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Poly(3-alkyltellurophene)s Are Solution-Processable Polyheterocycles

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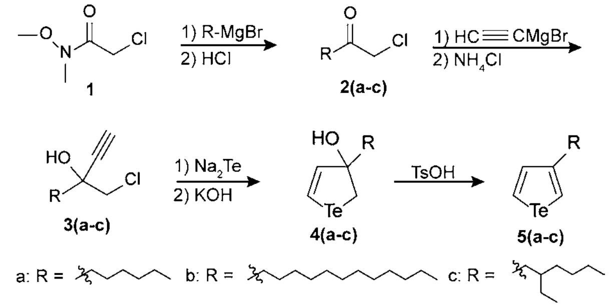
Supporting Information

ABSTRACT: The synthesis and characterization of a series of poly(3-alkyltellurophene)s are described. Polymers are prepared by both electrochemical and Kumada catalyst transfer polymerization methods. These polymers have reasonably high molecular weights (M_n = 5.4−11.3 kDa) and can be processed in a manner analogous to that of their lighter atom analogues. All examples exhibit red-shifted optical absorption, as well as solid-state organization, as evidenced by absorption spectroscopy and atomic force microscopy. Overall, the synthesis and characterization of these materials open up a wide range of future studies involving tellurium-based polyheterocycles.

Polythiophenes have arguably been the most well studied, well characterized, and important organic electronic materials.[1] While furan[2] and selenophene[3] analogues have emerged in recent years, there have been very few reports of soluble tellurophene-containing polymers[4] and no examples of soluble tellurophene homopolymers. Polytellurophenes represent a significant synthetic challenge, particularly in the development of monomers suitable for metal-catalyzed condensation polymerizations. "Heavy" heterocycles offer certain advantageous properties relative to their lighter analogues, including a narrow optical band gap,[5] the ability to be polarized,[6] the ability to form extended valence adducts,[7] enhanced planarity,[3e] and a distinct solid-state structure.[8] Herein we report for the first time that a series of alkyltellurophene homopolymers, including the tellurium analogue of the ubiquitous poly(3-hexylthiophene) (P3HT), can be prepared by a novel methodology. We further demonstrate their potential for use in organic electronics by characterizing both their solution and solid-state properties.

For this study, alkyl-substituted tellurophene monomers were prepared by a ring-closing reaction that places the desired alkyl chain in the 3-position (Scheme 1). While certain aspects of this synthetic pathway were adapted from previously published work on 3-hexylselenophene,[9] we have significantly modified the first step to improve the yield, as well as the ring-closing step for the use of tellurium (in place of selenium). Specifically, the synthesis begins with the preparation of the Weinreb amide 2-chloro-*N*-methoxy-*N*-methylacetamide (**1**).[10] This precursor was then treated with hexylmagnesium bromide to afford 1-chloro-2-octanone (**2a**) in high yield (92%) without the need for purification. We find that the Weinreb amide route is superior to the previously published procedure for **2a** that begins with chloroacetyl chloride and requires a challenging purification step. Treatment of **2a** with ethynylmagnesium bromide affords 3-(chloromethyl)-1-nonyn-3-ol (**3a**), the precursor to the five-member ring product, in 94% yield. Addition of **3a** to a solution of sodium telluride in ethanol gives the intermediate **4a**, which is dehydrated without further purification to give 3-hexyltellurophene (**5a**) in 37% yield. All three novel 3-alkyltellurophenes can be prepared in this manner.

Scheme 1. Synthesis of 3-Alkyltellurophenes



One of the hallmarks of 3-alkylthiophenes is their ability to be electropolymerized at relatively low oxidative potentials. Thus, for our initial investigations, we performed electrochemical polymerization on 3-hexyltellurophene (**5a**) to determine if these compounds could indeed be electropolymerized. It should also be noted that oxidative polymerization is the most common way in which previous polytellurophenes have been synthesized.

