Polymers, Composites, and Characterization of Conducting Polyfuran and Poly(2-bromoaniline)

Ayşegül Gök,[1] Bekir Sari,[2] Muzaffer Talu[2]

[1]Süleyman Demirel University, Faculty of Arts and Science, Department of Chemistry, 32260 Isparta, Turkey
[2]Gazi University, Faculty of Science, Department of Chemistry, 06500 Ankara, Turkey

ABSTRACT: Polyfuran (PFu), poly(2-bromoaniline) (P2BrAn), and poly(2-bromoaniline)/polyfuran (P2BrAn/PFu) composites were synthesized by coupling using various solvents and oxidants. 2-Bromoaniline (2BrAn) was polymerized using $FeCl_3$ and $(NH_4)_2S_2O_8$ in aqueous HCl medium. PFu was synthesized using $FeCl_3$ and $SbCl_3$ in anhydrous media ($CHCl_3$, CH_3CN). Furan was polymerized using both salts in $CHCl_3$ medium, whereas it could be polymerized using only $FeCl_3$ in CH_3CN medium. The new electrically conducting composites were prepared by chemical oxidative polymerization using polyfuran synthesized with $SbCl_3$ and poly(2-bromoaniline). The polymers and composites were characterized using conductivity, magnetic susceptibility, infrared spectra (FTIR), UV-Vis spectra, thermal analysis (TGA), and scanning electron microscopy (SEM) measurements. It was found that $PFu(SbCl_3)$ has the lowest thermal stability. Thus, the thermal stability of PFu was increased by preparing composites. The chemical structures of P2BrAns and composites have been found from UV-Vis results to contain quinone-imine units along the polymer chain. Magnetic susceptibility measurements indicated that the polymers and composites were diamagnetic or paramagnetic. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 2048–2057, 2005

Key words: conducting polymers; conjugated polymers; oxidative polymerization; poly(2-bromoaniline); polyfuran

INTRODUCTION

In recent years, conducting polymers have been studied extensively because of their potential application in light-emitting diodes,[1] batteries,[2] electromagnetic shielding,[3] antistatic coatings or fibers,[4] gas sensors,[5] corrosion protection,[6] and activators.[7] Particularly, polyaniline, polypyrrole, and polythiophene are most frequently used for these studies, because they are stable in air with high electrical conductivity and they can be easily synthesized through electrochemical or chemical polymerization.[8,9] On the other hand, much less attention has been devoted to the electrochemical or chemical synthesis and characterization, in terms of structural and electroconducting properties, of polyfurans, probably because of their less well-defined structures and poor stability.[10,11] Moreover, films of the electrically conductive polymers synthesized through electrochemical polymerization, which provides homogeneous electrical conductivity across their surface areas, have limited utility because they are not easily melted, owing to the strong intermolecular attractive force. Powders of the electrically conductive polymers synthesized through chemical poly-merization also require complicated post-treatment procedures for their applications.

Recently, extensive efforts have been directed toward improving the processability of electrically conductive polymers, by making substituted derivatives, colloidal dispersions, and coated latices. So far, although composites and copolymers of polyanilines and alkylsubstituted polyanilines have been commonly investigated,[12,13] there are fewer studies involving composites[14] and copolymers[15] of halogen substituted polyanilines, especially poly(2-bromoanilines).[16] Similarly, studies with both polyfuran and its composites are limited in number.[17]

The present study aimed to prepare and investigate polyfuran and poly(2-bromoaniline) by changing polymerization conditions. The resulting polymers and composites have been characterized by various experimental techniques. Particularly, we synthesized P2BrAn/PFu composites, which have not been investigated before, and investigated the effect of polymerization conditions upon some of their properties.

EXPERIMENTAL

Materials

Furan (Merck, Germany) and 2-bromoaniline (Merck, Germany) were distilled under vacuum prior to use. Ammonium peroxydisulfate [$(NH_4)_2S_2O_8$], antimony(III) chloride ($SbCl_3$), anhydrous ferric chloride

(FeCl$_3$), chloroform (CHCl$_3$), diethyl ether, HCl, acetonitrile (CH$_3$CN), and absolute ethanol were purchased from Merck and used as received.

Characterization

The dc electrical conductivities of polymers and composites were measured by use of a four-probe technique at room temperature. The polymer samples were made into pellets, and their conductivity levels were measured using a Nippon NP-900 multimeter (Nippon, Osaka, Japan). The magnetic susceptibility measurements of polymers were carried out using a Sherwood Scientific Model MKI Gouy Scale (Sherwood, St. Louis, MO), corresponding to the procedure reported elsewhere.[18] Fourier transform infrared (FTIR) spectra of polymers and composites were recorded using a Mattson-1000 Model spectrophotometer (Ati Unicam Ltd., Cambridge, UK) by use of the KBr disc technique. UV-Vis spectra of samples were recorded using a Unicam UV-2 Model spectrophotometer (Ati Unicam Ltd., Cambridge, UK), using DMF in the reference cells. Thermal properties were measured using TGA (Dupont 951 Model, Boston, MA) at a heating rate of 10°C/min under nitrogen atmosphere. Scanning electron microscopy measurements of polymers were done by use of a JEOL JEM 100 CX II electron microscope (JEOL, Peabody, MA).

Synthesis of P2BrAn and PFu

P2BrAn was synthesized as follows: About 100 mL of a 1.5M HCl solution containing 17.5 mmol of oxidant (FeCl$_3$ or (NH$_4$)$_2$S$_2$O$_8$) were added dropwise to 100 mL of a 1.5M HCl solution with 8.76 mmol (1.51 g) of 2-bromoaniline with stirring under a nitrogen atmosphere. The synthesis temperature was optimized (35°C for FeCl$_3$ and 30°C for (NH$_4$)$_2$S$_2$O$_8$). The reaction product was collected on a filter; washed with 1.5M HCl, distilled water, and diethyl ether; and dried in a vacuum at 70°C.

PFu was synthesized using FeCl$_3$ both in CH$_3$CN and CHCl$_3$ media, and SbCl$_3$ only in CHCl$_3$ medium. The oxidant/monomer ratio was taken as 1.5. Then the collected product was dried in vacuum at 70°C.

Synthesis of P2BrAn/PFu composites

To synthesize P2BrAn/PFu composites, P2BrAn and the synthesis salt (SbCl$_3$) of PFu were placed in a three-neck round flask and stirred in CHCl$_3$. After the SbCl$_3$ was completely dissolved, a solution of furan in CHCl$_3$ was added dropwise with vigorous stirring. The reaction was allowed to proceed for 24 h with stirring. The precipitated powder was washed with CHCl$_3$ and finally dried in vacuum at 70°C for 24 h.

