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Thermoresponsive Gating Characteristics of Poly(*N*-isopropylacrylamide)-Grafted Porous Poly(vinylidene fluoride) Membranes**Yan Li, Liang-Yin Chu,* Jia-Hua Zhu, Hai-Dong Wang, Su-Lan Xia, and Wen-Mei Chen***School of Chemical Engineering, Sichuan University, Chengdu, Sichuan 610065, China*

A series of thermoresponsive gating membranes, with a wide range of grafting yields, were prepared by grafting poly(*N*-isopropylacrylamide) (PNIPAM) onto porous poly(vinylidene fluoride) (PVDF) membrane substrates with a plasma-induced pore-filling polymerization method. The effect of grafting yield on the gating characteristics of thermoresponsive gating membranes was investigated systematically. The results showed that the grafting yield heavily affected both the water flux responsiveness coefficient and the thermoresponsivity of the membrane pore size. When the grafting yield was smaller than 2.81%, both the flux responsiveness coefficient and the thermoresponsivity of the membrane pore size increased with an increase in the grafting yield; however, when the grafting yield was higher than 6.38%, both the flux responsiveness coefficient and the thermoresponsivity of the membrane pore size were always equal to 1; i.e., no gating characteristics existed anymore. Diffusional permeation experiments showed that two distinct types of temperature responses were observed, depending on the grafting yield. The diffusional coefficient of a solute across membranes with low grafting yields increased with temperature, while that across membranes with high grafting yields decreased with temperature. To get a desired or satisfactory thermoresponsive gating performance, the membranes should be designed and prepared with a proper grafting yield.

Introduction

Much attention has been drawn to polymeric membranes whose permeability can be controlled in response to environmental stimuli such as temperature, pH, light, electric field, and chemical or biological species.^{1–10} These environmental responsive membranes may find applications ranging from controlled drug delivery, to chemical separation, to water treatment, to bioseparation, to chemical sensor, to tissue engineering, etc. There is an increasing interest in these intelligent membranes.

One type of stimuli-responsive membrane is prepared by grafting stimuli-responsive polymers possessing functional groups onto porous membrane substrates. The porous substrate provides mechanical strength and dimensional stability, while the conformational changes of the grafted functional polymers result in environment-responsive characteristics. The permeability of these membranes can be controlled or adjusted by the grafted polymer according to the external chemical and/or physical environment. Two main advantages can be obtained from grafting techniques in preparing these intelligent membranes. One is that the grafted chains are chemically bonded to the membrane substrate compared with those prepared by coating and adsorption 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 comparison with hydrogels with typical cross-linked network structures.

Various grafting techniques, including chemical grafting, plasma-induced grafting, and radiation-induced grafting and so on, have been employed to prepare stimuli-responsive membranes by grafting different functional polymers onto either the external membrane surface or both the external surface and the inside surface of the pores.^{1–9,11–18} However, a comprehensive understanding of the thermoresponsive gating characteristics, including that of the hydraulic permeability (pressure-driven convective flow of solvents) responsiveness, the thermoresponsivity of the membrane pore size, and the diffusional permeability (concentration-driven molecular diffusion of solutes) response, is still lacking.

In this study, a series of thermoresponsive gating membranes, with a wide range of grafting yields, were prepared by grafting poly(*N*-isopropylacrylamide) (PNIPAM) onto porous poly(vinylidene fluoride) (PVDF) membrane substrates with a plasma-induced pore-filling polymerization method. Investigations were carried out on the examination of grafting, the effect of grafting yield on the thermoresponsive hydraulic permeability, the flux responsiveness coefficient, the thermoresponsivity of the membrane pore size, and the diffusional permeability response.

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Experimental Section

Materials. Porous PVDF membranes were used as the flat porous membrane substrates. The PVDF substrate, with a pore size of 0.22 μm and a thickness of 62.5 μm , was supplied by Xidoumen Membrane Co. Ltd., China. The *N*-isopropylacrylamide (NIPAM) was kindly provided by Kohjin Co., Ltd., Japan, and was used after purification by recrystallization in hexane and acetone and then drying in vacuo at room temperature. The water used in the experiment was well-deionized, and its resistance was larger than 16 M Ω .

