Electrochemical Copolymerization and Characterization of Aniline and Isoprene in Aqueous *p*-Toluene Sulfonic Acid Solution

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ABSTRACT: Uniform and adherent copolymer coating of poly(aniline-*co*-isoprene) was successfully formed on low-carbon-steel electrodes by potentiostatic electropolymerization. Electropolymerization was performed by using aqueous *p*-toluene sulfonic acid solution as electrolyte. Applied potential and feed ratios of monomers (aniline and isoprene) were systematically varied and the reactions were done under aqueous conditions. The copolymer coatings were characterized by infrared spectroscopy and the formation of copolymer was confirmed by the presence of aliphatic secondary amine, aromatic secondary amine, and aliphatic CH stretch groups. The electronic structure of the copolymers was further investigated by using UV/Vis absorption spectroscopy. The electrochemistry of the formation of copolymers was studied by using cyclic voltammetry. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 184–192, 2002; DOI 10.1002/app.10298

INTRODUCTION

In general, polymers are insulating materials. However, in the past 20 years, a new class of organic polymers was synthesized with a remarkable ability to conduct electricity. This has paved the way for potential applications in the field of rechargeable batteries, electrolytic capacitors, and electrochromic displays.

In 1862, polyaniline was the first conducting polymer to be synthesized.[1] It was also the first conducting polymer to be commercialized. Polyaniline can exist in three different oxidation states, such as leucoemeraldine base (fully reduced state), emeraldine base (partially oxidized state), and pernigraniline base (fully oxidized state).

When doped with suitable anions, they exist in corresponding salt form.

Sulfonated polyanilines were found to have self-doping characteristics. This kind of polyaniline is readily processible. In terms of conductivity, sulfonated polyanilines are very useful, as they retain high conductivity even in neutral pH.[2]

Polyaniline was synthesized by electrochemical process by using noble or inert electrodes as the working electrodes. Freestanding polyaniline films were synthesized by electrochemical polymerization on platinum and gold electrodes.[3] The electrochemical synthesis of polyaniline on carbon fibers was also reported.[4–6] It is difficult to coat polyaniline on nonnoble working electrodes because of preferential dissolution and passivation of the substrates by the formation of poorly conducting salt or oxide films during anodic polymerization.
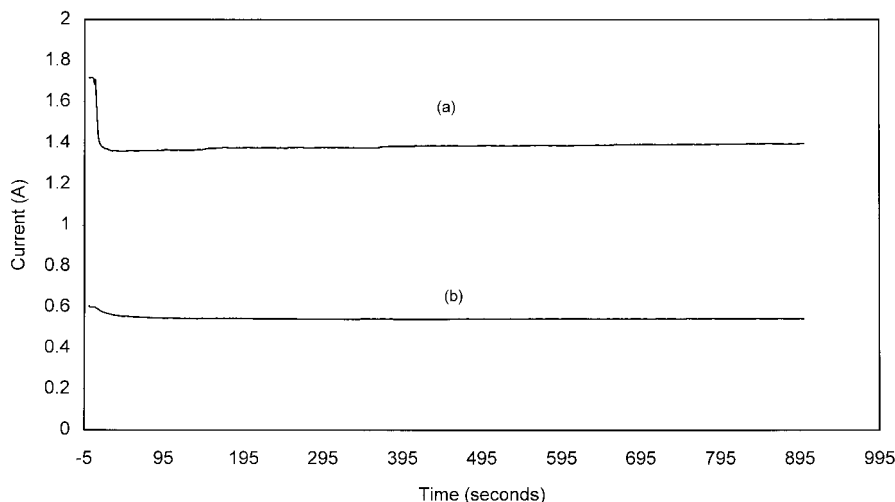
It is interesting to note that polyaniline can be formed on reactive metals such as steel and alu-

Figure 1 *I-t* curves monitored for reactions done at an applied potential of 2.0 V versus SCE for 15 min on low-carbon steel using aqueous toluene sulfonic acid solution (0.5*M*) as electrolyte along with (a) isoprene only and (b) aniline only.

