Surface Modification of Microporous Polypropylene Membranes by Plasma-Induced Graft Polymerization of α-Allyl Glucoside

ARTICLE *in* LANGMUIR · JULY 2003

Impact Factor: 4.46 · DOI: 10.1021/la0345486

Surface Modification of Microporous Polypropylene Membranes by Plasma-Induced Graft Polymerization of α-Allyl Glucoside

Rui-Qiang Kou,† Zhi-Kang Xu,*,† Hong-Tao Deng,† Zhen-Mei Liu,† Patrick Seta,‡ and Youyi Xu†

Institute of Polymer Science, College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, People's Rebublica of China, and Institut Européen des Membranes, UMR CNRS n°5635, 34293 Montpellier, Cedex 05, France

Received March 31, 2003. In Final Form: May 29, 2003

To change the surface property from hydrophobic to hydrophilic and to improve the antifouling property, the N_2-plasma-induced graft polymerization of sugar-containing monomer [α-allyl glucoside (AG) in this work] was carried out on microporous polypropylene hollow fiber membranes (PPHFMs) for the first time. The chemical and morphological changes of the membrane surface were confirmed by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy, pure-water contact-angle, and protein adsorption measurements. It was found that the AG grafting degree increased slightly with the increase of AG monomer concentration for coating and adsorption on the membrane surface, and then it decreased when the AG concentration exceeded 0.25 g/mL. The static contact angle of pure water on the grafted membrane decreased significantly from 120 to 36° with the increase of the AG grafting degree from 0 to 3.46 wt %, which indicated that the membrane surface was distinctly changed from hydrophobic to hydrophilic. Most importantly, the contact-angle measurements also revealed that the hydrophilicity was permanent, and no hydrophobic recovery was observed. The pure-water flux of PPHFMs grafted with 2.50 wt % AG reached tremendously to 3.82×10^3 kg/(m^2·h). Furthermore, modification by AG grafting made the membrane surface less susceptible to the adsorption of bovine serum albumin. The modified membranes also give high flux recoveries after cleaning, indicating that the antifouling property of the membrane was improved.

Introduction

It is well recognized that the surface chemical and physical properties play a dominant role in determining the separation characteristics of membranes.[1,2] For commercial applications such as aqueous solution treatment and bioseparation, hydrophilic and antifouling membrane surfaces are normally favored. Therefore, there has been much interest in developing surface treatment methods to modify the chemical and physical properties of membrane materials.[3−21] In fact, surface modification of membranes is thought to be equally as important to the membrane industry as membrane material and process development. One of the simplest methods is to treat the membranes with a surfactant or impregnate them with a polymer solution and then evaporate the solvent. However, it is difficult to sustain the surfactant for long time with repeated uses because the surfactants are only physically adsorbed and do not bind chemically to the surface of the membranes. In the past 10 years, therefore, more complex and advanced technologies have been used to modify or improve the surface properties of membranes. Among them, surface graft polymerization is one of the most commonly used methods, which includes radical,[3−7] radiation,[8−10] plasma,[11−14] and UV[15−21] initiated graft polymerization. Typical monomers used for this purpose include AA, acrylamides, various acrylates or methacrylates, *N*-vinyl pyrrolidone, 4-vinyl-pyridine, and so on. However, one major limitation for this method is that the hydrophilicity of the modified membranes does not reach the desirable level with a low grafting degree, while at a relatively high grafting degree, the membrane pores are usually blocked by the grafted chains.[5−7] Pore blocking causes an obvious decrease for the water permeation of

* To whom all correspondence should be addressed. E-mail: xuzk@ipsm.zju.edu.cn.

† Zhejiang University.

‡ Institut Européen des Membranes.

(1) Zeman, L. J.; Zydney, A. *Microfiltration and Ultrafiltration: Principles and Applications*; Marcel Dekker: New York, 1996.

(2) Lloyd, D. R., Ed. *Material Science of Synthetic Membrane*; ACS Symposium Series 269; American Chemical Society: Washington, DC, 1985.

(3) Carroll, T.; Booker, N. A.; Meier-Haack, J. *J. Membr. Sci.* **2002**, *203*, 3.

(4) Wang, Y.; Kim, J.-H.; Choo, K.-H.; Lee, Y.-S.; Lee, C.-H. *J. Membr. Sci.* **2000**, *139*, 269.

(5) Gabriel, E. M.; Gillberg, G. E. *J. Appl. Polym. Sci.* **1993**, *48*, 2081.

(6) Garg, D. H.; Lenk, W.; Berwald, S.; Lunkwitz, K.; Simon, F.; Eichhorn, K.-J. *J. Appl. Polym. Sci.* **1996**, *60*, 2087.

(7) Xu, Z.-K.; Wang, J.-L.; Shen, L.-Q.; Meng, D.-F.; Xu, Y.-Y. *J. Membr. Sci.* **2002**, *196*, 221.

(8) Kang, J. S.; Shim J. K.; Huh, H.; Lee, Y. M. *Langmuir* **2001**, *17*, 4352.

(9) Shim, J. K.; Na, H. S.; Lee, Y. M.; Huh, H.; Nho, Y. C. *J. Membr. Sci.* **2001**, *190*, 215.

(10) Kim, M.; Saito, K. *Radiat. Phys. Chem.* **2000**, *57*, 167.

(11) Liang, L.; Shi, M.; Viawanathan, V. V.; Peurrung, L. M.; Young, J. S. *J. Membr. Sci.* **2000**, *177*, 97.

(12) Yamaguchi, T.; Suzuki, T.; Kai, T.; Nakao, S. *J. Membr. Sci.* **2001**, *194*, 217.

(13) Wavhal, D. S.; Fisher, E. R. *J. Membr. Sci.* **2002**, *209*, 255.

