

# Synthesis and Characterization of Nylon 6/Polyalkylaniline Conducting Composites

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**ABSTRACT:** Conducting composite films of polyalkylanilines with nylon 6 as the insulating matrix were electrochemically synthesized and characterized. The electrochemical properties of the alkyanilines and their composites were investigated with a cyclic voltammetry technique. The magnetic properties of the polymers and composites were analyzed, and their conducting mechanisms were found to be of bipolaron nature. With Fourier transform infrared spectra, it

was clarified that polymerization occurred via the  $\text{—NH}_2$  group in a head-to-tail mechanism. Through thermogravimetric analyses, the thermal properties of the polymers and their composites were elucidated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1693–1701, 2003

**Key words:** nylon; composites; conducting polymers

## INTRODUCTION

Conductive polymers have been attracting interest in many scientific and technological fields in recent years. Among these polymers, polyaniline (PAN) has been found to have several interesting applications in the areas of electronics, optics, and biology.<sup>1,2</sup> The main disadvantages of conducting polymers are their poor processability, mechanical properties, and environmental stability. For improved physical properties and for feasibility, conducting polymers are usually blended with other insulating or conducting polymers. This is called *composite preparation*. The aim of this process is to prepare mixtures with good mechanical properties and good electrical conductivity.<sup>3–7</sup> Conducting polymers have also been used in textile technology.<sup>8,9</sup> A process has been developed to polymerize pyrrole or aniline on the surface of every single fiber of a textile composite.<sup>8</sup> Smooth and coherent films on the surfaces of textile materials have been obtained in this way. There are two basic methods used to synthesize PAN-containing composites. In the first, composites are obtained by the polymerization of aniline in the presence of another polymer.<sup>10–14</sup> In the second, composites are synthesized by the dissolution of PAN in a solution or in a melt of another polymer.<sup>15–18</sup> Moreover, there are various ways to prepare composites with PAN and other conducting polymers. For instance, the dip-coating method<sup>19–24</sup> is a success-

ful method of electrochemical composite preparation. In this method, the working electrode is dipped into a dilute insulating polymer solution, and in this way, the electrode surface is coated with a polymer film. Then, by the electrochemical polymerization of the monomer solution, conducting composites are synthesized on the electrode surface. This electrode is used for the electrolysis of a monomer solution, and conducting composites are synthesized.

In this study, conducting polymers of some alkyanilines and their conducting composites, with nylon 6 (PA6) as an insulating matrix, were electrochemically synthesized, and their electrochemical, structural, thermal, and electrical properties were characterized.

## EXPERIMENTAL

### Chemicals

Alkyanilines (Merck) were distilled *in vacuo* before use. Sulfuric acid, *m*-cresol, PA6 (in a granular form), and acetone were obtained from Merck and used as received.

### Materials and measurements

Electrochemical polymerization experiments were carried out at constant potentials with a PGS 2000 D model potentiostat. The electrolysis cell consisted of working, counter, and reference electrodes. Working and counter electrodes were made of platinum plates with a surface area of 2.5 cm<sup>2</sup>. A saturated calomel electrode was used as the reference electrode. Cyclic voltammograms (CVs) of the monomers were taken in acidic media with Linseis LY-1600 recorder.

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**TABLE I**  
Conductivities of Polyalkylanilines

| Polymer | Conductivity (S/cm)   |
|---------|-----------------------|
| POT     | $1.74 \times 10^{-3}$ |
| P2EAn   | 0.17                  |
| PNMAn   | 0.20                  |
| PNEAn   | 0.11                  |

**TABLE II**  
Conductivities of PA6/Polyalkylaniline Composites

| Composite | Conductivity (S/cm)   |
|-----------|-----------------------|
| PA6/POT   | $1.29 \times 10^{-3}$ |
| PA6/P2EAn | $7.63 \times 10^{-4}$ |
| PA6/PNMAn | 0.07                  |
| PA6/PNEAn | 0.08                  |

The conductivities of the synthesized polymers were measured with the four-probe technique. The magnetic susceptibility of the polymers was determined previously in another article.<sup>25</sup>

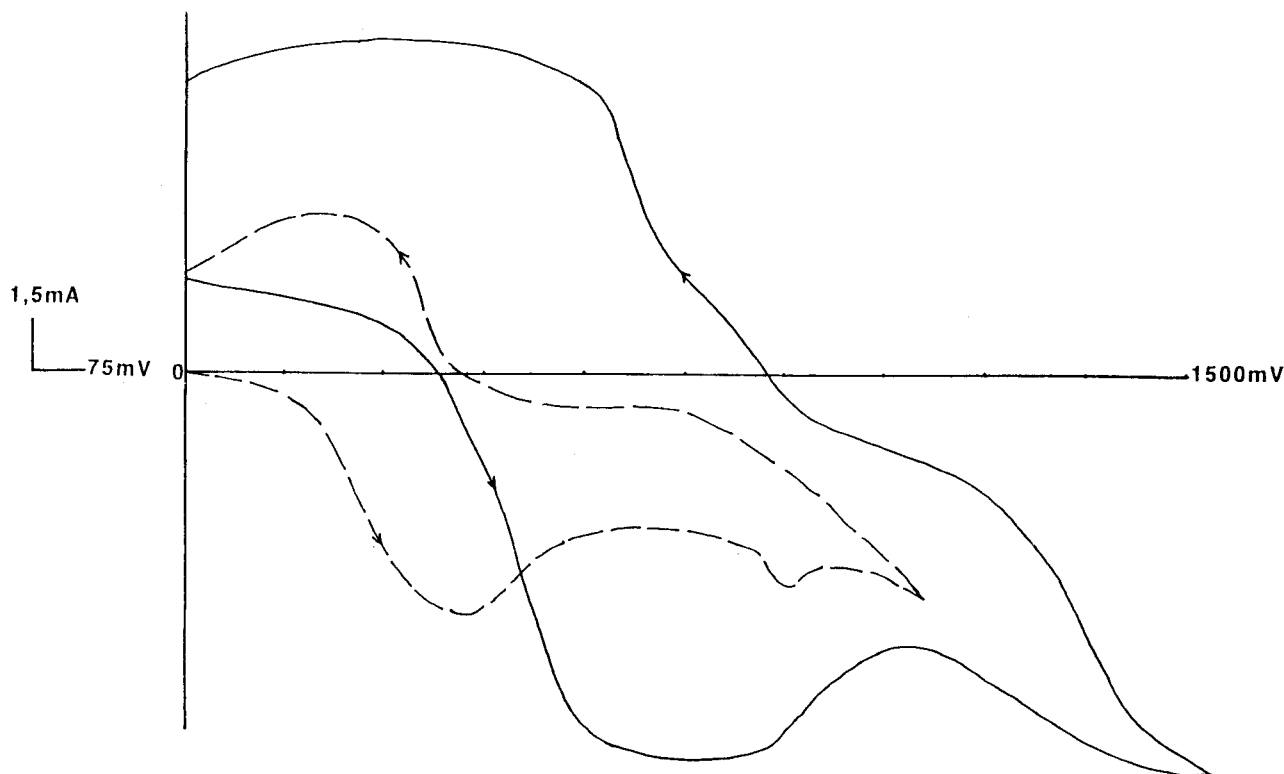
Fourier transform infrared (FTIR) spectra of the polymer samples were taken on KBr disks and were recorded on a Mattson 1000 spectrometer.

