Novel Functionalized Conjugated Polythiophene with Oxetane Substituents: Synthesis, Optical, Electrochemical, and Field-Effect Properties

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Conjugated polymers are currently the subject of a broad research area, especially for the applications in electronic and electrochemical devices such as organic field-effect transistors (OFETs),[1] organic light-emitting diodes (OLEDs),[2] polymer solar cells (PSCs),[3] and sensors.[4] OFETs have drawn great attention recently because of their promising applications in integrated circuit, low-cost large area memories, smart cards, and driving circuits for large-area displays.[5] A notable feature of conjugated polymers lies in the versatility of their molecular structure which affords wide space to construct new polymers with improved properties. Among the conjugated polymers, polythiophene derivatives (PTs) attracted the most intensive studies. In order to improve the optoelectronic properties to meet the request for different applications, chemical modifications of PTs have been well performed.[6,7] One method to modulating the electronic properties of the conjugated polymers is the introduction of substituents with functional groups.[8]

Recent work reported that oxetane-substituted small molecules or polymers can be used in multilayer OLEDs[9,10] as hole transporting layer and liquid-crystal displays.[11] On the other hand, for high-performance OFETs-based integrated circuits and flat displays, fast operation and large aperture ratios are needed.[12] For these applications the channel length and total device size should be as small as possible. Thus, micron-sized polymeric patterns fabricated using conjugated polymer materials are highly desired. Photolithography, which is the technique of choice for the patterning of inorganic and organic electronic materials, remains the most attractive pattering technique in microelectronic technologies.[13] The cross-linkable oxetane groups can be polymerized cationically under UV illumination with a high polymerization rate and result in insoluble and stable material with high conversions. Furthermore, the polymerization process of oxetanes is accompanied by very small volume shrinkage and negligible modification of the electrical and optical properties of the material.[9−11] The oxetane-functionalized polymers would open up new opportunities in organic optoelectronics field.

On the other hand, almost all polymer semiconductors used chloroform, THF, or chlorobenzene as solvents during the fabricating procedure. The problem is that these solvents are not environmentally friendly but toxic or expensive, which limited the practical application including straightforward processing to large area substrates. Although considerable efforts have been taken in the development of new polymer semiconductors, up to now almost all of the known polymer semiconductors are still limited in normal solvents, and only a few can be truly dissolved in environmentally friendly and cheap solvents such as water or ethanol.[6e−g] Therefore, design and synthesis of new conjugated polymer semiconductors with special functional substituents are highly desirable.

In this paper we report on the use of oxetane-functionalized cross-linkable conjugated PTs as functional photoresists and semiconductors. The polymer could be patterned in a way similarly to ordinary photoresists using standard lithographic techniques. Optical and electrochemical properties of the polymer, in both the soluble and cross-linked forms, are studied. The possibility to prepare micrometer size patterns by a photocross-link method of this material is also explored. The performance of OFETs containing a cross-linked layer was compared with a reference device based on the non-cross-linked material. In our experiments, solution preparation, deposition, and device measurements were all performed in air conditions.

The oxetane-substituted conjugated polymer PTHOT was prepared by a Still coupling reaction; the synthesis route is illustrated in Scheme 1. Another analogous polymer PTHOBT was also synthesized as comparison (Figure 1). Monomer A was obtained from compound **4** by bromination of NBS under acetic acid conditions. The polymer PTHOT was obtained as a dark-red powder and can be easily dissolved in conventional organic solvents such as chloroform, toluene, and THF. Interestingly, the resultant polymer can be also dissolved in ethanol. The good solubility can be partially attributed to the rich of oxygen atom and steric hindrance arose from bulk side chains. However, the obtained analogous polymer PTHOBT could not be dissolved in ethanol probably due to its more rigid structure (^{1}H NMR spectra, Figure S1c in Supporting Information). Therefore, PTHOT was chosen to operate further investigation using THF and ethanol as solvents separately. The solubility of PTHOT was about 4 mg mL^{-1} in ethanol and about 15 mg mL^{-1} in THF. The regioregularity of the polymer was 82%, which was calculated from the ration of the integral area of the two peaks (4a, 4b) at 2.5−2.8 ppm in ^{1}H NMR spectra[14] (Figure S1b in Supporting Information). The photoinitiator [4-(2-hydroxy-3-butoxy-1-propoxy)phenyl]phenyliodonium hexafluoroantimonate (compound **6**) was synthesized according to the literature.[15]

