

Surface Modification of Polypropylene Microporous Membrane by Grafting Acrylic Acid Using Physisorbed Initiators Method

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ABSTRACT: Surface modification of microporous polypropylene (PP) membrane was performed by graft polymerization of acrylic acid using physisorbed initiators method. The factors effecting on the grafting degree such as monomer concentration, reaction temperature and initiator density were determined. The morphological and microstructure changes of the membrane were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and Fourier transform infrared spectroscopy (FTIR). The pure water contact angle, protein adsorbed amount, water flux, and antifouling property of the grafted membrane were investigated. The results indicated that the pore size and porosity of the grafted membrane were reduced and the static contact angle of pure

water on the grafted membrane decreased from 108° to 40° with the increase of grafting degree. The amount of protein adsorbed on the grafted membrane decreased about 30% compared to the virgin polypropylene membrane when the grafting degree was 18.71%. Though the water flux reduced, the flux recovery of the grafted membrane increased 82.66% with the grafting degree 16.0%. The hydrophilic and antifouling property of the grafted membrane also were improved. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3728–3735, 2009

Key words: physisorbed initiator; polypropylene microporous membrane; surface modification; BSA adsorption; antifouling

INTRODUCTION

It is well known that the physical and chemical properties of membrane surface are very important in the membrane industry.^{1–2} As many membrane surfaces are hydrophobic, the pollutants are accessible to deposit on the membrane, which results in reducing the flux and selectivity, increasing the separation cost, it is the main drawback in the extensive use of membranes for microfiltration and ultrafiltration process.^{3–4} So many researchers draw much attention to the surface modification of membranes. In recent years, a large number of methods have been reported for hydrophilic modification of membrane surface including physical and chemical methods.^{5–8} In summary, the physical methods treating the membranes with hydrophilic agents such as alcohols, surfactants or coating with hydrophilic compounds are simple, but the hydrophilicity of the modified membrane is not permanent and changes

easily to hydrophobic after a little time. Surface graft polymerization^{9–11} including plasma, radiation and UV initiated graft polymerization has been regarded as an effective method, which is commonly used and has several advantages. But the plasma treatment is slow and expensive, the irradiation can damage the membrane structure over long time exposures and the UV light is harmful to human health. So these methods are difficult to scale up in industry.

Polypropylene (PP) microporous membranes are widely used in a variety of industrial applications such as wastewater treatment,¹² membrane separation^{13,14} because of its good mechanical, thermal and chemical stability and low cost. However, the hydrophobicity of PP microporous membrane limits its use in the membrane industry. Many methods, such as UV,^{15,16} plasma,^{17–20} γ -ray,^{21,22} and O₃²³ initiated graft polymerization have been used to graft monomers onto the PP microporous membrane resulting in hydrophilic membrane, but the disadvantages of these methods have been discussed in earlier. Hu²⁴ describes a versatile grafting method: physisorbed initiator (1) preadsorb a hydrophobic initiator onto the bulk polymer surface, (2) exploit the polarity disparity between the initiating radicals and an aqueous polymerization medium, and (3) perform

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surface grafting of hydrophilic monomers via physisorbed free radical species. This method offers a new technique for the surface modification of membranes.

In this study, surface modification of polypropylene microporous was performed by graft polymerization of acrylic acid using physisorbed initiators method. The technique used water as solvent instead of organic solution²⁵ or supercritical carbon dioxide,²⁶ it reduced the pollution to the environmental and the cost, and had the great potential to scale up. The effects of graft polymerization conditions on the grafting degree were investigated and the grafted membranes were characterized with ATR-FTIR, SEM, and AFM as well. The amounts of proteins adsorbed and the antifouling were compared between virgin and grafted membranes using a bovine serum albumin (BSA) protein solution.

EXPERIMENTAL

Materials

Flat sheets of polypropylene microporous membrane (Celgard 2400, Celgard Company, North Carolina) was used as the grafting substrate. Its pore size was $125 \times 50 \text{ nm}^2$ with a thickness of $25 \text{ }\mu\text{m}$ and a porosity of 40%. Acrylic acid (AA, Beijing Chemical Reagent Company, A.R. grade, Beijing, China) was used for grafting without purification; Benzoyl peroxide (BPO, Beijing Chemical Reagent Company, A.R. grade, Beijing, China) was recrystallized twice from methanol. Acetone (Tianjin Deen Chemical Reagent Company, A.R. grade, Tianjin, China) was used to wash the PP membrane; Bovine serum albumin (BSA, Sigma, St. Louis, MO) was used for testing the antifouling property of the PP membranes.

Graft polymerization

The PP membranes were cut into a round shape with a diameter of 3 cm and washed with acetone to remove any chemicals, then dried at 30°C for 24 h and stored in a desiccator before using.

