

# A 316 Steel Electrode Coated with Polycarbonate for Electropolymerization of Aniline

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**ABSTRACT:** In this study, homogenous and flexible conductive polymer films with improved mechanical properties were obtained by the electrochemical polymerization of aniline on polycarbonate-coated 316 steel electrodes. The optimal thickness of polycarbonate coating was found to be 20  $\mu\text{m}$  in order to obtain free-standing, high-quality conducting films. The polyaniline/polycarbonate films obtained on 316 steel electrodes were more homogenous than those obtained on platinum electrodes. The maximum conductivity was observed for 10% polyaniline content; increasing the polyaniline content did not affect the conductivity to a significant extent. The films were found to be a suitable sensor against ammonia gas in a concentration range of 0.1–1.0%. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1103–1111, 1997

**Key words:** conductive polyaniline/polycarbonate films; electropolymerization; 316 steel electrode

## INTRODUCTION

Polyaniline (PANI) is expected to be an attractive conductive polymer for industrial applications due to its environmental stability, chemical stability, and cost-effective raw materials, such as aniline. Conductive PANI can easily be obtained by electrochemical or chemical methods.<sup>1–5</sup> The chemical technique gives a powder product while it is possible to obtain a conductive polymer film form by the electrochemical method. One of the techniques to improve the mechanical properties of the conductive polymer is precoating of the electrode surface with an insulating polymer and carrying out the polymerization of aniline on the modified electrode.<sup>6–8</sup>

Electrochemical polymerization of aniline on a nitrile rubber-coated platinum (Pt) electrode resulted in a conducting composite.<sup>9,10</sup> On the other

hand, the polymerization of aniline was reported to take place at a polyurethane-Pt interface when a polyurethane-coated electrode was used.<sup>11</sup>

By this technique, monomer, solvent, and electrolyte anions diffuse through the insulating polymer layer and the polymerization takes place at the electrode metal/insulating polymer interface. This type of polymerization may be limited to the interface,<sup>11</sup> or the conducting polymer may penetrate into the insulating polymer to form a conducting film.<sup>6–9,12</sup>

The electrochemical polymerization of PANI is generally carried out on noble metal electrodes such as Pt, Au in acidic media by continuous scan, or constant potential electrolysis.<sup>13–15</sup> In recent reports, steel electrodes were used as working electrodes: These are generally in patented literature.<sup>16,17</sup>

Troch-Nagels et al.<sup>18</sup> investigated the electrochemical polymerization of monomers, which can give conductive polymers such as aniline, pyrrole, and thiophene on a steel surface for corrosion protection studies on mild steel. Similarly, DeBerry<sup>19</sup> reported that stainless steel electrodes coated

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with thin films of PANI remain passive for long periods of time in acid solutions in which they are normally active and subjected to high rates of corrosion.

The synthesis of conductive PANI/insulating polymer films on a steel electrode is of great industrial importance, since the use of much cheaper electrode material, instead of highly expensive inert electrodes such as Pt and Au, enables us to work with electrodes with much bigger dimensions. In this work, the electropolymerization of aniline on a 316 steel electrode was investigated where polycarbonate (PC) was used as the insulating polymer to coat the steel electrode. This modified electrode was used to obtain conductive PANI/PC film. Conductive PANI/PC films were characterized by scanning electron microscopy, ultraviolet, infrared, and conductivity measurements. The sensor properties of these films against ammonia gas were also investigated.

## EXPERIMENTAL

### Materials

Aniline (BDH, UK) was distilled in vacuum. The steel electrode was made of 316 stainless steel (16–18% Cr, 10–14% Ni, 1.75–2.75% Mo, and 0.1% C). PC (density = 1.20 g/cm<sup>3</sup>,  $T_g$  = 150°C) (Scientific Polymer Products, USA) was used as supplied.

### Cyclic Voltammetry and Electrolysis

The cyclic voltammograms were taken by using 2-mm-long Pt wire or 3-mm-long 316 steel wire as working, Ag/Ag<sup>+</sup> as reference, and 2-cm-long Pt wire as counter electrodes at 25°C. The electrolysis was carried out in three electrode H-type cells, the specifications of which were detailed previously.<sup>20</sup> The working electrodes used during the electrolysis were 1 × 1.5 cm<sup>2</sup> Pt and 316 steel plates. The electrolysis was performed in 1.0M H<sub>2</sub>SO<sub>4</sub> at 0.7-V constant potential. The solution was saturated with nitrogen prior to the electrolysis and kept under nitrogen atmosphere thereafter.

