

SURFACE MODIFICATION OF MICROPOROUS POLYPROPYLENE MEMBRANES BY GRAFT POLYMERIZATION OF *N,N*-DIMETHYLAMINOETHYL METHACRYLATE*

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Abstract Surface modification of microporous polypropylene hollow fiber membranes was performed by radical-induced graft polymerization of *N,N*-dimethylaminoethyl methacrylate (DMAEMA). The influences of temperature, monomer concentration and pre-adsorbed amount of benzoyl peroxide on grafting degree were studied respectively. It was found that the appropriate graft temperature was 75 °C, at which the grafting degree was the highest and the hydrolytic decomposition of DMAEMA the lowest. Scanning electron photomicrography and the average pore diameters of the modified membranes demonstrated that part of the micropores on the membrane surface was plugged by the grafted polyDMAEMA chains, especially at high grafting degree. Contact angle and water swelling experiments showed that a moderate grafting degree could improve the hydrophilicity of the membranes. In the range of 11.3%–12.0% grafting degree, the water swelling percentage reached its maximum (51.1%) and the contact angle reached its minimum (74 degrees). The bovine serum albumin (BSA) adsorption experiment indicated that the grafted polyDMAEMA had a dual effect on protein adsorption. At the first stage, the BSA adsorption decreased with increasing of DMAEMA grafting degree. As the interaction between BSA and polyDMAEMA on membrane surface increased, the BSA adsorption increased with increasing of DMAEMA grafting degree.

Keywords Polypropylene hollow fiber membrane, *N,N*-Dimethylaminoethyl methacrylate, Surface modification, Graft polymerization, BSA adsorption

INTRODUCTION

The importance of membrane surface chemistry and physics in deciding the separation characteristics is well recognized^[1–3]. In recent years, therefore, there has been much interest in developing surface treatment technologies to alter the chemical and physical properties of membrane surfaces. Different methods such as hydrophilizing agent coating, plasma modification, corona discharge and flame treatment can be applied to modify the membrane surfaces, *e.g.* to increase or to reduce hydrophilicity, adsorption of molecules, ionic change, biocompatibility *etc.*, without affecting their bulk properties. One of the simplest modification methods is to treat the membrane with hydrophilizing agents such as alcohols, surfactants, polyelectrolyte complexes, or a coating with hydrophilic compounds. However, it is difficult to sustain the initial hydrophilicity. The micropores of the alcohol-wetted membranes remain hydrophilic during immersion in water, but once the membrane is dried, its hydrophilicity is instantly lost. In the case of a surfactant-impregnated membrane, its hydrophilicity decreases with time, as the surfactant tends to leak out from the pores. Although these techniques are extremely simple, they do not impart permanent hydrophilicity to the membrane because the surfactants adsorb only

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physically and do not bind chemically to the surface of the membrane. Therefore, surface graft polymerization has been developed as one of the most efficient methods to control the hydrophilic monomer on the membrane surface and to modify durably the surface properties of membrane. During the graft polymerization, active sites are first introduced on the membrane surface commonly by radicals^[4–7], radiation^[8, 9], plasma^[10, 11] and UV^[12–18], and then initiate monomer for polymerization. The monomers used for this purpose include acrylic acid, acrylamides, various acrylates or methacrylates, *N*-vinyl pyrrolidone, 4-vinyl-pyridine and so on.

N,N-Dimethylaminoethyl methacrylate (DMAEMA) is a useful monomer containing both ester and dimethyl amino groups. Chen *et al.*^[19] synthesized hydrogels based on DMAEMA by photopolymerization in water solutions. The hydrogels were proved to be both thermosensitive and pH-sensitive, which had a potential for application in modulated drug-delivery because the polymers not only respond to external stimuli but also control the release rate of drugs^[20]. Grassi *et al.*^[21] established the model of solute transporting across a temperature sensitive poly(DMAEMA-*co*-AAm) gel membrane. By group transfer polymerization, Triftaridou *et al.*^[22] synthesized three isomeric, linear, equimolar, amphiphilic ABC triblock copolymers containing the ionizable hydrophilic DMAEMA and found that the different distributions of monomer units in the copolymers resulted in different supramolecular structures with different colloidal stabilities. Surface modification with DMAEMA would result in desirable properties such as hydrophilicity, biocompatibility and positive charging potential. Richey *et al.*^[23] prepared functional balloon catheters by photo-grafting DMAEMA on polyethylene surfaces in order to immobilize argatroban, a potent anti-thrombin agent. Yang *et al.*^[24] reported the graft polymerization of DMAEMA on SBS membrane to fabricate SBS-*g*-DMAEMA copolymer membrane by UV photo-grafting. The biocompatibility of the resultant membranes was evaluated by measuring the contact angle and the protein adsorption of fibrinogen and albumin on surfaces.

