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Regioregular Poly(3-alkoxythiophene)s: Toward Soluble, Chiral Conjugated Polymers with a Stable Oxidized State

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ABSTRACT: Chiral poly(3-(3,7-dimethyloctyloxy)thiophene)s were prepared using three different methodologies, rendering polymers with different degrees of regioregularity. In a first attempt, 3-alkoxythiophene was polymerized using $FeCl_3$, resulting in a highly regioirregular poly(3-alkoxythiophene). Second, the GRIM methodology was applied, which yielded poly(3-alkoxythiophene)s with relatively high, but not perfect, degrees of regioregularity. Finally, an alternative methodology was used, which consisted of the exclusive formation and subsequent polymerization of 2-bromomagnesio-3-(3,7-dimethyloctyloxy)-5-bromothiophene) and which resulted in poly(3-alkoxythiophene)s with (almost) perfect regioregularity. The degrees of regioregularity were evaluated with ^{1}H NMR, UV−vis, and CD spectroscopy and cyclic voltammetry. These (regioregular) poly(3-alkoxythiophene)s show a very high λ_{max}, indicating very high conjugation lengths. Moreover, the polymers could easily be oxidized and they were stable in both neutral as well as oxidized state. This stability can be correlated with the decrease in oxidation potential. The reproducibility and reversibility of the oxidation was demonstrated by UV−vis spectroscopy. Finally, the chiral properties of the polymers were investigated with circular dichroism spectroscopy. These experiments demonstrated again the difference in regioregularity of the polymers.

Introduction

Poly(3-alkylthiophenes) (P3ATs) represent a class of soluble, conjugated polymers, which show moderate to excellent conductivities in the doped (oxidized) state. They are of great interest in oLEDs, photovoltaic cells, and field-effect transitors, among others.[1]

The properties of P3ATs greatly depend on the degree of regioregularity, which can be defined as the percentage of head-to-tail (HT) couplings: more regioregularity leads to less steric hindrance between adjacent thiophene units and, consequently, to higher conjugation lengths. As a consequence, planar structures are impossible in regioirregular P3ATs, which leads to poor packing and also small conjugation lengths. In regioregular P3ATs (HT-P3ATs), on the other hand, the planarity allows high degrees of molecular overlap, which leads to high conductivities, lower badgaps, and lower oxidation potentials. In films or nonsolvents, the material consists of aggregates, composed of coplanar strands.[1] The degree of regioregularity has also a profound effect on the packing of the chains in films.[2] In chiral HT-P3ATs, the strands pack in a chiral way and the supramolecular chirality leads to, for instance, large bisignate Cotton effects.[3] Unfortunately, since 3-alkylthiophene is an unsymmetrical molecule, HT-P3ATs can only be obtained if the monomer is polymerized in a regiospecific way. Several synthetic pathways have been developed to produce regioregular P3ATs.[1b,e,4]

The major drawbacks of regioirregular as well as regioregular P3ATs are the instability of the oxidized (conductive) state and the difficulty in doping the material reproducibly. This greatly limits the possibilities of these materials to be used in electrical applications and to study their properties in the doped state. One possibility to diminish, but not fully exclude, this instability is to create holes in the alkyl phase, in which the counterion can incorporate.[5] Another approach consists of lowering the oxidation potential of the polymers. An excellent example is poly(3,4-ethylenedioxythiophene) (PEDOT).

Here, we show that regioregular poly(3-alkoxythiophene)s (HT-P3AOTs) are a class of soluble, conjugated polymers with excellent stability in both neutral and oxidized state and that the incorporation of chiral side chains leads to chiral, supramolecular packing, analogous to HT-P3ATs. The influence of the regioregularity on the properties is discussed.