minum. The formation of strongly adherent polyaniline coatings on mild steel using aqueous oxalic acid and *p*-toluene sulfonic acid as electrolytes was reported.[7–8] The formation of polyaniline on lead and aluminum by electrocatalytic synthesis was also reported.[9]

One of the main applications of polyaniline on reactive metals is corrosion protection. Polyaniline doped with *p*-toluene sulfonic acid was found to show good corrosion-resistance properties when formed on low-carbon steel.[10–14] It is also reported that polyaniline shows better corrosion resistance in the undoped form.[15–17]

The major disadvantage of polyaniline is poor processibility and mechanical properties. This was overcome by the formation of polyaniline blends and composites. The mechanical properties of polyaniline can be improved by forming a blend or a copolymer with an unsaturated hydrocarbon such as polyisoprene.

Akbulut et al. have shown that isoprene can be electropolymerized by using constant potential electrolysis.[18] It was shown that oxidation peak potential of isoprene occurs at 2.0 V versus Ag^0/Ag^+. It was also reported that monomers such as isoprene and indene, which has a large applied peak potential difference, can be copolymerized by using a constant potential process.[19]

In this article, we report a novel method of synthesizing copolymers of aniline and isoprene by electrochemical method. The influence of electrochemical deposition parameters such as
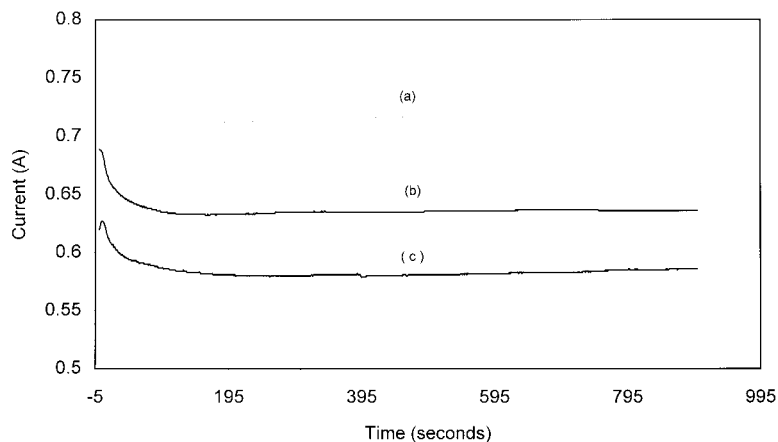
feed ratio of monomers and the applied potential on the formation of copolymers was also studied.

EXPERIMENTAL

All chemicals were purchased from Aldrich Chemical Co., Inc. and the aqueous solutions were made by using deionized water. QD low-carbon-steel panels were provided by Q-Panel Co. The substrates were degreased ultrasonically with acetone for about 15 min prior to the electrochemical polymerization.

Electrochemical Reactions

Aqueous electropolymerization was performed by using a single-compartment polypropylene electrochemical cell. A 0.5-mm-thick QD low-carbon-steel panel was used as the working electrode. The counter electrodes comprised two stainless steel plates. A saturated calomel electrode (SCE) manufactured by Corning Co. was used as the reference electrode. An EG and G Princeton Applied Research 273A Potentiostat/Galvanostat was used as the source of supply. Controlled potential coulometry was used to form the copolymers of aniline and isoprene on steel. The applied potential varied from 1.5 to 2.5 V versus SCE. The molar ratio of the initial concentration of the comonomers (aniline and isoprene) was varied from 1 : 9 to 9 : 1, respectively. The concentration

Figure 2 *I-t* curves monitored as a function of feed ratio of monomers for reactions done at an applied potential of 2.0 V versus SCE for 15 min on low-carbon steel using aqueous toluene sulfonic acid solution (0.5M) as electrolyte along with (a) aniline-0.025M, isoprene-0.225M (1 : 9); (b) aniline-0.125M, isoprene-0.125M (1 : 1); (c) aniline-0.09M, isoprene-0.01M (9 : 1).

of aqueous *p*-toluene sulfonic acid was kept constant at 0.5M. The volume of the aqueous solution used for each experiment was 100 mL and the area of the coated substrate was 8 cm^2. The coated samples were obtained by stopping the reactions at predetermined reaction times. At the end of each experiment, the coated substrate was removed from the solution and rinsed thoroughly with methanol, so as to eliminate any loosely contacted species. The sample was then dried in an oven at 100°C for about 2 h.

