# Conductive Polyaniline/Poly(methyl methacrylate) Films Obtained by Electropolymerization

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## SYNOPSIS

Electrochemical polymerization of aniline, on a Pt foil electrode coated with poly(methyl methacrylate) (PMMA), produces a homogeneous, free-standing, flexible, and conductive polymer film. The conductivity of the films depends on the aniline content and reaches 0.1–0.2 S/cm for films having aniline content of 15% or more. The optimum thickness of precoated PMMA to obtain durable conducting films was found to be in the range of 10–15 $\mu$m. Cyclic voltammetric investigation revealed that aniline exhibits a similar electrochemical behavior on a PMMA coated platinum electrode similar to a bare Pt surface. The film gives a fast and reproducible response against ammonia gas within a concentration range of 1.0–0.01%. Scanning electron micrographs indicate that the films have a rough structure consisting of globular regions. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Conducting polymers have attracted the interest of scientific and technological researchers in recent years. These materials have widespread applications, such as solar energy conversion, batteries, electronics, sensors, and corrosion etc., along with probable uses in the future. Among all of the electrically conductive polymers, polyaniline (PANI) is a particularly attractive material because it has moderately high conductivity upon doping with acids, is easily synthesized by chemical or electrochemical oxidation of aniline, and has good thermal and oxidative stability.

The polymerization of aniline has been investigated extensively since the beginning of this century.[1] However, considerable studies have been devoted to PANI since MacDiarmid et al.[2] reinvestigated it as a conducting polymer.

PANI is normally obtained as a powder material, either by electrochemical or chemical synthesis in aqueous solutions. The main disadvantage of PANI for industrial use is its powdered form, which results in poor processability and mechanical properties. To overcome these disadvantages, various approaches have been reported.

Processability has been achieved recently by rendering PANI soluble and thereby processable.[3–5] An alternative method for soluble PANI is the preparation of blends or composites of PANI with the insulating polymer having desirable physical properties.[6–11] In these studies the aim was to combine the conductivity of PANI with the good mechanical characteristics of the insulating polymer. Conductive blends and composites of PANI with polyacrylamide,[6] poly(ethylene terephthalate),[7] cellulose acetate,[8] poly(vinyl chloride),[9] and poly(alkyl methacrylate),[10,11] prepared by chemical oxidative polymerization of aniline, have been reported.

It is also possible to obtain a conductive film by electrochemical oxidation of aniline on an electrode precoated with an insulating polymer. In that case, monomer and solvent molecules and electrolyte anions are expected to diffuse into the insulating polymer coating. As a result polymerization starts in the interface between the electrode surface and the polymer film. The electrochemically obtained conductive polymers grow into a film, forming an electrically conducting polymer layer.[12,13] The electrochemical polymerization of aniline on a nitrilic rub-

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ber coated Pt working electrode was reported to yield a conductive and electroactive elastomeric film.[14] Based on experimental data, Pei and Bi[15] reported that aniline was electropolymerized, mainly at the polyurethane film–Pt interface when Pt anodes coated with polyurethane film were used as the working electrode. Poly(ethylene imine),[16] nylon 6,[17] and poly(carbonate)[18,19] have also been used by various workers for coating of the working electrode as an insulating polymer.

There are some advantages of the electrochemical polymerization of aniline compared to the chemical methods. The PANI obtained by the electrochemical polymerization method is free from the contamination of the oxidizing agent. The electrical properties of the PANI/insulating polymer films can be varied simply by changing the electrolysis conditions.[20]

In this study, we report the preparation and characterization of the conducting PANI/poly-(methyl methacrylate) (PMMA) films obtained by the electrochemical method. PANI/PMMA films were characterized by their electrical conductivity, UV-visible spectroscopy, and scanning electron microscopy (SEM). Temperature dependence of electrical conductivity and the $NH_3$ gas sensitive characteristics of these films were also examined.

## EXPERIMENTAL

### Materials

Aniline (Merck) was doubly distilled under vacuum. PMMA with a viscosity-average molecular weight of 150,000 was synthesized by solution polymerization using benzoyl peroxide.

### Procedures and Measurements

PANI/PMMA conducting films were prepared by constant potential electrolysis at +0.8 V vs. $Ag^0$/ $Ag^+$ reference electrode, using a Pt foil electrode (1.5 $cm^2$) precoated with PMMA film.

