

Increased Stability of Polythiophene in the Presence of Aniline in Acetonitrile

Nuran Pekmez Özçiçek,¹ Kadir Pekmez,¹ Rudolf Holze,² Attila Yıldız¹

¹Hacettepe University, Department of Chemistry, Beytepe, Ankara 06532, Turkey

²Technische Universität Chemnitz, Institut für Chemie, D-09107 Chemnitz, Germany

Received 29 May 2002; accepted 10 June 2002

ABSTRACT: The conductance behavior of copolymers of aniline and thiophene with varying concentration ratios were studied in acetonitrile/tetrabutylammonium tetrafluoroborate using cyclic voltammetry and *in situ* conductance measurements. These studies revealed that compared with homopolymers, the copolymers have extended ranges of stability (even at very positive applied potentials), lower

conductivities, and reversible doping/undoping characteristics. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 862–866, 2003

Key words: copolymerization; conducting polymers; electrochemistry; degradation

INTRODUCTION

Polyaniline (PA) and polythiophene (PT) have received considerable attention due to their electroactivity, low density, high electrical conductivity, environmental stability, ease of preparation, and attractive applications.^{1–4} PT possesses a large number of special physical properties, such as, thermochromism, electrochromism, solvatochromism, luminescence, and photoconductivity. However, PA has always been the most studied conjugated polymer because of its unique reversible protonic dopability, excellent redox recyclability, and chemical stability. Because PA and PT are intractable, there is a need to modify them to make them as processable as conventional organic polymers. This need is driven by the growing number of potential applications of these materials. The use of substituted monomers and post-treatment processes (sulfonation, secondary doping) are possible routes of modification. One other approach in this search for processability is copolymerization.

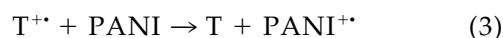
In recent years, a few studies have been published about the synthesis of copolymers of aniline and thiophene or their derivatives, with physical properties that are different from those of homopolymers, that were prepared by electrochemical^{5–7} and chemical^{8–10} methods. Hu et al. reported the electrochemical preparation of bithiophene and aniline copolymer in aqueous/organic mixed medium.⁵ In another study about electrochemical copolymerization of thiophene and aniline, polythiophene was coated with polyaniline,

and the resulting system was a composite. On the other hand, when polyaniline was coated with polythiophene, the system was claimed to be a copolymer.⁶ The main difficulty with electrochemical copolymerization of aniline with thiophene is the large difference in the electrooxidation potentials between the two types of monomers. This problem can be solved by controlling the concentration of monomers and adjusting the polymerization potential at a defined concentration of monomer. Bithiophene can also be used for copolymerization instead of thiophene, but thiophene is more conventional.

In previous studies from our laboratory, electrochemical preparation and properties of polyaniline and polythiophene in acetonitrile were extensively elucidated.^{7, 11, 12} In one of these studies, the effects of thiophene on electropreparation and properties of polyaniline were investigated on Pt electrode in acetonitrile.⁷ The presence of thiophene in aniline solutions in acetonitrile accelerates the formation and causes an improvement in the conductivity of polyaniline films. A catalytic mechanism related to the role of thiophene cation radicals, which involves chemical and electrochemical oxidation steps, is proposed. Electrolytically produced thiophene cation radical chemically oxidizes aniline and also polyaniline chains, forming the polypernigriline form during deposition:



and



Correspondence to: A. Yıldız (yildiz@hacettepe.edu.tr).