The Pt or 316 steel electrodes were coated with PC using a 1% PC solution in chloroform. Each electrode surface was coated with 0.4 mL of solution in a dropwise manner and then dried and used in electrolysis as the working electrode.

When the electrolysis was completed, the work-

ing electrode was removed from the cell and the PANI/PC film formed on the surface was washed thoroughly with water and methanol. Then, it was kept in 1.0M H<sub>2</sub>SO<sub>4</sub> solution for half an hour and dried under vacuum at 40°C. All of the experiments were carried out using a Bank Elektronik ST 88 potentiostat, a Bank Elektronik VSG 2000 function generator, and a Karl Kolb Servagor X-Y recorder.

### Characterization

The 316 steel and Pt plates were weighed after being thoroughly dried, covered with PC, dried under vacuum at 40°C, and reweighed, and the amount of PC covering the electrode was then calculated. The same procedure was repeated after the electrolysis to determine the amount of PANI in the PANI/PC film.

The UV-visible spectra were measured using a Shimadzu 160 A model spectrophotometer.

The IR spectra were measured with a Perkin Elmer 1710 model FTIR. The PANI/PC film on the electrode was peeled off from the surface after the electrolysis. PANI formed in the solution was filtered off and dried. The IR of the film was taken directly, while powder PANI was pelletized with KBr.

The conductivity of the PANI/PC composite films was determined using four- or two-probe methods at 25°C and 55% humidity. The micrographs were taken using a JEOL model JEM scanning electron microscope.

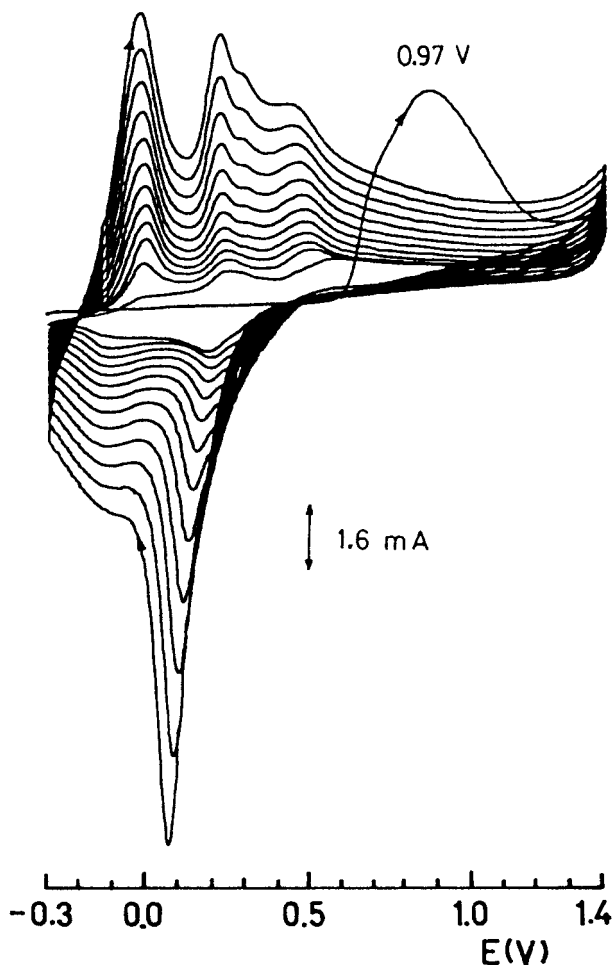
### Response to Ammonia Gas

The response of PANI/PC films to ammonia gas was investigated in a chamber with two stopcocks. The samples were placed in the chamber, and ammonia gas with a known concentration was sent through one of the stopcocks with a flow rate of 50 mL/min. The resistance of the film was continuously monitored throughout the 3-min feeding period. Then, the stopcock from which the ammonia gas was sent was closed and the film was exposed to air for 3 min by opening the other stopcock. These experiments were repeated for several pulses. All of the experiments were carried out at 25°C, and the concentration of ammonia gas was adjusted with dry nitrogen.

