# Comparison Between Different Conditions of the Chemical Polymerization of Polyaniline on Top of PET Films

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**ABSTRACT:** Composites produced during the *in situ* chemical polymerization of aniline on top of a poly(ethylene terephthalate) (PET) film, in different conditions, were studied by open-circuit potential (Voc), ultraviolet-visible, and infrared spectroscopy, electrical conductivity measurements, scanning electron microscopy, and atomic force microscopy. The polymerization monitoring by Voc showed a maximum associated with the intermediate pernigraniline oxidation state and a final formation of polyaniline (PANI) in the doped emeraldine salt (ES) form. Furthermore, high electrical conductivity values were obtained for the PANI–ES coating prepared under selected conditions. A globular formation was observed for the doped PANI–ES coating with globules of sizes of the same order and same shape of the PET, demonstrating the influence of the substrate on the coating morphology. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1220–1229, 2001

**Key words:** conducting polymers; polyaniline; composite; coating, morphology

## INTRODUCTION

The mechanical performance and technological potential of conducting polymers can be significantly increased and the final cost usually decreased by the development of blends and composites with high-performance polymers. Several examples are described in the literature[1–4] on the production of blends and composites of polyanilines with polyolefins, polycarbonate, nylons, polyesters, and other polymers. Among them, composites of polyester prepared in the form of fibers, fabrics, or films coated by the chemical deposition of polyaniline (PANI) or polypyrrole have attracted great industrial interest and have been studied by several researchers[4–13] due to their technological potential in applications such as microelectronic devices, electromagnetic interference shielding, and static charge dissipation.

Although it is known that the synthesis conditions used greatly affect the structure, morphology, and final properties of conducting polymers, there is a lack of a systematic study monitoring the PANI deposition on top of poly(ethylene terephthalate) (PET) and comparing different synthesis conditions including some methods recently reported in the literature.[14–17] Therefore, the aim of the present article was to monitor the *in situ* chemical polymerization of aniline on top

**Table I Electrical Conductivity of Polyaniline Deposited on Top of PET Films Under Different Chemical Syntheses' Conditions for a Constant Polymerization Time (2 h)**

| Synthesis Conditions | | Synthesis Conditions No. | Conductivity (S/cm) |
|---|---|---|---|
| Monomer : oxidant, (M : O) | (4 : 1) | | |
| $T_p$ = 0°C | (4 : 1) | 1 | $5.0 \pm 1.0$ |
| Polymerization temperature | | | |
| $T_p$ = 25°C | (4 : 1) | 2 | $9.0 \pm 1.0$ |
| | (4 : 1) + salt | 3 | $(2.0 \pm 1.0) \times 10^{-2}$ |
| | (4 : 1) + benzoic acid | 4 | $(2.0 \pm 1.0) \times 10^{-3}$ |
| | Pretreatment of PET film | | |
| | PET + aniline (4 h, 25°C) | 5 | $4.5 \pm 1.0$ |
| | PET + aniline (0.75 h, 90°C) | 6 | $3.6 \pm 1.0$ |
| | PET + aniline + benzoic acid (4 h, 25°C) | 7 | $(2.0 \pm 1.0) \times 10^{-3}$ |
| | PET + aniline + benzoic acid (0.75 h, 90°C) | 8 | $(1.0 \pm 1.0) \times 10^{-3}$ |
| Vapor oxidation | PET + aniline (4 h) $T_p$ = 30°C | 9 | $<10^{-6}$ |
| M : O (1 : 1) | $T_p$ = 25°C | 10 | $(6.0 \pm 1.0) \times 10^{-1}$ |

$T_p$, polymerization temperature

of PET films and to compare the characteristics of the composites produced under different conditions, by open-circuit potential (Voc), ultraviolet-visible (UV-vis), and infrared spectroscopy, electrical conductivity measurements, scanning electron, and atomic force microscopy (AFM).

## EXPERIMENTAL

### Composite Preparation

Double axially oriented PET films (12 $\mu$m thick), named Terphane 19.10, produced by Rhodia-Ster Filmes Ltda. (Cabo, Brazil) were used as a substrate for the deposition of PANI, after cleaning with acetone. Aniline (Aldrich, São Paulo, Brazil) was used after distillation under reduced pressure. Benzoic acid (Synth, São Paulo, Brazil) and all other chemicals (Merck, São Paulo, Brazil) were used as received.

