Quinoid-Resonant Conducting Polymers Achieve High Electrical Conductivity over 4000 S cm$^{-1}$ for Thermoelectrics

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New conducting polymers polythieno[3,4-b]thiophene-Tosylate (PTbT-Tos) are prepared by solution casting polymerization. Through tuning the alkyl group of TbT, the electrical conductivity can be effectively enhanced from 0.0001 to 450 S cm$^{-1}$. Interestingly, the electrical conductivity of PTbT-C1-Tos increases significantly from 450 S cm$^{-1}$ at room temperature to 4444 S cm$^{-1}$ at 370 K, which is disparate from polyethyleneoxide-thiophene-Tos exhibiting metallic conducting behavior. Quasi-reversible phase transformation with temperature from 3D crystallites to lamellar-stacking coincides with the increasing electrical conductivity of PTbT-C1-Tos with heating. Methyl-substituted PTbT-Tos with the best electrical property is further utilized for thermoelectrics and a power factor as high as 263 µW m$^{-1}$ K$^{-1}$ is obtained. It is believed that PTbT-Tos will be a promising family of conducting polymers for solution-processed organic electronics.

Conducting polymers have received great attentions since the pioneering works by Alan MacDiarmid, Hideki Shirakawa, and Alan J. Heeger, who found that serendipitous polyacetylene shows metallic conducting property after doped by iodine.[1]

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These new generation of polymers featuring conjugated backbones combine both the chemical and the mechanical properties of the plastics and the metallic conducting behavior. In the recent several decades, polyacetylene, polythiophene, polypyrrole, polyaniline (PANI), polyparaphenylene vinylene, polyethyleneoxide-thiophene (PEDOT), etc. have been developed and their conducting property were investigated systematically by chemical or electrochemical doping.[2] Moreover, these polymer conductors have shown great prospect for next generation of optoelectronic devices including organic light-emitting diodes, optical transparent electrodes, ion-storage layer, etc.[3] Recently, conducting polymers have been successful employed in thermoelectric applications because of their intrinsically low thermal conductivity and high electrical conductivity.[4] Because of the unique quinoid-enhancing effect,[5,6] (Scheme 1), the ring-fused polythiophene derivatives including PITN, PTP, polythieno[3,4-b]thiophene (PTbT), etc. can achieve both narrowed energy bandgaps and enhanced π-conjugation.[7] After doping, the induced charge carriers can transport smoothly on these conjugated backbones, from which a high electrical conductivity may be achieved as the charge carriers can be stabilized by the quinoidization effect. The family of polymers have been developed since 1997.[7] The first soluble PTbT was synthesized by Pomerantz et al. through oxidation polymerization of TbT monomers by FeCl$_3$, which led to a low optical bandgap of 0.92 eV and electrical conductivity of 0.0031 S cm$^{-1}$ after doped by FeCl$_3$.[8] Neef et al. developed phenyl substituted PTbT by electrochemical polymerization with a more narrowed bandgap of 0.85 eV obtained.[9] PTbT polymers without alkyl group were developed by Sotzing and Lee through electrochemical polymerization of the TbT monomer[10] and dimers,[11] which showed high stability for both n-type and p-type doping. Because of more than two reaction sites on these monomers, network-like homo–polymers were formed. The conductivity of these PTbT homo–polymers were determined to be 10$^{−5}$ S cm$^{-1}$ in the neutral state, which increased to 0.2 S cm$^{-1}$ by four orders of magnitude in the doped state. The water dispersion PTbT-PSS were also synthesized by the same group,[12] with drop-cast films showing a conductivity
of 0.02 S cm\(^{-1}\) with a bandgap lower than 1.0 eV. Bendikov and co-workers developed a solid-state polymerization method\(^{[13]}\) by directly heating TBT-2Br monomer on a hot-plate for more controlled polymerization. Pressed pellets of PTbT showed an electrical conductivity of 6 S cm\(^{-1}\) with a bandgap of 0.96 eV. To date, the low electrical conductivity of doped PTbTs makes it quite difficult for practical applications.\(^{[14]}\)