Thermogravimetric analyses (TGAs) of the polymers were performed with a DuPont General V2.2A 9900 thermogravimetric analyzer. Thermograms of the samples were taken under a nitrogen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$  and within a temperature range of  $0\text{--}800^\circ\text{C}$ .

#### Procedure

In the experiments, previously described electrochemical cells and methods were used.<sup>25</sup> Monomer solutions were prepared from 0.1M alkyylanilines and 0.2M sulfuric acid solutions in a volumetric flask. Then, the

CVs were performed separately for each monomer in the anodic direction within a range of  $0\text{--}1.0\text{ V}$  ( $1.5\text{ V}$ ). Peak potentials were determined for *o*-toluidine, 2-ethylaniline, *N*-methylaniline, and *N*-ethylaniline at 0.75, 0.90, 1.24, and 0.57 V, respectively. Therefore, poly(*o*-toluidine) (POT), poly(2-ethylaniline) (P2EAn), poly(*N*-methylaniline) (PNMAn), and poly(*N*-ethylaniline) (PNEAn) were synthesized and deposited onto the working electrode for 16 h under the aforementioned controlled potential conditions. Then, the polymers were peeled off from the electrode surface and washed with the supporting electrolyte solution ( $0.2\text{M H}_2\text{SO}_4$ ), twice distilled water, and acetone successively.<sup>26,27</sup> Finally, they were dried at  $75^\circ\text{C}$  in a vacuum oven for 24 h. For the synthesis of the composites, the following method was used. The working electrode was dried at  $50^\circ\text{C}$  in a vacuum oven. The electrode, which was coated with a PA6 film via dip coating from a 1% solution of PA6 in *m*-cresol for 24 h, was dried under the aforementioned conditions. PA6/polyalkylaniline conductive



**Figure 1** CVs of (—) *o*-toluidine and (---) 2-ethylaniline in a  $0.2\text{M H}_2\text{SO}_4$  solution at a scanning rate of  $100\text{ mV s}^{-1}$ .

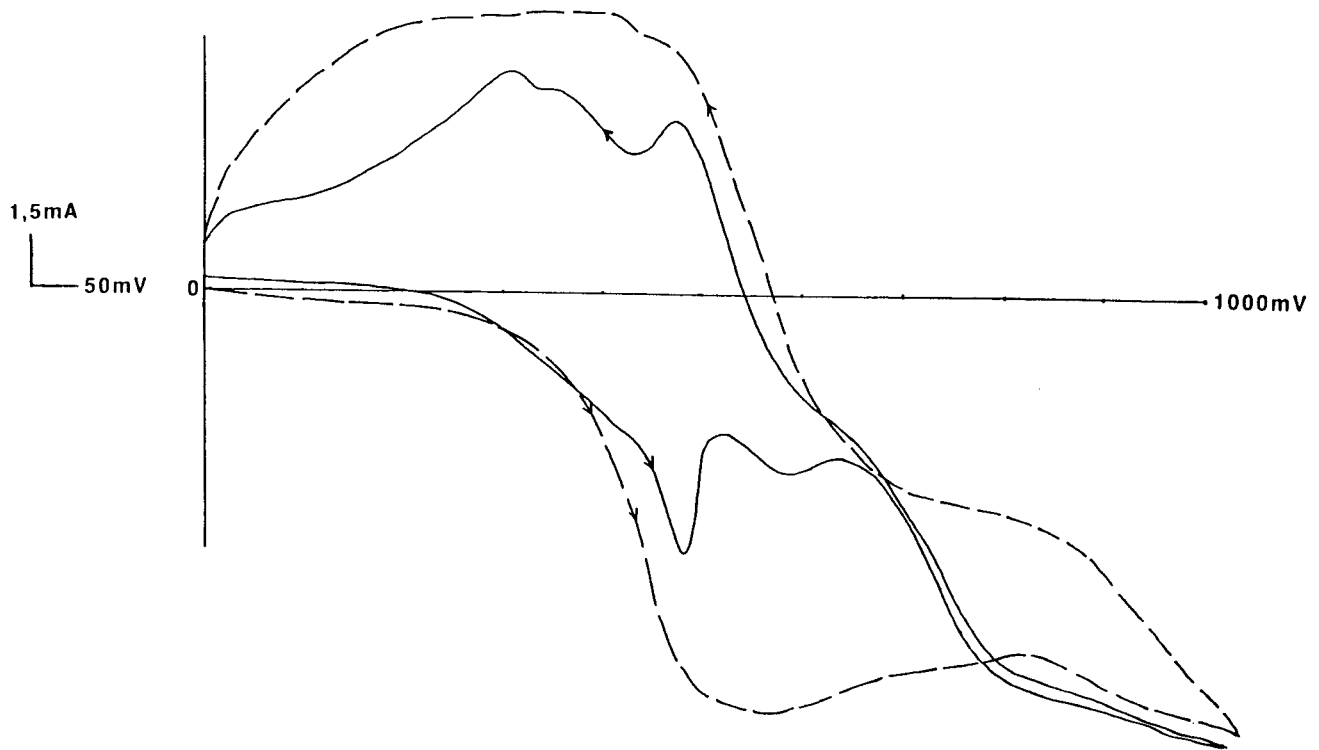


Figure 2 CVs of (—) *N*-methylaniline and (---) *N*-ethylaniline in a 0.2M H<sub>2</sub>SO<sub>4</sub> solution at a scanning rate of 100 mV s<sup>-1</sup>.