The electrochemical properties of **5a** were investigated by cyclic voltammetry (CV) in acetonitrile, revealing two irreversible oxidation peaks at 0.56 and 0.90 V (all potentials are reported vs ferrocene/ferrocenium). Repeated CV cycling to 0.78 V did not produce a well-defined film on the surface of a platinum working electrode, but a small increase in current and shift to lower oxidation potential are observed in the voltammogram, indicating that electrochemical polymerization occurs to some extent (Figure 1a). Similar results were obtained upon repeating the process and increasing the CV cycling range to 1.08 V [see the Supporting Information (SI)]. When an electrochemical cell containing **5a** was held at a constant potential (0.58 V) for a sustained period, however, the

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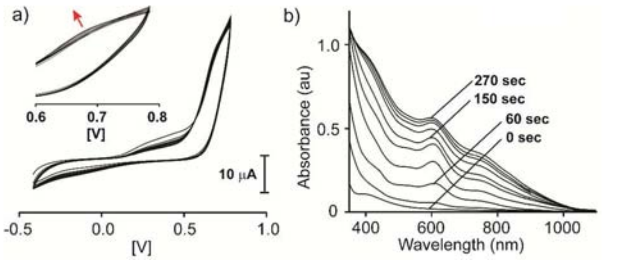
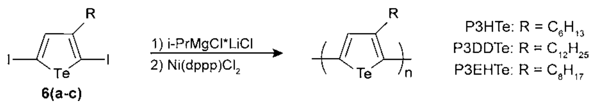


Figure 1. Characterization of 3-hexyltellurophene by (a) cyclic voltammetry and (b) pulsed spectroelectrochemistry. All potentials are relative to Fc/Fc$^+$.

solution changed from colorless to blue and produced a blue precipitate. Based on this observation, we decided to perform spectroelectrochemical measurements on **5a** in dichloromethane to further investigate the electropolymerization process. Time-resolved spectroelectrochemical measurements were conducted using a platinum gauze working electrode held at a constant potential (0.58 V) for 30 s intervals, after which the absorbance profile was measured (Figure 1b). The absorbance in the visible region increases with each successive pulse, producing results consistent with the formation of poly(3-hexyltellurophene) (P3HTe). After 10 pulses the spectrum has an absorbance maximum at 599 nm with a well-defined shoulder at ~750 nm. During the course of this experiment, trace amounts of an insoluble blue film were also noted to coat the surface of the working electrode. Overall, electrochemical and absorption spectroscopy measurements show that the electrochemical polymerization of **5a** occurs under these conditions.

Another significant advantage of polythiophenes (and selenophenes) is their ability to be synthesized under controlled chain-growth polymerization methods.[11] This has led to the formation of narrow polydispersity homopolymers with relatively high molecular weight as well as distinct block-type[12] and gradient-type[13] copolymers. Based on this, we next prepared 3-alkyltellurophene monomers to specifically test their ability to be polymerized under the widely used Kumada catalyst transfer polymerization. For this, 3-alkyltellurophene compounds were iodinated in the 2- and 5-positions by treatment with *sec*-butyllithium followed by electrophilic quenching with iodine to afford the desired 2,5-diiodo-3-alkyltellurophenes (**6a–c**). With these halogenated monomers in hand, polymers were prepared by activation with an *iso*-propylmagnesium chloride–lithium chloride complex, followed by addition of [1,3-bis(diphenylphosphino)propane]nickel(II) chloride catalyst (Scheme 2). Polymerization reactions were conducted in methyl-THF at 80 °C to maintain the solubility of the growing chain, and typical reaction times were 24–48 h to afford the highest possible molecular weight. After this time, the reaction mixtures were added to methanol to precipitate the polymer products, which were then collected and purified by Soxhlet extraction with various solvents, depending on the side-chain substituent (see the SI). For example, P3HTe was washed successively with methanol, hexanes, and chloroform before collection of the remaining insoluble material (the desired product). Poly(3-(2′-ethyl)hexyltellurophene) (P3EHTe) is much more soluble than P3HTe and was washed with methanol and ethyl acetate before being extracted in hexanes.

