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Helical Conjugated Polymers by Design

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ABSTRACT: Some alternating phenylene−furan units can lead to conformationally locked conjugated polymers. Depending upon the substitution pattern, rigid-rod-like or helical structures can be rationally designed. The presence of helical structure in poly(1,4-(2,3-dialkoxyphenylene)-*alt*-2,5-furan)s has been demonstrated by adding chiral side chains and by performing circular dichroism measurements. In a good solvent, this polymer exhibits some chiroptical properties which decreases upon aggregation in poor solvents. In contrast, rigid-rod-like poly(1,4-(2,5-di-(*S*)-2-methylbutoxyphenylene)-*alt*-2,5-furan) only shows chiroptical properties upon aggregation.

Introduction

One great challenge in polymer science is certainly the prediction of the structure and properties of synthetic polymers from only knowledge of the structure of their monomeric units.[1] This goal is similar to those devoted to the understanding of the molecular tools developed and utilized by nature to construct complex polymeric structures. In both areas, the overall conformation (and possibly function) of the macromolecules is encoded within the molecular building blocks. Among all possible conformations, the self-organization of macromolecules into helical structure is certainly of fundamental importance.[2] The significance of helical structures in polypeptides and DNA is well established, but synthetic helical polymers have also attracted great attention. In particular, the development of helical conjugated polymers has been the subject of many studies due to their possible utilization as polarized luminescent materials, asymmetric electrodes, etc.[3] These investigations include the development of chiral polyacetylenes,[4] oligo- and poly(phenylene ethynylene)s,[5] polythiophenes,[6] and polyanilines[7] based on helical backbones (or supramolecular organizations) with an excess of one-handed screw sense. Helical structures have also been recently obtained from complexation of cationic conjugated polymers with negatively charged DNA substrates.[8]

Along these lines, ab initio calculations performed on various conjugated dimers have revealed that some alternating phenylene−furan units can lead to conformationally locked conjugated macromolecules.[9] Moreover, depending upon the substitution pattern, a rigid-rod (zigzag coplanar) or helical structure seems possible (see Scheme 1). As mentioned above, such shape-persistent photoactive and electroactive polymers could lead to materials with interesting anisotropic properties (e.g., liquid crystalline or chiroptical properties). In this regard, we report here the synthesis and characterization of helical conjugated poly(1,4-(2,3-dialkoxyphenylene)-*alt*-2,5-furan)s bearing chiral substituents. This study seems to indicate that it is possible to make a rational design of novel helical conjugated polymers.

Results and Discussion

As revealed in a previous theoretical investigation on dimer model compounds,[9] favorable interactions between the oxygen atoms (of the furan moieties or alkoxy groups) and the hydrogen atoms connected to the aromatic rings combined with a delocalization energy in an anti coplanar (180°) or nearly planar conformation should lead to conformationally locked alternating poly(dialkoxy-1,4-phenylene-*alt*-2,5-furan)s (Scheme 1). The 0° (syn) conformation is less stable by about 5 kcal/mol of repeat unit, and a second minimum energy is observed near 45° but is less stable than the 180° conformation by about 3 kcal/mol of repeat unit. Therefore, owing to this unusual and asymmetric energy potential, it can be anticipated that poly(1,4-(2,3-dialkoxyphenylene)-*alt*-2,5-furan)s (Scheme 1, structure a) should adopt a helical structure. For this purpose, pre-monomer 3,6-diiodocathecol[10] was prepared and substituted with various side chains (see Scheme 2a). These monomers were then copolymerized with 2,5-bis(trimethylstannyl)furan to yield the desired alternating conjugated copolymers.[9,11] In general, the resulting alternating copolymers are soluble in chloroform or tetrahydrofuran and exhibit a number-average molecular weight of about 5−7 kDa (measured against polystyrene standards) with a polydispersity index of about 1.5 (degree of polymerization of ca. 20) (see Table 1). First experiments were carried out with achiral (octyloxy) substituents (**pPF-1**). Circular dichroism (CD) measurements in different solvents did not reveal any chiroptical properties. These results could indicate an equal preference for either right- or left-handed helices. To prove the formation of a helical structure in dilute solutions, chiral substituents were introduced; such chiral substituents usually inducing a preferred handedness along the backbone associated with the presence of chiroptical properties.

