Synthesis of Amphiphilic Poly(phthalazinone ether sulfone ketone)-*graft*-Poly(ethylene glycol) Graft Copolymers via Williamson Etherification

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ABSTRACT: Amphiphilic graft copolymers consisting of poly(phthalazinone ether sulfone ketone) (PPESK) backbones and poly(ethylene glycol) (PEG) side chains were synthesized via reaction of chloromethylated PPESK (CMPPESK) with a sodium alkoxide of methoxyl PEG (PEG-ONa). The reactive precursor, CMPPESK, was prepared by the chloromethylation of PPESK with chloromethylether (CME) using concentrated H_2SO_4 as reaction medium. FTIR spectroscopy, ^{1}H-NMR and Solid-state ^{13}C CP-MAS NMR analysis confirmed the covalent linking of PEG with PPESK backbones. The PEG content in the graft copolymers from ^{1}H-NMR analysis varied from 21.0 to 37.2 wt %, which was approximately in agreement with that calculated from TGA tests. The graft products have good solubility in many aprotic polar solvents and can be slightly swelled by water and ethanol, but water insoluble. Contact angle measurements revealed that the hydrophilicity of PPESK was significantly improved by the introduction of PEG graft chains, indicating the graft copolymer is a potential hydrophilic additive for PPESK membranes. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2973–2979, 2007

Key words: amphiphilic graft copolymers; poly(phthalazinone ether sulfone ketone); poly(ethylene glycol); Williamson ether synthesis

INTRODUCTION

Poly(phthalazinone ether sulfone ketone) (PPESK) is a newly-developed amorphous copolymer containing rigid phthalazinone moieties and aromatic structure, showing excellent thermal stability and chemical resistance. This polymer is dissolvable in some polar aprotic solvents and is easily cast into porous membranes by traditional phase inversion technique.[1,2] Jian et al. have successfully applied PPESK as membrane material for gas separation (GS), ultrafiltration (UF), and nanofiltration (NF), etc.[3,4] Despite its advantages as membrane material, the hydrophobic nature of PPESK can result in membrane fouling in water treatment because of the adsorption of protein or natural organic matter (NOM) on membrane surface and inside membrane pores. Many efforts have been made to improve the hydrophilicity and separation performances of PPESK membrane. Methods currently used include PPESK sulfonation,[5–7] quaternization,[8] synthesis of PPESK containing carboxyl,[9] interfacial polymerization on PPESK support membrane,[10,11] etc. However, rare work is done to promote the properties of PPESK membrane through a chemical graft method.

In recent years, amphiphilic graft copolymers having hydrophobic backbone and hydrophilic side chains have absorbed many researchers' attention because of their particular characters and convenient synthesis process.[12] Poly(ethylene glycol) (PEG) is widely used as the hydrophilic side chains for amphiphilic graft copolymer, thanks to its low cost and inherent biocompatibility.[13–16] On the basis of previous reports, there are usually two routes for the preparation of amphiphilic PEG-grafted copolymers: one is copolymerization of vinyl monomers with PEG macromonomers, the other is the conjugation of polymeric precursors with the active functionalized group of PEG.[13] From the latter, the resulting products with comb-like PEG side chains often show enhanced hydrophilicity and biocompatibility compared to the polymeric precursors.

Several authors synthesized graft copolymers having polysulfone backbones and PEG side chains via reaction of an alkoxide formed from PEG and sodium hydride with chloromethylated polysulfone. The resulting copolymers were added into casting solution to perform a surface modification for polysulfone membranes.[17] In the present work, analogous approach was employed to perform a chemical modification for PPESK resin. Hydrophilic PEG chains were introduced to the rigid PPESK back-

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bones through a modified Williamson reaction. The obtained PPESK-g-PEG graft copolymer is a potential hydrophilic additive to improve the hydrophilicity and antifouling properties of PPESK phase inversion membranes.

