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Photolithography of Polyaniline on Solid Substrates Using Photoassisted Polymerization of Aniline

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The time span of the induction period, present in aniline oxidative polymerization, is reduced by illumination of the solution with UV light. In that way, aniline polymerization rate is increased. Based on such effect a photolithographic process to produce conductive polyaniline patterns is demonstrated.

Keywords Photoassisted; photolithography; polyaniline; polymerization

Introduction

Polyaniline (PANI) is one of the most promising materials for technical applications in batteries, supercapacitors, electrochromic displays, sensors, etc. [1]. In some applications, patterning of conductive polymer layers onto solid substrates is of great interest [2]. Therefore, different patterning schemes of PANI layers have been devised including: contact printing [3], oxidation with photosensitizers [4], photochemical reduction [3], formation of insoluble domains [4] and conventional lithography [5]. We found that chemical lithography of nitrosated polyaniline could be used to produce conductive PANI patterns [6].

The photolithographic patterning of spin coated PANI films is also the basis of a practical process for the production of plastic solid state circuits [7]. In the present communication, we report a photochemical effect on the polymerization of aniline, which could be used to design a photolithographic process to produce PANI.

Experimental

General

Aniline (Merck) was twice distilled under reduced (20 mm Hg) pressure and stored below 4°C under nitrogen. All other reagents were of analytical quality. All

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Address correspondence to César Barbero, Programa de Materialies Avanzados, Universidad Nacional de Rio Cuarto, ruta 8, km 601, Rio Cuarto 5800, Argentina. E-mail: cbarbero@exa.unrc.edu.ar solutions were prepared with Millipore high quality water (18 MΩ). The bulk polymer was synthesized by the established procedure [8]: chemical oxidation of aniline (0.1 M) in acidic (1 M HCl) solution with ammonium persulfate (equimolar with aniline). We performed it in the dark and under illumination for comparison. After the polymerization ends, the polymer is filtered off and deprotonated by stirring in 0.1 M NH_4OH solution during 24 hs. The polymer powder is then washed with water and dried under vacuum for 48 hs. To study its chemical structure, in situ deposited polymer films were produced onto quartz or glass plates under illumination. The plates were removed when the polymer is still in its pernigraniline state and the films were converted to emeraldine salt by immersion (15 min) in oxidant free aniline solution (0.1 M aniline/1 M HCl). Then, the polymer is converted to its emeraldine base form by immersion during 30 min in 0.1 M NH_4OH solution.

Characterization

UV-visible transmission spectra of films on quartz were obtained using a scanning UV-vis spectrophotometer (Shimadzu 1103 P), with a quartz plate as reference. To obtain spectra of films from bulk polymer, they were deposited from a solution (0.5% w/v) of its base form in N-methylpyrrolidone (NMP). The residual NMP was removed by ten protonation-deprotonation cycles [9]. The UV-visible spectra of polymerization solutions were taken using a dispersion spectrophotometer, because diode array spectrophotometers irradiate the sample with UV light, effectively inducing polymerization. To measure the infrared spectrum of the bulk polymer, the powder was dispersed in KBr. In the cases of films, the material used was scrapped off from glass slides. Pellets were then produced using a steel dye under 10.000 ton/cm^2 of pressure. Transmission spectra of the pellets were obtained using a Nicolet Impact 400 FTIR with a resolution of 4 cm^{-1}. The conductivity of the films was measured using the four point probe method [10] on films deposited onto glass. The thickness was estimated from the optical absorption of the film at 400 nm [11].

Potentiometric Monitoring. The potentiometric measurements were made using a high impedance electronic potentiometer (Orion 160) connected with a X-t recorder (radiometer RE61). The sensing electrode was a Pt wire (0.5 mm dia., 1 cm long). The reference electrode was a miniature Ag/AgCl in 3 M KCl (BAS). The cell was a standard 1 cm pathlength quartz cuvette. The solution was kept mixed by use of a small magnetic bar driven by an external magnetic stirrer. The ratio of oxidant ($S_2O_8(NH_4)_2$) to monomer (aniline) is always 1:1. The oxidant was injected by addition 200 μl of solution in water, using a dispensing pipette. Between runs all parts of the cell was cleaned by immersion, for at least 8 hs., in sulfonitric cleaning solution (1:1 mixture of conc. sulfuric and nitric acid) to remove any traces of PANI. The monochromatic illumination was performed using a photolyzer (Photon Technology Industries) that comprises a 150 W Xe lamp and a high irradiance monochromator. The average power in the cell was higher than 10 mW. The temperature was measured with a thermistor based digital thermometer (CheckTemp). It is important to note that traces of PANI could also decrease the span of the induction time; therefore all traces of PANI have to be removed from the reaction vessel to observe the photoeffect.

