Regioregularity in Poly(3-alkoxythiophene)s: Effects on the Faraday Rotation and Polymerization Mechanism

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Summary

Poly(3-alkoxythiophene)s with different degrees of regioregularity were prepared using three different methodologies. It is shown that their Faraday rotation is highly dependent on the degree of regioregularity. The origin of the differences in regiospecificity of the methodologies is discussed.

Introduction

Substituted polythiophenes, s. a. poly(3-alkylthiophene)s (P3ATs), represent an important class of soluble, conjugated polymers, which show moderate to excellent conductivities in the doped (oxidized) state.^[1-4] The (conductive) properties are greatly affected by the degree of regioregularity, which can be expressed as the percentage of head-to-tail (HT) couplings. The higher the regioregularity, the less steric hindrance between the substituents and adjacent thiophenes moieties is present. As a consequence, planar structures and high conjugation lengths are impossible in regiorregular P3ATs. In regioregular P3ATs (HT-P3ATs), on the other hand, aggregates, composed of coplanar strands, are formed in nonsolvents or films. The planarity is reflected in an efficient molecular overlap, which leads to lower bandgaps and lower oxidation potentials. The regular molecular structure allows a good stacking, resulting in good conductivities and charge carrier mobilities.

The major drawbacks of regiorregular as well as regioregular P3ATs are the instability of the doped (oxidized, for instance with I₂) (conductive) state and the difficulty to dope the material reproducibly. Therefore, (regioregular) poly(3-alkoxythiophene)s (P3AOTs) were developed.^[5-6] In a previous manuscript, we synthesized chiral P3AOTs with different degrees of regioregularity, using different polymerization methodologies and studied the effect of the regioregularity on the properties.^[5b] Regioregular P3AOTs appeared to be soluble, highly conjugated polymers with a stable oxidized state and very large chiral (Cotton) effects. It was also shown that minor changes in regioregularity, which hardly effect λ_{max} , can have tremendous effects on the stacking, which was visualized by circular dichroism. In this manuscript, we evaluate the influence of the regioregularity of poly(3-octyloxythiophene)s, prepared by the different methodologies, on a particular and easy-to-measure property, applicable on chiral as well as achiral materials, Faraday rotation. Finally, the origin of the differences in regiospecificity of the methodologies is discussed.

Experimental part

Materials

All starting materials were purchased from Acros Organics, Fluka, Merck or Aldrich and were used as received. Tetrahydrofuran (THF) and *n*-hexane were dried over a Na/K alloy. **1** was synthesized according to a literature procedure^[7].

Synthesis of 3-octyloxythiophene **2**

A solution of **1** (8.55 g, 75.0 mmol), octanol (19.5 g, 150.0 mmol) and NaHSO₄ (0.45 g) in dry toluene (25 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 NaHCO₃-solution and dried over MgSO₄. The solvents were removed and the crude product was purified by vacuum distillation.

Yield = 10.7 g (67%). b.p. = 91 °C/ 0.4 mm Hg. ¹H-NMR (CDCl₃): δ = 7.16 (dd, J = 5.1 Hz, 3.1 Hz, 1H), 6.75 (dd, J = 5.1 Hz, 1.5 Hz, 1H), 6.22 (dd, J = 3.1 Hz, J = 1.5 Hz, 1H), 3.93 (t, 2H), 1.76 (qu, 2H), 1.44 (m, 2H), 1.30 (m, 8H), 0.88 (t, 3H). ¹³C-NMR (CDCl₃): δ = 158.2, 124.6, 119.7, 97.1, 70.4, 32.0, 29.5, 29.4, 26.2, 22.8, 14.2. MS: m/z = 212 (M⁺), 100 (M⁺ - C₈H₁₆).

Synthesis of 2,5-dibromo-3-octyloxythiophene **3**

Under argon atmosphere, *N*-bromosuccinimide (NBS) (8.90 g, 50 mmol) was added in small portions to a solution of **2** (5.30 g, 25 mmol) in chloroform (20 mL) and acetic acid (10 mL). 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 NaHCO₃-solution, with a Na₂S₂O₃-solution and finally dried over MgSO₄. The solvents were removed and the product was purified by column chromatography (silicagel; 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 = 5.5 g (59%) $^1\text{H-NMR}$ (CDCl_3): δ = 6.76 (s, 1H), 3.99 (t, 2H), 1.73 (qu, 2H), 1.43 (m, 2H), 1.30 (m, 8H), 0.89 (t, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ = 154.0, 121.0, 109.7, 90.7, 72.7, 31.9, 29.5, 29.4, 29.3, 25.9, 22.8, 14.2. MS: m/z = 370 (M^+), 258 ($\text{M}^+ - \text{C}_8\text{H}_{16}$).