The PP membrane was immersed into an acetone solution of BPO (w/v) for 15 min, then dried in a vacuum oven at room temperature for 24 h to get the BPO treated PP membrane. The density of the initiator BPO adsorbed on the PP membranes was calculated from the following equation:

$$\text{initiator density}(d) = (W_b - W_0)/s \quad (1)$$

where W_0 and W_b were the weight of the PP membranes before and after adsorbed BPO respectively, s stands for the area of the PP membranes. A monomer solution of AA with various concentrations in 50 mL water was purged by nitrogen gas for 30 min.

The BPO treated PP membrane was transferred into the sealed glass vessel containing the AA solution and reacted at a temperature $70\text{--}85^\circ\text{C}$ in nitrogen atmosphere. After a desired reaction time, the grafted membrane was taken out and washed with acetone and extracted in a Soxhlet extractor using methanol for 24 h to remove AA homopolymer. The grafted membrane was dried in a vacuum oven at 40°C to constant weight. The degree of grafting was calculated from the following equation:

$$\text{Dg}(\%) = (W_1 - W_0)/(W_0 \times 100) \quad (2)$$

where W_0 and W_1 are the mass of the virgin and grafted PP membrane, respectively.

Characterization

ATR/FTIR (attenuated total reflectance technique) spectra of virgin and grafted membranes were obtained using a Bruker Fesor 27 FTIR (Germany) equipped with ATR cell, 16 scans were taken for each spectrum at a resolution of 4 cm^{-1} . Thermal stability was measured using thermogravimetric analyzer (TG, Shimadzu DT-40, Japan). TGA measurements were performed at the scanning rates of $10^\circ\text{C min}^{-1}$ in the presence of nitrogen gas. Scanning electronic microscopy (SEM) was carried out on AMARY-1000B to investigate the changes in the surface morphology of virgin and grafted membranes. Atom force microscopy (AFM) was conducted with a SPIB 800N microscope (Seriko Instruments, Japan). The water contact angle on the PP membranes was measured using a DATA Physics System (OCA20, Germany). BSA was used as a model protein to evaluate the protein fouling characteristic of the PP membranes. The membrane was immersed in ethanol for 10 min for pre-wetting then put into a BSA solution with different concentration whose pH was adjusted to 8.0 with 0.1M phosphate buffer. An area of 7 cm^2 PP membranes was soaked in 20 mL BSA solution for 24 h at ambient temperature. The amount of protein adsorbed on the membrane surface was obtained from the decreased concentration of the BSA solution, the concentrations of BSA solution were determined on the basis of the absorbance at 280 nm using a UV spectrophotometer (U-3010, Japan).

A dead-end cell filtration was employed to test the water flux of PP membranes. The active membrane area was 7.0 cm^2 . Before the measurements, the PP membranes were wetted with ethanol for 30 min and then precompact at 0.15 MPa for 30 min. The transmembrane pressure was stepwise increased in intervals of about 0.02 MPa and water flux as a function of pressure up to 0.1 MPa was measured. When the pressure was 0.1 MPa, the water flux of the PP membranes was defined as J_0 ,

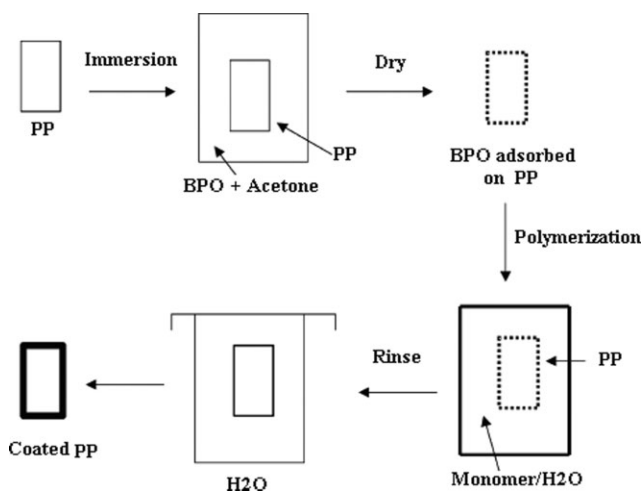


Figure 1 Schematic process of grafting PAA on the surface of PP membrane using physisorbed initiators method.

then the water was replaced of 1 g L^{-1} BSA solution, the BSA flux was denoted as J_p . After the BSA solution filtration, the water flux (J_1) was measured at 0.1 MPa again. The reduction of flux (RF) and flux recovery (FR) were calculated as follows:

$$\text{RF}(\%) = (1 - J_p/J_0) \times 100 \quad (3)$$

$$\text{FR}(\%) = (J_1/J_0) \times 100 \quad (4)$$

RESULTS AND DISCUSSION

Grafting

The schematic process of grafting PAA on the surface of polypropylene membrane using physisorbed initiators method is shown in Figure 1. The hydrophobic initiators were preadsorbed on the bulk surface of PP membranes, exploited the polarity disparity between the initiating radicals and an aqueous polymerization medium, the PAA was grafted on the PP membranes via physisorbed free radical species.

