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Preparation and Characterization of Polyaniline *N*-Grafted with Poly(ethyl acrylate) Synthesized via Atom Transfer Radical Polymerization

Bakhshali Massoumi,[1] Mahdi Abdollahi,[2] Somayyeh Jahed Shabestari,[1] Ali Akbar Entezami[3]

[1]Department of Chemistry, Payame Noor University, P.O. Box 19395-3697, Tehran, I.R., Iran

[2]Polymer Engineering Department, Faculty of Chemical Engineering, Tarbiat Modares University, P. O. Box 14115-114, Tehran, I.R., Iran

[3]Laboratory of Polymer, Faculty of Chemistry, Tabriz University, Tabriz, I.R., Iran

Correspondence to: B. Massoumi (E-mail: b-massoumi@pnu.ac.ir or bakhshalim@yahoo.com) or M. Abdollahi (E-mail: abdollahim@modares.ac.ir)

ABSTRACT: Polyaniline (PANI) *N*-grafted with poly(ethyl acrylate) (PEA) was synthesized by the grafting of bromo-terminated poly (ethyl acrylate) (PEA-Br) onto the leucoemeraldine form of PANI. PEA-Br was synthesized by the atom transfer radical polymerization of ethyl acrylate in the presence of methyl-2-bromopropionate and copper(I) chloride/bipyridine as the initiator and catalyst systems, respectively. The leucoemeraldine form of PANI was deprotonated by butyl lithium and then reacted with PEA-Br to prepare PEA-*g*-PANI graft copolymers containing different amounts of PEA via an *N*-grafting reaction. The graft copolymers were characterized by Fourier transform infrared spectroscopy, elemental analysis, and thermogravimetric analysis. Solubility testing showed that the solubility of PANI in chloroform was increased by the grafting of PEA onto PANI. The morphology of the PEA-*g*-PANI graft copolymer films was observed by scanning electron microscopy to be homogeneous. The electrical conductivity of the graft copolymers was measured by the four-probe method. The results show that the conductivity of the PANI decreased significantly with increasing grafting density of PEA onto the PANI backbone up to 7 wt % and then remained almost constant with further increases in the grafting percentage of PEA. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

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INTRODUCTION

Since the discovery that a conjugated polymer could be made to conduct electricity through doping,[1] a tremendous of research has been carried out in the field of conducting polymers.[2,3] Polyaniline (PANI) is an excellent example of a conjugated polymer that can be tailored for specific applications through the doping process.[4] Since its conducting properties were rediscovered in the early 1980s, PANI has been studied for many other potential applications, including lightweight battery electrodes,[5] electromagnetic shielding devices,[6] and anticorrosion coatings.[7]

It is essential to modify the properties of a polymer according to tailor-made specifications designed for target applications. There are several means for modifying polymers properties, namely, blending, grafting, and curing. *Grafting* is a method wherein monomers are covalently bonded (modified) onto the polymer chain.[8] PANI is inherently brittle and poor in processability because of its insolubility in comment solvents. Its poor solubility has limited the industrial applications of PANI.[9,10] To improve its processability, various methods have been reported to increase the solubility of PANI. For example, it has been reported that the incorporation of the alkyl side groups into PANI can enhance its solubility and processability and change its properties.[11–13] The growth of aniline onto functionalized polystyrene has also been reported.[14] To improve the melt and solution processability, the *N*-grafting of brominated polystyrene[15] and brominated poly(styrene-*co*-methyl styrene)[16] synthesized via atom transfer radical polymerization (ATRP) onto PANI has also been reported. Flexible alkyl,[17] poly(ethylene glycol),[18] and polyether[19] chains have been incorporated onto the PANI via an *N*-alkylation method. Also, water-soluble PANI-*graft*-poly(*N*-isopropylacrylamide) copolymers have been synthesized by the ATRP of *N*-isopropylacrylamide in the presence of PANI macroinitiators.[20]

