Copolymers of Aniline and 3-Aminophenol Derivatives with Oligo(oxyethylene) Side Chains as Novel Water-Soluble Conducting Polymers

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ABSTRACT: A novel water-soluble copolymer of aniline and aminophenol (AP) grafted with oligo-(oxyethylene) (PEO) side chains (AP-*g*-PEO) was synthesized. The AP-*g*-PEO macromononer was prepared starting from an N-protected 3-aminophenol (protection group: *tert*-butoxycarbonyl) followed by the substitution of tosylated oligo(oxyethylene) on the hydroxide moiety of the AP and deprotection. Finally, AP-*g*-PEO was copolymerized with aniline at various feed mole ratios (AP-*g*-PEO/aniline). The copolymers and various intermediates were characterized by FTIR, MS, NMR, GPC, UV−vis, and chemical elemental analysis. The increase of the aniline content and the decrease of the PEO side chain length generated lower oligo(oxyethylene) grafted concentrations and solubilities in water but longer conjugation lengths and higher conductivities. Four AP-*g*-PEOs were prepared from four oligo(oxyethylene) methyl ethers with M_n = 164, 350, 750, and 2000. The poly((AP-*g*-PEO-750)-*co*-aniline) at a feed mole ratio of 3/1 was water-soluble and possessed a relatively high conductivity (0.12 S/cm). AP-*g*-PEOs were found to have low reactivities and to generate low homopolymerization degrees because of the torsional effects of the PEO side chains on the backbone of the copolymer. A possible copolymerization mechanism was suggested. Furthermore, the copolymers with high PEO content had lower oxidation and doping levels of their backbones, which were confirmed by X-ray photoelectron spectroscopy.

Introduction

Polyaniline has been extensively studied in the past 20 years, as one of the important conducting polymers, because of its thermal stability and high conductivity.[1−4] However, this polymer was found to have low solubilities in the common solvents and poor processability. Numerous investigations have been carried out for the improvement of the solubility and processability by introducing various side chains such as alkyl,[5] alkoxy,[6] benzyl,[7] and aryl[8] substituents either at the aromatic ring or at nitrogen. The grafted side chains in these aniline derivatives increased the solubility of the PANI backbones. Water-soluble poly(aniline derivatives) could be also prepared by the direct polymerization of water-soluble aniline derivative monomers containing a sulfonic acid moiety at the phenyl ring or nitrogen.[9−13] The withdrawing effect of the sulfonic group caused, however, difficulties in homopolymerization and also decreased the conductivity. The copolymerizations of sulfonated aniline and aniline have been successfully carried out.[14−18] Another pathway was the modification of the backbone of polyaniline through grafting water-soluble side chains at either the ring or nitrogen. A typical example is the directly sulfonated polyaniline (SPAN) reported by Epstein et al.[19] A decrease of the conductivity because of the withdrawing effect was observed.[19−21] Yamaguchi et al. prepared PANI grafted with hydrophilic poly(ethylene oxide) (PEO) through a "graft from" process, in which a ring-opening polymerization of an epoxide occurred on the active anionic nitrogens of the PANI backbone.[22] Wang et al. grafted PEO chains to the active anionic nitrogens of PANI via a direct attachment under very strict experimental

conditions. A lower grafting degree, below 30%, was, however, achieved through this "graft onto" process.[23] Less attention was paid to the grafting of PEO side chains to the phenyl ring, even though the modification that occurs at nitrogen was expected to produce a higher decrease of the conductivity than that which occurs at a phenyl ring. Park et al.[24] suggested a synthesis strategy in which poly(ethyleneoxy)-3-aminobenzoate was prepared by reacting 3-aminobenzoic acid with trityl chloride, followed by the chlorination and esterification of the benzoic acid moiety. After deprotection in acidic conditions, the resulted macromonomer could be copolymerized with aniline. The presence of benzoic acid or of its ester decreased the reactivity of the macromonomer because of their electron-withdrawing effect, resulting in a low-grafted copolymer (<35%).The aniline derivatives with a short-chain alkoxyl grafted on the phenyl ring, such as 2- or 3-methoxyaniline or 2- or 3-ethoxyaniline, were easily homopolymerized to generate conducting polymers with conductivities as high as that of polyaniline because the alkoxyl is an electron donor.[25] The homopolymerization of 2- or 3-aminophenol in acidic conditions has been also reported.[26] The low conductivity achieved, below $10^{−8}$ S/cm, might have been caused by the inductive effect of the hydroxide moiety of the AP.

In previous papers, we reported the preparation of a water-soluble polydiphenylamine (PDPA) with poly-(ethylene oxide) (PEO) grafted onto the nitrogens of the PDPA backbone.[27] The grafting was achieved by substituting the tosyloyl end group of PEO-tosylate with an amine of the PDPA under mild conditions. The resulted PDPA-*g*-PEO with a comb-shaped architecture became soluble in organic solvents, such as chloroform or tetrahydrofuran, and even became water-soluble for PEO side chains of molecular weight M_n = 2000. The

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Scheme 1. Synthesis Pathway of Copolymers of AP-*g*-PEO and Aniline
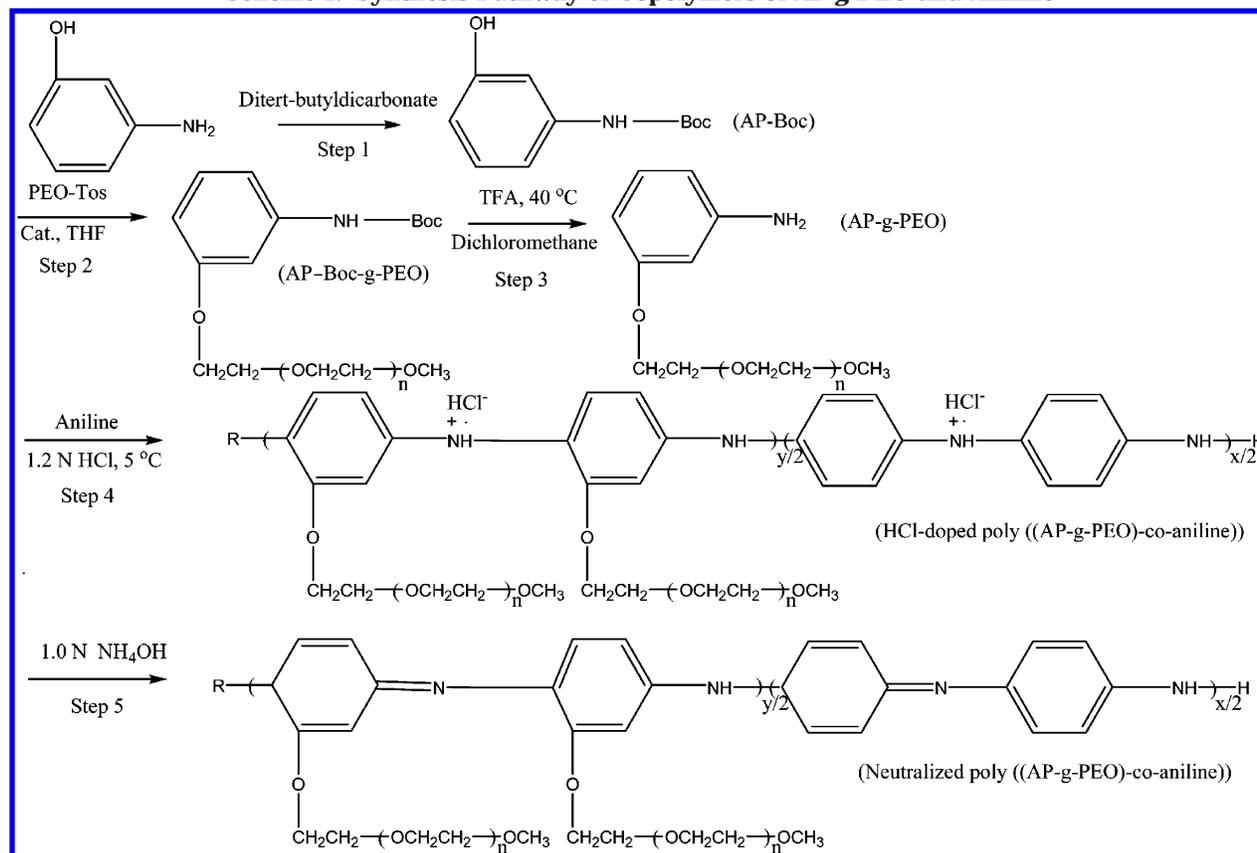
PEO-grafted polyaniline can be employed as battery material and biomaterial.[28−31]

