

SYNTHESIS OF AN AMPHIPHILIC PPESK-*g*-P(PEGMA) GRAFT COPOLYMER VIA ATRP AND ITS USE IN BLEND MODIFICATION OF PPESK MEMBRANES*

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Abstract Preparation of an amphiphilic graft copolymer having poly(phthalazinone ether sulfone ketone) (PPESK) as main chains was carried out by atom transfer radical polymerization (ATRP). The precursor, chloromethylated PPESK (CMPESK), was prepared by using chloromethylether as chloromethylation agent. Then, poly(ethylene glycol) methyl ether methacrylate (PEGMA) was used as monomer to synthesize PPESK-*g*-P(PEGMA) by ATRP method under the catalysis of a cuprous chloride/2,2'-bipyridyl system. PPESK/PPESK-*g*-P(PEGMA) blend membranes were prepared and characterized. Chemical structures of the products were confirmed by FT-IR spectroscopy and ¹H-NMR analysis. The thermal properties of PPESK-*g*-P(PEGMA) were analyzed by thermal gravity analysis (TGA). XPS method was used to analyze the composition of the blend membrane. FESEM was employed to investigate the morphology of the membranes. The hydrophilicity of blend membranes was measured by water contact angle test. It turns out that the hydrophilicity and surface wettability were enhanced after modification. However, the thermal properties were negatively affected.

Keywords: Amphiphilic; Poly(phthalazinone ether sulfone ketone); Graft copolymer; Atomic transfer radical polymerization; Blend membranes.

INTRODUCTION

Poly(phthalazinone ether sulfone ketone) (PPESK) has been one of the most focused materials used in membranes quite recently because of its outstanding thermal properties and good solubility in many organic solvents. Microfiltration, ultrafiltration and nanofiltration membranes are easily acquirable by solution phase inversion process using PPESK^[1–5]. However, it is often difficult to control the structure of membranes due to the diversity of membrane-forming parameters. Moreover, PPESK is a naturally hydrophobic and weak-polaritic material, making it more difficult to prepare water medium filtration membranes with high flux and anti-fouling ability.

Many modification methods have been investigated in order to improve the properties of PPESK membranes such as thermal properties. Those previous works including ultrafiltration and nanofiltration membranes with higher *T_g*, permeation flux and solute rejection ratio were obtained by sulfonating PPESK using oil of vitriol and oleum by Dai *et al*^[6]. A novel PPESK carrying carboxyl lateral groups, which owns good thermal properties and hydrophilicity and can easily dissolved in nitrobenzene and pyridine, was synthesized by Xuan *et al*^[7].

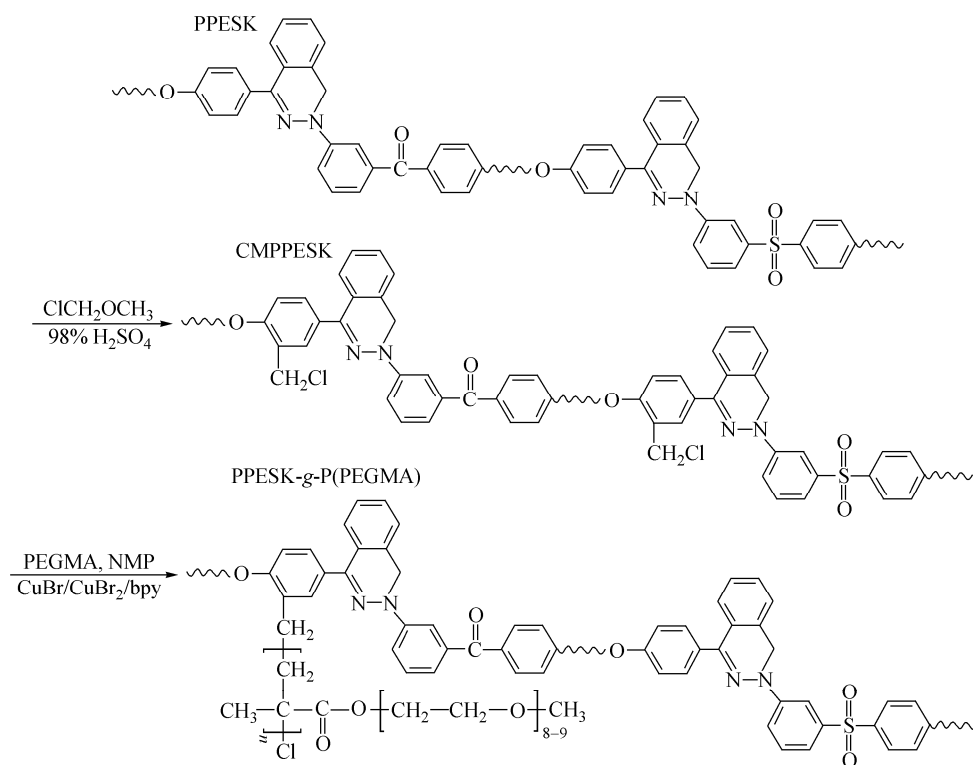
PPESK, as a member of PES family, is a suitable candidate for separation membranes for having non-coplanar structure, which prevents polymer chains from pulling close, and thus enlarges the free volume of the polymer. But few work have been conducted concerning PPESK modification by ATRP. Friedel-Crafts substitution of the aromatic rings in the main chain of PPESK by chloromethylation has been reported in our

