Modification of Poly(ether imide) Membranes via Surface-Initiated Atom Transfer Radical Polymerization

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Introduction

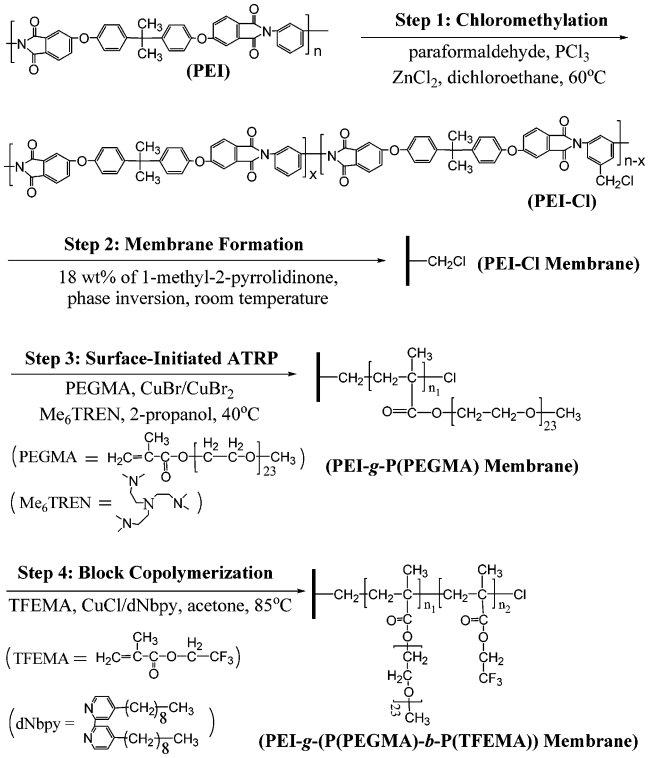
Polyimides (PIs) exhibit outstanding thermal, mechanical, physicochemical, and dielectric properties. They have been widely used in membranes, electronics, photonics, and optics and in the aerospace industry.[1−9] However, there are some drawbacks for PIs, such as poor adhesion to materials, poor solubility, and hydrophobicity. Efforts have been devoted to modifying PIs to provide them with enhanced solubility, optical transparency, photosensitivity, photorefractivity, and nonlinear optical properties, while maintaining their excellent thermal and intrinsic properties.[10−14] Although general physical treatments[15] are quick and easy to implement, chemical modification ensures reproducibility and durability. Among the major chemical modification methods, atom transfer radical polymerization (ATRP) has been successfully applied to the preparation of well-defined polymer brushes on various surfaces. Preparations of polymer brushes on silicon, SiO_2, gold, and polymers have been reported.[16−25] Poly(pentafluorostyrene) brushes have been synthesized by ATRP on fluorinated PIs.[26] A prerequisite for this method is the introduction of reactive chemical groups (ATRP initiators) on the substrate chain or surface. Electrophilic substitutions of the aromatic rings in the main chain of PIs, e.g. by chloromethylation, have been reported.[27,28]

Poly(ether imide) (PEI), as a member of the PI family, is a suitable candidate for biomedical application due to its good membrane-forming properties.[29−31] The polymer backbone of PEI possesses functional groups that are accessible via chemical modification to tailor the resulting membrane materials for specific application.[32] In this work, chloromethylation of PEI chains was first carried out to introduce the ATRP initiators onto their backbones and the surface, including the pore surface, of the resulting microporous membranes. Amphiphilic poly(poly(ethylene glycol) methyl ether methacrylate)-*block*-poly(2,2,2-trifluoroethyl methacrylate), or P(PEGMA)-*b*-P(TFEMA), copolymer brushes were incorporated via consecutive surface-initiated ATRPs from the alkyl halide sites on the PEI microporous membrane. The synthetic pathway is shown in Scheme 1. The present study thus illustrates an approach to the preparation of novel PEI microporous membranes with "dormant" surface sites for further functionalization via surface-initiated ATRP.

