

NMRP 중합법을 이용한 전도성 폴리아닐린-수식 고분자의 제조와 특성

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Synthesis and Characterization of Conductive Polyaniline-Modified Polymers via Nitroxide Mediated Radical Polymerization

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Abstract: The paper describes the preparation and characterization of conductive polyaniline-modified polymers by growing of aniline onto functionalized poly(styrene-*co*-*p*-methylstyrene) [P(St-*co*-MSt)]. For this purpose, P(St-*co*-MSt) was synthesized via nitroxide mediated radical polymerization (NMRP) and then *N*-boromosuccinimide was used for introduction of bromine to the benzylic positions of copolymer. Afterwards, 1,4-phenylenediamine was linked to the brominated P(St-*co*-MSt) and functionalized copolymer [P(St-*co*-MSt)-NH₂] was prepared. The graft copolymerization of aniline monomers onto functionalized P(St-*co*-MSt) was initiated by oxidized phenylamine groups after addition of ammonium peroxydisulfate (APS), and *p*-toluenesulfonic acid-doped PANI was chemically grafted onto P(St-*co*-MSt) via oxidation polymerization. The obtained terpolymer was studied by FTIR and UV-Vis spectroscopy and its thermal behaviour were examined by DSC and TGA analyses. The conductivity of terpolymer was measured by four-point probe method and electroactivity was measured by cyclic voltammetry (CV). The solubility of P(St-*co*-MSt)-*g*-PANI was examined in common organic solvents.

Keywords: poly(styrene-*co*-*p*-methylstyrene), NMRP, graft copolymer, conductive polyaniline, modification, solubility.

Introduction

Polyaniline (PANI) has been the subject of considerable recent interest because of their unique properties such as high electrical conductivity, good environmental stability in doped and neutral states,¹ ease of synthesis and numerous potential applications including rechargeable batteries,^{2–4} energy storage devices, electromagnetic interference shielding, electronic and optical devices,^{5,6} smart windows and light emitting diodes.⁷ However polyaniline is inherently brittle and poor in processability due to its insolubility in common organic solvents. Its poor solubility has limited the industrial applications of polyaniline.^{8,9} To improve its processability, various procedures have been adapted. For example, self doped PANI with sulfonic acid groups substituted onto the polymer has been synthesized. Several ring and *N*-sub-

stituted PANI, soluble in common organic solvents, have been prepared directly from polymerization of the corresponding aniline monomers.¹⁰ Another approach toward modified polyaniline is copolymerization of aniline with suitable substituted aniline to produce copolymers. The obtained copolymers have improved in solubility and processability.¹¹ Among PANI derivatives, sulfonated polyaniline (SPANI) is the most successful candidate for practical applications in electronic devices due to its water solubility, electroactive properties, thermal stability, optical properties, unique self-doping and external doping mechanism.^{12–14} However, strong electron-withdrawing of sulfonic acid's functional groups make conductivity of SPANI much lower than that of PANI.¹⁵

In recent years, “controlled/living” radical polymerization (CRP), have developed rapidly for facile preparation of a variety of polymeric materials with predetermined molecular weight (M_n) and low polydispersity index (PDI), and high degrees of chain-end functionalization.¹⁶ Compared with

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conventional living anionic polymerizations, CRP techniques have the advantage of the variety of applicable monomers and more tolerant experimental conditions. The most widely used CRP methods are atom transfer radical polymerization (ATRP),^{17–20} reversible addition fragmentation chain transfer (RAFT) polymerization,^{21,22} and nitroxide-mediated radical polymerization (NMRP).^{23,24} Nitroxide mediated radical polymerization method is a controlled free radical methodology, which allows the synthesis of star and graft copolymers with controlled molecular weight under mild conditions. This polymerization method is based on the use of traditional radical initiator (e.g., B.P.O) in the presence of stable nitroxide radical (e.g., TEMPO).

