Chemical Modification of Polyaniline by N-Grafting of Polystyrene Synthesized via ATRP

Homa Gheybi, Mojtaba Abbasian, Peyman Najafi Moghaddam, Ali Akbar Entezami

Laboratory of Polymer, Faculty of Chemistry, University of Tabriz, Tabriz, Iran

ABSTRACT: The N-substituted polyaniline (PANi) was synthesized by incorporation of bromine-terminated polystyrene (PS-Br) onto the emeraldine form of polyaniline. End brominated polystyrene was synthesized by atom transfer radical polymerization (ATRP) technique and then deprotonated polyaniline was reacted with PS-Br to prepare PS-grafted PANi (PS-*g*-PANi) copolymer through N-grafting reaction. The degree of N-grafting can be controlled by adjusting the molar feed ratio of PS-Br to the number of repeat units of PANi. The microstructure and compositions of the PS-*g*-PANi copolymers with different degrees of N-substitution were characterized by FT-IR, elemental analysis, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The cyclicvoltammetry shows that the electroactivity of N-substituted PANi is strongly dependent on the degree of N-grafting. The solubility of PS-*g*-PANi copolymers in common organic solvents such as tetrahydrofuran and chloroform was improved by increasing the degree of N-grafting, and also the samples are partially soluble in xylene. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3495–3501, 2007

Key words: conducting polymer; polyaniline; polystyrene; ATRP; N-substitution

INTRODUCTION

Polyaniline has been the subject of considerable scientific inquiry because of its unique electrical behavior, its potential as an environmentally stable conducting polymer[1] and wide applications in different fields, such as microelectronics,[2,3] sensors,[4,5] electrodes,[6,7] corrosion protection,[8,9] and release devices.[10,11] 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 (PANi).[12,13] To improve its processability, various procedures have been adapted. For example, self doped PANi with sulfonic acid groups substituted onto the polymer[14,15] have been synthesized. Several ring- and N-substituted PANi, soluble in common organic solvents, have been prepared directly from polymerization of the corresponding aniline monomers.[16–18] The incorporation of the side groups into polyaniline has enhanced its solubility and processability and changed its properties.[19,20] Hosseini was reported the growing of aniline onto functionalized polystyrene.[21] Another approach toward soluble polyaniline is copolymerization of aniline with a suitable substituted aniline to produce copolymers. The obtained copolymers have improved in solubility.[22] To improve melt and solution processability, the majority of polyaniline modifications to date have been made by the incorporation of substituents on the polymer backbone.[13] Flexible alkyl chains,[23] poly(ethylenglycol) chain,[24] and polyether chain[25] have been incorporated onto PANi through N-alkylation method. In this article, a new N-substituted PANi is synthesized by insertion of bromine-terminated polystyrene (PS-Br) onto the polyaniline backbone. Polystyrene is gaining wide recognition as it possesses many unique properties, such as solubility in organic solvents and good mechanical properties. Thus, incorporation of polystyrene into polyaniline may endow the resulted copolymer with new and interesting properties. For instances, the process may enhance the solubility and the processability of polyaniline. PS-Br was synthesized via atom transfer radical polymerization (ATRP) technique.[26–29]

EXPERIMENTAL

Materials

Aniline from Merck was distilled twice under a reduced pressure before use. Styrene from Tabriz petrochemical company was distilled under a reduced pressure. Ammonium persulfate (Merck) was recrystallized at room temperature from EtOH/water. 2.2′-bipyridine (Merck) was used as received. Copper (I) chloride (Merck) was purified by stirring in glacial

---

acetic acid, then washing with methanol, and finally drying under reduced pressure. Butyllithium (BuLi) was purchased from Merck and titrated with diphenylacetic acid before use. Benzylbromide (Merck) was purified by distillation under vacuum. Dimethylsulfoxide (Fluka) was totally dried and then distilled under reduced pressure. Freshly tetrahydrofuran was dried and distilled under argon atmosphere.

Preparation of polyaniline

Polyaniline was synthesized by oxidative polymerization of aniline according to the method reported in the literature.[1] Thus, 0.1 mol of aniline was dissolved in 123 mL of $1.7M$ HCl. The solution was kept at 0°C under an argon atmosphere. A prechilled solution of 0.1 mol of ammonium persulfate in 134 mL of $1.7M$ HCl was added slowly with vigorous stirring. The reaction mixture was agitated continuously for another 5 h. The precipitate was subsequently filtered, washed several times with methanol, and finally a colorless filtrate was obtained. The collected green-black polyaniline salts were added into ammonia solution ($1.7M$) and stirred for 2 h. The undoped polyaniline was filtered and washed several times with water. The resulted powder was dried at 50°C under reduced pressure.

