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Synthesis of pH-Responsive Polyethylene Terephthalate Track-Etched Membranes by Grafting Hydroxyethyl-Methacrylate Using Atom-Transfer Radical Polymerization Method

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ABSTRACT: pH-responsive polyethylene terephthalate (PET) track-etched membranes were synthesized by grafting 2-hydroxyethyl-methacrylate (HEMA) on the surface of the membrane via atom transfer radical polymerization. The controllability of grafting polymerization of HEMA on membrane surface is systematically investigated. The pH-responsive characteristics of PET-*g*-poly(2-hydroxyethyl-methacrylate) (PHEMA) gating membranes with different grafted PHEMA chain lengths are measured by tracking the permeation of water solution with different pH values. The results show that the grafting polymerization is controllable, and the permeation of grafted membranes is affected by the grafted PHEMA chain lengths on the surface of membrane. The results also demonstrate that the grafted PET membranes exhibit reversible pH-response permeation to environmental pH values. Desired pH-responsive membranes are obtained by controlling the grafted PHEMA chain lengths via atom transfer radical polymerization method. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40912.

KEYWORDS: grafting; membranes; stimuli-sensitive polymers

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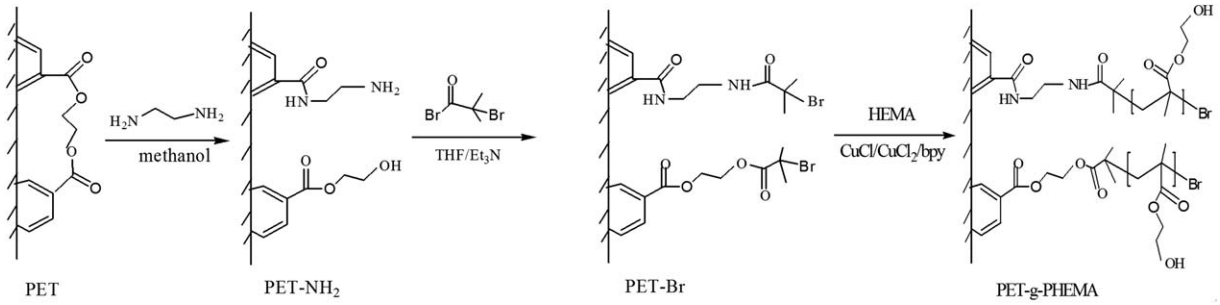
INTRODUCTION

Environmental stimuli-responsive membranes have gained considerable attention because of their excellent chemical and physical responses to the various ambient conditions. Compared with traditional membrane separation technology, the application of this new type of membranes can be extended to waste water treatment, bio-separation, chemical sensors, etc. Its distinctive features and diverse applications innovate the extensive study of the preparation and the properties.[1–5]

Many of the functional membranes have been synthesized by different "grafting from" methods, such as chemical grafting,[6,7] radiation-induced grafting,[8] photografting,[9,10] and plasma-induced grafting.[11] However, difficult control of the grafting polymer chain length is the primary disadvantage for those methods. Surface-initiated atom transfer radical polymerization (ATRP) is proposed as a solution to modify membranes. In this method, the initiator is anchored on the membrane surface in advance, and the initiated polymerization of the monomers only occurs on the surface rather than in the solution. Some other advantages, such as the facile polymerization conditions and wide adaptive monomer range, also make this method a versatile technique for the modification of membrane.[12]

Based on our previous work,[13,14] we chose the polyethylene terephthalate (PET) track-etched membranes with discrete pores[15] as the thin films to prepare stimuli-responsive membranes in this research. 2-Hydroxyethyl-methacrylate (HEMA) was chosen as the functional monomer because of the reversible pH-response of poly(2-hydroxyethyl-methacrylate) (PHEMA) polymer chains. Currently, some studies about grafting PHEMA chains from various substrates have been published.[16–20] The membranes were functionalized with pH-responsive capability by immobilizing PHEMA chains on the surface of PET track-etched membrane with ATRP method (as shown in Scheme 1). The grafting amount of PHEMA chains on the surface of the membrane was controlled by adjusting the polymerization time. Therefore, the grafted chains provide a "pore valve" by which membrane separation characteristics and trans-membrane flux can be varied in response to solution pH value. The surface structure of the membrane is well defined with a facile control of the grafting density and grafted chain length by this method. In the current work, X-ray photoelectron spectroscopy (XPS), attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and water flux measurement



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

were used to test the chemical and physical performances of the grafted membranes.

