Electrochromic Pattern Formation by Photo Cross-linking Reaction of PEDOT Side Chains

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Abstract: An electrochemically and photochemically polymerizable monomer, 2-((2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxy)ethyl methacrylate (EDOT-EMA), was explored for patterning of poly(3,4-ethylenedioxythiophene) (PEDOT) via side chain cross-linking. The polymer from EDOT-EMA was deposited electrochemically to produce polymeric EDOT (PEDOT-EMA), which was directly photo-patterned by UV light as the side EMA groups of PEDOT-EMA were polymerized to give cross-linked EMA (PEDOT-PEMA). Absorption and FTIR studies of the UV-exposed film (PEDOT-PEMA) indicated that the photo-patterning mainly originated from the photo cross-linking of the methacrylates in the side-chain. After irradiation of the film, the conductivity of the irradiated area decreased from 5.6×10^{-3} S/cm to 7.2×10^{-4} S/cm, possibly due to bending of the conductive PEDOT channel as a result of the side chain cross-linking. The patterned film was applied to a solid state electrochromic (EC) cell to obtain micro-patterned EC cells with lines up to 5 μm wide.

Keywords: PEDOT, side chain cross-linking, electrochemical, photo-pattern, conductivity, electrochromic.

Introduction

Patterning of active polymer films at micro scales is important for the development of organic electronics, optics, and bio-engineering.[1,2] In particular, the micro-lithographic formation of conducting patterns is a key prerequisite for various practical applications, such as in integrated circuits, field-effect transistors, multichannel molecular recognition, region-specific cell growth or protein fixation, optical memory storage devices, and electroluminescent and electrochromic displays.[3-11] Several methods, including top-down and bottom-up patterning of polymers, have been suggested for the generation of conducting patterns[12] (e.g., plasma etching, micromolding, photolithography, printing techniques, self-assembly of block copolymers, and instability-induced patterning). These methods lead to increased control over the pattern resolution and conductivity, rendering them highly valuable methods for various micro- to nano-technological applications. The photolithography and plasma patterning of conductive copolymers have successfully been used to fine-tune conductive nanostructures; however, these methods require multi-step patterning processes including an etching process. Thus, tools to pattern conductive polymers in a predictable and simple manner are indispensable.

PEDOT has attracted considerable attention because it

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gives highly stable thin films with sufficient electrical conductivity for applications as an electrode in organic electronics after secondary doping.[13-17] The conductivity is highly sensitive to the structural change in PEDOT main chain, and structural distortion by dopants and any external stimuli affects the electrical conductivity of PEDOT. In this context, selective disconnection of the conducting channel by a photon method is of interest because it would provide a new and simple patterning method for PEDOT film. Several different approaches to create photolithographically defined patterns of poly-3-alkylthiophenes on insulating or conducting substrates has been reported.[18] Acrylate-functionalized 3-alkylthiophene copolymer produced negative-tone images by irradiating a spin-coated film of the polymer through a mask and then development of the latent image with chloroform. The photoinduced decrease in the solubility of the acrylate-functionalized 3-alkylthiophene copolymer is due to cross-linking of the acrylate side groups. A poly-3-alkylthiophene containing an acid-labile tetrahydropyranyl (THP) group in the side chain affords photolithography to pattern the material by acid-catalyzed removal of the THP group.[19,20]

Photocurable EDOT monomers could be interesting as it can induce high degree of cross-linking and can be combined with other monomers to tailor polymer properties. As an example, MDOT (EDOT-methylene methacrylate) was copolymerized and applied for photolithographic grating-pattern formation.[21,22] However, unlike the side chain func-

tionalized PEDOTs, studies on the EDOT modified photo-curable monomers are few.

In this paper, we report a simple dry procedure to generate high-resolution conductive patterns via a photo-induced polymerization of the side chain in conducting polymers using a EDOT modified photocurable monomer; we also describe the physicochemical characterization and application of the resulting surface patterns.

