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Water-Soluble Conducting Poly(ethylene oxide)-Grafted Polydiphenylamine Synthesis through a “Graft Onto” Process

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ABSTRACT: A synthesis method to prepare a fully grafted polydiphenylamine (PDPA) with poly(ethylene oxide) (PEO) through a “graft onto” process is reported. Three graft copolymers, PDPA-*g*-PEO-350, PDPA-*g*-PEO-750, and PDPA-*g*-PEO-2000, were obtained by substituting the tosyloyl end group of tosylate PEO with an amine-functionalized PDPA. The latter polymer was prepared via an acid-mediated chemical polymerization of diphenylamine. These graft copolymers became water-soluble when the grafted PEO molecular weight (M_n) was above 750. Furthermore, the copolymers can be oxidized, in aqueous acidic solutions in the presence of air, to produce PDPA in a conducting state, containing, depending on the degree of oxidation, the *N,N′*-diphenylbenzidine radical cation ($DPB^{\bullet+}$) or the *N,N′*-phenylbenzidine dication (DPB^{2+}). The conductivities of the HCl-doped graft copolymers were found to be in the range 10^{-1}−10^{-4} S/cm, dependent on the grafted PEO side-chain length. As expected, the PDPA-*g*-PEO copolymers with longer PEO side chains possessed lower conductivities. Furthermore, for the HCl-doped PDPA-*g*-PEO-2000, the crystallization of the PEO-2000 side chains appears to be responsible for the low conductivity. Its conductivity could be raised 10-fold upon heating at 55 °C, above the PEO-2000 melting point (50 °C).

Introduction

In the past decades, polyaniline has attracted increasing attention, owing to its high electronic conductivity and environmental stability.[1−4] This conductive polymer can be easily prepared by electrochemical or chemical oxidation of aniline in aqueous acidic media. However, its poor processability and solubility in organic compounds because of the stiffness of its backbone and the hydrogen-bonding interaction of the inter-amino moieties of adjacent chains have stimulated attempts for their improvement. Numerous investigations have been carried out regarding its processability and solubility by introducing various side chains into the rigid PANI backbone. The PANI combined with alkyl,[5] alkoxy,[6] benzyl,[7] and aryl[8] substituents on the aromatic ring or nitrogen has been successfully prepared. The grafted side chains increased the solubility of PANI by increasing the entropy of dissolution and decreasing the interactions between the main chains.[9] Sometimes, the densely grafted PANI with side chains looks like a comb or a brush.[10−12] The microstructure of the brushed PANI is expected to provide some unique physical properties and special molecular conformations.[11]

Poly(ethylene glycol) (PEG) has been frequently employed, owing to its unique physical and biochemical properties.[13,14] The incorporation of PEG into a PANI backbone can endow the modified PANI with a number of properties, including higher water solubility, more facile processability, and biocompatibility.[15,16] Recently, it was found a most useful application in secondary lithium polymer batteries.[17,18] PEO side chains were grafted on PANI, and this allowed lithium salts to dissolve in the polymer matrix.[18] In general, the modification by grafting could be carried out using three synthetic routes: “graft onto” (coupling attachment of the side chains to the main chain), “graft from” (direct grafting polymerization of the monomer to form side chains from active points on the backbone), and “graft through” (homopolymerization of macromonomers).[20−22] Moon suggested a typical grafting through route by the oxidative homopolymerization of an aniline substituted with PEO.[20] Yamaguchi successfully prepared PANI grafted with PEO through a “graft from” process, in which a ring-opening polymerization of an epoxide proceeded on active anionic nitrogens of the PANI backbone.[21] Wang et al.[22] grafted PEO chains to the active anionic nitrogens of PANI via direct attachment under very strict experimental conditions. A lower grafting degree, below 30%, was, however, reached through this “graft onto” process.

Polydiphenylamine (PDPA) was prepared mostly by electrochemical polymerization of diphenylamine, which because of the phenyl substituent on nitrogen, occurred via a 4,4′ C−C phenyl−phenyl coupling mechanism. This mechanism differs from the preferential head-to-tail polymerization of aniline.[8,23−27] Thus, the resulting structure is intermediate between that of PANI and that of poly(*p*-phenylene) and allows a more facile dissolution of its dedoped form in organic compounds, such as tetrahydrofuran or chloroform, etc. In contrast, the dedoped form of PANI can dissolve only in some special solvents, such as *N*-methyl-2-pyrrolidinone (NMP). Recently, Wen et al. synthesized PDPA by a chemical method in a 3 N methanesulfonic acid solution.[28]

In a previous paper we reported the synthesis of polysulfonic diphenylamine salt and of its water-soluble PEO block copolymer.[29] In the present paper, we suggest a simple synthesis strategy for polydiphenylamine-*graft*-PEO (PDPA-*g*-PEO), which is also expected to be water-soluble. First, diphenylamine was polymerized in a highly concentrated HCl aqueous solution (3 N) using ammonium persulfate as initiator. PDPA was neutralized with a 1 N ammonium aqueous solution, followed by reduction with hydrazine to produce a secondary amine-functionalized PDPA. Second, tosylate-ended PEO chains were grafted onto the nitrogens of the PDPA

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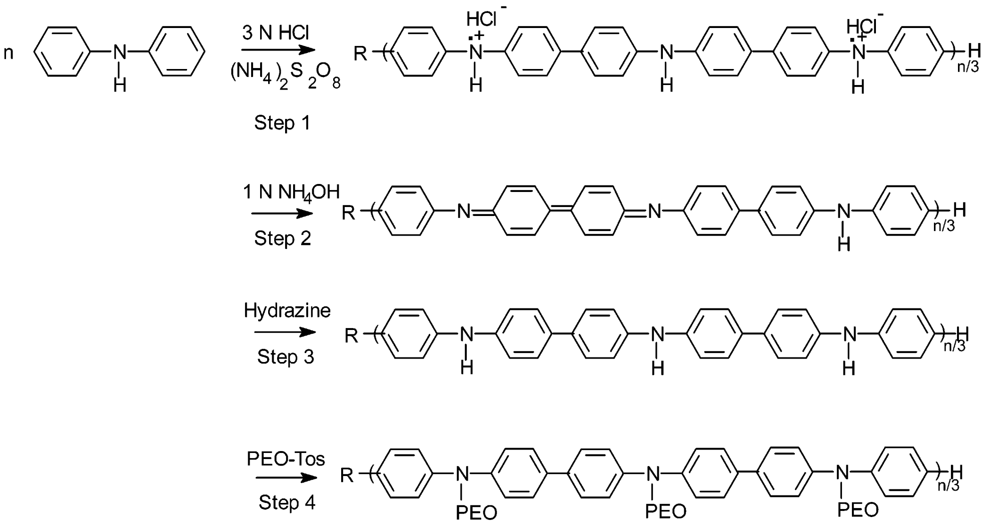
Scheme 1. Synthesis Strategy of Polydiphenylamine Grafted with Poly(ethylene oxide) (PDPA-*g*-PEO) through a "Graft Onto" Process