(14) Wavhal, D. S.; Fisher, E. R. *Langmuir* **2003**, *19*, 79.

(15) Piletsky, S.; Matuschewski, H.; Schedler, U.; Wilpert, A.; Piletska, E.; Thirle, T. A.; Ulbricht, M. *Macromolecules* **2000**, *33*, 3092.

(16) Ulbricht, M.; Richau, K.; Kamusewitz, H. *Colloids Surf., A* **1998**, *138*, 353.

(17) Pieracci, J.; Crivello, J. V.; Belfort, G. *J. Membr. Sci.* **1999**, *156*, 223.

(18) Pieracci, J.; Crivello, J. V.; Belfort, G. *Chem. Mater.* **2002**, *14*, 256.

(19) Ma, H.; Kakim, L. F.; Bowman, C. N.; Davis, R. H. *J. Membr. Sci.* **2001**, *189*, 255.

(20) Ma, H.; Bowman, C. N.; Davis, R. H. *J. Membr. Sci.* **2000**, *173*, 191.

(21) Peng, T.; Cheng, Y.-L. *Polymer* **2001**, *42*, 2091.

10.1021/la0345486 CCC: $25.00
Published on Web 07/08/2003

the porous membranes.[5−6] Nevertheless, if the grafted chains are chemical- or thermosensitive, "smart" (valve) membranes can be prepared by this method.[11]

It is envisaged that using the derivatives of native substances existing in the biological systems (such as phospholipid and carbohydrates) to modify those hydrophobic membranes can overcome this problem. Because carbohydrates exist in many forms and play important roles in living systems, their highly hydrophilic character together with their innate compatibility with biomolecules has led to considerable interest in their polymer syntheses.[22−26] Besides their versatile potentials in the fields of medicine and biotechnology, these polymers are expected to serve as useful functional materials, such as nonionic surfactants, surface modifiers, hydrogels, and chiral templates, for asymmetric synthesis and optical resolution of organic compounds.

To our knowledge, no data have been reported to date for membrane surface modification with the graft polymerization of the sugar-containing monomer. In this paper, therefore, α-allyl glucoside (AG), which can be synthesized simply, was grafted on a hydrophobic microporous polypropylene (PP) membrane by a simple two-step plasma treatment method. First, the PP membrane was immersed into an AG solution for a certain time to coat AG physically on the membrane surface. Then, the coated AG was grafted chemically onto the PP membrane surface by N_2-plasma radiation. The chemical and morphological changes of the membrane surface were studied. The grafted AG polymer chains are highly hydrophilic due to the multiple hydroxyl groups in each sugar moiety. Especially, the hexacyclic glucoside groups are large enough and difficult to be rotated or buried into the interior of the PP membrane. Therefore, an excellent and permanent hydrophilicity can be achieved.

Experimental Section

Materials. Microporous hydrophobic PP hollow fiber membranes were prepared with a melt-extruded/cold-stretched method in our lab.[7] The inner and outer diameters of this hollow fiber were 240 and 290 μm, respectively, with a porosity of 40−50% and an average pore diameter of 0.070 μm. Before the surfaces of PPHFM were modified, they were washed with acetone to remove any chemicals and wetting agents adsorbed on the membrane surfaces, dried in a vacuum oven at room temperature for 24 h, and then stored in a desiccator before use. *N*,*N*-Dimethylformamide (DMF) was a commercial product and was purified by distillation under a reduced pressure. Allyl alcohol, anhydrous glucose, and tris(hydroxymethyl)aminomethane were used as received without further purification. AG was synthesized according to the method reported by Talley[27] et al. The chemical structure is shown in Figure 1. Bovine serum albumin (BSA, pI = 4.8, M_w = 66 kDa) was purchased from Sino-American Biotechnology Co. and used as received.

Modification of PP Membranes. A typical two-stage procedure was used for surface modification. First, polypropylene hollow fiber membranes (PPHFMs) were dipped into an AG solution of DMF for a predetermined time, and the solvent was evaporated in a vacuum oven. Then, the coated AG monomer was grafted chemically on the membrane surface by N_2-plasma radiation. The second step was carried out in a glow-discharge plasma reactor connected with a diffusion pump and two rotary pumps. A tubular-type Pyrex reactor (10 × 150 cm) was rounded with a pair of copper electrodes. These two electrodes were powered through a matching network by a 13.56 MHz radio frequency generator. The PPHFMs were placed in the middle of the reactor tube. On the basis of systematic experiments considering the membrane damage and monomer grafting degree induced by the plasma, 100 W was chosen as the applied radio frequency power for all the experiments described here. The entire system was first evacuated to a pressure of ~3.76×10^{-5} Pa (5 mTorr), and N_2 gas was purged into it, a minimum of three times. By adjusting the gas flow rate, the pressure in the reactor was then set to 4.51×10^{-4} Pa (60 mTorr) and the plasma was run for a predetermined time. The N_2-plasma treatment time was varied from 5 to 40 min, but each membrane sample was retained in the reactor to keep the grafting reaction time at 60 min. After this, the modified PPHFM was taken out from the reactor, washed with excess water and acetone to remove any residual monomer and AG homopolymer, and dried in a vacuum oven at 50 °C to constant weight. The grafting degree, D_g, was calculated by following equation:

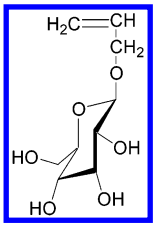

Figure 1. Molecular structure of AG.

$$D_g = (W_t - W_0)/W_0$$

where W_t is the mass of the membrane after grafting and drying and W_0 is the mass of the nascent membrane. All the results were the average of two parallel experiments. The standard error for the result is below 10% of the average value.