Figure 2 shows the effects of BPO concentration and immersed time on d (initiator density), it can be seen that the d increased with the increase of BPO concentration and the immersed time, and leveled off in 15 min, this is because the PP membranes had reached the adsorption equilibrium after 15 min. Because of the limited pore size and porosity, the maximum d was obtained when the BPO was 10% (w/v) and the immersed time was 15 min.

Figure 3 shows the effect of AA monomer concentration on the degree of grafting (Dg). It is found that Dg increased with the increase of AA concentration and reaction time. This is easy to understand that increasing the AA concentration and reaction

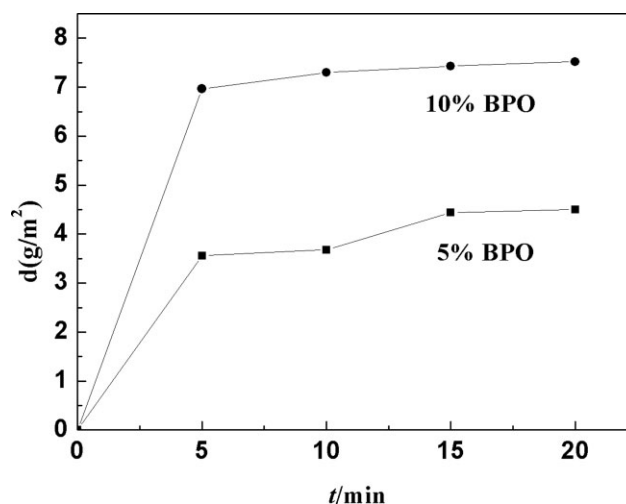


Figure 2 Effects of BPO concentration and immersed time on initiator density (d).

time, much more AA monomer reached to the surface of PP membrane, and reacted with the active sites on the membrane surface, thus more monomer can be grafted onto PP backbone. However, when the AA concentration exceeded 20% (w/v), the Dg did not increase. It might be that the amount of active sites generated on the surface was limited, so the reacted monomer was not infinite. Meanwhile, the viscosity of the monomer solution increased with the increase of monomer concentration, this hindered the diffusion of the AA monomer from the solution to the membrane surface. Therefore, it led to the Dg slow down at higher monomer concentrations.

Figure 4 demonstrates the dependence of grafting degree on reaction temperature. It can be seen from that increasing the reaction temperature gives rise to the enhancement of Dg, on the other hand,

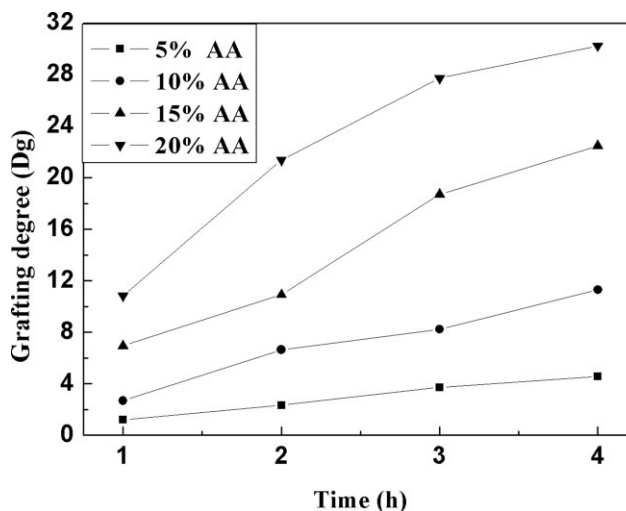


Figure 3 Effect of AA monomer concentration on the degree of grafting ($T = 80^\circ\text{C}$, $\text{BPO} = 3.5 \text{ g cm}^{-2}$).

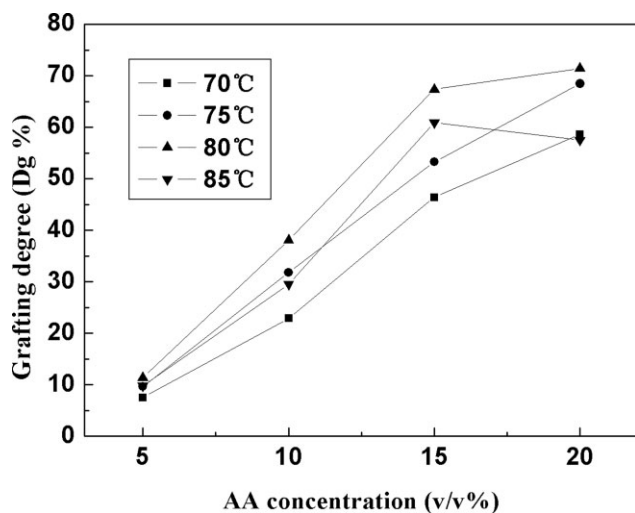


Figure 4 Effect of reaction temperature on the degree of grafting ($t = 4$ h, BPO = 6.9 g cm^{-2}).

maximum Dg was obtained at about 80°C in different AA monomer concentration. This phenomena can be explained that the number of free radicals by the thermodecomposition of the initiator increased at higher temperature, as a result, the active area of the membrane surface become larger, high temperature accelerated the diffusion of the monomer to the membrane surface as well and higher Dg was achieved. However, excessive temperature induced to the growth of the viscosity of solution reducing the diffusion of AA monomer. Therefore, the Dg decreased at 85°C .