EXPERIMENTAL

Materials

PET track-etched membranes (pore size 0.4 μm, 25 mm diameter) were purchased from Whatman Co. HEMA (97%) and 2-bromoisobutyryl bromide (2-BIB, 98%) were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. Anhydrous tetrahydrofuran (THF, 99.9%), methanol (99.8%), triethylamine (≥99.5%), CuCl (>99%), $CuCl_2$ (>99%), ethyl alcohol (99.5%), and 2,2-bipyridyl (bpy, >99%) were purchased from Beijing Reagent Corp. Ethylenediamine (99%) was purchased from Alfa Aesar.

Membrane Surface Grafting

Immobilization of ATRP Initiator. To anchor the ATRP initiator on the surface of PET track-etched membrane by reacting with acyl bromide group, PET track-etched membrane was pretreated to introduce active amido groups. PET track-etched membrane was first immersed in the ethylenediamine methanol solution (1 mol/L) in a three-necked flask with moderate agitation. The PET track-etched membranes were removed after 2 h reaction and washed with methanol for multiple times. The amino-functionalized membranes were obtained after drying in vacuum at room temperature for 8 h. The product membranes were then immersed in the anhydrous THF solution consisting of triethylamine and 2-BIB (THF/triethylamine/2-BIB = 70/6/1 (volume ratio)) in the three-necked flask, which had been backfilled with argon for 30 min before the addition of raw materials. The reaction proceeded with moderate agitation for 2 h in argon to immobilize the ATRP initiator on the surface of PET membranes. The anchored PET membranes were washed with deionized water for multiple times, dried, and then stored for use. All the above reactions were allowed to proceed at room temperature.

Surface-Initiated ATRP of HEMA. High performance liquid Chromatography (HPLC) water, HEMA, copper (I) chloride, bpy, copper (II) chloride dehydrate (HEMA/CuCl/bpy/$CuCl_2$ = 100/1/3/0.3 (mol ratio)), and the membranes anchored with initiator were added into a three-necked flask. The flask was backfilled with argon for 15 min before polymerization. The reaction proceeds at room temperature in argon for 15 to 60 min. The membranes were washed in deionized water for three times at room temperature, 45°C, and room temperature sequentially after polymerization and then dried in vacuum oven.

Characterization

The surface chemical compositions of PET track-etched membranes were analyzed by XPS on ESCALAB 250 spectrometer using a monochromatized Al Ka X-ray source at a constant analyzer. An ATR-FTIR spectrometer (Spectrum RX-I) was used to detect the functional groups on the surface of the blank and grafted membranes. TGA was carried out using a SDT Q600 (TA Co., USA) under nitrogen atmosphere. Samples (about 10 mg) were heated from room temperature to 500°C at a heating rate of 10°C/min. The surface morphology of the PET track-etched membranes with different grafting times was investigated by SEM on Hitachis-4700 SEM at an accelerating voltage of 20 kV. The membranes were mounted on the sample studs by double-sided adhesive tapes and coated with a thin layer of palladium before measurement.

The amount of polymer chains grafted on the membranes was estimated by the grafting degree (D, eq. (1)), which is the ratio of increased weight of grafted membrane to membrane area:

$$D = \frac{M_g - M_o}{A} \quad (1)$$

where M_g is the weights of grafted membranes, M_0 is the weight of initiator-anchored membranes, and A is the area of membrane.