The PMMA film was coated on the electrode surface from a 10 g/L chloroform solution of PMMA. The coating was performed by dropping 0.8 mL of this solution onto each surface of the working electrode. The PMMA-coated electrode was then placed into the three-electrode cell[21] having separated compartments and containing 0.1$M$ aniline in an aqueous solution of 1.0$M$ $H_2SO_4$. The counter electrode was 2 $cm^2$ Pt foil. A nitrogen stream was passed through the solution in the cell for 20 min before

each experiment to remove the dissolved oxygen. The films were peeled off the electrode, washed with diluted $H_2SO_4$, and dried under vacuum.

The PANI content of the films was found gravimetrically. The PMMA-coated Pt foil electrode was weighed before and after electrolysis. The percent PANI content was calculated from weight differences.

The thickness of the films were determined by a micrometer within a sensitivity of ±0.001 mm.

The electronic apparatuses used were a Bank Electronik LB 75 L potentiostat, a Bank Elektronik VS 72 function generator, and a Karl Kolb Servogor recorder.

The UV-visible absorption spectra measurements were taken on a Shimadzu model 160 A spectrophotometer.

SEM studies of the films coated with gold were performed on a JEOL model JEM-100 CX II microscope.

Conductivities of free-standing PANI/PMMA films were measured by using the standard four- or two-probe method.

The temperature dependence of the electrical conductivity of PANI/PMMA films was measured over a temperature range from 203 to 298 K. The sample was placed in a temperature controlled chamber with a heating rate of 2–3°C/min, and the resistivity of the sample was recorded as temperature varied.

The response of PANI/PMMA films to $NH_3$ gas was determined using a chamber connected with a two way stopcock; the sample was placed in the chamber and fed with $NH_3$ gas for 3 min while its resistance was measured. The two way stopcock was then opened to air (with 60% relative humidity) for 3 min and the resistance values were recorded. The experiment was carried out at 24°C using ammonia gas diluted with nitrogen having a flow rate of 50 mL/min.

## RESULTS AND DISCUSSION

### Cyclic Voltammetry

A typical cyclic voltammogram (CV) recorded during the potentiodynamic polymerization of aniline in sulfuric acid on a bare Pt electrode are shown in Figure 1(a). It is similar to those presented by other authors and discussed in detail in the literature.[22,23] Performing the same experiment with a PMMA-coated Pt working electrode gave very similar CV curves as shown in Figure 1(b).
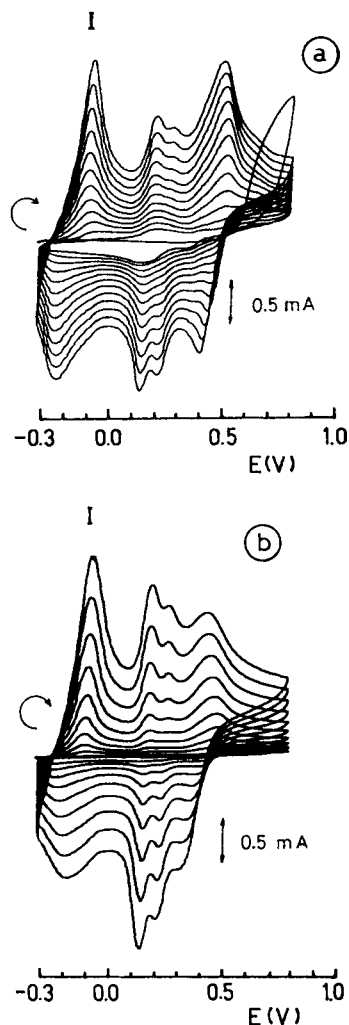
I

0.5 mA

| | | | |
|-|-|-|-|
|-0.3|0.0|0.5|1.0|

E(V)

I

0.5 mA

| | | | |
|-|-|-|-|
|-0.3|0.0|0.5|1.0|

E(V)

**Figure 1**    Multisweep cyclic voltammograms recorded in $0.1M$ aniline $+1.0M$ $H_2SO_4$ by potential sweeping between $-0.3$ and $+0.8$ V at a scan rate of 50 mV/s: (a) on a bare Pt electrode and (b) on a PMMA-coated Pt electrode. Cyclic voltammograms were recorded at every fifth scan for the PMMA-coated Pt electrode.

