

Synthesis of Controlled Thermoresponsive PET Track-Etched Membranes by ATRP Method

Kai Pan,^{1,2} Ruimin Ren,¹ Yi Dan,² Bing Cao¹

¹College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China

²State Key Laboratory of Polymer Materials Engineering (Sichuan University), Chengdu 610065, China

Received 22 November 2010; accepted 15 January 2011

DOI 10.1002/app.34265

Published online 13 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Controlled thermoresponsive PET track-etched membranes were synthesized by grafting *N*-isopropylacrylamide (NIPAAm) onto the membrane surface via atom transfer radical polymerization (ATRP). The initial measurements were made to determine the anchoring of ATRP initiator on PET membrane surface. Thereafter, polymerization was carried out to control the mass of polymer by controlling reaction time grafted from the membrane surface and, ATR-FTIR, grafting degree measurements, water contact angle measurements, TGA, and SEM were used to characterize changes in the chemical functionality, surface and pore morphology of membranes

as a result of modification. Water flux measurements were used to evaluate the thermoresponsive capacity of grafted membranes. The results show the grafted PET track-etched membranes exhibit rapid and reversible response of permeability to environmental temperature, and its permeability could be controlled by controlling polymerization time using ATRP method. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2047–2053, 2011

Key words: PET track-etched membrane; atom transfer radical polymerization (ATRP); thermoresponsive; poly(*N*-isopropylacrylamide); control grafting

INTRODUCTION

The stimuli-responsive membranes have attracted a lot of attentions for their intelligent properties in recent years,^{1–5} including pH, thermo, ionic strength responsibilities, and so on. Compared with traditional membrane separated technology, the using field of membrane was extended. The stimuli-responsive membranes could be used as wastewater treatment, bioseparation, chemical sensors, etc. Usually, stimuli-responsive membranes are prepared by grafting stimuli-responsive polymers onto the substrate membranes. Many of the intelligent membranes have been synthesized by “grafting from” methods, such as chemical grafting,⁶ radiation-induced grafting,⁷ photografting,⁸ and plasma-induced grafting.⁹ Recently, Atom transfer radical polymerization (ATRP) became a versatile method to membrane surface modification. The precise control of the polymer structure made it have promi-

nent advantages on membrane modification and attract more attentions.^{10,11}

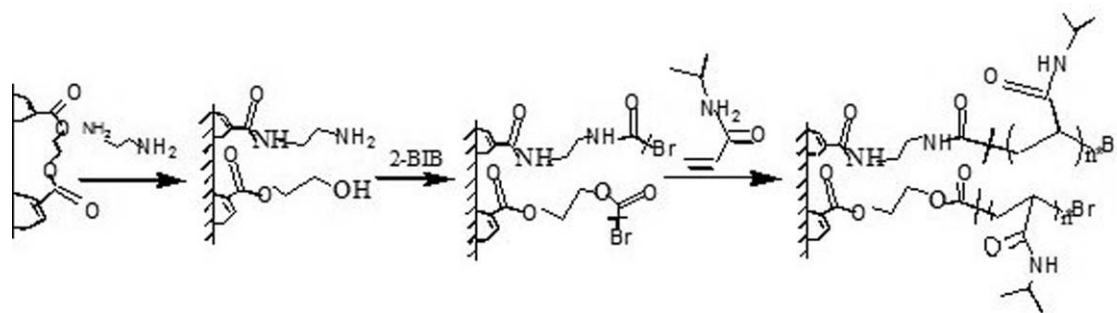
Polymer track-etched membranes are thin polymer films with discrete pores that are formed through a combination of heavy ions bombardment and chemical etching.¹² By choosing appropriate conditions for irradiation and etching, it is possible to prepare a wide range of polymer track-etched membranes. The pore size, shape, and density can be varied in a controllable manner.¹³ Track-etched membranes have found diverse applications in biotechnology, medicine, ecology, etc.¹² Modification of such a membrane by grafting it with polymers, especially stimuli-responsive polymers, would extend the possibility of their use.^{14,15}

In this work, we immobilized thermoresponsive PNIPAAm polymers on PET track-etched membranes by ATRP method (as shown in Scheme 1) that offers an important advantage to other grafting methods. Polymerization time was used as the independent variable to manipulate the amount of grafted PNIPAAm on the membrane surface. Thus, the grafted chains provide a “pore valve” by which membrane separation characteristics and *trans*-membrane flux can be varied in response to simple solution temperature. Through this method, well-defined surface structures can be achieved, the grafting density and grafted chain length are controlled well. In our experiment, XPS, ATR-FTIP, SEM, TGA, and water flux measurement were used to test the

Correspondence to: B. Cao (bcao@mail.buct.edu.cn).