Synthesis of PS-Br via ATRP

Styrene (10.4 g, 100 mmol, 100 equiv), benzyl bromide (1 mmol, 1 equiv) (initiator), bipyridine (0.468 g, 3 mmol, 3 equiv) (ligand), CuCl (0.0995 g, 1 mmol, 1 equiv) (catalyst) were added into a glass tube. The mixture in the tube was degassed by freeze–pump–thaw cycles for five times to remove the oxygen. Then the tube was sealed under vacuum and shacked in the oil bath at (90 ± 1)°C. After a predetermined polymerization time, the tube was opened and the mixture was poured in a suitable nonsolvent (methanol) to precipitate the polymer. The resulted polymer was dissolved in acetone completely and then filtered to remove the insoluble salts and most of the bipyridine. The filtered polymer solution was poured into methanol to precipitate the polymer. After repeating the dissolution and precipitation process another two times to remove the catalyst, the polymer dried under reduced pressure at 50°C.[30,31]

Preparation of graft copolymer

The reaction flask was dried and kept under an inert atmosphere throughout the reactions by a constant flow of argon. The emeraldine base form of polyaniline (0.1 g) was dissolved in 40-mL DMSO. The solution was cooled to 0°C and predetermined amount of BuLi was added with stirring. The color of the solution changed from dark blue to green-black. In other dried flask, PS-Br was dissolved in 10 mL of tetrahydrofuran (THF) under argon atmosphere. This solution was added to the reaction mixture. The reaction was stirred under argon atmosphere at 60°C for 24 h. The color of the solution turned blue gradually. The amount of PS-Br added dictated the resulting copolymer composition. The reaction mixture was poured into methanol to precipitate the copolymer. The precipitate was filtered, added to cyclohexane, and refluxed to remove the residual amount of unreacted PS-Br. Low and moderate PS grafted copolymers were insoluble in hot cyclohexane, high PS grafted copolymer is partially soluble in hot cyclohexane, while unreacted PS-Br is completely soluble in hot cyclohexane.

Characterization

FT-IR spectra were recorded using Shimadzu FT-IR-8101 M. The samples were prepared in the pellet form using spectroscopic grade KBr powder. The contents of C, H, and N in the samples were determined by elemental analysis using Heareus CHN-ORAPID instrument. C/N ratios indicated the degree of N-grafting. Morphological studies were performed with the help of LEO 440 i scanning electron microscope. Differential scanning calorimetry (DSC) analysis was performed on a Mettler 4000 TA thermal analytical system up to 400°C at a heating rate of 10°C/min. Molecular weight of PS-Br determined by gel permeation chromatography (GPC) with a maxima 820 GPC analysis instrument using polystyrene (10^6, 10^5, 10^4 Å) calibration standards with a THF mobile phase. Cast films were prepared, using solutions containing 4–5 mg of copolymer powder in 2 mL of tetrahydrofuran, which evaporate easily, allowing the formation of a thin copolymer film onto a glass carbon (GC) electrode for electrochemical studies.

RESULT AND DISCUSSION

ATRP is one of the living polymerization methods which allows for the controlled polymerization of many vinyl monomers, such as styrene and acrylonitrile by a radical approach.[32] Inherent in the mechanism of ATRP is the incorporation of the halogen at the chain ends. Halogen ATRP of styrene in bulk have been proceeded with various types of alkyl halides as initiators and CuX (X=Cl, Br)/2, 2'- bipyridine complex as catalyst.[33,34] The molecular weight of PS-Br was determined by GPC. M_n = 4560; (M_w = 6360; polydispersity = 1.39).
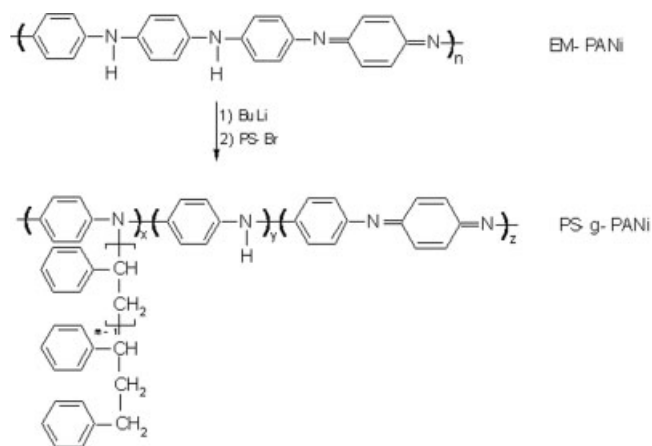
Scheme 1 Synthetic route of N-grafted polyaniline.

