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A novel method of surface modification on thin-film composite reverse osmosis membrane by grafting poly(ethylene glycol)

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Abstract

A novel method of surface modification by grafting hydrophilic poly(ethylene glycol) (PEG) chains onto the surface of a thin-film composite (TFC) polyamide reverse osmosis (RO) membrane was performed. Aminopolyethylene glycol monomethylether (MPEG-NH_2) was used as grafting monomer. The membranes were characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The changes in chemical composition and morphology of the membranes' surface indicated the successful grafting process. Furthermore, a preliminary experiment confirmed that the grafting of PEG chains improved membrane antifouling property.

Keywords: Surface modification; TFC membrane; Poly(ethylene glycol)

1. Introduction

The development of thin-film composite (TFC) membrane is an important breakthrough in the field of reverse osmosis (RO) technology. During the past two or three decades, RO process has gained extensive attention in water reclamation and separation of organics from aqueous streams [1–3]. However, the successful utilization of RO technology is greatly limited by fouling, which is a major obstacle for the membrane application [4,5].

By far, to mitigate this problem and promote the RO technology application, numerous ways were examined including pretreatment processes [6], designing special modules [7] and preparation of antifouling membranes. Meanwhile, surface modification was considered as a potential route to prepare antifouling membrane by improving the hydrophilicity or charge properties of membrane surface. The surface modification methods ranged from simple physical adsorption [8–10] to chemical bond formation [11–20]. Considering the long-term effect, covalent grafting methods by chemical coupling [13–15], UV-induced [16] or plasma-initiated [20] were desirable. Such approaches showed the promise of the increase in antifouling property. However, most of them needed special instruments or modification conditions that restricted their application. In our present paper, we attempt to perform a novel and easy method for surface modification of the TFC membrane.

The above approaches were based on the introduction of active functional groups or free radicals to the membrane surface for further chemical coupling between grafting monomers and the membrane. In addition, the active layer of aromatic polyamide composite membranes fabricated by interfacial polymerization contained carboxylic acid groups [1]. They were formed by the eventual hydrolysis of the acyl chloride groups that did not react with amine. Therefore, it was

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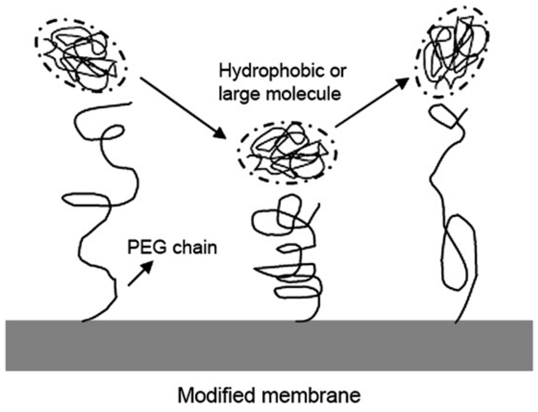


Fig. 1. Schematic diagram of steric repulsion mechanism of macromolecule by surface grafting PEG chain.

possible to modify the nascent composite membrane surface using these unreacted acyl chloride groups before their hydrolysis.

On the other hand, among various hydrophilic monomers used for surface grafting, poly(ethylene glycol) (PEG) and its derivates were used widely. PEG is an uncharged water-soluble polymer with the chemical formula of $HO-(CH_2CH_2O)_n-H$. Its extraordinary antifouling ability, e.g. especially to resist protein adsorption, is due to its hydrophilicity, flexible long chains, large exclusion volume and unique coordination with surrounding water molecules in an aqueous medium [21]. Surface-bounded PEG molecules can be very effective in preventing adsorption of hydrophobic or large molecules from membrane surface, following the steric repulsion mechanism demonstrated in Fig. 1. The steric repulsion effect is due to the loss of configurational entropy resulting from volume restriction and osmotic repulsion of PEG chains. In recent years, surface modification by the immobilization of PEG molecules was investigated to improve membrane antifouling property, particularly in ultrafiltration [13,16,20].