The deposition of PANI on top of the PET films was made by chemically synthesizing the parent PANI in the presence of a PET film immersed into the polymerization solution, under several conditions, as described in Table I. The first synthesis condition used was a modification of the conventional chemical synthesis reported in the literature,[14,18] in dilute conditions at the temperature of 0°C using aniline in excess and a monomer: oxidant ratio of 4:1. In this case, aniline (4 mL 0.0438 mol) was dissolved in 300 mL of 1.0$M$ HCl

and ammonium peroxydisulfate (2.3 g, 0.0101 mol) in a solution of 200 mL of 1.0$M$ HCl. In all the conditions used, the oxidant solution was added to the monomer solution upon stirring. For the synthesis in the presence of a salt (synthesis condition #3, Table I), reported in the literature to produce high molecular PANI,[14] 3.0$M$ CaCl$_2$ was used in the HCl solution for both the monomer and oxidant solutions. In the synthesis condition #4 (Table I), 20 mg of benzoic acid was added to the monomer solution. When indicated (syntheses conditions #5–9), a pretreatment of the PET with aniline and/or benzoic acid[17] was used as an attempt to diffuse the monomer into the substrate. In the vapor-oxidation synthesis (synthesis condition #9), the aniline-treated PET was exposed only to the vapor of the oxidant solution for 4 h. Another attempt (synthesis condition #10) was to have an equimolar amount of the monomer and oxidant (1:1). The PET/PANI composites produced were washed several times with 1.0$M$ HCl to eliminate residues and then dried for 72 h in a desiccator under a vacuum to obtain PANI in the doped emeraldine salt (ES) oxidation state.

### Characterization

The syntheses were monitored by measuring *in situ* the Voc of the reaction mixture using a saturated calomel electrode (SCE) and a platinum electrode. The UV-vis absorption spectra from the PET/PANI–ES composite were obtained using a

Perkin–Elmer Model Lambda-9 spectrophotometer. Electrical conductivity measurements were made using the four-probe method. Measurements of UV-vis absorbance, conductivity, and thickness as a function of polymerization time were made on different samples placed in the reaction mixture and taken out at the given times. These samples were washed with HCl and dried before the analysis. FTIR spectra were obtained in a Bomem Model MB 102 spectrometer by scratching KBr powder on the surface of the PANI–ES deposited on top of the PET in order to make a pellet of KBr + PANI–ES. Scanning electron microscopy (SEM) was performed on a Zeiss microscope Model DSM 960 operated at 20 kV for samples coated with a thin layer of gold.

AFM measurements were carried out on a Topometrix Discoverer TMX 2000 instrument in the standard contact mode using 200 $\mu$m-long V-shaped cantilevers with a nominal spring constant of about 0.06 N/m and $Si_3N_4$ pyramidal tips integrated onto the underside of the end of the cantilever. The scan rate was 1.25 Hz. The reported AFM images were captured with 300 $\times$ 300 data points. The surface roughness was evaluated using the software of the Topometrix instrument to calculate the average roughness ($Ra$) and root mean square (rms) given by

$$R_a = \frac{1}{N}\sum_i^N |Z_i - \bar{Z}|$$

where $\bar{Z}$ is the average of $Z$; $Z_i$, the height $Z$ at a given location; and $N$, the number of data points (locations) and

$$\text{rms} = {}_{f1}^{f2}\left(\int P(f)df\right)^{1/2}$$

where $P(f)$ is the power spectral density, defined as the square magnitude of the Fourier transform.

## RESULTS AND DISCUSSION

Several syntheses' strategies were tested to compare the characteristics, especially the conductivity, of each PANI coating formed on top of a PET film. A summary of the conditions used and the respective conductivity values obtained are presented in Table I. The first interesting observation is that the conductivity for synthesis condition #2 carried out at room temperature [conductivity ($\sigma$) of 9.0 $\pm$ 1.0 S/cm] is slightly higher than that obtained in the conventional method at 0ºC ($\sigma$ = 5.0 $\pm$ 1.0 S/cm for synthesis condition #1). The conductivity of the latter is consistent with the values reported in the literature for a pressed pellet of the as-synthesized doped PANI powder.[14–18] This is a great advantage, since from the technological point of view, it is much easier and cheaper to prepare the PANI coating at room temperature.

The polymerization using a PET film pretreated with the aniline monomer produced no improvement in the conductivity or adhesion of the PANI coating. The use of a carrier was also tested, since, as reported elsewhere,[17] it favors dye penetration into PET films and could possibly also favor the aniline penetration. To further evaluate the possibility of aniline penetration into PET, higher temperature (90ºC) as well as both higher temperature and use of a carrier were tested, resulting, however, in no further improvement in the adhesion of the PANI to the PET film (evaluated by a conventional tape test). Improvement in adhesion was satisfactorily obtained by thermally treating the samples, as will be discussed later in this article. The use of a carrier was further studied using benzoic acid with HCl into the reaction mixture during the polymerization. Among the polymerization conditions tested, samples produced on four different conditions were selected to be studied in greater detail:

(a) Polymerization using an excess of the monomer; monomer:oxidant (4:1) (synthesis condition #2, Table I);
(b) Polymerization in the presence of a salt; (4:1) + salt (synthesis condition #3, Table I) (similar to the high molecular weight method[14]);
(c) Polymerization in the presence of a carrier (synthesis condition #4, Table I); and
(d) Polymerization using no excess of the monomer; monomer:oxidant ratio 1:1 (synthesis condition #10, Table I).