Results and Discussion

Polymer Synthesis. In this paper, three chiral P3AOTs (in casu poly(3-(3,7-dimethyloctyloxy)thiophene)) were prepared using three different methods, yielding P3AOTs with different degrees of regioregularity (Scheme 1). In a first approach, 3-(3,7-dimethyloctyloxy)thiophene (**3**) was oxidatively polymerized with $FeCl_3$, rendering **pol 1**. **3** itself was obtained via a transetherification reaction from **1**.[6] Oxidative polymerization of 3-alkoxythiophenes with, for instance $FeCl_3$, have already been carried out and this methodology has shown to produce highly irregular P3AOTs.[7] To produce regioregular P3AOTs, a regiospecific polymerization procedure is required. It is well-known that the GRIM (Grignard metathesis) methodology produces P3ATs with a high degree of regioregularity from 2,5-dibromo-3-alkyl thiophene derivatives.[8a] The reason for this regioregularity is *not* the exclusive formation of only one isomer of the monomer (since both 2-bromomagnesio-3-alkyl-5-bromothiophene and 2-bromo-3-alkyl-5-bromomagnesiothiophene are formed), but the selectivity of the catalyst: due to steric hindrance, HH-couplings are not promoted by the catalyst.[8b] Therefore, in a second approach, **3** was dibrominated with NBS to afford **4**,

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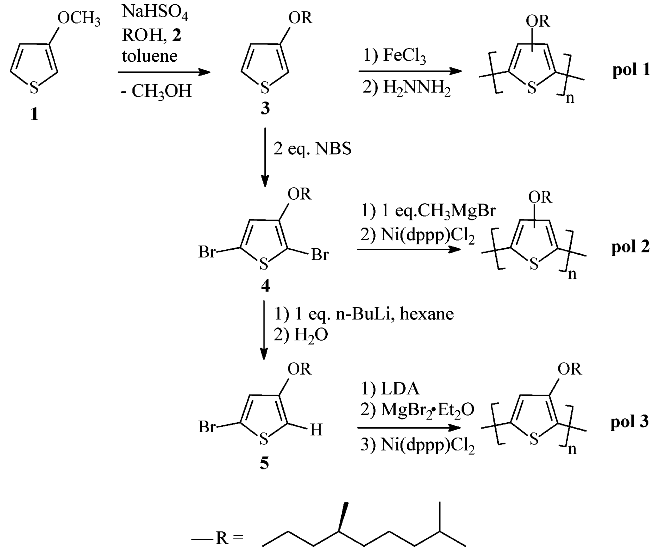
Scheme 1. Synthesis of the Monomers and Pol 1−3



which was subsequently transformed into the Grignard derivative with methylmagnesium bromide and polymerized with a Kumada cross-coupling reaction, catalyzed by bis(diphenylphosphinopropane)nickel(II) dichloride (Ni(dppp)Cl$_2$). As will be shown, this methodology fails to produce perfectly regioregular P3AOTs. Therefore, an alternative procedure to prepare regioregular P3AOTs was used, which consisted in the formation and subsequent polymerization of only one of the above-mentioned isomers, i.e., 2-bromomagnesio-3-(3,7-dimethyloctyloxy)-5-bromothiophene. This reaction sequence is very similar to the original McCullough methodology, which was developed for the production of HT-P3ATs,[1b] but differs from the latter in the fact that the actual monomer is not 2-bromo-3-alkoxy-5-bromomagnesiothiophene but instead 2-bromomagnesio-3-alkoxy-5-bromothiophene. This modification is crucial: On one hand, if 2-bromo-3-alkoxythiophene is lithiated (in order to form, after cation exchange, 2-bromo-3-alkoxy-5-bromomagnesiothiophene), large amounts of scrambling occur, which results in a mixture of both isomers, and consequently, regioirregular P3AOTs.[9] On the other hand, the difficulty to *fully* convert 2-bromo-3-alkoxy-5-bromomagnesiothiophene into 2-bromomagnesio-3-alkoxy-5-bromothiophene in THF also leads to a mixture of both isomers. [Evidence for the fact that the conversion of 2-bromo-3-alkoxy-5-bromomagnesiothiophene into 2-bromomagnesio-3-alkoxy-5-bromothiophene does not run to completion in THF is the fact that the treatment of **4** with *n*-BuLi in THF leads to a mixture of isomers (vide infra).] However, if **5** is lithiated, the most stable isomer is formed. Therefore, this approach prevents scrambling and, as a consequence, the formation of regioirregular P3AOTs. The enhanced regioregularity of **pol 3** compared with **pol 2** was proven by ^{1}H NMR spectroscopy (Figure 1), but also by cyclic voltammetry and UV−vis and CD spectroscopy.

Thus, **4** was selectively debrominated in the 2-position with *n*-BuLi in hexane. Quenching experiments with H$_2$O indicated that hexane must be used as solvent instead of tetrahydrofuran (THF) or diethyl ether (Et$_2$O), since no selective debromination took place in the latter cases. Finally, **5** was lithiated with lithium diisopropyl amide (LDA), and the intermediate was converted to the desired Grignard reagent, which was finally polymerized.

