Effect of Graft Yield on the Thermo-Responsive Permeability Through Porous Membranes with Plasma-Grafted Poly(N-isopropylacrylamide) Gates*

CHU Liangyin(褚良银)**, **ZHU Jiahua(朱家骅) and CHEN Wenmei(陈文梅)**
School of Chemical Engineering, Sichuan University, Chengdu 610065, China

NIITSUMA Takuya, YAMAGUCHI Takeo and NAKAO Shin-ichi
Department of Chemical System Engineering, University of Tokyo, Tokyo 113-8656, Japan

Abstract The effect of graft yield on both the thermo-responsive hydraulic permeability and the thermo-responsive diffusional permeability through porous membranes with plasma-grafted poly(N-isopropylacrylamide) (PNIPAM) gates was investigated. Both thermo-responsive flat membranes and core-shell microcapsule membranes with a wide range of graft yield of PNIPAM were prepared using a plasma-graft pore-filling polymerization method. The grafted PNIPAM was formed homogeneously throughout the entire thickness of both the flat polyethylene membranes and the microcapsule polyamide membranes. Both the hydraulic permeability and the diffusional permeability were heavily dependent on the PNIPAM graft yield. With increasing the graft yield, the hydraulic permeability (water flux) decreases rapidly at 25°C because of the decrease of the pore size; however, the water flux at 40°C increases firstly to a peak because of the increase of hydrophobicity of the pore surface, and then decreases and finally tends to zero because of the pore size becoming smaller and smaller. For the diffusional permeability, the temperature shows different effects on the diffusional permeability coefficients of solutes across the membranes. When the graft yield was low, the diffusional coefficient of solute across the membrane was higher at temperature above the lower critical solution temperature (LCST) than that below the LCST; however, when the graft yield was high, the diffusional coefficient was lower at temperature above the LCST than that below the LCST. It is very important to choose or design a proper graft yield of PNIPAM for obtaining a desired thermo-responsive "on/off" hydraulic or diffusional permeability.

Keywords thermo-responsive membrane, poly(N-isopropylacrylamide), plasma-graft pore-filling polymerization, graft yield, hydraulic permeability, diffusional permeability

1 INTRODUCTION

In the past decade, much attention has been drawn to modified porous polymeric membranes whose surface and permeation properties can be triggered by external chemical and/or physical environmental stimuli such as temperature, pH, light, electric field, and chemical or biological species[1−10]. These environment response membranes may find various applications including controlled drug delivery, bioseparation, water treatment, chemical separation, chemical sensor, tissue engineering, etc. There is an increasing interest in these intelligent membranes.

A convenient way of preparing the above-mentioned membranes is to graft monomers possessing functional groups onto the pore surface of porous membrane substrates. The substrate provides mechanical strength and dimensional stability, while the grafted functional polymer provides the environment responsive characteristics, i.e., altering its conformation and physical structure as the environmental conditions vary. As a result, the permeability of these membranes can be controlled or adjusted by the grafted gates according to the external chemical and/or physical environment. Two main advantages can be benefited from grafting techniques in

preparing these membranes. One is that the grafted chains are chemically bonded to the membrane matrix compared with those prepared by coating techniques, so that they will not be dissolved as solvent permeates through the membrane. The other is that the grafted chains have freely mobile ends so that the prepared membranes respond faster to the environmental stimuli in compared with hydrogels with typical crosslinked network structures.

Up to date, various grafting techniques, including chemical grafting, plasma-induced grafting, and radiation-induced grafting and so on, have been introduced to prepare environment-responsive membranes by grafting different functional polymers either onto the external membrane surface or onto both the external surface and the inside surface of the pores[1−7,9−18]. All the prepared membranes have been reported to have environment responsive hydraulic permeability (pressure-driven convective flow of solvents) or diffusional permeability (concentration-driven molecular diffusion of solutes). However, the effects of graft yield and graft location on both the hydraulic and the diffusional permeability response have not been well investigated yet.

