

Electrochemical Preparation of Poly(2-bromoaniline) and Poly(aniline-co-2-bromoaniline) in Acetonitrile

Yücel Şahin,¹ Sabriye Perçin,² Mutlu Şahin,¹ Güleren Özkan²

¹Anadolu University, Department of Chemistry, 26470 Eskişehir, Turkey

²Süleyman Demirel University, Department of Chemistry, 32260 Isparta, Turkey

Received 3 December 2002; accepted 2 April 2003

ABSTRACT: Electrochemical preparation of poly(2-bromoaniline) (PBrANI) and poly(aniline-co-2-bromoaniline) [P(An-co-2-BrAn)] was carried out in an acetonitrile solution containing tetrabutylammonium perchlorate (TBAP) and perchloric acid (HClO₄). The cyclic voltammograms during the copolymerization had many features similar to those for the usual polymerization of aniline. The copolymer exhibits a higher dry electrical conductivity value than that of PBrANI and a lower one than that of PANI. The observed

decrease in the conductivity of the copolymer relative to PANI is attributed to the incorporation of bromine moieties into the polyaniline chain. The structure and properties of the polymer and copolymer were elucidated using cyclic voltammetry (CV), FTIR, and UV-vis spectroscopy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2460–2468, 2003

Key words: electrochemistry, copolymerization; polyaniline; conducting polymer

INTRODUCTION

Polyaniline (PANI) has been studied extensively as a special member of the conducting polymer family because of its stability in the presence of air and humidity. PANI has shown many promising applications in industries related to high technologies. PANI and its derivatives can be used in active electrodes,¹ rechargeable batteries,² indicators,³ electrochromic devices,⁴ microelectronics,⁵ etc. However, its applications are strongly limited by its poor processibility. Electropolymerization of aniline derivatives has been widely investigated for the improvement of processibility and other properties of conductive PANI. Substituted PANIs are used to increase the processibility of the polymer. Substituted PANI can be prepared by modifying the polymer chain in the following ways⁶: (i) the post-treatment of parent PANI; (ii) the chemical or electrochemical polymerization of aniline derivatives; and (iii) the copolymerization of aniline with ring or *N*-substituted derivatives. The effect of electron-donating groups (alkoxy, alkyl, etc.) on the solubility and conductivity of PANI has been reported in the literature.^{7–11} There are also a few studies about the polymerization of aniline containing electron-withdrawing groups as substituents. The sulfonic acid dopants can improve the solubility of polymers in common organic solvents and in water. Introducing a —SO₃H group on the PANI chain affects the properties of the parent

PANI without substantially changing the conductivity and is of specific interest for several reasons such as solubility, environmental stability, and processibility.^{12–15}

Halogen-substituted PANIs, such as fluoro-substituted,^{6,16–19} chloro-substituted,^{19–22} and iodo-substituted,²³ have been synthesized and characterized. The polymers, which have electron-donating groups, are soluble in common organic solvents but exhibit lower electrical conductivity values (10⁻³–10⁻¹ S/cm) than those of unsubstituted PANI and the electrical conductivity of the copolymers is strongly dependent on the amount of substituted aniline incorporated.^{7–11} D'Aprano et al. reported that alkoxy monosubstituted anilines exhibit lower conductivities than those obtained with the alkyl derivatives.²⁴ Kang and Yung reported that substitution by an electronegative group (F and Cl) lowers the conductivity of a polymer (<10⁻⁶ S/cm).¹⁹ Neoh et al. also measured the conductivity of iodine- and chlorine-substituted PANI to be smaller than 10⁻⁶ S/cm.²⁵ These results indicate that the side groups may markedly affect the conductivity and processibility of a polymer. Roy et al. reported on the chemical synthesis of poly(*o*-bromoaniline) and poly(aniline-co-*o*-bromoaniline) using methane sulfonic acid as a dopant in an aqueous solution.²⁶ Stejskal et al. synthesized brominated PANI by the reaction of PANI with bromine in an aqueous medium.²⁷ The content of bromine in the modified polymer increased with the amount of bromine introduced into the reaction mixture. The conductivity of poly(2-bromoaniline) (PBrANI) was found to be 3.9 × 10⁻⁵ S/cm in the same work. However, electrochemical polymer-

Correspondence to: Y. Şahin (ysahin@anadolu.edu.tr).

ization of 2-bromoaniline and copolymerization of it with aniline in an acetonitrile solution were not encountered in the literature.

In this work, we report on the electrochemical synthesis of PBrANI (homo polymer) and poly(aniline-co-2-bromoaniline) [P(An-co-2-BrAn)] (copolymer) in an acetonitrile solution containing TBAP and HClO₄. The dry electrical conductivity values of the polymer and copolymer were measured by the four-probe technique. The structure and properties of the polymer and copolymer were elucidated using cyclic voltammetry (CV), FTIR, and UV-vis spectroscopy.

EXPERIMENTAL

Aniline (Aldrich, Milwaukee, WI) was vacuum-distilled (67°C) and kept under a nitrogen atmosphere. 2-Bromoaniline (Aldrich, Milwaukee, WI) was used without further purification. Acetonitrile (Merck, Li-Chrosolv, Darmstadt, Germany), perchloric acid (70%, Aldrich), and tetrabutylammonium perchlorate (TBAP) (Aldrich, Steinheim, Germany) was used as a solvent, as an acid, and as a supporting electrolyte, respectively. The preparation of TBAP was described by Şahin et al.²⁸ All electrochemical experiments were carried out under a nitrogen atmosphere. The electrochemical cell used was of the three-electrode type with separate compartments for the reference electrode (Ag/AgCl, sat.) and the counter electrode (Pt, spiral). The acetonitrile containing a 0.1M TBAP solution in the reference electrode compartment was saturated with AgCl. The working electrode for the cyclic voltammetric studies was a Pt disc (area, 0.0132 cm²). The working electrode was cleaned by polishing with an Al₂O₃ slurry. The macrosamples of the polymer and copolymer films were prepared on a Pt foil (area, 1.0 cm²) cleaned by holding it in a flame for a few minutes. The electrodes were rinsed with acetonitrile and dried before use. Electrodeposition was performed by cyclic potential sweeping in the potential range between -0.30 and +1.90 V (versus Ag/AgCl, sat.) at a sweep rate of 100 mV/s. The films prepared electrochemically were immersed in acetonitrile to remove TBAP and the soluble oligomers and dried under a vacuum at room temperature. Because of their porosity, the films were pressed under a pressure of 5 tons cm⁻² before measuring the dry electrical conductivity of the films.

