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Fabrication of a poly(*N*-vinyl-2-pyrrolidone) modified macroporous polypropylene membrane via one-pot reversible-addition fragmentation chain-transfer polymerization and click chemistry

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Jin Zhou contributed to the characterization and permeation and antifouling properties examination of the unmodified and modified macroporous polypropylene membranes. Bing Hu contributed to the preparation of the clickable membrane and the grafting of poly(N-vinyl-2-pyrrolidone) onto the macroporous polypropylene membrane surface.

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ABSTRACT: In this study, a macroporous polypropylene membrane (MPPM) was grafted with hydrophilic poly(*N*-vinyl-2-pyrrolidone) (PNVP) based on a one-pot reversible-addition fragmentation chain transfer (RAFT) polymerization and click chemistry. First, we prepared the clickable membrane by bromination and following S_N2 nucleophilic substitution reaction; then, click chemistry and RAFT polymerization were performed in one-pot to graft PNVP to the MPPM surface. The surface characterizations, including attenuated total reflectance/Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and field-emission scanning electron microscopy, illustrated that PNVP was really grafted onto the MPPM surface. The permeation and antifouling characteristics of the MPPMs were measured by the filtration of a bovine serum albumin dispersion; this showed that in contrast to the nascent membrane, the grafted membrane efficiently obstructed protein molecules because of the compactly grafted polymer chains. The hydrophilicity and antifouling properties of MPPM were greatly ameliorated after modification. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42649.

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INTRODUCTION

Polypropylene membranes have many attractive properties (e.g., chemical inertness, well-controlled porousness, very high porosity[1–4]) and is commonly used for lithium-ion battery isolation membrane, bipolar membrane substrate, and so on. In the field of water treatment, the macroporous polypropylene membrane (MPPM) can be used as an ultrafiltration, microfiltration separation membrane. Its application field continues to expand. However, the surface wettability and hydrophilicity of polypropylene is very poor; this leads not only to low water flux but also to serious membrane fouling. This restricts the potential applications of these membranes in biomedical systems and the separation of aqueous solutions. Therefore, the preparation of hydrophilic MPPM is becoming urgent for expanding its applications.

Many studies have shown that membrane fouling could be abated by the enhancement of the hydrophilicity of the membrane surface.[5–7] Different approaches have been explored to ameliorate the hydrophilicity of MPPM, including blending,[8] coating,[9] surface modification,[10–12] and click chemistry. Click chemistry, a kind of reaction with modularity, has advantages of a high efficiency, fewer side effects, and a high selective reactivity.[13] Among the click reactions, the Huisgen 1,3-dipolar cycloaddition reaction of azide-alkyne catalyzed by Cu^I as the most common one,[14,15] is widely used in the field of polymer synthesis nowadays.

N-Vinyl-2-pyrrolidone (NVP), a nonionic and hydrophilic monomer, has many distinctive properties, including biological and chemical inertia, biocompatibility, and exceptional aqueous solubility. Moreover, polymeric substrates containing poly (*N*-vinyl-2-pyrrolidone) (PNVP) can availably counteract nonspecific protein adsorption; thus, they have potential applications in health-related domains, such as biomedicine, food, and cosmetics. NVP has been widely used to modify different materials via multifarious kinds of grafting methods, including Co^{60} γ-ray preirradiation,[16–18] low-temperature plasma treatment,[19] UV irradiation[16–21] and SI-ATRP (surface-initiated atom transfer radical polymerization).[22] Although the antifouling performance could be improved, these surface modification approaches have significant drawbacks involving tedious chemical reactions

or requiring complicated machines. Therefore, a method that is efficient, controllable, and easy to scale up to graft PNVP onto the polyolefin membrane is highly desirable. A one-pot reaction satisfies these requirements well with its advantages of easy operation, high efficiency, and the ability to graft short polymer chains; this may improve the hydrophilicity and water flux without blocking the membrane pores.

In this study, to obtain a hydrophilic membrane, NVP was grafted onto the MPPM surface via reversible-addition fragmentation chain transfer (RAFT) polymerization combined with click chemistry reaction in one-pot. Various characterization techniques were used to verify the successful of grafting PNVP onto the membranes. The antifouling performances of the membranes before and after PNVP grafting were examined by the filtration of the bovine serum albumin (BSA) dispersion.

