Temperature-Sensitive Membranes Prepared by the Plasma-Induced Graft Polymerization of *N*-Isopropylacrylamide into Porous Polyethylene Membranes

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ABSTRACT: A temperature-responsive polymer, poly(*N*-isopropylacrylamide) (PNIPAAm), was grafted onto porous polyethylene membranes by a plasma-induced graft polymerization technique. A wide range of grafting was achieved through variations in the grafting conditions, including the postpolymerization temperature, time, monomer concentration, and graft-reaction medium. The active species induced by plasma treatment was proven to be long-living via a postpolymerization time of 95 h. Different solvent compositions, that is, water, methanol, benzene, and water/methanol, were used as reaction media, and water showed a much higher polymerization rate than the organic solvents. Based on the hydrophilicity of the active species, a mechanism explaining the solvent effect in plasma-induced graft polymerization was examined. Characterizations by scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), and micro Fourier transform infrared showed that the grafted polymers were located on both the outer surface and inside pores of the membranes. The XPS analysis also confirmed that the polar amide groups tended to distribute more outward when grafted PNIPAAm was in its expanding state than when it was in its shrinking state. Water permeation experiments showed that the permeability of the grafted membranes varied dramatically with a slight temperature change in the vicinity of the lower critical solution temperature (LCST) of PNIPAAm. The effective pore radii of the grafted membranes above and below the LCST could be depicted by Hagen-Poiseuille's law. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3180–3187, 2003

Key words: graft copolymers; plasma polymerization; polyethylene (PE); membranes

INTRODUCTION

Low-temperature plasma has extensively been studied to modify the surface properties of polymer membranes. The major method is either plasma polymerization, in which a thin, crosslinked polymer layer is deposited on the membrane surface, or plasma-induced graft polymerization, in which grafted polymer chains are introduced onto the surface region of the membrane. Most previous works have reported that treating a porous membrane with plasma only affects the outer surface, allowing the bulk properties to remain unchanged.[1] However, Yasuda and Hsu_2 reported radical formation in the bulk when a nonporous polyethylene (PE) film was treated with plasma. They reported that these radicals formed because of ultraviolet radiation from the plasma. Recently, using porous high-density PE films as a plasma-treated substrate, Yamaguchi et al.[3] reported radical formation on the pore surfaces inside the membrane and growth of graft polymers from these radicals.

The permeability of polymeric membranes can be changed in response to environmental stimuli such as the temperature, pH, light, and chemical media.[1,4–6] Poly(*N*-isopropylacrylamide) (PNIPAAm) exhibits its lower critical solution temperature (LCST) near 32°C and has a remarkable hydration–dehydration change in aqueous solutions in response to a relatively small change in temperature. Below the LCST, PNIPAAm chains hydrate to form an expanding structure; and above the LCST, PNIPAAm chains dehydrate to form a shrinking structure. This property is due to the reversible formation and cleavage of hydrogen bonds between groups of NH or C═O in PNIPAAm chains and surrounding water with a small change in the temperature.[7,8]

The thermally induced phase transitions of PNIPAAm hydrogel membranes have extensively been studied, and several applications have been proposed in a variety of areas, including sensors, drug devices, and solute separation.[9,10] However, most polymer hydrogels respond slowly to environmental stimuli, and the lower mechanical strength of hydro-

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gels is also a problem for making thin films. For such problems to be overcome, PNIPAAm has been grafted onto porous membranes by various grafting techniques, including plasma,[11,12] ion-beam,[13,14] and chemical methods.[15] The advantage of such a membrane is that the porous substrate acts as a dimensionally stable matrix for mechanical support, whereas the conformational changes of the graft polymer induced by environmental stimuli lead to permeability changes. In addition, the stimulus response of the grafted PNIPAAm chain may be faster than that of the crosslinked PNIPAAm network in the hydrogel. Because the grafted chain should have a freely mobile end, distinct from the typical crosslinked network structure with a relatively immobile chain end, a more rapid conformation change is expected.

In this study, temperature-sensitive membranes were prepared by the plasma-induced graft polymerization of *N*-isopropylacrylamide (NIPAAm) onto porous PE membranes. The grafting conditions, such as the temperature, time, monomer concentration, and graft-reaction medium, were investigated. The details of the grafted PNIPAAm, on both the outer surface and inside pores of the membrane, were observed. The temperature-dependent permeation of water through the grafted membranes was described.

