Electrochemical Polymerization of Fluoro- and Chloro-Substituted Anilines and Copolymers with Aniline

Yücel Şahin,[1] Sabriye Perçin,[2] Mutlu Şahin,[1] Güleren Özkan[2]

[1]*Department of Chemistry, Anadolu University, 26470 Eskişehir, Turkey*
[2]*Department of Chemistry, Süleyman Demirel University, 32260 Isparta, Turkey*

ABSTRACT: Poly(2-fluroaniline) and poly(2-chloroaniline) were synthesized by an electrochemical method in an acetonitrile solution containing tetrabutylammonium perchlorate and perchloric acid. Also, the electrochemical copolymerization of aniline with 2-fluroaniline and 2-chloroaniline was carried out in the same medium. Cyclic voltammograms of the deposited films were recorded in neutral, acidic, and basic solutions. The electrochemical behavior of the films showed the same characteristic results as conventional polyaniline. The observed decrease in the dry electrical conductivity of the copolymers with respect to polyaniline was attributed to the incorporation of the fluoro- and chloro-substituted anilines into the polyaniline chain. Further characterization of the polymer and copolymer products was performed through dry electrical conductivity measurements, ultraviolet–visible spectroscopy, and Fourier transform infrared spectroscopy. The relative solubility of the films was determined in various common organic solvents. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2302–2312, 2004

Key words: halogenated anilines; conducting polymers; copolymerization; electropolymerization

INTRODUCTION

Conducting polymers in highly extended conjugated electron systems in the main chain have recently attracted much attention from both fundamental and practical perspectives. Polyaniline (PANI) has been studied extensively as a special member of the conducting polymer family because of its stability and potentially attractive economics. This polymer and its derivatives can be used in rechargeable batteries, electromagnetic interference shielding, electrochromic display devices, sensors, and electrocatalysis.[1–3] Attempts to overcome the associated difficulty of PANI in applications due to its restricted solubility in common organic solvents have been made by many researchers using different approaches. One of the methods used to improve the solubility of PANI is the use of sulfonic acids as dopants. Introducing a —SO_3H group into the PANI chain affects the properties of the parent PANI without substantial conductivity and is of specific interest for several reasons, such as solubility, environmental stability, and processability.[4–10] Also, the polymers of substituted anilines have shown better solubility. The substituent groups present in the units of the polymer chain cause a decrease in the stiffness of the polymer chain and result in better solvation. Several substituted PANIs with electron-donating groups (alkoxy, alkyl, etc.) have been re-

ported in the literature;[11–15] these polymers are soluble in common solvents but exhibit lower electrical conductivity values (10^{-3} to 10^{-1} S/cm) than unsubstituted PANI. These results indicate that the side groups may markedly affect the polymerizability of anilines.[11] Borole et al.[16] prepared PANI, poly(o-toluidine) (POT), and polyaniline-co-poly(o-toluidine) (PANI–POT) thin films doped by several organic salts with cations of various sizes, using an aqueous solution of H_2SO_4 as an electrolyte. The conductivities of PANI, POT, and PANI–POT films were determined in a solution containing $0.1M$ monomer and $1M$ H_2SO_4 to be 0.0972, 0.0563, and 0.0765 S/cm, respectively. PANI, poly(2,5-dimethoxyaniline) (PDMA), and copolymers of 2,5-dimethoxyaniline with aniline were prepared by Huang et al.[17] The electrical conductivity values of PANI, PDMA, and PANI–PDMA were measured to be 1.36, 5.49×10^{-5}, and 0.34 S/cm, respectively. A lower conductivity of the copolymer, with respect to PANI, was expected to arise from the steric effect of the substituent (—OCH_3), which could provide torsional twists in the polymer backbone, reducing the coplanarity and average electron delocalization length. When they changed the ratio of the monomers, different conductivity values were observed, between 0.34 and 6.08×10^{-4} S/cm for the copolymer. The synthesis of different homopolymers and copolymers derived from anilines bearing electron-withdrawing groups has been reported. The electrochemical polymerization of halogen-substituted anilines was performed potentiostatically in a single-compartment cell equipped with a gold-coated ceramic plate as an an-
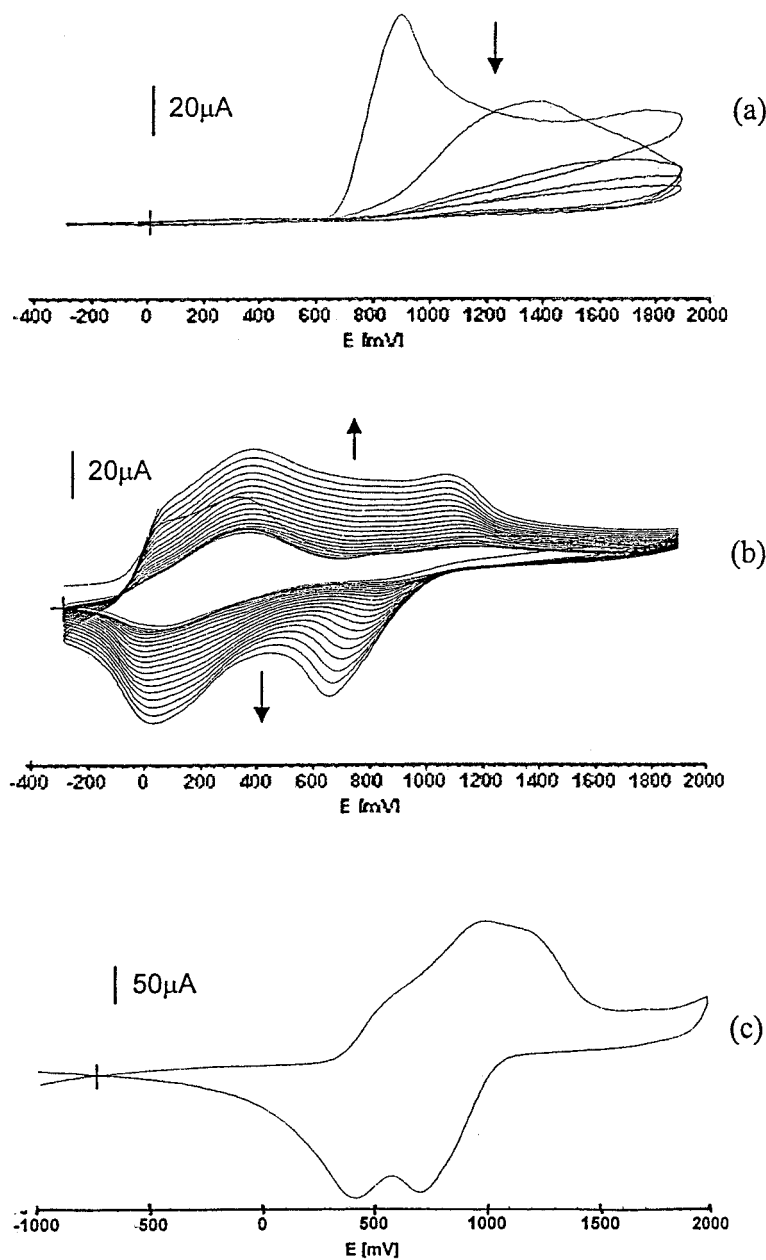
Figure 1 Cyclic voltammograms of an acetonitrile solution containing 75 m*M* aniline and 30 m*M* HClO$_4$/0.1*M* TBAP: (a) the five initial cyclic voltammograms, (b) the subsequent multisweep cyclic voltammograms, and (c) the electrochemical behavior of the polymer film in a neutral blank solution (0.1*M* TBAP). The scanning rate was 100 mV/s.

