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Photoinduced Doping and Photolithography of Methyl-Substituted Polyaniline

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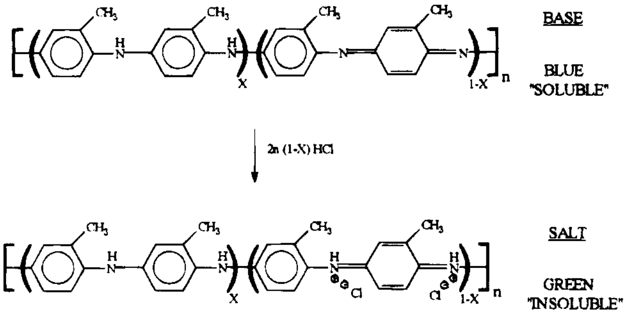
The soluble base form of methyl-substituted polyaniline, poly(*o*-toluidine) (POT), can be converted to the insoluble and electrically conductive salt form upon doping with Bronsted acids such as hydrochloric acid (HCl). With an aim of making submicron features in an intrinsically conductive polymer, we investigated the doping of thin films of POT using a nonionic photo acid generator (PAG) which produces sulfonic acid when irradiated with ultraviolet (UV) light. Although only a marginal increase in conductivity was observed in the photodoped POT films made thus far, the material exhibited the insolubility that is characteristic of the salt form of POT. By using 248 nm UV radiation, 1 μm wide lines and spaces have been delineated in PAG-containing POT films. The conductivity of photodoped films can be increased further by exposure to HCl. Changes in the UV−visible and infrared spectra of POT upon photodoping are identical to those observed after doping with HCl. Infrared spectroscopy also suggests that partial photodoping is caused by only partial decomposition of the PAG in the system.

Introduction

While reports about polyanilines have been found in the literature dating back to the late 19th century[1], recent investigations[2] of this class of polymers have been sparked by the observation of their relatively high electronic conductivities. Polyaniline (H instead of CH_3 in Scheme 1) is usually synthesized in the emeraldine form ($x = 0.5$). Like many other conductive polymers, it is relatively insoluble in organic solvents. Relatively soluble forms have been synthesized by substituting alkyl groups for hydrogen in the ortho or meta positions of the benzyl and quinoidal rings.[3] One such soluble form where the ortho position contains a methyl group (Scheme 1) is poly(*o*-toluidine) (POT), the polymer of interest in this study. Other forms of polyaniline, where the substituents reside on the nitrogen instead of the ring carbon, have also been synthesized.[4]

The electrical conductivity of the polyaniline class of polymers depends not only on the level of oxidation but also on the degree to which they have been protonated. This protonation (or doping) is believed to take place at the imine nitrogens[2] and is also shown in Scheme 1 for POT. The undoped, insulating polymer is referred to as the base form and the doped, conductive polymer is called the *salt* form. Commonly used proton donors include hydrogen chloride (HCl), hydrochloric acid and sulfuric acid. In most polyaniline systems the solubility of the base form is much better than that of the salt form. However, a number of exceptions have been discovered recently.[5]

Scheme 1



The ease with which polyanilines are synthesized and their relative stability have made them attractive materials for several recent applications. These include electroluminescent displays,[6] field-effect transistors,[7] electrochromic displays,[8] and electrode materials[9] for batteries. For many of these applications it is essential that the conductive polymer be photodefinable so it can be patterned on specific substrates. Several materials and processes are available for microlithography using nonconductive polymers.[10] One approach to making lithographic materials based on conductive polymers is to incorporate cross-linkable groups either within the polymers or as a second component. Dao et al.[11] have copolymerized aniline with *N*-allylaniline to make a

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soluble copolymer. They suggest that exposing the material to UV or electron-beam radiation should cross-link the allyl groups, hence making it insoluble and providing lithographic properties. In another study,[12] poly(3-octylthiophene) was treated with *N*-hydroxysuccinimide-functionalized perfluorophenyl azide using electron-beam or UV radiation. The azide is believed to form a reactive nitrene which then inserts itself into the octyl chain of the polymer to form an insoluble product. Micron-sized patterns have been generated using electron-beam exposure.

