Regioregular Poly(3-(4-alkoxyphenyl)thiophene)s: Evidence for a Two-step Aggregation Process

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Keywords: annealing, chiral, conjugated polymers

Summary

A chiral, regioregular poly(3-(4-alkoxyphenyl)thiophene) has been prepared and studied. Films prepared by fast evaporation of the solvent, consists of random-coils, while films prepared by slow evaporation are composed of chirally aggregated, coplanar strands. Heat treatment transforms the random-coil to the aggregated films via an intermediate state, which was characterized as chiral, coplanar, unaggregated polymer strands.

Introduction

Conjugated polymers have attracted a lot of attention. They are of great interest in oLEDs, photovoltaic cells, field-effect transistors, amongst others. Especially regioregular poly(3-alkylthiophene)s (HT-P3ATs) are of particular interest, since they are soluble and, due to the high amount of order in the solid state, highly conjugated^[1]. Recently, also regioregular poly(3-alkoxythiophene)s, which show the additional advantage of a good stability of the oxidized state, and, consequently, conductivity, have been developed^[2]. Finally, also poly(3-(4-alkoxyphenyl)thiophene)s (P3AOPTs)^[3] and poly(3-(4-alkylphenyl)thiophene)s (P3APT)s^[3d, 4] with poor to moderate degrees of regioregularity have been prepared.

As other conjugated polymers HT-P3ATs show remarkable thermo- and solvatochromism in solution^[5]. This can be explained by a transition from a poorly conjugated state, in which the polymer strands are present as random coils, to aggregates, which are composed of coplanar, highly conjugated polythiophene strands. However, no direct evidence was given to indicate whether this transition is a two-step process (in which the strands first planarize and then aggregate or vice versa), or a one-step process. Up till now, the presence or absence of a clear isosbestic point in the UV-vis spectra associated with this transition, was used to distinguish between these two possibilities. In films, curing is a common technique and is used to change (optimize) the macroscopic order. Possible changes in UV-Vis and CD spectra of films of these polymers upon heat treatment then reflect an altered supramolecular order, rather than a transition from the random-coil to the aggregated state.

In this paper, we report the synthesis of regioregular, chiral P3AOPTs. These polymers are comparable with HT-P3ATs, but the presence of the phenyl groups, directly attached to the polythiophene backbone, restricts the molecular mobility. As a consequence, a potential intermediate state in the transition from random-coils to aggregates in films is present and visualized. This intermediate state is a clear evidence for a two-step aggregation process in

films and gives more insight in the aggregation of poly(3-substituted)thiophenes in general. The combination of UV-Vis and CD spectroscopy will be used to study this transition.

Experimental part

Materials

All starting materials were purchased from Acros Organics, Fluka, Merck or Aldrich and were used as received. Tetrahydrofuran (THF) was dried over a Na/K alloy and diisopropylamine was distilled over CaH_2 and further dried on molecular sieve (4Å).

3-(4-octyloxyphenyl)thiophene 2a and (S)-(-)-3-[4-[(3,7-dimethyl)octyloxy]phenyl]thiophene 2b

A solution of 4-iodoalkoxybenzene **1a-b** (10.0 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.3 mmol, 347 mg) in DME (30 ml) was purged with argon and a solution of 3-thiophene boronic acid (11.0 mmol, 1.41 g) in DME (10 ml) was added. The mixture was slightly heated until complete dissolution and a Na_2CO_3 -solution (20 ml, 1M in water) was added. The reaction mixture was refluxed for 30 min, cooled and poured into water. After extraction with diethylether, the combined organic layers were dried over MgSO_4 . The solvents were removed and the crude product was purified by recrystallization from chloroform/methanol and isolated as a white solid.

2a: Yield = 1.82 g (63 %); m.p. = 93.9 °C; $^1\text{H-NMR}$ (CDCl_3): δ = 7.51 (d, 2H, $J=8.8$ Hz), 7.34 (m, 3H), 6.92 (d, 2H, $J=8.8$ Hz), 3.98 (t, 2H), 1.79 (qu, 2H), 1.2-1.5 (m, 10H), 0.89 (t, 3H).

2b: Yield = 1.29 g (41 %); m.p. = 74.5 °C; $[\alpha]_D^{25} = -0.94 \text{ deg}\cdot\text{dm}^{-1}\cdot\text{mol}^{-1}\cdot\text{l}$ ($c = 1$ in CHCl_3); $^1\text{H-NMR}$ (CDCl_3): δ = 7.51 (d, 2H, $J=8.7$ Hz), 7.34 (m, 3H), 6.92 (d, 2H, $J=8.7$ Hz), 4.01 (m, 2H), 1.83 (m, 1H), 1.4-1.8 (m, 3H), 1.1-1.4 (m, 6H), 0.95 (d, 3H), 0.87 (d, 6H).