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 the flat membrane according to the method described previously.^{1–4} In the experiments, the 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 plasma power was changed from 10 to 30 W. The NIPAM concentrations in the monomer solutions were 1 and 3 wt %, respectively. The grafting time was from 60 to 240 min. The grafting yield of the membrane was defined as the weight increase of the membrane after the grafting and could be calculated according to the equation

$$Y = \frac{W_g - W_0}{W_0} \times 100\% \quad (1)$$

where Y stands for the grafting yield [%] of PNIPAM on the membrane substrate and W_g and W_0 stand for the mass [g] of the membrane after and before grafting, respectively.

Morphological Analysis. Fourier transform infrared (FT-IR) spectra of the ungrafted and PNIPAM-grafted membranes were measured on a spectrophotometer (Spectrum one, P–E Com., USA) to ascertain the grafted PNIPAM formation.

To observe the microscopic configuration of PNIPAM-grafted membranes with different grafting yields, a scanning electron microscope (SEM; JSM 5900LV, Hitachi, Japan) was used. The cross-sectional structures of the membranes were observed by putting the membranes into liquid nitrogen, cutting the membranes with a slice, and then gilding the membranes.

Thermoresponsive Filtration Experiments. The hydraulic permeability experiments or filtration experiments of membranes were carried out with a transmembrane pressure of 90 kPa. The diameter of the effective membrane area for filtration was 60 mm. The temperature of the feedwater was controlled using a thermostatic unit. The temperature range in the experiments was from 25 to 40 °C. The hydraulic permeability through the ungrafted and PNIPAM-grafted membranes at different temperatures was studied by measuring the water flux.

Thermoresponsive Diffusion Experiments. The diffusional permeability experiments of membranes were carried out using a standard side-by-side diffusion cell. The diffusion cell was located in a constant-temperature water bath to keep the diffusional temperature constant. Each test membrane was soaked first in ethanol to wet the membrane and then immersed in the permeant solution overnight before starting the diffusion experiments. The solute was sodium chloride. Well-deionized water was used as the liquid in the receptor cell. After a check for leakage, 300 mL of well-

Table 1. Prepared PVDF-*g*-PNIPAM Membranes with Different Grafting Yields

| membrane code | experimental parameter | | | |
|---------------|------------------------|--|---------------------|--------------------|
| | argon plasma power [W] | NIPAM concn in monomer solution [wt %] | grafting time [min] | grafting yield [%] |
| P24 | 10 | 3 | 60 | 0.19 |
| P5 | 30 | 1 | 120 | 0.79 |
| P9 | 30 | 1 | 240 | 0.80 |
| P12 | 20 | 3 | 60 | 2.81 |
| P4 | 30 | 3 | 60 | 6.38 |
| P20 | 30 | 3 | 90 | 7.94 |
| P3 | 30 | 3 | 120 | 14.03 |
| P2 | 30 | 3 | 180 | 14.95 |
| P8 | 30 | 3 | 210 | 16.61 |

deionized water and 0.2 mol/L of a NaCl solution were added simultaneously to the receptor and donor cells, respectively, and stirred with a pair of magnetic stirrers. The concentration of NaCl was determined by measuring the electrical conductance with an electrical conductivity meter. The membranes were washed by well-deionized water and soaked in a NaCl solution at least for 12 h before a new diffusion experiment was started at a different temperature, and each new diffusion experiment was started with a fresh NaCl solution and freshwater in the donor and receptor compartments, respectively.

The diffusion coefficient of the solute across the flat membrane can be calculated using the following equation, derived from Fick's first law of diffusion:

$$D = -\frac{VL}{2A} \frac{1}{t} \ln \left[1 - 2 \frac{(C_2)_t}{(C_1)_0} \right] \quad (2)$$

where D is the diffusional coefficient [cm^2/s], $(C_1)_0$ and $(C_2)_t$ are the initial and intermediary concentrations (at time t) of the solute in the donor and receptor compartments, respectively [mol/L], V is the volume of the liquid in the donor compartment and that in the receptor compartment [cm^3], L is the thickness of the dry membrane [cm], and A is the effective diffusion area of the membrane [cm^2].