In this study, a plasma-graft pore-filling polymer-

ization method[3,4,9,10,19,20] was introduced to prepared both thermo-responsive flat membranes and core-shell microcapsule membranes with a wide range of graft yield by grafting poly(N-isopropylacrylamide) (PNIPAM) onto porous membrane substrate. Investigations were carried out on the examination of the graft location, the effect of graft yield on the hydraulic permeability response, and the effect of graft yield on the diffusional permeability response.

2 MODELS FOR DIFFUSIONAL PERMEABILITY

2.1 Diffusion through microcapsule membranes

The model was derived from Fick's first law of diffusion. In developing the diffusion model the following assumptions have been made[21,22]: (1) The diffusion within the core of the microcapsule is much faster than diffusion through the membrane wall; therefore a uniform concentration in the inner core could be assumed; (2) The solubility of the diffusing species in the extra-capsular solution is equal to its solubility in the inner core (partition coefficient equal to one); (3) The extra-capsular solution is well mixed; therefore the bulk concentration is uniform (no concentration gradients exist); (4) Diffusivity of the diffusing species through the microcapsule membrane is constant with respect to the membrane structure and the concentration; (5) Linear concentration gradient exists across the membrane; and (6) Pseudo steady-state diffusion through the membrane of the microcapsule is established immediately and is maintained throughout. A schematic illustration of the diffusion of solute from intracapsular liquid into the bulk solution is shown in Fig. 1(a).

The permeating rate of diffusing species from the intracapsular liquid can be described by Fick's first law of diffusion as follows[23,24]

$$\frac{dM}{dt} = -AD\left(\frac{\partial c}{\partial r}\right) = AD\left(\frac{\Delta c}{\delta}\right) \tag{1}$$

The rate of change in bulk solute concentration, dc_t/dt, can be obtained by dividing the total change in amount of solute by the bulk volume

$$\frac{dc_t}{dt} = \frac{1}{V_s}\frac{dM}{dt} = \frac{DA}{V_s}\left(\frac{\Delta c}{\delta}\right) \tag{2}$$

From the conservation of the total amount of solute in the system

$$c_i V_s + c_{im} V_m = c_t V_s + c_{tm} V_m = c_f(V_s + V_m) \tag{3}$$

The diffusion driving force reads

$$\Delta c = c_{tm} - c_t = \frac{c_f(V_s + V_m) - c_t V_s}{V_m} - c_t$$

$$= (c_f - c_t)\frac{V_s + V_m}{V_m} \tag{4}$$

Then, Eq. (2) upon substitution of Eq. (4) becomes

$$\frac{dc_t}{dt} = \frac{DA}{\delta}\frac{(V_s + V_m)}{V_m V_s}(c_f - c_t) \tag{5}$$

Integrating Eq. (5), the diffusion coefficient across the microcapsule membrane is derived

$$D = \frac{\delta}{A}\frac{V_s V_m}{(V_s + V_m)}\frac{1}{t}\ln\frac{c_f - c_i}{c_f - c_t} \tag{6}$$

Because it is difficult to measure the thickness of the microcapsule membrane exactly, the diffusional permeability coefficient P instead of diffusion coefficient D is used as follows