Structure Analysis and Properties Measurement. To investigate the changes in chemical structure between the unmodified original PPHFM and the AG-grafted membranes and to confirm that the poly(α-allyl glucoside) formed on the surface of the PPHFM, Fourier transform infrared spectroscopy (FT-IR; Vector 22 FT-IR, Brucker Optics, Switzerland) with an attenuated total reflection (ATR) unit (KRS-5 crystal, 45°) was used. X-ray photoelectron spectroscopy (XPS) spectra of virgin and grafted membranes were also recorded with a PHI 5000C XPS spectrometer (Perkin-Elmer Instruments, U.S.A.) using a monochromatic Al Kα X-ray source at a 45° take-off angle. The analysis of the high-resolution XPS spectra for the unmodified and modified membranes was based on the reference measurements of Beamson and Grigg.[28] In all cases, a Gaussian peak shape was used. All the spectra were charge corrected for the C(1s) peak at 284.7 eV. Scanning electron microscopy (SEM) images of virgin and grafted membranes were taken with a Hitachi S-570 microscope operated at 20 kV. All the samples were coated with a 20-nm gold layer before SEM analysis.

Static water contact angles of the membrane surface were measured by the sessile drop method at 25 °C under an atmosphere of saturated water vapor with a contact angle goniometer (KRÜSS DSA10-MK, Germany) equipped with video capture. The use of video capture for measuring the contact angle of porous materials has been discussed recently by Wavhal and Fisher.[13−14] Following the reported process, comparison of these values between samples provides a semiquantitative measure of the differences in the wettabilities for porous membranes and, to a certain extent, removes issues associated with porous media. In a typical acquisition, a water drop (~0.8 μL) was dispensed on the membrane surface. Then, an image was recorded every 2 s, and a water contact angle was determined for each image with the imaging software. The contact angle as a function of the age of the drop was plotted to determine a constant value. Unless

(22) Yamada, K.; Minoda, M.; Miyamoto, T. *Macromolecules* **1999**, *32*, 3553.
(23) Jia, W.; Ikuyoshi, T. *Macromolecules* **2001**, *34*, 4294.
(24) Carneiro, M. J.; Fernandes, A.; Figueiredo, C. M.; Fortes, A. G.; Freitas, A. M. *Carbohydr. Polym.* **2001**, *45*, 135.
(25) Manning, D. D.; Hu, X.; Beck, P.; Kiessling, L. L. *J. Am. Chem. Soc.* **1997**, *119*, 3161.
(26) Sakamoto, N.; Suzuki, K.; Kishida, A.; Akashi, M. *J. Appl. Polym. Sci.* **1998**, *70*, 965.
(27) Talley, E. T.; Vale, M. D.; Yanovsky, E. *J. Am. Chem. Soc.* **1945**, *67*, 2037.
(28) Beamson, G.; Grigg, D. *High Resolution of XPS of Organic Polymers*; Wiley: New York, 1992.

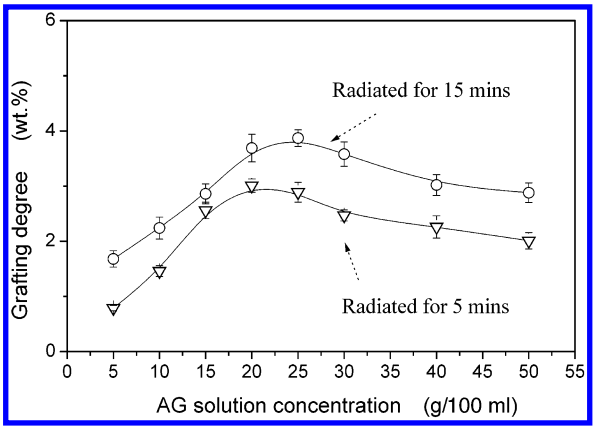

Figure 2. Effect of AG concentration on the grafting degree.

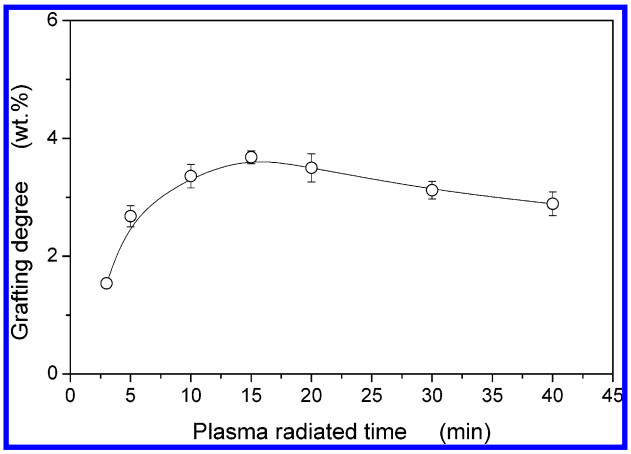

Figure 3. Effect of plasma radiation time on the AG grafting degree (AG concentration: 10 wt %).

otherwise noted, contact-angle measurements were made within 1 hr of the modification and at least 10 contact angles were averaged to get a reliable value.

BSA was used as a model protein to evaluate the protein fouling characteristics of nascent and grafted membranes. In this work, membrane fouling was evaluated by two methods: static BSA adsorption and protein filtration. For the first method, the membranes were immersed in ethanol for 10 min for prewetting and then put into a BSA solution with various concentrations, whose pH was adjusted to 8.0 with 0.1 M Tris-HCl buffer. This buffer can facilitate the hydrophobic interaction and inversely depress the electrostatic binding between the protein and the polymer surface.[29] The mixture was incubated at 30 °C for 24 h to reach an adsorption−elution equilibrium. The amount of protein adsorbed on the membrane surface was calculated from the decreased concentration of the BSA solution. The concentrations of the BSA solutions were determined on the basis of the absorbance at 280 nm using a UV spectroscope. The reported data were the mean values of triplicate samples for each membrane. For the second method, membranes of about 9.08 cm^2 were bundled into a U shape, and their open ends were fastened with epoxy resin to fabricate a module.[7] The module was wetted with ethanol and flushed thoroughly with ultrapure water. Then, ultrapure water at 25 °C was forced to permeate through the membranes at a constant permeation pressure of 0.08 MPa, and the flux, J_0, was measured at equal intervals for 1 h. The membranes were then exposed to 5 mg/mL BSA in a Tris-HCl buffer solution for 1 h without permeation. After that, the permeate flux of the BSA solution, J_p, was then collected at equal intervals at 0.08 MPa also. The membrane was cleaned with caustic by filtering a 0.1 M NaOH solution for 30 min. Then, the membrane module was filled with ultrapure water and shaken for 1 min three times, and the water flux was measured (J_1) to see if the original water flux could be recovered. The mean values of triplicate modules for each membrane with the standard deviation were reported.

