

Self-Orienting Head-to-Tail Poly(3-alkylthiophenes): New Insights on Structure-Property Relationships in Conducting Polymers

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Due to their stability and solubility, poly(3-alkylthiophenes)¹ have been the focus of a large number of physical studies aimed at understanding the chemistry and physics of conducting organic polymers.² However, correlating the material's electronic and macromolecular structure to the observed electrical and optical properties have been difficult due to the lack of structural integrity of the materials under investigation. In particular, physical studies are performed on polymers containing a number of structural types and defects, which can lead to difficulties in data interpretation and erroneous conclusions. The major problem is that the theories used to explain electrical and optical properties often are based on a single structural type and the measurements are made on structural mixtures.

We have recently prepared poly(3-alkylthiophenes) (PATs) containing virtually one structural type³ ($\approx 98\%$ head-to-tail (HT) couplings). Herein we present, for the first time, physical property data that clearly show the structure-property relationships in this class of materials. We find that these HT poly(3-alkylthiophenes) undergo solid-state macromolecular self-assembly and give self-oriented structures, as determined by X-ray diffraction studies. In addition, we find, contrary to other studies,⁴ that PATs with longer alkyl side chains (e.g., $C_{12}H_{25}$) produce the structures with the most desirable electronic, electrochemical, and optical properties and induce the formation of planar main-chain structures. The HT poly(3-dodecylthiophene) (PDDT) exhibits reversible electrochemistry, is the most highly electrically conductive, and has the greatest effective conjugation length, following by HT poly(3-octylthiophene) (POT), HT poly(3-hexylthiophene) (PHT), and HT poly(3-butylthiophene) (PBT).

The HT poly(3-alkylthiophenes) used in this physical property study were prepared by a new synthetic method developed in our

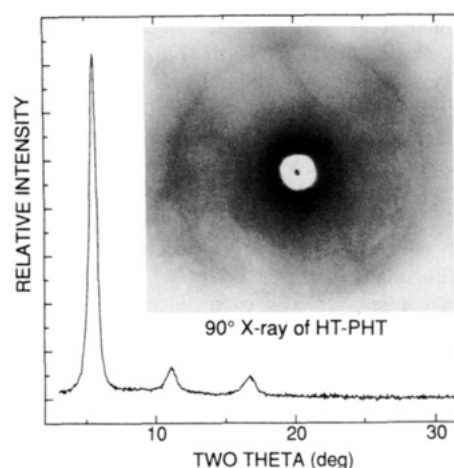


Figure 1. X-ray diffraction pattern of a cast head-to-tail poly(3-hexylthiophene), on a 70- μ m coverslip, from scans of intensity of vs 2θ . Inset: X-ray film data taken at a 90° angle of incidence to the coverslip.

lab, in which 2-bromo-5-(bromomagnesio)-3-alkylthiophene is polymerized with catalytic amounts of $Ni(dppp)Cl_2$, leading to $\approx 98\%$ HT couplings.³ It is interesting to note that HT-coupled PHT can also be obtained by the self-coupling of a mixture containing 90% of 2-bromo-5-(bromozincio)-3-hexylthiophene and $Ni(dppe)Cl_2$,⁵ making the method rather general. Simple air evaporation of filtered 2–5% xylene solutions of PATs onto 70- μ m glass coverslips surprisingly leads to very highly oriented structures, as determined by film X-ray studies. Both X-ray film data, at a 5° angle of incidence to the coverslip surface, and scans of intensity vs 2θ (Figure 1)⁶ show strong intensity in three small-angle reflections, which correspond to a well-ordered lamellar structure with an interlayer spacing, in the case of PHT, of 16.0 ± 0.2 Å (Figure 2). A narrow (0.1-Å half-width), single wide-angle reflection is observed at a 90° angle of incidence to the coverslip (Figure 1, inset), corresponding to 3.81 ± 0.02 Å, which represents the stacking distance of the thiophene rings between two polymer chains (Figure 2). The minimum energy structure for a HT 3-hexylthiophene tetramer can be calculated using molecular mechanics⁷ and is shown in Figure 2. The molecule has been arranged in Figure 2 to fit the X-ray data. These structures mirror those presented in the elegant work of Winokur and co-workers on stretch-oriented PATs.⁸ However, an important point is that in all other PAT samples examined to date, the wide-angle peak is quite broad.^{8,9} Our observation of a very narrow width in the wide-angle region indicates that along the polymer chain conformational order gives rise to virtually a single stacking distance and not a distribution of stacking distances. The narrow widths of all these dominant X-ray features indicate self-oriented, highly ordered crystalline domains in PHT.¹⁰ It appears, however, that the samples are disordered from domain to domain, which gives rise to the wide-angle ring found in the