backbone through a "graft onto" process via a nucleophilic substitution mechanism. The chemical structures of various prepolymers and graft copolymers with various PEO chain lengths were characterized by FTIR, ^{1}H or ^{13}C NMR, UV−vis, and GPC, and their electronic conductivities were determined.

Experimental Section

Materials. Diphenylamine (99%), hydrochloric acid (37 wt %), ammonium persulfate (98 wt %), hydrazine (98 wt %), *p*-toluenesulfonyl chloride (99+ wt %), and potassium *tert*-butylate (>95 wt %) were purchased from Aldrich and used without further purification. 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, such as acetone, diethyl ether, and tetrahydrofuran (THF) from Aldrich and chloroform from Fisher, were of HPLC purity.

Preparation of Polydiphenylamine. Polydiphenylamine (PDPA) was prepared by the chemical oxidation method in a 3 N aqueous HCl solution using ammonium persulfate as initiator. The synthesis method is sketched in step 1 of Scheme 1. Diphenylamine (6.0 g, 0.0354 mol), 120 mL of 3 N HCl solution, and 150 mL of ethanol were introduced into a 500 mL round-bottom flask. The system was subjected to intensive magnetic stirring for a few minutes and then cooled to 5 °C in an ice−water bath. Ammonium persulfate (3.01 g, 0.0132 mol) was dissolved in 15 mL of 3 N HCl solution and added dropwise into the flask. The color of the reaction solution changed from transparent to green, indicating the start of polymerization. The system was subjected to intensive stirring for 16 h. A green precipitate, PDPA, was separated using a supercentrifuge (Dupont, RC-5) at 3500 rpm for 30 min. The PDPA particles were washed with ethanol/water mixtures (3/1, v/v) a few times (30 mL each time), until no green supernatant was identified, and finally dried under vacuum at room temperature for at least 24 h. The yield was 35%.

Neutralization and Reduction of PDPA. To prepare an amine-functionalized PDPA with secondary amine moieties on the PDPA backbone, the HCl-doped PDPA was neutralized after polymerization with a 1 N ammonium aqueous solution, followed by reduction with hydrazine as shown in steps 2 and 3 of Scheme 1. HCl-doped PDPA (1.8 g), 5 mL of ethanol, and 20 mL of 1 N NH_4OH solution were introduced into a 50 mL round-bottom flask and mixed with intensive stirring. The neutralization has taken place at room temperature for 18 h. The neutralized PDPA was separated by centrifugation at 3500 rpm for 30 min. The precipitate was washed a few times with ethanol/water mixtures (3/1) until no colored supernatant was observed. The dark purple PDPA particles were dried under vacuum at room temperature for at least 24 h.

The reduction was carried out in an inert nitrogen atmosphere at room temperature. The dried and neutralized PDPA (1.5 g), hydrazine (2.5 g), and 25 mL of ethanol were introduced into a 50 mL flask and mixed with intensive stirring. Nitrogen was bubbled through the mixture for half hour to remove the dissolved oxygen. The color of the reaction system changed from dark purple to light red. The reduction reaction was continued for 36 h. After reaction, 2.5 mL of water was added to the reaction system to precipitate the polymer. The reduced PDPA was separated by centrifugation at 3500 rpm for 30 min and washed with ethanol/water (5/1, v/v), followed by drying under vacuum at room temperature for at least 24 h. The polymer was protected under a nitrogen atmosphere before its further use. The yields for neutralization and reduction were 90 and 70%, respectively.

Graft Reaction of PEO and PDPA through a Graft Onto Process. Hydroxyl-ended PEO was first converted to tosylate-functionalized PEO as described in refs 29−31. The tosylates can be substituted by secondary amines on a reduced PDPA backbone via a nucleophilic substitution mechanism.[29] PEO chains fully grafted the PDPA backbone when the amount of PEO-Tos was 3 times that of the amine moieties of the reduced PDPA. All operations were carried out under a nitrogen atmosphere. The reduced PDPA (0.52 g, 0.003 07 mol of amine moieties), PEO-Tos-350 (3.23 g, 0.009 28 mol), potassium *tert*-butylate (0.9 g), and 20 mL of dry THF were introduced into a 100 mL round-bottom flask and mixed with intensive stirring for a few minutes. The system was kept at room temperature for 6 days. Then, 20 mL of dry THF was added to produce precipitation. The precipitate was removed by centrifugation (3500 rpm, 30 min). The remaining THF solution was concentrated using a rotary evaporater. The concentrated THF solution was added to a 3.5-fold volume of diethyl ether to precipitate red particles. The thus-obtained PDPA-*g*-PEO was further purified through dissolution−precipitation in THF/diethyl ether (1/3.5, v/v) and dried under vacuum at room temperature for at least 24 h. PDPA-*g*-PEO-350 was obtained from PEO-Tos-350, PDPA-*g*-PEO-750 from PEO-Tos-750, and PDPA-*g*-PEO-2000 from PEO-Tos-2000. The yields in all three cases were about 65%.