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20804002.

Contract grant sponsor: Opening Project of State Key Laboratory of Polymer Materials Engineering (Sichuan University); contract grant number: KF200904.



Scheme 1 The schematic of NIPAAm polymerization initiated from PET track-etched membrane by ATRP.

chemical and physical performances of the grafted membranes.

EXPERIMENTAL MATERIALS AND METHODS

Materials

PET track-etched membranes (pore diameter 0.4 μm , 25 mm diameter) were purchased from Whatman Co. *N*-isopropylacrylamide (NIPAAm) (97%) and 2-bromoisobutyryl bromide (2-BIB, 98%) were purchased from Sigma-Aldrich and used without further treatment. Anhydrous tetrahydrofuran (THF, 99.9%), methanol (99.8%), triethylamine ($\geq 99.5\%$), copper (I) chloride ($>99\%$), ethyl alcohol (99.5%), 2,2-bipyridyl ($>99\%$) were purchased from Beijing Reagent corp. Ethylenediamine (99%) was purchased from Alfa Aesar.

Membrane surface modification

Immobilization of ATRP initiator on the membrane surface

To immobilize the ATRP initiator onto PET track-etched membrane surface by virtue of the reaction with acyl bromide group, PET track-etched membrane should be pretreated to introduce active amido group. First, PET track-etched membrane was immersed in three-neck flask which containing ethylenediamine solution in methanol (1 mol/L), during the reaction, moderate agitation was used. After 2 h reaction, the PET track-etched membrane was removed from the solution, and washed with multiple methanol, then dried in vacuum at room temperature at least 8 h. Second, the aminofunctionalized surface was immersed in three-neck flask containing anhydrous THF solution, triethylamine and 2-bromoisobutyryl bromide (2-BIB) were added [THF/triethylamine/2-BIB = 70/6/1 (volume ratio)]. Before addition, the three-neck flask was backfilled with argon for at least 30 min. The reaction proceeded with moderate agitation for different time

during emptying the oxygen of the state by inletting argon. After the reaction, the functionalized PET membrane was purified by multiple washing with water. All above reactions were allowed to proceed at room temperature.

Surface initiated ATRP of *N*-isopropylacrylamide (NIPAAm)

HPLC water, *N*-isopropylacrylamide (NIPAAm), copper (I) chloride, 2, 2-bipyridyl [NIPAAm/CuCl/bpy = 280/1/1.8 (mol ratio)], and the membrane anchored with initiator were added into a three-neck flask. Before polymerization, the flask was backfilled with argon for 15 min. The reaction time ranged from 0.5 h to 2 h, during which the flask was deoxygenated by inletting argon. All the reaction steps were undertaken at room temperature. After polymerization, the membranes were washed in water for three times at the temperatures of room temperature, 45°C, and room temperature in sequence. The membranes were then dried at vacuum drying oven.

Characterization

X-ray photoelectron spectroscopy (XPS) characterization. The surface chemical compositions of blank, aminated, initiator anchored, and grafted PET track-etched membranes were analyzed by X-ray photoelectron spectroscopy (XPS). XPS analysis was carried out on ESCALAB 250 spectrometer using a monochromatized Al K α X-ray source at a constant analyzer.

ATR-FTIR characterization. A Fourier transform infrared attenuated total reflection spectrometer (ATR-FTIR) spectrometer (Spectrum RX-I) was used to detect the functional groups on the surface of the blank and grafted membranes.