EXPERIMENTAL

Materials and reagents

PPESK(sulfone/ketone = 1 : 1) (Intrinsic viscosity of 0.65 dL/g, in chloroform at 25°C) was provided by Dalian New Polymer (People's Republic of China) and was vacuum dried at 100°C for 24 h prior to use. Methoxyl poly(ethylene glycol) (PEG-OH) (average molecular weight of 350 and 750, respectively) and sodium hydride (NaH) were purchased from Aldrich. Commercially available N-methyl-2-pyrrolidone (NMP) (Shanghai Wulian chemical plant, People's Republic of China, reagent grade) served as solvent and was purified by vacuum distillation from calcium hydride before use. Chloromethylether (CME) was obtained from Shanghai Haiqu Chemical Company. All other reagents were commercially analytical grade and used without further purification.

Chloromethylation of PPESK

The synthesis of PPESK-g-PEG copolymers contained two steps, as illustrated in Figure 1. In the first step, chloromethylated PPESK (CMPPESK) was prepared as an intermediate to synthesize the graft copolymer. The chloromethylation of PPESK followed a reported procedure.[8,18,19] In a typical procedure, 10 g of PPESK resin was dissolved in 150 mL of 98% concentrated H_2SO_4 under vigorous stirring at room temperature. Forty milliliter of CME was added dropwise into the PPESK solution, and the reaction

was performed under stirring for 5 h. Then, the reaction mixture was precipitated in cool de-ionized water under mechanical agitation, and was repeatedly washed with de-ionized water until the washed water was neutral. After filtering and completely drying, the obtained CMPPESK was used for characterization and the next synthesis.

The ^{1}H-NMR spectra of CMPPESKs were recorded by a Bruker Avance DMX 500 MHz instrument using deutrated chloroform as the solvent. The degree of chloromethylation (DCM) was calculated according to the ^{1}H-NMR spectra.

Preparation of PPESK-g-PEG copolymer

A modified Williamson etherification was employed for the synthesis of PPESK-g-PEG.[17] In a typical procedure, an alkoxide solution was prepared by adding dropwise 40 mL of 10.0 mmol PEG-OH solution into 40 mL of 10.0 mmol NaH solution using NMP as the solvent. The PEG-OHs with molecular weight of 350 and 750 g/mol were used and labeled as PEG-OH$_{350}$ and PEG-OH$_{750}$, respectively. The mixture was stirred for 2 h at room temperature. Then, the obtained alkoxide solution was added dropwise to a solution of 3 g CMPPESK dissolved in 60 mL NMP. The reaction was performed at room temperature under an argon atmosphere for 72 h and then was terminated through neutralizing the mixture with a certain amount of acetic acid. At last, the reaction mixture was precipitated into an adequate amount of de-ionized water. After filtrated and dried, the product was repeatedly refined with NMP and ethanol. The resultant product was extracted for 48 h by methanol using a Soxhlet extractor and vacuum dried at 60°C overnight.

Characterization of PPESK-g-PEG

Fourier transform infrared (FTIR) spectra were recorded using a Vector22 (Bruker Co. Germany) instrument. The ^{1}H-NMR spectra of CMPPESKs and PPESK-g-PEGs in deutrated chloroform were determined using a Bruker Avance DMX 500 MHz instrument. Solid-state ^{13}C CP-MAS NMR spectra for virgin PPESK and PPESK-g-PEG copolymers were acquired on a Bruker Avance AV 400 MHz spectrometer using a standard Bruker broad-band MAS 4-mm probe. All samples were examined with the MAS spinning speed of 5 kHz, the CP contact time of 1 ms and the recycle delay of 3 s. Thermogravimetric analysis was performed at a heating rate of 10°C/min under a protective nitrogen atmosphere using a Pyris 6 TGA (Perkin-Elmer, Germany) instrument.
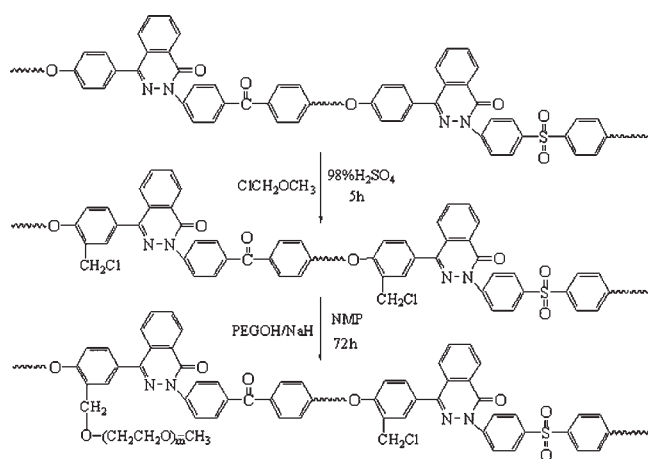

Figure 1 Schematic diagram for the synthesis of PPESK-g-PEG graft copolymers.