(29) Hofstee, B. H. J. *Biochem. Biophys. Res. Commun.* **1975**, *63*, 618.

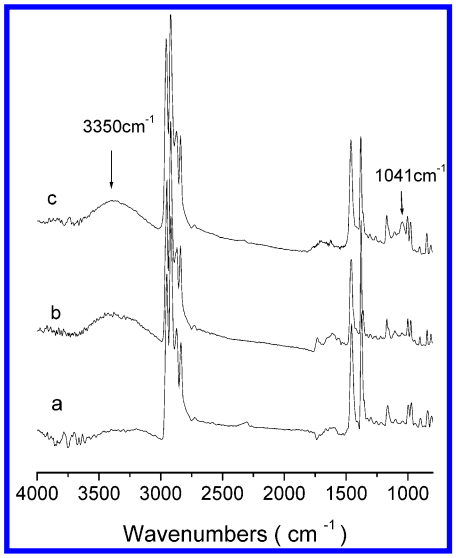

Figure 4. IR spectra of PP membranes (a, nascent PP membrane; b, 1.12 wt % AG-grafted PP membrane; c, 3.46 wt % AG-grafted PP membrane).

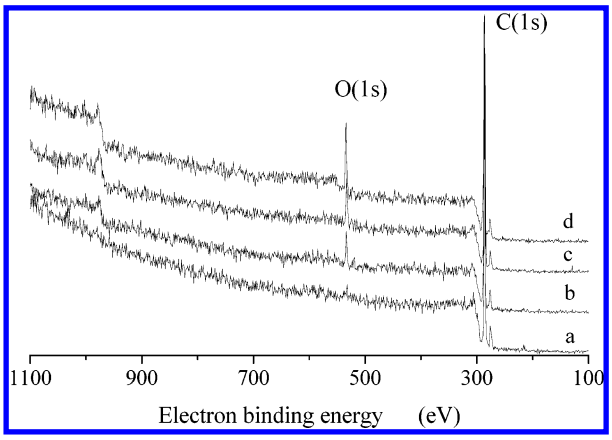

Figure 5. XPS spectra of PP membranes (a, nascent PP membrane; b, 10-min N_2-plasma-treated PP membrane; c, 1.12 wt % AG-grafted PP membrane; d, 3.46 wt % AG-grafted PP membrane).

Results and Discussion

Graft Polymerization of AG. Figure 2 shows the effect of the AG monomer concentration on the grafting degree (D_g). It can be seen that the D_g increased with the increase of AG concentration at first and then decreased when the monomer concentration exceeded 250 g/L. It seems that raising the AG concentration from 50 to 200 g/L increased the amount of monomers adsorbed and coated on the membrane surface, which in turn increased the grafting degree. In our experiments, the PPHFMs were dipped into an AG solution for a predetermined time, and the solvent was evaporated in a vacuum oven before plasma treatment. Therefore, the monomer coated on the membrane surface should contain the adsorbed monomer layer and the residual monomer layer when the solvent of the AG solution filled in the membrane pores was evaporated. Obviously, the thickness of the residual monomer layer increased with increasing the monomer concentration. However, low-temperature plasma techniques are very surface selective. When the monomer layer coated on the membrane surface was thick enough, the reactive sites in