Scheme 2. Nickel-Catalyzed Polymerization of Diiodo-alkyltellurophenes



P3HTe: R = C_6H_{13}
P3DDTe: R = $C_{12}H_{25}$
P3EHTe: R = C_8H_{17}

Having obtained soluble polymers, we next conducted a series of NMR experiments to further characterize the polymers and determine if regioregular materials had been prepared. Regioregularity is very important for solid-state organization and charge transport properties. Poly(3-dodecyltellurophene) (P3DDTe) and P3EHTe have ^{1}H NMR resonances at 7.40 ppm, which we assign as the aromatic tellurophene proton. This is downfield from the aromatic resonances of poly(3-hexylthiophene) and poly(3-hexylselenophene) (P3HS), which are at 6.98 and 7.12 ppm, respectively. This is consistent with the trend that a heavier group 16 atom leads to a downfield shift in the aromatic resonance. Integration of the two methylene signals confirms that P3EHTe is 93% regioregular (Figure 2). P3DDTe does not have a second (regiorandom) methylene peak in the proton spectra (see the SI), which is indicative of a high degree of regioregularity. However, due to the weak signal, an exact value cannot be determined. Due to solubility limitations, the ^{1}H NMR of P3HTe was not obtained.

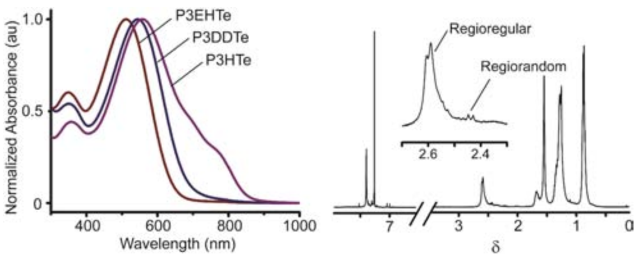


Figure 2. Solution absorption spectra of poly(3-alkyltellurophene)s and P3EHTe ^{1}H NMR spectra.

Chain-length approximation by gel permeation chromatography relative to polystyrene standards (conducted in 1,2,4-trichlorobenzene at 140 °C) was conducted to confirm the polymeric nature of the materials. These data show that P3HTe and P3DDTe have similar M_n values, 9.9 (PDI = 2.2) and 11.3 kDa (PDI = 2.0), respectively, while P3EHTe is lower (5.4 kDa, PDI = 1.9). The ethylhexyl side chains likely hinder the nickel-catalyzed chain growth due to steric effects, which explains this trend.[14] Based on the monomer:catalyst ratio, we would expect a degree of polymerization of 100, leading to M_n = 26–35 kDa for all polymers. Shorter than expected chains for all three polymers is likely due to chain termination before complete monomer consumption. This may be due to either solubility limitations or a weaker association of the Ni catalyst with the tellurophene chain. Given the lack of previously reported polytellurophenes, however, these molecular weights are reasonably high, confirming that polymeric materials were prepared.

To better understand the properties of polytellurophenes, optical studies on all three samples were performed in chlorobenzene. P3HTe and P3DDTe have maximum absorption peaks (558 and 545 nm, respectively) that occur at notably longer wavelengths than P3HT (455 nm) or P3HS (500 nm), which is consistent with theory that predicts polytellurophenes will have a narrower HOMO–LUMO gap than thiophenes and selenophenes. For P3EHTe, a blue-shift in absorption maximum (to 512 nm) is observed relative to P3HTe and P3DDTe, likely due to backbone twisting that results from the bulky ethylhexyl side chain.[15] Although P3HTe and P3DDTe have similar maximum absorption peaks, a well-defined shoulder is observed in the long-wavelength region of the P3HTe absorbance spectrum. We assign this as the presence of aggregated chains that arise from the limited solubility of this polymer, consistent with NMR studies. Upon heating to 95 °C in 1,2,4-trichlorobenzene, P3HTe is fully dissolved, and this shoulder is no longer present (see the SI). The molar absorptivities of the three polymers were obtained in chlorobenzene. P3HTe, P3DDTe, and P3EHTe have molar absorptivities of 3900, 5100, and 6400 M^{-1} cm^{-1} (calculated per repeat unit), respectively, revealing that all three polymers are strong light-absorbers.

It is worth noting that all three P3ATes have a second, weaker, high-energy absorption band in their solution absorption spectra. Consistent with this observation, time-dependent density functional theory calculations on a pentamer model predict a high-energy transition with an oscillator strength of 0.14 compared to 1.49 for the lower energy transition (see the SI). The high-energy transition is a HOMO−1 to LUMO+1 transition, while the lower energy transition is HOMO to LUMO. This high-energy band is also predicted for P3HT and P3HS but occurs at a lower wavelength and therefore is not often observed in the wavelength range that is typically reported for these polymers in solution.