Results and Discussion

Grafting Yield of the PNIPAM-Grafted Membranes. A series of PNIPAM-grafted membranes, with a wide range of grafting yields, were prepared by altering the plasma power, the monomer concentration, and the grafting time. The prepared membranes with different grafting yields are listed in Table 1. Because the grafting temperature and the experimental parameters of the plasma treatment (except plasma power) were unchanged, the grafting yield was dependent on the plasma power, the monomer concentration, and the grafting time. With an increase in the plasma power, the monomer concentration, or the grafting time, the graft yield of PNIPAM on the membrane increased.

Morphological Analyses of the PNIPAM-Grafted Membranes. FT-IR spectra of ungrafted and PNIPAM-grafted membranes are illustrated in Figure 1. After PNIPAM is grafted onto the PVDF substrate, two characteristic peaks of PNIPAM, the C=O peak at 1658.9 cm^{-1} and the amide II peak at 1548.6 cm^{-1} , appeared newly in the spectrum compared with that of the ungrafted membrane. The comparison result veri-

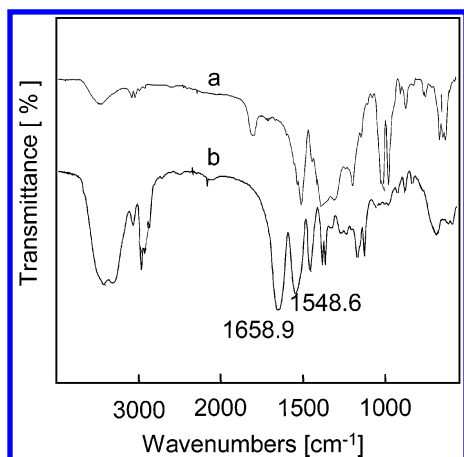


Figure 1. IR spectra of (a) an ungrafted PVDF membrane and (b) a PNIPAM-grafted PVDF membrane.

fied that PNIPAM was grafted on the membrane substrate by plasma-induced pore-filling polymerization.

Figure 2 shows SEM micrographs of the cross sections of ungrafted and PNIPAM-grafted membranes with different grafting yields. The cross sections of the ungrafted and PNIPAM-grafted membranes are seen to have significantly different structures. As seen from Figure 2a, the ungrafted membrane is obviously featured with a porous structure and a thin functional top layer. The cross sections of the grafted membranes, as

shown in Figure 2b–d, are seen to have thicker graft layers with an increase in the grafting yield. When Figure 2a is compared with Figure 2b–d, it is obviously found that the membrane cross section becomes denser and the porosity of the membrane becomes smaller with an increase in the grafting yield. That is to say, the graft of PNIPAM was formed not only on the surface but also in the pores of the membrane.

Thermoresponsive Hydraulic Permeability. Figure 3 shows the effect of temperature on the hydraulic permeability ranging from 25 to 40 °C. For the ungrafted membrane, the water flux increases slowly with an increase in the environmental temperature, which is due to the decrease of the liquid viscosity resulting from the temperature increasing. After PNIPAM is grafted onto the porous membrane substrates, the hydraulic permeability for the grafted membranes with certain grafting yields (such as membranes P24, P9, P5, and P12) changes dramatically at about 32 °C. 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;¹⁹ however, it becomes hydrophobic and shrinks dramatically when the temperature is raised above the LCST. When the environmental temperature is below the LCST, the grafted PNIPAM chains in the membrane