The effect of initiator density on the Dg is illustrated in Figure 5. As can be seen, d has a great influence on Dg. Dg increased obviously with the initiator density at first and then decreased when the d was above 7.43 g m^{-2} . This also can be explained that increasing the initiator density, more

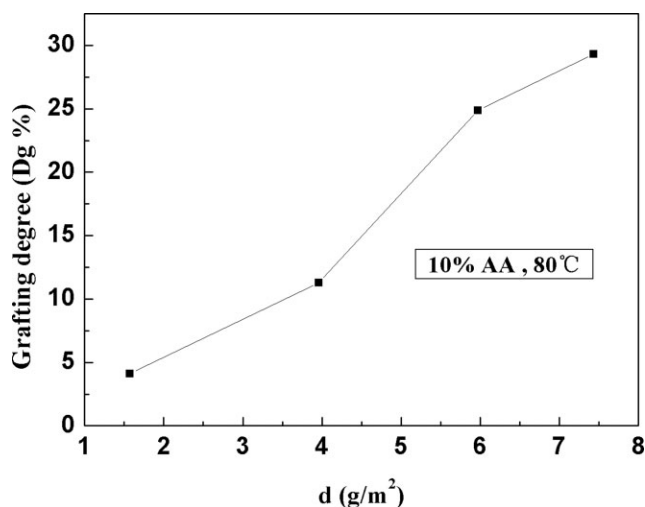


Figure 5 Effect of initiator density on the degree of grafting ($t = 4$ h).

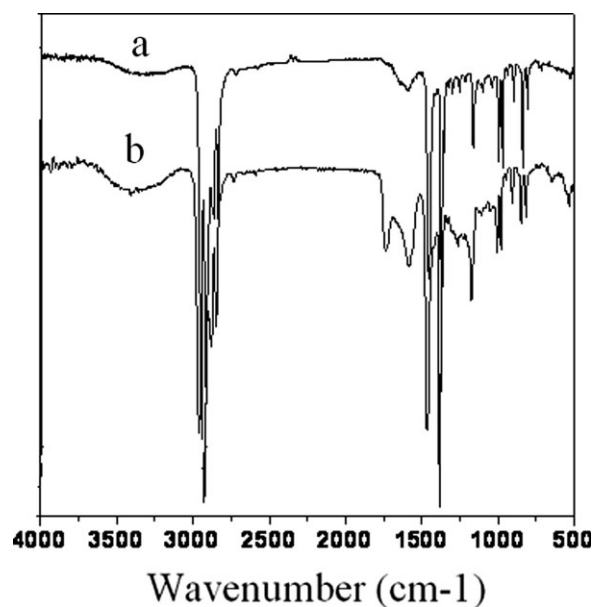


Figure 6 ATR-FTIR spectra of (a) virgin PP membrane and (b) grafted PP membrane with Dg of 18.18 wt % PAA.

active sites were generated; subsequently more AA monomer was grafted on the membrane surface. But increasing initiator density also produced the increase of the density of the propagating chain radicals, which results in intensive termination reactions and block further growth of the grafted chains. Moreover, higher initiator density disturbed the contact of monomer and the membrane surface and increased the homopolymerization. Thus, the Dg was reduced as the initiator density was enhanced. These results indicate that the grafting degree can be controlled easily by the monomer concentration, reaction temperature and initiator density.

Characterization and properties of PP and grafted PP membranes

The ATR-FTIR can confirm that the AA was grafted onto the surface of PP membrane. Figure 6 depicted

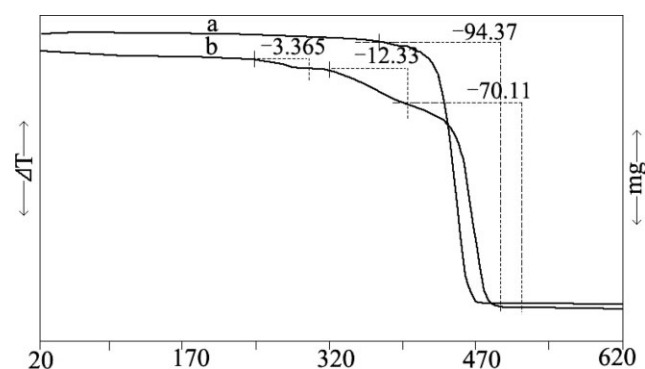


Figure 7 TG curves of (a) virgin PP membrane (b) grafted PP membrane with Dg of 8.76 wt % PAA.