A second approach, suggested by Bargon et al.,[13] involves patterning a poly(vinyl chloride) film containing ferric chloride ($FeCl_3$) and then allowing the $FeCl_3$ to oxidatively polymerize pyrrole vapor into electrically conductive polypyrrole in the patterned regions. In this case, the conductive material is a composite of polypyrrole and PVC.

A third technique, which is particularly suited to polyanilines, is to start with a mixture of a photoacid generator and the base form of the polyaniline. Upon irradiation, the PAG produces a Bronsted acid which can then protonate the polyaniline to form the conductive salt form. If the solubility of the base form is significantly different from that of the salt form it should be possible to use a selective solvent to pattern the polymer. Angelopoulos et al.[14] have used triphenylsulfonium hexafluoroarsenate salt, an ionic photoacid generator, to dope polyaniline films cast from *N*-methylpyrrolidinone by exposing the system to 240 nm wavelength ultraviolet (UV) or electron-beam radiation. Conductivities of the order 0.1 S/cm and the generation of patterns using electron-beam have been demonstrated.

This paper describes a method to pattern poly(*o*-toluidine) (POT), methyl-substituted polyaniline, using nitrobenzyl sulfonate esters, nonionic photoacid generators (PAGs). POT was chosen because in its base form it is known to be quite soluble in a number of common organic solvents and is hence relatively easier to process and characterize than polyaniline.[3] Therefore, instead of a basic solvent like NMP (the best known organic solvent for polyaniline), nonbasic ones which do not hinder the photoacid generating process can be used. In addition, the photoacid generator used is metal-free and nonionic and can generate the acid without abstracting protons from the surrounding lattice. Patterns generated by this technique may be used as electrodes in flat-panel displays and also in applications which require features with large differences in electrical conductivities or dielectric constants from their surroundings, such as anisotropic interconnections and optical memory storage devices.

Experimental Section

Materials. POT was synthesized by the oxidation of *o*-toluidine by ammonium persulfate in an acidic medium. About 10.7 g of *o*-toluidine was dissolved in 300 mL of 1 M HCl.[3] The solution was placed in an ice/water bath and cooled; a few grains of ferrous sulfate were added to it as a catalyst. A solution of ammonium sulfate (4.6 g in 100 mL of 1 M HCl) was cooled in an ice/water bath and added dropwise to the *o*-toluidine solution over a period of about 10 min with vigorous stirring. As the polymerization proceeded, the solution turned green and the salt form of POT (POT-S) began to precipitate. After all the ammonium persulfate had been added, the mixture was cooled in a refrigerator for 2 h. It was then filtered using a Buchner funnel, washed with about 300 mL of 1 M HCl and dried in a vacuum oven at room temperature for about 48 h. This dried conducting salt form of POT was then stirred for 48 h in an aqueous solution of 0.1 M ammonium hydroxide (NH_4OH, 100 mL for every gram of solid) in order to convert it to the insulating base form (POT-B). NH_4OH (1 M) was added to the suspension to maintain a pH of around 10. The base form was then filtered using a Buchner funnel, washed with a 1:1 mixture of methanol and 0.2 M NH_4OH and allowed to dry in a vacuum oven for 48 h.

The PAG that was used was one of a series of 2-nitrobenzylsulfonate esters that was synthesized by Houlihan et al. at AT&T Bell Laboratories.[15] Upon UV irradiation the PAG is known to undergo a photochemically induced intramolecular rearrangement which generates sulfonic acid. The acid was photogenerated by exposing the PAG to a UV light source operating either at 254 or at 248 nm.