In the present paper, an N-protected aniline derivative was first prepared by reacting 3-aminophenol (AP) with *tert*-butoxycarbonyl (*t*-Boc) as a temporary protecting group.[32] The protection was followed by the grafting of an oligo(oxyethylene) side chain at the 3-position by substituting the tosyloyl end group of tosylate oligo-(oxyethylene) with the hydroxide moiety of the AP under mild conditions[31,33] to generate AP-Boc-*g*-PEO. Further, the AP-Boc-*g*-PEO was deprotected with trifluoroacetic acid (TFA) to obtain an aniline macromonomer possessing an oligo(oxyethylene) side chain at the 3-position (AP-*g*-PEO), which was (co)polymerized via chemical oxidation in the presence of 1.2 N HCl aqueous solution (see Scheme 1). The molecular structures of the amino-protected oligomers and copolymers were characterized by FTIR, MS, NMR, GPC, and elemental chemical analysis. Furthermore, the oxidation levels of these copolymers upon doping or undoping were examined by X-ray photoelectron spectroscopy (XPS).

Experimental Section

Materials. 3-Aminophenol (99%), aniline (99%), di-*tert*-butyldicarbonate (97%), hydrochloric acid (37 wt %), ammonium persulfate (98 wt %), trifluoroacetic acid (TFA, 99%), triethylamine (99 wt %), *p*-toluenesulfonyl chloride (99+ wt %), and potassium *tert*-butylate (>95 wt %) were purchased from Aldrich and used without further purification. Oligo-(oxyethylene) methyl ethers with different molecular weights, such as tri(ethylene glycol) monomethyl ether (PEO-150, M_n = 164) and poly(ethylene oxide) methyl ethers (PEO-350 (M_n = 350), PEO-750 (M_n = 750), and PEO-2000 (M_n = 2000)) were also purchased from Aldrich and used without further purification. The solvents, dimethylformamide (DMF), diethyl ether, and tetrahydrofuran (THF) from Aldrich and dichloromethane and chloroform from Fisher, were of HPLC purity.

Amino Protecting Reaction. 3-Aminophenol (0.1 mol), di-*tert*-butyldicarbonate (0.1 mol), and 40 mL of DMF were introduced into a round flask under a nitrogen atomosphere. The system was subjected to intensive magnetic stirring for a few minutes and then cooled to 0 °C in an ice−water bath. A triethylamine (0.105 mol) solution in DMF (40 mL) was added dropwise within 1 h. The reaction lasted an additional 12 h at 0 °C. Further, 300 mL of chloroform and 100 mL of water were introduced to generate two layers. The pH of the top layer (the water phase) was carefully adjusted, using a 0.1 N HCl aqueous solution, at pH = 7, and extracted with chloroform three times (30 mL each time). The combined chloroform phases were first washed with a saturated NaHCO₃ aqueous solution and then washed with water until neutral. The chloroform solution was dried with Na₂SO₄, and the solvent was evaporated on a rotary evaporator. A light brown solid, N-protected aminophenol (AP-Boc), was obtained with an yield of 89%. ¹H NMR (CDCl₃) δ = 7.01−6.10 (1,3-Ph, 4 H), 4.57 (−OH, 1H), 3.66 (−NH₂, 2 H). Anal. Calcd for C₁₁H₁₅O₃N: C, 63.15; H, 7.18; O, 22.97; N, 6.70. Found: C, 63.12; H, 7.16; O, 22.99; N, 6.73. MS (*m/z*): 209.1.

Substitution Reaction of Tosylated Oligo(oxyethylene) (PEO-Tos) to the Hydroxide Moiety of the Phenol of AP-Boc. AP-Boc (0.050 mol), potassium *tert*-butylate (0.050 mol), and dry THF (250 mL) were introduced into a round flask under a dry nitrogen atmosphere and subjected to intensive stirring. PEO-Tos with controlled oxyethylene chain length (PEO-150, PEO-350, PEO-750, and PEO-2000) was prepared via the tosylation of the oligo(oxyethylene) methyl ether with tosyol chloride as reported in a previous paper.[27] PEO-Tos (0.055 mol) was dissolved in 50 mL of THF, and this solution was added dropwise to the flask. The system was subjected to intensive stirring for 3 days. The mixture became light red, and a precipitate appeared, indicating the start of grafting. Dichloromethane (300 mL) and 100 mL of water were introduced to generate two layers. The top layer (the water phase) was extracted with dichloromethane three times (30 mL each time), and the extracted oil phase was combined with the previous dichloromethane phase. The total oil phase was

washed with water three times (100 mL each time) and dried with Na$_2$SO$_4$. The dichloromethane was removed on a rotary evaporator. Further purification was carried out via a chromatographic method. A light brown liquid, namely AP-Boc-*g*-PEO, was thus obtained with an yield of about 70%.

Deprotecting Reaction of AP-Boc-*g*-PEO and Copolymerization with Aniline. AP-Boc-*g*-PEO (0.030 mol), TFA (0.060 mol), and dichloromethane (40 mL) were introduced into a round flask equipped with a condensor, subjected to intensive stirring, and its temperature raised to 40 °C. The reaction lasted 2 h at 40 °C, after which the solvent and the excess of TFA were removed on a rotary evaporator under high vacuum at a temperature <30 °C. A brown liquid, AP-*g*-PEO, was obtained with a yield of 98%.