We next designed experiments to further understand the solid-state properties of the chemically synthesized polytellurophenes. Thermogravimetric analysis of powder samples shows that the polymers experience 5% mass loss at 305, 312, and 250 °C for P3HTe, P3DDTe, and P3EHTe, respectively. Thin films were then prepared by spin-casting solutions of polymers from hot chlorobenzene followed by annealing (100 °C, 1 h), and then optical properties of the films were measured. P3HTe and P3DDTe have structured solid-state absorption spectra with long-wavelength shoulders that are indicative of interchain π-stacking (Figure 3a). This further supports the conclusion that these polymers are regioregular, as these vibronic peaks are characteristic of the solid-state order typically associated with regioregular materials.[16] For P3EHTe, the long-wavelength shoulder is not as well pronounced, which could be due to the shorter chain length of the polymer or backbone twisting as described earlier. The optical HOMO−LUMO gaps of P3HTe and P3DDTe, determined by onset of absorption, are 1.44 eV, while P3EHTe has a 1.57 eV optical HOMO−LUMO gap. To probe the samples further, we conducted atomic force microscopy imaging (Figure 3b and SI). This experiment shows that P3EHTe forms nanofibrils as a thin film. X-ray diffraction and differential scanning calorimetry also confirm the presence of crystalline domains in films of all three polymers (see the SI). It thus appears that all three polymers are organized, at least to some degree, in the solid state.

We then examined the electrochemical properties of a P3HTe film spun-cast onto an ITO working electrode. A reversible oxidation with an onset at 0.02 V was observed, and repetitive scanning (10 times) to 0.25 V resulted in a 14% loss of current. A second oxidation with an onset at 0.25 V (Figure 3c) was observed, and at higher oxidation potentials (up to 1 V) irreversible oxidation altered the reverse scan (see the SI). During reductive scanning, a peak with an onset around −1.35 V was also observed, indicating an electrochemical HOMO−LUMO gap of 1.37 eV, which is significantly narrower than for polyselenophene.[3a] The observed reversibility of the oxidative wave at lower potentials prompted us to conduct spectroelectrochemistry experiments on a film of P3HTe.

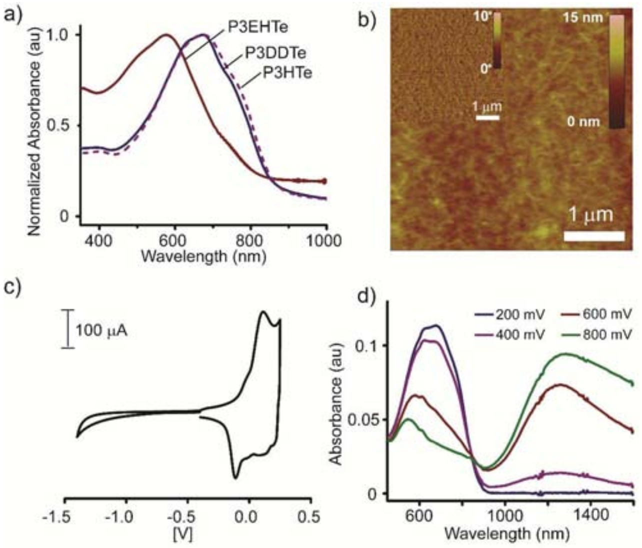


Figure 3. (a) Thin-film absorption spectra of all three polymers. (b) AFM image of P3EHTe spun-cast onto a glass substrate and annealed for 1 h at 100 °C; the inset shows the corresponding phase image. (c) Cyclic voltammogram and (d) spectroelectrochemistry of P3HTe spun-cast onto an ITO substrate. All potentials are relative to Fc/Fc$^+$.