Synthesis of 2-bromo-4-octyloxythiophene 4

A solution of **3** (1.85 g, 5.0 mmol) in dry *n*-hexane (50 mL) was purged with argon and cooled to -78°C . To this solution, *n*-BuLi (2.0 mL, 5 mmol; 2.5 M in hexane) was added drop wise. 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 (silicagel; eluent: hexane/dichloromethane (95:5 v/v) and isolated as a colorless oil.

Yield = 1.3 g (93%). $^1\text{H-NMR}$ (CDCl_3): δ = 6.73 (d, J = 1.9 Hz, 1H), 6.10 (d, J = 1.9 Hz, 1H), 3.88 (t, 2H), 1.74 (qu, 2H), 1.2-1.5 (m, 10H). $^{13}\text{C-NMR}$ (CDCl_3): δ = 157.0, 122.8, 111.7, 98.7, 70.2, 32.0, 29.5, 29.4, 29.2, 26.1, 22.8, 14.2. MS: m/z = 292 (M^+), 180 ($\text{M}^+ - \text{C}_8\text{H}_{16}$).

Polymer synthesis

The three polymers, **pol 1**, **pol 2** and **pol 3**, were synthesized in three different ways.

pol 1:

A solution of **2** (1.27 g, 6.0 mmol) in dry chloroform (20 mL) was added drop wise 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 reduced by addition of hydrazine and purified by Soxhlet extraction using hexane. The polymer was isolated via Soxhlet extraction with chloroform, precipitated into methanol, filtered off and dried.

Yield = 0.375 g (30%). $^1\text{H-NMR}$ (CDCl_3): δ = 7.1-6.7 (s, (br), 1H), 4.13 (s, (br), 2H), 1.86 (s, 2H), 1.3 (m, 10H), 0.87 (s, 3H).

pol 2:

MeMgBr (1.67 mL, 5.0 mmol, 3 M in Et_2O) was added to a solution of **3** (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 (271 mg, 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 extractions with hexane using a Soxhlet apparatus. Finally, the polymer itself was extracted with chloroform, precipitated into methanol, filtered off and dried.

Yield = 0.889 g (85%). $^1\text{H-NMR}$ (CDCl_3): δ = 6.94 (s, 1H), 4.16 (s, 2H), 1.88 (s, 2H), 1.31 (m, 10H), 0.89 (s, 3H).

pol 3:

Under argon atmosphere, *n*-BuLi (0.93 mL, 2.4 mmol, 2.57 M in hexane) was added at room temperature to a solution of freshly distilled diisopropylamine (0.291 g, 2.88 mmol) in dry THF (10 mL). This LDA-solution was added to a solution of **4** (0.582 g, 2.0 mmol) in dry THF (5 mL) at -78°C . After stirring for 30 min at -78°C , this mixture was added to $\text{MgBr}_2\cdot\text{OEt}_2$ (0.62 g, 2.4 mmol) and Ni(dppp)Cl_2 (10.8 mg, 0.02 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 via Soxhlet extraction using hexane. The polymer was isolated via Soxhlet extraction with chloroform, precipitated into methanol, filtered off and dried.

Yield = 480 mg (76%). $^1\text{H-NMR}$ (CDCl_3): δ = 6.93 (s, 1H), 4.16 (s, 2H), 1.86 (s, 2H), 1.3 (m, 10H), 0.88 (s, 3H).

Results and discussion

Three poly(3-octyloxythiophene)s with different degrees of regioregularity were prepared using three different methods which we previously employed for the synthesis of chiral P3AOTs: an oxidative polymerization,^[6b] the GRIM methodology^[2a-b, 5] and a “reversed McCullough” procedure.^[5b]

So, in a first approach, 3-octyloxythiophene (**2**) was oxidatively polymerized with FeCl_3 , rendering **pol 1** (Scheme 1). **2** itself was obtained via a transesterification from **1**.^[8] A second sample of poly(3-octyloxythiophene) (**pol 2**) was obtained using the GRIM method. Therefore, **2** was dibrominated with NBS to afford **3**, which was subsequently transformed into the Grignard derivative with methyl magnesium bromide and polymerized with a Kumada cross-coupling reaction, catalyzed by bis(diphenylphosphinopropane)nickel^(+II) dichloride ($\text{Ni}(\text{dppp})\text{Cl}_2$). Finally, **pol 3** was prepared from 2-bromo-4-alkoxythiophene using a “reversed McCullough” method*. Therefore, **3** was selectively debrominated in the 2-position with *n*-BuLi in hexane. It appeared that hexane must be used instead of THF or diethyl ether, since no selective debromination took place in the latter cases. Finally, **4** was lithiated with lithium diisopropyl amide (LDA) and the intermediate was converted into the desired Grignard reagent with magnesium bromide diethyletherate, 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 by hydrazine. For purification, the crude

