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Electrochemical Polymerization of Para-Substituted Haloanilines

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Polyhaloanilines: poly(4-fluoroaniline) (P4FAN), poly(4-chloroaniline) (P4CAN), and poly(4-bromoaniline) (P4BAN), are synthesized from para-substituted haloaniline monomers; 4-fluoroaniline (4FAN), 4-chloroaniline (4CAN), and 4-bromoaniline (4BAN), respectively, via constant potential electrolysis (CPE) in acetonitrile-water mixture (1 : 1 v/v) with NaClO₄ as supporting electrolyte. Prior to CPE, electrochemical behavior of the monomers were investigated in organic medium utilizing cyclic voltammetry (CV). The course of CPE was monitored using in-situ UV-VIS spectroscopic technique. Characterization of polymer products have been carried out using FT-IR and NMR spectroscopic techniques and thermal behaviors were studied using differential scanning calorimeter (DSC). Polyhaloanilines synthesized by electrochemical oxidation were doped using iodine and the change in the paramagnetic behavior was monitored by ESR, UV-VIS, and FT-IR.

Keywords electrochemical polymerization, para-substituted haloanilines, iodine doping

Introduction

Polyaniline (PANI) is one of the most extensively studied conducting polymers because of its unique conduction mechanism and good environmental stability in the presence of oxygen and water. On the other hand, its insolubility in common organic solvents and its infusibility are disadvantages for industrial applications. Recent works have been focused on how to solve these problems by substituted aniline derivatives functionalized especially by electron withdrawing groups. Snauwaert and his coworkers (1) reported the synthesis of polyhaloanilines by chemical and electrochemical oxidation, but the polymers were not fully characterized. Synthesis of dihalogenated anilines using various oxidizing agents were reported by Diaz et al. (2) and synthesis of polychloroaniline via electrochemical oxidation by Athawale et al. (3). Kwon and his coworkers (4) investigated the polymerization of fluoro-substituted anilines by chemical oxidation. Earlier, we investigated the polymerization of three different fluoro-substituted anilines (i.e., 4FAN, 3FAN, and 2FAN) via chemical (5) and electrochemical (6) oxidation. It is found that both methods of polymerization yielded soluble polyfluoroanilines which become

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conductors after I₂ doping. Recently, Prakash et al. (7) investigated the electrochemical copolymerization of 4FAN with o-toluidine and reported that 4FAN does not give electroactive film in aqueous acidic medium.

Herein, the aim of the work is to investigate the effect of the para-substituents halogens, on the polymerization of aniline and to achieve soluble and conducting polymers by electrochemical polymerization.

Experimental

Chemicals

The monomers 4BAN and 4CAN (Aldrich Chemical Co.) were used without any further purification and 4FAN monomer (Aldrich Chemical Co.) was dried over CaH₂ for 48 h and distilled under reduced pressure. Acetonitrile (Aldrich Chemical Co.), deionized water and NaClO₄ (Aldrich Chemical Co.) as supporting electrolyte were used without further purification for CV measurements and for CPE.

Cyclic Voltammetry

The electrochemical behavior of the monomers were investigated utilizing CV. Pt-wire, Pt-coil, and saturated calomel electrode (SCE) were used as working, counter, and reference electrodes, respectively. CV measurements were carried out using a potentiostat (Bank Pos 73), an X-Y recorder (Lloyd PL-3), in a mixture of acetonitrile-water (1 : 1 v/v) with NaClO₄ as supporting electrolyte at room temperature.

Polymer Synthesis

Electrochemical polymerization of haloanilines was performed in a classical three-electrode cell at a constant potential referenced to SCE. Acetonitrile-water mixture (1 : 1 v/v) and 0.1 M NaClO₄ were used as a solvent-electrolyte couple for CPE. At the end of the electrolysis, the solution from the anode compartment was concentrated by removing the solvent under vacuum. The electrolyte and unreacted monomers from the remaining mixture were removed by extraction with dichloromethane and water, and the polymer was dried under vacuum at 80°C for 24 h. The black polymer film deposited on the working electrode was dissolved by using acetone after washing with water and then dried under vacuum.