Sample Preparation and Doping. Thin blue films of POT (thicknesses ranging from 0.1 to 1 μm), with or without PAG, were formed by spin-casting or just solvent-casting from methyl ethyl ketone (MEK) or chloroform solutions. POT films that were spun cast from chloroform solutions were dried before exposure to UV since residual chloroform could cause some doping of the POT upon exposure. The solutions were made by stirring 0.2 g of POT in 20 mL of solvent overnight and then filtering through a 0.5 μm filter. The POT + PAG solution was made by dissolving the required amount of PAG into the filtered POT solution. The POT:PAG mole ratios referred to in the following text correspond to the ratio of moles of PAG to that of the *o*-toluidine repeat units in the POT. Films of POT + PAG were doped by exposing to UV radiation either from a UVGL-58 Mineralight lamp operating at 254 nm or from an excimer laser operating at 248 nm. Radiation dosage for the 254 nm source was measured by a UVX-25 Radiometer.

Characterizing. UV–visible spectroscopy was performed on a Varian Cary 4 UV–visible spectrophotometer. Samples were made by spin-casting from solution onto quartz substrates. Film thicknesses were measured using a Dektak Model 3030ST. Infrared spectra were obtained on a BIORAD Digilab FTS-60 FTIR spectrometer. IR samples were made by solvent-casting onto silicon substrates. Conductivity measurements were carried out using a Quad Tech 1865 Megohmmeter.

Preliminary evaluation of the performance of the POT–PAG system as a photoresist was carried out by exposure to 248 nm UV radiation on a GCA Laserstep deep-UV exposure tool. Patterns were examined by a Zeiss Axiophot photomicroscope or a JEOL scanning electron microscope.

Results and Discussion

The UV–visible spectra of a POT film (thickness ~ 0.3 μm) before (A) and after (B) exposure to HCl are shown in Figure 1. The band with a maximum around 600 nm (Figure 1A) has been assigned to an intermolecular and/or intramolecular charge-transfer process from the benzenoid to the quinoid ring,[16] leading to the formation of a molecular exciton. The other absorption band in the spectrum of the base has a maximum at 300 nm and is due to a $\pi-\pi^*$ transition.[17] With

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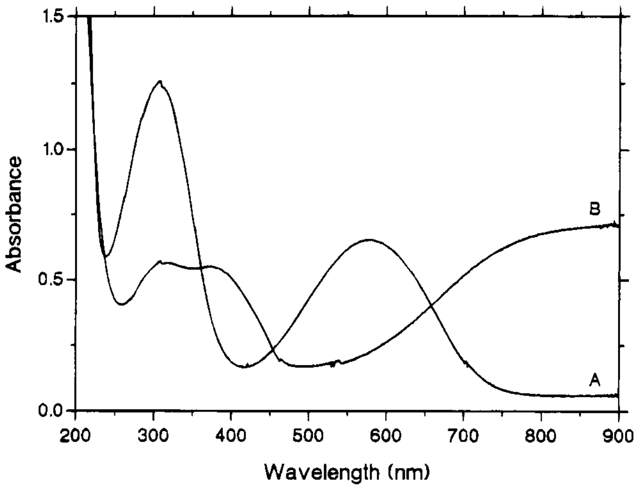

Figure 1. UV–visible spectra of (a) poly(*o*-toluidine) base form and (b) poly(*o*-toluidine) salt form. The salt form was obtained by exposing the base to hydrochloric acid.