To achieve high electrical conductivity for doped PTbTs, linear polymerization and high doping level is essential. In this work, a new family of doped PTbTs, namely PTbT-Tos, is carrier concentration, \(\mu\) is charge mobility, \(\sigma\) is electrical conductivity, \(n\) is carrier charge, electrical conductivity (\(\sigma\)) is determined by the charge transport ability (\(\mu\)) and doping levels (\(n\)). Ultraviolet-visible near-infrared spectroscopy (UV–vis–NIR), ultraviolet photoelectron spectroscopy (UPS), and X-ray photoelectron spectroscopy (XPS) measurements are performed to investigate doping level of PTbT-Tos with different alkyl groups in thin films. As shown in the UV–vis–NIR spectra (Figure 2a), the absorption peaks at around 500–1500 nm disappear gradually from PTbT-C8-Tos to PTbT-C1-Tos, being replaced by wide charge-resonance band extending over 2500 nm. The increased absorption bands imply enhanced doping level (oxidation process) with shortening of alkyl chain from C8 to C1. The closure of bandgap in PTbT-C1-Tos, similar to the metal gates. Meanwhile, different from the absence of ESR response for PEDOT-Tos with bipolaron transport, the PTbT-C1-Tos film exhibits a strong ESR signal (Figure 1d) at \(g = 2.00643\), possibly indicating polaron-dominant transport mode.

According to the equation: \(\sigma = n\mu q\), where \(\sigma\) is electrical conductivity, \(n\) is carrier concentration, \(\mu\) is charge mobility, \(q\) is charge carrier, electrical conductivity (\(\sigma\)) is determined by the charge transport ability (\(\mu\)) and doping levels (\(n\)). Ultraviolet-visible near-infrared spectroscopy (UV–vis–NIR), ultraviolet photoelectron spectroscopy (UPS), and X-ray photoelectron spectroscopy (XPS) measurements are performed to investigate doping level of PTbT-Tos with different alkyl groups in thin films. As shown in the UV–vis–NIR spectra (Figure 2a), the absorption peaks at around 500–1500 nm disappear gradually from PTbT-C8-Tos to PTbT-C1-Tos, being replaced by wide charge-resonance band extending over 2500 nm. The increased absorption bands imply enhanced doping level (oxidation process) with shortening of alkyl chain from C8 to C1. The closure of bandgap in PTbT-C1-Tos, similar to the metal absorption, should facilitate the generation of free carriers by thermal activation and charge transport.\(^{[18]}\) The S(2p) peak at the binding energy of 166–170 eV in XPS spectra is attributed to the sulfur of Tos\(^{-}\) that is coupled with the positive charge on PTbT chain,\(^{[16,17]}\) representing the doping levels. As shown in Figure 2b and Figure S4 (Supporting Information), the intensity of this sulfur peak of Tos\(^{-}\) increases gradually with shortening of the alkyl chain length together with the binding energy near 164 eV assigned to sulfur on TBT shifting toward lower value, which is consistent with the increasing doping levels.

On the other hand, the doping induced charged TBT units shifts the most intense peak near 164 eV (Sulfur in PTbT) toward lower binding energy, in accordance with the shifts of the vacuum level and valence band spectra as discussed below due to the band bending effect, also suggests a higher doping level with decreasing length of the alkyl substituent. From the UPS data, the work function is found to significantly shift from
4.04 eV for PTbT-C6-Tos downward to 4.50 eV for PTbT-C1-Tos as depicted in low kinetic energy region (Figure 2c). Meanwhile, the binding energy as shown in the highest occupied molecular orbital (HOMO) onset region in the UPS spectra (Figure 2d; Figure S5, Supporting Information) is significantly shifting toward lower values going from 0.38 (C8) to ~0 eV.

Figure 1. a) The electrical conductivity (logarithm) of PTbT-Tos with alkyl groups from C8 to C0. b) Electrical conductivity (logarithm) of PTbT-C1-Tos and PEDOT-Tos changes with elevated temperature. c) Electrical conductivity of PTbT-C1-Tos film with heating and cooling (three cycles). d) ESR spectra of PTbT-C1-Tos and PEDOT-Tos films.