$$P = \frac{V_s V_m}{A(V_s + V_m)t}\ln\frac{c_f - c_i}{c_f - c_t} \tag{7}$$

That is, if the surface area and volume of the microcapsule and the volume of bulk solution are known, the diffusional permeability of a solute across the microcapsule membrane could be calculated by measuring the change of the solute concentration in the bulk solution with time.
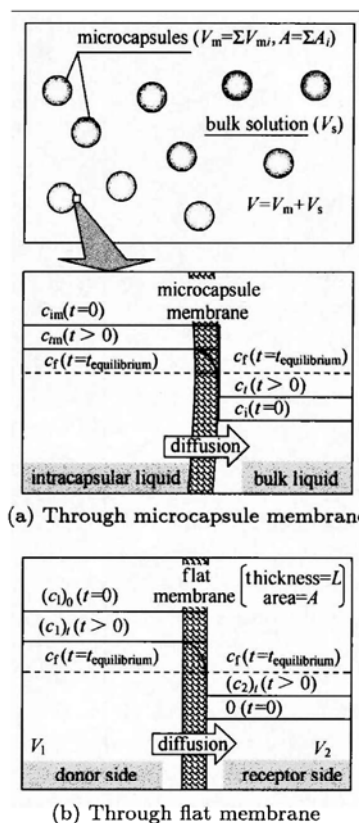

(a) Through microcapsule membrane

(b) Through flat membrane

Figure 1 Schematic illustrations of the diffusion of solutes through the microcapsule membrane (a) and flat membrane (b)

2.2 Diffusion through flat membranes

A schematic illustration of the diffusion of solute from the donor side into the receptor side of flat membrane is shown in Fig. 1(b). Similar to the case of

microcapsule membranes, the diffusion coefficient of solute across the flat membrane D can be calculated using the following equation

$$D = \frac{V_1 V_2}{(V_1 + V_2)} \cdot \frac{L}{A} \cdot \frac{1}{t} \cdot \ln \frac{(c_1)_0}{(c_1)_t - (C_2)_t} \qquad (8)$$

3 EXPERIMENTAL

3.1 Materials

Porous polyethylene (PE H2100) film was used as the flat porous membrane substrate. The PE H2100 substrate, with a thickness of $100\,\mu m$, a porosity of 69%, and a pore size of $0.28\,\mu m$, was supplied by Asahi Chemical Co. Ltd, Japan. The porous microcapsule membrane substrates were prepared using the interfacial polymerization method as described in an earlier publication[3]. Terephthaloyl dichloride (TDC) was purchased from Tokyo Kasei Kogyo Co., Ltd, Japan. Ethylene diamine (EDA), sodium dodecyl sulfate (SDS), benzene, xylene, sodium carbonate, sodium chloride, carbazochrome sodium sulfonate (CCSS), and vitamin B_{12} (VB_{12}) were all purchased from Wako Pure Chemical Industries, Ltd, Japan. The solvents used were all of reagent grade. All these chemicals were used as received. The N-isopropylacrylamide (NIPAM) was kindly provided by Kohjin Co., Ltd, Japan, and was used after purifying by recrystallization in hexane and acetone, and then dried *in vacuo* at room temperature.

3.2 Grafting PNIPAM gates by plasma-graft pore-filling polymerization

Plasma-graft pore-filling polymerization was employed to graft the linear PNIPAM chains into the pores of either the flat membrane or the microcapsule membranes according to the method described previously[3,4,9,10,19,20]. In the experiments, the plasma power was 30 W, plasma treatment time was 60 s, the reaction atmosphere was argon gas, the pressure was 10 Pa, and the grafting temperature was 30°C. The NIPAM concentrations in the monomer solutions for PE flat membranes were 1% and 5% respectively, while that for the microcapsule membranes was 1% only. The grafting time for the PE flat membranes were from 56 to 1282 min, and that for the microcapsule membranes were from 20 to 240 min. The quantitative index of grafting onto the membrane was defined as the mass increase of the membrane after the grafting. Because the porous microcapsules were very small (mean diameters about $40\,\mu m$), it was very difficult to prevent their loss in the washing water. Therefore, the quantitative data of grafting mass onto the microcapsule membrane was not obtained in this study. The graft yield of the PE flat membrane was defined as the mass of the grafted polymer per square centimeter of the substrate film. Because the grafting temperature and the experimental parameters of the plasma treatment were unchanged, the grafted yield was dependent on the monomer concentration and the

grafting time. The graft yield was proven to be directly proportional to the monomer concentration or the grafting time.