EXPERIMENTAL

Materials

A porous PE tubular membrane supplied by Asahi Kasei Corp. (Tokyo, Japan) was used as the substrate. The porous membrane was hydrophilic on its surface, had a pore size of 0.25 μm, a porosity of 75%, an outer diameter of 3 mm, and an inner diameter of 2 mm. NIPAAm (CAS 2210-25-5), supplied by Kohjin Co., Ltd. (Tokyo, Japan), was used as the grafted monomer. The monomer was used without further purification. The solvents, methanol and benzene, were purified by distillation before use.

Plasma pretreatment and graft polymerization

The graft polymerization of PNIPAAm to a PE membrane was carried out in two steps. First, the PE membrane was inserted into a glass tube (2 cm in its inner diameter and 15 cm long). The system was evacuated and filled with argon three times. After the system was evacuated to 3 Pa, the membrane was irradiated by plasma for 60 s at a power of 15 W. The apparatus used for the plasma exposure was homemade. The radio-frequency generator for generating plasma irradiation was at 13.56 MHz and had a maximal output power of 200 W. The radio frequency was supplied from the generator to the reactor through a capacitively coupled system with two electrodes wound on the outside of the glass reactor. Second, the activated substrate was instantly placed into contact with a 20-mL monomer solution (3–15 wt %) that had previously been purged with argon gas. The graft polymerization was carried out in a shaking constant-temperature bath for a predetermined length of time. The grafted membrane was washed with distilled water and then soaked in water for 48 h for the removal of the nonreacted monomer and the possible homopolymer. The grafted membranes were dried at 50°C *in vacuo*. The amount of grafting of PNIPAAm was expressed as follows:

$$\text{Amount of grafting (mg/cm}^2) = (W_g - W_0)/A \quad (1)$$

where W_0, W_g, and A represent the weight of the substrate membrane, the weight of the grafted membrane, and the outer surface area of the substrate membrane, respectively.

Morphological observations

The surface of the membrane was vacuum-deposited with gold. The morphological details of the NIPAAm-grafted membrane and the substrate membrane were observed with scanning electron microscopy (SEM; S900, Hitachi, Tokyo, Japan).

X-ray photoelectron spectroscopy (XPS) spectra were obtained with a VG Escalab MK-II electron spectrometer (UK) with a Mg Kα X-ray source (1249 eV at 12 kV and 20 mA) at a pressure of 10^{-7} Torr and an electron takeoff angle of 45°.

An ultrathin slice of a cross section of the membrane was made with an ultramicrotome, and the composition of the slice was analyzed with micro Fourier transform infrared (micro-FTIR; Nicolet Magna 550 with Nic-Plan, Nicolet, WI). The measurement region was scanned in 20-μm steps.

Water permeability

The water permeability was investigated with an effective membrane area of 6.28 cm^2. The water temperature was changed from 10 to 50°C. The applied pressure for the feed side was kept at 0.02 MPa. The reversible permeability test of the grafted membrane was performed at a pressure of 0.01 MPa with a temperature cycle between 24 and 40°C.

RESULTS AND DISCUSSION

Graft polymerization

Graft temperature

To prevent overetching or weight loss produced on the substrate surface by an excessive plasma treatment, we applied a moderate plasma pretreatment (plasma power

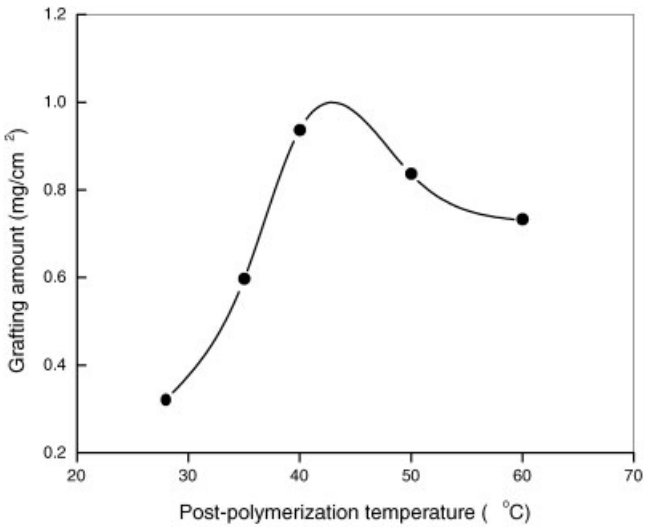

Figure 1 Relationship between the amount of grafting and the postpolymerization temperature under the following conditions: 5% NIPAAm in water for 20 h.

