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Synthesis and Properties of Polymer Having Electronegative Terthiophene Pendants Based on Cyclopenta[*c*]thiophene

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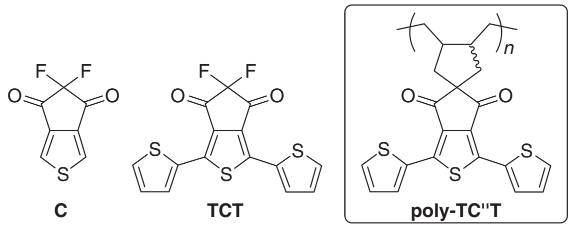
We have designed a new pendant-type polymer having an electronegative terthiophene at pendant positions. This polymer was successfully synthesized by the combination of Stille coupling reaction and palladium-catalyzed cyclopolymerization. To investigate the properties of the polymer, electronic absorption and fluorescence spectra as well as cyclic voltammogram were measured.

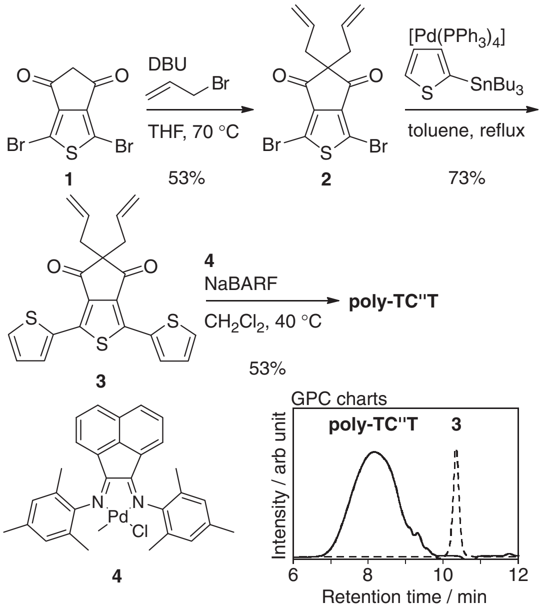
Development of π-conjugated systems can be realized by versatile protocols of transition-metal-catalyzed cross-coupling reactions.[1,2] Thiophene-based oligomers and polymers are extensively investigated π-conjugated systems because of their applicability to electronic materials such as organic field-effect transistors (OFETs) and photovoltaic devices (OPVs).[3] The majority of such application has been devoted to hole-transporting (p-type) organic semiconductors. On the other hand, the investigation of electron-transporting (n-type) π-conjugated compounds, which are an essential component for realizing organic complementary circuits, has been limited.[4] This is due to the difficulty of molecular design aimed at lowering the lowest unoccupied molecular orbital (LUMO) energy level. Previously, we have reported an electronegative terthiophene **TCT**, which contains difluorodioxocyclopenta[*c*]thiophene **C** as an electron-accepting central unit (Figure 1).[5] Owing to the ring annelation with cyclopentene, the **C** unit has the advantage of enhancing electronegative character without disturbing effective conjugation. Furthermore, we have revealed that solution-processable n-type OFET materials involving the **C** unit showed moderate electron mobility.[6] For further improving the OFET characteristics, it is important to control molecular ordering in the solid state while maintaining low LUMO energy level. We thus focused on the design of a pendant-type polymer incorporating electronegative π-conjugated oligothiophenes. This strategy is based on the followings: (i) electronegative characteristics of structurally defined oligothiophenes can be fine-tuned by modification of the electron-accepting unit; (ii) the distance between neighboring oligothiophenes in the polymer can be controlled by the design of connecting groups; (iii) furthermore, solubility of polymers toward organic solvents are ensured by the presence of connecting alkyl groups. To realize this strategy, we have utilized the palladium-catalyzed cyclopolymerization of 1,6-diene[7] and synthesized new electronegative polymer **poly-TC″T** (Figure 1). Herein, we present the synthesis and properties of pendant-type polymer having electronegative terthiophenes at pendant positions.



C **TCT** **poly-TC″T**

Figure 1. Chemical structures.

The synthetic route to the target polymer is shown in Scheme 1.[8] Allyl-substituted thiophene **2** was obtained by the reaction of **1**[9] with allyl bromide in the presence of DBU. The key monomer unit **3** was synthesized by the palladium-catalyzed Stille coupling reaction of **2** with 2-tributylstannylthiophene in a yield of 73%. Finally, cyclopolymerization of **3** in the presence of a catalytic amount of Pd diimine complex **4** and NaBARF (BARF: $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$) at 40 °C gave a target polymer **poly-TC″T**, which exhibits moderate solubility in organic solvents such as chloroform and fluorobenzene. The resulting polymer was purified through precipitation from methanol, followed by preparative gel-permeation chromatography (GPC). The number-average molecular weight (M_n) of this polymer was determined by analytical GPC using a polystyrene standard to be 5.6 kg mol^{-1}, corresponding to a degree of polymerization of ca. 14 with a polydispersity index of 1.48.