TABLE I
Conductivity and Magnetic Susceptibility Values of Polymers

Polymer	Conductivity (S cm^{-1})	Magnetic susceptibility (μ_e, BM)
PFu (FeCl$_3$)[a]	2.93 × 10^{-5}	+152
PFu(FeCl$_3$)[b]	1.18 × 10^{-5}	+144
PFu(SbCl$_3$)	1.44 × 10^{-5}	−51
P2BrAn(FeCl$_3$)	1.64 × 10^{-5}	+1830
P2BrAn[(NH$_4$)$_2$S$_2$O$_8$]	1.37 × 10^{-5}	−35
P2BrAn(FeCl$_3$)/PFu(SbCl$_3$)	7.89 × 10^{-5}	−102
P2BrAn[(NH$_4$)$_2$S$_2$O$_8$]/Fu(SbCl$_3$)	8.33 × 10^{-5}	+1440

μ_e, effective magnetic moment; BM, Bohr magneton.
[a] PFu synthesized in CH$_3$CN medium.
[b] PFu synthesized in CHCl$_3$ medium.

RESULTS AND DISCUSSION

Electrical conductivity and magnetic susceptibility

The electrical conductivities and magnetic susceptibilities of homopolymers and composites are summarized in Table I. The conductivity values of P2BrAn are low as compared with those of nonsubstituted PAns[19] and similar to those shown by alkylsubstituted and halogen substituted PAns.[20,21] P2BrAns have higher values than those of Cl and Br dihalogaNeted PAns.[22] However, P2BrAns synthesized using FeCl$_3$ and (NH$_4$)$_2$S$_2$O$_8$ salts have nearly the same conductivity values (10^{-5} Scm^{-1}); these values are higher than some literature values.[23] Similarly, the conductivities of PFu obtained using different media are similar to each other; however, these values are higher than those given in literature for PFu.[17]

Among the composites, the highest conductivity value obtained is 8.33 × 10^{-5} S cm^{-1} for P2BrAn-[(NH$_4$)$_2$S$_2$O$_8$]/PFu(SbCl$_3$). It can be seen from Table I that the conductivities of composites are to some extent higher than those of homopolymers. The higher regioregularity on the polymer backbone in the composites may be responsible for the higher conductivities.

Magnetic susceptibility data of the polymers are also given in Table I. The values obtained from Gouy measurements demonstrated that the prepared polymer samples had both diamagnetic and paramagnetic properties, and their conducting mechanisms are of "bipolaron" and "polaron" natures.[24] The reason for high positive values in polymers synthesized using FeCl$_3$ may be attributed to Fe(III) counter-ions remaining in the polymer; though it is interesting that, different from P2BrAn[(NH$_4$)$_2$S$_2$O$_8$] and PFu (SbCl$_3$) homopolymers, their composite has a polaron structure.

FTIR spectroscopy

The IR spectra of the monomer and P2BrAn[(NH$_4$)$_2$S$_2$O$_8$] are displayed in Figures 1a and b, respectively. The
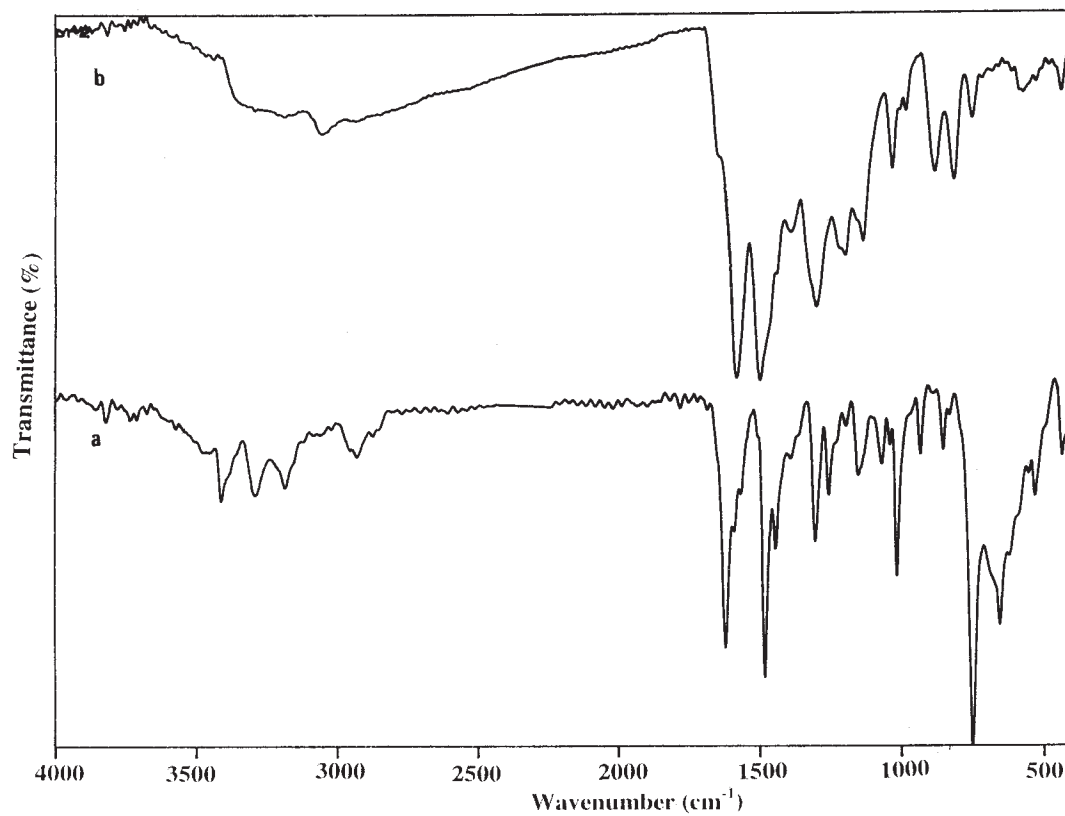
Figure 1   FTIR spectra of (a) 2BrAn (monomer), and (b) P2BrAn[$(NH_4)_2S_2O_8$].
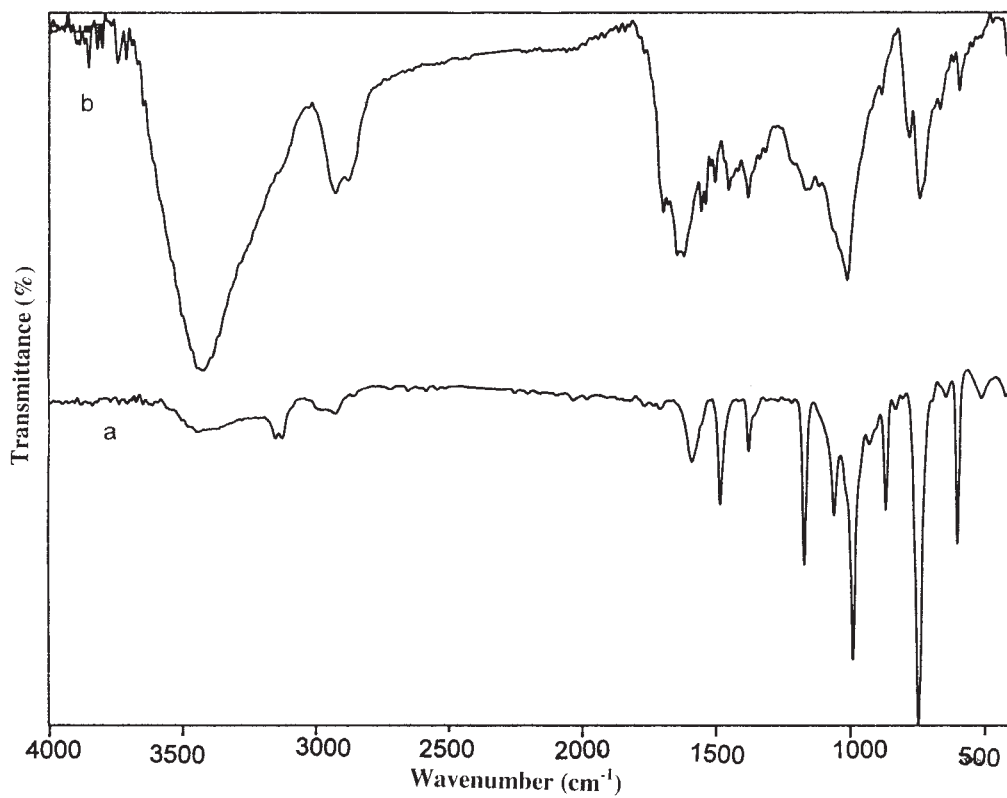

