

# Preparation of Thermal-Responsive Poly(propylene) Membranes Grafted with *N*-Isopropylacrylamide by Plasma-Induced Polymerization and Their Water Permeation

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**ABSTRACT:** Poly(propylene) (PP) membrane grafted with poly(*N*-isopropylacrylamide) (PNIPAAm), which is known to have a lower critical solution temperature (LCST) at around 32°C, was prepared by the plasma-induced graft polymerization technique. Graft polymerization of PNIPAAm onto a PP membrane was confirmed by microscopic attenuated total reflection/Fourier transform IR spectroscopy. The grafting yield of PNIPAAm increased with the concentration of *N*-isopropylacrylamide monomer and the reaction time of graft polymerization. The average pore size of the PP membrane also affected the grafting yield. From the field emission scanning electron microscopy (FE-SEM) measurement, we observed a morphological change in the PP-*g*-PNIPAAm membrane under wet conditions at 25°C below LCST. The permeability of water through the PP-*g*-PNIPAAm membrane was controlled by temperature. The PP-*g*-PNIPAAm membrane (PN05 and PN10) exhibited higher water permeability ( $L_p$ ) than the original PP substrate membrane below LCST. As the temperature increased to above LCST,  $L_p$  gradually decreased. In addition, the graft yield of PNIPAAm and the average pore size of the PP substrate influenced water permeability. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1168–1177, 2002; DOI 10.1002/app.10410

**Key words:** poly(propylene) (PP); *N*-isopropylacrylamide; plasma polymerization; graft polymerization; water permeation

## INTRODUCTION

There have been many studies to develop polymers with specific physicochemical properties.<sup>1–3</sup> The surface modification of polymers has been of special interest, with particular attention being paid to such applications as adhesives, biomaterials, and membranes.<sup>4–19</sup> Their surfaces can be readily modified, and such modifications can have significant influences on materials applications.

Therefore, many methods such as ultraviolet irradiation,<sup>6,7</sup> ion-beam irradiation,<sup>8,9</sup> electron-beam irradiation,<sup>10</sup>  $\gamma$  irradiation,<sup>11,12</sup> plasma treatment,<sup>13–19</sup> and chemical treatment<sup>20</sup> have been used to modify polymers and membranes for specific applications.

Among these methods, the plasma treatment technique<sup>13–19</sup> provides a unique approach for alteration of material surfaces without alteration of their bulk properties. In addition, plasma-induced graft polymerization has some advantages. It provides economic feasibility, due to small-sized instruments, commercially available product, and low-energy power. This plasma method is an environmentally compatible process that is

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dry and avoids harmful waste. Also, high efficiency can be achieved with a short treatment time of only a few seconds or minutes. With the use of various specific gases, such as oxygen, argon, nitrogen, and hydrogen, and active monomers, a wide range of surface properties can be designed for a particular application.<sup>13–19</sup> Particularly, the modification of polymer surfaces by means of plasma treatment is a very important and useful technique in the biomedical materials area.<sup>13,19</sup>

Poly(propylene) (PP) has many advantages, such as chemical and physical stability, good resistance to biodegradation, and low cost. However, it is not possible to modify PP with conventional chemical methods.<sup>21–24</sup>

Irradiation-induced grafting is frequently used to modify polymeric materials, especially polyolefin films such as polyethylene and PP. Many researchers have shown that the wettability, adhesion, dyeability, and biocompatibility properties of a given polymer can be changed by the graft modification of its surface.<sup>21–24</sup>

There are many kinds of polymers that respond to changes in environmental conditions. The polymers can change their physical characteristics or chemical structures, depending on several external physicochemical factors.<sup>1–3</sup>

It is well known that poly(*N*-isopropylacrylamide) (PNIPAAm) in aqueous solution has a lower critical solution temperature (LCST) at around 32°C.<sup>25–32</sup> Recently, PNIPAAm has received growing interest in the fields of separation, drug delivery, cell and tissue engineering, and those of other switching devices because of its unique thermal property changes.<sup>25–32</sup> PNIPAAm has not only hydrophilic groups (NH, C=O) but also hydrophobic groups (isopropyl) and thus hydrophilic interaction and hydrophobic interaction may play a dominant role in the thermoshrink transition.

This is a continuing study to develop a cell separator with a thermoresponsive polymer. In the field of tissue engineering, efficient cell separation is important as a prerequisite to the functional analysis of specialized cell types with complex biological systems. There have been many studies to develop a more successful system for cell separation depending on cell density (specific gravity), cell size, and light scattering or the fluorescent emission of labeled cells sorted electronically by flow cytometry.

However, a new technology is still required to achieve an inexpensive system with high yield.

Therefore, we considered a cell separation system with thermosensitivity and an affinity of antibodies to the cell surface, which could be controlled by a change in temperature and could separate specific cells by affinity to an antibody.

The goal of this work was to introduce thermally sensitive PNIPAAm groups on the surface of a nonwoven PP substrate membrane. In addition, we sought to prepare a temperature-sensitive membrane with high water permeability by using a nonwoven PP membrane with a large average pore size. In this study, we considered a plasma treatment technique consisting of two successive steps for the graft polymerization of *N*-isopropylacrylamide (NIPAAm) onto nonwoven PP. The first step was the formation of radicals on the PP membrane surface by the irradiation of argon plasma. This treatment was immediately followed by the graft polymerization of the NIPAAm monomer.

