Low Protein Fouling Polypropylene Membrane Prepared by Photoinduced Reversible Addition-Fragmentation Chain Transfer Polymerization

Bing Hu,[1,2] Liang Wang,[1] Xiu-Min Wu,[1] Song Yang,[1] Jia-Shan Gu,[1] Hai-Yin Yu[1]

[1]*Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Key Laboratory of Molecular-Based Materials, College of Chemistry and Materials Science, Anhui Normal University, East Beijing Rd. 1, Wuhu, Anhui 241000, China*
[2]*Department of Chemistry and Food Science, Chizhou University, Chizhou, Anhui 247000, China*

Received 26 April 2011; accepted 6 June 2011
DOI 10.1002/app.35034
Published online 22 September 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: In this study, 2-hydroxyethyl methacrylate and *N*-isopropyl acrylamide was block grafted onto the polypropylene macroporous membrane surface by photo-induced reversible addition-fragmentation chain transfer (RAFT) radical polymerization with benzyl dithiobenzoate as the RAFT agent. The degree of grafting of poly(2-hydroxyethyl methacrylate) on the membrane surface increased with UV irradiation time and decreased with the chain transfer agent concentration increasing. The poly(2-hydroxyethyl methacrylate)- grafted membranes were used as macro chain transfer agent for the further block graft copolymerization of *N*-isopropyl acrylamide in the presence of free radical initiator. The degree of grafting of poly(*N*-isopropyl acrylamide) increased with reaction time. Furthermore, the poly(2-hydroxyethyl methacrylate)-grafted membrane with a degree of grafting of 0.48% (wt) showed the highest relative pure water flux and the best antifouling characteristics of protein dispersion. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 3668–3674, 2012

Key words: block graft polymerization; 2-hydroxyethyl methacrylate; *N*-isopropyl acrylamide; photo-induced reversible addition-fragmentation chain transfer radical polymerization; poly-(propylene) macroporous membrane

INTRODUCTION

For membranes, the surface properties are as important as their bulk properties, but it is often difficult to find a material that provides a suitable combination of both. To solve this problem, surface modification has been widely used to enhance the membrane performance such as flux and selectivity without changing the bulk properties.[1–3] Membrane surface modification is an important area for both applied and basic research. A number of surface modification techniques such as plasma treatment, photo-induced graft were adopted, most of which are via the traditional free-radical polymerization process.

Unfortunately, for surface modification using traditional free-radical grafting technique, it is not easy to control the chain structure or to graft block copolymer on materials surface in most cases. Covalent attachment of polymer chains to solid substrates by surface-initiated controlled radical polymerization is an effective method for tailoring surface properties.[4,5]

Among them, reversible addition fragmentation chain transfer polymerization (RAFT) is unarguably the most adaptable to controlled radical polymerization of versatile monomers under a variety of conditions.[6–8] This process also allows the synthesis of a wide range of functional polymers with fine structures in one step without group protecting.

Poly(2-hydroxyethyl methacrylate) (PHEMA) surface-modified membranes have many technological applications, including enzyme immobilization, hydrophilicity, biocompatibility, and antifouling characterization, as a result of the presence of hydroxyl groups in the side chains of the polymer.[9–11] Therefore, tethering PHEMA to the membrane surface through graft polymerization of HEMA has received much attention. Although HEMA can be grafted on macroporous polypropylene membrane (PPMM) by ozone treatment and γ-ray irradiation,[12,13] it is difficult to graft PHEMA on PPMM surface by the conventional one-pot photo-induced polymerization. Using benzophenone (BP) together with $FeCl_3 \cdot 6H_2O$ as the photosensitizer, PHEMA has been grafted on PPMM surface under UV irradiation.[9] Nevertheless, block copolymer cannot be obtained by this technique.

Correspondence to: H.-Y. Yu (yhy456@mail.ahnu.edu.cn).
Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20871003.