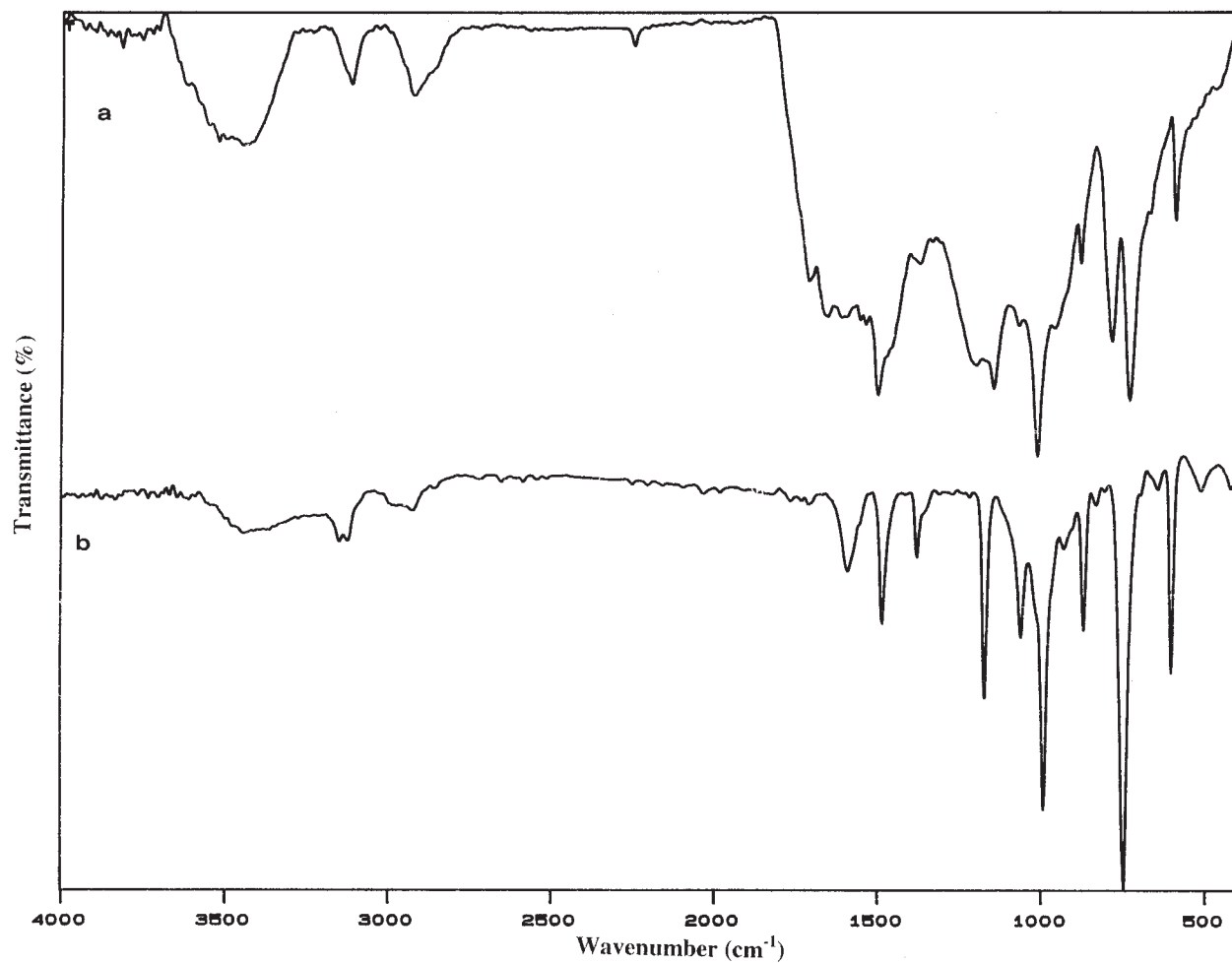**Figure 2**   FTIR spectra of (a) furan, and (b) PFu ($SbCl_3$).
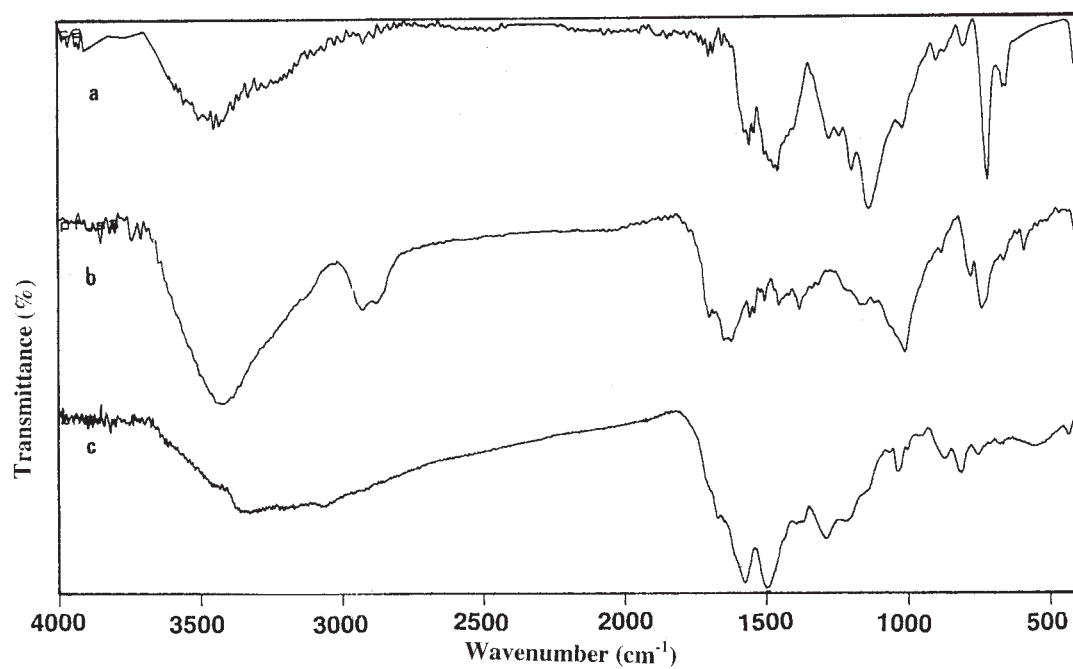
Figure 3   FTIR spectra of (a) furan, and (b) PFu (FeCl$_3$).