At the next step, reaction of EM-PANi with BuLi caused partial deprotonation of NH groups, and subsequent treatment with PS-Br provided graft copolymers. The degree of N-grafting can be controlled by adjusting the molar ratio of BuLi and PS-Br to the number of repeat units of PANi. Synthetic route of N-grafted polyaniline is shown in Scheme 1.

The elemental analysis was carried out to know about the composition of the copolymers with various elements such as C, H, and N present in the polymer matrix. Table I shows the compositions of the PS-g-PANi samples prepared under different feed ratios of BuLi and PS-Br to aniline in EM. The higher values of %C and %H in PS-PANi samples are obviously due to the presence of the PS chains on the nitrogen atoms. As shown in Table I, the degree of N-grafting reasonably increased with increase in the amount of BuLi and PS-Br, however, it was somewhat lower than the value calculated from the amount of BuLi per the NH group, which may arise from incomplete deprotonation of NH groups by BuLi[35] or incomplete reaction of PS-Br with nitrogens of PANi having negative charge, perhaps due to the effect of steric hindrance on grafting. Figure 1 shows the FT-IR spectra of the PANi and graft copolymers. In PS-g-PANi samples, the charac-

teristic absorption band of polyaniline, namely, the C=N in the quinoidal units which appears at 1585 cm^{-1}, the benzenoid stretches at 1490 cm^{-1}, the N—H stretches at 3270 cm^{-1}, and the aromatic C—H stretches at 3020 cm^{-1} were observed.[36] The C$_{aromatic}$—N stretching band of an aromatic amine appears at 1300 cm^{-1}.[19] The absorption peak at 1157 cm^{-1} is characteristic of electron-like absorption of the N=Q=N vibration (where Q denotes the quinoid ring).[37] The presence of the absorption peak at 1223 cm^{-1} attributed to the aliphatic C—N stretching suggests that the polystyrene chains are linked on the nitrogens of polyaniline, while neither the position nor the intensity of the aromatic C—N stretching band at 1300 cm^{-1} changes after grafting.[38] The absorption band at 827 cm^{-1}, characteristic of the out-of-plane bending vibration of the 1, 4-disubstituted benzene ring, together with the absence of a splitting of this peak into two peaks at 820 and 870 cm^{-1}, indicates that no ring substitution occurred in the grafting reaction.[19,39] Polystyrene has characteristic peaks at 2919 and 2852 cm^{-1}, attributed to aliphatic C—H stretchings, and 758 and 697 cm^{-1} corresponded to out-of-plane hydrogen deformation that indicate the existence of the polystyrene chains in our samples.[40] The solubilities of the N-grafted copolymers in common organic solvents are shown in Table II. Polystyrene has excellent solubility in nonpolar solvents. Because of incorporation of polystyrene to the polyaniline backbone, solubility of PS-g-PANi samples are increased in the low boiling point solvents such as THF, CH$_2$Cl$_2$, and CHCl$_3$. Also PS-g-PANi samples are partially soluble in xylene, whereas polyaniline is not. The concentration used in the solubility tests was 10 mg of copolymers in 1 mL of solvents (10%). The increase in solubility can be attributed to the lowering in polarity and stiffness of the polymer chains by an incorporation of the polystyrene chains. But highly polar solvents such as N-methyl 2-pyrrolidone (NMP) and DMSO, which are good solvents for PANi, are no longer good solvents for these N-grafted polyanilines, resulting from the lack of amine hydrogen in the N-grafted polyanilines to provide hydrogen bonding

TABLE I
Compositions of the PS-g-PANi Copolymers

Polymers	Feed amount[a]		Compositions[b]			Degree of N-grafting
	BuLi	PS-Br	C%	H%	N%	
Polyaniline	–	–	76.1	4.6	14.2	–
PS-g-PANi no. 1	0.2	0.07	80.4	6.0	8.3	0.03
PS-g-PANi no. 2	0.4	0.14	81.9	6.1	6.3	0.05
PS-g-PANi no. 3	0.6	0.21	83.0	6.5	5.2	0.07