## RESULTS AND DISCUSSION

### Cyclic Voltammetry

Figure 1 shows a typical cyclic voltammogram of aniline (0.1M) in 1.0M H<sub>2</sub>SO<sub>4</sub> using a Pt working



**Figure 1** The multisweep cyclic voltammograms recorded between  $-0.3$  and  $1.4$  V in  $0.1M$  aniline +  $1.0M$   $H_2SO_4$  using a Pt electrode at a scan rate of  $50$  mV/s.

electrode between a potential range of  $-0.3$  and  $1.4$  V. The single peak observed during the first scan at  $0.97$  V corresponds to the oxidation of aniline. The decrease in acid concentration shifts the potential to lower values.<sup>21</sup>

Figure 2(a) shows the cyclic voltammetric curves of 316 steel,  $1.0M$  in  $H_2SO_4$  without aniline. As seen from this figure, 316 steel gives a single peak at  $1.1$  V in  $1.0M$   $H_2SO_4$  and the increase in the number of scans does not cause a significant change either in the position or in the height of this peak. The peak observed at  $1.1$  V is a typical oxidation peak of Cr present in 316 steel.<sup>22</sup>

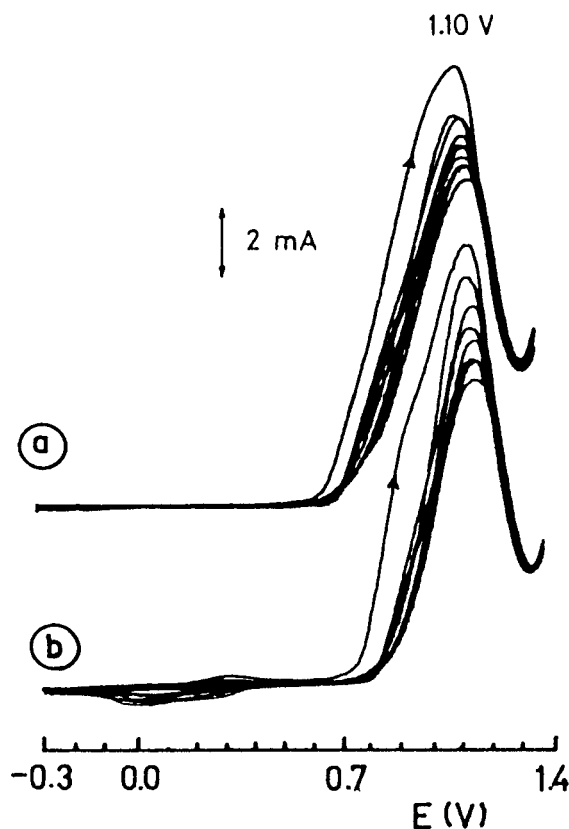
The addition of  $0.1M$  aniline to the medium results in the cyclic voltammogram given in Figure 2(b). The peak at  $1.1$  V reappears during the first scan. The peak observed at  $0.97$  V occurred

on the Pt surface during the first scan (Fig. 1), possibly under the oxidation peak of Cr at  $1.1$  V.

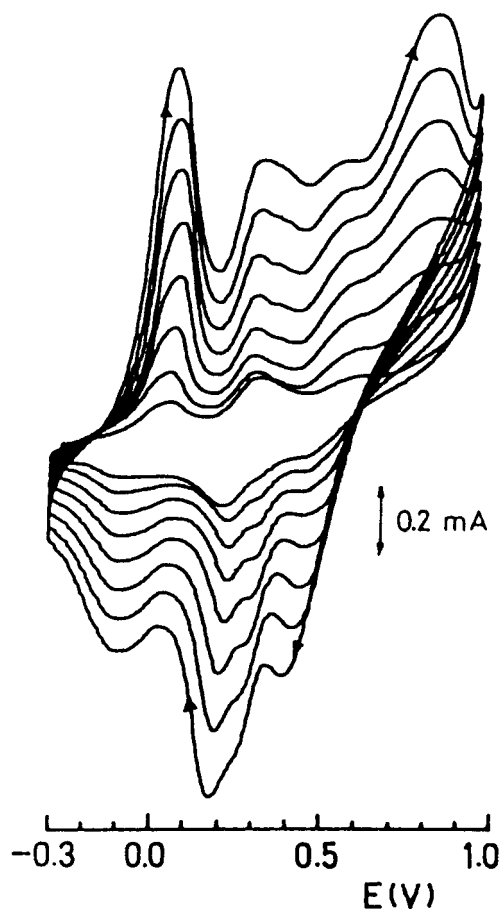
The cyclic voltammograms of aniline in  $1.0M$   $H_2SO_4$ , using the 316 steel electrode and taken between  $-0.3$  and  $1.0$  V with higher sensitivity, give the curves in Figure 3. Figure 4 also shows the cyclic voltammogram curves obtained with the Pt electrode under the same conditions as in Figure 3.