UV−vis absorption spectra of the PTHOT in diluted THF solution (Figure 2) exhibited a main absorption with λ_{max} at 478 nm, while the absorption spectra of spun coated film showed main absorption with λ_{max} at 530 nm. The absorption showed a red shift from solution to film probably result from the stronger interchain interaction of the polymer in the solid state. In addition, this red shift in absorption from solution to film (50 nm) is smaller than those of regioregular polythiophenes such as regioregular P3HT (ca. 100 nm) and poly(didodecylquarterthiophene) (PQT-12; ca. 75 nm),[1h] suggesting that the PTHOT might have more twisted conformation due to the introduction of bulk oxetane groups. A similar result was found in spectra of PTHOBT (Figure S2 in Supporting Information). On the other hand, the film absorption exhibited a small blue shift (∼15 nm) after illumination under UV lamp ($\lambda = 365$ nm) for about 10 s with presence of photoinitiator. It indicated that after photochemically process the polymer showed shorter effective

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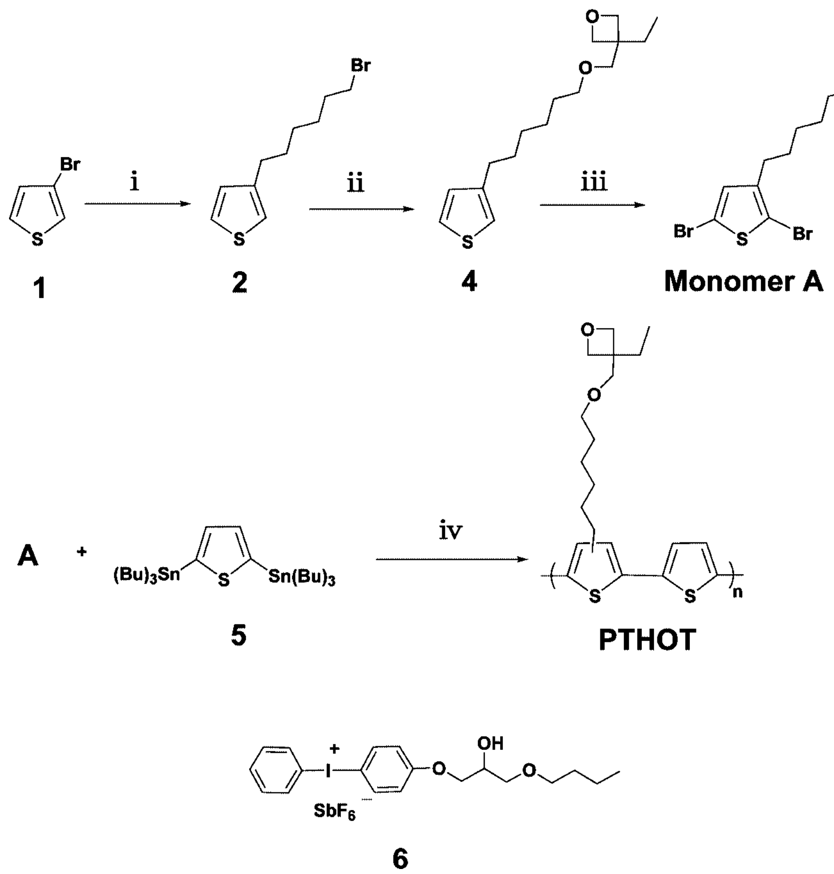
Scheme 1. Chemical Structure and Synthetic Route of PTHOT[a]



[a] (i) BuLi, hexane, THF, reflux, 6 h; (ii) 3-ethyl-3-oxetanemethanol (compound **3**), NaOH, hexane, reflux, 10 h; (iii) NBS, $CHCl_3$/HOAc, 2 h; (iv) $Pd(PPh_3)_4$, toluene, Ar, reflux, 12 h.

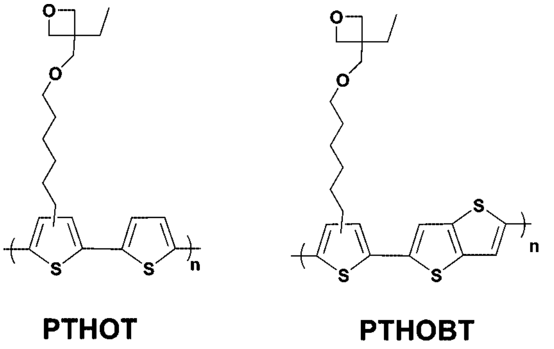


Figure 1. Chemical structures of the polymers with oxetanes.