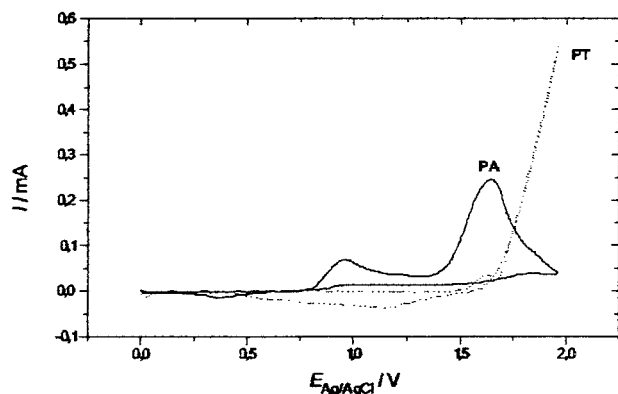
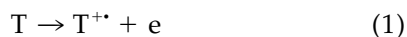


Figure 1 Cyclic voltammograms of (a) aniline and (b) thiophene in 0.1 M TBABF₄/acetonitrile ($v = 0.1 \text{ V sn}^{-1}$).

In acidic solutions containing higher thiophene-to-aniline concentration ratios, thiophene enters into the structure of the polymer, thereby forming a copolymer. The properties of this copolymer were elucidated by cyclic voltammetry, gas chromatography mass spectroscopy (GCMS), elemental analysis, and differential scanning calorimetry (DSC) methods.⁷



This article deals with the results obtained by cyclic voltammetry, *in situ* conductivity measurements of aniline–thiophene copolymers deposited at constant potential (1.7 V versus Ag, AgCl) using experimentally determined concentrations of monomers on an Au electrode in acetonitrile. The properties of these copolymers were investigated and compared with those of homopolymers. Possible structures for copolymers are proposed.

EXPERIMENTAL

Acetonitrile (Merck, LiChrosolv) was purged with nitrogen prior to use. Aniline (Merck) was distilled at reduced pressure and stored under nitrogen atmosphere at -10°C in darkness. Thiophene (Aldrich) and diethylether complex of tetrafluoroboric acid (HBF₄) (Aldrich) were kept at -10°C in darkness under a nitrogen atmosphere and used directly. Electrolyte solutions were prepared from tetrabutylammonium tetrafluoroborate (TBABF₄; Aldrich) without purification.

Electrochemical measurements were carried out under a nitrogen atmosphere in a three-electrode-type cell with separate compartments for the reference electrode [Ag, AgCl (sat) in acetonitrile] and the counter electrode (Pt wire). The working electrode for the cyclic voltammetric studies, which was cleaned by polishing with an Al₂O₃ slurry, was an Au disc with an area of 0.078 cm².

For *in situ* conductivity measurements, the polymer was deposited on a the two-band Au electrode¹³ in a three-electrode-type cell. A Pt wire was used as a counter electrode, and an Ag, AgCl (sat) electrode served as a reference electrode. All potentials in this report are quoted against this reference electrode. The experimental equipment consisted of two-band electrode in the cell and a specially designed electrical circuit supplying 10 mV of direct current (dc) across the two Au strips.¹³

RESULTS AND DISCUSSION

The cyclic voltammetric behavior of two monomers, aniline and thiophene, in 0.1 M TBABF₄/acetonitrile is shown in Figure 1. As seen from the figure, the potential scan should result in coating polyaniline with polythiophene by electrolysis due to the large difference in the electrooxidation potentials of aniline and thiophene (0.90 and 2.0 V, respectively, versus Ag/AgCl). To avoid this phenomenon, aniline–thiophene copolymers were deposited at an experimentally determined constant potential (1.7 V) instead of potential scanned electrolysis. Polyaniline, polythiophene, copolymer A, copolymer B, and copolymer C were deposited on an Au electrode from solutions described in Table I.

Cyclic voltammograms were recorded after deposition of polyaniline and polythiophene (Figure 2a and 2b, respectively) and after deposition of copolymer A, copolymer B, and copolymer C (Figure 3a, 3b, and 3c, respectively) at 1.7 V in 0.1 M TBABF₄/acetonitrile (blank solution). Cyclic voltammograms of copolymers have broad peaks like those of polythiophene, but their peak currents are different from each other. The cyclic voltammogram of copolymer B has the smallest peak current. No significant differences between the voltammograms of copolymers were found except for the intensities of the peak currents.

