Effects of Side-Chain Length and Shape on Polytellurophene Molecular Order and Blend Morphology

Joseph Razzell-Hollis,¹ Franziska Fleischli,² Ashlee A. Jahnke,³ Natalie Stingelin,² Dwight S. Seferos,³ Ji-Seon Kim¹,*

1. Department of Physics and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, United Kingdom
2. Department of Materials and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, United Kingdom
3. Department of Chemistry, University of Toronto, Toronto, Ontario M5S 3H6, Canada

KEYWORDS
Resonant Raman Spectroscopy, Molecular Order, Polytellurophenes, Organic Electronics, OFETs.

ABSTRACT
We investigate the molecular order and thin film morphology of the conjugated polymer polytellurophene, in order to understand how the tellurium atom and the choice of side-chain influence the conjugated polymer’s backbone planarity and performance in organic transistors. We find that poly(3hexyltellurophene) (P3HTe) continues the trend from polythiophene (P3HT) to polyselenophene (P3HS): substitution with Tellurium leads to a more planar backbone, evident from the shifts of the C=C vibrational peak to lower wavenumbers (~1389 cm\(^{-1}\)) and a smaller optical band-gap (~1.4 eV). Resonant Raman spectroscopy revealed that molecular order was highly dependent on the structure of the P3ATe alkyl side-chain: a longer chains introduces kinetic hindrance, reducing the fraction of ordered phase obtained at room temperature, while a branched side-chain introduces steric hindrance, with intrinsic disorder present even when deposited at higher temperatures. When blended with the insulator HDPE, all three polymers exhibit little additional disorder and instead form phase-separated networks of high molecular order that are beneficial to percolated charge transport in transistors. We find that molecular order, as measured by Raman, correlates well with reported transistor mobilities and provides a greater understanding of the structure-property relationships that determine the performance of these novel organometallic polymers in electronic devices.

INTRODUCTION

Conjugated polymers are a promising class of semiconducting materials being investigated for use in a number of low-cost electronic devices, including organic photovoltaics (OPVs), organic field effect transistors (OFETs) and organic light-emitting diodes (OLEDs).\(^1\)\(^-\)\(^3\) The performance of these polymers in electronic devices is to depend strongly on their thin film morphologies, based on organization of the polymer at length scales ranging from molecular order (i.e. planarity
of the conjugated backbone) up to micron-scale aggregation and phase separation. The soluble polythiophene poly(3-hexylthiophene) (P3HT) is one of the most thoroughly studied and industrially important semiconducting polymers currently available,\textsuperscript{4-6} achieving reasonable efficiencies of up to \textasciitilde{}5\% in OPVs,\textsuperscript{7} and charge carrier mobilities of up to 0.1 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} in transistors.\textsuperscript{8} However, it still suffers from certain disadvantages: it has a large optical band-gap of 1.9 eV, far greater than the optimal \textasciitilde{}1.2 eV for OPVs;\textsuperscript{9} and a morphology that is very sensitive to processing conditions, requiring careful optimization to form highly-ordered domains with good \(\pi\)-\(\pi\) stacking essential to intermolecular charge transport.\textsuperscript{8,10-12} In recent years, selenophene and tellurophene analogues of P3HT have been developed to try and improve its properties by replacing the sulfur atom of thiophene with heavier Group 16 elements such as selenium or tellurium.\textsuperscript{13,14} This has met with some success, poly(3-hexylselenophene) (P3HS) was reported to have a smaller optical band-gap of 1.6 eV, and formed larger aggregates with a high degree of molecular order that favours \(\pi\)-\(\pi\) stacking.\textsuperscript{13,15} Continuing down Group 16, the synthesis of organometallic poly(3-hexyltellurophene) (P3HTe) was first reported in 2013 and produced a polymer with an optical band-gap of 1.4 eV, close to the optimal value of 1.2 eV, and evidence of aggregation into nanofibres.\textsuperscript{14,16} This nanoscale organization was found to depend on the structure of the polymer’s alkyl side-chain, with a marked impact on charge carrier mobility when used as the active material of semiconductor:insulator blends for OFET applications.\textsuperscript{16} Consequently, it is important to characterize the thin film morphology of novel polymers such as polytellurophene in greater detail, in order to better understand the relationships between their molecular order, thin film microstructure and device performance.

To complement the measurements of microstructure reported previously, the aim of this study is to investigate long- and short-range molecular order using absorption spectroscopy and
resonant Raman spectroscopy respectively. Absorption can provide information about long-range organization, in terms of effective conjugation length and aggregation. Resonant Raman is a simple, effective tool for probing the vibrational modes of molecules, and is particularly suited to studying the conjugated backbones of organic semiconductors. Under resonant conditions, when the excitation energy exceeds the materials’ optical band-gap, vibrational modes associated with the conjugated backbone become sensitive to its conformation through strong electron-phonon coupling, exhibiting distinctive spectral changes between the planar and twisted polymer backbones of ordered (crystalline) and disordered (amorphous) domains. In practice, this allows the use of Raman to monitor changes in the overall degree of molecular order within thin films, as we have demonstrated previously with P3HT and P3HS. In this study, we will investigate the impact of the heavy tellurium atom, different side-chains and processing conditions on the molecular order of three polytellurophenes, depicted in Figure 1, with a standard linear hexyl chain (P3HTe), a longer linear dodecyl chain (P3DDTe) and a branched 2’-ethylhexyl chain (P3EHTe). By comparing the behavior of these polymers under different deposition conditions, the structure-property relationships between side-chain, solid state molecular order and reported device performance can be identified.
EXPERIMENTAL METHODS