After polymerization, all polymers were precipitated in methanol and filtered off. **pol 1** was collected in the oxidized state and was reduced with hydrazine. For purification, the crude material was extracted first with hexane (to remove the lower-molecular weight fraction) and then with chloroform. Finally, the concentrated chloroform solution was added dropwise to methanol and dried.

Characterization of the Polymers. GPC Analysis. The physical properties of the three polymers are listed in Table 1. The polymers are soluble in common organic solvents. The yield and molecular weight of the first (oxidative) polymerization methodology are very low, which can be attributed to the fact that the polymer is formed in the oxidized, and hence poorly soluble, state. The yields and molecular weight of **pol 2−3** are comparable with those of P3ATs prepared by a Kumada cross-coupling reaction in the classical McCullough and GRIM methodologies.[1b,8a]

^{1}H NMR Spectroscopy. The degree of regularity of the polymers was evaluated using ^{1}H NMR spectroscopy; the aromatic signal is used. As presented in Figure 1, **pol 1** is highly irregular, which can be attributed to its asymmetric synthesis. **pol 2**, on the other hand, shows a sharper signal, as well as some small peaks at 7.4−8.0 ppm. Since the molecular weight is quite high (Table 1), these peaks cannot be attributed to end groups and some regioirregularities must be presented. As a consequence, this indicates that, in contrast to 3-alkylthiophenes, the GRIM methodology renders no perfectly regioregular polymers when 3-alkoxythiophenes are used. The reason for this failure must be ascribed to the catalyst. Either the reduction of steric hindrance for the production of a HH-coupling with alkoxy groups and/or the affinity of Ni for oxygen can be the reason for this loss of specificity. The aromatic proton in **pol 3**, finally, shows only one signal, which indicates that this methodology produces P3AOTs with a very large degree of regioregularity.

UV—Vis Spectroscopy. From all polymers, λ_{max} was measured in both film and solution in neutral as well as oxidized state. As displayed in Table 1, the λ_{max} values for these polymers are significantly red-shifted compared with those of P3ATs ($\lambda_{max} \sim 520$ nm in films). In fact, the values reported here are, to the best of our knowledge, the highest reported for any alkyl, thioalkyl ($\lambda_{max,film} \sim 555$ nm), mono- ($\lambda_{max,film} \sim 545-580$ nm) or dialkoxy ($\lambda_{max,film} \sim 545$ nm) substituted polythiophenes.[1,3,10,11] Due to this red-shift, these polymers could be of great interest for photovoltaic applications.

Since λ_{max} is proportional to the conjugation length and, consequently, to the regioregularity, the determination of λ_{max} is a tool to evaluate the degree of regioregularity. It is again clear that **pol 3** is the most regioregular and **pol 1** the least. Moreover, in contrast to **pol 1−2**, a vibronic fine-structure is present in films of **pol 3** (Figure 2). Such fine-structure is only possible in highly regular structures; hence, this again points at a difference in regioregularity of the polymers and regiospecificity of the applied polymerization methodologies.

Interestingly, λ_{max} of HT-P3AOTs (**pol 3**) are also red-shifted compared to poly(3,3′-dialkoxybithiophene)s, which are essentially P3AOTs which consists of alternating HH- and TT-couplings.[10e] Due to their regularity, a relatively high λ_{max} as well as a vibronic fine structure are present in these materials. However, the red-shift