Grafting degree measurements. The amount of polymer chains grafted on the membranes is estimated by the grafting degree [D , eq. (1)], which is the ratio of

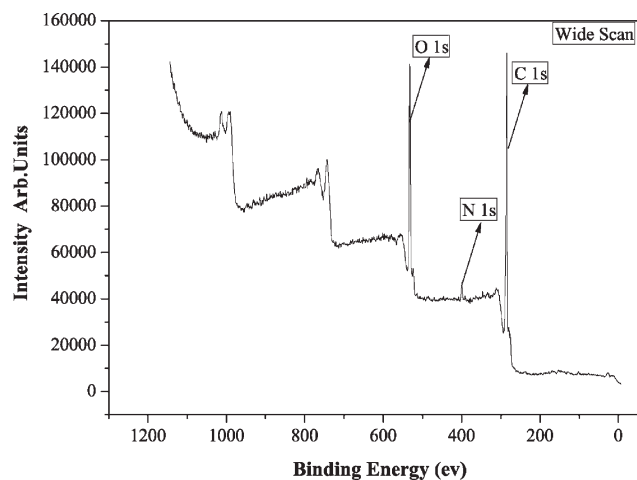


Figure 1 The XPS spectra of aminated PET track-etched membrane.

increased weight of grafted membrane to membrane area:

$$D = M_g - M_0/A \quad (1)$$

where M_g and M_0 represent weights of grafted and initiator anchored membranes, respectively. A represents the area of membrane.

Water contact angle measurements. The hydrophilic of the membranes was tested by water contact angle measurements instrument (JC2000C, Shanghai Zhongchen Co., China). Before the samples were tested, they were fully dried. Five different locations were chosen for each value.

Thermal analysis. Thermogravimetric analysis was carried out using a SDT Q600 (TA Co.) under nitrogen atmosphere. Samples (about 10 mg) were heated from room temperature to 500°C at a heating rate of 10°C/min.

Scanning electron microscopy (SEM). The surface morphology of the PET track-etched membranes with different grafted time was investigated by scanning electron microscopy (SEM) on Hitachi-4700 SEM. The membranes were mounted on the sample studs by means of double-sided adhesive tapes. A thin layer of palladium was sputtered onto the membrane surface before the SEM measurement. The measurements were performed at an accelerating voltage of 20 kV.

Thermoresponsive permeability measurement of grafted membranes. The permeation properties of the blank and grafted PET track-etched membranes were examined in different temperature buffer solutions. The water flux measurements were obtained using 25 mm diameter unmodified and modified membranes to study the temperature modulated permeability properties of membranes with surface-grafted

TABLE I
The XPS Spectra of Blank, Aminated, and Initiator Anchored PET Track-Etched Membranes

Membrane	C (at. %)	O (at. %)	N (at. %)	Br (at. %)
Blank	77.77	22.24	0	0
Aminated	76.10	21.75	2.15	0
Initiator anchored	71.84	25.22	2.44	0.50

PNIPAAm. Feed pressures were set at 0.17 Mpa by a pump at a rate and the change in permeate mass was monitored over time using a balance.

RESULTS AND DISCUSSION

XPS of the initiator-functionalized membrane

To anchor the ATRP initiator 2-BIB on membrane surface, PET track-etched membranes should be pretreated by aminated reaction. Then the initiator 2-BIB could be anchored onto the surface of PET track-etched membranes by reacting with the amido group of pretreated membranes surface. XPS measurements were used to detect the surface chemical compositions of blank, aminated and initiator anchored PET track-etched membranes.

Figure 1 presents XPS wide-scan spectra for aminated membrane. The spectra of nitrogen element can be seen around 400(eV). And the atom contents are shown in Table I. The nitrogen content on the surface increased up to 2.15% after aminated reaction while the nitrogen content of the raw material was 0%. Figure 2 presents XPS wide-scan spectra for initiator anchored membrane. The spectra around 180eV and 70eV are Br 3p and Br 3d spectra, indicating that the initiator had been anchored on the membrane surface. The atom contents are also

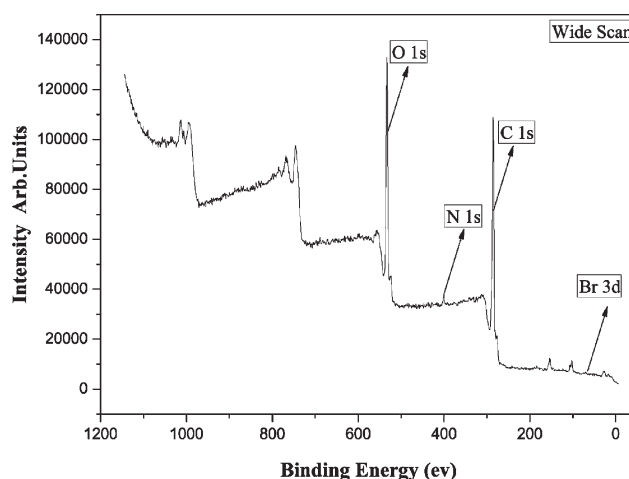


Figure 2 The XPS spectra of initiator anchored PET track-etched membrane.

