Structure−Property Relations of Regiosymmetrical 3,4-Dioxy-Functionalized Polythiophenes

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ABSTRACT: We present the synthesis and characterization of novel homo- and copolymers containing mono- and dialkylated 3,4-propylenedioxythiophenes with the purpose of creating new π-conjugated polymers to be exploited in the field of polymer electronics and photonics. We show that the large seven-membered dioxepine ring attached to the thiophene moiety causes unfavorable steric interactions, especially in the homopolymers; it thus prevents the polymers from adapting a coplanar structure with a short π-stacking distance in the solid state. We furthermore show that incorporation of less space filling units in the form of unsubstituted thiophene units into the polymer chain reduces these unfavorable interactions and therefore allows for a more coplanar polymer backbone orientation and a shorter π-stacking distance in the solid state. These findings are based on absorption spectroscopy, electrochemical measurements, X-ray powder diffraction, and conductivity measurements.

Introduction

Polythiophenes appear as one of the most important classes of π-conjugated polymers, primarily because they meet the essential requirements of solubility, processability, and the possibility for incorporating a wide variety of functionalities through substituent modifications.[1] The early work in this field dealt primarily with unsymmetrical thiophene units substituted in the 3-position, and pioneering work by McCullough and others[2,3] has clearly shown that control of regiochemistry is decisive for the conductive properties of poly(3-alkylthiophene) (PAT) thin films. The discovery of the symmetrical poly(3,4-ethylenedioxythiophene) (polyEDOT)[4,5] as a new modified polythiophene with a high chemical stability and a high electrical conductivity in the doped form[6−8] launched numerous investigations based on the development of new regiosymmetrical thiophene-based polymer systems; these investigations have primarily been focused on systems closely related to EDOT, but completely novel systems encompassing alternative substitution patterns, other heteroatoms, or an unconventional connectivity have been presented as well.[9−12] In an effort to identify new systems which encompass the advantage of symmetrical thiophene units as well as the possibility to graft solubilizing chains onto the polymer without disrupting the symmetry, we have focused our studies on new symmetrical members of the 3,4-alkylenedioxythiophene family. Our approach has been to extend the six-membered 1,4-dioxine ring to a seven-membered 1,4-dioxepine ring, thus creating a 3,4-propylenedioxythiophene (ProDOT) with a propylene bridge between the oxygen atoms instead of an ethylene bridge, as also seen in works from Reynolds and others;[5,11,13−15] this facilitates functionalization with solubilizing chains on the central carbon atom without loss of regiosymmetry. To overcome some of the main problems encountered with the symmetrically substituted thiophenes including the dialkylated ProDOTs, namely increased steric interactions and an increased volume of alkyl chains, we have furthermore developed new symmetrical polythiophenes with less space-filling alkyl chains per thiophene unit by incorporating unsubstituted thiophene units into the ProDOT-based polymer in a symmetrical fashion, an approach also seen in work from Frechet and co-workers.[16,17]

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Results and Discussion

Homopolymer Synthesis. As depicted in Scheme 1, ProDOT-hexyl (**2a**), ProDOT-dihexyl (**2b**), and ProDOT-didecyl (**2c**) were all synthesized in good yields from 3,4-dimethoxythiophene (**1**) by transetherification with an alkylated 1,3-propanediol; the subsequent bromination with NBS afforded compounds **3a**−**3c** in high yields. The oxidative polymerization protocol with ferric chloride developed by Sugimoto was applied to the ProDOT monomers (**2a**−**2c**) to create the PolyProDOTs **Poly2a**−**Poly2c** as shown in Scheme 2. The reaction was carried out by adding a 0.2 M solution of the ProDOT monomer in chloroform to a 0.2 M solution of ferric chloride in chloroform, whereupon the reaction mixture was stirred for 24 h at room temperature; the polymer was subsequently precipitated into methanol and purified by Soxhlet extraction. Yields varied greatly with the aliphatic moiety on the monomer, in that PolyProDOT-hexyl (**Poly2a**) was formed in a 5% yield whereas PolyProDOT-dihexyl (**Poly2b**) and PolyProDOT-didecyl (**Poly2c**) were formed in an 82% yield and an 80% yield, respectively. As an alternative polymerization route, the GRIM procedure developed by McCullough and co-workers were applied to the dibrominated ProDOT monomers (**3a**−**3c**) to create the PolyProDOTs **Poly3a**−**Poly3c** as illustrated in Scheme 3. Grignard metathesis in THF with 1 equiv of Grignard reagent followed by the addition of $Ni(dppp)Cl_2$ and reflux for 20 h promoted polymerization by a Kumada-type cross-coupling. Again, the polymer was precipitated into methanol and purified by Soxhlet extraction; yields followed the trend observed for the Sugimoto protocol since PolyProDOT-hexyl (**Poly3a**) only was formed in a 5% yield whereas PolyProDOT-dihexyl (**Poly3b**) and PolyProDOT-didecyl (**Poly3c**) were formed in a 37% yield and a 40% yield, respectively.

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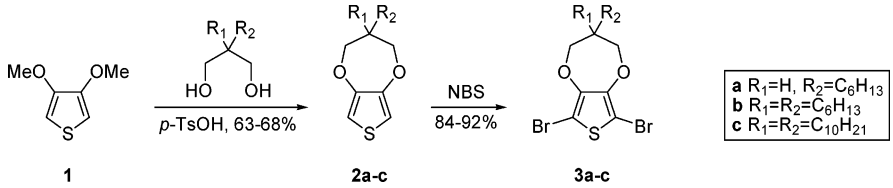
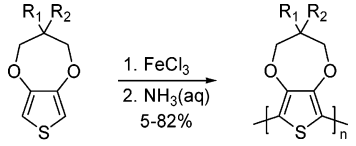
Scheme 1. Monomer Synthesis



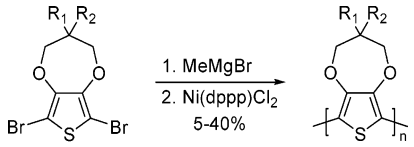
1 2a-c 3a-c

Scheme 2. Homopolymer Synthesis (Sugimoto Method)



2a-c Poly2a-c

Scheme 3. Homopolymer Synthesis (GRIM Method)



3a-c Poly3a-c

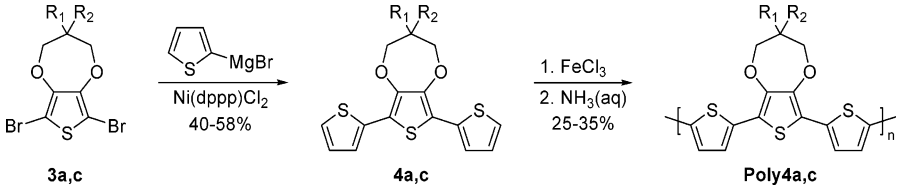
Alternating Copolymer Synthesis. For the controlled synthesis of perfectly alternating two-component copolymers (AB-type copolymers) organometallic reactions must be considered. An attempt to metalate both α-positions of compounds **3a**−**3c** and then react the resulting Grignard reagent in situ with 2,5-dibromothiophene under Kumada-type conditions showed that only one of the two α-positions was metalated; thus, the only polymeric material obtained was **Poly3a**−**Poly3c**. Another strategy utilizing a Suzuki coupling involved the pinacol ester of thiophene-2,5-bisboronic acid, which was reacted with compounds **3a**−**3c** in the presence of a palladium catalyst. In this case, the alternating connectivity was obtained, but with a very low efficiency affording very low molecular weight material in a low yield. Instead, focus was turned toward synthesis of regioregular terthiophenes, as depicted in Scheme 4. By a nickel-catalyzed Kumada coupling with 2-thienylmagnesium bromide in THF, compounds **3a** and **3c** were converted to the regiosymmetrical terthiophenes **4a** and **4c** in moderate yields. These are set up for a Sugimoto-type polymerization, which affords Poly(Tp_2ProDOT-hexyl) (**Poly4a**) in a 25% yield and Poly(Tp_2ProDOT-didecyl) (**Poly4c**) in a 35% yield after purification by Soxhlet extraction.