= 15 W and exposure time = 60 s). Figure 1 shows the curve of the amount of grafting versus the grafting temperature. The amount of grafting initially increases with the temperature and then tends to decrease with a maximum at 40°C. The plasma-induced polymerization can proceed easily at a lower temperature, but a higher graft polymerization temperature is beneficial to monomer diffusion into the pores so that a pore-filled grafted membrane is obtained.

PNIPAAm in an aqueous medium has an LCST of 32°C. As the temperature increases to the LCST, PNIPAAm chains drastically change from a hydrophilic state to a hydrophobic state. For graft temperatures below the LCST, the grafted PNIPAAm chains form hydrogen bonds with water and exist in a gel form; above the LCST, the hydrogen bonds break down and the shrunken PNIPAAm chains tend to trap the PNIPAAm macroradicals. It can be deduced that the monomer molecule should diffuse more easily to the PNIPAAm macroradical in the swelling state. Consequently, a remarkable change should be observed in the curve of the amount of grafting versus the temperature in the vicinity of 32°C. However, such a change is not shown in Figure 1. Kawaguchi et al.[16] reported from his protein adsorbed experiments that the hydrophobicity of the shrunken PNIPAAm was not extremely high but moderate. In our study, we believe that the shrunken PNIPAAm should not suppress the monomer diffusion enough to make the diffusion rate the controlling step of the graft polymerization rate above the LCST. The graft rate is only affected by the graft temperature in this situation.

Monomer concentration

The relationship between the amount of grafting and the monomer concentration is shown in Figure 2. The amount of grafting of the membranes is proportional to the monomer concentration in the range of 0–15%. This result coincides with the classical kinetic model of radical polymerization.

Grafting time

It has previously been reported that plasma-induced polymerization, in which monomers grow from species in solution produced by plasma pretreatment, tends to possess long-living active species and to easily produce an ultrahigh molecular weight polymer. Once the monomers are initiated by the plasma exposure, they can be postpolymerized for days and even weeks without a chain-terminated reaction.[17] Figure 3 shows the amount of grafting as a function of the postpolymerization time in the graft system. The amount of grafting is proportional to the graft polymerization time within 95 h when the grafting is performed in 1:1 water/methanol mixed solvent. The LCST of PNIPAAm is 32°C in water and is below 32°C in a 1:1 water/methanol mixed solvent.[18] The solutions should appear cloudy to simple visual observation if any PNIPAAm homopolymers are produced in the solutions above LCST. However, the graft solutions are clear during the whole grafting period at the graft temperature of 60°C, whether in water or in a water/methanol mixed solvent. These phenomena indicate no presence of PNIPAAm homopolymers in the graft solutions, and this suggests that the possible transfer reaction of radicals on the substrate surface to the NIPAAm monomer and methanol does not happen. The amount of the active species, which is at a low concentration on the substrate surface, should be constant because no additional active species would

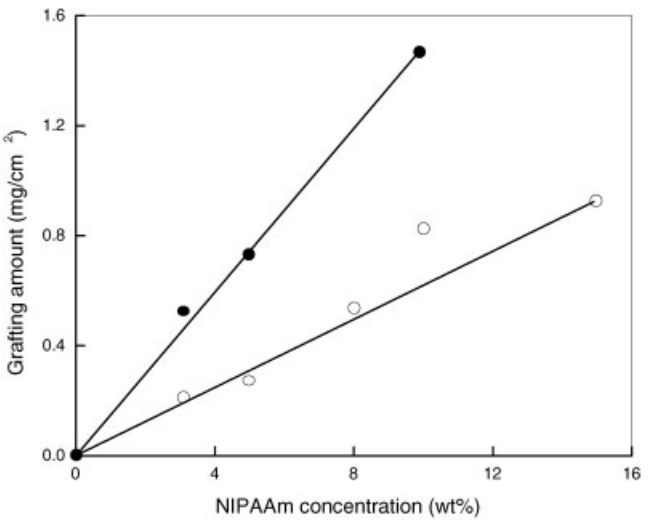

Figure 2 Relationship between the amount of grafting and the NIPAAm concentration under the following conditions: (●) in water for 20 h at 60°C and (○) in 1:1 water/methanol for 45 h at 60°C.