Poly(ethyl acrylate) (PEA) is an outstanding engineering material, which is generally used in textile applications because of its good mechanical and thermal properties and low cost. PEA has gained wide recognition as it possesses many unique properties, including solubility in organic solvents and good mechanical properties. To our knowledge, there has been no report on the *N*-grafting of PANI with end-functionalized PEA. A new *N*-substituted PANI was synthesized in this study by the incorporation of different amounts of bromo-terminated poly(ethyl acrylate) (PEA-Br) synthesized by ATRP onto the deprotonated PANI backbone. The PEA-*g*-PANI graft copolymers were characterized by Fourier transform infrared (FTIR) spectroscopy, elemental analysis, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and conductivity measurements. It was expected that the incorporation of PEA onto PANI would result in a graft copolymer with new and interesting properties, such as improved solubility and processability of the PANI.[21,22]

EXPERIMENTAL

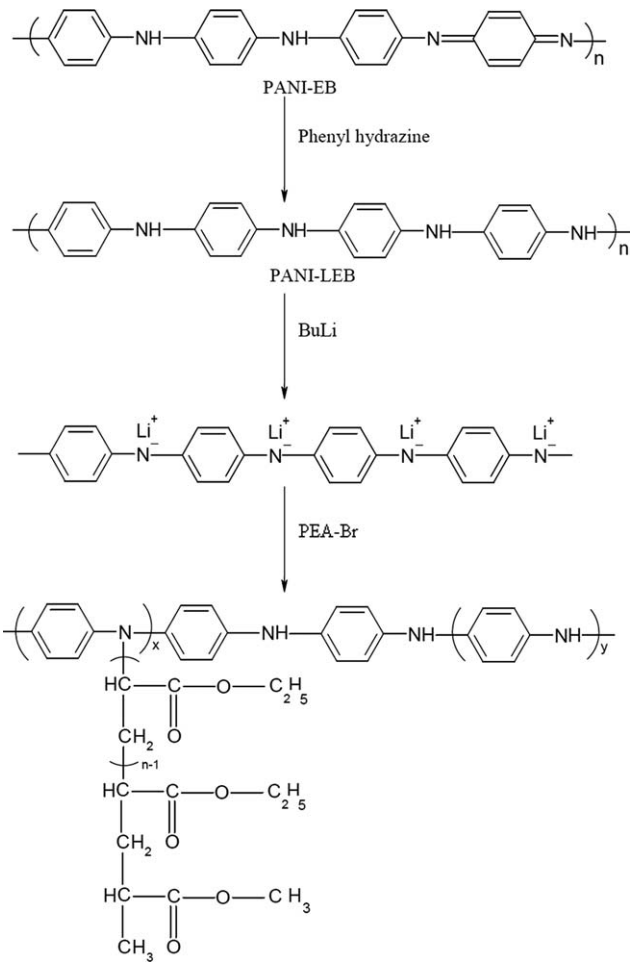
Materials

Aniline (Merck) was purified by double distillation under reduced pressure before use. Ethyl acrylate (EA; Merck) was washed twice with an aqueous solution of sodium hydroxide (5 wt %) and twice with distilled water. The organic portion was dried with anhydrous sodium carbonate by overnight stirring, then filtered, and finally distilled under reduced pressure over calcium hydride. Ammonium persulfate (Merck) was recrystallized three times from ethanol/water. 2,2′-Bipyridine (Bpy) and methyl 2-bromopropionate (MBrP; Merck) were used as received. Copper(I) chloride (CuCl; Merck) was washed with glacial acetic acid (three times), absolute ethanol, and diethyl ether in turn and then dried *in vacuo*. Fresh tetrahydrofuran (THF) was dried and distilled under an argon atmosphere. Butyl lithium (BuLi) was purchased from Merck. *N*-Methyl-2-pyrrolidone (NMP), carbon tetrachloride, chloroform ($CHCl_3$), acetone, methanol, sulfuric acid, phenyl hydrazine, *n*-hexane, diethyl ether and ammonia (all from Fluka) were used as received.