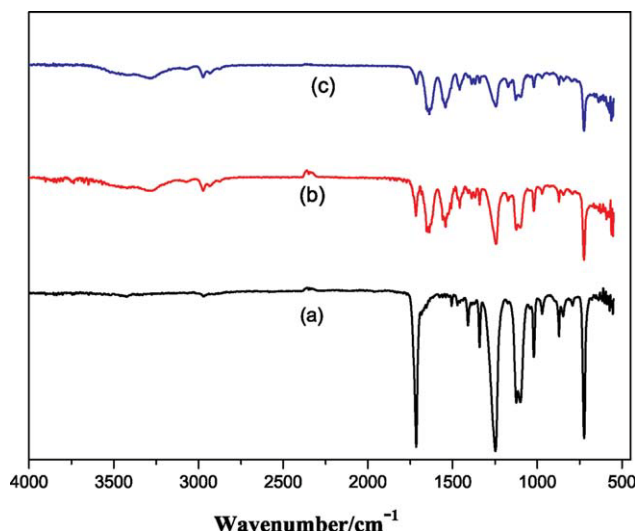


Figure 3 ATR-FTIR Spectra of blank and grafted PET track-etched membrane.(a)blank membrane; (b) PNIPAAm grafted membrane (grafted for 1 h); (c) PNIPAAm grafted membrane (PNIPAAm grafted for 2 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shown in Table I. The bromo content on the surface increased up to 0.50% after 2 h reaction while the bromo content of the unmodified material was 0%.

ATR-FTIR characterization of the grafted membranes

Chemical compositions of grafted membranes before and after immobilization of PNIPAAm are verified by ATR-FTIR spectra. Figure 3 presents ATR-FTIR spectra for the raw and grafted with PNIPAAm membranes prepared by surface-initiated ATRP for 1 h and 2 h. As shown in Figure 3(b,c) curves, the peak at 1639 cm^{-1} is attributed to a strong stretching mode of carbonyl groups of the amides, the peak at 1549 cm^{-1} is caused by deformation vibration of the group of $-\text{NH}$, the peak at 1469 cm^{-1} is the result of asymmetrical bending vibration of the methyl group, and the double peaks at 1391 cm^{-1} and 1369 cm^{-1} are formed by the symmetrical deformation vibration of the twin methyl groups in the membrane with grafted PNIPAAm. After polymerization, the surface of the membrane was covered by a layer of PNIPAAm. As a result, the peak at 1069 cm^{-1} in the spectrum of grafted membrane diminished in intensity comparing with the spectrum of RC membrane, which is attributed to hydroxyl groups of cellulose. So it is confirmed that the polymerization of PNIPAAm is successful. We can also see from Figure 3 that with the increasing of grafting time, the intensity of spectrum of PET track-etched membranes becomes weak. That is because the layer of PNI-

AAm became much thicker with the extension of grafting time.

ATRP grafting polymerization on PET track-etched membrane surface and the controllability

In this work, grafting degree (D) was the unit area increase of grafted PET track-etched membranes. Because all the initiators were anchored on the membrane surface and the chain propagation only occurred on the membrane surface, we can get the logarithmic conversion data $\ln([M]_0/[M]_t)$ ($[M]_0$ and $[M]_t$ are the concentration of monomer at time 0 and t , respectively). Figure 4 shows the time dependence of $\ln([M]_0/[M]_t)$ and grafting degree. From Figure 4 we can see that the grafting degree increased with grafting time increasing from $2.39 \times 10^{-4}\text{ g/cm}^2$ to $6.74 \times 10^{-4}\text{ g/cm}^2$ during 2 h. Figure 4 also shows the polymerization kinetic was first order (linear fit correlation coefficient R is 0.9834) in monomer, and the concentration of growing species kept constant during the polymerization.