In this work, we report on the surface modification of polypropylene macroporous membrane by the photo-induced RAFT polymerization of HEMA, benzyl dithiobenzoate (BDTB) was used as the chain transfer agent (CTA). To verify the living character of CTA, the HEMA-grafted membrane was used as macro CTA for further block graft copolymerization with *N*-isopropyl acrylamide (NIPAAm) in the presence of free radical initiator, 2,2′-azobisisobutyronitrile (AIBN).

EXPERIMENTAL SECTION

Materials

Polypropylene macroporous membrane (PPMM) with a porosity of 45–50% and an average pore diameter of about 0.10 μm, 2,2′-azobisisobutyronitrile (AIBN), benzophenone (BP), 2-hydroxyethyl methacrylate (HEMA), and *N*-isopropyl acrylamide (NIPAAm, 98%) were used as purchased. Benzyl dithiobenzoate (BDTB) was synthesized according to the literature.[14,15] Characterization was done by 1H NMR: ($CDCl_3$, 300 MHz) (ppm): 4.61 (s, 2H); 7.23–7.43 (m, 8H); and 8.02 (m, 2H). Bovine serum albumin (BSA, purity > 98%, pI = 4.8, M_w = 66 kDa) was purchased from Sino-American Biotechnology Co. and used as received. BSA was mixed in a phosphate buffered saline (PBS) solution at pH 7.4.

Membrane surface modification

Membrane surface modification was performed according to our previous work with minor modifications.[16] Preweighed PPMMs were soaked for 60 min in 50 mL BP solution in heptane, each side of the membranes was subjected to UV irradiation for 15 min. The photo-induced grafting polymerization was conducted in a degassed and sealed flask under UV irradiation in the presence of 50 mL 0–5.0 mmol/L BDTB and 5% (v/v) HEMA solution in anhydrous ethanol. Finally, the HEMA-modified membrane, NIPAAm (10% (wt)) and AIBN (0.10 mol/L) were introduced into 40 mL of 2-propanol, and the polymerization was initiated by AIBN at 60°C. The BP immobilized, HEMA modified, and the NIPAAm graft copolymerized membranes were designated as PPMM-BP, PPMM-*g*-PHEMA, and PPMM-*g*-PHEMA-*b*-PNIPAAm, respectively.

After each step of surface modification, the samples were taken out of the reaction system and washed with ethanol and pure water in a shaking water bath at 30°C for 24 h, then dried completely in vacuum at 40°C to a constant weight. The degree of grafting of PHEMA (DG_2) and PNIPAAm (DG_3) were calculated as follows:

$$DG_2 = \frac{(W_2 - W_0)}{W_0} \times 100\% \quad (1)$$

$$DG_3 = \frac{(W_3 - W_2)}{W_0} \times 100\% \quad (2)$$

where DG_2 and DG_3 are the degrees of grafting of PHEMA and PNIPAAm on the membrane surface, % (wt); W_0 is the weight of the blank membrane, W_2 and W_3 are the weights of the membranes in the second and the third step, respectively.

Characterization of the modified membranes

Membrane characterization by attenuated total reflection—Fourier transform infrared spectroscopy (FTIR/ATR), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), and mean membrane pore size analysis, were conducted as described before.[17]

Membrane filtration

The permeation properties of PPMMs were examined in a stirred dead-ended ultrafiltration test cell connected to a 2 L feed tank.[18] The deionized water fluxes ($J_{0,u}$) and ($J_{0,m}$) were obtained by measuring permeate through the unmodified and modified membranes. Then, 1 g/L BSA dispersion in phosphate buffer solution at pH 7.4 was used as the feed solution; the flux at the end of the BSA filtration was recorded as J_p. The membranes were subsequently cleaned with deionized water and 0.1*M* NaOH solution, the fluxes (J_1 and J_2) were then measured after water and caustic cleaning. The volumetric fluxes were divided by $J_{0,u}$ to obtain the relative fluxes.

RESULTS AND DISCUSSION

RAFT-mediated block graft of PHEMA and PNIPAAm on the PPMM surface

In this study, the photo-induced RAFT-mediated block graft copolymerization of HEMA and NIPAAm was carried out as proposed in Ref. [18]. BP was immobilized on the membrane surface under UV irradiation in the first step. In the second step, HEMA was grafted on the membrane surface with the functional benzodithioic moieties linked at the tail of the grafting chain. In the third step, PPMM-*g*-PHEMA was used as surface macro CTA; PNIPAAm was further block grafted onto the membrane surface initiated by AIBN.