Random Copolymer Synthesis. An approach to incorporate thiophene units with less space-filling substituents into the PolyProDOT chain in a random fashion was initially attempted by polymerizing a mixture of equimolar amounts of ProDOT monomer and thiophene under the same Sugimoto-type conditions as for the homopolymerization. Characterization of the resulting polymers revealed that thiophene was not incorporated in detectable amounts for any of the polymers; apparently, the process is solely governed by oxidation potentials. As another strategy for incorporation of a less steric demanding monomer in the polymer chain, EDOT was added as the second component instead of thiophene in the Sugimoto-type polymerization. Again, the choice of a regiosymmetrical monomer eliminated the concerns about regioregularity; furthermore, EDOT is believed to have an oxidation potential close to that of the ProDOTs due to the high structural resemblance, and therefore one can imagine more favorable conditions for a competitive reaction governed by both ionization potentials and steric properties during the polymerization process. The reaction, which is only carried out for the ProDOT-didecyl monomer (**2c**), is depicted in Scheme 5. Indeed, EDOT (**5**) is incorporated in the resulting polymer as evident from both the ^{1}H and ^{13}C NMR spectrum (see Figure 1); integration gives that the copolymer **Poly5c** consists of approximately 30% EDOT units and 70% ProDOT-didecyl units.

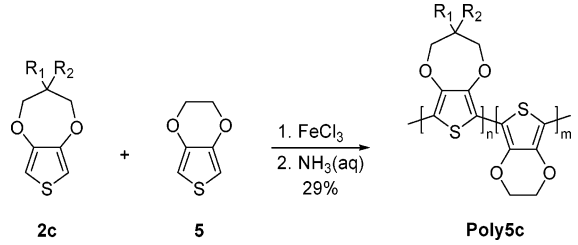
Molecular Weight Characterization. All synthesized polymers were analyzed with size exclusion chromatography (SEC) in order to determine the polystyrene equivalent molecular weights; the results are listed in Table 1. For most of the polymers, a severe tailing effect in the chromatograms, which are also reported by Welsh and co-workers,[14] indicates that the polymers have a tendency to interact unexpectedly with the column. Furthermore, there is a highly significant difference between the spectral data from SEC and the spectral data obtained from regular solution spectroscopy prior to SEC analysis; in most cases the absorption maxima of the eluted polymer fractions are markedly blue-shifted compared to the absorption maxima of the original polymer fractions. These findings strongly indicate that the highest molecular weight polymer fraction is not passing the size separating column as expected. In general, the degree of polymerization based upon the weight-average molecular weight from SEC corresponds to around 20 thiophene units, except **Poly4c** characterized by a degree of polymerization of 22 corresponding to 66 thiophene units and **Poly5c** with an average of only 11 thiophene units per polymer chain. Here it should be mentioned that **Poly5c** has an exceptionally large discrepancy between the optical characteristics before and after SEC analysis. The molecular weights presented herein are in general comparable to previous studies of PolyProDOTs.[14,18] Because of the likely presence of both hydrogen and halogen atoms in the polymer end-group positions, estimation of molecular weight from NMR end-group analysis is not possible.

Optical Spectroscopy. Comparison of the optical absorption data for the polymers in chloroform solution and as films cast from chloroform solution reveals a moderate red shift upon the phase transfer in all cases (Table 1). This typical behavior for polythiophenes indicates that the degree of conjugation is increased in the dense thin films compared to solution due to ordering effects in the solid state. The red shift, however, is not as significant as seen for regioregular PATs, indicating either a certain degree of preaggregation in solution or a lower degree of order in the solid state for the ProDOT-based homo- and copolymers presented herein; a small concentration dependence (5−10 nm) of the absorption data in solution indicates that preaggre-

Scheme 4. Alternating Copolymer Synthesis



Scheme 5. Random Copolymer Synthesis



gation indeed occurs to some extent in solution. For the homopolymers, **Poly2a**−**c** and **Poly3a**−**c**, we note that the extinction coefficient per monomer increases with increasing number of alkyl chains per monomer as well as with increasing length of the alkyl chain. For comparable degrees of polymerization, the tendency should be opposite due to the increasing proportion of alkyl chains relative to thiophene units, a fact indicating that the grafting of longer alkyl chains or additional alkyl chains onto the monomers provides a higher degree of polymerization. From the data in Table 1 it is obvious that both the homo- and copolymers containing the monoalkylated ProDOT moiety (**Poly2a**, **Poly3a**, and **Poly4a**) have significantly blue-shifted absorption maxima both in solution and in the solid state as well as diminished red shifts when going from solution to the solid state compared to the corresponding dialkylated polymer systems, an observation indicating relatively poor self-organizing properties and low degrees of coplanarity for the monoalkylated ProDOT-based polymers. Because of the uncertainties associated with the molecular weight characterization, it is not possible to rule out the fact that these poorer self-organizing properties are a consequence of a lower degree of polymerization more than a consequence of the difference in the substitution pattern. When comparing the dialkylated PolyProDOTs prepared by the Sugimoto-type polymerization (**Poly2b** and **Poly2c**) with the corresponding polymers prepared by the Kumada coupling (**Poly3b** and **Poly3c**), it is evident that the Kumada-type polymers have slightly longer effective conjugation lengths in solution and markedly longer effective conjugation lengths in the solid state than the corresponding Sugimoto-type polymers; they are thus better to adapt a more ordered and coplanar structure upon the phase transfer from solution to thin film. Since this comparison involves identical polymers from different synthetic routes, the explanation for better self-organizing properties most likely relates to an increased degree of polymerization for the Kumada-type polymers compared to the Sugimoto-type polymers; no evidence of structural defects in either type of polymer is present. The observations pointed out above are all supported by the finding that vibronic resolution is observed in the optical absorption spectra for the dialkylated PolyProDOTs but not for the monoalkylated PolyProDOTs.

When a less electron-rich component such as unsubstituted thiophene is incorporated into the polymer chain, the expected increase in oxidation potential compared to the corresponding PolyProDOT is supported by a blue-shifted absorption maximum both in solution and in the solid state as observed for both **Poly4a** and **Poly4c**; the red shift associated with the phase transition is comparable to what is observed for the homopolymers. The copolymers have a larger proportion of thiophene units relative to alkyl chains than the corresponding homopolymers, and as expected this causes an increase in the extinction coefficient. Moreover, it is observed that the extinction coefficient increases when going from **Poly4a** to **Poly4c**, i.e., when increasing the proportion of alkyl chains, hereby again implying that a higher proportion of alkyl chains provides a higher degree of polymerization. Copolymer

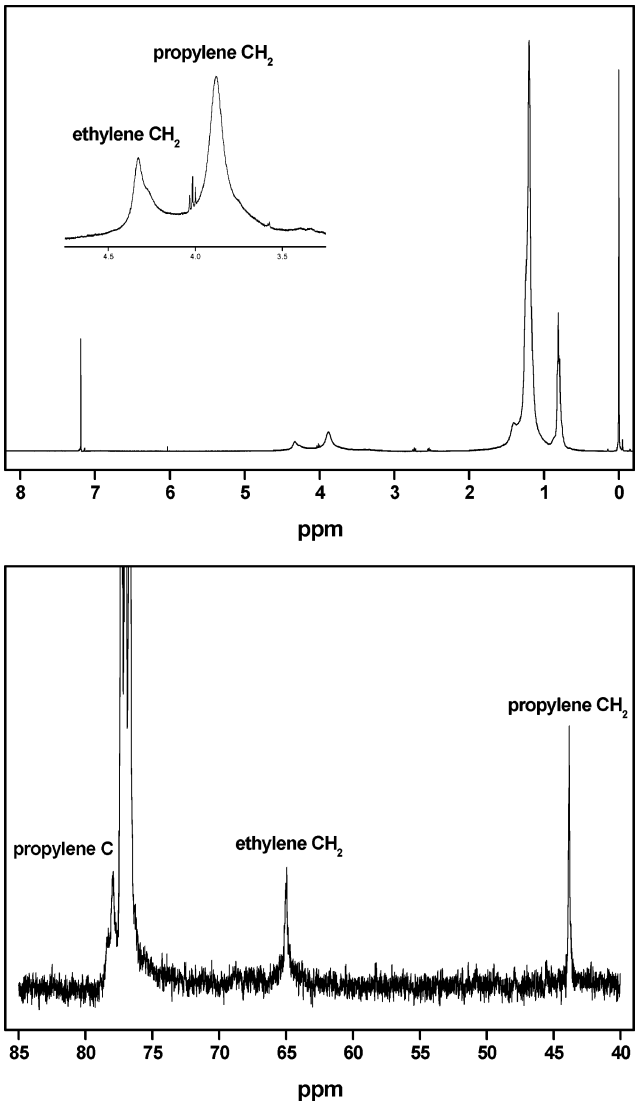


Figure 1. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **Poly5c**; insertion shows an expansion of the 4.75−3.25 ppm area, indicating the presence of both EDOT and ProDOT units in the polymer.