Oxidation of the Graft Copolymers. The graft copolymers in the reduced state were oxidized in air to produce oxidized states.[32,33] PDPA-*g*-PEO-350 (0.16 g), PDPA-*g*-PEO-750 (0.22 g), and PDPA-*g*-PEO-2000 (0.84 g) were ground into fine powders and each dispersed into 10 mL of 3 N HCl solutions in 50 mL centrifuge tubes. Compressed air was bubbled through the solutions in order to oxidize the graft copolymers. The bubbling at room temperature lasted for at

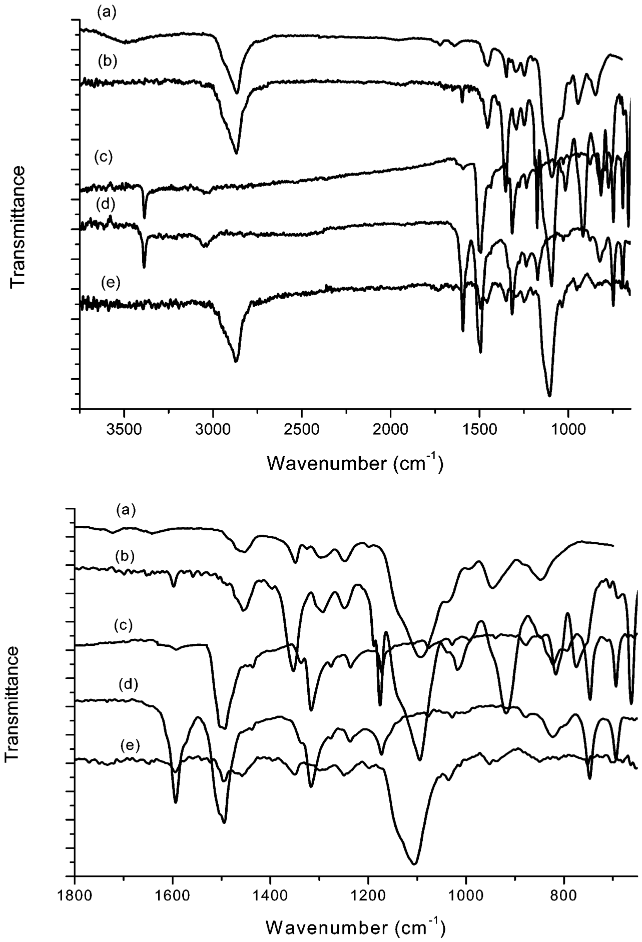


Figure 1. FTIR spectra of PEO-2000, PEO-Tos-2000, neutralized PDPA, reduced PDPA, and neutralized PDPA-*g*-PEO-2000: (a) PEO-2000, (b) PEO-Tos-2000, (c) reduced PDPA, (d) neutralizaed PDPA, and (e) neutralized PDPA-*g*-PEO-2000.

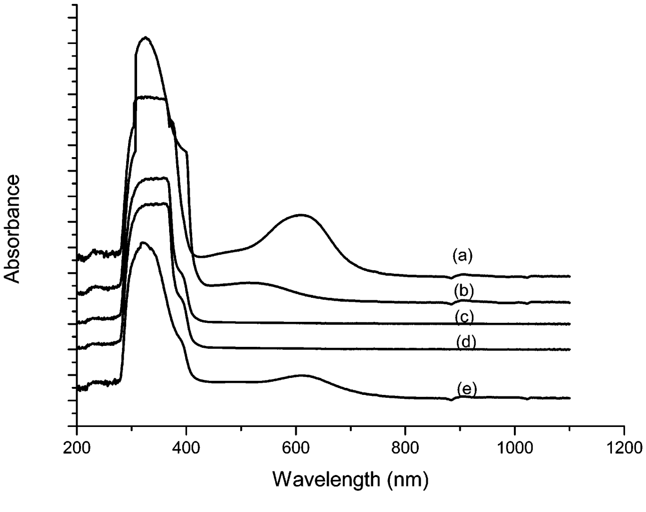


Figure 2. UV−vis spectra of HCl-doped PDPA, neutralized PDPA, reduced PDPA, PDPA-*g*-PEO-2000 and HCl-doped PDPA-*g*-PEO-2000 in THF: (a) HCl-doped PDPA, (b) neutralized PDPA, (c) reduced PDPA, (d) PDPA-*g*-PEO-2000, and (e) HCl-doped PDPA-*g*-PEO-2000.

least 72 h. The color changed from red to green. A small sample was taken out periodically and its UV−vis spectrum determined. When the UV−vis spectrum displayed no change, the water was removed using a rotary evaporater under vacuum. The HCl-doped green graft copolymers were further dried under vacuum at room temperature for at least 24 h.

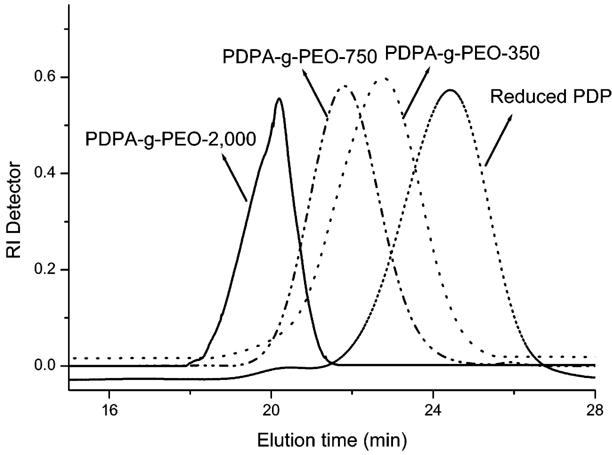


Figure 3. GPC traces of the reduced PDPA and various graft copolymers.

Characterization. Proton (^{1}H) and carbon (^{13}C) NMR, UV−vis absorption, and FTIR measurements were carried out on a 400 MHz INOVA-400, 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. Gel permeation chromatography (GPC, Waters) was used to obtain the molecular weights and the polydispersity indexes of the prepolymers and the graft copolymers on the basis of a polystyrene calibration curve. The GPC was equipped with three 30 cm long columns filled with Waters Styragel, a Waters HPLC 515 pump, and a Waters 410 RI detector. The GPC measurements were carried out using THF (containing 0.5 wt % triethylamine)[34] as eluent at 37 °C, with a flow rate of 1.0 mL/min and 1.0 cm/min chart speed. The 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 various prepolymers and graft copolymers were determined using the conventional four-point probe method. The temperature dependence of the conductivity was determined using compressed pellets in a homemade heating stage possessing a temperature controller. Every determination was recorded after the pellet film was heated and stabilized for at least 5 min at the selected temperature. Differential scanning calorimetery (DSC, Perkin-Elmer, DSC-7) was carried out using a heating rate of 15 K/min in the range from −100 to 200 °C. The XRD of the polymer particles was recorded on a SIEMENS, D500, X-ray diffractometer, operated at 30 MA and 40 KVP MAX.