AP-*g*-PEO and aniline, with feed mole ratios of AP-*g*-PEO/ aniline of 10/1, 6/1, 3/1, 1/1, or 1/2, and a total concentration of 1.2 N were dissolved in 45 mL of 1.2 N HCl aqueous solution with intensive stirring, and the system was cooled to 5 °C. Ammonium persulfate (0.010 mol) dissolved in 1.2 N HCl aqueous solution (15 mL) was added dropwise into the flask. The color of the mixture changed slowly from brown to green, indicating the beginning of copolymerization. After 18 h, a green precipitate was separated using a supercentrifuge (Dupont, RC-5) at 3500 rpm for 30 min. The green particles of the copolymers were washed with water several times until no red supernatant was identified. Further purifications of the HCl-doped copolymers were carried out through dissolution−precipitation in diethyl ether. The yields were 32, 57, 62, 67, and 75% for feed mole ratios of 10/1, 6/1, 3/1, 1/1, and 1/2, respectively. The dedoping was carried out through the neutralization of the above HCl-doped copolymers with a 1.0 N NH$_4$OH aqueous solution. A blue solid was obtained with an yield above 90% in all cases.

The homopolymerization of AP-*g*-PEOs was also carried out for comparison purposes. The yield was in all cases below 37%.

Characterization. Proton (^{1}H) NMR, MS, UV−vis absorption, and FTIR measurements have been carried out on a 400 MHz INOVA-400, Mass Spectroscope (PHI 7200 model), a Thermo Spectronic Genesys-6, and a Perkin-Elmer FTIR 1760, respectively. The NMR solutions were prepared by dissolving the polymer in deuterated water or deuterated chloroform (5 g/L). Gel permeation chromatography (GPC, Waters) was used to evaluate the molecular weights of the homopolymers and copolymers on the basis of a polystyrene calibration curve. The GPC was equipped with three 30 cm long columns filled with a Waters Styragel, a Waters HPLC 515 pump, and a Waters 410 RI detector. The GPC measurements have been carried out using DMF as eluent at 60 °C, at a flow rate of 1.0 mL/ min and 1.0 cm/min chart speed.

The chemical elemental analysis of the polymer samples was carried out on a Perkin-Elmer model 2400 C, H, N analyzer. The chlorine and sulfur contents were determined by the oxygen flask method. The room temperature conductivities of the compressed pellets of the various copolymers were determined using the conventional four-point method. The surface elemental analysis of compressed disks was carried out on a VG ESCA/SIMSLAB MK II with a Mg Kα radiation source (1253.6 eV). Each copolymer sample was first dissolved in DMF, and subsequently DMF was removed using a rotary evaporator. The solid sample was dried under high vacuum at room temperature for at least 7 days under a nitrogen atmosphere and ground into a powder which was compressed into a disk (of thickness around 1 mm) between two Teflon films.

Results and Discussion

Synthesis and Characterization. The copolymers of aminophenol with oligo(oxyethylene) side chains at the 3-position of the phenyl ring (AP-*g*-PEO) and aniline were prepared via the successive four steps of Scheme 1. The *t*-Boc-N-protected aminophenol (AP-Boc) was grafted via substitution with tosylated oligo(oxyethylene) (PEO-Tos-150, PEO-Tos-350, PEO-Tos-750, or PEO-Tos-2000 prepared from PEO-150 (M_n = 164), PEO-350
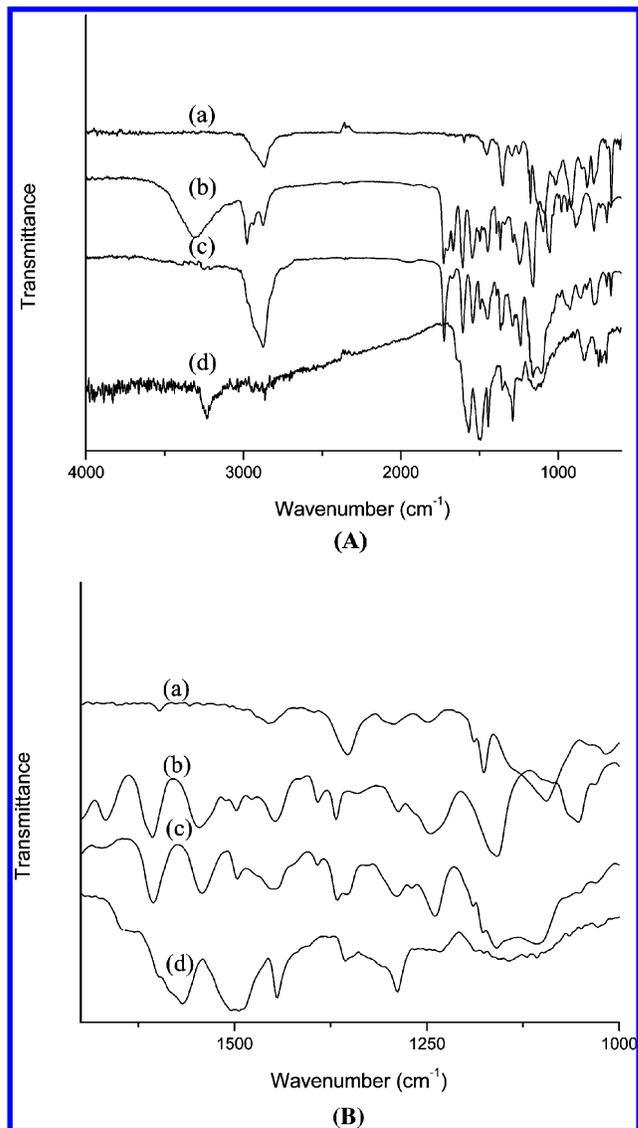
Figure 1. FTIR spectra of (a) PEO-750-Tos, (b) AP-Boc, (c) AP-Boc-*g*-PEO-750, and (d) poly(AP-*g*-PEO-750)-*co*-aniline) (3/1).
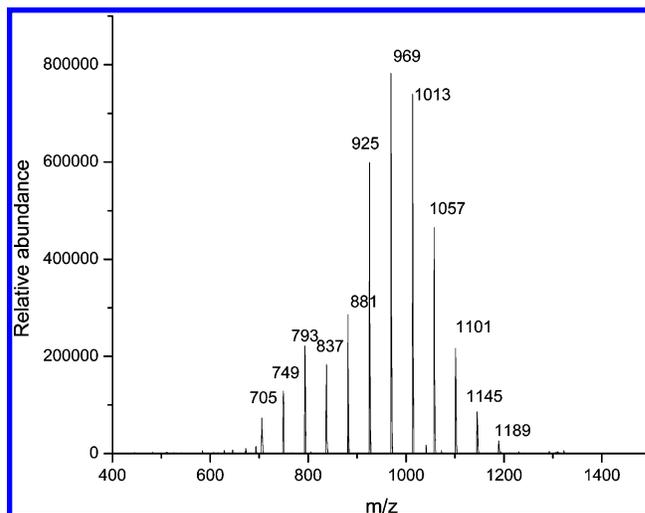
Figure 2. MS spectrum of AP-Boc-*g*-PEO-750.