The peaks observed at lower potentials after the first scan using both electrodes show a redox reaction of PANI taking place on the electrode surface. These results have been previously reported in detail.<sup>4,14</sup>

Figure 5 shows the cyclic voltammograms obtained for PC-covered steel electrodes. The peaks are similar to those observed with naked Pt and steel electrodes (Figs. 3 and 4). This shows that the thickness of PC coverage is sufficient to allow reactants to diffuse toward the electrode.



**Figure 2** The multisweep cyclic voltammograms recorded between  $-0.3$  and  $1.4$  V in (a)  $1M$   $H_2SO_4$  and (b)  $0.1M$  aniline +  $1.0M$   $H_2SO_4$  using a 316 steel electrode at a scan rate of  $50$  mV/s.



**Figure 3** The multisweep cyclic voltammograms recorded between  $-0.3$  and  $1.0$  V in  $0.1M$  aniline +  $1.0M$   $H_2SO_4$  using a 316 steel electrode at a scan rate of  $50$  mV/s.

#### Preparation of PANI/PC Films and Conductivities

The thickness of the insulating film coated on the electrode surface is of importance because it must be thin enough to allow the diffusion of the reactants to the electrode. The concentration of the PC solutions, to be used to coat the electrodes, varied between  $0.1$  and  $5\%$  in chloroform. These solutions were dropped on the 316 steel surface, and the most satisfactory results were obtained with the dropwise addition of  $0.4$  mL of  $1\%$  PC solution on each surface of the electrode. This resulted in a  $20\text{-}\mu\text{m}$ -thick PC coating. Thicker coatings did not allow aniline polymerization due to inadequate diffusion, while thinner coatings resulted in weak PANI/PC films, which were difficult to remove intact from the electrode surface.

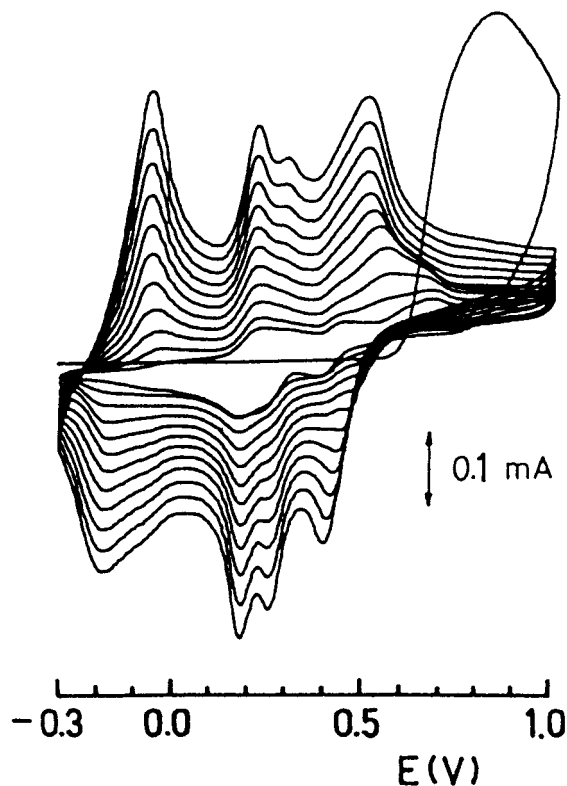
The PANI/PC films prepared by the use of the Pt plate electrode are usually uniformly colored. The studies carried out with a PC-coated 316 steel

electrode gave more homogeneously colored PANI/PC films. The UV absorption values of five different regions of  $10.8\%$  PANI-containing films obtained with Pt and 316 steel electrodes were measured at two wavelengths (Table I). The extent of local variation of absorption values is the measure of the uniformity of the dispersion of PANI in PANI/PC film.