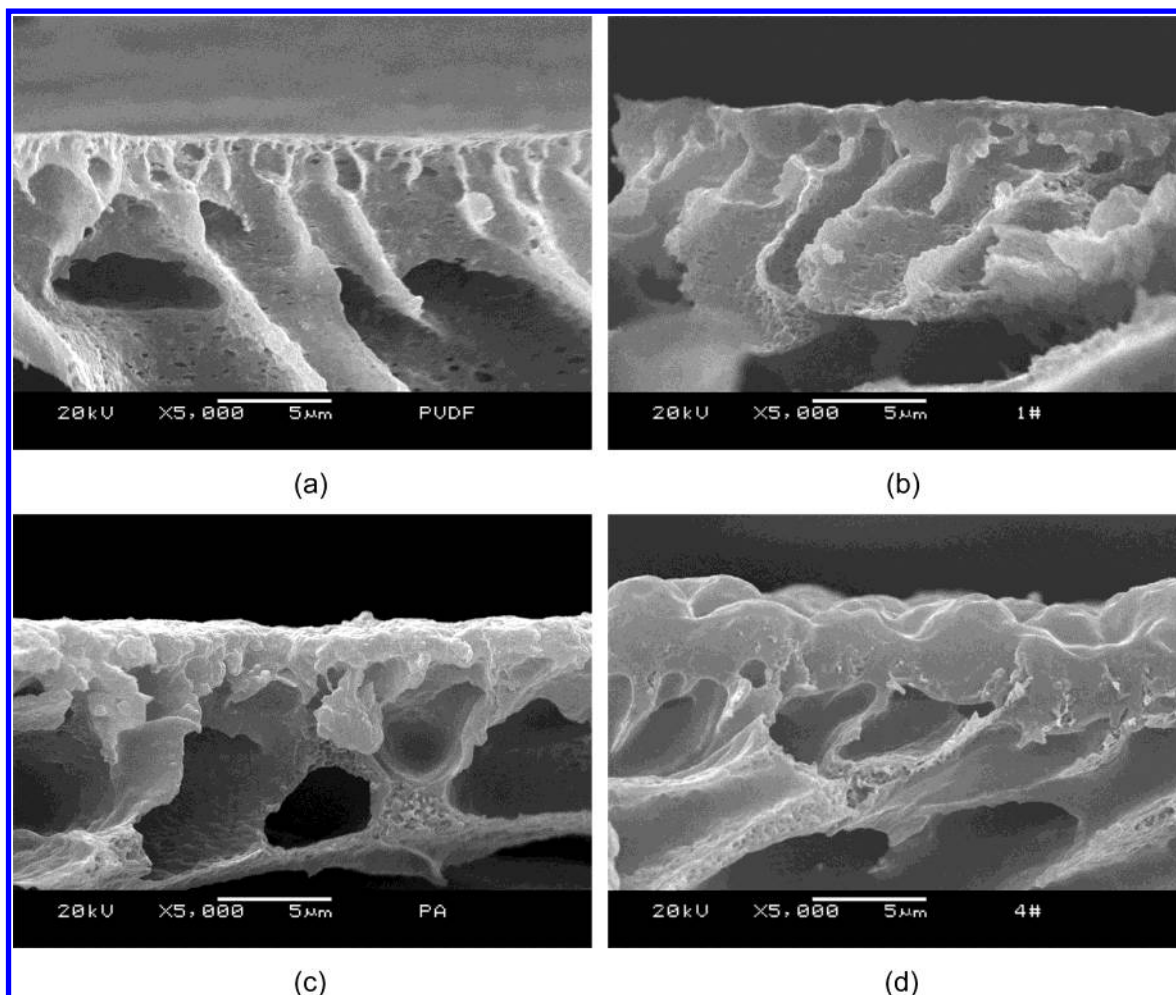


Figure 2. SEM micrographs of the cross sections of (a) an ungrafted PVDF membrane, (b) a PVDF-*g*-PNIPAM membrane with a grafting yield of 2.81%, (c) a PVDF-*g*-PNIPAM membrane with a grafting yield of 7.94%, and (d) a PVDF-*g*-PNIPAM membrane with a grafting yield of 16.61%.

