Enantiomeric Substituents Determine the Chirality of Luminescent Conjugated Polythiophenes

K. Peter R. Nilsson,*,† Johan D. M. Olsson,‡ Peter Konradsson,‡ and Olle Inganäs†

Department of Physics and Measurement Technology, Biology, and Chemistry, Linköping University, SE-581 83 Linköping, Sweden

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ABSTRACT: Chiral isomers of 3-substituted polythiophenes with amino acid functiontionalized side chains are compared. The polymers show pH-dependent absorption, emission, and circular dichroism spectra in buffered aqueous solution. At pH equal to pI of the amino acid, the backbones adopt nonplanar helical conformations, and the polymer chains are separated from each other. Increasing pH leads to more planar conformations of the backbones and an aggregation of the polymer chains occurs. A lower pH will also lead to more planar conformation of the backbones, but aggregation of the polymer chains appears to be absent. The nonplanar to planar transition of the polymer backbone and the separation/aggregation of different polymer chains is not affected by stereochemistry of the zwitterionic side chain. The two isomers have almost identical pH-dependent absorption and emission spectra. However, the chirality of the zwitterionic side chain is reflected in the conformation of the polymer backbone, giving rise to a right-handed and left-handed helical form of polythiophene chains since the induced circular dichroism patterns of the two polymers are mirror images.

Introduction

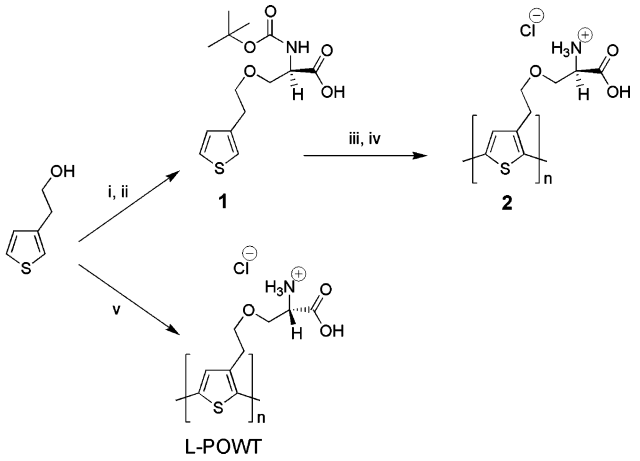
Chiral conjugated polymers (CPs) with a well-defined structure are of interest, due to their potential for being used in optoelectronic devices, biosensors, and as artificial enzymes. Especially, polythiophenes (PTs)[1−8] with an optically active substituent in the 3-position have been studied for these purposes. Chiral polythiophenes normally exhibit optical activity in the $\pi-\pi^*$ transition region, derived from the main-chain chirality when the polymer chains are forming supramolecular, π-stacked self-assembled aggregates in a poor solvent or at low temperature, whereas they show no activity in the UV−vis region in a good solvent or at high temperatures.[5,9−12] Recent studies,[13−16] using optically inactive CPs that become chiral upon addition of a chiral guest, show that chirality introduction can also be a result of an acid−base complexation between the CP and the chiral guest, forming a one-handed helical structure with a preferred twist reflecting the stereochemistry of the chiral guest.[13−16]

Natural biopolymers, such as proteins and DNA, frequently have one-handed helical conformations that contribute to the three-dimensional ordered structure and the specific function of the biopolymer. The preferable twists of the helical conformations are caused by homochirality of their components (D-sugars and L-amino acids). Normally, a polypeptide made from L-α-amino acid residues forms a right-handed helix, and the exclusive one-handed helical conformation is of great importance, as the stereochemistry of biomolecules are widely used to create biospecific interactions and the specificity of enzymatic reactions.

Previous studies[4,17,18] of a polythiophene, with a free L-amino acid side chain, poly(3-[(*S*)-5-amino-5-carboxyl-3-oxapentyl]-2,5-thiophenylene hydrochloride), L-POWT (Scheme 1), have shown pH-dependent optical phenomena due to different electrostatic interactions and hydrogen-bonding patterns within the polymer chain and between adjacent polymer chains. At a pH equal to the pI of the amino acid, the backbone adopts a nonplanar right-handed helical conformation, and the polymer chains are separated from each other. Increasing pH leads to a more planar conformation of the backbone, and an aggregation of the polymer chains occurs. A lower pH will also lead to a more planar conformation of the backbone, but aggregation of the polymer chains appears to be absent. The polymer adopts a right-handed helical form, so apparently the nature of the L-amino acid is reflected in the helical conformation of the polymer backbone. Consequently, it would be of great interest to synthesize the polymer using the D-form of serine to see if the twist of the helix is reversed.

