Synthesis and Characterization of Poly(ethylene glycol)-Grafted Polyaniline

Peng Wang and K. L. Tan

Department of Physics, National University of Singapore, Kent Ridge, Singapore 119260

Fu Zhang, E. T. Kang,* and K. G. Neoh

Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 119260

Poly(ethylene glycol) (PEG)-grafted polyaniline (PANi) copolymers were prepared by incorporating a chlorine end-capped methoxy PEG (mPEGCl) of molecular weight of about 2000 onto the leucoemeraldine form of PANi via N-alkylation. The microstructures and compositions of the mPEG-grafted PANi (mPEG-*g*-PANi) copolymers were characterized by FT-IR, elemental analysis, UV−visible absorption spectroscopy, thermogravimetric (TG) analysis and X-ray photoelectron spectroscopy (XPS). The graft concentration (degree of N-alkylation) can be controlled by adjusting the molar feed ratio of mPEGCl to the number of repeat units of PANi. The mPEG-*g*-PANi copolymers showed enhanced solubility in common organic solvents and water. The electrical conductivity of the mPEG-*g*-PANi copolymer film decreased by a factor of 5 at the mPEG graft concentration of 0.05. The mPEG-*g*-PANi copolymer with a high graft concentration was very effective in preventing platelet adhesion.

Introduction

Recent investigations[1] into the century-old[2,3] aniline family of polymers have rekindled intense research interest in these materials. The aniline polymers generally have controllable electrical conductivity, environmental stability, and interesting redox properties associated with the chain nitrogens.[4] They have been extensively studied for their unique characteristics and potential applications in electrical devices, such as polymer electrodes and sensors. The aniline polymers have the general formula $[(-B-NH-B-NH-)_y(-B-N=Q=N-)_{1-y}]_x$, in which B and Q denote the C_6H_4 rings in the benzenoid and quinonoid forms, respectively. Thus, the aniline polymers are basically poly(*p*-phenyleneamine)s, in which the intrinsic oxidation states can vary from that of the fully reduced leucoemeraldine (LM, $y = 1$), through that of the 50% intrinsically oxidized emeraldine (EM, $y = 0.5$), to that of the fully oxidized pernigraniline (PNA, $y = 0$). The polymer can achieve its highly conductive state either through the protonation of the imine nitrogens ($=N-$) in its EM oxidation state, or through the oxidation of the amine nitrogens ($-NH-$) in its fully reduced LM state.[5]

The emeraldine form of PANi is obtained as a dark powder which exhibits only limited processability. This characteristic is believed to have resulted from the stiffness of the polymer backbone and the hydrogen-bonding interaction between adjacent chains. The limited solubility has impeded not only its industrial applications but also a complete understanding of the polymer structure.[6] Great effort has been devoted to the modification of the aniline polymers with various functional groups to enhance their processability. For example, self-doped PANi with sulfonic acid groups substituted onto the aniline ring has been synthesized by treating EM base with fuming sulfuric acid.[7,8] Copolymerization of aniline with *o*-alkoxyaniline has been carried out to produce soluble, conductive polymers.[9] Flexible alkyl chains have been incorporated into PANi through N-alkylation of the LM base form. It was found that the solubility of the polymer in common organic solvents improved remarkable with alkylation.[10] On the other hand, Mikhael et al.[11] reacted EM base and its anions with various alkylating and acylating agents.

Poly(ethylene glycol) (PEG) is gaining wide recognition as it possesses many unique physical and biochemical properties, such as nontoxicity, biocompatibility, and miscibility with many solvents.[12] Therefore, PEG and its derivatives are finding an ever-expanding range of

* Fax: (65) 779−1936. E-mail: cheket@nus.edu.sg.

(1) MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F; Epstein A. J. *Synth. Met.* **1987**, *18*, 285.

(2) Green, A. G.; Woodhea, A. E. *J. Chem. Soc.* **1910**, 1117.

(3) Green, A. G.; Woodhea, A. E. *J. Chem. Soc.* **1910**, 2388.

(4) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog. Polym. Sci.* **1998**, *23*, 277.

(5) Ray, A.; Asturias, G. E.; Kershner, D. L.; Richter, A. F.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1989**, *29*, E141.

(6) Li, S.; Cao, Y.; Xue, Z. *Synth. Met.* **1987**, *20*, 141.

(7) Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. *J. Am. Chem. Soc.* **1991**, *113*, 2665.

(8) Kang, E. T.; Neoh, K. G.; Woo, Y. L.; Tan K. L. *Polym. Commun.* **1990**, *32*, 412.

(9) Liao, Y. H.; Angelopoulos, M.; Levon, K. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 2725.

(10) Zheng, W. Y.; Levon, K.; Laakso, J.; Österholm, J. E. *Macromolecules* **1994**, *27*, 7754.

(11) Mikhael, M.; Padius, A. B.; Hall, H. K. *J. Polym. Sci. Part A: Polym. Chem.* **1994**, *27*, 7754.

biomedical and industrial applications.[13] In addition, PEG has also found useful applications in secondary lithium polymeric batteries.[14] Thus, incorporating PEG into PANi may endow the century-old aniline polymer with new and interesting properties. For instances, the process may enhance the solution, including aqueous solution, and the processability of PANi, as well as improve the biocompatibility of PANi for applications as biosensors or as biomedical materials for implants. In the present work, we report on the synthesis and characterization of PEG-grafted polyaniline.

Experimental Section

1. Materials. Anhydrous-grade dimethyl sulfoxide (DMSO) was obtained from Merck Chemical Co. Aniline, thionyl chloride ($SOCl_2$), sodium hydride (NaH), methoxy poly-(ethylene glycol) (mPEG) with a molecular weight of about 2000, and all other reagent-grade chemicals were purchased from Aldrich Chemical Co. and were used as received.

