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Photografting Modification of PET Nucleopore Membranes

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ABSTRACT

PET nucleopore membranes were modified by photografting polymerization. The grafted membrane has a well-defined structure. Grafting polymerization is confined on the membrane surface; no graft occurs inside membrane pores. The grafted PAA was characterized with ESCA, and the morphology of grafted membranes was observed by SEM. The high monomer concentration, temperature and UV intensity is beneficial to the increase of grafting degree (D_g). BP as initiator has an optimized concentration due to the self-screening. Membrane surface was changed into hydrophilic via 10 sec. treatment. The competition of water affinity of membrane surface and swelling-cover effect of grafted layer result in the filtration rate of grafted membranes varied with the D_g. At low D_g, flux is larger than that of blank membrane; at high D_g, the swelled PAA chains on the membrane surface cover the membrane pores and thus the flux decreases dramatically even close to zero, whereas SEM shows that the membrane pores are still open in dry state.

Key Words: Photografting; Nucleopore membranes; Surface modification; Grafting modification.

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INTRODUCTION

Nucleopore membranes are widely applied in fine separation due to their peculiarities, high mechanical strength, cylindrical pores and the quite narrow pore size distribution. However, the hydrophobic nature not only results in more filtration resistance to aqueous solution, but also makes membranes easily protein-polluted. Grafting modification is an effective solution to those problems.

The grafting modification of nucleopore membranes was mainly concentrated on the high-energy irradiation and plasma grafting. N. I. Shtanko and co-workers[1] studied the relationships between grafting yield and dose rate, pre-irradiation dose and storage time by radiation grafting of styrene on PET nucleopore membranes. By irradiation grafting hydrophilic poly(methylvinyl pyridine), the membranes have an increase of flux at a low graft yield. The gas flow rate is decreased due to the decrease of pore size.[2] When thermo-sensitive poly(N-isopropylacrylamide) was grafted onto the nucleopore membranes, environmental sensitive character was obtained.[3] H. Iwata et al.[4,5] grafted poly(acrylic acid) (PAA) onto polycarbonate nucleopore membranes by low temperature plasma pre-treatment.

Since 1990s, photografting was used for membranes modification.[6–11] To our knowledge, its application on nucleopore membranes has not been reported. Compared with other grafting techniques, photografting has more advantages: UV light has poor penetrability than other high-energy radiation. Thus, the substrate is less affected by UV radiation. Furthermore, it does not need high vacuum and expensive reaction devices. The process can be a continuous operation, therefore, the photografting is a facile and practical method for nucleopore membranes modification.

Based on the above viewpoints, we initiated a project of photografting modification of commercial nucleopore membrane with the aim of improving their performances and developing new functional membranes. In this paper, the grafting chemistry and the effect of the photografting on the membrane structure and flux have been studied. The pH-responsive character will be discussed in following reports.

EXPERIMENTAL

Materials

The commercial PET nucleopore membranes were purchased from the Institute of Atomic Energy (P. R. China). Their structure parameters are shown in Table 1. Before use,

Table 1. Properties of PET nucleopore membranes.

Pore size (μm)	Pore density (/cm^2)	Thickness (μm)
0.2	1×10^8	10
0.4	3×10^7	10
1.5	1.2×10^5	28

the membranes were extracted with acetone for 12 h, then dried in vacuum at room temperature. Acrylic acid (AA) (Beijing Yili Fine Chemical Co.) was purified by distillation under reduced pressure. Benzophenone (BP) (Shanghai Reagent Factory) was used as received. Distilled water was used for filtration and grafting.

Photografting

Photografting polymerization was carried out in a photo reactor, as shown in Fig. 1. The pre-weighed membranes were fixed on the holder and immersed into the aqueous solution of BP and AA. The solution thickness on the membrane surface was kept at about 0.5 mm. This assembly was radiated for a given time under nitrogen atmosphere with a high-pressure mercury lamp (1 kW, Beijing Institute of Electric Light Source). After radiation, the grafted membranes were extracted with hot water in Soxhlet extractor and dried in vacuum at 50°C for about 10 h until a constant weight.

Characterization

The grafting degree (D_g) was calculated with the following equation.

$$Dg = \frac{m - m_0}{m_0} \times 100\% \tag{1}$$

where m_0 is the weight of blank membranes, m is the weight of grafted membranes.