Plasma-induced graft polymerization of NIPAAm was performed under various conditions to investigate the optimum conditions and influencing factors. This study also dealt with the characterization of the graft-polymer-modified surface by microscopic attenuated total reflection/Fourier transform infrared (ATR/FTIR) spectroscopy and field emission scanning electron microscopy (FE-SEM) measurements. In addition, the effect of the modification on the permeability of water through a PP membrane grafted with a PNIPAAm membrane was evaluated as a function of temperature.

## EXPERIMENTAL

### Materials

Three nonwoven PP membranes purchased from Millipore (Bedford, MA) were used as substrates for graft polymerization. They had a diameter of 47 mm, and their average pore sizes were 5.0, 10.0, and 30  $\mu\text{m}$  (catalog numbers AN5004700, AN1H04700, and AN3H04700), respectively. NIPAAm was used as a graft monomer. NIPAAm was supplied from Tokyo Kasei Chemical Co. (Tokyo, Japan) and was used after recrystallization in *n*-hexane and toluene (40/60 vol %). Argon used for argon plasma irradiation was pure grade (99.995% purity). Ultrapure water was used after purification with a Milli-Q plus system (Waters, Millipore). All other chemicals were extrapure re-

**Table I** Conditions of Plasma Treatment and Graft Polymerization of NIPAAm and Properties of the Nonwoven PP Substrate Membranes

	Power (W)	Time (s)	Pressure (Pa)	Atmosphere
Condition of Plasma Treatment	10	60	10	Ar
		Grafting Temperature (°C)	Grafting Time (h)	Monomer Concentration (wt %)
Condition of Graft Polymerization of NIPAAm		60	0.5–48	1–10
	Sample	Average Pore Size (μm)		Catalog Number
Properties of Nonwoven PP Membrane	PP05	5.0		AN5004700
	PP10	10.0		AN1H04700
	PP30	30.0		AN3H04700

agent grade and were used as purchased without further purification.

#### Preparation of the Poly(propylene) Membrane Grafted with Poly(N-isopropylacrylamide) (PP-g-PNIPAAm)

The NIPAAm monomer, purified by recrystallization, was dissolved in ultrapure water (1–10 wt %). To remove any oxygen remaining in the solution, we bubbled nitrogen gas into the solution at room temperature for 30 min. Then, the monomer solution was degassed by a repeated freeze and thawing procedure under a vacuum of 1–2 Pa.

The plasma graft polymerization of NIPAAm on the PP membrane was carried out in two successive steps. The first step was a plasma irradiation treatment to form polymer radicals on the PP substrate membrane; the second step was the grafting and polymerization of NIPAAm monomer from radicals.

The conditions of the plasma treatment and graft polymerization of NIPAAm and the properties of PP substrate membranes are described in Table I. A preweighed PP substrate membrane was fixed in the center of a tubular Pyrex glass reactor (35 cm long and 4.5 cm in diameter). The whole system was evacuated for at least 30 min, and the system was filled with argon gas. After the system was evacuated to 10 Pa, the PP membrane was treated with a high frequency generator (13.56 MHz) (Samco. Ltd., Kyoto, Japan) connected with two external copper electrodes (distance between two electrodes = 9 cm)

surrounding the reactor. The power and period of argon plasma treatment were fixed at 10 W and 60 s, respectively.

The plasma-treated PP substrate membrane was connected with the degassed NIPAAm monomer solution in the liquid phase. The graft polymerization of NIPAAm onto the plasma-treated PP membrane was performed for a predetermined period in a constant-temperature water bath (60°C). We washed and agitated the grafted PP membrane in ultrapure water for 24 h at room temperature to eliminate the unreacted monomer and homopolymer probably formed on the surface, and then we dried the membrane in a vacuum oven at room temperature.

#### Microscopic ATR/FTIR Measurement

ATR/FTIR spectroscopy was used to examine the surface of the PP membrane.

The spectra were collected at 4 cm<sup>-1</sup> resolution with an ATR/FTIR microscopic spectrometer (Micro FT/IR-200, Jasco, Japan) over 50 scans. The sampling area was 25 μm<sup>2</sup>, coupled with an attenuated total reflection accessory and a 45° KRS-5 crystal.

#### Graft Yield of the PP-g-PNIPAAm Membrane

The graft polymerization was evaluated from weight increases after the graft polymerization. The grafting amount of PNIPAAm on the treated PP membrane was calculated as follows:

$$\text{Graft Yield } (\mu\text{g}/\text{cm}^2) = \frac{W_1 - W_0}{A} \quad (1)$$

where  $W_1$  and  $W_0$  represent the weight of the membrane after and before grafting, respectively;  $A$  is the area of poly(propylene) membrane.