Figure 4   FTIR spectra of polymers: (a) P2BrAn[(NH$_4$)$_2$S$_2$O$_8$]/PFu(SbCl$_3$), (b) PFu(SbCl$_3$), and (c) P2BrAn[(NH$_4$)$_2$S$_2$O$_8$].
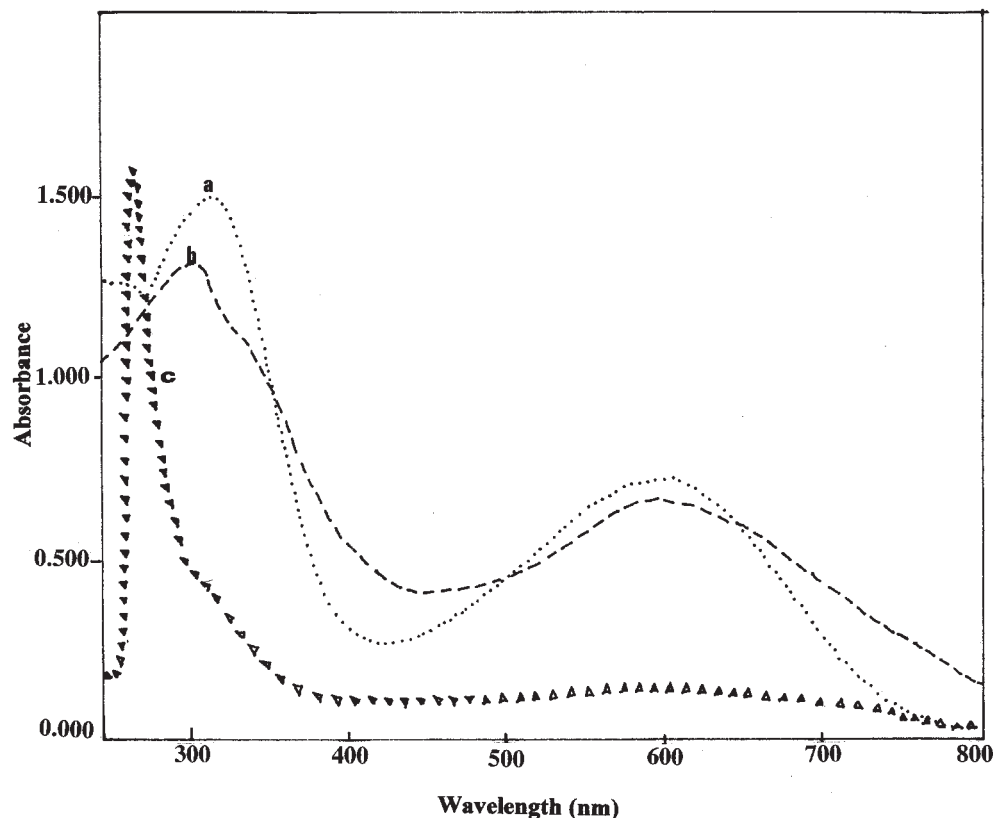
Figure 5   UV-Vis spectra of doped (a) P2BrAn[(NH$_4$)$_2$S$_2$O$_8$], (b) P2BrAn(FeCl$_3$), and (c) P2BrAn[(NH$_4$)$_2$S$_2$O$_8$]/PFu(SbCl$_3$).

main peaks of the IR spectra of P2BrAns are located in the region from 450 to 1800 cm^{-1}, as expected from the benzene-ring absorption. However, special attention has to be directed to the absorptions at 1580 and 1490 cm^{-1} assigned to C=C stretching of the quinoid and benzenoid units, respectively, because their intensities provide information related to the potential conductivity of the polymer.[14] The infrared spectra of P2BrAn salts are similar to each other. In the region of 1010–1170 cm^{-1}, aromatic C-H in-plane-bending modes are usually observed. For P2BrAn, a band characteristically appears at 1150 cm^{-1}, which has been explained as an electronic band or a vibrational band of nitrogen quinone.[25]

The C-H out-of-plane bending mode has been used as a key to identify the type of substituted benzene. For the P2BrAn salts, this mode was observed in the range 840–880 cm^{-1}, such as was reported for a 1,4-substituted benzene.[26] The IR spectrum of P2BrAn[(NH$_4$)$_2$S$_2$O$_8$] closely matches with that of P2BrAn (FeCl$_3$) salts.

The FTIR spectra of PFu(SbCl$_3$) and PFu(FeCl$_3$)^a (Figs. 2 and 3) show C-H deformation in the region of 760 and 740 cm^{-1}, and 733 and 796 cm^{-1}, attributable to deformation of the aromatic and olefinic hydrogen atom, respectively.[27] The presence of the conjugated PFu is supported with symmetric and asymmetric C=C bands in 1171 and 1151 cm^{-1} of the furan ring

and C-O-C bands corresponding to plane deformation in 1022 and 1016 cm^{-1}.[28] Furthermore, presence of C-H deformation in the region of 760–740 cm^{-1} and 796–733 cm^{-1} indicates that coupling of the radical cation is α, β instead of α, α coupling.[29]

The FTIR spectrum (Fig. 4a) of the P2BrAn-[(NH$_4$)$_2$S$_2$O$_8$]/PFu(SbCl$_3$) composite contains the main bands of both PFu and P2BrAn (Figs. 4b and 4c). Similar results were also obtained for the polyaniline/ poly(ethylmethacrylate) (PEMA) composite.[30] The intensities of the infrared bands of composites are different from in the pure polymers.