Scheme 1. Synthesis of **poly-TC″T** and analytical GPC charts.

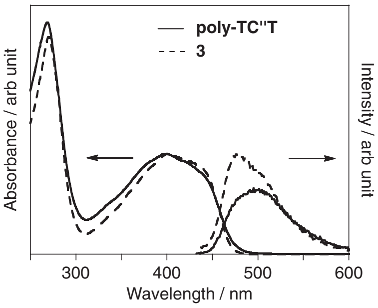


Figure 2. UV–vis spectra and fluorescence spectra with excitation at absorption maximum in chloroform.

Table 1. Photophysical[a] and electrochemical data[b]

Compds	λ^{abs}/nm	λ^{em}/nm	$E^{\mathrm{red}}{}_{1/2}$/V	$E_{\mathrm{p.c}}$/V
poly-TC″T	400	501	−1.82	−1.88
3	402	479	−1.84	−1.90
TCT[c]	467	535		−1.34[d]

[a]In $CHCl_3$. [b]In C_6H_5F, 0.1 M $TBAPF_6$, V vs. Fc/Fc^+. [c]Ref. 5. [d]Irreversible.

We investigated the photophysical properties of the synthesized polymer. Figure 2 shows the electronic absorption and fluorescence spectra of **poly-TC″T** and **3** in chloroform. Table 1 collected the maximum wavelengths. To avoid the influence of intermolecular interactions, the concentrations of solutions for all fluorescence experiments were adjusted to yield an absorptivity of $A < 0.1$ in the absorption spectra. The UV–vis absorption spectrum of **poly-TC″T** showed an absorption peak corresponding to the π–π^* transition band of the pendant units at 400 nm, whose profile is essentially unchanged from that of the absorption spectrum of **3**, indicating that the electronic properties of the π-conjugated system are maintained even after polymerization. On the other hand, the maximum emission wavelength of **poly-TC″T** is red-shifted as compared to that of **3** with decreasing the relative intensity. This phenomenon is attributed to the occurrence of intramolecular interactions between neighboring terthiophenes in the polymer.

To judge the suitability as electron-transporting materials, the electrochemical properties of **poly-TC″T** and **3** were studied by cyclic voltammetry. Figure 3 shows cyclic voltammograms (CVs) of these compounds in fluorobenzene containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$), and their electrochemical data are summarized in Table 1. The reported potentials are relative values to the redox couple of ferrocene/ferrocenium (Fc/Fc^+). The CV of **poly-TC″T** showed reversible reduction wave with the reduction potential of −1.88 V. This value is almost identical with that of **3** (−1.90 V), indicating that the difference between allyl groups and spiro-cyclopentane ring has little influence on the electrochemical properties. Importantly, the appearance of the reduction process implies that the cyclopenta[*c*]thiophene unit contributes to increase the electron affinity. However, the reduction potentials of these compounds are negatively shifted as compared to that of **TCT** (−1.34 V) because of the absence of electron-withdrawing fluorine atoms. The resulting weakened donor–acceptor–donor configuration in **poly-TC″T** and **3** caused the blue shift of absorption maxima relative to that of **TCT** (Table 1).

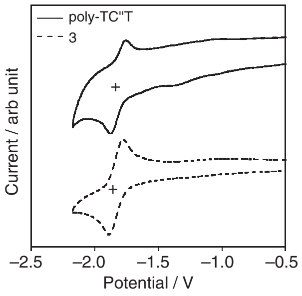


Figure 3. CVs of **poly-TC″T** and **3** in fluorobenzene containing 0.1 M $TBAPF_6$ at a scan rate of 100 mV s^{-1}.

In summary, we have successfully designed and synthesized pendant-type polymer incorporating dioxocyclopenta[*c*]thiophene-based terthiophenes. The photophysical measurements indicated intramolecular interactions between terthiophenes in the excited state. Electrochemical measurements revealed the electron affinity of the developed polymer. Our preliminary results make this polymer a candidate for n-type solution-processable OFET materials. Further investigation on film-forming properties of **poly-TC″T** as well as the molecular design to decrease the LUMO energy level is underway in our laboratory.

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