Microporous polypropylene membranes as supported-layers were eye-catching for their high void volume, well-controlled porosity, chemical inertness and low cost. To improve its hydrophilicity and anti-fouling property, DMAEMA was also used to modify microporous polypropylene membranes by Ma *et al.*^[16, 17] with UV photo-grafting and Carroll *et al.*^[25] with free radical grafting based on a macroinitiator of poly(trimethyl-2-pentene-*alt*-maleic acid anhydride), respectively. However, no data concerning the graft polymerization itself was reported. In our previous paper^[7], acrylic acid (AA) was grafted onto the surface of microporous polypropylene hollow fiber membranes using a free radical method. The water-alcohol separation performance of the AA-grafted polypropylene hollow fiber membranes by pervaporation was also described^[26]. In this work, the graft polymerization of DMAEMA onto the surface of polypropylene hollow fiber membranes by a simple free radical method was investigated. The chemical and morphological changes of the membrane surface were examined. It is envisaged that the introduction of polyDMAEMA onto the surface of microporous polypropylene membrane could improve both its hydrophilicity and biocompatibility.

EXPERIMENTAL

Materials

Microporous polypropylene hollow fiber membranes were prepared by a melt-extruded/cold-stretched (MECS) method in our lab. The inner and outer diameters of this hollow fiber were 240 μm and 290 μm , respectively, with a porosity of 40% and an average pore diameter of 0.070 μm . DMAEMA with 99% purity was kindly supplied by Xinyu Chemical Co. Limited, Wuxi, China, and was distilled under vacuum before use. Benzoyl peroxide (BPO), as the initiator, was A.R. grade and was recrystallized three times before use. Bovine serum albumin (BSA) was purchased from Sino-American Biotechnology Co. Ltd. and used as received. The other reagents were A.R. grade, and purified before use. Ultra-pure water with a conductivity of 18 S/cm was used as polymerization medium and for water permeability measurement.

Graft Polymerization

The nascent microporous polypropylene membranes were soaked in acetone for a week, washed two times to remove any chemicals absorbed on the membrane surface, and were dried in vacuum at room temperature for

24 h before initial weight (W_1) was measured. The pre-weighed membrane was soaked in BPO/ CHCl_3 solution for several hours to adsorb BPO on the surface of the membrane, and then dried in vacuum at room temperature till constant weight. Hereafter, the weight of BPO-adsorbed membranes was measured (W_2). The membranes were put into flasks and immersed in DMAEMA aqueous solutions of different concentrations. The flasks were purged with nitrogen for 10 min and sealed, then placed in an oil bath at a temperature of 65–80 °C for polymerization. During polymerization, the flasks were shaken at a shaking speed of 120 r/min. After the completion of graft polymerization, the membranes were taken out of the reaction flasks and washed with 95% ethanol for at least three times to extract the homopolymer adsorbed on the membrane surface. Then, the membranes were dried and weighed (W_3). The grafting degree (D_g) of DMAEMA was defined as

$$D_g(\%) = \frac{W_3 - W_1}{W_1} \times 100$$

where W_3 and W_1 were the weights of the grafted and initial membrane, respectively.

Characterization

Attenuated total reflectance (ATR) FT-IR spectra of the virgin and grafted PP membranes were obtained from a Bruck 22 FT-IR spectrometer, and the surface morphology of the membranes was studied by scanning electron microscopy (SEM) with a Hitachi S-570 electron microscope. The contact angle of pure water on polypropylene membranes was measured to estimate the membrane's hydrophilicity. The average pore diameter (r_{av}) was measured using a mercury porosimeter. A weighed amount of fiber membrane was introduced into a chamber filled with mercury. Then the pressure was increased to force mercury into the micropores of the membrane. By monitoring the volume change of mercury and the corresponding pressure, the average pore diameter of membrane could be obtained.