Electronic absorption spectra

P2BrAn salts and composites were dissolved in DMF, but only small quantities of the samples were soluble in DMF. The electronic absorption spectrum of the solution was recorded. The absorption spectra of P2BrAn [(NH$_4$)$_2$S$_2$O$_8$] and its composite are shown in Figure 5. The spectrum of PFu was not recorded due to its insolubility in common solvents. The UV-Vis spectra of P2BrAn composites resemble the spectrum of the emeraldine salt P2BrAn. The maximum absorbance wavelengths of the polymers are listed in Table II. The absorption maxima (λ_{max}) are seen at λ_1(nm) and λ_2(nm) for the doped P2BrAns and composites.

TABLE II
UV-Vis Results of Polymers

Polymer	λ_1 (nm)	λ_2 (nm)
P2BrAn(FeCl$_3$)	315	579
P2BrAn[(NH$_4$)$_2$S$_2$O$_8$]	313	598
P2BrAn(FeCl$_3$)/PFu(SbCl$_3$)	279	602
P2BrAn[(NH$_4$)$_2$S$_2$O$_8$]/PFu(SbCl$_3$)	269	607

The absorption bands that appear at $\lambda_1 = 269$–315 nm in the case of polymers are due to $\pi \rightarrow \pi^*$ transitions,[31] and the absorption bands that appear in the visible region at $\lambda_2 = 579$–607 nm show an excitation transition due to the high conjugation of the aromatic polymeric chains.[32] The excitation transitions associated with the polymer conductivities are shifted to lower energies. The variations at wavelengths of the composites may be the effect of composite formation of P2BrAn with PFu.

Thermal studies

Thermal analysis patterns of the polymers show the relative thermal stability of doped P2BrAns, PFus, and the composites, respectively, in Figures 6–8. In all the thermograms, a small weight loss of 3–8%, below 100°C, occurs, presumably due to the loss of water and low molecular weight oligomers for P2BrAns and composites.[33] For polyfurans, the reason of the weight loss may be attributed to the residue solvent, monomer, and low molecular weight oligomers. TGA results were also tabulated in Table III. As seen from Table III, decomposition temperatures (T$_i$, T$_m$, T$_f$) of polymers are different from each other. PFu(FeCl$_3$)^a, PFu(FeCl$_3$)^b, P2BrAn(FeCl$_3$), and P2BrAn(FeCl$_3$)/PFu(SbCl$_3$) decompose with two steps, whereas P2BrAn[(NH$_4$)$_2$S$_2$O$_8$]/PFu composite and P2BrAn[(NH$_4$)$_2$S$_2$O$_8$] with one step, and PFu(SbCl$_3$) with three steps. A significant weight loss starts at the second step, and this weight loss represents a dopant loss.[34] At the third step, degradation of the polymer backbone starts to occur.[35]