3.3 Morphological analysis

The grafted polymer formation profile of the flat porous substrate was measured using the microscopic Fourier transform infrared (FT-IR) mapping method (MAGNA-IR 560 with Nic-Plan, Nicolet, USA). The PE-g-PNIPAM membrane sample was sliced using a microtome, and the sliced sample was scanned by FT-IR. The spectra were collected in up to 10-μm steps along the membrane axial thickness. The aperture size of each measurement was $10 \times 50\,\mu m^2$. The profile of the grafted polymer formation was obtained by measuring the ratio of the characteristic PNIPAM peak (amide II peak, $1550\,cm^{-1}$) to the characteristic polyethylene substrate peak (methylene peak, $1450\,cm^{-1}$).

As the membrane thickness of the prepared microcapsule was too small (about $2\,\mu m$) to be analyzed by the FT-IR mapping method, a field emission scanning electron microscope (FE-SEM S-900S, Hitachi, Japan) was used to observe the freeze-dried ungrafted and PNIPAM-grafted microcapsules. The cross-sectional structures of the microcapsules were observed by cutting the microcapsules with a microtome knife.

3.4 Thermo-responsive filtration experiments

The hydraulic permeability experiments or filtration experiments of the flat membranes were carried out with trans-membrane pressure being 50 kPa. The diameter of the effective membrane area for the filtration was 40 mm. The temperature of the feed water was kept at a constant 25°C or 40°C using a thermostatic unit (COOLNIT CL-80F, TAITEC, Japan). The hydraulic permeability through the ungrafted and the PNIPAM-grafted membranes at temperatures both below and above the LCST was studied by measuring the filtrate.

3.5 Thermo-responsive diffusion experiments

The diffusional permeability experiments of the flat membranes were carried out using a standard side-by-side diffusion cell. The diffusion cell was located in a constant-temperature incubator (EYELA LTI-601SD, Tokyo Rikakikai Co., Ltd., Japan) to keep the diffusional temperature constant. Each test membrane was immersed in the permeant solution overnight before starting the diffusion experiments. The solute was CCSS. Deionized water was used as the liquid in the receptor cell. The concentration of CCSS was determined using a UV-visible recording spectrophotometer (U-3310, Hitachi, Japan) at wavelength of $\lambda = 363\,nm$.

The permeability of the solute across the microcapsule membranes was measured by determining the increase in the solute concentration of the surrounding medium with time, after mixing a known volume of microcapsule dispersion with a known solute concentration, with the same volume of deionized water.

During the measurements, the liquid temperature was kept constant using a thermostatic unit. The solutes used were NaCl and VB$_{12}$. The concentration of NaCl was determined by measuring the electrical conductance with an electrical conductivity meter (TOA EC Meter 50AT, TOA Electronics Ltd, Japan), and that of VB$_{12}$ was determined using the UV-visible recording spectrophotometer at wavelength of 361 nm.

4 RESULTS AND DISCUSSION

### 4.1 Morphological analyses of the PNIPAM-grafted membranes

Figure 2 shows a profile of the FT-IR absorbance ratio of the amide II peak to the polyethylene peak in the PE-g-PNIPAM membranes. The height ratio of the characteristic PNIPAM peak (amide II peak) to the characteristic polyethylene substrate peak (methylene peak at 1450 cm^{-1}) was used to quantitatively characterize the grafting composition of PNIPAM across the membrane thickness. The absorbance ratio was plotted against the distance from the membrane surface. The results show that a homogeneous graft was formed throughout the entire thickness of the membrane.
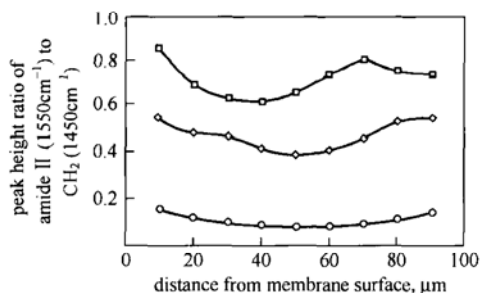