The dry electrical conductivity values depending on the film thickness were measured using a four-probe technique at room temperature. Gold-plated probes were used to avoid any errors that might arise from the ohmic contacts. At least 10 different current values were used in the measurement of the potential decreases. The electrochemical instrumentation consisted of a Bank Wenking POS 88 Model potentiostat and a Bank 175 model integrator. The current-voltage curves were recorded with a universal software program.

UV-vis spectra of the polymer and copolymer solutions in DMSO were recorded on a Perkin-Elmer spectrophotometer. The polymer and copolymer structures were determined by an FTIR spectrophotometer also using a Perkin-Elmer instrument.

RESULTS AND DISCUSSION

The oxidation of aniline and 2-bromoaniline was recorded at the peak potential of +0.90 V [Fig. 1(a)] and +1.10 V [Fig. 2(a)] (versus Ag/AgCl), respectively, in a TBAP/acetonitrile medium. The first step in the development of a PANI-like structure is often the oxidation of monomers to radical cations. These species are reactive toward most nucleophiles. When the potential scan was reversed toward the cathodic direction, no reduction peak appeared.

Figure 1(a) shows the initial five cyclic voltammetric sweeps taken during the oxidation of 75 mM aniline + 30 mM HClO₄ in a 0.1M TBAP/acetonitrile solution. The potential was scanned from -0.30 to +1.90 V (versus Ag/AgCl) at scan rate of 100 mV/s. The oxidation peak of the aniline shifts to higher anodic potentials and gradually disappears. It shows the formation of a film on the electrode surface and behaves differently from that of a bare Pt working electrode. Figure 1(b) demonstrates the subsequent sweeps obtained in the same solution. The formation and growth of the polymer film can easily be seen in this figure. The oxidation and reduction peaks of the film increase in intensity as the film grows. Two broad oxidation and reduction peaks are observed during the growth of the film. The first oxidation peak at the potential of +0.40 V belongs to the formation of a leucoemeraldine cation radical from leucoemeraldine. The reverse reduction process occurs with a peak potential of +0.025 V. The leucoemeraldine cation radical is further oxidized to emeraldine at the peak potential of +1.10 V with a corresponding cathodic peak at +0.70 V belonging to the reverse process. The electrochemical behavior of the film, in an acetonitrile solution containing 0.1M TBAP (neutral blank solution), is shown in Figure 1(c). The film exhibits two broad oxidation and two reduction peaks related to the blank solution. As seen in this figure, the electroactivity of the film did not deteriorate in the neutral blank solution.

Figure 2(a) illustrates the first five cyclic voltammograms during electrochemical polymerization of 75 mM 2-bromoaniline + 30 mM HClO₄ in a 0.1M TBAP/acetonitrile solution. The potential was scanned from -0.30 to +1.90 V (versus Ag/AgCl) at a scan rate of 100 mV/s. The intensity of the oxidation peak of 2-bromoaniline decreased and shifted to higher anodic potentials. A polymeric film was deposited onto the electrode surface during electrooxidation of 2-bromoaniline. The electrochemistry of the monomers (aniline and 2-bromoaniline) was quite similar.