For *in situ* conductivity measurements, polyaniline and polythiophene were deposited from a solution described in Table I at 1.7 V on an Au bandgap electrode. The resistivity versus the applied electrode po-

TABLE I
Solution Conditions for Deposited Homopolymers and Copolymers

Polymer	Solution
Polyaniline	175 mM aniline 75 mM HBF ₄
Polythiophene	175 mM thiophene 75 mM HBF ₄
Copolymer A	175 mM aniline 75 mM HBF ₄ , 150 mM thiophene
Copolymer B	175 mM aniline 75 mM HBF ₄ , 175 mM thiophene
Copolymer C	175 mM aniline 75 mM HBF ₄ , 200 mM thiophene

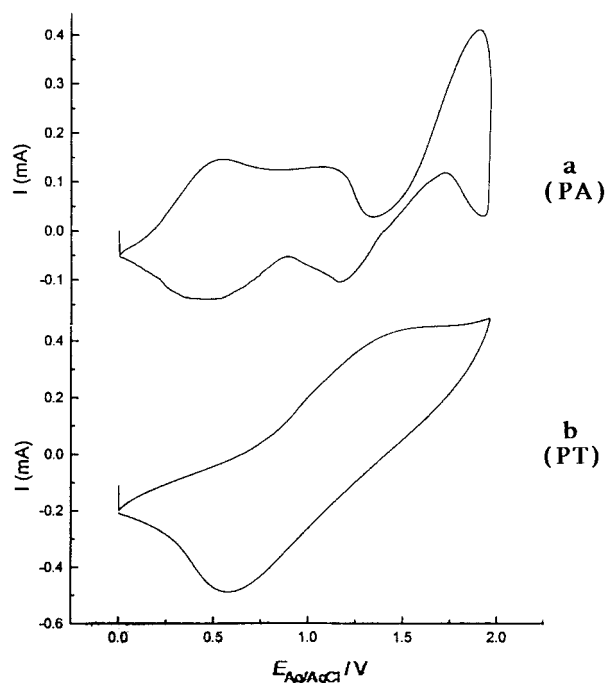
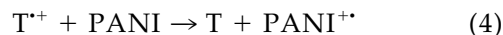


Figure 2 Cyclic voltammograms of (a) polyaniline and (b) polythiophene in blank solution ($v = 0.1 \text{ V s}^{-1}$).

tential (0.0–1.3 V) plots of polyaniline and polythiophene in blank solution containing 15 mM HBF_4 are shown in Figure 4. The same measurements in the range 0.0–1.9 V are shown in Figure 5. When the applied potential was increased, the resistivity of polyaniline decreased sharply by three orders of magnitude after 0.3 V and then increased sharply after 0.9 V (Fig. 4a). This behavior is similar to that reported in the literature.^{14–17} Polythiophene showed a slow decrease of about four orders of magnitude in electrical resistivity after 0.5 V (Fig 4b). In the potential interval between 1.4 and 1.9 V, the resistivity of polythiophene increased slowly compared with that of polyaniline, in accordance with the literature (Fig. 5b).¹⁸ On initial oxidation, the conducting species (radical cation of polymers) are produced, and further oxidation corresponds to overoxidation of polymers.¹⁹ When the potential shift direction was reversed from 1.3 to 0.0 V, the conductivities of two polymers were almost completely restored (Figs. 4a and 4b). If the potential shift direction was reversed from 1.9 to 0.0 V (Figs. 5a and 5b), the conductivity of polyaniline was almost restored, whereas the conductivity of polythiophene was not restored. The resistivity of polythiophene is irreversible because of a degradation process.¹⁹ In the aqueous medium, polyaniline gives quinonediimines, and quinone-type degradation products cause an irreversible increase in its resistivity.¹⁹ On the other hand, in acetonitrile, the resistivity of polyaniline was almost restored under the same conditions (Fig. 5a), with a slight irreversible change of resistivity that may be

