A Soluble Polyaniline Substituted with t-BOC: Conducting Patterns and Doping

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ABSTRACT: A soluble polyaniline (PANi) was synthesized by modifying with a photolabile, acid-labile, and thermolabile *tert*-butoxycarbonyl (t-BOC) group in this study. The prepared PANi(t-BOC) is highly soluble and thermodynamically stable in low-boiling solvents such as THF, dioxane, and $CHCl_3$. This soluble form of PANi(t-BOC) was converted to the insoluble and electrically conductive emeraldine salts upon photodoping with only a catalytic amount of photoacid generators such as *N*-(tosyloxy)- or (camphorsulfonyloxy)norborneneimide or -onium salts. As a result of this solubility difference, conducting patterns of high resolution were produced by conventional photolithography process. Further, upon removal of the t-BOC groups in PANi(t-BOC) by acid doping, no obvious morphology change of the films was observed, and such conversion recovered the original conductivity level of the doped PANi. Since the t-BOC protecting groups are easily removed in doping or acid-catalyzed reaction by chemical amplification or thermal bake, the PANi(t-BOC) can be used as conductive matrix polymers for negative type photoimaging or printing materials or for novel solution-processed applications in various microelectronic devices.

Introduction

Conducting polymers have attracted much attention as organic electronic materials for applications ranging from microelectronic devices to mechanical actuators.[1−3] Functional components such as diodes,[4] transistors,[5] and light-emitting diodes (LEDs)[6] have been also fabricated from conjugated polymers in prototype forms. Most of these applications require the formation of patterned microstructures of conducting polymers with feature sizes less than 100 μm. Various approaches have been reported so far for this purpose: photolithographic techniques based on photoinduced doping/dedoping,[7] photochemical reaction,[8] chemical amplication,[9] and nonphotolithographic methods[10] such as selective electrochemical deposition, microcontact printing, micromolding, ink-jet,[11] and screen printing,[12] and electrochemical dip-pen nanolithography.[13]

The material we are investigating in this report is polyaniline (PANi). This material is probably the most important conducting polymer, being environmentally stable as well as commercially available. Unfortunately, the conductive emeraldine base and especially salt form of PANi have long been considered as an intractable material. Its poor solubility in most common solvents has limited the industrial application of PANi. To improve melt and solution processability, the majority of PANi modifications to date have been made by the incorporation of substituents on the polymer backbone. However, as is well-known, chemical modification of the conjugated backbone generally leads to a decrease in its electrical conductivity.[14] Hence, a design strategy enhancing solubility without sacrificing the conductivity will be valuable for maintaining inherent conductive applications. Recently, Zhang et al. reported the synthesis of t-BOC-protected PANi through step-growth polymerization of a bifunctional dimeric monomer via palladium-catalyzed amination chemistry.[15] The method we demonstrate here is a photolithographic technique that involves modification of the polyaniline (PANi) with a thermolabile and acid-labile *tert*-butoxycarbonyl (t-BOC) group. The t-BOC group has long been used as a protecting group in peptide synthesis.[16] We have introduced it into the backbone to obtain a soluble PANi in self-recoverable form when doped. Spatially resolved conversion can then be achieved in a lithographic process by employing photoacid generators (PAGs), so that the PANi is made into a negative photoresist capable of generating high-resolution conducting lines. In this paper we present the detailed imaging process and spectroscopic/microscopic evaluation of the resultant conducting patterns. In view of the ease with which PANi(t-BOC) can be spin-coated into thin films using common solvents such as $CHCl_3$ or THF, this simple and selective method for the generation of patterns by development with common solvent is promise for various practical applications.