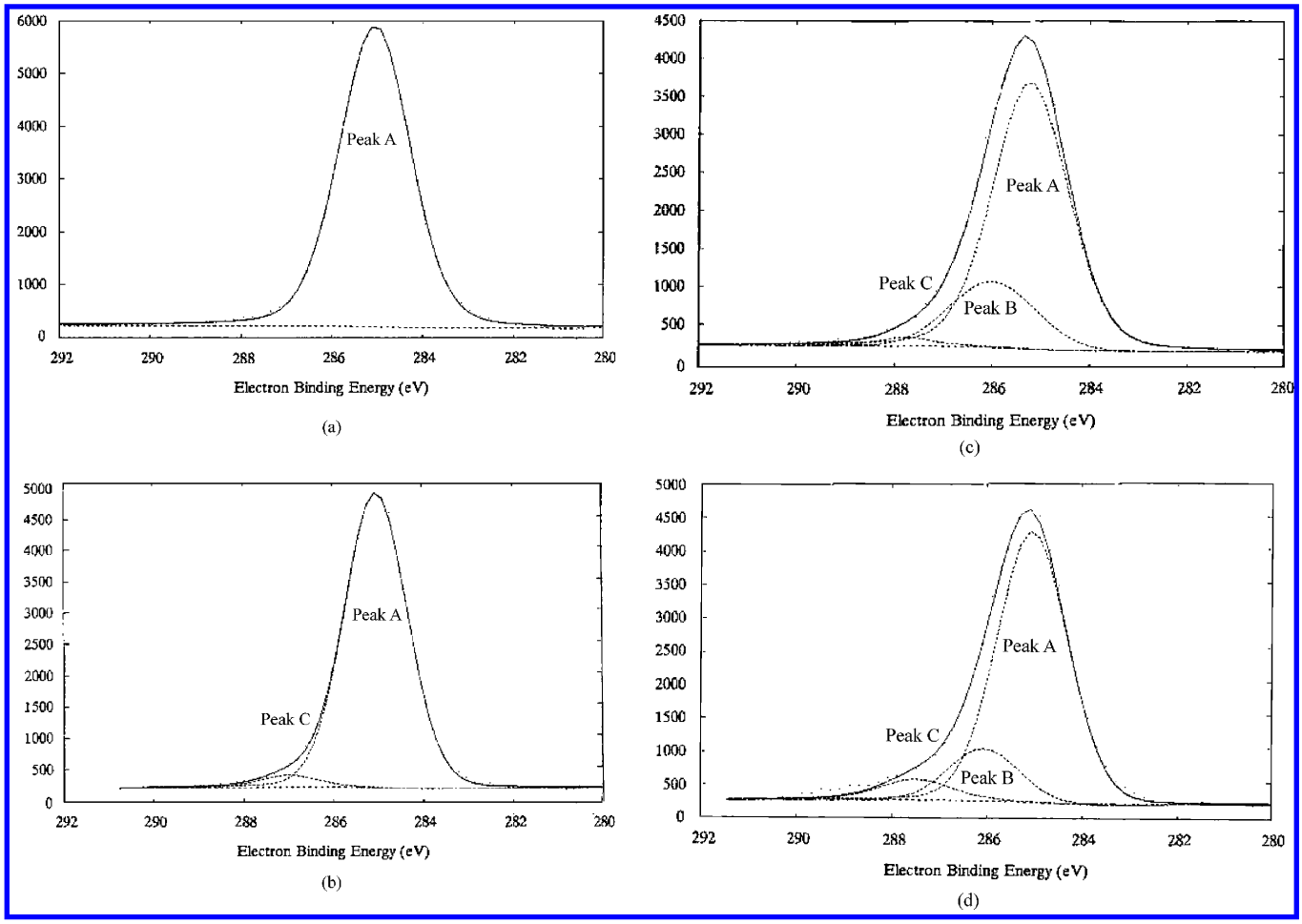

Figure 6. Resolved XPS spectra of C(1s) for PP membranes (a, nascent PP membrane; b, 10-min N_2-plasma-treated PP membrane; c, 1.12 wt % AG-grafted PP membrane; d, 3.46 wt % AG-grafted PP membrane).

the atmosphere could not attack directly on the membrane surface and no active sites were generated on the membrane surface for monomer grafting. The monomers might be only linked with each other. This part of AG was washed away after plasma radiation. With the use of a similar process, cross-linking glucose (20 g of glucose solvated in a 60 mL of ethanol/40 mL of water mixture) on the membrane surface was tried also. However, no weight increase was observed. The results indicated that only a sugar-containing vinyl monomer can be grafted on the PPHFM.

Figure 3 shows the dependence of the grafting degree of AG on the plasma radiation time. It was found that D_g first increased with the plasma radiation time and then decreased slightly when the radiation time exceeded 15 min. This was because with the increase of the plasma radiation time, more active species were produced on the membrane surface and relatively more monomers were grafted on the membrane surface. Nevertheless, the membrane surface was partially etched in the process of plasma radiation at the same time (see Supporting Information). Therefore, a long plasma radiation time indicated an apparent decrease for the grafting degree.

From both Figure 2 and Figure 3, it can also be seen that the highest grafting degree was about 3.5 wt %. This could be ascribed to the relatively poor polymerization ability of the monomer due to its solid state on the membrane surfaces. In fact, a higher grafting degree normally filled or blocked the pores of the porous membrane, which was undesirable.[7] Therefore, to some extent, a low grafting degree was expected if the hydrophilicity and antifouling properties of the membrane can be improved effectively.

Characterization. Figure 4 depicts the FT-IR ATR spectra of the nascent and modified PP membranes. There was no absorption peak around 3350 cm^{-1} in the spectrum of the nascent PP membrane. However, one broad absorption band can be seen at 3350 cm^{-1}, and another peak around 1041 cm^{-1} was obvious for the spectra of the grafted PP membrane, which can be attributed to the hydroxyl groups of the AG pendants.

In an attempt to gain further information about the graft polymerization of AG on PP membranes, the composition of the membrane surface was also analyzed by XPS. Because photoelectrons can only escape from a few nanometers underneath solid surfaces, XPS can provide some information about the atoms, their bonding types, and their chemical compositions on the polymer surface. Figure 5 shows the XPS spectra of the nascent and the N_2-plasma-treated membranes as well as the AG-grafted membranes. For the unmodified PP membrane, a major emission peak corresponding to a 284.7-eV binding energy of C(1s) was observed. However, for the modified membrane, an additional emission peak (533.8-eV binding energy) of O(1s) was detected, as is shown in Figure 5b−d. Furthermore, the peak intensity for O(1s) increased with the grafting degree of AG. The high-resolution spectra of the PP membrane corresponding to C(1s) and O(1s) are shown in Figures 6 and 7, respectively, to distinguish the different types of functional groups on the membrane surface. A single symmetry peak A (284.7 eV binding energy) can be observed for C(1s) of the nascent PP