related to crosslinking between linear polymer chains.¹⁹

The resistivities of the three copolymer films prepared were reversible when the potential shift direction was reversed from 1.9 V in the same blank solution containing 15 mM HBF_4 (Fig. 6). In the case of copolymer A (Fig. 6a), there was a small decrease in electrical resistivity after 0.3 V, but the resistivity value remained almost unchanged in the potential interval between 0.0 and 1.0 V. When the potential shift direction was reversed from 1.9 to 0.0 V, the resistivity of this copolymer was completely restored. This finding can be interpreted as indicating the formation of a polyaniline-based copolymer that is interrupted by thiophene units. During polymerization, longer polyaniline chains get oxidized to the polypernigriline state because of the catalytic effect of the thiophene cation radicals that are present:⁷



Only shorter polyaniline chains contribute to the conductivity, and, accordingly, the conductivity of the

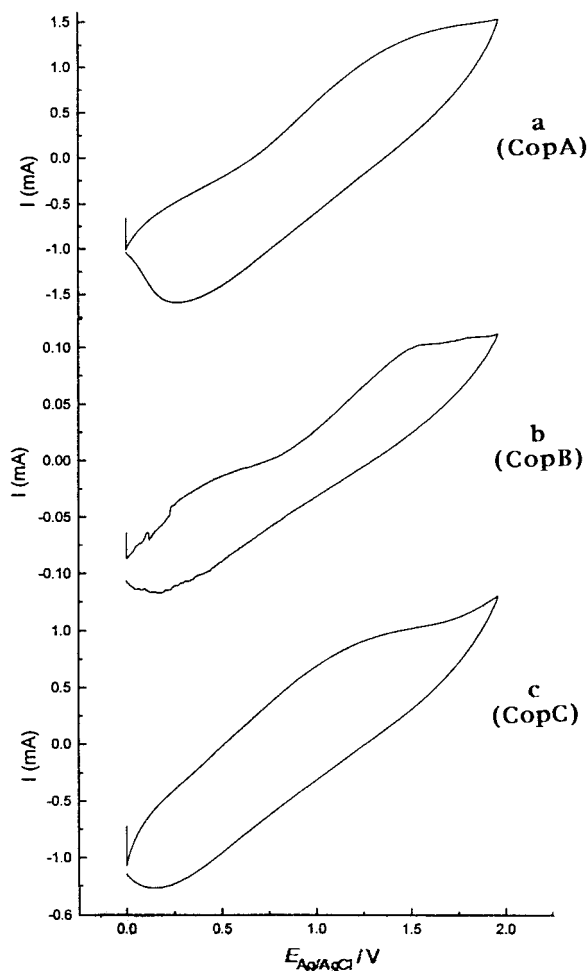


Figure 3 Cyclic voltammograms of (a) copolymer A, (b) copolymer B, and (c) copolymer C in blank solution ($v = 0.1 \text{ V s}^{-1}$).