### Wet FE-SEM Observation

The morphology of the PP-*g*-PNIPAAm membrane surface was observed with a wet field emission scanning electron microscope (SM-300, Topcon Co., Tokyo, Japan). The instrument was operated at an accelerating voltage of 10 kV. We observed the surface of original PP and PP-*g*-PNIPAAm membranes in both dry and wet states at 25°C. To investigate the morphology of a membrane under wet conditions, we carried out the FE-SEM observation after the membranes were stored in water for 24 h.

### Water Permeation of the PP-*g*-PNIPAAm Membrane

The water permeability ( $L_p$ ) through unmodified PP and PP-*g*-PNIPAAm membranes was measured with a permeation cell (LS-47V, Advantec MFS, Inc., Tokyo, Japan) apparatus. An active membrane area of 17.3 cm<sup>2</sup> was used. The pure water was supplied from a reservoir to the PP membrane installed in the permeation cell, which connected to a pressure transducer (PG-101G, Copal Electronics, Tokyo, Japan). The water permeability was determined by recording the flux ( $J$ ) of water at controlled hydrostatic pressure ( $\Delta P$ ) and was repeatedly measured by a timed collection of filtrate until a stable value was observed.

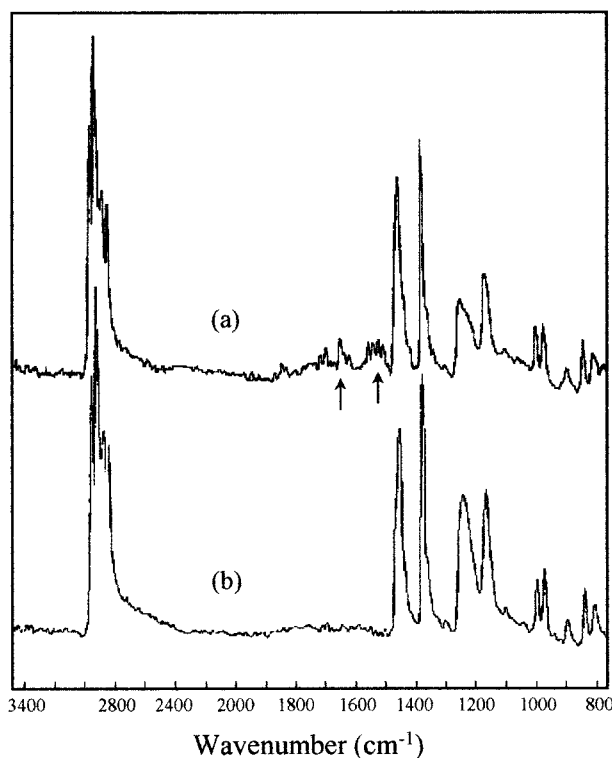
$L_p$  (m/Pa s) of the membrane was evaluated in terms of  $L_p$ , defined as<sup>33,34</sup>

$$J = Q/A = \varepsilon r^2 \Delta P / 8 \eta \tau \Delta \chi \quad (2)$$

$$Q/A = L_p \Delta P \quad (3)$$

where  $J$  is the water flux through the membrane at a driving force of  $\Delta P / \Delta \chi$ , where  $\Delta P$  is the pressure difference and  $\Delta \chi$  is the membrane thickness. The proportionality factor contains the pore size radius  $r$ , the liquid viscosity  $\eta$  (Pa s), the surface porosity of the membrane  $\varepsilon$  ( $n \pi r^2$ /surface area), and the tortuosity factor  $\tau$ .

A constant temperature was maintained by circulation of thermostated fluid through the outside water jackets. The permeation of water, through untreated PP and PP-*g*-NIPAAm membranes, was measured as a function of temperature to



**Figure 1** Microscopic ATR/FTIR spectra of the PP membrane grafted with NIPAAm and the original PP membrane: (a) PP membrane after plasma-induced polymerization and (b) original PP membrane before plasma-induced polymerization.

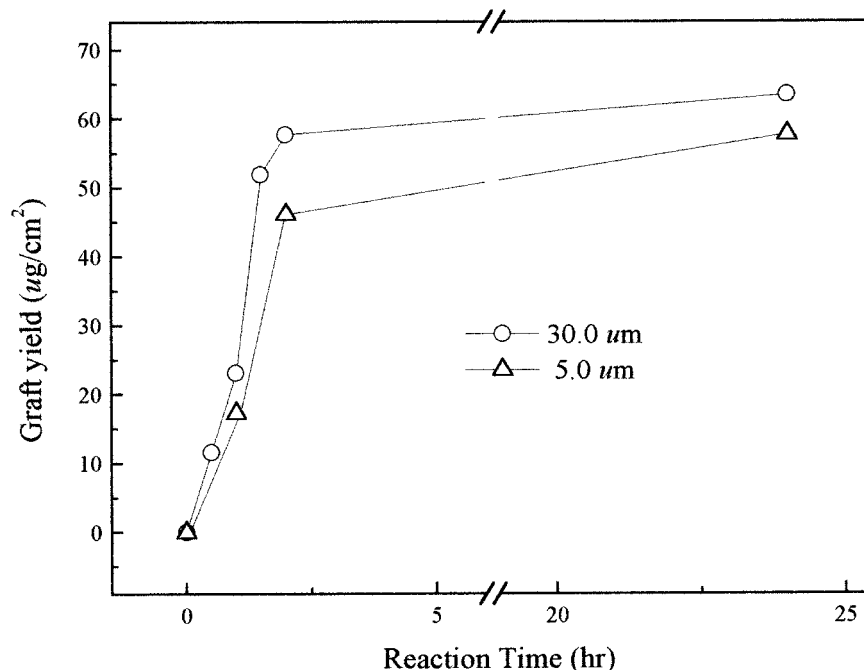
observe the difference of permeation between at below and above the LCST of PNIPAAm.