Film preparation and contact angle measurement

Polymer films were prepared by casting from 0.05 g/mL polymer solutions in chloroform against the glass slides. Prior to use, the glass slides were cleaned and fully dried. After controlled evaporation of the solvent, the films were dried in a vacuum oven at room temperature for 24 h to ensure removal of residual chloroform. And then the films were removed from the glass slide substrates and used for the measurements of contact angle.

The contact angles of pure water on the films were obtained using an OCA20 contact angle goniometer (Dataphysics Instruments GmbH, Germany). The measurements were performed at ambient conditions with 25°C and 60% relative humidity. For each sample, the average of five measurements was reported. From values of the water contact angle, the work of adhesion of dispersion for polymers was calculated by the combined Young-Dupre equation[20]:

$$W_{sl} = \gamma_l \, (1 + \cos \, \theta) \tag{1}$$

where γ_l is the surface tension of water, 72.8 mN/m and θ is the equilibrium water contact angle on the solid surface.[21] Values of the adhesion work, W_{sl}, indicate the hydrophilicity of the polymers.

RESULTS AND DISCUSSION

Preparation and characterization of CMPPESK

Chloromethylation provides PPESK with active group, —CH$_2$Cl, for the subsequent graft reaction, as shown in Figure 1. The chloromethylation of aromatic polymers is an electrophilic Fridel-Crafts substitution reaction, and the substitution position depends on the type of activating substituents linked to the phenyl ring. PPESK resin used in this work is a random copolymer, in which the mole ratio of the connected units sulfone (S) and ketone (K) is 1 : 1. In the chemical structure of PPESK, the oxygen of phenyl ether is an electron-donating substituent leading to selective ortho- and para-substitution, while phthalazinyl, carbonyl, and sulfone are electron-withdrawing substituents which favor the metha-substitution. So the substitution of the —CH$_2$Cl occurs at the carbon atom adjacent to the ether bond, as shown in Figure 2.[5,22]

PPESK reacted with CME in the presence of concentrated H$_2$SO$_4$ as the reaction medium and catalyst, and this led to a successful introduction of —CH$_2$Cl into the polymer backbone. Figure 2 presents a typical ^{1}H-NMR spectrum of CMPPESK. A series of peaks at 7.0–8.1 ppm correspond to the protons of PPESK main chain and they are difficult to assign detailedly because of the random connec-
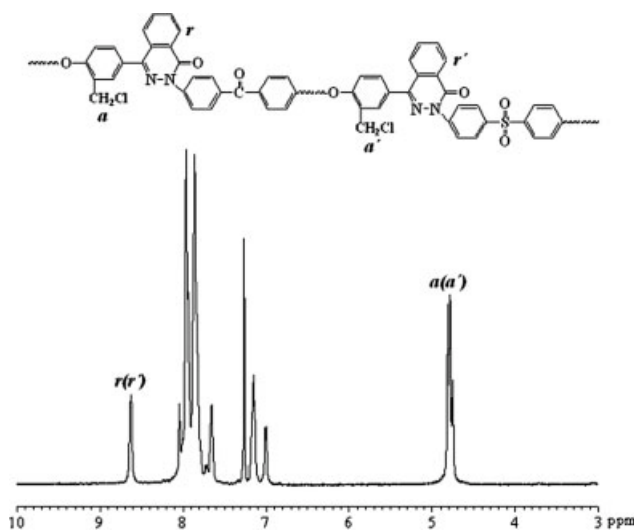

Figure 2 ^{1}H-NMR spectrum of CMPPESK (C-4).

tivity and complexity of the repeat units. However, a specific signal of —CH$_2$Cl protons is observed at about 4.8 ppm (*a* (*a′*)), and there is only a slight difference between sulfone unit and ketone unit. The introduction of chloromethyl group was also verified by the FTIR spectra, as shown in Figure 3. Compared to the virgin PPESK, the FTIR spectrum of CMPPESK presents a new strong absorbance at 754 cm^{-1}, which is attributed to the stretching vibration of C—Cl bond.