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earlier study^[8]. The chloromethyl groups in the main chains provide an available agent to initiate ATRP on PPESK membrane surfaces. In this work, we try to graft hydrophilic poly(ethylene glycol) methyl ether methacrylate (PEGMA) onto chloromethylated PPESK by ATRP aiming to obtain an amphiphilic graft copolymer, and the properties of PPESK/PPESK-*g*-P(PEGMA) blend membranes are also studied in this paper. The synthetic pathway is shown in Scheme 1.



Scheme 1 Synthesis route of PPESK-*g*-P(PEGMA) graft copolymers

EXPERIMENTAL

Materials

PPESK (sulfone/ketone ratio = 1:1) was purchased from Aldrich Chemical Co. It was vacuum dried at 120°C for 4 h prior to use. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, 99%, $M_n = 475$) was obtained from Aldrich Chemical Co. It was passed through a column to remove inhibitor and then stored in refrigerator. Chloromethylether (CME, 99%) was obtained from Shanghai Bangcheng Chemical Co. and was used as received. Cuprous chloride (CuCl, 99%) was supplied by Aldrich Chemical Co. and was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with anhydrous ethanol and finally dried under reduced pressure at room temperature, restored under an argon atmosphere. Polyethylene glycol (PEG, $M_n = 600$) was supplied by Shanghai Chemical Regent Company (Shanghai, China) and was used as received. 2,2'-Bipyridyl (bpy, 97%) is supplied by Aldrich Chemical Co. and was used as received. NMP (97%) was supplied by Aldrich Chemical Co. and was purified by vacuum distillation.

Chloromethylation of Poly(phthalazinone ether sulfone ketone) (PPESK)

In a 100 mL, three-necked, round-bottom flask equipped with a nitrogen inlet, 20 g of PPESK was dissolved in 200 mL of concentrated sulfuric acid under stirring at 18°C for 4–6 h. Then CME was added slowly to the mixture under a nitrogen atmosphere. The reaction mixture was stirred at 18°C for 48 h and then poured into deionized water. The precipitate was filtered and rewashed for several times. Finally, the precipitate was dried under reduced pressure at 40°C for at least 24 h until a constant weight was obtained.

Synthesis of PPESK-*g*-P(PEGMA) by ATRP

Synthesis of PPESK-*g*-P(PEGMA) was accomplished in a 250 mL, three-necked, round-bottom flask equipped with a nitrogen inlet. 5.0 g of CME-PPESK was first dissolved in 50 mL of NMP stirring under a nitrogen atmosphere at room temperature for 12 h to remove dissolved oxygen. Then 8.0 g of PEGMA, 0.113 g of bpy, 0.06 g of CuCl were added into the mixture. The polymerization was carried out at 85°C for 3 days. At the end of polymerization, the copolymer was precipitated in ether and redissolved in NMP and reprecipitated in ether for at least 3 times and then dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained.

Preparation of PPESK/PPESK-*g*-P(PEGMA) Blend Membrane

Membrane casting solutions were prepared by dissolving PPESK and PPESK-*g*-P(PEGMA) with different weight ratio, 8/2 and 9/1 respectively, in NMP. The concentration of blend PPESK/PPESK-*g*-P(PEGMA) was a constant, 18%. PEG ($M_n = 600$) was added to the solutions as a pore-forming agent, and its mass concentration was 6%. After the mixtures were stirred until stable and even mixtures were obtained, the PPESK/PPESK-*g*-P(PEGMA) solutions were cast on a substrate of non-woven fabric on a glass plate to improve the membrane mechanical strength. The glass plate was subsequently immersed in deionized water. After the non-woven fabric detached from the glass plate, it was extracted in a second bath of deionized water at 70°C for 12 h. The microporous membrane so-obtained based on non-woven fabric was dried at room temperature and then stored in desiccator.

