Patterned Conductive Polyaniline Films Fabricated Using Lithography and *In Situ* Polymerization

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ABSTRACT: In this article, we describe a novel bottom-up technique for the preparation of transparent conductive films of polyaniline (PANI). A UV-curable photoresist was formulated containing an acrylate-endcapped urethane oligomer [UA(PPG400)], acrylic acid, a photoinitiator, and a reactive diluent (tripropylene glycol diacrylate), and the lithography techniques were used to pattern the structure with line widths/spaces of 100 μm/100 μm, 10 μm/10 μm, and 5 μm/5 μm on a polyethylene terephthalate substrate. The carboxylic acid units on the surface of the patterned photoresist interacted with the aniline monomer units to form anilinium complexes; using ammonium persulfate as a chemical oxidant, we then synthesized a layer of conductive PANI on the surface of the patterned resist through *in situ* polymerization. The optimal conductivity of the PANI conductive film was ca. 10 S/cm. The thin film was characterized, and its physical properties investigated using Fourier transform infrared spectroscopy, UV–Vis spectroscopy, differential scanning calorimetry, optical and atomic force microscopy, and four-point probe conductivity measurements. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2271–2276, 2010

Key words: atomic force microscopy (AFM); FTIR; lithography; photoresists

INTRODUCTION

The field of flexible electronics has the potential to enable useful devices, such as flexible paper-like displayers, woven electrotextiles, low-cost identification tags, printed transistor circuits, and electromagnetic wave interference shielding mesh films.[1–5] To develop flexible electronics, it is necessary to pattern the electrodes and active semiconductor layers. Nano-silver paste is an appropriate material for preparing the electrodes because of its high electrical conductivity and operational stability. It can be patterned using several approaches, such as inkjet printing, roll-to-roll (R2R) production techniques, and soft imprint lithography.[6–8] These materials tend to crack, however, during annealing because of the large intrinsic volume reduction that accompanies complete sintering of the nanoparticles, resulting in weak substrate adhesion and poor cohesion within the metal films.[9] As a result, many researchers have investigated the application of conjugated polymers (CPs) in place of the inorganic materials. For example, Haberko printed patterns of surfactant on Ag substrates using a poly(dimethylsiloxane) stamp and spin-coated the polyaniline/polystyrene composite to manufacture microscale patterns via self-organization.[10] Mustonen et al. used multiwalled carbon nanotube and Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) composites to form conducting patterns through inkjet printing.[11]

Polyaniline (PANI) is a useful CP that exhibits good environmental stability, high electrical conductivity, and interesting redox properties.[12,13] The processing of PANI is, however, difficult because of its very low solubility in common organic solvents and because its decomposition temperature is below its glass transition temperature (T_g).[14,15] Thus, attempts have been made to modify the PANI polymer chain[16,17] or blend it with another matrix[10] to improve its processability; nevertheless, the crystallinity and the degree of conjugation—and, hence, the electronic properties[18]—are usually lower than those of PANI homopolymers.

In this article, we describe the development of a novel bottom-up process for the preparation of patterned PANI films. We used lithography techniques to pattern a UV-curable photoresist containing acrylate-endcapped urethane oligomer, acrylic acid, photoinitiator, and reactive diluent [tripropylene glycol diacrylate (TPGDA)] onto a polyethylene terephthalate (PET) substrate. The carboxylic acid groups on the surface of the photoresist interacted with the aniline (Ani) monomer units through electrostatic

interactions. Using ammonium persulfate (APS) as a chemical oxidant, we then synthesized a conducting PANI layer through *in situ* polymerization. We characterized the patterned PANI films in terms of their transparency, conductivity, and morphology.

EXPERIMENTAL

Materials

Acrylic acid, hydroxyethyl acrylate (HEA), Ani, and APS were purchased from Acros. Hexamethylene diisocyanate (HDI) was purchased from TCI. The poly(oxypropylene glycol) (PPG400) was obtained from Arco. The T-12 catalyst [DBDT(catalyst Sn% = 18)] was purchased from Aldrich. TPGDA was obtained from SANDOTEX. The photoinitiator (Irgacure651) was purchased from Ciba Specialty Chemicals.