A more detailed discussion about the synthesis, purification, and characterization of CMPPESK was previously reported elsewhere.[19] Differently in this work, instead of chloromethyl butyl ether, CME was employed as chloromethylation agent. In Figure 2, the peak at 8.63 ppm is assigned to the proton adjacent to C=O group at phthalazinone, and its relative intensity is unchanged after chloromethylation, so is selected as reference peak. The average number of chloromethyl group per PPESK repeat unit (containing a sulfone unit and a ketone unit) is defined as degree of substitution (DS) of chloromethylation, and its value is calculated by the ratio of peak intensity at about 4.8 ppm to that at 8.63 ppm. A series of CMPPESKs were prepared in various reaction conditions. The DS values of different samples are listed in Table I. The DS of CMPPESK strongly depended on the reaction conditions, including reaction temperature, reaction time, the amount of CME, and concentration of reactants, etc. Obviously, the ratio of CME to PPESK is the main factor to influence the DS, and the value of DS increases observably with the ratio of reactants. In this study, CMPPESKs with the DS varying from 0.81 to 3.22 were obtained. Considering the sulfonation and chain degradation of PPESK might occur at a high temperature in presence of concentrated H$_2$SO$_4$, the reaction was performed at
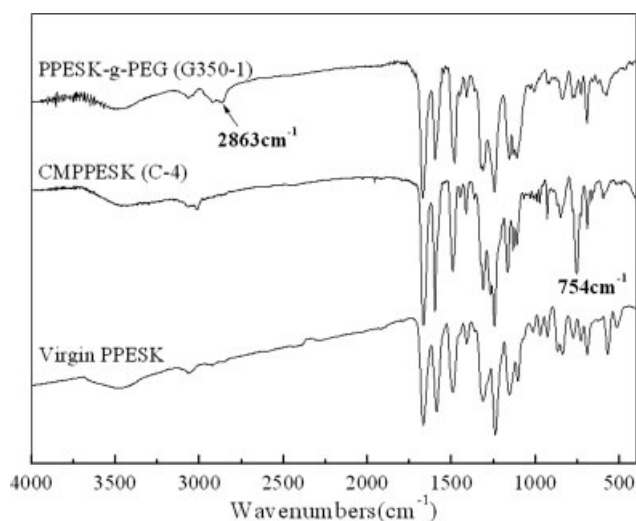
Figure 3 FTIR spectra of PPESK, CMPPESK, and PPESK-*g*-PEG.

Figure 4 [^1]H NMR spectrum of PPESK-*g*-PEG (G350-1).

below 30°C. In the temperature range of 20–30°C, the DS climbed to a maximum degree within about 5 h. The elevation of reaction temperature speeded the chloromethylation process, but the ultimate DS declined. This phenomenon might be due to the occurrence of side reaction at higher temperature or in longer reaction time. The optimal reaction condition based on substantial experiments was: reaction temperature, 20°C; reaction time, 5 h. In this condition, the DS of CMPPESK can be conveniently regulated at an anticipative range by the dosage of CME.

Synthesis of PPESK-*g*-PEG copolymers

After PPESK was chloromethylated, the resultant CMPPESK reacted with a sodium alkoxide formed from PEG-OH with NaH to prepare PPESK-*g*-PEG graft copolymers. Because the sodium alkoxide was highly sensitive to moisture and water, the reactants and solvent were required to sufficiently dry. And,

TABLE I
DS of CMPPESK in Various Reaction Conditions[a]

| | Reaction conditions | | | |
Sample label	Mole ratio of CME/PPESK repeat unit	Temperature/ °C	Time/ h	DS
C-1	11.5	20	2	0.81
C-2	34.5	20	2	1.65
C-3	57.5	20	2	3.03
C-4	57.5	20	5	3.22
C-5	57.5	20	10	2.96
C-6	57.5	30	10	2.47

[a] In all chloromethylation experiments, the amounts of concentrated H_2SO_4 were 15 mL/g PPESK.

the reaction must be performed under a protective inert gas atmosphere. The purpose of selecting mono hydroxyl PEG as the graft agent was to avoid the crosslinking of reactants and the gelation of reaction system. The molecular weight of PEG-OH used in this work included 350 and 750 g/mol.