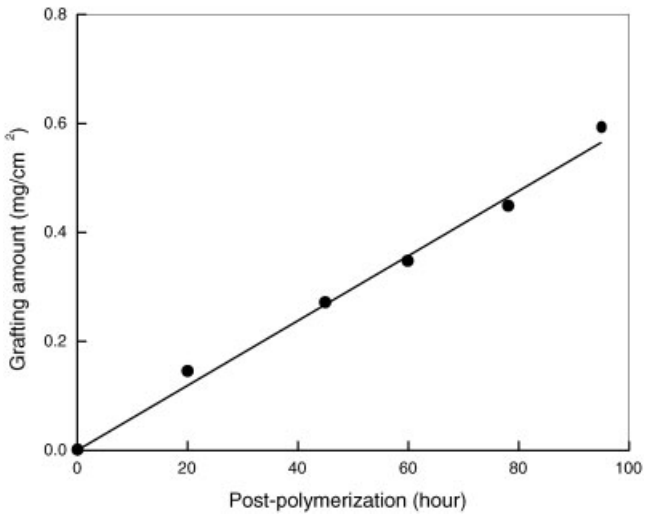

Figure 3 Relationship between the amount of grafting and the postpolymerization time under the following conditions: 5% NIPAAm in 1:1 water/methanol for 60°C.

be reformed during the postpolymerization period. The long-living active species is confirmed. It is expected that the molecular weight of the grafted polymer and the amount of grafting can be controlled through different postpolymerization times.

Graft medium

Previous researchers have realized the solvent effect in plasma-induced polymerization, that the monomer polymerizes more rapidly in an aqueous medium and more slowly in organic solvents.[19,20] In this study, we investigated the solvent effect in a graft polymerization system. The solvents applied were water, a 1:1 water/methanol mixed solvent, methanol, and benzene. The experimental data are shown in Figure 4. The solvents greatly affect the graft polymerization rate; water shows a much higher polymerization rate than the organic solvents. When water is used as the solvent, the amount of grafted PNIPAAm on the membrane (1.51 mg/cm^2) is 5 times and 8 times as great as the amounts in a 1:1 water/methanol mixed solvent and in methanol, respectively, and almost no PNIPAAm-grafted polymers form in benzene.

The lower grafting amounts grafted in media containing methanol cannot be interpreted simply through the chain-transfer reaction of the solvents, as indicated previously. Osada et al.[19] reported that a significant increase in the electrical conductivity was detected when dimethylformamide was exposed to plasma, and the presence of both ions and radicals was considered. It should also be mentioned that high water wettability was attained after PE films were exposed to argon plasma.[21] It can be concluded from these studies that plasma-induced active species and their derivatives are more hydrophilic. One of the factors that could explain the solvent effect in plasma graft polymerization is the high hydrophilicity of the active species. Although the graft temperature is above the LCST when the grafting is performed in an aqueous medium, the shrunken PNIPAAm would possess a moderate, not extreme, hydrophobicity, as discussed previously, and it would not suppress the monomer diffusion significantly. The collision ability of the hydrophilic active species with the aqueous NIPAAm molecules reaches a relatively high value. The reaction rate constants of both initiation and propagation increase. The case is something like a reaction in a homogeneous reaction system. However, when the grafting is performed in organic solvents, although PNIPAAm chains can dissolve freely in methanol and benzene without an LCST, both the initiation and propagation rates fall to a lower value. The reason is that the hydrophilic active species are less compatible with the organic media. This is like a reaction in a heterogeneous system.

It is widely accepted that plasma-induced polymerization proceeds by a radical mechanism, as proven by the inhibition experiment carried out in the presence of radical polymerization inhibitors, by the tacticity distribution of the polymers, and by the monomer/copolymer composition relationship of the resulting copolymers.[17] However, the long-living macroradical and the solvent effect cannot be described by the classical kinetic model of radical polymerization. In fact, some phenomena of plasma-induced polymerization, such as the easy synthesis of ultrahigh molecular weight polymers, the long-living active species, and the stronger dependence of the polymerization rate on the solvent properties, are similar to those commonly observed in ionic polymerization. However, because of the complex composites in the plasma atmosphere