The water swelling percentage of membrane was measured using the following procedure. The weighed membrane sample (W_4) was immersed in ultra-pure water at 25 °C for 24 h. Then the membrane was taken out and excess water on membrane outer surface was blotted out with filter paper and the weight of the membrane was measured immediately (W_5). The water swelling percentage of the grafted membrane was calculated by the following equation.

$$\text{Water swelling percentage (\%)} = \frac{W_5 - W_4}{W_4} \times 100$$

The hollow fiber membrane about 20 cm long was positioned in a U-configuration. Ultra-pure water was forced to permeate through the pores radially outwards at a constant permeation pressure. The flow rate of the water penetrating the outside surface of the hollow fiber was measured, and the pure water flux was calculated by dividing the flow rate by the inside surface area of the hollow fiber ($Q = \text{L/m}^2 \cdot \text{h}$). All the measurements were performed at 25 °C and 0.01 MPa pressure.

The BSA adsorption of grafted membrane was studied by the following approach. The membrane was first washed several times with ethanol and ultra-pure water to remove the pollutants, then immersed in 10 mL BSA/buffer solution ($\text{Na}_2\text{HPO}_4\text{-KH}_2\text{PO}_4$, pH = 8) of various concentrations. The mixture was sealed and incubated at 35 °C for 24 h. After reaching adsorption-elution equilibrium, the membrane was taken out and the concentration change of BSA solution was determined by UV spectroscopy at 280 nm. The protein adsorption on the membrane surface was calculated from the concentration decrease of BSA solution.

RESULTS AND DISCUSSION

Graft Polymerization

To obtain membrane with excellent bulk properties and anti-fouling surface characteristics is one of the goals of current research efforts. In this respect, graft polymerization is an efficient way to chemically attach hydrophilic species to hydrophobic membranes such as polypropylene (PP), polyethylene (PE) and polytetrafluoroethylene

(PTFE). For the graft polymerization of DEAEMA on the surface of PP microporous hollow fiber membrane, several factors would influence the graft process.

The effect of reaction temperature on the graft polymerization was studied at 65°C, 70°C, 75°C and 80°C, respectively, and the results are shown in Fig. 1. It can be seen that the grafting degree increased gradually from 65°C to 75°C, reached a maximum value near 75°C, and then declined with increasing temperature. The favorable impact of temperature on graft polymerization could be attributed to (a) the enhancement of diffusion of monomer into the membrane pores; (b) the increase of the mobility of monomer molecules and their collisions with macroradicals; (c) the increase of the propagation of grafted chains and (d) the increase of the number of free radicals generated by thermo-decomposition of BPO, which perhaps resulted in forming more reactive sites on the membrane surface. On the other hand, the negative influence on graft polymerization at and above 75°C might be due to (a) the increase of the termination rate of grafted polymer chains by disproportionation and (b) the enhancement of chain transfer to monomer molecules. For the above reasons, the most appropriate temperature in our work was 75°C.

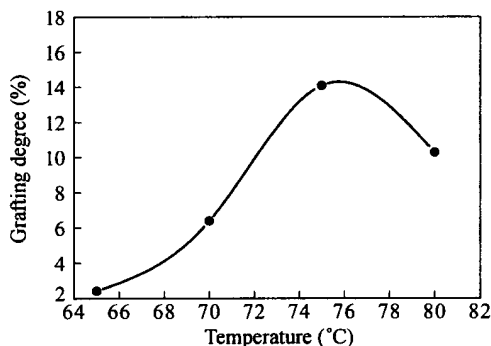


Fig. 1 Effect of temperature on the graft polymerization of DMAEMA
Reaction time: 13 h; Monomer concentration: 9.0 wt%

Figure 2 shows the effect of monomer concentration on graft polymerization at 75°C. It is evident that the grafting degree of DMAEMA increases with the monomer concentration. Figure 3 illustrates the effect of the amount of BPO adsorbed on membrane surfaces. It was found that the grafting degree increased with the amount of adsorbed-BPO. This was reasonable because, at the same graft temperature, more BPO was adsorbed, and more active site was produced on the membrane surface.