Photolithography

Photolithographic patterns were obtained by irradiation of cooled, down to 5°C, polymerization solution layers (ca. 2 mm thick) retained on glass slides. The aniline concentration used is 0.05 M to decrease the polymerization rate. In that way, it is easier to wash the plate with the film when the film is deposited only in the exposed region. The irradiation is effected from the back, trough two masks (negative and positive Swiss cross) made with black masking tape, using a broadband UV-lamp (Raytech LS 88). After 10 min, the plates are immersed in oxidant free aniline solution (0.1 M aniline/ 1 M HCl) for 15 min, to convert the pernigraniline film onto the more stable emeraldine film. Then, the films were converted into its emeraldine base form by immersion in 0.1 M NH_4OH solution during 30 min. The polymer film images were then acquired using an Astra 610 P (UMAX) scanner, without size changes.

Results and Discussion

We have found that aniline polymerization seems to occur faster under irradiation with UV light than in the dark. To measure quantitatively the effect, we use potentiometry, which have been used before to monitor aniline polymerization [12]. While the polymerization mechanism of aniline is still under discussion in the literature [13], it is clear that aniline oxidative polymerization presents an induction time [14]. During that period, the concentration of aniline remains nearly unchanged and formation of polymer molecules is not observed. After that period, the concentration of aniline begins to decrease and polymer molecules could be detected. Adding polyaniline or other fine particles to the solution reduces the extent of the induction time. We have found a similar catalytic effect by light irradiation. The comparison between polymerization in absence and presence of light is depicted in Figure 1.

In dashed line is shown the potential monitoring during aniline (0.1 M Aniline/ 1 M $HClO_4$) polymerization, in the dark, in absence of catalysts. The profile is similar to the one reported before [15,13]. The initial potential (ca. 0.51 V) of the aniline solution shifts to 0.72 V upon addition of the oxidant and remains stable for an induction time (A). The solution is colorless at this stage. After this period, the potential shifts to ca. 0.82 V and the solution becomes progressively blue, indicating the beginning of polymer formation. It has been reported [16], that pernigraniline form of PANI is formed at this stage. After a polymerization period (B), the potential decreases slowly signaling the end of polymerization. The green solution contains a polyaniline in its emeraldine salt state. The walls of the cell and any surface present become covered with a green film. The effect of light irradiation is also apparent in Figure 1. The potentiometric profile taken under irradiation with light of $\lambda = 280$ nm (full line), shows a reduced span of the induction period (A). Therefore the total polymerization time decreases. The polymerization period (B), related with the growth of polymer chains, has a quite similar duration in both measurements, suggesting that the effect of light is mainly to promote the initial polymerisation during the induction period. After a first layer of polyaniline is formed, the polymer itself, through the autocatalytic mechanism [7], promotes film growth. The catalytic effect is observed when light of wavelength from 200 to 380 nm is used. Light of higher wavelength (lower energy) seems to produce no effect.

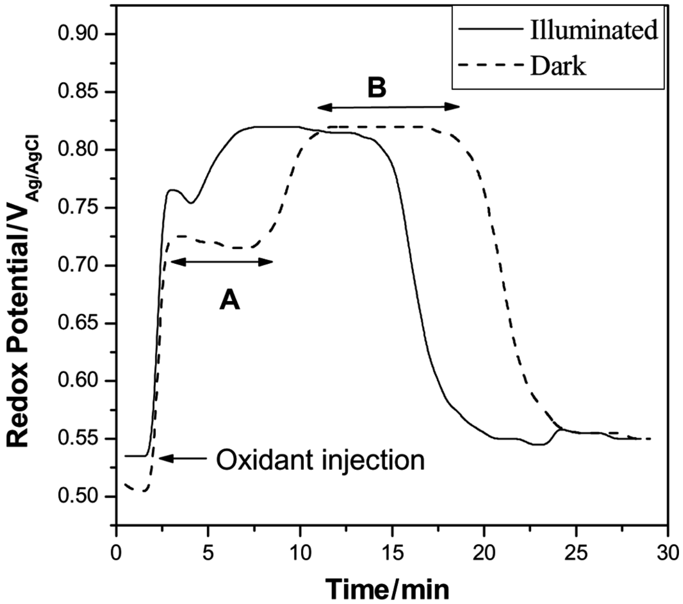

Figure 1. Potentiometric monitoring of aniline polymerization by persulfate, in absence of light (dashed line) and under illumination with light of 280 nm (full line). Solution = 0.1 M aniline/0.1 M $S_2O_8^{2-}$/1 M $HClO_4$. Potentials reported vs Ag/AgCl (sat). T = 15.4°C.