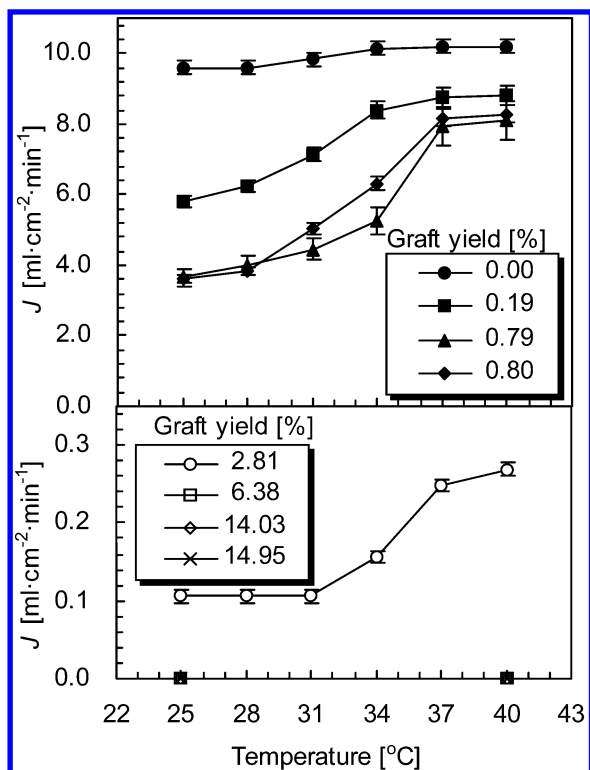


Figure 3. Thermoresponsive characteristics of the water flux of PVDF-*g*-PNIPAM membranes with different grafting yields.

pores are in the swollen state; therefore, the pore size is decreased or closed. As a result, the water flux is small. When the environmental temperature is above the LCST, the grafted PNIPAM chains in the membrane pores are in the shrunken state; therefore, the pore size is increased or open. As a result, the water flux is large. The grafted PNIPAM chains in the membrane pores can act as intelligent thermoresponsive gates. The thermoresponsive characteristics of the water flux of the membranes with different grafting yields are different. In the case that too much PNIPAM is grafted into pores, the membrane pores could not be opened anymore even when the grafted PNIPAM chains are in the shrunken state; consequently, the water flux through the membrane at temperatures both above and below the LCST tends to zero (see membranes P2, P3, and P4). That is to say, with a too large grafting yield, the grafted PNIPAM chains in the pores could not act as thermoresponsive gates effectively anymore.

Thermoresponsive Gating Characteristics. The architectures and relatively physicochemical properties of the grafted PNIPAM chains, such as the length and density of the PNIPAM chains and the thermoresponse time of these chains, will change with the variation of the grafting yield. Consequently, the thermoresponsive gating characteristics of PNIPAM-grafted membranes with different grafting yields are different from each other. Figure 4 shows the effect of the grafting yield on the thermoresponsive gating characteristics of PVDF-*g*-PNIPAM membranes, in which the thermoresponsive gating coefficient or so-called flux responsiveness coefficient R is defined as

$$R = J_{40}/J_{25} \quad (3)$$

where J_{40} and J_{25} are the measured water fluxes at environmental temperatures of 40 and 25 °C, respectively [$\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$].

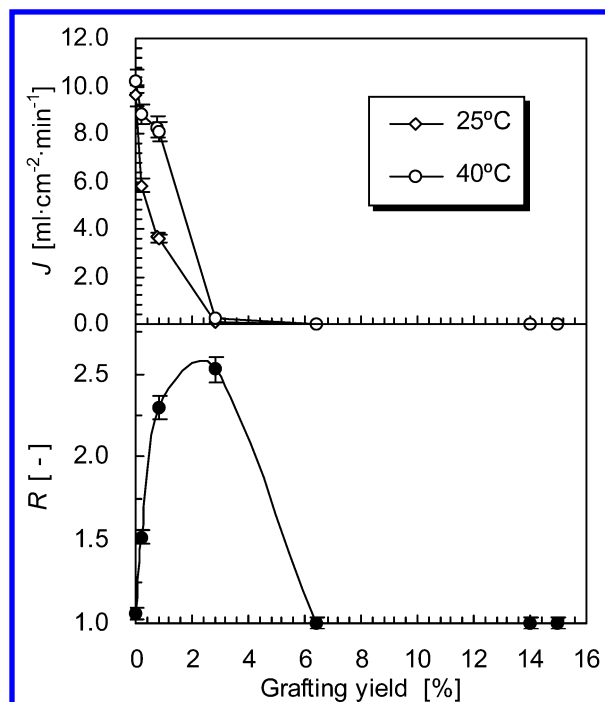


Figure 4. Effect of the grafting yield on the thermoresponsive gating characteristics of PVDF-*g*-PNIPAM membranes.

If the water fluxes are both zero at 25 and 40 °C, the flux responsiveness coefficient R is defined as 1. That is, the PNIPAM-grafted membrane has no gating function in that case.