ode, platinum as a cathode, and lithium perchlorate as a supporting electrolyte by Snauwaert et al.[18] Neoh et al.[19] reported the chemical copolymerizations of aniline with mono-ortho-halogenated anilines (2-chloroaniline and 2-iodoaniline), and they showed that the presence of Cl- or I-substituted groups in the ortho position did not adversely affect the polymerization. The measured electrical conductivity of the homopolymers, poly(2-chloroaniline) (PClANI) and poly(2-iodoaniline) (PIANI), was less than 10^{-6} S/cm, and the electrical conductivity of the copolymers was strongly dependent on the amount of the substituted aniline incorporated. Recently, we investigated the

electrochemical polymerization of 2-iodoaniline[20] and 2-bromoaniline[21] and their copolymerization with aniline in an acetonitrile solution. We obtained soluble homopolymers and copolymers in common organic solvents. Palaniappan[22] reported the synthesis of poly(aniline-*co*-2-chloroaniline)-*p*-toluene-sulfonate and poly(aniline-*co*-2-chloroaniline) [P(An-*co*-2-ClAn)] formate salts from an aqueous solution of aniline and *o*-chloroaniline by chemical polymerization. The electropolymerization of aniline with *o*-chloroaniline was synthesized with a pulse potentiostatic method in an aqueous medium by Rajendran et al.[23] Poly(dichloroaniline-*co*-aniline) was synthesized by the chemical

copolymerization of aniline with dichloroaniline in 1M aqueous hydrochloric acid with potassium dichromate as an oxidizing agent by Diaz et al.[24] Mav and Zigon[25] reported the chemical copolymerization of 2-methoxyaniline with 2- or 3-substituted anilines (—SO$_3$H, —COOH, —Cl, —F, —NO$_2$ and —CH$_3$). Sharma et al.[26] reported the chemical synthesis and characterization of poly(aniline-*co*-fluoroaniline). Kang and Yun[27] carried out a polymerization study of
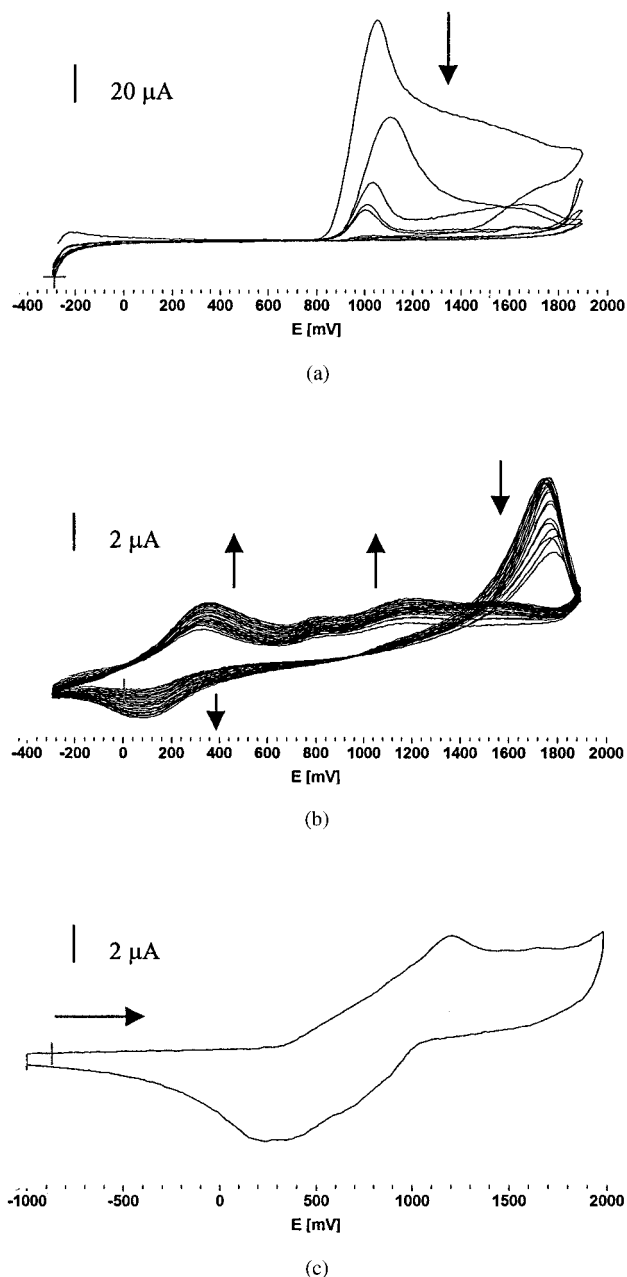

Figure 2 Cyclic voltammograms of an acetonitrile solution containing 75 mM 2-fluoroaniline and 30 mM HClO$_4$/0.1M TBAP: (a) the five initial cyclic voltammograms, (b) the subsequent multisweep cyclic voltammograms, and (c) the electrochemical behavior of the polymer film in a neutral blank solution (0.1M TBAP). The scanning rate was 100 mV/s.