Experimental Section

Materials. PEI (Ultem 1000) was purchased from GE Plastics. It was dried at 150 °C for 4 h before use. Poly(ethylene glycol) methyl ether methacrylate (PEGMA, 97%, M_n = 1100 g mol^{-1}, containing 23 ethylene glycol units (n = 23)) was obtained from Aldrich Chemical Co. (Milwaukee, WI). It was dissolved in THF and passed through an inhibitor removing column, concentrated in a rotary evaporator, and then dried under reduced pressure. 2,2,2-Trifluoroethyl methacrylate (TFEMA, 99%) was obtained from Aldrich Chemical Co. and was used as received. Paraformaldehyde (95%), copper(I) bromide (CuBr, 99+%), and 4,4′-dinoyl-2,2′-bipyridyl (dNbpy, 97%) were supplied by Aldrich Chemical Co. and were used as received. Phosphorus trichloride (PCl_3) was obtained from Merck (Schuchardt, Germany). Zinc chloride (analytical reagent) was obtained from General Scientific Co. Sdn Bhd (Singapore). Copper(I) chloride (CuCl, 98+%) 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. Copper(II) bromide ($CuBr_2$, 99+%), obtained from Aldrich Chemical Co., was dissolved in deionized water, filtered, concentrated under reduced pressure at 30 °C, crystallized in a vacuum oven with P_2O_5, filtered, and dried. Tris(2-(dimethylamino)ethyl)amine (Me_6TREN) was synthesized following the procedures reported previously.[33] 2-Propanol (analytical reagent) and 1-methyl-2-pyrrolidinone (NMP, analytical reagent) were obtained from Fisher Scientific Co. (Leics, UK). All other solvents (reagent or HPLC grade) were obtained from either Fisher Scientific Co. or Aldrich Chemical Co. and were used as received.

Scheme 1. Schematic Diagram Illustrating the Preparation of a Chloromethylated PEI Microporous Membranes and the Consecutive Surface-Initiated ATRPs To Produce a Grafted Amphiphilic Block Copolymer on the Membrane[a]



[a] PEI = poly(ether imide); PCl_3 = phosphorus trichloride; $ZnCl_2$ = zinc chloride; PEI-Cl = chloromethylated poly(ether imide); PEGMA = poly(ethylene glycol) methyl ether methacrylate; CuBr = copper(I) bromide; $CuBr_2$ = copper(II) bromide; Me_6TREN = tris(2-(dimethylamino)ethyl)amine; P(PEGMA) = poly(poly(ethylene glycol) methyl ether methacrylate); TFEMA = trifluoroethyl methacrylate; CuCl = copper(I) chloride; P(TFEMA) = poly(trifluoroethyl methacrylate); dNbpy = 4,4′-dinoyl-2,2′-bipyridyl; ATRP = atom transfer radical polymerization.

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Chloromethylation of Poly(ether imide) (PEI). In a 100 mL, three-necked, round-bottom flask equipped with a condenser (with a drying tube attached at the top) and an argon inlet, 5 g of PEI (equivalent to 8.4 mmol of the repeat units) was dissolved in 40 mL of dichloroethane under stirring at 60 °C. Paraformaldehyde (1.5 g), phosphorus trichloride (10 g), and zinc chloride (5 g) were added slowly to the reaction mixture under an argon atmosphere. The mixture was stirred at 60 °C for 48 h and then poured into 400 mL of methanol. The precipitate was filtered, redissolved, and reprecipitated into a water/methanol mixture (50/50, v/v) and then dried under reduced pressure at 80 °C for at least 24 h until a constant weight was obtained. The chloromethylated PEI, or PEI-Cl, so-obtained was further purified by dissolving in *N*,*N*-dimethylformamide and then reprecipitating in methanol.