Results and Discussion

Preparation of PDPA-*g*-PEO Copolymers. The synthesis strategy of graft copolymers is schematically presented in Scheme 1. The grafting process was carried out through a “graft onto” process, i.e., the tosylate-functionalized PEO reacted with the amine moieties on the PDPA backbone. The fully reduced PDPA was used in this process in order to avoid side reactions such as the cross-linking.[35] A high excess of PEO-Tos compared to that of the secondary amine moieties of PDPA ([tosylate]/[NH] = 3/1) ensured the generation of a fully grafted PDPA. The tosylate PEO was obtained via the esterification of HO-ended PEO with tosylol chloride, as described in ref 31.

Figure 1 presents the FTIR spectra of PEO-2000, PEO-2000-Tos, neutralized PDPA, reduced PDPA, and neutralized PDPA-*g*-PEO-2000. The neutralized PDPA possesses the following characteristic bands: 3420, 1595, 1494, and 754 cm^{-1}, which can be assigned to

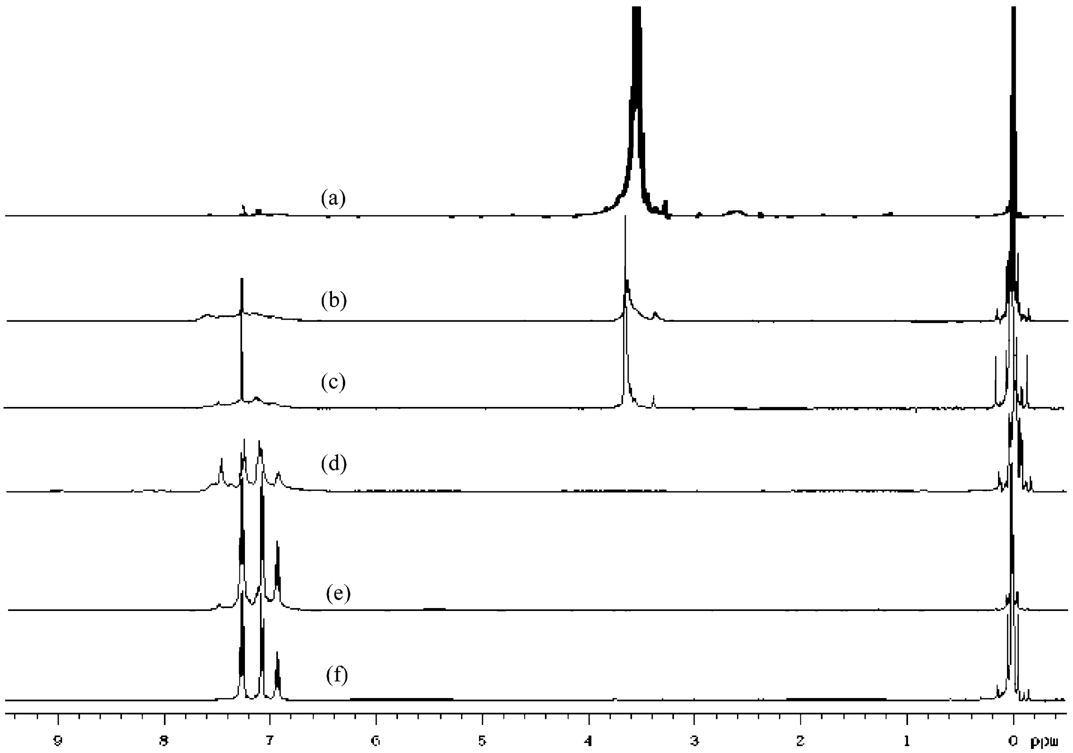


Figure 4. ^{1}H NMR spectra of DPA monomer, HCl-doped PDPA, neutralized PDPA, and graft copolymers with various PEO chain lengths in deuterated chloroform: (a) PDPA-*g*-PEO-2000, (b) PDPA-*g*-PEO-750, (c) PDPA-*g*-PEO-350, (d) reduced PDPA, (e) HCl-doped PDPA, and (f) DPA monomer.

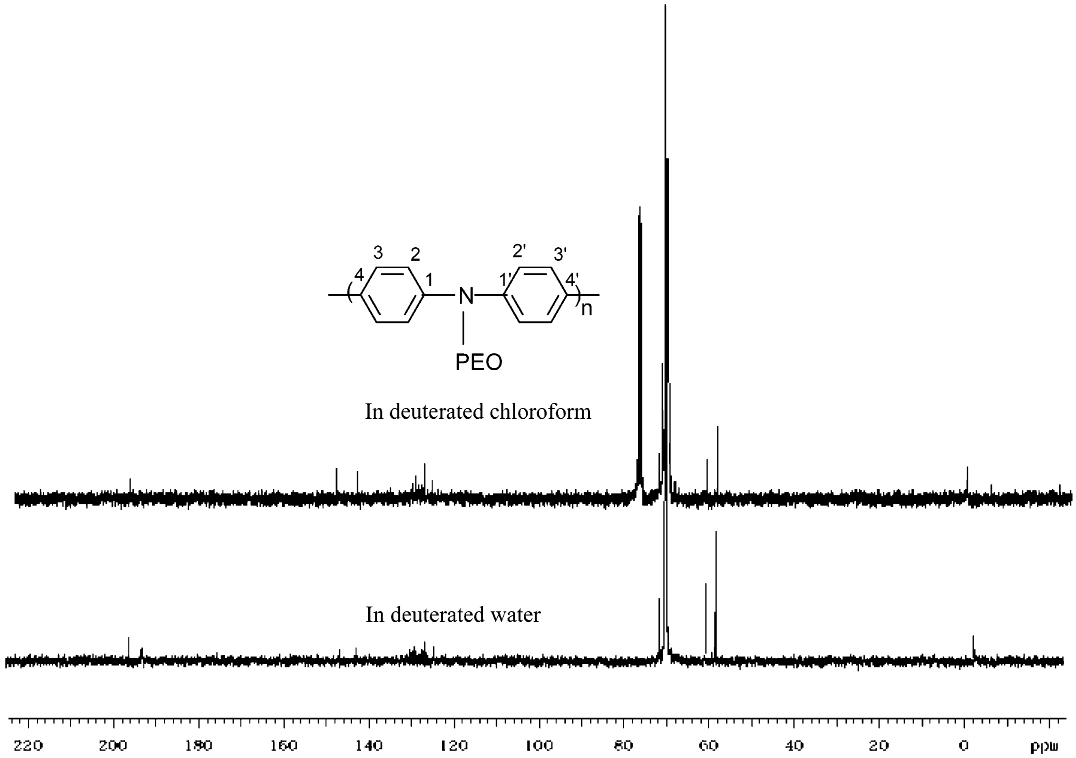


Figure 5. ^{13}C spectra of PDPA-*g*-PEO-2000 in deuterated water and in deuterated chloroform.