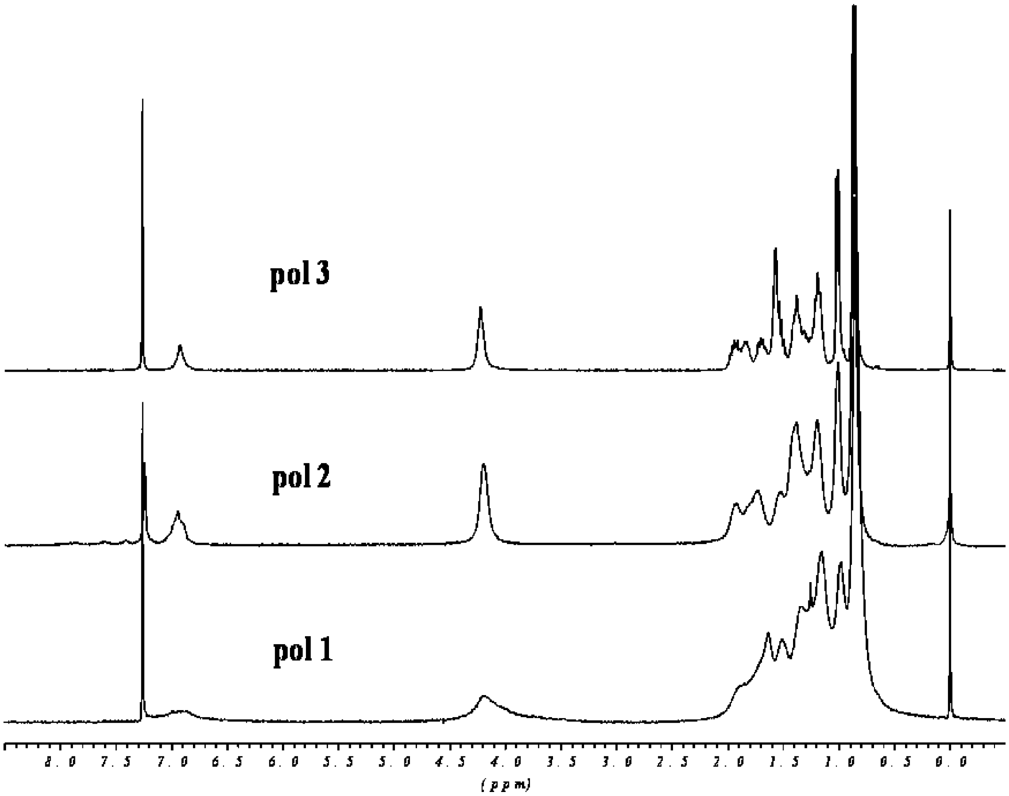


Figure 1. ^{1}H NMR spectra of **pol 1–3**.

Table 1. Physical Properties of Pol 1–3

polymer	yield/%	$\bar{M}_n{}^a/10^3$ g·mol^{-1} (DP^b)	D^c	$\lambda_{max,neutral}$/nm solution	$\lambda_{max,neutral}$/nm film	$\lambda_{max,ox}$/nm solution	$\lambda_{max,ox}$/nm film	$E_{pa}(1)^d$/V	σ^e/S·cm^{-1}
pol 1	12	2.2 (9)	2.0	542	553	827	835	0.82	0.1
pol 2	72	16.5 (69)	1.4	590	615	858	911	0.62	10
pol 3	61	13.5 (57)	1.9	602	635	901	913	0.49	18

[a] Determined by GPC in THF toward polystyrene standards. [b] Mean number of repeating units. [c] Polydispersity, determined by GPC ($D = \bar{M}_w/\bar{M}_n$). [d] Potential of the peak anodic current of the first oxidation, measured with cyclic voltammetry in CH_3CN at 50 mV/s vs Ag^+/Ag. [e] Conductivity, measured with a four-point probe, of spin-coated films.

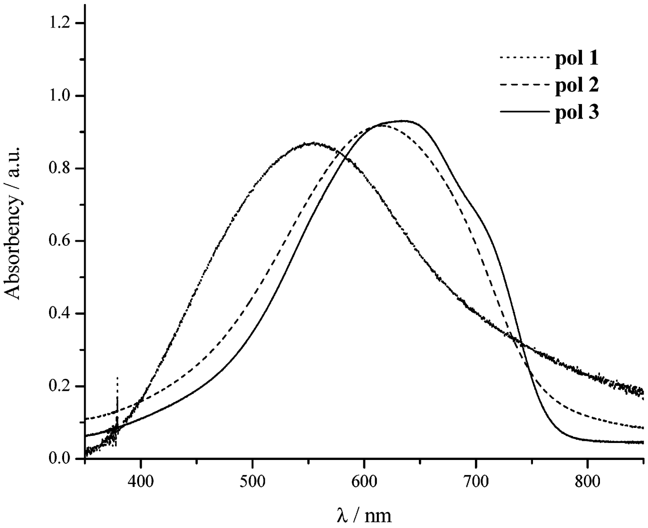


Figure 2. UV–vis spectrum of films of **pol 1–3**.

which is observed for the HT-P3AOTs presented here, indicates a lower conjugation length in poly(3,3′-dialkoxybithiophene)s, which can be attributed to the presence of HH-couplings.