With an increase in the grafting yield, the water flux decreases at both 25 and 40 °C. When the grafting yield is less than 2.81%, the flux responsiveness coefficient increases with an increase in the grafting yield; however, when the grafting yield is larger than 6.38%, the water flux through the membrane tends to zero at both 25 and 40 °C, and the flux responsiveness coefficient tends to 1. It can be seen that only when the grafting yield is less than 6.38% can the grafted PNIPAM chains in the membrane pores act as thermoresponsive gates or adjusting valves of the water flux, whereas when the grafting yield is larger than 6.38%, the length and density of the grafted PNIPAM chains in the membrane pores are too long and large, resulting in the chains losing the function of thermoresponsive gates or adjusting valves of the water flux. For the environmental stimuli-responsive gating membrane, the larger the flux responsiveness coefficient is, the better the gating property. Therefore, the grafting yield must be kept in a proper range in order to obtain a satisfactory gating characteristic for the membrane.

Thermoresponsive Control of the Membrane Pore Size. The thermoresponsive change of the pore size of PVDF-*g*-PNIPAM membranes can be calculated using Hagen–Poiseuille's law. According to Hagen–Poiseuille's law, the water flux of a skinless porous membrane can be expressed as

$$J = \frac{n\pi d^4 P}{128\eta l} \quad (4)$$

where J stands for the water flux [$\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$], n for the number of pores per unit area [m^{-2}], d for the pore diameter [m], P for the transmembrane pressure [Pa], η for the viscosity of the flowing liquid [$\text{Pa} \cdot \text{s}$], and l for the membrane thickness [m].

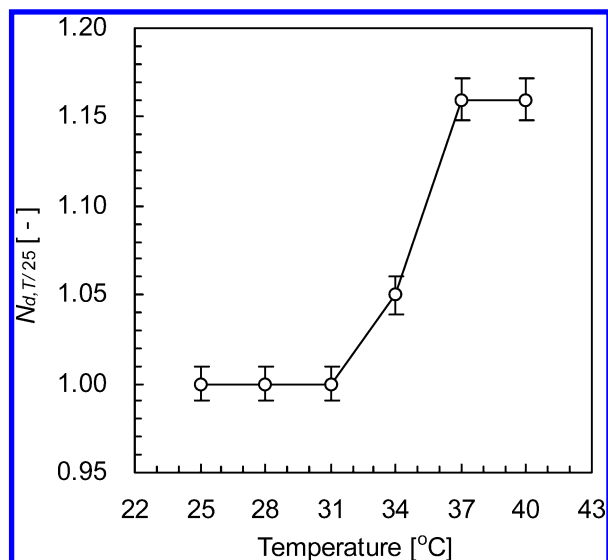


Figure 5. Thermoresponsive control of the pore size of a PVDF-*g*-PNIPAM membrane (membrane P12 in Table 1).

In a plasma-grafted membrane, the grafted PNIPAM forms a skin layer on the inner surface of the membrane pore.⁴ As indicated in eq 1, the water flux is governed by the fourth power of the pore diameter. Thus, the conformational change of PNIPAM chains that grafted on the inner surface of membrane pore, i.e., coil globule, affects the water flux greatly. As known from eq 1, the ratio of the effective pore diameter of the PNIPAM-grafted membrane at T [°C] to that at 25 °C, which is defined as the thermoresponsive gating factor of the membrane pore size, can be evaluated using the measured water fluxes and viscosities of water at different temperatures with the following formula:

$$N_{d, T/25} = \frac{d_{g, T}}{d_{g, 25}} = \left(\frac{J_T \eta_T}{J_{25} \eta_{25}} \right)^{\frac{1}{4}} \quad (5)$$

where $N_{d, T/25}$ is the thermoresponsive gating factor of the membrane pore size, $d_{g, T}$ and $d_{g, 25}$ are the effective pore diameters of the PNIPAM-grafted membranes at T [°C] and 25 °C, respectively [m], J_T is the measured water fluxes at the environmental temperature T [°C] [$\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$], and η_T and η_{25} are the viscosity coefficients of the flowing liquid at T [°C] and 25 °C, respectively [Pa·s].

Thermoresponsive control of the effective pore size of membrane P12 is illustrated in Figure 5. As expected, the effective pore size of the PNIPAM-grafted membrane changes dramatically at temperatures around the LCST of PNIPAM as a result of the conformational change of the grafted PNIPAM chains. When the environmental temperature is less than 31 °C or larger than 37 °C, the effective pore size remains nearly unchanged. This is due to the fact that the conformation of the grafted PNIPAM chains presents a steady state at these temperature ranges.