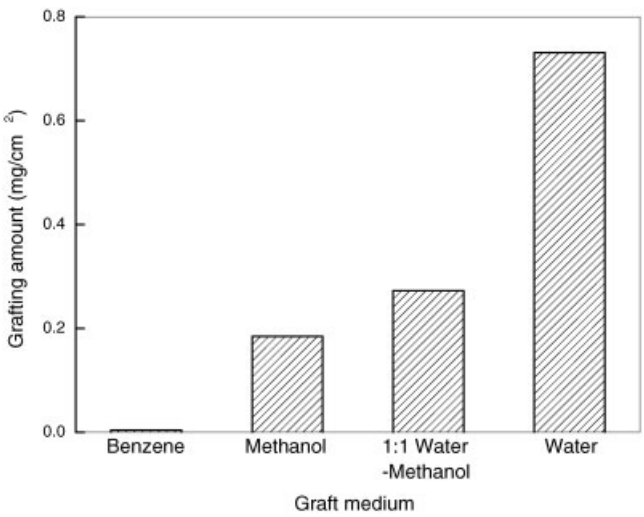

Figure 4 Effects of the different solvents on the amount of grafting under the following conditions: 5% NIPAAm for 45 h at 60°C.

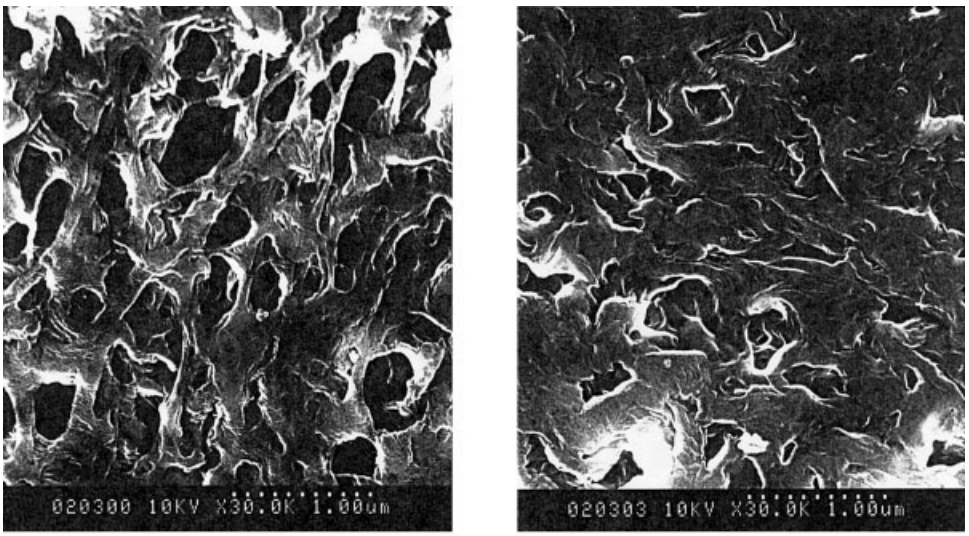

Figure 5 SEM micrographs of the outer surfaces of (A) the substrate membrane and (B) the grafted membrane with the amount of grafting equal to 0.58 mg/cm^2.

and the absence of detective methods, the detailed mechanism of the plasma-induced polymerization has not been well determined yet.

Morphological evaluation

In Figure 5 are shown the SEM microphotographs of the outer surfaces on both a substrate membrane and an NIPAAm-grafted membrane. The substrate membrane exhibits some dark holes indicating membrane pores with a mean pore size of 0.5 μm, whereas the grafted membrane shows much brighter areas indicating the skin-grafted layers of PNIPAAm. The grafted polymers aggregate to form discontinuous, cloud-shaped layers and cover most of the membrane pores.

Surface morphology changes were analyzed by XPS. The membranes were each grafted at 1.07 mg/cm^2; one was dried above the LCST, and the other was dried by a freeze-drying technique. The freeze-drying technique captures the configuration of the expanded PNIPAAm chain below the LCST. Figure 6 shows the XPS spectrum changes for the two membranes. The XPS spectra and the N/C ratios are similar to the results of Sugiyama et al.,[22] who also grafted PNIPAAm onto a PE substrate by a plasma method. In Figure 6, the N1s peak appearing at 400.0 eV is from the amide group of PNIPAAm,[1,22] and this is consistent with the presence of PNIPAAm on the membrane surfaces as shown by the SEM results previously described. In addition, the N1s peak of the membrane dried below the LCST (N/C ratio = 0.033) is higher than that of the membrane dried above the LCST (N/C ratio = 0.025). The XPS analysis is thought to give a surface signal less than 100 Å deep. This result shows that the polar amide groups tend to distribute outward when grafted PNIPAAm is in an expanding state, whereas the amide groups tend to be enveloped by the nonpolar main chain when PNIPAAm in its shrinking state. This result is consistent with the PNIPAAm chain hydrophilicity when the membrane is dried below the LCST and its hydrophobicity when the membrane is dried above the LCST.