Chiral poly(1,4-(2,3-di-(*S*)-2-methylbutoxyphenylene)-*alt*-2,5-furan) (**pPF-2**) was then prepared and characterized in dilute solutions. In chloroform (a good solvent), this polymer exhibits a broad absorption band with a maximum at 392 nm (see Figure 1a). As shown in Figure 1b, CD measurements revealed some optical activity with a bisignate Cotton effect for this polymer

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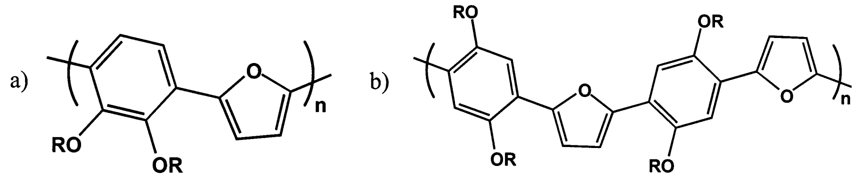
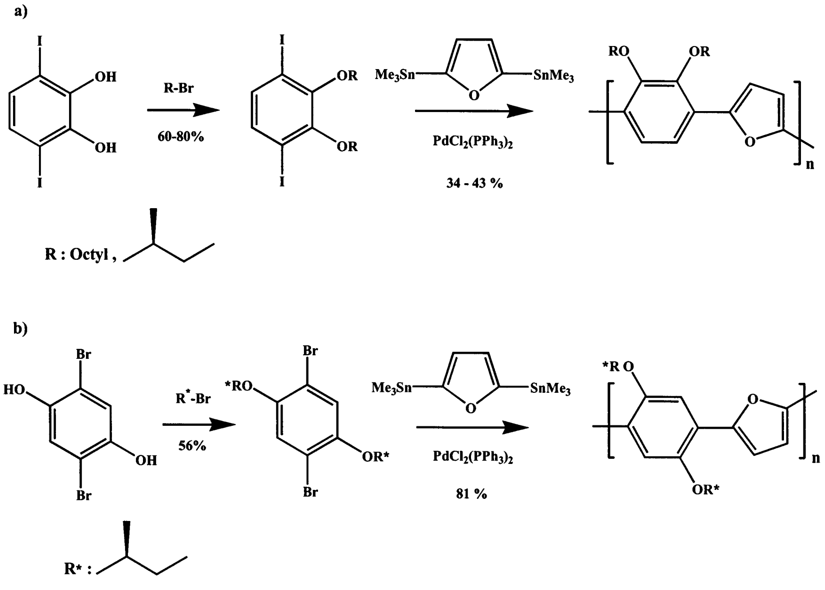
Scheme 1



Scheme 2



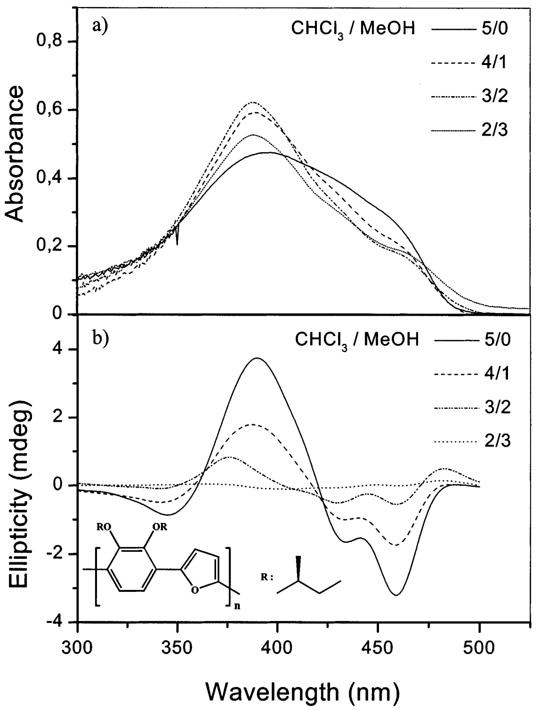


Figure 1. Solvatochromic studies of poly(1,4-(2,3-di-(*S*)-2-methylbutoxyphenylene)-*alt*-2,5-furan) in different solvents: (a) UV–vis measurements; (b) CD measurements.

solution (a maximum *g* value of 3.2×10^{-4} being obtained at 464 nm). This behavior seems to indicate a predominant one-handed helical structure for this polymer. Similar properties were recently reported for some polyacetylenes[4] or polythiophenes[6g] in a molecularly dispersed state (dissolved in a good solvent at low concentrations). This behavior is different from chiral superstructures resulting from intermolecular $\pi-\pi$ stacking observed with some conjugated polymers bearing chiral substituents.[6]