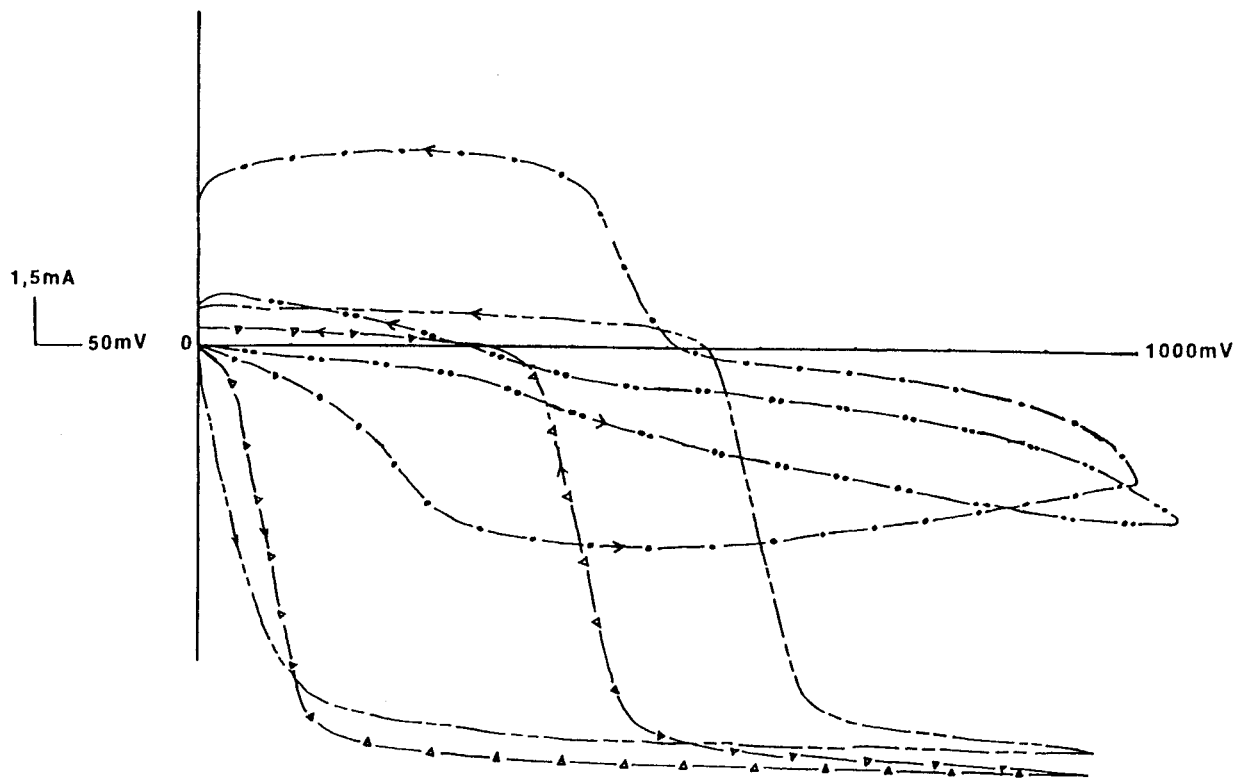


Figure 3 CVs of (-·-) PA6/POT, (···) PA6/P2EAn, (-▽-) PA6/PNMAAn, and (—) PA6/PNEAn composite films in a 0.2M H<sub>2</sub>SO<sub>4</sub> solution at a scanning rate of 100 mV s<sup>-1</sup>.

**TABLE III**  
Gouy Balance Measurements of Polyalkylanilines and Composites

| Polyalkylaniline or composite | Gouy balance measurements<br>[ $\mu_{\text{eff}}^*$ (BM)] <sup>a</sup> |
|-------------------------------|--|
| POT                           | -32  |
| P2EAn                         | -15  |
| PNMAn                         | -37  |
| PNEAn                         | -10  |
| PA6/POT                       | -32  |
| PA6/P2EAn                     | -31  |
| PA6/PNMAn                     | -35  |
| PA6/PNEAn                     | -32  |

<sup>a</sup> Effective magnetic moment. BM = Bohr magneton.

films were synthesized on the PA6/Pt electrode at the determined constant potentials for 16 h. Then, they were washed again with the supporting electrolyte solution, twice distilled water, and acetone successively. Finally, they were dried at 75°C in a vacuum oven for 24 h.

## RESULTS AND DISCUSSION

The conductivities of the polyalkylanilines were determined, and the results are given in Table I. PNMAn had the highest conductivity (0.20 S cm<sup>-1</sup>), whereas

POT had the lowest conductivity (1.74 × 10<sup>-3</sup> S cm<sup>-1</sup>). The significant difference between the conductivities of the polyalkylanilines could be attributed to electron contribution effects. *N*-Alkyl groups are electron-donating groups that augment the  $\pi$ -electron density along the conjugated polymeric chain and increase the basicity of the imine units and their conductivities.<sup>28</sup>

The conductivities of the composites were measured, and the results are given in Table II. PA6/PNEAn had the highest conductivity (0.08 S cm<sup>-1</sup>), whereas PA6/P2EAn had the lowest conductivity (7.63 × 10<sup>-4</sup> S cm<sup>-1</sup>). This contradiction can be explained as follows. First, it is difficult to polymerize the ortho- and meta-substituted aniline derivatives because of the steric and weak inductance effects of the substituents. Second, short polymer chains form in the composites. Third, hydrogen bonding forms between P2EAn and PA6 and results in a conductivity decrease.<sup>29,30</sup>

The electrochemical properties of the polymers and their composites were determined from their CVs. The CVs of *o*-toluidine and 2-ethylaniline are given in Figure 1. The CVs of *N*-methylaniline and *N*-ethylaniline are given in Figure 2. The CVs of 2-ethylaniline and *o*-toluidine (Fig. 1) are similar. As seen in Figure 1, *o*-toluidine had a broad anodic current peak, and 2-ethylaniline had two anodic current peaks. The first