In this article, we report the synthesis and the optical properties of a polythiophene with a free D-amino acid

Scheme 1[a]



[a] (i) TsCl, pyridine, $CHCl_3$, 86 %; (ii) *N*-*t*-Boc-D-Ser, K_2CO_3, DMF, 35 °C, 57 %; (iii) CH_2Cl_2/TFA (1:1), quant.; (iv) $FeCl_3$, TBA-trifluoromethanesulfonate, $CHCl_3$, 15 °C, 61 %; and (v) Andersson et al.[4]

* Corresponding author. E-mail: petni@ifm.liu.se.
† Department of Physics.
‡ Department of Chemistry.

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side chain, poly (3-[(*R*)-5-amino-5-carboxyl-3-oxapentyl]-2,5-thiophenylene hydrochloride), D-POWT (see Scheme 1), and the comparison of the chiral isomers.

Experimental Procedures

General Methods. Normal workup means drying the organic phase with $MgSO_4$ (s) or Na_2SO_4 (s), filtering, and evaporation of the solvent in vacuo at ~45 °C. All dry solvents were collected onto 4 Å predried molecular sieves (Merck). Thin-layer chromatography (TLC) was carried out on 0.25 mm precoated silica gel plates (Merck silica gel 60 F_{254}) detected by UV-abs. (254 nm) and/or by charring with PAA-dip (ethanol/sulfuric acid/*p*-anisaldehyde/acetic acid 90:3:2:1) followed by heating to ~250 °C. FC means flash column chromatography using Silica gel (MERCK 60 (0.040−0.063 mm)). ^{1}H and ^{13}C NMR spectra were performed on a Varian Mercury 300 MHz instrument at 25 °C. Chemical shifts are given in ppm relative to TMS in $CDCl_3$ (δ 0.00) for ^{1}H and ^{13}C or CD_3OD (δ 3.31) for ^{1}H and CD_3OD (δ 49.0) for ^{13}C NMR. Optical rotations were recorded at room temperature with a Perkin-Elmer 141 polarimeter. IR spectra were recorded as KBr pellets on a Perkin-Elmer SPECTRUM 1000 FTIR spectrometer.

Synthesis of (*R*)-2-*tert*-Butoxycarbonylamino-3-(2-thiophen-3-yl-ethoxy)-propionic Acid (1). 3-Thiopheneethanol (0.75 g, 5.85 mmol) was dissolved in $CHCl_3$ (30 mL) and cooled to 0 °C. Pyridine (1.5 mL, 18.64 mmol) and *p*-toluenesulfonyl chloride (2.78 g, 14.58 mmol) were added. After 24 h, the reaction was quenched by adding H_2O (6 mL) and was diluted with Et_2O (40 mL). The organic layer was washed with 2 M HCl (2 × 15 mL), sat. $NaHCO_3$ (aq) (2 × 15 mL), and H_2O (2 × 15 mL) and was subjected to normal workup. FC (toluene) and recrystallization from EtOAc/hexane afforded 2-(3-thienyl)ethanol tosylate (1.42 g, 5.03 mmol, 86%) as white crystals (R_f = 0.74, toluene/EtOAc 4:1). ^{1}H NMR was in accordance with those previously reported.[19] *N*-*t*-Boc-D-Ser (1.85 g, 9.02 mmol) and tosylated product (1.42 g, 5.03 mmol) were dissolved in dry DMF (100 mL) under N_2 atmosphere. The solution was heated to 35 °C, and K_2CO_3 (2.42 g, 17.51 mmol) was added. After 26 h, the mixture was poured over cold 2 M HCl (aq) (150 mL) and washed with Et_2O (3 × 50 mL). The organic layer was washed with 1 M HCl (aq) (2 × 50 mL) and H_2O (2 × 50 mL), subjected to normal workup, and purified by FC (toluene/EtOAc 4:1) to give **1** (0.90 g, 2.87 mmol, 57%) as a colorless syrup. R_f = 0.57 (toluene/EtOAc 1:1); $[\alpha]_D$ = +6.1 (*c* 2.0, $CHCl_3$) (for the S-enantiomer $[\alpha]_D$ = −6.1 (*c* 2.0, $CHCl_3$)).