To describe quantitatively the effect of the grafting yield on the pore gating behavior of the PNIPAM-grafted membranes, a special thermoresponsive gating factor of the pore size, which is named the pore size responsivity here, is defined as

$$N_{d, 40/25} = d_{g, 40} / d_{g, 25} \quad (6)$$

where $N_{d, 40/25}$ is the pore size responsivity of the

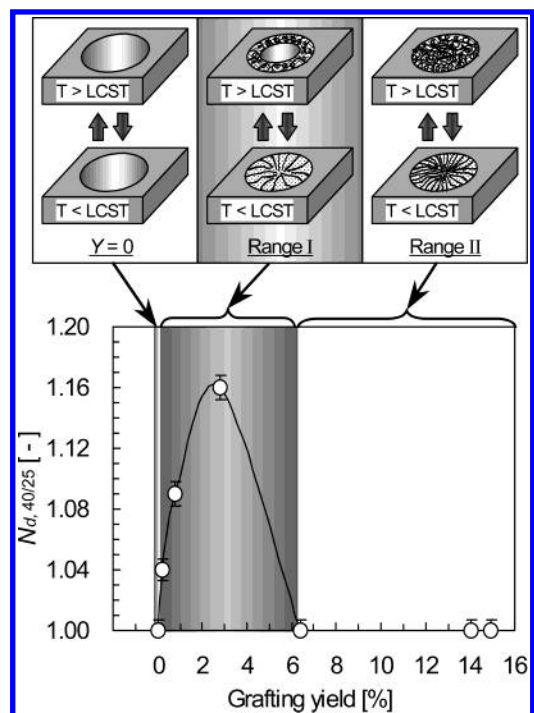


Figure 6. Effect of the grafting yield on the thermoresponsivity of the membrane pore size and schematic illustration of the thermoresponsive control of the pore size.

membrane and $d_{g, 40}$ is the effective pore diameter of the PNIPAM-grafted membrane at 40 °C.

Figure 6 shows the effect of the grafting yield on the thermoresponsivity of the membrane pore size and the schematic illustration of the thermoresponsive control of the pore size. For the membrane substrate, the pore size does not change with variation in the environmental temperature. For the PNIPAM-grafted membranes, the thermoresponsivity of the pore size is heavily affected by the grafting yield. When the grafting yield is too small, the grafted PNIPAM chains are too short, resulting in a small responsivity of the membrane pore size. With an increase in the grafting yield, the length of the grafted PNIPAM chains increases; consequently, the thermoresponsivity of the pore size also increases. However, when the grafting yield increases too much, the grafted PNIPAM chains become too long and the conformational change of the PNIPAM chains cannot bring any obvious change of the pore size anymore. That is, the membrane pores have been “choked” by the grafted polymers. The influence behavior of the grafting yield on the flux responsiveness coefficient and that on the thermoresponsivity of the pore size are similar to each other. This verifies again that the thermoresponsive flux change of the PNIPAM-grafted membranes is controlled by the thermoresponsivity of the pore size.

In summary, it is very important to choose a proper grafting yield for obtaining an ideal “on/off” gating response. In the present study, it was suggested to set the grafting yield in the range 0.5–3.0% for the membrane to get an effective thermoresponsive gating property.

Thermoresponsive Diffusional Permeability. Figure 7 shows the thermoresponsive diffusional permeability through PVDF-*g*-PNIPAM membranes with different grafting yields. When the grafting yield is zero (i.e., the substrate membrane), the diffusional coefficient of the solute across the membrane increases slightly with an increase in the environmental temperature in