Figure 1 shows the synthesis monitoring by the Voc as a function of polymerization time for each different polymerization condition described above. It can be observed that in all cases the Voc goes through a maximum between 0.75 and 0.8 V (SCE) in the first stage of polymerization and
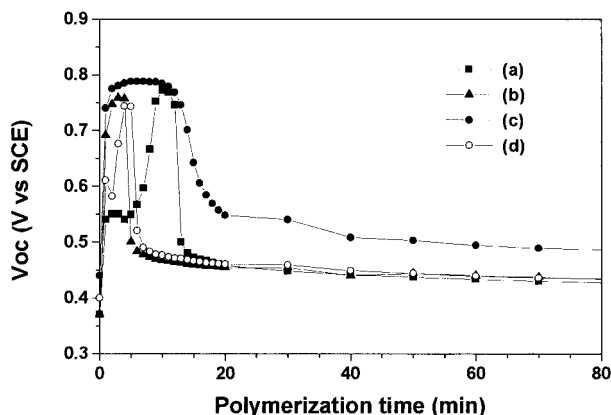
**Figure 1** Voc as a function of polymerization time of PANI–ES deposited on top of PET films under different chemical syntheses conditions: (a) polymerization using excess of monomer (synthesis condition #2, Table I); (b) polymerization using no excess of monomer (synthesis condition #10); (c) polymerization in the presence of a salt (synthesis condition #3); (d) polymerization in the presence of a carrier (synthesis condition #4).

then decreases to a constant value below 0.55 V. Such a peak is associated with the formation of an intermediate, pernigraniline,[19] the fully oxidized PANI state. According to the literature,[19] pernigraniline acts as an oxidizing agent to the remaining aniline monomers, whereas it is itself reduced to the polymer in the half-oxidized emeraldine state, leading to the decay of the Voc. Such decay in the Voc is accompanied by the precipitation of most of the polymer, as reported in the literature[19] and supported by our results of UV-vis spectroscopy and thickness increase (of the PANI–ES coating) detected by AFM versus polymerization time, as will be later presented. The Voc also offers a good indication of the polymerization kinetics, as previously reported.[14,20] When there is monomer in excess, the polymerization has an initial induction period before it initiates [Fig. 1(a)]. By increasing the amount of oxidant relative to the monomer [Fig. 1(b)], the reaction starts earlier and the monomer is consumed also in a shorter period. By adding salt to the media, the propagation step of the polymerization (associated with the slope of the Voc decay) is delayed, as previously reported,[14] leading to a longer maximum range and also to a less steep decay of the Voc potential. This is explained by the Donnan potential effect,[14] in which case the salt screens the charged growing polymer sites, allowing a greater approach of the also positively charged monomer species, leading, consequently, to the

polymerization of a higher molecular weight polymer which usually possesses a molecular weight ($M_w$) two to four times greater than in the conventional method.[14] The synthesis in the presence of the carrier showed an induction period and an extremely atypical short period at the maximum, indicating the lowest polymerization propagation rate and the lowest PANI deposition as evidenced by the UV-vis analysis. It is supposed that such a decrease in the polymer formation was due to the decrease in the formation of the pernigraniline intermediate.

As it has already been mentioned, the UV-vis absorbance spectra (Fig. 2) corroborates the polymerization behavior observed using the Voc monitoring. For a constant deposition time (90 min), the highest amount of PANI was deposited from the polymerization in the presence of salt [Fig. 2(c)], whereas the lowest amount was obtained in the presence of the carrier, in great agreement with the polymerization interpretation given in the Voc analysis described above, where the highest propagation rate was observed for the synthesis carried out in the presence of salt and the lowest for that with benzoic acid. It should be noted that the maxima observed at the UV-vis spectra at 350 and 840 nm, associated, respectively, with $\pi$–$\pi$* and excitonic transitions, and the shoulder at 440 nm are consistent with the literature.[2,21]
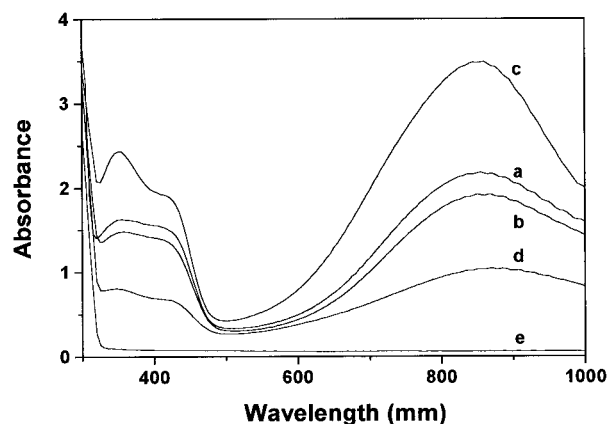