Characterization

Reflection–absorption infrared spectra (RAIR) of the sample were measured by a Bio-Rad FTS-40

FTIR spectrometer (Bio-Rad, Richmond, CA). Angular specular reflectance attachment was set to an incident angle of 50°. Spectra were obtained by using a resolution of 8 cm^{-1} and averaged over 256 scans. A background spectrum of a bare polished steel substrate was subtracted from the acquired spectra in all cases.

UV/Vis absorption spectroscopy was done by using a U-3000 UV/Vis spectrometer. The copolymers and the homopolymers were dissolved in *N*-methyl pyrrolidone. The samples were scanned over a range of 200–1100 nm.

The electrochemistry of the formation of coatings was studied by using cyclic voltammetry. The reactions were done over a scan range of −1.0–1.75 V versus SCE at a scan rate of 20 mV/s.
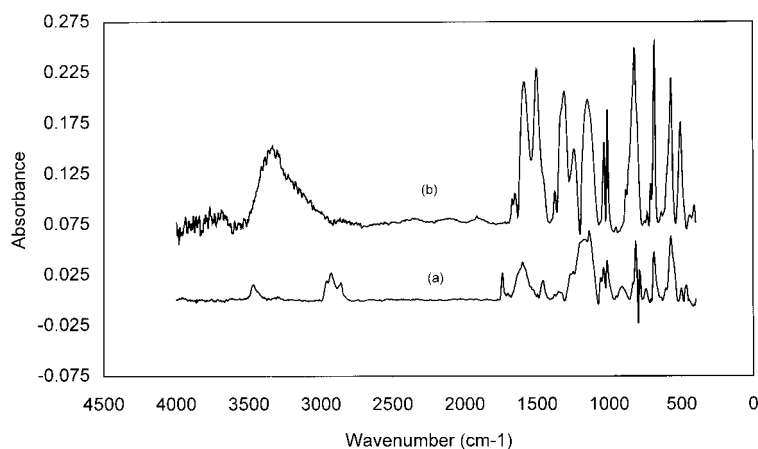
Figure 3 RAIR spectra for reactions done at an applied potential of 2.0 V versus SCE for 15 min on low-carbon steel using aqueous toluene sulfonic acid solution (0.5M) as electrolyte along with (a) isoprene only and (b) aniline only.
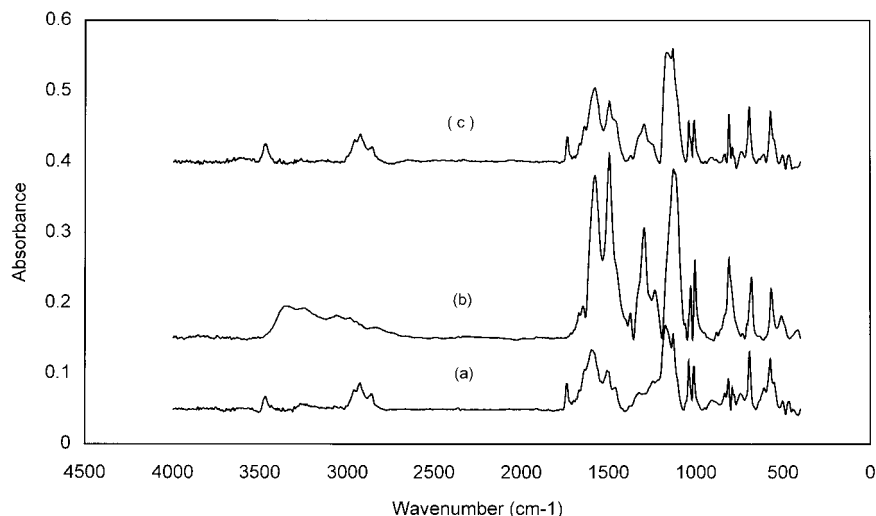
Figure 4   RAIR spectra as a function of feed ratio of monomers for reactions done at an applied potential of 2.0 V versus SCE for 15 min on low-carbon steel using aqueous toluene sulfonic acid solution (0.5M) as electrolyte along with (a) aniline-0.025M, isoprene-0.225M (1 : 9); (b) aniline-0.125M, isoprene-0.125M (1 : 1); (c) aniline-0.09M, isoprene-0.01M (9 : 1).