Experimental

Materials. 3,4-Dimethoxythiophene, 3-chloro-1,2-propanediol, *p*-toluenesulfonic acid monohydrate, 2-hydroxyethyl methacrylate, anhydrous toluene, anhydrous dimethylformamide, anhydrous methylene chloride and potassium carbonate were purchased from Aldrich Chemicals and used without further purification. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from TCI (Japan). 2-Chloromethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (CMEDOT) was synthesized according to the method reported in the literature.[23]

2-((2,3-Dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxy) Ethyl Methacrylate (EDOT-EMA). To two necked 50 mL flask equipped with N_2 purge was added CMEDOT (0.5 g, 2.6 mmol), 2-hydroxyethyl methacrylate (HEMA, 0.338 g, 2.6 mmol), K_2CO_3 (3.6 g, 26 mmol) and 30 mL of dry DMF. The solution was stirred at 60 °C. After 72 h, the solution was allowed to room temperature and resulting mixture was mixed with water and MC was added. Then organic layer was separated and washed with HCl (aq) and then with distilled water many times. After removal of the solvent, remaining crude product was isolated by chromatography to give yellow liquid as a final product (yield 65%). ^1H NMR (CDCl$_3$, 400 MHz): δ 6.34 (m, 2H, Th), 6.14-5.57 (m, 2H, C=CH$_2$), 4.38-4.35 (m, 2H, -OCH$_2$CH), 4.29-4.24 (m, 2H, O=C-OCH$_2$-), 4.16 (m,1H, -CHCH$_2$O-), 3.73-3.62 (m, 4H, -CH$_2$OCH$_2$-), 1.93 (s, 3H, -CH$_3$). FTIR (neat, cm^{-1}): 2939, 1716, 1633, 1479, 1429, 1369, 1180, 1242, 1060, 1016, 933, 759.

Electrochemical Polymerization. An anhydrous dichloromethane solution of tetrabutylammonium hexafluorophosphate (TBAP, 0.1 M) was prepared. Monomers were electropolymerized by successive scanning at a concentration of 0.01 M in the abovementioned dichloromethane/TBAP solution. The condition was composed of a three-electrode assembly equipped with ITO working electrode, stainless steel as the counter electrode, and an Ag/AgCl electrode as the reference electrode. Measurements were examined at room temperature. Electropolymerization of monomer (EDOT-EMA) was carried out for fabricating conductive thin films onto ITO glass in scanning between -1.2 and 1.7 V. The thickness of film depended on number of scanning cycles.

Patterning Method. Pattern formation was carried out using UV light with photomask coated Cr. The coated con-

ductive polymer on ITO glass was placed under the photomask and the gap between ITO glass and photomask was about 100 μm. The conductive polymer film was irradiated and after irradiation the irradiated area was bleached and showed patterns. The pattern size and shape were controllable by photomask having different pattern size and shape.

Preparation of Electrochromic Cell. Methoxy poly(ethylene glycol) 1000 monomethacrylate (MPEGM) (0.3 g), PEGDMe (0.6 g), triallyl-1,3,5-triazine-2,4,6-(1H, 3H,5H)-trione (0.072 g) were mixed. Lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$, 0.06 g) was dissolved to the above mixture and stirred for 2 h.[24] Electrochromic devices (ECDs) were assembled by introducing the optimized electrolyte solution between conductive polymer coated and patterned ITO glass and ITO glass. The space between two substrates was controlled by placing an insulating polyimide tape (60 μm).