(M_n = 350), PEO-750 (M_n = 750), and PEO-2000 (M_n = 2000), respectively) to generate the corresponding oligomer (AP-Boc-*g*-PEO). Figure 1 presents the FTIR spectra of PEO-750-Tos (spectrum a), AP-Boc (spectrum
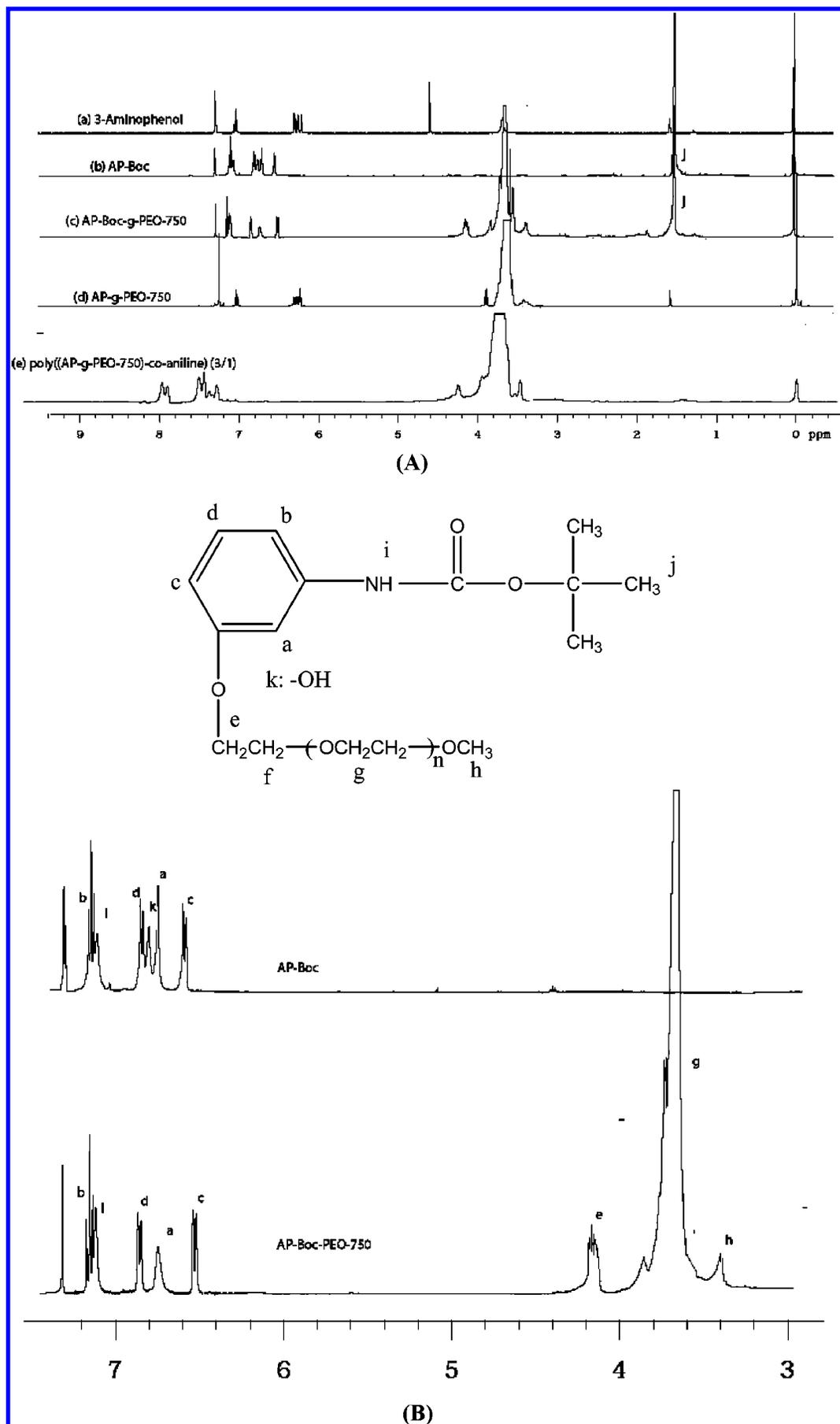
Figure 3. (A) ^{1}H NMR spectra of (a) 3-aminophenol, (b) AP-Boc, (c) AP-Boc-*g*-PEO-750, (d) AP-*g*-PEO-750, and (e) poly((AP-*g*-PEO)-*co*-aniline) (3/1) in CDCl$_3$, 5 g/L. (B) Two expanded ^{1}H NMR spectra of (b) AP-Boc and (c) AP-Boc-*g*-PEO-750 in CDCl$_3$, 5 g/L.
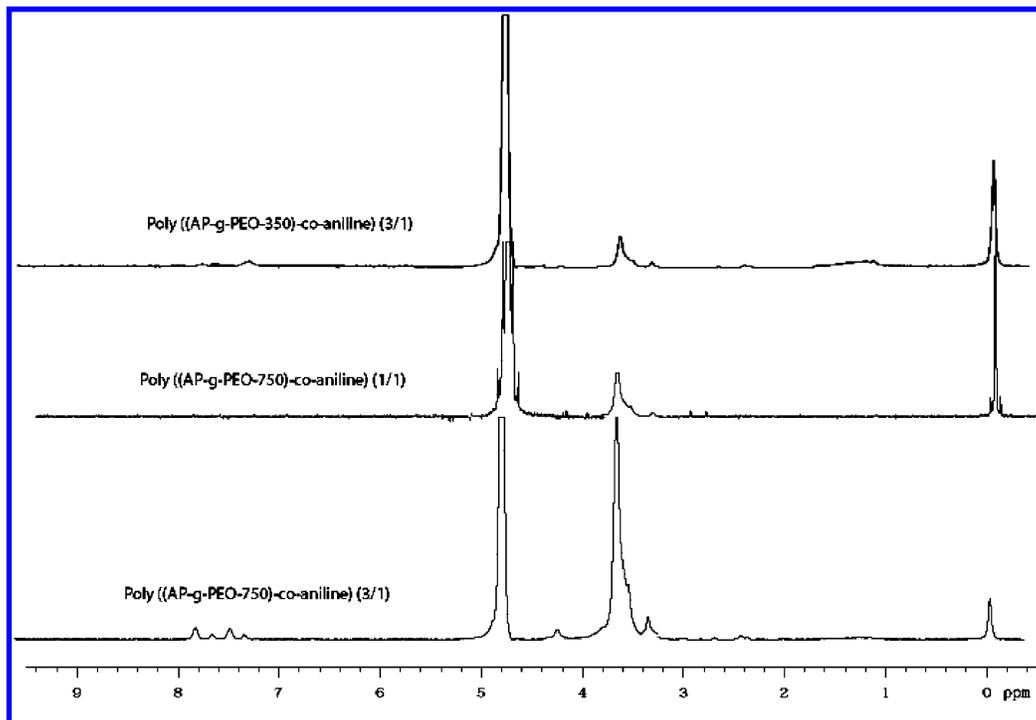
Figure 4. ^{1}H NMR spectra of copolymers in D$_2$O, 5 g/L: (a) poly((AP-*g*-PEO-750)-*co*-aniline) (3/1), (b) poly((AP-*g*-PEO-750)-*co*-aniline) (1/1), and (c) poly((AP-*g*-PEO-350)-*co*-aniline) (3/1).

