Micropatterning of Conducting Polymer Thin Films on Reactive Self-assembled Monolayers

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Organic semiconducting materials, such as π-conjugated polymers, continue to be the subject of intense research due to their unique optical and electronic properties.[1,2] The processing advantages, together with the versatility of molecular structures and tunable physical properties, make these organic electroactive materials attractive for a wide range of applications ranging from electronic devices to mechanical actuators.[3–5] The development of polymer-based microelectronics and optoelectronics is based largely on simple and reliable methods that are available for patterning of high-definition micrometer and sub-micrometer scale features of these materials.[6] In addition to the traditional photolithography processing, various non-photolithographic patterning techniques including soft lithography,[7,8] ink-jet printing,[9] and screen printing[10] have been studied for the spatial deposition of conducting polymers. The non-photolithographic approach avoids the photopatterning process that often results in damage of the polymer structures and associated physical properties. Microcontact printing (μCP) is a soft lithographic method of depositing patterned self-assembled monolayers (SAMs) of compounds such as thiols and silanes onto gold and silicon substrates, respectively.[11] μCP of SAMs has also been used in conjunction with other techniques such as electropolymerization[12,13] and

the Langmuir–Blodgett (LB)[14] technique to yield conjugated polymer patterns, in which SAMs act as molecular resists to block the selective areas on the substrates. We report here a simple method for the generation of patterned conducting polymer films by directly utilizing the reactivity of functional groups on patterned SAMs. The well-known luminescent polymer, poly(phenylene vinylene) (PPV), has been used as a model structure in this work. PPV and its derivatives are being widely used as active matrixes for polymeric light-emitting diodes and have had a greater impact to date in the field of molecular electronics and optoelectronics.[15–18] For this work, a reactive alkanethiolate SAM presenting interchain carboxylic anhydrides was patterned by microcontact printing and served as a template for further deposition of amino-substituted poly(phenylene vinylene) (PPV) from solution. The PPV was expected to covalently bond to the surface through the feasible condensation reaction between amines and carboxylic anhydride groups of the SAM.

Scheme 1 outlines the synthetic approach to PPV with amino groups on side chains (polymer **II**). The precursor polymer (polymer **I**) was synthesized by the palladium-catalyzed Heck coupling reaction of *p*-divinylbenzene with dihalide **1**, which was prepared by the reaction of 2,5-diidohydroquinone with 5-[(*tert*-butoxycarbonyl)-amino]-1-pentyl bromide. Removal of the protecting BOC groups in polymer **I** was performed in THF with CF_3COOH as the acid.[19,20] Deprotection in HCl/dioxane was unsuccessful, resulting in black insoluble polymers. It was believed that the conjugated polymer backbone was destroyed under strong acidic conditions.[21] Polymer **II** is soluble in most common organic solvents, such as THF, chloroform, and DMF. GPC measurements in THF, using polystyrene as a standard, indicate a weight-average molecular weight (Mw) of approximately 30 kDa with a polydispersity of 2.13. The structures of the polymers were confirmed by spectroscopic studies and elemental analysis. In the ^1H NMR spectrum of polymer **II**, the chemical shifts of two vinyl protons appear at 7.17 ppm and those of aromatic protons appear at 7.24 and 7.51 ppm (details are provided as Supporting Information).

A poly(dimethylsiloxane) (PDMS) stamp with hollow squares (5 × 5 μm) was inked with 16-mercaptohexadecanoic acid in ethanol and placed in contact with gold surfaces using literature procedures.[22–24] The thickness of 16-mercaptohexadecanoic acid SAM is about 2 nm,