2. Preparation of the Graft Copolymer. *Chlorine End-Capped mPEG (mPEGCl).* mPEG (10 g, 0.005 mol) was dissolved in 40 mL of CCl_4, containing also 0.005 mol of dry pyridine. Thionyl chloride (0.015 mol), dissolved in 10 mL of CCl_4, was added dropwise over a period of 1 h under reflux. The mixture was stirred at 60 °C overnight. The pyridine salt was removed by filtration. The CCl_4 and excess $SOCl_2$ were removed by pumping under reduced pressure. The adduct was dissolved in CH_2Cl_2, dried over anhydrous K_2CO_3, and filtered. The filtrate was precipitated into 10-fold excess of cold diethyl ether. The chlorinated mPEG (or mPEGCl) precipitated out as a white powder and was dried under reduced pressure for 24 h.[15,16] The chlorination of mPEG was studied by both the FT-IR absorption spectroscopy and the elemental analysis. The chlorine end-capped mPEG (mPEGCl) can be identified from the changes in the IR absorption characteristics. The OH absorption band for mPEG in the 3300–3500 cm^{-1} region has disappeared, with the corresponding appearance of the C–Cl absorption band at 671 cm^{-1}. On the other hand, elemental analysis reveals the presence of 1.6 wt % of Cl in the compound. The result suggests that about 90% of the mPEG molecules have been converted to mPEGCl.

Synthesis of the mPEG-Grafted Polyaniline (mPEG-g-PANi) Copolymers. Polyaniline was synthesized by oxidative polymerization of aniline according to the method reported in the literature.[4,5] Thus, 0.05 mol of aniline was dissolved in 800 mL of 1 M HCl. The solution was kept at 0 °C under an argon atmosphere. A prechilled solution of 0.05 mol of ammonium persulfate in 200 mL of 1 M HCl was added slowly with vigorous stirring. The reaction mixture was agitated continuously for another 5 h. The precipitate was subsequently filtered and collected. It was converted to the EM base by treatment with excess 0.5 M aqueous NH_4OH and dried by pumping under reduced pressure. The fully reduced LM was prepared by treating the EM base powders with hydrazine in ethanol for 24 h under an argon atmosphere. The light gray LM powders were washed thoroughly with ethanol and THF, in that order, to remove the excess reducing agent and the low-molecular-weight LM species. The LM powders were then dried under reduced pressure at room temperature.

A 40 mL aliquot of DMSO and 0.115 g (0.0048 mol) of NaH were introduced into a 100 mL round-bottom flask. The reaction flask was kept under an inert atmosphere throughout the subsequent reactions by a constant flow of argon. The mixture was stirred at 60 °C until the NaH was completely

dissolved. A solution of methylsufinyl carbanion in DMSO was formed as described in the literature.[10,17] About 0.4 g (0.0044mol) of LM powder was added to the sodium methylsufinyl carbanion solution at 60 °C. A dark-yellow anion solution formed after 4 h of reaction time. The solution was cooled to 40 °C, and a predetermined amount of mPEGCl was added with vigorous stirring. The amount of mPEGCl added dictated the resulting copolymer composition. The color of the solution turned blue gradually, suggesting the oxidation of the LM backbone to the EM state.[4] The reaction was allowed to continue for 24 h.

Separation and Purification of the Copolymer Adduct. Different separation and purification methods were adopted according to whether the product was soluble in water or not. The water solubility, in turn, was determined by the concentration of the grafted mPEG chains. For the product that was insoluble in water, the reaction mixture was poured into a 10-times excess volume of doubly distilled water, under vigorous stirring, to precipitate the copolymer. The precipitate was recovered by filtration and washed exhaustively with doubly distilled water to remove the residual amount of unreacted species. The product so obtained was dried under reduced pressure at ambient temperature. For the product that was soluble in water, the reaction mixture was first precipitated into a large excess of diethyl ether. The precipitate was dialyzed against doubly distilled water for 48 h. The water was allowed to evaporate under reduced pressure at ambient temperature. The product was then collected and subjected to further drying under reduced pressure. The copolymer samples were characterized by elemental analysis, FT-IR spectroscopy, UV–visible absorption spectroscopy, thermogravimetric (TG) analysis, and X-ray photoelectron spectroscopy (XPS).

Preparation of Copolymer Thin Films. The copolymer samples were dissolved in NMP to form the 1 wt % solutions. The solutions were cast onto glass plates and heated in a constant temperature oven at 110 °C for 2 h to form lightly cross-linked films, similar to the method used for the preparation of PANi films.[18] The films so obtained were dried under reduced pressure at room temperature for 24 h to remove the NMP.

Platelet Adhesion. Heparinized blood from a healthy dog (supplied by the Animal Holding Unit, National University of Singapore) was used in this study. The blood was centrifuged at 200 G for 15 min to obtain the platelet-rich plasma (PRP). The PRP was diluted with PBS to give a concentration of about 1×10^5 platelets/μL. About 0.1 mL of the diluted platelet suspension was placed onto the polymer film surface of about 0.8 cm × 0.8 cm in area. The film was incubated at 37 °C for 30 min under a static condition. After incubation, the film surface was rinsed with PBS gently, but thoroughly, to remove the loosely adhered platelets on the film surface. After the thorough rinsing with PBS, the films were allowed to dry at room temperature.[19]