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(6) The intensity vs 2θ scans were obtained with a Rigaku Geigerflex operated in the θ - θ mode. The film data (inset Figure 1) were obtained with an Elliot rotating anode Type GX21 in 6 h, with nickel-filtered, pinhole collimated Cu K α radiation with a 90° angle of beam incidence through the back of the coverslip.

(7) All molecular mechanics calculations were performed using Charmm software (Polygen, Inc.) on a Silicon Graphics Iris 4D computer.

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(10) An intensity vs 2θ scan on a greenish-gold free-standing film of POT (cast from $CHCl_3$) reveals more structural order in our HT POT than in stretch-oriented POT: Prosa, T. J.; Winokur, M. J.; McCullough, R. D., unpublished results.

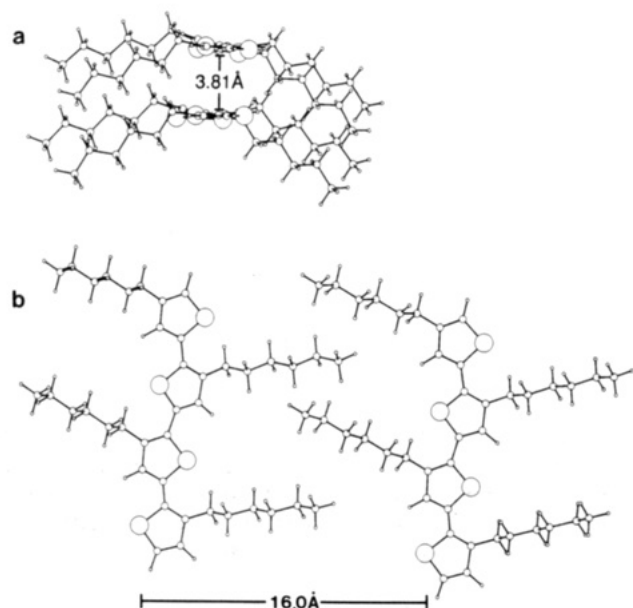


Figure 2. Calculated structure for a HT 3-hexylthiophene tetramer using molecular mechanics. These globally minimized tetramers have been "docked" in an idealized manner to fit the X-ray structural parameters from PHT thin films. (a) Intermolecular π stacking between thiophene rings inferred from 90° X-ray pattern of HT-PHT film. (b) Lamellar stacking inferred from X-ray scans of intensity vs 2θ data.

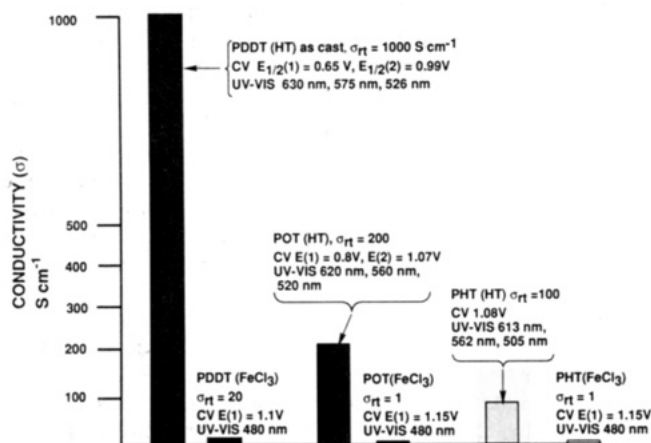


Figure 3. Electrical conductivity and electrochemical and optical absorption data on thin films of HT poly(3-alkylthiophenes).

90° picture (Figure 1, inset). In striking contrast, PHT prepared from FeCl_3 (work in other labs and ours)^{8,9,11} shows much weaker intensity reflections in the small-angle region, with a d spacing of $17.3 \pm 0.5 \text{ \AA}$ and a very broad amorphous halo centered at 3.8 \AA . These results indicate an unprecedented structural order for our PATs, indicating that the self-order is induced by the regiochemical perfection derived from the synthetic method used to prepare these samples.