Stability of the Oxidized State. As mentioned above, the main disadvantage of regioirregular as well as regioregular P3ATs is their instability of the oxidized state, which limits both possible electrical applications and fundamental studies of (chiral) conducting polymers in the oxidized state. Indeed, P3ATs cannot be oxidized in solution; in film, they are dedoped within a few minutes to hours, depending on the dopant. In contrast, P3AOTs show a moderate to good stability, which is also dependent on the degree of regioregularity: films of **pol 1** are reduced in 1–2 days, while films of **pol 3** remain oxidized for almost 2 weeks. Solutions of **pol 1–3** remain oxidized for several weeks.

This increase in stability of the oxidized state can be correlated with the oxidation potential of the materials. Indeed, regioregular poly(3-octylthiophene) shows a pseudo-reversible oxidation at $E_{pa}(1) = 0.80$ V.[1a] In the P3AOTs presented here, this potential is shifted to lower voltages, again depending on their degree of regioregularity (Table 1). Moreover, also the nature of the redox behavior (reversible vs irreversible) is dependent on the degree of regioregularity: in the case of **pol 3**, the oxidation becomes reversible.

Next, the reversibility and reproducibility of the oxidation and reduction of these polymers was investigated. Therefore, I_2 ($\sim 10^{-3}$ M in THF) was added to a polymer solution (THF). Upon oxidation, the peak around 600 nm gradually disappears and a new peak near 900 nm appears. When the polymer was fully

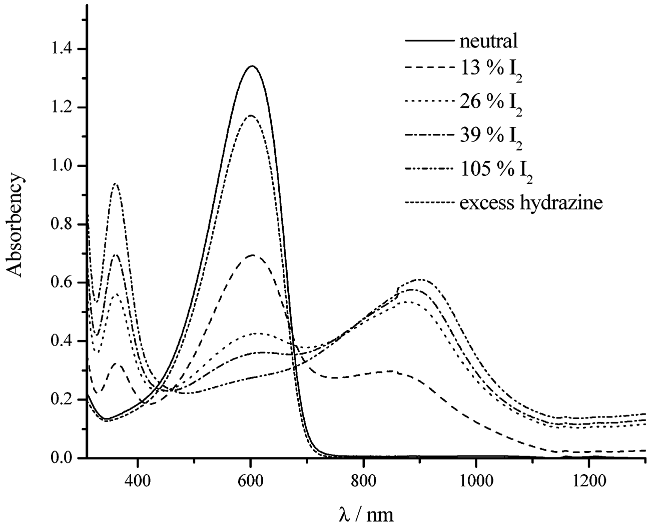


Figure 3. Oxidation and back reduction of **pol 3**.

oxidized, the system was back reduced by addition of hydrazine ($\sim10^{-1}$ M, THF). The oxidation and back reduction is visualized for **pol 3** in Figure 3. As can be seen, the oxidation/reduction could easily be controlled and proved to be reversible, without any visible decomposition, since—apart from dilution—the UV−vis spectra of the polymer solution before and after oxidation/reduction are identical.Next, we performed conductivity measurements on oxidized, spin-coated films of **pol 1−3**. These experiments reveal a weak to good conductivity, which was dependent on the degree of regioregularity (Table 1). This behavior can be explained by the improvement in supramolecular packing in films upon increasing degrees of regioregularity, which enhances hopping between stacked chains. Since sample preparation has proven to play a crucial role in the conductivity of a film and that this factor has not yet been optimized, these polymers show great potential as conductive polymer materials.