**Figure 2** UV-vis spectra of PANI–ES deposited on top of PET films under different chemical syntheses conditions: (a) polymerization using excess of monomer (synthesis condition #2, Table I); (b) polymerization using no excess of monomer (synthesis condition #10); (c) polymerization in the presence of a salt (synthesis condition #3); (d) polymerization in the presence of a carrier (synthesis condition #4); (e) raw PET film. Samples taken at a polymerization time of 90 min.
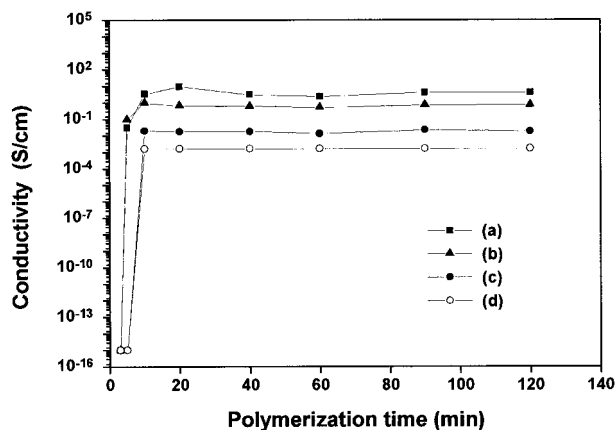
**Figure 3** Electrical conductivity as a function of polymerization time of PANI–ES deposited on top of PET films under different chemical syntheses conditions: (a) polymerization using excess of monomer (synthesis condition #2, Table I); (b) polymerization using no excess of monomer (synthesis condition #10); (c) polymerization in the presence of a salt (synthesis condition #3); (d) polymerization in the presence of a carrier (synthesis condition #4).

The variation of the conductivity during the polymerization, presented in Figure 3, demonstrates that high values of conductivity are already obtained for the very first stage of PANI deposition and they are maintained practically constant until the end of the reaction time. The conductivity values achieved in the present work ($10^{-2}$ to $10^1$ S/cm) are higher than those recently reported in the literature[22] ($10^{-6}$ to $10^{-4}$ S/cm) for PANI/PET composites. It should be mentioned that although the pernigraniline state maximum was detected below about 20 min for all synthesis, depending on the conditions used, the conductivity results of Figure 3 correspond to the polymer in the ES state. That is the case because the Voc was measured *in situ* but the conductivity (the same for the other measurements such as UV-vis) was performed on samples taken out of the solution and washed with aqueous 1$M$ HCl, which promotes reduction of more oxidized PANI forms to the ES state.[19] The highest conductivity values [Fig. 3(a)] were obtained for the synthesis containing the monomer in excess (synthesis condition #2), followed by the synthesis containing an equimolar amount of the monomer–oxidant, and the lowest ones for that in the presence of a salt and for the synthesis using benzoic acid.

The best film, in terms of conductivity as well as of homogeneity of the coating surface, was that obtained by the synthesis using an excess of the monomer (condition #2, Table I). Such film was therefore studied in greater detail. A possible explanation for the good quality of this film is that the presence of the monomer in excess minimizes the occurrence of undesirable side reactions, which contribute to lowering the conductivity, as reported elsewhere.[23] On the other hand, the presence of salt and benzoic acid, used in the other synthesis conditions, seems to contribute to these side reactions, as evidenced by FTIR analysis (Fig. 4). Degradation peaks, associated with less conductive underoxidized species, were observed at 1330 and 1380 cm$^{-1}$ for all synthesis studied except for the synthesis condition #2 which contained an excess of aniline. The other IR bands characteristic of PANI in the emeraldine form[14] at about 1708, 1592, 1502, 1450, 1300, 1240, 1160, and 806 cm$^{-1}$ were present for all films.