IR ν_{max} cm^{-1}: 778, 1060, 1164, 1367, 1506, 1716, 2976, 3436.

^{13}C NMR ($CDCl_3$) δ: 28.2 (3C), 29.3, 55.7, 63.2, 65.2, 80.1, 121.7, 125.7, 128.1, 137.5, 155.7, 170.8.

^{1}H NMR ($CDCl_3$) δ: 1.44 (s, 9H), 2.99 (t, 2H, J = 6.9 Hz,), 3.82 (dd, 1H, J = 3.6, 11.1 Hz), 3.89 (dd, 1H, J = 3.9, 11.1 Hz), 4.37 (m, 3H), 6.96 (dd, 1 H, J = 1.2, 4.8 Hz), 7.04 (m, 1H), 7.26 (dd, 1H, J = 3.0, 4.8 Hz).

Synthesis of Poly(3-[(*R*)-5-amino-5-carboxyl-3-oxapentyl]-2,5-thiophenylene Hydrochloride) (2). Compound **1** (107 mg, 0.34 mmol) was dissolved in CH_2Cl_2/TFA (1:1, 4 mL). The reaction was quenched after 4 h by adding MeOH (10 mL) and coconcentrated with toluene (3 × 10 mL). The ammonium salt and TBA-trifluoromethanesulfonate (0.164 g, 0.42 mmol) were dissolved in dry $CHCl_3$ (2 mL), and the solution was cooled to 13 °C. A slurry of anhydrous $FeCl_3$ (0.56 g, 3.45 mmol) in dry $CHCl_3$ (1 mL) was added dropwise to this solution under Ar atmosphere. After 26 h, the reaction was quenched with H_2O (4 mL) and diluted with $CHCl_3$ (3 mL). The organic layer was washed with H_2O (3 × 3 mL). The aqueous solution was diluted with acetone (30 mL), and conc. HCl (2 mL) was added. After 2 h, the mixture was centrifuged (4 min/2500 rpm). The red salt was washed with acetone (2 × 35 mL), dissolved in H_2O (2 mL), and precipitated from acetone/concentrated HCl (25:1, 26 mL). The washing procedure was repeated twice to give **2** (52 mg, 0.207 mmol, 61%) as a red−orange powder. The ^{1}H NMR in CD_3OD and the IR were identical with those earlier published for the S-enantiomer of the polymer.[4]

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectroscopy (MALDI-TOF-MS). A total of 0.5 μL of an aqueous solution of the polymer and 0.5 μL of α-cyano-4-hydroxy-*trans*-cinnamic acid (CHCA) in 0.1% TFA/acetonitrile (1:1) were mixed and evaporated on a target plate. The spectra were recorded in linear positive mode with a Voyager-DE STR Biochemistry Workstation.

Spectroscopic Experiments. A stock solution containing 5.0 mg of polymer/mL (L-POWT or D-POWT) in deionized water was prepared and placed on a rocking table for 1 h. The following buffer solutions were prepared:

20 mM sodium acetate (pH 4.0), 20 mM Mes (pH 5.9), and 20 mM sodium carbonate (pH 10.0). All the chemicals used were of analytical grade.

For the absorption, emission, and circular dichroism (CD) measurements, 15 μL of the stock solution was diluted with one of the buffer solutions to a final concentration of 37.5 μg of polymer/mL solvent, and the sample was placed on a rocking table for 1 h before the spectrum was recorded. The procedure was repeated for all the buffer system and deionized water. Optical spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/NIR spectrophotometer for UV/vis, a Hitachi F4500 Fluorescence Spectrophotometer for fluorescence, and an I. S. A. Jobin-Yvon CD6 (5 mm quartz cell) for CD.

Results and Discussion

3-Thiophene ethanol was converted to corresponding tosylate as described earlier[20] and then displaced by a protected unnatural amino acid, *N*-*t*-Boc-D-Ser. The Boc group was removed in CH_2Cl_2/TFA to readily enable the ammonium salt for polymerization. There are many well-known methods to polymerize thiophenes, which have been reviewed by, for example, McCullough.[21] Because of the functional groups of the amino acid substituted thiophene monomer, the polymerization was performed by a method reported by Sugimoto et al. using chemical oxidation with anhydrous ferric chloride in chloroform[22,23] (see Scheme 1). The water-soluble polymer was then precipitated by adding acetone and concentrated hydrochloric acid.