Figure 5 presents XPS wide-scan spectra for NIPAAm grafted membrane. The atom contents are shown in Table II. The bromo content on the surface of NIPAAm grafted membranes was 0.11%. Though the percent of bromo was declining, the even appearance of bromo was a strong proof to prove the grafting polymerization is ATRP polymerization.

Combing the above results, we can conclude that the grafting polymerization was an ATRP polymerization, and the concentration of growing species kept constant during grafting polymerization. This polymerization should be a controlled grafting polymerization. Only the molecular weight and molecular weight distribution of grafted polymer chains were difficult to detect because it is hard to know where the grafted polymer chains can be divided from membrane surface.

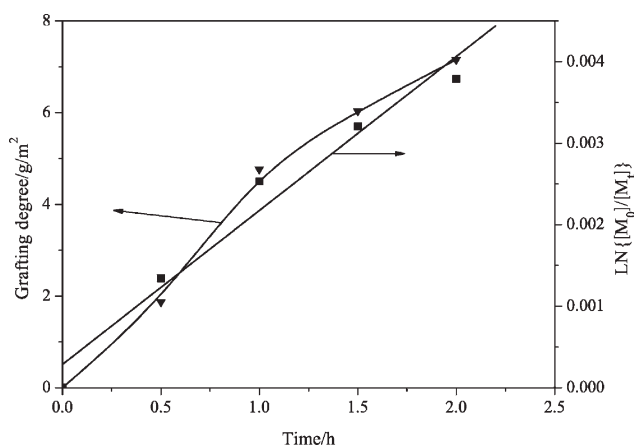


Figure 4 Time dependence of $\ln([M]_0/[M]_t)$ and Grafting degree of NIPAAm grafted by ATRP method. (NIPAAm/CuCl/bpy = 280/1/1.8 (mol ratio))

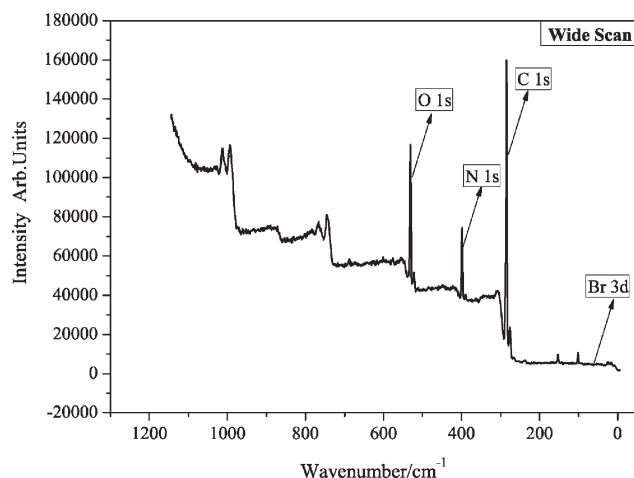


Figure 5 The XPS spectra of grafted PET track-etched membrane.

Water contact angle measurements of the grafted membranes

The hydrophilic property of PET track-etched membranes was shown in Figure 6. From Figure 6 we can see that the water contact angle of blank membrane was 79°, with increasing of reaction time, the water contact angle of grafted membranes linearly decreased from 70° (grafted 0.5 h) to 51° (grafted 2 h). The results showed that the hydrophilicity of PET membranes would be increased by grafting PNIPAAm onto membrane surface. The linear decreasing of water contact angle with grafting time also told us that this grafting polymerization process could be controlled by grafting time using ATRP method.

TGA of the grafted membranes

TGA results of the blank and grafted PET track-etched membrane with PNIPAAm are presented in Figure 7. The thermogram of the grafted membrane is different from the blank one. It undergoes a two-step thermal degradation process. The first step is a small weight loss at low temperature range (47–70°C), corresponding to the loss of absorbed water and small molecules by the chain of PNIPAAm compared with the blank membrane, the thermal degradation of grafted membrane [Fig. 7(b)] showed one pyrolysis, which began at about 405°C. While the thermal degradation of blank PET membrane started

TABLE II
The XPS Spectra of Grafted PET Track-Etched Membrane

Membrane	C (at. %)	O (at. %)	N (at. %)	Br (at. %)
Blank	77.77	22.24	0	0
Grafted	76.22	13.67	9.99	0.11