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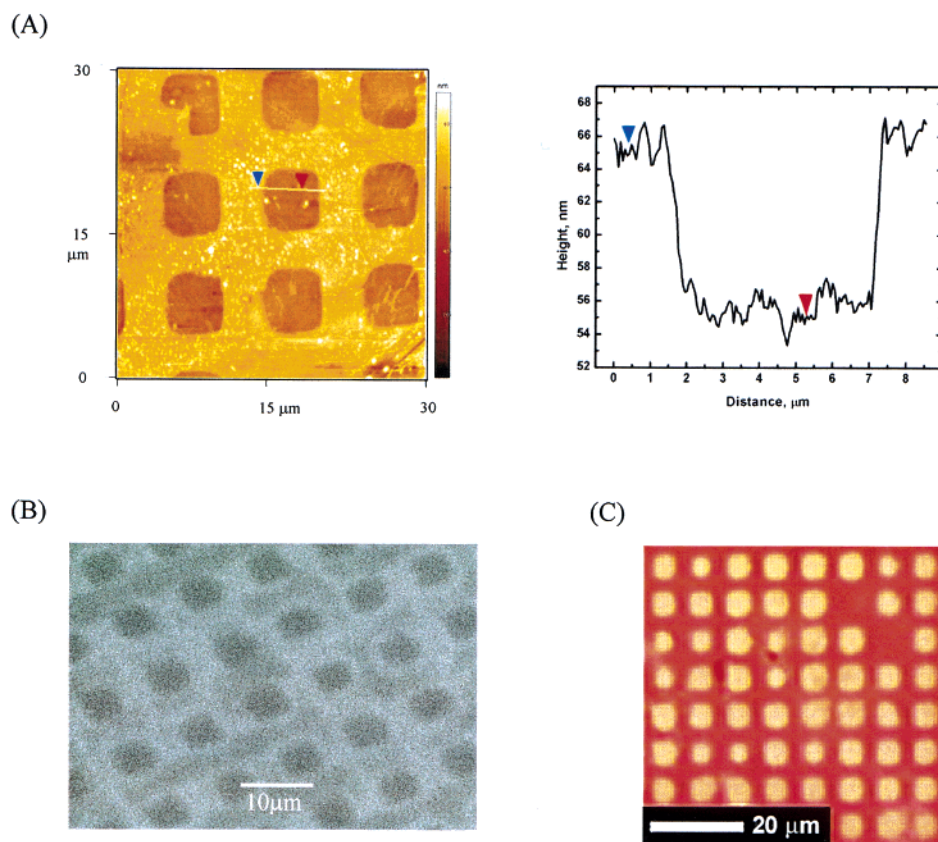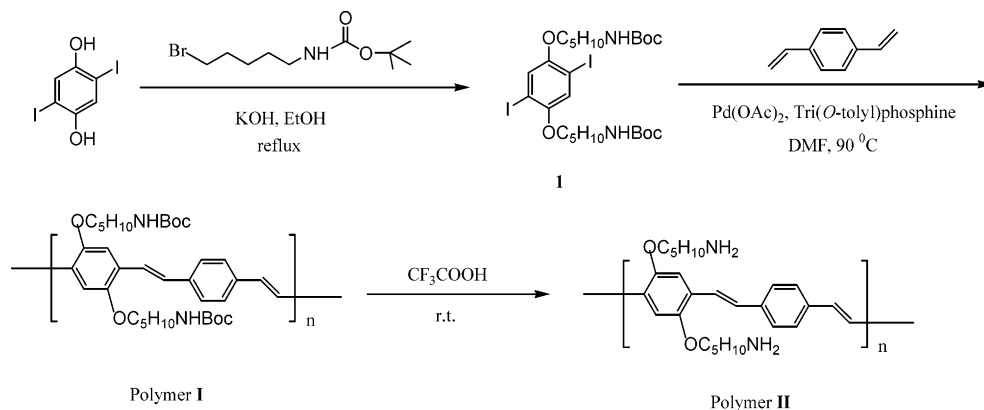(23) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498.

(A)

(B)

(C)

Figure 1. (A) Tapping-mode AFM image and section analysis (B) SEM image and (C) optical micrograph of the patterned PPV thin films.

Scheme 1. Synthesis of Amino-Substituted PPV

Polymer **I**

Polymer **II**

measured by tapping-mode atomic force microscopy (AFM). The patterned SAM of 16-mercaptohexadecanoic acid was treated with trifluoroacetic anhydride to generate a reactive SAM terminated with interchain carboxylic anhydrides.[25−27] The film was immersed in 1 wt % solution of polymer **II** in THF for 2 h, which leads to the immobilization of the polymer on the reactive areas of the surface. The film was then rinsed with THF and sonicated in CH_2Cl_2 to remove physisorbed materials before drying with nitrogen. As shown

in Figure 1, a well-defined pattern of PPV thin films was illustrated by AFM, scanning electron microscopy (SEM), and optical microscopy. AFM images indicate that edge roughness of the PPV micropattern is at the sub-micrometer scale (<500 nm). Line analysis in AFM suggests that the average thickness of the patterned PPV thin films is approximately 6−7 nm. This height corresponds to approximately 4 "monolayers" of polymer **II**. The optical microscopy image shown in Figure 1C indicates that the pattern exists over a large scale, 1 × 1 cm (not shown in full).

The interactions between polymer **II** and the SAM were analyzed by polarized external reflectance spectroscopy (EFTIR) and X-ray photoelectron spectroscopy (XPS). Figure 2 shows the EFTIR spectra of (A) the SAM presenting carboxylic acids, (B) the SAM presenting interchain carboxylic anhydrides, and (C) the chemi-