Table 1. Summarized Molecular Weight Characteristics and Optical Properties of the Presented ProDOT Homo- and Copolymers

	M_w [kDa]	PDI	λ_{max}(SEC) [nm]	λ_{max}(sol) [nm]	ϵ_{max} [M^{-1} cm^{-1}]	λ_{max}(film) [nm]
Poly2a	4.9	1.53	483	512	5.3×10^3	522
Poly2b	6.9	1.58	468	533	6.2×10^3	550 (sh 588)
Poly2c	9.3	1.50	470	534	8.5×10^3	550 (591)
Poly3a	5.2	1.31	503	495	5.0×10^3	503
Poly3b	5.8	1.48	462	541 (sh 580)	9.8×10^3	(555) 597
Poly3c	6.9	1.37	462	547 (sh 581)	1.2×10^4	(554) 600
Poly4a	2.4	1.62	460	496	1.9×10^4	510
Poly4c	13.1	2.80	480	514	2.6×10^4	537 (sh 587)
Poly5c	3.9	1.66	416	513	2.7×10^3	550

Table 2. Summarized Electrochemical Properties (First ($E_{pa,1}$) and Second ($E_{pa,2}$) Anodic Peak), Structural Characteristics from XRD (Lamellar Repeat Distance (d_1), Lamellar Coherence Length (L_1), and Alkyl Chain Packing Distance (d_2)) and Electrical Conductivities of the Presented ProDOT Homo- and Copolymers

	$E_{pa,1}$ [V]	$E_{pa,2}$ [V]	d_1 [Å]	L_1 [Å]	d_2 [Å]	ρ [g/cm^3][a]	σ [S/m]
Poly2a	0.57		21.2	51	4.5	1.09	$<10^{-3}$
Poly2b	0.48	0.77	18.9	27	4.7	1.58	$<10^{-3}$
Poly2c	0.51	0.81	21.5	35	4.5	1.96	$<10^{-3}$
Poly3a	0.56						$<10^{-3}$
Poly3b	0.49	0.84					0.17
Poly3c	0.49	0.79	21.6	27	4.5	1.95	30
Poly4a	0.50	0.76	24.0		4.4	0.55	8.4
Poly4c	0.57	0.80	27.7	70	4.6	0.68	46
Poly5c	0.46	0.79	26.0	67	4.5	1.23	0.68

[a] Densities (ρ) were calculated from the XRD data using d_1, d_2, and 7.6 Å as the three dimensions in a unit cell containing a dimeric thiophene unit.

Poly5c can be seen as **Poly2c** with 30% of the ProDOT-didecyl units exchanged with EDOT units, a modification which causes only minor changes, such as less vibronic resolution and a smaller extinction coefficient, in the optical characteristics indicating a slight decrease in effective conjugation length.

Electrochemistry. Typical electrochemical behavior for polythiophene thin films is revealed by characterization of solution cast thin films of the homo- and copolymers on conducting indium tin oxide (ITO) glass plates (Table 2). For all three substitution patterns, the Sugimoto-type PolyProDOTs (**Poly2a**−**Poly2c**) and the Kumada-type PolyProDOTs (**Poly3a**−**Poly3c**) display very similar electrochemical properties, and in general the oxidative behavior of **Poly2a**−**Poly2c** and **Poly3a**−**Poly3c** is in good agreement with previously described PolyProDOTs.[19,20] According to McCullough and Ewbank, an increase in coplanarity along the polythiophene backbone will increase the molecular orbital overlap and hence stabilize both polaronic (radical cationic) and bipolaronic (dicationic) states; this will lower the oxidation potentials and make both states accessible during solid-state electrochemistry.[1] Thus, the presence of two oxidation peaks for the dialkylated PolyProDOTs indicates that these systems organize with a higher degree of coplanarity in the solid state than the monoalkylated PolyProDOTs, which only show one characteristic oxidation peak. Corroborating this argumentation as well as the spectroscopic data, we note that the dialkylated PolyProDOTs have very similar oxidation potentials around 0.50 V for the first oxidation process, while the monoalkylated PolyProDOTs have a somewhat higher first oxidation potential at 0.56−0.57 V.

All the synthesized copolymers exhibit two oxidation peaks, indicating a relatively high degree of coplanarity in the solid state (Table 2). Comparison of **Poly2c** and **Poly5c** indicates that the incorporation of roughly 30% EDOT units in a random way has a positive effect on the effective conjugation length in the solid state since the oxidation potential is slightly lowered, whereas the conclusions come out more vaguely when comparing **Poly4a** and **Poly4c** with the corresponding homopolymers (**Poly2a** and **Poly2c**). Insertion of unsubstituted thiophene units in the polymer chain is expected to cause an increase in oxidation potential since the number of electron-donating 3,4-dioxythiophene moieties is reduced. On the other hand, if the unsubstituted thiophenes bring steric relief to the system and thereby induce a more coplanar conformation in the solid state, then the oxidation potential is expected to decrease. For the monoalkylated system, going from the homopolymer to the copolymer brings a small decrease in oxidation potential, indicating that the effect from an increased effective conjugation length is the most decisive; the opposite is observed for the dialkylated system since **Poly4c** has a slightly higher oxidation potential than **Poly2c**.

X-ray Powder Diffraction. X-ray powder diffraction (XRD) gives diffraction patterns typical for polythiophenes encompassing two rather broad peaks (Figure 2): a low-angle peak correlated to the lamellar repeat distance (d_1 in Table 2) between polymers and a high-angle peak correlated to alkyl chain packing (d_2 in Table 2). The X-ray powder diffraction patterns give no clear information about the π-stacking; no valuable information can be extracted from the broad wide-angle peaks arising from a fairly disordered alkyl chain packing. The polymer powders all possess a rather small degree of crystallinity; the coherence lengths L_1 (calculated from the Scherrer equation) listed in Table 2 indicate that only a few lamellar repetitions exist within

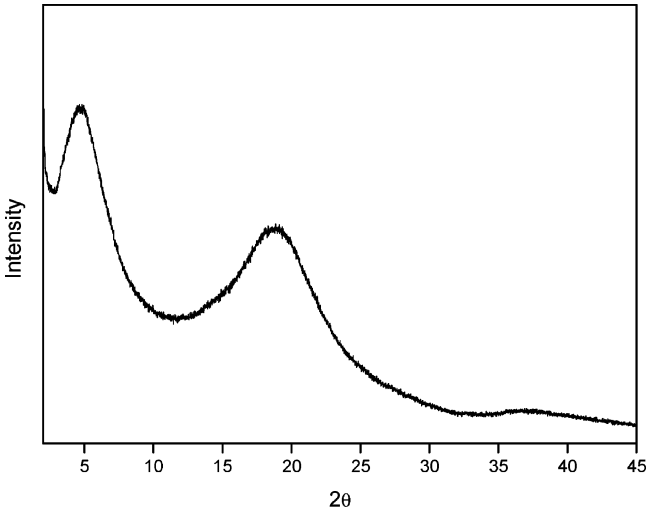


Figure 2. Powder X-ray diffraction spectrum of Sugimoto-type PolyProDOT-dihexyl, **Poly2b**.