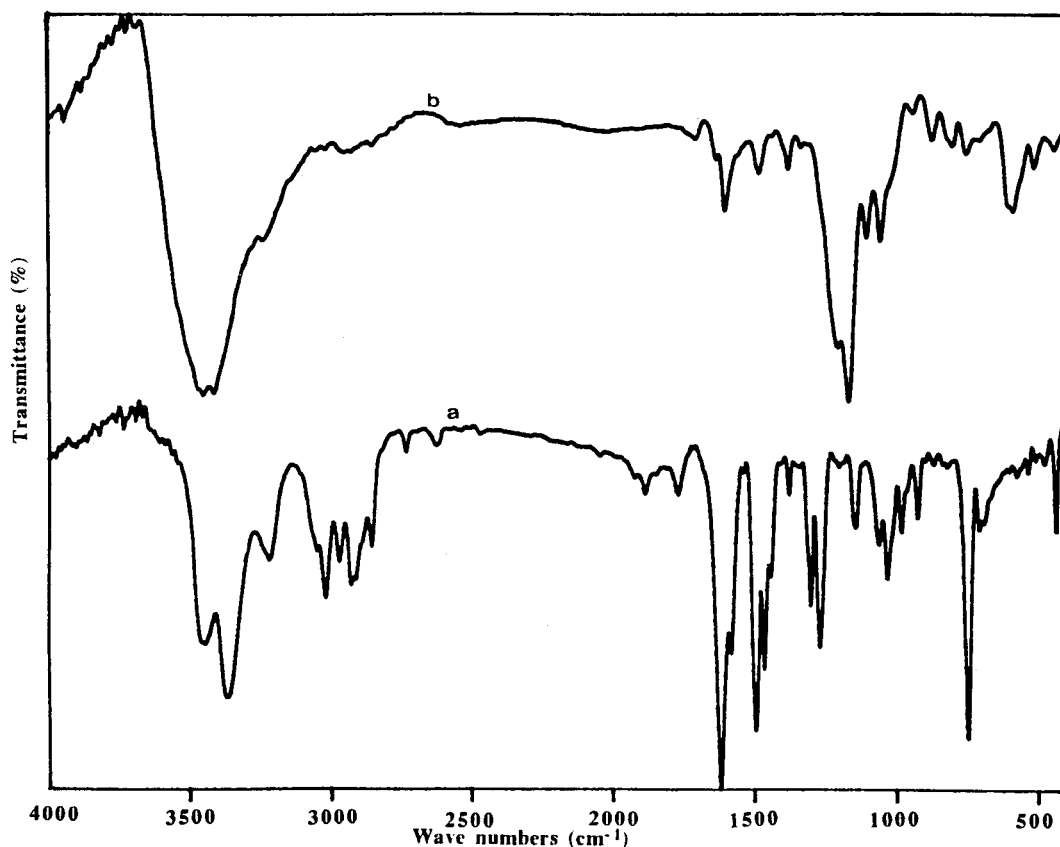


Figure 4 FTIR spectra of (a) *o*-toluidine and (b) POT.

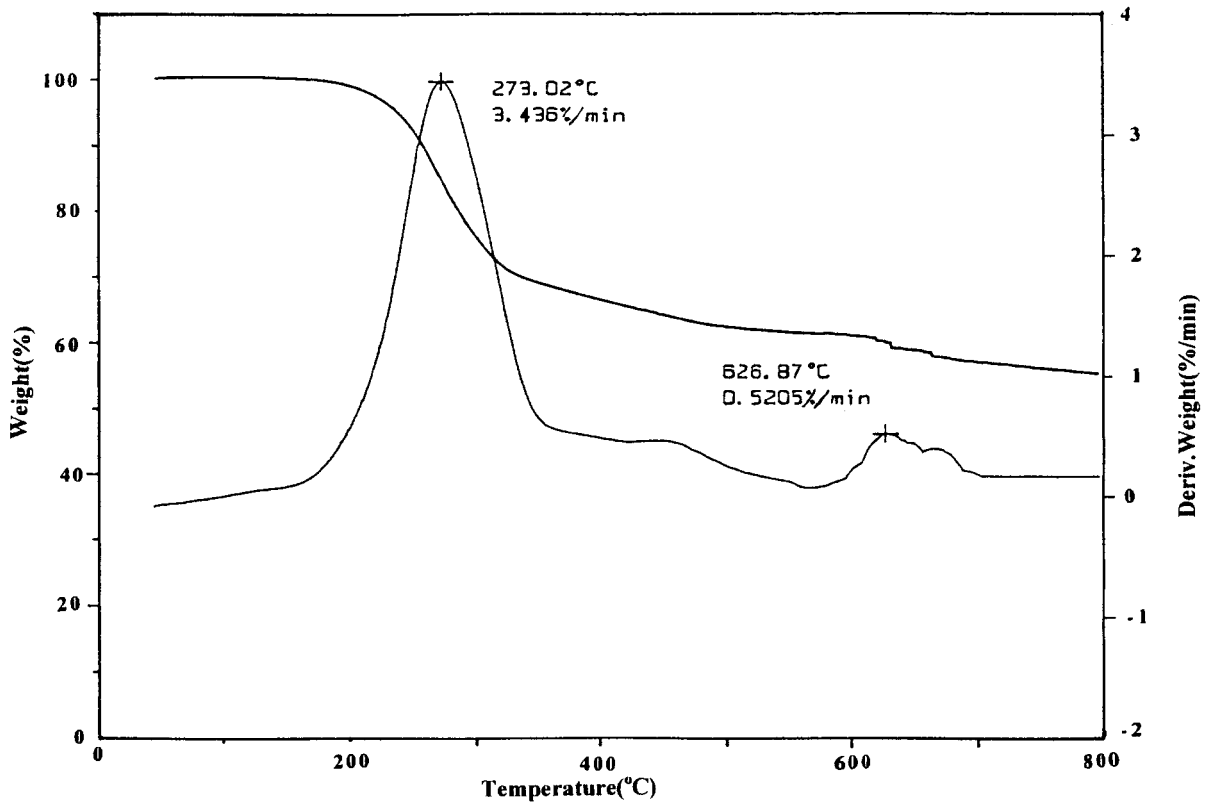


Figure 5 TGA of POT.