EXPERIMENTAL

Materials

MPPM (average pore size = 0.20 μm, thickness $\approx$ 160 μm, and porosity $\approx$ 75%, Membrana GmbH, Germany) was purchased for the permeation and antifouling performance characterization. Polypropylene membranes without pore were used for water contact angle (WCA) experiments. A clickable polypropylene membrane, that is, an azide-functionalized macroporous polypropylene membrane (MPPM-N_3), was synthesized according to ref. 23. The chain-transfer agent (CTA) with an alkyne end groups was synthesized by a published method.[24] NVP, $CuSO_4{\cdot}5H_2O$, and sodium ascorbate were purchased from Sinopharm Chemical Reagent Co., Ltd. BSA (weight-average molecular weight = 66 kDa, pI = pH 4.8, purity > 98%) was purchased from Sino-American Biotechnology Co. The BSA dispersion was confected with a buffer solution at pH 7.4 as the solvent. All of the reagents were used as provided.

Grafting NVP onto the Surface of MPPM

A one-pot reaction of RAFT polymerization and click chemistry was used to fabricate hydrophilic MPPM. A piece of MPPM-N_3 [grafting degree (GD) $\approx$ 1.35 wt %] of about 0.046 g, 0.4 g (0.957 mmol) of alkyne-terminated CTA, 15.9 g (0.14 mol) of NVP, 25 mL of dimethyl sulfoxide, 0.010 g (0.04 mmol) of $CuSO_4{\cdot}5H_2O$ in 3 mL of water, 0.017 g (0.085 mmol) of sodium ascorbate dissolved in 3 mL of water, and 0.015 g (0.09 mmol) of initiator (AIBN) were mixed in a Schlenk flask. The flask was vacuumed and charged with argon three times to remove oxygen and then heated to 65°C for a specific time under pure argon. We terminated the RAFT polymerization terminated by chilling the flask in an ice–water bath. PNVP with alkyne end groups was obtained from solution by precipitation in cold methanol. The membrane was washed with a solvent mixture (ethanol/water = 1 : 1) to remove the physically adsorbed polymer and then vacuum-dried (for 12 h at 45°C). The method was similar to one reported in the literature.[25]

GD of PNVP on the membrane was calculated as follows:

$$\mathrm{GD}\ (\mathrm{mmol/m^2}) = [(m_1 - m_0)/(2A \times 3500)] \times 1000 \qquad (1)$$

where m_1 is the weight of MPPM-*g*-PNVP, m_0 is the weight of nascent MPPM, and 3500 is the molecular weight of the alkyne-PNVP (calculated from NMR data). GD of every sample was averaged from three parallel results.

Characterization

Attenuated total reflectance (ATR)/Fourier transform infrared (FTIR) spectroscopy was carried out (Vector 22 FTIR Bruker Optics, Switzerland) with an ATR cell of KRS-5 crystal (45°).[23]

X-ray photoelectron spectroscopy (XPS) was conducted on an XPS spectrometer (PHI 5000c, PerkinElmer Instruments) with Al Kα radiation (1486.6 eV) to analyze the chemical composition of the MPPM surface. Broad-scan spectra were acquired under a background pressure of 1×10^{-5} Pa and a pass energy of 150 eV. The signal of C1s at 284.7 eV was chosen for energy standardization.

The surface structures of the original and grafted MPPMs were scrutinized with field-emission scanning electron microscopy (FESEM; Hitachi S-4800, Japan) handling at 5 keV.

The WCA values of the MPPMs were surveyed by the sessile drop method (CTS-200, Mighty Technology Pvt., Ltd., China) at ambient temperature. About 2 μL of water was slowly dropped onto the sample surface with a microsyringe. The data of WCA was determined by the built-in software. Each sample was measured more than five times at different surface locations. The average value is given as the final result.

Permeation and Antifouling Property Examination

The water permeation of the membranes was tested by a dead-ended ultrafiltration cell with stirring. The ultrafiltration cell was connected to a feed tank (full of 2 L of water), which was pressurized by the adjustment of Ar gas. The detailed experimental setup and procedures were done according to the literature.[23] The normalized flux of pure water and the flux recovery ratio after cleaning with water were defined as follows:

$$\text{Normalized flux} = J_{0,m}/J_{0,u} \qquad (2)$$

$$\text{Flux recovery ratio} = J_1/J_{0,m} \qquad (3)$$

where $J_{0,u}$ is the deionized water flux of the unmodified membrane, $J_{0,m}$ is the deionized water flux of the modified membrane, and J_1 is the deionized water flux after BSA permeation and deionized water cleaning.