3. Physical Measurement. FT-IR spectra of the polymer and copolymer powders were obtained from a Bio-Rad FTS 135 FT-IR spectrophotometer. Each spectrum was collected by cumulating 16 scans at a resolution of 4 cm^{-1}. The UV–visible absorption spectra of the polymer and copolymer solutions or thin films coated onto quartz substrates were monitored on an UV–vis–NIR scanning spectrophotometer (Shimadzu UV-3101 PC). The bulk C and N atomic ratios were determined by elemental analyses on a Perkin-Elmer 2400 elemental analyzer. The Cl content was determined, on the other hand, by the Schöniger combustion method[20] at the Microanalysis Centre of the National University of Singapore. For the TG analysis, the polymer and copolymer samples were heated to 700 °C at a heating rate of 20 °C/min under a dry nitrogen atmosphere in the Du Pont thermal analyst 2100 system, equipped with a TGA 2050 thermogravimetric thermal ana-

(12) Lee, J. H.; Lee, H. B.; Andrade, J. D. *Prog. Polym. Sci.* **1995**, *20*, 1043.

(13) Harris, J. M. *J. Macromol. Sci. RMCP* **1983**, *C25* (3), 325.

(14) Novak, P.; Müller, K.; Santhanam, K. S. V.; Haas, O. *Chem. Rev.* **1997**, *97*, 207.

(15) Zalipsky, S.; Gilon, C.; Zilkha, A. *Eur. Polym. J.* **1983**, *19*, 1177.

(16) Ha, C. S.; Choi, H. Y.; Cho, W. J. *Polym. Bull.* **1991**, *25*, 185.

(17) Takayanagi, M.; Katagose, T. *J. Polym. Chem. Ed.* **1981**, *19*, 1133.

(18) MacDiarmid, A. G.; Min, Y.; Wiesinger, J. M.; Oh, E. J.; Scherr, E. M.; Epstein, A. J. *Synth. Met.* **1993**, *55*, 753.

(19) Kulik, E.; Ikada, Y. *J. Biomed. Mater. Res.* **1996**, *30*, 295.

(20) Walton, H. F. *Principles and Methods of Chemical Analysis*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1964; pp 175–178.
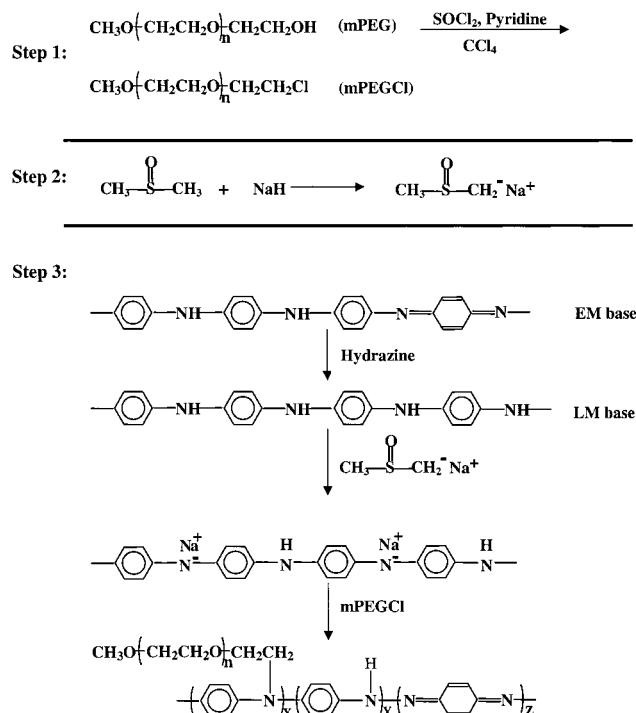
Figure 1. Schematic diagram illustrating the synthesis of the mPEG-*g*-PANi graft copolymer.

lyzer. The electrical conductivity of the cross-linked polymer films was measured by the four-probe method. XPS measurements were made on a VG ESCALAB MkII spectrometer with a Mg Kα X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The polymer films were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level signals were obtained at the photoelectron takeoff angle (α, with respect to the sample surface) of 75°. The X-ray source was run at a reduced power of 120 W. The pressure in the analysis chamber was maintained at 7.5×10^{-9} Torr or lower during each measurement. All binding energies (BEs) were referenced to the C1s neutral carbon peak at 284.6 eV. In peak synthesis, the line width (full width at half-maximum, or fwhm) for the Gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak–area ratios and were reliable to ±10%. The static water contact angles of cross-linked polymer thin films were measured at 25 °C and 60% relative humidity using a sessile drop method in a telescopic goniometer (Rame-Hart model 100-00(230)). The telescope with a magnification power of 23× was equipped with a protractor of 1° graduation. For each angle reported, at least five sample readings from different surface locations were averaged. The angles reported were reliable to ±3°. The adhered platelets on the polymer film surface were studied by scanning electron microscopy (SEM), using a JEOL 6320 electron microscope. The films were mounted on the sample studs by means of double-sided adhesive tapes and were shadowed with gold prior to SEM measurements. The SEM measurements were performed at an accelerating voltage of 10 kV.

Results and Discussion

Synthesis of the mPEG-*g*-PANi Copolymers. The processes for the synthesis of the mPEG-*g*-PANi copolymer are shown schematically in Figure 1. The compositions of the mPEG-*g*-PANi samples, prepared under different feed ratios of mPEGCl to aniline in LM, are summarized in Table 1. The graft concentration and volume and weight fractions of the grafted mPEG in the copolymer are calculated from elemental analysis. Thus,

the graft concentration is defined as the number of mPEG units (of MW ~2000) per aniline unit of PANi. It can be seen that the graft concentration increases with the increase in feed molar ratio of the mPEGCl to aniline units.