For the first time, the nitroxide mediated radical polymerization (NMRP) was employed to prepare the conductive polyaniline-modified polymers. In synthesis process, P(St-*co*-MSt) was synthesized via NMRP technique and then the benzylic hydrogen's of P(St-*co*-MSt) was brominated. Thus brominated copolymer was synthesized using *N*-bromosuccinimide (NBS) and 2,2'-azobis(isobutyronitrile) (AIBN). Afterwards, 1,4-phenylenediamine was linked to the brominated copolymer by using an effective chemical route. Poly(styrene-*co*-*p*-methylstyrene)-*grafted*-polyaniline [P(St-*co*-MSt)-*g*-PANI] was synthesized by adding solution of ammonium peroxydisulfate and *p*-toluenesulfonic acid to the solution of aniline monomers and functionalized P(St-*co*-MSt).

Experimental

Materials. Aniline monomers from Merck was dried with NaOH and fractionally distilled under reduced pressure from sodium or CaH₂. Ammonium peroxydisulfate (APS) from Merck was recrystallized at room temperature from ethanol/water. Styrene and *p*-methylstyrene monomers were purchased from Merck and distilled under reduced pressure before used. *N*-Bromosuccinimide (NBS) from Merck was purified by recrystallization in water at 70 °C. 2,2'-Azobis(isobutyronitrile) (AIBN) from Aldrich were recrystallized in ethanol at 50 °C. TEMPO (2, 2, 6, 6-tetramethylpiperidinyloxy) was prepared in our laboratory. All other reagents were purified according to the literature.

Instrumentations. Fourier-transform infrared (FTIR) spectra were obtained on Shimadzu 8101 M FTIR. The samples were prepared by grinding the dry powders with KBr and compressing the mixture to form disks. The disks were stored in a desiccator to avoid moisture absorption. Spectra were recorded at room temperature. Proton nuclear magnetic resonance (¹H NMR) spectra were obtained at 25 °C on FT

NMR (400 MHz) Bruker spectrometer. Sample for ¹H NMR spectroscopy was prepared by dissolving about 10 mg of products in 5 mL of deuterated chloroform. The molecular weight of polymer was measured with a gel permeation chromatograph (GPC) (Maxima 820 GPC Analysis Report) using polystyrene (10⁶, 10⁵, 10⁴ Å) calibration standard with a THF mobile phase at a flow rate of 1 mL/min and column temperature at 30 °C. The thermal properties of P(St-*co*-MSt) and P(St-*co*-MSt)-*g*-PANI were investigated with thermogravimetric analysis (TGA-PL, England). About 10 mg of samples were heated between 25–600 °C at the heating rate of 10 °C min⁻¹ under nitrogen flow. Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH (Germany) – DSC 200 F3 Maia. The sample was first heated to 200 °C and kept for 5 min to eliminate thermal history. The sample was then cooled down at a rate of 10 °C/min. Then the sample was reheated to 200 °C at a rate of 10 °C/min. The entire test was performed under nitrogen purging at a flow rate of 50 mL min⁻¹.

Synthesis of P(St-*co*-MSt) via NMRP. 5 mL styrene (43.7 mmol), 5 mL *p*-methylstyrene (38.1 mmol), 0.15 g (0.62 mmol), dibenzoyl peroxide and 0.14 g (0.9 mmol) TEMPO were placed in an ampoule, degassed with several freeze-pump-thaw cycles, and sealed off under vacuum and placed in an oil bath at 95 °C for 4 hrs. At the end of this period, temperature was increased to 130 °C for another 12 hrs. The product was cooled, diluted with tetrahydrofuran (THF) and precipitated into excess methanol. This product was dried overnight under vacuum at room temperature. The *p*-methylstyrene content in the copolymer was 46% (by mole) based on peak at 2.28 ppm (–CH₃) in the ¹H NMR spectrum.

Synthesis of P(St-*co*-MSt)-Br. A 100 mL three-necked flask containing 30 mL CCl₄ and 3.31 g (30 mmol) poly(styrene-*co*-*p*-methylstyrene) was equipped with a mechanical stirrer under argon atmosphere. In a separate container 4.27 g (24 mmol) NBS and 4.04 g (21 mmol) AIBN was dissolved in 30 mL of dried CCl₄. This mixture was added to the polymer solution and was stirred for 2 hrs at 70 °C under argon atmosphere. The mixture was then cooled to room temperature and the brominated copolymer was recovered by filtration in large amount of methanol. The product was dried overnight under vacuum at room temperature.