Characterization

The structures of PPESK, CMPESK and PPESK-*g*-P(PEGMA) were determined by ^1H -NMR spectra in deuterated chloroform (CDCl_3) on an Avance DMX 500 MHz spectrometer.

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra for the original and modified PPESK membranes were obtained using a Vector22 spectrometer.

Thermal gravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris 1 calorimeter (Germany) in dry nitrogen atmosphere, and the thermograms were recorded while heating from 50°C to 700°C at 10 K/min to determine the thermal stability of the original and modified PPESK.

The chemical compositions on the surface of the blend membranes were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA system).

A field emitting scanning electronic microscope (FESEM, SIRION-100, FEI Co., Ltd., Netherlands) was used to investigate the surface and cross-sectional morphologies of the unmodified and modified membranes. To prevent pore collapse, the membrane samples were dried by critical point drying after dehydrated in a series of gradient ethanol-water solutions, as reported by Singh *et al.*^[9]. To avoid destroying the cross-section structure, the membrane samples were fractured in liquid nitrogen and then sputtered with gold before observation.

Hydrophilicity of PPESK and modified PPESK membranes was measured by water contact angle test with an contact angle system OC (OCA20, Dataphysics, Germany). To minimized experimental error, the contact angles were measured five times for each sample and then averaged.

RESULTS AND DISCUSSION

Structure Characterization

The structures of PPESK, CMPESK and PPESK-*g*-P(PEGMA) were studied by ^1H -NMR. Their ^1H -NMR spectra are shown in Figs. 1(A), 1(B) and 1(C), respectively. Compared with spectrum of PPESK (Fig. 1A), a new chemical shift at $\delta = 4.80$ which can be assigned to the methylene protons of $-\text{CH}_2\text{Cl}$ ^[10], is found in the spectrum of CMPESK (Fig. 1B), indicating that $-\text{CH}_2\text{Cl}$ groups are covalently tethered on the PPESK main chain. When comparing spectrum (B) and (C), it is found that the chemical shift at $\delta = 4.80$ disappears in the spectrum of PPESK-*g*-P(PEGMA) (Fig. 1C), while new chemical shifts appeared at $\delta = 1.95$ and 3.48 which can be assigned to the methyl protons of terminated group $-\text{CH}_3$ in the P(PEGMA) chain. Meanwhile, the shift at $\delta = 2.51$ can be assigned to methylene protons ($-\text{CH}_2$) that co-joints PPESK and P(PEGMA) chains. Moreover,

the shift at $\delta = 2.98$ and 4.25 can be assigned to ether methylene protons ($\text{O}-\text{CH}_2-$) and ester methylene protons ($\text{COO}-\text{CH}_2-$), respectively. These results indicate that P(PEGMA) chains were successfully grafted onto CMPESK chains.