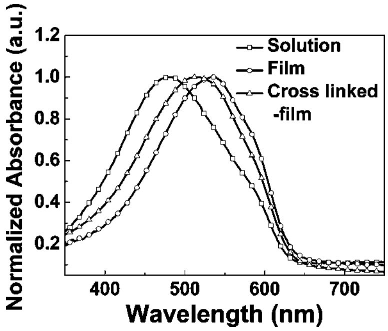


Figure 2. UV absorption spectra of the PTHOT in THF with the concentration of ca. 5.0×10^{-5} M; absorption of films before and after cross-linking by spin-coating THF solution on a quartz plate.

Table 1. Optical and Electrochemical Properties of the Polymer PTHOT before and after Cross-Linking

	UV−vis absorption spectra		CV		
polymer	solution λ_{max} (nm)	film λ_{max} (nm)	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)
PTHOT	478	530	−4.97	−2.63	2.34
cross-linked PTHOT	478[a]	512	−5.04	−2.73	2.31

[a] No change was found after UV illumination, probably due to the solution was very diluted and difficult to find difference.

conjugated length, probably due to the cross-linked structure make the main chain distorted slightly.

The electrochemical property of the polymer was investigated by cyclic voltammetry (CV). As shown in Figure S3 in the Supporting Information, the polymer showed similar reversible p-doping/dedoping (oxidation/rereduction) and n-doping/dedoping (reduction/reoxidation) processes before and after photo-cross-linking. The results of the electrochemical measurements are listed in Table 1. The HOMO level of the PTHOT, as determined by cyclic voltammetry, is about 5.0 eV, ~0.3 eV greater than that of regioregular P3HT (4.8 eV),[1h] measured under identical conditions. This probably contributed to the increasing of flexibility and reducing of π overlap for the backbone. This HOMO level matches well with the work function of gold (ca. −5.1 eV) and can ensure effective hole injection between the electrode and semiconductor and tend to improve the device performance. Interestingly, the electrochemical performance of the polymer was almost maintained after cross-linking, revealing that the photoprocess influences a little on the electronic property.

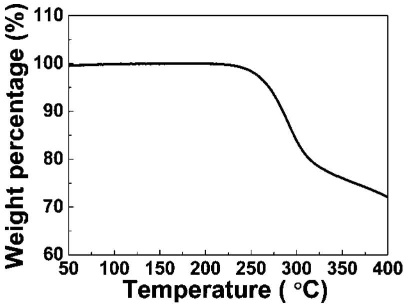


Figure 3. TGA plots of the PTHOT with a heating rate of 10 °C/min under an inert atmosphere.

Figure 3 shows the thermal gravimetric analysis (TGA) curve of PTHOT under a nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Thermal decomposition of PTHOT starts at about 230 °C, and 5% weight loss was recorded at 275 °C. The results indicate that the thermal stability of the polymer is enough for the application in optoelectronic devices. Differential scanning calorimetry (DSC) of the polymers did not show obvious peak before 200 °C.

The crystallization and structure order of the polymer films were investigated by atomic force microscope (AFM) and film X-ray diffraction (XRD). Figure S5 in the Supporting Information shows the AFM topographic images of PTHOT film (thickness: ~70 nm) by spin-coating THF solution (10 mg mL^{-1}) on *n*-octadecyltrichlorosilane (OTS)-modified SiO$_2$/Si substrate before and after cross-linking and annealing at 180 °C for 30 min. The non-cross-linked film showed morphology with small granule crystallite. In contrast, more rough morphology was found after the film was cross-linked. Figure S6 in the Supporting Information shows the AFM topographic images of PTHOT film (thickness: ~40 nm) by spin-coating ethanol solution (4 mg mL^{-1}) on OTS-modified SiO$_2$/Si substrate annealing at 100 and 150 °C for 30 min. The film annealed at 100 °C exhibited smoother and more homogeneous morphology. However, pin holes were observed when the film was annealed at 150 °C, which may be attributed to the sudden aggregate formation in the thin polymer layer. The XRD measurements were carried out for the thin films prepared on OTS-modified SiO$_2$/Si substrates by spin-coating polymer solutions. As shown in Figure S7 in the Supporting Information, the XRD patterns of the annealing films spin-coated THF solutions exhibited higher crystalline patterns than that of film spin-coated ethanol solutions. The XRD pattern of the polymer film spin-coated THF solutions before and after cross-linking exhibited crystalline patterns with a similar strong primary diffraction peak, which arose from the ordered interlayer stacking of the polymers (Figures S7b and S7c). However, the crystalline pattern from 20° to 25°, arising from $\pi-\pi$ stacking order, changed weak when the film was cross-linked. This probably attributed to the cross-linked more distorted conformation made the packed lamellar structures more loosely.