Figure 2 Grafted PNIPAM formation profiles on the cross-sections of PE-g-PNIPAM membranes with different graft yields
graft yield, mg·cm^{-2}: —□— 6.06; —◇— 3.04; —○— 1.41

Figure 3 shows FE-SEM micrographs of the cross-sections of ungrafted and PNIPAM-grafted microcapsule membranes. The cross-sections of the ungrafted and PNIPAM-grafted microcapsule membranes are seen to have significantly different structures. After grafting PNIPAM onto the inner pore surface of the porous membrane with NIPAM monomer concentration (N_{NIPAM}) as 1.0% and grafting time (t_g) as 20 min, the pore size decreased. With increasing N_{NIPAM} to 3.0% and t_g to 240 min, the graft yield increased largely, and the grafted membrane even looked to be a dense one. The observation indicates that the porous structure across the cross-section of the microcapsule membranes was covered homogeneously by the grafted PNIPAM throughout the entire membrane thickness.
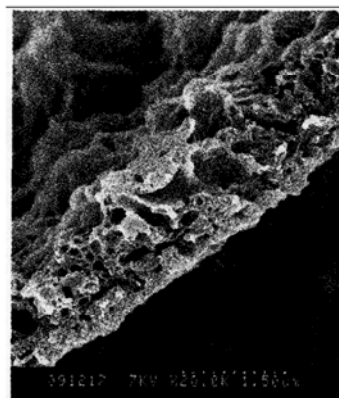
(a) ungrafted
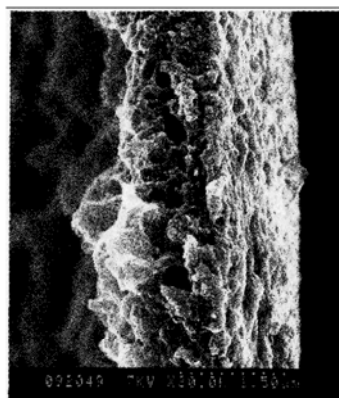
(b) PNIPAM-grafted ($N_{\mathrm{NIPAM}} = 1.0\%$, $t_g = 20$ min)
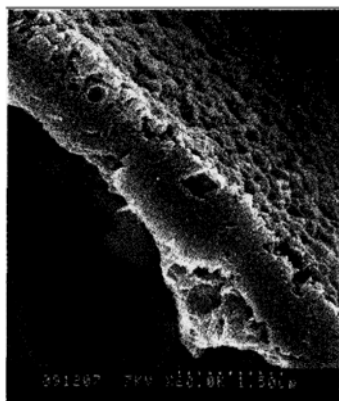

(c) PNIPAM-grafted ($N_{\mathrm{NIPAM}} = 3.0\%$, $t_g = 240$ min)

Figure 3 FE-SEM micrographs of the cross-sections of microcapsule membranes

4.2 Thermo-responsive hydraulic permeability

Figure 4 shows the effect of graft yield on the thermo-responsive hydraulic permeability through the PE-g-PNIPAM membranes. When the PNIPAM graft yield is zero, the water flux at 40℃ is larger than that at 25℃, because the viscosity decreases with temperature increasing. After grafting PNIPAM onto the porous membrane substrates, the hydraulic permeability changes dramatically and strongly depends on the PNIPAM graft yield. PNIPAM has been well known as a smart hydrogel material, because of its unique feature of hydrophilicity and volume change