The rejection of the BSA dispersion was calculated from the feeding and permeating concentration and defined with the following equation:

$$\text{Rejection} = 1 - C_p/C_f \qquad (4)$$

where C_p and C_f are the BSA concentrations of the permeating and feeding solution, respectively. The BSA dispersion was freshly confected for each filtration experiment, and the concentration was obtained by the UV-absorbency examination of the sample solution at 280 nm.

RESULTS AND DISCUSSION

Coupling PNVP to the MPPM Surface via One-Pot Click Chemistry and RAFT Polymerization

A two-step route for coupling alkyne-PNVP to the MPPM surface is schematically displayed in Figure 1. First, the clickable MPPMs (MPPM-N_3) were prepared according to ref. 23. Second,

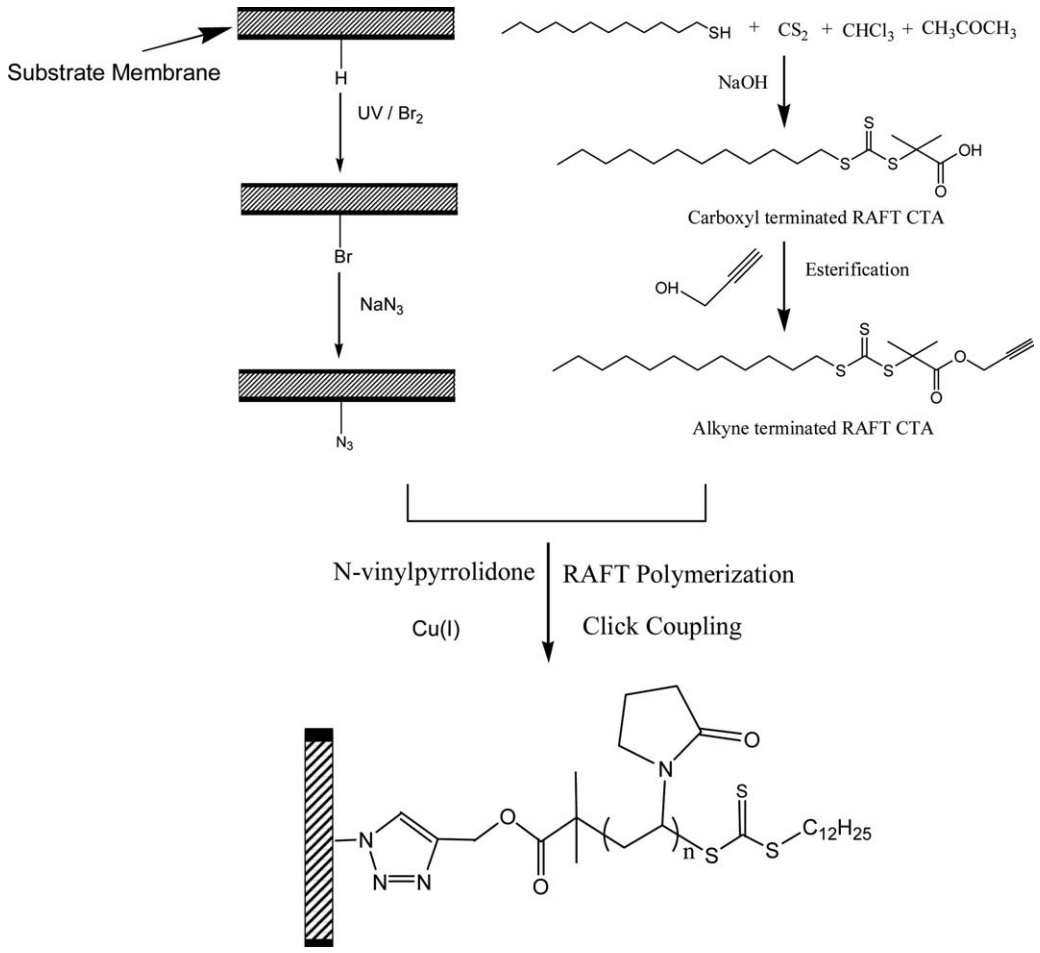

Figure 1. Surface modification of the polypropylene macroporous membrane via one-pot RAFT polymerization and click chemistry.

the grafting of PNVP to the membrane surface was carried out with a one-pot RAFT polymerization and click chemistry. Thus, a triazole five-membered ring containing NVP was generated. The experiment lacked an independent RAFT polymerization and a postprocessing step; this made the membrane surface modification more convenient.

