LeCN): (○) LiCl; (△) PEG600; (□) PEG2000.

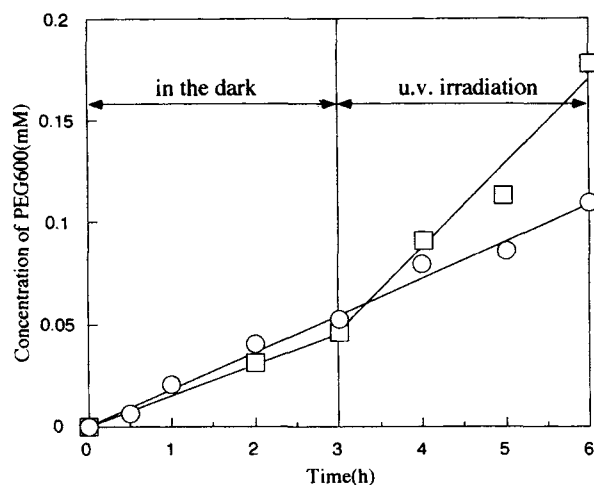


Figure 9 Changes in concentration of PEG600 permeated on R side through the GF membrane grafted with poly(NIPAAm–LeCN) in the dark and upon UV irradiation at 25 and 35°C. The initial concentration of PEG600 in L side was 1.7 mM: (○) 25°C; (□) 35°C.

Photodissociation of LeCN molecules gave fixed cations and free anions in the membrane system. Before UV irradiation, the GF membrane grafted with poly(NIPAAm–LeCN) was in the shrunken state at 35°C. The increase of the hydrophilicity and osmotic pressure between the inside of the membrane and the external aqueous solution due to the formation of ionic species raised the phase-transition temperature of the poly(NIPAAm–LeCN) segments. Consequently, the isothermal photochemical phase transition from the shrunken state to the swollen state is induced by photodissociation of LeCN molecules at 35°C. The increase of the permeation rate is interpreted in terms of the increase of the micro-pore size of the membrane due to the photochemical phase transition of poly(NIPAAm) segments.

CONCLUSION

GF membrane grafted with poly(NIPAAm–LeCN) was prepared by graft polymerization of NIPAAm and LeCN monomer on the GF membrane treated

with 3-methacryloxypropyltrimethoxysilane. UV irradiation on the GF membrane grafted with poly(NIPAAm–LeCN) brought about the photodissociation of LeCN molecules, providing fixed cations and free anions. The increases of the hydrophilicity and osmotic pressure due to the formation of ionic species brought about the change in the phase-transition temperature of the poly(NIPAAm–LeCN) segments grafted on the GF membrane. The photocontrol of the permeation of PEG600 through the GF membrane grafted with poly(NIPAAm–LeCN) can be achieved by UV irradiation at 35°C, resulting in the phase transition of poly(NIPAAm) segments from the shrunken state to the swollen state.

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