Synthesis of PANI and PEA-Br

PANI was prepared via the chemical interfacial polymerization of aniline.[23] Aniline (0.064 mol) was dissolved in 200 mL of chloroform as the organic phase. Ammonium persulfate (0.016 mol) as the oxidant was dissolved in 200 mL of 1*M* H_2SO_4 as the dopant acid solution. The organic solution was added to the aqueous solution gently and with minimal agitation along the sides of the vessel. The resulting two-phase system was left undisturbed at room temperature for 24 h. The PANI was filtered, washed several times with water and methanol, respectively, and desiccated *in vacuo*.

The obtained doped PANI, emeraldine salt, was dedoped by washing with a 1*M* ammonia aqueous solution ($NH_3{\cdot}H_2O$) to form the emeraldine-base polyaniline (EB-PANI). To maximize the degree of substitution, the completely reduced form of PANI, leucoemeraldine base (LEB), was prepared by the treatment of EB-PANI powder in diethyl ether with phenyl hydrazine (Scheme 1). Phenyl hydrazine (2.5 mL) as a reducing agent was added to 0.5 g of EB-PANI and stirred for 1 h. The reaction



Scheme 1. Reaction mechanism of PEA-*g*-PANI.

mixture was diluted and precipitated with 75 mL of diethyl ether. The collected gray–white powder was further washed with 50 mL of diethyl ether. The resulting powder was dried in a vacuum oven in the dark.

A typical ATRP of EA was carried out as follows.[24] CuCl (9.8×10^{-4} mol) was placed in a flask. It was then purged with argon for 15 min. Bpy (19.6×10^{-4} mol), EA (9.8×10^{-2} mol, already degassed by purging with argon for 30 min before use), and finally, the initiator, MBrP (9.8×10^{-4} mol), were added to the flask in sequential order via a dried and purified syringe at ambient temperature with continuous stirring. The reaction vessel was sealed with a rubber septum, immersed in a thermostated oil bath maintained at a temperature of 90°C, and stirred for 5 h under an argon atmosphere. After a specific time, the reaction was quenched by cooling. The final polymer was passed three times through a column of neutral alumina to remove the catalyst and was then dried in a vacuum oven at 50°C.

Synthesis of the graft copolymer (PEA-*g*-PANI)

The reaction flask was dried and kept under an inert atmosphere throughout the reactions by a constant flow of argon. The leucoemeraldine-base polyaniline (LEB-PANI; 0.2 g) was dispersed in 20 mL of THF. The reaction mixture was cooled to 0°C, and a predetermined amount of BuLi (0.8 mL) was added

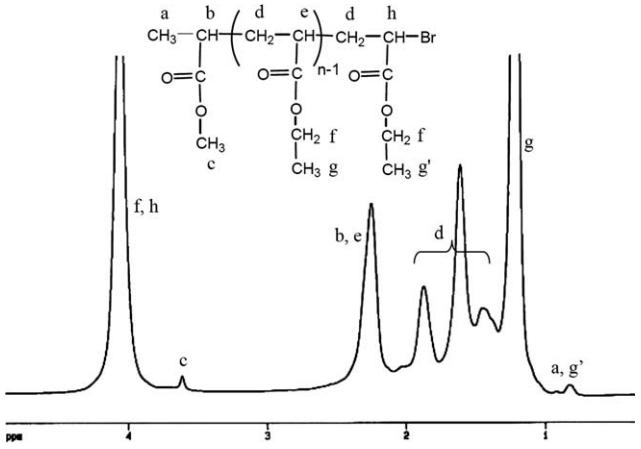


Figure 1. ^{1}H-NMR spectrum of PEA-Br synthesized via ATRP of EA initiated by MBrP.

with stirring. The color of the reaction mixture changed from dark blue to green–black. In another dried flask, PEA-Br (0.2, 0.3, or 0.6 g) was dissolved in 10 mL of THF under an argon atmosphere. This solution was added to the reaction mixture. The reaction was stirred under an argon atmosphere at 60°C for 24 h (Scheme 1). The color of the solution gradually turned blue. After a specific time, the reaction mixture was poured into methanol to precipitate the graft copolymer. The precipitate was filtered, washed further with water and methanol to remove residual amounts of salts and unreacted PEA, and then desiccated *in vacuo*. Then, three PEA-*g*-PANI graft copolymers (i.e., PEA-*g*-PANI4, PEA-*g*-PANI7, and PEA-*g*-PANI10) were obtained. The numbers indicate the grafting percentage of PEA as determined by TGA (see the Results and Discussion section). It should be noted that the low-molecular-weight PEA synthesized in this study was fully soluble in the methanol.