RESULTS AND DISCUSSION

Electrodeposition Process

Figure 1 shows the current-time (*I*-*t*) transients for the electropolymerization of homopolymers formed at an applied potential of 2.0 V versus SCE. The curves show a general trend of a sharp drop in the current at very short times, which is followed by a steady current regime. Figure 1(a) shows the *I*-*t* curves for reactions done using only isoprene (in the absence of aniline). The steady current value is higher when compared to the reactions done using only aniline (i.e., in the absence of isoprene) [Fig. 1(b)]. As we vary the feed composition of the monomers, the steady current value increases with an increase in the concentration of isoprene [Figs. 2(a)–2(c)]. Comparing Figures 1 and 2, it is shown that the steady current values of the copolymers (Fig. 2) lie between that of the homopolymers (Fig. 1).

Infrared Spectroscopy

Figure 3 shows the infrared spectra of the individual homopolymers (polyaniline and polyisoprene). The infrared spectrum of polyisoprene shows a group of the CH stretching vibration bands between 2800 and 3000 cm^{-1}, a CH$_3$ asymmetrical bending vibration at 1460 cm^{-1}, and a

symmetrical CH$_3$ bending vibration at 1385 cm^{-1}. Our results agree well with the literature.[18] The infrared spectrum of polyaniline is different from that of polyisoprene. The characteristic peaks of polyaniline occurring at 3250, 1600, 1500, 1300, and 830 cm^{-1} are observed. The peaks at 1600 and 1500 cm^{-1} occur because of the benzenoid and quinonoid deformation. The presence of these peaks suggests that polyaniline exists in emeraldine form. Both the infrared spectra of polyaniline and the polyisoprene show peaks at 1030 and 1010 cm^{-1} because of the sulfonate groups. The presence of these peaks suggests that both polyaniline and polyisoprene exist in doped form.

Figure 4 shows the infrared spectra as a function of feed ratio of comonomers. The infrared spectra show peaks due to both polyaniline and polyisoprene. The most prominent peaks occur at 3000–2800, 1600, 1500, 1460, 1300, 1140, 1030, 1010, and 830 cm^{-1}. The peak at 1140 cm^{-1} suggests the presence of an aliphatic secondary
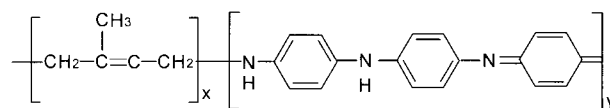
Figure 5   Block copolymer of polyaniline and polyisoprene.
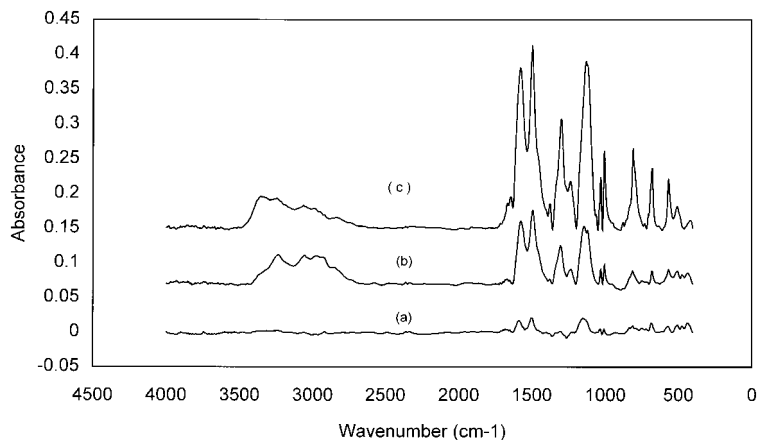
Figure 6   RAIR spectra as a function of reaction time for electropolymerization of aniline-0.125M, isoprene-0.125M (1 : 1) along with aqueous toluene sulfonic acid (0.5M) as electrolyte at an applied potential of 2.0 V versus SCE. (a) 1 min; (b) 5 min; (c) 15 min.

amine group. This suggests that there is a chemical bond between polyaniline and polyisoprene units. Additionally, the presence of all the characteristic peaks of polyaniline and polyisoprene indicates the formation of block copolymer of polyaniline and polyisoprene. The proposed structure of the copolymer is shown in Figure 5.