Synthesis of P(St-*co*-MSt)-NH₂. A 100 mL three-necked flask containing 30 mL of DMF/CH₂Cl₂ (50/50 v/v) and 1 g (8.50 mmol) of P(St-*co*-MSt)-Br that was prepared in previous section was equipped with a mechanical stirrer and maintained at temperature of 75 °C by an external oil bath. Then 0.5 g (4.62 mmol) of 1,4-phenylenediamine, 1

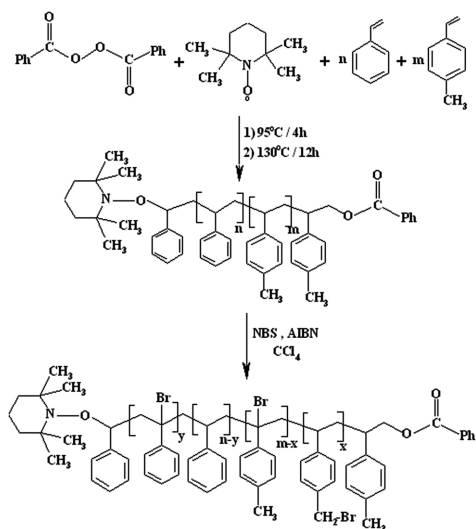
g (9.43 mmol) of anhydrous pulverized sodium carbonate, and 1 mL (12.4 mmol) of pyridine were added to the flask and the resulting mixture was stirred and heated for 4 hrs. At the end of the reaction, the polymer solution was filtered and precipitated into excess methanol. The product was washed with methanol and dried over night under vacuum.

Preparation of P(St-*co*-MSt)-*g*-PANI. P(St-*co*-MSt)-NH₂ (0.5 g) was completely dissolved in 30 mL of DMSO. Then, 1 g (10.74 mmol) of aniline and 0.5 g (2.57 mmol) of *p*-toluenesulfonic acid were added to the solution. The mixture was vigorously stirred and temperature was reduced to 5 °C. In a separate container, 2 g (8.76 mmol) of ammonium peroxydisulfate (APS) was dissolved in 10 mL of *p*-toluenesulfonic acid solution (1 M). The oxidant solution was slowly added at a rate of 5 mL/min to the mixture. The mixture was stirred for about 4 hrs, and then the polymer solution was filtered into excess methanol. The product was washed successively by distilled water and methanol.

The crude product was extracted with tetrahydrofuran (THF) for three times, in order to remove pure polyaniline. Polyaniline is partially soluble in THF. The polymer solution was filtered and precipitated into excess methanol. Afterwards, the product was added into cyclohexane, and refluxed to remove any residual ungrafted P(St-*co*-MSt). Poly(styrene-*co*-*p*-methylstyrene)-*g*-polyaniline is partially soluble in cyclohexane, while ungrafted P(St-*co*-MSt) is completely soluble in cyclohexane.

Results and Discussion

The graft copolymer materials prepared from hydrophilic polymers, PSt-*g*-PANI, could be appropriate for various

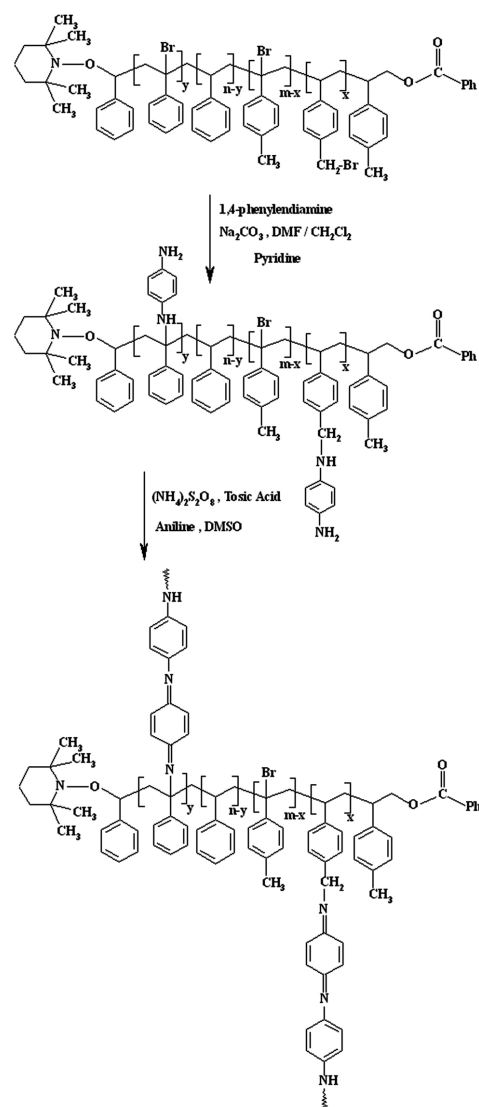


Scheme 1. Synthesis of P(St-*co*-MSt) and P(St-*co*-MSt)-Br.