Lately, MALDI-TOF-MS has been developed as a powerful tool when analyzing synthetic polymers, both for chain-length studies and for end-group analysis of different polymers. Different techniques considering the use of matrix, cationization agents, and the matrix/analyte ratio have also been investigated, regarding the use of MALDI-TOF-MS as a tool for the determination of the chain-length distribution in conjugated polymers.[24−26] The length of the polythiophene backbone of the conjugated polymers described herein was further elucidated by MALDI-TOF-MS.

An aqueous solution of the polymer was mixed with a CHCA in 0.1% TFA/acetonitrile (1:1) as matrix. This matrix has earlier shown low grade of fragmentation for oligo- and polythiophenes.[26] Other matrixes known for a low grade of fragmentation (e.g., dithranol and dihydroxybenzoic acid (DHB)) were also tried, but the best spectra were achieved using CHCA as matrix. The MALDI-TOF-MS spectra of the product from polymerization with $FeCl_3$ in $CHCl_3$ showed polymers with a molecular weight mainly between 2600 and 3900 following ion series corresponding to $[213_n]^+$, $[213_n + 35]^+$, or $[213_n + 70]^+$ (see Figure 1). Recently, McCarley et al. reported that polymers made by $FeCl_3$ polymerization and characterized by MALDI-TOF-MS adduct chlorine atoms at the α-carbon ends of the polymer backbone when ionized by MALDI-TOF-MS.[27] So the series $[213_n + 35]^+$ and $[213_n + 70]^+$ corresponds to serinesubstituted thiophene (ST) units and chlorine

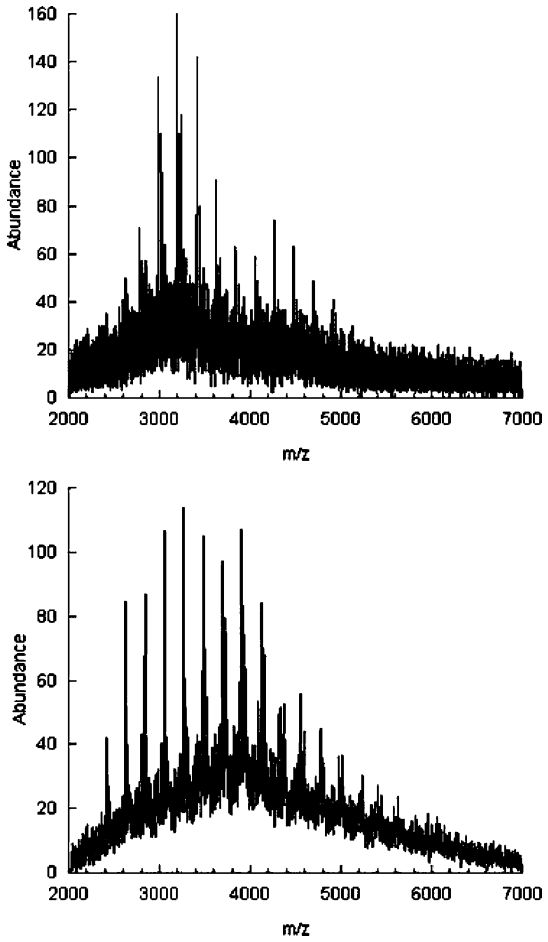

Figure 1. MALDI-TOF-MS spectra for poly(3-[(*S*)-5-amino-5-carboxyl-3-oxapentyl]-2,5-thiophenylene hydrochloride) (top) and poly(3-[(*R*)-5-amino-5-carboxyl-3-oxapentyl]-2,5-thiophenylene hydrochloride) (bottom) recorded in linear positive mode.

atoms as end groups, $[ST_n + Cl]^+$ and $[ST_n + 2\ Cl]^+$, where n is the number of ST in the backbone. The covalently bound chlorine atoms originate from the oxidizing agent $FeCl_3$, which are known to give impurities of iron or chlorine,[28] or originate from the hydrochloride form of the polymer. The spectrum corresponds to polymers containing between 13 and 19 ST units in the backbone. Even though traces of small peaks down to $n = 11$ and up to $n = 22$ can be found, the backbone length can be approximated to $n = 16 \times b1\ 3$. The D-POWT and L-POWT show similar length distribution.