each crystallite. A rather long lamellar repeat distance of 21 Å is observed for PolyProDOT-hexyl (**Poly2a**), a shorter distance of 19 Å for PolyProDOT-dihexyl (**Poly2b**), and a somewhat longer distance of nearly 22 Å for PolyProDOT-didecyl (**Poly2c** and **Poly3c**). This indicates that the alkyl chains are fairly extended in the crystalline structure of the monoalkylated PolyProDOTs, while the introduction of a second alkyl chain introduces a tilt, increased conformational disorder, or pronounced alkyl chain interdigitation, which bring the lamellae closer to each other. When going from **Poly2b** to **Poly2c**, thus extending the alkyl chains with four methylene units and therefore the lamella with eight methylene units, the lamellar distance is only increased with 2.6 Å; for comparison, the corresponding change for PATs is more than 7 Å. This also points toward a strongly interdigitated side-chain packing pattern, a phenomenon also described by Bauerle and co-workers in their extensive studies of oligo- and polythiophenes by means of scanneling tunneling microscopy.[1,21−24]

Comparing the XRD data for the random copolymer of EDOT and ProDOT-didecyl (**Poly5c**) with the homopolymer of ProDOT-didecyl (**Poly2c** and **Poly3c**), a significant difference in lamellar distance is observed; the 4.5 Å longer lamellar distance for the copolymer suggests that the alkyl chains possess a less tilted conformation or alternatively experience less intermolecular interdigitation. The same observations are made for the ABA-type copolymers, **Poly4a** and **Poly4c**; when they are compared to the PolyProDOTs of the same alkyl substitution pattern, a significant increase in lamellar distance (5−6 Å) is observed.

In light of the presented XRD data for both homo- and copolymers, the packing in the solid state seems to have a strong dependency upon the degree of alkylation; both the monoalkylated homopolymers (**Poly2a** and **Poly3a**) and the copolymers (**Poly4a**−**c** and **Poly5c**), which all have a relatively low proportion of alkyl chains, have fairly long lamellar repeat distances compared to the dialkylated homopolymers (**Poly2b**−**c** and **Poly3b**−**c**), where the higher proportion of alkyl chains seems to induce a more dense and interdigitated packing pattern. These differences in lamellar distances also find expression in the calculated densities presented in Table 2.

Significant variations in lamellar packing distances are also observed for regioregular HT PATs, which prove to have two distinct packing structures according to Winokur and co-workers.[25−27] Type I is the most common packing pattern characterized by a well-ordered lamellar structure with partial interdigitation of the alkyl side chains. The metastable type II packing structure is characterized by a more interdigitated alkyl packing pattern which causes a decrease in the lamellar distance of roughly 30%. While the type I packing structure has a $\pi-\pi$ packing distance of 3.8 Å, the corresponding stacking distance is 4.5 Å for the type II structure. These variations in lamellar repeat distances hold a strong resemblance to the observations reported in Table 2 for our ProDOT-based homo- and copolymers; it seems like the dialkylated PolyProDOTs adopt a type II-like packing structure while the copolymers adopt a more type I-like packing structure.

Conductivity. Preliminary measurements of electrical conductivity of iodine-doped thin films of the synthesized polymers give low values compared to those observed for PATs, PolyEDOTs, and other PolyProDOTs; the values, which are obtained from a simple two-probe resistance measurement on solution cast thin films, are presented in Table 2. All three Sugimoto-type PolyProDOTs (**Poly2a**−**Poly2c**) and the Kumada-type PolyProDOT-hexyl (**Poly3a**) proved unable to conduct a measurable electrical current upon iodine doping with this experimental setup, whereas the dialkylated Kumada-type PolyProDOTs (**Poly3b** and **Poly3c**) responded to the doping process. **Poly3b** and **Poly3c** showed conductivities of 0.17 and 30 S/m, respectively. The nearly 200-fold increase in conductivity caused by lengthening the alkyl chains is surprisingly large; generally the conductivity upon doping increases only slightly with increasing length of the alkyl chain as observed for both PATs and PolyEDOT-alkyls.[1,8] The longer alkyl chains seem to induce a more structurally ordered packing in the solid state which results in a higher electrical conductivity upon doping. For comparison, Welsh and co-workers have reported conductivities between 200 and 700 S/m for a Kumada-type PolyProDOT-dibutyl.[14] To the best of our knowledge, no electrical conductivity has so far been reported for Sugimoto-type PolyProDOTs.

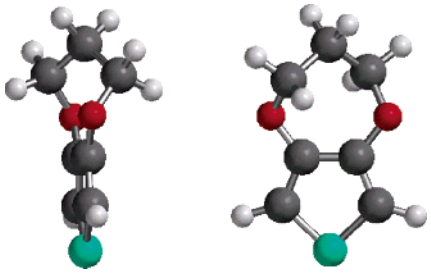


Figure 3. Side-view (left) and front-view (right) of the most stable ProDOT monomer conformation as predicted by semiempirical calculations.

While none of the Sugimoto-type homopolymers presented herein showed electrical conductivity upon iodine doping, the ProDOT-based copolymers, which were also synthesized by the Sugimoto polymerization protocol, responded to the doping process, and low conductivities were measured for all three copolymers (Table 2). The conductivity was 8.4 S/m for **Poly4a** and 46 S/m for **Poly4c**. When these values are compared to the results for the Sugimoto-type homopolymers **Poly2a** and **Poly2c**, it is obvious that the incorporation of two unsubstituted thiophene units per ProDOT unit has an extremely positive effect on the electrical properties in the solid state. Furthermore, increasing conductivity was yet again observed with increasing length of the alkyl chains. The random copolymer **Poly5c** showed a rather low conductivity, but when it is compared to **Poly2c**, it becomes clear that the incorporation of even a small amount of EDOT units in a completely random fashion has a highly positive effect on the resulting polymer with respect to the electrical conductivity.

Discussion. From the well-known crystal packing of regioregular HT PATs one finds that effective π-stacking with the optimal $\pi-\pi$ distance of 3.8 Å leaves a projected area of 29 Å^2 within a dimeric thiophene unit, which due to the transoid orientation of adjacent thiophene units is the natural crystallographic repeat unit.[28,29] When this area is compared with the projected area of 18−20 Å^2 for an alkyl chain, it is obvious that two alkyl groups within a dimeric unit, as is the case for PolyProDOT-dialkyl, will force the $\pi-\pi$ distance to increase, an increase which is highly unfavorable for the interchain charge transport and thus for the mac-

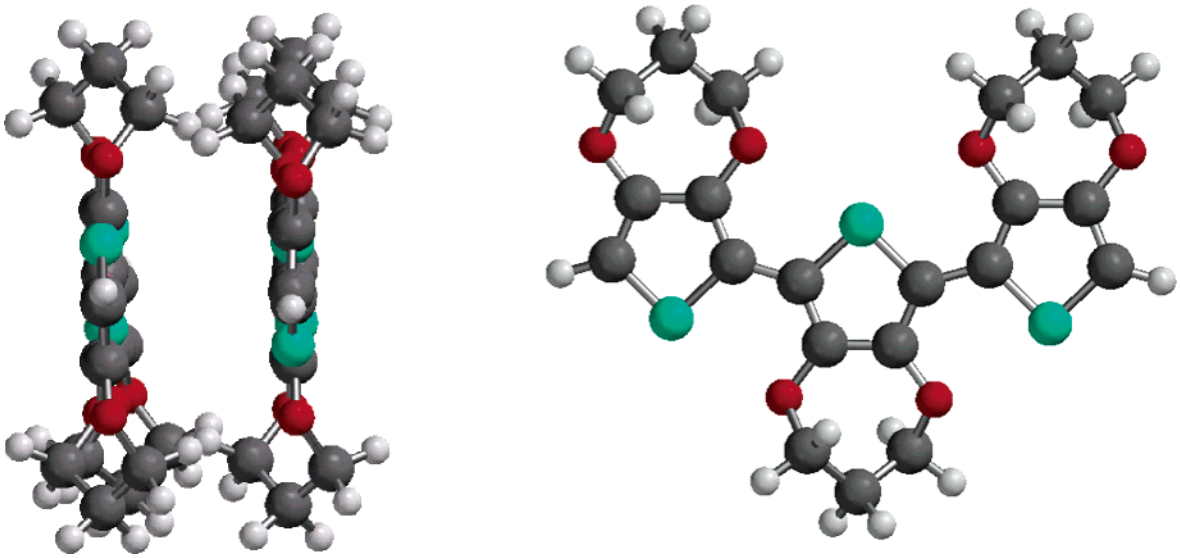


Figure 4. Left: side view of two coplanar PolyProDOT segments with a favorable $\pi-\pi$ distance of 4.2 Å; right: front-view of a single PolyProDOT segment.