The hydrophilicity of the membranes was tested by water contact angle measurements instrument (JC2000C, Shanghai Zhongchen Co., China). The samples were fully dried before testing. Each value was averaged by the data taken at five different locations.

pH-Responsive Permeation Measurement of Grafted Membranes

To investigate the pH-responsiveness of grafted membranes, different pH value buffer solutions (pH = 2, 3, 4, 4.6, 4.9, 5.6, 7, and 8) were permeated through the membranes. The water flux measurements were performed with 25 mm diameter membranes to study the pH modulated permeation of membranes by a diffusion cell. Feed pressures were set at 0.14 MPa, and the change in permeate mass was monitored over time. The membrane was immersed in the permeate solution for 12 h before testing.

The membrane grafted for 30 min was chosen to investigate the reversible pH-response permeation by buffer solution with

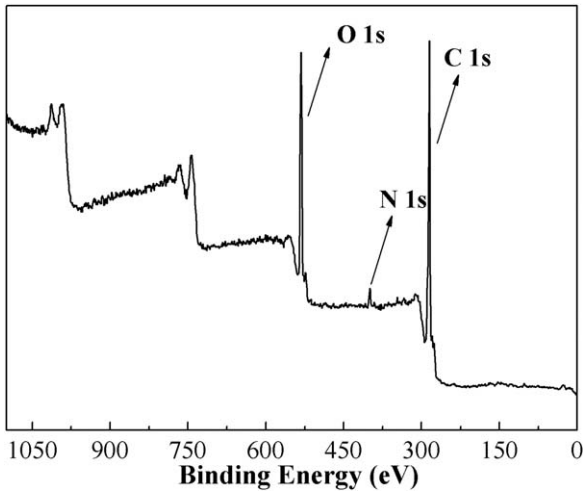


Figure 1. The XPS spectrum of aminated PET track-etched membrane.

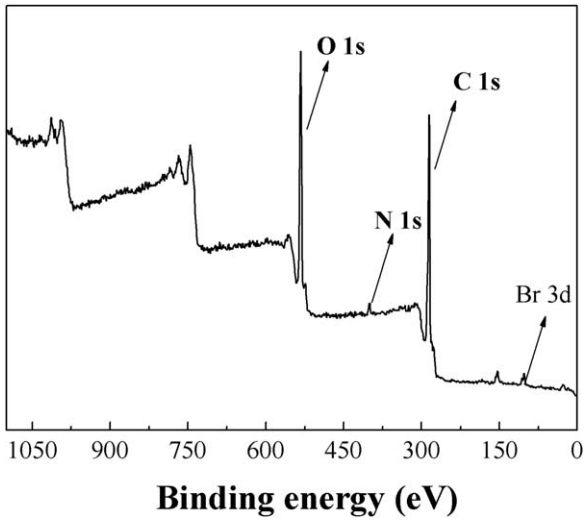


Figure 2. The XPS spectrum of initiator-anchored PET track-etched membrane.

pH = 3 and 7, respectively. The membrane was immersed in the solution for 12 h before penetration.

RESULTS AND DISCUSSION

XPS of the Initiator-Functionalized Membrane

The ATRP initiator 2-BIB was anchored on the surface of PET membrane by reacting with the amido group on the pretreated membrane surface. XPS measurements were conducted to detect the surface chemical composition of blank, aminated, and initiator-anchored PET track-etched membranes.

Figure 1 shows the XPS wide-scan spectrum of aminated membrane. The peak relating to nitrogen can be seen observed at about 400 eV. The atomic percentages of all samples are shown in Table I. According to this table, the surface nitrogen content increased up to 5.48% after aminated reaction, whereas the value of blank membrane was 0%. The XPS wide-scan spectrum of initiator-anchored membrane is illustrated in Figure 2. The peaks at 180 and 70 eV refer to Br 3p and Br 3d spectra, indicating that the initiator had been anchored on the membrane surface. From Table I it can be seen that the bromo content on the surface increased up to 0.48% after 2 h reaction whereas no bromo was detected on the surface of blank membrane. The XPS results confirm that the ATRP initiator 2-BIB has been successfully anchored on the surface of PET membrane.