Figure 3 Cyclic voltammograms of an acetonitrile solution containing 75 mM 2-chloroaniline and 30 mM HClO$_4$/0.1M TBAP: (a) the five initial cyclic voltammograms, (b) the subsequent multisweep cyclic voltammograms, and (c) the electrochemical behavior of the polymer film in a neutral blank solution (0.1M TBAP). The scanning rate was 100 mV/s.
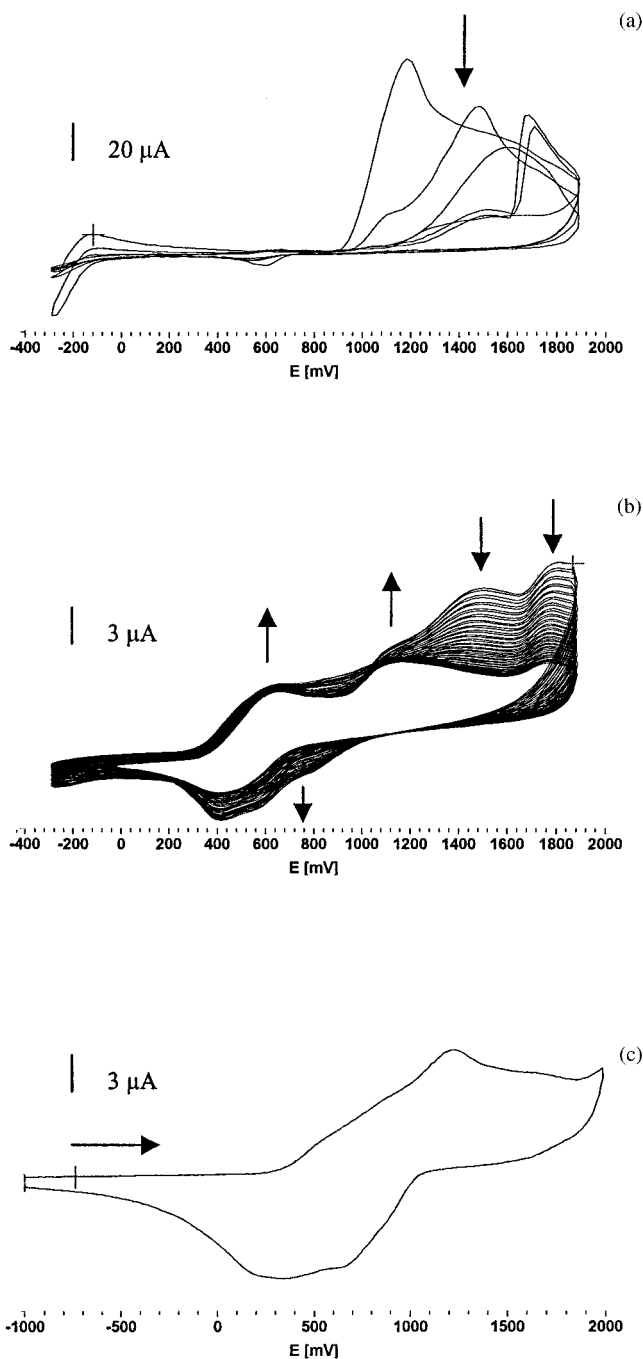
2-fluoroaniline and 2-chloroaniline with chromic acid at various pHs. Their results indicated that substitution by an electronegative group lowered the conductivity of a polymer. Thus, PClANI had a conductivity of 7.9×10^{-5} S cm^{-1}, whereas poly(2-fluoroaniline) (PFANI) had a conductivity of 8.3×10^{-6} S cm^{-1}. Cihaner and Önal[28] reported the synthesis of fluorine-
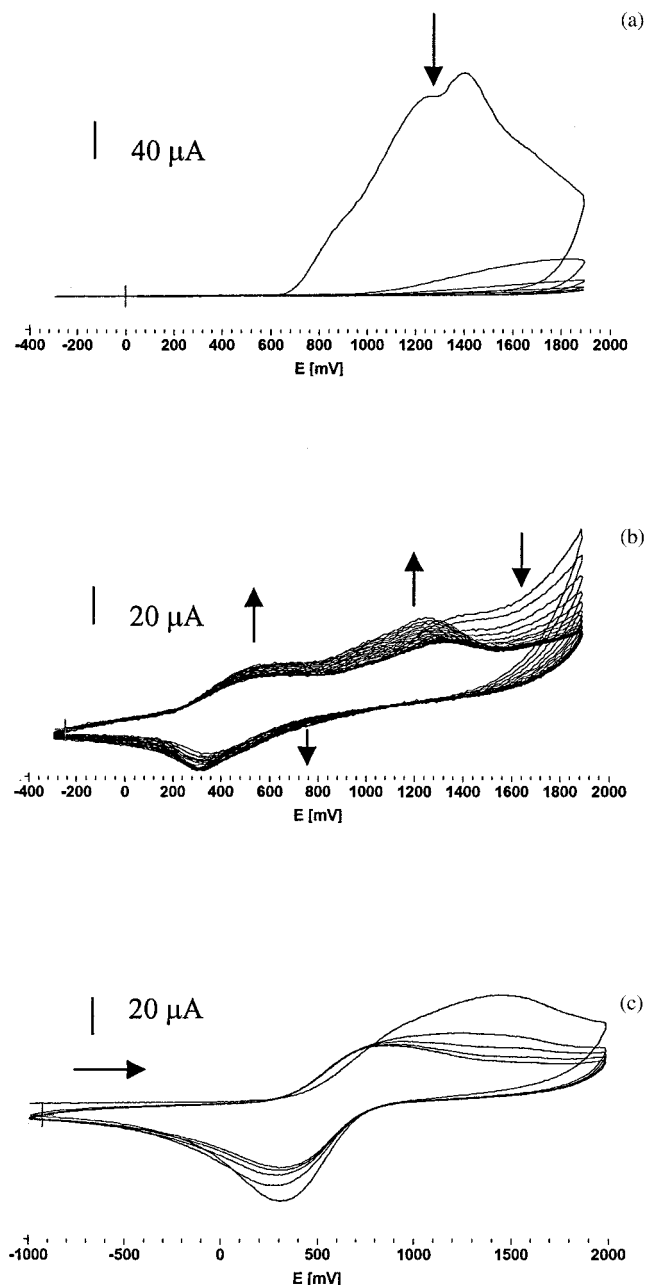
aniline and their copolymerization with aniline in an acetonitrile solution containing tetrabutylammonium perchlorate (TBAP) and perchloric acid. The structures and properties of the polymers and copolymers were elucidated with dry electrical conductivity measurements, cyclic voltammetry, Fourier transform infrared (FTIR), and ultraviolet–visible (UV–vis) spectroscopy. The relative solubility of the polymers and copolymers was determined in various organic solvents.
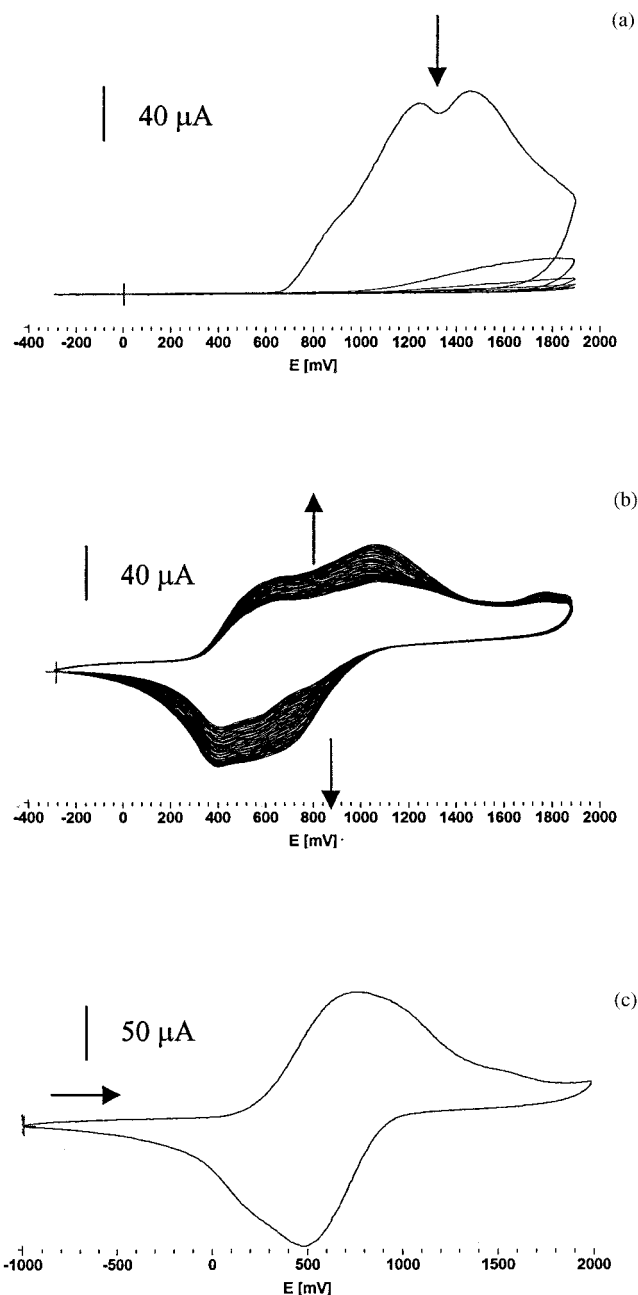

Figure 4 Cyclic voltammograms of an acetonitrile solution containing 75 mM 2-fluoroaniline, 150 mM aniline, and 30 mM HClO$_4$/0.1M TBAP: (a) the five initial cyclic voltammograms, (b) the subsequent multisweep cyclic voltammograms, and (c) the electrochemical behavior of the polymer film in a neutral blank solution (0.1M TBAP). The scanning rate was 100 mV/s.

substituted PANIs from 2-, 3-, and 4-fluoroaniline monomers with K$_2$Cr$_2$O$_7$ as an oxidizing agent. They also investigated the electrochemical behavior and electrochemical polymerization of fluoro-substituted anilines.[29] Soluble polymers were obtained from an acetonitrile–water solution containing NaClO$_4$ (as a supporting electrolyte) by constant potential electrolysis.