The reaction conditions of bromination and S_N2 substitution were fixed to prepare the clickable MPPMs. As shown in Figure 2(a), GD increased with increasing Br molar content.[23] Because the grafting sites increased with Br molar content, more and more polymer chains were grafted to the MPPM surface; this resulted in an increase in GD.

The Br molar content on the membrane surface was not controllable; this was ascribed to the free-radical photochemical pathway. Therefore, to analyze the variation of the NVP molar concentration with GD, a lot of membrane bromination experiments were conducted under identical conditions. Then, the membranes with almost the same Br molar content on the surfaces were chosen to perform the S_N2 substitution under the same conditions. The variation of the NVP concentration with GD was investigated. The result is shown in Figure 2(b); GD increased as the monomer concentration increased. Because the monomer concentration mightily affected its diffusivity to the reaction zone, the grafting rate and the final GD varied with the monomer concentration. These results show that the grafting density could be controlled well by the monomer concentration and Br molar content on the membrane surface.

Surface Characterization

The existence of C—Br and C—N_3 in MPPM-Br and C—N_3 was substantiated with ATR/FTIR and XPS spectra. Regrettably, the signals of the Br—C stretching vibrations at 571, 640, and 661 cm^{-1} did not emerge in the ATR/FTIR spectra because the detector resolution was not high enough.[26] The peak at 1730 cm^{-1} shown in Figure 3(d) was attributed to C=O, which was from CTA. The azide stretching vibrations at 2100 cm^{-1} [20] indicated the successful exchange of azide with Br on MPPM-Br. After PNVP grafted onto the MPPM surface, the characteristic peaks from NVP at 1650 cm^{-1} of amide carbonyl stretching and the C=N peak at 1260 cm^{-1} were observed.

XPS survey scans were conducted to examine the elemental composition of the sample surface, and the spectra are shown in Figure 4. The signal peak at 284.7 eV belongs to the binding energy of C1s for the unmodified MPPM. The O1s signal in the spectrum for the unmodified MPPM may have stemmed from surface oxidation.[27] As shown in Figure 4(b), the existence of Br3d5, Br3p3, and Br3s at binding energies of 73, 185, and 259 eV illustrate that a bromine functional group was really introduced into the membrane via bromination. These values

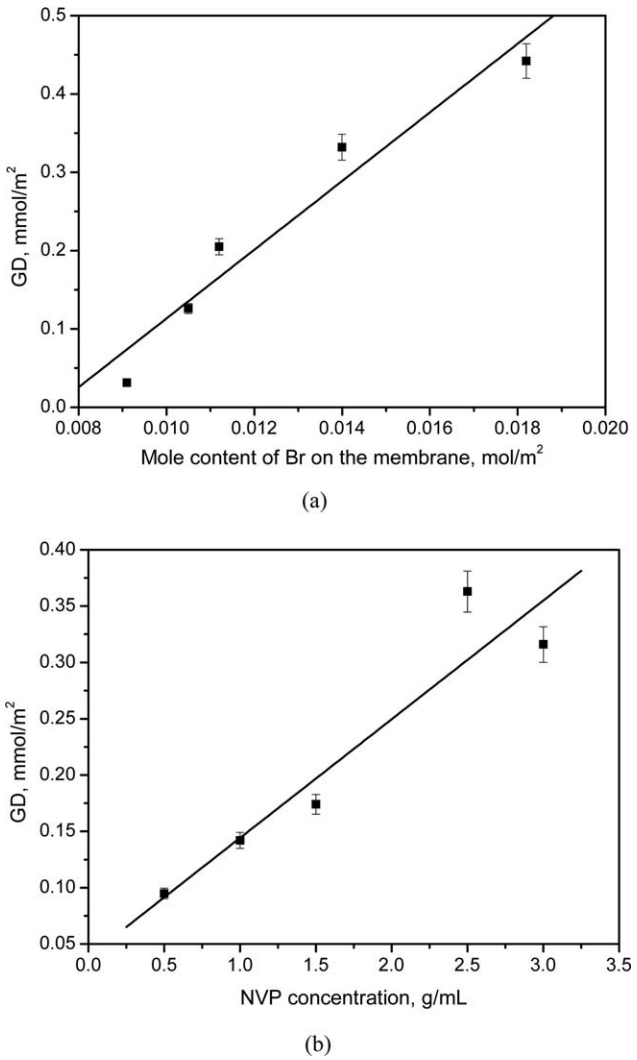

Figure 2. Variation of GD of PNVP on the membrane with (a) the Br molar content and (b) the monomer concentration.