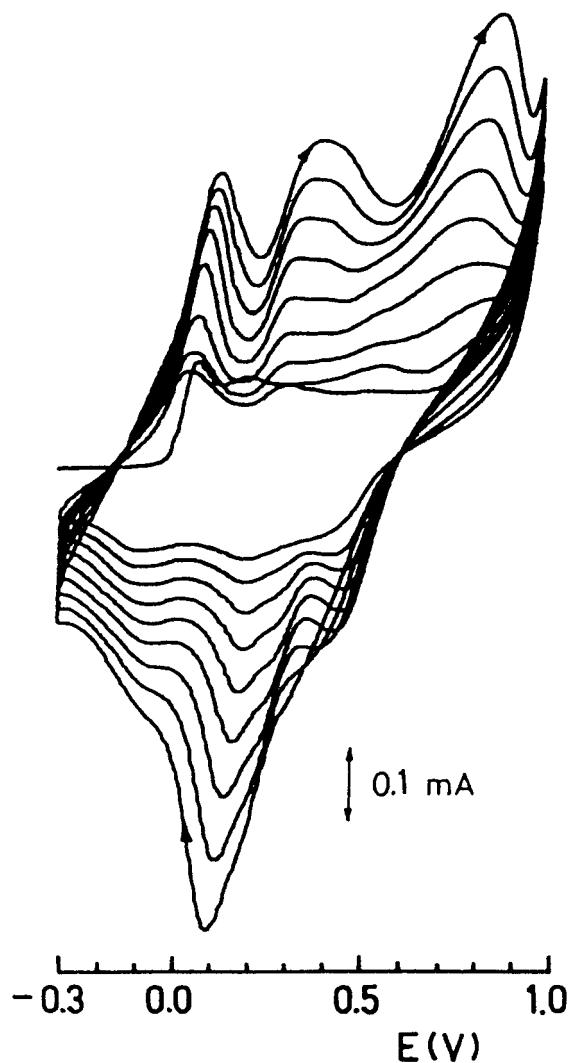
As seen from Table I, the absorption values measured from the different regions of the film obtained by the use of the 316 steel electrode are quite close to each other. On the other hand, the absorption values of the film obtained by the use of the Pt electrode are quite different.

It was reported that a passive metal oxide film forms on the electrode surface and that PANI deposition takes place on the passive film. Once the electrode surface is covered by the passive film, aniline polymerization takes place in a fashion similar to that on inert electrodes.<sup>19</sup>

The PANI/PC composite films were peeled off from the electrode surface after the electrolysis was completed, and no liquid accumulation was



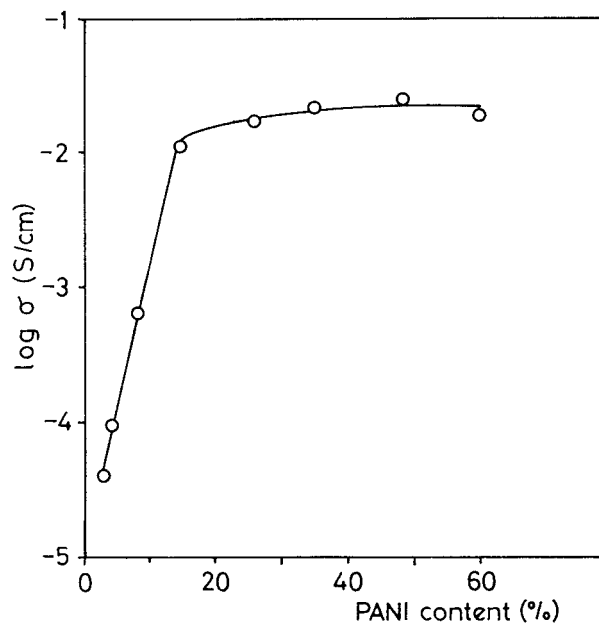
**Figure 4** The multisweep cyclic voltammograms recorded between  $-0.3$  and  $1.0$  V in  $0.1M$  aniline +  $1.0M$   $H_2SO_4$  using a PC-covered 316 steel electrode at a scan rate of  $50$  mV/s.



**Figure 5** The multisweep cyclic voltammograms recorded between  $-0.3$  and  $1.0$  V in  $0.1M$  aniline +  $1.0M$   $H_2SO_4$  using a Pt electrode at a scan rate of  $50$  mV/s.

**Table I** Absorbance Values of  $10.8\%$  PANI Containing PANI/PC Films Obtained Using Pt and 316 Steel Electrodes at  $400$  and  $800$  nm

| Absorbance of Film Obtained Using 316 Steel Electrode |        | Absorbance of Film Obtained Using Pt Electrode |        |
|---|--------|--|--------|
| 400 nm  | 800 nm | 400 nm   | 800 nm |
| 0.581   | 0.516  | 0.545  | 0.479  |
| 0.586   | 0.532  | 0.643  | 0.520  |
| 0.572   | 0.515  | 0.510  | 0.412  |
| 0.576   | 0.526  | 0.686  | 0.364  |
| 0.589   | 0.523  | 0.490  | 0.591  |