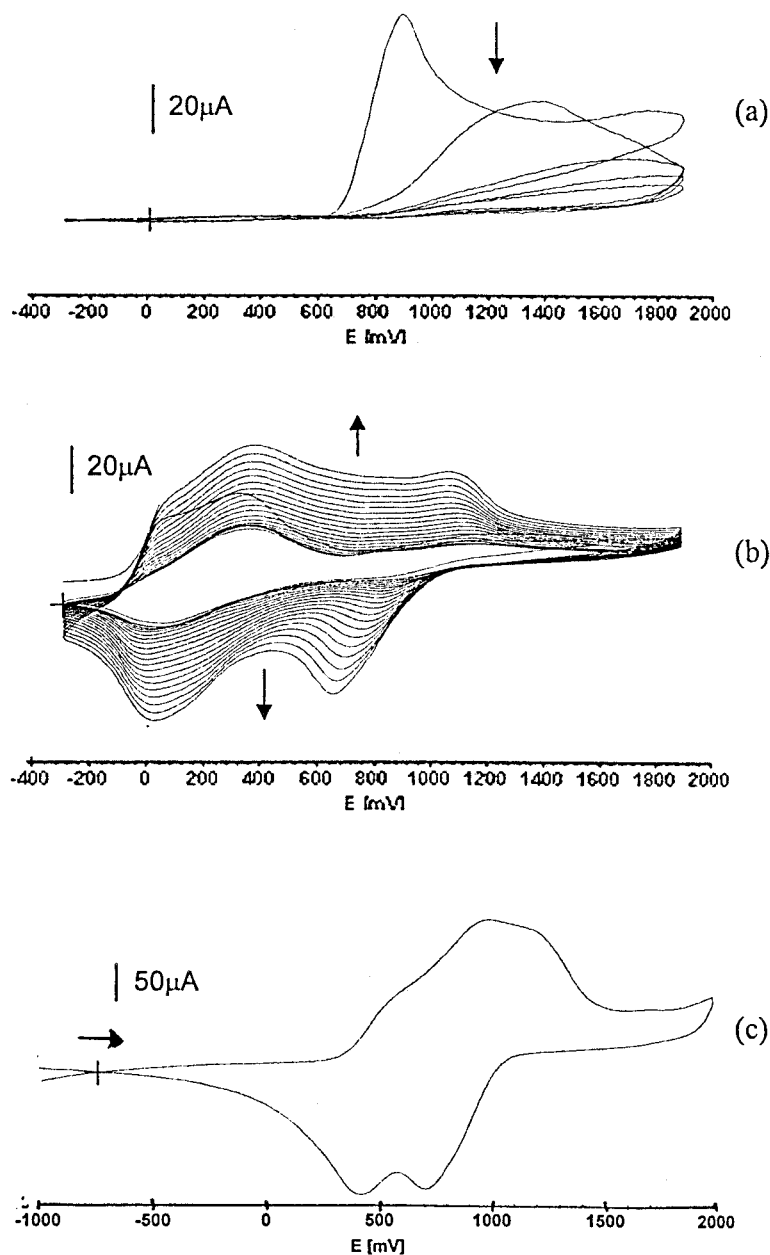


Figure 1 Cyclic voltammograms of the acetonitrile solution containing 75 mM aniline + 30 mM HClO_4 /0.1M TBAP: (a) initial five cyclic voltammograms; (b) subsequent multisweep cyclic voltammograms; (c) electrochemical behavior of the polymer film in neutral blank solution (0.1M TBAP). Scan rate: 100 mV/s.

However, the growth rate of the polymer film was significantly slower [Fig. 2(b)] than that of PANI [Fig. 1(b)]. The voltammogram of 2-bromoaniline involves three oxidation and two reduction peaks [Fig. 2(b)]. The first oxidation peak at about +0.40 V belongs to the formation of a leucoemeraldine cation radical from leucoemeraldine. The reverse reduction process occurs with a peak potential of +0.15 V. The leucoemeraldine cation radicals further oxidized to emeraldine at the peak potential of +0.80 V, with a corresponding cathodic peak at +0.70 V belonging to the reverse process. The third oxidation peak, which appears at +1.20 V, is due to the oxidation of emeraldine to an

emeraldine cation radical. The electrochemical behavior of the film in the neutral blank solution is seen in Figure 2(c). The film did not lose its electroactivity in this medium.

Figure 3 shows the cyclic voltammetric sweeps taken during the oxidation of 75 mM 2-bromoaniline + 150 mM aniline in an acetonitrile solution containing 0.1M TBAP and 30 mM HClO_4 . The films were grown in aniline solutions in the range of 25–200 mM by cycling of the potential between -0.30 and $+1.90$ V (versus Ag/AgCl) for the same period of time (30 min) at a scan rate of 100 mV/s. The optimum aniline concentration was found to be 150 mM. There was a

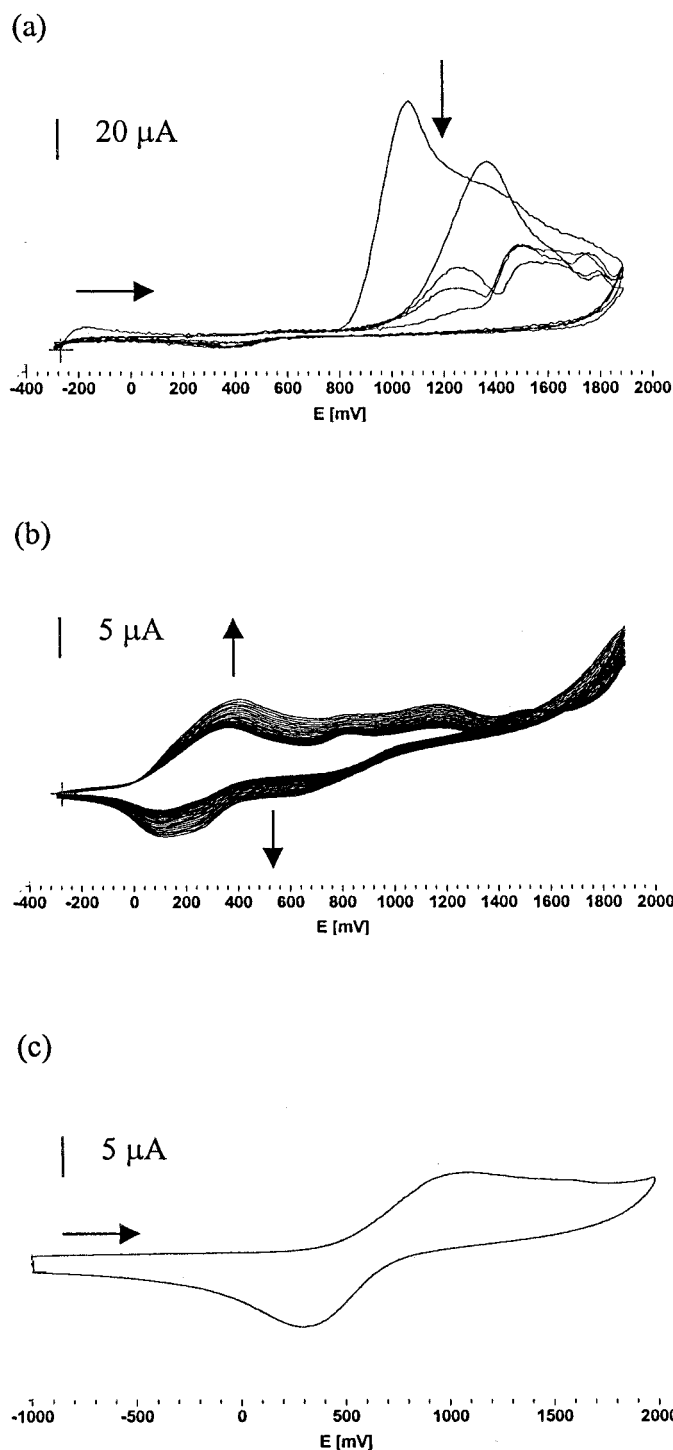


Figure 2 Cyclic voltammograms of the acetonitrile solution containing 75 mM 2-bromoaniline + 30 mM HClO_4 /0.1M TBAP: (a) initial five cyclic voltammograms; (b) subsequent multisweep cyclic voltammograms; (c) electrochemical behavior of the polymer film in neutral blank solution (0.1M TBAP). Scan rate: 100 mV/s.