CD Spectroscopy. Finally, we performed some circular dichroism (CD) experiments of spin-coated films of **pol 1−3**. CD has proven to be a very powerful tool for the determination of the regioregularity of P3ATs and the supramolecular chirality of HT-P3ATs and poly(3,4-dialkoxythiophene)s.[3,11] As mentioned earlier, the regioregularity allows the formation of coplanar strands, which are stacked in a chiral way. This supramolecular chirality leads to very large, bisignate Cotton effects. It is clear that regioregularity is crucial for this stacking. As displayed in Figure 4, spin-coated films of **pol 1** show almost no CD, and films of **pol 2** show a moderate effect, while films of **pol 3** show an extremely high CD response. The degree of circular polarization in absorption, as defined by $g_{\text{abs}}(\Delta\epsilon/\epsilon)$, was 3×10^{-4} ($\lambda = 737$ and 523 nm) for **pol 2** and even 10^{-2} ($\lambda = 745$ nm) and 6×10^{-3} ($\lambda = 532$ nm) for **pol 3**. These values are approximately 1 order of magnitude higher than those found in films of chiral HT-P3AT and regioregular poly(3,4-dialkoxythiophene)s.[2,11]

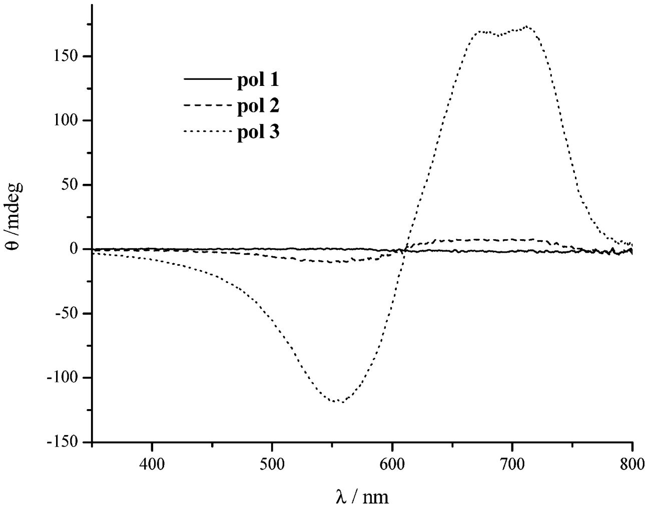


Figure 4. CD spectrum of films of pol **1−3**.

This work is an improvement in the development of chiral polymer conductors. A first approach to prepare chiral, conducting polymers consisted of the electrochemical polymerization of chiral thiophene and mainly pyrrole monomers, yielding conductive polymer films. However, these materials are insoluble, and they do not show any evidence of supramolecular chirality, probably due to the regioirregular nature of the polymer and/or the bulkiness of the chiral side-chain, which prevents a (chiral) stacking.[12] A second approach consists of doping achiral conducting polymers (e.g. PANI) with chiral dopants or to use chiral templates.[13] In a last approach, regioregular, chiral polythiophenes with a stable oxidized state are prepared. Recently, this was achieved by polymerizing chiral EDOTs.[14a] However, these polymer materials are insoluble and no evidence of supramolecular chirality in neutral nor oxidized state was presented. We have shown that chiral, *N*-substituted polythieno[3,2-*b*:2′,3′-*d*]pyrroles are a class of soluble, conducting polymers with a stable oxidized state and which show (supramolecular) chirality in both neutral as well as oxidized state and are therefore soluble, chiral polymer conductors.[14b] Unfortunately, due to their limited solubility, only low molecular weight, soluble material can be obtained and relative small Cotton effects are observed. Regioregular P3AOTs, on the other hand, show a remarkable solubility and processability and very large Cotton effects. Unfortunately, it was not possible to record CD-spectra in the oxidized state, since the wavelength range of our CD spectrometer is limited to 800 nm.

Experimental Section

Reagents. All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka, and Avocado. Reagent grade solvents were dried when necessary and were purified by distillation.

Gel permeation chromatography (GPC) measurements were done with a Waters apparatus with a tunable absorbance detector and a differential refractometer in tetrahydrofuran (THF) as eluent toward polystyrene standards. ^{1}H nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz. UV−vis spectra were recorded with a Varian Cary 400.

Synthesis of the Monomers. Synthesis of (*S*)-(—)-3-(3,7-Dimethyloctyl)oxythiophene (3). A solution of **1** (8.55 g, 75.0 mmol), (*S*)-3,7-dimethyloctanol (**2**) (23.7 g, 150 mmol), and $NaHSO_4$ (0.45 g) in dry toluene (30 mL) was heated during 3 h and approximately 10 mL of an azeotropic mixture of methanol and toluene was distilled off. After reaction, the catalyst was filtered off and the organic layer was washed with a saturated $NaHCO_3$-solution until neutral and finally dried over $MgSO_4$. The solvents were removed, and the crude product was purified by vacuum distillation.