[a] Molar ratio of BuLi and PS-Br per the polyaniline unit.
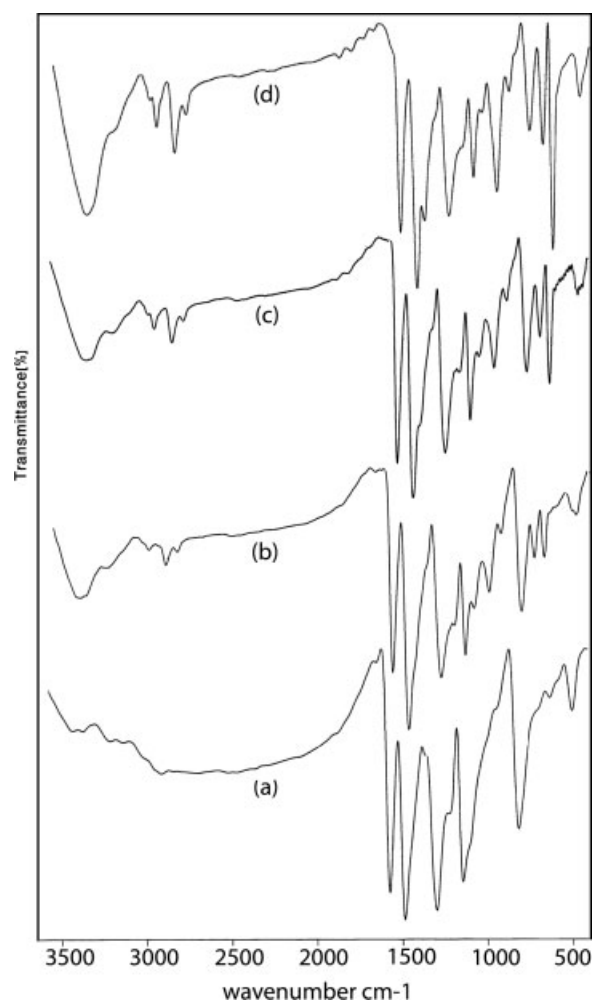[b] Determined by elemental analysis.

Figure 1 FT-IR spectra of the PANi and graft copolymers (a) Polyaniline (b) Low PS grafted PANi (PS-*g*-PANi no. 1) (c) Moderate PS grafted PANi (PS-*g*-PANi no. 2) (d) High PS grafted PANi (PS-*g*-PANi no. 3).

interaction with and solvation by the solvents.[41] Figure 2 shows the DSC thermogram of PS-*g*-PANi copolymers. Curve *a* in Figure 2 shows the thermogram obtained in the case of low PS grafted copolymer (sample 1). The endothermic peaks seen at 69 and 117°C in this curve have been attributed to the evaporation of any residual water and solvent. A

strong exothermic peak appears at 305°C that indicates the degradation of this copolymer. Curve *b* is the thermogram observed in the case of moderate PS grafted copolymer (sample 2). Two endothermic peaks appear at 74 and 116°C attributed to the evaporation of water and solvent molecules present in the polymer matrix. The exothermic peak at 301°C is due to degradation of this copolymer. The transition observed at 176°C can be designed as the glass transition temperature. Curve *c* shows the thermogram of high PS grafted copolymer (sample 3). This curve exhibits an endothermic peak at 79°C corresponding to evaporation of eventual water and an exothermic peak at 292°C corresponding to the degradation of copolymer. The transition appears at 196°C can be attributed to the glass transition of this sample. We notice that the exothermic peak in all curves appears at lower temperatures with the increasing of polystyrene concentration in the copolymer. Polystyrene chains bonded to the backbone of PANi lead to more flexibility in copolymer structure and cause to the degradation at lower temperatures. The thermogram also confirms the absence of any melting (T_m) for all of the samples.

Scanning electron microscopy (SEM) is used to characterize the morphology of PS-*g*-PANi samples. As shown in Figure 3, SEM reveals some variations in the morphological structure of polyaniline and PS-*g*-PANi samples. Polyaniline exhibits a sponge-like structure with small particle size, whereas in grafted samples, particles become larger that lead to the compressed structures. This variation can be explained by grafting of polystyrene chains onto the nitrogen atoms of polyaniline backbone, which results in bulky structures in obtained copolymers. The degree of N-grafting was found to affect the PS-*g*-PANi morphology. The increase in mole ratio of polystyrene in grafting process, leads to more compressed structures. As shown in Figure 3(a–c), the structure of the samples with moderate mole ratio of polystyrene [Fig. 3(c)] is more compressed than the sample with lower values of polystyrene [Fig. 3(b)]. Figure 4(a,b) show voltammograms of two samples of PS-*g*-PANi copolymers with low and high PS grafting. The polymer films were prepared on GC