The fully reduced LM was used in this study in order to avoid the side reactions, such as the cross-linking reaction.[11] The LM dissolves well in DMSO in the presence of NaH. The blue product formed during the grafting reaction indicates the presence of autoxidation[4] of the aniline polymer backbone. The changes in intrinsic oxidation states ($[=N-]/[-NH-]$ ratios) of PANi are revealed by FT-IR spectroscopy and XPS. Figure 2 shows the FT-IR spectra of the LM base, the EM base and the mPEG-*g*-PANi base (graft concentration = 0.046) powders. The absorption peaks at 1595 and 1503 cm^{-1} are attributable to the quinoid unit and benzenoid unit of PANi, respectively.[21] The predominance of the absorption band at 1503 cm^{-1} for the LM base is consistent with the fully reduced nature of the LM state of PANi. On the other hand, the approximately equal intensities for the 1595 and 1503 cm^{-1} bands for the EM base are consistent with a 50% intrinsically oxidized PANi structure. For the spectrum of the mPEG-*g*-PANi sample, two new absorption bands have appeared. They correspond to that at 952 cm^{-1} for the methylene rocking mode and that at 1105 cm^{-1} for the C−O−C stretching mode. These are the typical absorption bands of PEG.[15] In addition, the intensity of the absorption band at 1595 cm^{-1} from the original LM base has become comparable to that of the absorption band at 1503 cm^{-1}, suggesting an increase in the intrinsic oxidation state of LM compared to that of EM during the grafting and purification processes. The phenomenon is commonly observed in reactions involving LM, especially in the presence of oxygen.[4] The auto-oxidation effect can be minimized by carrying out the purification of the copolymers under an inert atmosphere. Nevertheless, the oxidation of the copolymer backbone to the EM state is inconsequential as the subsequent characterization, processing, and application of the copolymers are carried out under atmospheric conditions.

Figure 3a–e shows the UV−visible absorption spectra of the LM and EM bases and three mPEG-*g*-PANi samples (graft concentration = 0.023, 0.046, and 0.257, respectively) in NMP. For the LM base, only one absorption peak at 340 nm, which originates from the $\pi-\pi^*$ transition of the benzenoid rings,[22] is observable. For the EM base and the mPEG-*g*-PANi samples, each spectrum consists of two absorption maxima, one at around 330 nm and another at around 630 nm, which are attributable to the $\pi-\pi^*$ transition of the benzenoid rings and the absorption of the quinoid rings, respectively.[23] Further studies revealed that the benzenoid absorption peak for the mPEG-*g*-PANi samples exhibits a blue shift and the shift increases with the graft concentration. The phenomenon indicates that the non-planar conformation of the PANi backbone, which leads to a decrease in effective conjugate length, is increased

(21) Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth. Met.* **1988**, *24*, 231.

(22) Barbero, C.; Miras, M. C.; Haas, O.; Kötz, R. O. *J. Electroanal. Chem.* **1993**, *55*, 3591.

(23) Pouget, J. P.; Józefowicz, M. E.; Epstein, A. J.; Tang, X.; MacDiarmid, A. G. *Macromolecules* **1991**, *24*, 779.

Table 1. Compositions of the mPEG-*g*-PANi Copolymers

polymers	feed mol ratio[a]	C/N mol ratio[b]	graft concn[c]	vol frac. of mPEG (%)[b,d]	wt frac. of mPEG (%)[b]	wt frac. of mPEG (%)[e]	surf. graft concn[f,g]	vol frac. of mPEG (%)[d,f]
polyaniline		5.96		0	0	0	0	0
mPEG-*g*-PANi#1	1:20	7.09	0.012	28.4	20.9	23	0.01	23
mPEG-*g*-PANi#2	1:10	8.12	0.023	43.4	33.8	33	0.02	37
mPEG-*g*-PANi#3	1:8	9.26	0.035	54.2	44.1	43	0.03	51
mPEG-*g*-PANi#4	1:6	10.3	0.046	61.1	50.3	54	0.04	58
mPEG-*g*-PANi#5	1:1.5	37.1	0.257	91.8	88.3	85	[h]	[h]

[a] Ratio of mPEGCl per aniline unit. [b] Determined by elemental analysis. [c] Defined as the number of mPEG units (MW ~2000) per aniline unit of PANi. It is determined from the C/N molar ratio of each copolymer, taking into account that the C/N molar ratio for PANi is 6 and there are about 90 carbons per mPEG chain. Thus, the graft concentration is calculated from the expression $([C/N] - 6)/(84 + [C/N])$. [d] Based on the experimentally determined density for the lightly cross-linked PANi film = 1.5 g/cm^3 and the density of mPEG = 1.0 g/cm^3 specified in the Aldrich catalog. [e] From TG analysis. [f] From XPS analysis. [g] Determined from the XPS-derived CO component and N1s spectral areas using the expression $([CO]/90)/[N]$. [h] mPEG-*g*-PANi#5 cannot be cast into a free-standing film, due to the high content of grafted mPEG.
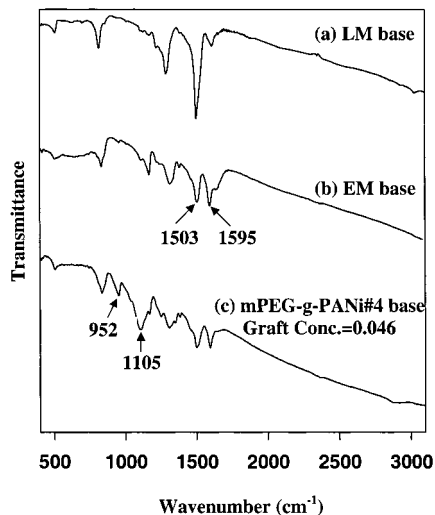