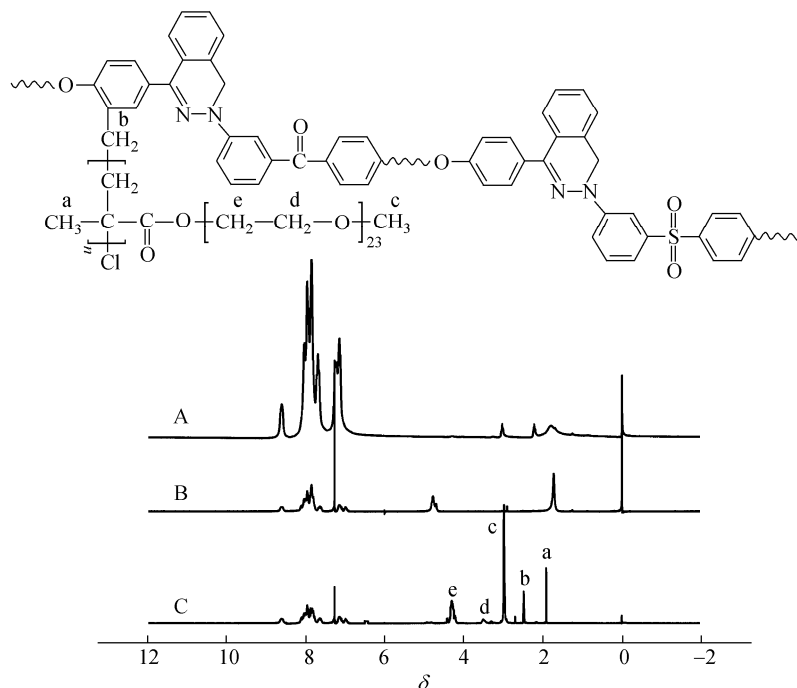


Fig. 1 ^1H -NMR spectra of (A) PPESK, (B) CMPESK and (C) PPESK-*g*-P(PEGMA)

The introduction of $-\text{CH}_2\text{Cl}$ and P(PEGMA) onto PPESK chains was further confirmed by FT-IR spectroscopy (Fig. 2a–2c). The characteristic peak at 754 cm^{-1} in Fig. 2(b) can be assigned to symmetric stretching of $\text{C}-\text{Cl}$, indicating the existence of $-\text{CH}_2\text{Cl}$ on PPESK chains. Compared with Fig. 2(b), a new characteristic peak at around 1722 cm^{-1} shows up in the spectrum of PPESK-*g*-P(PEGMA) (Fig. 2a) which can be assigned to the absorption bands of carbonyl groups that belong to the ester on the P(PEGMA) chain. Moreover, the absorption bands of the ether bond at 1098 cm^{-1} , $\text{C}-\text{H}$ at $3100\text{--}2800\text{ cm}^{-1}$ and hydroxyl group at 3500 cm^{-1} are all strong proofs that PEGMA has been grafted onto the PPESK main chain.

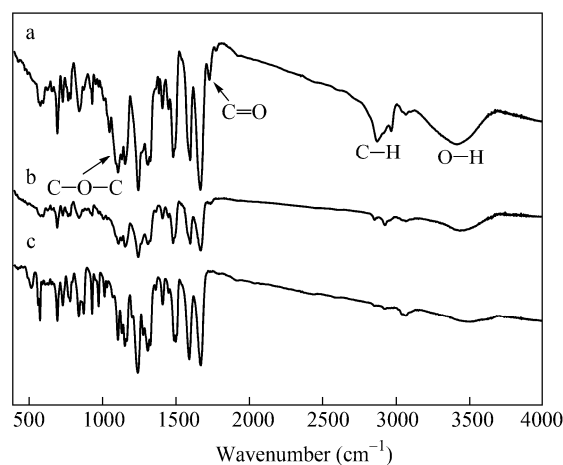


Fig. 2 FT-IR spectra of (a) PPESK/PPESK-*g*-P(PEGMA) blend membrane, (b) CMPESK and (c) PPESK

Thermal Analysis

TGA analysis was employed to examine the thermal stability of PPESK, CMPESK and PPESK-*g*-P(PEGMA). As shown in Fig. 3, the onset weight-loss temperature of PPESK is about 490°C. The TGA curves for CMPESK and PPESK-*g*-P(PEGMA) are characterized by two distinct regions of mass loss: (i) decomposition of chloromethyl groups and P(PEGMA) chains at 200–350°C and 130–400°C, respectively, (ii) degradation of PPESK segments at 480°C. We can note that the thermal stability of PPESK decreases due to the introduction of PEGMA. Furthermore, it can be determined that the grafting yield of P(PEGMA) on the PPESK is about 12% by calculating the weight loss ratios at the first decomposition step.

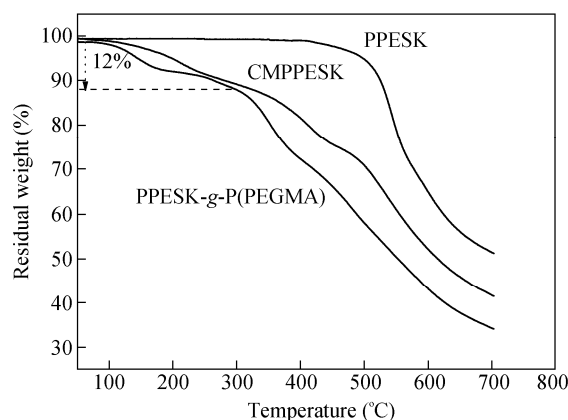


Fig. 3 TGA curves of PPESK, CMPESK and PPESK-*g*-P(PEGMA)