The composition of the cross section of the grafted membrane (grafting amount = 0.58 mg/cm^2) was analyzed by micro-FTIR. Figure 7 shows the micro-FTIR spectra of a cross section from the outer surface to the inner surface of a tubular membrane with a stage step size of 20 μm. The two characteristic peaks of PNIPAAm, the absorption of the carbonyl (C═O) stretching vibration and the combined absorption of

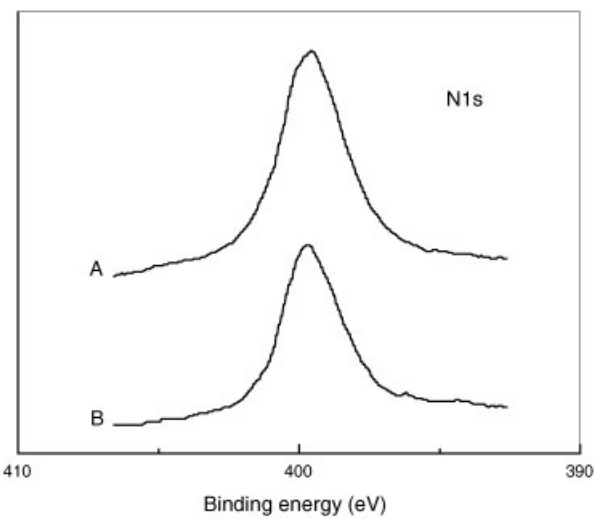

Figure 6 XPS spectra of N1s for grafted membranes (1.07 mg/cm^2) dried (A) below LCST and (B) above LCST.

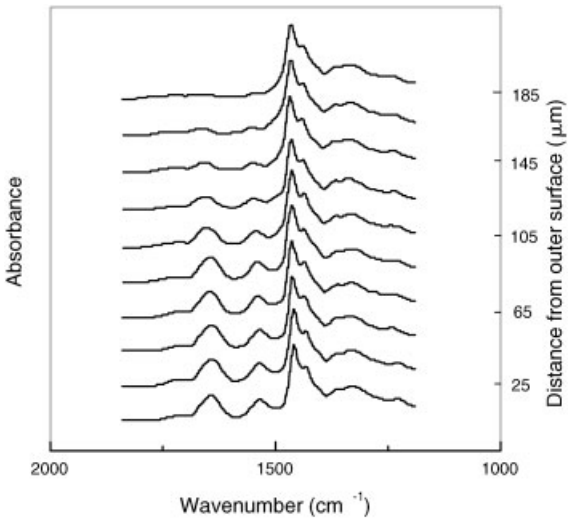

Figure 7 Micro-FTIR spectra of a cross section from the outer surface to the inner surface of a grafted membrane (0.58 mg/cm^2) with a stage step of 20 μm.

both the N—H bending vibration and C—N stretching vibration, are at 1650 and 1550 cm^{-1}, respectively. Both characteristic peaks exist within 165 μm from the outer surface of the membrane, and the peak areas indicate that the graft amount goes into the membrane pore with a nonlinear profile. The SEM and micro-FTIR analyses show that the graft polymerization can occur simultaneously both on the outer surface of the substrate membrane and on the inner surfaces of the membrane pores with plasma graft technology.

Most previous works have shown that treating a membrane with plasma only affects the outer surface, allowing the bulk properties to remain unchanged.[1] However, the aforementioned micro-FTIR analysis indicates that graft polymerization can take place at least 165 μm into the membrane pores by a plasma graft technique. This result shows that a plasma treatment would initiate the radicals inside the membrane pores, and grafted polymers would grow from those radicals. The PNIPAAm chains grafted onto the inner surfaces of membrane pores can be designed to act as a chemical valve, in which the on–off can be carried out through a slight temperature change around the LCST.