Sample Preparation: P3HTe, P3DDTe and P3EHTe (with weight-average molecular weights \( M_w \) of \( \sim 21.8 \) kDa, \( \sim 22.9 \) kDa and \( \sim 13.8 \) kDa respectively, and corresponding polydispersities of 2.2, 2.0 and 1.5) were synthesized and purified at the University of Toronto according to published protocols. P3EHTe had a regioregularity of 93% according to \(^1\)H NMR, no data was available for P3HTe or P3DDTe due to limited solubility. RR-P3HT and HDPE were purchased from Sigma Aldrich (\( M_w \) of \( \sim 35 \) kDa and \( \sim 125 \) kDa respectively) and used as received. For wire-bar coating, each polymer was dissolved in 1,2,4-trichlorobenzene at 140 °C to produce neat solutions, or co-dissolved with HDPE with a weight ratio of 60:40 to produce blend solutions, all at a total polymer concentration of 5 mg/mL. Bar-coated films were deposited onto glass substrates that were either at room temperature or heated to 140 °C, the latter were kept at 140 °C for a further minute after solvent evaporation and then cooled to room temperature. Films for XRD were prepared using neat solutions of each polymer in
chlorobenzene, at concentration of 10 mg/mL, which was spin-coated onto Si/SiO₂ (for XRD measurements) at 2000 rpm for 120 sec and then blow-dried with a nitrogen gas gun.

**UV-Visible Spectroscopy:** Absorption spectra were obtained using a Shimadzu 2550 spectrophotometer.

**XRD:** X-Ray Diffraction measurements were done on thin films using an X’Pert PRO PANalytical diffractometer. The source was a nickel-filtered Cu Kα1 beam, operating under a current of 40 mA and an accelerating voltage of 40 kV. Intensity was measured against twice the scattering angle (2θ), from 2 to 20°. Exposure times were 40 minutes for RR-P3HT and 30 minutes for P3ATe.

**Raman Spectroscopy:** Raman spectra were obtained using a Renishaw inVia microscope with a 50x objective in a back-scattering configuration. To reduce photo-degradation, samples were measured in a Linkam thermal stage under N₂ purging and the laser spot was defocused to ~10 μm. The laser powers and acquisition times used at each excitation wavelength were as follows: 0.16 mW, 30 sec (457 nm); 0.45 mW, 30 sec (488 nm); 0.11 mW, 30 sec (514 nm); 0.12 mW, 10 sec (633 nm); 1.3 mW, 10 sec (785 nm). All spectra were background-corrected using a linear baseline between 1250 and 1600 cm⁻¹. Optical microscopy was done using the inVia microscope, in reflection mode using the 50x objective.

**DFT simulations:** oligomers of P3ATe were simulated by the Gaussian 09 software package,²⁰ using a mixed basis set: B3LYP 6-31G(d,p) for H and C atoms, LANL2DZ with a core electron pseudo-potential for tellurium atoms. Molecular structures were first optimized in the gas phase and then theoretical Raman spectra were calculated. Raman shifts were adjusted using an empirically obtained 0.960 scaling factor according to the 6-31G(d,p) basis set.²¹ An oligomer with 6 repeat units (a hexamer) was found to give the most realistic Raman spectrum after
optimization. The effect of molecular order (backbone planarity) on vibrational properties of the polymers was investigated by calculating Raman spectra for a hexamer with varying dihedral angles between 0 and 40°. Alkyl side-chains were reduced to methyl groups to aid computation time.

RESULTS AND DISCUSSION

A Comparison of P3HT and P3HTe

In order to understand the effect of the heavy tellurium atom on the optical and structural properties of polymer thin films, we first compared P3HTe to its polythiophene analogue P3HT. Figure 2 demonstrates that a film of neat P3HTe exhibited a single major absorption peak reaching a maximum ($\lambda_{\text{max}}$) at 612 nm and an onset at $\sim$850 nm, compared to a $\lambda_{\text{max}}$ of 519 nm and an onset of $\sim$650 nm for a film of neat P3HT. The red-shift of absorption from P3HT to P3HTe is consistent with a smaller optical band-gap ($E_g$) for tellurophene compared to thiophene or selenophene. For the polymers, we calculated optical band-gaps of 1.9 eV for P3HT, 1.6 eV for P3HS (which has a reported $\lambda_{\text{max}}$ of 585 nm)\textsuperscript{15} and 1.4 eV for P3HTe. The P3HTe absorption peak was very broad (with a full-width-half-maximum of 292 nm, versus 160 nm for P3HT), which suggests the polymer adopts a wide range of distinct conformations in the solid state, with different degrees of $\pi$-delocalization. The red-shift and breadth of the absorption peak cannot be solely attributed to conformation, however, as the Te atom will also have a direct impact on electronic energy levels. The size and metallic nature of Te atom make it easily polarized, and thus will be highly sensitive to intermolecular packing. Although P3HTe did not exhibit the distinctive vibronic features that are associated with aggregation, namely a well-defined 0-0 transition shoulder at longer wavelengths (i.e. 605 nm for P3HT),\textsuperscript{22} earlier work identified the absorption around $\sim$800 nm to aggregation of this polymer in solution, which was not observed
for P3DDTe or P3EHTe. P3HTe exhibits very promising optical properties for use in OPVs: its low band-gap of 1.4 eV is much closer to the often-quoted ideal value of 1.2 eV, and suggests that polytellurophene will be a useful material for efficiently absorbing a greater portion of the solar spectrum. However, we must also consider the solid-state organization of the polymer and the impact that it will have on charge transport.