The introduction of PEG chains to the PPESK is qualitatively confirmed by FTIR spectroscopy, as shown in Figure 3. In comparison with CMPPESK, the C—Cl absorbance peak for PPESK-*g*-PEG drastically shrinks. Moreover, a new peak occurs at 2863 cm^{-1}, which is attributed to the stretching vibration of C—H in PEG chains. But FTIR analysis cannot provide sufficient evidence for the covalent linking of PEG with the PPESK backbones, so further NMR measurements were performed.

Figure 4 shows a representative [^1]H-NMR spectrum of PPESK-*g*-PEG. The signals of methylene protons (denoted in Fig. 4 as *c*) and terminal methyl protons (denoted in Fig. 4 as *d*) appear at about 3.7 and 3.4 ppm, respectively. They are the characteristics of the PEG chains. The peaks at about 4.35 ppm are attributed to the protons between phenyl and PEG chains, as denoted in Figure 4 as *b* and *b'*. Comparison of Figure 4 with Figure 2, the relative intensity of the peaks at about 4.8 ppm corresponding to the protons of —CH_2Cl (*a* and *a'*) is greatly reduced after the grafting of PEG. In addition, solid-state [^13]C CP-MAS NMR spectra of the virgin PPESK and PPESK-*g*-PEG are shown in Figure 5. In the spectrum of PPESK-*g*-PEG, a series of new peaks are observed at 38–70 ppm, which is attributed to the introduction of PEG chains. The peaks for the carbon of methyl and methylene in PEG chains occur at about 58 and 69 ppm, respectively. It is worth noting
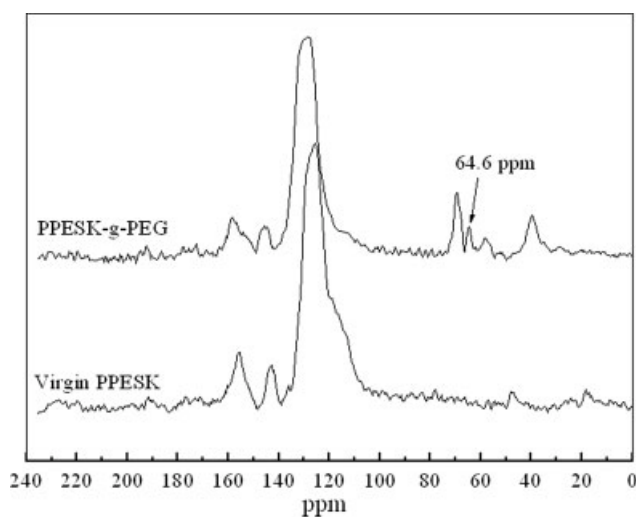
Figure 5 Solid-state ^{13}C CP-MAS NMR spectra of PPESK and PPESK-*g*-PEG (G350-1).

that the new peak at 64.6 ppm is corresponding to the carbon linking PPESK with PEG. From these results, it is concluded that PEG chain is covalently linked to PPESK backbones assuredly.

The grafting degree (GD) of PEG onto PPESK, defined as the average number of grafted PEG chains per PPESK repeat unit (containing a sulfone unit and a ketone unit), was determined according to the ratio of peak intensity at 4.35 ppm (*b(b′)*) to that at 8.6 ppm (*r(r′)*) in Figure 4. The grafting efficiency (namely the percentage of —CH$_2$Cl conversion into —CH$_2$O—PEG) was calculated according to the ratio of PEG GD to the corresponding DS of CMPPESK. The results are listed in Table II. From NMR analysis, PEG incorporation onto PPESK varied from 21.0 to 37.2 wt %. At same reaction conditions, the GD of PEG-OH$_{350}$ was higher than that of PEG-OH$_{750}$, and same trend was found for the grafting efficiency. This phenomenon might be attributed to a high chemical activity of hydroxyl group in a short PEG-OH molecular chain. Furthermore, a

shorter molecular chain provides the reactive groups with a bigger contacting probability for reaction. For same PEG-OH, the grafting efficiency decreased with the increase of the DS of used CMPPESK in spite of an increasing GD of PEG-OH. This phenomenon mainly is owed to the stereo resistance of molecular chains to PEG grafting, since the steric conformation effect will hinder the collisions among the reactive sites on the macromolecules. For all these samples, the grafting efficiencies were lower than 46.1%. That is to say, only a small portion of —CH$_2$Cl were translated into —CH$_2$O-PEG.