Water permeability

The influence of the water permeability of the membranes on the temperature change is shown in Figure 8. the permeability of the grafted membranes depends little on the temperature below 30°C, but in the vicinity of the LCST, the permeability increases sharply with increasing temperature. The permeability rates are 82.9 (34°C) and 16.3 kg/h·m^2 (31°C) for the high-grafted membrane and 89.6 (34°C) and 52.9 kg/h·m^2 (31°C) for the low-grafted membrane. Therefore, the permeability ratios above and below the LCST (34 and 31°C) are 5.1 and 1.7 for the high-grafted membrane and the low-grafted membrane, respectively. By contrast, the permeability rate of the substrate membrane increases linearly with increasing temperature, and this is caused by the decrease in the viscosity of the flowing liquid. The result shows that the grafted PNIPAAm chain exhibits a volume phase transition as the PNIPAAm hydrogel does. Below the LCST, the grafted PNIPAAm chains in pores exist in a hydrated structure, and the membrane pores should be closed. Above the LCST, the grafted PNIPAAm chains shrink and recoil to the membrane surface, and this results in membrane pores being opened and, therefore, the permeability increasing. The grafted PNIPAAm on the outer surface of the membrane behaves similarly. Consequently, the grafted PNIPAAm chains should act as a sensor of the temperature and a valve regulating the permeability of the membrane with a slight change in the temperature around the LCST. However, Chu et al.[11] prepared PNIPAAm-grafted microcapsules by a plasma method and reported an opposite effect of temperature on the permeability. If the amount of grafting is high enough, because there is too much grafted polymer in the membrane pores, the permeability will decrease with increasing temperature (above the LCST); that is, the pores are choked by the dense hydrophobic polymer. This is opposite to the behavior shown in Figure 8 with a lower grafting amount.

Hagen-Poiseuille's law can more quantitatively depict the features of the temperature-sensitive membrane.[1] The permeability of the porous membrane can be expressed as follows:

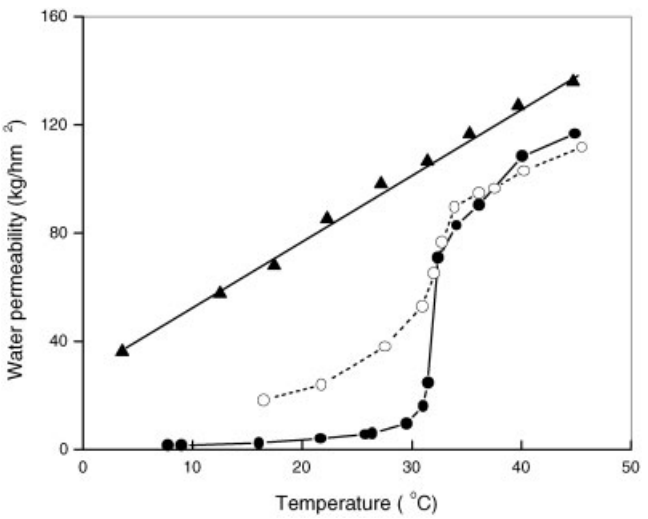

Figure 8 Water permeability versus the temperature for various membranes: (●) a grafted membrane (0.48 mg/cm^2), (○) a grafted membrane (0.19 mg/cm^2), and (▲) a substrate membrane.

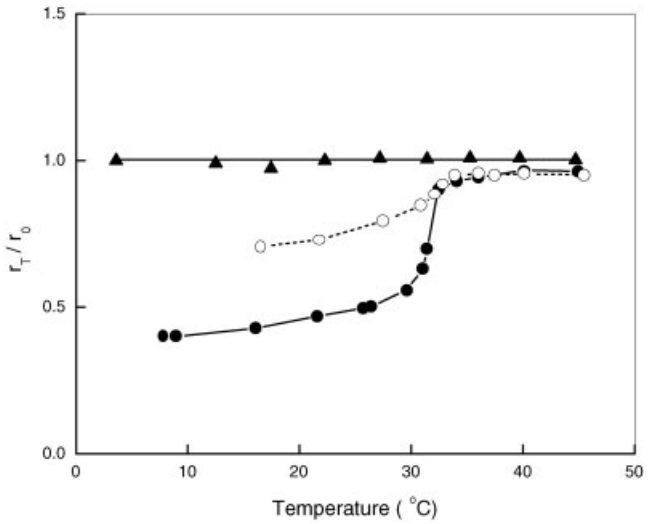

Figure 9 Relative pore radius (r_T/r_0) versus the temperature for various membranes: (●) a grafted membrane (0.48 mg/cm^2), (○) a grafted membrane (0.19 mg/cm^2), and (▲) a substrate membrane.