roscopic conductivity. PolyProDOT-monoalkyl, with only one alkyl chain on each side of the plane within a dimeric unit, on the other hand, seems to be able to pack with an optimal $\pi-\pi$ distance, but the seven-membered dioxepine ring itself takes up a large amount of space as illustrated in Figure 3. Investigating the interaction between two antiplanar PolyProDOT segments (trimers) with a simple model (Figure 4) reveals that the optimal $\pi-\pi$ distance is increased to 4.2 Å, compared to the 3.8 Å distance for PATs, due to the space-filling dioxepine rings; if the antiplanar constraint is removed during the model fitting, the middle thiophene unit rotates ~60° away from antiplanarity and the $\pi-\pi$ distance is further increased to 4.6 Å.[30]

The model thus suggests that neither mono- nor dialkylated PolyProDOTs are optimal material for polymer electronics due to the large dioxepine ring, whereas they might be interesting candidates for polymer photonics as also demonstrated by Reynolds and co-workers.[13−15,31] With regard to conductive applications, our results indicate likewise that severe disadvantages are associated with the PolyProDOTs; fairly poor self-organizing properties, a rather loose packing motif and low conductivities characterize both mono- and dialkylated PolyProDOTs, which also indicate that it is mainly the large seven-membered ring that induces the structural disorder and not the presence of one or two alkyl chains per thiophene unit. Grafting of longer or extra alkyl chains onto the system seems to favor the polymerization process, thus causing an increased effective conjugation length and therefore slightly improved self-organizing and conductive properties. Also, the Kumada-type polymerization process appears superior compared to the Sugimoto-type with respect to obtaining higher molecular weight material.

To verify the hypothesis that the dioxepine ring is the major reason for unfavorable steric interactions preventing ideal structural ordering in the solid state, we have investigated several copolymers, where a fraction of the large ProDOT units is exchanged with less space-filling thiophene units. In copolymer **Poly5c**, randomly, 30% of the seven-membered dioxepine units are replaced with six-membered dioxine units via a Sugimoto-type polymerization; the outcome is significant since a conductivity of 0.68 S/m in the doped state was measured, whereas all the Sugimoto-type homopolymers showed no enhanced conductivity upon iodine doping. Going a step further, in copolymers **Poly4a** and **Poly4c** two-thirds of the ProDOT units are replaced with unsubstituted thiophenes in a regular fashion. From the conductivity measurements, which show relatively high values for Sugimoto-type polymers, we find reason to assume that **Poly4a** and **Poly4c** due to their unsubstituted thiophene spacers can organize with a much more favorable $\pi-\pi$ stacking distance than the corresponding PolyProDOTs. Again all results indicate that the self-organizing properties increase with increasing degree of alkylation, most likely as a result of increased solubility, which allows for higher molecular weight material to form.

Conclusions. We find that the ProDOT homopolymers, both mono- and dialkylated on the central carbon atom, are unable to pack with an optimal $\pi-\pi$ stacking distance in the solid state due to unfavorable steric interaction caused by the highly space-filling nature of the seven-membered dioxepine ring. These unfavorable interactions can be diminished to a great extent if smaller thiophene moieties, like EDOT or unsubstituted thiophene, are incorporated into the polymer chain. We have proven that this steric relief can be introduced by the design and synthesis of regiosymmetrically functionalized terthiophenes, but also by a simpler synthetic route utilizing a random polymerization process between two regiosymmetrical thiophenes. The degree of alkylation plays an important role also; increasing the length and/or the number of alkyl chains obviously results in polymers with better self-organizing properties, most likely as a consequence of the formation of higher molecular weight material. Work is in progress in our laboratories to further investigate the properties of these ProDOT-based polymers.

Experimental Section

Measurements. Elemental analyses were obtained with a Carlo Elba FLASH 1112 apparatus. Mass spectrometry was carried out on a Hewlett-Packard 59 GC-MS, while high-resolution mass spectrometry was accomplished using a four-sector JEOL HX110/HX110 instrument. NMR spectra were all recorded in $CDCl_3$ on a Varian Unity 400 instrument, and the chemical shifts are listed relative to tetramethylsilane. SEC

was performed in chloroform with a Shimadzu 10A HPLC system equipped with a TSK-GEL separating column; molecular weights were referenced to a series of polystyrene standards. Absorption spectroscopy was carried out on a Perkin-Elmer Lambda 5 spectrophotometer. All electrochemical experiments were conducted under nitrogen in dry acetonitrile using tetrabutylammonium tetrafluoroborate (0.10 M) as the supporting electrolyte, an ITO glass plate as the working electrode, a coiled platinum wire as the auxiliary electrode, and an Ag/AgCl electrode as the reference system; calibration was carried out as described by Johansson and coworkers:[32] all potentials are reported vs Ag/AgCl under the assumption that the redox couple ferrocene/ferrocenium ion has a redox potential of 0.326 V vs Ag/AgCl. The powder X-ray diffraction was measured on a STOE powder diffraction system in transmission geometry with the wavelength fixed at 1.54 Å corresponding to the Cu Kα line. The electrical conductivity was measured using a simple two-electrode system fabricated by thermal evaporation of chromium (5 nm) and subsequently gold (100 nm) onto a glass substrate through a simple mask, after which the polymer film was solution cast onto the electrode system from chloroform; the electrode gap was 2 mm, the polymer film typically covered an area of 20 mm^2 between the electrodes, and alligator clips and aluminum foil were used as contacts. A fixed potential of 100 mV was applied, and the current was subsequently measured as a function of time while the film was subjected to iodine vapor. When doping was complete and the resistance had reached a minimum, current was measured as a function of potential (−100 to 100 mV) to achieve $I-V$ curves from which the electrical conductivity was derived.

Materials. 3,4-Dimethoxythiophene (**1**) was prepared as previously described in the literature.[33,34] The syntheses of 2-hexylpropane-1,3-diol, 2,2-dihexylpropane-1,3-diol, and 2,2-didecylpropane-1,3-diol are presented in the Supporting Information. All reactions were carried out with oven-dried glassware and dry solvents in a nitrogen atmosphere unless otherwise stated. Anhydrous ferric chloride, *N*-bromosuccinimide, methylmagnesium bromide (1.0 M solution in dibutyl ether), 2-thienylmagnesium bromide (1.0 M solution in THF), and *p*-toluenesulfonic acid monohydrate were obtained from Aldrich, [1,3-bis(diphenylphosphino)propane]nickel(II) chloride was obtained from Fluka, and 3,4-ethylenedioxythiophene (EDOT, Baytron M) was obtained from H.C. Starck; all chemicals were used without further purification. For column chromatography, silica gel 0.060−0.200 mm (pore diameter 6 nm) from Acros Organics was used.