Experimental Section

Materials and Instrumentation. PANi was synthesized according to the standard procedure.[17] *N*-(10-Camphorsulfonyloxy)norborneneimide (CSNBI) and *N*-(tosyloxy)norborneneimide (TSNBI) were prepared according to the procedure reported elsewhere.[18] Triphenylsulfonium triflate (TPSOTf) was purchased from Kumho Co. ^{1}H NMR spectra were recorded on a Varian Gemini 200 spectrometer of Perkin-Elmer using $CDCl_3$. Infrared spectra were recorded on a Nicolet 800 spectrophotometer (Nicolet Instrument Co). Molecular weights were measured by gel permeation chromatography (GPC) using a GPC-717 plus autosampler (Waters Instrument Co). UV spectra were recorded on a Shimadzu model UV-1606 spectrophotometer. Thermal properties of polymers were analyzed by model DSC 2010 and model 2050 of TA Instruments (heating rate: 10 °C/min). The dc conductivity measurements of the films were performed with a four-probe technique using the picoamperometer Keithley 237 at room temperature, and graphite glue was used for better contact.

Synthesis of PANi(t-BOC). To a solution of PANi (4.9 g, 0.014 mol) and 13 mL (0.16 mol) of pyridine in 100 mL of *N*-methylpyrrolidinone (NMP) was added slowly di-*tert*-butyl dicarbonate (DTBDC) (9.0 g, 0.041 mol) in 50 mL of NMP at

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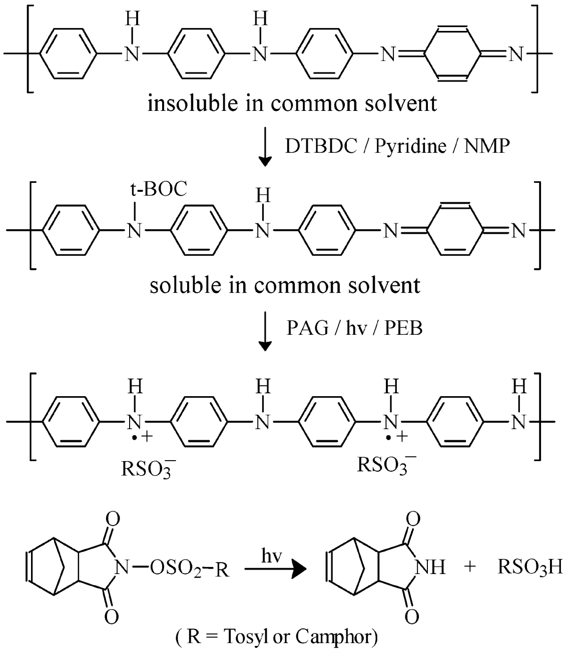
Scheme 1. Schematic Drawings for the Preparation of PANi(t-BOC) and Its Conversion into PANi Salt as Well as Structures for PAG, *N*-(10-Camphorsulfonyloxy)norborneneimide (CSNBI), and *N*-(Tosyloxy)norborneneimide (TSNBI)



80 °C. The mixture was stirred for 3 h under a nitrogen atmosphere. The reaction mixture was filtered, and the filterate solution was precipitated into methanol and dried to give a polymer PANi (t-BOC) as pale dark red powders in 2.8 g (yield 45%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.5 (s, 9H, t-BOC), 6.8−7.2 (broad, 16H, aromatic). IR (KBr): ν 2900−3100 (C−H stretching), 1707 (C=O of t-BOC), 1597 (quinoid ring), 1507 (benziod ring). UV (NMP, 1.0×10^{-4}, PANI-t-BOC): λ_{max} 317 nm ($\pi-\pi^*$), 585 nm (exiciton). UV (MNP, 1.0×10^{-4}, PANi): λ_{max} 328 nm ($\pi-\pi^*$), 637 nm (exiciton).

Spatially Resolved Conversion. The polymer (t-BOC) and 3 wt % CSNBI, TSNBI, or TPSOTf as a PAG were dissolved in THF. The solutions were filtered through a 0.2 μm membrane filter and spin-coated using a Headway Research spin-coater to make about 0.5 μm thick films after soft baking at 50 °C for 1 min. Quartz plates were used for UV spectroscopy and silicon wafers for conducting patterns as the substrate. UV exposure was performed with illuminator of Ushio Inc. (Japan) equipped with a 500 W Hg−Xe lamp and a narrow band-pass filter at 250 nm wavelength (intensity of 23 mW/cm^2). The spin-cast film of PANi(t-BOC) with PAG was exposed to UV through a photomask in a contact mode followed by postexposure bake at 110 °C for 1 min to bring about acid-catalyzed deprotection. The photographs of the conducting patterns were taken with laser scanning microscopy (LSM) of Carl Zeiss Co (LSM 5 PASCAL).