Based on the analysis above, a novel idea was introduced in the present paper to modify TFC RO membrane. Aminopolyethylene glycol monomethylether (MPEG-NH_2) was used as grafting monomer. The surface chemical composition and morphology of membranes were investigated using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). A preliminary fouling experiment was performed.

2. Experimental section

2.1. Materials

Solvents and reagents were purchased from commercial sources and in analytical grade. Polysulfone support membranes were prepared by phase inversion method. 1,3,5-Benzenetricarbonyl trichloride (TMC), *m*-phenylene-diamine (MPD) and monomethoxy-poly(ethylene glycol) (MPEG) with a molecular mass of about 5000 g/mol were purchased from Aldrich company.

The MPEG-NH_2 was synthesized from MPEG with classical Gabriel synthesis method according to Refs. [22,23], which is summarized in Scheme 1. The MPEG-NH_2 with the end amine group was prepared and used as grafting monomer for its higher activity than MPEG.

2.2. Fabrication of TFC RO membranes

The membranes were fabricated according to interfacial polymerization method described elsewhere [1,24]. The preparation process of modified membranes was similar, the differences were: after initial polymerization reaction between TMC (0.1%, w/v) and MPD (2.0%, w/w), excess hexane solution was removed, subsequently the membrane surface was covered with a solution of MPEG-NH_2 (5.0%, w/w) in deionized water for 5 min, then the membranes were rinsed and dried in an oven for a few minutes. The whole fabrication process was performed at room temperature. All membranes were thoroughly washed with deionized water and stored in deionized water.

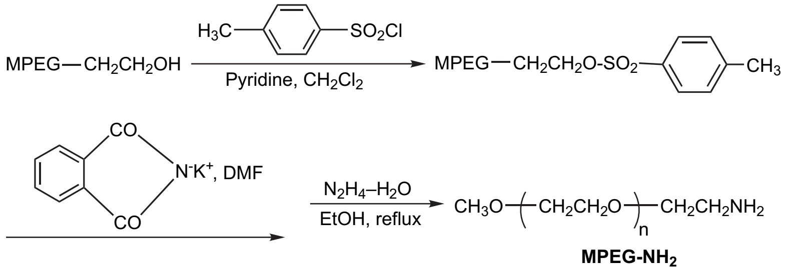
2.3. Spectroscopic analysis

2.3.1. ATR-FTIR spectroscopy

In order to investigate chemical composition changes between the unmodified and modified membranes and confirm the grafting of PEG onto RO membrane surface, Fourier transform infrared spectroscopy (Equinox 55) with an attenuated ATR unit (ZnSe crystal, 45°) was employed. The membrane samples were dried in vacuum oven before analysis. IR spectra of the membranes were recorded in the range of wave number 800−4000 cm^{-1} at 25 °C.

2.3.2. X-ray photoelectron spectroscopy

XPS spectra were recorded on a Leybold LHS-12 ESCA unit employing Mg Kα excitation radiation (1253.6 eV). The



Scheme 1. Synthesis schematic diagram of MPEG-NH_2.

X-ray source was run at a power of 200 W (10.0 kV, 20 mA). The surface elemental stoichiometries were determined from peak area ratios after correcting with experimentally determined instrumental sensitivity factors.

2.3.3. Atomic force microscopy

The membranes' surface topography was structurally characterized by AFM using a Nanoscope III equipped with 1553D scanner (Digital Instruments Inc., Santa Barbara). The tapping mode in air was preferable and used to take AFM images [10]. The AFM images of 10 μm scans were acquired by scanning the sample in air under ambient laboratory conditions at a scan rate of 2 Hz. The roughness of the membrane surface was assessed by measuring the roughness parameters.