SEM analysis also corroborates the better performance of the film prepared with the monomer in excess, since such a film presented a more compact and cohesive structure which contributes better to the conductivity than do those prepared in the presence of salt and without the monomer in excess, as shown in Figure 5. In the latter two cases, a more open and porous morphology was obtained. It should be pointed out that, although a compact morphology was also obtained for the synthesis carried out in the presence of benzoic acid, the lowest conductivity was obtained in this
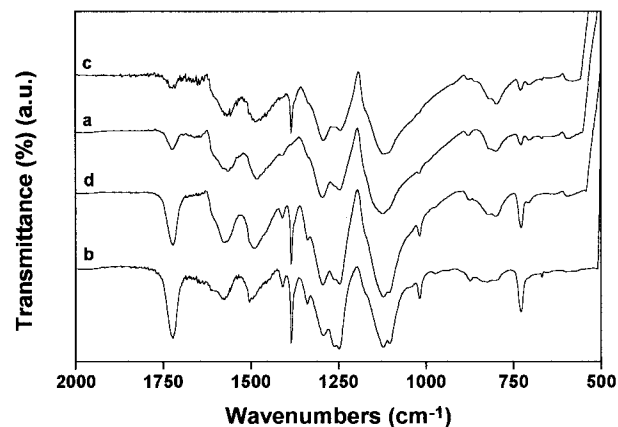


**Figure 4** FTIR spectra of PANI–ES deposited on top of PET films under different chemical syntheses conditions: (a) polymerization using excess of monomer (synthesis condition #2, Table I); (b) polymerization using no excess of monomer (synthesis condition #10); (c) polymerization in the presence of a salt (synthesis condition #3); (d) polymerization in the presence of a carrier (synthesis condition #4).
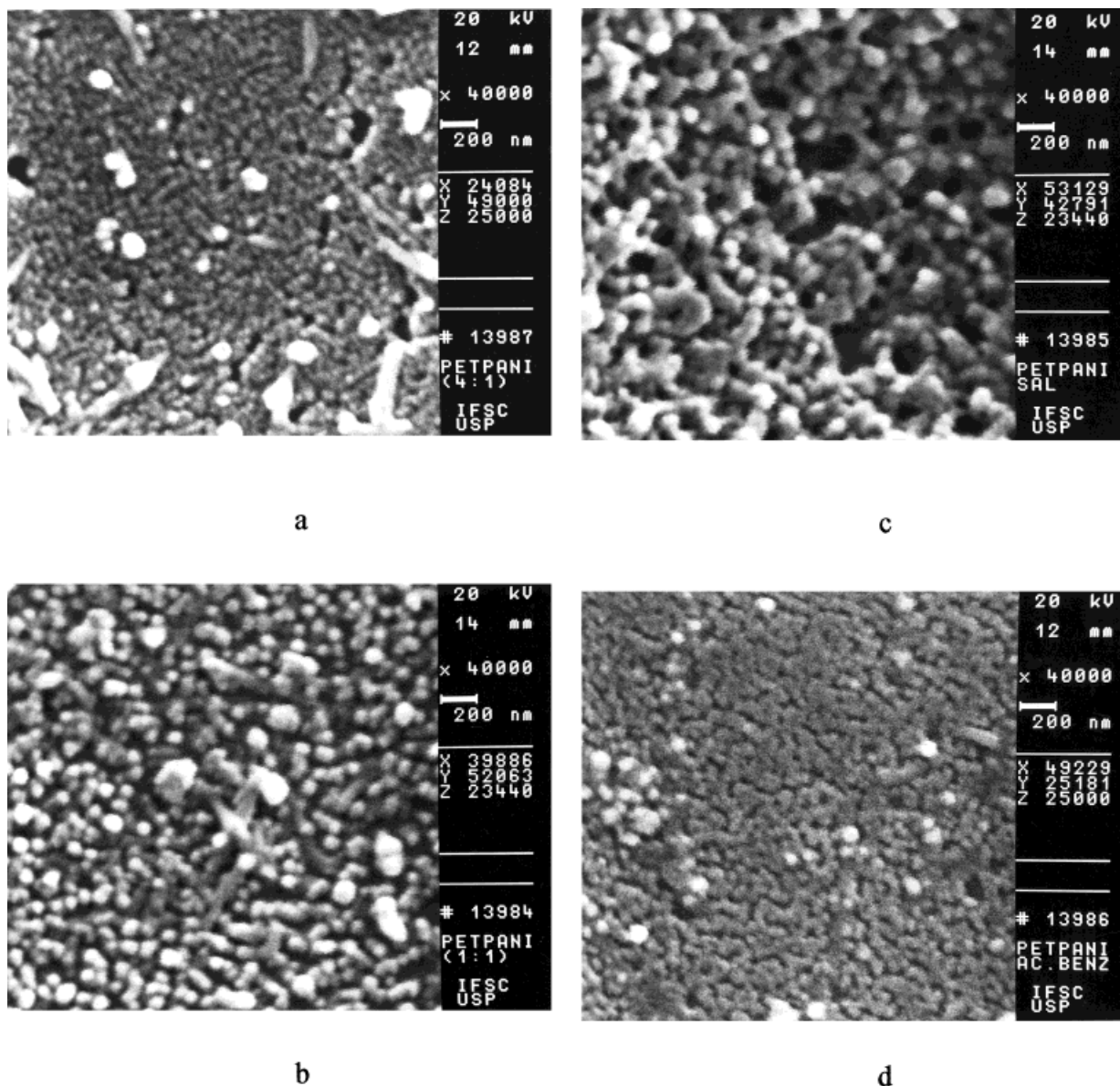
**Figure 5**  Scanning electron micrographs of PANI–ES deposited on top of PET films under different chemical syntheses conditions: (a) polymerization using excess of monomer (synthesis condition #2, Table I); (b) polymerization using no excess of monomer (synthesis condition #10); (c) polymerization in the presence of a salt (synthesis condition #3); (d) polymerization in the presence of a carrier (synthesis condition #4).