Figure 1 shows the effect of the reaction time and CTA concentration on the degree of grafting of PHEMA on PPMM (DG_2). In the CTA adding process, DG_2 increases very slowly during the reaction time of 0–30 min, which indicates that the process is somehow inhibited within the first 0–30 min. An ideal RAFT process should be fast and the

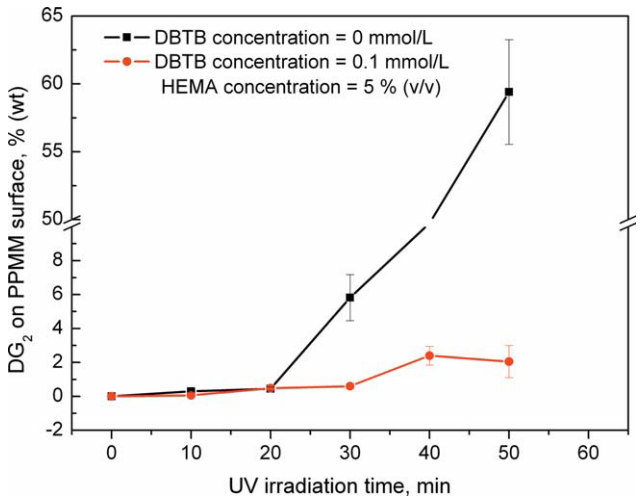

Figure 1 Effect of the reaction time and chain transfer agent concentration on degree of grafting of PHEMA on PPMM (DG_2). Monomer concentration of HEMA is 5 % (v/v). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

intermediate RAFT-adduct radical should be short lived.[19] However, an obvious reduction of the rate was been observed,[19,20] indicating that the slow fragmentation of the intermediate macro-RAFT radicals may be the primary cause.[21] After 30 min reaction, DG_2 increases a bit quickly with reaction time, which may be due to chain entanglement and self-autoacceleration.[22]

For the conventional process ([BDTB] = 0), DG_2 increases with reaction time, especially after 20 min the increase is obvious, which resulted from the self-autoacceleration in a traditional free radical polymerization process.[23] This phenomenon is in good agreement with the conventional graft polymerization process initiated by free radicals. In addition, the conventional process always gains a higher DG_2 than the corresponding RAFT-mediated process.

Figure 2 shows the effect of the CTA concentration on DG_2. It can be found that at the reaction time of 60 min and monomer concentration of 5 % (v/v), DG_2 decreases with the increase of CTA concentration. This result indicates that as CTA concentration is reduced, the normal events of radical polymerization becomes more dominant than the RAFT-mediated process.[24] The grafting chains are initiated by the RAFT agent and the decomposition of the surface initiator PPMM-BP, that is, the number of the initiating sites increased with the prolongation of UV irradiation time in the second step. As a result, the polymerization was not a living process. The RAFT agents were really introduced to the grafting chains via the reversible termination process.[18]

It is not easy to synthesize block copolymers with conventional free radical polymerization strategies. Favorably, block copolymers can be easily obtained just by sequential addition of different monomers to the reaction system during the living polymerization process. This is the distinct characteristic of living polymerization. Herein, PPMM-*g*-PHEMA containing CTA functional groups was used as macro-CTA,[25] and NIPAAm was block grafted on PPMM-*g*-PHEMA surface without UV irradiation in the presence of free radical initiator, AIBN, which cannot produce new initiating sites on the membrane surface. The degree of grafting of PNIPAAm (DG_3) on the membrane surface is shown in Figure 3. It can be found that DG_3 increases with reaction time, which indicates that the grafted HEMA chains can really be served as the surface macro CTA for the subsequent surface-initiated block graft copolymerization of PNIPAAm. Thus, the here reported method can be a very simple way to graft block polymeric chains on the membrane surface and prepare multifunctional responsive membranes.[26]