The surface and cross-section morphology of grafted membranes were observed by SEM (Cambridge 250 MK3) under high vacuum. The atomic composition of the grafted surface was determined by X-ray photoelectron spectroscopy (XPS) (ESCA Lab220i-XL, VG Scientific) with an Al Kα large area source. The filtration experiments were carried out under a 100 kPa feed pressure in a self-made ultra-filtration cell. The flux of membranes (J) was calculated using the following equation:

$$J = \frac{V}{S \cdot t} \tag{2}$$

where V is the volume of filtrate, S is the effective filtration area and t is the time of filtration.

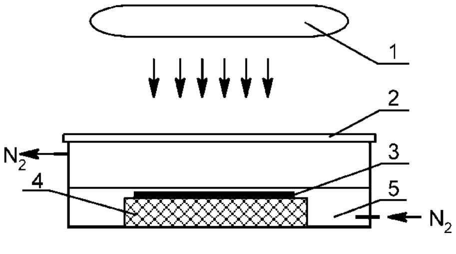

Figure 1. Schematic of photografting device. 1—UV lamp; 2—quartz glass; 3—membrane; 4—membrane holder; 5—reaction solution.

RESULTS AND DISCUSSION

Photografting Polymerization of AA

BP was used as an initiator in the photografting modification of nucleopore membranes. Figure 2 shows the chemistry of the photografting polymerization. Under UV radiation, BP undergoes photoreduction with the presence of the hydrogen donor, PET substrate. Photoreduction gives surface free radicals and semi-pinacol radicals. Surface free radicals initiate polymerization of AA. At last, the PAA was grafted onto the membranes.

The surface of grafted membrane was analyzed by XPS; the results are shown in Fig. 3 and Table 2.

Figure 3(a) and (b) are the O_{1s} spectra, the peak at 531.5 eV is attributed to the OH and C—O, and the peak at 533.1 eV is attributed to C═O. After grafting, the peak strength at 531.5 eV increased considerably. On the contrary, the peak strength at 533.1 eV decreased. In C_{1s} spectra (Fig. 3c and d), the peak strength at 286.1 eV that is assigned to C—C—O of the PET decreased. This indicated that the content of PET on the surface became lower. These results suggest that PAA has been grafted onto the surface of PET membranes. Table 2 shows the percentage of O_{1s} on the membranes surface increased. This is also attributed to the grafting of PAA.

D_g as a function of radiation time, temperature and UV intensity was shown in Fig. 4. It was seen that D_g increased with the prolongation of radiation time. When the temperature increased from 30°C to 50°C, D_g increased dramatically. To UV intensity, the same trend was observed, i.e., D_g increased with the increase of UV intensity because the high UV intensity excited more initiating species on the membrane surface. All of those indicated that the long radiation time, high temperature and UV intensity are beneficial to the grafting polymerization.

Figure 5 shows the relationship of initiator concentration (C_{BP}) and grafting degree.

With the increase of BP concentration, the D_g firstly increased to a maximum, and then decreased. This results can be explained by the self-screening of BP. Generally, the increase of C_{BP} is beneficial to grafting polymerization because of increasing the initiating species. However, with the increase of C_{BP}, the UV absorbability of reaction solution is enhanced which leads to the decrease of UV intensity on the membranes surface. The variation of D_g is a result of the increasing initiating species counter balanced by the self-screening of BP.

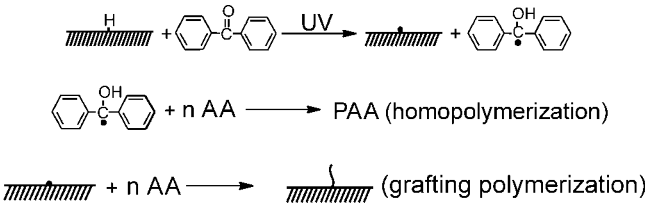

Figure 2. Schematics of photografting polymerization chemistry.