were highly congruent with the published data for the Br—C bonds.[26,28] The signal intensity of O1s increased for MPPM-Br in comparison with the original MPPM because of UV oxidation during the bromination process.[29] According to this literature, C—O and C═O could be specified in the oxygen-related groups.[14] The reduction of the Br peak intensity and the emergence of the N1s signal around 402.3 eV [Figure 4(c)] verified the transformation of bromine atoms in the MPPM-Br into azide groups because of S_N2 nucleophilic substitution. After PNVP grafting [Figure 4(d)], sulfur, which came from CTA, was detected on the MPPM-PNVP membrane surface. These results obviously show that PNVP was successfully grafted onto MPPM by the one-pot RAFT polymerization and click chemistry.

The elemental molar contents of the MPPM samples are shown in Table I. O/C of the blank film was 1.09 mol %; this indicated the surface oxidation of the unmodified membrane. After UV bromination, O/C rose to 5.35 mol % and Br/C from 0 mol % to 3.62 mol %. These results suggest that Br and O atoms were

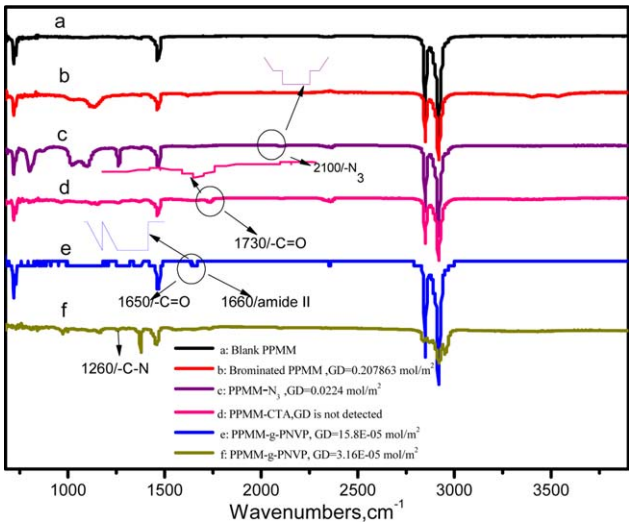

Figure 3. ATR/FTIR spectra of the (a) blank MPPM, (b) brominated MPPM (MPPM-Br), (c) MPPM-N_3, (d) MPPM-*g*-CTA, and (e,f) MPPM-*g*-PNVP with GDs of 0.158 and 0.0316 mmol/m^2, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

introduced onto the membrane surface after UV bromination. The content of bromine obviously decreases and that of nitrogen element increases after S_N2 nucleophilic substitution. Mol ratio of N/C ascends from 0.00 mol % to 0.90 mol %, showing that bromine was successfully replaced by azide groups. With the rise of PNVP GD, the atomic ratio of N/C increased.

The morphological changes of MPPMs at each step were distinctly observed by FESEM (Figure 5). After bromination, the pore size and porosity obviously decreased compared to those of the original membrane. The pore size shrank with increasing molar content of Br atoms. When Br was replaced by the azide groups [Figure 5(b,c)], the membrane pore sizes showed no obvious change. The membrane pore size shrank further after the grafting of PNVP; this demonstrated that a lot of polymer chains were successfully grafted onto the membrane surfaces.

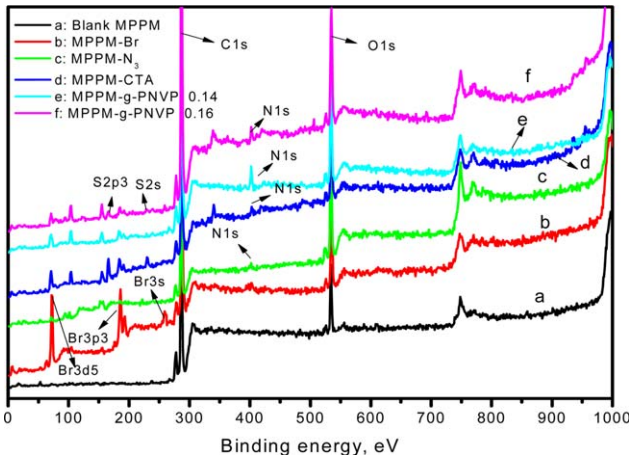

Figure 4. Wide-scan XPS spectra of the unmodified and modified MPPMs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Atomic Ratio Compositions of the Membranes with a Deviation of Approximately ±1.0%