case probably due to the drastic changes that have taken place during the synthesis compared to synthesis condition #2, as previously described. It was reported in the literature[16,18,22–23] that the dopant counterion plays a really important role in the doping mechanism and, consequently, in the conductivity of PANIs. Therefore, in the case of the synthesis with benzoic acid, the presence of the counterion might have competed with the Cl⁻

ions in the doping process, leading to the changes observed.

Moreover, adhesion of the PANI layer to the PET film could be greatly increased from 65% (untreated sample) of the area of the PANI coating removed from the PET by a conventional tape test to 0% of the area removed after a thermal treatment at 180ºC for 2 h. The explanation for such improvement is related to crosslinking for-
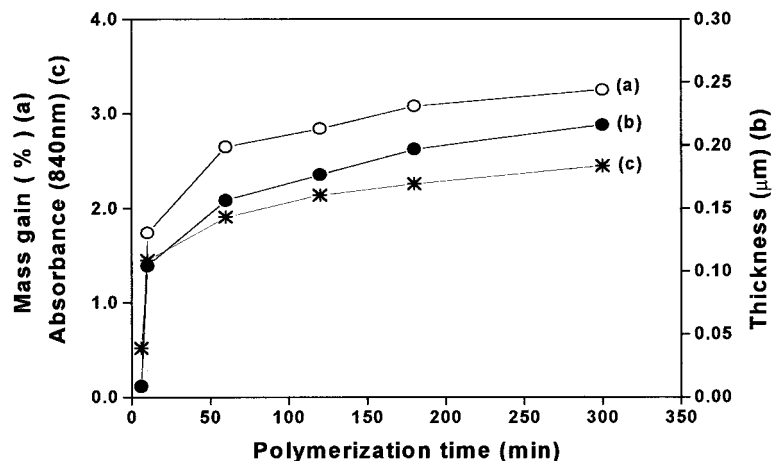
**Figure 6** Results of (a) mass gain, (b) coating thickness, and (c) absorbance of PANI–ES deposited on top of PET films for the polymerization using excess of monomer (synthesis condition #2, Table I).

mation and morphological changes, as will be shown in a detailed work[24] to be published elsewhere. These samples had to be redoped (1.0$M$ HCl, 2 h) to regain a conductivity of $3 \times 10^{-2}$ S/cm, since at this temperature there was HCl evaporation and conductivity loss. The lower value of the conductivity obtained after redoping is consistent with the formation of crosslinking at the imines, which decreases the doping sites, leading to a lower doping and conductivity level.

In Figure 6, the mass gain, UV-vis absorbance, and thickness determined by AFM are plotted as a function of polymerization time. Indeed, one observes, as has been previously mentioned in the present article, that most of the polymer (ca. 80%) is deposited in the first stage of polymerization (first 60 min), although the reaction time lasts for a much longer period (300 min), for further polymer formation and stabilization of the final Voc potential. It should be pointed out that the total amount of polymer deposited on the PET leads to only 3% of gain in its weight. Based on the results of thickness and weight, the density of the PANI–ES coating layer could be estimated to be in the range of 1.25–1.44 g/cm$^3$. These results indicate that conductivity does not change with the thickness of the PANI–ES coating being deposited, since there is practically no increase in conductivity after 10 min of polymerization, but an increase in thickness is observed, for instance, from 0.10 to 0.16 $\mu$m, respectively, for 10 and 60 min of polymerization. Such an observation supports the comparison of the conductivity values done for the different polymerization conditions (Fig. 3).