The course of electrolysis was followed by *in-situ* monitoring the changes in the electronic absorption spectra of the monomer solutions in two different solvent electrolyte couples (i.e., acetonitrile/water-NaClO₄ and aqueous acidic medium) at room temperature. The changes in the high energy part of the electronic absorption spectrum were recorded at 5 min time intervals by a UV-VIS HP 8453A Diode Array Spectrophotometer. On the other hand, the changes in the 300–1100 nm region were monitored using ITO working electrode. ESR spectra of the electrochemically prepared polymers, (un)doped with iodine, were recorded by using a Varian E12 ESR Spectrometer.

Polymer Characterization

¹H-NMR spectra of the polymers were taken by a Bruker Instrument-NMR Spectrometer (DPX-400) in CDCl₃ or in d-DMSO. FT-IR spectra of the polymers were obtained on

a Nicolet 510 FTIR Spectrometer using KBr pellet. A DSC 910S/TA instrument was used for DSC analysis.

Results and Discussion

Electrochemical Behaviors of Aniline and Para-Substituted Haloanilines

CVs of aniline and 4BAN measured in acetonitrile-water mixture are given in Figure 1. The appearances of the voltammograms for all haloanilines are very similar to each other.

The first oxidation peak appears around 0.8 V vs. SCE (Figure 1) and a new reversible peak intensifies at about 0.25 V vs. SCE during successive anodic scans. The reversible peak corresponds most likely to the transition of leucoemeraldine to emeraldine (8). However, no new reversible peak for the transition of emeraldine to pernigraniline was observed, indicating that polyhaloanilines formed on the surface of working electrode are in the base form. Lack of emeraldine-pernigraniline transition is most probably due to lower basicity of para-substituted polyhaloanilines than that of PANI (1, 2).

Electrochemical Synthesis

Electrochemical synthesis of polyhaloanilines were carried out by CPE at the predetermined peak potential of the corresponding monomer at room temperature. Acetonitrile-water mixture (1 : 1 v/v) was used as solvent and NaClO_4 was used as the electrolyte. Soluble polymers were obtained both from the working electrode surface and from the bulk of the anolyte at the end of the CPE. Since the polymer quality did not allow

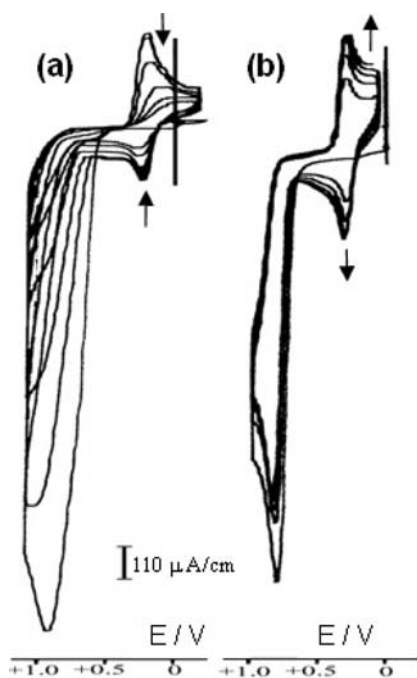


Figure 1. Cyclic voltammograms of (a) aniline (1.0×10^{-3} M) and (b) 4BAN (1.0×10^{-3} M) in acetonitrile-water (1 : 1 v/v)- NaClO_4 (0.1 M) mixture, voltage scan rate = 150 mV/sec.

peeling off the film from the anode surface, it was isolated by dissolving the film using acetone, and then evaporating the solvent. In the case of polymer obtained from the anolyte, the solution was concentrated and the electrolyte was removed by an extraction method, as explained in the experimental part.

The structural analyses of the polymers were done by FT-IR, $^1\text{H-NMR}$, and UV-VIS spectroscopic methods.