* The sequence to prepare the actual monomer (**3a**, see also scheme 2) and the concept to prepare only one of the possible isomers, resembles the original McCullough methodology,^[1b] but in the original method, **3b** is formed starting for **5**, while in the “reversed McCullough” method, the other isomer (**3a**), is prepared from **4**. If the McCullough method would be applied on alkoxythiophenes, scrambling would occur – since the less stable isomer is formed - resulting in a mixture of isomers. As will be shown, this modification is crucial.

polymer material was extracted first with hexane and then with chloroform. Finally, the concentrated chloroform-solution was added drop wise to methanol.

The molecular weights and polydispersities were measured by GPC in THF towards polystyrene (Table 1). It must be noted that it is shown that the molecular weights, determined in this way, are underestimated.^[9]

¹H-NMR spectroscopy was used to get a first indication of the differences in regioregularity - the aromatic signal was 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 one singlet, and some small peaks at 7.34, 7.59 and 7.85 ppm. Since the molecular weight is quite high, these peaks cannot be attributed to end-groups only and, consequently, some regioirregularities must be present. **pol 3**, finally, shows only one small shoulder, indicating that the polymer is almost perfectly regioregular.

Also UV-vis spectroscopy can be used to probe differences in regioregularity, since regioirregularities, especially HH-couplings, lead to nonplanar structures, causing a blue-shift. UV-vis spectra of all polymers were recorded in both neutral and oxidized state in THF solution as well as in thin spin coated films. The films were oxidized by exposure to I₂-vapour for 5 seconds and the solutions were oxidized by addition of an I₂-solution. As displayed in Table 1, the λ_{max} values for these polymers are significantly red-shifted compared with those of P3ATs ($\lambda_{\text{max}} \sim 520$ nm in films). Also a red-shift is observed when the polymer is transformed from solution to film. This is a common feature in conjugated polymers and can be ascribed to the formation of more planar structures in the solid state. If the three polymers are compared, it is clear that **pol 1** is significantly blue-shifted, but that **pol 2** and **pol 3** show almost the same λ_{max} .

Although differences in the regioregularity can be visualized by UV-vis or NMR spectroscopy, these methods are not sensitive to small variations (a few percent) of the

regioregularity. On the other hand, we have demonstrated that circular dichroism is a very powerful technique to visualize small differences in regioregularity. CD measurements demonstrated large differences between P3AOTs prepared via the different methods.^[5b]

However, it is clear that this technique can only be applied on *chiral* materials.

Faraday rotation is a nonlinear optical process that consists of the rotation of the plane of polarization of linear polarized light in the presence of a parallel magnetic field. The magnitude of the rotation is proportional to the strength of the magnetic induction field (B), the pathlength (L) and a material-constant, the Verdet constant (V) (Eq. 1).

$$\theta = B \cdot L \cdot V \quad \text{Eq. 1}$$

Faraday rotation is very wavelength-dependent and can be measured in both chiral and achiral materials. Recently, we have shown that poly(3-alkylthiophene)s and poly(3-alkoxythiophene)s show remarkable high Verdet constants.^[10] Although the reason for this high Faraday rotation is not completely understood, (nonlinear) optical processes are in general very sensitive to conjugation and supramolecular organization. Hence, Faraday rotation can be a promising tool to probe (small) differences in regioregularity in chiral as well as achiral polythiophenes.

Faraday rotation measurements were performed with diodelaser (830 nm). After passing through a polarizer, the linearly polarized light was incident on the sample, which was placed in a parallel AC magnetic field (50 - 1000 Hz, 0.005 - 0.0250 T). After passing through an analyzer (rotated 45° with respect to the first polarizer), the changes in output intensity - as a consequence of polarisation rotation - were detected with a photodiode and a lock-in amplifier.

From the Faraday rotation measurements, significant differences in Verdet constants are observed (Table 1). Since λ_{max} of all samples is more or less the same (especially for **pol 2** and **pol 3**), the large variations of the Verdet constant cannot be ascribed to a wavelength

dependency, but instead reflect significant differences between the materials. Because the polymers only differ in regioregularity, the observed differences in Verdet constant must be due to variations in degree of regioregularity. Consequently, Faraday rotation is an easy and promising technique to probe (small) differences in molecular structure, such as regioregularity, in both chiral and achiral conjugated polymers.