Composition of the Membranes

XPS analysis was employed to determine the chemical compositions of the blend membrane. Figure 4 shows the wide scan, C 1s and O 1s of pure PPESK membrane and blend membrane with PPESK/PPESK-*g*-P(PEGMA) weight ratio of 8/2 and 9/1, respectively. Three emission peaks can be observed in Fig. 4 at the BEs of about 287, 402, and 534 eV which are attributable respectively to the C 1s, N 1s, and O 1s, respectively. The persistence of a N 1s signal at the BE of 400 eV (Fig. 5) indicates that the thickness of grafted P(PEGMA) on the PPESK membrane is less than the probing depth of the XPS technique (*ca.* 8 nm in an organic matrix^[11]). The decreases of N 1s, S 2s and S 2p₃ emission peaks are due to the increase of P(PEGMA) content at the membrane surfaces.

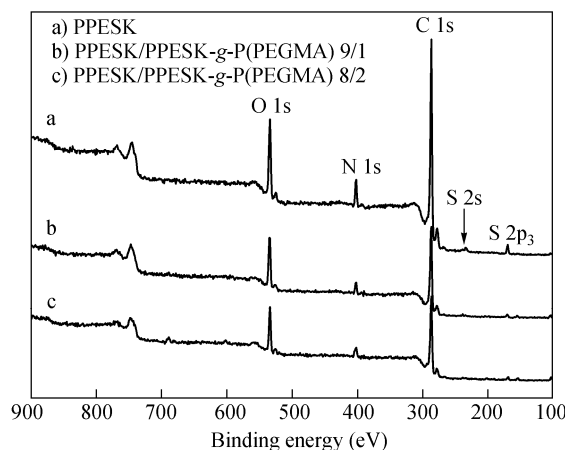


Fig. 4 Typical XPS wide scans for PPESK and PPESK/PPESK-*g*-P(PEGMA) blend membranes with different PPESK/PPESK-*g*-P(PEGMA) ratio of 8/2 and 9/1