Synthesis of acrylate-endcapped urethane oligomer

The PPG400 and HEA were degassed separately under vacuum at 75°C overnight. In a three-necked flask, PPG400 (20 g, 1 equiv) and a trace amount of the catalyst (T-12) were mixed at 75°C using a mechanical stirring apparatus. HDI (16.8 g, 2 equiv) was added dropwise into the flask. After the characteristic IR spectroscopic peak of isocyanate groups (at 2270 cm^{-1}) had reduced to half of its original intensity, HEA (11.6 g, 2 equiv) was added dropwise. This mixture was stirred at 75°C until the signal at 2270 cm^{-1} disappeared completely. The resultant viscous mixture was kept in a dark glass bottle until required for further use.

Photoresist composition

Table I. Photoresist compositions

Lithography

Blade coating was used to form uniform photoresist films. Masks with various line width/space patterns (5 μm/5 μm, 10 μm/10 μm, 100 μm/ 100μm) were used to define the patterns on the PET films. A 365-

TABLE I
Photoresist Compositions

Sample designation	Acrylate-endcapped urethane oligomer(PPG400) + TMPTA (UA, mol %)	Acrylic acid (AA, mol%)
70UA-30AA	70	30
50UA-50AA	50	50
30UA-70AA	30	70
15UA-85AA	15	85
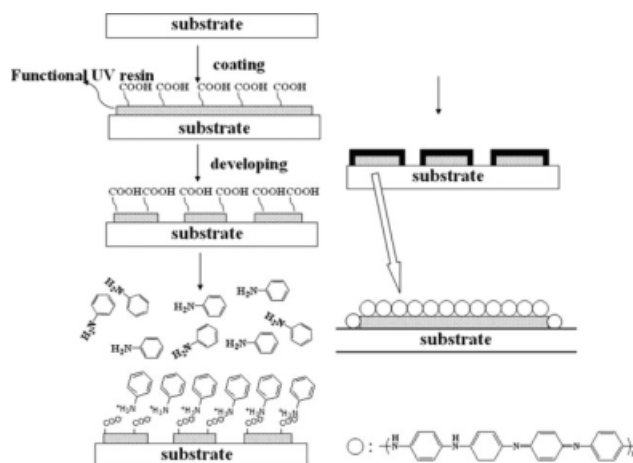
**Scheme 1** Microlithography process used to prepare patterned polyaniline films.

nm UV lamp was used as the light source; isopropanol was used to develop the patterns.

In situ polymerization of Ani

The patterned film (5 cm × 5 cm) was placed into a solution containing 0.2M aqueous Ani (100 mL) at 5°C for 2 h and then 0.2M aqueous APS (50 mL), which had been cooled to 5°C, was added slowly (over 10 min) to the Ani solution. After 4 h, the resultant film was washed several times sequentially with water and acetone to remove any residual reagents and then it was dried in an oven at 60°C. Scheme 1 outlines the process used to prepare the nanometer-thick patterned films of conducting PANI.