To start the cross-linking reaction, we blended the polymer with small amounts (<0.5 wt %) of compound **6** as a photoinitiator that donated a proton upon exposure to UV light. By exposing only certain areas of a thin polymer film through a shadow mask, the selectively film became insoluble. Afterward, the film was rinsed with THF, and only the unexposed regions were dissolved (Figure 4). Thus, this polymer effectively works as negative photoresist, and thin films of this polymer can be directly structured via photolithography.

The devices employing the polymer as semiconductor layers were fabricated by spin-coating ethanol and THF solutions of polymer onto OTS-modified SiO$_2$/Si substrates with top-contact

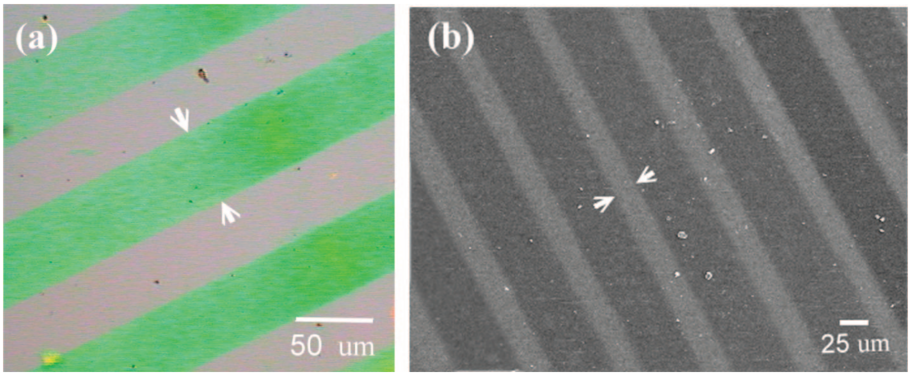


Figure 4. (a) Optical image of PTHOT spin-coated on Si/SiO$_2$ substrate irradiated using UV lamp (λ = 365 nm) under a mask and etched with THF (see the area which the arrow indicated) and (b) SEM images of PTHOT spin-coated on Si/SiO$_2$ substrate irradiated using UV lamp under another mask and etched with THF (see the area which the arrow indicated).

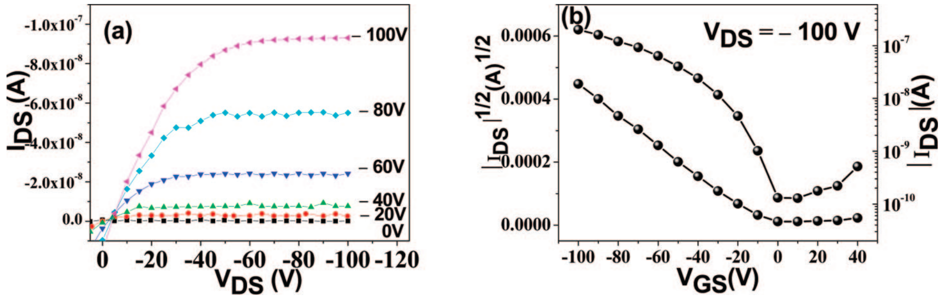


Figure 5. OFET characteristics of PTHOT device spin-coating ethanol solution (4 mg mL^{-1}) on OTS-modified substrate (channel length = 50 μm, channel width = 3000 μm) and annealed at 100 °C: (a) output curves at different gate voltages, (b) transfer curve in saturated regime at constant source-drain voltage of −100 V and square root of the absolute value of current as a function of gate voltage.