In this study, we used a cyclic voltammetry method for the polymerization of 2-fluroaniline and 2-chloro-

Figure 5 Cyclic voltammograms of an acetonitrile solution containing 75 mM 2-chloroaniline, 150 mM aniline, and 30 mM HClO$_4$/0.1M TBAP: (a) the five initial cyclic voltammograms, (b) the subsequent multisweep cyclic voltammograms, and (c) the electrochemical behavior of the polymer film in a neutral blank solution (0.1M TBAP). The scanning rate was 100 mV/s.
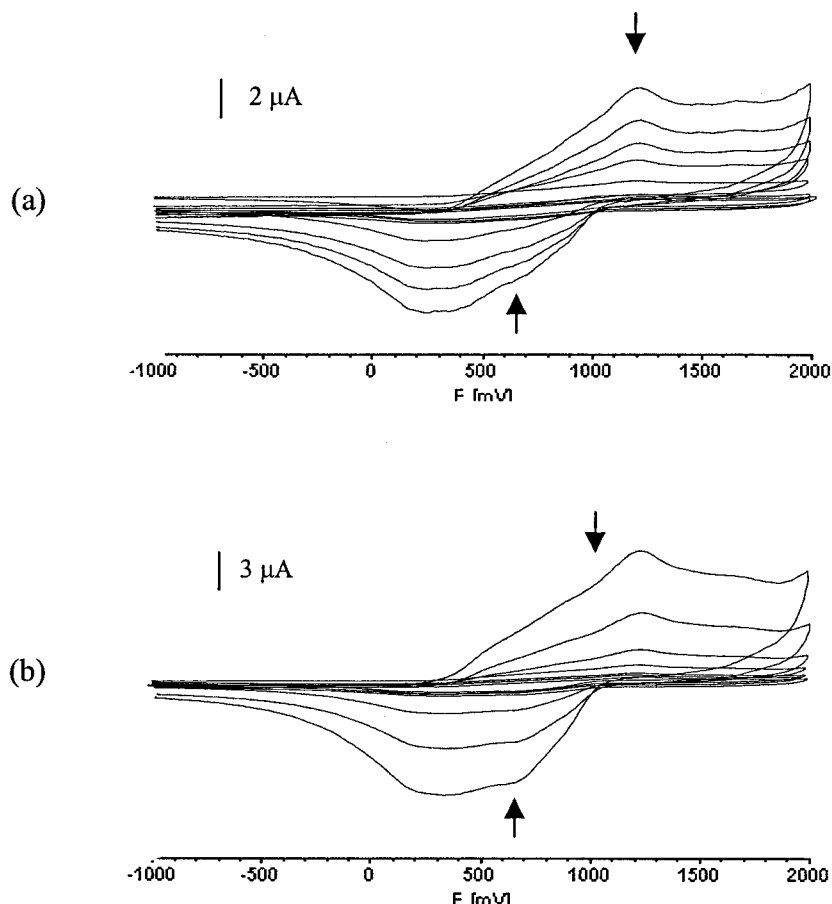
Figure 6 Electrochemical behavior of films obtained from (a) 75 mM 2-fluoroaniline and 30 mM HClO$_4$/0.1M TBAP and (b) 75 mM 2-chloroaniline and 30 mM HClO$_4$/0.1M TBAP in a basic blank solution (pyridine/TBAP). The scanning rate was 100 mV/s.

EXPERIMENTAL

Aniline (Aldrich, Milwaukee, WI), 2-fluroaniline (Aldrich, Steinheim, Germany), and 2-chloroaniline (Aldrich, Steinheim, Germany) were vacuum-distilled and kept under a nitrogen atmosphere. Acetonitrile (LiChrosolv, Merck, Darmstadt, Germany), perchloric acid (70%; Aldrich, Steinheim, Germany), and TBAP were used as a solvent, as an acid, and as a supporting electrolyte, respectively. The preparation of TBAP was described by Şahin et al.[30] All electrochemical experiments were carried out under a nitrogen atmosphere. The electrochemical cell used was the three-electrode type with separate compartments for the reference electrode (Ag/AgCl, saturated) and the counter electrode (Pt spiral). The acetonitrile-containing 0.1M TBAP solution in the reference electrode compartment was saturated with AgCl. The working electrode for the cyclic voltammetry studies was a Pt disc (area = 0.0132 cm^2). The working electrode was cleaned through polishing with Al$_2$O$_3$ slurry. The macrosamples of the polymer and copolymer films were prepared on Pt foil (area = 1.0 cm^2) cleaned by being held 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 (vs Ag/AgCl, saturated) at a sweep rate of 100 mV/s. The films prepared electrochemically were immersed in acetonitrile to remove TBAP and the soluble oligomers and were dried *in vacuo* at room temperature. Because of their porosity, the films were pressed under a pressure of 490 MPa before the dry electrical conductivity of the films was measured.

The dry electrical conductivity values, depending on the film thickness, were measured with a four-probe technique at room temperature. Gold-plated probes were used to prevent any errors that might arise from the ohmic contacts. At least 10 different current values were used in the measurement of the potential drops.

The electrochemical instrumentation consisted of a Bank Wenking POS 88 potentiostat (Bank Elektronic, Germany) and a Bank Wenking EVI 95 Voltage Integrator (Bank Elektronic). The current–voltage curves were recorded with a universal software program.