Among the polyfurans, PFu(FeCl$_3$)^b synthesized in chloroform media has the highest thermal stability and PFu(SbCl$_3$) has the lowest thermal stability, according to initial decomposition temperature. It was seen that P2BrAns are thermally more stable than PFus. The reason for this may arise from the lower molecular weight of PFus. Especially, among all the homopolymers, P2BrAn[(NH$_4$)$_2$S$_2$O$_8$}] is the most stable. To increase thermal stability of PFu(SbCl$_3$), its composites with P2BrAns were prepared. Consequently, as seen from Table III, the thermal stability of P2BrAn/PFu composites is higher than that of PFu(SbCl$_3$). However, its thermal property lies between those pure P2BrAn and pure PFu, which it contains in its structure. Thus, these data confirm the enhanced thermogravimetric stability of the P2BrAn/PFu composite relative to that of PFu.
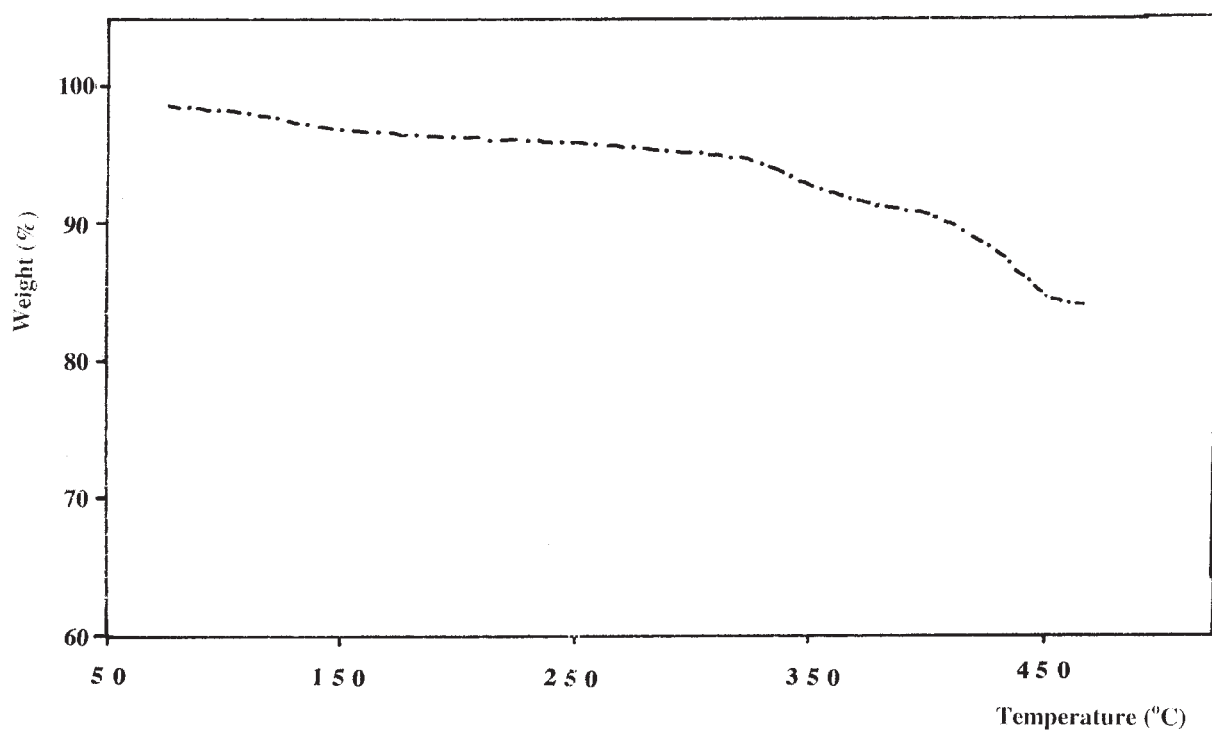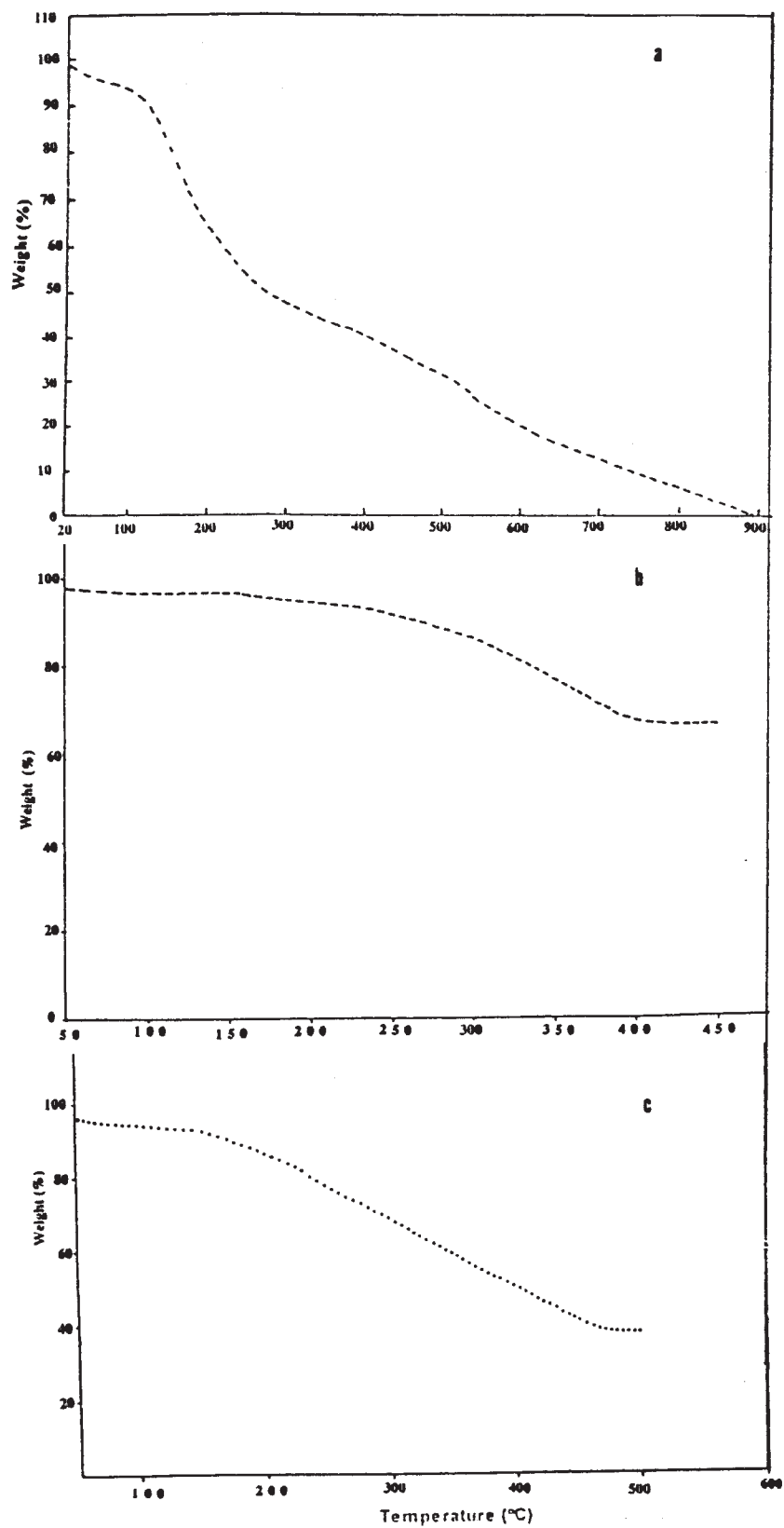

Figure 6 TGA thermogram of P2BrAn[(NH$_4$)$_2$S$_2$O$_8$].

Figure 7 TGA thermograms of polyfurans (a) PFu(SbCl$_3$), (b) PFu(FeCl$_3$)[a], and (c) PFu(FeCl$_3$).
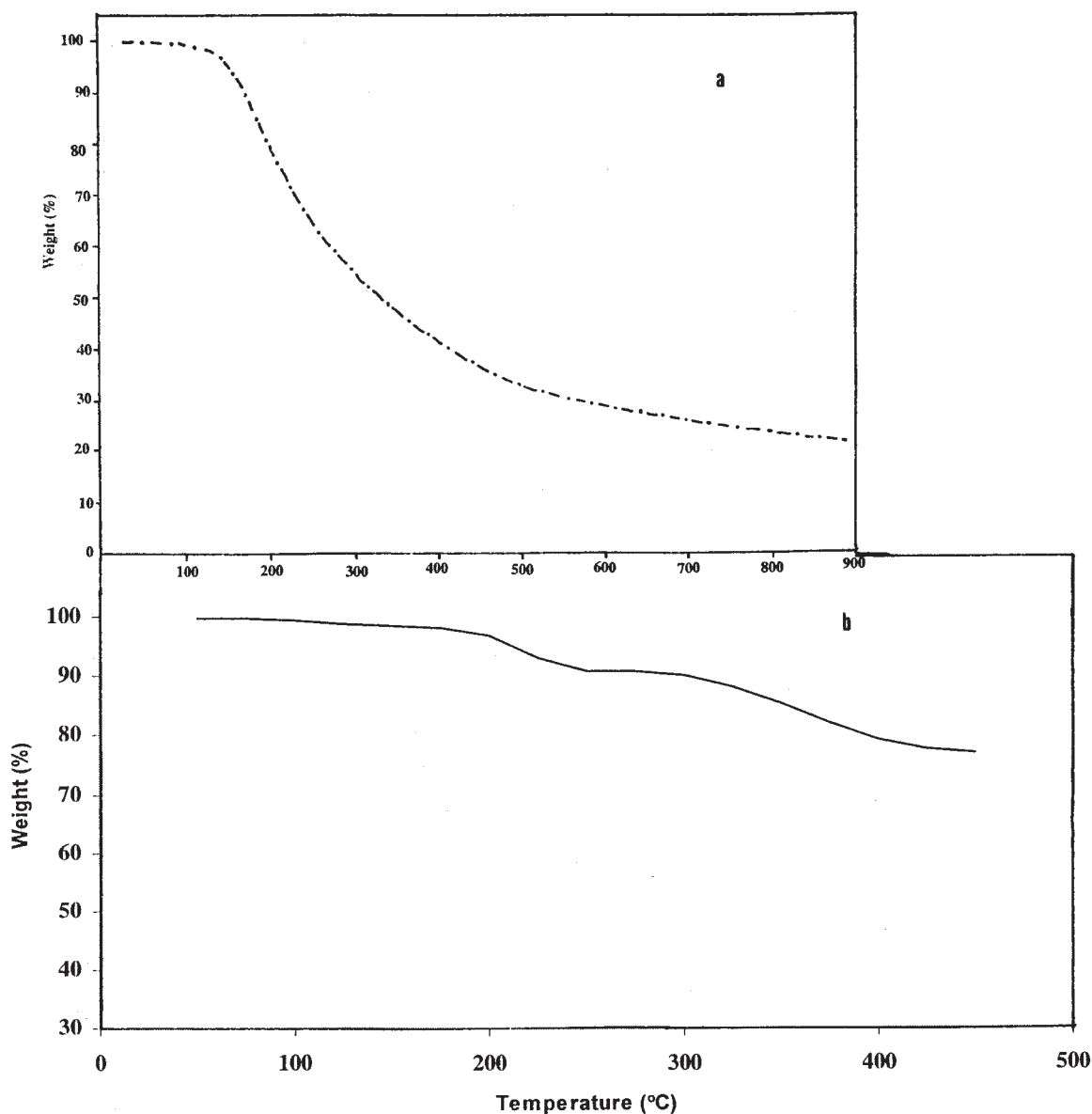
Figure 8   TGA thermograms of composites (a) P2BrAn[(NH$_4$)$_2$S$_2$O$_8$]/PFu(SbCl$_3$), and (b) P2BrAn(FeCl$_3$)/PFu(SbCl$_3$).