PEA-*g*-PANI itself is insulating material. It was converted into a semiconducting material by doping with sulfuric acid. For this purpose, the PEA-*g*-PANI graft copolymers were protonated by immersion in a 1*M* H_2SO_4 solution for 2 h. To remove excess acid from the polymer, the dark green powder was then washed by H_2O and dried under reduced pressure.

Characterization

FTIR spectra were recorded with a Shimadzu FT-IR 8600s spectrometer (Shimadzu, Kyoto, Japan). The samples were prepared in the pellet form with spectroscopic-grade KBr powder. The ^{1}H-NMR spectrum was recorded on a Bruker 400-MHz spectrometer. The sample was analyzed in a deuterated chloroform solution. A Philips 515 scanning electron microscope was used to study the surface morphology of the graft polymer film. The contents of C, H, and N in the samples were determined by elemental analysis with a Heareus CHN-ORAPID instrument. The electrical conductivity was measured on compression-molded films with the usual four-probe technique (ASTM 991-89) by a four-point probe with a direct current source (Azar Electric Co., Iran). All measurements were done in air at room temperature and were converted to conductivity by the following equation:[16]

$$\rho = 1/\delta = V/I\omega\pi/\ln 2 \quad (1)$$

where ρ is the resistivity (Ω cm), δ is the conductivity (S/cm), V is the potential difference (mV), I is the applied constant current (mA), and ω is the thickness (cm).

TGA was performed under a nitrogen purge on a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments, New Castle, DE) in a temperature range of 25–700°C at a heating rate of 20°C/min. The intrinsic viscosity of the PEA-Br homopolymer in a benzene solution was measured at 30°C by the viscometry method. The molecular weight of the PEA-Br homopolymer was then calculated with the Mark–Houwink equation with $k = 2.77 \times 10^{-2}$ (mL/g) and $\alpha = 0.67$. The solubilities of the PANI and PEA-*g*-PANI graft copolymer were checked at room temperature in various solvents, including NMP, carbon tetrachloride, chloroform, and acetone.

The apparent (i.e., polystyrene-equivalent) molecular weight and polydispersity of PEA-Br dissolved in THF was determined by a Waters 150C gel permeation chromatograph (GPC Waters 150C, Milford, MA) equipped with a 10^4-, 10^3-, and 500-Å set of Ultrastyragel columns and a refractive-index detector. Polystyrene standards with narrow molecular weight distributions and molecular weights in the range of the analyzed molecular weights were used to calibrate the columns. THF was used as an eluent with a flow rate of 1 mL/min at 35°C.

RESULTS AND DISCUSSION

Structural characterization of the PANI-based polymers

The synthetic route of *N*-grafted PANI with PEA (PEA-*g*-PANI) and its proposed reaction mechanism are shown in Scheme 1. The reaction of LEB-PANI with BuLi in THF caused deprotonation of the NH groups and produced an anion of LEB-PANI. The subsequent reaction of the deprotonated LEB-PANI with PEA-Br provided the graft copolymer (Scheme 1). PEA-Br was prepared via ATRP of EA in the presence of methyl-2-bromopropionate and CuCl/Bpy as the initiator and catalyst systems, respectively. Inherent in the mechanism of ATRP was the incorporation of a halogen at the chain ω end (Figure 1).[25–27]

The structure of the low-molecular-weight PEA synthesized via the ATRP technique was analyzed by ^{1}H-NMR spectroscopy (Figure 1). All signals in the ^{1}H-NMR spectrum were assigned to the corresponding protons.[24] The number-average molecular weight of PEA-Br, calculated from the intensities of the signals appearing at 3.7 and 4.1 ppm, was 4600 g/mol; this was in good agreement with the molecular weight estimated from the viscometry measurement (3200 g/mol). The number-average molecular weight and polydispersity index of the synthesized PEA-Br were also measured by gel permeation chromatography to be 6760 g/mol and 1.48, respectively.