considerable decrease in the yield of the copolymer formation below and above this aniline concentration. As shown in Figure 3, the cyclic voltammograms during the copolymerization have many features similar to those for the usual polymerization of aniline and 2-bromoaniline as shown in Figures 1 and 2. These

similar voltammograms hint that the structure of the copolymer is not substantially different from PANI and PBrANI.

The electrochemical behavior of the films in basic and acidic solutions is given in Figures 4 and 5, respectively. PANI and poly(2-iodoaniline) (PIANI) lose

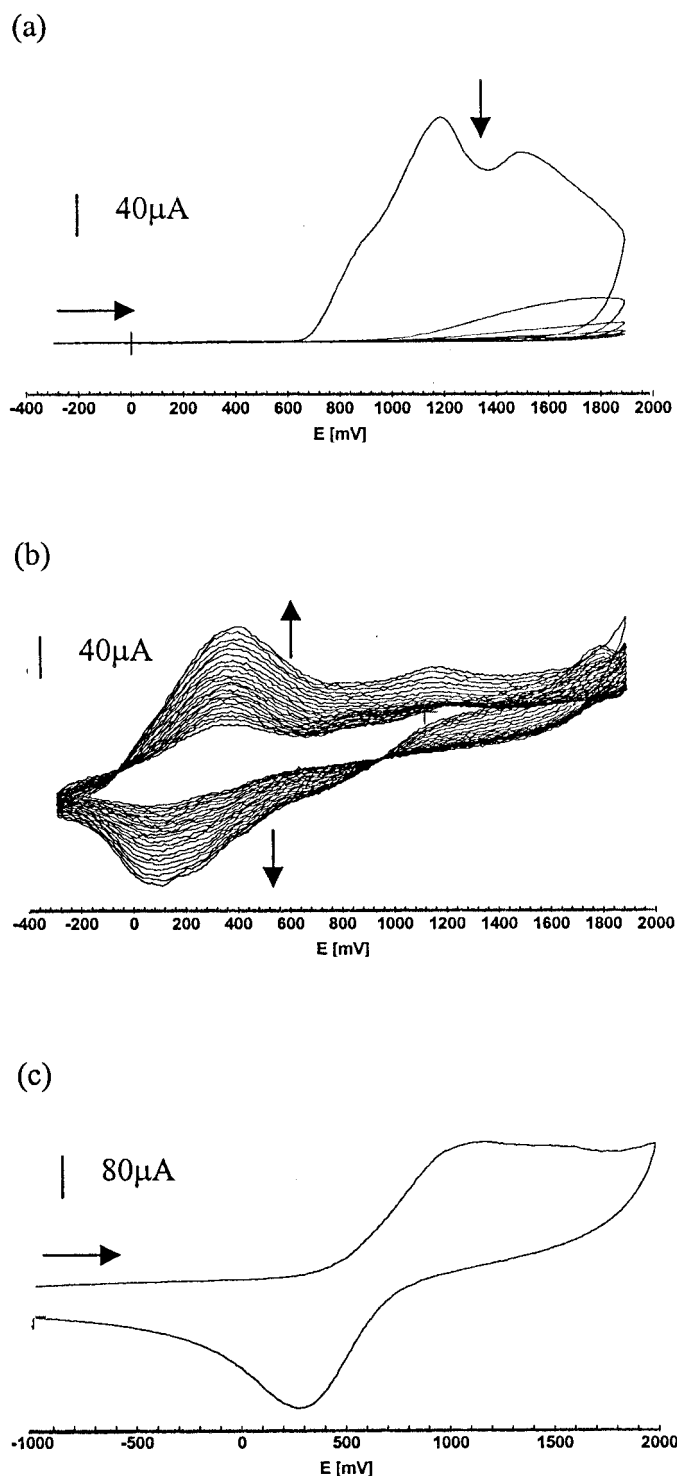


Figure 3 Cyclic voltammograms of the acetonitrile solution containing 75 mM 2-bromoaniline + 150 mM aniline + 30 mM HClO_4 /0.1M TBAP: (a) initial five cyclic voltammograms; (b) subsequent multisweep cyclic voltammograms; (c) electrochemical behavior of the polymer film in neutral blank solution (0.1M TBAP). Scan rate: 100 mV/s.

their electroactivities completely even after a few cycles by the addition of small amounts of pyridine (5 mM) into the TBAP/acetonitrile solution.^{23,29} In the cyclic voltammograms of the PBrANI and P(An-co-2-BrAn) films in a basic blank solution, containing 0.1M TBAP and 5 mM pyridine, the oxidation and reduc-

tion peak of the films disappeared after a few potential scans (Fig. 4), whereas they remained almost unchanged in the neutral blank solution [Fig. 2(c)]. Pyridine causes a rapid loss of electroactivity. The films did not lose their electroactivities in the acidic blank solution, which contained an excess amount of HClO_4

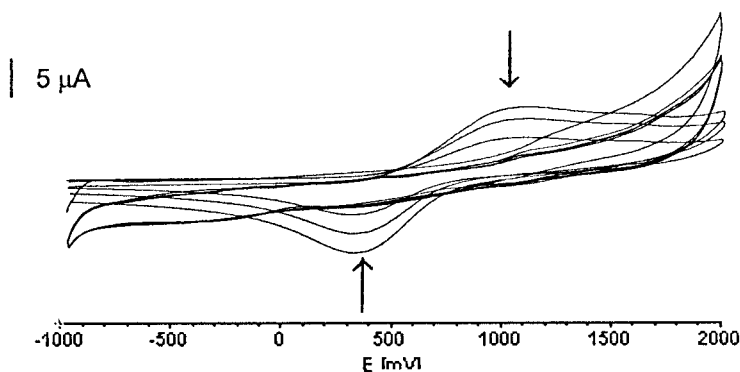


Figure 4 Electrochemical behavior of the film, obtained from 75 mM 2-bromoaniline + 30 mM HClO_4 /0.1M TBAP in basic blank (pyridine/TBAP) solution. Scan rate: 100 mV/s.