The absorption spectra for L-POWT and D-POWT in deionized water and different buffer solutions are shown in Figure 2. The polymers undergo a pH induced yellow to orange color (a shift of the absorption maximum from 405 to 450) change, indicating that deprotonation and protonation of the amino and carboxyl groups have an influence on the coil-to-rod (nonplanar to planar) conformation transition of the polymer backbones. The nonplanar conformations are most abundant in deionized water and in the pH 5.9 buffer solutions. As the side chains become charged, either positive or negative, the polymer chains adopt a more planar conformation, observed as a red shift. The polymers are probably adopting the rod-shaped conformation due to electrostatic repulsion forces between the polymer side chains[29,30] or from hydrogen bonding[31] and hydrophobic assembly between nearby polymer chains, as these molecular forces are highly influenced by the charge of the polymer side chains. Interestingly, the alteration of the stereochemistry of the side-chain is not influencing the absorption properties of the polymer backbone, as the pH induced conformational changes of the polymer backbone are the same for the two polymers. The absorption maxima from L-POWT and D-POWT are slightly different, but this is probably due to the difference in chain-length distributions between the two polymers. The altered stereochemistry of the chiral center on the zwitterionic side chain does not affect the absorption properties of the polymer backbone.

The pH-induced conformational changes of the polymer chains will also alter the emission spectra for the polymer solutions (see Figure 2). The polymers emit light with a longer wavelength, as the net charge of the polymer side chains becomes more negative. At pH 10, where almost all the amino groups are neutral and all the carboxyl groups are negatively charged, the polymers emit light with a wavelength around 605 nm. When the pH decreases and the net charge of the polymers become close to neutral, light with a shorter wavelength is emitted, and at pH 5.9 (pI for serine), the peak is shifted to approximately 550 nm. Earlier studies[17,18] of POWT have shown an analogous trend in the photoluminescence (PL) of intra- and interchain phenomena in the polymer. As the chains were separated, the PL maximum was blue-shifted by approximately 105 nm, as compared to emission in the solid state using dense packing of the polymer chains. This observation indicates that the two distinct separated peaks in the emission spectra of POWT originate from an intrachain event (550 nm) and an interchain event (605 nm). At pH 10, a mixture of these two states is present in the solution. Aggregation of the polymer chains seems to be encouraged at higher pH where the polymer backbone adopts a more planar conformation, and this could also been seen in the sample used, as the polymer precipitate at an alkaline pH. A solution of POWT in the 20 mM Mes buffer (pH 5.9) remains stable for a couple of months, but in the 20 mM carbonate buffer (pH 10), the polymer precipitates after a couple of days. Apparently, the deprotonation of the amino groups is important for the polymer chains to form aggregates. A deprotonated amino group will be able to function as a hydrogen bond acceptor, suggesting that hydrogen bonding is important for directing aggregation. The intensity of the fluorescence for the aggregated phase of polythiophenes derivatives, as compared with the fluorescence for the single chain, has previously been shown to be weaker by approximately 1 order of magnitude,[10,12] in agreement with the results in this study. The earlier studies of thin films of POWT also showed an analogous trend, as the PL quantum efficiency increased from 4 to 16% in the absence of the interchain event.[17]

Surprisingly, in the nonplanar-to-planar conformational transition of the backbone at pH 4, where the net charge of the polymer chains becomes more positive, light with a slightly longer wavelength is emitted, but the intensity of the fluorescence is not decreasing in the same way as for the solution with pH 10. These results indicate that the emitted light is due to an intrachain event. Consequently, the positive net charge of the polymer seems to favor a more rod shape conformation of the polymer chain, but aggregation of the polymer chains is most likely absent. The rod shape form of the polymer chains at acidic pH could be induced by