To further characterize the electrochemical properties, we examined the spectroelectrochemistry of the chemically synthesized P3HTe film. A well-defined absorption in the near-infrared (NIR) region of the spectrum appears upon oxidation and increases with potential, while a concurrent decrease in intensity of the absorbance in the visible region occurs (Figure 3d). This NIR absorption is suggestive of the formation of a polaron. Changes observed in the spectra are reversible up to potentials of 0.40 V (see the SI). At higher potentials however, where even larger changes in the NIR region are observed, the process is no longer reversible.

In conclusion, we have synthesized the first series of poly(3-alkyltellurophene)s using both electrochemical and chemical polymerization methods. The polymers have the potential to have many of the advantageous properties of polythiophenes, including regioregularity and the ability to organize in the solid state. They also have new properties that arise from the distinction that they are tellurophenes, including red-shifted optical properties and a narrow electrochemical HOMO−LUMO gap. The polymers can be prepared by both electrochemical oxidation and Kumada catalyst transfer polymerization, leading to materials that are reasonably well defined and can be readily handled in the ambient laboratory environment. For all of these reasons, these tellurophene homopolymers open up many avenues for future developments in their controlled polymerization chemistry as well as the exploration of the optoelectronic properties of materials that are based on the distinct chemistry of tellurium.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, compound characterization, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93. (b) Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202. (c) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169.

(2) (a) Kaur, S.; Findlay, N. J.; Kanibolotsky, A. L.; Elmasly, S. E. T.; Skabara, P. J.; Berridge, R.; Wilson, C.; Coles, S. J. *Polym. Chem.* **2012**, *3*, 2277. (b) Ferrón, C. C.; Delgado, M. C. R.; Gidron, O.; Sharma, S.; Sheberla, D.; Sheynin, Y.; Bendikov, M.; Navarrete, J. T. L.; Hernández, V. *Chem. Commun.* **2012**, *48*, 6732. (c) Bijleveld, J. C.; Karsten, B. P.; Mathijssen, S. G. J.; Wienk, M. M.; de Leeuw, D. M.; Janssen, R. A. J. *J. Mater. Chem.* **2011**, *21*, 1600.

(3) (a) Heeney, M.; Zhang, W.; Crouch, D. J.; Chabinyc, M. L.; Gordeyev, S.; Hamilton, R.; Higgins, S. J.; McCulloch, I.; Skabara, P. J.; Sparrowe, D.; Tierney, S. *Chem. Commun.* **2007**, *47*, 5061. (b) Patra, A.; Wijsboom, Y. H.; Zade, S. S.; Li, M.; Sheynin, Y.; Leitus, G.; Bendikov, M. *J. Am. Chem. Soc.* **2008**, *130*, 6734. (c) Chen, Z.; Lemke, H.; Albert-Seifried, S.; Caironi, M.; Nielsen, M. M.; Heeney, M.; Zhang, W. M.; McCulloch, I.; Sirringhaus, H. *Adv. Mater.* **2010**, *22*, 2371. (d) Hollinger, J.; Jahnke, A. A.; Coombs, N.; Seferos, D. S. *J. Am. Chem. Soc.* **2010**, *132*, 8546. (e) Patra, A.; Bendikov, M. *J. Mater. Chem.* **2010**, *20*, 422. (f) Lee, W.-H.; Son, S. K.; Kim, K.; Lee, S. K.; Shin, W. S.; Moon, S.-J.; Kang, I.-N. *Macromolecules* **2012**, *45*, 1303. (g) Khim, D.; Lee, W.-H.; Baeg, K.-J.; Kim, D.-Y.; Kang, I.-N.; Noh, Y.-Y. *J. Mater. Chem.* **2012**, *22*, 12774. (h) Atak, S.; Içli-Özkut; Önal, A. M.; Cihaner, A. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4398. (i) Li, L.; Hollinger, J.; Jahnke, A. A.; Petrov, S.; Seferos, D. S. *Chem. Sci.* **2011**, *2*, 2306. (j) Klein, M. F. G.; Pfaff, M.; Müller, E.; Czolk, J.; Reinhard, M.; Valouch, S.; Lemmer, U.; Colsmann, A.; Gerthsen, D. *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 198. (k) Hollinger, J.; DiCarmine, P. M.; Karl, D.; Seferos, D. S. *Macromolecules* **2012**, *45*, 3772.