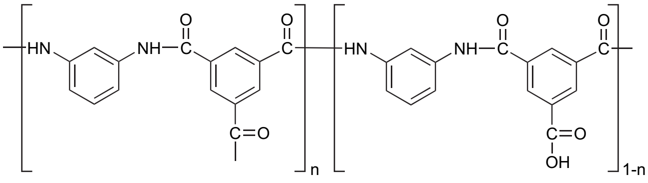
2.4. Fouling experiments

Membrane fouling experiments were performed with a laboratory-scale crossflow test unit. Each membrane was compacted with deionized water until the permeate flux became almost constant. Subsequently the contaminant was added to the reservoir and the permeate experiment was performed for a due course time. Then the membrane was rinsed with deionized water to investigate the flux recovery. The test was conducted at 1.6 MPa and 25 °C. Evaluation of the fouling extent of unmodified and modified membranes was based on the value of relative flux, which was calculated by comparing the water flux before and after fouling or cleaning.

3. Results and discussion

3.1. The feasibility analysis of grafting MPEG-NH_2

The feasibility of grafting PEG chains onto TFC membrane surface was analyzed. As mentioned before, the surface of some polyamide composite membranes such as FT-30 membrane contained carboxylic acid groups [1] and its chemical structure is described in Scheme 2. It had been confirmed that polymerization reaction occurred in organic phase during interfacial polymerization process [1]. In other words, amine should continually cross the water–organic interface, diffuse through the polyamide layer already formed, and then contact with acyl halide in the organic solvent side of the polyamide layer. With the increasing thickness of polyamide layer, there would be fewer and fewer amine groups on the organic phase side. The acyl chloride groups without reacting with amine to form amide bonds would be eventually hydrolyzed to carboxyl acid groups. Meanwhile, since the hydrolysis reaction of acyl chloride was a relatively slow process, the nascent membrane would contain numerous acyl halide groups on the surface (Fig. 2).



Scheme 2. Chemical structural formula of barrier layer in aromatic composite membrane.

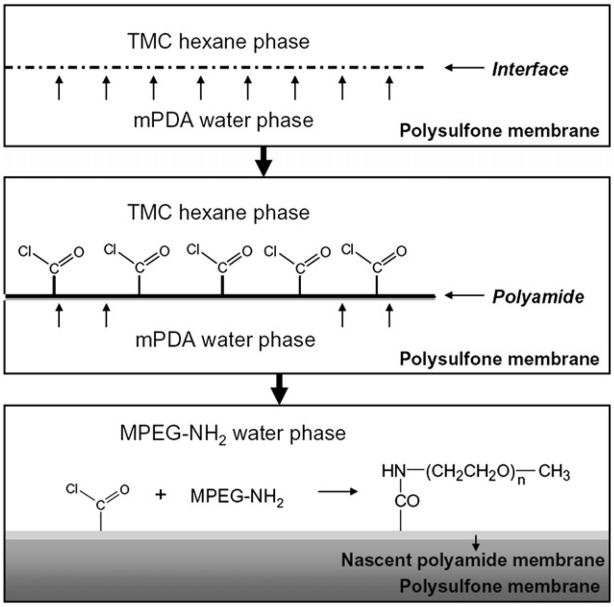


Fig. 2. Procedure of MPEG-NH_2 modification on nascent polyamide composite membrane surface.

As a result, it was possible to modify the nascent polyamide composite membrane surface with these unreacted acyl halide groups by chemical coupling with MPEG-NH_2. The schematic illustration of grafting process is summarized in Fig. 2.

3.2. Spectroscopic analyses

3.2.1. ATR-FTIR spectroscopy

ATR-FTIR measurement was performed to confirm the successful grafting reaction of PEG chains onto the membrane surface. ATR-FTIR spectroscopy provides a convenient and effective way for determination of the composition of the outmost part in a TFC membrane. Since the active layer is very thin, the IR spectrum of the composite samples shows information of both active layer and PSF support membrane. The spectra of unmodified and modified RO membranes with some bands of PSF such as 1584 cm^{-1} and 1243 cm^{-1} is presented in Fig. 3.