Instruments. The electrochemical property was studied using an electrochemical analyzer (CH Instruments Inc, CHI624B). The UV-vis spectra were recorded for electrochemically polymerized films onto ITO glass with AvaSpec (AvaSpec-2048. Light source: AvaLight-DHS). The UV light (PowerArc UV100, 13.05 mW/cm^2) was used for irradiation. The morphology of the resulting polymer was measured with JEM 2100 (JEOL) transmission electron microscope (TEM). For the TEM measurement the conductive polymer films on ITO were peeled off and dispersed in a small amount of ethanol. Then the solution was dropped on copper TEM grid and the grid was dried for 2 days in desiccators. FTIR spectra were obtained from a Bio-Rad Digilab Division FTS-80. The ^1H NMR spectrum was determined by a Bruker ARX-400 spectrometer. The patterns in the conductive polymer films were examined by optical microscopy (Bimeince, USA) and a digital camera (Model: Canon Power Shot A640). Conductivity of the film was determined from the four-point method using, ALS CO. LTD, Japan.

Results and Discussion

Synthesis of a Photo Cross-linkable EDOT (EDOT-EMA) and Its Polymer (PEDOT-EMA). For formation of the conductive polymer pattern, 3,4-ethylenedioxythiophene (EDOT) was modified with a photo-reactive group. The monomer was synthesized from 2-chloromethyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (CMEDOT)[12] and 2-hydroxyethyl methacrylate (HEMA) (see Scheme I). The monomer (EDOT-EMA) was polymerized by bonding the thiophene units chemically or electrochemically to produce conductive polymers with a cross-linkable methacrylic unit in the side chain similar to the method reported in ref. 18, 21 and 22.

Cyclic voltammograms recorded during the electropolymerization of the monomer (EDOT-EMA, 0.01 M) solution on bare ITO electrodes are shown in Figure 1(a). During the initial anodic sweep, no Faradic current is apparent until
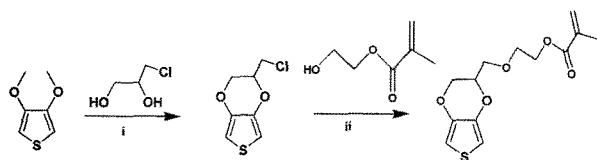
i: *p*-toluenesulfonic acid monohydrate/ toluene, reflux. ii: K_2CO_3/dry DMF, 60 °C.

Scheme I. Synthesis of the monomer, EDOT-EMA.

~1 V (vs. Ag/AgCl), at which the current increases significantly, corresponding to the onset of monomer oxidation and subsequent electropolymerization.[25] On the return sweep, polymerization continues at potentials higher than +0.80 V. This difference between the onset potential and the minimum potential required to sustain polymer growth creates a "nucleation loop," characteristic of the electropolymerization of conductive polymers.[26] The peak current at the new oxidation peak near 0.5 V and reduction peak at -0.3 V showed a continuous increase with continued cycling of the potential.

After three cycles of voltammetric scan from -1 to +1.8 V with a scan rate of 0.1 V/s, a blue-colored film of 70 nm thickness was deposited on an ITO film. The color intensified upon further cycles. The increase in thickness, as determined by a surface profilometer, and absorbance of the film at 601 nm were linearly dependent on the number of potential cycles up to 10-13 cycles, as shown in Figure 1(b). This result indicates that the thickness can be controlled by electrochemical polymerization at nanometer to sub-micrometer scales. After 13 cycles, the thickness and absorbance increase deviated from the linear dependence, possibly due to the nucleation of the polymers and inhomogeneous growth of the film.[26]

Photoreaction of PEDOT-EMA. The PEDOT-EMA film was bleached within a few minutes of UV irradiation with a

dose less than 2 J/cm². Absorption in the visible region was significantly decreased. As the visible bands are responsible for electronic conduction in PEDOT main chain, the spectral change indicates that the conduction paths are broken. The bleaching of the conductive polymer film indicates that the conductivity of the film is decreased by the photoreaction.