The FTIR spectra of the EB-PANI, LEB-PANI, and PEA-*g*-PANI7 polymers are shown in Figure 2. The characteristic absorption bands of PANI, namely, C=N in the quinoidal units at 1591 cm^{-1}, benzenoid stretches at 1502 cm^{-1}, and N—H stretching at 3382 cm^{-1}, were observed in the FTIR spectrum of EB-PANI [Figure 2(a)]. The $C_{aromatic}$—N stretching band of an aromatic amine appeared at 1303 cm^{-1}. The absorption peak at 1159 cm^{-1} was characteristic of the electron-like absorption of the N=Q=N vibration (where Q denotes the quinoidal ring).

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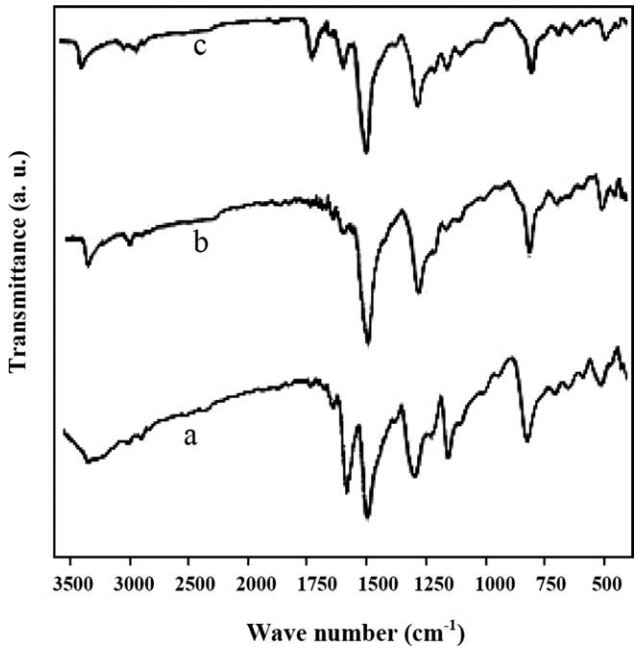

Figure 2. FTIR spectra of the (a) EB-PANI, (b) LEB-PANI, and (c) PEA-*g*-PANI7.

In the spectrum of the completely reduced PANI [Figure 2(b)], the absorption peak at 1591 cm^{-1} of the quionoidal units was removed. However, the intensity of the bands appeared at 1502 cm^{-1} (benzenoid stretching), and the N—H stretching at 3382 cm^{-1} increased.

In the spectrum of the PEA-*g*-PANI7 graft copolymer [Figure 2(c)], two new absorption bands appeared at 2852 and 2923 cm^{-1} for the asymmetric and symmetric aliphatic C—H stretching vibrations, respectively, of the PEA chain. Also, the absorption band at 1726 cm^{-1} was attributed to the carbonyl group (C=O) of PEA. The absorption band at 813.9 cm^{-1}, characteristic of the out-of-plane bending vibration of the 1,4-disubstituted benzene rings, together with the absence of a splitting of this peak into two peaks at 813 and 870 cm^{-1}, indicated that no ring substitution occurred in the grafting reaction. The presence of the absorption band of an ether group at 1251 cm^{-1} overlapped with the PANI peaks.[11,28] Similar spectra were also observed for the two other graft copolymers, that is, PEA-*g*-PANI4 and PEA-*g*-PANI10. The FTIR results showed that PEA-Br was successfully been grafted onto the PANI via the *N*-grafting reaction.

The elemental analysis was carried out to evaluate composition of the copolymer with various elements, such as C, H, and N in the polymer matrix. Only one sample from the graft copolymers was subjected to elemental analysis. Table I shows the composition of the PANI and PEA-*g*-PANI7 samples. It is clear from Table I that the PEA chain, with a viscosity-average molecular weight of 3200, was grafted onto the PANI backbone.