To investigate further this point, solvatochromic studies were performed with poly(1,4-(2,3-di-(*S*)-2-methylbutoxyphenylene)-*alt*-2,5-furan). As shown in Figure 1, when adding a poor solvent (i.e., methanol), some aggregation is taking place which results in some modifications (a more defined vibronic structure) of the UV–vis absorption spectrum. As reported for many other classes of solvatochromic conjugated polymers, the determination of the relative contribution of conformational changes and interchain electronic interactions is still a very difficult task.[9,12] This solvatochromic effect influences also the CD spectrum, and the *g* value decreases. As a first approximation, it can be assumed that a planarization occurs upon aggregation which disturbs the helical organization.

For comparison purposes, poly(1,4-(2,5-di-(*S*)-2-methylbutoxyphenylene)-*alt*-2,5-furan) **(pPF-3)** was synthesized (Scheme 2b) and characterized. In agreement with previous results obtained with similar but achiral polymers,[9] this polymer with a relatively rigid and planar backbone (Scheme 1, structure b) exhibits two absorption maxima at 470 and 500 nm in a good solvent (i.e., chloroform) (see Figure 2a). In contrast to its previous geometrical isomer, this chiral polymer does not exhibit any chiroptical properties in chloroform (see Figure 2b). However, in a poor solvent, a relatively strong bisignate Cotton effect is observed which can be tentatively explained by an aggregation of the polymer chains into a chiral superstructure. The *g* value increases until a maximum of 8.0×10^{-3} at 403 nm, just before precipitation of the polymer. Similar effects have been observed with various chiral polythiophene derivatives.[6] This aggregation of the polymer chains affects

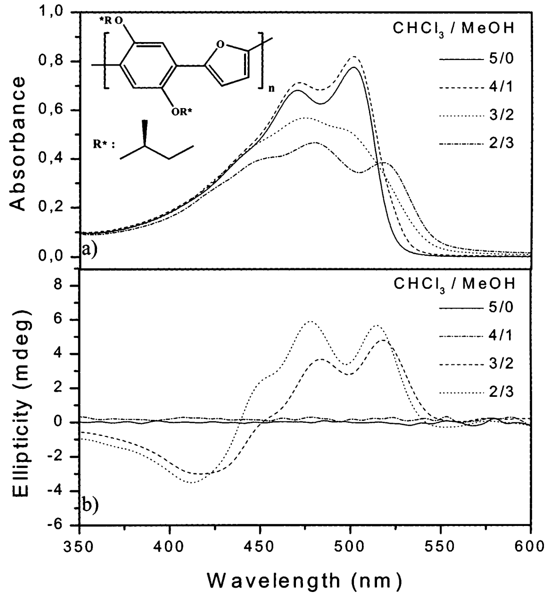


Figure 2. Solvatochromic studies of poly(1,4-(2,5-di-2-(*S*)-methylbutoxyphenylene)-*alt*-2,5-furan) in different solvents: (a) UV−vis measurements; (b) CD measurements.

also its UV−vis absorption spectrum by inducing a weak blue shift of the maximum of absorption together with the appearance of a new peak at lower energies (ca. 520 nm). Similar features have been previously reported with achiral poly(1,4-(2,5-dioctyloxyphenylene)-*alt*-2,5-furan)[9] and have been related to the presence of some excitonic effects upon aggregation without any significant modification of the main chain conformation.

From all these results, it therefore seems that it is possible to make a rational design of helical conjugated polymers only on the basis of the structure of their respective repeat unit. Furthermore, previous theoretical calculations[13] have indicated that alternating phenylene−pyrrole copolymers should exhibit similar features as those reported in this study due to hydrogen bonding between the oxygen atom of the alkoxy side chain and the hydrogen atom bound to the pyrrole ring. These new stiff conjugated polymers should be synthesized and characterized in the near future as well as new water-soluble shape-persistent electroactive and photoactive polymers.

Conclusions

This study has clearly shown that attractive interactions between the oxygen atoms of alkoxy side chains or furan units and hydrogen atoms connected to aromatic rings can allow a fine-tuning of the overall conformation of conjugated polymers. By varying the substitution pattern, rigid-rod-like or helical conformational structures can be obtained from alternating poly(dialkoxy-1,4-phenylene-*alt*-2,5-furan)s. Interestingly, helical poly(1,4-(2,3-di-(*S*)-2-methylbutoxyphenylene)-*alt*-2,5-furan) exhibits some chiroptical properties in a molecularly dispersed state which decreases upon aggregation whereas an opposite behavior is observed with poly(1,4-(2,5-di-(*S*)-2-methylbutoxyphenylene)-*alt*-2,5-furan). All these results shed some light on the structure−property relationships in conjugated polymers and should contribute to the rational design of novel materials with optimized electrical, optical, and electrooptical properties.