						Atomic ratio (mol %)		
Membrane	C1s	O1s	Br	N1s	S	O/C	Br/C	N/C
Blank MPPM	98.92	1.08	0.00	0.00	0.00	1.09	0.00	0.00
MPPM-Br[a]	91.77	4.91	3.32	0.00	0.00	5.35	3.62	0.00
MPPM-N_3[b]	94.27	3.16	1.72	0.85	0.00	3.35	1.82	0.90
MPPM-*g*-PNVP[c]	78.16	12.74	1.46	2.07	0.71	16.30	1.87	2.65

[a] GD of Br on the membrane surface was 207.9 mmol/m^2.
[b] GD of azide groups on the membrane surface was 22.4 mmol/m^2.
[c] GD of PNVP on the membrane surface was 0.14 mmol/m^2.

WCA is not adequate at definitely interpreting the hydrophilicity and hydrophobicity of porous membranes; this is ascribed to heterogeneity and roughness.[30] As a result, the relative hydrophilicity of the membranes was obtained with nonporous polypropylene films by a WCA test. Figure 6 shows the WCAs of the polypropylene films at each modification stage. WCA for the unmodified film was about 98°, the hydrophilicities of the brominated and azide-functionalized ones (WCAs ≈ 92 and 94°) only showed a little change. After the PNVP chains were grafted to the polypropylene film surface, WCA dramatically decreased. Moreover, WCA continuously decreased with increasing PNVP GD. WCA was about 62.7° for the polypropylene film with a GD of 8.92 mmol.%. These results clearly demonstrate that the hydrophobic MPPM was greatly hydrophilically modified by the grafting of PNVP; this could rather ameliorate the antifouling characteristic of MPPM, as shown in the following section.