Table I. Results of the CHN Analysis of the PANI and PEA-*g*-PANI7 Samples

		Test method ASTM D 5291		
Sample	Unit	C content	H content	N content
PANI	Mass %	77.6	5.2	13.9
PEA-g-PANI7	Mass %	73.9	5.7	11.4

To further verify the grafting of the PEA chain onto the PANI backbone, the graft copolymers were subjected to TGA. The TGA thermograms of PANI, PEA-*g*-PANI4, PEA-*g*-PANI7, and PEA-*g*-PANI10 in the temperature range of 25–700°C are shown in Figure 3. The weight loss from 50 to 150°C was attributed to contaminating water and solvent in the polymer.[29,30] In the TGA thermogram of the PEA-*g*-PANI graft copolymers, major weight losses were observed over two temperature ranges, around 240–450 and 450–700°C. The thermograms of the PEA-*g*-PANI graft copolymers from 450 to 700°C exhibited a decomposition pattern similar to that of the parent PANI (Figure 3).[31] Therefore, it is clear from Figure 3 that the weight loss from 240 to 450°C was related to the cleavage of PEA chains,[32] and the weight loss after 450°C was attributed to the thermal decomposition of the main chain of the PANI.[31] These results confirmed that the PEA chain with a viscosity-average molecular weight of 3200 was successfully grafted onto the PANI backbone. Also, the synthesized PEA-*g*-PANI graft copolymers had a relatively good thermal stability. It was reported that PEA completely degrades in the temperature range of 250–450°C.[32] Therefore, the grafting percentage (G), which was defined as the weight of PEA chains grafted onto 100 g of PANI, could be calculated from the TGA thermograms with weight loss in the temperature range of 200–450°C [eq. (2)]:

$$G(\%) = \frac{m_{200} - m_{450}}{m_{450}} \times 100 \qquad (2)$$

where m_{200} and m_{450} indicate the residual masses of the samples used in TGA at 200 and 450°C, respectively. From the TGA thermograms (Figure 3), the grafting percentages of PEA onto the PEA-*g*-PANI4, PEA-*g*-PANI7, and PEA-*g*-PANI10 graft copolymers were estimated via eq. (2) to be about 4.2, 7.0, and 10.1 wt %, respectively, from which the grafting density was then

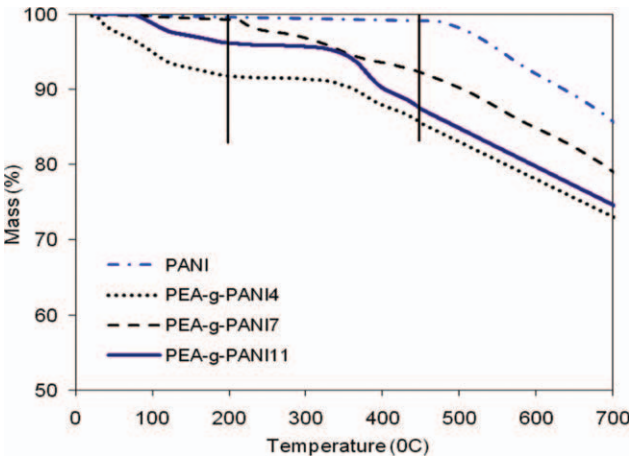

Figure 3. TGA thermograms of the PANI and PAE-*g*-PANI graft copolymers at a heating rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