−NH stretching vibration, stetching vibrations of quinoid ring, phenyl hydrogen, and C−H plane vibration of the para-substituted aromatic ring, respectively. The reduced PDPA has a very weak absorption at 1595 cm^{-1}, indicating that most quinoid rings disappeared because of reduction and acquired the structure presented in step 3 of Scheme 1. The spectrum of the neutralized PDPA-*g*-PEO-2000 displays a combination of the bands of neutralized PDPA and PEO-2000. The characteristic bands at 1109, 1595, and 1494 cm^{-1} can be assigned to the C−O−C stretching vibration of oxyethylene of the PEO side chain and the quinoid ring and phenyl group of the PDPA backbone, respectively. Furthermore, the characteristic −NH stretching vibration of PDPA is no longer present, owing to its replacement by the C−N connection between PEO and the PDPA backbone. The

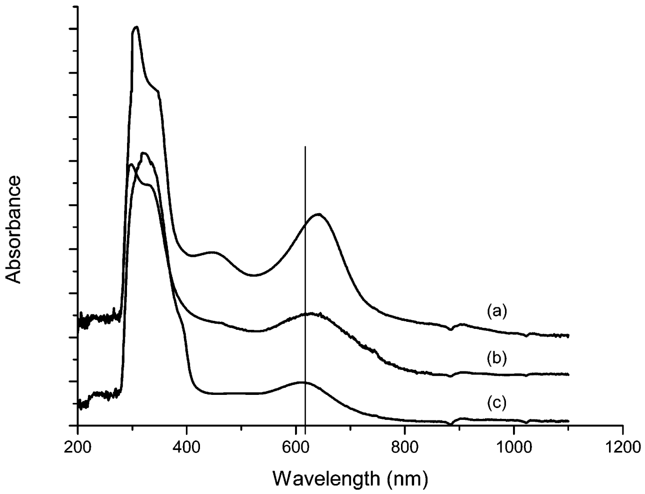


Figure 6. UV−vis spectra of the graft copolymers with various PEO chain lengths in THF: (a) HCl-doped PDPA-*g*-PEO-350, (b) HCl-doped PDPA-*g*-PEO-750, and (c) HCl-doped PDPA-*g*-PEO-2000.

absence of the peak in the graft copolymer due to −NH at 3420 cm^{-1} demonstrates that a full substitution with PEO on the PDPA backbone has taken place. In addition, the characteristic absorption at 1182 cm^{-1}, which can be assigned to the stretching vibrations of C−O in S−O−C of PEO-Tos-2000, disappeared because the tosylate has been removed through the substitution reaction (step 4 of Scheme 1).

Figure 2 presents the UV−vis spectra in THF of HCl-doped PDPA, neutralized PDPA, reduced PDPA, PDPA-*g*-PEO-2000, and HCl-doped PDPA-*g*-PEO-2000. For HCl-doped PDPA, the two absorption bands at 320 and 630 nm can be assigned to the $\pi-\pi^*$ transition of the benzenoid ring and polaron structure, respectively.[6−8] After neutralization, the band at 630 nm experienced a blue shift to 520 nm, which can be assigned to an exciton transition, consistent with the FTIR results. However, in the spectrum of reduced PDPA, the band at 630 nm fully disappeared whereas the band at 320 nm due to the benzenoid ring remained. Before oxidative doping, the PDPA-*g*-PEO-2000 exhibited a spectrum similar to that of the reduced PDPA, indicating that in reduced state the PDPA and the graft copolymer are nonconductive. After oxidation, the spectrum of HCl-doped PDPA-*g*-PEO-2000 exhibited a band at 610 nm due to the generation of *N,N′*-diphenylbenzidine radical cation (DPB$^{\bullet+}$), which constitutes the polaron form of the PDPA unit.[6] This issue will be discussed in detail later.

The GPC traces of the three grafted copolymers and reduced PDPA in Figure 3 demonstrated, as expected, that the molecular weight became larger with increasing PEO side chain length (M_ns of PDPA, PDPA-*g*-PEO-350, PDPA-*g*-PEO-750, and PDPA-*g*-PEO-2000 are 13 400, 35 600, 64 000, and 176 500, respectively). The polydispersity indexes (PDIs) of PDPA-*g*-PEO-350, PDPA-*g*-PEO-750, and PDPA-*g*-PEO-2000 were relatively large, 1.9, 2.3, and 2.6, respectively. The reduced PDPA had a PDI of 3.0, whereas the three grafted PEO side chains (PEO-350, PEO-750, and PEO-2000) had PDIs of 1.12, 1.10, and 1.10, respectively.