Figure 6 shows the infrared spectra as a function of reaction time for reactions done using a 1 : 1M feed ratio of comonomers. The peak intensity of the infrared spectra increases with an increase in the reaction time. This suggests that the coating becomes thicker with an increase in the

reaction time. At very short times, the infrared spectra do not show any distinct peaks [Fig. 6(a)].

The infrared spectra as a function of applied potential show that the peaks in the 3000- to 2800-cm^{-1} regions become more distinct with an increase in the applied potential (Fig. 7). This shows that the copolymers start to form at higher applied potential ($\geq$ 2.0 V versus SCE).

UV/Vis Absorption Spectroscopy

The UV spectrum of polyaniline shows two characteristic bands at 300 and 600 nm, respectively
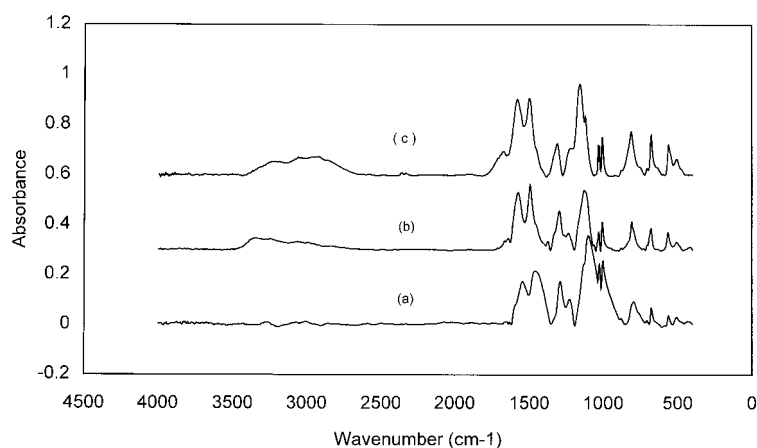
Figure 7   RAIR spectra as a function of applied potential for the copolymer coatings formed because of the electropolymerization of aniline-0.12M, isoprene-0.125M (1 : 1) along with aqueous toluene sulfonic acid solution after 15 min of reaction. (a) 1.5 V versus SCE; (b) 2.0 V versus SCE; (c) 2.5 V versus SCE.
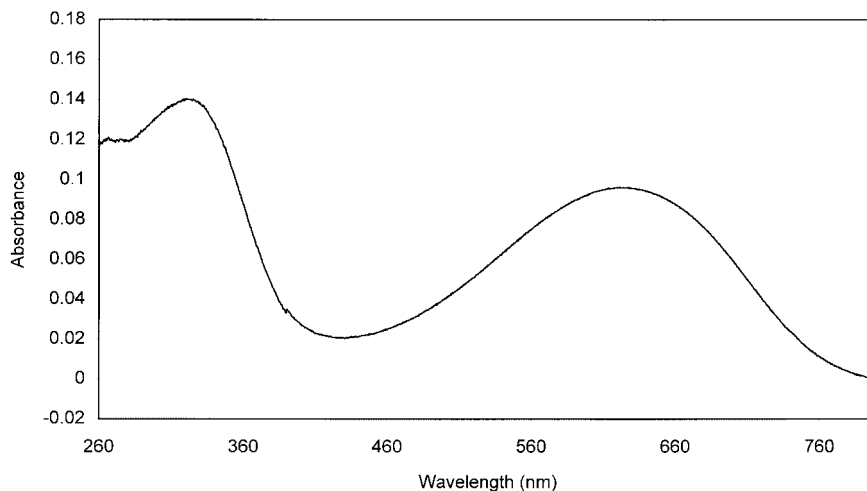
Figure 8 UV/Vis absorption spectra of polyaniline formed by the electropolymerization of aniline (0.25M) along with aqueous toluene sulfonic acid (0.5M) as electrolyte using an applied potential of 2.0 V versus SCE after 15 min of reaction.