Measurements

Conductivity was measured using a Hewlett–Packard HP4338B milliohm meter under ambient conditions. Two parallel conducting electrode lines (1.5 mm × 20 mm) were coated by Ag paste; they were aligned 20 mm apart and perpendicular to the patterned lines. Fourier transform infrared (FTIR) spectra were recorded using a BIO-RAD FTS-3000 spectrometer equipped with an attenuated total reflectance sample stage. UV–Vis spectra were recorded using a UNICAM HEλIOS-Gamma spectrometer. Modulated differential scanning calorimetry was performed using a TA LT-Modulate DSC 2920 instrument operated under the following conditions: sample size, 5–10 mg; heating rate, 10°C/min; carrying gas, N$_2$. Optical microscopy (OM) images of the patterns were obtained using a ZOOMKOP microscope. Atomic force microscopy (AFM) images and the thickness of conductive films were recorded under ambient conditions on a Digital Instruments
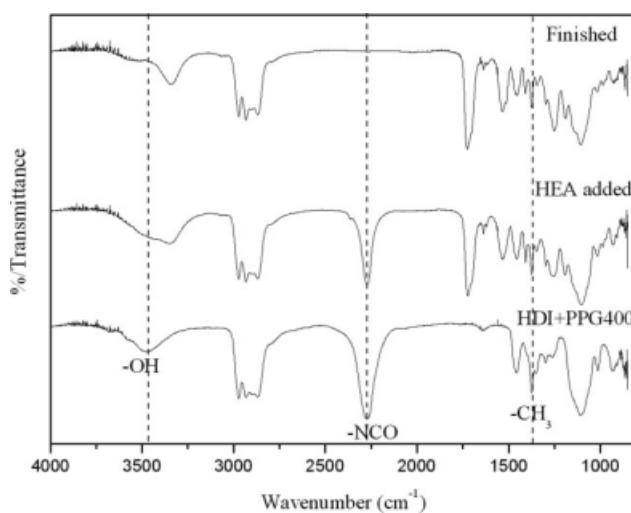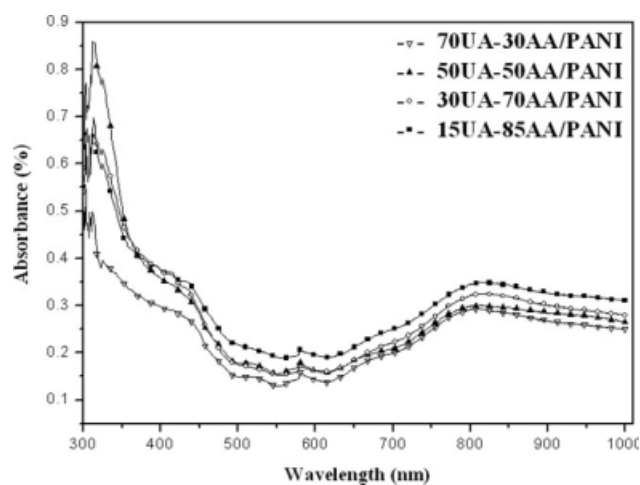
Figure 1 FTIR spectra recorded at various stages during the synthesis of the acrylate-endcapped urethane oligomer.

Figure 2 UV–Vis spectra of UA-AA/PANI samples containing various AA contents (reaction time: 2 h).

Dimension-3100 Multimode, operated in a tapping mode using Si cantilevers.

RESULTS AND DISCUSSION

The FTIR spectra in Figure 1 display the characteristic peaks monitored during the synthesis of the acrylate-endcapped urethane oligomer. The urethane prepolymer was synthesized through the reaction of a polyol (1 equiv) and a diisocyanate (2 equiv). The urethane linkage was deemed to have formed when the intensity of the signal of the isocyanate (NCO) groups (at 2270 cm^{-1}) had halved and the broad signal of the hydroxyl (OH) groups (at 3500 cm^{-1}) had disappeared. The viscosity increased during the reaction providing further evidence for the formation of a high-molecular-weight compound. After HEA had been added, the remaining NCO groups reacted with the OH groups of HEA. At this stage, we observed that the signal for the NCO groups had disappeared, suggesting that the HEA units had completely end-capped the urethane prepolymer to form our target product. Thus, the FTIR spectra in Figure 1 confirmed the syntheses of both the urethane prepolymer and the acrylate-endcapped urethane oligomer. Note, however, that because of the molecular weight distribution of PPG, we obtained a mixture of acrylate-endcapped oligomers, rather than a species having a precise molecular weight. The resultant mixture was kept in a dark glass vial and used without any further purification.

