

# Poly[3-(5-octyl-thienylene-vinyl)-thiophene]: A side-chain conjugated polymer with very broad absorption band†

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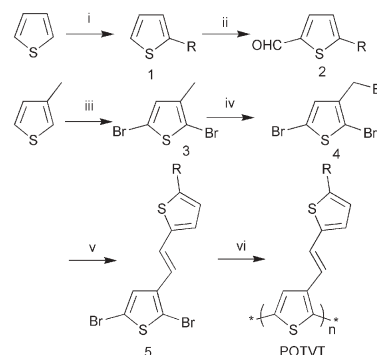
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A novel polythiophene derivative, poly[3-(5-octyl-thienylene-vinyl)-thiophene] (POTVT) with conjugated thienylene vinyl side-chain, was synthesized, and the POTVT film shows a very broad absorption band-width covering from 300 nm to 700 nm after thermal annealing at 130 °C for 10 min.

Polythiophenes (PTs) are very important conjugated polymers that can be used as optoelectronic polymer materials in many fields.<sup>1</sup> To improve their properties and explore the full application potential of the materials, chemical modifications of PTs have been actively performed.<sup>2</sup> Some of this work has focused on changing the band gap of PTs. As we know, the band gap of conjugated polymers is related to the effective conjugation length and the functional groups on the conjugated chains of the polymers. For this purpose, some PT derivatives were synthesized, such as PITN<sup>3</sup> and poly(3-alkoxythiophene)s.<sup>4</sup> The band gap of these PTs was reduced effectively by enlargement of the conjugated system or by alteration of functional groups on the conjugated chain.

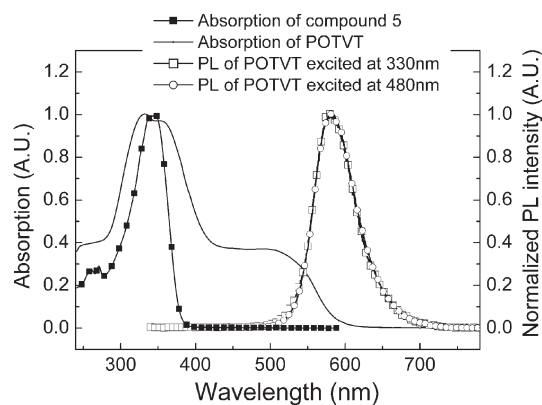
We have synthesized a side-chain conjugated PT derivative with phenylene vinyl side chains for improving the absorption of PTs.<sup>5</sup> In this paper, we designed a new side-chain conjugated PT derivative: (poly[3-(5-octyl-thienylene-vinyl)-thiophene]), POTVT, intending to reduce its bandgap. The synthesis route and structure of POTVT are shown in Scheme 1. Main chain of POTVT was linked with a 5-alkylthienyl through a *trans* carbon to carbon double bond (which was proved by <sup>1</sup>H NMR as shown in Fig. S1 in ESI†) by the Honor–Emours reaction. The polymerization was performed by the Grim method,<sup>6</sup> and the product is a dark-red powder with number-average molecular weight of 34 kg mol<sup>-1</sup>, and polydispersity of about 2. TGA result (see Fig. S2 in ESI†) indicates that the polymer of POTVT is stable in opening atmosphere below 280 °C.

Fig. 1 shows the absorption and PL spectra of POTVT chloroform solution. There are two absorption peaks located at *ca.* 350 nm and 510 nm respectively. In comparison with the absorption spectrum of monomer **5** (also shown in Fig. 1), obviously, the absorption peak in UV range results from the conjugated side-chains while that in the visible range corresponds to the  $\pi$ - $\pi^*$  transition of the conjugated main chains. The PL spectra of the polymer in chloroform solution were measured with