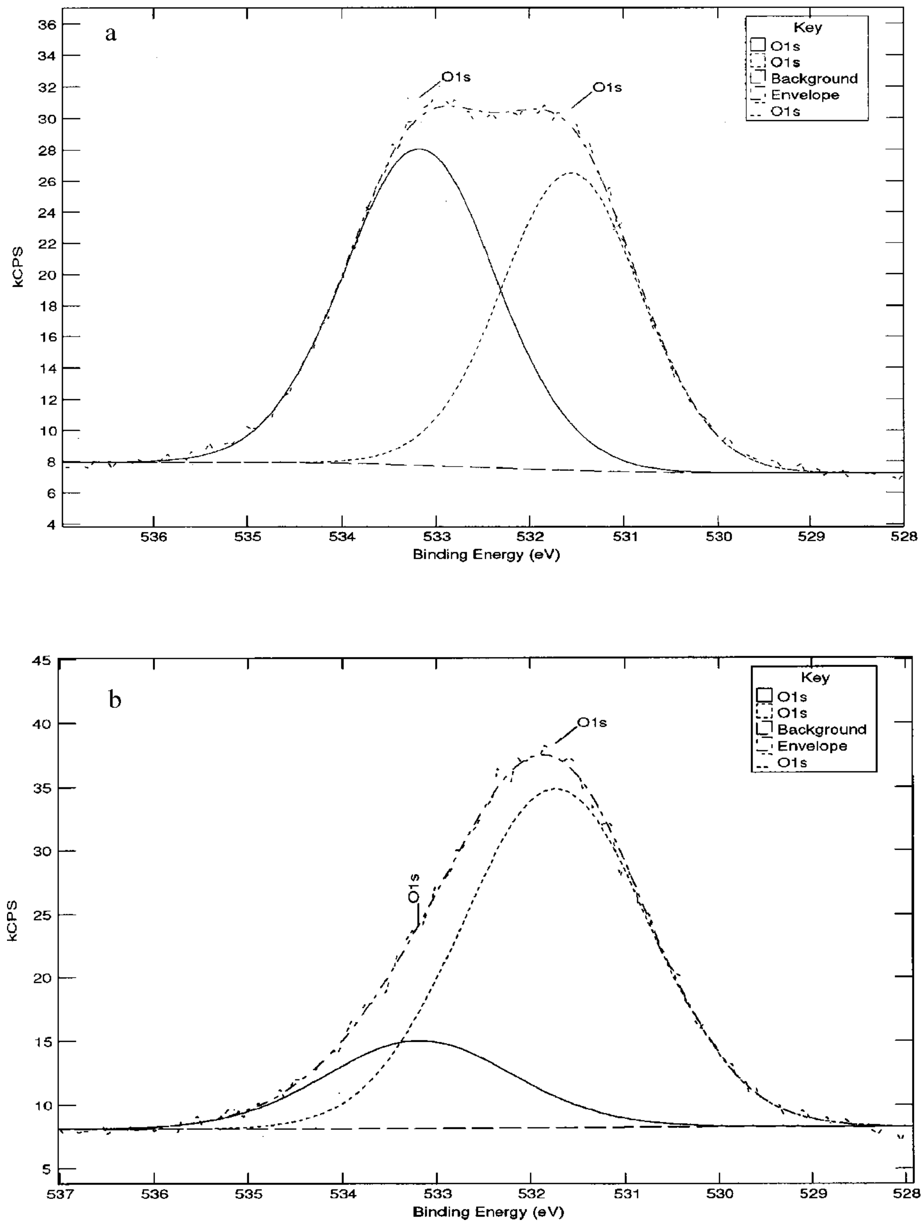

Figure 3. XPS spectra of control and the grafted membranes with a D_g of 2.07% (a) O_{1s} of control membrane; (b) O_{1s} of grafted membrane; (c) C_{1s} of control membrane; (d) C_{1s} of grafted membrane.