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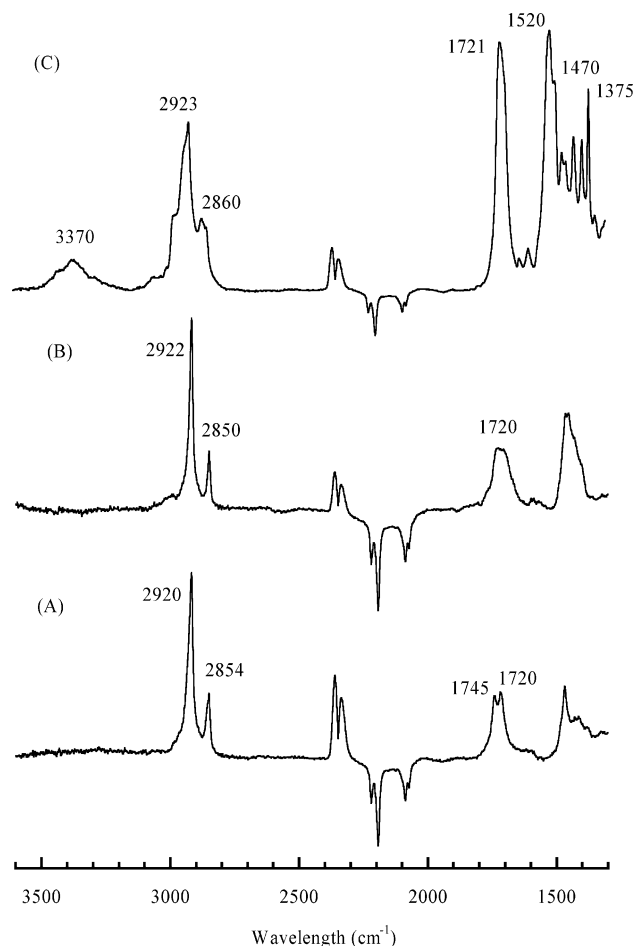
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Figure 2. EFTIR spectra of (A) the SAM presenting carboxylic acids, (B) the SAM presenting interchain carboxylic anhydrides, and (C) the chemisorbed PPV film. Absorption bands in the range of 2500−2000 cm^{-1} are due to the presence of residual CO_2 in the IR sample chamber.

Figure 3. UV/vis and photoluminescence spectra of polymer **II** in THF and as thin films.

sorbed PPV film. In the spectrum of C, a new peak, which corresponds to a N−H stretch of amides or amines, appears at about 3370 cm^{-1}. The hydrocarbon region of the spectrum provides additional support for the deposition of the polymer. The intensity of the absorption band for the C−H stretch is much stronger in spectrum C (2920 cm^{-1}) than those in SAMs (spectra A and B). In the range of 1900−1300 cm^{-1}, the key difference among spectra A, B, and C is that several fine absorption bands appear around 1500 cm^{-1}, which can be assigned to the amide I peak (C=O stretching) and amide II peak (N−H mixed mode).[28,29] The presence of these characteristic bands argues strongly that polymer **II** is chemically bound to the surface through the formation of amide bonds after the reaction between amines and carboxylic anhydrides. The formation of the covalent bond renders great stability of the pattern. For example, the PPV patterned film has been treated ultrasonically in solvents for several hours and the micropatterns keep intact. The XPS showed a strong N(1s) signal at 400.3 eV in chemisorbed PPV film. The

intensities of the Au peaks in the film are much weaker than those in the surface covered by SAMs, which also suggests that a polymer film was formed on the surface. Figure 3 shows the UV/vis and fluorescence spectra of polymer **II** in solution and as solid films. A typical absorption maximum due to the $\pi-\pi^*$ transition of the polymer backbone was observed at about 450 nm for polymer **II** in THF and slightly blue-shifted to 445 nm in the thin film. The fluorescence of the polymer thin film is red-shifted compared to the maximum in solution due to aggregation in the films.[30] Polymer **II** solution has a emission peak at ca. 505 nm and a shoulder around 530 nm, features typical of dialkoxy-substituted PPVs, while the thin film shows one broad emission at ca. 535 nm.

In summary, we have synthesized a new PPV polymer containing amino functional groups. This polymer has been covalently linked to surface-confined, reactive monolayers, which leads to a well-defined and robust micropattern over a large scale. We believe that this procedure based on a combination of μCP and chemical coupling reaction provides a simple and convenient route to pattern many other types of conducting polymers with a wide range of organic functionalities. The expansion of this approach toward complex multilayers of conjugated polymer systems and evaluation of patterned PPV films in light-emitting devices are in progress.

Supporting Information Available: The synthetic procedures and characterization data for polymers **I** and **II**, experimental procedures for the preparation of patterned reactive SAMs, and XPS data for SAMs and chemisorbed PPV film (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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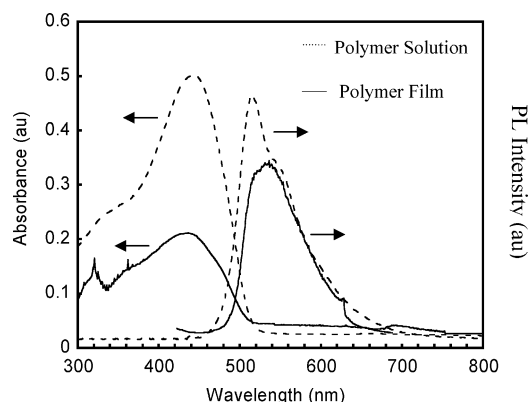
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