Spectro-Electrochemical Investigations

In-situ UV-VIS Study. The electronic absorption spectra of the monomers 4FAN, 4BAN, and 4CAN in acetonitrile-water mixture consist of three bands at about 205, 245, and 296 nm. During CPE of the monomers, the band intensity at 245 nm decreased, whereas the band intensity at 296 nm increased (6). A new broad band also appeared at around 496 nm, together with two isosbestic points at 218 nm and 240 nm, suggesting only one-step electrode reaction taking place in the electrolyte solution.

When compared with the UV-VIS spectra of PANI, the introduction of an electron-withdrawing group in the aromatic ring of aniline produces a blue shift (4, 9). Thus, the band located at 296 nm most probably corresponds to $\pi-\pi^*$ transition in the benzenoid ring and the new band that intensifies during CPE corresponds to the transition of quinoid ring.

In order to compare the initial rate of polymerization of haloanilines, the increasing intensity of 496 nm band was monitored and plotted as a function of time (Figure 2).

As seen from Figure 2, the initial rate of polymerization changes drastically depending on the substituent. Since bromine is a better leaving group than the others, one might expect higher rates in the case of 4BAN; however, this is not the

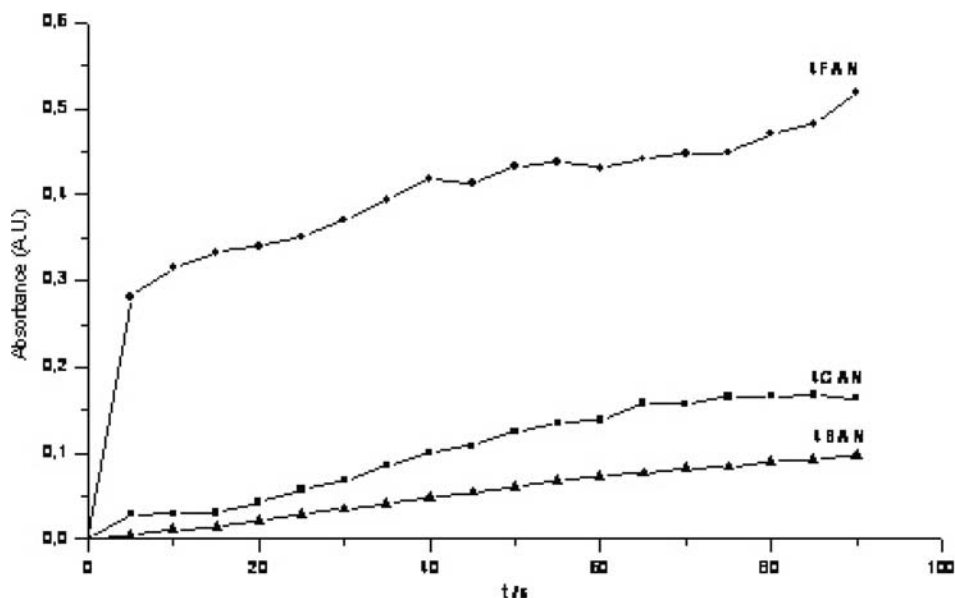


Figure 2. Time traces of 496 nm band obtained during CPE of 1×10^{-4} M solutions of 4FAN, 4BAN, and 4CAN in acetonitrile-water mixture using 6.0×10^{-2} M of NaClO_4 as supporting electrolyte.

case. The highest rate was obtained for 4FAN. The observed trend might be explained due to the bulkiness of bromine group that will influence the rate if this group is not eliminated during the electrochemical polymerization. The following order was found for the initial rate of polymerization of haloanilines: 4FAN > 4CAN > 4BAN. This order is consistent with elimination ratios reported by Snauwaert and his coworker (1).