(*continued*)

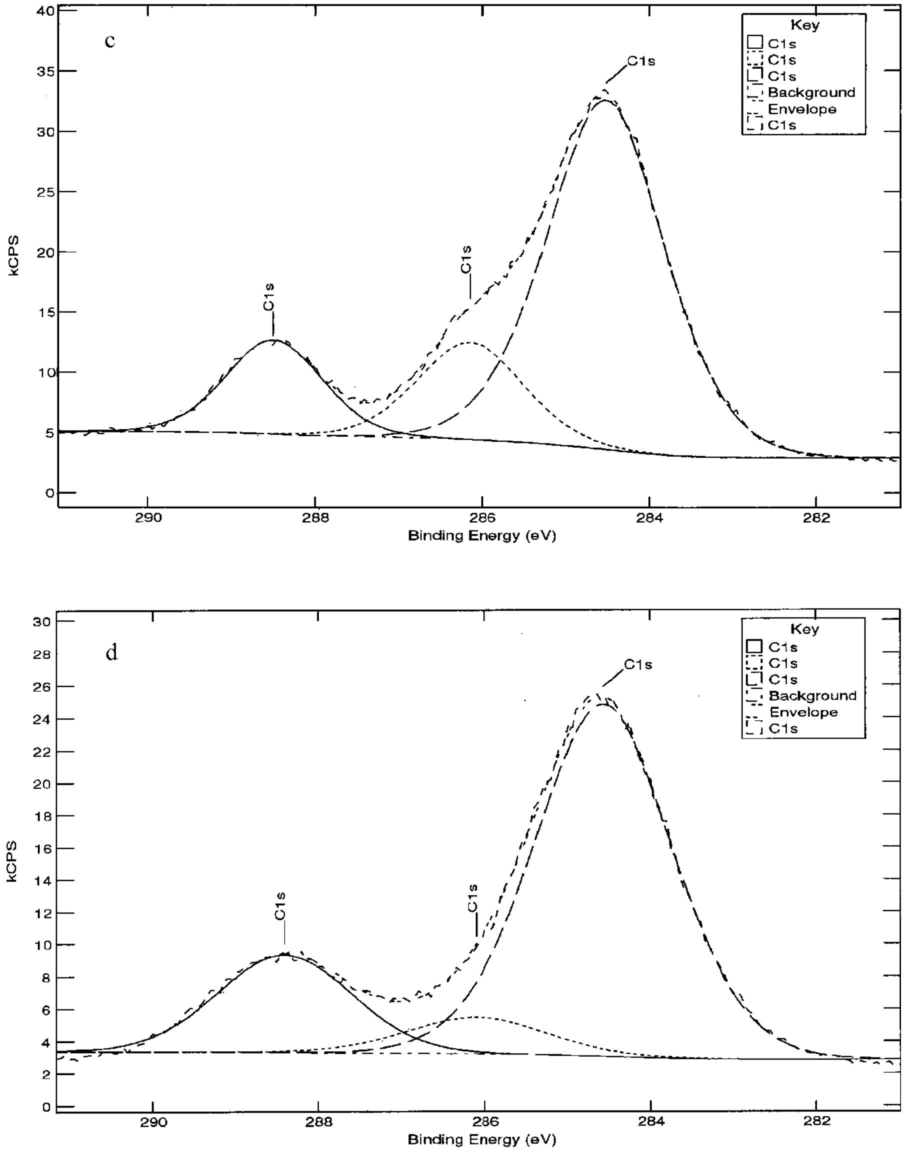

Figure 3. Continued.

The relationship of monomer concentration and D_g was presented in Fig. 6. It was found that the D_g rose with the increase of C_{AA}.

By adjusting the reaction parameters, grafted membranes with different D_g were prepared.

Table 2. XPS spectra of the membrane surface[a].

	Control membrane		Grafted membrane	
	Binding energy (eV)	Percentage (%)	Binding energy (eV)	Percentage (%)
O_{1s}	533.0	25.530	531.85	31.183
C_{1s}	284.55	74.470	284.65	68.817

[a] The membrane pore sizes are 0.4 μm. The D_g of grafted membrane is 2.07%.

Sites of the Photografting

Photografting polymerization is a heterogeneous interface reaction. The grafting sites depend on the UV light and the morphology of membranes. The role of the far UV in photografting polymerization and the screening property of PET film to the far UV radiation had been investigated in detail.[12] The far UV (254 nm) radiation is a decisive factor in the photografting initiated by BP; however, it cannot reach the deep of the membranes due to the strong absorption of PET. Furthermore, self-screening of the reaction solution and the small included angle between UV light and pore-wall also decreases the light intensity on the pore-wall. This is proof that the graft polymerization only occurs on the membrane surface exposed to the UV light and there was no change inside of the membrane pores. This also showed the grafted membranes has an asymmetric structure as seen in Fig. 7.