Figure 2 displays UV–Vis spectra of the conducting PANI film. Among the four oxidation states of PANI—leucoemeraldine, pernigraniline, emeraldine base, and emeraldine salt—the doped emeraldine salt has the highest conductivity.[19] We assign the band at 820 nm to a localized polaron corresponding to the localization of charge carriers by a π-polaron transition; we observed a second polaron band at 430 nm that was dependent on the doping level. The presence of these two bands indicated that proton-doped PANI products existed in their conducting form (i.e., the emeraldine salt form of PANI). Furthermore, broad signals appeared in the near-infrared region (>850 nm), due to the delocalization of charge carriers; we assign the absorption band at 320 nm to π–π* transition.[20–22] In Figure 2, we observe that these bands increased in intensity at higher Acrylic acid (AA) contents. Therefore, from these UV–Vis spectra, it was evident that the PANI thin films had formed on the PET substrate after a reaction time of 2 h.

The glass transition temperature is a thermal property that determines the possible applications of polymers. Figure 3 displays the glass transition
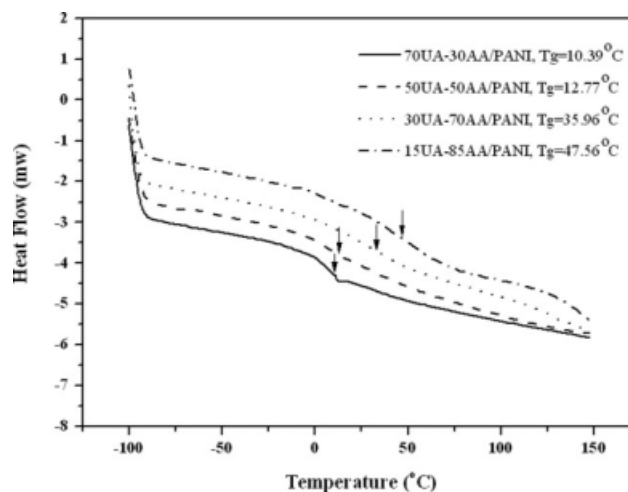
Figure 3 DSC traces of UA-AA/PANI samples containing various AA contents (PANI polymerization time: 2 h).
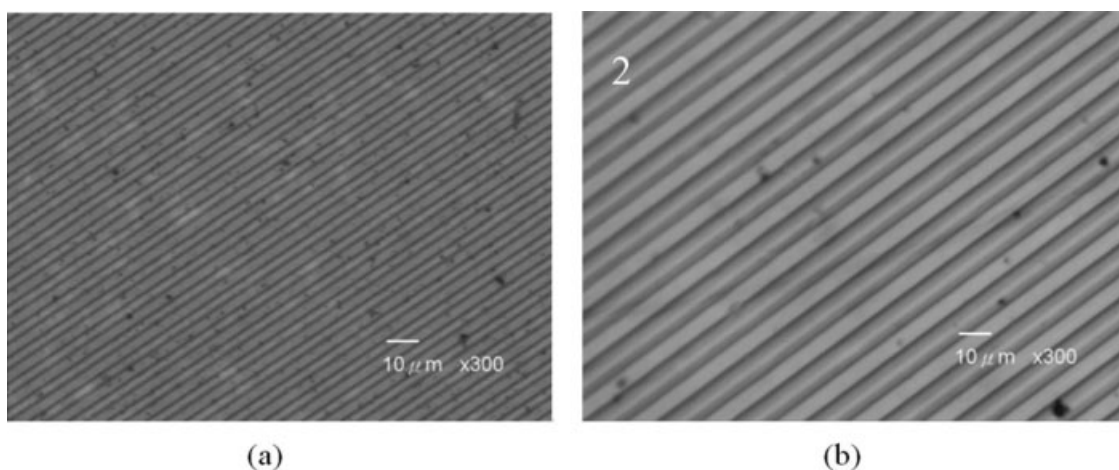
Figure 4 OM images of patterned photoresist films (15UA-85AA) having line widths/spaces of (a) 5 μm/5 μm and (b) 10 μm/10 μm.

temperatures—as measured using differential scanning calorimetry (DSC)—of the PANI thin films prepared from the urethane oligomers. As the AA content increased, the values of T_g increased. The glass transition temperature can be viewed as a measure of a polymeric system's degree of flexibility; therefore, Figure 3 suggests that higher AA contents resulted in lower atomic flexibility. Because PANI has a rigid rod-like structure, it constricts the mobility of the acrylic-endcapped urethane resin. Thus, we conclude that increasing the AA content increased the amount of PANI synthesized. This feature was also evident from the relationship between the conductivity and the AA content (see below).