b), and AP-Boc-*g*-PEO-750 (spectrum c); the characteristic peak of the hydroxide moiety at 3300 cm^{-1} disappeared in AP-Boc-*g*-PEO-750 because of the formation of an ether bond after substitution, and the ether bond peaks (C–O–C) of the PEO side chains and of the phenoxyl (=C–O–C) appeared around 1108 cm^{-1} as a multipeak. The carbonyl vibration peak at 1734 cm^{-1}, which can be assigned to *t*-Boc, is still present in the two compounds, indicating that the *t*-Boc was not eliminated during substitution. Figure 2 displays a typical MS spectrum of AP-Boc-*g*-PEO-750 (ESI MS), where the values of the main molecular ionic peaks in the MS spectra reflect the following formula:

$$M_n = 23(Na^+) + 31(-OCH_3) + 208 \; (\text{structure}) + 44 \; (-CH_2CH_2O-)n$$

where *n* is the number of ethylene oxides in the oligo-(oxyethylene) side chains. Furthermore, in the ^{1}H NMR spectra (CDCl$_3$, Figure 3A), the signals in the range 8.0–6.0 ppm of the phenyl rings of AP-Boc or AP-Boc-*g*-PEO-750 were shifted downfield compared with those of 3-aminophenol because of the deshielding effect caused by the *tert*-butoxycarbonyl. The characteristic signal at 1.44 ppm, which can be assigned to the protons of methane of *t*-Boc, remained almost the same in the two cases (spectra b and c in Figure 3A), indicating that the protecting groups were not lost during substitution. In Figure 3B of the expanded NMR spectra of AP-Boc and AP-Boc-*g*-PEO-750, the protons of the phenyl ring could be assigned to the chemical formula inserted. The signals at 4.18, 3.65, and 3.41 ppm can be assigned to the protons of phenoxymethylene, the oxyethylene, and oxymethyl of the PEO side chains, respectively. The NMR spectrum of AP-*g*-PEO-750 obtained after deprotection (spectrum d of Figure 3A) shows that the signals at 7.10 ppm (peak i) and 1.40 ppm (peak j) present in AP-Boc-*g*-PEO-750 (which can be assigned to the pro-

tons of the amide (–CONH–) and methyl (–CH$_3$) of the *t*-Boc, respectively) disappeared. The signals due to the protons of the phenyl ring were shifted upfield because the deshielding effect caused by the *tert*-butoxycarbonyl was no longer present. The main peaks in the MS spectrum after deprotection were found to differ from those of AP-*g*-Boc-*g*-PEO-750 (see Figure 2) by 108 Da, corresponding exactly to the molecular weight of the *t*-Boc moiety.

Figure 1c also contains a typical FTIR spectrum of neutralized poly(AP-*g*-PEO-750-*co*-aniline) prepared for a feed mole ratio of AP-*g*-PEO-750/aniline = 3/1. The characteristic vibrations at 1585 and 1490 cm^{-1} can be assigned to the stretching vibrations of the quinoid and benzenoid rings, respectively, indicating the generation of conjugation along the backbone (oxidated state). Its NMR spectrum (CDCl$_3$, spectrum e of Figure 3A) displays two groups of signals at 8.00–7.00 and 4.00–3.00 ppm, which can be assigned to the protons of the phenyl ring of polyaniline main chain and the oxyalkyl protons of PEO side chains, respectively. However, in deuterated water (D$_2$O), the signals due to the protons of the phenyl ring became weak. Particularly for the copolymer prepared from a feed mole ratio of 1/1, these signals could be hardly identified (see Figure 4). This is probably related to the aggregation of the hydrophobic polyaniline backbones in water.[27]

Copolymerization of AP-*g*-PEOs and Aniline. The copolymerization of aniline derivatives and aniline has been investigated because most derivatives with side chains attached either to the phenyl ring or to the nitrogen have low reactivities because of the torsional and electronic withdrawing effects of the side groups. The methoxy- or ethoxyaniline can homopolymerize as aniline because the methoxy or ethyoxy moieties are electron donors, thus almost complementing the loss of reactivity due to the torsional effects. Table 1 shows that the poly(2-methoxyaniline) (poly(*o*-anisidine)) and polyaniline exhibit comparable polymerization degrees (153.0

Table 1. Physical Parameters of the Copolymers of AP-*g*-PEOs and Aniline

name	HCl concn, temp	AP-*g*-PEO/ aniline,[a] feed mole ratio	M_n (polymerization degree)[b]	AP-*g*-PEO/ aniline in copolymer (y/x)[c]	PEO wt fraction in copolymer[d]	conductivity, S/cm[e]
polyaniline	1.2 N, 5 °C		15760 (169.5)			4.57
poly(*o*-anisidine)	1.2 N, 5 °C		18970 (153.0)			3.53
poly (AP-*g*-PEO-150)	3.0 N, 5 °C		9550 (36.4)			2.34×10^{-3}
poly (AP-*g*-PEO-350)	3.0 N, 5 °C		11350 (24.0)			5.43×10^{-5}
poly (AP-*g*-PEO-750)	3.0 N,5 °C		5675 (6.50)			$<10^{-7}$
poly (AP-*g*-PEO-2000)	3.0 N, 5 °C		12060 (5.7)			$<10^{-7}$
poly((AP-*g*-PEO-750)-*co*-aniline)	1.2 N, 5 °C	10/1	9650 (13.7)	4.0	0.850	7.4×10^{-5}
poly((AP-*g*-PEO-750)-*co*-aniline)	1.2 N, 5 °C	6/1	20460 (30.4)	3.2	0.845	4.8×10^{-4}
poly((AP-*g*-PEO-750)-*co*-aniline)	1.2 N, 5 °C	3/1	56450 (98.6)	1.7	0.821	0.12
poly((AP-*g*-PEO-750)-*co*-aniline)	1.2 N, 5 °C	1/1	41690 (102.7)	0.7	0.757	0.30
poly((AP-*g*-PEO-750)-*co*-aniline)	1.2 N, 5 °C	1/2	40630 (125.1)	0.44	0.702	0.83
poly((AP-*g*-PEO-150)-*co*-aniline)	1.2 N, 5 °C	3/1	27590 (126.9)	2.4	0.504	0.67
poly((AP-*g*-PEO-350)-*co*-aniline)	1.2 N, 5 °C	3/1	37480 (112.1)	2.0	0.693	0.44
poly((AP-*g*-PEO-2000)-*co*-aniline)	3.0 N, 5 °C	3/1	26540 (17.6)	0.4	0.858	$<10^{-7}$