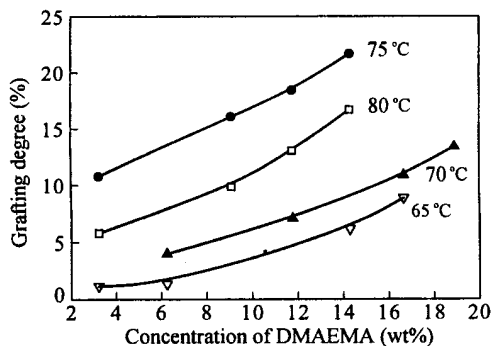


Fig. 2 Relationship between the grafting degree and DMAEMA concentration at different temperatures

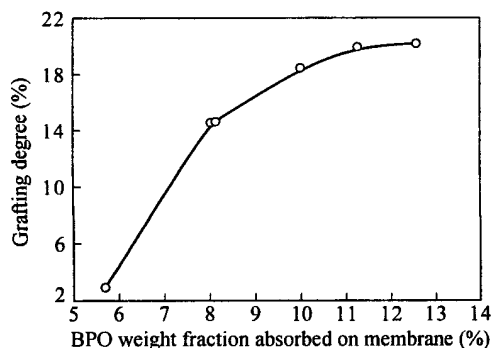


Fig. 3 Effect of the amount of BPO absorbed on membranes on grafting degree
Reaction temperature: 75°C; DMAEMA concentration: 10.0 wt%; Reaction time: 12 h

Characterization and Properties of the Modified Membranes

After graft polymerization, a thin layer of polyDMAEMA was generated on the surface of PP membrane. Figure 4 shows the ATR FT-IR spectra of original and grafted membranes. From the spectra of the grafted membranes (Fig. 4b to 4e), one absorption peak ($\approx 1730\text{ cm}^{-1}$) can be seen, which is attributed to the stretching vibration of C=O group in DMAEMA. Because DMAEMA was relatively easy to hydrolyze during polymerization in aqueous solution, the effect of graft temperature on DMAEMA hydrolysis was studied by ATR FT-IR spectroscopy. As can be seen from Fig. 4, at 80°C , there is an obvious absorption peak above 3000 cm^{-1} , indicating the existence of $-\text{OH}$ groups. Combining with the absorption peaks appeared near 1650 cm^{-1} and 1550 cm^{-1} , which are attributed to the $-\text{COOH}$ and $-\text{COO}^-$ groups respectively, it seems that DMAEMA was slightly hydrolyzed at 80°C . However, at other graft temperatures, the hydrolysis of DMAEMA was ambiguous.

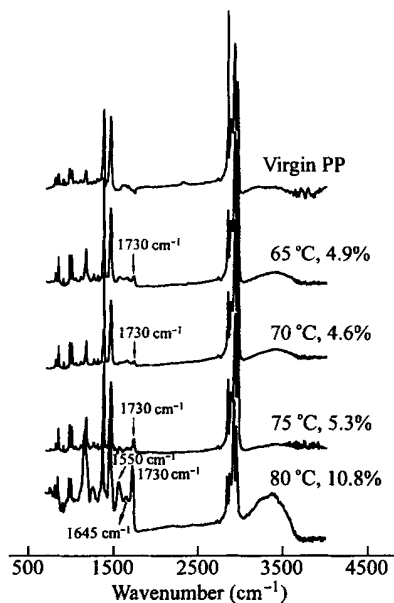


Fig. 4 ATR FT-IR spectra of nascent PP membrane and DMAEMA-grafted membranes

Scanning electron microscopy (SEM) was employed to examine the surface morphology of typical modified membranes. The SEM pictures for the outer surface of hollow fiber membranes are shown in Fig. 5. It seems that part of the surface pores was somewhat plugged, especially at high grafting degree, because polyDMAEMA chains cover the original surfaces of the PP membrane. Compared with the micrograph of unmodified membrane (Fig. 5a), it was observed that some pores become smaller and more spherical in shape. This can be further confirmed by the average pore diameters of nascent and modified membranes, which are listed in Table 1. The data reveal that the average pore diameter for the modified membranes decreases with the increase of grafting degree. The SEM pictures of modified membranes with similar grafting degree at different graft temperature are also given in Fig. 6. It is evident that the microporous structure of membranes is not obviously changed by the grafting temperature.

DMAEMA is an amphiphilic monomer. Therefore, the graft polymerization of DMAEMA on the PP membrane surface could alter the surface property from hydrophobic to comparatively hydrophilic. The water swelling characteristics of the grafted membranes is shown in Fig. 7. It was found that the water swelling percentage increased at low grafting degree. Near the point of 11.3% grafting degree, the water swelling percentage reached its maximum value. Hereafter, it decreased with the increase of grafting degree. These results can be explained on the basis of the moderate hydrophilicity of polyDMAEMA and pore-plugging effect. With the increase of grafting degree, the hydrophilicity of the membrane increases, which enhances the water swelling

percentage. At high grafting degree, however, part of the micropores is plugged. Therefore, water entrapped in the porous cavities is reduced. As a total result, the apparent water swelling percentage decreases at high grafting degree.