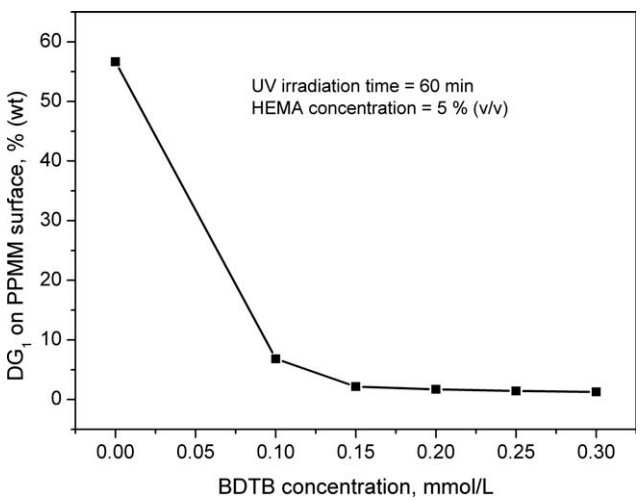

Figure 2 Variation of degree of grafting of PHEMA on PPMM (DG_2) with CTA concentration.

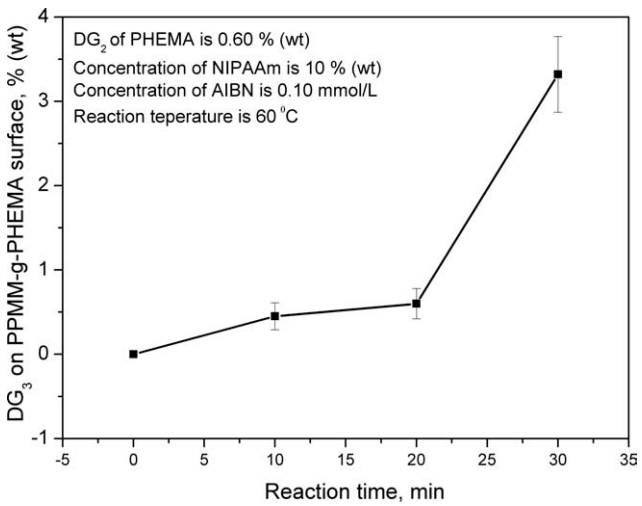

Figure 3 Variation of degree of grafting of PNIPAAm (DG_3) on PPMM-*g*-PHEMA with the reaction time.

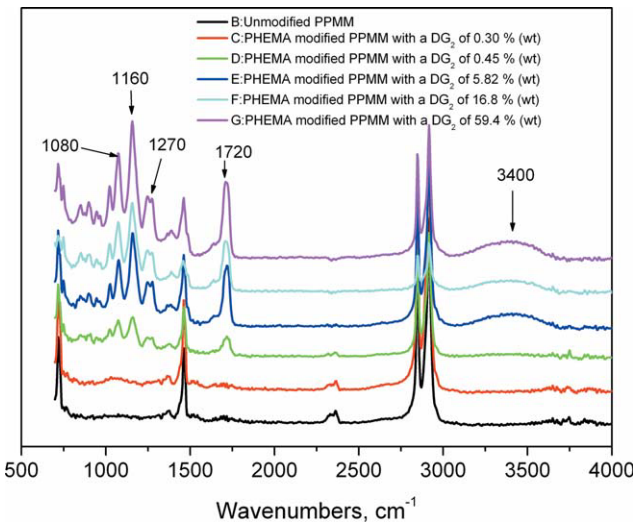

Figure 4 FTIR/ATR spectra for the unmodified membrane and HEMA-grafted membrane with different degree of grafting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization

HEMA was grafted onto the membrane surface, which was confirmed by the FTIR/ATR analysis (Fig. 4). A broad absorption band at 3400 cm^{-1} ascribed to the —O—H stretching vibration appears, indicating —OH groups on the membrane surface. An obvious absorption band at 1720 cm^{-1} characteristic of the C=O stretching vibration of esters in PHEMA is found for the modified membranes. Other new absorption bands appearing at 1160 cm^{-1}, 1270 cm^{-1}, and 1080 cm^{-1} are characteristic of the C—O—C stretching vibration, the C—O stretching vibration and the O—H deformation vibration of the C—O—H group, respectively.[9] The intensity of these absorption bands increase with the degree of grafting of PHEMA (DG_2) on the membrane surface.