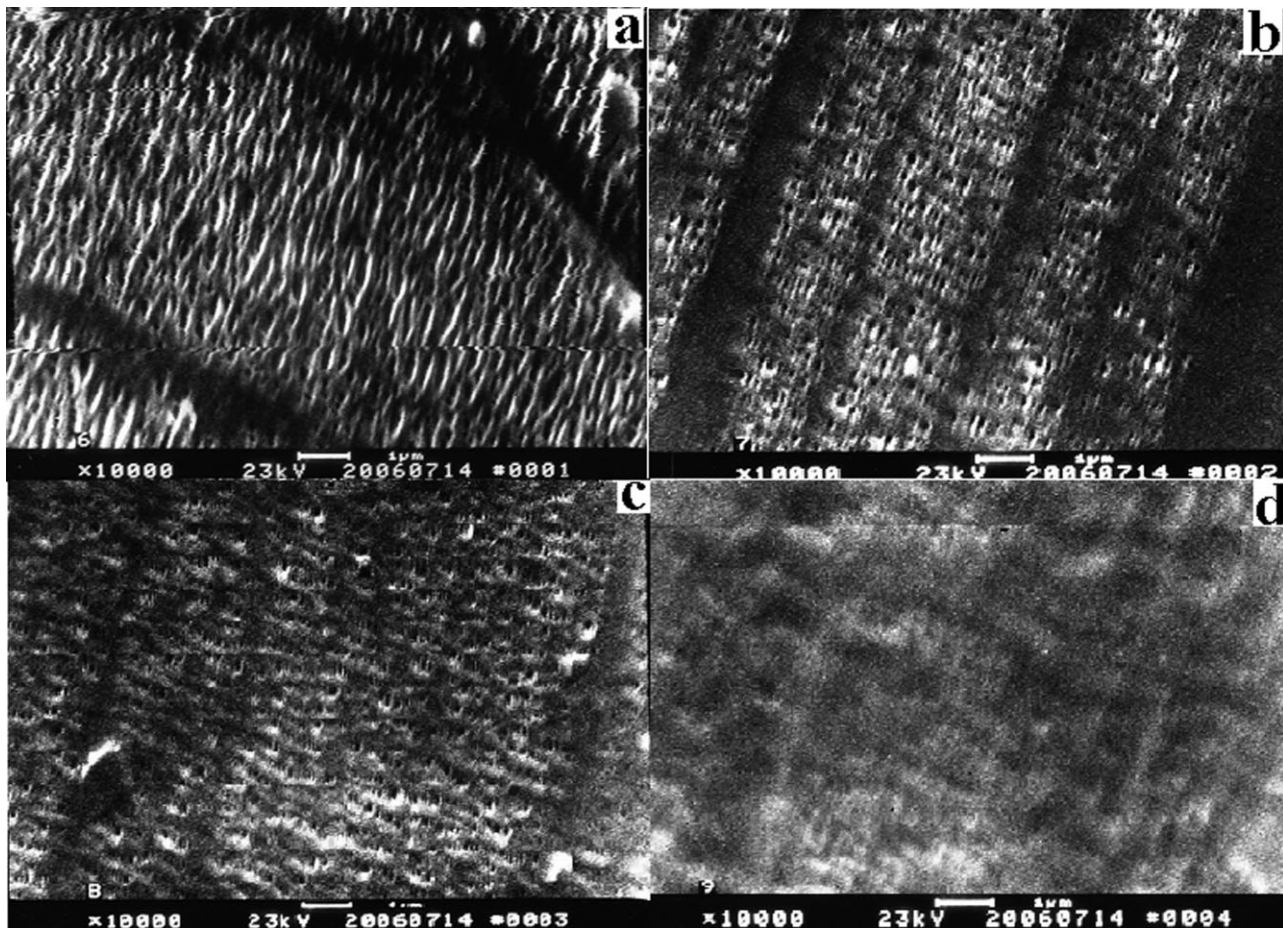


Figure 8 SEM photographs of (a) virgin PP membrane (b) grafted PP membrane with Dg of 8.76 wt % (c) grafted PP membrane with Dg of 17.2 wt % (d) grafted PP membrane with Dg of 35.8 wt % PAA.

the ATR-FTIR spectra for virgin PP and grafted PP membranes. As can be seen, the structure of PP was characterized with absorbance peaks at 1367cm^{-1} , 1452cm^{-1} and $2800\text{--}3000\text{cm}^{-1}$ in the spectra of vir-

gin PP and grafted PP membranes. It is noted that there was an absorption peak around 1725cm^{-1} and 3500cm^{-1} in the spectra of the grafted PP membrane, which can not be observed for the virgin PP