Figure 2. FT-IR spectra of (a) the pristine LM base powder, (b) the pristine EM base powder, and (c) the mPEG-*g*-PANi#4 powder (graft concn = 0.046).

upon the incorporation of the flexible mPEG side chains.[24] The UV−visible absorption spectrum of an aqueous solution of the mPEG-*g*-PANi sample with a graft concentration of 0.257 is also shown in Figure 3f. It can be seen that both of the absorption maxima at 314 and 601 nm exhibit even more remarkable blue shifts in an aqueous solution when compared to those observed in the NMP solution. This phenomenon may be due to the hydrogen-bonding effect of NMP[25] which promotes a thermodynamically more stable PANi chain conformation and restricts the polymer to lower energy, higher-planarity states. Alternatively, the decrease in the effective conjugation length of the PANi backbone becomes more drastic in the presence of strong polar group interactions between the mPEG side chain and the aqueous medium.[7]

Thermal Analysis. The mPEG-*g*-PANi copolymers are also subjected to TG analysis. Figure 4 shows the respective TG analysis curves of the pristine EM base, the mPEG-*g*-PANi copolymers of graft concentrations of 0.012, 0.023, 0.035, 0.046, and 0.257, and the pristine mPEG. The mPEG-*g*-PANi samples (curves 2−6) show intermediate weight loss behavior in comparison to that of the mPEG (curves 7) and that of the EM base (curves 1). A distinct two-step degradation process is discernible
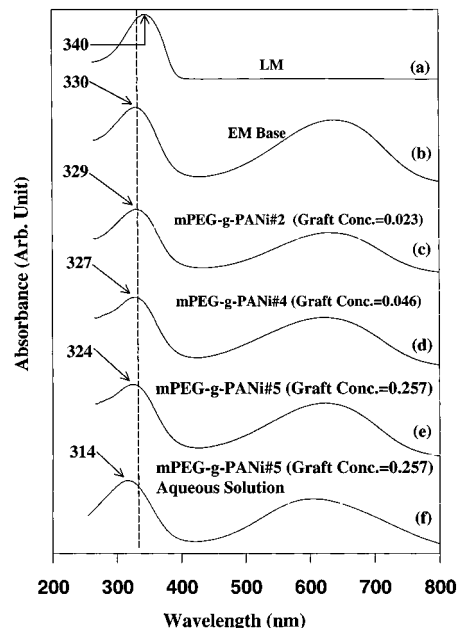

Figure 3. UV−visible absorption spectra of NMP solutions of (a) the pristine LM base, (b) the pristine EM base, (c) the mPEG-*g*-PANi#2 (graft concn = 0.023), (d) the mPEG-*g*-PANi#4 (graft concn = 0.046), (e) the mPEG-*g*-PANi#5 (graft concn = 0.257), and an aqueous solution of (f) the mPEG-*g*-PANi#5 (graft concn = 0.257).

for the copolymer samples. The onset of the first major weight loss at about 280 °C corresponds to the decomposition of the grafted mPEG side chains. The second major weight loss begins at about 500 °C, corresponding to the decomposition of the PANi backbone in the EM state.[26] For each copolymer, the weight fraction of the mPEG side chains derived from the first major weight loss step in the TG analysis curve is also shown in Table 1. In each case, the percent weight loss coincides approximately with the weight fraction of mPEG in the copolymer determined from the elemental analysis results. The decomposition of the PANi backbone is affected by the grafted mPEG chains only at high extents of grafting. For sample with a high graft concentration of 0.257, the onset temperature for the second major weight loss is reduced to about 420 °C. Obviously, the tertiary aromatic amines substituted by alkyl groups are thermally less stable than the secondary amines.[10]

(24) Moon, H. S.; Park, J. K. *Macromolecules* **1998**, *31*, 6461.
(25) Chen, S. A.; Lee, H. T. *Macromolecules* **1993**, *26*, 3254.

(26) Kang, E. T.; Neoh, K. G.; Tan, T. C.; Khor, S. H.; Tan, K. L. *Macromolecules* **1990**, *23*, 2918.
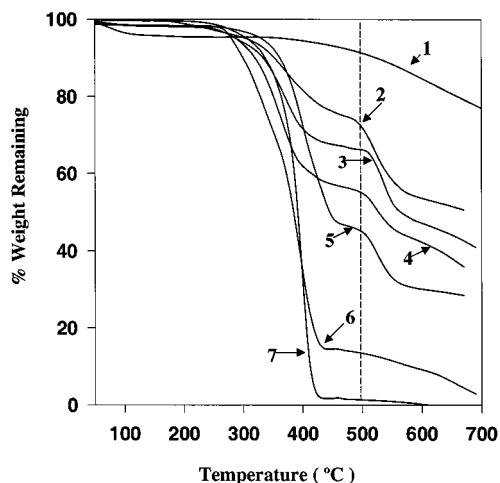
Figure 4. TG analysis curves of (1) the pristine EM base, (2) the mPEG-*g*-PANi#1 (graft concn = 0.012), (3) the mPEG-*g*-PANi#2 (graft concn = 0.023), (4) the mPEG-*g*-PANi#3 (graft concn = 0.035), (5) the mPEG-*g*-PANi#4 (graft concn = 0.046), (6) the mPEG-*g*-PANi#5 (graft concn = 0.257), and (7) the mPEG sample.