Thermal stability and solubility

PPESK is an amorphous copolymer with rigid phthalazinone moieties and aromatic structure. The grafting of flexible PEG chains had a great influence on PPESK's thermal properties. The TGA curves for PPESK, CMPPESK, and PPESK-*g*-PEGs are shown in Figure 6. The weight loss temperature (5% loss) of virgin PPESK is at 476°C, exhibiting an outstanding thermal stability. Two decomposition steps are observed in the curves of CMPPESK and PPESK-*g*-PEGs. The first, from 250 to 320°C, is attributed to the decomposition of chloromethyl groups and PEG chains. The second decomposition step, beginning at about 480°C, is corresponding to the damage of PPESK backbones. From the weight loss ratios at the first decomposition step, the GD of PEG on the PPESK was also calculated. Because of the graft products containing unreacted CMPPESK, the weight loss ratio of CMPPESK must be considered when calculating the GD of PPESK-*g*-PEG. As shown in Table II, the results from TGA are approximately in agreement with the data calculated from ^{1}H-NMR analysis, suggesting that the unreacted PEG-OH had completely been removed from the products by reprecipitation and extraction. In spite of the deteriorated thermal stability for PPESK after the grafting of PEG, the bulk of PPESK membranes with the graft

TABLE II
The Grafting Degree (GD), PEG Incorporation, and Grafting Efficiency of PPESK-*g*-PEGs

Sample label[a]	DS of used CMPPESK	GD of PEG		[b]PEG incorporation/wt %	[c]Grafting efficiency/%
		^{1}H-NMR	TGA		
G350-1	3.22	1.18	1.09	29.2	36.6
G350-2	2.47	0.94	0.91	24.8	38.1
G350-3	1.65	0.76	–	21.0	46.1
G750-1	3.22	0.79	0.71	37.2	24.5
G750-2	2.47	0.66	–	33.1	26.7
G750-3	1.65	0.52	–	28.1	31.7

[a] The first number in the sample label indicates the molecular weight of used PEG-OH.
[b] PEG content calculated according to the grafting degree from ^{1}H NMR analysis.
[c] Grafting efficiency denoted the conversion percentage of —CH$_2$Cl and calculated from ^{1}H-NMR analysis.

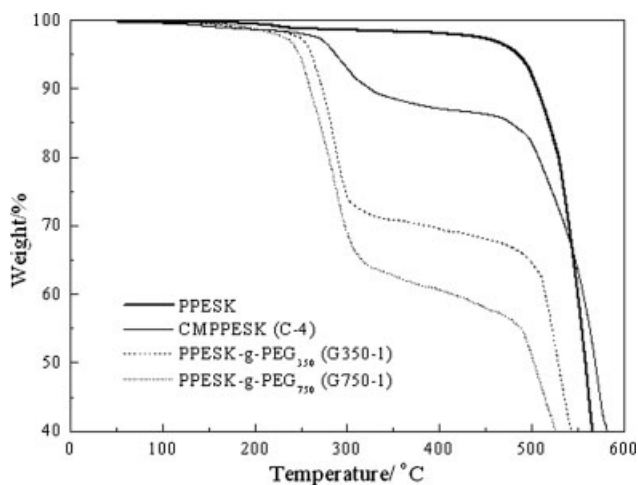**Figure 6** The TGA curves of PPESK, CMPPESK, and PPESK-*g*-PEGs.

TABLE III
The Solubilities of PPESK, CMPPESK, and
PPESK-*g*-PEG in Different Solvents

Solvent	PPESK	CMPPESK	PPESK-*g*-PEG
Water	I	I	SW
Ethanol	I	I	SW
Dichloromethane	S	S	S
Chloroform	S	S	S
Benzene	I	I	I
Acetone	I	I	I
Tetrahydrofuran	I	SW	SW
N,N-dimethylformamide (DMF)	S	S	S
N,N-dimethylacetamide (DMAc)	S	S	S
N-methyl-2-pyrrolidone (NMP)	S	S	S
Dimethyl sulfoxide (DMSO)	S	SW	I
Concentrated H_2SO_4	S	S	S

S, soluble; I, insoluble; SW, swelling.

copolymers as hydrophilic additives maintained a good thermal resistance because the additive was preferentially excluded to the membrane surface during membrane formation. This problem isn't further discussed in this work.