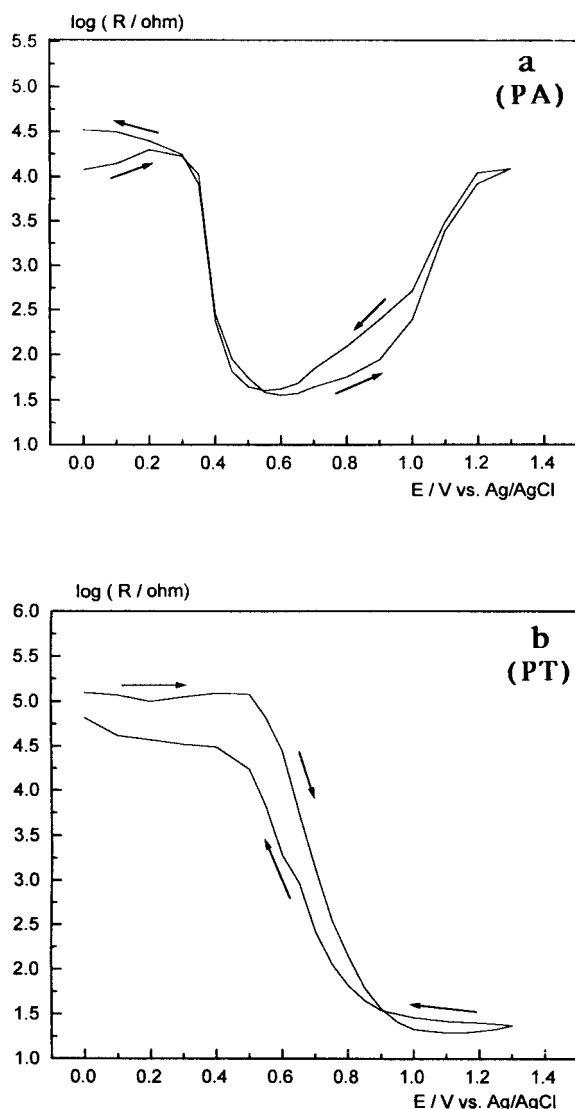


Figure 4 Resistivity versus electrode potential plots between 0.0 and 1.3 V of (a) polyaniline and (b) polythiophene in blank solution containing 15 mM HBF_4 .

copolymer was almost constant up to 1.0 V (Fig. 6a). In addition, the magnitude of the conductance of copolymer A was ~ 2.5 orders of magnitude lower than that of pure polyaniline.

In the case of copolymer C, the resistivity measurements resulted in a slow decrease after 0.5 V, like the case of polythiophene (Fig. 6c). However, the conductivity of this copolymer did not diminish between 1.0 and 1.7 V, unlike that of polythiophene. Nevertheless there was a small decrease in the conductivity value beyond 1.7 V. When the potential shift direction was reversed from 1.9 to 0.5 V, the conductivity of copolymer C was not restored and remained constant, like that of polythiophene. This copolymer has conductivity properties similar to those of polythiophene, except that the conductivity remains almost constant between 1.4 and 1.9 V. The other difference is the slow

increase in electrical conductivity by about three orders of magnitude beyond 0.5 V. These observations imply the formation of a polythiophene-based copolymer that is interrupted by aniline units. The presence of these aniline units between polythiophene chains apparently prevents degradation of polythiophene. The electrical properties of copolymer B were similar to those of copolymer C (Fig. 6b).

The observed *in situ* conductivity properties are not the sum of those of the two individual homopolymers. This result eliminates the possibility that the copolymers A, B, and C can be considered as block copolymers. It can only be concluded that copolymers A and C have structures approaching those of polyaniline-based random copolymer and polythiophene-based random copolymer, respectively. The average length of polyaniline chains decreases with increasing amounts of thiophene in the polymerization solution. Copolymer B, on the other hand, has a structure approaching that of block copolymer, having longer polythiophene chains and shorter polyaniline chains than copolymer A.