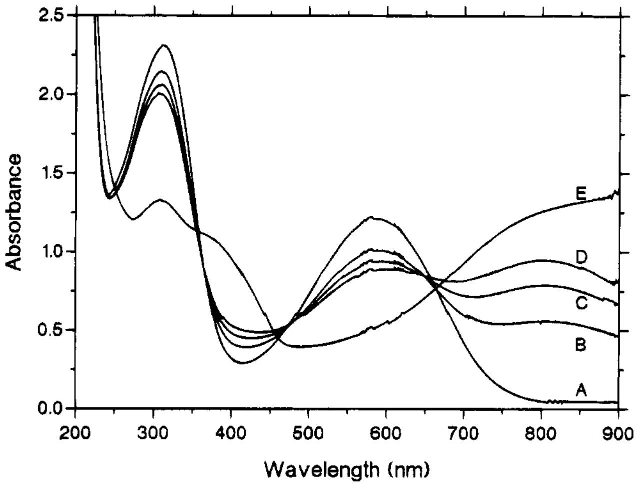

Figure 2. UV–visible spectra of a film of poly(*o*-toluidine) with photoacid generator. The four spectra correspond to the sample after exposure to (A) 0, (B) 300, (c) 900, and (D) 1800 mJ/cm^2 of 254 nm UV radiation. Spectrum (E) corresponds to sample (D) after exposure to hydrochloric acid.

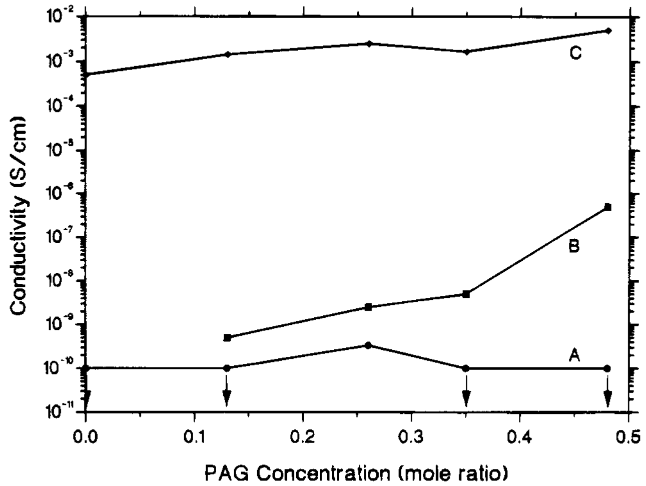

Figure 3. Conductivities of various concentrations of POT–PAG mixtures: (A) as-cast samples, (B) after treatment with UV 1000 mJ/cm^2 of 254 nm UV radiation, and (C) after exposure to hydrochloric acid vapor.

exposure to HCl, the band centered at around 600 nm nearly disappears while the band at around 300 nm shows a significant reduction in intensity. The disappearance of the former suggests the absence of the exciton in the polaron lattice that is formed upon doping.[17] The decrease in the absorption of the latter suggests that the number of species undergoing the $\pi-\pi^*$ transition has decreased. Accompanying these changes two new bands are visible, one centered around 800 nm and the other around 400 nm. These bands have been assigned to transitions from the highest and the second highest valence bands to the polaron band situated in the middle of the bandgap.[17]

Figure 2 shows the changes that take place in the spectrum of the POT–PAG film (thickness ~0.6 μm) upon exposure to UV radiation at 254 nm. The four different spectra represent four different exposure doses for the same sample (see Figure 2 for exposure doses). The first spectrum (Figure 2A) was obtained prior to any UV exposure and shows features similar to Figure 1A. With increasing UV exposure the spectrum registers changes analogous to those seen upon exposure of POT to HCL (Figure 2A-D). There is a decrease in the intensity of the $\pi-\pi^*$ transition band. The intensity of the band assigned to the charge-transfer process (at around 600 nm) decreases with increased exposure to UV radiation, suggesting the possible disappearance of either the quinoid or benzenoid group. Finally, two new bands become visible, one at around 800 nm and the other at around 400 nm, suggesting the formation of mid gap states in the material.[17]

Comparing Figure 1A with Figure 2D we find that although in both cases the $\pi-\pi^*$ absorption intensity has decreased, the decrease is much less pronounced in the photodoped case, suggesting that the photoinduced doping process is incomplete. The same argument can explain why the peak at 400 nm, attributed to a transition into the polaron band, is more intense in HCl-doped POT than in the photodoped POT. The doping process can be pushed much further by exposing the photodoped samples to HCl vapor. This process is illustrated in Figure 2E, which shows the UV spectrum of a photodoped sample after a 5 min exposure to HCl (the spectrum of the photodoped sample before exposure to HCl is as shown in Figure 2D). Further reduction in the intensity of the $\pi-\pi^*$ transition band and increase in the intensity of the 400 nm polaron transition band are seen after exposure to HCl. Accompanying these changes is a slight increase in the intensity of the 800 nm polaron transition band.