**Figure 6** The change of the conductivities of PANI/PC films with PANI content.

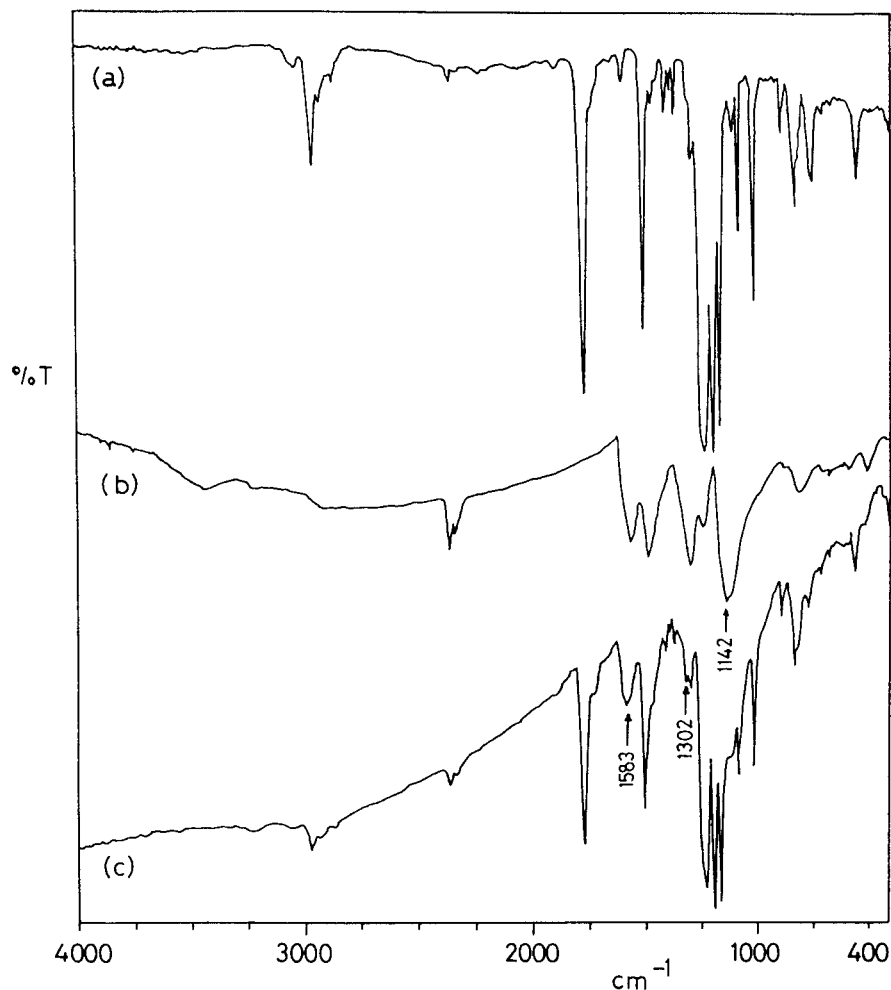
observed. The electrode was seen to maintain its brightness at the beginning of the electrolysis. There was no evidence of PANI formation or accumulation or any variation of color at any region of the electrode surface.

Figure 6 shows the variation of conductivities ( $\sigma$ ) of PANI/PC films depending on the PANI content. The conductivities are closely related to the amount of PANI in the PANI/PC films. The highest conductivity is observed at a PANI content of  $10\%$ . A further increase in PANI content did not change the conductivity to a significant extent. Since sufficient PANI is inserted into the film to provide its own conductivity pathway at threshold value, further inclusion of PANI into the film does not change this maximum conductivity value.

### IR Spectra

The Fourier transform IR (FTIR) spectrum of the pure PANI isolated from the solution during the formation of PANI/PC composite film (in  $0.1M$  aniline +  $1.0M$   $H_2SO_4$  at  $0.7$  V) is given in Figure 7(b). The fundamental absorption bands are in good agreement with values found in the literature.<sup>4,23</sup>

Figure 7(a) and (c) show the FTIR spectra of PC and conductive PANI/PC films ( $14.9\%$  PANI), respectively. The spectrum of PANI/PC films contains typical bands of pure PC and pure PANI.