in response to temperature changes. It shows a hydrophilic and swollen state in water below the lower critical solution temperature (LCST) around 32°C[25],
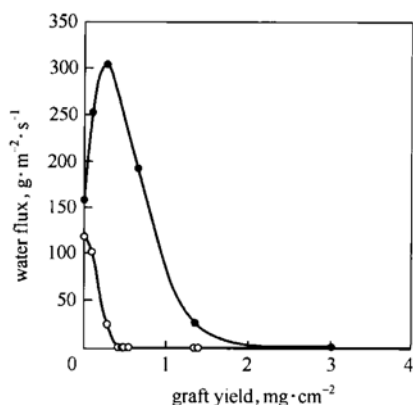
Figure 4   Effect of graft yield on the thermo-responsive hydraulic permeability through the PE-*g*-PNIPAM membranes(pressure 50 kPa)
T, °C: —O— 25; —●— 40

however it becomes hydrophobic and shrinking dramatically when the temperature is raised above the LCST. At 25°C (below the LCST), the grafted PNIPAM chains in the membrane pores are in the swollen state, therefore the pore size decreased rapidly with increasing the PNIPAM graft yield. As a result, the water flux decreases rapidly. The case at 40°C (above the LCST) is quite different. Because the grafted PNIPAM chains are in the shrinking state, the membrane pores are still "open" at low graft yield, and the hydrophobicity of the inside pore surfaces increases [as illustrated in Fig. 5(a)]. Owing to the stronger hydrophobicity of the inside pore surface, lower frictional drag force is resulted for the water flowing through the membrane. Therefore, at low graft yield, the water flux of PNIPAM-grafted membrane at 40°C is larger than that of the ungrafted membrane. With keeping on increasing the graft yield, the pore size decreases gradually, resulting in decrease of water flux. In the case that too much PNIPAM grafted into the pores, the pores could not be opened any more even when the grafted PNIPAM chains are in the shrunken state, consequently the water flux through the membrane tends to zero.

It is indeed very important to choose a proper graft yield for obtaining an ideal "on/off" gating response. In the present study, it was suggested to set the graft yield in the range 0.4—0.8 mg·cm^{-2} for the membrane to get an effective thermo-responsive "on/off" hydraulic permeability.

4.3 Thermo-responsive diffusional permeability

Figure 6 shows the effect of graft yield on the thermo-responsive diffusional permeability through the PE-*g*-PNIPAM membranes, and Fig. 7 shows the

(a) Filtration
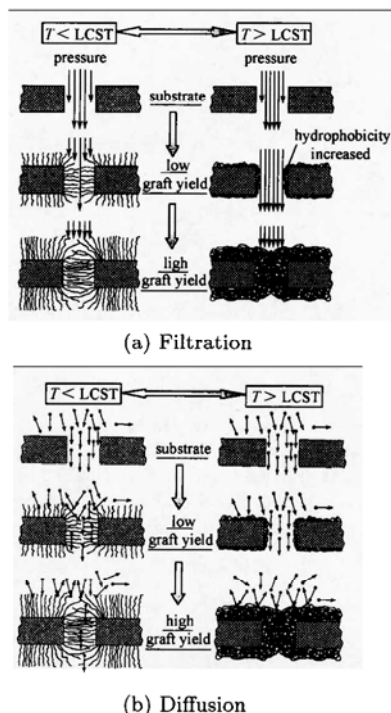
(b) Diffusion

Figure 5   Schematic illustration of the hydraulic and diffusional permeability through PNIPAM-grafted membranes with different graft yields
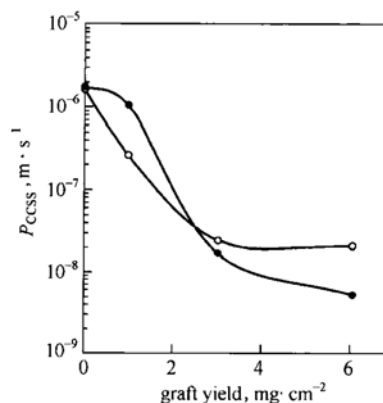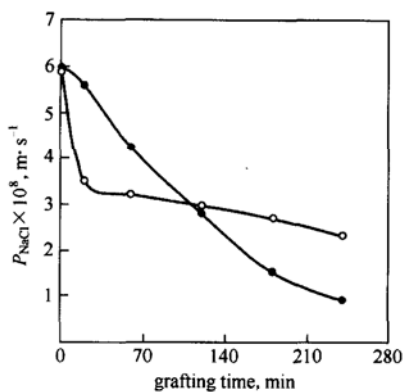