Figure 3 shows the conductivities for POT films with different POT–PAG mole ratios. The as-cast samples exhibited very low conductivities, typically less than 10^{-9} S/cm (curve A). Samples that were photodoped with photoacid produced by exposure to 1000 mJ/cm^2 of 254 nm UV radiation showed only a slight increase in conductivity, giving values between 10^{-9} and 10^{-7} S/cm (curve B). This small increase is consistent with the partial doping of the POT that was suggested by UV–visible spectroscopy and occurs either because of incomplete decomposition of the photoacid generator or due to the consumption of the photogenerated acid elsewhere in the system. Incomplete decomposition may be due to significant absorption by the POT in the 254 nm region of the UV spectrum (Figure 1A).[16b] As is evident from curve B, exposure of samples containing a larger amount of PAG yields films with slightly higher

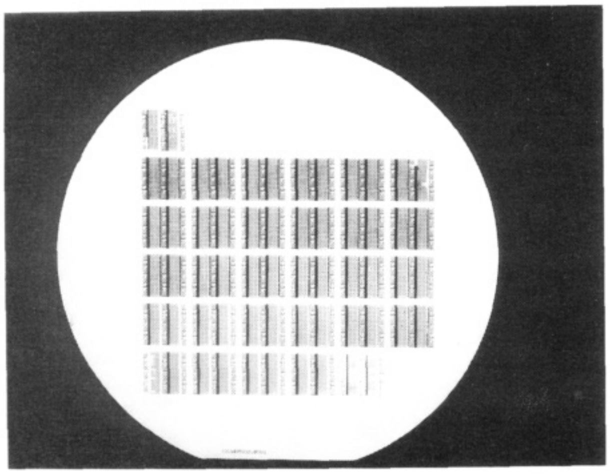

Figure 4. Patterns of POT on a 5 in. silicon wafer. Exposure doses for the dies ranged from 500 mJ/cm^2 to 3000 mJ/cm^2 at 248 nm.

conductivities. However at mole ratios ≥0.35, the PAG in the POT−PAG mixture tended to form macrophases and the resulting films were inhomogenous. The maximum mole ratio of 0.5 was chosen because it is the composition at which complete protonation of the imine nitrogens (Scheme 1) is expected to take place, assuming complete decomposition of the PAG. Upon exposing the photodoped samples to HCl vapor a significant increase in conductivities (curve C) was observed. This is in agreement with the trend shown by the UV spectra. Typically conductivity values for these films ranged from 10^{-4} to 10^{-3} S/cm. Typical literature values for the conductivity of POT are in the 10^{-2} S/cm regime.[3] The lower conductivity seen in our HCl-doped samples may be because our samples are vapor doped instead of doped with HCl solution or due to synthesis conditions.