(Fig. 8). The spectrum obtained is characteristic of the emeraldine form of polyaniline and is similar to that reported in the literature.[8] The band at 300 nm is attributed to the π-π^* transition of the benzenoid groups. The absorption in the visible region is characteristic of the quinone diamine structure and of the degree of oxidation of the polymer.

The UV spectra of the copolymers also show the two characteristic bands of polyaniline (Fig. 9). The intensity of these bands increase with an increase in the concentration of aniline. The pres-

ence of the characteristic bands of polyaniline is in complete agreement with the results of the infrared spectroscopy. This further confirms the formation of a block copolymer of polyaniline and polyisoprene.

Cyclic Voltammetry

Reactions without Monomer

Cyclic voltammogram of low-carbon steel electrode polarized in 0.5M aqueous toluene sulfonic
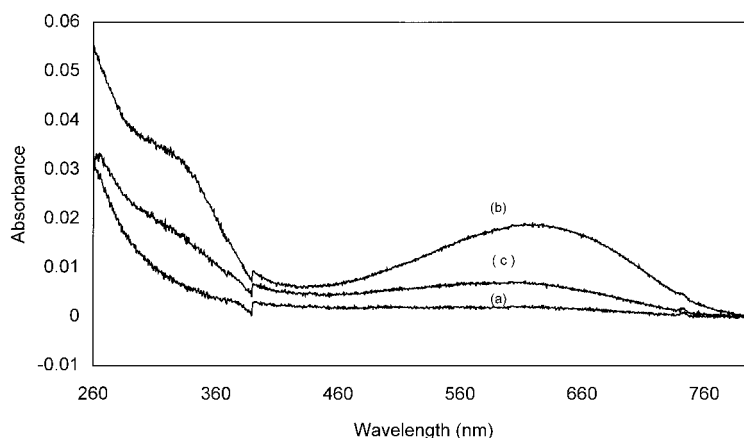
Figure 9 UV/Vis absorption spectra as a function of feed ratio of comonomers for reactions done using aqueous toluene sulfonic acid solution (0.5M) as electrolyte at an applied potential of 2.0 V versus SCE after 15 min of reaction. (a) Aniline-0.025M, isoprene-0.225M (1 : 9); (b) aniline-0.125M, isoprene-0.125M (1 : 1); and (c) aniline-0.09M, isoprene-0.01M (9 : 1).
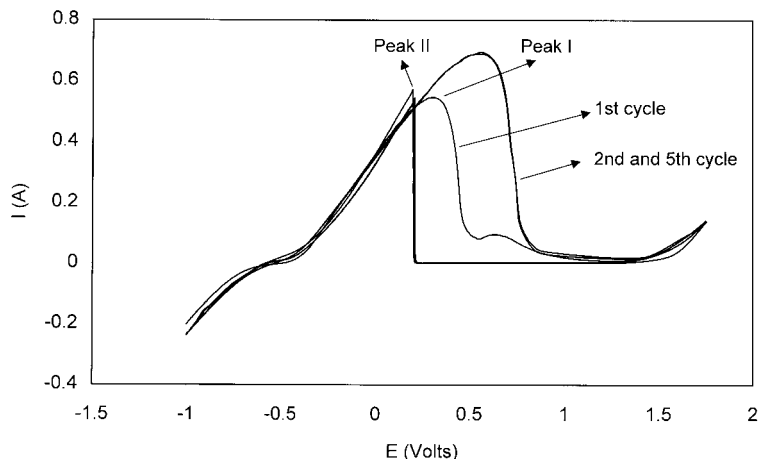
Figure 10 Potentiodynamic polarization of low-carbon steel electrode in 0.5*M* aqueous toluene sulfonic acid solution at a scan rate of 20 mV/s.