(Fig. 5). The voltammetry of PBrANI shows characteristics similar to those of PIANI²³ in both basic and acidic solutions.

During the electrooxidation of both aniline and 2-bromoaniline, a dark-purple-colored material was observed near the electrode which diffused away from the surface into the bulk solution. It indicates the formation of soluble oligomers or low molecular weight polymers. When the cyclic voltammogram of the colored solutions was taken, by the cycling of the potential between -0.30 and $+1.90$ V (versus Ag/AgCl) at a scan rate of 100 mV/s, no new peak was observed in the cyclic voltammograms for both aniline [Fig. 6(b)] and 2-bromoaniline [Fig. 6(d)]. As shown in Figure 6, the cyclic voltammograms of the initial electropolymerization solutions of aniline and 2-bromoaniline [Fig. 6(a,c), respectively] were quite similar to those for the final colored solutions [Fig. 6(b,d)].

The acid concentration is very effective in increasing the amount and quality of the PANI films in acetonitrile solutions. In other words, the extent of protonation of the film is the major factor in its autocatalytic growth. If no proton was present in the medium, highly conducting polyemeraldine would be further oxidized to the less conducting polypernigriline form. Protonation of the quinoid-type nitrogen centers in the

moderately acidic medium also prevents the loss of the NH proton of the leucoemeraldine nitrogen to the quinoid N-centers, thus causing extra stability for the emeraldine. The presence of excess acid, in the medium in which the PANI backbone is growing, also impedes the polymer growth as a result of the protonation of the end amino group.³⁰ The presence of moderate amounts of acids not only improves the stability of aniline cation radicals but also causes the preferred protonation of these species which are primarily involved during the growth of highly conducting PANI.

Efficient polymer growth occurs in moderately acidic medium in an acetonitrile solution. To determine the effect of the acid (HClO_4) concentration on the growth of the polymer film, the films were grown in the range of 5–75 mM acid concentrations by cycling the potential between -0.30 and $+1.90$ V (versus Ag/AgCl) at the same time interval (30 min). The charge, passed during the electrooxidation of these films in the neutral blank solution, was measured (Fig. 7). Then, the charge during the first oxidative cycle of the cyclic voltammograms of the film in the blank solution was measured. The anodic charge, which should be proportional to the thickness of the deposit, was found to increase with an increasing acid concen-

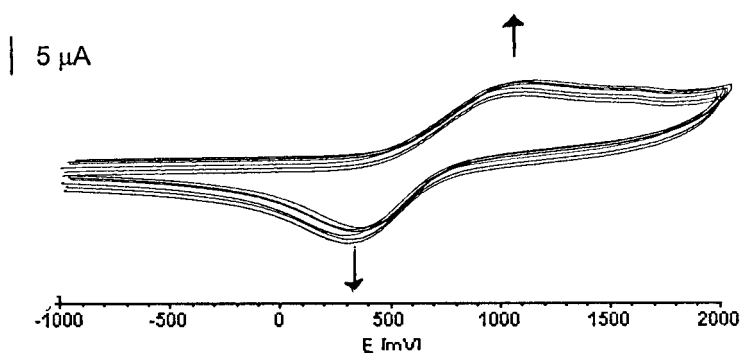


Figure 5 Electrochemical behavior of the film, obtained from 75 mM 2-bromoaniline + 30 mM HClO_4 /0.1M TBAP in acidic blank (HClO_4 /TBAP) solution. Scan rate: 100 mV/s.