3-Hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (2a). A solution of 2-hexylpropane-1,3-diol (1.603 g, 10.00 mmol), 3,4-dimethoxythiophene (1.457 g, 10.10 mmol), and *p*-toluenesulfonic acid monohydrate (191 mg, 1.00 mmol) in 30 mL of toluene was refluxed for 24 h. The reaction mixture was washed with water and concentrated to a dark oil. The oil was purified by column chromatography using toluene/dichloromethane/heptane (3:1:1) as eluent to yield 3-hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (1.51 g, 6.28 mmol, 63%) as a yellow oil. EA: calcd for $C_{13}H_{20}O_2S$: C 64.96, H 8.39, S 13.34; found C 64.76, H 8.37, S 13.32. MS (GC-MS): *m/z* (rel int) 69 (84), 83 (29), 116 (100), 127 (20), 141 (14), 155 (7), 169 (7), 240 (M^+, 82). HRMS (FAB^+): *m/z* calcd for $C_{13}H_{21}O_2S$ (MH^+) 241.1262; found 241.1264. ^1H NMR: δ 6.47 (s, 2H), 4.13 (dd, 2H), 3.86 (dd, 2H), 2.16 (m, 1H), 1.29 (m, 10H), 0.89 (t, 3H). ^{13}C NMR: δ 149.95, 105.35, 74.45, 42.35, 31.54, 29.27, 27.79, 26.78, 22.46, 13.92.

3,3-Dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (2b). As **2a**; 2,2-dihexylpropane-1,3-diol (1.478 g, 6.046 mmol); 3,4-dimethoxythiophene (0.887 g, 6.151 mmol); *p*-toluenesulfonic acid monohydrate (117 mg, 0.615 mmol). Column chromatography using toluene/dichloromethane/heptane (3:1:1) as eluent afforded 3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (1.33 g, 4.10 mmol, 68%) as a colorless oil. EA: calcd for $C_{19}H_{32}O_2S$: C 70.32, H 9.94, S 9.88; found C 70.37, H 9.81, S 9.93. MS (GC-MS): *m/z* (rel int) 55 (94), 69 (100), 83 (66), 97 (48), 116 (61), 127 (21), 141 (17), 169 (15), 324 (M^+, 63). HRMS (EI): *m/z* calcd for $C_{19}H_{32}O_2S$ (M^+) 324.2123; found 324.2128. ^1H NMR: δ 6.41 (s, 1H), 3.85 (s, 2H), 1.29 (m, 10H), 0.89 (t, 3H). ^{13}C NMR: δ 149.59, 104.48, 77.41, 43.62, 31.78, 31.63, 30.03, 22.67, 22.53, 13.96.

3,3-Didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (2c). As **2a**; 2,2-didecylpropane-1,3-diol (3.750 g, 10.51 mmol), 3,4-dimethoxythiophene (1.466 g, 10.17 mmol), *p*-toluenesulfonic acid monohydrate (193 mg, 1.01 mmol). Column chromatography using heptane/dichloromethane (2:1) as eluent afforded 3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (2.87 g, 6.57 mmol, 65%) as a yellowish brown oil. EA: calcd for $C_{27}H_{48}O_2S$: C 74.25, H 11.08, S 7.34; found C 74.04, H 11.17, S 7.35. MS (GC-MS): *m/z* (rel int) 43(100), 55 (69), 69 (58), 83 (44), 97 (47), 116 (38), 127 (15), 141 (9), 436 (M^+, 18). HRMS (FAB^+): *m/z* calcd for $C_{27}H_{49}O_2S$ (MH^+) 437.3453; found 437.3454. ^1H NMR: δ 6.41 (s, 1H), 3.85 (s, 2H), 1.37 (m, 2H), 1.27 (broad s, 16H), 0.89 (t, 3H). ^{13}C NMR: δ 149.62, 104.50, 77.43, 43.63, 31.80, 31.75, 30.37, 29.51 (broad), 29.43, 29.23, 22.70, 22.58, 14.00.

6,8-Dibromo-3-hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (3a). 3-Hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (1.97 g, 8.20 mmol) was dissolved in 330 mL of chloroform. The mixture was stirred for 0.5 h, and then NBS (4.38 g, 24.6 mmol) was added in one portion. The solution was stirred at room temperature overnight, after which the solvent was evaporated and the crude product was purified by column chromatography using heptane/dichloromethane (2:1) as eluent to afford 6,8-dibromo-3-hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (2.75 g, 6.91 mmol, 84%) as a colorless oil. EA: calcd for $C_{13}H_{18}Br_2O_2S$: C 39.22, H 4.56, Br 40.14, S 8.05; found C 39.40, H 4.55, Br 40.34, S 7.80. MS (GC-MS): *m/z* (rel int) 41 (100), 55 (67), 69 (80), 83 (27), 123 (31), 125 (32), 272 (29), 274 (62), 276 (35), 396 (M^+, 18), 398 (37), 400 (18). ^1H NMR: δ 4.20 (dd, 2H), 3.97 (dd, 2H), 2.21 (m, 1H), 1.43 (t, 2H), 1.29 (m, 8H), 0.89 (t, 3H). ^{13}C NMR: δ 147.16, 91.30, 74.75, 42.16, 31.57, 29.21, 27.81, 26.76, 22.49, 14.02.

6,8-Dibromo-3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (3b). As **3a**; 3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (1.62 g, 4.99 mmol); 200 mL of chloroform; NBS (2.67 g, 15.0 mmol). Column chromatography using heptane/dichloromethane (2:1) as eluent afforded 6,8-dibromo-3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (2.22 g, 4.60 mmol, 92%) as a colorless oil. EA: calcd for $C_{19}H_{30}Br_2O_2S$: C 47.31, H 6.27, Br 33.13, S 6.65; found C 47.90, H 6.31, Br 33.14, S 6.74. MS (GC-MS): *m/z* (rel int) 41 (100), 55 (93), 69 (94), 83 (45), 97 (40), 111 (19), 272 (23), 274 (45), 276 (22), 480 (M^+, 11), 482 (24), 484 (16). HRMS (EI): *m/z* calcd for $C_{19}H_{30}Br_2O_2S$ (M^+) 480.0333; found 480.0339. ^1H NMR: δ 3.91 (s, 2H), 1.39 (m, 2H), 1.29 (broad s, 8H), 0.89 (t, 3H). ^{13}C NMR: δ 147.01, 90.52, 77.91, 43.90, 31.60, 31.54, 29.95, 22.58, 22.53, 13.97.

6,8-Dibromo-3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (3c). As **3a**; 3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (1.60 g, 3.66 mmol); 150 mL of chloroform; NBS (2.00 g, 11.2 mmol). Column chromatography using heptane/dichloromethane (2:1) as eluent afforded 6,8-dibromo-3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (1.97 g, 3.31 mmol, 91%) as a yellow oil. EA: calcd for $C_{27}H_{46}Br_2O_2S$: C 54.55, H 7.80, Br 26.88, S 5.39; found C 54.66, H 7.92, Br 27.23, S 5.51. MS (GC-MS): *m/z* (rel int) 43 (100), 55 (59), 69 (41), 83 (33), 97 (34), 111 (20), 125 (12), 272 (17), 274 (33), 276 (17), 592 (M^+, 8), 594 (18), 596 (9). HRMS (EI): *m/z* calcd for $C_{27}H_{46}Br_2O_2S$ (M^+) 592.1585; found 592.1599. ^1H NMR: δ 3.91 (s, 2H), 1.38 (m, 2H), 1.26 (broad s, 16H), 0.88 (t, 3H). ^{13}C NMR: δ 147.06, 90.53, 77.93, 43.91, 31.80, 31.50, 30.27, 29.50 (broad), 29.40, 29.22, 22.59 (broad), 14.00.