acid is shown in Figure 10. The first scan shows broad anodic maxima at around 0.3 V versus SCE (peak I). This peak is attributed to the electrode passivation process. During the reverse scan, a sharp oxidation peak is observed in the potential range of 0–0.3 V versus SCE (peak II). This observation is in complete agreement with the literature.[8] The reversed oxidation maxim was attributed to an oxidation process, which causes partial destruction of the passive layer.[19]

Formation of Polyaniline

The first scan of the electropolymerization of aniline, shown in Figure 11, is similar to that ob-

served in the absence of aniline (peak I and peak II). As the number of scan cycles is increased, both peaks I and II shift cathodically and also the oxidation currents start to decrease. This is due to the growth of the polyaniline film on the steel electrode, which is dark green in color. As the number of cycles is increased, we see another anodic maxima at around 0.2 V versus SCE. This is due to the conversion of the leucoemeraldine form of polyaniline to the emeraldine form of polyaniline.

Formation of Copolymers

Figures 12-14 show the cyclic voltammogram of the electropolymerization of comonomers by us-
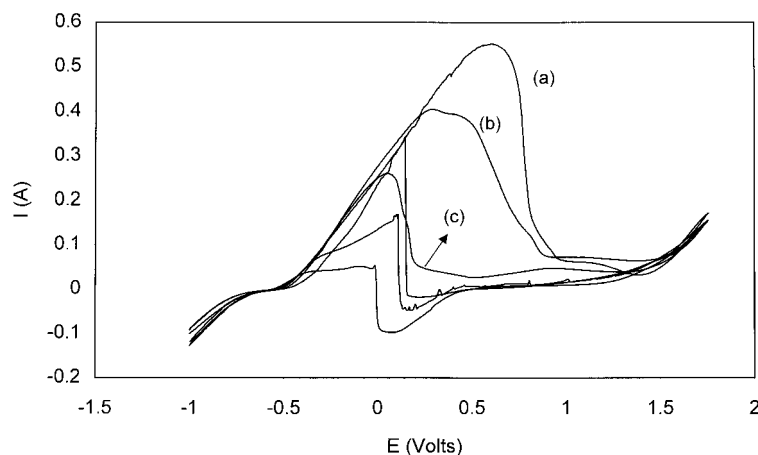
Figure 11 Cyclic voltammogram of electropolymerization of aniline (0.25*M*) using aqueous toluene sulfonic acid solution (0.5*M*) as electrolyte using a scan rate of 20 mV/s. (a) First cycle; (b) fourth cycle; (c) fifth cycle.
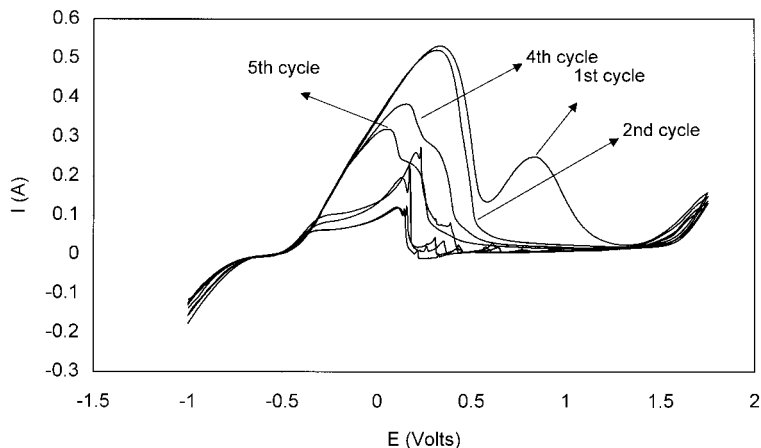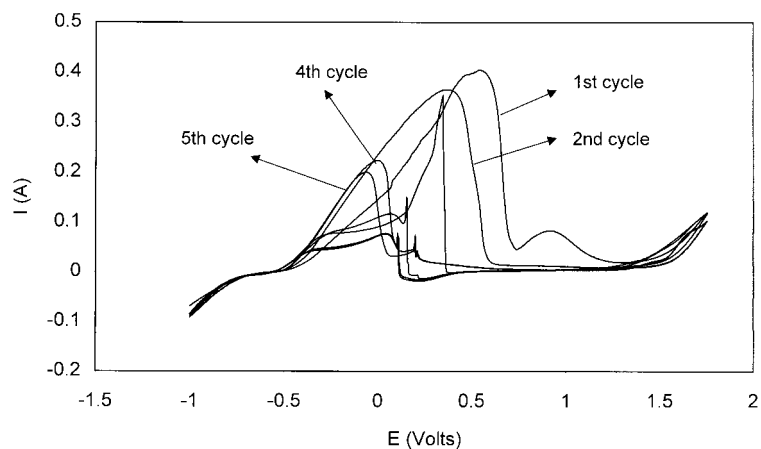
Figure 12 Cyclic voltammogram of electropolymerization of aniline-0.09*M*, isoprene-0.01*M* (9 : 1) using aqueous toluene sulfonic acid solution as electrolyte on low-carbon steel using a scan rate of 20 mV/s.