**Figure 2.** Normalized absorption spectra for thin films of the polythiophene P3HT and the polytellurophene P3HTe.

The decrease in $E_g$ due to substitution of the heteroatom with heavier Group 16 elements is typically attributed to a combination of greater planarity of the conjugated backbone, which increases $\pi$-orbital delocalization along the chain; and a deeper energy level for the lowest-unoccupied-molecular-orbital (LUMO). This was corroborated by DFT simulations of P3HT, P3HS and P3HTe oligomers, however, we note that the reliability of these simulations was hindered by the limitations of finding a functional and basis set capable of predicting the electronic properties of conjugated organometallic polymers with sufficient accuracy. Consequently, we were not able to use the results of these simulations to conclusively describe
the relationship between the identity of the heteroatom and the electronic/vibrational properties of the polymer, and must instead infer from experimentally observed trends from P3HT to P3HS to P3HTe.

To this end, we examined P3HT and P3HTe using resonant Raman spectroscopy in order to directly probe the backbone planarity of polytellurophene, and infer the impact of the larger, heavier tellurium atom on the polymer’s organization. Under 488 nm excitation, there is a strong resonance with the absorption of both polymers that enables us to exploit the sensitivity of resonant Raman spectroscopy to molecular order that has been described in detail previously.\textsuperscript{11,17}

The Raman spectrum of P3HTe was found to be similar to that of P3HT, with the same vibrations of C=C and C-C bonds along the conjugated backbone assigned to peaks at lower frequencies than in P3HT, plus a number of overlapping peaks at 1160-1220 cm\textsuperscript{-1} assigned to the hexyl side-chain. The largest down-shift in frequency was for the two major peaks of the spectrum, assigned to the C=C and C-C in-plane symmetric stretching modes of the tellurophene ring, which were shifted from 1449 to 1389 cm\textsuperscript{-1} and 1380 to 1340 cm\textsuperscript{-1} respectively. We conclude that the down-shift, particularly of these modes associated with the conjugated ring, is due to the Te atom’s impact on electronic distribution along the polymer, and thus on the vibrational frequencies of the conjugated bonds. This continues the reported trend from P3HT to P3HS,\textsuperscript{15} the latter having a C=C peak at 1470 cm\textsuperscript{-1} and a C-C peak at 1360 cm\textsuperscript{-1}, both down-shifted with respect to P3HT but up-shifted relative to P3HTe.
Figure 3. a) Normalized resonant Raman spectra for P3HT and P3HTe under 488 nm excitation. Colored labels indicate the assignments of major Raman modes to vibrations of particular chemical bonds on polytellurophene. b) Deconvolution of P3HTe C=C peak into ordered and disordered contributions based on fitting.

Under resonant conditions, the C=C peak of highly-ordered (planar) regioregular P3HT has a Raman shift of 1449 cm\(^{-1}\), while highly disordered (twisted) regiorandom P3HT is at a much higher frequency of 1475 cm\(^{-1}\) (see ESI for spectra). A peak shift to higher frequencies due to twisting the polymer is associated with reduced \(\pi\)-electron delocalization along the conjugated backbone, a less quinoidal structure and an increase in force constant for the C=C bond. Similar behavior has been reported for P3HS, with a greater disparity between ordered and disordered C=C peak frequencies leading to a distinctly bimodal peak.\(^{15}\) For P3HTe we observed a very
broad C=C peak that was distinctly bimodal, comprising of a narrow peak at 1389 cm\(^{-1}\) (responsible for the peak maximum) overlapping with a much broader peak that covers a range of 1400 to 1480 cm\(^{-1}\). Based on the similarity between spectra of P3HT, P3HS and P3HTe, we therefore conclude that the narrow low-wavenumber peak at 1389 cm\(^{-1}\) represents more planar polymer conformations, i.e. the ordered phase of P3HTe; while the broader higher-wavenumber peak at 1440 cm\(^{-1}\) is from more twisted conformations, i.e. the disordered phase. This behavior was corroborated by DFT simulations of polytellurophene oligomers with different torsion angles, shown in the ESI, though the reliability of the chosen basis set is treated with the same note of caution mentioned earlier.