Results and Discussion

Synthesis and Properties of PANi(t-BOC). The emeraldine base form has two amine nitrogens followed by two imine nitrogens along the chains. The t-BOC-substituted PANi as a target polymer is shown in Scheme 1. The present soluble PANi was synthesized by reacting the parent PANi with DTBDC in NMP as solvent. Interestingly, the mono-t-BOC-substituted products were always obtained in 37−45% yield as confirmed by NMR, IR, and TGA. The ^{1}H NMR spectra of PANi-(t-BOC) showed a singlet peak at 1.5 ppm for 9H of t-BOC and broad double peaks at 6.8−7.2 ppm for 16H of aromatic protons in the benzenoid and quinoid rings. In its IR spectrum a characteristic absorption band at 1707 cm^{-1} corresponding to the carbonyl groups of t-BOC was also identified. Furthermore, the complete removal of the t-BOC groups in the PANi(t-BOC) to amine units in the benzenoid ring occurred at 180 °C with a mass loss of 22% confirmed by an endothermic event in TGA and DSC thermograms, as shown in Figure 1. The amount of the mass loss and NMR data agree well with the theoretical value of the composition of one t-BOC group for four aromatic rings in the polymer. It is probable that the amine groups adjacent to t-BOC-substituted amine groups did not undergo substitution reaction due to steric hindrance as well as reduced basicity by the neighboring electron-withdrawing t-BOC group, thereby resulting in one-half substitutions.

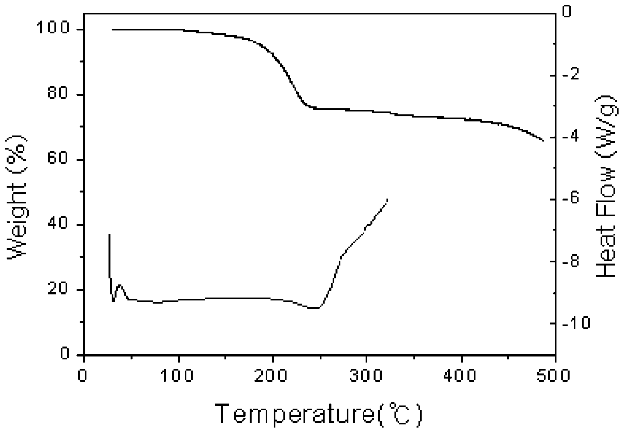


Figure 1. DSC (bottom) and TGA (top) thermograms of the PANi(t-BOC) measured under a nitrogen atmosphere.

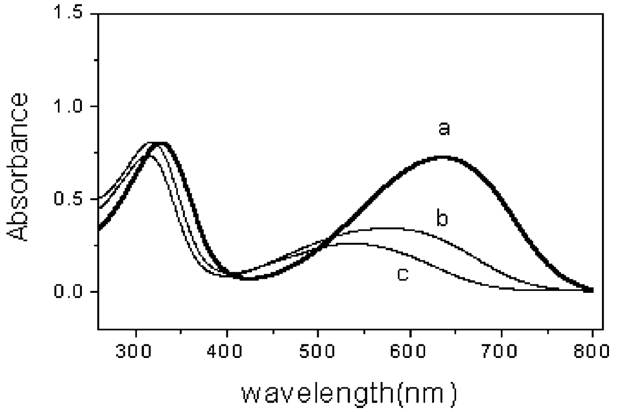
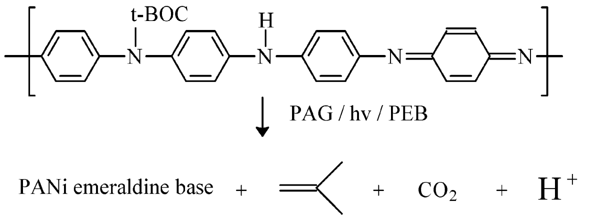


Figure 2. UV absorption spectra of (a) PANi(emeraldine base), (b) PANi(t-BOC) in NMP, and (c) PANi(t-BOC) in $CHCl_3$.