Figure 6   Effect of graft yield on the thermo-responsive diffusional permeability through the PE-*g*-PNIPAM membranes
(The initial concentration of CCSS in donor side is 8.56×10^{-3} mol·L^{-1}, and that in receptor side is zero)
T, °C: —O— 25; —●— 40

effect of grafting time on the thermo-responsive diffusional permeability through PNIPAM-grafted microcapsule membranes. Because the graft yield has been verified to be directly proportional to the grafting time in the plasma-graft pore-filling polymerization when all other experimental conditions being the same[19], the results in Fig. 7 reflect the effect of the graft yield on the diffusional permeability. Figs. 6 and 7 show the similar permeability-response patterns in these two different membranes. When graft yield is zero, the diffusional coefficient of solute across the membrane at 40°C is slightly larger than that at 25°C, because the diffusivity of solute increases with increasing
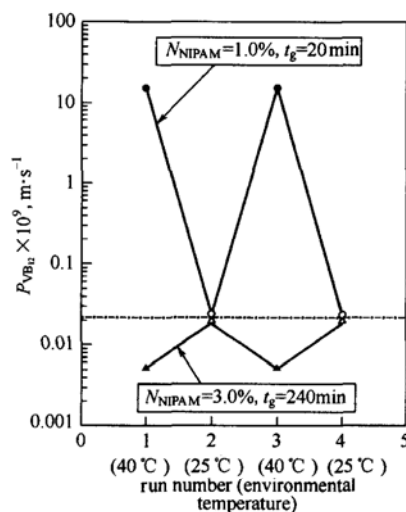
Figure 7   Effect of grafting time on the thermo-responsive diffusional permeability through PNIPAM-grafted microcapsule membranes
(The initial concentration of NaCl in intracapsular liquid is 0.324 mol·L^{-1}, and that in bulk liquid is 0.162 mol·L^{-1})
T, °C: —○— 25; —●— 40

the environmental temperature. After grafting PNIPAM, the temperature has an opposite effect on the diffusional permeability coefficients of solutes across the membranes with low graft yields as opposed to those with high graft yields. When the graft yield was low, the diffusional coefficient of solute across the membrane was higher at temperature above the LCST than that below the LCST, owing to the pores of the membrane being controlled open/closed by the shrinking/swelling mechanism of the grafted PNIPAM gates. While, when the graft yield was high, the diffusional coefficient was lower at temperature above the LCST than that below the LCST, owing to the hydrophilic/hydrophobic phase transition of the grafted PNIPAM gates. Because the solutes used in the experiments were water-soluble, any solute diffusion within the membranes occurred primarily within the water-filled regions in the spaces delineated by the grafted PNIPAM chains. Therefore, it is easier for the solute to find water-filled regions in the membranes with hydrophilic PNIPAM gates rather than in the membranes with hydrophobic PNIPAM gates. A schematic illustration of the diffusional permeability through PNIPAM-grafted membranes with different graft yields is shown in Fig. 5(b).

Figure 8 shows the reversible thermo-responsive diffusional permeability through PNIPAM-grafted microcapsule membranes with low graft yield and high graft yield respectively, in which the upper line is that of the microcapsule membranes with low graft yield and the lower one is that with high graft yield. The results show again that the temperature has an obviously opposite effect on the diffusional permeability coefficients of solutes across the membranes with low graft yield as opposed to those with high graft yield. The diffusional permeability response was found to be reversible and reproducible, indicating that the grafted PNIPAM gates retained their thermal swelling/shrinking and hydrophilic/hydrophobic properties intact, although they underwent repeated

temperature changes across the LCST. Therefore, it is also very important to choose a proper graft yield for obtaining a desired "on/off" thermo-responsive diffusional permeability.