applications in science and technology because of the good mechanical properties and their electrical conductivity. This article consists of four parts: (1) preparation of P(St-*co*-MSt) via nitroxide mediated radical polymerization; (2) synthesis and characterization of brominated P(St-*co*-MSt); (3) preparation of functionalized copolymer [P(St-*co*-PMSt)-NH₂] by linking of 1,4-phenylenediamine to the brominated copolymer; (4) synthesis and characterization of P(St-*co*-MSt)-*g*-PANI by growing of aniline onto functionalized copolymer. The methodology is shown in Scheme 1 and Scheme 2.

Synthesis of P(St-*co*-MSt) via Living Radical Polymerization.

Living polymerization is characterized by a linear increase of the molecular weight with conversion and reaction time, and a narrow molecular weight distribution as evidenced



Scheme 2. Synthesis of P(St-*co*-MSt)-NH₂ and P(St-*co*-MSt)-*g*-PANI.

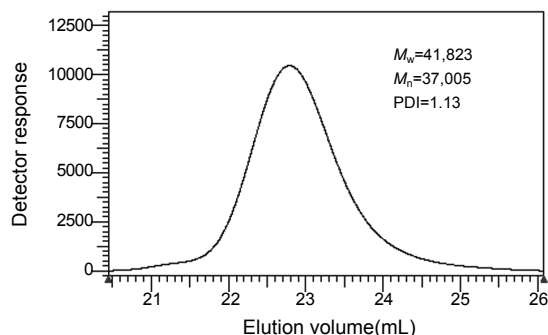


Figure 1. GPC chromatogram of P(St-co-MSt).

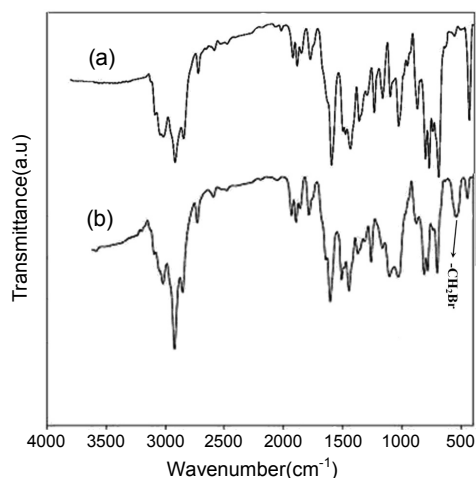


Figure 2. FTIR spectra of P(St-co-MSt) (a); P(St-co-MSt)-Br (b).

by a polydispersity index ($PDI = M_w/M_n$) approaching 1.²⁵ Figure 1 represents the GPC chromatogram of the P(St-co-MSt) that molecular weight distribution by GPC is 1.13. The single peak of the GPC chromatogram of the product indicated that the product could not be the blend of PSt homopolymer and PMSt homopolymer; if so, the GPC chromatogram should appear as two peaks, one for the PSt homopolymer and the other for the PMSt homopolymer.

Synthesis of P(St-co-MSt)-Br. Figure 2 shows the FTIR spectra of the P(St-co-MSt) and brominated copolymer. The FTIR spectra of P(St-co-MSt) shows the characteristic absorption bands due to stretching vibrations of aromatic and aliphatic C-H in the $3100\sim 2850\text{ cm}^{-1}$ region, weak aromatic overtone and combination bands in the $2100\sim 1670\text{ cm}^{-1}$ region, C=C stretching vibrations at 1606 and 1485 cm^{-1} , the absorption bands at 1445 and 1372 cm^{-1} characteristic of the $-\text{CH}_2$ bending vibrations and CH-out-of-plane bending of the phenyl ring at 768 and 709 cm^{-1} . The bromination takes place in the aliphatic chain and not in the aromatic ring. The C-Br stretching peak is observed at 557 cm^{-1} .