The anodic peak (peak I) shows the oxidation of PANI deposited on the electrode surface[24] that corresponds to the conversion of amine units to radical cations.

The amount of polymer growth on the electrode surface can be determined by calculating the area under peak I.[25] Figure 1(b) shows the scans recorded at every fifth scan. It can be seen that the anodic current of peak I in Figure 1(b) moderately decreased compared with peak I in Figure 1(a). This observation revealed that the rate of formation of PANI decreases when a PMMA-coated Pt working electrode is used in electrochemical polymerization of aniline.
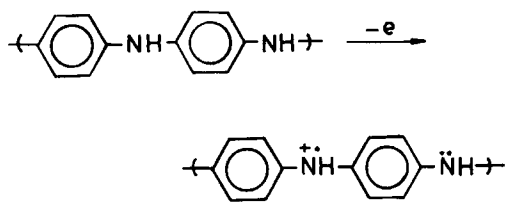
Figure 2(a) shows the first and the 10th CV curves of the aniline solution containing $0.1M$ aniline and $1.0M$ $H_2SO_4$ scanned between $-0.3$ and $+1.4$ V on the bare Pt electrode. The peak observed in the first cycle at $+0.9$ V corresponds to aniline oxidation.[26] When a PMMA-coated electrode was used instead of a bare Pt electrode, the oxidation peak of aniline was not observed [Fig. 2(b)]. In the electrochemical polymerization of aniline on an insulating polymer-coated electrode, aniline and supporting electrolytes can penetrate through the insulating polymer layer onto the Pt electrode surface. Because the PMMA layer exerts a strong limitation on the diffusion rate of the reactants, the intensity of the aniline oxidation peak in Figure 2(a) was not enough for detection purposes on the PMMA-coated electrode [Fig. 2(b)] in our experimental condition. In the consequent cycles, new oxidation peaks appeared indicating that the radical cations generated at the electrode surface undergo further reaction to give oligomer species that are more readily oxidized. And after a few cycles, the intensity of peak I increased (see Figs. 1, 2), an indication of PANI growth.[25]

CV of the PMMA-coated Pt electrode in $1.0M$ $H_2SO_4$ (without aniline) is shown in Figure 2(c). It can be seen that there is no oxidation peak between the $-0.3$ and $+1.4$ V. This observation indicates that the PMMA chosen as an insulating polymer is stable and cannot be electrooxidized in $1.0M$ $H_2SO_4$ aqueous solution within the selected potential range.

The stability of precoated PMMA was also checked with a separate control experiment. For this purpose the PMMA-coated Pt electrode was kept at $+0.8$ V for 30 min in $1.0M$ $H_2SO_4$ containing no aniline. The IR spectrum of the peeled film after the electrolysis was compared with that of original PMMA. There was no significant difference between these two spectra. This also shows that no chemical or electrochemical reaction takes place on the precoated PMMA layer in our reaction conditions.

## Conductivity

The electrochemical polymerization of aniline on the PMMA-coated Pt working electrode gave rise to a green to dark green, uniform, and flexible conducting film that could be easily peeled off from the electrode surface. Observation with the naked eye showed that the resultant conductive film was a homogenous mixture of PANI within PMMA matrix, and could not be separated into two layers by the adhesive tape test.
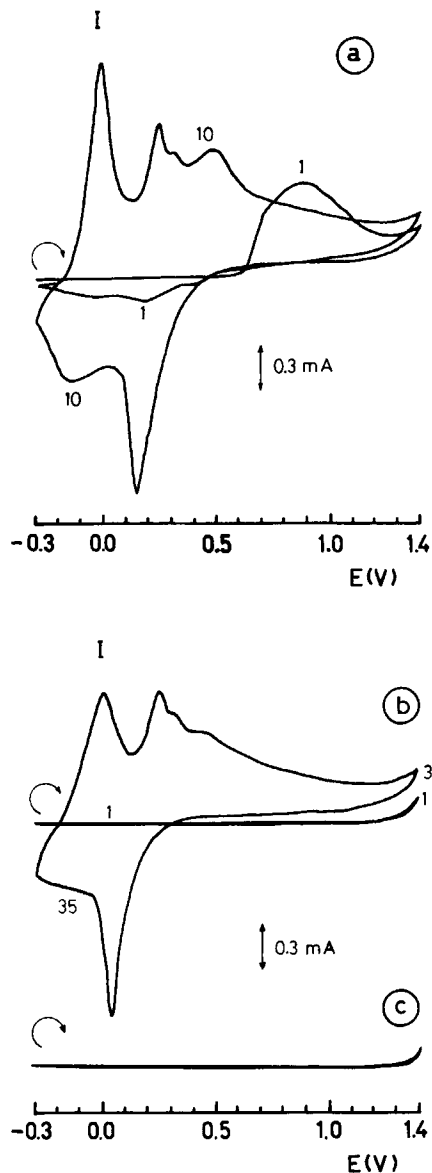
**Structure 1**