UV–vis spectra of the polymer and copolymer solutions in dimethyl sulfoxide (DMSO) were recorded on a PerkinElmer spectrophotometer (Lambda 20; PerkinElmer, CT). The polymer and copolymer struc-
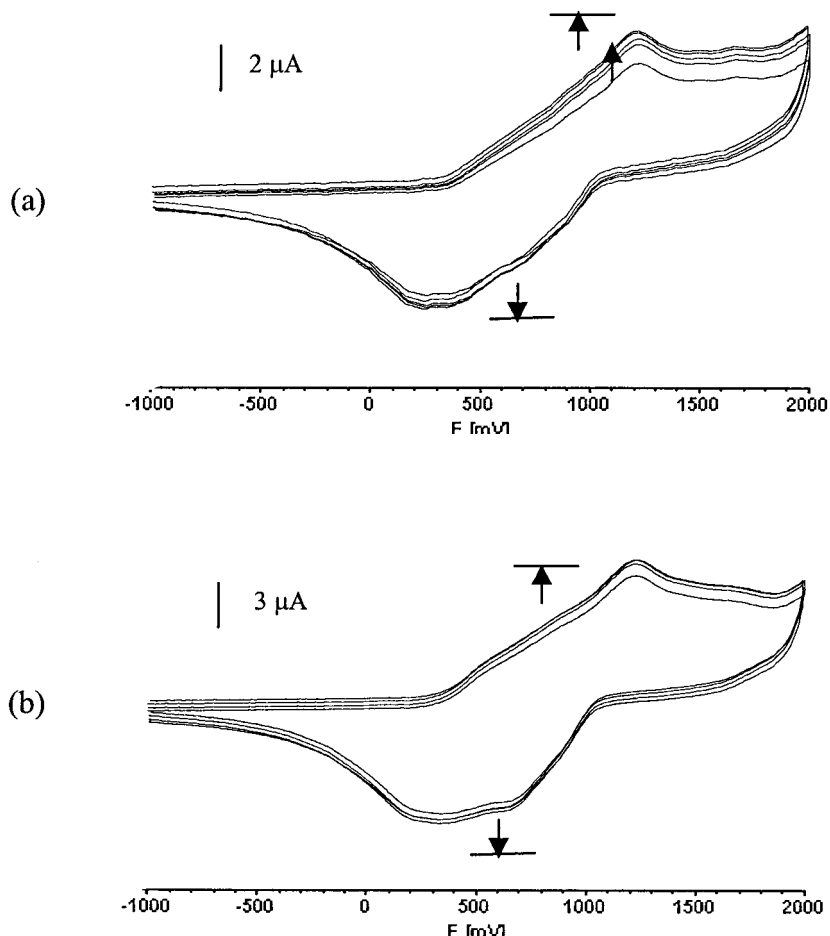
Figure 7 Electrochemical behavior of films obtained from (a) 75 mM 2-fluoroaniline and 30 mM HClO$_4$/0.1M TBAP and (b) 75 mM 2-chloroaniline and 30 mM HClO$_4$/0.1M TBAP in an acidic blank solution (HClO$_4$/TBAP). The scanning rate was 100 mV/s.

tures were determined with an FTIR spectrophotometer from PerkinElmer. The KBr pellet technique was used to prepare the samples for the recording of the IR spectra.

RESULTS AND DISCUSSION

Figure 1(a) shows the five initial cyclic voltammetry sweeps taken during the oxidation of 75 mM aniline and 30 mM HClO$_4$ in a 0.1M TBAP/acetonitrile solution. The potential was scanned from -0.30 to $+1.90$ V (vs Ag/AgCl) at scanning rate of 100 mV/s. The oxidation of aniline was recorded at the peak potential of $+0.90$ V (vs Ag/AgCl) in the same 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. 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 than 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 can be observed during the growth of the film. The first oxidation peak at the potential of $+0.40$ V belongs to the formation of the 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 peaks and two reduction peaks in the blank solution. The electroactivity of the film is not lost in the neutral blank solution.

Figures 2 and 3 show the electrochemical polymerization of 2-fluoroaniline and 2-chloroaniline in an acetonitrile solution. Figures 2(a) and 3(a) illustrate the
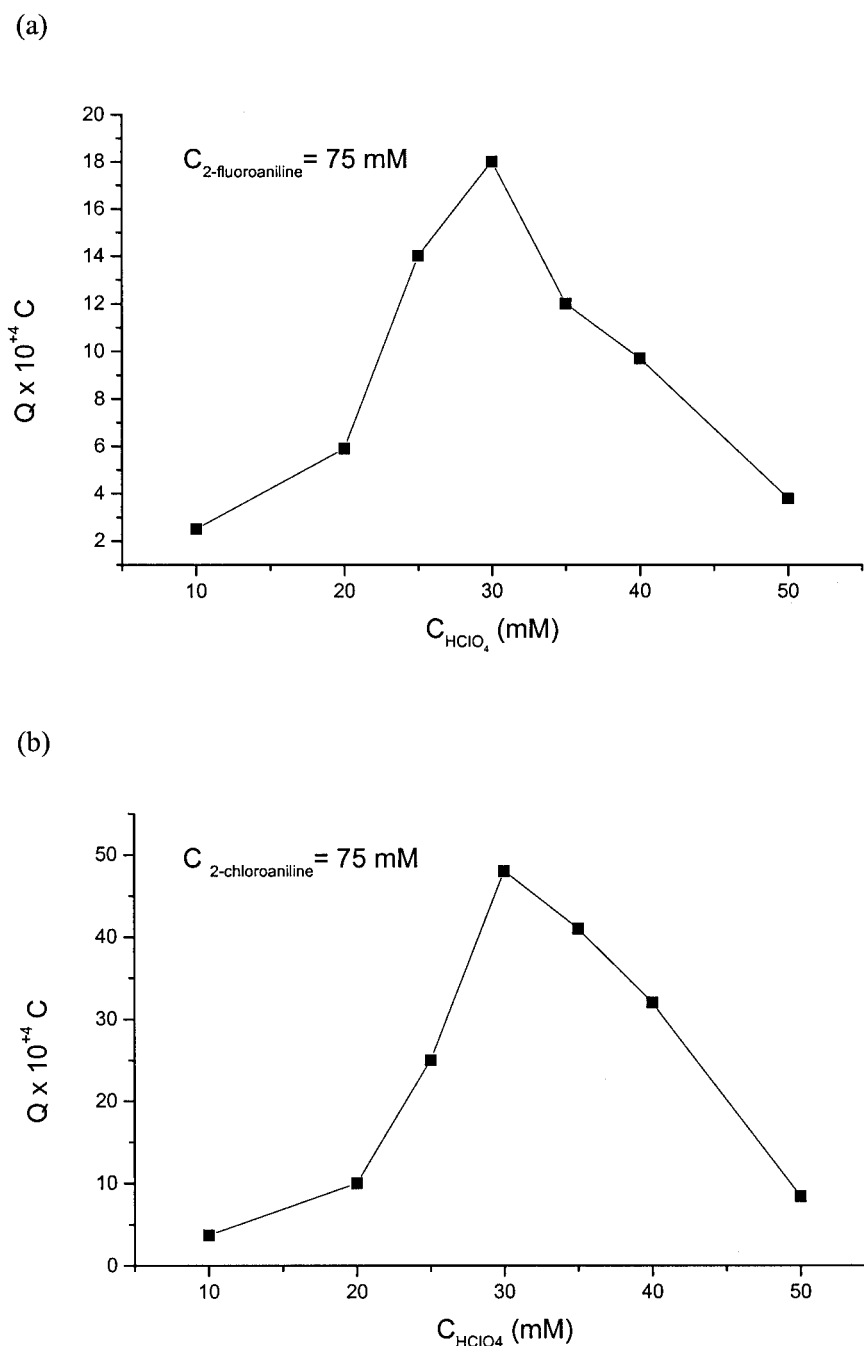
(a)

(b)

Figure 8 Plot of the charge passed during the electrooxidation of polymer films of (a) PFANI and (b) PClANI in 0.1M TBAP.

first five cyclic voltammograms during the electrochemical polymerization of 75 mM 2-fluoroaniline and 30 mM HClO$_4$ and of 75 mM 2-chloroaniline and 30 mM HClO$_4$, respectively, in a 0.1M TBAP/acetonitrile solution. The potential was scanned from −0.30 to +1.90 V (vs Ag/AgCl) at a scanning rate of 100 mV/s. The oxidation peaks were recorded at 1.08 and 1.20 V for 2-fluoroaniline and 2-chloroaniline, respectively. The intensity of the oxidation peaks of 2-fluoroaniline and 2-chloroaniline decreases and shifts to higher anodic potentials. The formation and growth of the polymer film can easily be seen in Figures 2(b) and 3(b).