TABLE II
Solubilities of the PS-*g*-PANi Samples in Common Organic Solvents

Polymers	NMP	DMSO	THF	CHCl₃	CH₂Cl₂	Cyclohexane	Xylene
Polyaniline	++	++	+	+	−	−	−
PS-*g*-PANi no. 1	++	++	+	+	+	−	−
PS-*g*-PANi no. 2	+	+	++	+	+	+	+
PS-*g*-PANi no. 3	+	+	++	++	++	++	++

++, soluble; +, partially soluble; −, insoluble.
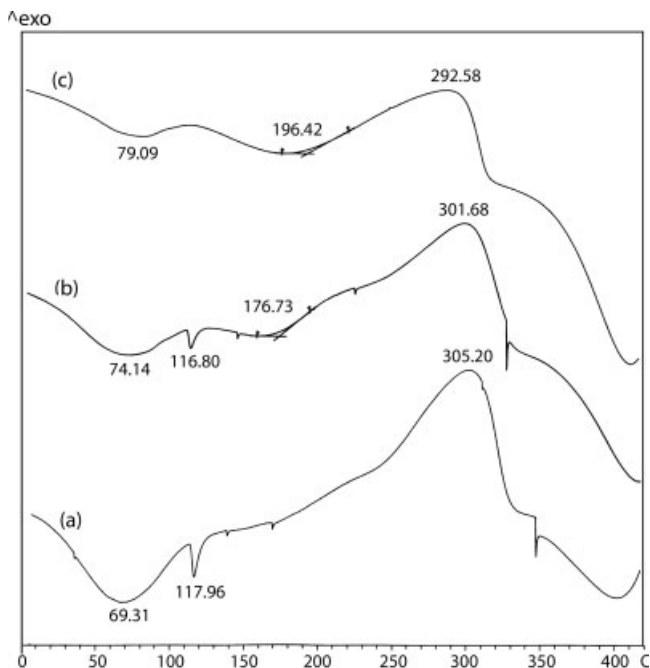The concentration used in the solubility test was 10 mg of each copolymer in 1 mL of solvents.

Figure 2 DCS thermograms of prepared copolymers (a) Low PS grafted PANi (PS-*g*-PANi no. 1) (b) Moderate PS grafted PANi (PS-*g*-PANi no. 2) (c) High PS grafted PANi (PS-*g*-PANi no. 3).