**Table I** Dependence of Electrical Conductivity of PANI/PMMA Films on PANI Content and Electrolysis Time

| Electrolysis Time (min) | PANI Content (%) | $\sigma \times 10^3$ (S/cm) |
|---|---|---|
| 3 | 7.3 | 0.3 |
| 7 | 10.0 | 12 |
| 11 | 15.3 | 100 |
| 16 | 21.3 | 110 |
| 21 | 33.3 | 130 |
| 25 | 41.6 | 210 |
| 29 | 55.3 | 190 |
| 35 | 65.6 | 200 |

A few minutes after the initiation of electrochemical polymerization at +0.8 V, the precoated colorless PMMA film began to develop a greenish color, indicating that PANI was synthesized within the PMMA matrix. The PANI content in these films can be controlled by changing the electrolysis time (Table I). As seen in Table I, the conductivity ($\sigma$) of PANI/PMMA films is also directly proportional to the electrolysis time (or weight fraction of PANI in the film).

Figure 3 shows the variation of conductivity with PANI content, found to be $\approx$ 0.2 S/cm with 25% PANI. Further increase in the PANI content did not show an appreciable effect on the conductivity. This implies that above 20 wt % PANI, PANI becomes dominant as far as the conducting mechanism is concerned in the PMMA matrix due to the direct contact of PANI chains.[27]
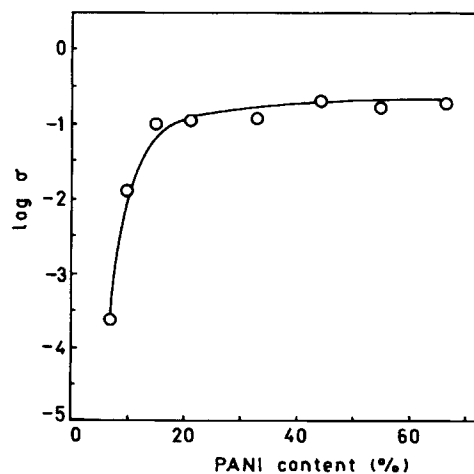


**Figure 2** (a) First and 10th cyclic voltammograms recorded in $0.1M$ aniline $+1.0M$ $H_2SO_4$ on a bare Pt electrode; (b) first and 30th cyclic voltammograms recorded in $0.1M$ aniline $1.0M$ $H_2SO_4$ on a bare Pt electrode; (c) first cyclic voltammogram recorded in $1.0M$ $H_2SO_4$ (without aniline) on a PMMA-coated Pt electrode by potential sweeping between $-0.3$ and $+1.4$ V at a scan rate of 50 mV/s.



**Figure 3** Dependence of electrical conductivity of PANI/PMMA film on the PANI content. The films were prepared in $0.1M$ aniline $+1.0M$ $H_2SO_4$ at $+0.8$ V.
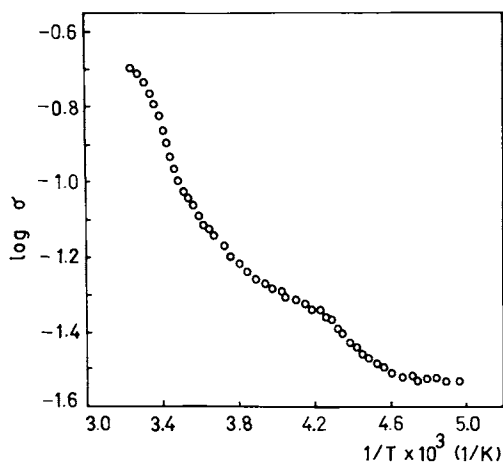
**Figure 4** Temperature dependence of the electrical conductivity of PANI/PMMA film.