Figure 4(a,b) displays OM images of the patterned films prepared using lithographic techniques with parallel line width/space patterns having line widths/spaces of 5 μm/5 μm and 10 μm/10 μm, respectively. We used AFM to measure the PANI thickness from the difference between the average film thickness before and after *in situ* polymerization. Figure 5(a,b) provides shape images of the clearly developed pattern having a line width/space of 10 μm/10 μm; nevertheless, we observed a slight degree of a footing effect at the patterns' edges, presumably due to the limitations of the resolution of the negative photoresist. Figure 5(c,d) presents topography images (5 μm × 5 μm) of the same film recorded at different spots of the conductive pattern and PET substrate, respectively; their surface morphologies are dramatically different. Because PANI features strong intermolecular hydrogen bonding, its polymer chains tend to coil to form a primary particle that undergoes further clustering to form agglomerates.[23] Thus, the surface of the conductive patterned line consisted of PANI primary particles, and the morphology of the conductive PANI line was rougher than that of the PET substrate.

Figure 6 reveals that the thickness of the PANI layers on the photoresists increased along with the polymerization time, becoming ca. 100 nm when polymerization time was greater than 2 h, for each constitution of the photoresist. The degree of *in situ* polymerization was obviously related to the reaction time, with more PANI molecules being attracted close to the film presenting the carboxyl acid groups. Nevertheless, this approach provided a new methodology for the preparation of conductive thin films.

We measured the surface resistances of the conductive films using a standard four-point probe method. The conductivity (σ) of each copolymer film was calculated using the equation

$$\sigma = 1/(R\,d) \tag{1}$$

where σ is the conductivity (in S/cm), R is the surface resistance (in $\Omega/\square$), and d is the the thickness of the conductive film (in cm).