The substituted PANi(t-BOC) had the number-average molecular weights (M_n) in the range 10 000−12 000 with polydispersities 1.5−1.8 as determined by GPC in THF. Note that PANi(t-BOC) displayed virtually weak exciton band (λ_{max}: 585 nm) and shifted to a shorter wavelength of $\pi-\pi^*$ (λ_{max}: 317 nm) compared to that of PANi emeraldine base, as shown in Figure 2. These results might be related to the low efficiency of exciton band formation due to the electron-withdrawing t-BOC groups increasing interchain distance. It is also interesting to note that the synthesized PANi(t-BOC) exhibits much better solubility than the parent PANi. It dissolves well and thermodynamically stable in common low-boiling organic solvents and thus allows the PANi process to be made compatible with the conventional process. We think that steric constraints along with

Scheme 2. Acid-Catalyzed Elimination of t-BOC from PANi(t-BOC)



removal of the mobile protons by the substituents disrupted inter- and intrachain hydrogen bonding responsible for low solubility and gelation at high concentrations. The solubility of the present PANi(t-BOC) is a highly desirable quality for its applications.

Photoinduced and Thermal Removal of t-BOC Groups in Polymer Films. Generally, the beneficial use of the t-BOC group as a leaving group is based upon the fact that the deprotection reaction is acid-catalyzed, i.e., chemically amplified as depicted in Scheme 2. To investigate whether the photoinduced removal of the present N-t-BOC groups is chemically amplified particularly in the PANi backbone, a solution of the PANi(t-BOC) with a catalytic amount (3%) of PAG was spin-coated onto substrates to make thin films. Three types of PAGs were employed: two norborneneimide compounds with different organic counter groups of tosyl and camphor (CSNBI, TSNBI) and one typical onium salt (TPSOTf). All of the polymers formed good-quality films by evaporating the solvent slowly or by spinning the solution and the films adhered well to the substrates. The deprotection of t-BOC groups in the polymer films was monitored by IR and UV spectral changes (Figure 3). The two IR absorption band intensities, the one at 1707 cm^{-1} associated with the carbonyl stretching vibration of the N-t-BOC groups and the other at 1597 cm^{-1} (quinoid ring) associated with PANi backbone, gradually decreased with increase in PEB temperature and exposure time. Simultaneously, the benzenoid absorption band intensity at 1507 cm^{-1} related to amine moiety increased by removal of t-BOC groups in the polymer films. However, the removal of t-BOC groups in the film was not complete at an employed PAC concentration of 3%, as observed from Figure 3. This incomplete removal is not necessarily due to the reduced reactivity of the acid-catalyzed deprotection of N-t-BOC compared to the usual O-t-BOC in the phenol derivatives.[19] Another explanation associated with the unique aspect of PANi backbone is the possibility of doping induced during UV exposure because irradiated PAGs act as a proton source. This localized photodoping process was confirmed by changes in the UV−vis spectra of the PANi-t-BOC/PAG film. Figure 3 (right) shows them before and after different doses of 250 nm UV exposure. The unexposed film displays two absorption peaks at 318 and 585 nm, characteristic of the undoped emeraldine base form of PANi. Upon exposure, the exciton band of 585 nm decreases and two new peaks appearing at 400 and 800 nm slightly increase with increasing exposure dose. These peaks are usually assigned to polaron bands originated from the conducting, i.e., doped, emeraldine salts. Further, visual inspection of the film showed color changes at the exposed areas. The pale dark red film on quartz substrate became slightly dark green after UV exposure followed by postexposure bake at 110 °C for 60 s.