(4) (a) Inoue, S.; Jigami, T.; Nozoe, H.; Aso, Y.; Ogura, F.; Otsubo, T. *Heterocycles* **2000**, *52*, 159. (b) Saito, H.; Ukai, S.; Iwatsuki, S.; Itoh, T.; Kubo, M. *Macromolecules* **1995**, *28*, 8363. (c) Ng, S. C.; Ding, H.; Chan, H. S. O. *Chem. Lett.* **1999**, *12*, 1325. (d) Jahnke, A. A.; Howe, G. W.; Seferos, D. S. *Angew. Chem., Int. Ed.* **2010**, *49*, 10140. (e) Jahnke, A. A.; Seferos, D. S. *Macromol. Rapid Commun.* **2011**, *32*, 943. (f) Lapkowski, M.; Motyka, R.; Suwinski, J.; Data, P. *Macromol. Chem. Phys.* **2012**, *213*, 29.

(5) (a) Das, S.; Zade, S. S. *Chem. Commun.* **2010**, *46*, 1168. (b) Das, S.; Bedi, A.; Krishna, G. R.; Reddy, C. M.; Zade, S. S. *Org. Biomol. Chem.* **2011**, *9*, 6963. (c) Chattopadhyaya, M.; Sen, S.; Alam, M. M.; Chakrabarti, S. *J. Chem. Phys.* **2012**, *136*, 094904.

(6) Zade, S. S.; Zamoshchik, N.; Bendikov, M. *Chem. Eur. J.* **2009**, *15*, 8613.

(7) McCormick, T. M.; Jahnke, A. A.; Lough, A. J.; Seferos, D. S. *J. Am. Chem. Soc.* **2012**, *134*, 3542.

(8) Patra, A.; Wijsboom, Y. H.; Leitus, G.; Bendikov, M. *Org. Lett.* **2009**, *11*, 1487.

(9) Mahatsekake, C.; Catel, J. M.; Andrieu, C. G.; Ebel, M.; Mollier, Y.; Tourillon, G. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *47*, 35.

(10) Shen, Z.; Dornan, P. K.; Khan, H. A.; Woo, T. K.; Dong, V. M. *J. Am. Chem. Soc.* **2009**, *131*, 1077.

(11) (a) Kiriy, A.; Senkovskyy, V.; Sommer, M. *Macromol. Rapid Commun.* **2011**, *32*, 1503. (b) Bronstein, H. A.; Luscombe, C. K. *J. Am. Chem. Soc.* **2009**, *131*, 12894. (c) Brusso, J. L.; Lilliedal, M. R.; Holdcroft, S. *Polym. Chem.* **2011**, *2*, 175. (d) Okamoto, K.; Luscombe, C. K. *Polym. Chem.* **2011**, *2*, 2424.

(12) (a) Wu, P. T.; Ren, G. Q.; Li, C. X.; Mezzenga, R.; Jenekhe, S. A. *Macromolecules* **2009**, *42*, 2317. (b) Yu, X. H.; Yang, H.; Wu, S. P.; Geng, Y. H.; Han, Y. C. *Macromolecules* **2012**, *45*, 266. (c) Zhang, Y.; Tajima, K.; Hashimoto, K. *Macromolecules* **2009**, *42*, 7008. (d) Wu, Z. Q.; Ono, R. J.; Chen, Z.; Bielawski, C. W. *J. Am. Chem. Soc.* **2010**, *132*, 14000.

(13) (a) Locke, J. R.; McNeil, A. J. *Macromolecules* **2010**, *43*, 8709. (b) Palermo, E. F.; McNeil, A. J. *Macromolecules* **2012**, *45*, 5948.

(14) Somanathan, N.; Radhakrishnan, S.; Thelakkat, M.; Schmidt, H. W. *Macromol. Mater. Eng.* **2002**, *287*, 236.

(15) Somanathan, N.; Radhakrishnan, S. *Int. J. Mod. Phys. B* **2005**, *19*, 4645.

(16) Brown, P. J.; Thomas, D. S.; Köhler, A.; Wilson, J. S.; Kim, J.-S.; Ramsdale, C. M.; Sirringhaus, H.; Friend, R. H. *Phys. Rev. B: Condens. Matter* **2003**, *67*, 064203.