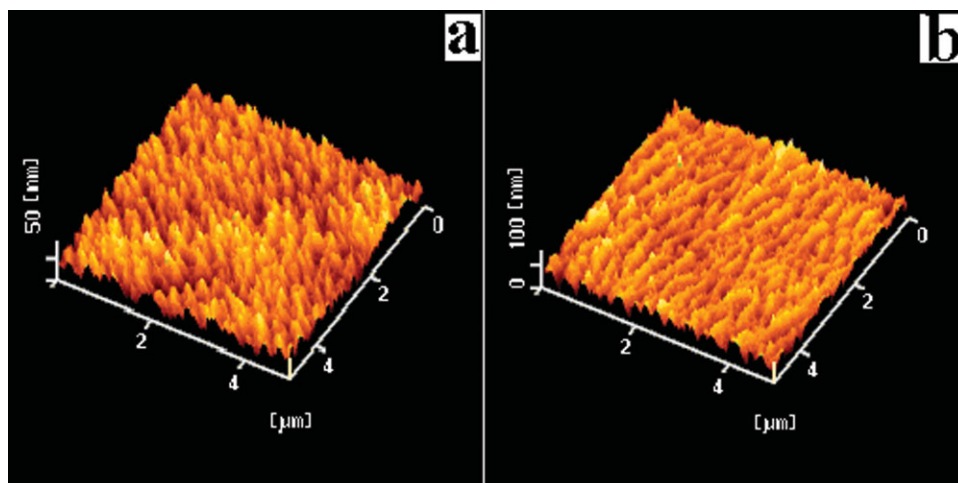


Figure 9 AFM photographs of (a) virgin PP membrane (b) grafted PP membrane with Dg of 13.5 wt % PAA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

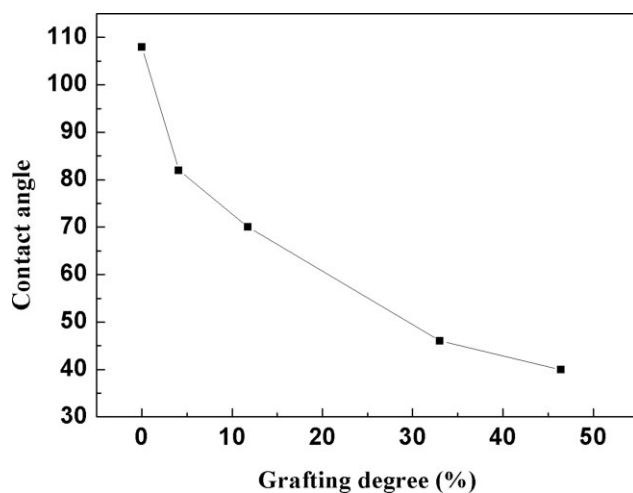


Figure 10 Effect of grafting degree on contact angle.

membrane. The adsorption peak at 1725 cm^{-1} and 3500 cm^{-1} can be attributed to the stretching of the C=O group and O—H group arising from the graft polymer, this indicates that the AA was successfully grafted onto the PP membrane surface.

The thermal properties of PP and grafted PP membranes were investigated in Figure 7. As can be seen from Figure 7, the PP membrane was thermally stable up to 380°C . There were slight weight loss at 220°C and 320°C for the grafted PP membrane; this was probably due to the decomposition of PAA grafted on the PP membrane. In summary, the decomposed temperature of grafted PP membrane decreased, which exhibited good thermal stability. It shows that the grafting does not change the matrix property of PP membrane.

To investigate the changes of the surface morphology of the grafted PP membrane, SEM and AFM photographs were carried out. Figure 8 illustrates the SEM images of the virgin and grafted PP membranes. As can be seen from Figure 8(a), the virgin PP membrane composed a large number of flat or elliptical pores. With the increase of Dg from 8.76% to 35.8%, the porosity and pore size of the grafted PP membrane were obviously decreased, because the grafted AA chains locked the surface pores and covered the PP membrane surface, there was no pore almost when the Dg was 35.8%. To further study the surface morphology of the grafted PP membrane, AFM was employed to compare the roughness of the virgin and grafted PP membrane. Figure 9 shows the AFM image of the virgin PP membrane surface, the surface was smooth, the R_a (mean roughness) was 10.12 and R_z (mean difference between the ten highest peaks and ten lowest values) was 74.38, however the surface roughness of the grafted PP membrane increased than the virgin membrane, when the Dg was 13.5%, the R_a was

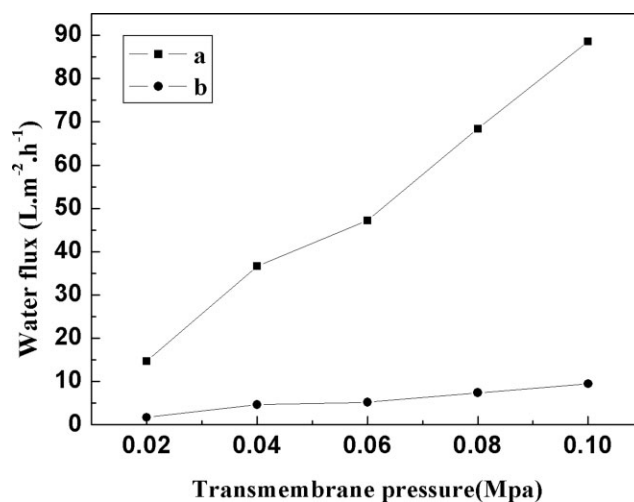


Figure 11 Effect of pressure on water flux of (a) virgin PP membrane (b) grafted PP membrane with Dg of 12.4 wt % PAA.