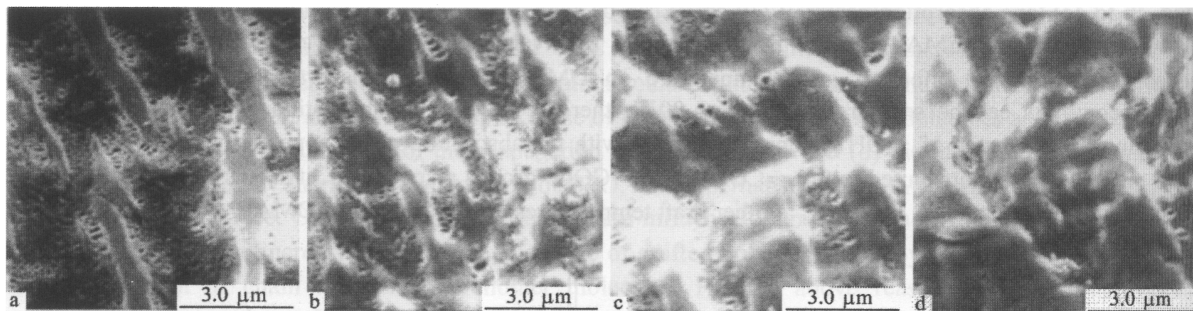


Fig. 5 Scanning electron photomicrographs of the outer surface of the nascent and modified PP hollow fiber membranes a) Virgin PPHFM; b) 2.1%, 75°C; c) 11.8%, 75°C; d) 20.3%, 75°C

Table 1. Average pore diameter of nascent and modified membranes

Grafting degree (%)	Average pore diameter (μm)
0	0.072 ± 0.005
1.3	0.053 ± 0.004
2.0	0.051 ± 0.005
3.7	0.045 ± 0.003
4.4	0.036 ± 0.005
5.8	0.031 ± 0.005
10.3	0.027 ± 0.005

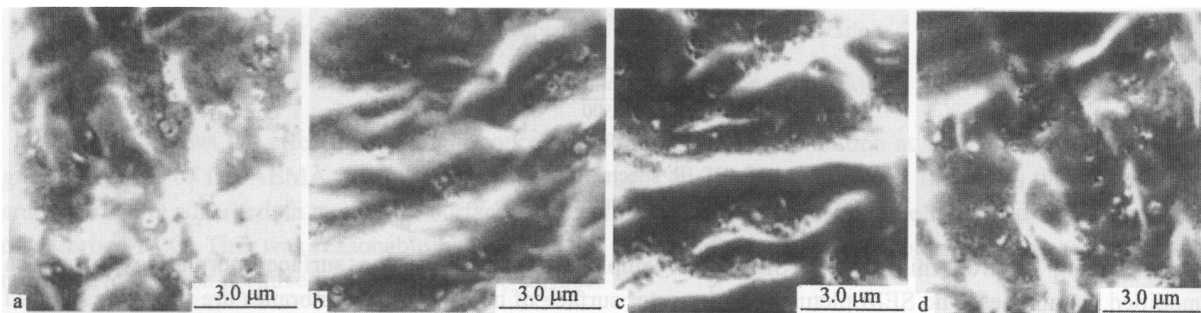


Fig. 6 Effect of reaction temperature on the SEM pictures of the outer surface of the modified PP hollow fiber membranes with similar grafting degree

a) 4.4%, 65°C, b) 4.6%, 70°C, c) 4.5%, 75°C, d) 4.8%, 80°C

To further estimate the hydrophilicity of modified membranes, pure water contact angle on membrane surface was measured and the results are shown in Fig. 8. Compared with the virgin membrane, it can be seen that the contact angle of grafted membrane decreases obviously with the increase of grafting degree. Near the point of 12.0% grafting degree, the contact angle reached its minimum value, which confirmed the view that DMAEMA grafted PP membranes were moderately hydrophilic. After this point, the contact angle increased slowly with the grafting degree. This could be explained as below. We assumed that grafted poly(DMAEMA) forms a monolayer on the membrane surface at relatively low grafting degree, with the hydrophobic side contacted with PP membrane surface and the hydrophilic side stretching outside, which greatly reduce the water contact angle. As the grafting degree increases, the monolayer transfers to multilayer with some hydrophobic side stretching outside, resulting in the increase of water contact angle. On the other hand, the micropores would be reduced or plugged at high graft degree, as demonstrated by SEM and average pore diameter measurement,