The thickness of the precoated PMMA layer on the electrode surface is an important criteria to obtain a free-standing conductive PANI/PMMA film. Our observation showed that only very thin free-standing films could be obtained because of the low penetration of the monomer into the PMMA. The optimum thickness for the precoated PMMA layer was found to be about 10–15 $\mu$m in our experimental conditions. The coating having this thickness can be obtained by dropping 0.8 mL of 10 g/L PMMA solution in chloroform onto each surface of the Pt foil (1.5 cm$^2$) electrode. The thinner coating resulted in the PANI/PMMA films having poor mechanical properties: they could not be peeled off from the electrode surface in a free-standing form.

There have been various models proposed for the electrical conduction mechanisms taking place in specific blends and composites obtained using various conducting and insulating polymers.[28,29] In spite of all these studies, the mechanism of conduction in the polymeric systems is yet to be clarified because it is affected by so many factors, such as dopant type and level, morphology of polymers, temperature, and density.

Nevertheless the dependency of conductivity on temperature for some heterocyclic polymers has been investigated, and conduction was found to be changed with $T^{-1/4}$ or $T^{-1/3}$ according to the following equations[28,29]:

$$\sigma = A \exp(-E_a/kT^{-1/3})$$

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Here $E_a$ is the activation energy, $T$ is the absolute temperature, $A$ is a constant for a given material, and $k$ is the Boltzmann constant.

The change of $\sigma$ with $T^{-1/4}$ or $T^{-1/3}$ implies the presence of a variable-range hopping mechanism for bipolarans operating between different chains in these types of materials.

However, when log $\sigma$ was plotted against $T^{-1/4}$ or $T^{-1/3}$ for PANI/PMMA films in a temperature range of 203–298 K, it yielded a nonlinear curve that showed that the above equations are not valid for conductivity of our polymer films.

Figure 4 shows the log $\sigma$ −1/$T$ plot of PANI/PMMA film within a temperature range of 203–298 K. The conductivity increases with the temperature but does not follow the Arrhenius law. The above observations indicated that the mechanism of conduction in the PANI/PMMA film shows a complicated behavior and is probably affected by two different types of mechanisms. Similar behavior was obtained for nylon 6/polypyrole.[30]

## UV-Visible Spectra

Figure 5 shows UV-visible absorption spectra of electrochemically prepared PANI/PMMA films from 400 to 800 nm. The spectra are directly recorded using free-standing films that have been peeled off the electrode surface.

During the electropolymerization the color of the PANI/PMMA films turned light green and gradually darkened and finally became dark green, depending upon the PANI content. It is clear that the transparency of the resulting films depends on the PANI content in their matrix. Because the visible light cannot pass through the film, the UV-visible ab-
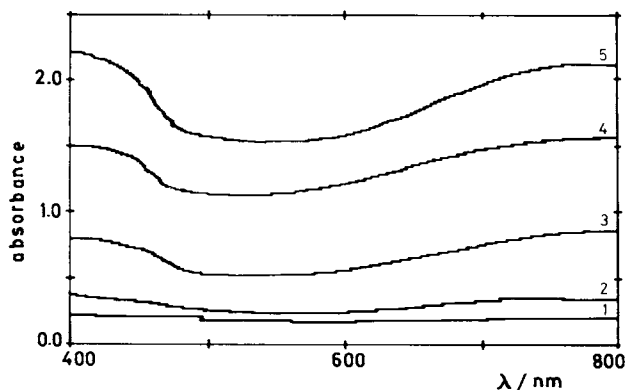