The conductivity of the polymer film on ITO glass was determined from an I-V curve by four-point probe measurement (Figure 2(a)). The electrical conductivity for the PEDOT-EMA film (0.76 μm in thickness) was 5.6×10^{-3} S/cm, comparable to the measured conductivity of the electrochemically synthesized PEDOT (3.9×10^{-3} S/cm) and reported values for an undoped PEDOT film ($3~6 \times 10^{-3}$ S/cm).[14]

The slope of the I-V curve for UV exposed area was smaller than the unexposed area, as compared in Figure 2(a). The conductivity of the UV exposed area was reduced to 7.2×10^{-4} S/cm. The conductivity of the polymer film was decreased upon exposure to light and the conductivity of the films with same thickness was same, within experimental error, under the same irradiation dose. The conductivity of the film was further decreased and reached a plateau, at which the photo cross-linking reaction of PEDOT-EMA was completed. Figure 2(b) shows evolution of the film conductivity change (σ_i/σ_o) against the irradiation dose, where σ_i is the conductivity at the corresponding light dose and σ_o is the conductivity of the film before UV exposure. For this experiment, an electrochemically deposited PEDOT-EMA film was scraped off from the ITO glass surface and loaded on a glass slide substrate. The conductivity of the film was steeply changed within 2.5 J/cm² and then saturated after light dose of 8.6 J/cm². Therefore the minimum energy for the conductivity change to pattern the film was estimated as 2.5 J/cm², which is similar dose for bleaching as described above. The conductivity decay was well correlated to the first exponential decay curve according to eq. (1):
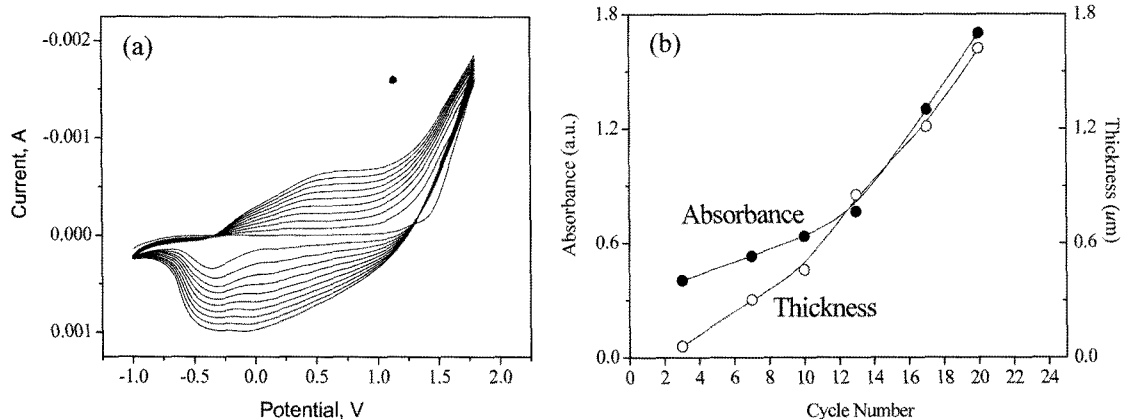