3-Hexyl-6,8-dithiophen-2-yl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (4a). 6,8-Dibromo-3-hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (386 mg, 0.969 mmol) and [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (27.8 mg, 0.051 mmol) were dissolved in 10 mL of THF. A solution of 2-thienylmagnesium bromide in THF (1.0 M, 2.6 mL, 2.6 mmol) was added, and the reaction mixture was refluxed for 72 h. The mixture was subsequently allowed to reach room temperature and then poured into dilute hydrochloric acid and extracted with diethyl ether. The organic extracts were

combined, washed with water, and dried over anhydrous magnesium sulfate. Evaporation of the solvent left a dark oil which was purified by column chromatography using 2% ethyl acetate in hexanes as eluent to yield 3-hexyl-6,8-dithiophen-2-yl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (0.23 g, 0.57 mmol, 58%) as a yellow oil. HRMS (EI): *m/z* calcd for $C_{21}H_{24}O_2S_3$ (M^+) 404.0938; found 404.0926. ^{1}H NMR: δ 7.15 (m, 4H), 6.94 (dd, 2H), 4.25 (dd, 2H), 3.93 (dd, 2H), 2.25 (m, 1H), 1.19 (m, 10H), 0.83 (t, 3H). ^{13}C NMR: δ 145.37, 134.56, 126.71, 124.31, 122.64, 114.14, 74.65, 42.41, 31.62, 29.31, 27.99, 26.89, 22.53, 13.99.

3,3-Didecyl-6,8-dithiophen-2-yl-3,4-dihydro-2*H*-thieno-[3,4-*b*][1,4]dioxepine (4c). As **4a**; 6,8-dibromo-3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (601 mg, 1.01 mmol); [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (28 mg, 0.052 mmol); 2-thienylmagnesium bromide in THF (1.0 M, 2.5 mL, 2.5 mmol); reflux 48 h. Column chromatography using heptane/dichloromethane (9:1) as eluent afforded 3,3-didecyl-6,8-dithiophen-2-yl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]-dioxepine (0.24 g, 0.40 mmol, 40%) as a yellow oil. HRMS (EI): *m/z* calcd for $C_{35}H_{52}O_2S_3$ (M^+) 600.3129; found 600.3120. ^{1}H NMR: δ 7.22 (m, 2H), 7.01 (dd, 1H), 4.01 (s, 2H), 1.48 (m, 2H), 1.29 (m, 16H), 0.90 (t, 3H). ^{13}C NMR: δ 145.21, 134.59, 126.69, 124.13, 122.60, 113.46, 77.75, 43.88, 31.82 (broad), 30.37, 29.53 (broad), 29.43, 29.25, 22.74, 22.59, 14.02.

Poly(3-hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]-dioxepine) (Poly2a). To a solution of anhydrous ferric chloride (1.37 g, 8.45 mmol) in 40 mL of chloroform a solution of 3-hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (490 mg, 2.04 mmol) in 11 mL of chloroform was added dropwise. The reaction mixture was stirred at room temperature for 24 h. The mixture was then poured into 700 mL of methanol, and the crude doped polymer was allowed to precipitate overnight. After isolation by filtration the filtrate was redissolved in chloroform and stirred vigorously overnight with 200 mL of 12.5% aqueous ammonia. The organic phase was washed with water and then concentrated to afford the crude undoped polymer as a black metallic film. After transfer to a Soxhlet apparatus the crude product was washed with methanol for 24 h and subsequently with hexanes for 24 h. Finally, thorough extraction with chloroform afforded poly(3-hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine) (23 mg, 5%) as a black metallic film. ^{1}H NMR: δ 4.24 (broad s, 2H), 3.85 (broad s, 2H), 2.26 (broad s, 1H), 1.19 (m, 10H), 0.84 (broad s, 3H).

Poly(3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]-dioxepine) (Poly2b). As **Poly2a**; anhydrous ferric chloride (1.38 g, 8.51 mmol); 3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*]-[1,4]dioxepine (652 mg, 2.01 mmol). Extraction afforded poly-(3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine) (531 mg, 82%) as a black metallic film. EA: calcd for $(C_{19}H_{30}O_2S)_n$: C 70.76, H 9.38, S 9.94; found C 69.02, H 9.27, Cl 1.06, S 9.76, residue 0.30. ^{1}H NMR: δ 3.95 (broad s, 2H), 1.48 (broad s, 2H), 1.32 (broad s, 8H), 0.90 (broad s, 3H). ^{13}C NMR: δ 144.91, 113.54, 77.89, 43.72, 31.75, 30.11, 29.62, 22.77, 22.60, 14.01.

Poly(3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]-dioxepine) (Poly2c). As **Poly2a**; anhydrous ferric chloride (1.39 g, 8.57 mmol); 3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*]-[1,4]dioxepine (874 mg, 2.00 mmol). Extraction afforded poly-(3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine) (697 mg, 80%) as a black metallic film. EA: calcd for $(C_{27}H_{46}O_2S)_n$: C 74.60, H 10.67, S 7.38; found C 73.80, H 10.66, Cl 0.19, S 7.48, residue 0. ^{1}H NMR: δ 3.88 (broad s, 2H), 1.41 (broad s, 2H), 1.19 (m, 16H), 0.81 (t, 3H). ^{13}C NMR: δ 31.87, 31.70, 30.53, 29.70, 29.62 (2C), 29.34, 22.89, 22.61, 14.02.

Poly(3-hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]-dioxepine) (Poly3a). To a solution of 6,8-dibromo-3-hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (400 mg, 1.00 mmol) in 25 mL of THF a solution of methylmagnesium bromide in dibutyl ether (1.0 M, 1.0 mL, 1.0 mmol) was added. The reaction mixture was refluxed for 1 h and was then allowed to cool to room temperature. [1,3-Bis(diphenylphosphino)-propane]nickel(II) chloride (14.0 mg, 0.026 mmol) was added, and the reaction mixture was refluxed for 20 h. The cooled mixture was then poured into 500 mL of methanol, and the crude polymer was allowed to precipitate overnight. The dark red precipitate was filtered directly into a Soxhlet thimble. After washing the crude polymer with methanol for 24 h and subsequently with hexanes for 48 h thorough extraction with chloroform afforded poly(3-hexyl-3,4-dihydro-2*H*-thieno[3,4-*b*]-[1,4]dioxepine) (13 mg, 5%) as a black metallic film. ^{1}H NMR: δ 4.23 (broad s, 2H), 3.85 (broad s, 2H), 2.26 (broad s, 1H), 1.19 (m, 10H), 0.84 (m, 3H).

Poly(3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]-dioxepine) (Poly3b). As **Poly3a**; 6,8-dibromo-3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (492 mg, 1.02 mmol); [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (14.3 mg, 0.026 mmol). Extraction afforded poly(3,3-dihexyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine) (123 mg, 37%) as a black metallic film. EA: calcd for $(C_{19}H_{30}O_2S)_n$: C 70.76, H 9.38, S 9.94; found C 68.23, H 9.24, Br 1.95, S 9.44, residue 1.33. ^{1}H NMR: δ 3.91 (broad s, 2H), 1.19 (m, 10H), 0.84 (broad s, 3H). ^{13}C NMR: δ 43.87, 31.72, 30.11, 29.59, 22.79, 22.57, 13.99.

Poly(3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]-dioxepine) (Poly3c). As **Poly3a**; 6,8-dibromo-3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (595 mg, 1.00 mmol); [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (13.3 mg, 0.025 mmol). Extraction afforded poly(3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine) (175 mg, 40%) as a black metallic film. EA: calcd for $(C_{27}H_{46}O_2S)_n$: C 74.60, H 10.67, S 7.38; found C 73.15, H 10.75, Br 1.75, S 7.36, residue 0.06. ^{1}H NMR: δ 3.95 (broad s, 2H), 1.48 (broad s, 2H), 1.27 (m, 16H), 0.88 (t, 3H). ^{13}C NMR: δ 31.86, 31.66, 30.56, 29.71, 29.63 (2C), 29.34, 22.99, 22.61, 14.02.