Remains to be known how the irradiation affects the induction time. One possible explanation would be the electronic excitation of dimers or higher oligomers. The radical cation of the dimer (4-aminodiphenylamine) presents an absorption band at 450 nm [17]. However, the UV-visible spectra of the polymerization solution during the induction period (taken in absence of strong illumination) do not show noticeable absorption in that region. Therefore, oligomer excitation could not be responsible of the catalysis. Moreover, if electronic excitation of oligomers would be the origin of rate increase, it would be expected that the polymerization period (B), where such oligomers are present, to be strongly affected which is not the case. While photothermal effects could not be excluded, we irradiated during 30 min oxidant free solution with light of $\lambda = 280$ nm and an increase of only 0.4°C was measured. This result suggests that thermal effects could not explain the observed changes in polymerization rate. Furthermore, illumination with chopped light also produces the effect, suggesting that local temperature increments do not cause the increased rate.

On the other hand, persulfate ion has an optical absorption spectrum with maxima at 215 nm and 308 nm [16]. It has been proved that persulfate could form radical anions thermally, [18], through the reaction:

$$S_2O_8^{2-} + e^- = SO_4^{2-} + SO_4^- \tag{2}$$

This reaction has a high oxidation potential (2.0 V_{NHE}), but proceeds with a slow kinetics and is irreversible [20]. Besides, it is well known that the photolysis of $S_2O_8^{2-}$ gives SO_4^- radical anions, thereby overcoming the kinetic barrier. As SO_4^- radical anions are strong oxidants, they are almost certainly the species responsible to oxidize aniline to radical cation to initiate the polymerization, as it has been suggested [17].

On the basis of the discussion above, it seems that photolyisis of persulfate is the most likely cause of aniline polymerization during the observed photocatalysis. Recently, a similar mechanism was suggested to account for simultaneous chemical and photochemical aniline polymerization, using bromate ion as oxidant, at the air-water interface [19]. In the best of our knowledge, our finding is novel and is important because it sheds some light on the mechanism of aniline polymerization with persulfate.

It is known that it is possible to deposit polyaniline films on transparent substrates by immersion of glass plates in the polymerization solution [20]. Indeed, we succeeded to deposit polymer films under illumination. The polymer films obtained (treated with base and dried) present a FTIR spectra (Fig. 3) in agreement with literature data of emeraldine base [21]. The UV-visible spectra of polymer films (Fig. 4), present bands at 310 y 610 nm, in agreement with the spectrum of polyaniline (emeraldine base) [22] and identical to a film of the bulk polymer, deposited from PANI solution.

Therefore, the observed photocatalytic effect can be used as a new way to deposit PANI on solid substrates. In particular, it is possible to implement a photolithographic deposition process by irradiation of a polymerization solution through a mask.

Figure 2 shows patterns of PANI created on quartz plates by illuminating a polymerization solution (0.05 M aniline/0.05 M $S_2O_8^{2-}$/1 M $HClO_4$) trough a glass slide with a UV broadband lamp. The plates are taken from the solution just after the induction period and quenched in 0.1 M Aniline/1 M HCl solution. In order to do that precisely, the polymerization rate was reduced by decreasing the concentration of reactants in the solution. If the plates are left in the solution during period B, the whole surface is covered.

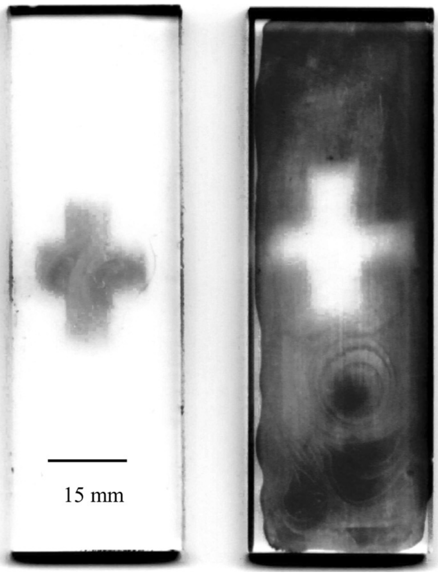

Figure 2. Images formed onto quartz plates by illumination of an aniline polymerization solution (0.05 M aniline/0.05 M $S_2O_8^{2-}$/1 M $HClO_4$) with a broadband UV lamp trough two masks (negative and positive cross).