In this study, we performed chemical oxidation polymerization to form the PANI layer on the photoresist. The acids used had two important roles: as the catalyst and as the dopant of the CP. Once CPs are doped, their conductivity can increase up to five orders of magnitude. Figure 7 reveals that the conductivities of patterned PANI films were similar for each line width/space of the patterned photoresist films, possibly because the constant area of the conductive PANI line in each pattern. Furthermore, as the AA content increased, the conductivity increased from 0.1 (AA = 30%) to 10 S/cm (AA = 85%). This phenomenon can be understood by considering that the presence of a greater content of AA leads to a greater number of carboxylic acid sites at which the PANI could be doped. On the other hand, measurements of the transparency provided further evidence for the increased doping level of PANI: as the
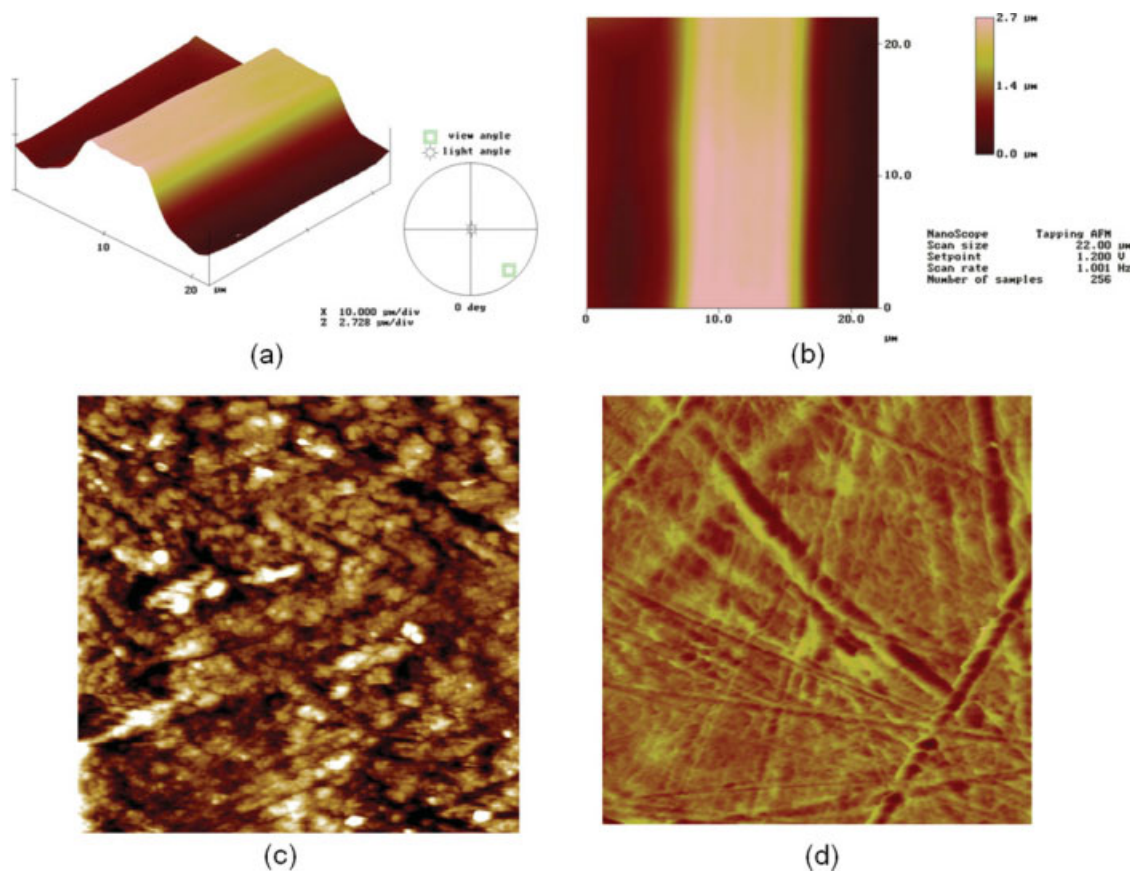
Figure 5 AFM images of the conductive pattern obtained after *in situ* polymerization of polyaniline (PANI polymerization time: 4 h; photoresist: 15UA-85AA): (a, b) topography at a line width/space of 10 μm/10 μm; (c) phase image of conductive patterned line of PANI; (d) phase image of PET substrate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

concentration of AA increased, the transparency decreased; i.e., more dark-green, emeraldine salt formed. In addition, the transparency was superior on the film patterned with smaller widths/spaces (Fig. 7); i.e., the line widths/spaces of the patterned films also influenced their transparency.