**Figure 5** UV-visible spectra (1) of pure PMMA and PANI/PMMA films containing (2) 7.3%, (3) 10.0%, (4) 15.3%, and (5) 21.3% polyaniline.
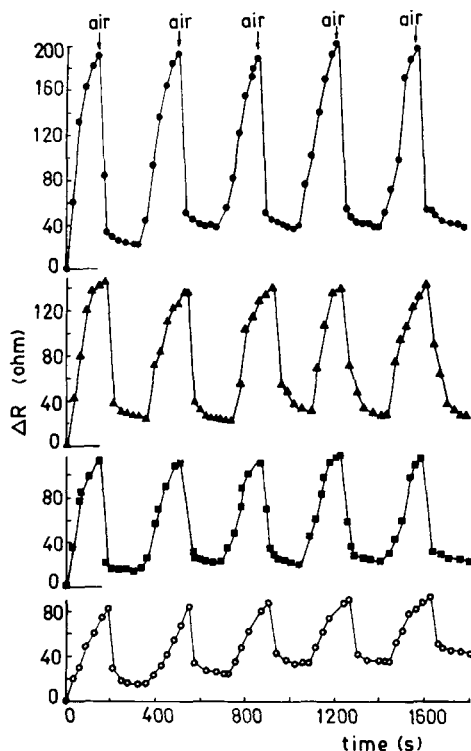
**Figure 6** Resistance changes at 24°C for PANI/PMMA film in $NH_3$ gas. $NH_3$ concentration: (O) 0.01%; (■) 0.1%; (▲) 0.5%; (●) 1%. Flow rate is 50 mL/min.

sorption spectra of films containing over 20% PANI cannot be obtained.

Figure 5 reveals two bands: one broad band about 425 nm was assigned to the emeraldine salt form of PANI; the other broad band from 600 nm upward, results from the free-carrier absorption from the partially filled band in a polaronic metal.[31] We may therefore conclude that the PANI synthesized in the PMMA matrix has essentially the same electronic structure as the pure form of the PANI obtained on an optically transparent electrode.[31,32]

## Response to $NH_3$ Gas

It is known that the resistance of some conducting polymers varies on exposure to certain gases, such as $NH_3$,[33] $NO_2$,[34] and some organic vapors.[35] These conducting polymers give fast and reversible resistance variation response against various gases and vapors. Conducting/insulating polymer blends and composites are superior to pure conducting polymers in respect to processability. These films have great potential to be used in gas sensor devices due to their free-standing ability, flexibility, and other mechanical properties resulting from the insulating polymer.

In this part of the study the response of PANI/PMMA films against $NH_3$ gas was investigated. Figure 6 shows the resistance change of 15% PANI containing PANI/PMMA film at various $NH_3$ concentrations. As seen from Figure 6 by the investigation of each pulse, the resistance of the film exposed to $NH_3$ gas showed an increase; however, when exposed to air its resistance dropped down to background value.

The increase in pulse number does not change the background resistance values of $NH_3$ concentration (1.0–0.1%) significantly. However, the background resistance at 0.01% $NH_3$ concentration tends to increase with the number of pulses.

PANI is knows to be a $p$-type semiconductor. $NH_3$ molecules act as a donor after being adsorbed and form an electric barrier near the surface of the sample. The barrier height increases with the adsorbed gas concentration.[33] This effect is clearly seen in Figure 7. Figure 7 was drawn by overlaying the third pulses obtained for each $NH_3$ concentration in Figure 6.

The reproducible resistance change of PANI/PMMA film with $NH_3$ concentration shows that these films can be used for $NH_3$ detection within a concentration range of 1.0–0.1%.

## SEM

The scanning electron micrographs of pure PMMA and 21.3 and 55.3% PANI-containing PANI/PMMA films are shown in Figure 8. It is clear from the SEM results that the pure PMMA film surface [Fig. 8(A)] has a smooth and relatively homogenous appearance, although there exist a few craters that may have formed during solvent evaporation. However, 21.3% PANI-containing film [Fig. 8(B)] has a rough
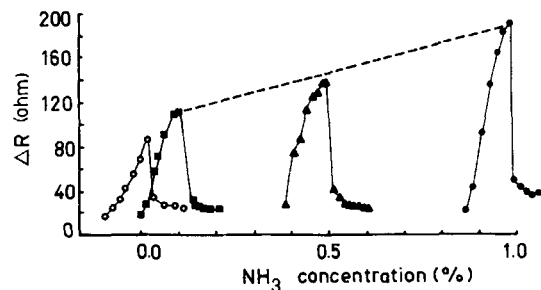