XPS was employed to analyze the chemical composition on the membrane surface (Fig. 5). It can be found a small O1s peak at 531.6 eV in spectra for the unmodified membrane due to oxidation of the membrane.[27] Compared with the virgin PPMM, it can be clearly seen that after the surface grafting of PHEMA, the intensity of the O1s increases. After the subsequent block grafting of PNIPAAm on the PPMM-*g*-PHEMA surface, a new peak at 402.3 eV corresponding to N1s appears. The N1s peak can be designated to the block graft copolymerization with PNIPAAm on the membrane surface. These results demonstrate that the block copolymer of PHEMA-*b*-PNIPAAm is successfully grafted on the membrane surface.

The surface morphology of the modified membranes was observed by FESEM observations (Fig. 6). Compared with the unmodified PPMM with high porosity [Fig. 6(a)], the surfaces of the modified PPMMs are covered with polymers gradually as the degree of grafting increases [Fig. 6(b–e)]. The membrane pores are plugged and the surface porosity decreases with the degree of grafting increasing. After the block graft copolymerization of PNIPAAm on the PHEMA-grafted membrane [Fig. 6(f)], the surface was further covered with a thicker layer of polymer, and the membrane pore size and surface porosity decrease continuously.

FESEM images were afterward treated with image analysis software (Image-Pro plus 6.0) to obtain more information on membrane pore size. Typical results are shown in Table I. It is found that the pore size and surface porosity decrease with the degree of grafting. This result is in good consistence with the FESEM observations.

Permeation and the antifouling characteristics

Variation of the relative pure water flux through PPMM-*g*-PHEMA with different DG_2 is shown in Figure 7. The relative pure water flux increases with DG_2, and has a maximum value of 1270 $Lm^{-2}h^{-1}$ (three times the values of the unmodified PPMM) for the PHEMA-modified PPMM with a DG_2 of 0.48% (wt), then it decreases with the further increase of DG_2. In the permeation process, the membrane permeability is determined mainly by two factors: one is the membrane structure, such as the thickness, pore size, and porosity; the other is the membrane surface hydrophilicity.[28] The surface hydrophilicity increases with the degree of grafting (the results of the water contact angles were not shown). When the DG_2 is low, the hydration of PHEMA chains results in a decreased resistance of

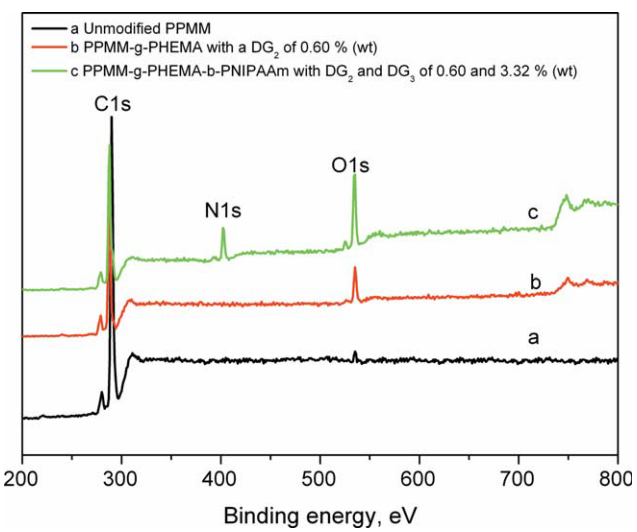

Figure 5 XPS spectra for the unmodified and modified PPMMs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