Figure 8 displays the relationship between the *in situ* polymerization time and the conductivity of the patterned 15UA-84AA/PANI films for each kind
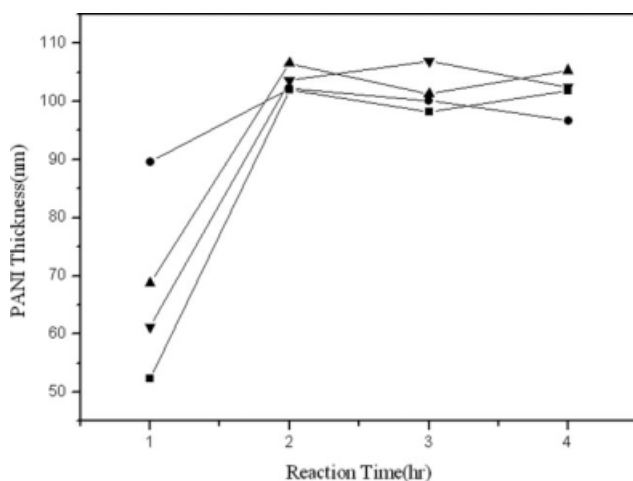
Figure 6 Thicknesses of UA-AA/PANI samples, plotted as a function of the reaction time, for AA contents (mol %) of (-■-) 30, (-●-) 50, (-▲-) 70, and (-▼-) 85%.
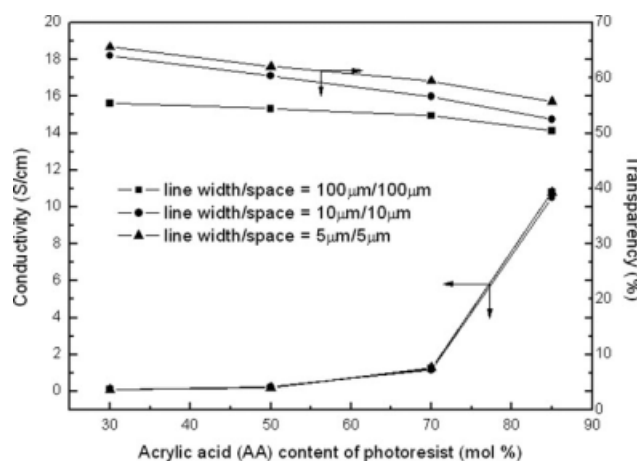
Figure 7 Conductivity and transparency of patterned PANI film, plotted as functions of the AA content in the photoresist (*in situ* polymerization time: 4 h).
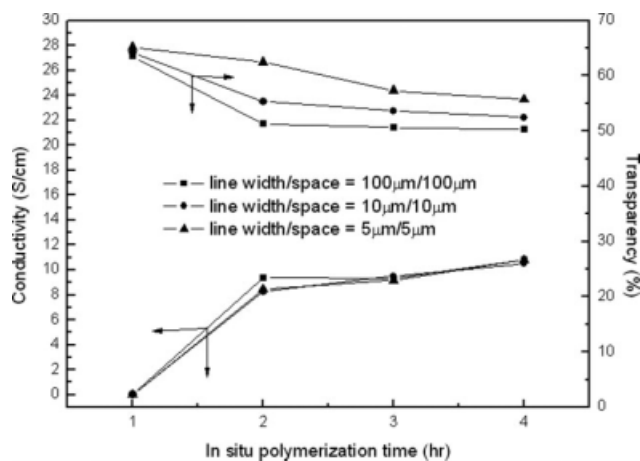
Figure 8 Conductivity and transparency of the 15UA-85AA/PANI patterned film, plotted as a function of the *in situ* polymerization time.

of line width/space. As expected, higher conductivities occurred after longer reaction times. Nevertheless, the conductivity became saturated after a polymerization time of 2 h. We also observed this trend for other photoresists containing different UA/AA ratios. This phenomenon suggested that most of the carboxyl acid sites were occupied after 2 h, leading to very few remaining reactive sites for the further polymerization of Ani. The trend for the transparencies was similar to those for the conductivities. The transparency decreased slightly after polymerization for 2 h; the conductive patterned PANI film having a line width/space of 5 μm/5 μm exhibited the best transparency.

CONCLUSION

We have developed a new bottom-up technique for the preparation of organic transparent conductive films through *in situ* polymerization; the optimal conductivity of the PANI film was ca. 10 S/cm. Using this process, PANI was readily patterned to formed a continuous conducting pathway without blending with another matrix. The conductivity and thickness of the PANI film were controlled by varying the carboxylic acid content of the photoresist and the polymerization time. The conductivity of the patterned PANI films was not influenced by the resolution of the pattern; the conductive patterned PANI film having a line width/space of 5 μm/5 μm

exhibited the best transparency. The conductivities of these PANI films are too large for them to be useful as high performance transparent conductive electrode; their applications are, therefore, limited to devices that do not require low electrical resistance (e.g., chemical and biological sensors).[24,25]

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