ATR-FTIR Characterization of the Grafted Membranes

The organic groups of grafted membranes before and after grafting PHEMA are characterized by ATR-FTIR spectra. Figure 3 illustrates the ATR-FTIR spectra for blank and PHEMA-grafted membrane prepared by surface-initiated ATRP for 60 min. On comparing those two curves shown in Figure 3, the peak at 2960 and 3450 cm^{-1} are attributed to a stretching mode of methyl and hydroxyl group of PHEMA, respectively. All of these results proved the successful grafting of PHEMA on the surface of PET membrane.

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	76.96	21.72	5.48	0
Initiator anchored	76.62	17.63	5.27	0.48

Controllability of ATRP Grafting Polymerization on Membrane Surface

The PHEMA chains were grafted on the surface of PET membrane by ATRP polymerization. The controllability of ATRP grafting polymerization on the surface of membrane was investigated by monitoring the grafting degree (D) during the polymerization. Grafting degree (D) is defined as the unit area mass increase of grafted PET track-etched membranes, as shown in eq. (1). Because all the initiators were anchored on the membrane surface and the chain propagation only occurred there,

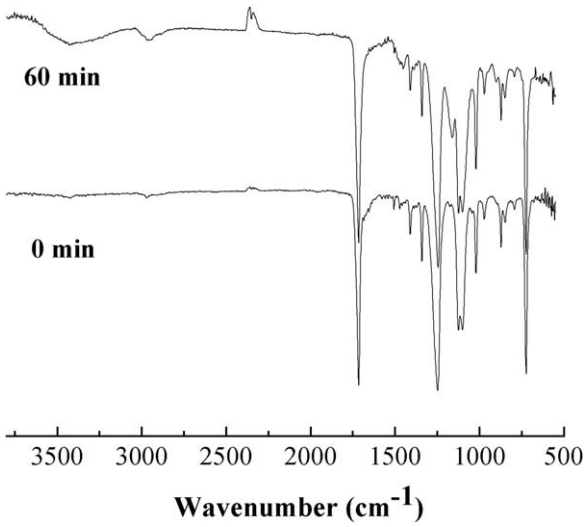


Figure 3. ATR-FTIR spectra of blank and grafted PET track-etched membranes. (A) Blank membrane; (B) PHEMA-grafted membrane (grafted for 60 min).

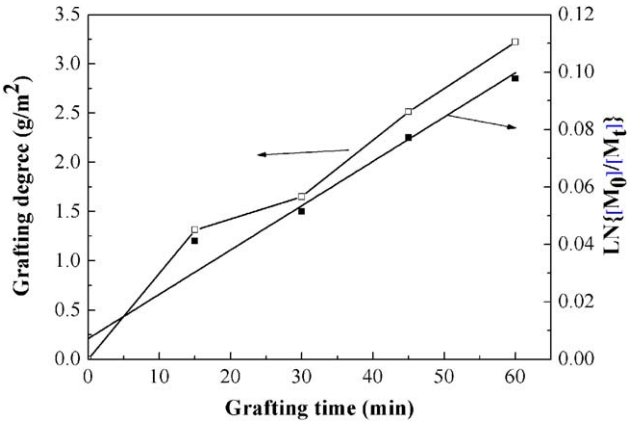


Figure 4. Time dependence of $\ln([M]_0/[M]_t)$ and grafting degree of PHEMA grafted by ATRP method (mol ratio: HEMA/CuCl/bpy/$CuCl_2$ = 100/1/3/0.3). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the logarithmic conversion data $\ln([M]_0/[M]_t)$ can be obtained by calculation ($[M]_0$ 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, which indicates that the polymerization kinetic was in first order, with a linear fit correlation coefficient R to be 0.982. The concentration of growing species is constant during the polymerization. With the increase in grafting time, the grafting degree increases from 1.2 to 2.85 $\times$ 10^{-4} g/cm^2. It can be concluded from the results discussed above that the grafting reaction was a controllable ATRP polymerization. During the reaction, it was difficult to detect the molecular weight and molecular weight distribution of the grafted polymer chains. The reason is that the grafted polymer chains are linked with the membrane by chemical bonds and thus hard to be divided, and when they are divided, it is hard to confirm where the bonds are divided. But the well-defined grafting method has many advantages for membrane modification and surface functionalization.