Polymeric films were deposited onto the electrode surface during the electrooxidation of 2-fluoroaniline and 2-chloroaniline. The voltammogram of 2-fluoroaniline involves three oxidation peaks and one reduction peak [Fig. 2(b)]. The first oxidation peak at about +0.40 V belongs to the formation of the leucoemeraldine cation radical from leucoemeraldine. The reverse reduction process occurs with a peak potential of +0.15 V. The leucoemeraldine cation radicals further oxidize into emeraldine at the peak potential of +0.80 V. The third oxidation peak, which appears at +1.20 V, is due to the oxidation of emeraldine to emeraldine

TABLE I
Dry Electrical Conductivity of PANI, PFANI, PCIANI, P (An-*co*-2-FAn),
and P (An-*co*-2-ClAn)

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-fluoroaniline + 30 mM HClO$_4$	PFANI	2.4×10^{-3}
75 mM 2-chloroaniline + 30 mM HClO$_4$	PCIANI	7.2×10^{-3}
150 mM aniline + 75 mM 2-bromoaniline + 30 mM HClO$_4$	P(An-*co*-2-FAn)	3.9×10^{-2}
150 mM aniline + 75 mM 2-bromoaniline + 30 mM HClO$_4$	P(An-*co*-2-ClAn)	4.7×10^{-2}

cation radical. The electrochemical behavior of the film in the neutral blank solution can be seen in Figure 2(c). The film does not lose its electroactivity in this medium. The growth voltammogram of 2-chloroaniline involves two oxidation peaks and two reduction peaks [Fig. 3(b)]. The first oxidation peak at about +0.68 V belongs to the formation of the leucoemeraldine cation radical from leucoemeraldine. The reverse reduction process occurs with a peak potential of +0.40 V. The leucoemeraldine cation radicals further oxidize into emeraldine at the peak potential of +1.16 V, a with corresponding cathodic peak at +0.80 V belonging to the reverse process. The film does not lose its electroactivity in this medium.

Figures 4 and 5 show the cyclic voltammetry sweeps taken during the oxidation of 75 mM 2-fluoroaniline and 150 mM aniline and of 75 mM 2-chloroaniline + 150 mM aniline, respectively, in an acetonitrile solution containing 0.1M TBAP and 30 mM HClO$_4$. The films were grown in aniline solutions in the range 25 of 200 mM by the cycling of the potential between −0.30 and +1.90 V (vs Ag/AgCl) for the same period of time (30 min) at a scanning rate of 100 mV/s. The optimum aniline concentration was found to be 150 mM for both copolymerization processes. There was a considerable decrease in the yield of copolymer formation below and above this aniline concentration.

The electrochemical behavior of the films in basic and acidic solutions is shown in Figures 6 and 7, respectively. PANI,[31] poly(2-bromoaniline) (PBrANI),[21] and PIANI[20] lose their electroactivities completely even after a few cycles by the addition of small amounts of pyridine (5 mM) into the TBAP/acetonitrile solution. In the cyclic voltammogram of PFANI and PCIANI films in a basic blank solution containing 0.1M TBAP and 5 mM pyridine, the oxidation and reduction peak of the films disappear after a few potential scans [Fig. 6(a,b), respectively], whereas they remain almost unchanged in a neutral blank solution [Figs. 2(c) and 3(c), respectively]. Also, the electroactivity of the copolymers disappears in the same basic medium. Pyridine causes a rapid loss of electroactivity. However, the films do not lose their electroactivities in an acidic blank solution containing an excess amount of HClO$_4$ [Figs. 7(a,b), respectively]. The

voltammetry of PFANI and PCIANI show characteristics similar to those of PBrANI[21] and PIANI[20] in both basic and acidic solutions.

The acid concentration is very effective, increasing the amount and quality of the PANI films in acetonitrile solutions. In other words, the extent of the protonation of the film is the major factor in its autocatalytic growth. If no proton were present in the medium, highly conducting polyemeraldine would be further oxidized into the less conducting polypernigraline 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 imparting extra stability to the emeraldine. The presence of excess acid in the medium in which the PANI backbone is growing also impedes polymer growth as a result of the protonation of the end amino group.[32] The presence of moderate amounts of acids not only improves the stability of the aniline cation radicals but also causes the preferred protonation of these species that are primarily involved during the growth of highly conducting PANI because efficient polymer growth occurs in a moderately acidic medium in an acetonitrile solution. To determine the effect of the acid (HClO$_4$) concentration on the growth of the polymer film, films were grown at acid concentrations of 5–75 mM by the cycling of the potential between −0.30 and +1.90 V (vs Ag/AgCl) at the same time interval (30 min). Then, the charge that passed during the first oxidative cycle of the cyclic voltammograms of the film in the blank solution was measured. The results are shown as graphs for PFANI and PCIANI in Figure 8(a,b), respectively. The anodic charge, which should be proportional to the thickness of the deposit, increases as the acid concentration increases, up to 30 mM. It can be concluded that the optimum acid concentration under these conditions is about 30 mM. There is 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 fluorine and chlorine can be seen in the conductivity of the
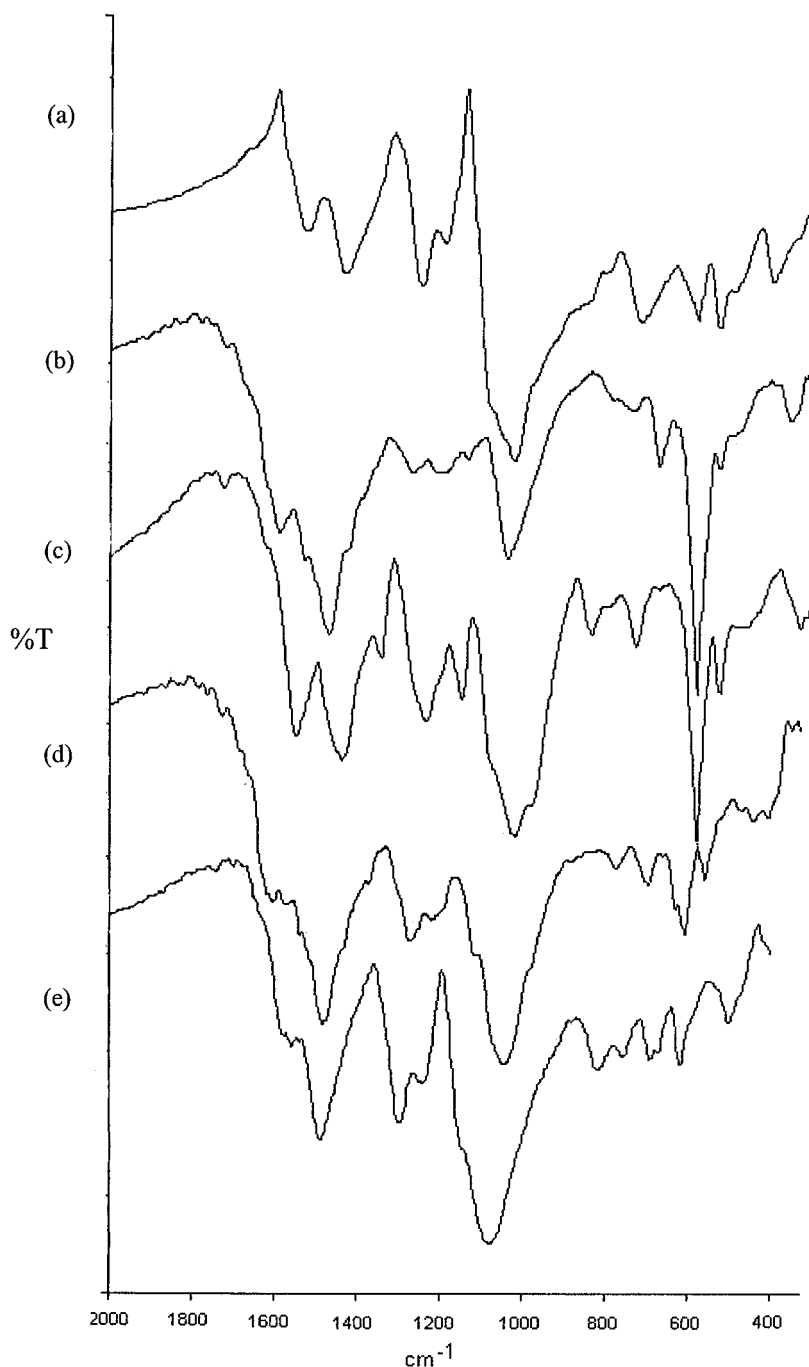
Figure 9 Baseline-corrected FTIR spectra (2000–400-cm^{-1} region) of (a) PANI, (b) PFANI, (c) PClANI, (d) P(An-co-2-FAn), and (e) P(An-*co*-2-ClAn).