$$J = \frac{n\pi r^4}{8\eta}\frac{\Delta P}{\Delta X} \tag{2}$$

where J is the permeability rate, n is the number of pores per centimeter squared, r is the effective pore radius, η is the viscosity of the flowing liquid, ΔP is the applied pressure, and ΔX is the thickness of the membrane. In a grafted membrane, grafted polymers form skin layers both on the surfaces in the pores and on the outer surface of the membrane. Therefore, the narrowest part of a channel, that is, the skin-grafted layer, determines the permeability rate. r_0 represents the effective pore radius for a substrate membrane calculated at 22°C, and r_T represents that at T (°C) for both substrate and grafted membranes. From eq. (2), with the increase in ΔX for grafted membranes neglected, the ratio of r_0 and r_T can roughly be expressed as follows:

$$\frac{r_T}{r_0} = \left(\frac{J_T\eta_T}{J_0\eta_0}\right)^{\frac{1}{4}} \tag{3}$$

where J_T, J_0, η_T, and η_0 are the permeability rates and viscosity of the flowing liquid under the same conditions. The r_T/r_0 ratio has been evaluated with the permeability rate and viscosity of water at each temperature. The results are shown in Figure 9. Clearly, in the vicinity of the LCST, the radius ratios change sharply, reflecting the volume phase transition of the grafted PNIPAAm chains. However, the radius ratios remain almost constant over the temperature regions both above and below the LCST. The level line in Figure 9 indicates the stable pore size of the substrate membrane.

Figure 10 shows the reversible changes in the water permeability rate when the temperature is cycled between 24 and 40°C. The water permeability rate maintains a fixed value in the recycling test whether at 24 or 40°C, and the temperature sensitivity is reversible and reproducible. The grafted PNIPAAm, but not the homopolymer of PNIPAAm, should be responsible for the temperature-sensitive behavior. The response time of the grafted membrane to a temperature change could not be determined quantitatively because at least 4 min is required for the set temperature to be reached when the temperature is switched. However, it is thought that the grafted PNIPAAm responds instantly to the temperature change in comparison with the PNIPAAm hydrogel because the grafted chain should have a freely mobile end, distinct from the crosslinked network structure with a relatively immobile chain end.

CONCLUSIONS

1. The possible chain-transfer reaction of active species to molecules of NIPAAm and methanol does not occur. The plasma-activated species seem to be long-living because the polymerization rate is proportional to the reaction time within 95 h.
2. The graft polymerization rate is strongly dependent on the reaction solvents used, and water shows a much higher polymerization rate than organic solvents. A mechanism explaining the solvent effect is proposed in which the hydrophilicity of plasma-activated species is responsible for the accelerated effect of water.
3. The morphology studies show that the grafted polymers can be obtained throughout the porous

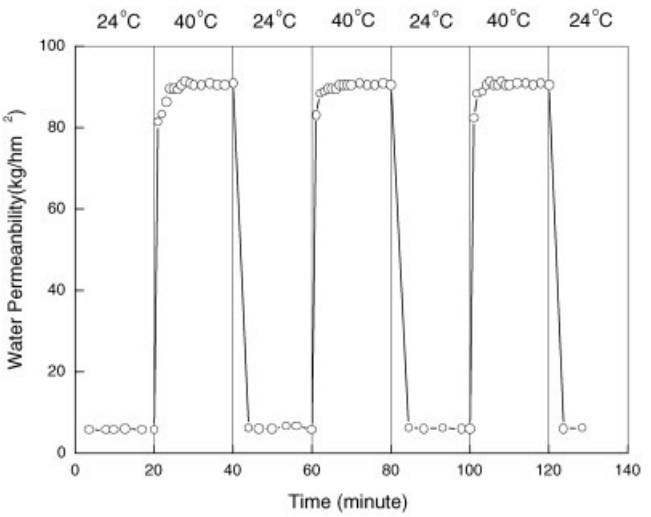

Figure 10 Reversible water permeability through a grafted membrane (0.48 mg/cm^2) in response to stepwise temperature changes between 24 and 40°C.

membrane, on both the outer surface and inside pores of the membrane, to a depth of at least 165 μm.

4. The XPS analysis gives evidence that the polar amide groups of grafted PNIPAAm below the LCST tend to distribute more outward than those of grafted PNIPAAm above LCST.
5. The grafted PNIPAAm chain can act as a sensor of the temperature and as a chemical valve regulating the pore radii with a slight temperature change in the vicinity of the LCST. The grafted membrane is stable in size and responds instantly to the temperature change.

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