[a] AP-*g*-PEOs denote aminophenol derivatives with various oligo(oxyethylene) side chains at the 3-position of 3-aminophenol. [b] Number-average molecular weights of the neutralized polymers were determined by GPC on the basis of a PS calibration curve; using DMF as eluent at a rate of 1 mL/min and at 60 °C. The polymerization degree is expressed as $DP_n = (M_{n,GPC} \times (1 + (y/x)))/((y/x) \times M_{n,AP-g-PEO} + M_{n,aniline} - 2)$. [c] The mole ratio of AP-*g*-PEO/aniline in copolymer, y/x, was determined from Table 3 via chemical elemental analysis, i.e., $y/x = (C/N - 6)/(7 - C/N + (M_n - 31)/22))$, where $M_{n,AP-g-PEO}$ is the molecular weight of the oligo(oxyethylene). [d] PEO weight fraction was calculated from footnote c using the expression $(M_{n,AP-g-PEO} \times (y/x))/((M_{n,AP-g-PEO} + 109) \times (y/x) + 91)$. [e] Conductivities of polymeric compressed pellets determined via the four-point method. Each polymer was dried under vacuum for at least 7 days before the measurement and ground into a powder which was further compressed into a disk.
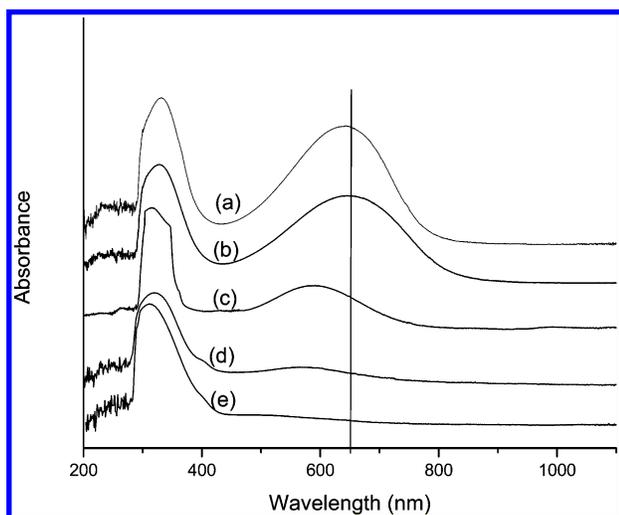
Figure 5. UV–vis spectra of (a) neutralized PANI, (b) neutralized poly(*o*-anisidine), (c) neutralized poly((AP-*g*-PEO-750)-*co*-aniline) (3/1), (d) neutralized poly(2-aminophenol), and (e) neutralized poly(AP-*g*-PEO-750) (all in DMF).

Figure 6. UV–vis spectra of (a) neutralized PANI, (b) neutralized poly((AP-*g*-PEO-750)-*co*-aniline) (1/2), (c) neutralized poly((AP-*g*-PEO-750)-*co*-aniline) (1/1), (d) neutralized poly-((AP-*g*-PEO-750)-*co*-aniline) (3/1), and (e) neutralized poly((AP-*g*-PEO-750)-*co*-aniline) (6/1) (all in DMF).

and 169.5, respectively). The UV–vis spectra of PANI and poly(*o*-anisidine) (spectra a and b of Figure 5) exhibit two absorbance peaks at 320 and 640 nm, which can be assigned to the $\pi-\pi^*$ transition of the benzenoid and the exciton transition of the quinoid rings, respectively. They show that their conjugations and conductivities are comparable. The UV–vis spectrum of poly-((AP-*g*-PEO-750)-*co*-aniline) (3/1) has a peak at 605 nm, which was blue-shifted in comparison with PANI, and a lower area integral, indicating a lower conjugation. Four AP-*g*-PEOs with various PEO side chains ($M_{n,PEO}$ = 164, 350, 750, and 2000) were homopolymerized under acidic conditions and produced low molecular weight homopolymers and low conductivities ($<10^{-3}$ S/cm). The polymerization degree decreased with increasing PEO side chain length, indicating that the reactivity of AP-*g*-PEOs has decreased in the same direction (see Table 1). Using AP-*g*-PEO-750 as an example, the UV–vis spectrum (Figure 5, spectrum e) of polyAP-*g*-PEO-750 provided a very weak peak around 600 nm in the

neutralized state and a very low conductivity ($<10^{-7}$ S/cm) in the HCl-doped state. However, the copolymerization between AP-*g*-PEO-750 and aniline with a feed mole ratio of 3/1 could produce high molecular weight copolymers (polymerization degree = 98.6). The mole ratio AP-*g*-PEO-750/aniline in the copolymers increased from 0.44 to 4.0 with increasing feed mole ratio of AP-*g*-PEO-750/aniline from 1/2 to 10/1, and the conductivity decreased in the same direction. In Figure 6, the blue shift compared to PANI increased with increasing feed mole ratio; i.e., the peak at 640 nm of the polyaniline was shifted to 595 nm for poly((AP-*g*-PEO-750)-*co*-aniline) at a feed mole ratio = 6/1, along with a decrease in the area integral, indicating a decrease of conjugation. Furthermore, the GPC traces of these copolymers (Figure 7) demonstrated that their molecular weight varied with the feed mole ratio. (The number-average molecular weights are listed in Table
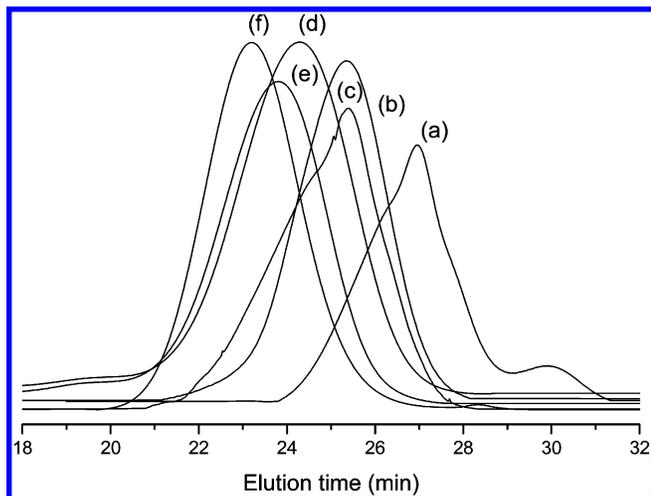
Figure 7. GPC traces of neutralized polymers: (a) poly(AP-*g*-PEO-750), (b) polyaniline, (c) poly((AP-*g*-PEO-750)-*co*-aniline) (6/1), (d) poly((AP-*g*-PEO-750)-*co*-aniline) (1/1), (e) poly((AP-*g*-PEO-350)-*co*-aniline) (3/1), and (f) poly((AP-*g*-PEO-750)-*co*-aniline (3/1).