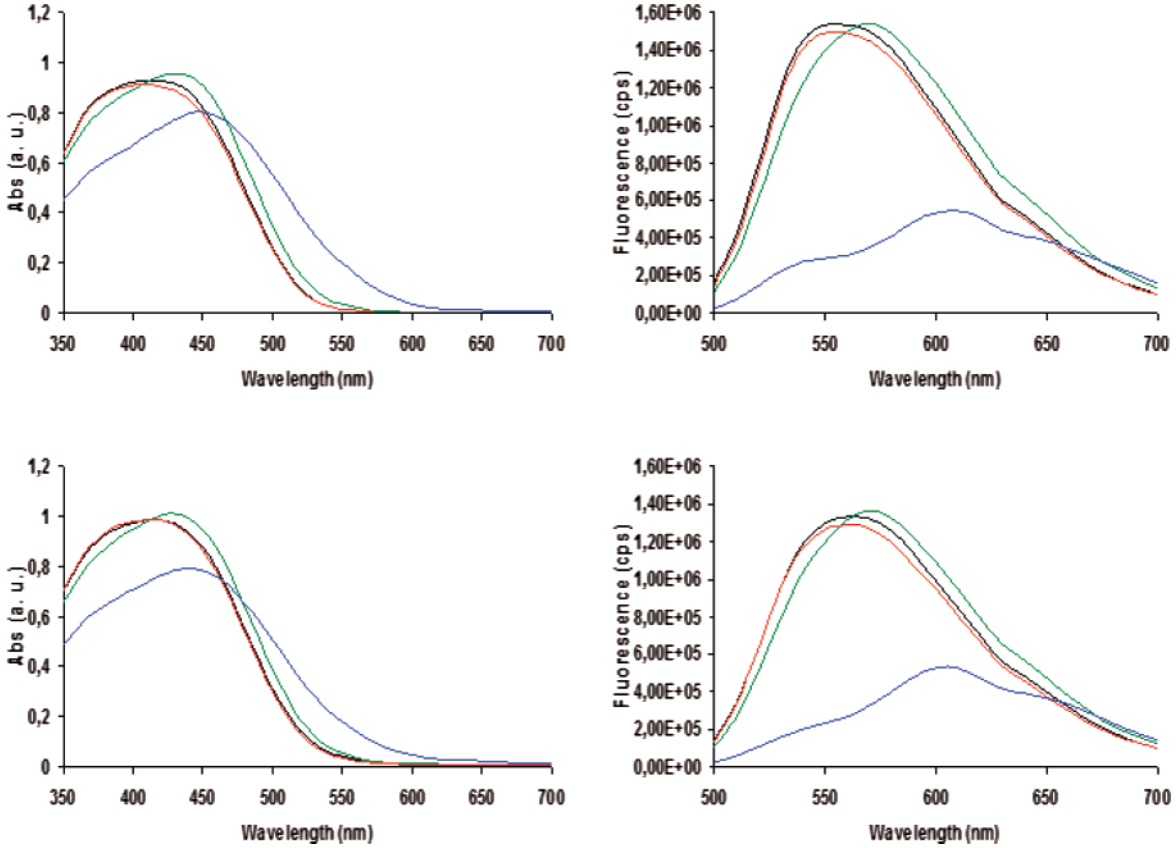

Figure 2. Absorption spectra (left) and emission spectra (right) of L-POWT (top) and D-POWT (bottom) after 30 min of incubation in deionized water (black line), pH 4.0 (green line), pH 5.9 (red line), and pH 10 (blue line). All the emission spectra were recorded with excitation at 400 nm.

electrostatic repulsion forces or by hydrogen bonding within the polymer chains. At acidic pH, the protonated carboxyl group will be able to function as a hydrogen bond donor, and this might encourage another type of hydrogen-bonding pattern, which will prevent aggregation but induce a more rod shape conformation of the polymer backbone. The polymer does not precipitate in solutions with acidic pH, in agreement with this assumption.

The different chirality of the polymer side chains does not seem to influence the emission properties from the polymer chains. Although there are minor differences between the emission spectra, an analogous pH-dependent trend is seen for the two isomers. Hence, the altered stereochemistry of the zwitterionic side chain is not reflected as an alteration of the nonplanar/planar transition of the polymer backbone or aggregation/separation of the polymer chains.

As previously reported[4,18] the polymers exhibit a split-type induced circular dichroism (ICD) in the $\pi-\pi^*$ transition region. The two major CD peaks observed in water, interpreted as due to syn conformers, disappeared in methanol where anti conformations dominate.[4] The CD spectra of L-POWT in different buffer solutions are shown in Figure 3. The red shifts in absorption, induced by different buffer systems, are accompanied with a decrease in the ICD, indicating that chirality induction may not be derived from π-stacked chiral aggregation of the polymer.[8−12] Instead, the ICDs is a result of main-chain chirality, such as a predominantly one-handed helical structure induced by the zwitterionic group of the polymer side chain.[13−16,18] The CD spectra show that near the zwitterionic point, the