14.07 and R_z was 138.4. This phenomenon may be due to the fact that the length of the grafted polyacrylic acid chain is different which leads to the non-uniformity of the membrane surface. It is well known that the surface roughness decreases the contact angle on the hydrophilic surface according to Wenzel equation,²⁷ so the enhancement of roughness is favored.

We all know that the contact angle measurement is an easy and effective way to characterize the hydrophilicity of a membrane surface. The water contact angles of the virgin and grafted PP membranes are shown in Figure 10. As seen from the Figure 10, the contact angle on the grafted PP membrane surface reduced greatly with the increase of the Dg. The contact angle of the virgin membrane

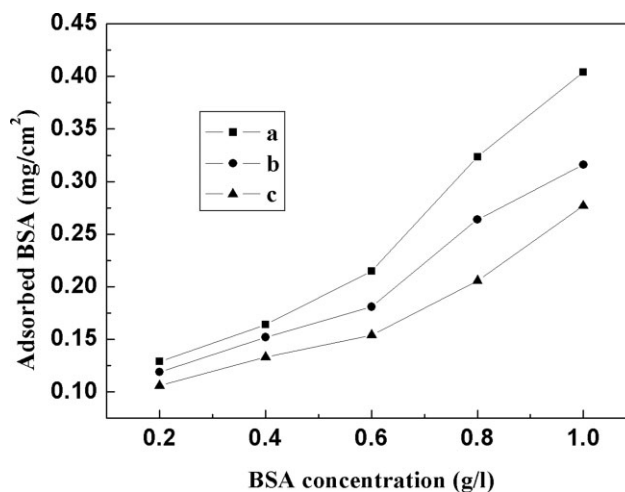


Figure 12 Amount of proteins adsorbed on the (a) virgin PP membrane (b) grafted PP membrane with Dg of 11.3 wt % PAA (c) grafted PP membrane with Dg of 18.71 wt % PAA.

TABLE I
Water Flux and BSA Flux of PP Membrane at 25°C and 0.1 MPa

PP membranes	J_0 (L m ⁻² h ⁻¹)	J_p (kg m ⁻² h ⁻¹)	J_1 (L m ⁻² h ⁻¹)	RF (%)	FR (%)
Virgin PP membrane	88.61	25.21	34.64	71.54	39.09
Grafted with Dg 4.76%	39.81	16.52	17.17	58.50	43.13
Grafted with Dg 11.5%	15.58	7.03	8.52	54.87	54.68
Grafted with Dg 16.0%	4.44	2.53	3.67	43.01	82.66

was 108°, the grafted PP membrane with the Dg 46.4% decreased to 40°, when the Dg reached to 33.03%, the tendency to decrease slowed down, it could be explained that after with the coverage of the grafted polyacrylic acid layer, the change of contact angle reduced.

Figure 11 illustrates the water flux for the virgin and grafted PP membrane at different transmembrane pressures. It can be found that the water flux approximately increased linearly with the transmembrane pressure for the virgin and grafted PP membrane, the virgin PP membrane could not filter water because of the hydrophobic of the membrane surface. In the study, the virgin PP membrane was treated with alcohol, so the water flux was relatively high. The water flux for the grafted PP membrane with Dg 12.4% was smaller than the virgin PP membrane, which was consistent with other articles.^{25,26,28,29} It could be understood that the pore size and porosity of membrane reduced after surface modification, resulting in decreasing the water flux although the surface hydrophilicity could increase the water permeability. The grafted polyacrylic plugged the pores of the membrane and reduced the channel for the water flow.

In the membrane separation industrial, membrane fouling should be reduced as much as possible. BSA adsorption measurements were employed to test the protein fouling. Figure 12 represents the amount of proteins adsorbed on the virgin and grafted PP membranes. As can be seen from the figure, the amount of proteins adsorbed on the grafted membranes decreased substantially with the increase of Dg, and was smaller than the virgin PP membrane. This phenomenon was not visible for the low BSA concentration.³⁰ When the BSA concentration was 1.0 g L⁻¹, the amount of proteins adsorbed on the virgin membrane was 0.4041 mg cm⁻², however 0.316 mg cm⁻² and 0.277 mg cm⁻² for the grafted PP membranes with Dg 11.3% and 18.71%, respectively.

The water and protein solution flux, RF and FR for the virgin and grafted PP membranes were compared in Table I. It can be found that the BSA solution filtration for the grafted membrane also decreased with the increase of Dg, but RF of the grafted PP membranes were lower than that of the virgin PP membrane, and reduced with the increase

of Dg. It is important to the grafted PP membranes that the flux recovery ratio increased markedly with increasing the Dg, the FR of the grafted PP membrane with Dg 16.0% was 82.66%, which improved 111.4% than that of the virgin PP membrane. Consequently, the antifouling property of the grafted PP membrane was greatly improved which has important significance in practical use.