electrode by casting. Cyclic voltammetry curves of PS-*g*-PANi samples recorded at different scan rates between −0.6 and 1.0 V vs. SCE in 0.5M camphorsulfonic acid show that they are electroactive polymers. As shown in Figure 4(a,b), cyclic voltammograms of PS-*g*-PANi copolymers exhibit some qualitative similarities with those of unsubstituted polyaniline. At a low scan rate (25 m V/s), the copolymer films show two oxidation peaks and two reduction peaks corresponding to the E_{pa} and E_{pc} values. The peaks are ascribed to polaronic and bipolaronic transitions for the first and second peaks, respectively.[42,43] As show in Figure 4(b), with the increasing of polystyrene percentage in copolymer composition, the voltammogram of copolymer exhibits only one peak at high scan rates. It can be explained by decreasing in electroactivity of obtained copolymer with high polystyrene grafting that caused to the resistance of this copolymer to oxidation. Figure 4(c) shows a linear relationship between the current and scan rate, indicating that adsorption-limited process.[44] Also these figures show the dependence of the electroactivity of the PS-*g*-PANi copolymers as a function of the concentration of polystyrene in the graft copolymer. The electroactivity of the copolymers exhibit a decrease with the increase in value of polystyrene in the copolymer. The sample with higher degree of N-grafting (sample 3) shows lower electroactivity.
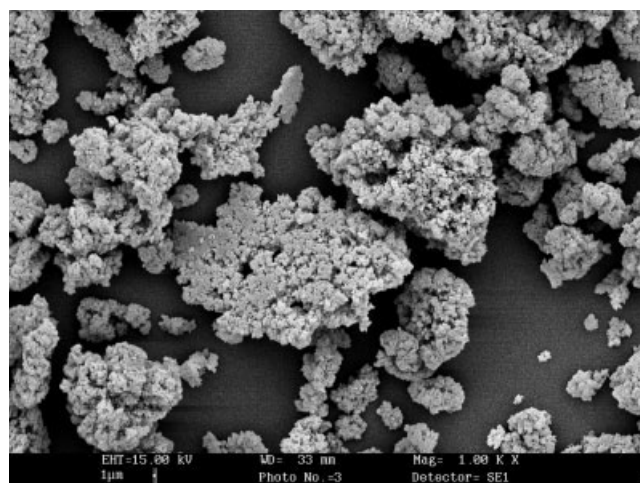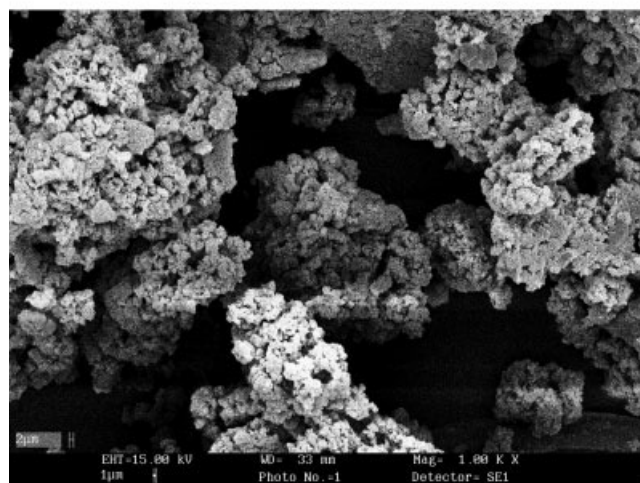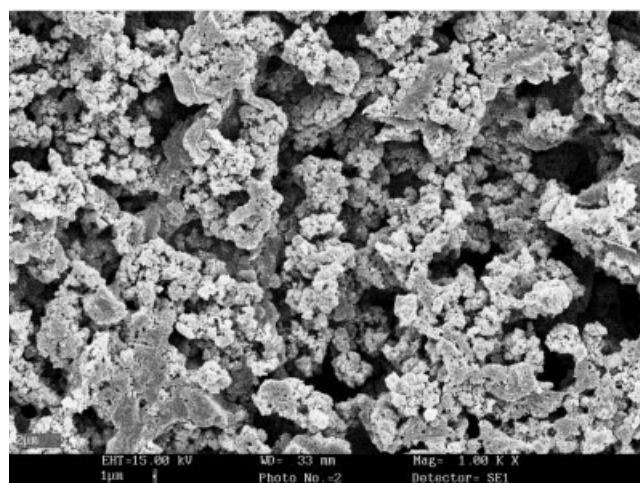
Figure 3 SEM of PS-*g*-PANi samples (a) Polyaniline (b) Low PS grafted PANi (PS-*g*-PANi no. 1) (c) Moderate PS grafted PANi (PS-*g*-PANi no. 2).
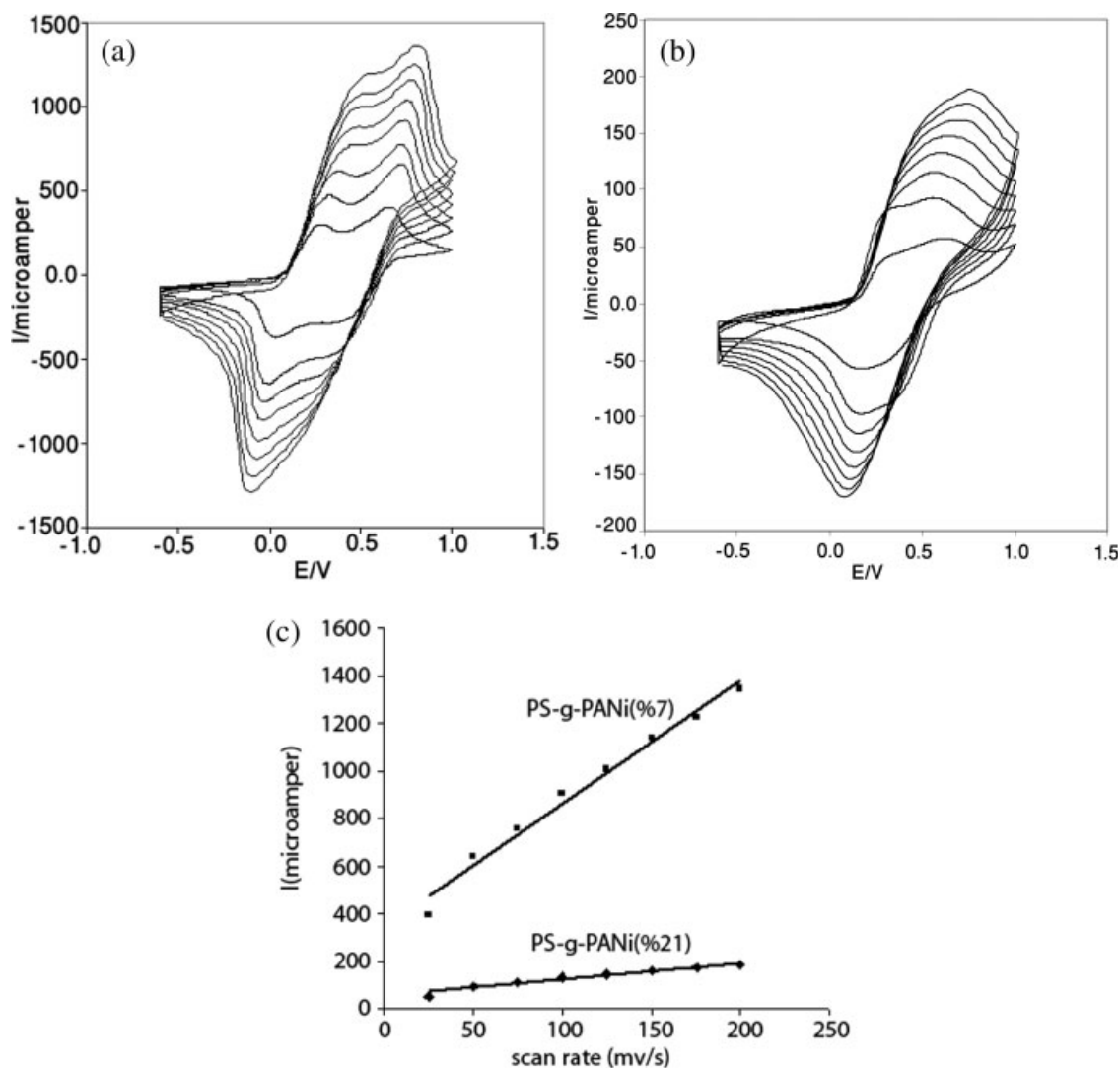
Figure 4 Cyclic voltammetry curves of PS-*g*-PANi samples (a) Low PS grafted PANi (PS-*g*-PANi no. 1) (b) High PS grafted PANi (PS-*g*-PANi no. 3) (c) Linear relationship between the current and scan rate.