Figure 1. (a) Cyclic voltammograms for electropolymerization of EDOT-EMA with a scan rate of 50 mV/s, in an electrolyte solution of TBAP (0.1 M) in dichloromethane using Ag/AgCl as a reference. (b) Plot of the thickness and absorbance of the film against the number of potential cycles in Figure 1(a).
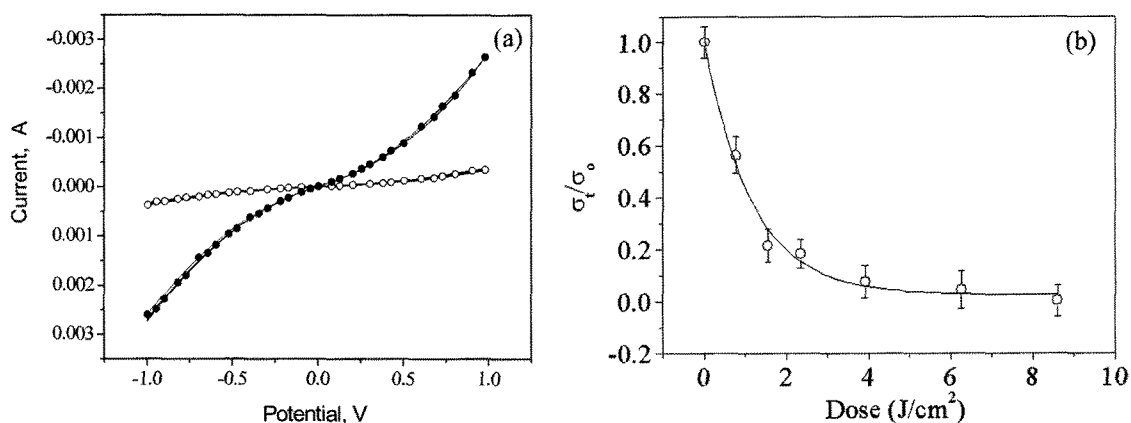
Figure 2. (a) I-V plot for a PEDOT-EMA film (thickness = 0.76 μm) before (●) and after (○) UV exposure between -1.0 V and 1.0 V, with a potential step increase by 0.1 V/s. (b) Conductivity change against dose of UV irradiation.

$$\sigma_t / \sigma_o = 0.98 \times \exp(-D/1.15) + 0.025 \qquad (1)$$

where D is the light dose (J/cm^2). Amperometric output is changed by a variety of molecular mechanisms, including charge localization, reduction in conjugation length, side chain charge perturbation, and segmental energy matching/ mismatching from adjacent redox-active sites.[27-35] It has been reported that the conductivity change after the photo cross-linking of the poly-3-alkylthiophene containing photoreactive end group was small.[18] However, in PEDOT-EMA, the content of photoreactive side chain is much larger than poly-3-alkylthiophene and thus the cross-linking at the side chain methacrylic groups may change the conduction channels and interpolymer interactions, to result in enhanced conductivity change. The conductivity change was also observed in PEDOT films functionalized with carboxylic acid side chains.[34]

Figure 3(a) shows FTIR spectra of the monomer, electro-chemically synthesized polymer, and UV-exposed polymer film. The peak at 3110 cm^{-1} for monomer is due to the 2,5-hydrogen atoms on the thiophene ring.[35,36] The peak at 3110 cm^{-1} was disappeared after electrochemical polymerization (dashed line). This result confirms the polymerization at the thiophene ring by the electrochemical method. The methacrylate transition[37] at the CH$_2$=CH- at 1637 cm^{-1} of the electrochemically deposited film showed similar intensity to that of the monomer, indicating that the methacrylate groups are intact during the electropolymerization. However, the CH$_2$=CH- at 1637 cm^{-1} of the methacrylate groups showed a red shift of about 15 cm^{-1} upon electropolymerization, possibly due to the steric congestion induced by the thiophene linkage. The peaks at ~2950 cm^{-1} can be attributed to the vibrational frequency of the C-H stretching of the methacrylates, and changed little after electrochemical polymerization.[38-41] The characteristic peak of the carbonyl transition (C=O) from the ester group was appeared as a large peak at 1720 cm^{-1} in all three samples. Thus the spectral region for C=O was cut in Figure 3(a) as its intensity was
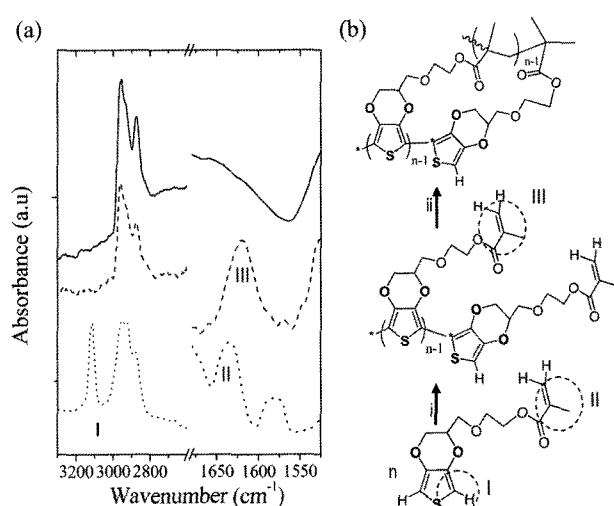
i: electrochemical polymerization; ii: photopolymerization.

