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Temperature-responsive poly(tetrafluoroethylene) membranes grafted with branched poly(N-isopropylacrylamide) chains

Chun-Chieh Han[a], Ta-Chin Wei[a], Chuan-Shao Wu[b], Ying-Ling Liu[a,*]

[a] *Department of Chemical Engineering and R&D Center for Membrane Technology, Chung Yuan Christian University, Chungli, Taoyuan 32023, Taiwan*
[b] *Department of Material and Fiber, Nanya Institute of Technology, Chungli, Taoyuan 32091, Taiwan*

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ABSTRACT

Temperature-responsive poly(tetrafluoroethylene) membranes grafted with branched poly(N-isopropylacrylamide) (PNIPAAm) chains have been prepared. The preparation method includes two reactions. The first step is grafts of poly(glycidylmethacrylate) (PGMA) chains to PTFE membrane surfaces through a surface-initiated free-radical polymerization, the second one is incorporation of PNIPAAm chains to PGMA segments through the addition reaction between the epoxide groups of PGMA and the amine groups of amino-terminated PNIPAAm. The chemical structures of the surface-modified PTFE membranes have been characterized with FTIR and XPS. The studies on their surface morphology have been carried out with SEM and AFM. The modified PTFE membranes display surface hydrophilicity and show a water flux of 7.6 kg m^{-2} h^{-1} at 25 °C and a 2-atm pressure drop. The water flux of the membrane at 40 °C is 34 kg m^{-2} h^{-1}, which is about 4.5 folds of that measured at 25 °C, demonstrating the temperature-responsive property of the PNIPAAm-modified PTFE membrane.

1. Introduction

Fluoropolymers, which have good mechanical properties and outstanding chemical stability, are one of the promising materials for filtration membranes. Poly(vinylidene fluoride) (PVDF) could be the most studied fluoropolymer for membrane application. Recently, poly(tetrafluoroethylene) (PTFE) also receives research attentions owing to their attractive properties such as excellent chemical resistance, high thermal stability, and good mechanical properties. Nevertheless, the applications of PTFE have been limited owing to its surface inertness and hydrophobicity. Hence, surface modification and functionalization are necessary and critical for PTFE to be applied to membrane separations [1]. Yamada et al. [2] prepared 2-(dimethylamino)ethyl methacrylate-modified PTFE membranes and studied their performance of protein separations. Incorporation of poly(ethylene glycol) (PEG) chains to PTFE membrane surfaces was also reported. The PEGylated PTFE membranes were endowed with surface hydrophilicity and protein repulsion ability [3,4]. Beside protein separations, surface-modified PTFE membranes have also been utilized in pervaporation separation processes [5–8]. As a result, the membranes displayed improved operation stability and separation performance.

Environment-responsive membranes having controllable permeation properties are attractive for some applications [9–13]. The most studied environment-responsive membranes are temperature-sensitive membranes. One general approach to bring the temperature-responsive characteristic to a membrane is incorporation of poly(N-isopropylacryamide) (PNIPAAm) chains to the membrane structure [14–18]. The chain conformation of PNIPAAm changes at the low critical solution temperature (LCST, about 32 °C) of PNIPAAm. This feature enables the permeation rates of the PNIPAAm-containing membranes changing with temperatures around the LCST of PNIPAAm. Yamada and coworkers [19–22] prepared PNIPAAm-grafted PTFE membranes by means of plasma treatments and photografting polymerization. Burillo and coworkers [23,24] reported their works on poly(acrylic acid) and PNIPAAm-modified PTFE membranes. The obtained membranes displayed temperature-induced changes of water contact angles, representing the thermo-responsive behavior of the membranes. Nevertheless, the studies on the PNIPAAm-modified PTFE membranes were rudimentary.

The PNIPAAm amount of PNIPAAm-modified PTFE membrane is critical for the thermo-sensitivity of the membrane [22,25,26]. A membrane has increased PNIPAAm amounts would display relatively high thermo-sensitivity. Building branched polymer brushes on membrane surfaces is an effective approach to increase the amounts of polymer chains on the surface-modified membranes. Meanwhile, branched polymer structures could also bring some distinctive physical and chemical properties to the surface-modified membranes [27–29]. Nevertheless, to our best knowledge, branched-PNIPAAm-modified PTFE membranes have not been ever reported. Therefore, in the present

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* Corresponding author. Tel.: +886 3 2654130; fax: +886 3 2654199.
E-mail address: ylliu@cycu.edu.tw (Y.-L. Liu).

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study we explore the preparation and characterization of branched-PNIPAAm-modified porous PTFE membranes as well as the temperature-controllable permeation rates of the membranes. The branched PNIPAAm chains change the PTFE membrane surface from hydrophobic to hydrophilic and endow the membrane a water flux of about 7.6 kg m^{-2} h^{-1} at 25 °C and a 2-atm pressure drop. While increasing the temperature to 40 °C, the water flux of the membrane increases to 34 kg m^{-2} h^{-1}, which is about 4.5 folds of the value measured at 25 °C. The temperature-induced change in the water permeation fluxes of the membrane demonstrates its thermo-responsive property.

2. Experimental

2.1. Materials

Expanded porous PTFE membranes with a thickness of 500 μm and pore sizes of 0.24 μm (diameter) were received from Yu-Min-Tai Co., Ltd., Taiwan. Glycidylmethacrylate (GMA Merck Co., 98 + %) was used as received. NIPAAm (TCI Co., Japan, 99%) was purified by recrystallization in hexane and acetone (50/50, v/v) prior to use [18]. 2-Aminoethanethiol hydrochloride (AET-HCl) and azobisisobutyronitrile (AIBN) received from Acros Co. were used as chain transfer agent and initiator, respectively, for the preparation of amino-terminated PNIPAAm. N,N-dimethylformamide (DMF, Fluka Chemie AG) was reluxed with potassium hydroxide and distilled prior to use. N-methyl-2-pyrrolidone (NMP, Fluka Chemie AG) was dehydrated with 4 Å molecule seives.