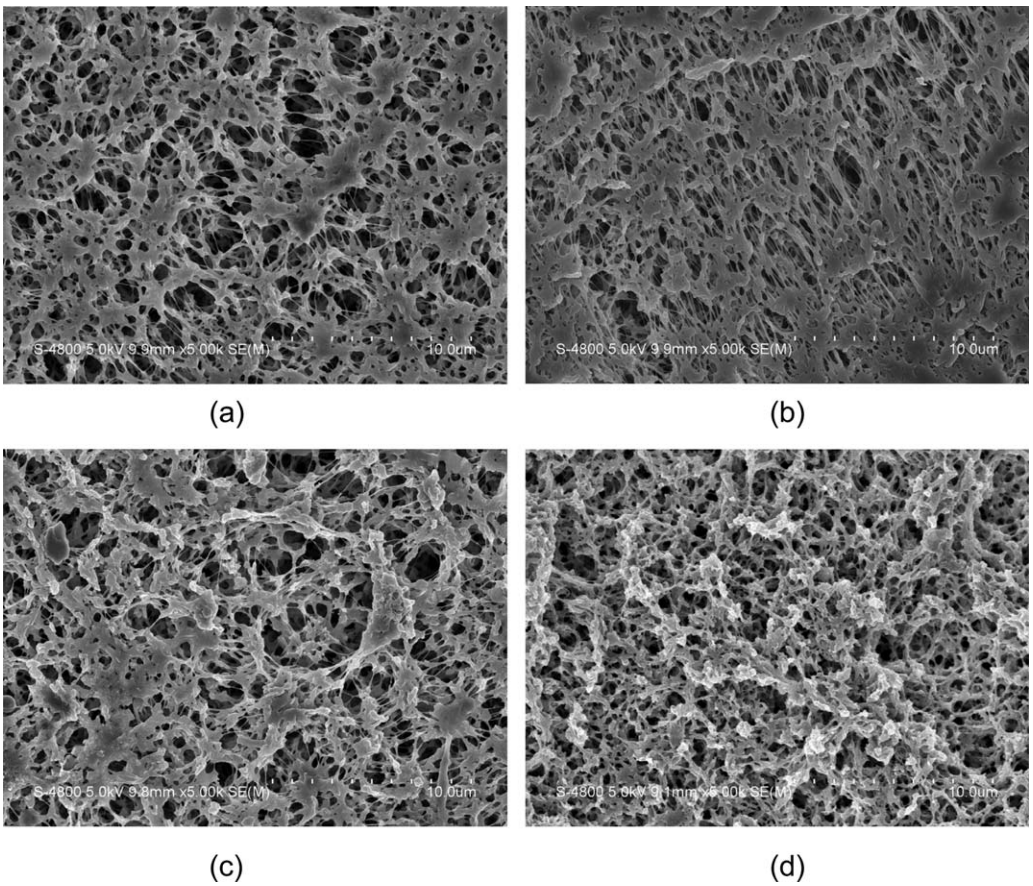

Figure 5. FESEM images for the (a) nascent membrane, (b) MPPM-Br (molar content of Br on the membrane = 19.60 mmol/m^2), (c) MPPM-N_3 (molar content of Br on the membrane = 22.4 mmol/m^2, molar content of azide on the membrane = 9.22 mmol/m^2), and (d) MPPM-*g*-PNVP (molar content of Br on the membrane = 27.3 mmol/m^2, molar content of azide on the membrane = 19.8 mmol/m^2, molar content of polymer chains on the membrane = 0.17 mmol/m^2). The images were obtained for different series of samples.

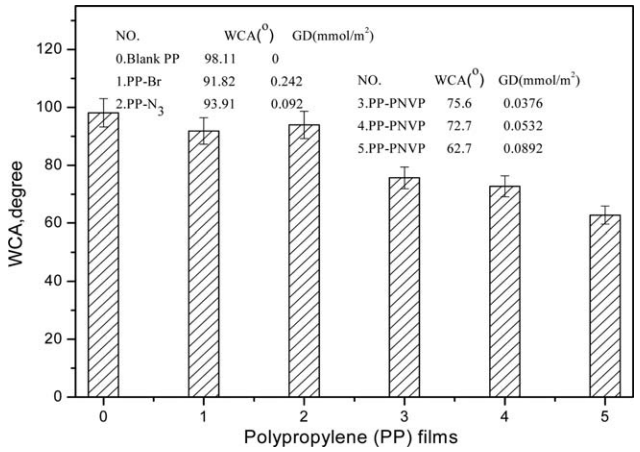

Figure 6. WCAs on different polypropylene films and GDs.

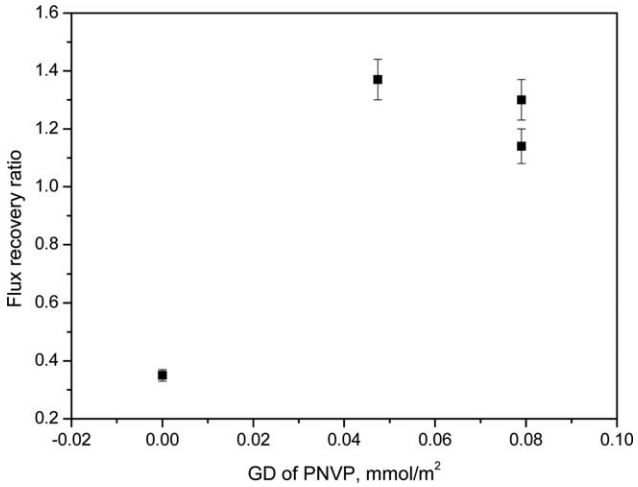

Figure 8. Effect of GD of PNVP on the flux recovery ratio of the BSA dispersion.

Permeation Performances

The filtration of ultrapure water and the BSA dispersion were carried out to explore the permeation and antifouling characteristics of the MPPM-*g*-PNVP membranes. As shown in Figure 7, the normalized water flux increased with increasing GD up to 0.045 mmol/m^2 and then dramatically decreased. This was attributed to the following reasons: the normalized water flux primarily depended on the hydrophilicity of the membrane when GD was low, and the normalized water flux increased with increasing hydrophilicity. When GD of PNVP was too high, it basically depended on the pore size. As shown in Figure 5, the pore size and porosity apparently decreased with increasing GD. Therefore, in contrast, the pure water permeation decreased when GD increased because the hydrophilicity was offset by the decrease in the pure water permeation because of the pore shrinkage and decrease in the porosity. Yu *et al.*[31] immobilized PNVP onto MPPM by plasma treatment; they found that the pure water flux increased with the immobilization degree; this was due to the surface hydrophilicity increased. However, the normalized flux showed a different trend in this study; this may have been caused by the reasons presented previously.