Figure 8   Reversible thermo-responsive diffusional permeability through PNIPAM-grafted microcapsule membranes with low graft yield (upper) and high graft yield (lower)

5 CONCLUSIONS

In this study, the effect of graft yield on both the thermo-responsive hydraulic permeability and the thermo-responsive diffusional permeability through porous membranes with plasma-grafted PNIPAM gates was investigated. Both thermo-responsive flat membranes and core-shell microcapsule membranes with a wide range of graft yield of PNIPAM were prepared using a plasma-graft pore-filling polymerization method. The PNIPAM was grafted homogeneously throughout the entire thickness of both the polyethylene flat membranes and the polyamide microcapsule membranes. Both the hydraulic permeability and the diffusional permeability were strongly dependent on the PNIPAM graft yield. With increasing the graft yield, the hydraulic permeability (water flux) decreases rapidly at 25°C because of the decrease of the pore size; however, the water flux at 40°C increases first to a peak because of the increase of the hydrophobicity of the pore surface, then decreases and finally tends to zero because of the pore size becoming smaller and smaller. For the diffusional permeability, the temperature has an opposite effect on the diffusional permeability coefficients of solutes across the membranes with low graft yields as opposed to those with high graft yields. When the graft yield was low, the diffusional coefficient of solute across the membrane was higher at temperature above the LCST than that below the LCST, owing to the pores of the membrane being opened/closed as controlled by the shrinking/swelling state change of the grafted PNIPAM gates. On the other hand, when the graft

yield was high, the diffusional coefficient was lower at temperature above the LCST than that below the LCST, owing to the hydrophilic/hydrophobic phase transition of the grafted PNIPAM gates. It is very important to choose or design a proper graft yield of PNIPAM for obtaining a desired thermo-responsive "on/off" hydraulic or diffusional permeability.

ACKNOWLEDGEMENTS

NOMENCLATURE

A	effective diffusion area of membrane, cm^2
c	concentration, $mol \cdot L^{-1}$
$(c_1)_0$	initial concentration of the solute in the donor compartment, $mol \cdot L^{-1}$
$(c_1)_t$	intermediary concentration (at time t) of the solute in the donor compartment, $mol \cdot L^{-1}$
$(c_2)_t$	intermediary concentration (at time t) of the solute in the receptor cell, $mol \cdot L^{-1}$
c_f	final concentration of solute in both bulk solution and intracapsular liquid, $mol \cdot L^{-1}$
c_i	initial concentrations in the bulk solution, $mol \cdot L^{-1}$
c_{im}	initial concentrations in the intracapsular liquid, $mol \cdot L^{-1}$
c_t	intermediary concentrations (at time t) in the bulk solution, $mol \cdot L^{-1}$
c_{tm}	intermediary concentrations (at time t) in the intracapsular liquid, $mol \cdot L^{-1}$
Δc	concentration difference between the bulk solution and intracapsular liquid, $mol \cdot L^{-1}$
D	diffusion coefficient, $cm^2 \cdot s^{-1}$
L	thickness of the dry membrane, cm
M	solute mass in the bulk solution, mol
N_{NIPAM}	NIPAM monomer concentration by mass, %
P	diffusional permeability coefficient, $m \cdot s^{-1}$
T	temperature, °C
t	time, s
t_g	grafting time, min
V_1	liquid volume in the donor compartment, cm^3
V_2	liquid volume in the receptor compartment, cm^3
V_m	total volume of microcapsules, cm^3
V_s	volume of the bulk solution, cm^3
δ	thickness of the membrane of microcapsule, cm

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