Membrane Preparation. The membrane was prepared by the phase inversion technique.[32] The PEI-Cl was dissolved in NMP to a concentration of 18 wt % at 80 °C. The PEI-Cl solution was cast on a glass plate. The glass plate was subsequently immersed in doubly distillated water. After the membrane had detached from the glass plates, it was extracted in a second bath of doubly distilled water at 70 °C for 30 min. The microporous membrane so-obtained with a thickness of about 50 μm was dried at room temperature under reduced pressure and then stored in a desiccator.

Surface-Initiated ATRP of PEGMA From the PEI-Cl Membrane. Surface-initiated ATRP of PEGMA on the PEI-Cl membrane was accomplished in a magnetically stirred glass tube (50 mL) by immersing the membrane (about 2 cm × 2 cm in size) into a reaction mixture containing 1.0 g (0.9 mmol) of PEGMA, 6.5 mg (0.04 mmol) of CuBr, 1.0 mg (0.004 mmol) of $CuBr_2$, 43 μL (0.13 mmol) of Me_6TREN, and 10 mL of 2-propanol. The reaction mixture was purged with argon for ~20 min to remove the dissolved oxygen. The tube was then sealed. Polymerization was carried out at 40 °C for 5 days. At the end of the polymerization reaction, the PEGMA graft copolymerized membrane (PEI-*g*-P(PEGMA)) was subjected to exhaustive washing and extraction with water and methanol and then dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained.

Block Copolymerization of TFEMA on the PEI-*g*-P(PEGMA) Membrane. Surface-initiated block copolymerization of TFEMA was carried out on the PEI-*g*-P(PEGMA) membrane, using the alkyl chloride group at the chain end of grafted P(PEGMA) as the ATRP macroinitiator. The procedure is similar to those used for the surfaced-initiated ATRP of PEGMA. In a 10 mL glass tube with provision for magnetic stirring, the membrane (about 1 cm × 1 cm in size) was immersed into a reaction mixture containing 1.0 mL (7.0 mmol) of TFEMA, 7.0 mg (0.07 mmol) of CuCl, 90.0 mg (0.22 mmol) of dNbpy, and 1.0 mL of acetone. The reaction mixture was purged with argon for ~20 min. The tube was then sealed. Polymerization was carried out at 85 °C for 15 h. At the end of the polymerization reaction, the membrane was subjected to exhaustive washing with acetone and then dried under reduced pressure at room temperature for at least 24 h until a constant weight was obtained.

Materials Characterization. ^{1}H NMR spectra were measured in deuterated chloroform ($CDCl_3$) on an Bruker ACF 300 MHz spectrometer at ambient temperature. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an AXIS HSi spectrometer (Kratos Analytical Ltd., Manchester, UK) with a monchormatized Al Kα X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. All binding energies (BEs) were referenced to the C 1s hydrocarbon peak at 284.6 eV. Field emission scanning electron microscopy (FESEM) images were recorded on a JEOL JSM-6700F FESEM at an accelerating voltage of 5 kV. The membrane samples were fractured in liquid nitrogen (for cross-sectional view) and mounted on the sample studs by means of double-sided adhesive tapes. A thin layer of platinum was sputter-coated on the sample for charge dissipation during FESEM imaging. The molecular weights and polydispersities of the polymers were determined using a Waters 1515 gel permeation chromatograph (GPC). The GPC was equipped with a refractive index detector, and HR1, HR3, and HR4 columns, to allow separation of polymers in the molecular weight range of 100−500 000. The columns were calibrated with polystyrene standards. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL min^{-1} at 30 °C.