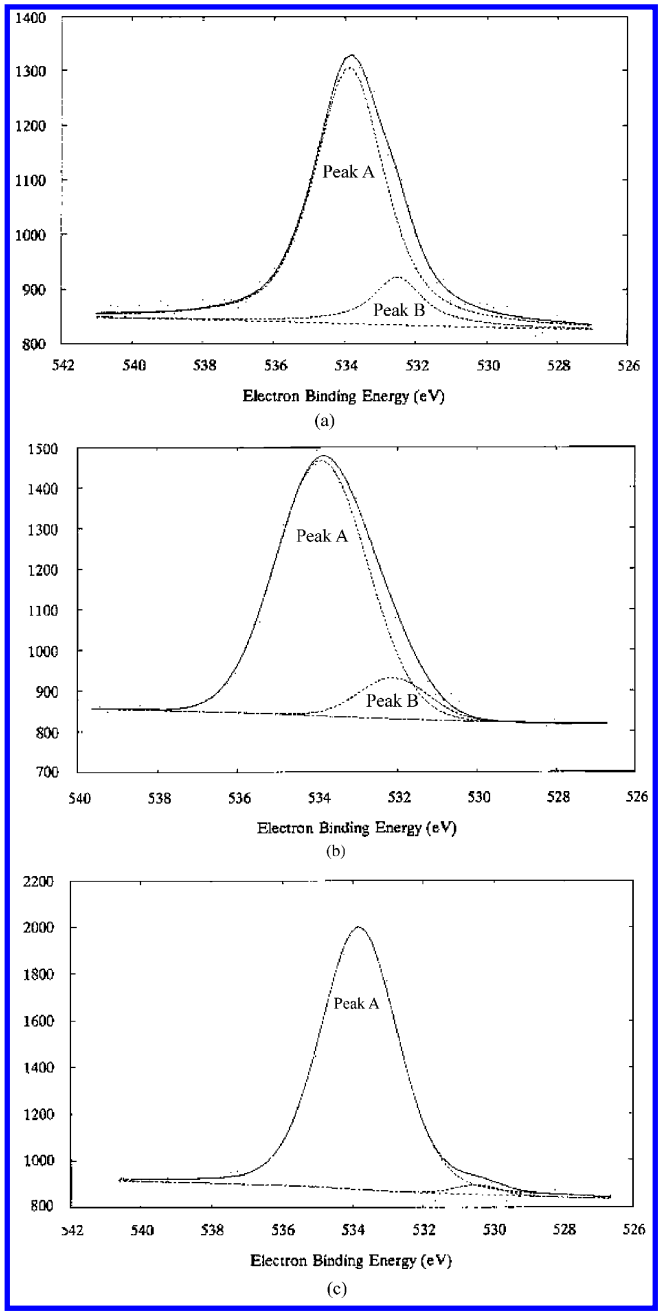

Figure 7. Resolved XPS spectra of O(1s) for modified PP membranes (a, 10-min N_2-plasma-treated PP membrane; b, 1.12 wt % AG-grafted PP membrane; c, 3.46 wt % AG-grafted PP membrane).

membrane, which corresponded to C—H and C—C, as shown in Figure 6a. For the N_2-plasma-treated membrane, as shown in Figure 6b, the C(1s) spectrum can be resolved into two peaks. Peak A at a binding energy of 284.7 eV was assigned to C—H and C—C. Peak C at a binding energy of 287.0 eV corresponding to C—O and/or C═O was caused by exposing the treated membrane to the atmosphere. However, for the AG-grafted membranes (Figure 6c,d), the C(1s) peak contained three peaks corresponding to C—H and C—C (peak A, 284.7-eV binding energy), C—O (peak B, 286.0-eV binding energy), and C═O (peak C, 287.4-eV binding energy). Consistent results can be concluded from the resulting O(1s) spectra. As can be seen from Figure 7, for the N_2-plasma-treated membrane and the AG-grafted membrane with a 1.12 wt % grafting degree, two components at 533.8 eV for C—OH and at about 532.4 eV for —C═O can be resolved. However, for

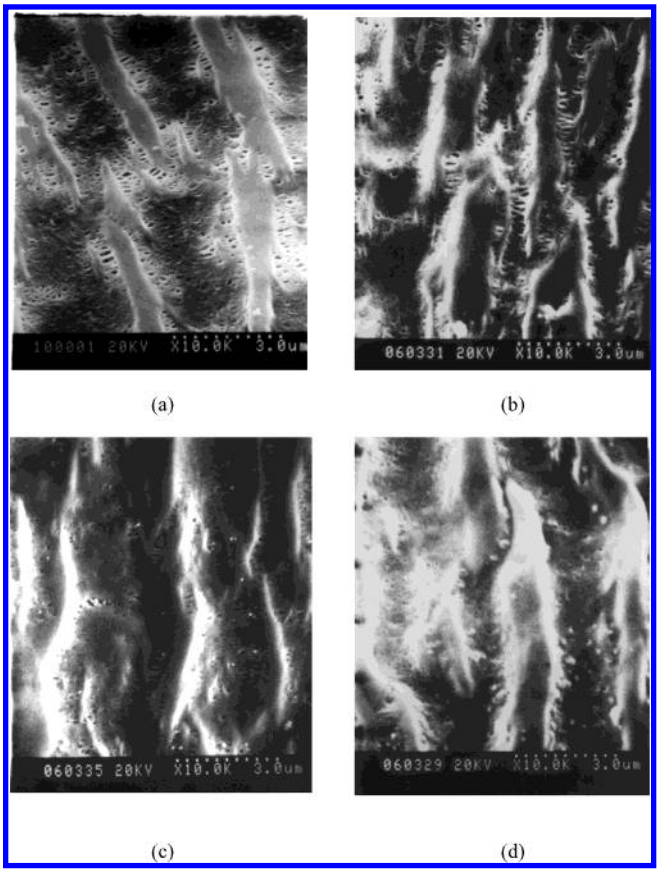

Figure 8. SEM pictures (×10 000) of nascent and modified PP membranes (a, nascent PP membrane; b, 0.82 wt % AG-grafted PP membrane; c, 1.86 wt % AG-grafted PP membrane; d, 3.46 wt % AG-grafted PP membrane).

the AG-grafted membrane with a 3.46 wt % grafting degree, only one main peak corresponding to C—OH can be observed. The small peak located at 530.5 eV might be a noise due to the high sensitivity of XPS.