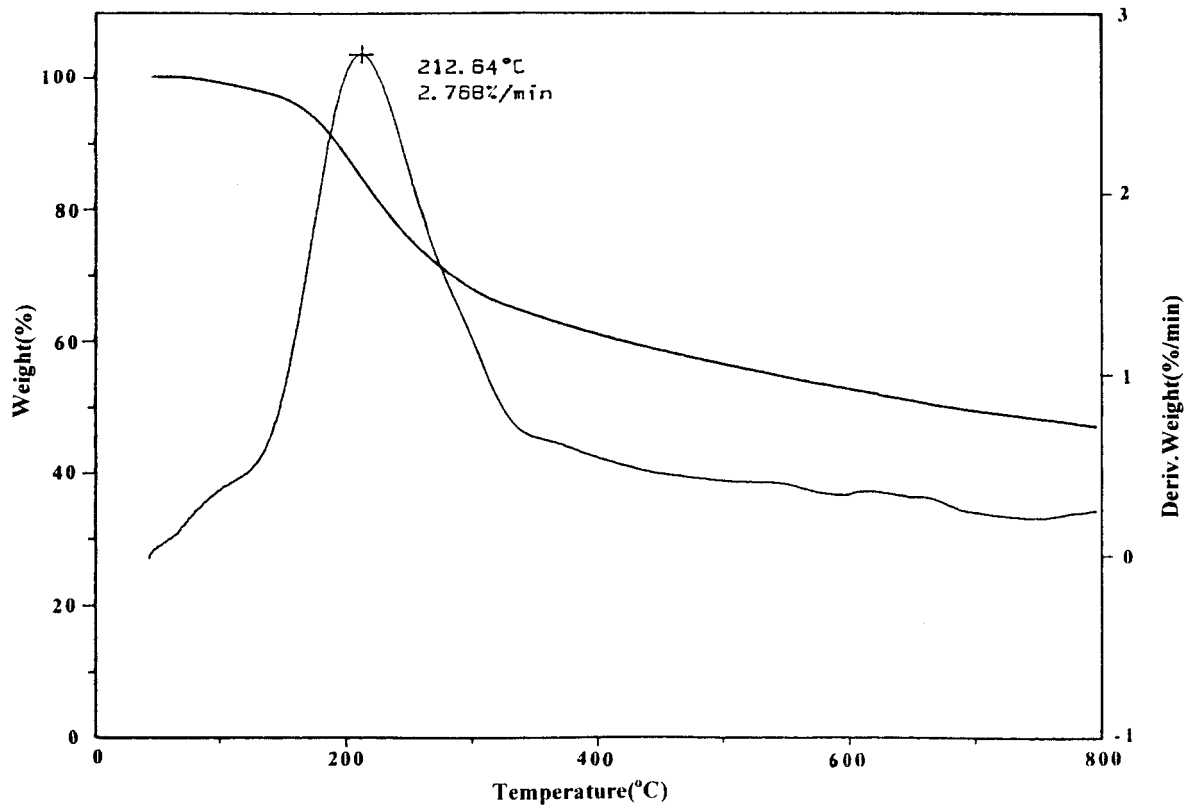


Figure 6 TGA of P2EAn.

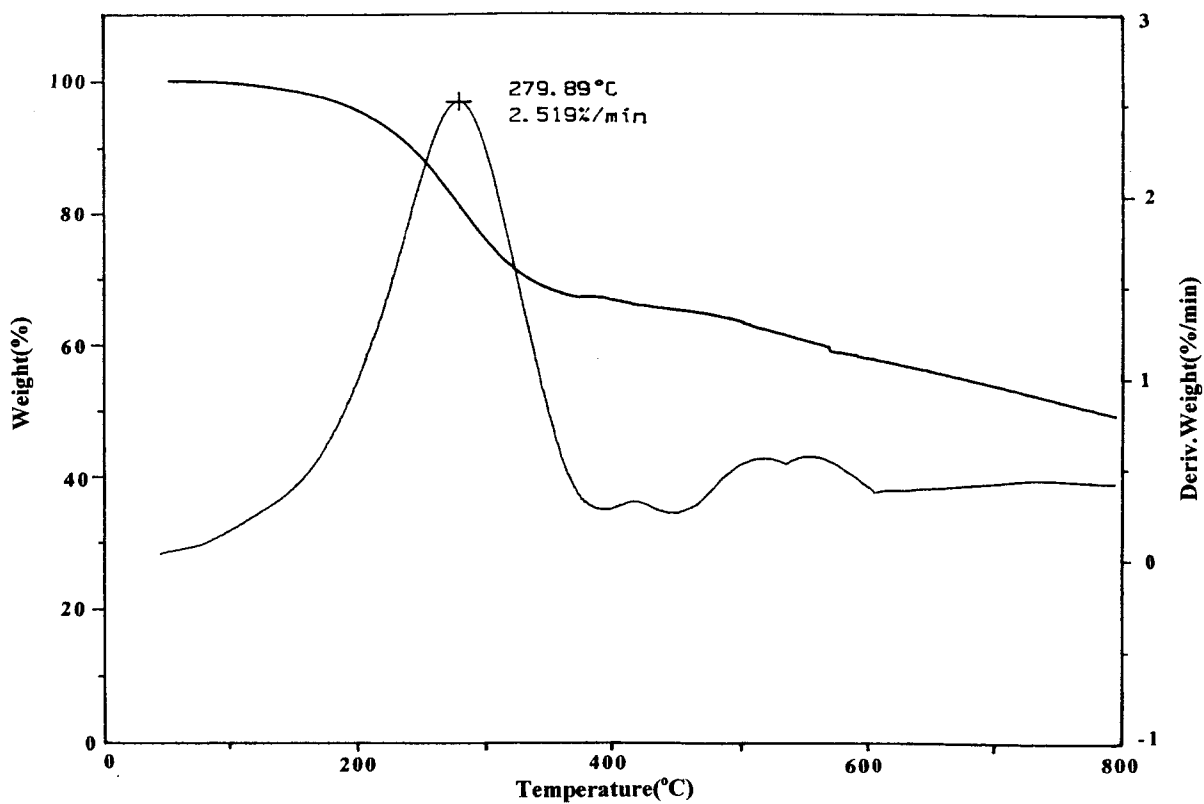


Figure 7 TGA of PNMA.