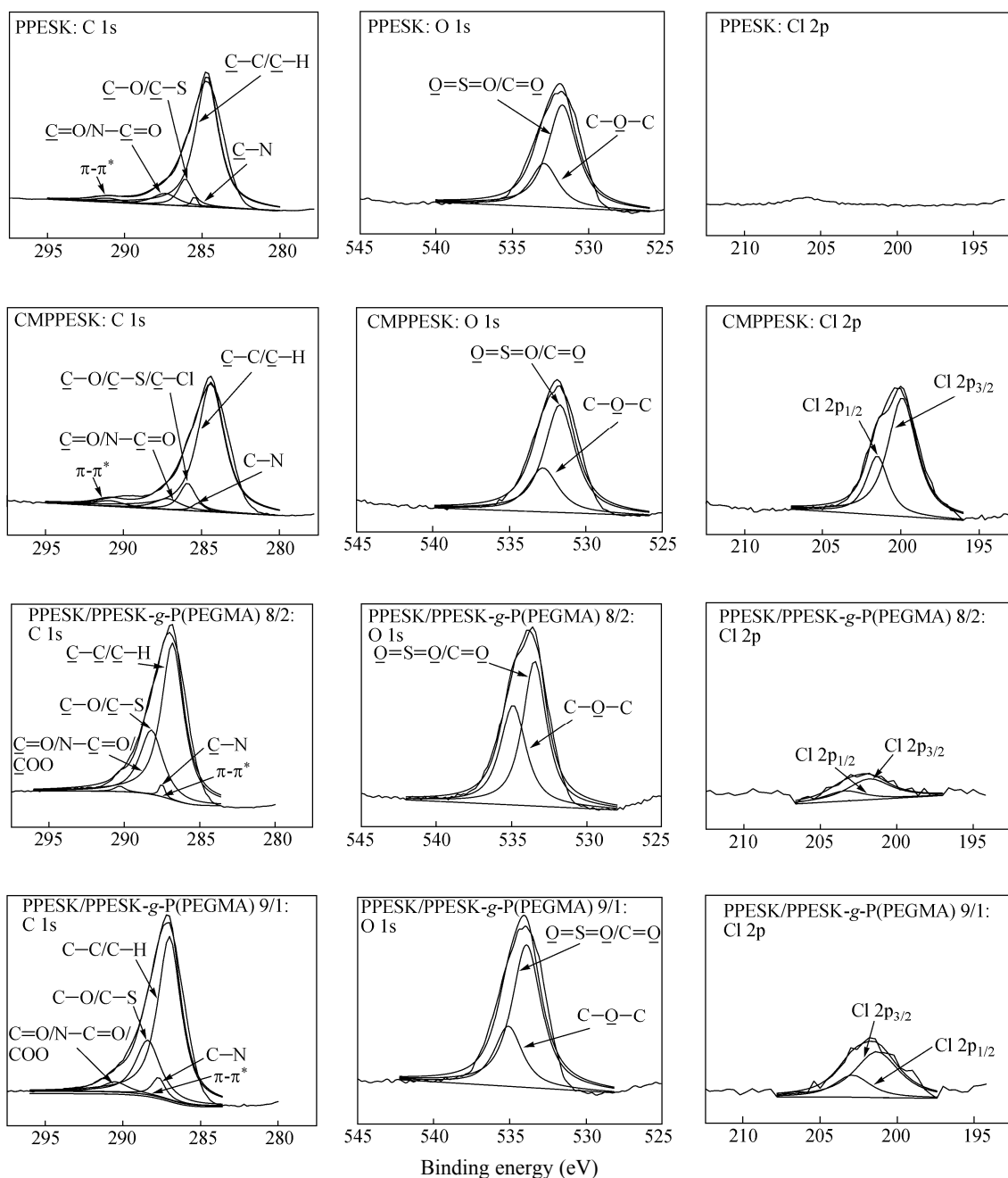


Fig. 5 X-ray photoelectron spectroscopy (XPS) of PPESK, CMPESK membranes and blend membranes with different PPESK/PPESK-g-P(PEGMA) ratio of 8/2 and 9/1

To further investigate the chemical composition of PPESK membrane and blend membranes, the C 1s, O 1s and Cl 1s regions of XPS spectra of membranes with different PPESK-g-P(PEGMA) contents are presented in Fig. 5. The C 1s peak components at the BEs of about 284.6, 285.4, 286.1, 288.2, and 291.2 eV are attributable to the C-H/C-C, C-N, C-O/C-S/C-Cl, C=O/N-C=O, and $\Pi-\Pi^*$ satellite species, respectively, in polymer^[12]. The percentages of each carbon component calculated from peak area for membranes are given in the Table 1. It can be clearly seen that the content of carbon in C-O (PEGMA) increases with the increase of

the PPESK-*g*-P(PEGMA)/PPESK ratio. Contrarily, the content of C—N(PPESK) decreases with the increase of the PPESK-*g*-P(PEGMA)/PPESK ratio. The O 1s peak components at the BEs of about 531.7, 532.8 are attributable to the O=S=O/C=O, C—O—C satellite species, respectively, in the polymer^[13, 14]. The O=S=O/C=O and C—O—C ratio of modified blend membrane, as determined from the curve-fitted O 1s core-level spectrum in Fig. 5, is about 0.575 and 0.425, respectively. In the neat PPESK membrane O1s core-level spectrum as is shown in Fig. 5, the O=S=O/C=O and C—O—C ratio is 0.72 and 0.28, respectively. This result is consistent with the substantial increase in intensity of the C—O—C emission peak at the BE of 532.8 eV in Fig. 5 when comparing spectra of pure PPESK membrane and blend membranes. This is because the presence of the grafted P(PEGMA) in the blend membranes increases the percentage of ether oxygen component. The Cl 2p peak components at about 199.9 and 201.5 eV are assigned to Cl 2p_{3/2} and Cl 2p_{1/2}, respectively^[10], and they are attributable to the covalently bonded chlorine (C—Cl). Calculating from the total areas of Cl and C peak, the Cl/C of the blend membrane with PPESK/PPESK-*g*-P(PEGMA) ratio of 8/2 is 0.056, while that of the blend membrane with PPESK/PPESK-*g*-P(PEGMA) ratio of 9/1 is 0.09. This is due to the graft of P(PEGMA) decreases the content ratio of Cl/C in the blend membrane.