Poly(3-hexyl-6,8-dithiophen-2-yl-3,4-dihydro-2*H*-thieno-[3,4-*b*][1,4]dioxepine) (Poly4a). As **Poly2a**; anhydrous ferric chloride (337 mg, 2.08 mmol); 3-hexyl-6,8-dithiophen-2-yl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (203 mg, 0.502 mmol). Extraction afforded poly(3-hexyl-6,8-dithiophen-2-yl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine) (51 mg, 25%) as a black metallic film. ^{1}H NMR: δ 7.02 (broad m, 4H), 4.28 (broad m, 2H), 3.94 (broad m, 2H), 2.26 (broad m, 1H), 1.19 (broad m, 10H), 0.84 (broad m, 3H). ^{13}C NMR: δ 126.76, 123.23, 74.80, 42.41, 31.63, 29.32, 28.02, 26.90, 22.55, 14.00.

Poly(3,3-didecyl-6,8-dithiophen-2-yl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine) (Poly4c). As **Poly2a**; anhydrous ferric chloride (210 mg, 1.29 mmol); 3,3-didecyl-6,8-dithiophen-2-yl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (171 mg, 0.285 mmol). Extraction afforded poly(3,3-didecyl-6,8-dithiophen-2-yl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine) (60 mg, 35%) as a black metallic film. EA: calcd for $(C_{35}H_{50}O_2S_3)_n$: C 70.18, H 8.41, S 16.06; found C 69.65, H 8.62, Cl 0.45, S 14.54, residue 5.01. ^{1}H NMR: δ 7.08 (broad m, 2H), 4.04 (broad m, 2H), 1.52 (broad m, 2H), 1.25 (broad m, 16H), 0.87 (broad m, 3H). ^{13}C NMR: δ 145.40, 136.12, 133.36, 126.77, 123.13, 113.75, 78.02, 43.94, 31.85 (2C), 30.43, 29.62, 29.58, 29.50, 29.30, 22.79, 22.61, 14.04.

Random Copolymer of 3,3-Didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine and 2,3-Dihydrothieno[3,4-*b*][1,4]dioxine (Poly5c). As **Poly2a**; anhydrous ferric chloride (1.41 g, 8.69 mmol); 3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*][1,4]dioxepine (447 mg, 1.02 mmol); 2,3-dihydrothieno[3,4-*b*][1,4]dioxine (144 mg, 1.01 mmol). Extraction afforded the random copolymer of 3,3-didecyl-3,4-dihydro-2*H*-thieno[3,4-*b*]-[1,4]dioxepine) and 2,3-dihydrothieno[3,4-b][1,4]dioxine (170 mg, 29%) as a black metallic film. EA: calcd for $(C_{27}H_{46}O_2S)_{0.7}$-$(C_6H_4O_2S)_{0.3}$: C 71.78, H 9.72, S 9.26; found C 69.11, H 9.23, Cl 1.09, S 9.96, residue 1.47. ^{1}H NMR: δ 4.33 (broad s, 0.8H), 3.88 (broad s, 2H), 1.20 (m, 18H), 0.81 (t, 3H). ^{13}C NMR: δ 144.89, 113.46, 77.83, 64.84, 43.72, 31.84, 31.67, 30.49, 29.70, 29.61, 29.32, 29.30, 22.81, 22.60, 14.01.

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Supporting Information Available: Synthetic procedures and full characterization of 2-hexylpropane-1,3-diol, 2,2-dihexylpropane-1,3-diol, and 2,2-didecylpropane-1,3-diol; proton NMR spectra, absorption spectra, and XRD spectra of all

presented homo- and copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) McCullough, R. D.; Ewbank, P. C. Regioregular, Head-to-Tail Coupled Poly(3-alkylthiophene) and Its Derivatives. In *Handbook of Conducting Polymers*; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; pp 225−258.
(2) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087−10088.
(3) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70−72.
(4) Jonas, F.; Schrader, L. *Synth. Met.* **1991**, *41*, 831−836.
(5) Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116−118.
(6) Pei, Q.; Zuccarello, G.; Ahlskog, M.; Inganas, O. *Polymer* **1994**, *35*, 1347−1351.
(7) Winter, I.; Reese, C.; Hormes, J.; Heywang, G.; Jonas, F. *Chem. Phys.* **1995**, *194*, 207−213.
(8) Groenendaal, L.; Zotti, G.; Jonas, F. *Synth. Met.* **2001**, *118*, 105−109.
(9) Nielsen, C. B.; Bjørnholm, T. *Org. Lett.* **2004**, *6*, 3381−3384.
(10) Ogawa, K.; Rasmussen, S. C. *J. Org. Chem.* **2003**, *68*, 2921−2928.
(11) Groenendaal, L.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481−494.
(12) Skabara, P. J.; Roberts, D. M.; Serebryakov, I. M.; Pozo-Gonzalo, C. *Chem. Commun.* **2000**, 1005−1006.
(13) Reeves, B. D.; Grenier, C. R. G.; Argun, A. A.; Cirpan, A.; McCarley, T. D.; Reynolds, J. R. *Macromolecules* **2004**, *37*, 7559−7569.
(14) Welsh, D. M.; Kloeppner, L. J.; Madrigal, L.; Pinto, M. R.; Thompson, B. C.; Schanze, K. S.; Abboud, K. A.; Powell, D.; Reynolds, J. R. *Macromolecules* **2002**, *35*, 6517−6525.
(15) Kumar, A.; Welsh, D. M.; Morvant, M. C.; Piroux, F.; Abboud, K. A.; Reynolds, J. R. *Chem. Mater.* **1998**, *10*, 896−902.
(16) Malenfant, P. R. L.; Jayaraman, M.; Frechet, J. M. J. *Chem. Mater.* **1999**, *11*, 3420−3422.
(17) Malenfant, P. R. L.; Frechet, J. M. J. *Macromolecules* **2000**, *33*, 3634−3640.
(18) Kloeppner, L. J.; Welsh, D. M.; Reynolds, J. R. *Polym. Prepr.* **1999**, *40*, 792.
(19) Dietrich, M.; Heinze, J.; Heywang, G.; Jonas, F. *J. Electroanal. Chem.* **1994**, *369*, 87−92.
(20) Groenendaal, L.; Zotti, G.; Aubert, P.-H.; Waybright, S. M.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 855−879.
(21) Bauerle, P.; Fischer, T.; Bidlingmeier, B.; Stabel, A.; Rabe, J. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 303−307.
(22) Soukopp, A.; Glockler, K.; Kraft, P.; Schmitt, S.; Sokolowski, M.; Umbach, E.; Mena-Osteritz, E.; Bauerle, P.; Hadicke, E. *Phys. Rev. B* **1998**, *58*, 13882−13894.
(23) Azumi, R.; Gotz, G.; Debaerdemaeker, T.; Bauerle, P. *Chem. Eur. J.* **2000**, *6*, 735−744.
(24) Mena-Osteritz, E.; Meyer, A.; Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W.; Bauerle, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 2680−2684.
(25) Prosa, T. J.; Winokur, M.; Moulton, J.; Smith, P.; Heeger, A. J. *Macromolecules* **1992**, *25*, 4364−4372.
(26) Prosa, T. J.; Winokur, M.; McCullough, R. D. *Macromolecules* **1996**, *29*, 3654−3656.
(27) Winokur, M. Structural Studies of Conducting Polymers. In *Handbook of Conducting Polymers*; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998; pp 707−726.
(28) Bjørnholm, T.; Hassenkam, T.; Reitzel, N. *J. Mater. Chem.* **1999**, *9*, 1975−1990.
(29) Reitzel, N.; Greve, D. R.; Kjaer, K.; Howes, P. B.; Jayaraman, M.; Savoy, S.; McCullough, R. D.; McDewitt, J. T.; Bjørnholm, T. *J. Am. Chem. Soc.* **2000**, *122*, 5788−5800.
(30) Semiempirical calculations performed with the AM1 method included in the PC SPARTAN PRO software program.
(31) Argun, A. A.; Cirpan, A.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 1338−1341.
(32) Johansson, T.; Mammo, W.; Svensson, M.; Andersson, M. R.; Inganäs, O. *J. Mater. Chem.* **2003**, *13*, 1316−1323.
(33) Zhang, Q. T.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5355−5362.
(34) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W. *J. Mol. Struct.* **2000**, *521*, 285−301.

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