CONCLUSIONS

Acrylic was grafted onto the surface of microporous PP membrane using physisorbed initiators method. This method is relatively simple, low cost and no pollution to environment, the grafting degree can be easily controlled by varying the monomer concentration, reaction temperature and initiator density. The water contact angle changed from 108° to 40° after surface modification, indicating the excellent hydrophilic for the grafted membrane. Although the water flux of the grafted PP membrane reduced with increasing the grafting degree, the results of BSA adsorption and filtration experiments revealed that the antifouling property of the grafted PP membrane was dramatically improved.

References

- Ma, H. M.; Bowman, C. N.; Davis, R. H. *J Membr Sci* 2000, 173, 191.
- Huang, S. L.; Qu, C. F.; Lai, J. Y. *J Membr Sci* 1999, 161, 21.
- Belfort, G.; Davis, R. H.; Zydney, A. L. *J Membr Sci* 1996, 96, 1.
- Yu, H. Y.; Xu, Z. K.; Xie, Y. J.; Liu, Z. L.; Wang, S. Y. *J Membr Sci* 2006, 279, 148.
- Akhtar, S. *J Membr Sci* 1995, 107, 209.
- Lang, W. Z.; Xu, Z. L.; Yang, H.; Tong, W. *J Membr Sci* 2007, 288, 123.
- Chung, T. C.; Lee, S. H. *J Appl Polym Sci* 1997, 64, 567.
- Bottino, A.; Capannelli, G.; Monticelli, O.; Piaggio, P. *J Membr Sci* 2000, 166, 23.
- Yu, H. Y.; Xu, Z. K.; Yang, Q.; Hu, M. X.; Wang, S. Y. *J Membr Sci* 2006, 281, 658.
- Li, Y.; Chu, L. Y.; Zhu, J. H.; Wang, H. D.; Xia, S. L.; Chen, W. M. *Ind Eng Chem Res* 2004, 43, 2643.
- Ying, L.; Yu, W. H.; Kang, E. T.; Neoh, K. G. *Langmuir* 2004, 20, 6032.
- Cao, J. H.; Zhu, B. K.; Hong, L.; Xu, Y. Y. *Desalination* 2005, 183, 431.
- Mulder, M. *Basic Principles of Membrane Technology*; Kluwer: The Netherlands, 1996; Chapter 6.
- Winston Ho, W. S.; Sirkar, K. K. *Membrane Handbook*; Van Nostrand Reinhold: New York, 1992; p 353.

15. Mika, A. M.; Childs, R. F.; Dickson, J. M. *J Membr Sci* 1999, 153, 45.
16. Ma, H. M.; Davis, R. H.; Bowman, C. N. *Macromolecules* 2000, 33, 331.
17. Liang, L.; Shi, M. K.; Viswanthan, V. V.; Peurrung, L. M.; Yong, J. S. *J Membr Sci* 2000, 177, 97.
18. Bae, B.; Chun, B. H.; Kim, D. *Polymer* 2001, 42, 7879.
19. Liu, M. Z.; Xu, Z. K.; Wang, J. Q.; Qian, Y.; Wu, J.; Seta, P. *Eur Polym J* 2003, 39, 2291.
20. Wavhal, D. S.; Fisher, E. R. *Langmuir* 2003, 19, 79.
21. Shim, J. K.; Na, H. S.; Moo, L. Y.; Hun, H.; Nho, Y. C. *J Membr Sci* 2001, 190, 215.
22. Liu, M. Z.; Xu, Z. K.; Wang, J. Q.; Qian, Y.; Wu, J.; Seta, P. *Eur Polym J* 2004, 40, 2077.
23. Wang, Y.; Kim, J. H.; Choo, K. H.; Lee, Y. S.; Lee, C. H. *J Membr Sci* 2000, 169, 269.
24. Hu, S. W.; Brittain, W. J. *Macromolecules* 2005, 38, 6592.
25. Xu, Z. K.; Wang, J. L.; Shen, L. Q.; Men, D. F.; Xu, Y. Y. *J Membr Sci* 2002, 196, 221.
26. Wang, Y.; Liu, Z. M.; Han, B. X.; Dong, Z. X.; Wang, J. Q.; Sun, D. H.; Huang, Y.; Chen, G. W. *Polymer* 2004, 45, 855.
27. Wenzel, R. N. *Ind Eng Chem* 1936, 28, 988.
28. Ulbricht, M. *React Funct Polym* 1996, 31, 165.
29. Ulbricht, M.; Yang, H. *Chem Mater* 2005, 17, 2622.
30. Kou, Q. Q.; Xu, Z. K.; Deng, H. T.; Liu, Z. M.; Patrick, S.; Xu, Y. Y. *Langmuir* 2003, 19, 6869.