**Scheme 1** Synthesis route and structure of POTVT. i) *n*-C<sub>4</sub>H<sub>9</sub>Li, THF, rt, 1 h, then *n*-C<sub>8</sub>H<sub>17</sub>Br, 6 h; ii) *n*-C<sub>4</sub>H<sub>9</sub>Li, THF, rt, 1 h, then *N*-carbaldehyde-piperidine, 6 h; iii) NBS, THF, rt, 1 h; iv) NBS, BPO, CCl<sub>4</sub>, reflux, 3 h; v) compound 4, P(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, 160 °C, 2 h, then NaOCH<sub>3</sub>, DMF, compound 2, 30 min; vi) CH<sub>3</sub>MgBr, THF, reflux, 1 h, then Ni(dppp)Cl<sub>2</sub>, 30 min.

the excitation at two wavelengths of 330 nm and 480 nm respectively, corresponding to the two absorption peaks. In order to avoid interchain interaction, the concentration of the solution was very low and its absorbance was only about 0.03. Interestingly, as shown in Fig. 1, the PL spectra excited at the two wavelengths are the same, which indicates that there is a thorough intramolecular energy transfer of the excitons from the conjugated side chains to the main chains when the polymer is excited at 330 nm.



**Fig. 1** Absorption spectra of POTVT and compound **5** solutions in chloroform and photoluminescence spectra of POTVT solution in chloroform excited at 330 nm and 480 nm respectively.

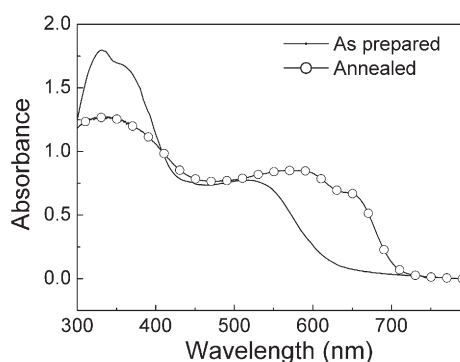
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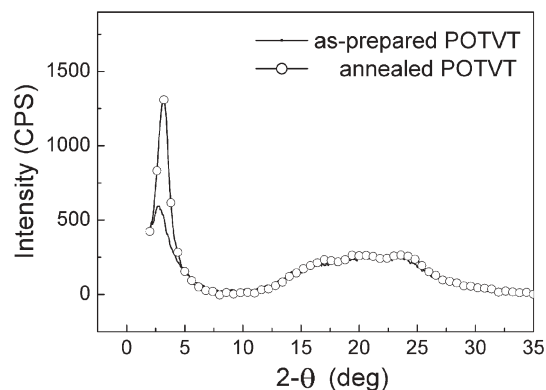
† Electronic supplementary information (ESI) available: experimental section, hole mobility measurement and photovoltaic properties. See DOI: 10.1039/b516576h

The absorption spectra of POTVT film are shown in Fig. 2. The spectrum of the as-prepared film shows two absorption peaks at *ca.* 344 nm and 520 nm respectively. In comparison with the absorption of POTVT solution (see Fig. 1), the absorption peak of the film in visible region red-shifted by *ca.* 10 nm. Very interestingly, after the film was annealed at 130 °C for 10 minutes, the visible absorption peak extended in the longer wavelength direction and broadened greatly, as shown in Fig. 2. The absorption of the annealed film covers a very broad wavelength range from 300 nm to 700 nm. The band gap of the polymer film is reduced from 2.03 eV to 1.77 eV after the thermal annealing. During the process of annealing, the color of the film changed from red to purple and then even to black. This kind of thermochromism phenomenon has been observed in other PTs,<sup>7</sup> but such a great spectrum change as that of the POTVT film has not been reported. In addition, the UV absorption peak at *ca.* 344 nm declined for some extent, while the visible absorption peak increased a little after the thermal annealing. The thermochromism could be explained as follows: Since the big planar side chains of thienylene-vinyl group are attached to every thiophene unit of POTVT, when the film was formed by evaporation of solvent, there may exist some steric hindrance of the side-chains on the alignment of the polymer main chains. However, when the film was thermally annealed, the polymer chains could rearrange to form a more regular morphology. So the conjugation of the polymer chains could be extended, and the band gap of the polymer film is reduced.