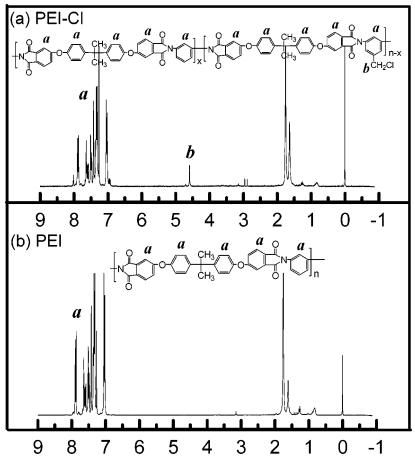

Figure 1. ^{1}H NMR spectra of (a) the chloromethylated PEI (PEI-Cl) and (b) the pristine PEI [PEI = poly(ether imide); PEI-Cl = chloromethylated poly(ether imide)].

Results and Discussion

Chloromethylation of PEI. The structure and composition of poly(ether imide) (PEI) before and after chloromethylation were studied by ^{1}H NMR spectroscopy. Parts a and b of Figure 1 show the respective ^{1}H NMR spectra (in $CDCl_3$) of chloromethylated PEI (PEI-Cl) and PEI. The chemical shifts at δ = 6.93−8.02 ppm (***a*** in Figure 1a,b) can be assigned to the aromatic protons of PEI-Cl and PEI polymers. After chloromethylation, a new chemical shift at δ = 4.59 ppm (***b*** in Figure 1a) can be assigned to the protons of benzyl chloride[27,34] in the PEI-Cl polymer, indicating the presence of chloromethyl (−CH_2Cl) groups covalently tethered on the PEI main chains. Furthermore, a ratio of about 39:1 for the aromatic protons (***a*** in Figure 1a) to the protons of benzyl chloride (***b*** in Figure 1a) indicates that the degree of chloromethylation (the number of chloromethyl groups per repeat unit of PEI) is about 0.22.

Surface-Initiated ATRP. The PEI-Cl was cast into membrane by phase inversion in water at room temperature from a 18 wt % NMP solution. The benzyl chloride groups on the PEI-Cl membrane surface can serve as the active ATRP initiator to produce the well-defined polymer brushes.[19,35] Sacrificial soluble initiators have been commonly used in surface-initiated ATRP to increase the concentration of initiating sites and to allow the system to self-equilibrate by the persistent radical effect.[20,36,37] The high degree of chloromethylation for the present membrane (about 0.22 per repeat PEI unit, both in the bulk and also at the membrane surface (see below)) makes the use of a sacrificial initiator unnecessary. Thus, the poly(poly(ethylene glycol) methyl ether methacrylate)-*b*-poly(2,2,2-trifluoroethyl methacrylate) (P(PEGMA)-*b*-P(TFEMA)) brushes were obtained by consecutive surface-initiated atom transfer radical polymerizations (ATRPs) of poly(ethylene glycol) methyl ether methacrylate (PEGMA) and 2,2,2-trifluoroethyl methacrylate (TFEMA) on the surface of the PEI-Cl membrane in the absence of any sacrificial soluble initiators (Scheme 1). The process involved (i) surface-initiated ATRP of PEGMA, using benzyl chloride groups on the PEI-Cl membrane as macroinitiators (PEI-*g*-P(PEGMA)), and (ii) block copolymerization via surface-initiated ATRP of TFEMA, using the alkyl halide groups at the chain ends of P(PEGMA) brushes as the macroinitiators (PEI-*g*-(P(PEGMA)-*b*-P(TFEMA))) (Scheme 1). The respective