Yield: 9.32 g (52%).

Bp: 80 °C/ 0.2 mmHg.

$[\alpha]_D^{20} = -0.83$ deg·dm^{-1}·g^{-1}·mL ($c = 57{,}2$ in CH_2Cl_2).

^{1}H NMR (CDCl$_3$): $\delta = 7.17$ (dd, $J = 5.1$ Hz, $J = 3.3$ Hz, 1H), 6.75 (dd, $J = 5.1$ Hz, $J = 1.5$ Hz, 1H), 6.23 (dd, $J = 3.3$ Hz, $J = 1.5$ Hz, 1H), 3.97 (m, 2H), 1.80 (m, 1H), 1.60 (m, 3H), 1.23 (m, 6H), 0.93 (d, 3H), 0.87 (d, 6H).

^{13}C NMR (CDCl$_3$): $\delta = 158.5$, 124.6, 120.0, 97.5, 69.0, 39.7, 37.7, 36.7, 30.3, 28.4, 25.3, 23.1, 19.5.

MS: $m/z = 240$ (M$^+$), 100 (M$^+$ − $C_{10}H_{20}$).

Anal. Calcd for $C_{14}H_{24}OS$: C, 69.95; H, 10.06. Found: C, 69.63; H, 9.86.

Synthesis of (*S*)-(−)-2,5-Dibromo-3-(3,7-dimethyloctyloxy)thiophene (4). A solution of **3** (3.61 g, 15 mmol) in chloroform (10 mL) and acetic acid (5 mL) was shielded from light and brought under argon atmosphere. Then, *N*-bromosuccinimide (5.72 g, 32.5 mmol) was added in small portions at 0 °C. After reaction (as monitored by TLC), NaOH (70 mL, 1 M) was added to the reaction mixture and the crude compound was extracted with dichloromethane. The combined organic layers were washed with a saturated $NaHCO_3$ solution and then with a $Na_2S_2O_3$ solution and finally dried over $MgSO_4$. The solvents were removed and the product was purified by column chromatography (silica gel; eluent = hexane/dichloromethane (98:2 v/v)). The product was isolated as a yellow oil and must be kept cold and in the dark.

Yield: 2.67 g (45%).

$[\alpha]_D^{20} = -0.34$ deg·dm^{-1}·g^{-1}·mL ($c = 16{,}6$ in CH_2Cl_2).

^{1}H NMR (CDCl$_3$): $\delta = 6.76$ (s, 1H), 4.03 (m, 2H), 1.77 (m, 1H), 1.66 (m, 1H), 1.55 (m, 2H), 1.1−1.4 (m, 6H), 0.93 (d, 3H), 0.87 (d, 6H).

^{13}C NMR (CDCl$_3$): $\delta = 154.3$, 121.2, 110.0, 90.9, 71.3, 39.9, 37.6, 36.8, 30.1, 28.4, 25.1, 23.1, 20.1.

MS: $m/z = 400$ (M$^+$), 260 (M$^+$ − $C_{10}H_{20}$).

Anal. Calcd for $C_{14}H_{22}Br_2OS$: C, 42.23; H, 5.57, Found: C, 41.98; H, 5.35.

Synthesis of (*S*)-(+)-2-Bromo-4-(3,7-dimethyloctyloxy)thiophene (5). A solution of **4** (1.99 g, 5.0 mmol) in dry *n*-hexane (50 mL) was purged with argon and cooled to − 78 °C. To this solution was added *n*-BuLi (2.0 mL, 5.0 mmol; 2.5 M in hexane) dropwise. The reaction mixture was stirred for 30 min at −78 °C, after which it was quenched with water and was extracted with diethyl ether. The combined organic extracts were washed with a saturated $NaHCO_3$ solution and dried over anhydrous $MgSO_4$. The solvents were removed and the product was purified by column chromatography (silica gel; eluent = hexane/dichloromethane (95:5 v/v)) and isolated as a colorless oil.

Yield: 1.38 g (86%).

$[\alpha]_D^{20} = +3.75$ deg·dm^{-1}·mol^{-1}·mL ($c = 3.6$ in CH_2Cl_2).

^{1}H NMR (CDCl$_3$): $\delta = 6.73$ (d, $J = 2.2$ Hz, 1H), 6.10 (d, $J = 2.2$ Hz, 1H), 3.91 (m, 2H), 1.75 (m, 1H), 1.55 (m, 3H), 1.1−1.4 (m, 6H), 0.93 (d, 3H), 0.86 (d, 6H).