## RESULTS AND DISCUSSION

### Preparation of the PP-*g*-PNIPAAm Membrane

Figure 1 illustrates the representative ATR/FTIR spectra of the PP membrane surface grafted with PNIPAAm and the original PP membrane. The spectrum of the unmodified PP membrane [Fig. 1(b)] indicated significant characteristic peaks, which are assigned to C—H of CH<sub>3</sub> stretching (2949 and 2868 cm<sup>-1</sup>), CH<sub>2</sub> bending (1454 cm<sup>-1</sup>), CH<sub>2</sub> stretching (2837 and 2916 cm<sup>-1</sup>), CH<sub>3</sub> bending (1375 cm<sup>-1</sup>), and C—C stretching (1164 cm<sup>-1</sup>).

For the grafted PP membrane, as shown in Figure 1(a), we observed several peaks at 1648, 1521, and 1375 cm<sup>-1</sup>, which can be attributed to the characteristic peaks of amide I, amide II, and the methyl group in —CH(CH<sub>3</sub>)<sub>2</sub>, respectively.



**Figure 2** Effect of reaction time on the graft yield of NIPAAm: NIPAAm monomer concentration = 3 wt %.

This proves the presence of PNIPAAm groups on the grafted PP membrane surface.

Also, the characteristics peaks at  $1631\text{ cm}^{-1}$  (C=C) and  $1413\text{ cm}^{-1}$  ( $\text{CH}_2=$ ) and C—H vinyl out-of-plane bending vibrations, believed to represent the NIPAAm monomer, were not present in this spectrum. This suggests that the PP-g-PNIPAAm membrane was washed thoroughly enough to remove unreacted NIPAAm monomer.

#### Graft Yield of PNIPAAm onto the PP Membrane

The grafting amount of PNIPAAm was measured as the weight of the grafted polymer per square centimeter of PP substrate membrane. Figure 2 illustrates the effect of reaction time on the graft yield of NIPAAm. As shown in Figure 2, with longer grafting time, graft yields increased. The maximum grafting of PNIPAAm at a concentration of 3 wt % of NIPAAm monomer was obtained after 24 h. In the case of reaction times longer than 24 h, however, we observed that the graft yield did not show a significant change. Accordingly, the reaction time in the graft polymerization after the plasma preirradiation was fixed at 24 h.

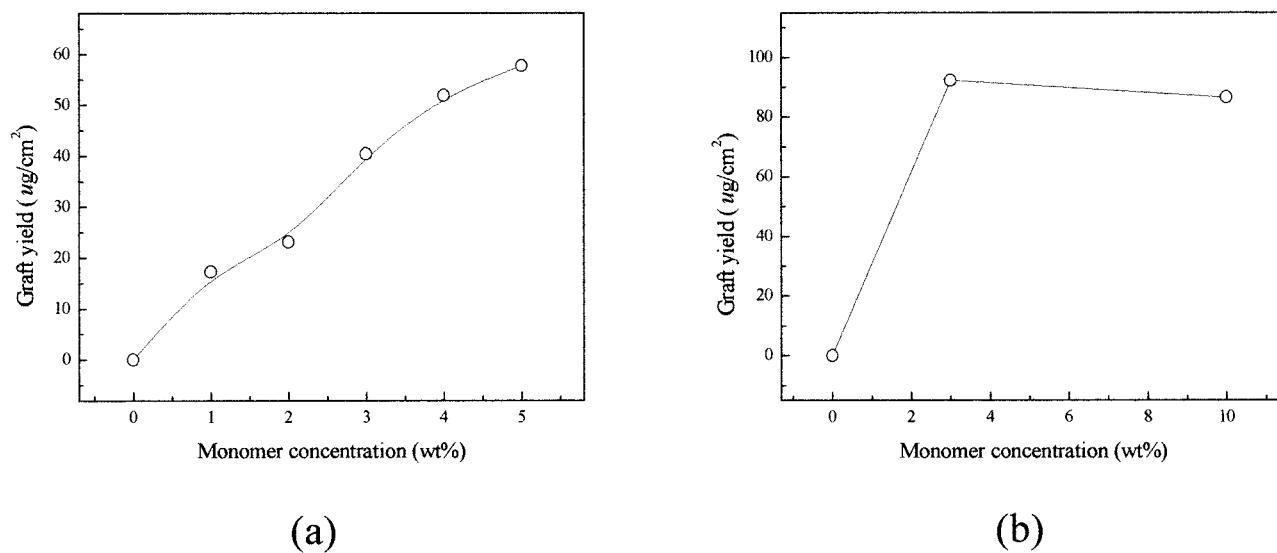
From the results shown in Figure 2, we could expect that this plasma-induced graft polymerization of NIPAAm (which involved the generation of

free radicals from the main chain of the polymer, followed by the initiation and propagation of the acrylic monomers) occurred rapidly in the early stage of polymerization.