Figure 3. (a) FTIR spectrum of the monomer (dotted), electro-chemically synthesized polymer (dashed), and then UV exposed polymer film (solid line). (b) Scheme of the polymerization for PEDOT-PEMA. i: electrochemical or chemical polymerization; ii: photo polymerization under UV light.

too large and intact in all samples.

As shown in Figure 3(a), the CH$_2$=CH- stretching intensity showed a dramatic decrease after UV exposure (solid line), thus confirming polymerization at the methacrylate groups. The peak at 1571 cm^{-1} is due to the conjugated C=C system, and is seen clearly in the film before UV exposure; however, the peak is not evident in the UV-exposed film. This finding indicates that UV exposure reduced the C=C conjugation and thus decreased conductivity of the film. Therefore, the observed spectral change confirms that the thiophene rings were polymerized electrochemically in the first step (Figure 3(b), i) and methacrylates were polymerized photochemically (Figure 3(b), ii). Although intra and

inter molecular cross-linking are possible for process ii, we depicted an intra molecular cross-linking reaction in Figure 3(b) as an example. Most of the thiophene unit is unlikely to be decomposed by UV light irradiation in the dose and wavelength range of this study because a number of stabilized states can exist in the PEDOT unit due to its π-conjugation in the long range.[42] The mechanism for the polymerization of PEDOT-EMA at each group could be described as shown in Figure 3(b).

As indicated by the FTIR study, the side chain methacrylate units of the conductive polymer are cross-linked. The photo-polymerization at the side chain forces structural changes in the thiophene main chain in order to covalently bond the methacrylate units in the polymer or between the polymer rods, to produce less conductive structures. To investigate if and how structural change occurs, the morphology of the film surface was characterized as described below.

The morphology of PEDOT-PEMA films was characterized with transmission electron microscope (TEM). Figure 4 shows TEM images of the conductive polymer film. Conductive polymer rods, similar to typical PEDOT rods,[43] are observed in the TEM image of the unexposed PEDOT-EMA sample (Figure 4(a)), which was collected after electrochemical polymerization and then loaded on a TEM grid. The polymer rods are straight, with an average diameter of ~90 nm. Surprisingly, the rods are curled and heavily bent in the UV-exposed sample, as shown in the TEM image in Figure 4(b). At greater magnification, the polymer rods appeared as linked as shown in Figure 4(b) (inset). The links must have originated from the non-conductive methacrylate units, and thus are irregular in shape and largely elongate.

Photo Patterning of PEDOT-EMA Films. We now consider one of the potential applications of the photo-induced conductivity change of the PEDOT-EMA film in patterning for displays. To pattern the conductive polymer film, a PEDOT-EMA film on ITO glass was irradiated with UV light through a photomask. Figure 5(a) and (b) shows the patterns generated from a photomask with line widths of
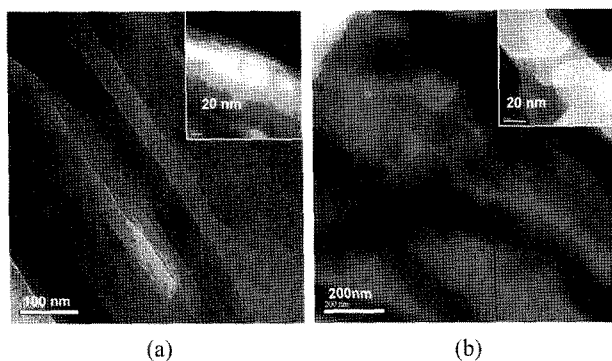
20 and 5 μm, respectively, in which the light-exposed areas appeared as bleached. The line resolution of the polymer film was limited to 5 μm though the photomask technique. These patterns were stable under ambient conditions.