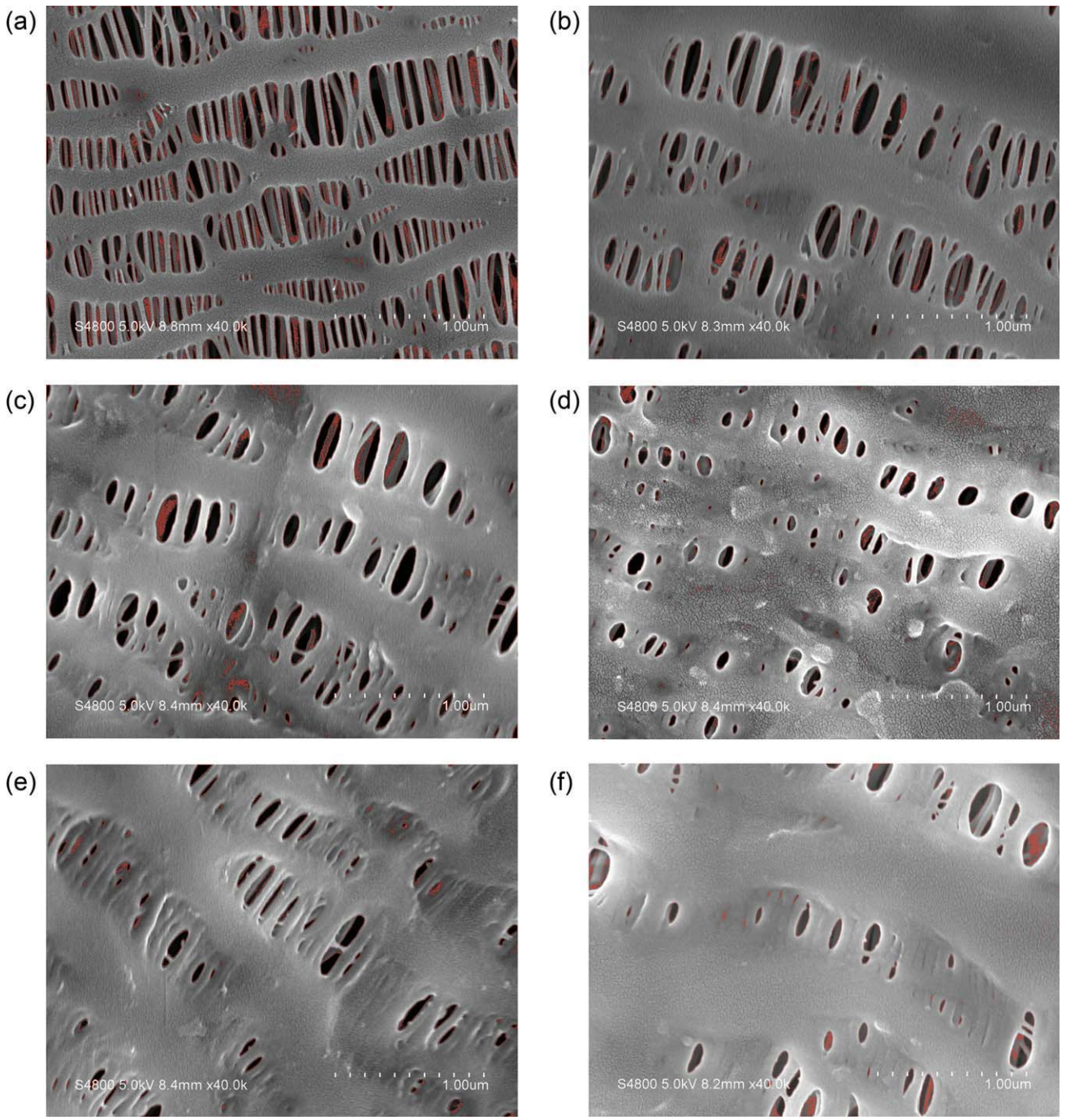

Figure 6 FESEM images (×40,000) for the PHEMA-grafted PPMMs. (a)–(e) with a DG_2 of 0, 0.48, 0.60, 2.40, and 4.05% (wt), respectively. (f) $DG_2 = 0.60\%$ (wt) and $DG_3 = 3.32\%$ (wt). The red circles are drawn by Image-Pro Plus automatically when calculating membrane pore size. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

water permeation and thus increases the water fluxes. For the membranes with high DG_2, the graft layer is thick and the expanded PHEMA conformation in aqueous circumstance tends to clog membrane pores, and consequently the water fluxes decrease.[29]