In order to investigate the structural change after the thermal annealing, X-ray diffraction analysis of the powder sample of POTVT was performed before and after the thermal treatment, as shown in Fig. 3. The as-prepared polymer exhibited a weak XRD peak at  $2\theta = 2.74^\circ$  (corresponding to an interlayer *d*-spacing<sup>8</sup> of 3.17 nm), and the annealed sample exhibited an enhanced diffraction peak at  $2\theta = 3.18^\circ$  (corresponding to a *d*-spacing of 2.77 nm). The interlayer *d*-spacing of the sample was reduced by 0.4 nm after the thermal annealing. The stronger XRD peak and smaller *d*-spacing of the thermally annealed sample indicate that the crystalline structure and ordering of the polymer chains were improved obviously after the thermal treatment. Probably, the heat treatment helps the polymer chains re-aligning and improves co-planarity of the polymer chains, which makes the *d*-spacing shrink and enhances the ordering structure. In addition, the improved ordering structure of the polymer chains should benefit



**Fig. 2** Absorption spectra of POTVT film spin cast from THF solution (solid line) and the film annealed at 130 °C for 10 min (rings).

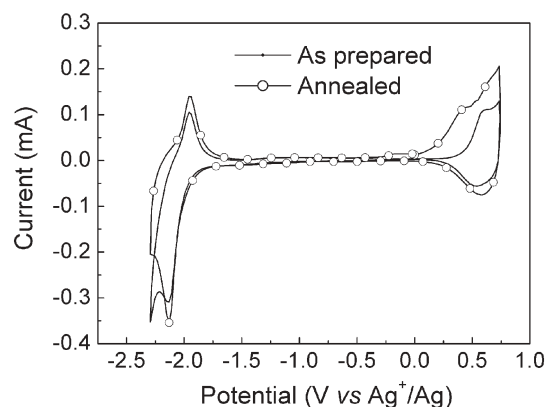


**Fig. 3** XRD patterns of POTVT powder precipitated from chloroform.

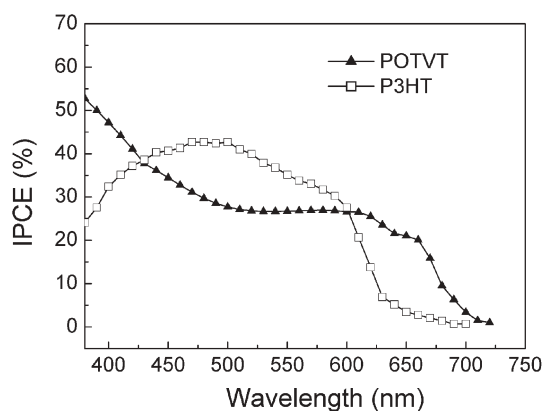
the extension of the conjugation length and decrease the band gap of the polymer. The interlayer *d*-spacing of the annealed POTVT is considerably larger than the 1.64 nm *d*-spacing of P3HT,<sup>8</sup> indicating that the bigger side-chains in POTVT make the interlayer *d*-spacing larger.

To check if there was some irreversible structural change during the thermal treatment, we dissolved the annealed sample in chloroform, and measured the absorption spectrum of the obtained solution. It was found that the solution possesses an identical absorption spectrum as that in Fig. 1 of the original POTVT solution. The result indicates that no chemical reaction occurred during the thermal treatment. So we think that the red-shift of the film absorption spectrum after the thermal annealing should result from the steric rearrangement of the polymer chains and the extension of the conjugation length of POTVT.