The formation of polymer film during CPE was also monitored using ITO electrode as the working electrode and the changes in the electronic absorption spectrum of 4FAN is given as an example in Figure 3. During the CPE of 4BAN, 4FAN, and 4CAN in acetonitrile-water mixture, a new band around 496 nm starts to intensify immediately as the polymer film grows on the surface of the electrode (Figure 3a). However, when the CPE is conducted in aqueous acidic medium, an additional new band at 730 nm was also observed (Figure 3b). This band, which is characteristic of conducting polymers, can be assigned to localized polarons (10). Comparison of Figure 3a with 3b indicates that the polymer film obtained in acetonitrile-water mixture is in the emeraldine base form that is consistent with our CV results. The electroactivity of P4FAN on the ITO electrode was also studied by recording the electronic absorption spectrum at different potentials and by recording the CV in acidic aqueous medium. It is found that P4FAN can be reversibly switched between -0.1 V and 0.3 V vs. Ag wire and the electronic absorption spectrum recorded at 0.0 V and 0.3 V are given in Figure 3c. The CV of P4FAN film on ITO exhibits a reversible oxidation peak at $+0.25$ V indicating doping and de-doping of the polymer film (Figure 4).

Polymer Characterization

The FT-IR spectra for polyhaloanilines obtained by electrochemical polymerization are depicted in Figure 5. In general, the essential structural units, quinoid diimine, and benzenoid diamine are confirmed by the presence of peaks at 1589 and 1487 cm^{-1} , respectively. Also, the peak at 3225 cm^{-1} is attributed to N-H stretching. The C-H of the ring and ClO^{4-} groups generate the strong absorption peaks at around 1097 and 623 cm^{-1} .

$^1\text{H-NMR}$ spectra of monomers and polyhaloanilines are very similar in terms of the peak positions. However, in general, the peaks are much broader in the spectra of polyhaloanilines. There are three distinct multiplets for aromatic protons between 6.7 and 8 ppm and a broad singlet at near 3.4 ppm appears due to the amine protons. In addition, some quinoid protons appear at about 6 ppm due to the quinoid structure. From our previous works (5, 6) $^{19}\text{F-NMR}$, as well as $^1\text{H-NMR}$ confirmed the presence of fluorine groups. The presence of fluorine, especially in the case of P4FAN, suggested that 100% elimination of fluorine is not taking place during the polymerization. Thus, polymerization, especially in the case of 4FAN, is taking place not only by 1,4 addition. Three possibilities, as suggested by Snauwaert and his coworkers (1): site blocking, formation of an sp^3 site or group elimination, maintaining the sp^2 hybridization and so the π -electron delocalization are likely to occur.

Thermal behavior of polymer samples have been studied by DSC, and resulting thermograms show an exothermic transition at about 200°C for polyhaloanilines, which has been attributed to decomposition of the polymers (Figure 6).

Doping, Conductivity and ESR Measurements

In this study, we synthesized the polymers from 4FAN, 4BAN, and 4CAN via electrochemical oxidation. Although, the monomers exhibit an intensifying reversible peak at