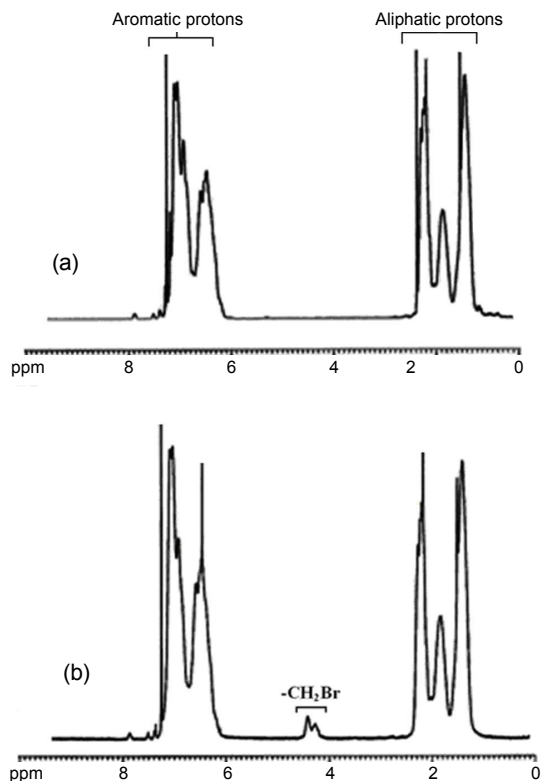


Figure 3. ^1H NMR spectra of P(St-co-MSt) (a); P(St-co-MSt)-Br (b).

The ^1H NMR spectra of P(St-co-MSt) and P(St-co-MSt)-Br are shown in Figure 3. The ^1H NMR spectra of P(St-co-MSt) shows the characteristic signals at 2.28, 1.86 and 1.43 ppm are assigned to $-\text{CH}_3$, $-\text{CH}$ and $-\text{CH}_2$ unit in P(St-co-MSt) respectively. Resonance at $6.13\sim 7.38$ ppm are assigned to aromatic protons (Figure 3(a)). After bromination, the ^1H NMR spectra shows the additional resonance at $4.14\sim 4.57$ ppm that is assigned to $-\text{CH}_2\text{Br}$ group in brominated copolymer (Figure 3(b)).

To calculate the extent of bromination for P(St-co-MSt) of a particular extent of bromination the following method was adopted. Let $[\text{P(St-co-MSt)}]_m - [\text{P(St-co-MSt)-Br}]_n$ represent the brominated P(St-co-MSt) copolymer. The mol% bromination is given by $n/(m+n) \times 100$. The area under the aliphatic region is given by $9n+5m$ and the area under the aromatic region is given by $9n+9m$. In Figure 3 solving the simultaneous equation with the integrated areas, it can be seen that $9n+5m=145.73$ and $9n+9m=154.1$ and therefore $n=2$ and $m=15.11$. Therefore the extent of bromination is $2/17.11 \times 100 = 11.68\%$.

Preparation of P(St-co-MSt)-g-PANI. Two kinds of cation radicals initiate PANI polymerization after addition of APS. One is oxidized phenylamine groups grafted to the brominated P(St-co-MSt), the other is oxidized aniline cation radicals.

As reaction time increasing, more aniline monomers join in the polymerization. Some are entrapped into the polymer chains initiated by oxidized phenylamine groups; others incorporate the polymer chains initiated by oxidized aniline cation radicals. This polymer chains could not be linked chemically to the P(St-co-PMSt).²⁶ To remove the ungrafted PANI chains, the crude product was purified as given in

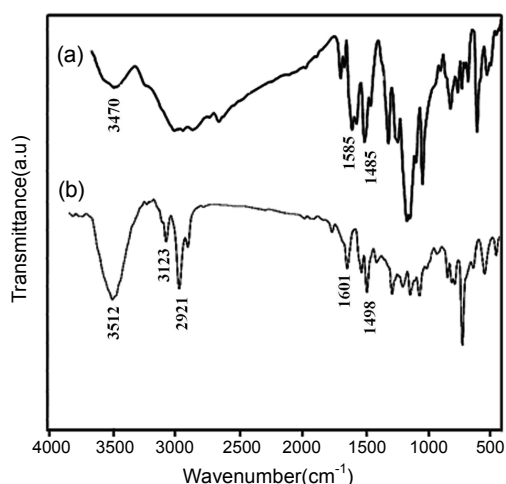


Figure 4. FTIR spectra of PANI (a); P(St-co-MSt)-g-PANI (b).

the experimental section.