The major characteristic bands of aromatic polyamide at 1660 cm^{-1} (amide I, C=O stretch) and 1544 cm^{-1} (amide II, N–H bend) are shown in Fig. 3. By comparing the IR spectrum between the unmodified and modified membranes, the latter showed some new or intensity increased peaks at 943 cm^{-1}, 1080 cm^{-1}, and 2875 cm^{-1}, which were ascribed to CH_2 rock and C–C stretch, C–O and C–C stretch, and the CH_2 symmetric stretch of PEG, respectively [25]. These observations suggested that the chains of PEG molecules should be effectively grafted on the surface of modified membrane.

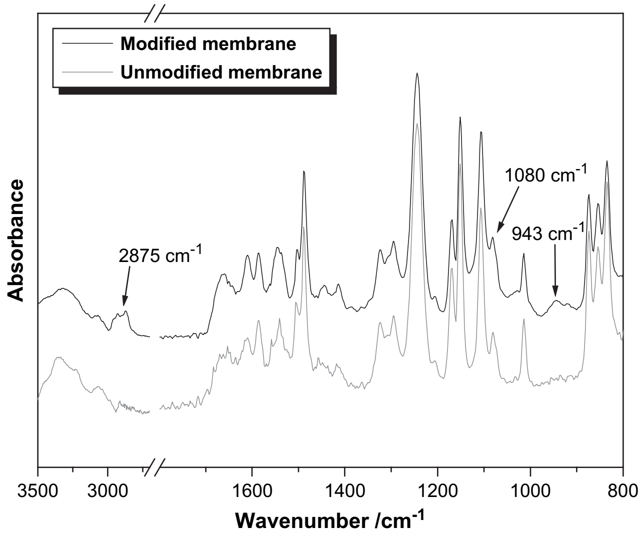


Fig. 3. ATR-IR spectrum analysis of unmodified and modified membranes.

Table 1
Relative surface atomic concentration of the unmodified and modified membranes calculated from XPS scan spectra

Sample	Atoms percent (mol%)			O/C
	C	O	N	
Unmodified membrane	72.6	16.5	10.9	0.227
MPEG-NH_2 (theoretical)	66.7	33.3	–	0.500
Modified membrane	69.3	21.3	9.4	0.307