Although it is clear that the “reversed McCullough” method produces (slightly) more regioregular P3AOTs than the GRIM methodology, the question remains what the origin of this difference is, especially since the McCullough and GRIM methodology, when applied for the synthesis of poly(3-*alkyl*thiophene)s, produce polymers which are equally regioregular. The generally accepted polymerization mechanism of mono- and dihalogenated 3-*alkyl*thiophenes is presented in scheme 2.^[11] The McCullough and GRIM method differ in the way the actual monomer (**3**) is prepared: in the McCullough method, **5** is exclusively converted to one isomeric monomer (**3b**), while in the GRIM methodology, Grignard metathesis of an *alkyl* Grignard reagent on **3** renders a mixture of both isomeric monomers **3a** and **3b**. The actual polymerization proceeds similarly: Upon addition of Ni(dppp)Cl₂, **3b** attacks the Ni-catalyst twice, which after intramolecular transfer, results in the formation of the real ‘initiator’, **6b**. Polymerization consists of oxidative addition of **3b** to the Ni-center and the intramolecular transfer of the Ni(0) to the terminal C-Br bond. Only **3b** reacts: the steric hindrance around the small Ni(dppp) center prevents this TT formation and therefore, **3a**, if present, is not consumed. Hence, the regioregularity in poly(3-*alkyl*thiophene)s is due to the Ni-catalyst. The polymerization is a living polymerization and essentially a chain-growth polymerization.

In case of poly*alkoxy*thiophenes, when **4** is polymerized in the “reversed McCullough” method, not **3b**, but **3a** is formed. The fact that **pol 3** is easily prepared, indicates that the addition of **3a** to Ni(dppp)Cl₂ readily occurs, although in this case, no TT-coupling, but a HH-

coupling is formed. The actual initiator is **6a** and not **6b**. The reason for this reduced specificity of the Ni-catalyst is probably the fact that an O-atom is smaller than a methylene group. Also the formation of S-O interactions in the growing polymer chain and/or interaction between oxygen and the Ni-center might explain the reduced specificity. The regioregularity, present in **pol 3**, therefore arises from the fact that only one isomer, the most stable one, is polymerized and *not* from the Ni(dppp)-catalyst.

In case of the GRIM polymerization for P3AOTs (**pol 2**), Grignard metathesis on **3** gives again rise to a mixture of isomers.^[5a] From the polymerization of **3**, it can be concluded that HH-couplings can be formed in P3AOTs using a Ni-catalyst. An exclusive formation of one initiator (**6b** or **6a**) and subsequent addition of only one isomer (**3b** or **3a** respectively), which would lead to regioregular P3AOT, can therefore be excluded. Instead, it is more likely that – due to the reduced regiospecificity of the Ni-catalyst – both initiators (**6b** and **6a**) are formed and that both isomers are built in. Consequently, some regioregularities must be present, which is also observed. Hence, in contrast to HT-P3ATs, which can be synthesized from a mixture of isomeric monomers by virtue of the Ni-catalyst preventing a HH-coupling, the regioregular polymerization of *alkoxy*thiophenes requires the formation of only one isomeric monomer. Efforts to further support this hypothesis are on-going.

Conclusions

Poly(3-alkoxythiophene)s with different degrees of regioregularity were prepared using three different methodologies. It was shown that their Faraday rotation is highly dependent on the degree of regioregularity and therefore, Faraday rotation seems to be a powerful technique to probe (small) variation in (supra)molecular structure of chiral as well as achiral conjugated polymers. The origin of the difference in regioselectivity of the GRIM and “reversed McCullough” method was explained: in contrast to poly(3-*alkyl*thiophene)s, the Ni-catalyst can promote HH-couplings in poly(3-*alkoxy*thiophene)s and, therefore, the formation of

regioregular poly(3-alkoxythiophene)s requires the use of only one, the most stable, of the isomeric monomers.

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Captions to figures and schemes

Figure 1: ^1H NMR spectra in CDCl_3 of **pol 1-3**

Scheme 1: Synthesis of the polymers **pol 1-3**.

Scheme 2: Polymerization mechanism of P3ATs and P3AOTs

Table 1: Physical properties of the polymers

Polymer	Yield ^a /	$\overline{M}_n$ /	D	$\lambda_{\text{max, neutral}}$ / nm		$\lambda_{\text{max, ox.}}$ / nm ^c		V /
	%	10^3 g mol^{-1}		solution ^b	film	solution ^b	film	$10^4 \text{ T}^{-1} \cdot \text{m}^{-1}$
pol 1	30	1.8	1.8	537	560	801	833	5.0
pol 2	85	4.6	2.1	586	621	903	919	40
pol 3	76	5.6	1.5	592	641	900	913	300

$$D = \frac{\overline{M}_w}{\overline{M}_n}$$

a) chloroform-soluble fraction after soxhlet extraction

b) In THF-solution

c) Oxidized with iodine

Figure 1

Scheme 1

Scheme 2

monomer formation

polymerization

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