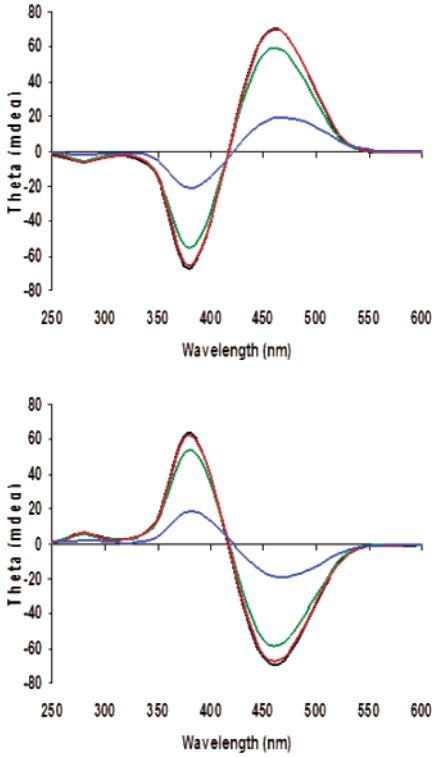

Figure 3. Circular dichroism (CD) spectra of L-POWT (top) and D-POWT (bottom) after 30 min of incubation in deionized water (black line), pH 4.0 (red line), pH 5.9 (green line), and pH 10 (blue line).

polymer chain will adopt the nonplanar syn conformation with a high helicity. In alkaline or acidic environ-

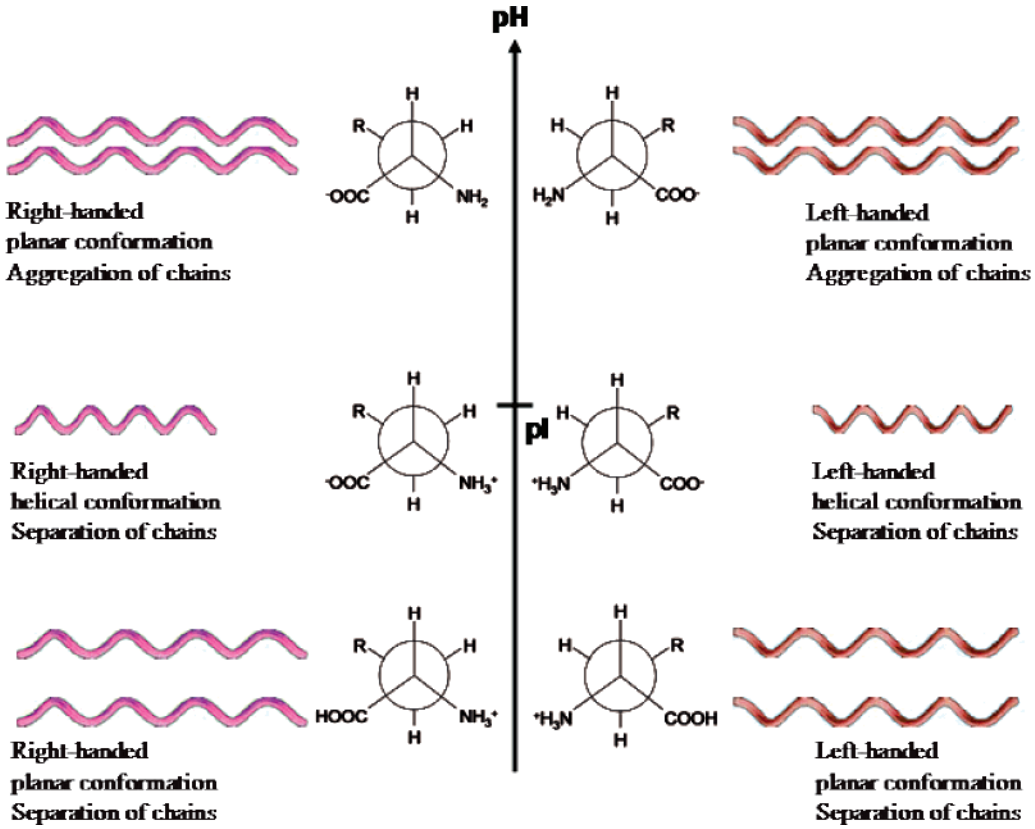

Figure 4. Newman projection of the zwitterionic side chain and schematic drawing of proposed backbone conformations of L-POWT (left) and D-POWT (right) at different pH.