Scheme 2. A Possible Copolymerization Mechanism
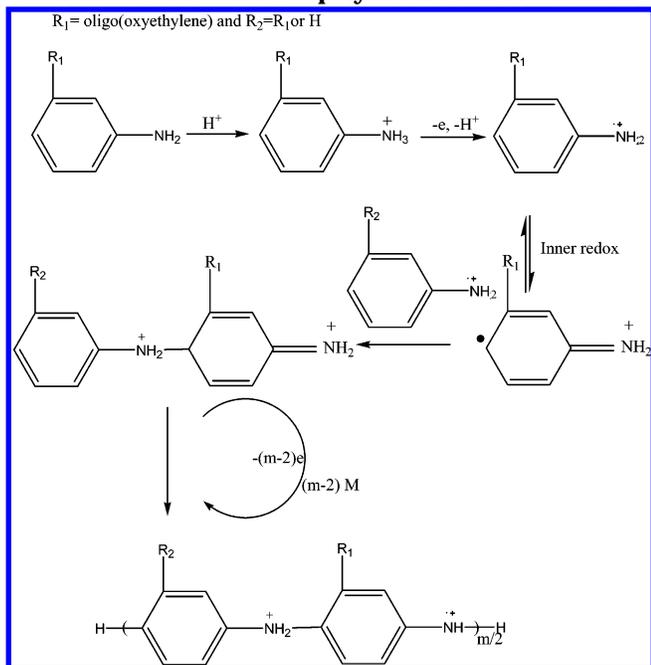
1.) The polymerization degrees of the copolymers prepared at the feed mole ratios of 1/2, 1/1, 3/1, 6/1, and 10/1 were 125.1, 102.7, 98.6, 30.4, and 13.7, respectively. As the feed mole ratio increased, the backbone length became shorter and possessed a lower conjugation. The grafted PEO-750 side chain of AP-*g*-PEO-750 provided a steric barrier which weakened the polaron formation under oxidation conditions, and as a result, the reactivity decreased. The higher diffusion barriers generated by the longer side chains regarding the propagation of the radical species decreased the rate of growth of the chains. Indeed, for the same feed mole ratio, the polymerization degree decreased as the oligo(oxyethylene) side chain length increased (see Table 1) because of the decreased reactivity of AP-*g*-PEO with longer side chains. A possible copolymerization mechanism via chemical oxidation under acidic conditions is suggested in Scheme 2. The copolymers resulted from AP-*g*-PEOs
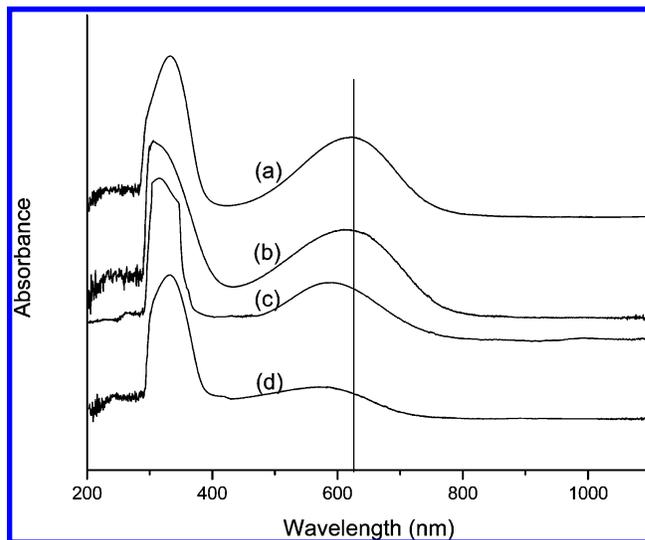
Figure 8. UV–vis spectra of (a) neutralized poly((AP-*g*-PEO-150)-*co*-aniline) (3/1), (b) neutralized poly((AP-*g*-PEO-350)-*co*-aniline) (3/1), (c) neutralized poly((AP-*g*-PEO-750)-*co*-aniline) (3/1), and (d) neutralized poly((AP-*g*-PEO-2000)-*co*-aniline) (3/1) (all in DMF).

with different side chains and the same feed mole ratio exhibited a blue shift in the UV–vis spectra, i.e., the peak at 625 nm of poly((AP-*g*-PEO-150)-*co*-aniline) (3/1) becoming 595 nm for poly((AP-*g*-PEO-2000)-*co*-aniline) (3/1) (see Figure 8).

Solubility. The solubility of the copolymers was dramatically improved by the grafting with oligo(oxyethylene) (Table 2). The copolymers prepared from AP-*g*-PEO-750 and aniline in the range of feed mole ratios 1/1 to 10/1 can dissolve in most commercial organic polar solvents. The poly((AP-*g*-PEO-750)-*co*-aniline) (3/1) exhibited a high water solubility and a relatively high conductivity (0.12 S/cm).

Surface Elemental Analysis of the Copolymers. The copolymers were also examined using X-ray photoelectron spectroscopy (XPS). In Table 3, the surface and bulk elemental stoichiometries of the copolymers prepared from various feed mole ratios are listed. The carbon and oxygen contents obtained by XPS were higher than those provided by the chemical elemental analysis, mostly because of the contamination of the surface (the adsorbed carbon dioxide), which occurs in any XPS analysis.[34] Figure 9 presents the wide-scale XPS spectra of the HCl-doped and neutralized polymers. They exhibited binding energies around 284, 398, and 533 eV, which can be assigned to C 1s, N 1s, and O 1s, respectively. The peaks due to S 2p and Cl 2p at 167 and 199 eV, respectively, could be hardly identified in the neutralized polymers, indicating that the chloride ions and the tosyol groups have been completely removed. Of course, the chloride peak appeared after HCl doping.

It should be noted that the C, N, and O cores are present in several energetic states which involve different components upon doping or dedoping (see Table 4). The oxidation and doping levels of the copolymers can be determined by analyzing the N 1s core levels.[35] In the XPS data analysis, the Shirley background was subtracted before the curve fitting.[36] The AugerScan Demo software was employed for curve fitting. The experimental spectra were fit into components of Gaussian–Lorentzian line shape. The component compositions were determined from the ratios among the area

Table 2. Solubility of the Various Copolymers in Neutralized State[a]

neutralized polymers	NMP	THF	chloroform	DMF	water
polyaniline	S	I	I	S	I
poly(*o*-anisidine)	S	PS	PS	S	I
poly (AP-*g*-PEO-150)	S	PS	PS	S	SS
poly (AP-*g*-PEO-350)	S	S	S	S	PS
poly (AP-*g*-PEO-750)	S	S	S	S	S
poly (AP-*g*-PEO-2000)	S	S	S	S	S
poly((AP-*g*-PEO-750)-*co*-aniline) (10/1)	S	S	S	S	S
poly((AP-*g*-PEO-750)-*co*-aniline) (6/1)	S	S	S	S	S
poly((AP-*g*-PEO-750)-*co*-aniline) (3/1)	S	S	S	S	S
poly((AP-*g*-PEO-750)-*co*-aniline) (1/1)	S	S	PS	S	PS
poly((AP-*g*-PEO-750)-*co*-aniline) (1/2)	S	PS	SS	S	SS
poly((AP-*g*-PEO-150)-*co*-aniline) (3/1)	S	PS	PS	S	SS
poly((AP-*g*-PEO-350)-*co*-aniline) (3/1)	S	S	S	S	PS
poly((AP-*g*-PEO-2000)-*co*-aniline) (3/1)	S	S	S	S	S

[a] Keywords: S = soluble up to 1.0g/L, stable for 1 month; I = insoluble; SS = slightly soluble, precipitation after 1 day, with a colored supernatant; PS = partially soluble, no precipitation within 1 week, but precipitation by centrifugation at 7000 rpm for 10 min.