2-bromo-3-(4-octyloxyphenyl)thiophene 3a and (S)-(+)-2-bromo-3-[4-[(3,7-dimethyl)octyloxy]phenyl]thiophene 3b

A solution of **2a-b** (5.00 mmol) in DMF (10 ml) was purged with argon and shielded from light. NBS (5.00 mmol, 890 mg) was added and the reaction mixture was stirred for 2h at room temperature. The mixture was poured into a NaHSO₃-solution and extracted with diethylether. The combined organic layers were dried over MgSO₄. The solvents were removed and the crude compound was purified by column chromatography (silicagel; eluent: petroleum ether) and collected as a colorless oil.

3a: Yield = 1.50 g (81 %); ¹H-NMR (CDCl₃): δ = 7.47 (d, 2H, J= 8.8Hz), 7.28 (d, 1H, J=5.9 Hz), 7.00 (d, 1H, J=5.9 Hz), 6.95 (d, 2H, J=8.8 Hz), 3.99 (t, 2H), 1.80 (qu, 2H), 1.2-1.5 (m, 10H), 0.89 (t, 3H); ¹³C-NMR (CDCl₃): δ = 159.1, 141.3, 130.2, 129.5, 127.7, 126.0, 114.7, 108.2, 68.4, 32.3, 29.7, 26.5, 23.1, 14.5; MS: *m/z* = 368 (M⁺), 256 (M⁺-C₈H₁₆).

3b: Yield = 1,70 g (85 %); $[\alpha]_D^{25} = -1.39 \text{ deg}\cdot\text{dm}^{-1}\cdot\text{mol}^{-1}\cdot\text{l}$ (c = 1 in CHCl₃); ¹H-NMR (CDCl₃): δ = 7.48 (d, 2H, J=8.7 Hz), 7.28 (d, 1H, J=5.9 Hz), 7.00 (d, 1H, J=5.9 Hz), 6.95 (d, 2H, J=8.7 Hz), 4.04 (m, 2H), 1.84 (m, 1H), 1.4-1.8 (m, 3H), 1.1-1.4 (m, 6H), 0.95 (d, 3H), 0.88 (d, 6H); ¹³C-NMR (CDCl₃): δ = 159.2, 141.3, 130.2, 129.5, 127.7, 126.1, 114.8, 108.2, 66.8, 39.8, 37.8, 36.7, 30.3, 28.5, 25.2, 23.2, 20.2; MS: *m/z* = 396 (M⁺), 256 (M⁺-C₁₀H₂₀).

Poly(3-(4-octyloxyphenyl)thiophene) 4a and poly((S)-3-[4-[(3,7-dimethyl)octyloxy]phenyl]thiophene) 4b

Under argon atmosphere, a solution of **3a-b** (0.7 mmol) in dry THF (1.5 ml) was added to a solution of LDA (0.84 mmol) [prepared from 1.05 mmol diisopropylamine and 0.84 mmol *n*-butyl lithium] in dry THF (3.5 ml) at -78 °C. The mixture was stirred for 30 min at -40 °C and anhydrous ZnCl₂ (0.84 mmol, 0.84 ml, 1 M in diethylether) was injected. The mixture was allowed to reach room temperature, Ni(dppp)Cl₂ (7.0 μmol, 4.0 mg) was added and the

reaction mixture was refluxed for 2 h. The polymer was precipitated in methanol (40 ml) and collected by filtration. For purification, it was washed with hexane using a Soxhlet extraction apparatus and extracted with chloroform. The chloroform-solution was concentrated and the polymer was precipitated in methanol. Finally, the polymer was filtered and dried under reduced pressure.

3a: Yield = 23.9 mg (12 %); $^1\text{H-NMR}$ ($\text{C}_2\text{D}_2\text{Cl}_4$): δ = 7.30 (d, 2H), 6.93 (d, 2H), 6.88 (s, 1H), 4.05 (t, 2H), 1.84 (m, 2H), 1.53 (m, 2H), 1.38 (m, 8H), 0.96 (t, 3H).