homopolymer (PFANI and PClANI) and copolymer films. As the halogen content of electron-withdrawing species increases, the conductivity of the film decreases. The observed decrease in the conductivity of the copolymer with respect to PANI can be attributed to the incorporation of the fluoroaniline and chloroaniline moieties into the PANI chain. The copolymers exhibit higher dry electrical conductivity values than the homopolymers and lower values than PANI.

The FTIR spectra of electrochemically prepared PANI, PFANI, PClANI, poly(aniline-*co*-2-fluoroani-

line) [P(An-*co*-2-FAn)], and P(An-*co*-2-ClAn) were recorded; a broad N—H stretching peak was observed around 3400 cm^{-1}, and a C—H vibration of the aromatic ring was observed at 3037 cm^{-1} (they are not shown in Fig. 9). The absorption of IR radiation at a wavelength below 2000 cm^{-1} is rich in molecular signatory information. For this reason, the IR peaks in the range of 2000–400 cm^{-1} are shown in Figure 9, respectively. The peak at about 1580 cm^{-1} is due to the C=C double bond of quinoid rings, whereas the peak at 1500 cm^{-1} arises from the vibration of the C=C dou-
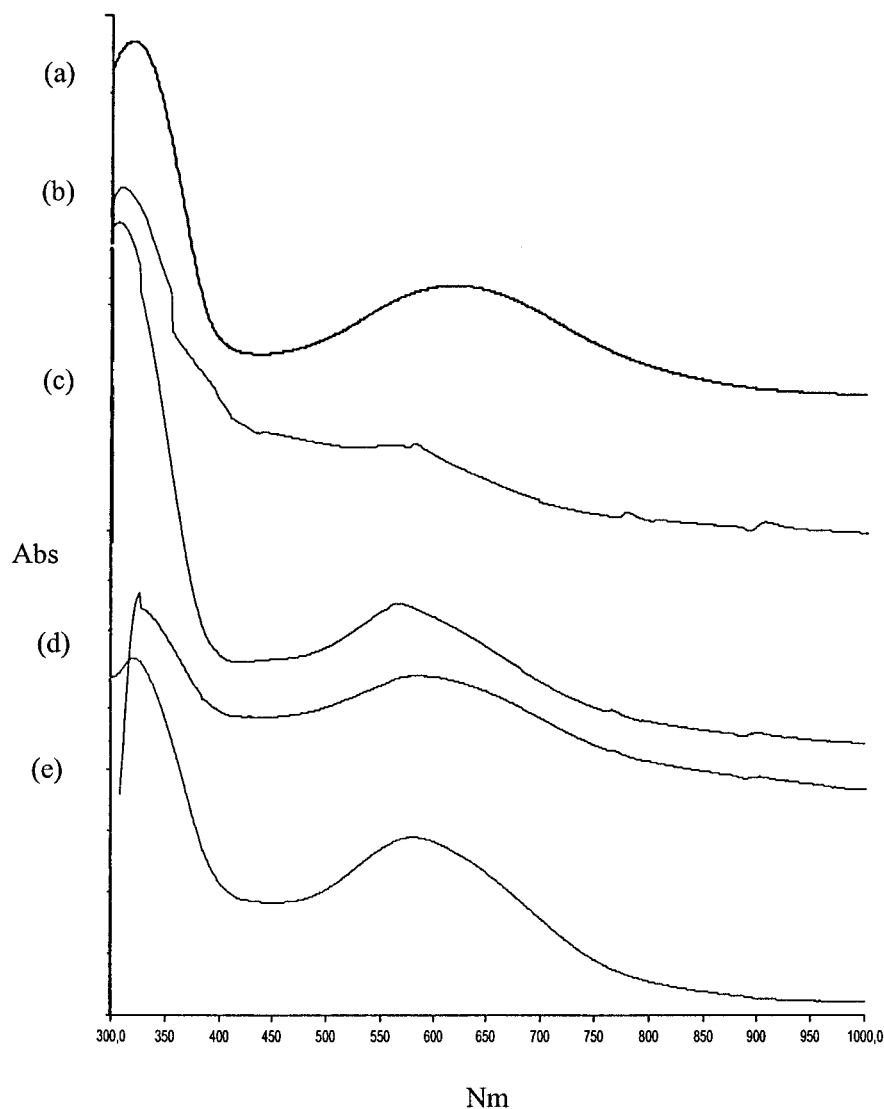
Figure 10 UV–vis absorption spectra of (a) PANI, (b) PFANI, (c) PClANI, (d) P(An-co-2-FAn), and (e) P(An-*co*-2-ClAn) in DMSO.

ble bond associated with the benzenoid ring. The band at about 1070–1170 cm^{-1}, primarily due to C—H in-plane deformation, was used by Chiang and MacDiarmid[33] as a measure of the extent of electron delocalization in the polymer. The peak at 804–831 cm^{-1} is due to aromatic C—H bending.[34] The peak observed at 625 cm^{-1} has been attributed to the ClO_4^- ion.[30] We also investigated the IR spectra of pure fluoroaniline and chloroaniline to determine the specific peaks of fluoro and chloro groups (not shown here). The vibration peak of the quinoid and benzenoid units shifts to higher wavelengths in halogen-substituted homopolymers and copolymers. The vibration bands found around 1309, 1184, and 680 cm^{-1} [Fig. 9(b,d)] are characteristic of fluoro groups.[35] This confirms the presence of the fluoro moieties in the PANI backbone. Two new bands can be observed at 1300–1340 and 700 cm^{-1} (this peak can easily be seen in the copolymer spectrum) in both PClANI and P(An-*co*-2-ClAn) spec-

tra [Fig. 9(c,e)]. These peaks are associated with the presence of chlorine groups in the halogen-substituted homopolymer and copolymer structure. The synthesized polymers are homopolymers of 2-fluoroaniline and 2-chloroaniline. The others are copolymers of aniline with 2-fluoroaniline and 2-chloroaniline and are not a mixture of the homopolymers.