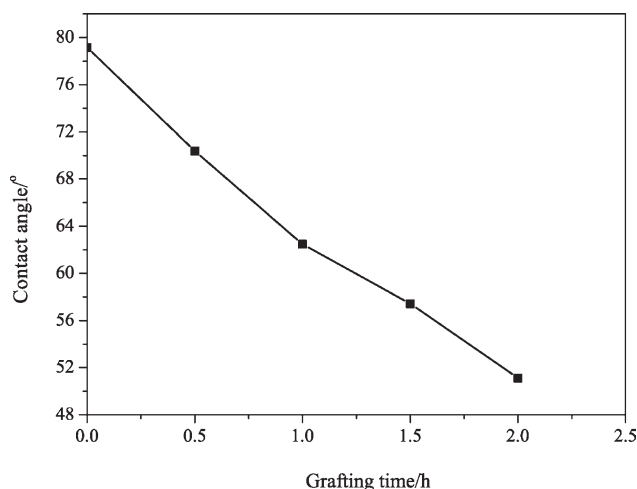


Figure 6 Time dependence of water contact angle.

at 431°C. These observations have clearly indicated that PET-g-PNIPAAm has low thermal stability compared with the blank PET track-etched membrane.

The surface morphology of membranes

Scanning electron microscopy (SEM) results (Fig. 8) showed that the pore density was reduced considerably, and the pore diameters became smaller after polymerization on the surface. Because ATRP is a controlled radical polymerization method, we can control the reaction by controlling the reaction time. Comparing Figure 8(a–e), it was observed that the surface morphology has significantly been varied more after the surface-initiated ATRP for more time. A dense layer of PNIPAAm formed on the PET track-etched membrane surface, completely covering the membrane surfaces, and few porous structures

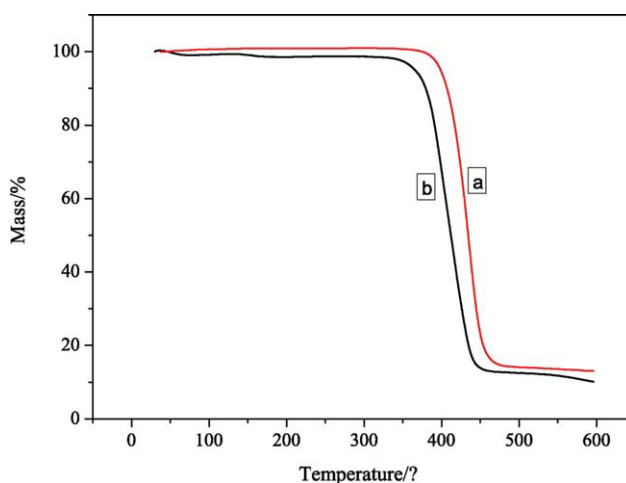


Figure 7 TGA spectra of blank and grafted PET track-etched membrane. (a) blank membrane; (b) PNIPAAm grafted membrane (grafted for 2 h). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