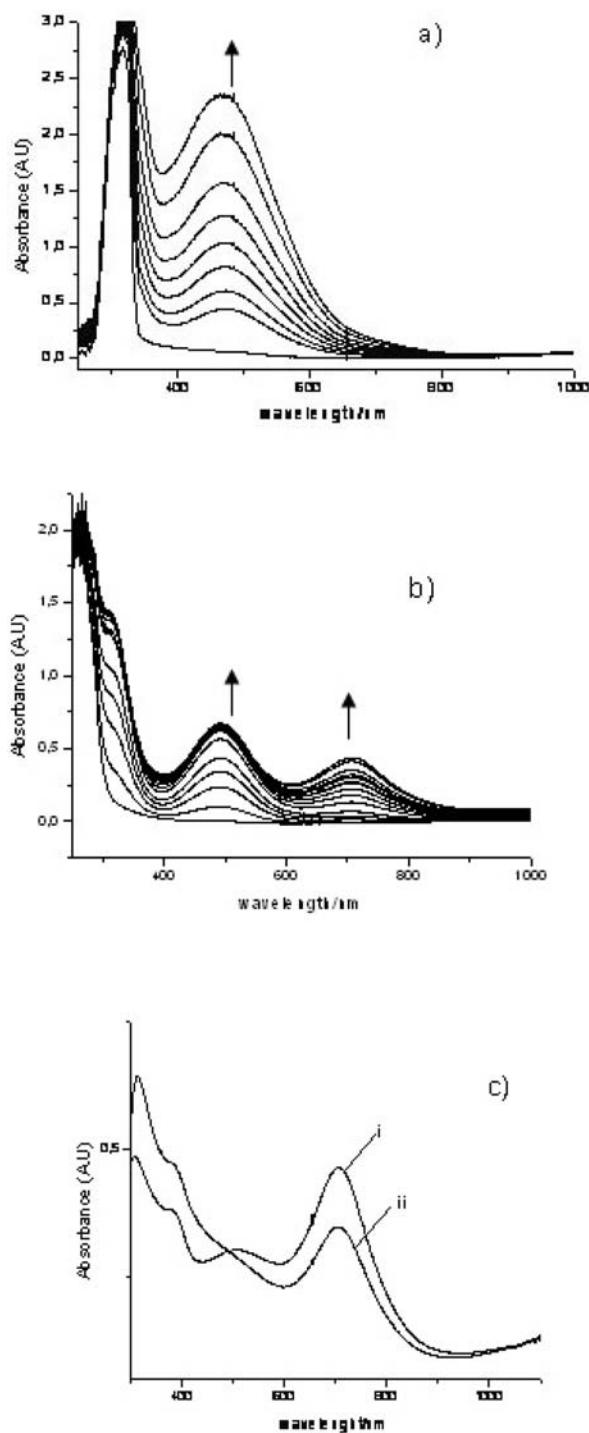


Figure 3. Absorption spectral changes of 4FAN on ITO working electrode during the CPE, a) in acetonitrile-water mixture, b) in aqueous acidic medium, and c) electronic absorption spectrum of P4FAN on ITO, i) at 0.3 V vs. Ag-wire and ii) at 0.0 V vs. Ag-wire.

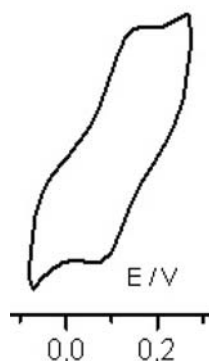


Figure 4. Cyclic voltammogram of P4FAN coated ITO in aqueous acidic medium.

0.25 V vs. SCE during successive scans characteristic of conducting polymer films, the polymers that are obtained by CPE of 4BAN, 4FAN, and 4CAN in acetonitrile-water mixture were found to exhibit very low conductivity. The polyfluoroanilines that we synthesized earlier by chemical and electrochemical oxidation were obtained in their undoped state, and they became conductors only after iodine doping (5, 6). Therefore, to impart electrical conductivity, polymers were doped by using iodine, in a separate glass cup under vacuum, at 50°C. It is observed that conductivity of all three polymers increases with increasing duration of the doping period (see Figure 7a). The mechanism of iodine