**Figure 7** The FTIR spectra of (a) PC, (b) PANI, and (c) PANI/PC film containing 14.9% PANI.

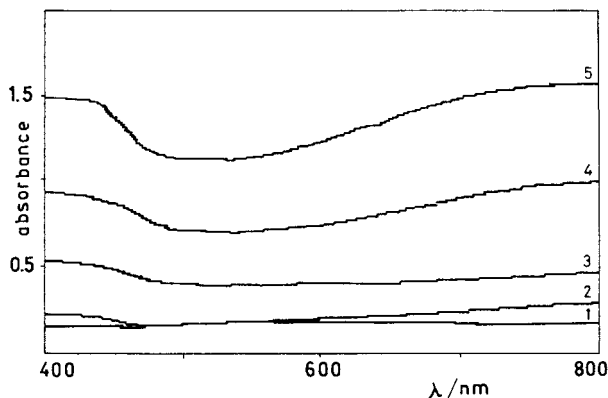
The baseline in the 4,000 to 2,000-nm region is lowered considerably due to the presence of PANI. Similarly, the band observed in pure PANI at 1,142 nm [Fig. 7(b)], which caused the broadening of the 1,000- to 1,250-nm region in the spectrum of the PANI/PC film [Fig. 7(c)], is characteristic of the conductive form of PANI and corresponds to charge delocalization on the conductive PANI.<sup>24</sup> PANI/PC film spectra also reveal bands corresponding to quinone benzene ring deformation at 1,583 nm and —CN— stretching of aromatic amines of 1,302 nm.<sup>4,23</sup>

#### UV-Visible Spectra

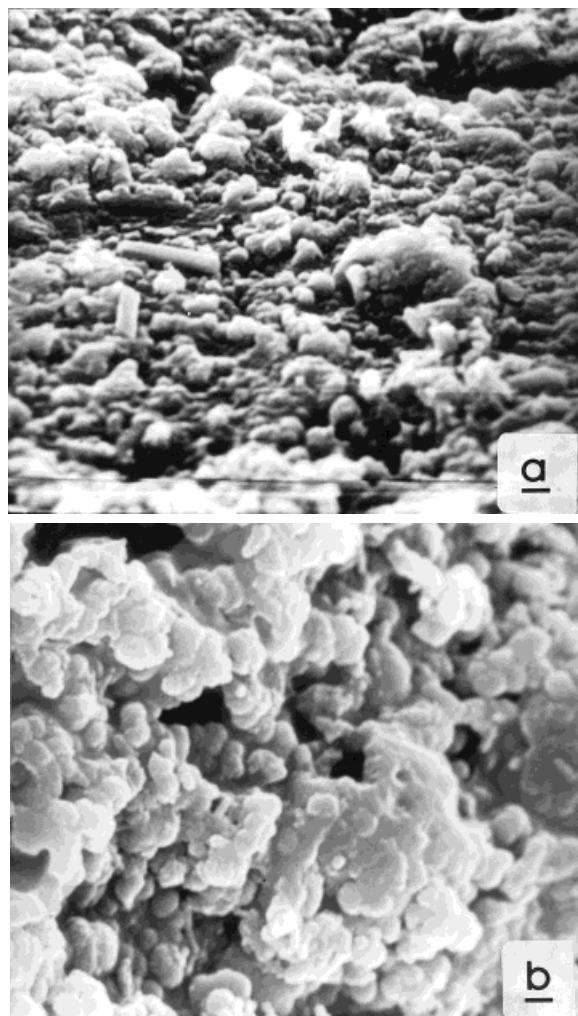
The transparent PC coating on the 316 steel electrode becomes darker as the electrolysis proceeds. The deepness of the color of the PANI/PC films

is dependent on the PANI content and can be controlled by the electrolysis time. The UV spectra of PANI films produced on the naked Pt or other bare metal electrodes cannot be obtained easily since those films are highly brittle and cannot be peeled off from the electrode surface. The UV spectra of PANI can be taken directly on transparent electrodes such as an indium tin/oxide-coated glass electrode.<sup>25–27</sup>

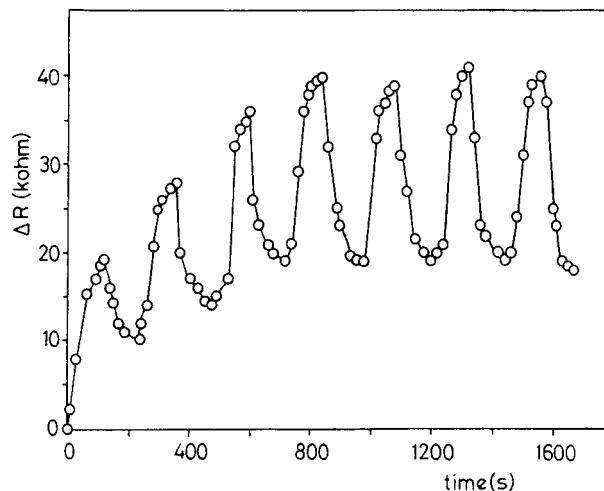
The PANI/PC films containing PANI around 15% and less are highly transparent. This transparency of these films enables one to take their UV spectra outside the solution. However, the transparency vanishes above 15% PANI content and the absorbance values exceed the detectable limit. Figure 8 shows the UV-visible spectra of pure PC and PANI/PC films containing various amounts of PANI.