Experimental Section

Instrumentation. ^{1}H (300 MHz) and ^{13}C (75.4 MHz) NMR spectra were recorded in $CDCl_3$ at room temperature with a Bruker AC-300 NMR spectrometer using tetramethylsilane as an internal standard. Molecular weights were evaluated by size exclusion chromatography (SEC) on a Waters Pl gel 10μ Mixed + Shodex KF804 columns in THF using a Waters instrument equipped with an absorbance detector (model 441). Calibration curves were obtained by using polystyrene standards. Optical rotation at the Na D line was measured with a Jasco DIP-360 polarimeter using a quartz cell with a path length of 1.0 dm at room temperature (20 °C). CD spectra were recorded on a Jasco J-710 spectropolarimeter using a quartz cell of 0.5 mm path length with at least 10 scans. UV−vis absorption spectra were recorded on Varian Cary 500 scan spectrophotometer. Sample preparation for solvatochromic measurements did proceed as follows: 0.2 mL of a polymer solution (4×10^{-4} M on a repeat unit basis) in chloroform was diluted with 2.5 mL of various proportions of good/poor solvents. For circular dichroism (CD) measurements, 0.5 mL of the above-mentioned polymer solution was diluted to 5 mL to obtain the desired good/poor solvent proportions. Solutions in pure chloroform were filtrated on 0.45 μm membranes to avoid any aggregation effect.

Materials. All commercial chemicals were obtained from Aldrich Co. and were used without further purification. HPLC grade THF, $CHCl_3$, and methanol were used for spectroscopic measurements. The synthesis of 1,4-diiodo-2,3-dihydroxybenzene has been developed by Zhu and Swager[10] whereas the synthesis of 2,5-dibromohydroquinone has been reported by Vahlenkamp and Wegner.[14]

1,4-Diiodo-2,3-dioctyloxyphenylene. To a solution of 1,4-diiodo-2,3-dihydroxybenzene (1.00 g, 2.7 mmol) in 20 mL of anhydrous ethanol, 0.62 g of potassium hydroxide was added, and the mixture was stirred under a nitrogen atmosphere. The mixture was heated to reflux for 1 h. 1.67 mL (9.6 mmol) of 1-bromooctane was added, and the mixture was refluxed for 48 h. The mixture was cooled, and the potassium bromide was filtered. Water was added, and the product was extracted twice with diethyl ether. The organic layers were combined and washed twice with water. The organic layer was dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on SiO_2, and the eluent was hexanes. 0.96 g (61%) of pure white solid, with a melting point of 50 °C, was obtained. Exact mass calculated for $C_{22}H_{36}O_2I_2$: 586.0805. Found: 586.0792.

NMR ^{1}H ($CHCl_3$, 300 MHz): δ (ppm) 7.21 (s, 2H), 3.98 (t, 4H), 1.82 (q, 4H), 1.45 (q, 4H), 1.4−1.2 (m, 16H), 0.85 (t, 6H).

NMR ^{13}C ($CHCl_3$, 75.4 MHz): δ (ppm) 152.8, 135.5, 93.7, 74.1, 32.1, 30.5, 29.6, 29.5, 26.3, 22.9, 14.3.

1,4-Diiodo-2,3-((*S*)-2-methylbutoxy)phenylene. To a mixture of 1,4-diiodo-2,3-dihydroxybenzene, 0.82 g (2.3 mmol) of cesium carbonate (2.90 g, 9.1 mmol) and potassium iodide (1.9 mg in 7 mL of dry DMF), 0.84 mL (6.8 mmol) of (*S*)-(+)-1-bromo-2-methylbutane was added. The mixture was heated 48 h at 80 °C under an inert atmosphere. The reaction was quenched with water, and the product was extracted with diethyl ether. The combined organic layers were washed with 5% NaOH aqueous solution, H_2O, and brine, then dried, and evaporated. The product was purified by flash chromatography, using hexanes as the eluent. The pure product is a colorless oil (0.92 g, 84%). $[\alpha]_D^{20} = +28.7$ (10 mg/mL in $CHCl_3$). Exact mass calculated for $C_{16}H_{24}O_2I_2$: 501.9866. Found: 501.9876.