Figure 3 shows the graft yield onto the PP membrane with  $10\text{ }\mu\text{m}$  average pore size as a function of the concentration of the NIPAAm monomer solution. The reaction times of the graft polymerization shown in Figure 1(a,b) were 1 and 24 h, respectively. The graft yield of PNIPAAm gradually increased with an increase in the concentration of monomer solution as shown in Figure 3(a).

As described previously, the grafting yield at a 24-h reaction time ( $92.3\text{ }\mu\text{g}/\text{cm}^2$ ) was greater than that at 1 h ( $40.4\text{ }\mu\text{g}/\text{cm}^2$ ) at the same monomer concentration of 3 wt %. When a monomer solution of 10 wt % was used, the grafting yield did not increase and showed some decrease, as illustrated in Figure 3(b). Evidently, the graft yield, depending on the monomer concentration, was nearly linear under comparatively low concentrations, but this enhancement of graft yield was not provided by monomer concentration beyond a certain monomer concentration. This could be attributed to the substantial amount of polymer grafted onto the membrane substrate, which inhibited the diffusion of monomer concentration into the PP for further grafting.



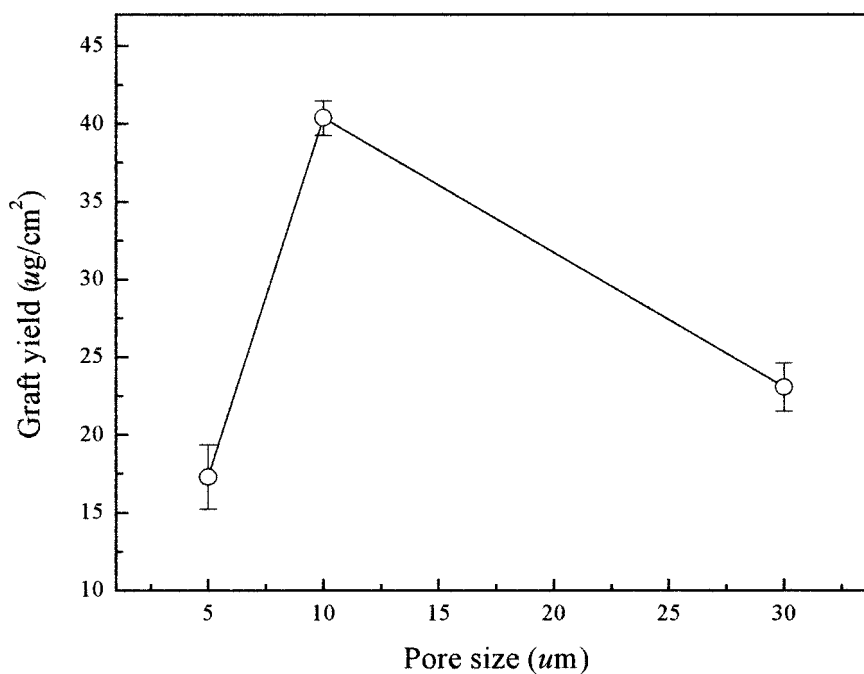


**Figure 3** Effect of the concentration of the monomer solution on the graft yield of NIPAAm onto the PP membrane ( $10\ \mu\text{m}$  of substrate): reaction time = (a) 1 and (b) 24 h.