Figure 4 shows the FTIR spectra of the PANI (a) and P(St-co-MSt)-g-PANI (b). The FTIR spectra of PANI shows the C=N in the quinoidal units which appears at 1585 cm^{-1} , the benzenoid stretches at 1485 cm^{-1} and the N-H stretches at 3470 cm^{-1} . The FTIR spectra of P(St-co-MSt)-g-PANI shows the absorption bands of polyaniline, the C=N in the quinoidal units which appears at 1601 cm^{-1} , the benzenoid stretches at 1498 cm^{-1} , the N-H stretches at 3512 cm^{-1} , and the aromatic C-H stretches at 3123 cm^{-1} were observed. The absorption peak at 1153 cm^{-1} is characteristic of electron-like absorption of the $\text{N}=\text{Q}=\text{N}$ vibration (where Q denotes the quinoid ring). Characteristic peaks at 2921 and 2853 cm^{-1} is attributed to the aliphatic C-H stretching's.

The solubility of P(St-co-MSt)-g-PANI terpolymer in

Table 1. Solubility of Polyaniline; P(St-co-MSt)-g-PANI in Common Organic Solvents

Solvent	DMSO	NMP	THF	CHCl_3	Xylene	DMF
PANI	+++	+++	+	+	-	++
P(St-co-MSt)-g-PANI	++	++	+++	++	+	+++

+++Soluble; +Partially Soluble; -Insoluble. The concentration used in the solubility test was 10 mg of each polymer in 1 mL of solvents.

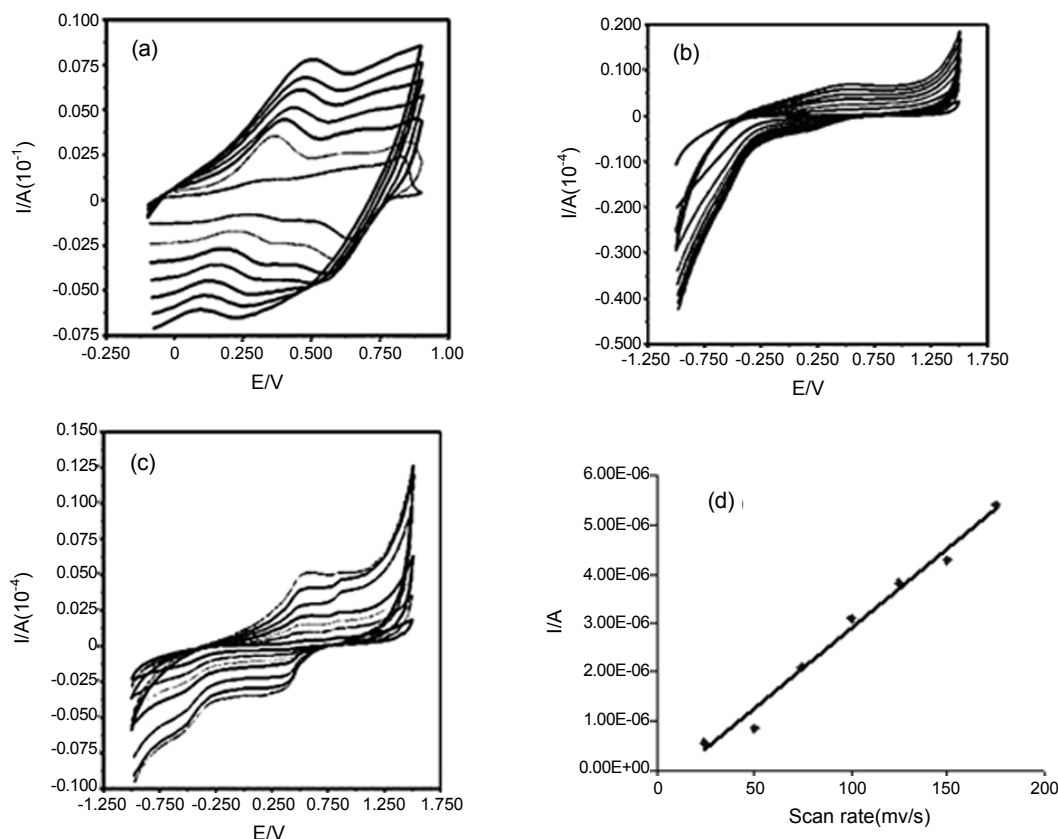


Figure 5. Cyclic voltammetry curves of PANI (a); P(St-co-MSt) (b); P(St-co-MSt)-g-PANI sample (c); linear relationship between the current and scan rate in P(St-co-MSt)-g-PANI (d).