2.2. Characterization

Fourier transform infrared (FTIR) spectra of the membrane surfaces were recorded with a PerkinElmer Spectrum One FTIR equipped with an attenuated total reflectance (ATR) accessory. Scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 field-emission SEM. X-ray photoelectron spectroscopy (XPS) analysis was conducted with a VG MICROTECH MT-500 ESCA (British) using a Mg Kα line as a radiation source. The background pressure in the analytical chamber was 1.0×10^{-5} Pa. Atomic force microscopy (AFM) images were acquired with a JPK Instruments AG multimode NanoWizard equipped with a NanoWizard scanner. A Si cantilevel of about 320 kHz resonant frequency from JPK was used for tapping-mode AFM. The environmental temperature in AFM measurement is around 25 °C. Water contact angles were measured with an angle-meter (Automatic Contact Angle Meter, Model CA-VP, Kyowa Interface Science Co., Ltd., Japan) at room temperature (around 25 °C). Distilled water (5 μL) in different temperatures was dropped on the sample surface at 10 different sites. The average of 10 measured values for a sample was taken as its water contact angle.

2.3. Synthesis of amino-terminated poly(NIPAAm) (PNIPAAm-NH$_2$)

PNIPAAm-NH$_2$ was synthesized from the free-radical polymerization of NIPAAm according to the reported method [30]. A solution of NIPAAm (10.1 g) in 55 mL DMF was charged into a 100 mL round-bottom flask. After addition of AIBN (9.2 mg) and AET-HCl (40 mg), the reaction system was degassed with the frozen-and-thaw process for three times. The polymerization reaction was then performed at 70 °C for 24 h under a nitrogen atmosphere. PNIPAAm-NH$_2$ was obtained with precipitation from excess diethyl ether and purified by repeated dissolution–precipitation process three times. The product was then dried in vacuum at room temperature (yield: 94%).

2.4. Preparation of poly(GMA) grafted PTFE (PTFE-g-PGMA) film

PGMA chains have been incorporated to PTFE membrane surfaces through the surface-initiated polymerization [29]. Surface treatments on porous PTFE membranes were performed with a hydrogen plasma (Dressler HF-Technik GmbH, Germany; model CESAR-1310) under the conditions of a hydrogen mass flow rate of 10 sccm (standard cm^3/min), a radio frequency of 13.56 MHz, a power of 50 W, a pressure of 0.1 Torr, and a reaction time of 180 s. The plasma-treated PTFE membranes were immersed in 80 mL isopropanol (IPA). A continuous O_3/O_2 mixture stream (flow rate: 6 L/min; O_3 concentration: 28 g/m^3) generated from an ozone generator (Ozone Group, Taiwan) was bubbled through the liquid at room temperature for about 15 min. The liquid was icy cooled. PTFE membranes were draw out and then dried at room temperature under vacuum.

The PTFE membranes were then introduced to a solution of GMA in 1,4-dioxane (25 wt%, 40 mL) in a 100 mL round-bottom flask. The reaction system was bubbled with an argon stream for 30 min and then reacted at 80 °C for 24 h. The PTFE membranes were draw out, washed with 1,4-dioxane, and dried under vacuum at room temperature. The PGMA graft yield (GY, μg cm^{-2}) of the PTFE-g-PGMA membrane was calculated from the weight differences of the PTFE membrane before and after graft-polymerization and the PTFE membrane area. The obtained PTFE-g-PGMA sample has a PGMA GY of 238 μg cm^{-2}.

2.5. Incorporation of PNIPAAm chains to PTFE-g-PGMA

PNIPAAm-NH$_2$ (1.5 g) was dissolved in 35 mL NMP. PTFE-g-PGMA membranes were immersed in the solution. The system was then allowed to react at 80 °C for 3 h. In the reaction, PNIPAAm chains added to PTFE-g-PGMA membranes through the addition reaction between the amino groups of PNIPAAm and the epoxide groups of PGMA. The PTFE membranes were draw out, washed with water, and dried under vacuum at 50 °C for 24 h. The obtained samples were coded as PTFE-g-(PGMA/PNIPAAm). The membrane has a PNIPAAm GY of about 163 μg cm^{-2}.

2.6. Water flux measurement

Water fluxes of the membranes were measured with a dead-end filtration cell at 2 atm trans-membrane pressure and various temperatures. The effective membrane area is 7.0 cm^2. The permeating water was collected in a baker place on an electronic balance. The collected mass versus time data were collected and differentiated numerically to give the flux values [31].

3. Results and discussion

3.1. Preparation of PTFE-g-(PGMA/PNIPAAm) membranes

Branched PNIPAAm chains have been incorporated to porous PTFE membrane surfaces through a two-step reaction (Fig. 1). The first step is to grow up PGMA chains on PTFE membrane surfaces through the plasma-induced grafting polymerization of GMA. In the second step, PNIPAAm chains react to the grafted PGMA chains through the addition reaction between the epoxide groups of PGMA chains and the amine groups of the amino-terminated PNIPAAm chains. The amount of PGMA grafted on the PTFE membrane surface is 238 μg cm^{-2}, which is determined from the weight difference of the PTFE membrane before and after PGMA grafting polymerization. The amount of PNIPAAm of the PTFE-g-(PGMA/PNIPAAm) membrane is 163 μg cm^{-2}.

Fig. 2 shows the FTIR spectra of the pristine and the surface-modified PTFE membranes. The pristine PTFE membrane exhibits typical absorption peaks at about 1202 and 1146 cm^{-1}. Besides