which means that the effect of micropores on the contact angle measurement would be reduced as grafting degree is increased, leading to the increase of contact angle also. The dynamic contact angle was measured to confirm the above assumption. As can be seen from Fig. 9, as the time for contacting membranes with water is increased, all the water contact angles of polyDMAEMA-modified membranes decrease, which is consistent with the above assumption.

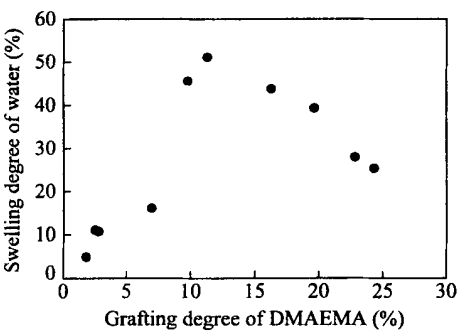


Fig. 7 Relationship between water swelling and DMAEMA grafting degree at 25°C

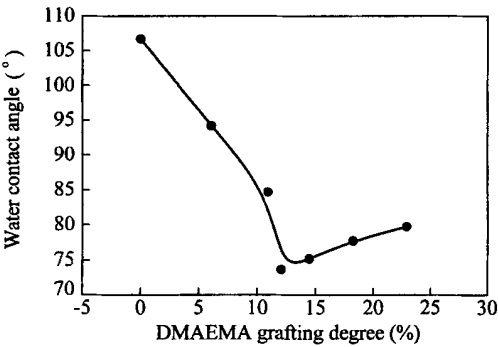


Fig. 8 Relationship between water contact angle and DMAEMA grafting degree

BSA is a typical non-selective protein and it is often used as a representative for protein adsorption experiment. Figure 10 shows the results of BSA adsorption on the membranes with different grafting degree. It was found that, at low grafting stage, the BSA adsorption decreased with the increase of DMAEMA grafting degree. When the grafting degree rose to 14.6%, the BSA adsorption reached its minimum value. Soon afterwards, the BSA adsorption increased with the increase of DMAEMA grafting degree. It was known that the amino groups in the grafted polyDMAEMA affected the BSA adsorption in two ways. First, these groups improved the hydrophilicity of the membrane surface, which could suppress the BSA adsorption. Second, they would facilitate the binding of proteins. At low grafting stage, the introduction of polyDMAEMA enhances membrane hydrophilicity more efficiently. With the increase of DMAEMA grafting degree, the membrane surface will be covered by polyDMAEMA, the effect of enhancing membrane hydrophilicity gradually gives way to the effect of protein binding. Therefore, it was clearly demonstrated that the BSA adsorption on the polyDMAEMA grafted PP membranes is significantly decreased when compared with that on the nascent PP membrane, but it is increased again when the grafting degree exceeds around 15%.

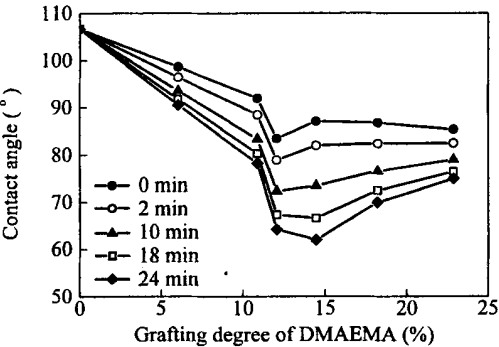


Fig. 9 Change of water contact angle with time for the DMAEMA modified PP hollow fiber membranes at 25°C

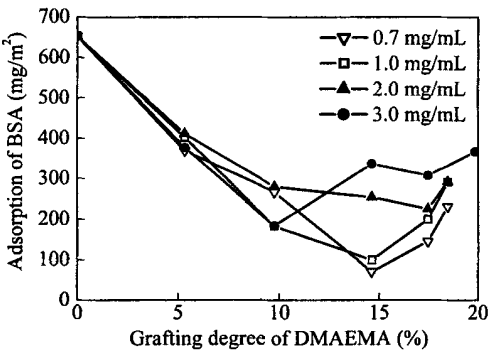


Fig. 10 Effect of DMAEMA grafting degree on BSA adsorption for the DMAEMA modified PP hollow fiber membranes at 25°C