3b: Yield = 58.0 mg (31 %); $^1\text{H-NMR}$ ($\text{C}_2\text{D}_2\text{Cl}_4$): δ = 7.21 (d, 2H), 6.84 (d, 2H), 6.79 (s, 1H), 4.00 (m, 2H), 1.78 (m, 1H), 1.5-1.7 (m, 3H), 1.1-1.4 (m, 6H), 0.93 (d, 3H), 0.86 (d, 6H);

Measurements

$^1\text{H-NMR}$ (300 MHz) and $^{13}\text{C-NMR}$ (75 MHz) measurements were carried out on a Bruker Avance 300 MHz. The number average molecular weights ($\overline{M}_n$) and polydispersity ($\overline{M}_w/\overline{M}_n$) were measured by gel permeation chromatography (GPC) with a Shimadzu 10A with a tuneable absorbency detector and a differential refractometer, using THF as an eluent towards polystyrene standards. The UV-VIS spectra were recorded on a Varian Cary 400. Optical rotations were measured with an Analis Optical Activity Polaar 20 apparatus. CD spectra were recorded on a AVIV 62 DS CD spectrometer.

Results and discussion

In this paper, we report the synthesis and some preliminary properties of regioregular, (a)chiral poly(3-(4-alkoxyphenyl)thiophene)s (P3AOPTs). The monomers were prepared starting from the respective 4-iodoalkoxybenzene derivatives **1a-b** (scheme 1). First, **1a-b** was coupled with 3-thiophene boronic acid by a Suzuki-Miyaura coupling reaction^[3a]. Next, the thiophene moiety was brominated in the 2-position with *N*-bromosuccinimide (NBS)^[6]. Finally, the polymers were prepared according to a McCullough methodology, but anhydrous

ZnCl₂ was used instead of anhydrous MgCl₂^[1a-b]. This renders P3AOPTs with high degrees (> 96 %) of regioregularities, as indicated by ¹H NMR spectroscopy. This is in contrast with P3AOPTs which were polymerized by chemical oxidation and which show low to moderate degrees of regioregularity^[3].

The yields of the polymers (**4a**: 12 %; **4b**: 31 %) are quite low. In both cases, a rather large insoluble fraction was formed. We assume that the polymers show a reduced solubility compared to their HT-P3ATs analogues. The presence of the branched side-chain in **4b** should increase its solubility. This is also reflected in GPC measurements. These experiments reveal good molecular weights for **4b** ($\overline{M}_n = 13.4$ kg/mol, D = 1.9), but rather poor for **4a** ($\overline{M}_n = 7.2$ kg/mol, D = 1.5). Since the polymers have both essentially the same molecular structure and are measured under the same conditions, we believe that in case of **4a**, only the lower-molecular weight fraction is soluble and measured.

DSC experiments reveal that the polymers do not melt, nor show a glass transition below 280 °C. This is rather surprising, since P3ATs melt at much lower temperatures^[7] and regioirregular poly(3-(4-octyloxyphenyl)thiophene) show a Tg near 22 °C^[3b]. Cyclic voltammetry (in acetonitrile, 0.1 M Bu₄NBF₄, versus Ag⁺/Ag) indicates that **4b** shows a reversible redox wave at E_{1/2} = 1,30 V.

UV-Vis spectroscopy of **4b** in chloroform (not shown) displays $\lambda_{\text{max}} = 465$ nm, with no vibronic fine-structure, which is comparable with HT-P3ATs ($\lambda_{\text{max}} \sim 445$ nm), and is attributed to the polymer backbone in its poorly conjugated (unordered) random-coil conformation. If films are prepared - either by spin-coating (2000 rpm) or drop-casting - the UV-VIS spectrum changes only slightly ($\lambda_{\text{max}} = 496$ nm) (Figure 1a). However, if the films were prepared from 1,2-dichlorobenzene (400 rpm), a dramatic red-shift ($\lambda_{\text{max}} = 608$ nm) was observed and a clear vibronic fine-structure at $\lambda = 528, 568, 608$ and 666 nm appeared. This corresponds to a band-edge of 1.86 eV. The same results could be obtained if a chloroform-

solution was evaporated very slowly. If the film was heated (150 °C for 1 min) a red-shift occurs and a fine-structure appears. A similar behaviour has been reported by Fell et al. in films of (achiral) poly(3-(4-octylphenyl)thiophene) with a high (~ 94 %) degree of regioregularity^[4b]. They concluded that films spincoated from chloroform-solution, are amorphous, but significantly gained crystallinity upon heat treatment. This transformation was accompanied with a drastic red-shift. We believe that the observed process here is the same transition from the poorly conjugated random-coil state, trapped by the fast evaporation of the solvent (chloroform, b.p.= 62 °C), to the aggregated state, consisting of coplanar polymer strands. This is supported by the fact that film prepared by spincoating from a high-boiling solvent, such as dichlorobenzene (b.p.= 180 °C) or by very slow evaporation of the chloroform-solution results in aggregated films.