common organic solvents are shown in Table 1. Polystyrene and poly(*p*-methylstyrene) has excellent solubility in non-polar solvents. The solubility of P(St-*co*-MSt)-*g*-PANI in common organic solvents improved compared to pure PANI, because aniline has grown onto polystyrene and poly(*p*-methylstyrene) backbone. The concentration used in the solubility tests was 10 mg of polymers in 1 mL of solvents.

Conductivity and Electroactivity Measurements. The most important physical properties of conductive polymers are conductivity properties. The conductivity of P(St-*co*-MSt)-*g*-PANI was measured by four-point probe technique. The conductivity value (σ) of terpolymer was obtained 0.084 Scm^{-1} .

Figure 5 shows the cyclic voltammograms of neat PANI, P(St-*co*-MSt) and P(St-*co*-MSt)-*g*-PANI. The polymer films were prepared on glass carbon (GC) electrode by casting. The cyclic voltammetry curves of samples were recorded at different scan rates. In Figure 5(a), the peak at 0.27 V in the anodic direction, which corresponds to the leucoemeraldine to emeraldine transition, is shifted to higher potential. For the P(St-*co*-MSt) no peaks are observed. Figure 5(b) shows that the P(St-*co*-MSt) is non-electroactive polymer. As shown in Figure 5(c), cyclic voltammogram of P(St-*co*-MSt)-*g*-PANI terpolymer exhibits some qualitative similarities with those of pure polyaniline. At a low scan rate, the terpolymer films shows two oxidation peaks and two reduction peaks corresponding to the Epa and Epc values. The peaks are ascribed to polaronic and bipolaronic transitions for the first and second peaks, respectively.^{27,28} Figure 5(d) shows a linear relationship between the current and scan rate, indicating that adsorption-limited process.

UV-Vis Spectroscopy. Figure 6(a) and (b) shows the electronic spectra of undoped PANI and undoped P(St-*co*-MSt)-*g*-PANI respectively in DMSO solvent. The UV-Vis spectra of PANI was characterized by two electronic transitions respectively at about 330 nm and 625 nm. As in the case of PANI-EB (Emeraldin form of polyaniline) the electronic transition at shorter wavelength is due to the benzene segments present in the PANI chain while the transition at longer wavelength is due to the quinoid (quinonimine) segments. The spectra of undoped P(St-*co*-MSt)-*g*-PANI characterized by only one electronic transition at about 597 nm that comparison to the pure PANI is lower. This shift to shorter wavelength ascribed by significantly lower the concentration of these quinoneimine units in the case of undoped P(St-*co*-MSt)-*g*-PANI in comparison to the undoped PANI.

When the P(St-*co*-MSt)-*g*-PANI is doped with HCl, a dramatic change in the electronic spectrum is observed (see Figure 6(c)). The band at about 600 nm completely disappears and is replaced by a new band at about 787 nm. The position of this band which is due to the formation of polarons (radical cations) occurs at considerable lower energy in the P(St-*co*-MSt)-*g*-PANI in comparison with pure PANI, which when doped with HCl.

Thermal Property Study. Figure 7 shows the DSC traces of P(St-*co*-MSt) (a) and P(St-*co*-MSt)-*g*-PANI (b). The P(St-*co*-MSt) is non-crystalline and therefore does not exhibit any crystallization or melting transitions. This co-polymer exhibits an endothermic peak approximately at 80 °C, corresponding to the glass transition temperature (T_g). Figure 7(b) shows the endothermic peak at 91 °C that has been attributed to the evaporation of any residual water and solvent molecules present in the polymer matrix. A strong exothermic peak appears at 171 °C that indicates the degradation of dopant (*p*-toluenesulfonic acid). The transition observed at 202 °C can be designed as the glass transition temperature of P(St-*co*-MSt)-*g*-PANI.