Figure 3b illustrates that it was possible to deconvolute the C=C peak into distinct peaks for the ordered and disordered phases, by fitting the peak with a single Gaussian-Lorentzian function to represent the ordered contribution (centered at 1387 cm\(^{-1}\), FWHM of 24 cm\(^{-1}\)) and two functions to fit the disordered contribution (centered at 1420 cm\(^{-1}\), FWHM of 65 cm\(^{-1}\); after addition). The difference in Raman shift and FWHM between the ordered and disordered contributions follows our understanding that the P3HTe film morphology can be represented by two distinct phases: an ordered phase with a narrow distribution of similar planar conformations, and a disordered phase with a broad range of twisted conformations. This correlates well with the very broad absorption peak observed for P3HTe, leading to the conclusion that the electronic impact of the large, metallic Te atom also broadens the range of C=C frequencies observed, and may be responsible for the decidedly asymmetric ‘disordered’ contribution. Although the peak area integrated intensity of the ordered contribution was estimated at 39% of the total C=C Raman intensity, it is not possible to convert this to an exact fraction of ordered phase without knowing the relative Raman scattering cross-sections of both the planar and twisted conformations under this
excitation wavelength. However, the relative intensity of the ordered phase can still be used as a qualitative indicator for the degree of molecular order, and is preferable to using the C=C peak position as the figure of merit, which tends to be dominated by a single contribution, i.e. the ordered phase at 1387 cm\(^{-1}\).

**Figure 4:** Dispersion of normalized Raman spectra for P3HT (a) P3HTe (b), P3DDTe (c) and P3EHTe (d), measured at five different excitation wavelengths.

We then investigated the distribution of molecular order within P3HTe by exploring its Raman spectrum at five different excitation wavelengths (457, 488, 514, 633 and 785 nm). In doing so, we exploit resonance with different electronic transitions of various conjugation lengths (see the absorption of P3HTe, Figure 2) in order to selectively probe the conformations of different chromophores within the film and obtain experimental evidence of the nature of P3HTe’s
ordered and disordered phases. Due to the nature of polytellurophene as a low band-gap material, none of the excitation sources used in this study had a low enough energy for true non-resonant Raman ($\lambda > 850$ nm). First, we examined the selective excitation of the most ordered and disordered phases: under 785 nm excitation we expect to be exclusively resonant with the low-energy electronic transitions of the ordered phase, and obtained a narrow C=C peak at low frequency (1373 cm$^{-1}$, FWHM of 30 cm$^{-1}$) with no apparent contribution from the disordered phase around 1420 cm$^{-1}$ (red trace, Figure 4b). In contrast, under 457 nm excitation there is a selective resonance is with the high-energy electronic transitions of the disordered phase, resulting in a much broader C=C peak with a maximum at higher frequency (1426 cm$^{-1}$, FWHM of 82 cm$^{-1}$), with a small contribution from the ordered contribution appearing as a shoulder around 1400 cm$^{-1}$ (purple trace, Figure 4b). The properties of the C=C peak measured under the two extreme excitation conditions appear similar to the ordered and disordered contributions obtained by fitting the 488 nm spectrum (as depicted in Figure 3b), and provides experimental evidence that the ordered phase (which is resonant with 785 nm) exhibits a much narrower distribution of highly-planar conformations while the disordered phase (which is resonant with 457 nm) exhibits a broad range of twisted conformations.

Across all excitation wavelengths used, there was a clear trend of increasing Raman intensity from the disordered contribution (around 1420 cm$^{-1}$) with higher excitation energy, indicative of an increasingly selective resonance with the high-energy disordered phase. The relative intensities of the ordered and disordered contributions measured under resonance gives us an indication of the overall degree of molecular order, although the overall C=C peak position was found to vary by only $\sim$15 cm$^{-1}$ (between 1373 and 1389 cm$^{-1}$) from 785 to 488 nm, as it was dominated by the sharp, narrow distribution of the ordered contribution. Between 488 and 457
nm the relative intensity of the disordered contribution increased significantly, shifting the maximum by a further ~37 cm\(^{-1}\) to 1426 cm\(^{-1}\). The total variation in position (referred to as the Raman dispersion) of the C=C peak was ~53 cm\(^{-1}\), far exceeding the ~8 cm\(^{-1}\) observed for P3HT under the same range of excitation wavelengths (see Figure 4a). In the case of P3HT, a large Raman dispersion for regiorandom-P3HT over regioregular-P3HT has been associated with a broader distribution of twisted conformations due to greater steric hindrance between side-chains.\(^{17}\) The two other polytellurophenes, one with a longer side-chain (P3DDTe) and one with a branched side-chain (P3EHTe), gave similar Raman dispersion values: ~48 cm\(^{-1}\) and ~60 cm\(^{-1}\) respectively. These values are determined by the difference between the most ordered and most disordered conformations being probed (under 785 and 457 nm excitation), and as such we propose that the three polymers exhibit similar distributions of conformation between those two extremes. However, we note that there is clearly a significant variation in the relative intensities of the ordered and disordered contributions when probed under intermediate excitation wavelengths (i.e. resonance with both phases), indicating that the different side-chains result in different proportions of ordered and disorder phase for each polymer.