Scanning electron microscopy (SEM)

Scanning electron micrographs of pure P2BrAn-[(NH$_4$)$_2$S$_2$O$_8$] and P2BrAn(FeCl$_3$) are illustrated in Figures 9a and b. The morphology of P2BrAns is greatly affected by the type of dopant salt used, as shown in Figures 9a and b.[36] P2BrAn[(NH$_4$)$_2$S$_2$O$_8$] shows a granular structure, whereas P2BrAn(FeCl$_3$) shows a practically porous structure with particles. The morphology of PFu (Fig. 9c) shows a structure changing from granular to uniform. The P2BrAn[(NH$_4$)$_2$S$_2$O$_8$]/PFu(SbCl$_3$) composite demonstrates both granular and uniform structures (Fig. 9d).

CONCLUSIONS

In this study homopolymers and composites based on 2-bromoaniline and furan were synthesized by

TABLE III
TGA Results of Polymers

Polymer	T_i (°C)	T_n (°C)	T_f (°C)
PFu(FeCl$_3$)[a]	164	207	249
	309	351	399
PFu(FeCl$_3$)[b]	168	198	231
	231	348	677
PFu(SbCl$_3$)	114	181	273
	273	341	409
	518	541	568
P2BrAn(FeCl$_3$)	250	267	279
	448	460	471
P2BrAn[(NH$_4$)$_2$S$_2$O$_8$]	324	343	358
P2BrAn(FeCl$_3$)/PFu(SbCl$_3$)	196	216	240
	310	345	383
P2BrAn[(NH$_4$)$_2$S$_2$O$_8$]/Fu(SbCl$_3$)	144	256	417

T_i, initial degradation temperature; T_m, maximum degradation temperature; T_f, final degradation temperature.
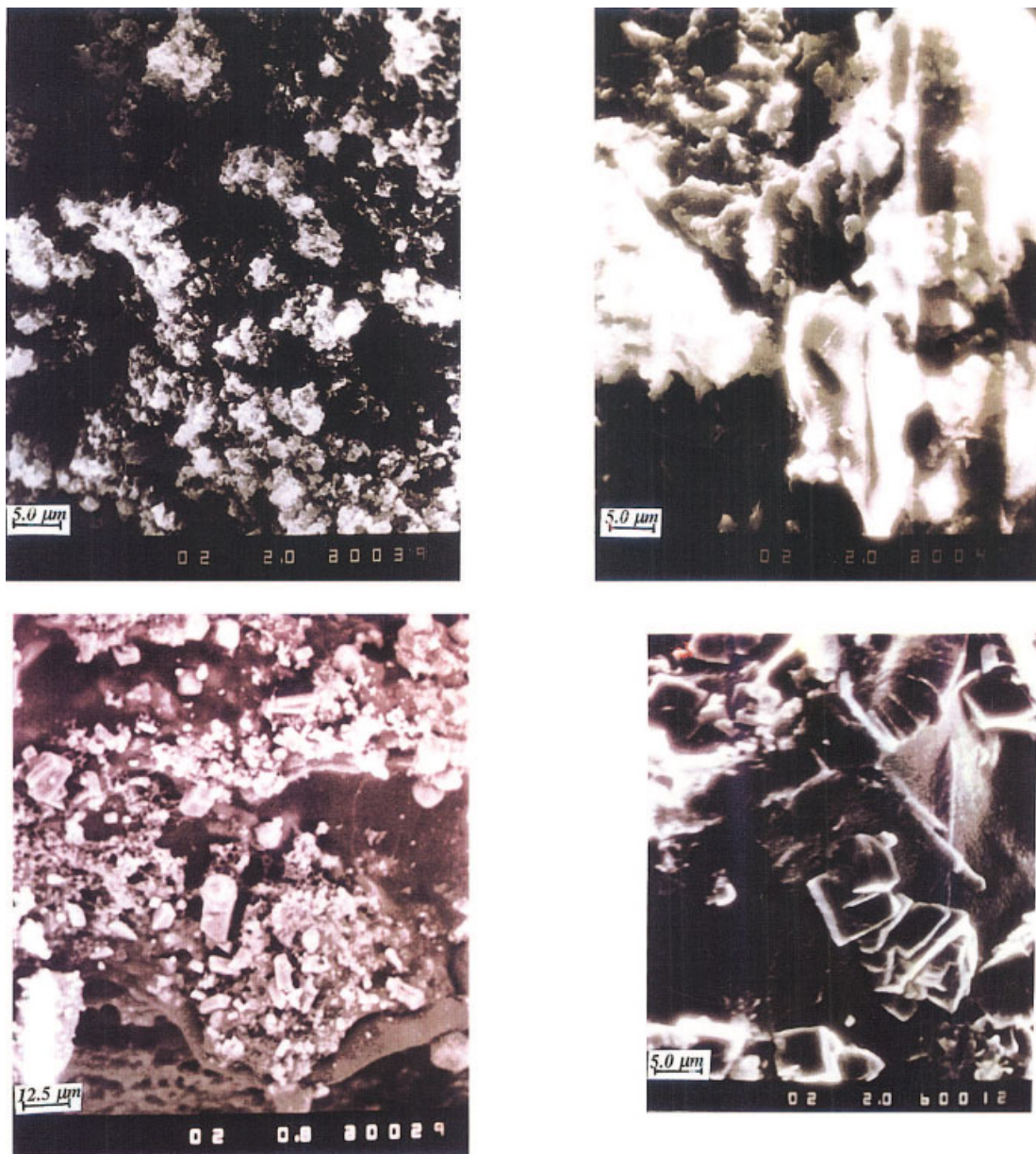
Figure 9 SEM micrographs of (a) P2BrAn[$(NH_4)_2S_2O_8$] ($\times$ 2000; bar = 5.0μm), (b) P2BrAn(FeCl$_3$) ($\times$ 2000; bar = 5.0μm), (c) PFu(SbCl$_3$) ($\times$ 800; 12.5μm), and (d) P2BrAn[$(NH_4)_2S_2O_8$]/PFu(SbCl$_3$) ($\times$ 2000; bar = 5.0μm). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