CONCLUSION

The reaction of polyaniline in the emeraldine state with PS-Br was investigated in this work. PS-Br was prepared by ATRP method. The substitution of the amine nitrogen of the polyaniline units results in the formation of negatively charged nitrogen by treatment of EM base with BuLi and subsequent incorporation of PS-Br chains onto polyaniline backbone. The properties of resulted copolymers are attributed to the degree of N-grafting. The PS-*g*-PANi copolymers exhibited enhanced solubility in common organic solvents (such as tetrahydrofuran, chloroform, cyclohexane, and xylene). With the increase in the degree of N-grafting, the electroactivity of copolymer is decreased. Investigation of thermal behavior of copolymers shows the increased flexibility due to the substitution.

References

1. Kaplan, S.; Conwell, E. M.; Richter, A. F.; MacDiarmid, A. G. Macromolecules 1989, 22, 1669.
2. Carswell, A. D. W.; O'Rear, E. A.; Grady, B. P. J Am Chem Soc 2003, 125, 14793.
3. Lee, C. W.; Kim, Y. B.; Lee, S. H. Chem Mater 2005, 17, 366.
4. Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. J Am Chem Soc 2003, 125, 314.
5. Hosseini, S. H.; Entezami, A. A. Polym Adv Technol 2001, 12, 482.
6. Cao, T.; Wei, L.; Yang, S. Langmuir 2002, 18, 750.
7. Gharibi, H.; Zhiani, M.; Entezami, A. A.; Mirzaie, R. A.; Kheirmand, M.; Kakaei, K. J Power Sourc 2006, 155, 138.
8. Jeyaprabha, C.; Sathiyanarayanan, S.; Venkatachari, G. J Appl Polym Sci 2006, 101, 2144.
9. Ahamad, N.; MacDiarmid, A. G. Synth Met 1996, 78, 103.
10. Lira, L. M.; Córdoba de Torresi, S. I. Electrochem Commun 2005, 7, 717.
11. Massoumi, B.; Entezami, A. A. Polym Int 2002, 51, 555.
12. Angelopoulos, M.; Ray, A.; MacDiarmid, A. G.; Epstein, A. J. Synth Met 1987, 21, 12.