Effects of Linear Side-Chain Length

First, we compared the standard polymer P3HTe to one with a dodecyl side-chain, P3DDTe (see Figure 1 for chemical structures). The impact of a longer linear side-chain on the packing of the polymer was immediately apparent in the diffractograms of the two neat polymers, shown in Figure 5, that were obtained using X-Ray diffraction (XRD). Diffraction peaks were observed at 2θ angles of 7.3 and 4.4° for P3HTe and P3DDTe respectively, and were both assigned to the first-order (100) reflection, associated with the lamellar packing distance (the \(a\) lattice parameter). The smaller angle of diffraction for P3DDTe confirms that the longer linear side-
chain increases the separation between edge-on polymer backbones, from 12.1 to 19.9 Å. We did not observe a shoulder for the P3HTe diffraction peak, which was reported by Jahnke et al. for bar-coated films and was attributed to a smaller lamellar separation induced by interdigitated side-chains. This may be a result of processing conditions, the films prepared for XRD measurements reported here were deposited by spin-coating rather than bar-coating, and a faster evaporation of solvent may have limited the formation of interdigitated domains. We observed second-order (200) diffraction peaks at 2θ = 14.3° for P3HTe and 8.9° for P3DDTe, giving lamellar distances of 12.3 and 19.8 Å respectively that were in good agreement with the first-order values. The exclusive detection of lamellar (h00) diffraction peaks suggests the formation of crystallites that are oriented edge-on with respect to the silicon substrate, this means that the π-π stacking direction is in-plane and the associated (0k0) peaks will be undetectable by out-of-plane measurements. Using XRD data alone, it is difficult to comment on the impact of the tellurium atom or the different side-chains on the π-π stacking distance. Instead, we use resonant Raman to probe molecular order, in order to understand the effect on backbone planarity and thus molecular packing in the π-π direction.
**Figure 5.** XRD diffractograms for spin-coated films of P3HTe, P3DDTe and P3EHTe on Si/SiO$_2$. Labels indicate the lamellar stacking distance associated with each (100) diffraction peak.

Figure 6a shows the normalized absorption spectra of P3HTe and P3DDTe, demonstrating that there is an appreciable blue-shift of the main absorption peak from a maximum of 612 nm (2.02 eV) for P3HTe to 580 nm (2.14 eV) for P3DDTe, suggestive of a shorter effective conjugation length for the polymer with a longer side-chain. This is corroborated by greatly reduced absorption at long wavelengths, at 700-800 nm, where P3HTe exhibited a broad shoulder that can be assigned to a 0-0 vibronic transition associated with the electronic transition of aggregated polymer. Although the appearance of a well-defined diffraction peak in the XRD data establishes the existence of crystalline domains within the film, the blue-shift in absorption and suppression of the vibronic shoulder at ~750 nm appears to indicate that the polymer’s morphology in the film is more dominated by disordered domains, compared to P3HTe. These domains, which lack long-range translational order, are difficult to detect with diffraction-based techniques, but their absorption and vibrational signatures are obvious.
Figure 6. Normalized absorption spectra (a) and normalized Raman spectra (b) for P3HTe, P3DDTe and P3EHTe films bar-coated at room temperature, under 488 nm excitation.

This was confirmed by resonant Raman spectroscopy, under 488 nm excitation there was a significantly larger contribution to the C=C peak from the disordered contribution at higher wavenumbers, shifting the C=C peak’s maximum to 1420 cm$^{-1}$ (see Figure 6b) as the Raman contribution from the ordered phase was reduced from 39% to 26%. This enables us to conclude that P3DDTe (with a longer linear side-chain) is significantly more disordered than P3HTe when bar-coated at room temperature. This was later found to be the effect of greater kinetic hindrance during deposition for the longer side-chains (vide infra).

Effect of a Branched Side-Chain
We then compared P3HTe to a third polytellurophene with a branched side-chain of similar length, P3EHTe (see Figure 1). The 2’-ethylhexyl side-chains of P3EHTe are expected to introduce significant steric hindrance between neighboring units on the same chain, but the XRD diffractogram of a neat film (see Figure 5) still shows a (100) diffraction peak at $2\theta = 6.2^\circ$, indicating a crystalline phase within the film. This angle corresponds to a lamellar spacing distance of 14.1 Å, ~2 Å larger than that of P3HTe despite having a similar side-chain length. This has been attributed to reduced interdigitation of side-chains, which reduces the effective lamellar spacing of P3HTe but is prevented by the branching of the ethylhexyl side-chains on P3EHTe.

In terms of absorption (Figure 6a), the $\lambda_{\text{max}}$ of P3EHTe was 634 nm, a red-shift of 22 nm with respect to P3HTe (1.96 vs 2.02 eV), and exhibited a stronger, more distinct vibronic shoulder at ~750 nm. This appears to suggest that despite any steric hindrance resulting from its branched side-chains, P3EHTe achieves a longer conjugation length than P3HTe, at least for neat films bar-coated at room temperature. This can be due to greater solubility afforded by the branched side-chain (compared to P3HTe, which suffered from near-insolubility in both trichlorobenzene and chlorobenzene unless heated), resulting in a slower deposition of P3EHTe and a ‘solvent annealing’ effect that favors long-range order. Optical microscopy reinforced this conclusion, as the P3HTe and P3DDTe films showed a number of micron-scale aggregates and a rough film structure indicative of irregular deposition and poor solubility, while P3EHTe formed a more uniform film (micrographs shown in Figure 8). Despite this, P3EHTe exhibited a Raman spectrum dominated by disorder (see Figure 6b), with a C=C peak maximum at 1420 cm$^{-1}$ and only a small contribution ordered phase at ~1390 cm$^{-1}$. After deconvolution by fitting, the relative intensity of the ordered contribution was estimated to be only 20%, much lower than that
of either P3HTe (40%) or P3DDTe (25%). Interestingly, P3EHTe exhibited a C=C peak broadened in both directions, with a greater intensity at both high wavenumbers (~1460 cm\(^{-1}\)) and surprisingly low wavenumbers (~1370 cm\(^{-1}\)). We consider that the low-wavenumber shoulder arises from the polymer chains that are responsible for the narrow C=C peak observed under 785 nm excitation (Figure 4d), the crystalline peaks observed in XRD and the absorption shoulder at ~750 nm associated with planar chains. Despite the steric hindrance expected of branched side-chains, P3EHTe appears to have achieved some degree of long-range molecular order, yet the broad C=C peak observed by Raman conclusively shows that P3EHTe also has the greatest proportion of short-range molecular disorder out of the three polymers we have investigated. This observation implies that while the branched side-chain is responsible for an increase in overall disorder it does not completely prevent the formation of aggregates with long-range order.