ing different molar ratios. When the concentration of aniline is higher than isoprene (9 : 1), we see a distinct anodic maxima at around 0.8 V in addition to peaks I and II in the first scan (Fig. 12). This should be due to the oxidation of aniline. As the number of cycles is increased, the film starts to grow on the steel electrode and the peaks (I and II) start to shift cathodically and the corresponding current maxima also decrease. New anodic maxima similar to that of polyaniline start to appear at 0.2 V versus SCE. When the molar feed ratio of the comonomers are equal, peak I and peak II start to decrease with an increase in the number of cycles and shift cathodically (Fig.

13). When the concentration of isoprene is higher than aniline, peak I and peak II do not shift much (Fig. 14).

CONCLUSION

The electropolymerization of poly(aniline-*co*-isoprene) coatings on low-carbon steel was successfully performed by varying the applied potential and feed ratio of comonomers. The presence of IR peaks at the 3100- to 2800-cm^{-1} region associated with the presence of aliphatic CH peaks and a secondary amine peak (1150 cm^{-1}) in the coatings

Figure 13 Cyclic voltammogram of electropolymerization of aniline-0.125*M*, isoprine-0.125*M* (1 : 1) using aqueous toluene sulfonic acid solution as electrolyte on low-carbon steel using a scan rate of 20 mV/s.
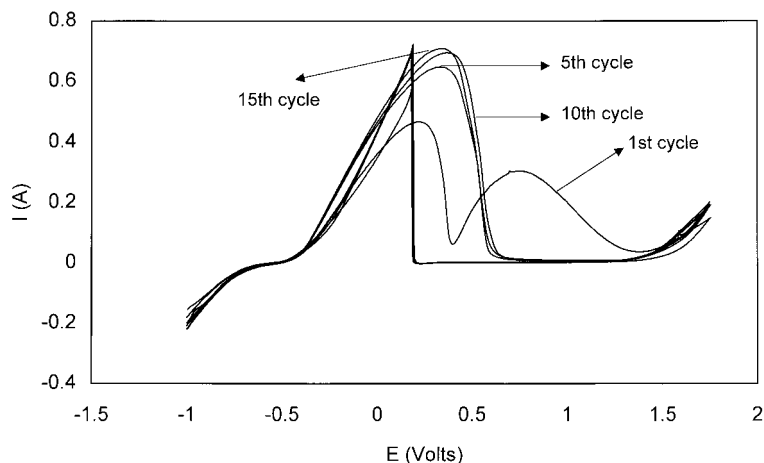
Figure 14 Cyclic voltammogram of electropolymerization of aniline-0.025*M*, iso-prene-0.225*M* using aqueous toluene sulfonic acid solution (0.5*M*) as electrolyte at a scan rate of 20 mV/s.

confirm the formation of block copolymers of polyaniline and polyisoprene. UV/Vis absorption spectroscopy suggests that the electronic structure of polyaniline is unaltered in the copolymers. Both infrared spectroscopy and UV/Vis spectroscopy suggest the formation of block copolymers of polyaniline and polyisoprene.

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