AFM analysis was used to determine the thickness, as has been presented, and to investigate the morphology of the PANI deposited on top of the PET film. In Figure 7, one observes that the raw PET film has a very smooth topography as compared to the PANI–ES deposited on top of the PET. The AFM image analyses indicate that the PET surface possesses an average height of 1.7 nm as compared to 26.5 nm of the PANI–ES deposited on top of the PET, indicating the rough morphology obtained for the PANI. This is confirmed by the calculated roughness $Ra$ of 0.6 and 13.3 nm and rms of 0.7 and 15.3 nm obtained from Figure 8, respectively, for PET and PANI–ES deposited on top of the PET film. It is important to point out that the morphology of the PANI–ES deposited on top of PET can be distinguished into two patterns: globules and agglomerates. The formation of a similarly globular morphology was also observed in other studies for PANI[25] as well as for polypyrrole[12] deposited in solid substrates. The globules are the more uniform background morphology seen in Figure 8(b), which is partially covered by some agglomerates distributed on its surface, seen in Figure 7(b). Despite these differences in height, roughness, and agglomerate formation, the diameter and shape of the globules found for PET and PANI–ES deposited on top of PET are identical (in the range from 47 to 123 nm for both of them). Their length varies between 85 to 226 nm for the PANI–ES deposited on top of PET, indicating a strong influence of the PET on the formation of PANI–ES globules. Such morphology is in agreement with the SEM analysis
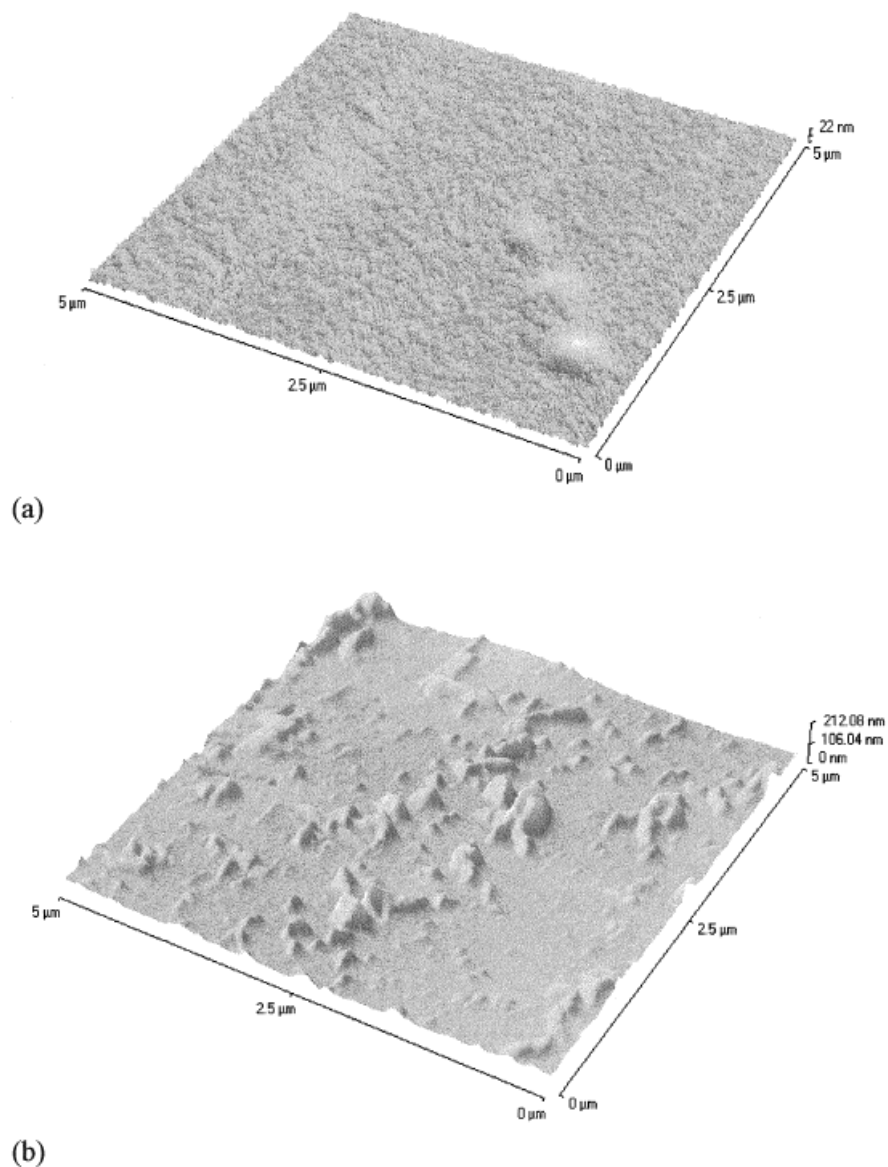
**Figure 7**  AFM images ($5 \times 5$ $\mu$m, contact mode) of (a) raw PET film and (b) PANI–ES deposited on top of PET film for the polymerization using excess of monomer (synthesis condition #2, Table I).

previously presented. It seems that the PET nucleates the growth of the PANI–ES globules, which reveals the surface morphology of this substrate. Concerning the agglomerates, they do not seem to be determined by the substrate, since only very few defects were detected for PET as illustrated in Figure 7(a), which occur in a much lower quantity and are about 10 times smaller (maximum $z$ range of about 22 nm) than for PANI–ES deposited on top of PET [212 nm, Fig. 7(b)]. Apparently, agglomerates are formed in the

second step of the deposition process, after the first PANI layer deposition.