oxidative coupling using different oxidants. The resultant composites of P2BrAn and PFu have better thermal stability, solubility, and conductivity according to PFu. The analysis results have shown compatibility between P2BrAn and PFu. Polyfuran displayed electrical conductivity several orders of magnitude higher than doped PFu obtained in previous studies. Thus, both PFu and composites are promising electroconducting materials for real applications to be explored.

References

1. Cao, Y.; Treacy, G. M.; Smith, P.; Heeger, A. J. J Appl Polym Sci 1992, 66, 1711.
2. Javadi, H. H. S.; Cromack, K. R.; MacDiarmid, A. G.; Epstein, A. J Phys Rev B 1989, 39, 3579.
3. Lu, W. K.; Elsenbaumer, R. L.; Wessling, B. Synth Met 1995, 71, 2163.
4. MacDiarmid, A. G.; Chiang, J. C.; Halpern, M. Polym Repr 1984, 25, 248.
5. Nigrey, P. J.; Macdiarmid, A. G.; Heeger, A. J. Mol Cryst Liq Cryst Sci Technol 1992, 83, 309.
6. Yeh, J. M.; Chen, C. L.; Chen, Y.C.; Ma, C. Y.; Lee, K. R.; Wei, Y.; Li, S. Polymer 2002, 43, 2729.
7. Kulkarni, V. G. ACS Symp Ser 1999, 735, 174.

8. Genies, E. M.; Boyle, A.; Lapkowski, M.; Tsintous, C. Synth Met 1990, 36, 139.

9. Ballav, N.; Biswas, M. Polym Int 2003, 52, 179.

10. Wan, X.; Zhang, W.; Jin, S.; Xue, G.; You, Q. D.; Che, B. J Electroanal Chem 1999, 470, 23.

11. Wan, X.; Li, L.; He, J.; Zhou, D. S.; Wang, T. W. J Appl Polym Sci 2002, 86, 3160.

12. Martins, C. R.; Freitas, P. S.; Paoli, M. A. Polym Bull 2003, 49, 379.

13. Cataldo, F.; Maltese, P. Eur Polym Mater 2002, 38, 1791.

14. Rubio, L. L.; Castillo-Ortega, M. M.; Rejon, L.; Olayo, R.; Cruz, G. J. J Polym Sci Part B: Polym Phys 2002, 40, 2130.

15. Sharma, A. L.; Saxena, V.; Annapoorni, S.; Malhotra, B. D. J Appl Polym Sci 2001, 81, 1460.

16. Kang, E. T.; Neoh, K. G.; Tau, K. L. Eur Polym Mater 1994, 30, 529.

17. Benvenuti, F.; Galleti, A. M. R.; Carlini, C.; Sbrana, G. Polymer 1997, 38, 4973.

18. Gok, A.; Sari, B. J Appl Polym Sci 1993 2002, 84.

19. Poussin, D.; Morgan, H.; Foot, P. J. S. Polym Int 2003, 52, 433.

20. Jiang, H.; Geng, Y.; Li, J.; Jing, X.; Wang, F. Synth Met 1997, 84, 125.

21. Sayyah, S. M.; Abd. EL-Khalek, A. A.; Bahgat, A. A.; Abd. El-Salam, H. M. Polym Int 2001, 50, 197.

22. Diaz, F. R.; Sanchez, C. O.; Del Valle, M. A.; Tagle, L. H.; Bernede, J. C.; Tregouet, Y. Synth Met 1998, 92, 99.

23. Roy, B. C.; Gupta, M. D.; Bhowmik, L.; Ray, J. K. J Appl Polym Sci 2002, 86, 2662.

24. Gupta, M. C.; Sindhimeshram, D. C. Ind J Chem 1994, 33A, 358.

25. Chan, H. S. O.; Ng, S. C.; Sim, W. S.; Tan, K. L.; Tan, B. T. G. Macromolecules 1992, 25, 6029.

26. Pavia, D. L.; Lampman, G. M.; Kriz, G. S. Introduction to Spectroscopy; Saunders College: Philadelphia, 1979.

27. Kuwabata, S.; Ito, S.; Yoneyama, H. J Electrochem Soc 1988, 13, 1691.

28. Wan, X.; Yan, F.; Jin, S.; Liu, X.; Xue, G. Chem Mater 1999, 11, 2400.

29. Demirboga, B.; Onal, A. M. Synth Met 1999, 99, 237.

30. Yang, S.; Ruckenstein, E. Synth Met 1993, 59, 1.

31. Dao, L. H.; Leclerc, M.; Guay, J.; Chevalier, J. W. Synth Met 1989, 29, E377.

32. Stafstorm, S.; Bredas, J. L.; Epstein, A. J.; Woo, H. S.; Tanner, D. B.; Huang, W. S.; Macdiarmid, A. G. Phys Rev Lett 1987, 59, 1464.

33. Wei, Y.; Hsuef, K. F.; Jang, G. W. Macromolecules 1994, 27, 518.

34. Wen, T. C.; Huang, L. M.; Gopalan, A. Synth Met 2001, 123, 451.

35. Traore, M. K.; Stevenson, W. T. K.; Mccormick, B. J.; Dorey, R. C.; Wen, S.; Meyers, D. Synth Met 1991, 40, 137.

36. Leonardo, G. P.; Mattoso, L. H. C. J Apply Polym Sci 2002, 83, 1309.