It is worth noting that the trend in thin-film absorption maxima differs from that reported previously for the three polytellurophenes with different side-chains, namely in that the absorption of P3DDTe is blue-shifted with respect to P3EHTe and not the other way around.\(^{14}\) However, the thin films described here were deposited via bar-coating from 1,3,5-trichlorobenzene, rather than spin-coating from chlorobenzene as was done previously, and the difference is attributed to variations in the materials’ respective solubilities and deposition kinetics.

**High-Temperature Bar-coating**

Thermal annealing is a commonly used processing treatment for manipulating and improving the morphology of organic thin films, and we have previously reported that annealing above the glass transition temperature of conjugated polymers like P3HT can have a significant effect on
their molecular order. The improvement is a consequence of heating the polymer above its glass transition temperature, at which point it becomes mobile and can reorganize, eventually adopting a thermodynamically-determined equilibrium morphology. A similar effect can be achieved by depositing films directly from solution onto hot substrates, effectively annealing the solid material as it precipitates out of the solution, and has the advantage of making it easier to process materials that are poorly soluble at room temperature.
Figure 7. Normalized absorption spectra (a,c,e) and normalized Raman spectra (b,d,f) for differently processed films of P3HTe (a,b), P3DDTe (c,d) and P3EHTe (e,f). Neat films were bar-coated at room temperature and 140 °C, P3ATE:HDPE blend films were bar-coated at 140 °C and were 2:1 by weight. Raman excitation λ was 488 nm.

When P3HTe was bar-coated onto a substrate heated to 140 °C it produced a much more uniform film morphology, as shown in Figure 8, that suggests a slower deposition and greater solubility. This led to a 33 nm red-shift of absorption from 612 to 643 nm (2.02 to 1.93 eV, see Figure 7a), indicative of a longer effective conjugation length and greater crystallinity. In terms of Raman, there was no change in the position of the C=C peak (1373 cm⁻¹, see Figure 7b) due to the dominance of the ordered contribution, but there was a significant increase in the relative intensity of the ordered phase, from 39% to 56%, due to suppression of the disordered phase contribution at 1420 cm⁻¹. Overall, it appears there was a marked improvement in the crystallinity and molecular order when the film was cast at high temperature, which can be attributed to a combination of greater solubility and annealing during deposition driving the film towards a highly-ordered equilibrium morphology.

P3DDTe also exhibited a more uniform morphology when bar-coated at 140 °C compared to room temperature (Figure 8), resulting in a 19 nm red-shift in absorption (see Figure 7c) from 580 to 599 nm (2.14 to 2.07 eV), due to greater absorption at longer wavelengths. Similarly, Raman spectra (Figure 7d) also demonstrated an increase in backbone planarity and molecular order: the relative intensity of the ordered phase rose from 26% to 42% and produced a down-shift of the C=C peak position from 1421 to 1391 cm⁻¹. The Raman spectra of both P3HTe and P3DDTe were very similar in shape when cast at high temperature, suggesting that both polymers have achieved similar degrees of molecular order despite the large differences
observed for films cast at room temperature. This leads us to conclude that both P3HTe and P3DDTe, possessing linear side-chains, have similar equilibrium morphologies dominated by highly planar conformations, which can be attained under thermodynamic deposition conditions (i.e. at high temperatures); this agrees with the transistor data reported by Jahnke et al., who reported that P3HTe and P3DDTe both exhibited a moderately good charge carrier mobility of $1.6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ when bar-coated at 140 °C, indicative of good π-π stacking for intermolecular charge transport.\textsuperscript{16} We propose that when P3DDTe is deposited at low temperatures, the longer side-chains introduce a large kinetic barrier that slows the reorganization of polymer chains, leading to a much more disordered polymer conformation in thin films at room temperature compared to P3HTe. This barrier appears to hinder the development of long-range order even at high temperatures: although the films exhibited almost identical Raman spectra when bar-coated at 140 °C, the absorption maximum of P3DDTe was less red-shifted towards longer wavelengths (longer conjugation lengths) compared to that of P3HTe.
Figure 8. Micrographs of P3HTe (left column), P3DDTe (middle column) and P3EHTe (right column) films, either neat films bar-coated at room temperature (top row), at 140 °C (middle row) or blend films bar-coated at 140 °C (bottom row).