This result is confirmed by the SEM and water contact angle. Figure 8 is the SEM photograph of control and grafted membrane. Figure 8(a) and (b) shows that the grafted

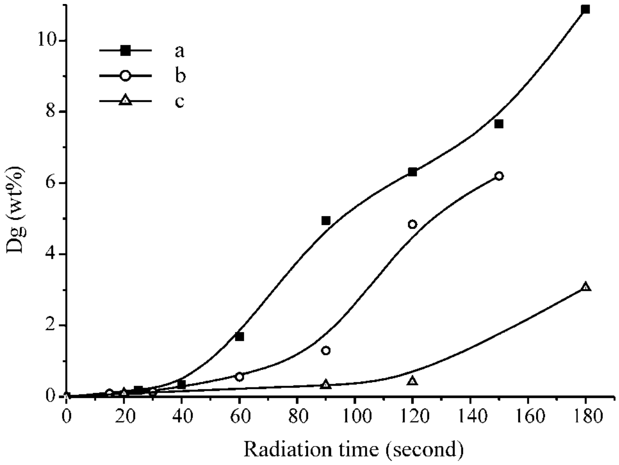

Figure 4. Effect of radiation time, temperature and intensity of UV light on degree of grafting. Reaction condition: (a) $I_0 = 8700\,\mu W/cm^2$, $T = 30°C$ is for (b); (a) $T = 50°C$; (b) $I_0 = 8700\,\mu W/cm^2$, $T = 30°C$; (c) $I_0 = 6700\,\mu W/cm^2$, $T = 30°C$. The pore size of membranes is 1.5 μm, $C_{AA} = 7\,mol/L$, $C_{BP} = 0.05\,mol/L$, I_0 is the intensity of UV light at the wavelength of 254 nm.

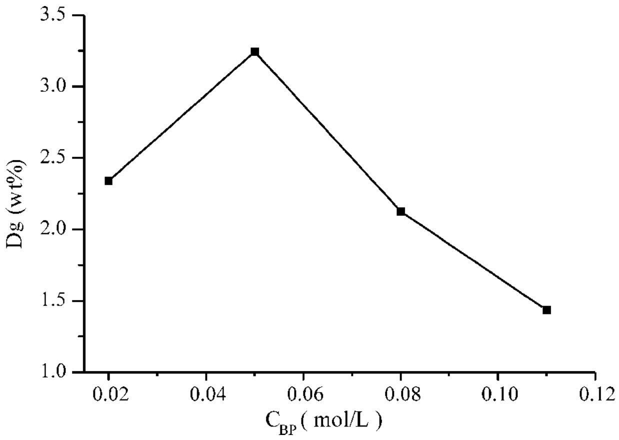

Figure 5. Effect of C_{BP} on D_g. The membrane pore size is 0.4 μm, T = 30°C, $C_{AA} = 7$ mol/L, t = 60 s.

membrane has both a dim pore shape and decreased pore size. In Fig. 8(d), a slice of grafting layer sticking on the membrane surface was seen. However, compared with the control membrane in Fig. 8(c), no difference was observed inside the pores. This suggests that the grafting layer was formed on the membrane surface, rather than inside the membrane pores.

The contact angle proved that the hydrophilic PAA grafting chains greatly improves the wetting capability of the grafted membranes. The blank membrane has a water contact angle of 73 ± 2 degree. After grafting, water spread completely on the grafted surface and easily penetrates into the pores, however, it is difficult to measure the water contact angle.

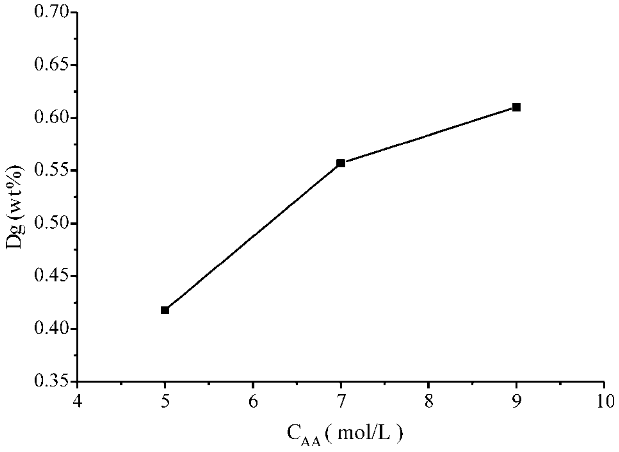

Figure 6. Effect of monomer concentration on the degree of grafting. Pore size is 1.5 μm, $C_{BP} = 0.05\,\text{mol/L}$, t = 60 s, T = 30°C.