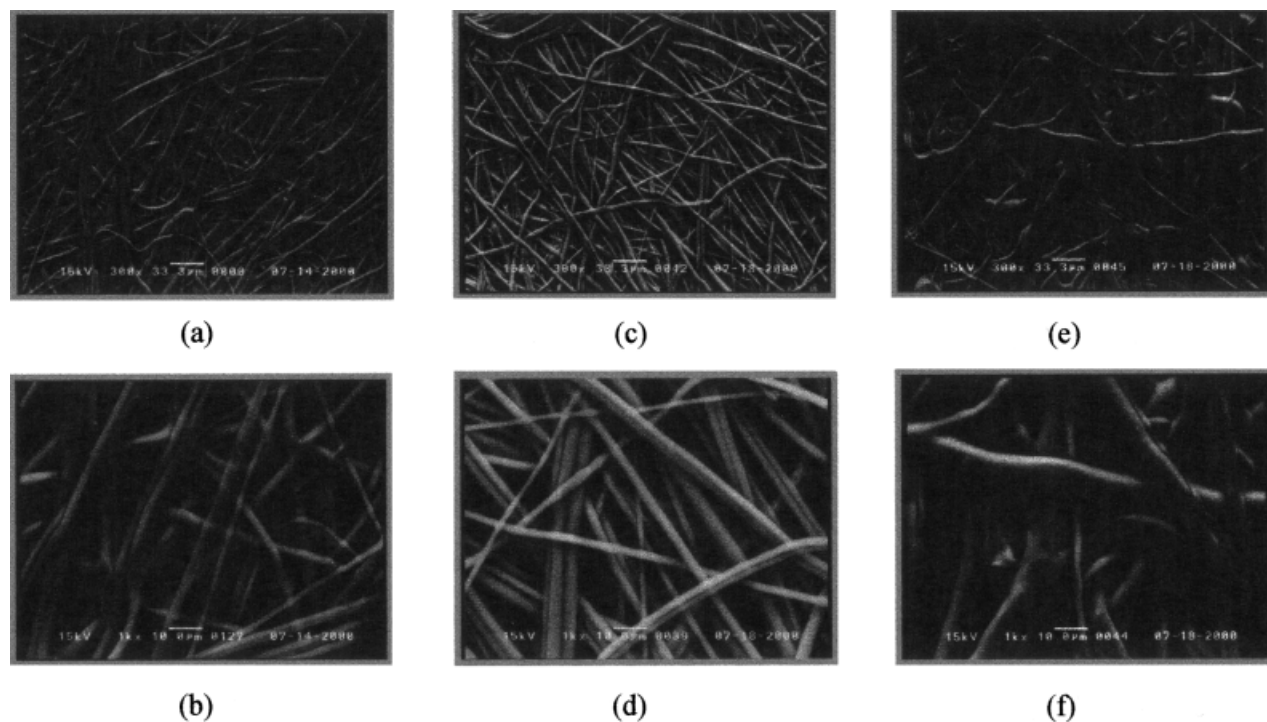
The influence of the average pore size of the PP substrate membrane on the grafting efficiency is illustrated in Figure 4. Figure 4 exhibits the graft yields of PP membranes with different average pore sizes, such as 5, 10, and  $30\ \mu\text{m}$ . Under the same reaction conditions (reaction time = 1 h, monomer concentration = 3 wt %), the graft

yields of PNIPAAm were significantly different, depending on the average pore size of the PP membrane.

As shown in Figure 4, the PP membranes with 30 and  $10\ \mu\text{m}$  average pore size exhibited higher graft yield than those with a PP membrane average pore size of  $5\ \mu\text{m}$ . It was also observed that



**Figure 4** Effect of pore size of the PP substrate membrane on the graft yield of NIPAAm: Reaction time = 1 h, NIPAAm monomer solution = 3 wt %.



**Figure 5** FE-SEM images of the untreated PP membrane (PP10, average pore size = 10  $\mu\text{m}$ ) and PP-g-PNIPAAm membrane (prepared with a PP membrane with an average pore size of 10  $\mu\text{m}$ , graft yield = 92.3  $\mu\text{g}/\text{cm}^2$ ): (a) original PP membrane in the dry state (300 $\times$ ), (b) original PP membrane in the dry state (1000 $\times$ ), (c) original PP membrane in the wet state (300 $\times$ ), (d) original PP membrane in the wet state (1000 $\times$ ), (e) PP-g-NIPAAm membrane in the wet state (300 $\times$ ), and (f) PP-g-NIPAAm membrane in the wet state (1000 $\times$ ).

the PP membrane with an average pore size of 30  $\mu\text{m}$  had a higher graft yield than that with an average pore size of 5  $\mu\text{m}$ , as shown in Figure 2, a plot of graft yield as a function of reaction time. These results on the relationship between the pore size of the substrate membrane and grafting yield coincide with those of other researchers.<sup>4,16</sup>

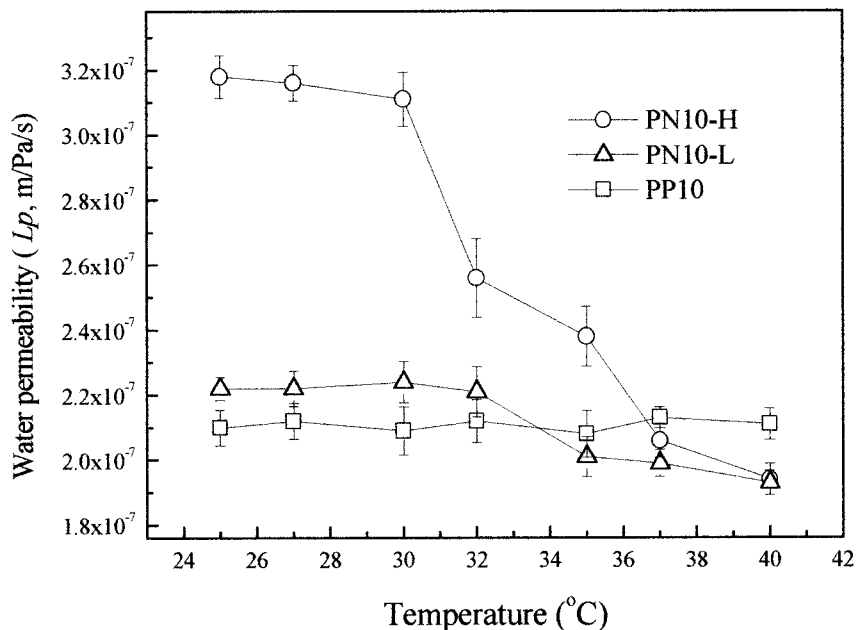
As represented in Figure 4, however, the graft yield of the PP membrane with an average pore size of 10  $\mu\text{m}$  was higher than that with an average pore size of 30  $\mu\text{m}$ . This could be attributed to the effective surface area of the PP nonwoven substrate for the graft polymerization of the NIPAAm monomer. Namely, as the average pore size of the nonwoven PP membrane increased, the effective area that could be grafted with the PNIPAAm chain could be reduced, even though the graft polymerization of the PNIPAAm chain onto the PP membrane became easier. The effective area of PP membrane with an average pore size of 30  $\mu\text{m}$ , which can be grafted, should be smaller than that with an average pore size of 10  $\mu\text{m}$ .