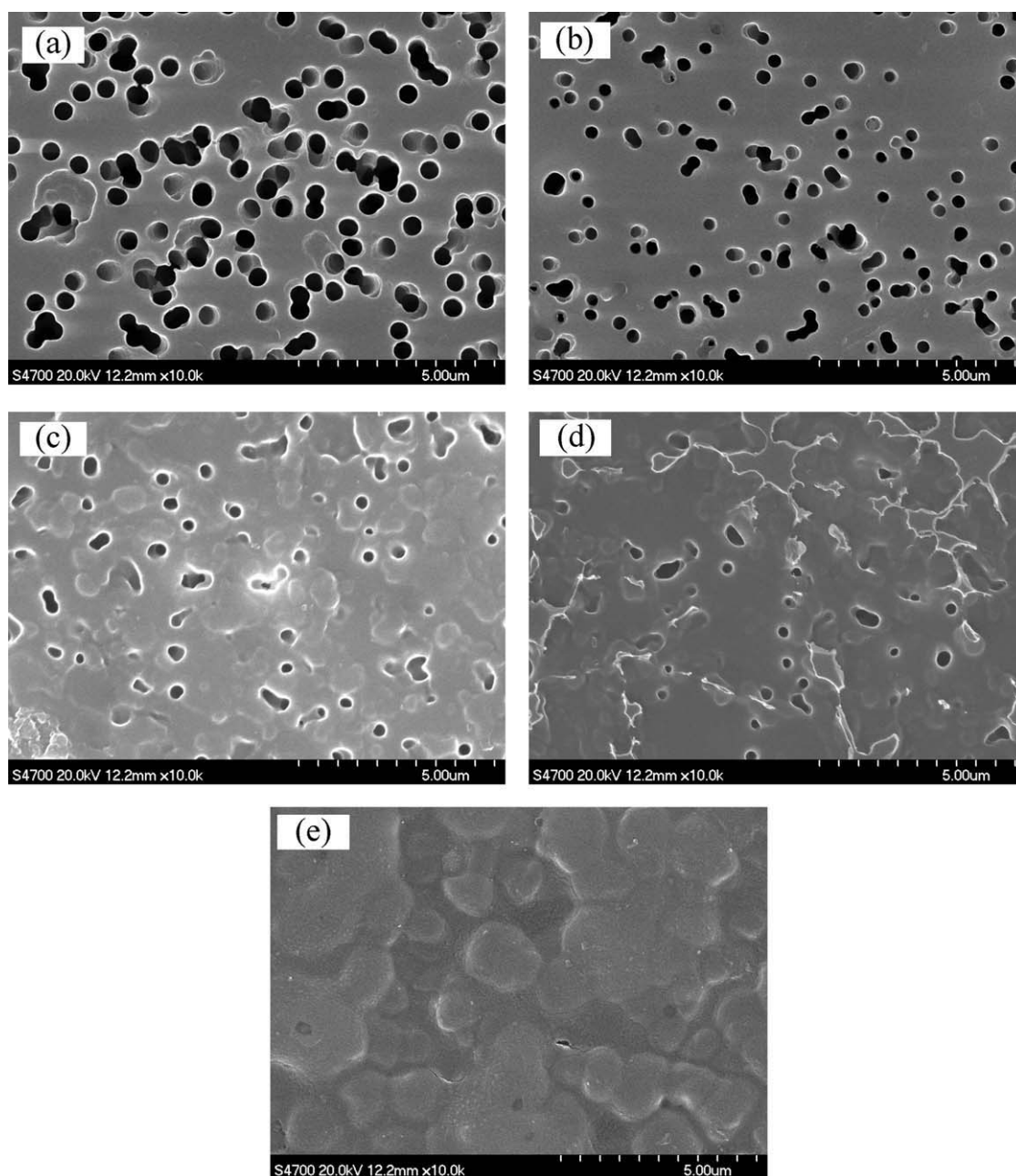


Figure 8 SEM images of blank and grafted PET track-etched membrane. (a) blank membrane; (b) grafted PNIPAAm for 0.5 h; (c) grafted PNIPAAm for 1 h; (d) grafted PNIPAAm for 1.5 h; (e) grafted PNIPAAm for 2 h.

were observed, because the PNIPAAm chains have completely filled the pore space, which was attributed to the longest reaction time, as shown in Figure 8(e).

Thermoresponsive permeability measurement of grafted membranes

To exam the thermoresponsive permeability of the grafted membranes, the flux was measured for modified membranes in different temperatures. Figure 9 give results for membranes grafted with PNIPAAm for 0.5 h, 1 h, 1.5 h, and 2 h. First, the flux

curve indicate that the permeate flux decreases with increasing of polymerization time, as expected. Second, it can be seen from the data of every grafted membrane, the permeate flux increased sharply while the temperature was 32°C. The temperature dependent behavior resulted from the thermodependent conformation of the PNIPAAm polymer side chains on the surface (including the pore surfaces). At a temperature lower than the LCST (lower critical solubility temperature) of the PNIPAAm polymer (32°C), the PNIPAAm polymer side chains are solvated. And the grafted PNIPAAm chains swelled on the surface of the membrane. This effect