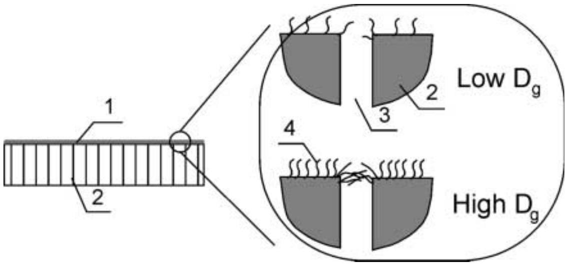

Figure 7. Schematic of sites of PAA grafting chains. 1—grafted layer; 2—membrane substrate; 3—membrane pore; 4—grafted PAA chains.

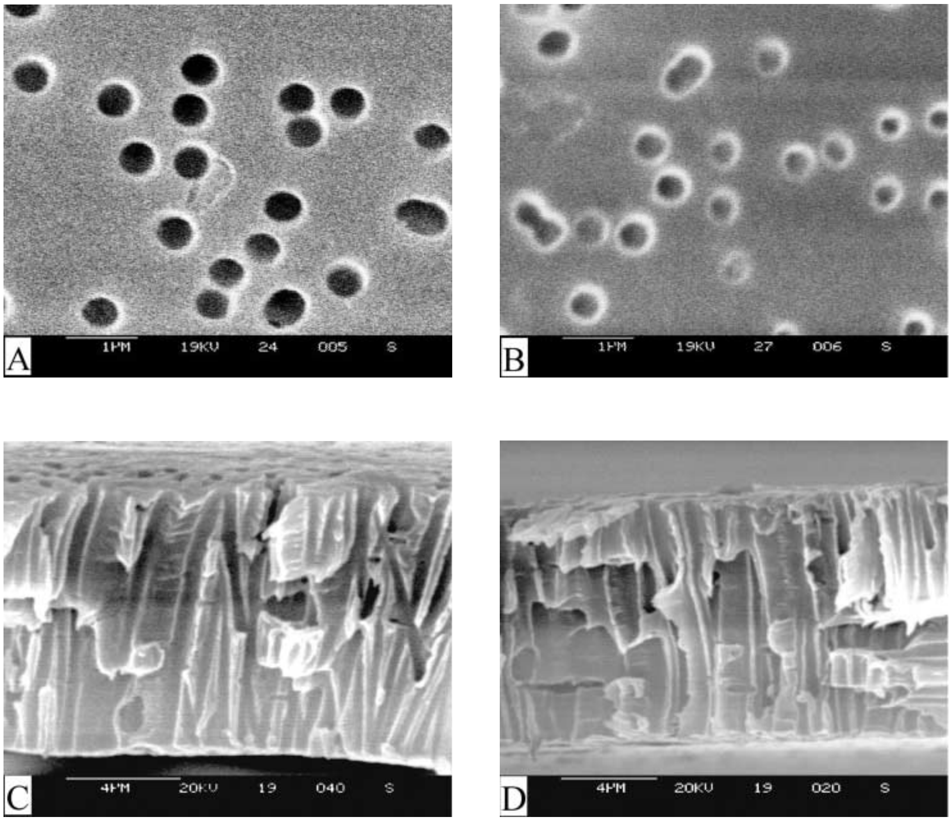

Figure 8. Surface and cross-section SEM of membranes with pore size of 0.4 μm. (A) Control membrane surface; (B) Grafted membrane surface ($D_g = 2.95\%$); (C) Cross-section of control membrane; (D) Cross-section of grafted membrane ($D_g = 2.95\%$).

A low D_g, such as 0.2%, is enough to change the membrane surface from hydrophobic into hydrophilic. On the contrary, the contact angle of the ungrafted surface, backside surface, has no change.