Figure 2. a) The UV–vis-NIR absorption spectra of PTbT-Tos with alkyl groups from C8 to C0. b) S(2p) XPS spectra of The PTbT-Tos polymers with alkyl group C6, C3, and C1. c) The low kinetic energy region and d) the low binding energy region (HOMO) of UPS spectra.
Moreover, the HOMO onset binding energy extending past zero as shown for PTbT-C1-Tos and PTbT-C0-Tos, imply that the Fermi level is overlapping with the HOMO energy level, facilitating the generation of carriers and consistent with the UV–vis–NIR absorption. Among them, the doping level of PTbT-C1-Tos with the shortest alkyl chain is the highest as concluded from the strongest S(2p) peaks in the XPS spectra and the most significant down-shift of Fermi level from the UPS spectra. As a result, we could deduce that the nonpolarity nature and steric hindrance of alkyl groups on TBT units might restrain the approaching of the oxidant, Fe(Tos)$_3$, to TBT and affect oxidative polymerization, which lead to lower doping levels for the PTbT-Tos polymers with longer alkyl chains. In comparison, the doping level of PTbT-C0-Tos without alkyl group is slightly higher than PTbT-C1-Tos as shown in Figures S4 and S5 of the Supporting Information. The increased doping level is consistent with the enhanced electrical conductivity going from PTbT-C8-Tos to PTbT-C1-Tos and PTbT-C0-Tos. Moreover, from the HOMO onset of PTbT-C1-Tos in UPS spectra (Figure 2d), the small slope of binding energy extending over zero is similar to PEDOT-PSS.$^{[15]}$ Together with the same strong ESR signal to PEDOT-PSS.$^{[15]}$ Together with the same strong ESR signal and electrical conductivity temperature-dependent behavior, the dominant charge carriers in PTbT-C1-Tos might be similar to the PEDOT-PSS (Polaron-dominant). As a result, the increased electrical conductivity with elevating temperature in PTbT-C1 may be partially attributed to the thermally activation hopping mechanism normally found in conducting polymers.$^{[19,20]}$

To explore the effect of the alkyl chain length on microstructures and charge transport in PTbT-Tos films, grazing incidence wide-angle X-ray scattering (GIWAXS) and scanning electron microscopy (SEM) measurements are conducted. The lamellar stacking distance is well resolved by the GIWAXS measurements (Figure 3c; Figure S3, Supporting Information). The low $q$ peaks below $q = 0.5$ Å$^{-1}$ correlate well with the side-chain lengths. Increasing the side chain length obviously increase the lamellar stacking distance, evidenced by the reduced $q$ value. The longer insulating alkyl groups inserting between polymer backbones are believed to influence the charge transport via its impact on the packing behaviors along the $\pi$-stacking direction and backbone direction. Intriguingly, the 1D GIWAXS profile of PTbT with the shortest alkyl length namely C1, show weak and broad peaks across the whole $q$ range, whereas other PTbT derivatives exhibit well-defined peaks, including the lamellar stacking peaks at $q < 0.5$ Å$^{-1}$, and 3D crystalline peaks ranging from $q = 1$ Å$^{-1}$ to $q = 2$ Å$^{-1}$. This observation may imply that the alkyl side chain with insufficient length is not capable of inducing highly ordered molecular arrangement.$^{[21,22]}$

Although PTbT-C1-Tos exhibits the least ordered edge-on lamellar crystallites, evidenced by the weak out-of-plane lamellar crystallite, it is seen that the PTbT-C1-Tos film has the highest electrical conductivity, higher than the other PTbT-Tos derivatives with alkyl side chains longer than C1. This suggests that morphological features other than the nanoscopic crystallization and aggregation may impose noticeable impact on the electrical properties. To this end, the mesoscopic topological information is probed by the SEM measurements and it is found that with longer alkyl chains larger surface domain is imaged (Figure 3a,b; Figure S2, Supporting Information), consistent with the trend observed from the GIWAXS results.