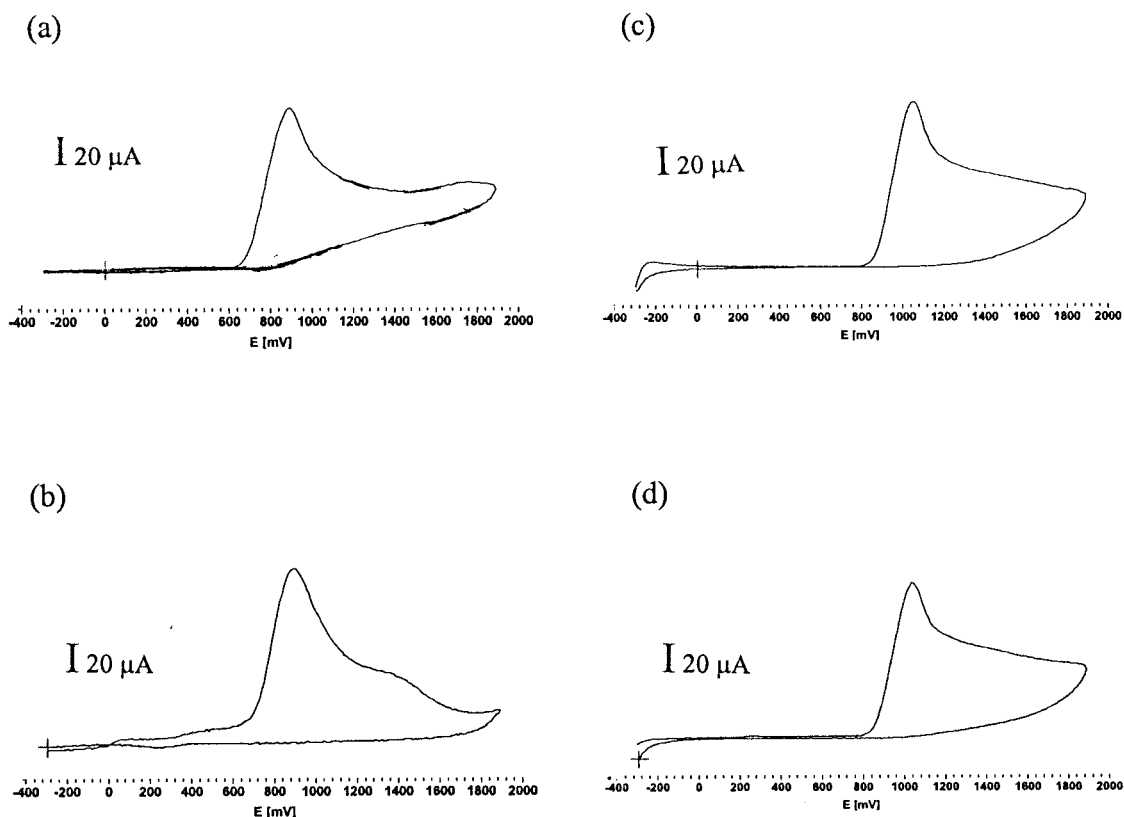


Figure 6 Cyclic voltammograms of the acetonitrile solution containing 75 mM aniline + 30 mM HClO_4 /0.1M TBAP: (a) before and (b) after electropolymerization. Cyclic voltammograms of the acetonitrile solution containing 75 mM 2-bromoaniline + 30 mM HClO_4 /0.1M TBAP: (c) before and (d) after electropolymerization. Scan rate: 100 mV/s.

tration up to 30 mM. It can be concluded that the optimum acid concentration under these conditions was about 30 mM. There was a considerable decrease in the yield of the polymer below and above this acid concentration.

The dry conductivity values of the deposited films obtained from the acetonitrile solutions are listed in Table I. The electron-withdrawing effect of bromine was seen on the conductivity of the PBrANI and P(An-co-2-BrAn) films. As the bromine content increased, the conductivity of the film decreased. The observed decrease in the conductivity of the copolymer, relative to PANI, is attributed to the incorporation of the bromoaniline moieties into the PANI chain. The copolymer exhibits a higher dry electrical conductivity value than that of PBrANI and lower than that of PANI. The conductivity of PBrANI in this study, 9.3×10^{-3} S/cm, is much higher than that reported by Stejskal et al.²⁷: 3.9×10^{-5} S/cm.

The FTIR spectra of the electrochemically prepared PANI, PBrANI, and P(An-2-BrAn) recorded in the range 2000–400 cm^{-1} are shown in Figure 8(a–c), respectively. The peak at about 1580 cm^{-1} is due to the $\text{C}=\text{C}$ double bond of quinoid rings, whereas the peak at 1500 cm^{-1} arises due to vibration of the $\text{C}=\text{C}$ double bond associated with the benzenoid ring. The

1308- cm^{-1} band is assigned to the $\text{C}-\text{N}$ stretch in a secondary aromatic amine.³¹ The band at about 1070–1170 cm^{-1} , primarily due to $\text{C}-\text{H}$ in-plane deformation, was used by Chiang and MacDiarmid³² as a measure of the extent of electron delocalization in the polymer. The peak at 804–831 cm^{-1} is due to aromatic $\text{C}-\text{H}$ bending.³³ The peak observed at 625 cm^{-1} was attributed to the ClO_4^- ion.²⁸ The absorption peak of the quinoid units shifted to higher wavelengths in PBrANI and P(An-2-BrAn). On the other hand, there was almost no change in the characteristic absorption

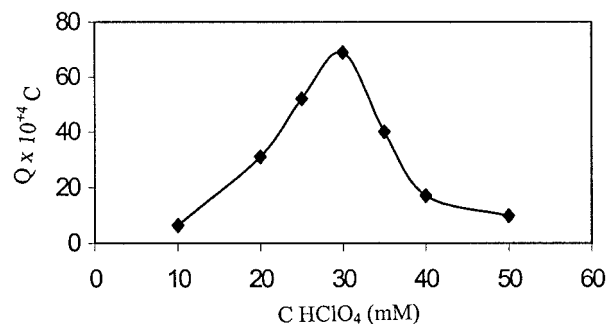


Figure 7 Plot of the charge passed during the electrooxidation of the polymer films in 0.1M TBAP.

TABLE I
Dry Electrical Conductivity Value of PANI, PBrANI, and P(An-co-2-BrAn)

Composition of the electropolymerization solution	Obtained film	Conductivity of the deposited film (S/cm)
75 mM aniline + 30 mM HClO ₄	PANI	2.1
75 mM 2-bromoaniline + 30 mM HClO ₄	PBrANI	9.3×10^{-3}
150 mM aniline + 75 mM 2-bromoaniline + 30 mM HClO ₄	P(An-co-2-BrAn)	6.5×10^{-2}

peak of benzenoid units (1500 cm^{-1}). The expected C—Br aromatic benzenoid and quinoid stretch at $1027\text{--}1032$ and 980 cm^{-1} (ref. 34) are exhibited by both PBrANI and P(An-co-2-BrAn) but are affected by the C—H in-plane deformation. Two new bands at about 800 cm^{-1} in both PBrANI and P(An-co-2-BrAn) and at 710 cm^{-1} in P(An-co-2-BrAn), related to the 1,2,4-trisubstituted benzene ring, are observed.²⁷ There was another band at about 1210 cm^{-1} in the copolymer [P(An-co-2-BrAn)] spectrum (probably C—Br stretching vibration). It is a fact that the synthesized polymer is a homopolymer of 2-bromoaniline and the other one is a copolymer of aniline with 2-bromoaniline and not a mixture of homopolymers. These results are also supported by UV-vis spectra of homopolymers and copolymers.