All of the facts proved that grafted membranes are single side modified and membrane pores are not affected.

Filtration Property of the Grafted Membrane

The performance of the grafted membranes was evaluated by water flux. Figure 9 presents the relationship between the grafting degree and water flux of the modified membranes. The value of J/J_0 denotes the variation of flux, where J is the flux of grafted membrane and J_0 is the flux of blank membrane. It was found that the curves of flux have a similar shape, despite the fact that the membranes pore size are different. At low D_g, the water flux of the grafted membrane is greater than that of the control membranes. The maximum fluxes of the grafted membranes with a pore size of 0.2 μm, 0.4 μm, and 1.5 μm reach 140%, 140%, and 200% of the flux of control membranes, respectively. When D_g is beyond a certain range, the fluxes begin to decrease. With a further increase of D_g, the fluxes drop and are close to zero.

This phenomenon can be understood by the improvement of surface hydrophilicity and swelling of PAA graft chains in water. The schematic illustrations in Fig. 7 show the effects at different D_g. The improvement in hydrophilicity reduces the resistance to aqueous solution and makes water pass easily through the membranes. At low D_g, the grafted polymer chains have little influence on the pore size, therefore, the flux is increased. With a further increase of D_g, the swelling of graft chains cannot be ignored. The swelled chains cover and block the pores. Thus, the effective pore size decreases.

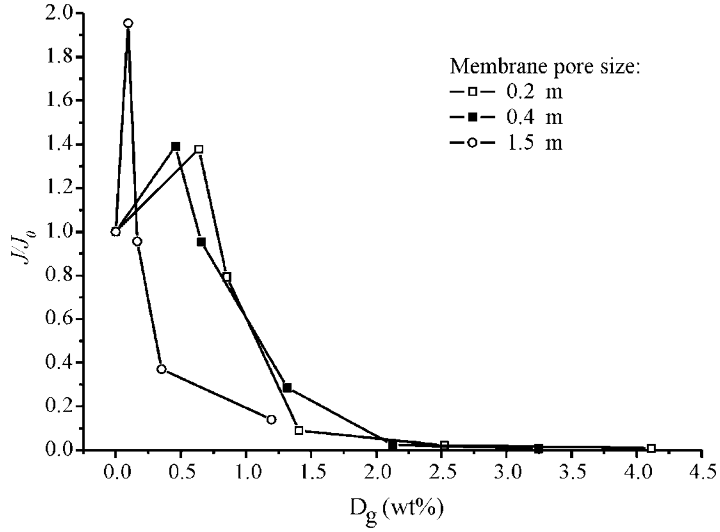

Figure 9. Effect of D_g on flux of grafted membranes.

The higher D_g is, the greater the covering effect. When the pores were completely blocked by swelling grafting polymer, the flux was close to zero.

The sample in Fig. 8 has a D_g of 2.95% and a flux of $0.02\ L\ h^{-1}\ cm^{-2}$. The flux is close to zero. It means that the pores have been blocked completely. However, the SEM picture shows that the grafted layer made the outline of pores blurry, whereas most of the pores were still open in a dry state. The sharp decrease in flux comes from the covering-block of the surface grafted layer of PAA.

According to these results, photografting has two potential applications. Firstly, we can increase flux and hydrophilicity of the nucleopore membrane surface by grafting hydrophilic monomer in a low D_g. Secondly, at a range of high D_g, the membrane pore size can be adjusted by accurately controlling the D_g. Thus, the filtration rate and separation property of membranes will be controllable. Furthermore, we may change a nucleopore membrane from microfiltration to ultrafiltration, nanofiltration, even reverse osmosis by gradually decreasing the effective pore size. Photografting provides a new method to prepare a series of functional membranes.

CONCLUSION

Using BP as a photoinitiator, PAA was photografted onto the PET nucleopore membranes. The membranes have a well-defined structure, single surface modified and no graft inside membrane pores. The modified surface was changed into hydrophilic. At low grafting degree, the membrane flux is higher than that of the blank membrane. With the further increasing of D_g, the flux decreases rapidly, even close to zero. The flux can be adjusted by control of the D_g. Photografting provides a simple and practical method for the modification of nucleopore membranes.

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