Pure water permeation flux was measured for the modified membranes. Typical results are shown in Table 2. Data reported by Ma *et al.*^[16, 17] and Carroll *et al.*^[25] are also cited in this Table for comparison. The

nascent PP membrane cannot allow water to flow across. The water flux of the ethanol-wetted membrane was 41.4 L/m² h but it decreased sharply within 2 h due to the flow-off of ethanol from membrane surface. Compared with ethanol-treated membrane, on the other hand, the water flux for the polyDMAEMA-modified membranes was more stable, as can be seen from Fig. 11. Table 2 also shows that, around the point of 1.60% grafting degree, the polyDMAEMA-modified membrane shows its maximum water flux of 57.7 L/m² · h. However, with the increase of grafting degree, the water flux decreases slowly to zero. This could be ascribed to the plugging effect of the grafted chains, which reduce the effective free pores for water permeation. Furthermore, the water flux of polyDMAEMA-modified membrane was much lower than those reported by Ma *et al.*^[16, 17] and Carroll *et al.*^[25]. This was mainly derived from the remarkable difference in the average pore size for the nascent PP membranes. Another reason for this was that polyDMAEMA was positively charged in an acid solution^[16, 17, 25] while in our situation the grafted layer was neutral. It is well known that the tertiary amine groups of polyDMAEMA can be easily charged positively or turned into quaternary amines. The hydrophilicity of positively charged polyDMAEMA is much higher than that of neutral polyDMAEMA. Further work concerning these membranes and their properties has been carrying out in our lab. This will be described in a forthcoming paper.

Table 2. Water flux of the membranes at 25°C

Average pore diameter of the original PP membrane (μm)	DMAEMA grafting degree (%)	Water flux (L/m ² · h)	Ref.
0.07	Treated with ethanol	41.4	This work ^a
	0.6	17.0	
	1.6	57.7	
	2.5	38.5	
	4.8	22.3	
	7.0	6.4	
	8.8	9.5	
	11.3	4.2	
0.22	15.0 and above it	0	[16] ^b
	Treated with ethanol	1100	
	4.0	1200	
0.20	Treated with ethanol	1480	[25] ^c
	4.4	1040	
	5.6	680	
	6.3	430	
	7.8	90	

^a The grafted polyDMAEMA was neutral and the values were measured at 0.020 MPa
^b The grafted polyDMAEMA was positively charged and the values were measured at 0.034 MPa
^c The grafted polyDMAEMA was positively charged and the values were measured at 0.050 MPa

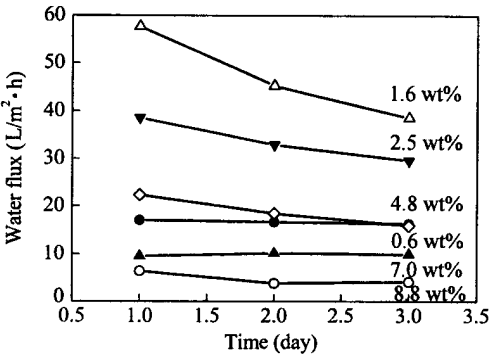


Fig. 11 Stability of water flux for the DMAEMA modified PP hollow fiber membranes at 25°C and 0.020 MPa

CONCLUSIONS

In this paper, microporous polypropylene membranes were modified by surface grafting of DMAEMA with BPO as initiator. Factors that influence graft polymerization were studied, respectively. ATR FT-IR spectra and SEM pictures together with average pore size analysis verify the chemical and morphological changes of the modified membranes. The static contact angle and water swelling as well as water permeation measurements revealed that relatively permanent hydrophilicity is achieved by grafting DMAEMA polymer on polypropylene membrane surfaces. The results of bovine serum albumin (BSA) adsorption measurement also indicate that the anti-fouling property of the membrane is improved. However, grafted membranes did not show high water flux because the grafting of DMAEMA plugged the pores of the membrane and the polyDMAEMA was moderately hydrophilic. High water flux could be expected when the grafted polyDMAEMA was positively charged and/or the tertiary amine groups in polyDMAEMA were turned into quaternary amines.

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