Table 2. Solubility of Polyaniline and mPEG-*g*-PANi Samples

	solvents[a]					
polymers[b]	NMP	DMSO	THF	CHCl₃	CH₂Cl₂	water
EM base	S	SS	SS	SS	I	I
mPEG	S	S	S	S	S	S
mPEGCl	S	S	S	S	S	S
mPEG-*g*-PANi#1	S	SS	SS	SS	I	I
mPEG-*g*-PANi#2	S	SS	SS	SS	I	I
mPEG-*g*-PANi#3	S	P	P	P	P	I
mPEG-*g*-PANi#4	S	S	S	S	S	I
mPEG-*g*-PANi#5	S	S	S	S	S	S

[a] Key: S, soluble (up to a concn of at least 1 g/100 mL); SS, slightly soluble; P, partially soluble; and I, insoluble. [b] The graft concentrations for the mPEG-*g*-PANi copolymers correspond to those of Table 1.

Solubility of the mPEG-*g*-PANi Samples. The mPEG-*g*-PANi samples with graft concentration greater than 0.035 are readily soluble in common organic solvents, such as NMP, CHCl₃, THF, and DMSO. Poly-(ethylene glycol) is well-known for its excellent solubility in both polar and nonpolar solvent.[12] The mPEG-*g*-PANi solutions with a concentration up to 1.0 g/100 mL are stable under ambient condition for months without precipitation. For the mPEG-*g*-PANi sample with a graft concentration of 0.257 and above, it is also soluble in water with a solubility up to 1.0 g/100 mL. The solubility results are summarized in Table 2.

Electrical Conductivity of the Doped mPEG-*g*-PANi Film. Figure 5 shows the dependence of the electrical conductivity of the 1 M HClO₄-protonated mPEG-*g*-PANi copolymer film as a function of the volume fraction of mPEG in the graft copolymer. The bulk conductivity of the HClO₄-protonated copolymer exhibits an approximately linear decrease with the increase in volume fraction of mPEG in the copolymer. The reduction in conductivity can be explained by the volumetric "diluting effect" of the grafted mPEG chains. The intermolecular steric effect introduced by the bulky mPEG side chains will have a diluting effect on the PANi chains and will thus contribute to the reduction in conductivity of the mPEG-*g*-PANi sample. The N-
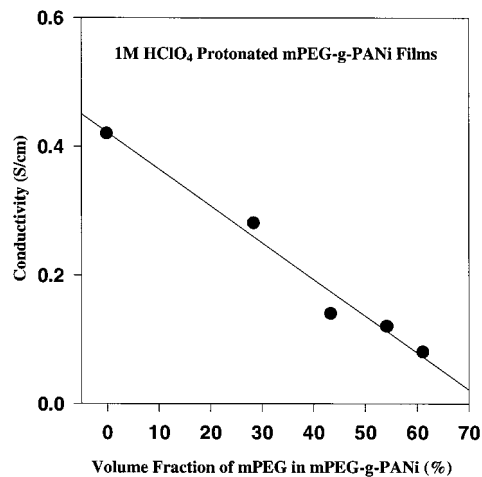

Figure 5. Effect of the mPEG graft concentration on the conductivity of the 1 M HClO₄-protonated mPEG-*g*-PANi films. (The point at 0 graft concn corresponds to that of the protonated EM homopolymer.)
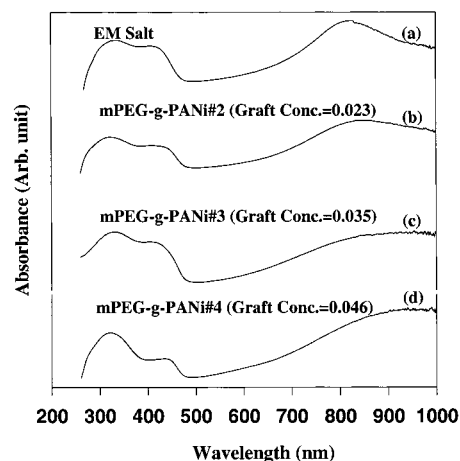

Figure 6. UV−visible absorption spectra of HClO₄-protonated coatings of (a) the pristine EM base, (b) the mPEG-*g*-PANi#2 (graft concn = 0.023), (c) the mPEG-*g*-PANi#3 (graft concn = 0.035), and (d) the mPEG-*g*-PANi#4 (graft concn = 0.046) on quartz substrates.

substituted mPEG chains can also alter the conformation of the PANi chain. The bulky side chains can induce nonplanar conformations, which in turn can cause a decrease in the effective conjugation length of the PANi backbone. In this way, the bulky side chain destabilizes the polysemiquinone radical cation and gives rise to higher redox potentials. Similar phenomenon has been reported in the literature for the substituted PANi derivatives.[27] Nevertheless, the nearly linear dependence of bulk conductivity on the volume fraction of mPEG in the copolymer suggests that the conformational effect is of less importance.