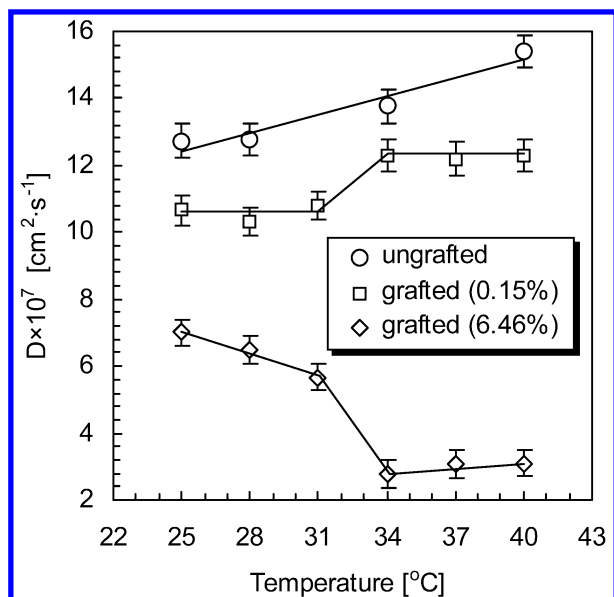


Figure 7. Effect of the grafting yield on thermoresponsive diffusional permeation.

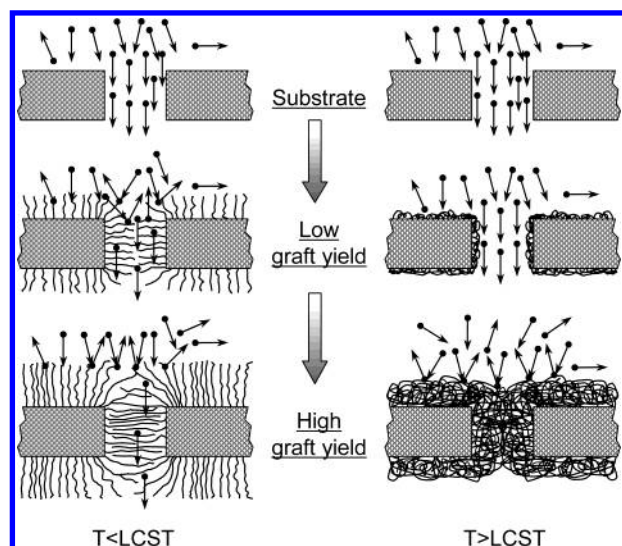


Figure 8. Schematic illustration of thermoresponsive diffusional permeability through PNIPAM-grafted membranes with different grafting yields.

the range of 25–40 °C, because the diffusivity of the solute increases with an increase of temperature. After PNIPAM is grafted, the diffusional coefficient of the solute across the membrane changes dramatically at temperatures around the LCST of PNIPAM, which is due to the conformational change of the PNIPAM chains grafted in membrane pores. As seen from Figure 7, the temperature has an opposite effect on the diffusional coefficients of the solutes across the membranes with low grafting yield as opposed to that with high grafting yield. A schematic illustration of the diffusional permeability through PNIPAM-grafted membranes with different grafting yields is shown in Figure 8. When the grafting yield was low, the diffusional coefficient of the solute across the membrane was higher at temperatures 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 grafting yield was high, the diffusional coefficient was lower at temperatures above the LCST than that below the LCST, owing to

the hydrophilic/hydrophobic phase transition of the grafted PNIPAM gates. Because the solute used in the experiments was 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.

Conclusions

In this study, thermoresponsive gating characteristics of PNIPAM-grafted porous PVDF membranes with a wide range of grafting yields were investigated systematically. The PVDF-*g*-PNIPAM membranes were prepared using a plasma-induced pore-filling polymerization method, and the spectra of FT-IR and the SEM micrographs of the membrane cross sections showed that PNIPAM was grafted homogeneously throughout the entire thickness of the porous PVDF membranes. Both the hydraulic permeability and the diffusional permeability through the PVDF-*g*-PNIPAM membranes were strongly dependent on the PNIPAM grafting yield. For the grafted membranes with moderate grafting yields (e.g., 0.5–3.0%), both the hydraulic permeability and the thermoresponsivity of the membrane pore size changed dramatically at about 32 °C. With an increase in the grafting yield, the hydraulic permeability (water flux) decreased rapidly at both 25 and 40 °C because of the decrease of the pore size. The diffusional permeability of the solute across the membranes also changed dramatically at temperatures around the LCST of PNIPAM. For the diffusional permeability, the temperature had an opposite effect on the diffusional coefficient of the solute across the membranes with a low grafting yield as opposed to that with a high grafting yield. To get a desired or satisfactory thermoresponsive gating performance, the PVDF-*g*-PNIPAM membranes should be designed and prepared with a proper grafting yield.

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