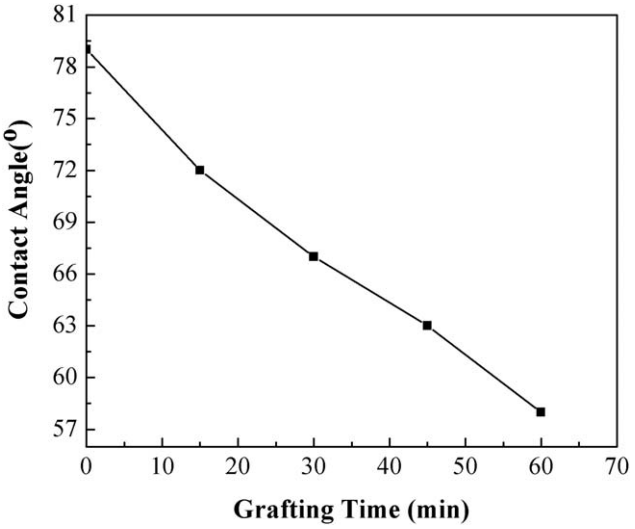


Figure 5. Time dependence of water contact angle.

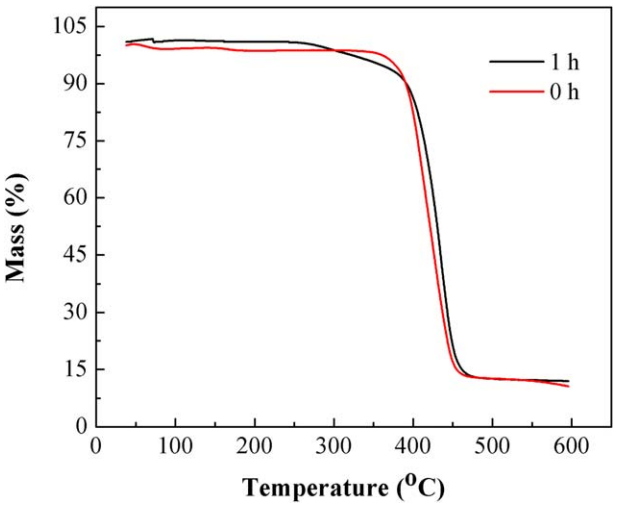


Figure 6. TGA curves of blank and grafted PET track-etched membranes. (A) Blank membrane; (B) PHEMA-grafted membrane (grafted for 60 min). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Water Contact Angle Measurement of the Grafted Membranes

The hydrophilic properties of the grafted membranes were characterized by contact angle measurement, and the result is shown in Figure 5. It can be seen that the water contact angle of blank membrane was 79°. With the increase in grafting time, the water contact angle of grafted membranes decreased linearly from 71° (grafted for 15 min) to 62° (grafted for 60 min), which is attributed to the increase in chain length of PHEMA. The results show that the hydrophilicity of PET membranes is increased by grafting PHEMA on the surface of membrane.

TGA Measurement of the Grafted Membranes

TGA results of the blank and grafted membranes are shown in Figure 6. The blank membrane (A) undergoes a two-step thermal degradation process, which occurs at the temperature range of 340°C −450°C. Compared with blank membrane, PHEMA-grafted membrane thermally degraded at earlier temperature (240°C),[21,22] illustrating that PHEMA chains have been grafted successfully on the surface of the membrane.