Since the process from random-coil to aggregates is slow in films and can therefore be visualized, these polymers enable us to determine whether this transition is a two-step process (in which the strands first planarize and then aggregate (Figure 2b) or vice versa (Figure 2c)), or a one-step process, in which the two processes happen simultaneously (Figure 2a). HT-P3ATs, for instance, cannot be used for this study, since their films, spincoated from chloroform or any other solvent, are already composed of aggregated polymer chains.

The CD spectrum of **4b**, spincoated from dichlorobenzene, shows a bisignate Cotton effect (Figure 1b). Combined with the UV-Vis spectrum, we can conclude that the polymer is present as chiral aggregates, composed of coplanar strands^[8]. This is the same as in chiral HT-P3ATs, although in those materials, the chiral effects are more pronounced. Probably, the reduced flexibility and/or the presence of the aromatic benzene moiety, restricts an efficient chiral stacking. The untreated films, spincoated from chloroform, show no circular dichroism. The film can be regarded as quenched from solution and mainly consists of random-coils, in which no chirality is present in the transition located at the backbone. Upon

heating (1 min at 70 °C, then 1 min at 100 °C, then at 150 °C for 1 min, then at 170 °C for 1 min, and finally at 190 °C for 1 min) the conjugation length increases, resulting in a red-shift, but the polymer strands remain essentially in their random-coil state. When heated to 150 °C for 1 min and further at 170 °C for 1 min, the polymer strands further planarize. A clear vibronic fine structure appears, together with a positive *monosignate* Cotton effect, centered near 600 nm. This clearly points at an unaggregated state, composed of chiral, highly conjugated (coplanar) rigid polymer strands. This state can be characterized as the intermediate state in which first planarization occurs (Figure 2c). If the polymer chain would first stack and then planarize, a gradual, continuing red-shift and a bisignate Cotton effect would be expected^[8]. Continuing the heat treatment (190 °C, 1 min) results in a UV-Vis spectrum in which the same bands are present, but with a small difference in the ratio of the intensities of the respective transitions. The CD spectrum, however, changes drastically. We believe that it is a superposition of the monosignate Cotton effect of the unaggregated state and a bisignate Cotton effect of the chirally aggregated state, as is the case from the dichlorobenzene-spincoated films.

These results clearly demonstrate that the transition from random-coil to aggregates in films of these polymers is a two-step process, which proceeds via unaggregated, coplanar strands. It is also worthwhile to note that the same results are obtained if tetrachloroethane (b.p. = 147 °C) was used instead of dichlorobenzene. Finally, if the polymer was aggregated in solution by addition of a nonsolvent (i. e. methanol), essentially the same results were obtained, but no intermediate state was observed. Clearly, the molecular motions are not restricted in solution and the aggregation process is very fast.

Conclusions

An achiral and chiral, regioregular poly(3-(4-alkoxythiophene) was prepared using a McCullough methodology. Slow evaporation of the solvent leads to films, composed of (chirally) ordered rigid, coplanar polymer strands, while fast evaporation of the solvent renders films of random-coils. Upon heat treatment, the random-coil films transform into aggregated films. It was shown by UV-vis and CD spectroscopy that this transition is a two-step process, in which the polymer strands first planarize and then stack. An intermediate state, consisting of rigid, (a)chiral, unaggregated, coplanar polymer strands was shown. This work contributes in the further understanding of the structure-properties relationship of films of conjugated polymers. Further research is on-going to characterize these three states in detail.

Acknowledgements

We are grateful to prof. C. Samyn for his practical advice. This work was supported by the Fund for Scientific Research-Flanders (FWO-Vlaanderen), the Katholieke Universiteit Leuven (GOA) and the Belgian Government (IUAP). G. K. is a postdoctoral fellow of the Fund for Scientific Research (FWO Vlaanderen) and D. C. is a doctoral fellow of the IWT.

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Captions to figures and schemes

Figure 1: UV-vis (a) and CD (b) spectra of films of **4b**, spincoated from CHCl_3 or dichlorobenzene and during the heat treatment.

Figure 2: Overview of the possible aggregation processes.

Scheme 1: Synthesis of the polymers.

Figure 1

The heat treatment consists of heating at 70 °C for 1 min, then at 100 °C for 1 min, then at 150 °C for 1 min, then at 170 °C for 1 min, and finally at 190 °C for 1 min.

Figure 2

Scheme 1

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A chiral, regioregular poly(3-(4-alkoxythiophene) was prepared. Slow evaporation of the solvent leads to films composed of chirally ordered, coplanar polymer strands, while fast evaporation renders films of random-coils. Heat treatment transforms the random-coil films into aggregated films in a two-step process, via an intermediate state, composed of chiral, coplanar, unaggregated polymer strands.