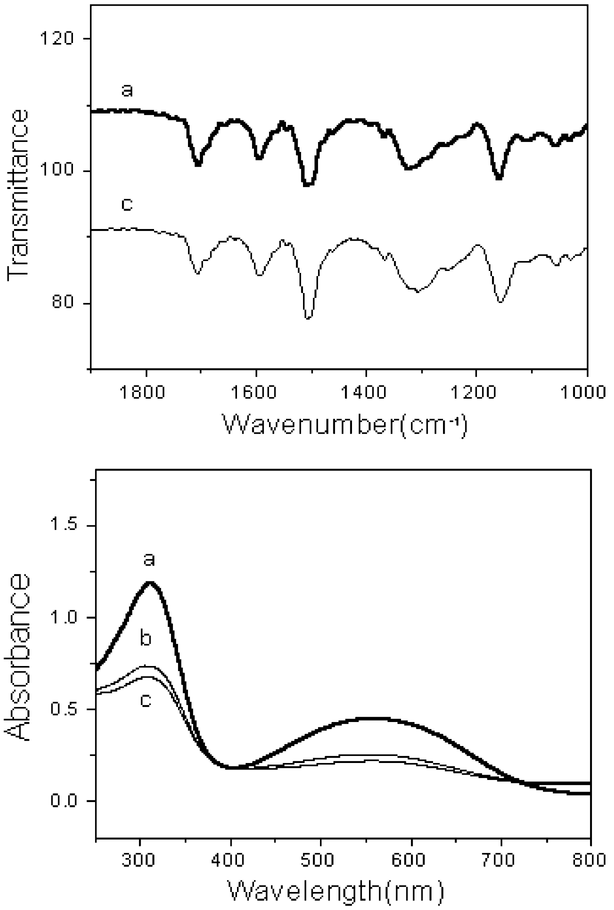


Figure 3. UV absorption spectra (top) of 0.9 μm PANi(t-BOC)-containing TSNBI (3 wt %) on a quartz plate and IR spectral changes (bottom): (a) before exposure, (b) after exposure without postexposure bake (PEB), and (c) after exposure with PEB.

To obtain the fully protonated polymer salt, a solution of the PANi-t-BOC/PAG(TSNBI) in a molar ratio of 2:1 was spin-coated onto substrates to make films. Among the PAGs investigated, TSNBI exhibited the best compatibility. The deprotection of t-BOC groups and doping level in these polymer films were monitored by IR and UV spectral changes (Figure 4). During UV exposure and postexposure baking, the imide (⟩N−O) carbonyl peak among two carbonyl species, one at 1707 cm^{-1} associated with the carbonyl stretching vibration of the N-t-BOC groups and the other at 1780 cm^{-1} associated with imide (⟩N−O) carbonyl of TSNBI, disappeared, and another imide (⟩N−H) carbonyl peak concurrently appeared at ca. 1700 cm^{-1}. This implies that TSNBI completely decomposed upon irradiation to generate protonic acid. However, the precise determination of the deprotection of t-BOC groups from these carbonyl peaks was rather difficult because the newly formed peak partly overlapped the N-t-BOC peak. Additional information obtained from the regenerated N−H stretching at 3300 cm^{-1} indicated that the deprotection of t-BOC group in the film was completed during 30 min postexposure baking at 110 °C. The complete removal of the t-BOC group was also confirmed by comparing the optical absorption spectra. Figure 4 (right) shows the spectra for PANi-t-BOC/PAG film before and after UV and thermal treatment. As noted already, the unexposed film displays two absorption peaks, at 318 and 585 nm. Upon treatments, the exciton band of 585 nm signifi-