Additionally, SEM was employed to elucidate the morphology of the membrane surface. Figure 8 shows the SEM pictures of the nascent and modified membranes. For the nascent membrane (Figure 8a), the pores ranged from 0.02 to 0.2 μm in the long dimension and up to 0.1 μm in width. It can be seen from Figure 8b—d that the pore size and the surface porosity were somewhat reduced because the grafted AG chains covered the original surfaces of the membrane.

Contact-angle measurements have been commonly used to characterize the hydrophilicity of polymer surfaces.[7—9,13—14,30] However, such measurements are difficult to interpret for synthetic porous membranes because of capillary forces within pores, contraction in the dry state, heterogeneity, roughness, and restructuring of the surfaces.[31—32] Nevertheless, the relative hydrophilicity or hydrophobicity of each sample can be easily obtained by this measurement. Furthermore, the use of video capture for measuring the contact angles of porous materials has been recently discussed by Wavhal and Fisher.[13—14] Following the reported process, comparison of these values between samples provides a semiquantitative measurement of the differences in the wettabilities for porous membranes and, to a certain extent, removes issues

(30) Cornelissen, E. R.; van den Boomgaard, Th.; Strathmann, H. *Colloids Surf., A* **1998**, *138*, 283.
(31) Taniguchi, M.; Pieracci, J. P.; Belfort, G. *Langmuir* **2001**, *17*, 4312.
(32) Taniguchi, M.; Belfort, G. *Langmuir* **2002**, *18*, 6465.

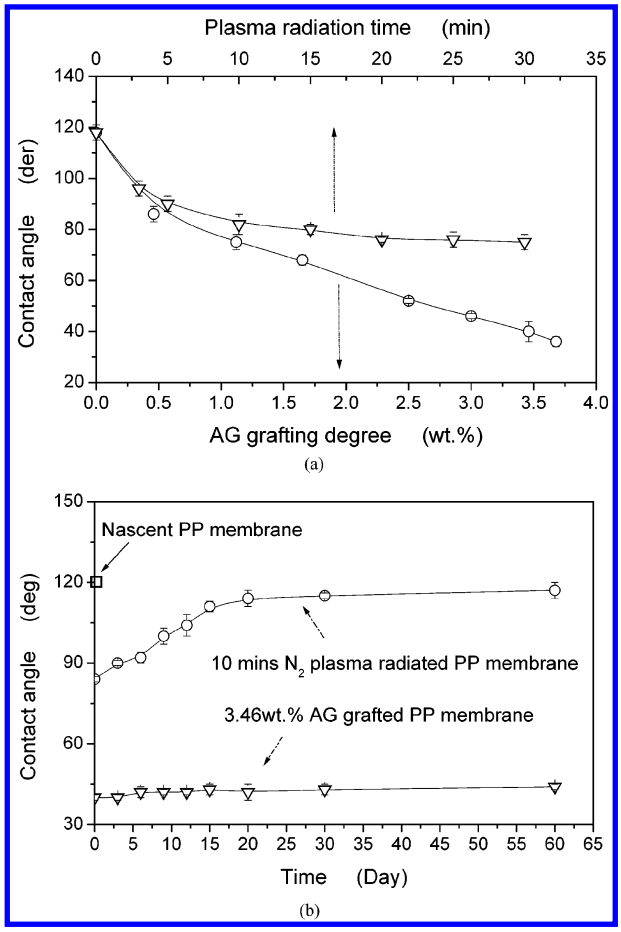

Figure 9. Pure-water contact angle of PP membranes (a, effect of the AG grafting degree and plasma radiation time; b, effect of the shelve time).

associated with porous media. Figure 9a shows the effect of the AG grafting degree and N_2-plasma radiation time on the pure-water contact angle (see also Supporting Information). The increase in the wettability after grafting modification for the membrane surface was evident from the results of the pure-water contact-angle measurement. It was found that the contact angle of PP membranes treated only with N_2 plasma without dip-coating the AG monomer decreased from 118 to 76° and no longer decreased when the plasma radiation time was over 20 min. However, for the AG-grafted membrane, the contact angle decreased to 34° as a result of the promising hydrophilicity of AG grafted on the membrane surface. Especially, the AG-grafted membrane can sustain the permanent hydrophilicity, as can be seen from Figure 9b. The contact angle of the N_2-plasma-treated membrane increased with time and became almost the same as the nascent membrane over 2 weeks. This phenomenon, called aging or "hydrophobic recovery", was one of the major drawbacks of plasma treatment. The physicochemical characteristics of the modified membrane surfaces, including surface composition, can be time dependent because the polar groups generated by the plasma treatment can reorientate in the surface region and bury in the interior of the membrane surfaces.[13] On the other hand, the contact angle of the AG-grafted membrane was unchanged over 2 months because the rotation of the polymer chains was prevented by the grafted AG chains; therefore, the hydrophilicity of the AG-grafted membrane can be sustained permanently.

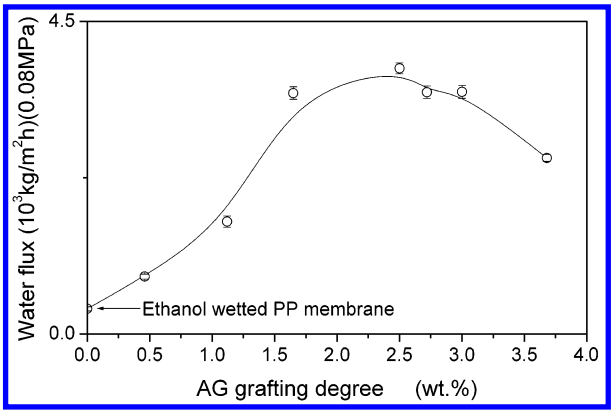

Figure 10. Effect of the AG grafting degree on the permeation flux of pure water at 25 °C and 0.08 MPa.