The solubility of the polymers was investigated by observing the solubility of 0.05 g polymer in 5 mL solvent. Table III presents the solubilities of PPESK, CMPPESK, and PPESK-*g*-PEG graft copolymer in some selected solvents. It can be found that PPESK and CMPPESK are soluble in some polar aprotic solvents (such as DMF, DMAc, and NMP) and chloridized solvents (such as dichloromethane and chloroform), and insoluble in some protic solvents such as water and ethanol. However, after the introduction of PEG chains, the obtained PPESK-*g*-PEG graft products can be slight swelled in water and ethanol because of the hydrophilicity of PEG, but water insoluble. It is worth noting that the solubility of PPESK-*g*-PEG is different with various graft degree. An excessive grafting of PEG should be avoided to prevent the graft products from being water soluble. The GD of PEG onto PPESK can be controlled by aforementioned approaches.

Water contact angle and hydrophilicity

The contact angle, an important parameter in surface science, is a regular measure of the surface hydrophilicity. In the present work, dense nonporous films were prepared for the measurements of contact angle. The contact angle values and the calculated adhesion work for various films are showed in Figure 7. The corresponding PEG incorporation ratio and GD for these samples have been listed in Table II. It can be seen clearly that the decline in the contact angle and increase in the adhesion work after PEG-OH was

grafted onto PPESK. In all samples, the virgin PPESK film has the biggest contact angle, 112.5°, and the smallest adhesion work, 44.94 mN/m. Whereas the film G750-1 with the PEG-OH_{750} incorporation of 37.2 wt % has the highest adhesion work 126.1 mN/m, indicating its excellent hydrophilicity. Both the length and the density of comb-like PEG chain have an influence on the hydrophilicity of the products. The order of adhesion work for these films is same as that of the PEG GD, namely G350-1 > G350-2 > G350-3 and G750-1 > G750-2 > G750-3, suggesting that more PEG graft chains bring higher hydrophilicity to the graft products. In a similar PEG content, such as G350-1 and G750-3, the graft copolymer with short but dense graft chains is more hydrophilic than that with long but sparse PEG chains. This phenomenon shows the density of PEG chains has a bigger contribution to the hydrophilicity than the chain length does.
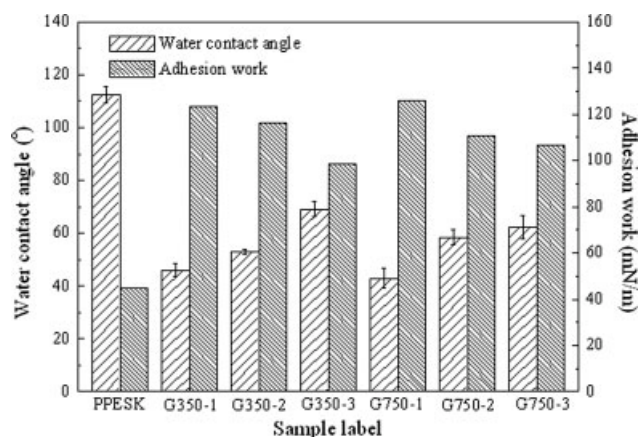

Figure 7 Water contact angle and adhesion work of the films.

CONCLUSIONS

Amphiphilic PPESK-*g*-PEG graft copolymers were successfully prepared by a modified Williamson ether synthesis. The comb-like hydrophilic PEG side chains were introduced into rigid PPESK backbones. The PEG incorporation ratio varied from 21.0 to 37.2 wt %. Two thermal decomposition steps were found in TGA analysis of the obtained graft copolymers. The GD of PEG calculated from ^{1}H-NMR was in approximately agreement with that from TGA tests. The graft products have good solubility in some aprotic polar solvents and can be slight swelled by water and ethanol, but water insoluble. The hydrophilicity of PPESK is significantly improved by the introduction of PEG graft chains, suggesting the graft copolymer is potentially useful as hydrophilic additive for PPESK phase inversion membranes.

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