The nonspecific adsorption of protein on the membrane surface and in the membrane pores is the main cause of membrane fouling in protein separation and purification. For the filtration of protein dispersion, membrane fouling should be reduced as much as possible. In this work, BSA was used as a model protein to investigate the antifouling characteristics of the unmodified and PHEMA-modified membranes; the results are also shown in Figure 7. It can be found that the water fluxes after BSA

filtration (J_p), followed by water (J_1) and caustic cleaning (J_2), shows the same trend as those of the modified PPMM ($J_{0,m}$). The values of fluxes through the modified membranes are higher than the corresponding ones of the unmodified membranes. Compared with $J_{0,m}$, J_p decreases dramatically, which is attributed to protein adsorption and/or convective deposition on membrane surface (cake formation). These results allow us to conclude that the antifouling ability of PPMM membrane is significantly improved after the introduction of hydrophilic PHEMA brushes. When the degree of grafting is too high, the membrane permeation flux will reduce, there should be an optimal value of degree of grafting for membranes permeate ability and membrane antifouling characteristics. These results indicate that the degree of grafting plays important role in membrane performances and should be carefully modulated.

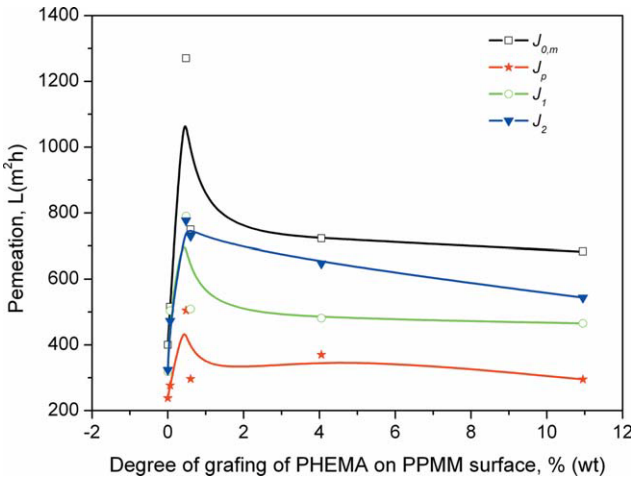

Figure 7 Flux changes for the PHEMA-grafted PPMMs with different degree of grafting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

Surface modification of polypropylene macroporous membranes were performed by the block grafting of poly(2-hydroxyethyl methacrylate) and poly(*N*-isopropyl acrylamide) via a photo-induced surface-initiated RAFT method. The degree of grafting of poly(2-hydroxyethyl methacrylate) increases with UV irradiation time and decreases with the concentration of the CTA. The poly(2-hydroxyethyl methacrylate)- modified membranes were used as macro CTA, and poly(*N*-isopropyl acrylamide) was block grafted on the membranes surfaces initiated by the free radical initiator. The degree of grafting of poly(*N*-isopropyl acrylamide) increases with reaction time. These results demonstrate that polymeric membranes can be block grafted with different monomers by the photo-induced RAFT method.

The PHEMA-modified membrane with a degree of grafting of 0.48% (wt) shows the highest pure water flux and the best antifouling characteristics.

TABLE I
Membrane Pore Size of the Nascent and PHEMA-Grafted PPMMs

Degree of grafting (wt %)	Mean diameter of pore size (μm)
0	0.119 ± 0.025
0.06	0.112 ± 0.030
0.48	0.095 ± 0.021
0.60	0.086 ± 0.022
2.40	0.079 ± 0.019
4.05	0.068 ± 0.015