Cast films of $7\text{--}12 \text{ }\mu\text{m}$, upon exposure to I_2 vapor, lead to maximum electrical conductivities of 1000 S cm^{-1} for PDDT, 200 S cm^{-1} for POT, and 150 S cm^{-1} for PHT as measured in air (Figure 3). Thin films of PATs prepared from the FeCl_3 method show maximum conductivities of between 20 and 0.1 S cm^{-1} . While the absolute values of the electrical conductivity are important, it is most critical to examine the relative values of thin films of similar thicknesses, history, and morphology.¹² We have found roughly the same conductivity in PATs prepared from FeCl_3 , whereas there is a clear trend in the electrical conductivity in HT PATs, decreasing in the series $\text{PDDT} > \text{POT} > \text{PHT} (> \text{PBT})$.¹³ Optical data show that the λ_{max} is at the highest

wavelength for PDDT thin films, with the wavelength decreasing uniformly from POT to PHT (to PBT)¹³ (Figure 3). These results can be interpreted by considering that PDDT has more extensive along the chain overlap and a larger number of highly conjugative domains relative to POT, PHT, and PBT.

The electrochemical properties of these self-oriented HT PATs exhibit similar trends (Figure 3). Cyclic voltammetry on thin-film samples of HT PDDT exhibited two reversible oxidation potentials of $\Delta E_{1/2}(1) = 0.65 \text{ V}$ and $\Delta E_{1/2}(2) = 0.99 \text{ V}$ (vs SCE); HT POT exhibited peaks at $E_{\text{pa}}(1) = 0.8 \text{ V}$ and $E_{\text{pa}}(2) = 1.07 \text{ V}$, and HT PHT exhibited a broad oxidation wave which peaked at $E_{\text{pa}} = 1.08 \text{ V}$. These results are in contrast to PATs prepared by other methods.¹⁴ We find that HT PDDT exhibits the lowest oxidation potential in the alkyl series, followed by POT and PHT.¹⁵ It is expected as the adjacent thiophene rings move toward coplanarity that the increase in molecular orbital overlap will help to stabilize both polaronic (radical cationic) and bipolaronic (dicationic) states, thus lowering the oxidation potentials.¹⁶

Experimental demonstration of structure–property relationships is of critical importance to the engineering design of organic materials,¹⁷ which include conducting polymers with highly desirable electronic and photonic properties. It remains to be seen if the use of side-chain-induced self-orientation can be used in order conducting polymers, such as alkylated polyanilines, poly(*p*-phenylenes), and polypyrroles with well-defined structures. However, it is clear that in structurally well-defined poly(3-alkylthiophenes), side chains play a heavy role in controlling the local and three-dimensional structure and hence the resultant physical properties.

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(12) All HT PAT and PAT from FeCl_3 thin-film samples are treated identically. All thin-film thicknesses were measured and film morphologies examined by SEM. It is also important to note that in the ultrathin-film regime, PATs have been shown to exhibit very highly ordered structures. These elegant studies show ultrathin films also exhibit increasing morphological disorder as the thickness increases from $6 (\lambda_{\text{max}} = 552 \text{ nm})$ to $190 \text{ nm} (\lambda_{\text{max}} = 510 \text{ nm})$. See: Yassar, A.; Roncali, J.; Garnier, F. *Macromolecules* **1989**, *22*, 804. In this present study, we are working in the "thick-film" regime relative to the aforementioned ultrathin-film work.

(13) HT PBT follows all of the trends as indicated; however, the numerical data are not included in this paper due to problems in uniform film formation. Nevertheless, the solid-state UV-vis data show absorptions at 610, 580, and 500 nm .

(14) The notation PDDT (FeCl_3) (used below) represents poly(3-dodecylthiophene) prepared from the FeCl_3 method of Sugimoto. See: Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635. Our measurements show that PDDT (FeCl_3) shows a broad potential of $E_{\text{pa}} = 1.1 \text{ V}$ and a small bump at $E_{\text{pa}} = 0.8 \text{ V}$; POT (FeCl_3) shows potential at 1.15 V and PHT (FeCl_3) at 1.07 V . The cyclic voltammetry of HT PBT exhibits a peak at $E_{\text{pa}} \approx 1 \text{ V}$.

(15) These results are based on numerous runs on films cast from both hot and cold solutions of xylene and films of varying thicknesses.

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