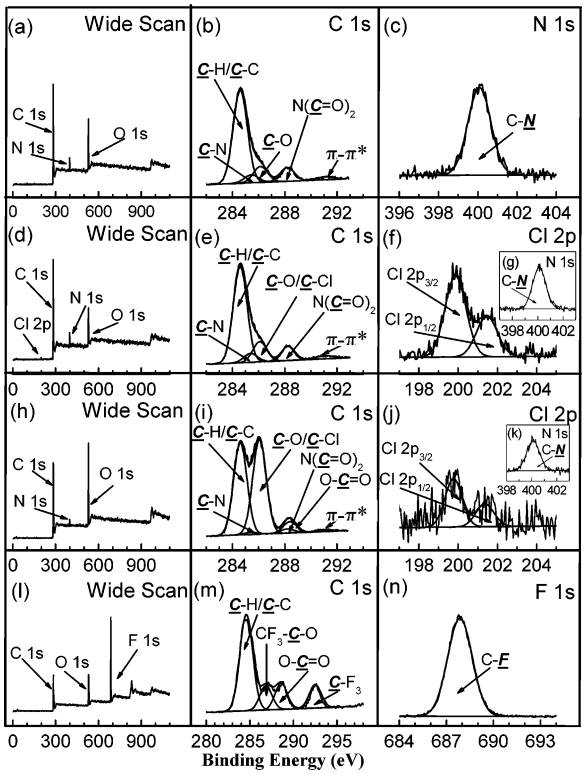

Figure 2. X-ray photoelectron spectroscopy (XPS) (a) wide scan, (b) C 1s, and (c) N 1s core-level spectra of the pristine PEI powders; (d) wide scan, (e) C 1s, (f) Cl 2p, and (g) N 1s core-level spectra of the PEI-Cl membrane surface; (h) wide scan, (i) C 1s, (j) Cl 2p, and (k) N 1s core-level spectra of the PEI-*g*-P(PEGMA) membrane surface; (l) wide scan, (m) C 1s, and (n) F 1s core-level spectra of the PEI-*g*-(P(PEGMA)-*b*-P(TFEMA)) membrane surface [PEI = poly(ether imide); PEI-Cl = chloromethylated poly(ether imide); P(PEGMA) = poly(poly(ethylene glycol) methyl ether methacrylate); P(TFEMA) = poly(trifluoroethyl methacrylate)].

number-average molecular weights, deduced from gel permeation chromatography (GPC), of the pristine PEI and PEI-*g*-P(PEGMA) are about 9500 and 17 000 g mol^{-1}. However, the polydispersity index (weight-average molecular weight/number-average molecular weight) after graft copolymerization has increased substantially from that of 1.51 for the pristine PEI because the surface-initiated ATRP has also given rise to an increased disparity in molecular sizes at and below the surface.

The chemical composition of the membrane surfaces at various stages of surface modification was determined by X-ray photoelectron spectroscopy (XPS). Figure 2a−c shows the XPS wide scan, C 1s, and N 1s spectra of the pristine PEI powders. The three peak components in Figure 2a at the BEs of about 285, 400, and 531 eV are attributable respectively to the C 1s, N 1s, and O 1s species of PEI. 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, N(*C*═O)$_2$, and $\pi-\pi^*$ satellite species, respectively, in the PEI polymer.[38] The [N(*C*═O)$_2$]/[*C*] ratio, as determined from the curve-fitted C 1s core-level spectrum, is about 0.11, in agreement with the theoretical ratio for the PEI polymer. The N 1s peak component at the BE of about 400.1 eV is attributable to the C−*N* species of PEI (Figure 2c).[1,38] After chloromethylation of PEI and subsequent membrane formation, a new peak component at the BE of 200 eV, attributable to the Cl species, has appeared in the wide scan spectrum of the PEI-Cl membrane (Figure 2d). Similar peak components as those of the pristine PEI are observed in the C 1s core-level spectrum of the PEI-Cl membrane (Figure 2e). The slightly enhanced C 1s peak component at the BE of about 286.1 eV is consistent with the presence of incorporated alkyl halide groups. The Cl 2p core-level spectrum of the PEI-Cl membrane (Figure 2f) consists of a doublet with the BEs for the Cl 2p$_{3/2}$ and Cl 2p$_{1/2}$ components at about 199.9 and 201.5 eV, respectively, attributable to the covalently bonded chlorine (C−*Cl*) species.[38] Furthermore, the surface composition of the PEI-Cl membrane can be estimated from the sensitivity factor-corrected Cl 2p and C 1s spectral area ratio and expressed as the [Cl]/[C] ratio. The observed [Cl]/[C] ratio of about 0.007 is in good agreement with the ratio of about 0.006, calculated from the ^{1}H NMR results (Figure 1a, with a degree of chloromethylation of 0.22). In addition, the appearance of a N 1s signal at the BE of about 400.1 eV is consistent with the presence of imide groups in the PEI-Cl membrane (Figure 2g).[38]