Electrochromic cells were fabricated with the anode consisting of a patterned polymer layer in contact with a solid polymer electrolyte layer, which was sandwiched between the patterned EC electrode and an ITO glass counter-electrode.[24] Upon application of + 2 V, the pattern was erased because the conductive polymer was oxidized. The pattern re-appeared upon application of – 2 V, returning the color of the original pattern as the conductive polymer was reduced. Figure 5(c) and (d) show photographs of a patterned electrochromic cell under an optical microscope for bleached and colored state, respectively. The electrochromic property of the patterned EC cell was reversible within step potential of ± 2 V. During the alternative voltage application, electrochromic switching in the UV exposed area was not detectable. This result indicates that the photopatterning of the PEDOT-EMA through side chain cross-linking is an effective method for EC patterning. It is noteworthy that the conductivity difference of the shaded region (5.6×10^{-3} S/cm) to the UV exposed area. (7.2×10^{-4} S/cm) is not large but enough to give electrochromic contrast between the two region. Further studies on photo curable EDOT derivatives are in progress to improve pattern resolution and quantify the charge perturbation through side chain cross-linking of conducting polymers.
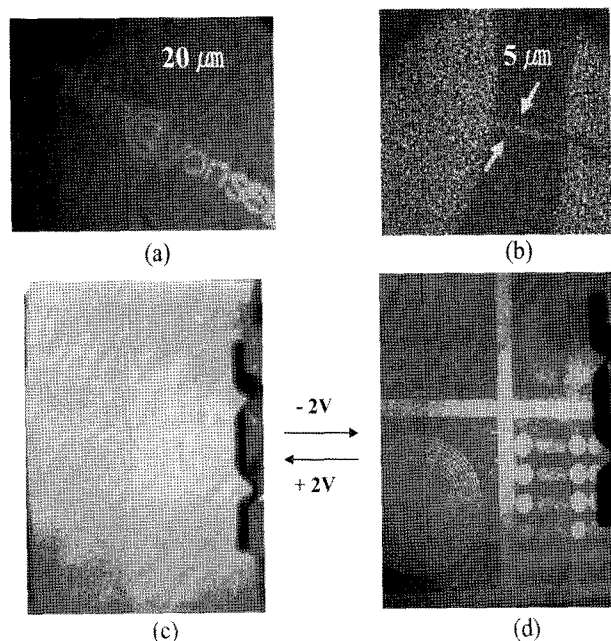

(a)   (b)

Figure 4. TEM and high-magnification TEM views in the inset for UV unexposed (a) and exposed sample (b). The scales are given as bar.

(a)   (b)

(c)   (d)

Figure 5. (a) An optical microscopic image of a patterned polymer film from electrochemically deposited PEDOT on an ITO glass in 20 μm and (b) 5 μm wide line. (c) Photographs of the patterned EC cell after application of potential from + 2 V to (d) -2 V for 10 sec.

Conclusions

We have demonstrated that PEDOT can be patterned directly by photo-sawing of side chains to afford micro-patterns of a conductive polymer circuit. FTIR study evidently showed cross-linking of the methacrylate side chains of the polymer after UV irradiation. TEM images of the UV-exposed polymer film showed that the conductive polymer rods are bent, indicating that conduction paths are broken, thereby decreasing the electrical conductivity. These patterns were applied to an electrochromic cell, which showed reversible electrochromic patterns. This constitutes an important step toward the fabrication of advanced simple method of conductive pattern formation useful in optoelectronic devices, including electrochromic and electrochemical light-emitting and solar cells.

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