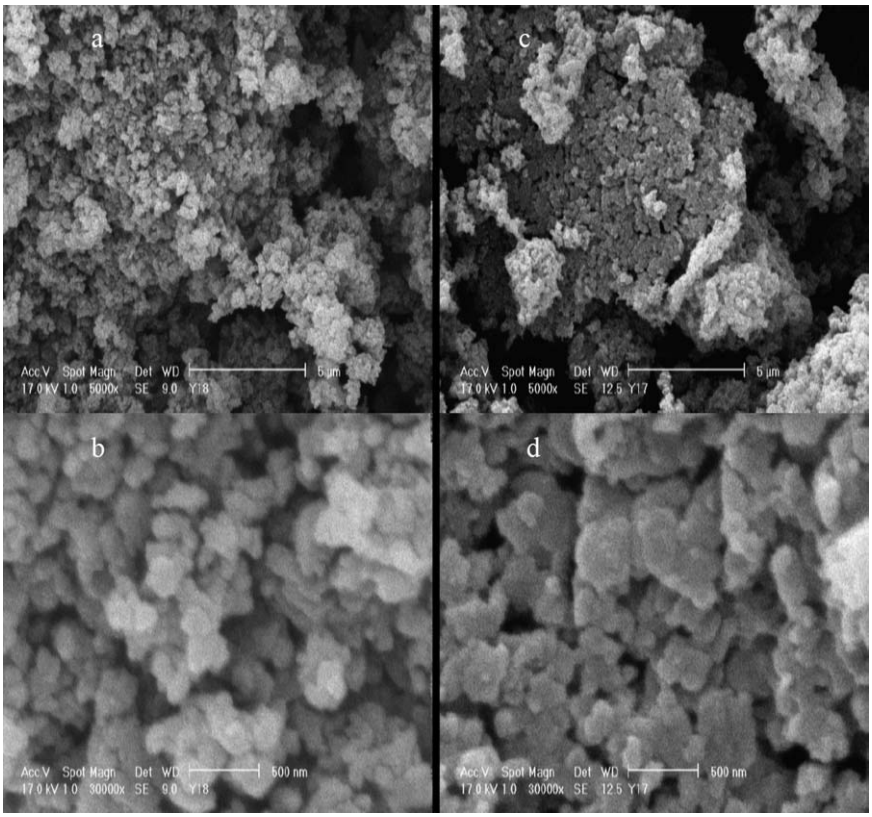

Figure 4. SEM images of (a) PANI, (b) 5000×, (b) 30,000×, and and PEA-*g*-PANI7 at (c) 5000 and (d) 30,000×.

estimated with the known number-average molecular weight of PEA (4600 g/mol) to be one PEA chain per about 1150, 650, and 450 aniline monomers in the PANI backbone, respectively.

The solubility of the PANI and PEA-*g*-PANI graft copolymers in various solvents, including NMP, carbon tetrachloride, chloroform, and acetone was tested. PANI was slightly soluble only in NMP, whereas the graft copolymers were partially soluble in chloroform (e.g., 1 wt % for PEA-*g*-PANI7) and NMP (e.g., 2 wt % for PEA-*g*-PANI7). The solubility of the graft copolymers was improved with increasing grafting percentage of PEA. Therefore, we concluded that the grafting of PEA onto the PANI backbone increased the solubility and, thereby, improved the processability of PANI.

SEM was used to characterize the morphology of PANI and the PEA-*g*-PANI7 graft copolymer. The SEM images in Figure 4 reveal some variations in the morphological structure of PANI and PEA-*g*-PANI7. PANI exhibited a spongelike structure with a nanoparticle size, about 45–100 nm [Figure 4(a,b)], whereas in PEA-*g*-PANI7, the particles became larger (150–200 nm), and this led to compressed structures [Figure 4(c,d)]. This variation could be explained by the grafting of the PEA chains onto the nitrogen atoms of the PANI backbone; this resulted in the bulky structure of the obtained graft copolymer.

Electrical conductivity of the acid-doped PEA-*g*-PANI graft copolymers

The PEA-*g*-PANI graft copolymers were converted into the semiconducting material by treatment with sulfuric acid. The electrical conductivity of the PEA-*g*-PANI graft copolymers protonated by sulfuric acid as a function of the grafting percentage of PEA are shown in Figure 5. It is clear from Figure 5 that electrical conductivity of the graft copolymers decreased significantly with increasing grafting percentage up to about 7 wt % and then remained almost constant with further increases in the grafting percentage. For example, the sulfuric acid-doped PEA-*g*-PANI7 graft copolymer showed an electrical conductivity of 0.31 S/cm at room temperature; this was lower than that of the