Characteristic TGA curves of P(St-*co*-MSt) and P(St-*co*-MSt)-*g*-PANI are shown in Figure 8. TGA results indicate

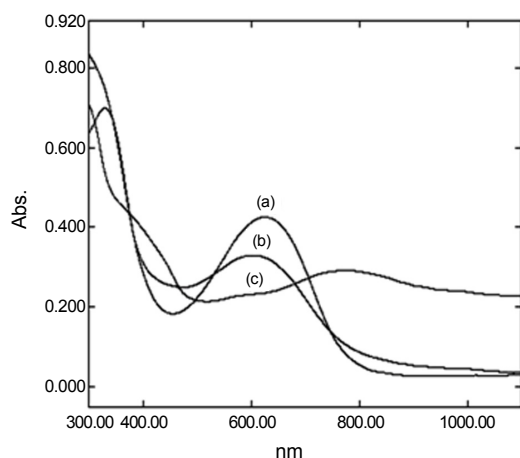


Figure 6. Electronic spectra of undoped PANI (a); undoped P(St-*co*-MSt)-*g*-PANI (b); doped P(St-*co*-MSt)-*g*-PANI with HCl (c) in DMSO solvent.

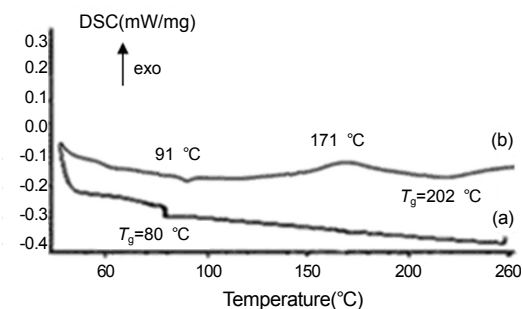


Figure 7. DSC traces of P(St-*co*-MSt) (a); P(St-*co*-MSt)-*g*-PANI (b).

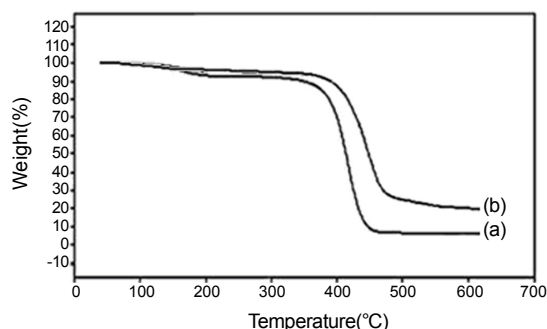


Figure 8. TGA curves of P(St-co-MSt) (a); P(St-co-MSt)-g-PANI (b).

improvement of the thermal stability for P(St-co-MSt)-g-PANI compared to P(St-co-MSt). The data of the onset of the degradation temperatures (at which 10% degradation occurs), the midpoint of the degradation temperatures (at which 50% degradation occurs) and the residue that was at 600 °C, were shifted to higher in the P(St-co-MSt)-g-PANI.

Conclusions

For the first time, synthesis of conductive polyaniline-modified polymers via nitroxide mediated radical polymerization (NMRP) was reported. The growing of aniline onto functionalized polystyrene and poly(*p*-methylstyrene) copolymer enhanced its solubility in common organic solvents, processability and changed its properties. The conductivity of P(St-co-MSt)-g-PANI was measured using four-point probe technique. The conductivity value of terpolymer was $\sigma=0.084 \text{ Scm}^{-1}$. The cyclic voltammograms of P(St-co-MSt)-g-PANI terpolymer showed some qualitative similarities with those of pure polyaniline. At a low scan rate, the terpolymer films showed two oxidation peaks and two reduction peaks corresponding to the Epa and Epc values. The cyclic voltammograms of P(St-co-MSt)-g-PANI exhibited that the synthesized terpolymer had relatively good electroactivity. The doped state of P(St-co-MSt)-g-PANI showed the polaronic band, at longer wavelength than that of the doped pure PANI in the UV-Vis spectroscopy. The thermal stability and glass transition temperature of P(St-co-MSt)-g-PANI improved observably in comparison with pure P(St-co-MSt).

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