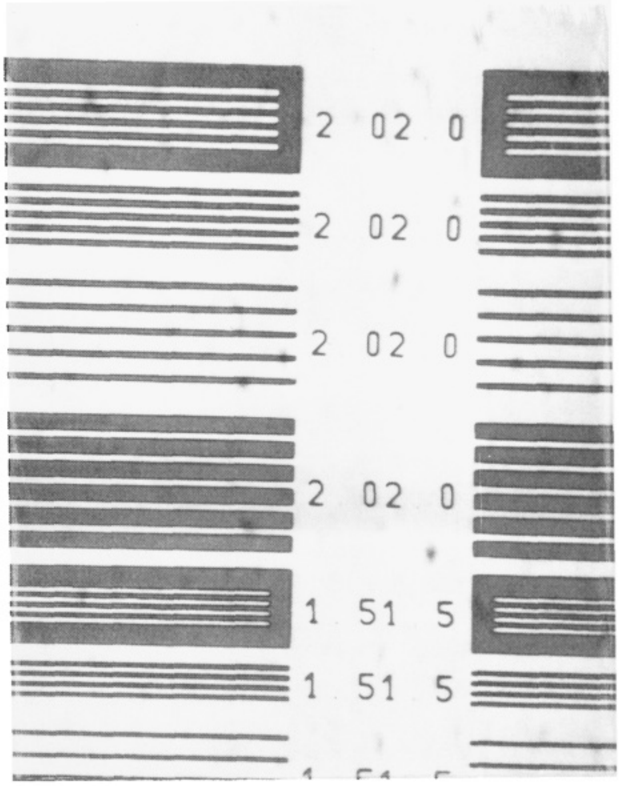

Figure 5. Optical photomicrographs showing 1.5 and 2 μm wide features made in a POT−PAG photoresist system.

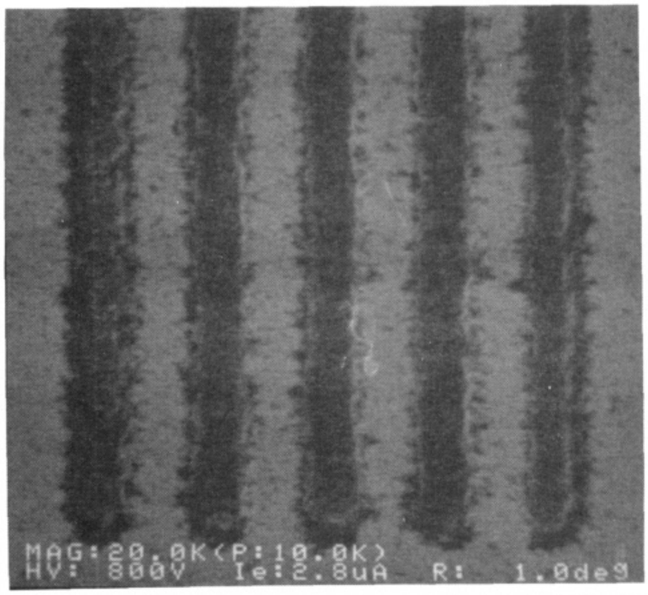

Figure 6. Scanning electron micrograph showing 0.8 μm features made in a POT−PAG photoresist system.

Although the photoinduced doping by itself was not sufficient to raise the conductivity of POT significantly, it created a large enough difference in solubility to differentiate the doped and undoped regions. Such a difference in solubility created by irradiation is essential to photoresist materials. Figure 4 shows a 5 in. silicon wafer with POT patterns. These patterns were produced by irradiating a spun-cast film of POT−PAG (mole ratio 0.25) through a projection mask and subsequently developing it with chloroform. Each square region (called a die) represents an area which was exposed to a specific amount of 248 nm UV radiation from an excimer laser. The lowest dose that was used was 500 mJ/cm^2 (bottom right) and an increment of 100 mJ/cm^2 was used for each successive die (moving in a zigzag fashion when hopping up from row to row). The exposure for the last die was aborted prematurely, this die is hence to be ignored for the purposes of this discussion. The very first die is not visible since it was washed away by the developer and suggesting that the sensitivity of the POT−PAG system is greater than 500 mJ/cm^2. In fact, clear lithographic features are visible only at patterns generated close to or above 1500 mJ/cm^2. These features become visible when the contents of a die are viewed through an optical microscope. One such set of features is shown in Figure 5 and demonstrates the ability of the POT system to delineate 1.5 and 2 μm lines and spaces. Figure 6 is a scanning electron micrograph of 0.8 μm features and shows that some optimization in the material or the process may be required in order to sharpen them.