We also measured the permeation characteristics of MPPM-Br. The normalized flux was 0.86; this indicated that the pure water flux of MPPM-Br was lower than that of the blank films. Because the hydrophilicity of MPPM-Br did not increase, and the pores shrank. This result indicate that the oxidation during the bromination process did not contribute to the permeation characteristics of MPPM-PNVP.

The antifouling properties of the grafted MPPMs were examined by the permeation experiment of the BSA dispersion through the blank and PNVP-grafted MPPMs. As shown in Figure 8, the flux recovery ratio increased with increasing GD up to 0.0474 mmol/m^2 and then slightly decreased. This was attributed to the membrane pore shrinkage when GD was greater than 0.0474 mmol/m^2. However, the flux recovery ratios were still greater than 1.0 (1.14 and 1.3); this demonstrated that the pure water flux was completely restored after cleaning with water. The antifouling properties were really improved by the grafting modification.

Compared with the literature results, we found that the relative flux recovery ratio was higher. The photoinduced grafting of NVP onto poly(ether sulfone) membranes was conducted; we also found that NVP, a neutral, strongly, and weakly charged monomer was very effective in suppressing protein fouling.[31] The flux

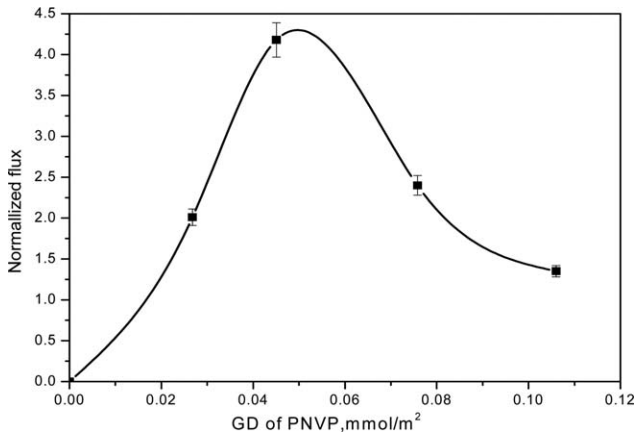

Figure 7. Dependence of the normalized flux on GD of PNVP.

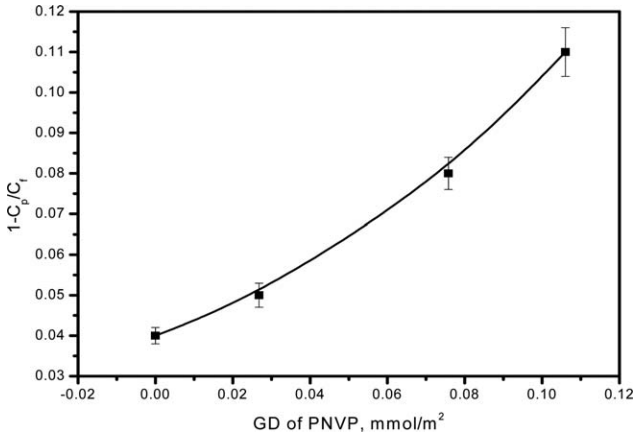

Figure 9. Effect of GD of PNVP on the rejection of the BSA dispersion.

recovery improved over 50% for the PNVP-grafted poly(ether sulfone) membrane by the photoinduced grafting of PNVP.[32]

The result in Figure 9 clearly shows that the BSA rejection increased with increasing GD; this was attributed to membrane pore shrinkage.

CONCLUSIONS

A novel one-pot technique was presented in this article; it could be generally used for membrane surface modification through the integration of RAFT polymerization with click chemistry. This new technique spares the complicated processing that has been generally used for membrane functionalization. Therefore, this new technique is environmentally friendly and time and cost saving.

To improve the hydrophilicity of MPPM, PNVP, a hydrophilic polymer, was grafted onto MPPM via click chemistry and RAFT polymerization in one pot. GD of PNVP on the MPPM surface increased with increasing Br molar content in the first step and NVP concentration in the one-pot reaction. GD of PNVP could be well controlled through the adjustment of the one-pot reaction conditions.

The normalized water flux increased along with increasing GD up to 4.96 mmol % because of the enhanced hydrophilicity; after that, it dramatically decreased because of pore shrinkage. The membrane fouling by protein was significantly suppressed; the flux recovery ratio and rejection of the grafted membrane for BSA was strengthened. The experimental results show that the antifouling characteristics of MPPM can be ameliorated by the grafting of a hydrophilic polymer, PNVP, onto the membrane surface.

ACKNOWLEDGMENTS

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