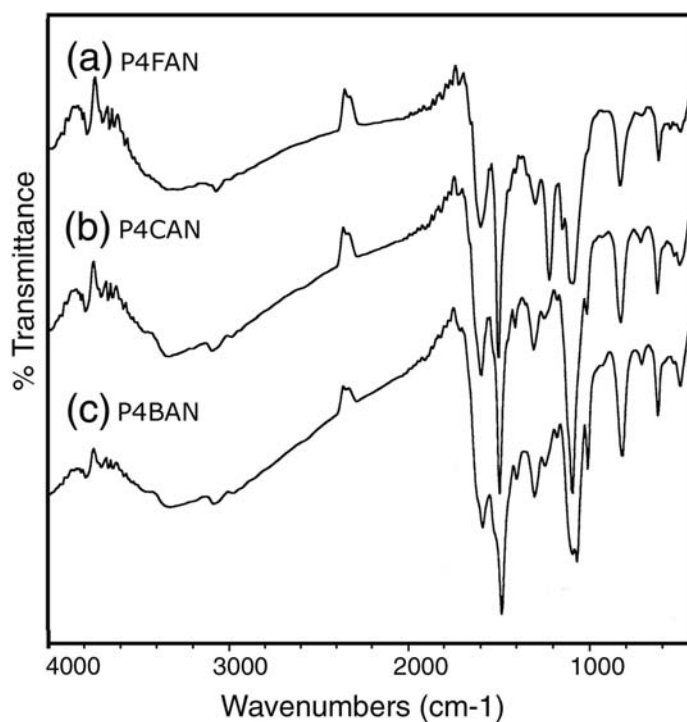


Figure 5. FT-IR spectra of (a) P4FAN, (b) P4CAN, and (c) P4BAN.

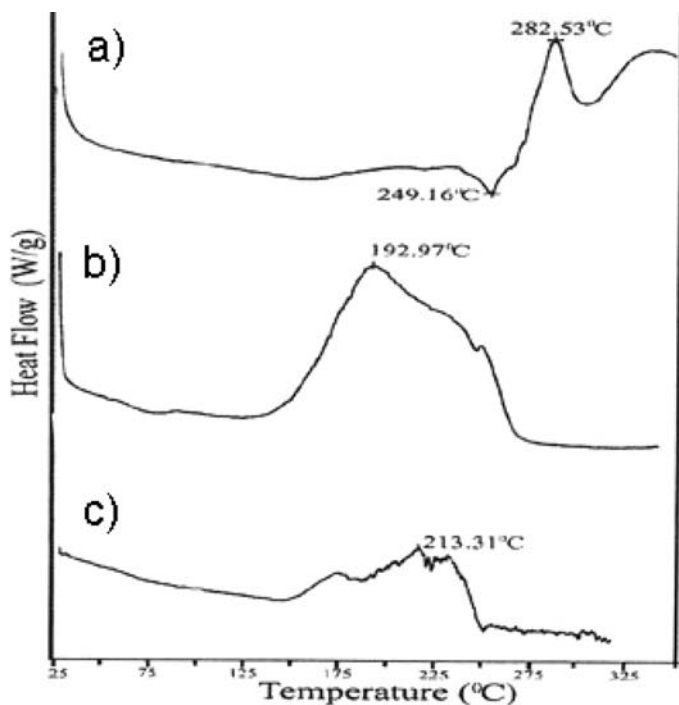


Figure 6. DSC Thermograms of a) P4FAN, b) P4CAN, and c) P4BAN.

doping for PANI was explained by R. Zeng et al. (11, 12). According to their mechanism, iodine doping mostly causes the conversion of some of the benzenoid units to the quinoid units, and polarons are formed as a consequence of intramolecular redox reaction in the quinoid units. The ESR spectra of the polymers, which consist of an asymmetric singlet with a line width of 10 G (6), was also monitored during iodine doping and a systematic increase in the ESR signal intensity was obtained (Figure 7b). This increase provides an evidence for the increase in the number of polarons in polyhaloanilines after iodine doping.

Quinoid structure for polyhaloanilines obtained with iodine doping was also checked by using a UV-VIS spectroscopic method. For this reason, a quartz window was coated with the polymer in question and doped using iodine, at the end of the doping period, UV spectrum was recorded. As seen from Figure 8, the broad peak beyond 500 nm represents the quinoid structure in the backbone of the polymer.

Also, oxidative doping reaction was checked by IR absorption measurements (Figure 9). After polyhaloanilines were doped with iodine, the absorption peaks of the quinoid units shifted from 1162 cm^{-1} to 1142 cm^{-1} . The imine units ($=\text{N}-$) decrease drastically as the cation radicals increase, which is consistent with the increase in ESR signal intensity. However, the iodine-doped polyhaloanilines could not form highly conjugated π systems in their chain structures while the protonic acids-doped could (11). There were more restrictions on the delocalization of the charges from the quinoid-diimine N-atoms to the neighboring benzenoid rings in the iodine-doped polyhaloanilines. As a result, there was no change at 1486 cm^{-1} , indicating that iodine