Reduction of band gap of conjugated polymers could be due to depression of LUMO or rise of HOMO. Cyclic voltammetry is often utilized to measure the HOMO and LUMO energy levels of the conjugated polymers.<sup>9</sup> To investigate the electronic structural change of the polymer after thermal annealing, we carried out cyclic voltammetry for the polymer film before and after the thermal treatment. As shown in Fig. 4, after annealing, the reduction onset potential remains unchanged, while the oxidation onset potential is decreased from 0.37 V to 0.12 V. The results indicate that the LUMO level of POTVT remains unchanged



**Fig. 4** Cyclic voltammograms of POTVT film on platinum electrode in 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub>-CH<sub>3</sub>CN solution for the as-prepared film (solid line) and the thermal annealed film (rings).



**Fig. 5** Input photon conversion efficiency of polymeric photovoltaic cell with structure of ITO/PEDOT:PSS/POTVT or P3HT:PCBM(1 : 1wt/wt)/Ca/Al.

while its HOMO level shifts upwards by 0.25 eV and the bandgap is reduced by 0.25 eV after the thermal annealing. The 0.25 eV bandgap reduction measured by the cyclic voltammetry agrees with the red-shift of the absorption spectrum for the thermal annealed samples.

Charge carrier mobility is another important parameter for the applications of the conjugated polymers. With good co-planarity and stronger intermolecular interaction of POTVT, we could expect a higher mobility. We measured the hole mobility of POTVT by the space-charge-limited current (SCLC) method<sup>10</sup> with a device structure of ITO/PEDOT:PSS/POTVT/Au. The hole mobility obtained in the thermally annealed POTVT film is *ca.*  $3.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  (see Fig. S3 in ESI<sup>†</sup>), which is a higher value among conjugated polymers.

In order to check if the broad absorption band of POTVT does make a contribution to the photoelectronic conversion in a polymer solar cell (PSC), the PSC device based on the blend of POTVT (as electron donor) and [6,6]-phenyl- $\text{C}_{60}$  butyric acid methyl ester (PCBM) (as electron acceptor) was fabricated with a weight ratio of POTVT : PCBM = 1 : 1. As a control, the device based on P3HT (which is the most conventional polythiophene derivative used in PSC) and PCBM was also fabricated with the same polymer to PCBM weight ratio. Fig. 5 compares the input photon to converted current efficiency (IPCE) of the two devices. The IPCE plot of the PSC based on POTVT covers a broad wavelength range from 380 nm to 700 nm in the visible region, which is quite similar to the absorption spectrum of the POTVT film after thermal annealing (see Fig. 2). The result indicates that the broad absorption of POTVT all makes contribution to the photon–electron conversion. In comparison with the PSC based on P3HT, the IPCE values of the PSC based on POTVT are much stronger in the wavelength ranges of 380 ~ 430 nm and 600 ~ 700 nm, but it is weaker in the range of 430 ~ 600 nm due to the weaker absorbance of the main chains of POTVT. Through the modulation of molecular structure of the polythiophene derivatives with the conjugated thienylene vinyl side chains, the absorbance of the main chains could be enhanced. The *I–V* curves and photovoltaic properties of the PSCs are shown in the ESI.<sup>†</sup>

In conclusion, we synthesized POTVT, a novel side-chain conjugated polythiophene derivative with thienylene vinyl side chains. The POTVT film after thermal annealing at 130 °C for 10 minutes shows a very broad absorption band in the UV-vis region covering from 300 nm to 700 nm, a lower bandgap of 1.77 eV with a higher HOMO energy level, an ordering structure with interlayer *d*-spacing of 2.77 nm and a higher hole mobility of *ca.*  $3.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . From IPCE data of the photovoltaic device based on POTVT and PCBM, the polymer shows better light utility in the wavelength ranges of 380 ~ 430 nm and 600 ~ 700 nm in comparison with P3HT. The strategy for synthesizing the polythiophene derivatives with conjugated thienylene vinyl side chains could be an effective way in looking for highly efficient conjugated polymers for photovoltaic cells.

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