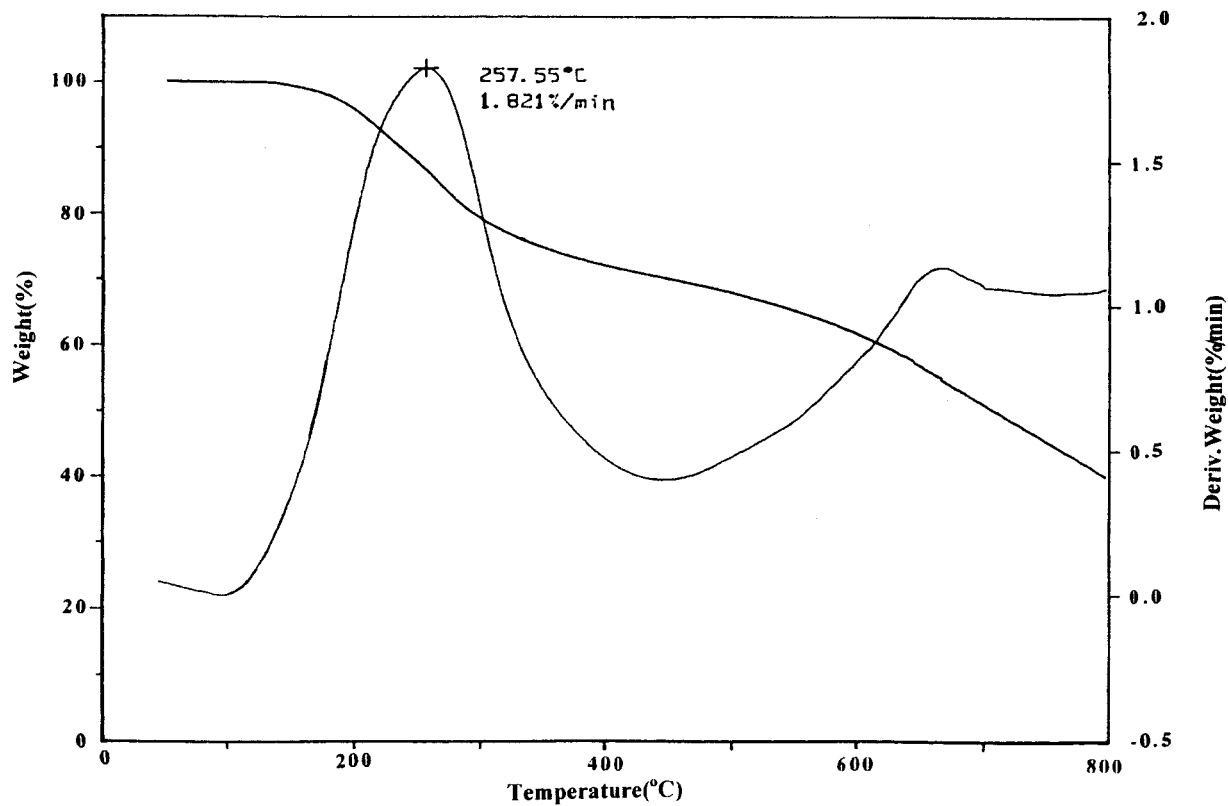


Figure 8 TGA of PNEAn.

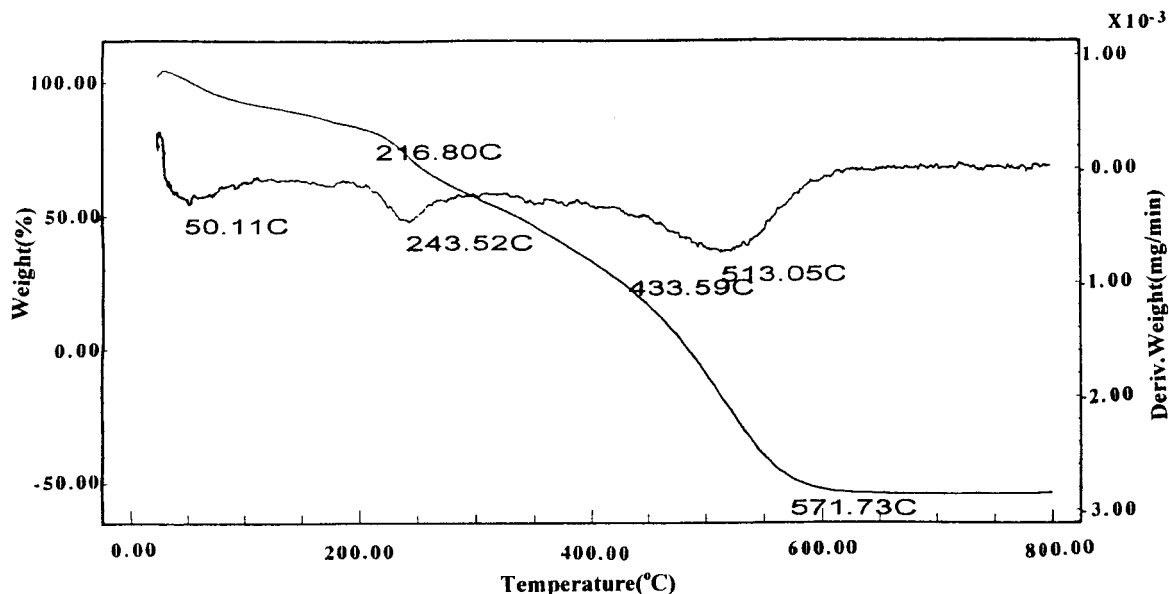


Figure 9 TGA of PA6/POT.

redox process (0.30 and 0.45 V) occurred because of the oxidation of the amine nitrogen atoms into radical cations. In this process, protonation and deprotonation could not be seen. The anodic current peaks in the middle and higher potentials (0.45, 0.60, and 0.90 V) pointed to emeraldine salts as the main products and pernigraniline salts.<sup>31</sup> As seen in Figure 2, the CVs of *N*-methylaniline and *N*-ethylaniline are different. Two redox couples were recorded at 0.48 and 0.50 V on the voltammograms of *N*-methylaniline. Moreover, two reductions in the observed current peaks belong to *N*-methylaniline at 0.48 and 0.31 V. The voltammogram of *N*-ethylaniline shows an oxidation current peak at 0.57 V, whereas, in reverse cycling, it shows a very broad reduction peak. *N*-Alkyl groups can change the  $\pi$ -electron distribution in the aromatic rings.<sup>32</sup> The steric effect of the *N*-alkyl groups would

cause different products to occur. The cyclic voltammetric curves (Fig. 2) indicate that, at low potentials (0.48 V), the major product was 4-aminodiphenylamine, and the side product was benzidine. The steric hindrance of alkyl groups that bonded to nitrogen atoms affected the head-to-head, head-to-tail, and tail-to-tail formation. Therefore, the current peak of benzidine was bigger than the current peak of *p*-aminodiphenylamine.<sup>33</sup> The oxidation and reduction current peaks observed in Figures 1 and 2 with a fast potential scan of 100 mV s<sup>-1</sup> indicate that the films were increasingly deposited on electrode surfaces. Unsymmetrical, tail-shaped potential waves indicated that reagents in the solution phase diffused into the polymer films on the electrode surfaces.<sup>34</sup> The CVs of composite films in a 0.2M H<sub>2</sub>SO<sub>4</sub> solution are shown in Figure 3. The CVs of PA6/POT and PA6/P2EAn are