Surface Morphology of Membranes

The surface morphology of membranes are analyzed with SEM, and the results of blank and grafted membrane surfaces with different length of grafted PHEMA chains are shown in Figure 7. Compared with the blank membrane, the PHEMA-grafted membranes have significantly different microstructures. As shown in Figure 7(B–E), after grafting PHEMA on the surface of the membrane, the pore density reduced considerably and the pore size became smaller. The length of grafted PHEMA as well as the pore size and density can be controlled by adjusting the reaction time for different grafting degree. Comparing Figure 7(A–E), a gradual change in membrane pore density and size was observed with increasing grafting time. Figure 7(E) shows a dense layer of the grafted PHEMA chains formed on the surface of PET track-etched membrane. It was observed that the layer covered the membrane surfaces completely and few pore structures were

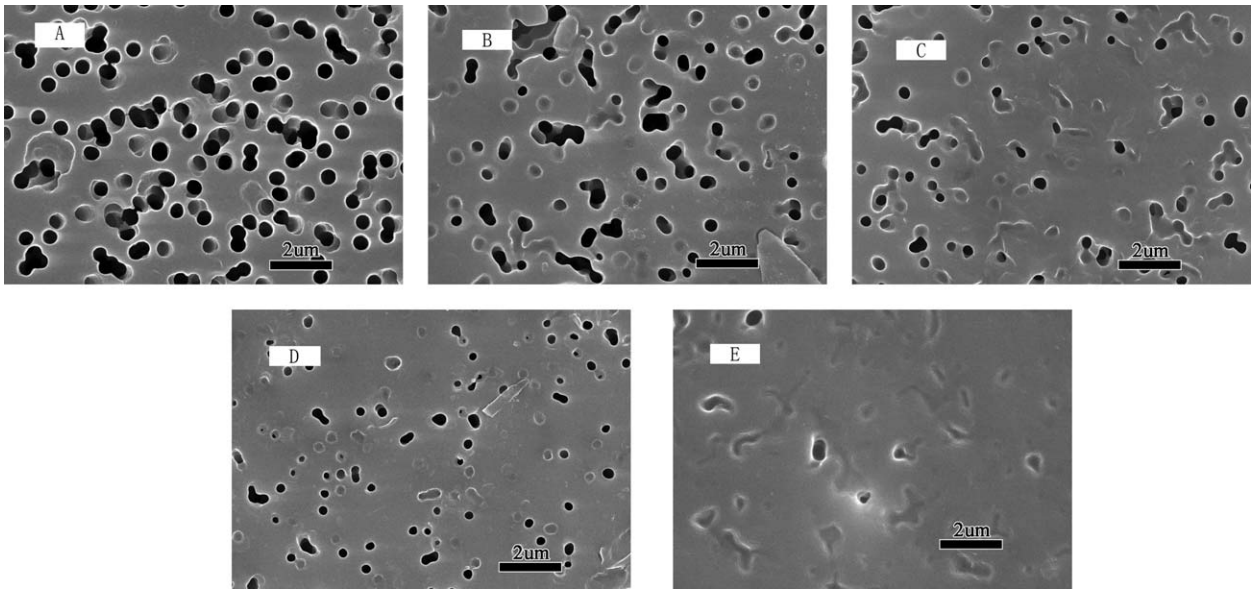


Figure 7. SEM images of blank and grafted PET track-etched membranes. (A) Blank membrane; (B) PHEMA grafted for 15 min; (C) PHEMA grafted for 30 min; (D) PHEMA grafted for 45 min; and (E) PHEMA grafted for 60 min.

observed. The reason is because the grafted PHEMA chains filled the pore completely if the grafting time is sufficiently long. The permeation of membranes would be influenced by the covering of polymer chains over the pores. By controlling the length of polymer chains, the permeability of membranes can be adjusted.

pH-Responsive Permeability of Grafted Membranes

To evaluate the pH-responsive permeability of the grafted membranes, the water flux of membranes at different pH values was measured. The results of membranes grafted with PHEMA for 15, 30, 45, and 60 min are presented in Figure 8. First, the results indicate that the permeate flux decreases with increasing grafting time, as expected. Second, the permeate flux decrease with increasing pH value for all grafted membranes excepted for 0 min. The water flux decreases sharply at the pH between 4 and 5, and the trend became mild at pH > 5. This behavior resulted from the pH-dependent configuration of the PHEMA polymer side chains on the surface (including the pore surfaces). At lower pH value (pH < 4), the hydroxyl (—OH) groups on the PHEMA chain formed hydrogen bond between each other, leading to the shrinkage of the PHEMA chains and the increase in virtual pore diameter. As a result, the water flux was increased. With the increase in pH value (pH > 4), hydrogen bond became weak, and the electrostatic repulsion led to the diffusion of PHEMA chains, which results in the decrease in water flux. When the pH value was beyond 5.6, the chains spread widest, and the water flux was constant.