The UV-vis spectra of the PANI, PBrANI, and P(An-co-2-BrAn) solutions in DMSO recorded at room temperature are shown in Figure 9(a–c), respectively. The spectra are dominated by two broad absorption bands at about 300 nm (peak 1) and 560–640 nm (peak 2). According to the general practice of peak assignment, peak 1 is attributed to the $\pi\text{--}\pi^*$ transition of the benzenoid moieties in the PANI linear structure or simply to the band gap of the polymer.³⁵ Peak 2 closely resembles the benzenoid–quinoid transition in the emeraldine form (middle oxidation state) of PANI.^{35,36} However, the actual band positions are blue-shifted with respect to PANI. The blue shift was induced by the presence of bromine units in the polymer and copolymer [Fig. 9(b,c)]. The electron-withdrawing character of bromine units restricts the effective dispersion of the electrical charge in the conjugated polymeric system, resulting in more locally oxidized polymeric units. The same effects were seen in sulfonated PANIs^{13–15} because of an electron-withdrawing effect of the sulfonate group. These spectra also suggest that the synthesized materials are PBrANI and P(An-co-2-BrAn).

The solubility of PANI, PBrANI, and P(An-co-2-BrAn) was tested in dimethyl sulfoxide (DMSO), 1-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), and tetrahydrofuran (THF) at room temperature. The homopolymer (PBrANI) and copolymer [P(An-co-2-BrAn)] showed improved solubility in those polar solvents compared to PANI. PANI was soluble in DMSO. However, it was not soluble in THF, NMP, and DMF. Unlike PANI, PBrANI and P(An-co-

2-BrAn) were soluble in NMP, THF, DMF, and DMSO. It was noticed that the presence of the halogen atom in the ring of aniline units can produce polymers and copolymers with better solubility in NMP, THF, DMF, and DMSO solvents. Thus, it is possible to cast film of the desired size of PBrANI and P(An-co-2-BrAn).

CONCLUSIONS

The cyclic voltammetric method was used to synthesize PANI, PBrANI, and [P(An-co-2-BrAn)] from acetonitrile solutions of aniline, 2-bromoaniline, and a mixture of aniline and 2-bromoaniline, respectively. The films did not lose their electroactivities in both acidic and neutral blank solutions. However, they lost their electroactivities in a basic blank solution. The dry electrical conductivity value of the copolymer was found to be lower than that of PANI and higher than that of PBrANI. Spectroscopic results (FTIR and UV-

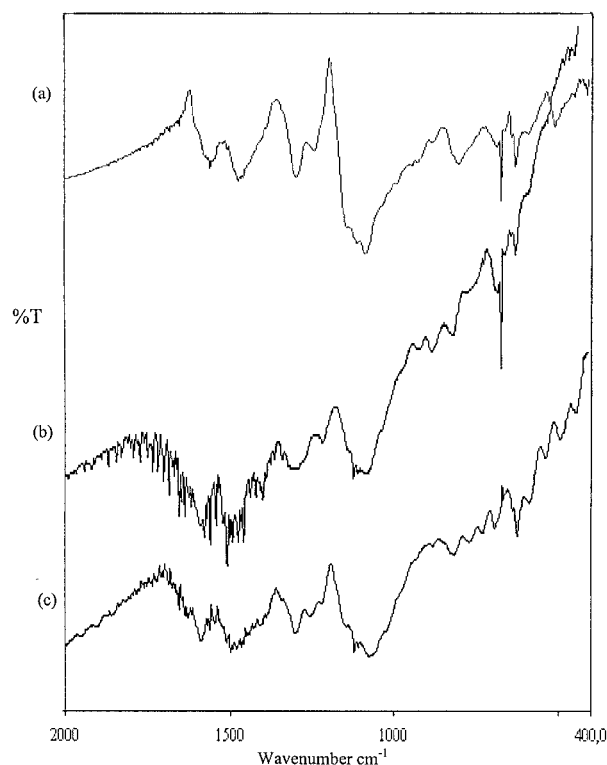


Figure 8 Baseline-corrected FTIR spectra, showing $2000\text{--}400 \text{ cm}^{-1}$ region, of (a) PANI (b) PBrANI, and (c) P(An-co-2-BrAn).