Table 3. Surface and Bulk Elemental Stoichiometries of the Neutralized Copolymers of AP-*g*-PEOs and Aniline

copolymers	atomic ratio in the bulk[a]	atomic ratio on the surface[b]
poly(*o*-anisidine)	$C_{7.38}H_{9.03}O_{1.05}N_{1.00}Cl_{0.01}S_{0.00}$	$C_{13.13}O_{2.42}N_{1.00}Cl_{0.00}S_{0.00}$
poly(AP-*g*-PEO-750)-*co*-aniline) (6/1)	$C_{31.70}H_{59.87}O_{13.20}N_{1.00}Cl_{0.00}S_{0.00}$	$C_{38.70}O_{19.02}N_{1.00}Cl_{0.01}S_{0.03}$
poly((AP-*g*-PEO-750)-*co*-aniline) (3/1)	$C_{27.20}H_{49.87}O_{10.91}N_{1.00}Cl_{0.00}S_{0.00}$	$C_{34.57}O_{16.10}N_{1.00}Cl_{0.00}S_{0.00}$
poly((AP-*g*-PEO-750)-*co*-aniline) (1/1)	$C_{19.86}H_{31.29}O_{7.10}N_{1.00}Cl_{0.00}S_{0.01}$	$C_{25.20}O_{10.61}N_{1.00}Cl_{0.01}S_{0.03}$
poly((AP-*g*-PEO-750)-*co*-aniline) (1/2)	$C_{16.29}H_{24.54}O_{5.20}N_{1.00}Cl_{0.01}S_{0.00}$	$C_{20.70}O_{7.90}N_{1.00}Cl_{0.01}S_{0.01}$

[a] Determined by chemical elemental analysis. [b] Each polymer was dried for at least 7 days under vacuum and ground into a powder, followed by compression as a disk. The disk surface concentrations were determined by XPS.
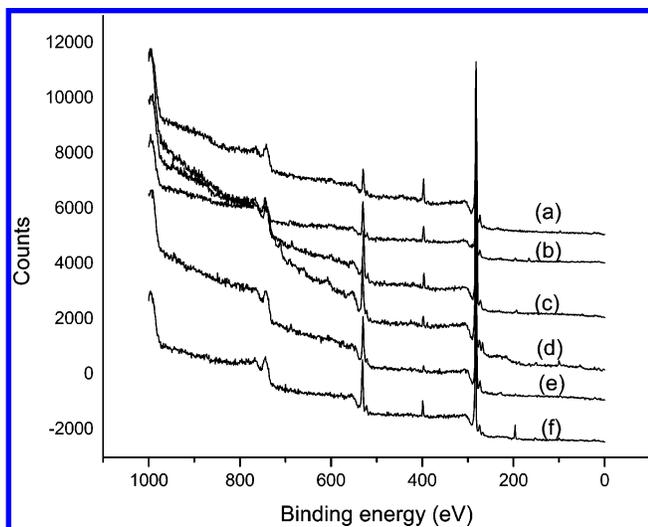
Figure 9. XPS spectra of copolymers: (a) neutralized poly-(*o*-anisidine), (b) neutralized poly((AP-*g*-PEO-750)-*co*-aniline) (3/1), (c) neutralized poly((AP-*g*-PEO-750)-*co*-aniline) (1/1), (d) neutralized poly((AP-*g*-PEO-350)-*co*-aniline (1/2), (e) neutralized poly(AP-*g*-PEO-750), and (f) HCl-doped poly((AP-*g*-PEO-750)-*co*-aniline) (3/1).

Table 4. Element Analysis of a Typical HCl-Doped Copolymer Poly((AP-*g*-PEO-750)-*co*-aniline) (3/1) by XPS

element (orbital)	possible components	binding energy (eV)	FWHM (eV)[a]	component conc, %
N 1s	=N−	398.20	1.09	2.3
	−NH−	399.41	1.86	53.3
	−N+−	400.83	2.68	36.7
	−N+H−	402.31	2.95	7.7
Cl 2p	Cl−	199.00	1.5	100

[a] FWHM denotes the full width at half-maximum of the fitted peak.

(*o*-anisidine). This indicates that in the copolymer the chain conformation produced a lower conjugation because of the higher steric barrier of the PEO side chains. Thus, the doping level was depressed, and the electron delocalization was weakened along the backbone. In this case, a lower conductivity was expected, which is consistent with the UV–vis results presented above. In a series of parallel XPS experiments, a decrease of the doping level was observed with increasing graft side chain length and feed mole ratio AP-*g*-PEO/aniline.

Conclusions

A simple synthetic strategy to prepare various soluble and processable copolymers of aniline and a macro-monomer, aminophenol, grafted with various oligo-(oxyethylene) side chains at the 3-position (AP-*g*-PEOs), was developed. The copolymerization and copolymer compositions were changed using various feed mole ratios AP-*g*-PEO/aniline and oligo(oxyethylene) side chain lengths. By increasing the aniline content of the feed mole ratio or decreasing the side chain length of PEO, the copolymerization produced longer chain copolymers with higher conjugation and conductivity. The copolymer of poly((AP-*g*-PEO-750-*co*-aniline) with a feed mole ratio of 3/1 was water-soluble and exhibited a relatively high conductivity (0.12 S/cm).

integrals of the fitted peaks. Figure 10 presents the core XPS spectra of N 1s of HCl-doped poly((AP-*g*-PEO-750)-*co*-aniline) (3/1) and HCl-doped poly(*o*-anisidine). The N 1s core has four fitted components for the core levels of 398.20, 399.41, 400.83, and 402.31 eV of Figure 10a, listed in Table 4. They can be assigned to the undoped imine and amine, doped imine, and positively charged amine, with the component concentrations 2.3, 53.3, 36.7, and 7.7%, respectively.[23,35,37] The doping level attained was 44.4%, which is much lower than the 62.4% of the HCl-doped poly(*o*-anisidine). (Its four N 1s core components have the compositions of 2.8, 34.8, 53.6, and 8.8% in Figure 10b.) The total oxidation level of 39.0% of the HCl-doped poly((AP-*g*-PEO-750)-*co*-aniline) (3/1) is much lower than the 56.4% of HCl-doped poly-

(a) N 1s

(b) N 1s

Figure 10. XPS N 1s core level spectra of (a) HCl-doped poly-((AP-*g*-PEO-750)-*co*-aniline) (3/1) and (b) HCl-doped poly(*o*-anisidine).

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