The UV–vis spectra of PANI, PFANI, PClANI, P(An-co-2-FAn), and P(An-*co*-2-ClAn) solutions in DMSO, recorded at room temperature, are shown in Figure 10(a–e), 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 π–π^* transition of the benzenoid moieties in the PANI linear structure or simply to the bandgap of the polymer.[36] Peak 2 closely resembles the benzenoid–quinoid transition in the emeraldine form (middle oxidation state) of PANI.[36,37] However, the actual

band positions are blueshifted with respect to PANI. The blueshift was induced by the presence of fluorine and chlorine units in the polymers and copolymers [Fig. 10(b–e)]. The electron-withdrawing character of fluorine and chlorine units restricts the effective dispersion of electrical charge in the conjugated polymeric system, and this results in more locally oxidized polymeric units. The same effects were seen in iodo- and bromo-PANIs[20,21] because of the electron-withdrawing effect of the sulfonate group. These spectra also suggest that the synthesized materials are PFANI, PClANI, P(An-*co*-2-FAn), and P(An-*co*-2-ClAn).

The solubility of PANI, PFANI, PClANI, P(An-*co*-2-FAn), and P(An-*co*-2-ClAn) was tested in DMSO, 1-methyl 2-pyrrolidone (NMP), dimethylformamide (DMF), and tetrahydrofuran (THF) at room temperature. The homopolymers (PFANI and PClANI) and copolymers showed improved solubility in those polar solvents with respect to PANI. PANI was soluble in DMSO. However, it was not soluble in THF, NMP, or DMF. Unlike PANI, PFANI, PClANI, P(An-*co*-2-FAn), and P(An-*co*-2-ClAn) were soluble in NMP, THF, DMF, and DMSO. We noticed that the presence of a halogen atom in the ring of the aniline units could produce polymers and copolymers with better solubility in NMP, THF, DMF, and DMSO. Thus, it is possible to cast films of the desired size of PFANI, PClANI, P(An-*co*-2-FAn), and P(An-*co*-2-ClAn).

CONCLUSIONS

Cyclic voltammetry was used to synthesize homopolymers and copolymers in acetonitrile solutions containing TBAP and $HClO_4$. The films did not lose their electroactivities in acidic or neutral blank solutions. However, they lost their electroactivities in basic blank solutions. The dry electrical conductivity values of the copolymers was found to be lower than that of PANI and higher than that of PFANI and PClANI. Spectroscopic results (FTIR and UV–vis) showed that the homopolymers (PFANI and PClANI) and copolymers were different from PANI. These spectra and the conductivity behavior of the films suggested that the synthesized materials were PFANI, PClANI, P(An-co-2-FAn), and P(An-*co*-2-ClAn).

References

1. Liu, M. L.; Visco, S. J.; Dejonghe, L. C. J Electrochem Soc 1991, 138, 1896.
2. Doeff, M. M.; Lerner, M. M.; Visco, S. J.; Dejonghe, L. C. J Electrochem Soc 1992, 139, 2077.
3. Liu, M. L.; Visco, S. J.; Dejonghe, L. C. J Electrochem Soc 1991, 138, 1891.
4. Yue, J.; Epstein, A. J. J Am Chem Soc 1990, 112, 2800.
5. Heeger, A. J. Synth Met 1993, 57, 3471.
6. Neoh, K. G.; Pun, M. Y.; Kang, E. T.; Tan, K. L. Synth Met 1995, 73, 209.
7. Cao, Y.; Smith, P.; Heeger, A. J. Synth Met 1992, 48, 91.
8. Şahin, Y.; Pekmez, K.; Yıldız, A. Synth Met 2002, 129, 107.
9. Şahin, Y.; Pekmez, K.; Yıldız, A. J Appl Polym Sci 2002, 85, 1227.
10. Şahin, Y.; Pekmez, K.; Yıldız, A. Synth Met 2002, 131, 7.
11. Leclerc, M.; D'Aprano, G.; Zotti, G. Synth Met 1993, 55, 1527.
12. Leclerc, M.; Guay, J.; Dao, L. H. Macromolecules 1995, 28, 1727.
13. Cattarin, S.; Doubova, L.; Mengoli, G.; Zotti, G. Electrochim Acta 1998, 33, 1077.
14. Geniès, E. M.; Penneau, J. F.; Laprowski, M. New J Chem 1998, 12, 765.
15. Wei, Y.; Focke, W. W.; Wnek, G. E.; MacDiarmid, A. G. J Phys Chem 1989, 93, 495.
16. Borole, D. D.; Kapadi, U. R.; Mahulikar, P. P.; Hundiwale, D. G. Mater Lett 2003, 57, 3629.
17. Huang, L.-M.; Wen, T.-C.; Gopalan, A. Met Lett 2003, 57, 1765.
18. Snauwaert, P. H.; Lazzaroni, R.; Riga, J.; Verbist, J. J. Synth Met 1986, 16, 245.
19. Neoh, K. G.; Kang, E. T.; Tan, X. L. Eur Polym J 1990, 26, 403.
20. Şahin, Y.; Perçin, S.; Alsancak, G. Ö. J Appl Polym Sci 2003, 89, 1652.
21. Şahin, Y.; Perçin, S.; Şahin, M.; Özkan, G. J Appl Polym Sci 2003, 90, 2460.
22. Palaniappan, S. Eur Polym J 1997, 33, 1735.
23. Rajendran, V.; Prakash, S.; Gopalan, A.; Vasudevan, T.; Chen, W.-C.; Wen, T.-C. Mater Chem Phys 2001, 69, 62.
24. Diaz, F. R.; Sanchez, C. O.; del Valle, M. A.; Torres, J. L.; Tagle, L. H. Synth Met 2001, 118, 25.
25. Mav, I.; Zigon, M. Synth Met 2001, 119, 145.
26. Sharma, A. L.; Saxena, V.; Annapaorni, S.; Malhotra, B. D. J Appl Polym Sci 2001, 81, 1460.
27. Kang, D. P.; Yun, M. S. Synth Met E 1989, 29, 343.
28. Cihaner, A.; Önal, A. M. Eur Polym J 2001, 37, 1767.
29. Cihaner, A.; Önal, A. M. Polym Int 2002, 51, 680.
30. Şahin, Y.; Pekmez, K.; Yıldız, A. Synth Met 2002, 129, 117.
31. Pekmez, N.; Pekmez, K.; Yıldız, A. J Electroanal Chem 1994, 370, 223.
32. Pekmez, N.; Pekmez, K.; Arca, M.; Yıldız, A. J Electroanal Chem 1993, 353, 237.
33. Chiang, J. C.; MacDiarmid, A. G. Synth Met 1986, 13, 193.
34. Quillard, S.; Louarn, G.; Lefrant, S.; MacDiarmid, A. G. Phys Rev B 1994, 50, 12496.
35. Sharma, A. L.; Annapoorni, S.; Malhotra, B. D. Curr Appl Phys 2003, 3, 239.
36. Lee, J. Y.; Cui, C. Q. J Electroanal Chem 1996, 403, 109.
37. 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.