Figure 2h−k shows the respective XPS wide scan, C 1s, Cl 2p, and N 1s spectra of the PEI-*g*-P(PEGMA) membrane via surfaced-initiated ATRP of PEGMA from the PEI-Cl membrane surface. The persistence of a N 1s signal at the BE of 400 eV (Figure 2h,k) indicates that the thickness of grafted P(PEGMA) on the PEI membrane is less than the probing depth of the XPS technique (~ 8 nm in an organic matrix[39]). The [*C*−H]/[*C*−O] peak component area ratio in Figure 2i would correspond to a P(PEGMA) layer coverage of about 4 nm. The C 1s peak components of the PEI-*g*-P(PEGMA) membrane surface at the BEs of about 284.6, 285.4, 286.1, 288.2, 288.4, and 291.1 eV are attributable to the *C*−H/*C*−C, *C*−N, *C*−O/*C*−Cl, N(*C*═O)$_2$, O−*C*═O, and $\pi-\pi^*$ satellite species, respectively, of the PEI-*g*-P(PEGMA) membrane (Figure 2i). The substantial increase in intensity of the *C*−O peak component at the BE of 286.1 eV in Figure 2i is consistent with the presence of the grafted P(PEGMA) in the PEI-*g*-P(PEGMA) membrane. In addition, the persistence of a Cl 2p$_{3/2}$ and Cl 2p$_{1/2}$ doublet at the BEs of about 199.8 and 201.4 eV, respectively, attributable to the covalently bonded chlorine (C−*Cl*) species (Figure 2j), indicates that the alkyl halide group remains intact after the surface-initiated ATRP of PEGMA. Thus, the PEI-*g*-P(PEGMA) membrane surface remains "dormant" and will allow the reinitiation of the ATRP process. The hydrophobic monomer containing fluorine, TFEMA, was used for the subsequent surface-initiated block copolymerization to produce the PEI-*g*-(P(PEGMA)-*b*-P(TFEMA)) membrane. The XPS wide scan spectrum of the membrane (Figure 2l) shows three peak components at the BEs of about 285, 531, and 687 eV, attributable respectively to the C 1s, O 1s, and F 1s species,[38] and is consistent with the presence of grafted P(TFEMA) polymer block on the PEI-*g*-(P(PEGMA)-*b*-P(TFEMA)) membrane. Figure 2m shows the C 1s core-level spectrum of the membrane surface. The four peak components at the BEs of 284.6, 286.8, 288.6, and 292.5 eV are attributable to the *C*−H/*C*−C, CF_3−*C*−O, O−*C*═O, and *C*−F_3 species, respectively,[38] and contributed mainly by the P(TFEMA) polymer. The F 1s core-level spectrum (Figure 2n) shows a peak component at the BE of 687.9 eV, attributable to the covalently bonded fluorine (C−*F*) species.[38] Furthermore, the surface [F]/[C] ratio of the PEI-*g*-(P(PEGMA)-*b*-P(TFEMA)) membrane is about 0.42, fairly close to the value of 0.5 expected for the TFEMA monomeric unit ($C_6H_7O_2F_3$), suggesting that the thickness of the P(TFEMA) layer is approaching the probing depth of the XPS technique (~8 nm in an organic matrix[39]). The XPS results thus indicate that an amphiphilic block copolymer, P(PEGMA)-*b*-P(TFEMA), has been covalently tethered on the PEI-Cl membrane surface (including the pore surfaces) via consecutive surface-initiated ATRPs.