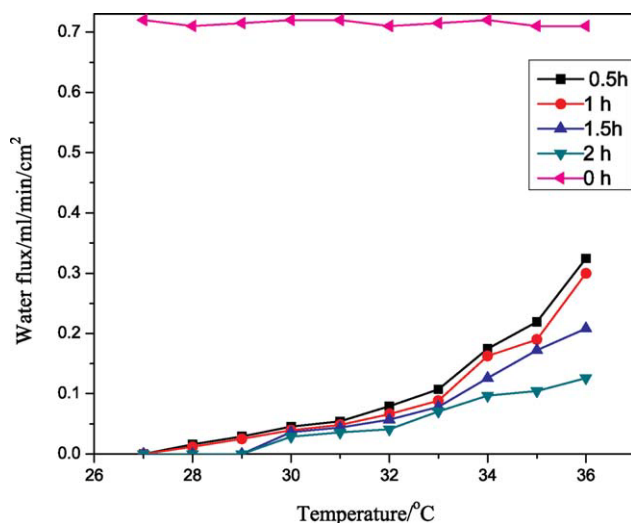


Figure 9 Water flux measurement of grafted PET track-etched membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

makes the surface pore stemmed by swelled chains, so the flux was small during this process. On the other hand, at temperatures higher than the LCST, the grafted PNIPAAm polymer chains shrank. The surface pore of membrane becomes big, resulting in the increasing of flux. From the results we can see that grafted PET track-etched membranes exhibit rapid and reversible response of permeability to environmental temperature, and its permeability could be controlled by controlling polymerization time using ATRP method.

CONCLUSIONS

PET track-etched membranes have been modified by grafting *N*-isopropylacrylamide (NIPAAm) onto the membrane surface via atom transfer radical polymerization (ATRP) for different periods of time. The grafted PET membranes were analyzed with ATR-FTIR, which confirmed that PNIPAAm had grafted onto the surface successfully. TGA result was also indicated the grafting of PNIPAM on membrane surface. XPS and grafting degree measurement showed that the grafting polymerization was an ATRP poly-

merization, and the concentration of growing species kept constant during grafting polymerization. This polymerization should be a controlled grafting polymerization. Water contact angle measurements showed the linear increasing of hydrophilic property of grafted membranes. From the SEM images, it can be seen a decreasing in pore diameter with increasing reaction time. To verify the thermal sensitivity of the membranes grafted with PNIPAAm, the fluxes of the membranes in buffers of different temperature were measured, indicating that flux values increases as the temperature rising. The results show the grafted PET track-etched membranes exhibit rapid and reversible response of permeability to environmental temperature, and its permeability could be controlled by controlling polymerization time using ATRP method.

References

- Ulbricht, M.; Ozdemir, S.; Geismann, C. *Desalination* 2006, 199, 150.
- Tarvainen, T.; Nevalainen, T.; Sundell, A.; Svarfvar, B.; Hyrsyla, J.; Paronen, P.; Jarvinen, K. *J Controlled Release* 2000, 66, 19.
- Abetz, V.; Brinkmann, T.; Dijkstra, M.; Ebert, K.; Fritsch, D. *Adv Eng Mater* 2006, 8, 328.
- Chapman, C. L.; Bhattacharyya, D.; Eberhart, R.; Timmons, R. B.; Chuong, C. J. *J Membr Sci* 2008, 318, 137.
- Ito, T.; Yamaguchi, T. *Langmuir* 2006, 22, 3945.
- Cheng, Z. P.; Zhu, X. L.; Kang, E. T.; Neoh, K. G. *Macromolecules* 2006, 39, 1660.
- Yamaki, T.; Asano, M.; Maekawa, Y.; Morita, Y.; Suwa, T.; Chen, J.; Tsubokawa, N.; Kobayashi, K.; Kubota, H.; Yoshida, M. *Radiat Phys Chem* 2003, 67, 403.
- Susanto, H.; Ulbricht, M. *Langmuir* 2007, 23, 7818.
- Xie, R.; Chu, L. Y.; Chen, W. M.; Xiao, W.; Wang, H. D.; Qu, J. B. *J Membr Sci* 2005, 258, 157.
- Singh, N.; Husson, S. M.; Zdyrko, B.; Luzinov, I. *J Membr Sci* 2005, 262, 81.
- Singh, N.; Chen, Z.; Tomer, N.; Wickramasinghe, S. R.; Soice, N.; Husson, S. M. *J Membr Sci* 2008, 311, 225.
- Zhitariuk, N.; Shtanko, N. *Eur Polym Mater* 1990, 26, 847.
- Ferain, E.; Legras, R. *Nucl Instrum Methods Phys Res Sect B* 2001, 174, 116.
- Yangi, B.; Yang, W. *J Macromol Sci Pure Appl Chem* 2003, A40, 309.
- Zhitariuk, N.; Shtanko, N. *Eur Polym Mater* 1990, 26, 847.