To investigate the reversible pH-response permeation of grafted membranes, the 30-min grafted membrane was chosen for alternative permeation by two different pH value buffer solutions (pH = 3 and 7). Figure 9 shows the reversible permeation

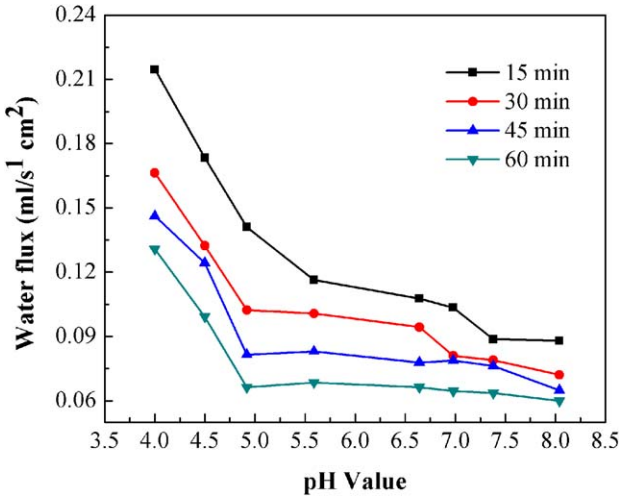


Figure 8. Water flux measurement of grafted PET track-etched membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

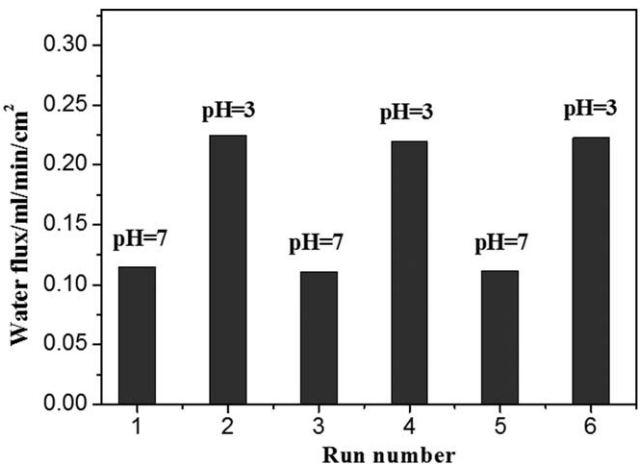


Figure 9. Reversible pH-responsive permeation measurement of 30-min grafted membranes under two different pH value solutions (pH = 3 and 7).

characteristic of the membrane. From the results it can be seen that the 30-min grafted PET track-etched membrane exhibit reversible response of permeability to the set pH value solutions, indicating that the grafted PHEMA chains on the membrane surface retain the pH shrunken/swollen properties although they undergo repeated pH value changes of environmental solutions.

CONCLUSIONS

In this study, the PHEMA was grafted on the surface of the PET track-etched membrane to prepare pH-responsive membranes by ATRP method. The grafting degree measurement showed that it was a controllable grafting polymerization and that the concentration of growing species was constant during grafting polymerization. By controlling the length of grafted PHEMA chains, the permeation of grafted membranes could be adjusted accurately. SEM images showed a decrease in pore diameter with the increase in grafting time. Water contact angle measurements showed the linear increase of hydrophilic property of grafted membranes.

The pH-response permeability of grafted membranes was studied by testing the water flux under different pH value buffer solutions. The results showed that the grafted PET-*g*-PHEMA membranes exhibit pH-response permeation to environmental solutions. The permeation for the same grafted membrane decreased with the pH value of buffer solutions increasing, and a sharp decrease could be observed between pH values of 4 and 5. The PHEMA-grafted membranes also showed well-reversible pH-response permeation to environmental solutions. The results can provide valuable guidance for designing and preparing stimuli-responsive membranes.

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