Some of the changes that occur in the structure of the POT during doping can be monitored by IR spectroscopy. Of particular interest is the region between 1400 and 1700 cm^{-1}, shown in Figure 7A for the base form of POT. Two peaks are visible: the first, at 1592 cm^{-1}, is assigned mainly to the stretching of the C=N group in the quinoid and the other, at 1492 cm^{-1}, is assigned mainly to the C=C stretch in the benzenoid.[18] Upon

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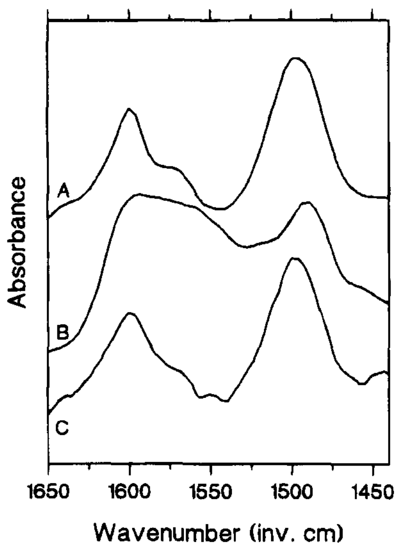


Figure 7. Infrared spectra of the C=N stretch region of poly(*o*-toluidine) without photoacid generator: (A) base form, (B) salt form obtained after doping the base form with hydrochloric acid, and (C) base form obtained after exposing the salt form to ammonia vapor.

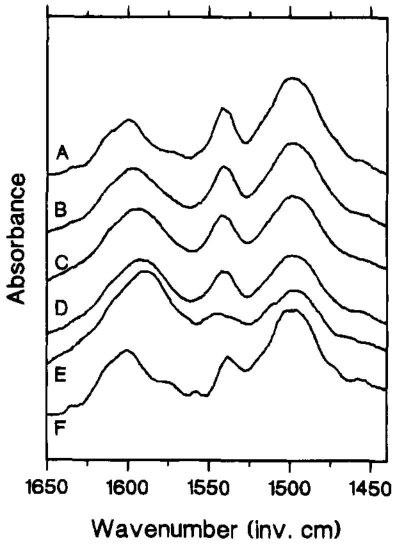
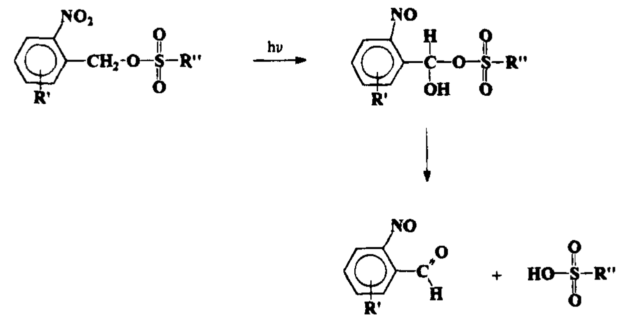


Figure 8. Infrared spectra of the C=N stretch region of poly(*o*-toluidine) with photoacid generator. Exposure times: (A) 0, (B) 300, (C) 900 (D) 1800, and (E) 27000 mJ/cm^2 of 254 nm UV radiation. Spectrum (F) was obtained after subsequent exposure to ammonia vapor.

Scheme 2



exposure to HCl the intensity of the first peak, relative to the second, increases (Figure 7B). This suggests that the salt form of POT has a more quinoidal structure than the base form. Alternatively, symmetry changes in the POT molecule upon protonation could lead to the change in relative intensities. Infrared-attenuated total reflection studies of polyaniline undergoing electrochemical doping have suggested that the metallic (salt) form of polyaniline has a more quinoidal character than the nonmetallic (base) form.[19] Furthermore, an increase in the quinoidal character has also been seen when polyaniline is doped with iodine.[18] This is probably due to a different phenomenon, however, since upon treatment with ammonia the transformation could not be reversed. In the present system the change in intensities of the two peaks upon doping could be reversed by undoping with ammonia vapors. Figure 7C shows the IR spectrum after the HCl-doped sample was exposed to ammonia vapor for 10 min. The original ratio of intensities is retrieved.