The chemical structures of these prepolymers and graft copolymers were also investigated by ^{1}H and ^{13}C NMR. In the proton NMR spectra of reduced PDPA and HCl-doped PDPA in deuterated chloroform, the wide multisignals in the range 6.8−7.8 ppm can be assigned to the aromatic hydrogens of the double-substituted phenyl rings of the PDPA backbone (see Figure 4). The spectra of the graft copolymers displayed a combination of those of PEO and PDPA. The wide multisignals in the range 6.8−7.8 and the signals at 3.60 and 3.37 ppm can be assigned to the aromatic hydrogens, oxyethylene hydrogens of ethylene oxide (EO) repeated units, and the end oxymethylene hydrogens of PEO side chains, respectively. The signal at 4.05 ppm, which can be assigned to the oxymethylene hydrogens connected with the tosylate, disappeared after substitution, being replaced by a new signal at 3.50 ppm, which can be assigned to the methylene hydrogens connected with the nitrogens of the PDPA backbone, indicating the connections between PEO side chains and PDPA backbone. Furthermore, the typical ^{13}C NMR spectra of PDPA-*g*-PEO-2000 in deuterated chloroform and deuterated water in Figure 5 display the characteristic resonance singals of the PEO side chains and PDPA backbone. The peaks at 69, 58, and 61 ppm can be assigned to the oxyethylene carbons of the EO units, the end oxymethylene carbon of the PEO chains, and the N−C connection between PEO and PDPA, respectively. The multisignals around 130 ppm are caused by the double-substituted phenyl rings of PDPA. The aromatic carbons (1 and 1′ in the inset of Figure 5) were shifted from 139 and 141 ppm to 142 and 148 ppm, respectively, by the oxyalkyl substitution at nitrogen,[5] further confirming

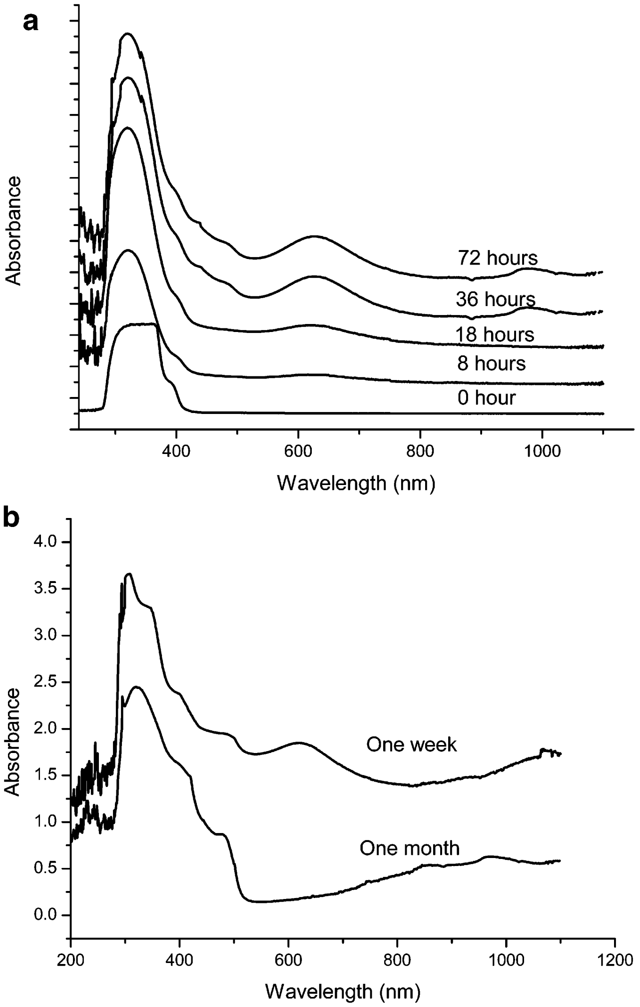
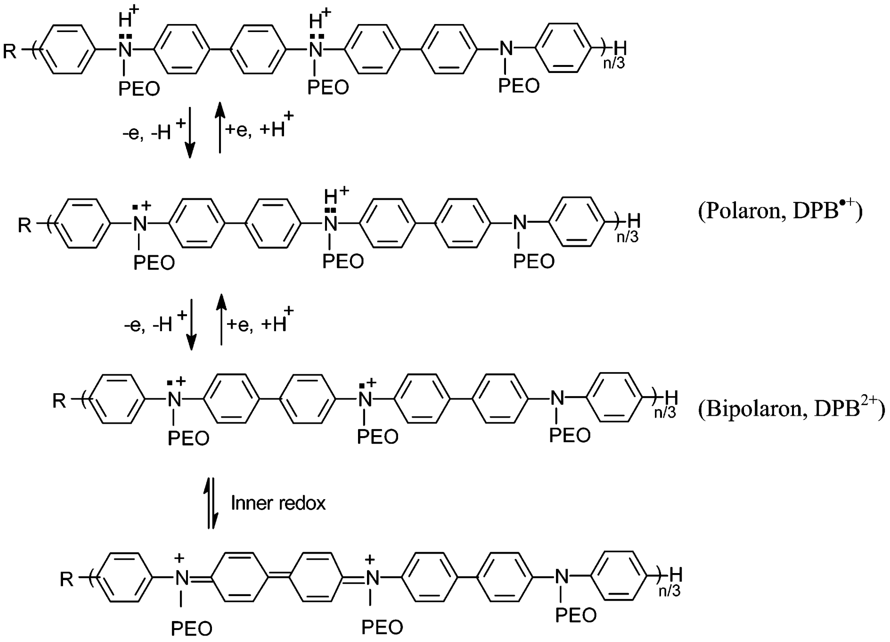


Figure 7. UV−vis spectra of the PDPA-*g*-PEO-2000 against the oxidation time in air in the presence of 3 N HCl solution (a) or 80% aqueous acetic acid solution (b).

Scheme 2. Reduction by Hydrazine and Oxidation in Air in the Presence of an Aqueous Acidic Solution



that the secondary amine groups of the PDPA have been almostly grafted with PEO side chains.

The elemental analysis showed that no sulfur was present in the grafted polymers after reduction. The Cl/N ratio of HCl-doped PDPA-*g*-PEO-350, PDPA-*g*-PEO-750, and PDPA-*g*-PEO-2000 were 0.47/1, 0.43/1, and 0.41/1, respectively, and as expected almost independent of the PEO chain length. Again as expected, the C/N ratio became larger in the sequence of doped-PDPA-*g*-PEO-350 (32.12) < doped-PDPA-*g*-PEO-750 (53.01) < doped-PDPA-*g*-PEO-2000 (118.05).

UV−vis Spectra. The three graft copolymers (PDPA-*g*-PEO-350, PDPA-*g*-PEO-750, and PDPA-*g*-PEO-2000) were oxidized in air for 3 days in the presence of 3 N HCl solutions. Their UV−vis spectra in the doped state in THF are presented in Figure 6. The two absorptions at about 320 and 620 nm can be assigned to the $\pi-\pi^*$ transition of the benzenoid rings and to the polaron form of the PDPA unit, as also observed for HCl-doped PDPA in a THF solution mentioned before. The latter absorption peak exhibited a blue shift, which increased with increasing side-chain length. This indicates that the planar conformation of the PDPA backbone became increasingly nonplanar with longer side chains because the longer PEO side chains caused greater torsional twists, thus decreasing the effective conjugation of the PDPA backbone.