CDV

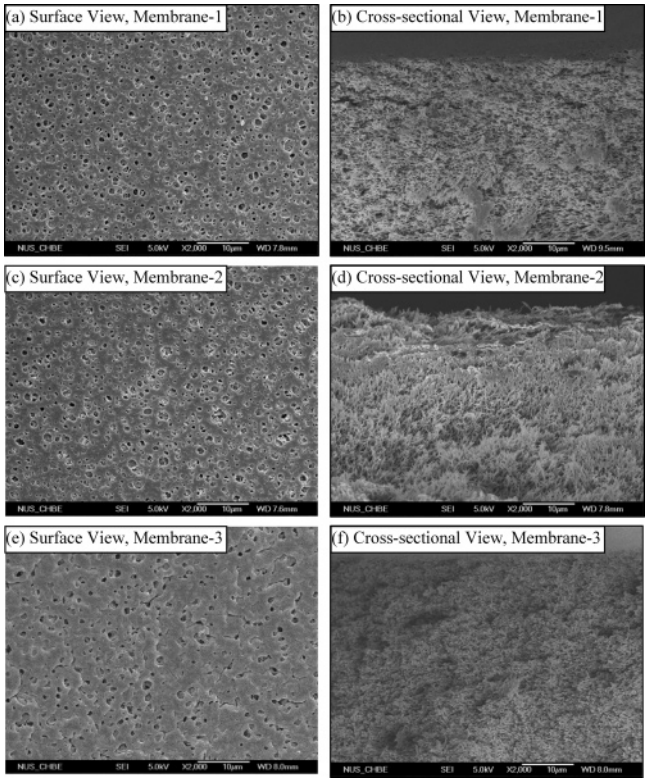

Figure 3. Field emission scanning electron microscopy (FESEM) images of (a) surface view and (b) cross-sectional view of the PEI-Cl membrane (membrane 1), prepared by phase inversion in water at room temperature from a 18 wt % NMP solution; (c) surface view and (d) cross-sectional view of the PEI-*g*-P(PEGMA) membrane (membrane 2); (e) surface view and (f) cross-sectional view of the PEI-*g*-(P(PEGMA)-*b*-P(TFEMA)) membrane (membrane 3) [PEI = poly(ether imide); PEI-Cl = chloromethylated poly(ether imide); P(PEGMA) = poly(poly(ethylene glycol) methyl ether methacrylate); P(TFEMA) = poly(trifluoroethyl methacrylate); NMP = 1-methyl-2-pyrrolidinone].

Morphology of the Membranes. The surface morphology of the microporous PEI membranes at various stages of surface modification was studied by field emission scanning electron microscopy (FESEM). Parts a and b of Figure 3 show respectively the surface view and cross-sectional view of the PEI-Cl membrane. The membrane has a symmetric and microporous structure. The pores have a mean diameter of about 1 μm. After graft copolymerization with PEGMA and TFEMA via surface-initiated ATRP, the pores of the corresponding PEI-*g*-P(PEGMA) membrane (Figure 3c,d) and PEI-*g*-(P(PEGMA)-*b*-P(TFEMA)) membrane (Figure 3e,f) became smaller than those of the pristine PEI-Cl membrane due to the presence of surface-grafted P(PEGMA) and P(TFEMA) polymer chains.

In summary, a novel method for preparing PEI membrane with surface "dormant" groups for further surface functionalization via "living"/controlled radical polymerization was demonstrated. Well-defined amphiphilic P(PEGMA)-*b*-P(TFEMA) brushes were covalently tethered on the PEI membrane surface, including the pore surface. The process involved (i) chloromethylation of the PEI polymer in dichloroethane, (ii) casting the chloromethylated PEI (PEI-Cl) into microporous membranes, (iii) surface-initiated ATRP of PEGMA, using the methyl chloride groups on the PEI-Cl membrane as the macroinitiators, and (iv) block copolymerization of TFEMA via surface-initiated ATRP, using the alkyl halide groups at the chain ends of P(PEGMA) brushes as the macroinitiators.

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