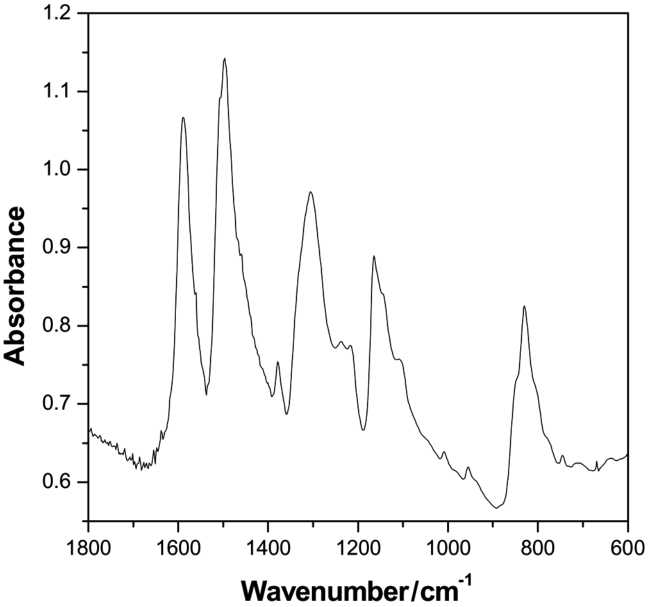

Figure 3. FTIR spectrum of the film (base form) produced by oxidative polymerization under illumination onto glass plates. The polymer is scraped and dispersed in a KBr pellet.

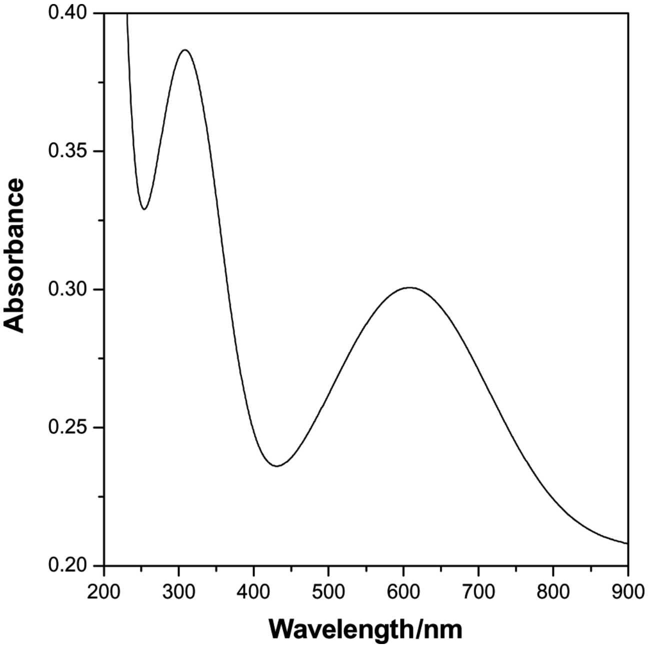

Figure 4. UV-visible spectrum of the film (base form) produced by oxidative polymerization under illumination onto quartz plates.

The mask patterns are clearly marked. Using appropriate masks, positive and negative patterns could be easily created. It is apparent that polymerization occurs faster in the illuminated areas, creating a polyaniline layer, whereas in the non illuminated areas the polymerization does not occur during the immersion of the plates in the solution. The conductivity of the film, protonated in 1 M HCl, was 0.5 S/cm, in the order of that of solid PANI [23]. The UV-visible and FTIR spectra of the covered part of the patterns are identical to that of PANI, suggesting that the structure and electronic properties are the same.

Conclusions

It has been shown that the time span of the induction period, present in aniline oxidative polymerization, is reduced by illumination of the solution with UV light. In that way, aniline polymerization rate is increased. Based on such effect, a photolithographic process to produce conductive polyaniline patterns is demonstrated. The method could be used to produce patterns of PANI which could be used as sensors [24]. It could also be combined with nanopatterning methods [25] to produce hierarchical surfaces.

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