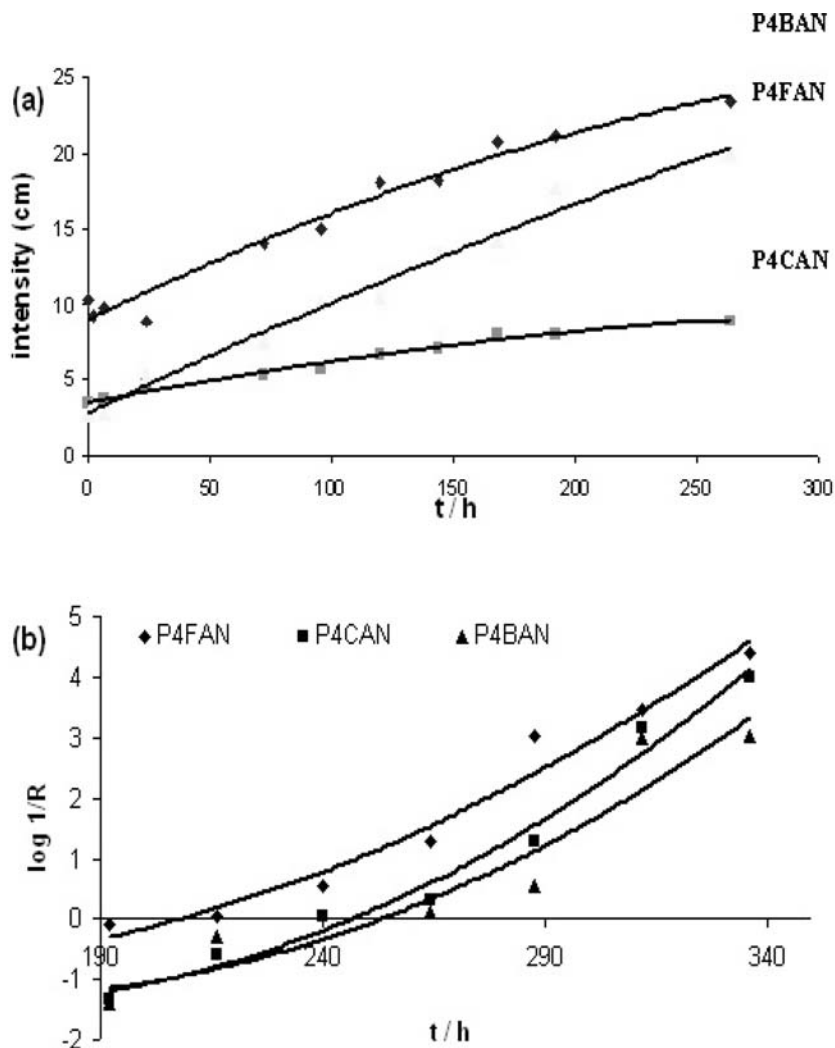


Figure 7. (a) Variation of resistance as a function of iodine doping period at 50°C and (b) variation of ESR signal intensity as a function of iodine doping period at 50°C.

doping reactions occurred at the quinoid units while benzenoid units remained essentially unaffected.

Conclusions

In this work, soluble polymers were synthesized from para-substituted haloanilines by CPE in acetonitrile-water mixture (1 : 1 v/v) using NaClO_4 as supporting electrolyte. Prior to the CPE, electrochemical behavior of the monomers were studied in the same solvent-electrolyte couple. A new reversible peak intensified during repeated cycling, indicating the transition from leucoemeraldine to emeraldine. However, emeraldine to pernigraniline transition was not observed for all monomers studied, including aniline. These results suggest that the polymers obtained by electrochemical oxidation in acetonitrile-water