Bar-coating neat P3EHTe at 140 °C had relatively little impact on the polymer’s absorption (see Figure 7e), resulting in a small decrease in absorption at longer wavelengths, notably of the vibronic shoulder at ~750 nm, with a minor ~6 nm blue-shift of $\lambda_{\text{max}}$ from 634 to 628 nm (1.96 to 1.97 eV). These changes in absorption suggest a poorer deposition but are too negligible to lead to any serious conclusions, and as such we must look at the impact on short-range molecular order according to Raman. Figure 7f demonstrates that there was a significant improvement in
molecular order for P3EHTe deposited at 140 °C, evident by an increase in the relative intensity of the ordered phase at ~1390 cm$^{-1}$ and a corresponding shift of the C=C peak maximum from 1420 to ~1410 cm$^{-1}$. The C=C peak did not resemble that of P3HTe or P3DDTe deposited under the same conditions, exhibiting a much larger disordered contribution at ~1420 cm$^{-1}$ and a broad C=C peak indicative of a broad distribution of different molecular conformations rather than the predominantly ordered phase that was observed for the other two polymers. This may explain why P3EHTe was reported to have a significantly lower charge carrier mobility (7.8 × 10$^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) compared to P3HTe and P3DDTe (1.6 × 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$),$^{16}$ which could be attributed to poorer π-π stacking due to the conformational disorder observed here. Considering that P3EHTe exhibited less of an improvement in order when cast at 140 °C compared to a polymer with larger, heavier side-chains (P3DDTe), we consider that the organization of P3EHTe is not limited by a kinetic energy barrier like that of P3DDTe, but that its equilibrium morphology is simply one with a lower degree of molecular order due to steric effects from its branched side-chains.

Effects of Blending with HDPE

We then examine the short and long-range molecular order of each semiconducting P3ATe polymer when blended with insulating high-density polyethylene (HDPE). P3ATe:HDPE blends were used previously as the active layer in bottom-gate bottom-contact field effect transistors (FETs), and exhibited reasonable charge transport characteristics (hole mobilities of ~10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$) despite containing ~40% insulating polymer by weight.$^{16}$ We have previously reported that blending P3HT with the fullerene acceptor PC$_{60}$BM resulted in a significant loss of molecular order, due to the formation of a mixed amorphous phase where P3HT organization is disrupted,$^{11,17}$ and as such it is important to study the impact of blending on the molecular order.
of polytellurophenes in order to understand the performance of P3ATe-based blend films in electronic devices.

Blending P3HTe with HPDE produced in a phase-separated film containing micron-scale domains, according to optical microscopy (Figure 8). HDPE did not contribute to either absorption or Raman spectra due to its lack of conjugation (see ESI for a comparison between 450 and 1800 cm\(^{-1}\)), but did affect the absorption and Raman of P3HTe: causing a \(\sim 9\) nm blue-shift of its main absorption peak from 643 to 634 nm (1.93 to 1.96 eV, see Figure 7a), and a small increase in the relative intensity of the disordered contribution to the C=C peak (Figure 7b) that reduced relative intensity of the ordered phase from 56% to 51%. These changes were relatively minor considering the blend contained 40% HDPE by weight, and as such it appears that the two materials have formed well-separated domains with relatively little interaction that would lead to disruption of P3HTe polymer molecular order. TEM imaging conducted previously indicated that the blends were formed of nanofibers and aggregated micron-scale spheroids set in a surrounding matrix, and Electron-Dispersive X-ray (EXD) mapping established that both the nanofibers and the matrix contained tellurium.\(^{16}\) We propose that these nanofibers are responsible for the highly-ordered component we observe using Raman, which is unaffected by blending, and that the small increase in disorder (responsible for the \(\sim 9\) nm blue-shift of absorption) is from a small quantity of P3HTe polymer that is mixed with HDPE in the amorphous matrix.

For P3DDTe:HDPE, the blend appeared to be highly phase separated at the micron-scale (Figure 8), as was observed for P3HTe:HDPE. Figure 7c revealed a very small \(\sim 7\) nm red-shift of absorption, from a \(\lambda_{\text{max}}\) of 599 to 606 nm (2.07 to 2.04 eV), due to decreased intensity at longer wavelengths, but the change was so minor that we consider blending had little impact.
However, Raman (Figure 7d) established that there was a clear increase in the disordered contribution to the C=C peak, around $\sim$1420 cm$^{-1}$, which resulted in a decrease in the estimated ordered phase fraction from 53% to 45%. It appears that P3DDTe:PCBM also forms a highly separated blend structure, preserving the polymer’s effective conjugation length, but with a slightly higher degree of intermixing evident in the greater disorder compared to P3HTe. TEM images reported previously showed that P3DDTe formed nanofibers in the neat film but that these were absent in the blend, while EXD revealed that tellurium was localized in one phase of the blend.$^{16}$ Consequently, it appears that although nanofibrillar structure is suppressed by blending, the film is still phase-separated and P3DDTe retains a significant percentage of its natural short-range molecular order. Interestingly, the P3DDTe:HDPE blend is reported to perform better than the neat film in FET devices, with a 3.6× increase in charge carrier mobility to $5.7 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, suggesting that the percolated network with good π-π stacking still exists despite the loss of nanofibres.$^{16}$ We propose that unlike P3HTe, the longer side-chains of P3DDTe allow it to better mix with HDPE but also possess enough flexibility that the conjugated backbone can retain its planarity despite this interaction, at the expense of longer-range lamellar organization (i.e. nanofiber formation).