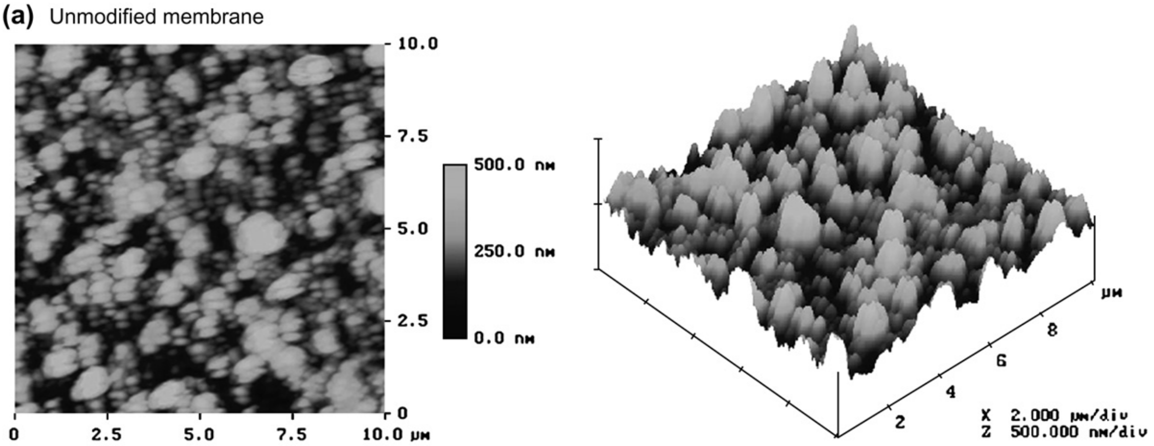
3.2.2. XPS analysis

XPS is particularly well suited for examining the skin layer of a composite membrane and the quantitative elemental composition of the top-most layer of the sample can be calculated from the spectrum [11]. Therefore, the membranes were analyzed for the chemical composition of skin layer through XPS analysis. As shown in Table 1, the oxygen content (16.5 mol%) of unmodified membrane surface was increased by the PEG modification (21.3 mol%) and the value of O/C also increased from 0.227 to 0.307. The results were consistent with the ATR-FTIR analysis indicating the successful immobilization of PEG chains onto the membranes.

3.2.3. AFM characterization

Atomic force microscope was used to investigate membrane surface properties demonstrated in Refs. [12,26]. Surface morphology of unmodified and PEG-modified membranes was determined using tapping mode AFM. Fig. 4 shows

(a) Unmodified membrane



(b) PEG modified membrane

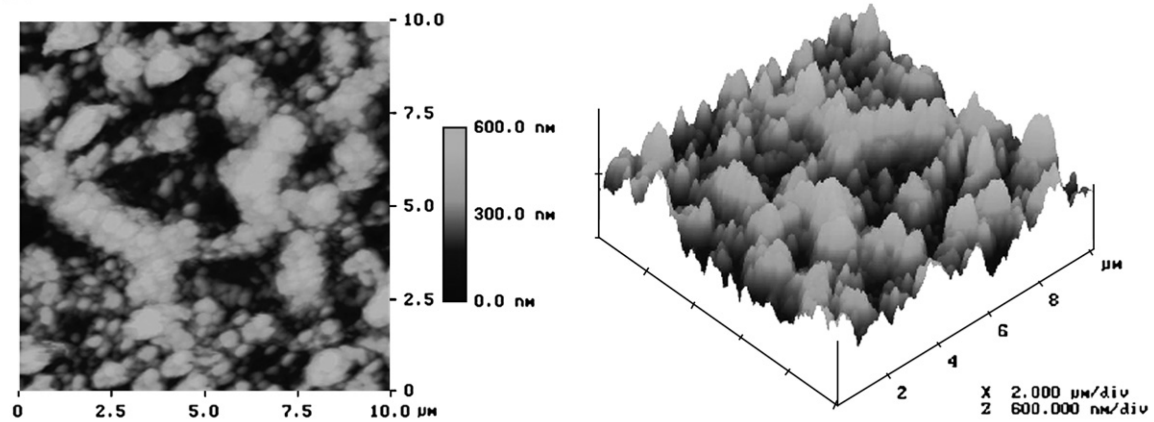


Fig. 4. AFM images of unmodified and modified membranes, with their *Z* (grey) scale of 500 nm and 600 nm, and their average roughness of (a) 58 nm and (b) 93 nm, respectively.

the images of two-dimensional and three-dimensional 10 μm scans for unmodified and PEG-modified membranes. It could be seen from the images, the unmodified membrane showed a unique and characteristic ridge-and-valley structure consistent with that in Ref. [1]. It appeared with homogeneous morphology and distribution features. While the modified membrane showed more irregularities, some new protuberances and unevenly distributed features arose. It may be due to the insufficient coverage of PEG chains on membrane surface. The steric repulsion effect of the initial grafted PEG chains in liquid surroundings was disadvantageous to the further grafting reaction. In addition, the grafted PEG chains may conglutinate with each other. As a result, the modified membrane surface was not completely covered by PEG and the uncovered area showed lower position. Therefore, the roughness parameters of the modified membrane increased compared to 93 nm unmodified, as compared with 58 nm of the unmodified membrane. It was noteworthy that the AFM analysis of the PEG layers was performed in dry state, and these values may change after surface wetting due to hydration of PEG chains [27].