**Figure 8** The UV-visible spectra of (1) pure PC film and PANI/PC films containing (2) 4.4%, (3) 8.0%, (4) 10.8%, and (5) 14.9% PANI.



**Figure 9** The scanning electron micrographs of PANI/PC film containing 40.2% PANI. Bars indicate (a) 5 mm and (b) 1.5 mm.



**Figure 10** The change of the resistance of PANI/PC films containing 14.9% PANI at an ammonia concentration of 1%. The film was exposed to ammonia gas for 3 min in each pulse and then exposed to air for the same period (the points where the film was exposed to air are marked on the figure).

As seen from Figure 8, pure PC film has no absorption peak between 400 and 800 nm. The UV-visible spectra of PANI/PC films give two peaks, at 440 and 800 nm. These peaks are characteristic for the conductive form of PANI.<sup>25</sup> The intensity of these peaks increases with the PANI content of the film.

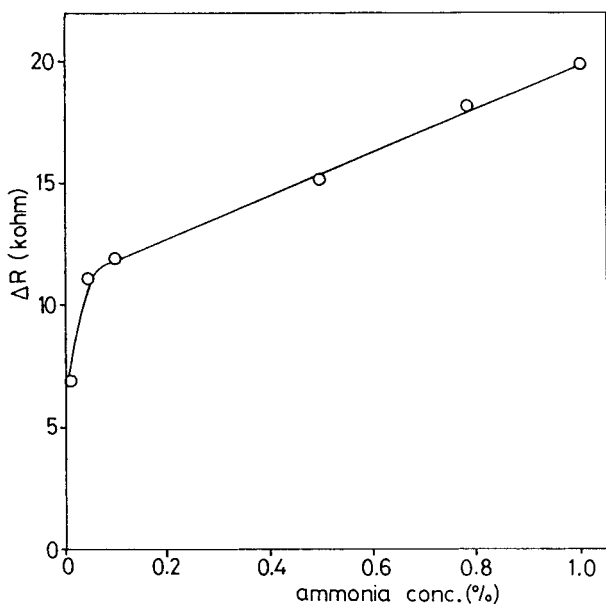
### Scanning Electron Microscopy

Figure 9 shows the micrograph of the PANI/PC film containing 40.2% PANI. The various size granules and semigranular structures are very apparent on the surface. The granular structure becomes much more visible at higher magnification [Fig. 9(b)].

### Sensor Properties Against Ammonia

The rapid and reversible change of the conductivities of some conductive polymers when subjected to various gases and organic vapors indicates that they can be used for sensing purposes.<sup>28,29</sup> The improved mechanical properties of conductive/insulating polymer composites provide various advantages for sensing purposes compared with pure conductive polymers.

Figure 10 gives the response of PANI/PC film



**Figure 11** The change of resistance of PANI/PC films containing 14.9% PANI with ammonia concentration (conc.).

containing 14.9% PANI against 1% ammonia gas. The resistance of the film shows a reversible change when the film is exposed to ammonia gas for certain periods. Change of resistance of the film becomes fully reversible following the first two or three pulses. Similarly, for other ammonia concentrations (0.01–1.0%), irreversible behavior for initial pulses was observed.

The change in resistance ( $\Delta R$ ) after the third pulse for ammonia concentration remained at the level of 20 kohm. Similar measurements were also carried out for other ammonia concentrations, and  $\Delta R$  values were plotted against the concentration (Fig. 11). The relation between  $\Delta R$  and gas concentration is linear within an ammonia concentration range of 0.1–1.0%. This shows that PANI/PC films are useable as ammonia sensors within this range.

## CONCLUSIONS

Aniline electrochemically polymerizes on a 316 stainless steel electrode and shows an electrochemical behavior on a steel surface similar to that on Pt. One can obtain conductive PANI/PC composites by covering the 316 steel electrode

with an insulating PC and allowing the polymerization of PANI on this surface.

PANI was found to be much more homogeneously distributed in PANI/PC films obtained with a 316 steel electrode than those obtained with a Pt electrode. These films are highly suitable for sensor usage due to their reversible resistance change by gas exposure and linear response against the gas concentration. The use of steel electrodes may enable us to work with electrodes with much bigger dimensions, since they would be much cheaper than conventional electrodes and consequently, it would be possible to obtain PANI/PC films in desired larger dimensions.

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