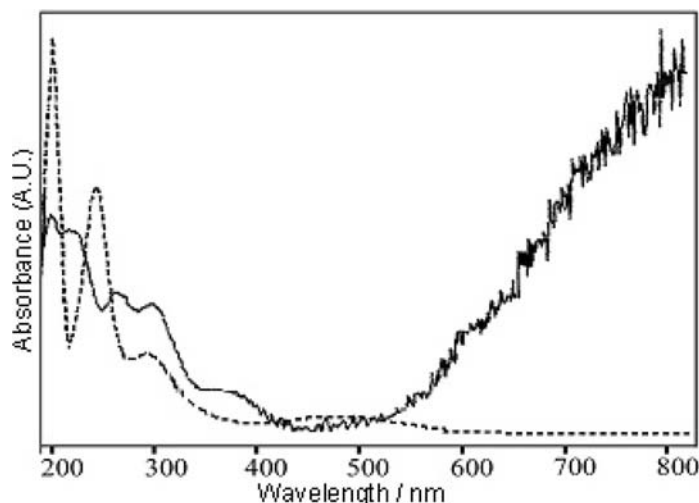


Figure 8. UV-VIS spectra of P4BAN before doping (dashed line) and P4BAN after doping (solid line) with iodine for 13 days at room temperature.

mixture are in emeraldine base form. *In-situ* UV-VIS studies on ITO electrode using the same solvent mixture also confirm this result. However, the polymer film obtained in aqueous acidic medium can be switched between -0.1 V and 0.3 V, reversibly.

In-situ UV-VIS studies also indicated that the initial rates of electrochemical polymerization increases in the following order: 4BAN < 4CAN < 4FAN.

Although, FT-IR results indicated that polymerization of the monomer proceeds mainly via 1,4-addition, other positions of the monomers should also take part without



Figure 9. FT-IR spectra of (a) P4BAN before doping and (b) P4BAN after doping with iodine for 13 days at room temperature.

any priority, because the para positions of the monomers are already occupied by corresponding halogens. This was proved by the existence of several peaks in ^{19}F -NMR spectra of the polymer P4FAN (6).

All the polymers synthesized by CPE exhibit very low conductivity, which can be enhanced by iodine doping. Iodine doping was monitored by recording ESR, FT-IR, and UV-VIS spectra of polymers before and after iodine doping.

It is interesting to note that soluble polymers can be coated on a glass surface (coated quartz for UV and ESR studies) and then they can gain conductivity upon iodine doping. This was also proved by ESR studies.

Acknowledgements

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References

1. Snauwaert, P.H., Lazzaroni, R., Riga, J., and Verbist, J.J. (1986) *Synth. Metals*, 16: 245–255.
2. Diaz, F.R., Sanchez, C.O., del Valle, M.A., Tagle, L.H., Bernede, J.C., and Tregouet, Y. (1998) *Synth. Metals*, 92 (2): 99–106.
3. Athawale, A.A., Patil, S.F., Deore, B., Patil, R.C., and Vijayamohanan, K. (1997) *Polym. J.*, 29 (10): 787–794.
4. Kwon, A.H., Conklin, J.A., Makhinson, M., and Kaner, R.B. (1997) *Synth. Metals*, 84 (1–3): 95–96.
5. Cihaner, A. and Önal, A.M. (2001) *Eur. Polym. J.*, 37: 1767–1772.
6. Cihaner, A. and Önal, A.M. (2002) *Polym. Int.*, 51: 680–686.
7. Prakash, S., Sivakumar, C., Rajendran, V., Vasudevan, T., Gopalan, A., and Wen, Ten-Chin (2002) *Materials Chemistry and Physics*, 74 (1): 74–82.
8. Duic, L., Mandic, Z., and Kovacicsek, F. (1994) *J. Polym. Sci., Part A: Polym. Chem.*, 32 (1): 105–111.
9. Lee, J.Y. (1992) *J. Appl. Electrochem.*, 22 (8): 738–742.
10. Inzelt, G., Scahok, E., and Kertesz, V. (2001) *Electrochimica Acta*, 46 (26–27): 3945–3962.
11. Zeng, X.R. and Ko, T.M. (1998) *Polymer*, 39 (5): 1187–1195.
12. Zeng, X.R. and Ko, T.M. (1997) *J. Polym. Sci., Part B: Polym., Phys.*, 35 (13): 1993–2001.