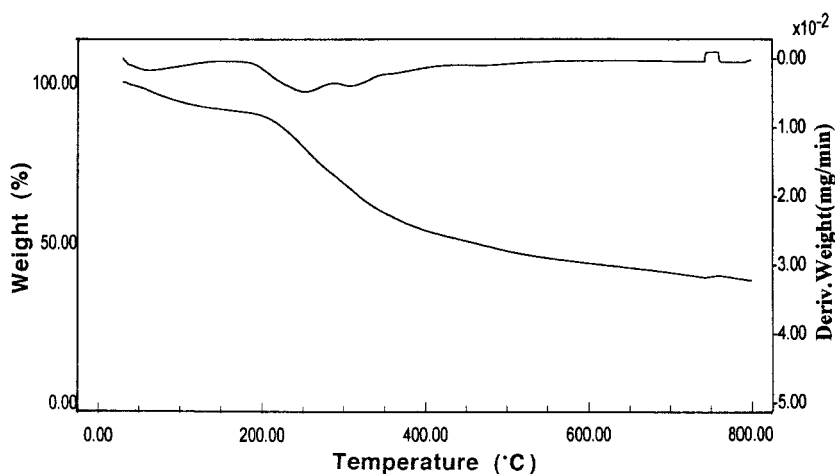


Figure 10 TGA of PA6/P2EAn.

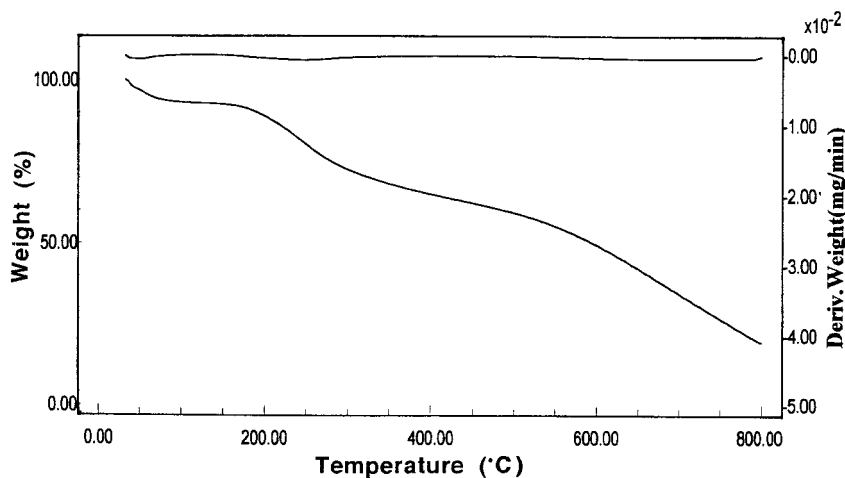


Figure 11 TGA of PA6/PNMAN.

similar. The voltammogram of PA6/PNEAn is also similar. When the four voltammograms were studied, we found that there were no peaks in the anodic and cathodic directions. These results reveal that these bipolymers were composites.<sup>25</sup> The curves obtained in a 0.2M H<sub>2</sub>SO<sub>4</sub> solution (Fig. 3) demonstrated very high anodic and cathodic currents. These phenomena revealed that the polyalkylaniline films had a significant tendency for hydrogen-ion decharging.<sup>35</sup>

The magnetic susceptibility data for the homopolymers and composites are given in Table III. The magnetic susceptibility values of all the polymers were negative. This reveals diamagnetism.<sup>36</sup> These analyses indicate that polyalkylanilines and their composites had diamagnetic properties and that their conducting mechanisms were of bipolaron nature.<sup>37</sup> Bipolaron structures are known as the major charge carriers in polymers.<sup>38</sup> Bipolaron structures clearly appeared in these alkyilanilines. Because aniline derivatives such as *o*-toluidine, 2-ethylaniline, *N*-methylaniline, and *N*-ethylaniline have elec-

tron-donating groups that increase the formation of imine units, these bipolaron structures are very stable.

IR spectra of *o*-toluidine and POT are given in Figure 4. Bands appear that support the polymerization. The doublet peak belongs to a —NH<sub>2</sub> group. The peak observed at 800–900 cm<sup>-1</sup> belongs to a *p*-substituted aromatic ring, and it proves that the polymerization proceeded in a head-to-tail fashion.<sup>39,40</sup>

TGA results for the polymers are given in Figures 5–12 and are also listed in Table IV. As seen in Table IV, the polyalkylanilines decomposed with a one-step weight loss. A PA6/POT composite decomposed in two steps, whereas other composites decomposed in one step. The one-step weight loss occurred between about 160 and 400°C. During this step, the polyalkylanilines decomposed in the skeletons of the polymers, along with the dopant salts. In the two-step decomposition of PA6/POT, the first step occurred between 217 and 434°C, and it could be attributed to the loss of the acid dopant bonded to the polymer chain. The second

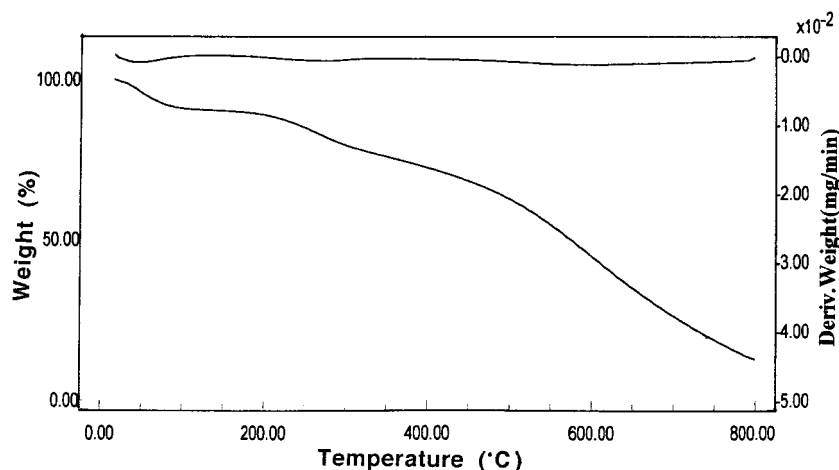


Figure 12 TGA of PA6/PNEAn.



**TABLE IV**  
**Results of TGA Analysis of Polyalkylanilines and Composites**

| Polyalkylaniline or composite | Decomposition temperature (°C) |             |         |
|-------------------------------|--------------------------------|-------------|---------|
|                               | $T_i^a$                        | $T_{max}^b$ | $T_f^c$ |
| POT                           | 228                            | 273         | 315     |
| P2EAn                         | 162                            | 213         | 289     |
| PNMAn                         | 211                            | 280         | 324     |
| PNEAn                         | 179                            | 258         | 317     |
| PA6/POT                       | 217                            | 244         | 434     |
|                               | 434                            | 513         | 572     |
| PA6/P2EAn                     | 205                            | 300         | 382     |
| PA6/PNMAn                     | 184                            | 245         | 295     |
| PA6/PNEAn                     | 214                            | 261         | 309     |

<sup>a</sup> Initial temperature.