The atomic force microscopy analysis results again confirmed that PEG chains were grafted on the membrane surface. However, an increasing roughness is not anticipated, and a further study of modification conditions should be further optimized to achieve a more even and homogeneous surface.

3.3. Fouling experiments

A 100 ppm tannic acid and a 100 ppm dodecyltrimethylammonium bromide (DTAB, a cationic surfactant) were used for fouling experiments. Tannic acid was a common contaminant of the surface waters, and DTAB could be adsorbed to the membrane by hydrophobic and/or ionic interactions with the membrane. The preliminary results are summarized in Fig. 5. As can be seen from the data provided, though the effect was not significant, the membrane modified according to the present method showed a relatively better antifouling property.

It was deemed that the effect of surface modification could be interpreted as follows. Firstly, grafting a hydrophilic PEG layer enhanced the hydrophilicity of membrane surface. Secondly, the modification process eliminated a portion of acyl halide groups by reaction with non-ionic PEG molecule, thus the surface of modification membrane was with less negative charge. Finally, end-on grafting of PEG chains presented a good steric repulsion effect. All these factors were helpful to restrain and prevent the adsorption of containment from membrane surface.

However, it should be mentioned again that the modified membrane had larger roughness which was disadvantageous to the membrane antifouling ability. If the modification conditions were further optimized and thus the modified membrane could have a more homogeneous and even surface, it was envisioned that the modification method in this study will show a better application potentiality.

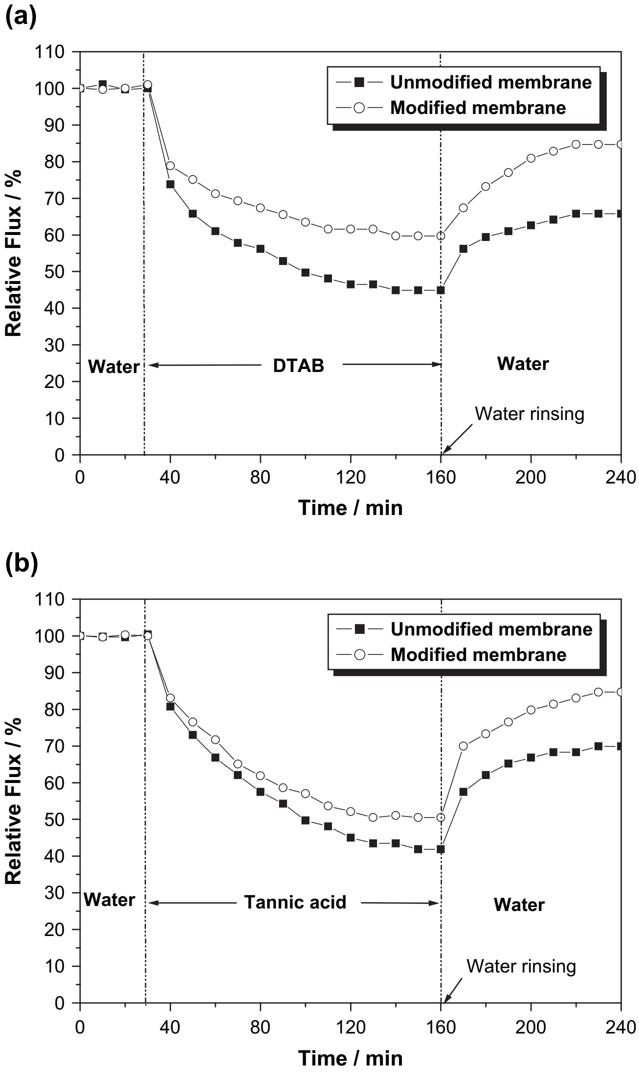


Fig. 5. Fouling experiments: (a) DTAB and (b) tannic acid for unmodified and modified membranes.