Therefore, this indicates that the effective surface area of the substrate more significantly influenced the graft yield of NIPAAm than did pore size beyond a certain average pore size (30  $\mu\text{m}$ ) for these nonwoven PP membranes.

Temperature also affected the graft polymerization of the NIPAAm monomer onto the PP membrane. Little graft polymerization of NIPAAm occurred when the temperature applied was 30 $^{\circ}\text{C}$  below the LCST. Therefore, in this study, 60 $^{\circ}\text{C}$  was chosen as the optimal temperature, which is generally used for the polymerization of NIPAAm.

#### Morphological Analysis by FE-SEM

To confirm the morphological change of the PP membrane grafted with PNIPAAm, untreated PP and PP-g-PNIPAAm membranes were observed by wet FE-SEM. Figure 5(a,b) exhibits the surface of the untreated PP membrane with an average pore size 10  $\mu\text{m}$  (PP10) in the dry state at 300 and 1000 $\times$  respectively. In addition, we ob-



**Figure 6**  $L_p$  through the original PP substrate membrane and PP-*g*-PNIPAAm membrane depending on temperature.

served the untreated PP and PP-*g*-PNIPAAm membranes in wet conditions after 24 h of storage in water. Figure 5(c,d) shows the FE-SEM images of the original PP membrane in the wet state after 24 h of storage in water at 300 and 1000 $\times$ , respectively. The PP-*g*-PNIPAAm membrane prepared with a PP membrane with an average pore size of 10  $\mu\text{m}$  (graft yield = 92.3  $\mu\text{g}/\text{cm}^2$ ) were also observed in the wet state after storage in water for 24 h, and the images are shown in Figures 5(e) (300 $\times$ ) and 5(f) (1000 $\times$ ).

As shown in Figure 5(a–d), there was not any morphological change in the untreated PP membrane between the dry and wet conditions. In Figure 5(e,f), which includes images of the PP membrane grafted with PNIPAAm in the wet state at 25 $^\circ\text{C}$ , we observed that the swollen nonwoven membrane was different from the untreated PP membrane. PNIPAAm has a LCST at around 32 $^\circ\text{C}$ . PNIPAAm forms hydrogen bonds with water and is extremely soluble in water below LCST. However, above LCST, intermolecular and intramolecular interactions in PNIPAAm are much stronger, resulting in precipitation. In this state, the hydrogen bonding between grafted PNIPAAm and water breaks down, and the mobility of polymer chain intermolecular and intramolecular interactions and the hydrophobic interactions due to the presence of the alkyl groups in the polymer chain increase.

Therefore, from the FE-SEM measurements, it was confirmed that graft polymerization of PNIPAAm onto the PP membrane occurred. Also, these images indicate that the PP-*g*-NIPAAm membrane became swollen at 25 $^\circ\text{C}$  in water, which led to an enlargement of PP fabrics with a PNIPAAm-grafted nonwoven PP membrane.

#### $L_p$ OF THE PP-*G*-PNIPAAm MEMBRANE DEPENDING ON TEMPERATURE

The effect of temperature on  $L_p$  through untreated PP and PP-*g*-NIPAAm membranes was determined. Figure 6 shows the relationship between the grafting yield of PNIPAAm and  $L_p$  as a function of temperature. For this permeation experiment, we used a PP membrane with the same average pore size of 10  $\mu\text{m}$ . PP10 is the original PP membrane, and the PN10-H and PN10-L membranes were PP membranes grafted with PNIPAAm, which had graft yields of 92.3 and 57.7  $\mu\text{g}/\text{cm}^2$ , respectively.

As shown in Figure 6 and as expected, the untreated PP membrane exhibited almost constant values of  $L_p$ , depending on temperature. In contrast, PP membranes grafted with PNIPAAm showed temperature-dependent permeation behavior of water. The  $L_p$ 's through PN10-H and PN10-L were greater than that of the untreated



**Table II** Permeation of Water Through the Original PP Membrane and PP-*g*-PNIPAAm with Different Average Pore Sizes

Sample	Average Pore Size of PP Membrane ( $\mu\text{m}$ )	Graft Yield ( $\mu\text{g}/\text{cm}^2$ )	$L_p$ (m/Pa s)	
			25°C	37°C
PP05	5	—	$1.99 \times 10^{-7}$	$1.97 \times 10^{-7}$
PP10	10	—	$2.10 \times 10^{-7}$	$2.13 \times 10^{-7}$
PP30	30	—	$2.51 \times 10^{-7}$	$2.59 \times 10^{-7}$
PN05	5	57.7	$2.36 \times 10^{-7}$	$1.80 \times 10^{-7}$
PN10	10	57.7	$2.22 \times 10^{-7}$	$1.99 \times 10^{-7}$
PN30	30	69.2	$2.16 \times 10^{-7}$	$1.90 \times 10^{-7}$

PP membrane at below LCST. Their  $L_p$ 's gradually decreased as the temperature changed from below LCST to above LCST.