Figure 6 shows the UV−visible absorption spectra of the HClO₄-protonated polyaniline and the mPEG-*g*-PANi coatings on quartz plates. Solutions (1 wt % NMP) of the respective copolymers were used for film casting on quartz plates. As in the case of all the other free-standing films cast from the copolymer solutions (see Experimental Section), the cast films on quartz plates were also heated in a constant temperature oven at 110 °C for 2 h to form a lightly cross-linked coating on each
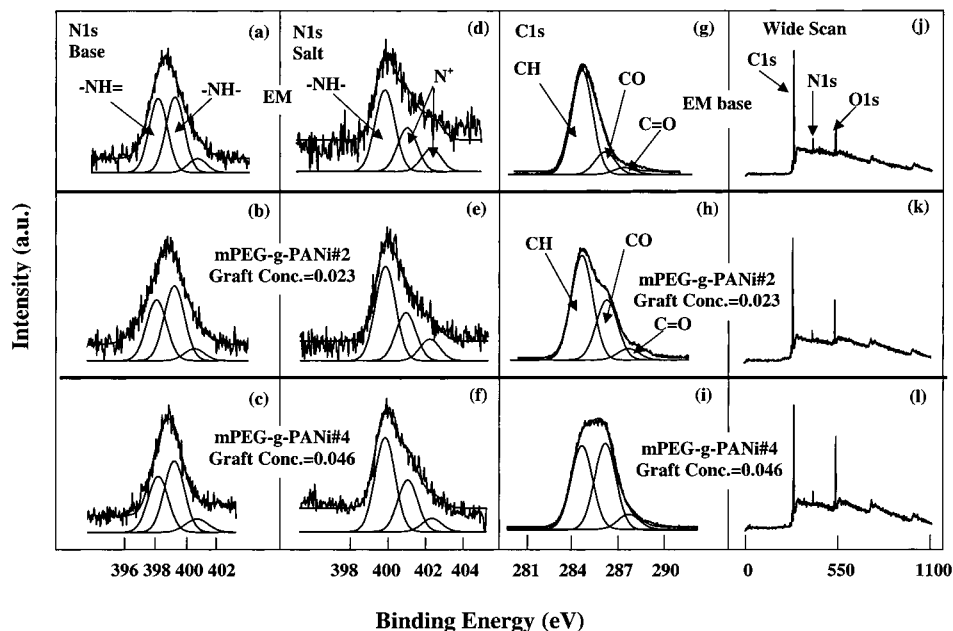
(27) Leclerc, M.; Daprano, G.; Zotti, G. *Synth. Met.* **1993**, *55*, 231.

Figure 7. XPS N1s core-level spectra of neutral and HClO4-protonated films of (a, d) the EM, (b, e) the mPEG-*g*-PANi#2 (graft concn = 0.023), and (c, f) the mPEG-*g*-PANi#4 (graft concn = 0.046). The corresponding C1s core-level and wide-scan spectra of (g, j) the EM base, (h, k) the mPEG-*g*-PANi#2 base, and (i, l) the mPEG-*g*-PANi#4 base are also shown.

quartz substrate. The UV−visible absorption spectrum of the doped polyaniline shows a characteristic polaron peak at 430 nm and a localized polaron absorption peak at 800 nm, together with a less well defined $\pi-\pi^*$ transition band at around 320 nm.[28] For the mPEG-*g*-PANi sample with a low graft concentration (~0.023) of mPEG, the characteristic of UV−visible absorption spectrum is similar to that of PANi. However, for the mPEG-*g*-PANi samples with higher graft concentrations, the localized polaron absorption band shifted to longer wavelengths of about 900−1000 nm. The result indicates that the grafted mPEG chains interfere with the doping process and the polaron delocalization.

Surface Characterization of the mPEG-*g*-PANi Films. The respective N1s core-level spectra of EM and two mPEG-*g*-PANi copolymers films before and after protonation by 1 M HClO4 are shown in Figure 7a−f. These spectra are deconvoluted into the following peak components:[4,29] imine (−N=) peak component with the binding energy (BE) at 398.2 eV, amine (−NH−) peak component with the BE at 399.4 eV, and two positively charged nitrogen (N[+]) peak components with the BEs above 400 eV, based on the fixed line width approach in peak synthesis adapted in the present work. It can be seen that for the mPEG-*g*-PANi base samples, the presence of approximately equal proportions of the imine and amine peak components is not unlike that of the EM base of PANi. This result gives further support to the conclusion that the original LM backbone has been oxidized to the EM state during the graft co-polymerization process. Protonation of the mPEG-*g*-PANi base samples results in the disappearance of the imine component and the appearance of a corresponding proportion of the positively charged nitrogen. This phenomenon is consistent with the fact that protonation of the EM base occurs preferably at the imine units.[4,5]

Thus, the protonation−deprotonation behavior of the PANi chains in the mPEG-*g*-PANi copolymer is not unlike that of the homopolymer of the EM base.

Figure 7g−l shows the corresponding C1s core-level and wide-scan spectra of the three films before protonation. In the case of the pristine EM base film, the C1s core-level spectra can be curve fitted with three peak components, with the BE at 284.6 eV for the C*H* species from benzene rings, at 286.2 eV for the C*O* species, and at 287.7 eV for the C=O species.[30] The appearance of trace amounts of the C*O* and C=O species may be attributed to surface oxidation of the film.[4] In the case of the mPEG-*g*-PANi samples, the C1s core-level spectra can be curve-fitted with three components which are similar to those found in the pristine EM base, except that the intensity of the C*O* species is substantially enhanced in each case. The enhancement of the C*O* peak component is consistent with the presence of the grafted mPEG side chain. The increase in surface oxygen content, as revealed by the corresponding wide-scan spectra, is also consistent with the increase in the C*O* peak intensity and the mPEG graft concentration. The surface graft concentration, defined as the number of mPEG units per aniline unit of PANi and derived from the C*O* component and N1s spectral area ratio, is also shown in Table 1. Thus, a good agreement between the bulk and surface graft concentration is observed. This result also suggests that the grafted mPEG units are distributed uniformly on all the PANi chains.

Figure 8 shows the dependence of the cosine of water contact angle of the mPEG-*g*-PANi film on the surface and bulk volume fractions of mPEG in the copolymer. The surface volume fraction was determined from the XPS-derived surface graft concentration (see Table 1). To a good approximation, the cosine of the contact angle varies linearly with both the surface and the bulk

(28) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1989**, *32*, 263.

(29) Tan, K. L.; Tan, B. T. G.; Kang, E. T.; Neoh, K. G. *Phys. Rev. B* **1989**, *39*, 8070.