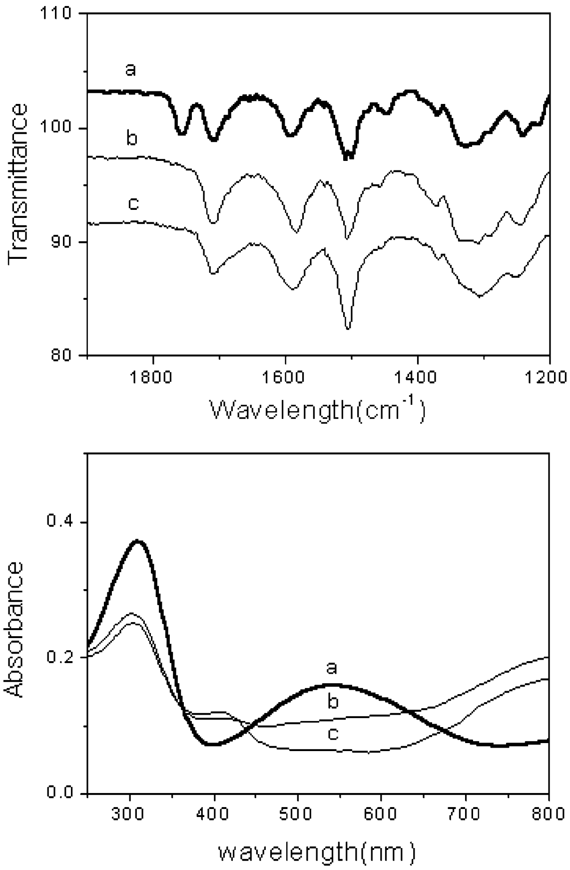


Figure 4. UV absorption spectra (top) of 0.5 μm PANi(t-BOC)-containing TSNBI (molar ratio of 2:1) on a quartz plate and IR spectral changes (bottom): (a) before exposure, (b) after exposure without PEB, and (c) after exposure with PEB.

cantly decreases while two new peaks appearing at 400 and 800 nm increase with increasing time. The most relevant information derived from these studies is that no significant changes are detected in the optical spectra of such films after such treatments when compared with those of the parent PANi immersed in HCl, indicating that the t-BOC could be cleanly removed, while leaving the PANi chain practically unperturbed. This observation, in conjunction with the acid-catalyzed nature of the deprotection process, provided the impetus for an attempt to examine chemically amplified photolithography of PANi-t-BOC in the presence of an equivalent photoacid generator (Scheme 1).

Formation of Patterns. As an example of the patterns, we show in Figure 4 the results of a lithographic process through the use of two different masks for polymer films of 0.5−0.7 μm thick containing 3 wt % TSNBI in a silicon wafer. Note that optical density of the polymer film at 254 nm was 0.5/μm. Since the exposed area was no longer soluble in low-boiling solvents, the relief image was obtained upon dissolution of the unexposed polymer in a solvent such as $CHCl_3$. Thus, a negative conducting pattern developed in $CHCl_3$. Numerous conducting stripes clearly came out. The fine lines in the range 1−10 μm were resolved here. These patterned images were uniform with smooth surfaces and closer to those of conventional resists in terms of lithographic performance of resolution, contrasts, etc.

In addition to these low molecular weight PAGs, we investigated UV-induced deprotection of blends of PANi(t-BOC) and poly(vinyl chloride) (PVC) using a similar technique. In this case, PVC acts as a polymeric PAG since HCl can be produced by photochemical degradation of the polymer. It showed the same features as the optical micrographs given in Figure 5. We feel that photolithographic patterns of submicron resolution for this blend can be achieved with synchrotron radiation.[20] Work is in progress to obtain nanopatterned lines using an X-ray lithography beamline.

Electrical Conductivity. Conductive polymers have various applications in microelectronics industry: electrostatic discharge or charge dissipators, conducting resists, metallization, and corrosion protection. The use of conducting polymers in devices or in interconnection technology requires a significant enhancement of the conductivity. We examined conductivities of resultant patterns using the four-line probe technique. The trend in conductivity indicates that higher conductivities are achieved with increasing PAG content up to about the PANi-t-BOC/PAG in a molar ratio of 2:1. Upon irradiation, a conductivity maximum of 1×10^{-3} S/cm was attained. However, the subsequent external doping of the treated film samples by HCl vapor resulted in a large increase in the conductivity up to 3−5 S/cm, similar to the conductivities of conventional free-standing PANi:HCl films, even though the conductivity of films of these materials is lower than PANi doped with functionalized sulfonic acids. This implies that the molecular conformation in the solid state of a PANi chain obtained by t-BOC removal of the PANi(t-BOC), which is a major factor in determining the electronic and electrical properties, is not much different from the conformation of a doped PANi chain in the solution from which it is cast. Further, we think that the solvent from which the solid PANi(t-BOC) polymer is obtained, its