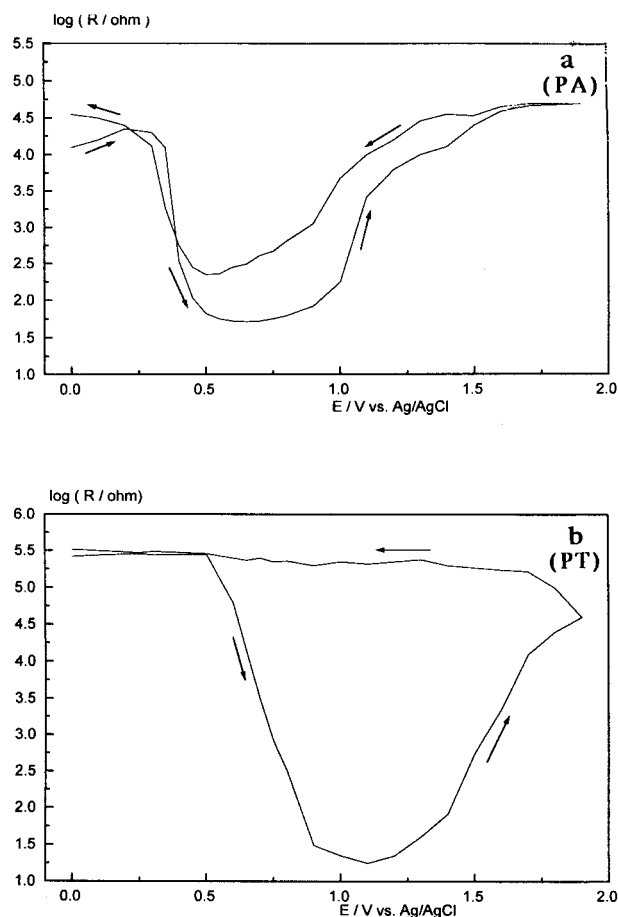


Figure 5 Resistivity versus electrode potential plots between 0.0 and 1.9 V of (a) polyaniline and (b) polythiophene in blank solution containing 15 mM HBF_4 .

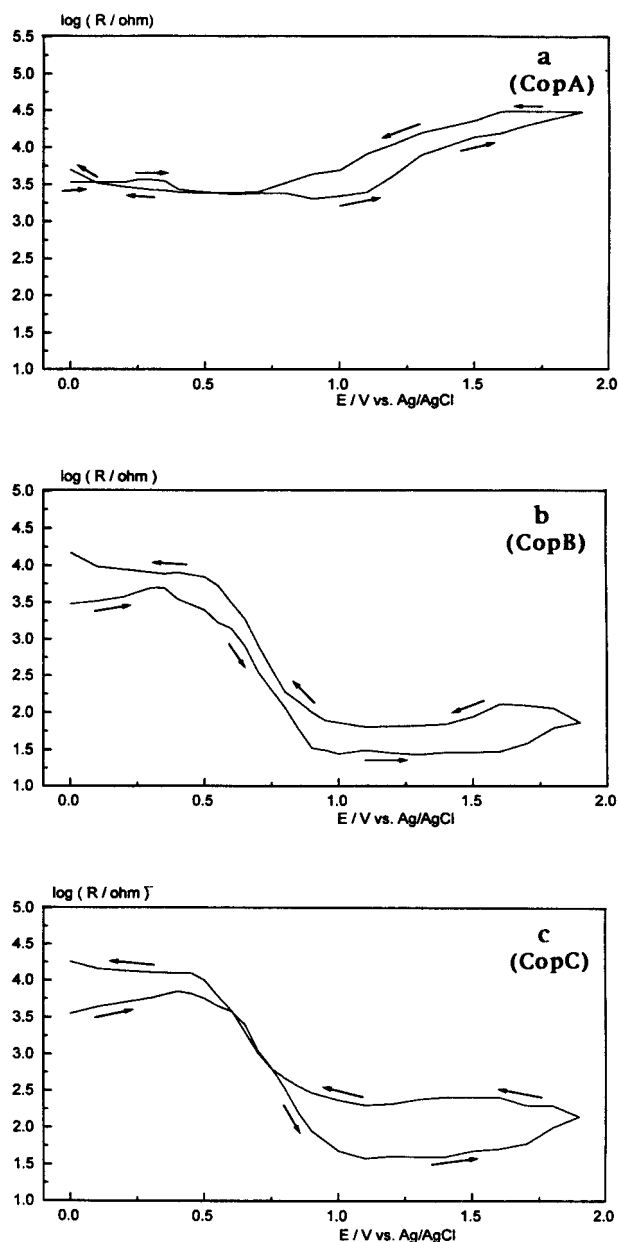


Figure 6 Resistivity versus electrode potential plots between 0.0 and 1.9 V of (a) copolymer A, (b) copolymer B, and (c) copolymer C in blank solution containing 15 mM HBF_4 .