Table 1 C 1s component peak areas as percentages of total area

Membrane ID	C—C/C—H	C—O/C—S	C=O/N—C=O/COO	C—N	Π-Π*
M0	80.11	7.21	5.11	6.63	1.94
M10	67.55	23.13	4.51	4.33	0.48
M20	68.01	27.89	2.53	1.41	0.07

Membrane Morphology

The effect of amphiphilic PPESK-*g*-P(PEGMA) on the surface morphology of PPESK was investigated by SEM as shown in Fig. 6. Typically, the blend membrane exhibits asymmetrical structure with porous surface. Usually, the top layer is responsible for the permeation and solute rejection, while the porous bulk acts as a mechanical support. It can be found that the surface of PPESK membrane becomes more tougher and porous after blending with amphiphilic PPESK-*g*-P(PEGMA). In addition, all membranes exhibit typical finger-like cross sections.

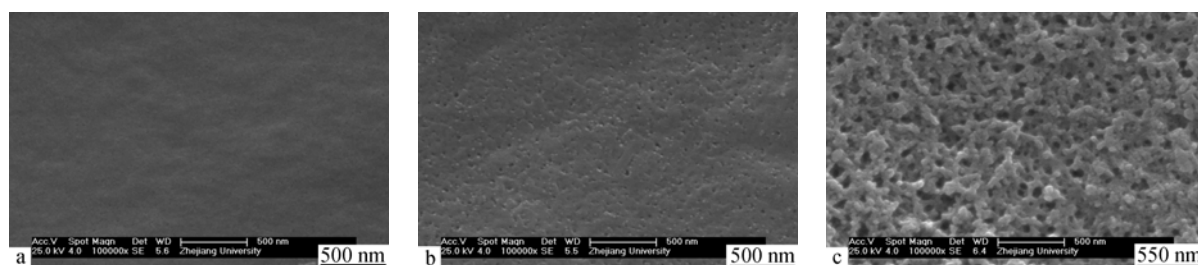


Fig. 6 Surface SEM images for (a) the original PPESK membrane, (b) CMPESK membrane and (c) the PPESK/PPESK-*g*-P(PEGMA) blend membrane

Hydrophilicity of the Membranes

Static water contact angle as a function of contact time on the pure PPESK and blend membranes is shown in Fig. 7. Pure PPESK membrane has the highest initial water contact angel (86.7°C), while the initial contact angle of the blend membrane with a PPESK/PPESK-*g*-P(PEGMA) ratio of 8/2 decreases to 74.1°C. At the meantime, the contact angle of pure PPESK and CMPESK membrane almost remains stable with prolongation of contact time. However, the contact angles on the surface of PPESK/PPESK-*g*-P(PEGMA) blend membranes reduce gradually within the measurement time. With increase of PPESK-*g*-P(PEGMA) content, the decreasing rate of contact angle increases, indicating that adding PPESK-*g*-P(PEGMA) into the PPESK membrane makes its surface very hydrophilic. This is due to surface location of the very hydrophilic PEGMA content maximizes the surface free energy and the increase of pore size on the membrane surface.

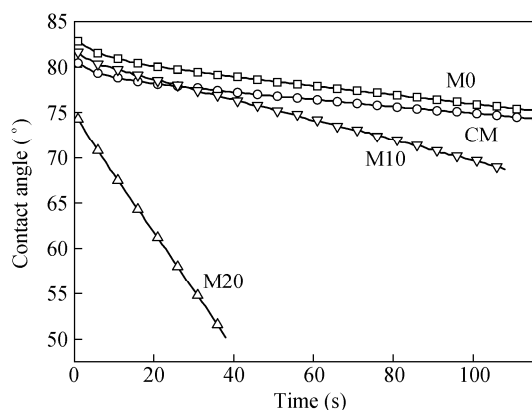


Fig. 7 Time dependence of water contact angle of membranes with different PPESK-*g*-P(PEGMA) content
The number behind M represents the weight content ratio of PPESK-*g*-P(PEGMA) in the blend membrane; CM represents CMPESK.

CONCLUSIONS

An amphiphilic PPESK-*g*-P(PEGMA) graft copolymers was prepared by ATRP, in which poly(poly(ethylene glycol) methyl ether methacrylate) was covalently coupled with chloromethylated PPESK. The grafting yield of PEGMA calculated from TGA test was around 12%. The graft products were blended with PPESK to prepare porous membranes by immersing precipitation method. The graft copolymers were excluded to membrane surface during membrane formation, and a hydrophilic surface modification was achieved for the PPESK membranes. The modified membranes exhibited enhanced hydrophilicity and surface wettability than the pure one, while the thermal properties were negatively affected. The blend membranes with different contents of hydrophilic PPESK-*g*-P(PEGMA) will exhibit different hydrophilicity.

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