Figure 8A shows a partial infrared spectrum for the POT–PAG system. The peak at 1540 cm^{-1} is due to the antisymmetric stretching of the NO_2 group in the PAG molecule. The IR spectra of this sample collected after different UV exposure times are shown in Figures 8B–E. With increase in exposure to UV the NO_2 peak gradually reduces in intensity indicating that some of the PAG has dissociated and that the NO_2 has been photochemically converted to the nitroso (Scheme 2). However, even after very long exposure, a NO_2 peak due to undissociated PAG is still visible (Figure 8E). This suggests that the reason for partial photodoping is the incomplete decomposition of the PAG and not due to unwanted side reactions involving photogenerated protons. The incomplete decomposition is most probably due to significant absorption by the POT in the 254 nm region of the UV spectrum (Figure 1A).[16b] Furthermore, the nitroso compound that is formed during photogeneration of the acid (Scheme 2) could undergo further photolysis to form highly absorbing products which increase the optical density of the film.[20] Even after the prolonged exposure the conductivity of the POT was only marginally better than that of the undoped POT. Hence, films much thicker than those used in this work may not be suitable for the photoinduced doping technique at 254 nm.

From Figure 8A–E, it is possible to see that the photogenerated acid has the same effect on the C=N and C=C peaks as HCl, i.e., the intensity of the C=N (quinoid) peak increases relative to that of the C=C (benzenoid) peak. Furthermore, just as in the HCl doped case, the original ratio of intensities is retrieved (Figure 8F) upon exposure to ammonia vapor. These results, like those from the UV–visible spectra, suggest that the changes in chemical structure induced by the photodoping method are similar to those induced by HCl and that both doping methods are reversible by dedoping with ammonia vapor. At present, it is not possible to comment unambiguously about the change in the quinoid:benzenoid ratio upon doping (by either method) since any change in the ratio of intensities of the C=C and the C=N peaks may be due to a alteration in the chemical structure upon protonation without a change in the quinoid:benzenoid ratio.

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In summary, although the photodoping step produced only a slight increase in the conductivities of the POT, it produced a large enough difference between the solubilities of the doped and undoped regions to allow the imaging of the POT–PAG system as a lithographic material. As suggested by curve c in Figure 3, once the patterns are generated it is possible to increase their conductivity to the order of 10^{-3} S/cm through standard doping techniques such as HCl vapor exposure. This ability to make transparent conducting patterns may be useful in display technology. For example, polyaniline electrodes have been used instead of indium–tin oxide to make flexible electroluminescent devices.[6] In addition, it may be possible to use this photodoping technique in applications which require patterns with large differences in electrical conductivity/dielectric constants, for example anisotropic interconnections or optical memory storage devices.

Conclusions

Poly(*o*-toluidine) films have been doped by an acid generated by the irradiation of a nonmetallic, nonionic photoacid generator with UV light. The optical and infrared spectra of the polymer obtained during photoinduced doping are similar to those obtained after doping with hydrochloric acid implying that the changes produced in the chemical and electronic structures of the polymer are identical. Under the present conditions, it appears as though the photoinduced doping process is only partially complete due to the partial decomposition of the photoacid generator under UV light irradiation. Significant absorption by the POT (and/or the photolysis products of the nitroso compound) in the 254 nm region of the UV spectrum is believed to be the cause of this limitation. While the conductivities of the photodoped polymers are only 1–3 orders of magnitude larger than those of the undoped polymers the photodoped polymers are insoluble in solvents that dissolve the undoped polymer. This allows the use of this material as a negative photoresist with typical sensitivities of around 1500 mJ/cm^2. Once patterned, the POT film can be exposed to hydrochloric acid vapor which raises the conductivity of the polymer film up to 10^{-3} S/cm.

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