## CONCLUSIONS

The present study has shown the differences in the characteristics of PANI–ES deposited on top of PET films prepared under various conditions. The Voc was a good tool for monitoring the synthesis, showing a maximum associated with the
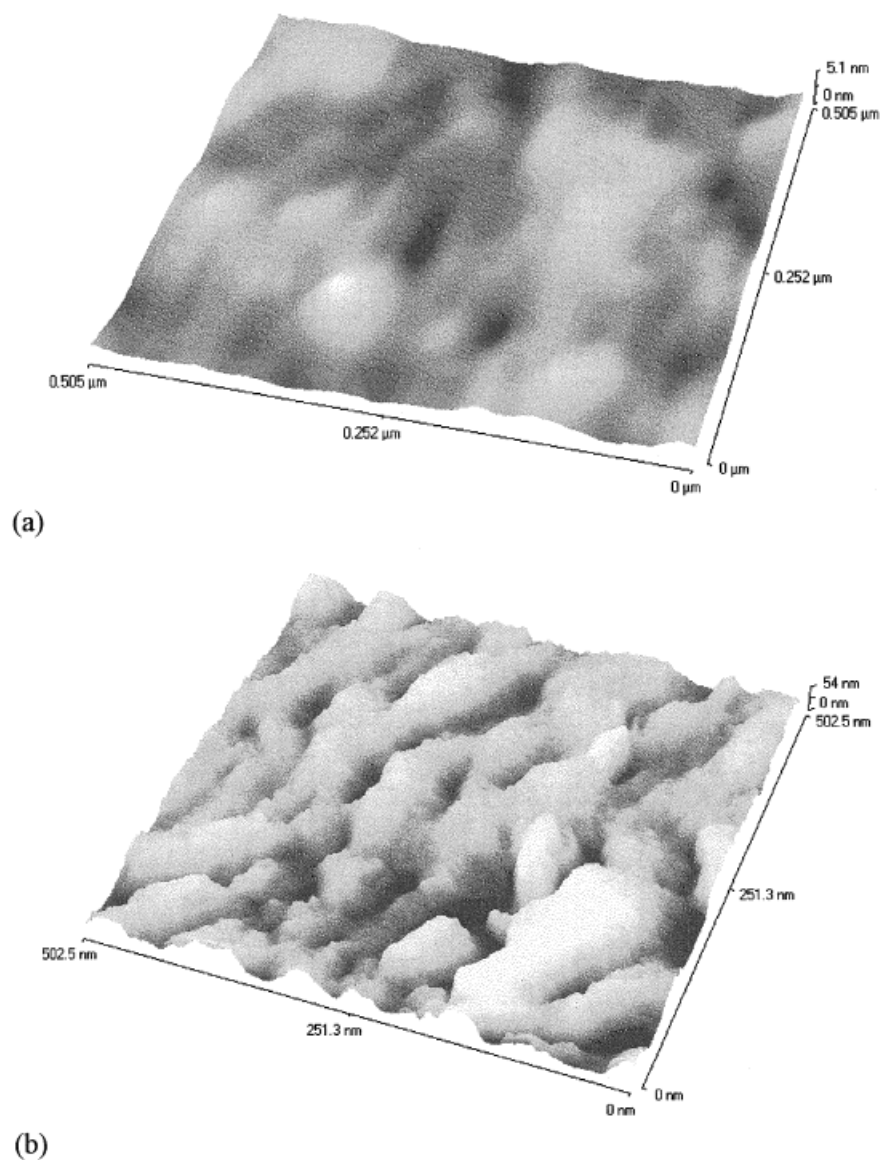
**Figure 8**   AFM images (550 × 500 nm, contact mode) of (a) raw PET film and (b) PANI–ES deposited on top of PET film for the polymerization using excess of monomer (synthesis condition #2, Table I).

intermediate pernigraniline oxidation state and a final formation of PANI in the doped ES form. It was also observed that most of the polymer is deposited in the first stage of polymerization as evidenced by Voc, UV-vis, and thickness analyses. Furthermore, high electrical conductivity values were obtained for the PANI–ES coating prepared under selected conditions. The conductivity of the PANI being deposited presents a great increase in the first stage of polymerization and remains constant with the polymerization time. The best PA-

NI–ES coating was obtained for the synthesis containing aniline in excess (synthesis condition #2, Table I), for which the formation of less conductive species is inhibited and a compact morphology is formed. Moreover, adhesion of the PANI layer to the PET film could be greatly increased after a thermal treatment. AFM analysis showed that the PANI–ES coating has a globular formation with sizes of the same order and same shape of the PET substrate, demonstrating the influence of the substrate on the morphology of the coating.

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