<sup>b</sup> Maximum temperature.

<sup>c</sup> Final temperature.

stage of decomposition occurred between 434 and 572°C. This step was due to the degradation of the skeletal bipolymer chain structure after the elimination of the dopant.<sup>41</sup> According to the initial decomposition temperature, among the polyalkylanilines, POT had the highest decomposition temperature (228°C). However, among the composites, PA6/POT had the highest decomposition temperature (217°C). Moreover, it is revealed in Table IV that the maximum decomposition temperatures of the composites were generally higher than the maximum decomposition temperatures of the polyalkylanilines. As a result, it can be concluded that the polymers and their composites had high thermal stability.

**CONCLUSIONS**

We have described the electrochemical synthesis, electrochemical properties, and characterization of some polyalkylanilines and their composites with a PA6 insulating matrix. The conductivities of the PA6/polyalkylaniline composites were different, and the thermal decomposition temperatures (initial, maximum, and final) of the composites increased significantly. The polyalkylaniline-based composites were found to be environmentally stable. We anticipate that these composite films will be used for innovative technological applications.

**References**

1. Genies, E. M.; Boyle, A.; Lapkowski, M.; Tsintavis, C. *Synth Met* 1990, 36, 139.
2. Uchiyama, S.; Sakamoto, H. *Talanta* 1997, 44, 1435.
3. Tassi, E. L.; De Paoli, M. A. *J Chem Commun* 1990, 155.

4. Galvin, M. E.; Wnek, G. E. *Polym Commun* 1982, 23,795.
5. Galvin, M. E.; Wnek, G. E. *J Polym Sci Part A: Polym Chem* 1989, 21, 2727.
6. Patil, R. C.; Ahmed, S. M.; Ogura, K. *Polym J* 2000, 32, 466.
7. Segal, E.; Haba, Y.; Narkis, M.; Siegmann, A. *J Polym Sci Part B: Polym Phys* 2001, 39, 611.
8. Gregory, R. V.; Kimbrell, W. C.; Kuhn, H. H. *Synth Met C* 1989, 28, 823.
9. Kelkar, D. S.; Bhat, N. V. *Polymer* 1983, 34, 986.
10. Yang, J.; Zhao, C.; Cui, D.; Hou, J.; Wan, M.; Xu, M. *J Appl Polym Sci* 1995, 56, 831.
11. Gospodinova, N.; Terlemezyan, L.; Mokreva, P.; Steiskal, J.; Kratochvil, P. *Eur Polym J* 1993, 29, 1305.
12. Steiskal, J.; Kratochvil, P.; Gospodinova, N.; Terlemezyan, L.; Mokreva, P. *Polymer* 1993, 33, 4857.
13. Steiskal, J.; Kratochvil, P.; Gospodinova, N.; Terlemezyan, L.; Mokreva, P. *Polym Int* 1993, 401, 32.
14. Yang, S.; Ruckenstein, E. *Synth Met* 1993, 59, 1.
15. Cao, Y.; Smith, P.; Heeger, A. J. *Synth Met* 1992, 48, 91.
16. Kulkarni, V. G.; Cambell, J. C.; Mathew, W. R. *Synth Met* 1995, 69, 213.
17. Davies, S. I.; Ryan, T. G.; Wilde, C. I.; Beyer, G. *Synth Met* 1995, 69, 209.
18. Ahlshog, M.; Isotalo, O.; Laahso, I.; Stubo, M.; Österholm, I. E. *Synth Met* 1995, 69, 213.
19. Doğan, S.; Akbulut, U.; Toppare, L. *Synth Met* 1992, 53, 29.
20. Karakışla, M. K.; Saçak, M.; Akbulut, U. *J Appl Polym Sci* 1996, 59, 1347.
21. Vatanserver, F.; Akbulut, U.; Toppare, L.; Hacaloğlu, J. *Polymer* 1996, 37, 1103.
22. Yiğit, S.; Hacaloğlu, J.; Akbulut, U.; Toppare, L. *Synth Met* 1996, 79, 11.
23. Vatanserver, F.; Hacaloğlu, J.; Akbulut, U.; Toppare, L. *Polym Int* 1996, 41, 237.
24. Pei, Q.; Bi, X. *Synth Met* 1989, 30, 351.
25. Sari, B.; Talu, M. *Synth Met* 1998, 94, 221.
26. Okabayashi, K.; Goto, F.; Abe, K.; Yoshida, T. *Synth Met* 1987, 18, 365.
27. Duic, L.; Mandic, Z.; Kovacicek, F. *J Polym Sci Part A: Polym Chem* 1994, 32, 105.
28. Mav, I.; Zigon, M. *Synth Met* 2001, 119, 145.
29. Syed, A. A.; Dinesan, M. K. *Talanta* 1991, 38, 815.
30. Byun, M. K.; Soon, S. *Polymer* 1992, 39, 485.
31. Daprano, G.; Leclerc, M.; Zotti, G. *Macromolecules* 1992, 25, 2145.
32. Mikhael, M. G.; Padias, A. B.; Hall, H. K., Jr. *J Polym Sci Part A: Polym Chem* 1997, 35, 1673.
33. Hand, R. L.; Nelson, R. F. *J Am Chem Soc* 1974, 96, 850.
34. Oyama, N.; Ohsaka, T. *Synth Met* 1987, 18, 375.
35. Talu, M.; Kabasakaloglu, M.; Oskoui, H. R. *J Polym Sci Part A: Polym Chem* 1996, 34, 2981.
36. Road, A. *Magnetic Susceptibility Balance: Instruction Manual; Christison Scientific Equipment: United Kingdom, 1993; p 8.*
37. Gupta, M. C.; Sindhimeshram, D. C. *Indian J Chem Sect A* 1994, 33, 558.
38. Kahol, P. K.; Dyakonov, A. J.; McCormick, B. *Synth Met* 1997, 89, 17.
39. Genies, E. M.; Penneau, J. F.; Lapkowski, M.; Boyle, A. *J Electroanal Chem* 1989, 269, 63.
40. Manohar, S. K.; McDarmid, A. G.; Cromack, K. R.; Ginder, J. M.; Epstein, A. J. *Synth Met* 1991, 29, 349.
41. Palaniappan, S.; Narayana, B. H. *J Polym Sci Part A: Polym Chem* 1994, 32, 2431.