13. Lee, C. W.; Seo, Y. H.; Lee, S. H. Macromolecules 2004, 37, 4070.
14. Yeu, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. J Am Chem Soc 1991, 113, 2665.
15. Mu, S. Macromol Chem Phys. 2005, 206, 689.
16. Wei, Y.; Focke, W. W.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G. J Phys Chem 1989, 93, 495.
17. Kulkarni, M.; Viswanath, A. K. Eur Polym J 2004, 40, 379.
18. Chevalier, J. W.; Bergeron, J. Y.; Dao, L. H. Macromolecules 1992, 25, 3325.
19. Hwang, G. W.; Wu, K. Y.; Hua, M. Y.; Lee, H. T.; Chen, S. A. Synth Met 1998, 92, 39.
20. Chen, Y.; Kang, E. T.; Neoh, K. G.; Ma, Z. H.; Tan, K. L. Macromol Chem Phys 2001, 202, 785.
21. Hosseini, S. H. J Appl Polym Sci 2006, 101, 3920.
22. Lee, X.; Guo, X.; Zhang, L.; Wang, Y.; Su, Z. J Appl Polym Sci 2007, 103, 140.
23. Zheng, W. Y.; Levon, K.; Laakso, J.; Osterholm, J. E. Macromolecules 1994, 27, 7754.
24. Wang, P.; Tan, K. L.; Zhang, F.; Kang, E. T.; Neoh, K. G. Chem Mater 2001, 13, 581.
25. Arsalani, N.; Khavei, M.; Entezami, A. A. Iranian Polym J 2003, 12, 237.
26. Tizpar, S.; Abbasian, M.; Afshar Taromi, F.; Entezami, A. A. J Appl Polym Sci 2006, 100, 2619.
27. Abbasian, M.; Rahmani, S.; Mohammadi R.; Entezami, A. A. J Appl Polym Sci 2007, 104, 611.
28. Abbasian, M.; Entezami, A. A. Polym Adv Technol 2007, 18, 306.
29. Shoaeifar, P.; Abbasian, M.; Entezami, A. A. J Polym Res 2007, 14, 45.
30. Bibiao, J.; Jianbo, F.; Yang, Y.; Qiang, R.; Wenyum, W.; Jianjun, H. Eur Polym J 2006, 42, 179.
31. Matyjaszewski, K.; Patten, T. E.; Xia, J. H. J Am Chem Soc 1997, 119, 674.
32. Wang, J. S.; Matyjaszewski, K. Macromolecules 1995, 28, 7901.
33. Neumann, A.; Keul, H.; Höcker, H. Macromol Chem Phys 2000, 201, 980.
34. Huang, J.; Jia, S.; Siegwart, D. J.; Kowalewski, T.; Matyjaszewski, K. Macromol Chem Phys 2006, 207, 801.
35. Yasuda, T.; Yamaguchi, I.; Yamamoto, T. Synth Met 2003, 139, 35.
36. Osaheni, J. A.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S.; Sun, Y.; MacDiarmid, A. G.; J Phys Chem 1992, 96, 2830.
37. Salaneck, W. R.; Liedberg, B.; Inganäs, O.; Erlandsson, R.; Lundströrm, I.; MacDiarmid, A. G.; Halpern, M.; Somasiri, N. L. D. Mol Cryst Liq Cryst 1985, 121, 191.
38. Zhao, B.; Neoh, K. G.; Kang, E. T.; Tan, K. L. Chem Mater 2000, 12, 1800.
39. Tang, J.; Jing, X.; Wang, B.; Wang, F. Synth Met 1998, 24, 231.
40. Tarkuc, S.; Sahin, E.; Toppare, L.; Colak, D.; Cianga, I.; Yagci, Y. Polymer 2006, 47, 2001.
41. Chen, S. A.; Lee, H. T. Macromolecules 1993, 26, 3254.
42. Manohar, S. K.; MacDiarmid, A. G.; Cromack, K. R.; Ginder, J. M.; Epstein, A. J. Synth Met 1989, 29, E349.
43. Travers, J. P.; Genoud, F.; Menardo, C.; Nechtschein, M. Synth Met 1990, 35, 159.
44. Entezami, A. A.; Rahmatpour, A. Eur Polym J 1998, 34, 871.