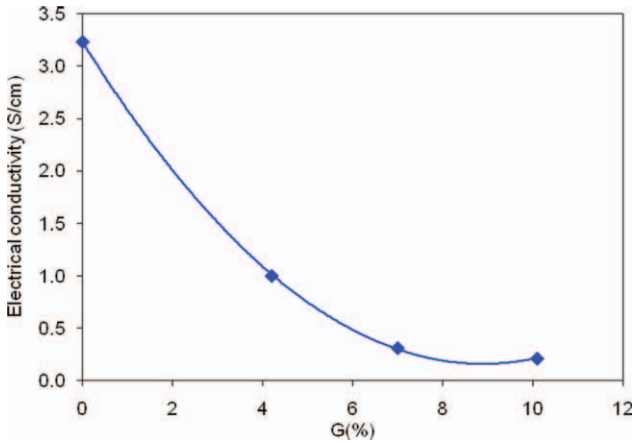

Figure 5. Electrical conductivity of the sulfuric acid-doped PEA-*g*-PANI graft copolymers as a function of the grafting percentage of PEA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EB-PANI protonated with sulfuric acid (3.233 S/cm). These variations in the electrical conductivity of the graft copolymers was attributed to the presence of nonconductive PEA chains in the graft copolymers and/or the effect of the PEA chains on the orientation of the PANI chains. The introduction of the nonconductive PEA side chains at the N position of PANI caused a decrease in the electrical conductivity. On the other hand, the higher grafting density of the PEA side chains may have caused orientations in the PANI backbone chains, which resulted in the increased electrical conductivity. Therefore, the electrical conductivity of the graft copolymers remained almost constant with further increases in the grafting density from 7 to 10 wt %.

The results obtained in this study were consistent with those reported in the literature for almost equivalent systems.[15,16,20,33] The conductivity of the PANI decreased with the incorporation of nonconductive polymer chains, such as methyl methacrylate and methacrylic acid chains.[33] The conductivity values of the pure PANI and poly(styrene-*co*-methyl styrene)-*g*-PANI terpolymer (degree of grafting = 2.5 wt %) were reported to be 1.25 and 0.17 S/cm, respectively;[16] this was consistent with results obtained in this study.

It should be noted that for some applications (e.g., corrosion inhibitors, electrochromic device), a high electrical conductivity may not be required, and an improvement in the processability may be more important.[29] Moreover, PEA-*g*-PANI is partially soluble in common solvents such as chloroform, whereas PANI is not soluble in these solvents at all. Also, the presence of PEA in the graft copolymer increased its flexibility and, to some extent, its solubility. Therefore, an improvement in the processability of PANI was expected by the *N*-grafting of PEA.

CONCLUSIONS

PANI is used as a conducting polymer for fiber and film compounds. The incorporation of side groups into PANI can enhance its solubility and processability and change its properties. PEA is a soluble, flexible, and dispersible polymer that is used in industry. Low-molecular-weight PEA-Br was prepared via ATRP of EA initiated with MBrP in the presence of a CuCl/Bpy catalyst system. PANI was prepared via chemical interfacial polymerization of aniline. *N*-Substitution of the PANI units with PEA chains was performed by the reaction of LEB-PANI with BuLi and the subsequent *N*-grafting of different amounts of PEA chains onto the PANI backbone (PEA-*g*-PANI4, PEA-*g*-PANI7, and PEA-*g*-PANI10). The successful synthesis of PEA, PANI, and the PEA-*g*-PANI graft copolymers were confirmed by FTIR spectroscopy, ^{1}H-NMR, CHN analysis, and TGA. The results of the electrical conductivity testing of the sulfuric acid doped PEA-*g*-PANI graft copolymers show that the electrical conductivity decreased significantly with increasing grafting percentage up to about 7 wt % and then remained almost constant with further increases in the grafting percentage. This was attributed to the presence of nonconductive PEA chains in the PEA-grafted PANI and to the effect of PEA chains on the orientation of the PANI backbone chains. The PEA-*g*-PANI graft copolymers were partially soluble in common solvents such as chloroform, whereas PANI was not soluble at all. The PEA-*g*-PANI graft copolymer is expected to be a flexible polymer with good film, fiber, dispersal, and conductivity properties.

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