As mentioned in the first section, the reduced graft copolymers are in a nonconductive state, and they should be oxidized to become conductive. They have been oxidized with air, as described in Experimental Section, and the oxidation process was followed by UV−vis. A series of UV−vis spectra of a PDPA-*g*-PEO-2000 graft copolymer are presented in Figure 7a. An absorption peak at about 610 nm was generated gradually through the bubbling of air for 8 h. This peak can be assigned to the polaron *N*,*N′*-diphenylbenzidine radical cation ($DPB^{\bullet+}$), induced in the benzenoid ring because of the removal by oxidation of one electron belonging to the nitrogen of a DPA unit. The peak intensity increased with increasing oxidation time because of increasing number of polarons. After 3 days, the UV−vis spectrum did no longer change. A similar behavior occurred when the oxidation process was carried out in the presence of 80 wt % aqueous acetic acid solution. However, if the latter system was subjected to oxidation for 1 week, the peak at about 610 nm was weakened and a new absorption peak above 700 nm appeared, which can be assigned to the bipolaron diphenylbenzidine dication (DPB^{2+} (see Figure 7b)). After 1 month of oxidation, only the peak above 700 nm remained, indicating that the polaron form of the PDPA unit was converted to the higher oxidative state of the bipolaron. However, the conductivities of the above two overoxidized systems were not improved as happened with PANI.[32,33,37] The mechanism for the oxidative doping described above is detailed in Scheme 2.

Solubility. The PDPA grafted with amphiphilic PEO side chains is expected to increase the water solubility of PDPA. The three grafted copolymers were introduced into water to reach concentrations of 1.0 g/L. The HCl-doped PDPA-*g*-PEO-2000 water solution remained stable under ambient conditions for several months. However, the HCl-doped PDPA-*g*-PEO-350 precipitated from solution after 1 day with a colored supernatant which exhibited absorptions in UV−vis as in Figure 6. The HCl-doped PDPA-*g*-PEO-750 could be precipitated under centrifugation at 7000 rpm for 10 min after 1 week. The solubility of the copolymers in the organic solvents, THF, chloroform, dichloromethane, ethanol, and NMP was also determined, and the results are listed in Table 1.

Conductivity. The HCl-doped polymers were ground into powders and compressed into films. The electronic conductivity of the film was determined by the four-probe method. The HCl-doped PDPA possessed the high conductivity of 0.37 S/cm, and could attain 0.45 S/cm upon heating at 55 °C, as a result of the thermal active effect.[35] The conductivity decreased with increasing PEO side-chain length. The reduction in conductivity can be explained by the volumetric “dilute effect”[36] of the fully grafted PEO chains which increases with increasing side-chain length (see Table 2). In addition, longer PEO side chains induced larger nonplanar conformations.

Table 1. Solubility of PDPAs and Graft Copolymers in Various Solvents[a]

	solvents					
polymer	NMP	THF	chloroform	ethanol	dichloromethane	water
HCl-doped PDPA	S	S	S	SS	PS	I
neutralized PDPA	S	S	S	PS	S	I
PDPA-*g*-PEO-350[b]	S	S	S	S	S	SS
PDPA-*g*-PEO-750[b]	S	S	S	S	S	PS
PDPA-*g*-PEO-2000[b]	S	S	S	S	S	S[c]

[a] Keywords: S = soluble up to 1.0 g/L, stable for 1 month; I = insoluble; SS = slightly soluble, precipitation after 1 day, with a colored supernatant; PS = partially soluble, not precipitation within 1 week, but precipitation by centrifugation at 7000 rpm for 10 min after 1 week. [b] The graft copolymers were oxidatively doped in air in the presence of a 3 N HCl solution for at least 72 h. [c] The dissolution process was carried out upon heating to 40 °C with intensive stirring for at least 2 min.

Table 2. Conductivities of HCl-Doped PDPA and PEO-Grafted PDPAs

polymers	HCl doping (S/cm)	heat treatment[c] (S/cm)	volume fraction of PDPA[d]
HCl-doped PDPA	0.37[a]	0.45	1.0
HCl-doped PDPA-*g*-PEO-350	0.042[b]	0.056	0.29
HCl-doped PDPA-*g*-PEO-750	0.007[b]	0.010	0.16
HCl-doped PDPA-*g*-PEO-2000	0.00056[b]	0.0051	0.065

[a] After HCl-mediated polymerization, PDPA was neutralized with a 1 N ammonium aqueous solution, followed by doping with a 3 N HCl solution. [b] The graft copolymers were oxidatively doped in air in the presence of 3 N HCl solutions for at least 72 h. [c] HCl-doped polymer samples were heated to 55 °C, where they were kept for 5 min, and then the conductivities were determined by the four-point method. [d] Based on the experimental density of PDPA film ($d_1 = 1.33$ g/cm^3) and the density of PEO specified in the Aldrich catalog ($d_2 = 1.10$ g/cm^3).

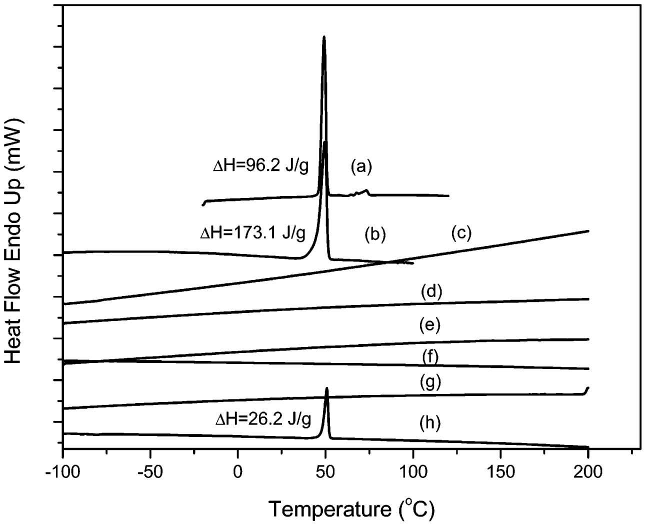


Figure 8. DSC profiles of PEO-2000, DPA monomer, HCl-doped PDPA, neutralized PDPA, reduced PDPA, neutralized PDPA-*g*-PEO-350, neutralized PDPA-*g*-PEO-750, and neutralized PDPA-*g*-PEO-2000: (a) DPA monomer, (b) PEO-2000, (c) HCl-doped PDPA, (d) neutralized PDPA, (e) reduced PDPA, (f) neutralized PDPA-*g*-PEO-350, (g) neutralized PDPA-*g*-PEO-750, and (h) neutralized PDPA-*g*-PEO-2000.