Permeation and Antifouling Properties. The measurements of pure-water permeability were carried out for typical modified membranes, and the process was repeated five times for each membrane module. The data were compared with those of nascent, ethanol-wetted, and acrylic acid (AA)-grafted membranes[7] in Figure 10 and Table 1,. The nascent membrane cannot let water flow across. The flux of the ethanol-wetted membrane was 0.42 $\times$ 10^3 kg/(m^2·h), while it increased sharply to 4.35 $\times$ 10^3 kg/(m^2·h) with the increase of the AG grafting degree. Especially, the water flux of the AG-grafted membranes was more stable with time than that of the ethanol-wetted membrane. However, the flux decreased when the grafting degree exceeded 2.5 wt %. This could be explained on the basis that the grafted AG plugged the pores of the membrane and, therefore, reduced the effective free cross section for water flow. Compared with that of the AA-grafted membranes, although the measurements were not carried out at the same permeation pressure, the data listed in Table 1 show us that the water permeation flux decreased according to the sequence of AG-grafted membranes $\gg$ ethanol-wetted membranes > AA-grafted membranes. This can be ascribed to the higher hydrophilicity of the AG-grafted membranes (contact angle 40°) than that of the AA-grafted membranes.

For efficient use in various applications, membrane fouling should be reduced as much as possible, especially for bioseparation. Usually, a hydrophilic surface will suppress the adsorption of biomolecules or cells on the membrane and reduce fouling. In this work, BSA was used as a model protein to evaluate the protein fouling

Table 1. Permeation and Antifouling Properties of PPHFMs at 25 °C

membrane	contact angle (deg)	J_{w0} [kg/(m^2·h)]	J_p [kg/(m^2·h)]	J_{w1} [kg/(m^2·h)]	RFR[c]	FRR[d]
ethanol-wetted[7]		49 ± 0.06[a]				
ethanol-wetted		364 ± 30[b]	102 ± 8	226 ± 12	72	62
2.95 wt % AA grafted[7]	75	4.3 ± 0.02[a]				
1.12 wt % AG grafted	75	1620 ± 82[b]	664 ± 45	1426 ± 72	59	88
2.50 wt % AG grafted	52	3826 ± 80[b]	1319 ± 52	2875 ± 78	61	85
3.01 wt % AG grafted	46	3488 ± 60[b]				

[a,b] Fluxes were measured at 0.02 MPa and 0.08 MPa, respectively. Shown are the averages plus and minus one standard deviation for three repeats. [c] Calculated from $(1 - J_p/J_{w0}) \times 100$. [d] Calculated from $J_{w1}/J_{w0} \times 100$.

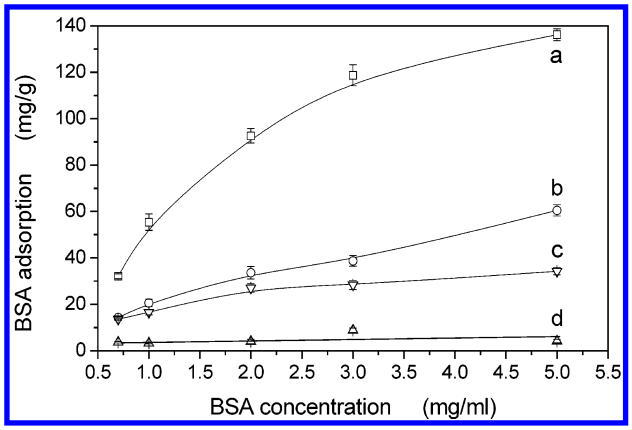

Figure 11. Effect of the AG grafting degree on BSA adsorption on the surface of the PP membranes (a, nascent PP membrane; b, 0.82 wt % AG-grafted PP membrane; c, 1.86 wt % AG-grafted PP membrane; d, 3.46 wt % AG-grafted PP membrane).

characteristics of the nascent and grafted membranes. Figure 11 is the result of BSA adsorption. It was found that the amount of BSA adsorbed on the membrane surface decreased obviously with the increase of the AG grafting degree, and a higher BSA concentration could lead to a slight increase of BSA adsorbed on the AG-grafted membrane with a relatively low D_g. However, when the grafting degree reached 3.46 wt %, it can be seen from Figure 11 that the BSA adsorption on the membrane surfaces kept almost constant. Filtration results of the BSA solution for the virgin and modified membranes are compared in Table 1. It can be seen that the relative flux reductions [defined as RFR (%) = $(1 - J_p/J_{w0}) \times 100$] of the modified membranes after protein fouling were lower than that of unmodified membrane. In addition, the flux recovery ratio [defined as FRR (%) = $(J_{w1}/J_{w0}) \times 100$] for the AG-modified membranes was relative high also. These results demonstrated that the antifouling properties were improved for PPHFMs by the graft polymerization of AG.

Conclusions

AG was grafted onto the surfaces of microporous PPHFMs by dipping the membranes in a monomer solution followed by N_2-plasma treatment. FT-IR ATR and XPS spectra together with SEM pictures indicated the chemical and morphological changes of the modified membranes. The static contact-angle and pure-water permeability measurements revealed that remarkable and permanent hydrophilicity was achieved by grafting sugar-containing polymer on the PP membrane surfaces. The results of BSA adsorption and filtration measurements also indicated that the antifouling property of the membrane was improved.

Acknowledgment. The financial support of the National Natural Science Foundation of China (Grant 20074033) and the High-Tech Research and Development Program of China (Grant 2002AA601230) is gratefully acknowledged.

Supporting Information Available: SEM pictures that demonstrate the effect of N_2-plasma treatment on the membrane morphology and typical dynamic curves for the water contact-angle measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

LA0345486