**Figure 7** (---) Dependence of resistance of PANI/PMMA film on $NH_3$ concentration. The curves show the third pulses of Figure 6. Maximum of each curve represents the change of resistance for (O) 0.01%, (■) 0.1%, (▲) 0.5%, and (O) 1% $NH_3$ concentrations.
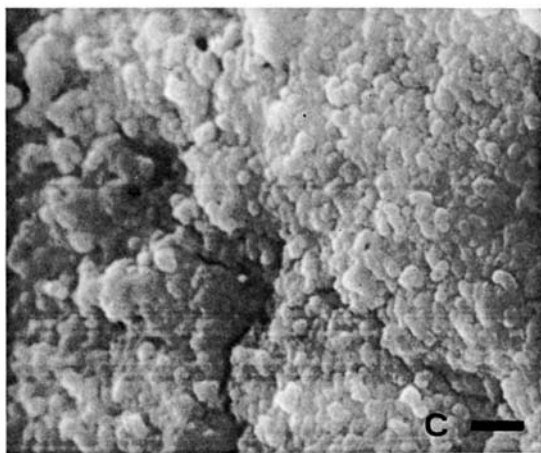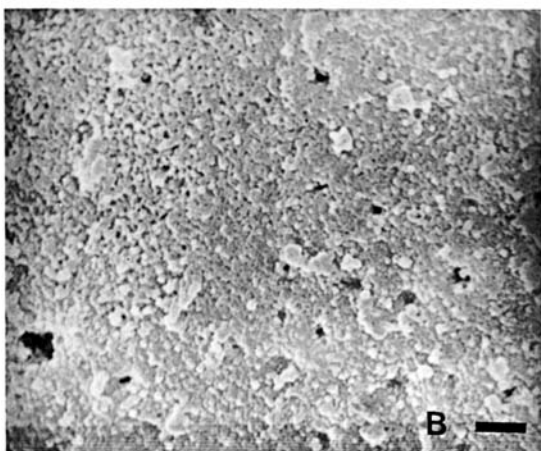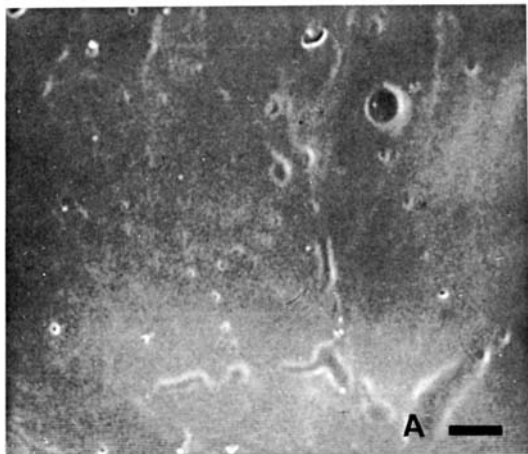
**Figure 8**  SEM micrographs of (A) pure PMMA film, (B) PANI/PMMA film (21.3 wt % PANI), and (C) PANI/PMMA (55.3 wt % PANI) prepared in 0.1$M$ aniline +1.0$M$ H$_2$SO$_4$ at +0.8 V (bar = 5 $\mu$m).

structure consisting of fine globular regions. By increasing the PANI content to 55.3%, the globular morphologies turned to larger globules [Fig. 8(C)].

## CONCLUSION

Our results showed that conductive films can be obtained by the electropolymerization of aniline on Pt electrodes precoated with PMMA. The importance of PANI/PMMA films stems from its combination of good optical properties of PMMA and conductivity of PANI. These films may have potential for applications in various optoelectronic devices.

The optimum thickness of a precoated PMMA layer to obtain high quality conductive film was found to be 10–15 $\mu$m. The films obtained at these conditions were mechanically strong and easily handled in free-standing form. Aniline behaves similarly on a PMMA-coated Pt electrode as it does on a bare Pt surface. However, the polymerization rate of aniline on a PMMA-coated Pt electrode caused a significant decrease due to diffusion hindrance.

The conduction values of PANI/PMMA films increase with an increase of PANI content (up to 25% PANI). This shows that the conductivity of PANI/PMMA film can be easily controlled electrochemically by controlling the PANI content. Response of PANI/PMMA films against NH$_3$ gas revealed that they have good potential to be used as sensors for NH$_3$.

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