References

1. Banihashemi, A.; Vakili, M. R.; Meratian, S. J Appl Polym Sci 2010, 118, 1.
2. Corrales, M.; Bierbrauer, K.; Sacristan, J.; Mijangos, C. Macromol Chem Phys 2010, 211, 1990.
3. Jackeray, R.; Jain, S.; Chattopadhyay, S.; Yadav, M.; Shrivastav, T. G.; Singh, H. J Appl Polym Sci 2010, 116, 1700.
4. He, D. M.; Ulbricht, M. Macromol Chem Phys 2009, 210, 1149.
5. Tomer, N.; Mondal, S.; Wandera, D.; Wickramasinghe, S. R.; Husson, S. M. Sep Sci Technol 2009, 44, 3346.
6. Xu, S. F.; Li, J. H.; Chen, L. X. J Mater Chem 2011, 21, 4346.
7. Li, J. W.; Yi, L. M.; Lin, H. M.; Hou, R. G. J Polym Sci Polym Chem 2011, 49, 1483.
8. Sogabe, A.; Flores, J. D.; McCormick, C. L. Macromolecules 2010, 43, 6599.
9. Hu, M.-X.; Yang, Q.; Xu, Z.-K. J Membr Sci 2006, 285, 196.
10. De Guzman, M.; Lee, K. R.; Lai, J. Y. Desalin Water Treat 2010, 17, 210.
11. Radhakumary, C.; Nair, P. D.; Mathew, S.; Nair, C. P. R. J Appl Polym Sci 2006, 101, 2960.
12. Kang, J. S.; Shim, J. K.; Huh, H.; Lee, Y. M. Langmuir 2001, 17, 4352.
13. Wang, Y.; Kim, J.-H.; Choo, K.-H.; Lee, Y.-S.; Lee, C.-H. J Membr Sci 2000, 169, 269.
14. Davies, M. C.; Dawkins, J. V.; Hourston, D. J. Polymer 2005, 46, 1739.
15. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 31, 5559.
16. Ulbricht, M.; Yang, H. Chem Mater 2005, 17, 2622.
17. Gu, J.-S.; Yu, H.-Y.; Huang, L.; Tang, Z.-Q.; Li, W.; Zhou, J.; Yan, M.-G.; Wei, X.-W. J Membr Sci 2009, 326, 145.
18. Yu, H.-Y.; Zhou, J.; Gu, J.-S.; Yang, S. J Membr Sci 2010, 364, 203.
19. Feldermann, A.; Coote, M. L.; Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. J Am Chem Soc 2004, 126, 15915.

20. Peklak, A. D.; Butte, A.; Storti, G.; Morbidelli, M. J Polym Sci Polym Chem 2006, 44, 1071.
21. Hao, X. J.; Heuts, J. P. A.; Barner-Kowollik, C.; Davis, T. P.; Evans, E. J Polym Sci Polym Chem 2003, 41, 2949.
22. Quinn, J. F.; Chaplin, R. P.; Davis, T. P. J Polym Sci Polym Chem 2002, 40, 2956.
23. Zhang, Z.; Zhu, X.; Zhu, J.; Cheng, Z. Polymer 2006, 47, 6970.
24. Ying, L.; Yu, W. H.; Kang, E. T.; Neoh, K. G. Langmuir 2004, 20, 6032.
25. Cheng, C.; Sun, G.; Khoshdel, E.; Wooley, K. L. J Am Chem Soc 2007, 129, 10086.
26. Yu, H.-Y.; Li, W.; Zhou, J.; Gu, J.-S.; Huang, L.; Tang, Z.-Q.; Wei, X.-W. J Membr Sci 2009, 343, 82.
27. Rjeb, A.; Letarte, S.; Tajounte, L.; El Idrissi, M. C.; Adnot, A.; Roy, D.; Claire, Y.; Kaloustian, J. J Electron Spectrosc 2000, 107, 221.
28. Yu, H.-Y.; Xu, Z.-K.; Lei, H.; Hu, M.-X.; Yanga, Q. Sep Purif Technol 2007, 53, 119.
29. Zhu, L.-P.; Dong, H.-B.; Wei, X.-Z.; Yi, Z.; Zhu, B.-K.; Xu, Y.-Y. J Membr Sci 2008, 320, 407.