3.4. Elucidation of the surface modification idea

On the basis of the results described above, though these are preliminary results, several meaningful conclusions were obtained. The method in this study is a novel idea to modify TFC membrane and improve its antifouling property. The application to the TFC membranes was technically and easily carried out. Furthermore, types of other hydrophilic monomers containing reactive groups can also be used for surface modification. In addition, the charge characteristics of TFC membrane surface may be changed by grafting anionic, neutral or cationic monomers. The method in this study is likely to provide a novel idea for surface modification of TFC membranes.

4. Summary

Our present research effort focused on the surface modification of grafting hydrophilic PEG chains onto TFC polyamide

RO membrane with a novel idea. PEG layers were created using a chemical coupling reaction during the fabrication of the TFC membrane. The characterizations of ATR-IR, XPS and AFM indicated clearly that the expected polymers were successfully grafted on the surface of the membrane. The preliminary fouling experiments showed that PEG-modified membrane had antifouling property. It was envisioned that the idea in this study may provide a novel framework for surface modification of TFC membranes. However, there were also some shortcomings present and further more efforts needed to be taken to achieve better modification effect.

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References

[1] Petersen RJ. J Membr Sci 1993;83:81−150.
[2] Kwak SY. Polymer 1999;40:6361−8.
[3] Huang J-C, Guo Q-H, Ohya H, Fang J. J Membr Sci 1998;144:1−11.
[4] Michaels A. Desalination 1990;77:5−34.
[5] Barger M, Carnahan BP. Desalination 1991;83:3−33.
[6] Qin J-J, Oo MH, Lee H, Kolkman R. J Membr Sci 2004;243:107−13.
[7] Boxtel A, Otten Z, Linden H. J Membr Sci 1991;58:89−111.
[8] Michelle CW, John P, Andrew Z. Desalination 1998;115:15−32.
[9] Louie JS, Pinnau I, Ciobanu I, Ishida KP, Ng A, Reinhard M. J Membr Sci 2006;280:762−70.
[10] Hachisuka H, Ikeda K. US Patent 6177011 B1; 2001.
[11] Belfer S, Purinson Y, Fainshtein R, Radchenko Y, Kedem O. J Membr Sci 1998;139:175−81.
[12] Freger V, Gilron J, Belfer S. J Membr Sci 2002;209:283−92.
[13] Nie F-Q, Xu Z-K, Ye P, Wu J, Seta P. Polymer 2004;45:399−407.
[14] Che A-F, Nie F-Q, Huang X-D, Xu Z-K, Yao K. Polymer 2005;46:11060−5.
[15] Huang X-J, Xu Z-K, Huang X-D, Wang Z-G, Yao K. Polymer 2006;47:3141−9.
[16] Thom V, Jankvoa K, Ulbricht M, Kops J, Jonsson G. Macromol Chem Phys 1998;199:2723−9.
[17] Chen R-X, Feng W, Zhu S-P, Botton G, Ong B, Wu Y-L. Polymer 2006;47:1119−23.
[18] Tu C-Y, Liu Y-L, Lee KR, Lai JY. Polymer 2005;46:6976−85.
[19] Combellas C, Fuchs A, Kanoufi F, Mazouzi D, Nunige S. Polymer 2004;45:4669−75.
[20] Wang J, Pan C-J, Huang N, Sun H, Yang P, Leng Y-X, et al. Surf Coat Technol 2005;196:307−11.
[21] Harris JM, editor. Poly(ethylene glycol) chemistry: biotechnical and biomedical applications. New York: Plenum Press; 1992.
[22] Pillai V, Mutter M. J Org Chem 1980;45:5364−70.
[23] Kohei K, Atsushi O, Takeshi U, Jun N. Polym J 1987;19:375−81.
[24] Cadotte. US Patent 4277344; 1981.
[25] Park Y, Won J, Kang Y. Langmuir 2000;16:9662−5.
[26] Nidal H, Mohammad A, Brian A, Darwish N. Desalination 2003;157:137−44.
[27] Jo S, Park K. Biomaterials 2000;21:605−16.