These permeation results are different from studies on the polymer-brush membrane, which is a porous membrane with introduced PNIPAAm chains.<sup>5,35</sup>

For the permeation behavior of water through this PP-*g*-PNIPAAm membrane system, we can consider two factors: one is the enhancement of hydrophilicity in hydrophobic PP substrate membranes by the graft polymerization of the hydrophilic monomer NIPAAm; the other is the effect of graft polymerization on the average pore size of the PP nonwoven membrane.

PNIPAAm is fully hydrated, with an expanded chain conformation in aqueous solution, when the temperature is below its LCST. Therefore, it could be expected that in the region below LCST, the grafting of hydrophilic PNIPAAm onto the hydrophobic PP membrane would lead to an increase in  $L_p$  by the enhancement of its hydrophilic properties. When the temperature was above 32°C, the LCST of PNIPAAm, the PNIPAAm polymer became hydrophobic due to the dissociation of ordered water molecules surrounding hydrophobic *N*-isopropyl groups. As a result,  $L_p$  through the PP-*g*-PNIPAAm membrane decreased with the rise of temperature. Finally,  $L_p$  was lower than that of the untreated PP membrane. This indicates that the effect of hydrophilicity was less than that of the average pore size with elevated temperature.

The temperature sensitivity of the  $L_p$  of the PP10-H membrane, with the higher graft yield of PNIPAAm, in particular was sharper than that of the PP10-L membrane with a lower graft yield.

With PP membranes having similar graft yields and different average pore sizes, their  $L_p$ 's

were investigated at below and above LCST, and these results are summarized in Table II. As shown in Table II, PP05, PP10, and PP30 were untreated PP membranes with average pore sizes of 5, 10, and 30  $\mu\text{m}$ , respectively. Their  $L_p$ 's showed similar values at 25 and 37°C.

On the other hand, for the PP-*g*-PNIPAAm membranes, which were PN05, PN10, and PN30, with similar graft yields and different average pore sizes of 5, 10, and 30  $\mu\text{m}$ , a temperature-dependent permeation of water was observed. The PN05 and PN10 membranes exhibited higher  $L_p$ 's than untreated the PP membrane at 25°C below LCST. However, the water permeability through the PN30 membrane was  $2.16 \times 10^{-7}$  m/Pa s, which was lower than the untreated PP30 membrane ( $2.51 \times 10^{-7}$  m/Pa s). This suggests that increasing hydrophilicity by the grafting of the hydrophilic monomer NIPAAm was not effective due to the large pore size of the membrane itself. At 37°C, which was above the LCST of PNIPAAm, all PP-*g*-PNIPAAm membranes showed decreased  $L_p$ .

Moreover, from these  $L_p$  experiments, we found that this PP-*g*-PNIPAAm membrane exhibited a relatively high thermal sensitivity, even though it had a high  $L_p$ , because the PP-*g*-PNIPAAm membranes were prepared with a nonwoven PP membrane with a large average pore size of 5–30  $\mu\text{m}$ .

## CONCLUSIONS

A temperature-sensitive membrane was prepared by plasma-induced graft polymerization. The graft polymerization of NIPAAm onto a nonwoven PP membrane was performed after the formation of radicals on the PP membrane surface by irra-

diation with argon plasma. The grafting of the PNIPAAm chain onto the PP membrane was identified by microscopic ATR/FTIR measurement. The graft yield of PNIPAAm was significantly influenced by several factors, including the concentration of NIPAAm monomer solution, reaction time of polymerization, reaction temperature, and the average pore size of the substrate membrane. From the FE-SEM measurements, morphological change in the PP-*g*-PNIPAAm membrane by swelling under wet conditions at below LCST was seen.

$L_p$  of the PP-*g*-PNIPAAm membrane showed sensitivity to temperature. Below LCST, the  $L_p$  of PP-*g*-PNIPAAm membrane with an average pore size of 10  $\mu\text{m}$  was higher than that of the untreated PP membrane, which gradually decreased with increasing temperature. As the graft yield of PNIPAAm was increased, the temperature dependency of  $L_p$  of the PP-*g*-PNIPAAm increased considerably.  $L_p$  was also influenced by the average pore size of the substrate membrane. Furthermore, the PP-*g*-PNIPAAm membrane system showed thermal sensitivity even with extremely high  $L_p$ .

Therefore, we conclude that the PP-*g*-PNIPAAm membrane, with its unique temperature sensitivity and high  $L_p$ , could be useful as a novel device for various biomedical applications. To obtain more information about the properties of this PP-*g*-NIPAAm membrane and to investigate its feasibility as a cell separator for tissue engineering, we are conducting further studies in our laboratory.

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