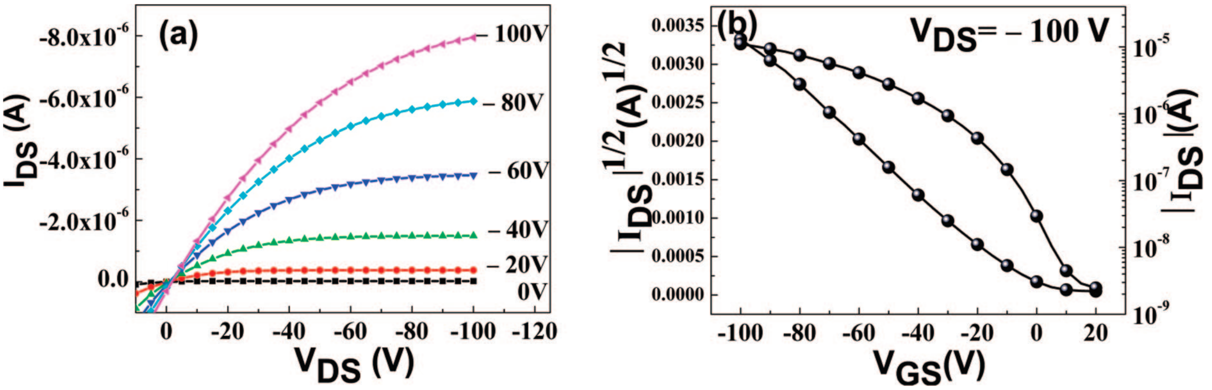


Figure 6. OFET characteristics of PTHOT device spin-coating THF solution (10 mg mL^{-1}) on OTS-modified substrate (channel length = 50 μm, channel width = 3000 μm) and annealed at 150 °C: (a) output curves at different gate voltages, (b) transfer curve in saturated regime at constant source-drain voltage of −100 V and square root of the absolute value of current as a function of gate voltage.

configuration. The devices were annealed at 100, 150, and 180 °C in vacuum for about 30 min and then measured in air conditions separately. They were found to exhibit typical p-type OFET characteristics and afforded very high hole mobility up to 7×10^{-3} cm^2 V^{-1} s^{-1} with an on/off ratio of 4.4×10^3 and threshold voltage of −4 V. The mobility, on/off ratio, and threshold voltage of the polymer devices are summarized in Table S1. The performance of annealed films (spin-coating THF solutions) can be found to improve obviously compared with that of films without thermal treatment, probably due to the formation of more highly crystalline morphology through annealing. The output and transfer characteristics of devices based on PTHOT film using ethanol solution annealed at 100 °C are shown in Figure 5 and using THF solution annealed at 150 °C are shown in Figure 6. The performance improved obviously when the solvent changed from ethanol to THF. This phenomenon is probably attributed to the different film morphology, which has been showed in the AFM images. In terms of carrier mobility, there is a small drop when the film was cross-linked and rinsed with THF, which is probably attributed to the decrease of the effective conjugation of backbone and increase of trapping density that arose from the remaining photoinitiator. This finding suggests that the introduction of cross-linkable groups is indeed a delicate balancing act: almost inevitably, this structural feature leads to a distortion of the polymer backbone, which comes at the expense of reduced charge mobility. It appears that the design of polymers is indeed hardly optimized, and these aspects need to be carefully balanced. The development of new substituted conjugated polymers which have the ability to charge transfer while limiting geometric distortion should therefore be a fruitful endeavor. Although the carrier mobility of PTHOT device is not as good as those of the best devices such as regioregular poly(3-hexylthiophene) (0.01−0.1 cm^2 V^{-1} s^{-1})[16] or some polymers with fused rings,[1b−h] it is among the best performance of OFETs based on the regiorandom polymers reported so far. The formation of a solid, stable, insoluble, and semiconducting layer will allow easy incorporation of this material in actual device structures. It was believed that this kind of functionalized conjugated polymers will open new opportunities for optoelectronics in the future.

In conclusion, a novel cross-linkable and ethanol soluble conjugated polythiophene derivative PTHOT with oxetane moieties attaching to the polymer backbone via an alkyl spacer was successfully synthesized by a facile synthesis method. The polymer was characterized carefully and photopatterned under UV in the presence of a photoinitiator. We attempted to apply this concept to OFETs, and the devices were fabricated by spin-coating ethanol and THF solutions separately. To our knowledge, there was few of polymer FETs to use environmental friendly solvent in the fabrication process. Further attention should be paid to this aspect. Importantly, the cross-linked film exhibited similar optical and electrical performance with non-cross-linked films. Therefore, this simple patterning technology for solution processed polymer semiconductors can provide not only microsized patterned areas but also high-performance devices. Consequently, we propose that this approach, which can be extended to a wide range of conjugated polymers, can be useful for the fabrication of micron-sized OFETs and may yet play a role in future organic electronics manufacturing efforts. The investigation of microelectronics is underway, and further improvements were expected with optimized conditions.

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Supporting Information Available: Experimental details, synthesis of the monomers and polymer, instrumentation and characterization procedures, ^{1}H NMR of the monomer and polymers, UV−vis absorption spectra of the PTHOBT, CV of the PTHOT films, TGA plots of the PTHOBT, AFM images, XRD patterns, and OFET performance. This material is available free of charge via the Internet at http://pubs.acs.org.

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