Polymer’s morphology changes with temperature would greatly influence charge transport in the polymer backbone. To explore the potential morphology changes with heating, temperature dependent XRD measurements are conducted on drop-cast films of PTbT-C1-Tos. As shown in the XRD profiles (Figure 4a; Figure S7, Supporting Information), the as-cast (black line) and annealed samples (red line) generate distinctively different diffractions. The different peak positions and widths between the as-cast film and the
annealed film suggest vastly different molecular packing patterns between the samples without and with thermal annealing. More specifically, Phase I (that predominantly exists at room temperature) exhibits intense and sharp diffraction peaks at high $q$ range over $q = 0.5 \, \text{Å}^{-1}$ with a weak but discernable lamellar diffraction at $q = 0.33 \, \text{Å}^{-1}$, corresponding to the lamellar spacing of 19.03 Å. This implies that the PTbT-C1-Tos molecules tend to form 3D crystallites with weak lamellar stacking. With thermal annealing, Phase I rapidly disappears, indicated by the elimination of sharp peaks at $1 < q < 1.5 \, \text{Å}^{-1}$ and broader diffraction peaks at $1 < q < 1.5 \, \text{Å}^{-1}$ along with a much stronger lamellar stacking peak at $q = 0.33 \, \text{Å}^{-1}$. Notably, the thermal annealing leads to considerably enhanced lamellar stacking, whereas the 3D feature of the PTbT-C1-Tos crystallites is observed to be highly suppressed, as evidenced by the reduced Å$^{-1}$, accompanied by the dominance of Phase II (that predominantly exists at high temperature), which displays less prominent diffraction at the high $q$ range. Intriguing, it is found that Phase I can be partially recovered when the temperature was set back to room temperature (see Figure 4a blue line; Figure S7, Supporting Information). The transformation of PTbT-C1 molecular arrangement correlates well with the DSC analysis with elevating temperature (Figure 4b), which shows obviously heat absorption double peaks starting from 60 °C and ending at 130 °C. The absence of any feature during the cooling process indicates that the crystallization process in PTbT-C1 is kinetically slow, which is in entire accord with the partially, rather than complete, recovery of Phase I, as evidenced by the XRD pattern recorded after returning room temperature. The temperature region of the increased electrical conductivity (Figure 1b; Figure S6a, Supporting Information), is consistent with the DSC and XRD trends. Besides, the activation energy of PTbT-C1-Tos calculated from Figure S6b,c of the Supporting Information, fitting to the Arrhenius equation, is determined to be 0.29 and 0.11 eV at low (300–340 K) and high temperature (350–370 K) region, respectively. In comparison to the reported highly doped conducting polymers, the relatively larger activation energy should be ascribed to the low ordered crystallites with amorphous character in PTbT-C1-Tos as concluded from GIWAXS measurements. The two different activation energies are consistent with the stacking transformation from Phase I to Phase II, which is similar to the zwitterion crystal, whose electrical conductivity has been shown to increase by nearly two orders of magnitude from 300 to 400 K. Consequently, it is believed that the molecular stacking changes and the thermal-assisted hopping mechanism may contribute to the significantly increased electrical conductivity with elevating temperature in PTbT-C1-Tos. The quasi-reversible transformations of electrical conductivity to near one order of magnitude and stacking mode with temperature are rare amongst reported conducting polymers, which provide a unique opportunity to understand the relationship between micro structural electrical properties.

The significantly increased electrical conductivity ($\sigma$) of the in situ PTbT-C1-Tos films with elevating temperature contributes to the enhanced thermoelectric performance following the equation: $PF = \sigma S^2$. Hence, the Seebeck coefficients ($S$) of the PTbT-C1-Tos films are determined by measuring the thermovoltages after providing a temperature difference on two sides of the films (Figure S8, Supporting Information). With increasing temperature, the Seebeck coefficients is gradually increased from 18.5 to 24.4 µV K$^{-1}$ (Figure 4c) and is reversible more than three times (Figure S9, Supporting Information). The power factor is enhanced from $13.0 \, \mu\text{W m}^{-1}\,\text{K}^{-2}$ at room temperature to $263 \, \mu\text{W m}^{-1}\,\text{K}^{-1}$ at 370 K, which is much higher than PEDOT-Tos-based device fabricated under the same conditions, 7.6 µW m$^{-1}$ K$^{-1}$ (Table S1, Supporting Information). Because of the acknowledged great challenge in the measurement of in-plane thermal conductivity ($\kappa_\parallel$) for organic thin film, $\kappa_\parallel$ of PTbT-C1-Tos film cannot be obtained at the present stage. However, the amorphous character of PTbT-C1-Tos is similar to PANI$^{[28]}$ and should contribute to an intrinsically low thermal conductivity, which should make PTbT an excellent material system for thermoelectric application (Table 1).$^{[26–29]}$

In conclusion, conducting polymers PTbT-Tos with different alkyl groups have been synthesized by in situ solution-casting polymerization. The electrical conductivity can be effectively tuned ranging from 0.0001 (n-octyl) to 450 (methyl) S cm$^{-1}$ by alkyl-chain length. The electrical conductivity of PTbT-C1-Tos enhances significantly from 450 S cm$^{-1}$ at room temperature to 4444 S cm$^{-1}$ at 370 K, disparate from PEDOT-Tos with metallic conducting behavior. Quasi-reversible phase transformation from 3D crystallites to lamellar-stacking is found in PTbT-C1-Tos, consistent well with the significantly enhanced electrical conductivity by heating. Highly conductive PTbT-C1-Tos polymer is promising for organic electronics, which has been demonstrated by thermoelectric application.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

cconducting polymers, conductivity, organic thermoelectrics, phase transformation, quinoid resonant

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Table 1. High-performance organic thermoelectric materials reported recently.

| Materials              | PF [µW m⁻¹ K⁻²] | Ref.     |
|------------------------|-----------------|----------|
| PyDI-SFPE-SnCl₂        | 80              | [26]     |
| BTBT₂(AsF₆)            | 88              | [27]     |
| P3HT-TCB               | 62.4            | [28]     |
| TDPPQ-Bi               | 113             | [29]     |
| PBTTT-F,TCNQ           | 120             | [24]     |
| Pt₆T-C1-Tos            | 263             | This work |

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