P3EHTe was reportedly the least miscible with HDPE, according to TEM and EXS mapping, and apparently formed a phase-separated network of P3EHTe nanofibrils in a pure HDPE matrix.$^{16}$ According to optical microscopy the film was phase-separated but the scale of individual domains was the smallest of the three blends (Figure 8). Figure 7e shows that blending had almost no impact on absorption, with no change in $\lambda_{\text{max}}$ and only a slight increase in absorption at $\sim$750 nm, the 0-0 vibronic transition associated with aggregation, compared to a neat film deposited at 140 °C. Figure 7f shows there was a corresponding increase in molecular
order, indicated by reduced intensity from the disordered component of the C=C peak. This improvement in both molecular order and conjugation length upon blending is very unusual; and does not follow our understanding that any degree of interaction leads to some disruption of molecular order, as shown by P3HTe and P3DDTe. However, we have previously observed that it is possible to obtain greater molecular order in blends of P3HT and polyethylene oxide (PEO) compared to a neat film deposited under the same conditions, due to their immiscibility driving the formation of an extremely phase-separated structure.³ We propose that a similar repulsion may occur in P3EHTe:HDPE blends, driving the two materials to form separate closely-packed structures in order to avoid contact with one another, resulting in greater backbone planarity and increased 0-0 absorption (i.e. J-like aggregation). This may explain why P3EHTe device performance was apparently improved by blending: closer aggregation and greater molecular order will aid π-π charge transport, in agreement with the reported 3.6x increase in charge carrier mobility to $2.8 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$.

CONCLUSIONS

Using absorption spectroscopy and resonant Raman spectroscopy, we have found that polytellurophene, a heavy organometallic analogue of polythiophene, exhibits some favorable opto-electronic and morphological properties as a result of the substitution of tellurium for sulfur. P3HTe exhibits a low optical band-gap of 1.4 eV, which will aid efficient sunlight harvesting for organic photovoltaic applications; while an increase in molecular order, i.e. greater planarity of the conjugated backbone, encourages aggregation and faster charge transport. Continuing the trend down Group 16 from polythiophene to polyselenophene, polytellurophene has a remarkable Raman spectrum with clearly defined vibrational peaks associated with ordered
and disordered polymer phases, dominated by a narrow distribution of planar conformations and a broad distribution of twisted conformations respectively.

By comparing three polytellurophenes with different side-chains, we have studied how both and deposition conditions and minor changes in chemical structure can influence the organization of the polymer at the nanoscale. We have established that increasing the length of a linear side-chain from a hexyl to a dodecyl moiety introduces a greater proportion of disordered phase at room temperature due to kinetic hindrance, but that both P3HTe and P3DDTe can achieve a similarly high degree of molecular order at higher processing temperatures. By contrast, using a branched 2-ethylhexyl side-chain introduces inherently greater conformational disorder through steric hindrance, which is still present even when deposited at high temperature and helps explain the poorer charge carrier mobility that has been reported for P3EHTe.16 When blended with the polymeric insulator HDPE, all three polymers exhibited relatively little disorder of the semiconducting polymer due to intermixing, instead forming phase-separated networks of good molecular order that are beneficial to percolated charge transport. Differences in reported charge carrier mobility can be attributed to variation in miscibility between their side-chains and HDPE, correlated to the impact on molecular order: P3DDTe was the most miscible, and exhibited the greatest disruption due to blending; P3HTe was less compatible with HDPE and retained its highly-ordered nanofibrillar structure, with no impact on mobility; while P3EHTe was the least compatible and actually exhibited greater molecular order when blended, with a corresponding improvement in charge carrier mobility.

We have shown that resonant Raman spectroscopy is a valuable tool for investigating the molecular order of conjugated polymers, an important morphological parameter that is influenced by a number of structural and processing parameters and in turn influences optical,
electronic and charge transport properties. Sensitivity to both the ordered phase and the
disordered phase makes Raman a powerful technique, revealing subtle changes in morphology
that were not immediately evident according to other techniques such as absorption spectroscopy
or XRD, and helps us develop a greater knowledge of the relationships between molecular
properties, morphological structure and device performance for this novel class of
organometallic conjugated polymer.

ASSOCIATED CONTENT

The following files are available free of charge.

Electronic supplementary information (PDF)

AUTHOR INFORMATION

Corresponding Author

* ji-seon.kim@imperial.ac.uk

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval
to the final version of the manuscript.

ACKNOWLEDGMENT

This work was funded by the EPSRC through the Plastic Electronics Doctoral Training Centre
(EP/G037515/1). We also acknowledge EPSRC support from EP/K029843/1, Cambridge
Display Technology (CDT) CASE studentship and Samsung GRO program.

REFERENCES


(15) Tsoi, W. C.; James, D. T.; Domingo, E. B.; Kim, J. S.; Al-Hashimi, M.; Murphy, C. E.; Stingelin, N.; Heeney, M.; Kim, J.-S. Effects of a Heavy Atom on Molecular Order and


(20) Frisch, M. J.; *et al.* Gaussian 09, Rev. A.02; Gaussian Inc.: Wallingford CT, 2009.


For Table of Contents only