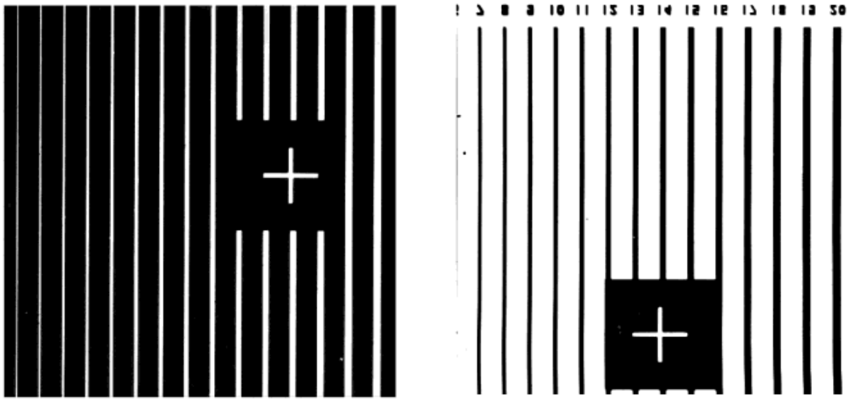


Figure 5. Laser scanning microscopy photographs of the conducting patterns generated by contact exposure on 0.6 μm thick film of the PANi(t-BOC) with 3 wt % TSNBI.

UV peaks being dependent on the solvent as shown in Figure 2, or the vapor to which it is exposed can play a significant role in the conductivity of the polymer as commonly observed in PANi.[21] Therefore, to be able to attain better conductivity properties for PANi(t-BOC), a new doping methodology is required.

Recently, Salavagione et al.[22] reported a similar method of acid-catalyzed PANi lithography using a removable NO group, nitrosated PANi, and produced conductive PANi images by the complete elimination of NO groups through acid hydrolysis. Wrighton et al.[23] have also used PANi amide formation/hydrolysis to reversibly modify polymer conductivity. These approaches toward modifying PANi using the removable functional groups can be certainly a desirable advantage to reversibly change polymer solubility and/or conductivity. However, we could not compare the efficacy of the different methods in the resolution of the patterns or their returned electrical conductivities due to the absence of the data in the literature. If we compare our results with patterns formed by irreversible solubility modifications reported in the literature,[24] there has obviously been an improvement in the conductivity behavior of our system. For an example, the methyl-substituted PANi, poly(*o*-toluidine),[25] more soluble than the parent PANi exhibited a conductivity on the order of 10^{-7} S/cm, and the conductivity was increased up to 10^{-3} S/cm by making the patterns further doping externally.

Conclusions

We have prepared photolabile and acid-labile PANi(t-BOC) by modification of PANi with di-*tert*-butyl dicarbonate in NMP. The t-BOC substitution reaction proceeded at the only one amine nitrogen of the two in the repeat structure of the emeraldine base form. The resultant PANi(t-BOC) is highly soluble and thermodynamically stable in low-boiling solvents such as THF, dioxane, and $CHCl_3$. These soluble PANi-containing t-BOC groups can act as negative conducting photoresists; that is, it is photo- and thermolabile and needs only a catalytic amount of PAGs to make photolithographic deep UV patterns. Upon removal of the t-BOC groups in PANi(t-BOC) by acid doping, no obvious morphology change of the films was observed, and such conversion recovered the original conductivity level of the doped PANi. The combination of this simple method for the generation of conducting patterns and the fact that PANi(t-BOC) completely returns to the parent PANi after photodoping and/or acid-doping or thermal treatment offer possibilities for novel applications of PANi in, for example, microelectronics.

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