NMR ^{1}H ($CHCl_3$, 300 MHz): δ (ppm) 7.22 (s, 2H), 3.87−3.71 (m, 4H), 2.46−2.31 (m, 2H), 1.66−1.61 (m, 2H), 1.32−1.27 (m, 2H), 1.09−0.93 (m, 12H).

NMR ^{13}C ($CHCl_3$, 75.4 MHz): δ (ppm) 152.7, 135.4, 93.2, 78.7, 35.7, 26.3, 16.7, 11.4.

1,4-Dibromo-2,5-((*S*)-2-methylbutoxy)phenylene. A mixture of 2,5-dibromohydroquinone (3.00 g, 11.2 mmol), potassium iodide (7 mg), and 14.6 g of cesium carbonate in 26 mL of anhydrous DMF was stirred under a nitrogen atmosphere for 30 min. (*S*)-(+)-1-Bromo-2-methylbutane (4.2 mL, 34 mmol) was added and heated to reflux for 48 h. After that, 3.00 g of cesium carbonate was added. After another 24 h of refluxing, the reaction was quenched with water. The mixture was extracted with diethyl ether; the organic layers were washed with 5% NaOH aqueous solution, water, and brine and then dried over $MgSO_4$. Solvent was removed under reduced pressure, and the residues were purified by flash chromatography using a hexanes−diethyl ether (98/2) mixture as eluent, to afford the desired product as a white solid (2.55 g, 56%); mp 44 °C.

$[\alpha]_D^{20} = -9.9$ (10 mg/mL in $CHCl_3$). Exact mass calculated for $C_{16}H_{24}O_2Br_2$: 406.0143. Found: 406.0136.

NMR ^1H ($CHCl_3$, 300 MHz): δ (ppm) 7.08 (s, 2H), 3.85−3.71 (m, 4H), 1.95−1.82 (m, 2H), 1.66−1.51 (m, 2H), 1.36−1.22 (m, 2H), 1.06 (d, $J = 6.6$ Hz, 6H), 0.95 (t, $J = 7.3$ Hz, 6H).

NMR ^{13}C ($CHCl_3$, 300 MHz): δ (ppm) 150.2, 118.3, 111.1, 75.0, 34.8, 26.1, 16.5, 11.3.

Polymerization. Polymerization reactions were carried out from Stille coupling between 1,4-iodo-2,3-dialkoxyphenylenes or 1,4-dibromo-2,5-dialkoxyphenylenes and 2,5-bis(trimethylstannyl)furan,[9,11] following well-established procedures reported in the literature.[9,11]

Poly(1,4-(2,3-dioctyloxyphenylene)-*alt*-2,5-furan) (pPF-1). Yield: 43%.

NMR ^1H ($CHCl_3$, 300 MHz): δ (ppm) 7.70−7.61 (broad, 2H), 7.10−7.00 (broad, 2H), 4.05−3.99 (m, 4H), 1.82−1.80 (m, 4H), 1.46−1.40 (m, 4H), 1.36−1.18 (m, 16H), 0.86−0.76 (m, 6H).

$M_n = 7000$; $M_w = 11\,000$.

Poly(1,4-(2,3-di-(*S*)-2-methylbutoxyphenylene)-*alt*-2,5-furan) (pPF-2). Yield: 34%.

NMR ^1H ($CHCl_3$, 300 MHz): δ (ppm) 7.65−7.63 (s (broad, 2H), 7.06−7.04 (s (broad), 2H), 3.86−3.77 (m, 4H), 1.95−1.91 (m, 2H), 1.56−1.50 (m, 2H), 1.25−1.23 (m, 2H), 1.04−0.94 (d, 6H), 0.82−0.76 (m, 6H).

$M_n = 6000$; $M_w = 8000$.

Poly(1,4-(2,5-di-(*S*)-2-methylbutoxyphenylene)-*alt*-2,5-furan) (pPF-3). Yield: 81%.

NMR ^1H ($CHCl_3$, 300 MHz): δ (ppm) 7.57−7.42 (s (broad), 2H), 7.15−7.02 (s (broad), 2H), 4.07−3.87 (m, 4H), 2.05−1.89 (m, 2H), 1.70−1.52 (m, 2H), 1.41−1.24 (m, 2H), 1.14−1.06 (d, 6H), 1.01−0.87 (m, 6H).

$M_n = 5000$; $M_w = 7000$.

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