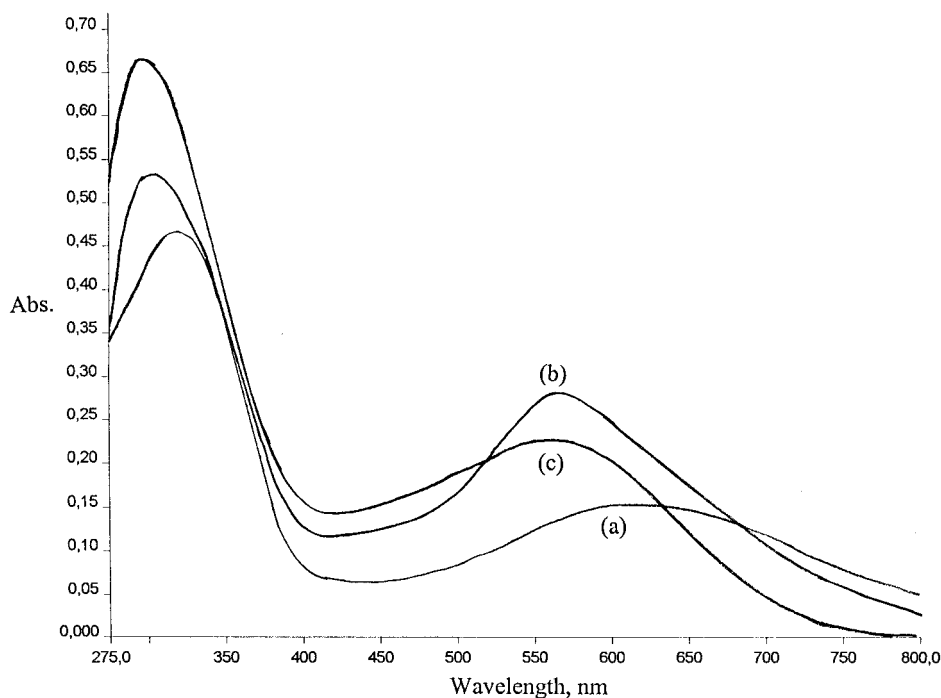


Figure 9 UV-vis absorption spectra of (a) PANI, (b) PBrANI, and (c) P(An-co-2-BrAn) in DMSO.

vis) showed that the polymer and copolymer were different from that of PANI. These spectra and the conductivity behavior of the films suggest that the synthesized materials are PBrANI and [P(An-co-2-BrAn)].

One of the authors (Y. S.) would like to thank Prof. Dr. Attila Yıldız and Assoc. Prof. Kadir Pekmez for measuring the dry electrical conductivity values of the films.

References

- Oyama, N.; Ohsaka, T. *Synth Met* 1987, 18, 191.
- Novak, P.; Muller, K.; Santhanam, K. S. V.; Haas, O. *Chem Rev* 1997, 97, 207.
- Barlett, P. N.; Birkin, P. R. *Synth Met* 1993, 61, 15.
- Katani, A.; Yano, J.; Sasaki, K. J. *J Electroanal Chem* 1980, 209, 227.
- Chao, S.; Wrighton, M. S. *J Am Chem Soc* 1987, 109, 6227.
- Mav, I.; Zigon, M. *Synth Met* 2001, 119, 145.
- Leclerc, M.; D'Aprano, G.; Zotti, G. *Synth Met* 1993, 55, 1527.
- Leclerc, M.; Guay, J.; Dao, L. H. *Macromolecules* 1995, 28, 1727.
- Cattarin, S.; Doubova, L.; Mengoli, G.; Zotti, G. *Electrochim Acta* 1998, 33, 1077.
- Genies, E. M.; Penneau, J. F.; Laprowski, M. *New J Chem* 1998, 12, 765.
- Wei, Y.; Focke, W. W.; Wnek, G. E.; MacDiarmid, A. G. *J Phys Chem* 1989, 93, 495.
- Yue, J.; Apstein, A. J.; Zhong, Z.; Gallogher, P. K.; MacDiarmid, A. G. *Synth Met* 1991, 41, 765.
- Şahin, Y.; Pekmez, K.; Yıldız, A. *Synth Met* 2002, 129, 107.
- Şahin, Y.; Pekmez, K.; Yıldız, A. *J Appl Polym Sci* 2002, 85, 1227.
- Şahin, Y.; Pekmez, K.; Yıldız, A. *Synth Met* 2002, 131(1-3), 7.
- Cihaner, A.; Onal, A. M. *Eur Polym J* 2001, 37, 767.
- Sharma, A. L.; Saxena, V.; Annapaorni, S.; Malhotra, B. D. *J Appl Polym Sci* 2001, 81, 1460.
- Kwon, A. H.; Conklin, J. A.; Makhinson, M.; Kaner, R. B. *Synth Met* 1997, 84, 95.
- Kang, D. P.; Yun, M. S. *Synth Met* 1989, 29, E343.
- Palaniappan, S. *Polym Int* 2000, 49, 659.
- Rajendran, V.; Prakash, S.; Gopalan, A.; Vasudevan, T.; Chen, W.-C.; Wen, T.-C. *Mater Chem Phys* 2001, 69, 62.
- Diaz, F. R.; Sanchez, C. O.; delValle, M. A.; Torres, J. L.; Tagle, L. H. *Synth Met* 2001, 118, 25.
- Şahin, Y.; Perçin, S.; Alsancak, G. Ö. *J Appl Polym Sci* 2003, 89, 1652.
- D'Aprano, G.; Leclerc, M.; Zotti, G. *J Electroanal Chem* 1993, 351, 145.
- Neoh, K. G.; Kang, E. T.; Tan, X. L. *Eur Polym J* 1990, 26, 403.
- Roy, B. C.; Gupta, M. D.; Bhowmik, L.; Ray, J. K. *J Appl Polym Sci* 2002, 86, 2662.
- Stejskal, J.; Trchova, M.; Prokes, J.; Sapurina, I. *Chem Mater* 2001, 13, 4083.
- Şahin, Y.; Pekmez, K.; Yıldız, A. *Synth Met* 2002, 129, 117.
- Pekmez, N.; Pekmez, K.; Yıldız, A. *J Electroanal Chem* 1994, 370, 223.
- Pekmez, N.; Pekmez, K.; Arca, M.; Yıldız, A. *J Electroanal Chem* 1993, 353, 237.
- Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth Met* 1988, 24, 231.
- Chiang, J. C.; MacDiarmid, A. G. *Synth Met* 1986, 13, 193.
- Quillard, S.; Louarn, G.; Lefrant, S.; MacDiarmid, A. G. *Phys Rev B* 1994, 50, 12496.
- Cattarin, S.; Mengoli, D. G.; Zotti, G. *J Electroanal Chem Interfac Electrochem* 1988, 239, 1077.
- Lee, J. Y.; Cui, C. Q. *J Electroanal Chem* 1996, 403, 109.
- McCall, R. P.; Ginder, J. M.; Lengs, J. M.; Ye, H. Y.; Manohar, S. K.; Astruios, G. E.; MacDiarmid, A. G.; Epstein, A. J. *Synth Met* 1997, 84, 97.