Particularly, HCl-doped PDPA-*g*-PEO-2000 had a very low conductivity, around 5.6×10^{-4} S/cm. However, upon heating above 55 °C, it increased up to 5.1×10^{-3} S/cm, a 10-fold increase. This increase might have been caused by the melting of the crystalline POE-2000 side chains.

Figure 8 presents the DSC profiles of diphenylamine monomer, PEO-2000, PDPA in various states, and the three graft copolymers. DPA and PEO-2000 have a similar melting point, around 50 °C. The neutralized PDPA and the reduced PDPA did not have melting transitions in the scanning range −100 to 200 °C, indicating that PDPA has an amorphous structure. Only the neutralized PDPA-*g*-PEO-2000 possessed a melting point, around 50 °C, which can be assigned to the crystalline structure of the ordered PEO-2000 side chain. The PEO crystallization in PDPA-*g*-PEO-2000 was confirmed by the XRD results presented in Figure 9. The XRD profile of the neutralized PDPA-*g*-PEO-2000 exhibited two characteristic peaks for 2θ of 19 and 23, near to those of PEO-2000. Therefore, the nonconductive PEO crystals provided resistance to the transport of charges among the PDPA domains. Upon heating above the PEO crystal melting point, the molten PEO segments could better contact among themselves, thus enhancing the contacts among the PDPA backbones.

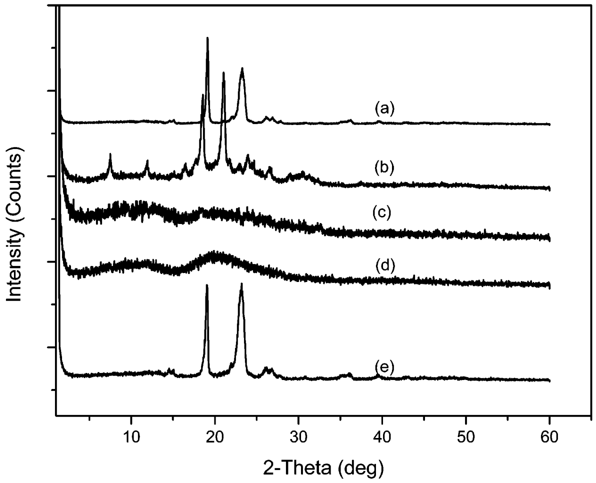


Figure 9. XRD profiles of PEO-2000, diphenylamine, reduced PDPA, neutralized PDPA-*g*-PEO-750, and neutralized PDPA-*g*-PEO-2000: (a) PEO-2000, (b) DPA monomer, (c) reduced PDPA, (d) PDPA-*g*-PEO-750, and (e) PDPA-*g*-PEO-2000.

Conclusions

A simple synthesis strategy to prepare polydiphenylamine grafted with poly(ethylene oxide) through a graft onto process was suggested. Three graft copolymers with various PEO chain lengths were obtained by substituting the tosylates of PEO-Tos on functionalized amines of the PDPA backbone. Their water solubilities were improved dramatically with the incorporation of PEO side chains. Furthermore, these copolymers can be oxidized in the presence of air and aqueous acidic solutions to generate a polaron (diphenylbenzidine radical cation) or a bipolaron (diphenylbenzidine dication). The conductivity decreased in the range 10^{-1}–10^{-4} S/cm with increasing PEO side chain length because of the volumetric "dilute effect" of the nonconductive PEO side chains as well as the increasing torsional effect. Especially for the doped PDPA-*g*-PEO-2000, the crystallization of PEO chains generates resistance to the charge transport. The increase of the conductivity of doped PDPA-*g*-PEO-2000 with temperature appears to be caused by the melting of the crystals of the ordered PEO-2000 side chains.

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(31) 32.75 g of PEO-350 (0.0936 mol), 25 mL of THF, and 5.59 g (0.1398 mol) of NaOH dissolved in 30 mL of water were introduced in a 250 mL round-bottom flask, after which the flask was located in a salt−ice bath around −5 °C. The first 5.5 g of TosCl dissolved in 30 mL of THF was added dropwise within 1 h, and another 12.75 g of TosCl dissolved in 25 mL of THF was added within another 1 h. The reaction was continued for 4 h at −5 °C, after which the temperature was raised to the room temperature and kept at that temperature for other 18 h. After reaction, 100 mL of diethyl ether was added for extraction three times. The diethyl ether solution was dried by passing through anhydrous Na_2SO_4 (30 g) columns, after which the diethyl ether was removed using a rotary evaporater. The PEO-Tos-350 prepared from PEO-350 was a transparent liquid, the PEO-750-Tos from PEO-750 was a paste, and PEO-Tos-2000 from PEO-2000 was a waxlike solid. The yield was in all three cases 90 wt %. The FTIR of PEO-Tos was 1594, 1182, and 784 cm^{-1}, which can be assigned to the stretching vibrations of the phenyl hydrogens, and of C−O and S−O in S−O−C. The ^1H NMR of PEO-Tos was 4.05 ppm (2H), due to the oxymethylene connected to tosylate, and 7.70 ppm (2H) and 7.22 (2H) ppm, which can be assigned to the double-substituted phenyl hydrogens of the tosylate moiety. The values of the main molecular ionic peaks in the MS spectra reflect the following formula: $M_n = 23\ (Na^+) + 15\ (-CH_3) + 155\ (CH_3-C_6H_4-SO_2-) + 44n\ (-OCH_2CH_2-)$, where n is the number of ethylene oxides in the PEO.
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