CONCLUSIONS

The cyclic voltammograms did not provide any evidence for the presence of copolymers. The patterns were all rather similar to that of polythiophene, but the peak currents of copolymers were different from each other. The conductivity of polyaniline in non-aqueous medium was almost restored when the potential shift direction was reversed, contrary to the reported data in the literature for aqueous systems. *In situ* conductivity measurements of copolymers A, B, and C were different from those of homopolymers.

The conductivity curve of copolymer A is similar to that of polyaniline except that its conductivity value is almost constant up to 1.0 V and 2.5 orders of magnitude lower than that of pure polyaniline. *In situ* conductivity behavior of copolymers B and C resemble that of polythiophene, but the important difference is that no degradation of these copolymers takes place between 1.4 and 1.9 V due to the presence of aniline units within the polythiophene chains. Unlike polythiophene, for which a complete loss of conductivity occurs during potential excursions up to 1.9 V, the range of stability of these copolymers is considerably extended. The reversible doping/undoping behavior of polyaniline is also reflected in this copolymer up to this potential limit, albeit with much lower overall conductivities. In other words, copolymers of aniline and thiophene combine the range of stability and reversible doping/undoping behavior advantages of both homopolymers.

Support of this work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie (RH), The Alexander von Humboldt Foundation (KP and AY), and TUBITAK (NP) is gratefully appreciated.

References

1. Arsov, L.D.; Plieth, W.; Kobmethl, G. *J Solid State Electrochem* 1998, 2, 235.
2. Kuo, C.T.; Chen, S.A.; Hwang, G.W.; Kuo, H.H. *Synth Met* 1998, 93, 155.
3. Hosokawa, C.; Higashiy, H.; Kusumoto, T. *Appl Phys Lett* 1993, 62, 3238.
4. Holze, R. In *Handbook of Electronic and Photonic Materials and Devices*, Vol. 8; Nalwa, H.S., Ed.; Academic: San Diego, 2000; p. 209.
5. Hu, X.; Wang, Gm.; Ng, H.; Wong, T.K.S. *Chem Let* 1999, 128, 1323.
6. Talu, M.; Kabasakalolu, M.; Oskovi, H.R. *J Polym Sci, Part A: Polym Chem* 1996, 34, 2981.
7. Can, M.; Pekmez, K.; Pekmez, N.; Yildiz, A. *Synth Met* 1999, 104, 9.
8. (a) Young, C.L.; Polis, D.W.; Bain, A.N.; Sapochak, L.S.; Dalton, L.R. *Macromolecules* 1990, 23, 3236; (b) Ng, S.C.; Xu, L.G.; Chan, H.S.O. *Synth Met* 1998, 94, 185.
9. Kang, E.T.; Neoh, K.G.; Tan, K.L. *Synth Met* 1993, 55–57, 1232.
10. Nagvekar, D.; Sankara, B.; Tan, L.S. *Polym Prepr (Am Chem Soc, Div Polym Chem)* 1998, 39, 548.
11. Pekmez, N.; Pekmez, K.; Arca, M.; Yildiz, A. *J Electroanal Chem* 1993, 353, 237.
12. Can, M.; Pekmez, K.; Pekmez, N.; Yildiz, A. *J Appl Polym Sci* 2000, 77, 312.
13. Holze, R.; Lippe, J. *Synth. Met* 1990, 38, 99.
14. Genies, E.M.; Hany, P.; Lapkowski, M.; Olmeda, L.; Santier, C. *Synth Met* 1988, 25, 29.
15. Genoud, F.; Kruszka, J.; Nechtschein, M.; Santier, C.; Davied, S.; Nicolau, Y. *Synth Met* 1991, 43, 2887.
16. Lippe, J.; Holze, R. *J Electroanal Chem* 1992, 339, 411.
17. Cai, L.T.; Yao, S.B.; Zhou, S.M. *J Electroanal Chem* 1997, 421, 45.
18. Zotti, G.; Schiavon, G. *Synth Met* 1990, 39, 183.
19. Pud, A.A. *Synth Met* 1994, 66, 1.