(30) Briggs, D. In *Surface Analysis of Polymers by XPS and Static SIMS*; Cambridge University Press: Cambridge, U.K., 1998; p 65.
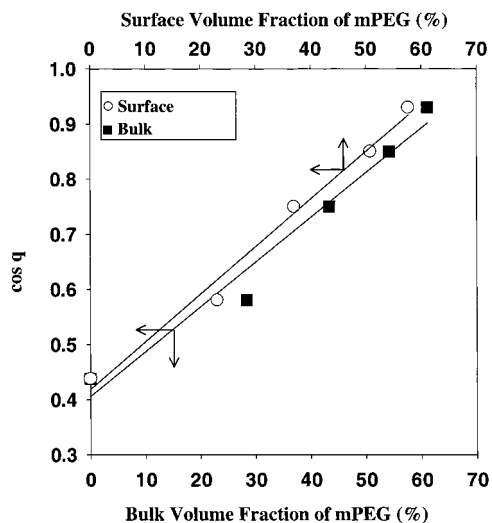
Figure 8. Dependence of the cosine of water contact angle (*q*) of the mPEG-*g*-PANi film on the surface and bulk volume fractions of mPEG in the copolymer.
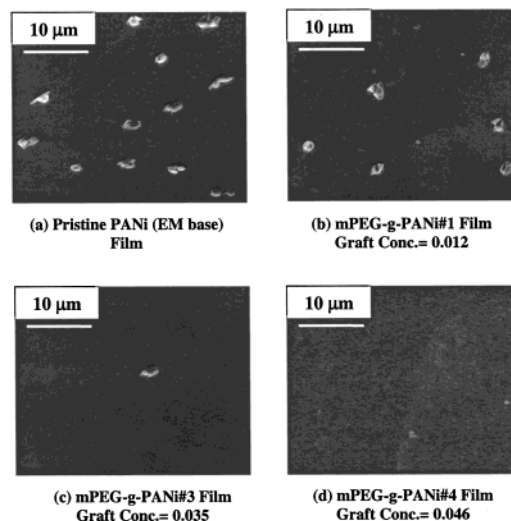

Figure 9. SEM images of the platelets adhered on (a) the pristine PANi (EM base) film surface, (b) the mPEG-*g*-PANi#1 film surface (graft concn = 0.012), (c) the mPEG-*g*-PANi#3 film surface (graft concn = 0.035), and (d) the mPEG-*g*-PANi#4 film surface (graft concn = 0.046).

volume fractions of the hydrophilic mPEG chains. By the Cassie relationship,[31] the wetting data have, thus, provided a surface measurement that mirrors the bulk. The contact angle data also suggest that the graft copolymer films have a rather homogeneous microstructure.[32]

Platelet Adhesion. For the platelet adhesion studies, PRP separated from the blood of a healthy dog was incubated on the pristine PANi and mPEG-*g*-PANi base film surfaces, and the extents of platelet adhesion on the surfaces were observed by SEM. Figure 9a–d shows the respective SEM images of the platelets adhered to the pristine EM base surface and three mPEG-*g*-PANi base film surfaces of different graft concentrations. It can be seen that the amount of platelet adhesion decreases with increasing mPEG graft concentration in the copolymer film. The mPEG-*g*-PANi film with a graft concentration of 0.046 is very effective in preventing platelet adhesion. The result thus suggests that the mPEG-PANi film cast from the copolymer sample with a moderate mPEG graft concentration (bulk) of 0.046 can exhibit nonfouling surface properties.

PEG-containing polymers are commonly used as blood-compatible materials.[12] The PEG component is well-known for its ability to minimize blood protein adsorption onto the surface. The blood protein adsorption is the first step in the thrombosis process. The second step of the thrombosis involves the platelet adhesion. Usually, the platelet adhesion will not occur to a significant extent if the blood protein cannot be adsorbed onto the surface.[33] The protein-repelling prop-

erty of PEG is believed to have resulted from its minimum interfacial free energy in water, its hydrophilicity, its high surface mobility, and its steric stabilization effects, as well as its unique solution properties and molecular conformation in water.[12] The PEG molecule has a large excluded volume in water. In an aqueous environment, a surface with hydrated flexible PEG chains and a large excluded volume tends to repel protein molecules that approach it. In the absence of protein adsorption, the platelet adhesion is suppressed.[34]

Conclusion

A new copolymer, methoxy poly(ethylene glycol)-grafted polyaniline, or mPEG-*g*-PANi, was successfully synthesized by incorporating the chlorine end-capped derivative of methoxy PEG (MW ~2000) onto PANi through the N-alkylation of the leucoemeraldine form of the PANi. The mPEG-*g*-PANi copolymers exhibited enhanced solubility in common organic solvents with only a moderate reduction in their electrical conductivity. For the mPEG-*g*-PANi sample with a graft concentration of 0.257, it also exhibited a solubility of up to 1.0 g/100 mL in water. The mPEG-*g*-PANi copolymer with a mPEG graft concentration ([mPEG]/[aniline]) above about 0.05 exhibited good resistance toward platelet adhesion, suggesting that the graft-modified electroactive polymer had been imparted with a nonfouling, blood-compatible surface.

(31) Cassie, A. B. D. *Discuss. Faraday Soc.* **1952**, *75*, 5041.
(32) Drelich, J.; Wilbur, J. L.; Miller, J. D.; Whitesides, G. M. *Langmuir* **1996**, *12*, 1913.

(33) Norde, W. *Adv. Colloid Interface Sci.* **1986**, *25*, 267.
(34) Kjellander, R.; Florin, E. *J. Chem. Soc., Faraday Trans.* I **1981**, *77*, 2053.