^{13}C NMR (CDCl$_3$): $\delta = 156.9$, 122.8, 122.6, 98.6, 68.4, 39.4, 37.4, 36.1, 29.9, 28.1, 24.8, 22.8, 22.7, 19.7.

MS: $m/z = 320$ (M$^+$), 180 (M$^+$ − $C_{10}H_{20}$).

Anal. Calcd for $C_{14}H_{23}BrOS$: C, 52.66; H, 7.26, Found: C, 52.24; H, 7.04.

Synthesis of the Polymers. Pol 1. A solution of **3** (1.27 g, 6.0 mmol) in dry chloroform (20 mL) was dropwise added to a solution of dry $FeCl_3$ (3.89 g, weighed under inert atmosphere, 24 mmol) in dry chloroform (30 mL). The whole mixture was stirred overnight at room temperature and the crude polymer was precipitated in methanol. The polymer was further purified by extraction with hexane using a Soxhlet apparatus. Finally, the polymer itself was extracted with chloroform, precipitated into methanol, filtered off, and dried.

Yield = 0.155 g (12%).

^{1}H NMR (CDCl$_3$): $\delta = 7.0$−6.7 (s, (br), 1H), 4.16 (s, (br), 2H), 2.0−1.1 (m, 10H), 1.00 (s, 3H), 0.86 (s, 6H).

Pol 2. MeMgBr (1.67 mL, 5.0 mmol, 3 M in Et_2O) was added to a solution of **4** (1.85 g, 5.0 mmol) in dry THF (30 mL) via a syringe. The reaction mixture was refluxed for 1 h under argon atmosphere. Ni(dppp)Cl_2 (0.271 g, 0.05 mmol) was added, and the reaction mixture was refluxed for 2 h. Then, a saturated $NaHCO_3$ solution was added and the polymer was extracted with chloroform. The combined organic layers were washed with a $NaHCO_3$ solution and dried over Na_2SO_4. The polymer solution was concentrated and the polymer was precipitated in methanol. The polymer was further purified by extraction with hexane using a Soxhlet apparatus. Finally, the polymer itself was extracted with chloroform, precipitated into methanol, filtered off, and dried.

Yield = 0.855 g (72%).

^{1}H NMR (CDCl$_3$): $\delta = 6.94$ (s, 1H), 4.20 (s, 2H), 2.0−1.1 (m, 10H), 1.00 (s, 3H), 0.86 (s, 6H).

Pol 3. *n*-BuLi (1.44 mL, 3.6 mmol, 2.57 M in hexane) was added at room temperature to a solution of freshly distilled diisopropylamine (0.405 g, 4.00 mmol) in dry THF (10 mL). This LDA solution was added to a solution of **5** (0.958 g, 3.0 mmol) in dry THF (5 mL) at −78 °C. After being stirred for 30 min at −78 °C, this mixture was added to $MgBr_2 \cdot OEt_2$ (0.78 g, 3.0 mmol) and Ni(dppp)Cl_2 (16.3 mg, 0.03 mmol). The reaction mixture was stirred at −78 °C for 30 min, warmed slowly to room temperature, and finally stirred overnight. The same amount of catalyst was added again, and stirring was continued for 5 h. The polymer was precipitated in methanol, and further purified by extractions with hexane using a Soxhlet apparatus. The polymer was isolated via Soxhlet extraction with chloroform, precipitated into methanol, filtered off, and dried.

Yield = 411 mg (61%).

^{1}H NMR (CDCl$_3$): $\delta = 6.92$ (s, 1H), 4.22 (s, 2H), 2.0−1.1 (m, 10H), 1.00 (s, 3H), 0.86 (s, 6H).

Conclusion

In conclusion, we have developed a new strategy which produces P3AOTs with much larger degrees of regioregularity in comparison with existing methodologies. The properties of the polymers were thoroughly investigated and evaluated for the degree of their regioregularity. Chiral regioregular P3AOTs show a unique combination of assets for conjugated polymers, i.e., solubility, chirality, conductivity, and stability of the oxidized state. These materials are therefore excellent candidates to be used in applications as well as in fundamental research of (chiral) conjugated materials in the oxidized state.

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