ment, when the side chains become more charged, negatively or positively, the helicity is reduced. Hence, the polymer chain adopts a more rod-like conformation, in agreement with the results previously seen in the absorption measurement. In water, the thiophene rings will be shielded from the solvent, and the polymer chains will probably form a micelle-like structure with the polar side chains pointing outward to the solvent. The helical structure is most likely stabilized by hydrophobic interactions, electrostatic interactions, or hydrogen bonding between the polymer side chains. As the magnitude of the Cotton effect is highest near the isoelectric point for serine and decreases with an alteration of the pH, the hydrogen bonded ion pair complex seems to favor the helicity of the polymer chains.

Previous studies of a stereoregular poly((4-carboxyphenyl)acetylene) forming acid−base complex with amines and amino alcohols in DMSO[13] indicate that R- and S-enantiomers induce split type ICD of mirror images. Interestingly, the S-form of serine used in the synthesis of L-POWT[4] gives a similar ICD pattern (negative/positive) as the primary S-amines in this earlier study.[13] The shape and sign of the ICD pattern are characteristic of a right-handed helical form of polythiophene first observed by Meier.[10,11] Normally, a polypeptide made from L-α-amino acid residues forms a right-handed helix, so apparently the nature of the amino acid is reflected in the helical conformation of the polymer backbone.

The CD spectra of D-POWT in different buffer solutions are shown in Figure 3. The intensity of the ICD signals follows the same analogous pH-dependent trend as seen for the L-POWT, with the highest helicity at pH 5.9. But the shape and the sign of the ICD pattern is a mirror image as compared with L-POWT, indicating that the altered chirality of the polymer side chain is influencing the helical twist of the polymer backbone. A positive and negative ICD pattern has previously been seen combining a stereoregular poly((4-carboxyphenyl)-acetylene) with primary R-amines,[13] supporting that the D-form of serine will induce a left-handed helical form of the polythiophene backbone. Likewise, polypeptides made from D-α-amino acids form left-handed helices.

A closer look at the CD spectra for L- and D-POWT shows a minor peak at approximately 280 nm, which is associated with the absorption of the thiophene ring. Interestingly, this peak has also opposite signs for the polymers, indicating that the chirality of the thiophene backbone is different for the two polymers and that the altered chirality of the side chain is reflected in the conformation of the polymer backbone. These peaks are also decreasing at alkaline and acidic pH, suggesting that the backbone becomes more planar in these environments. We also find that by mixing equal amounts of D- and L-POWT, we create racemic mixtures with no CD signal (within the error of solution mixing error). Also, we find that by mixing at different ratios, the CD signal is proportional to the difference between the concentration of D- and L-POWT in the solution, thus faithfully reflecting the stoichiometry. It is tempting to draw even stronger conclusions from these observations. It has been suggested that only in aggregation is chirality created for some classes of polythiophenes.[13−16] This should lead to the observation of vanishing chirality in dilute solutions, which is not observed here, where signals are remaining at dilutions of 550 μM polymer (on a monomer basis), and no aggregation of the polymer is observed. Also, if the D- and L-POWT are added in the same solution, these molecules are chemically

identical but different in the character of the chiral center. We do not see that the excess of one or the other of the two forms causes the other form to convert into the opposite chirality. This also argues against aggregation as the necessary condition for chirality. Here, chirality of the optical transitions on the main chain is due to the chiral geometry induced by chiral substituents.

Conclusions

By comparing two isomers of a conjugated polythiophene with a free amino acid side chain, we have shown that the nonplanar to planar transition of the polymer backbone and the separation/aggregation of different polymer chains is not affected by stereochemistry of the zwitterionic side chain. The two isomers have almost identical pH-dependent absorption and emission spectra. The chirality of the zwitterionic side chain is reflected in the conformation of the polymer backbone, giving rise to a right-handed and left-handed helical form of polythiophenes. The ICD patterns of the two polymers are mirror images. A schematic drawing of the different polymer chain conformations are summarized in Figure 4. Our future efforts in this system will be to determine the different types of interactions forcing the polymers to show this extraordinary behavior and how this can be used in different types of biosensor and bioelectronic systems. It would be of great interest to combine the different isomers with natural chiral biomolecules to see if the difference in chirality will cause a different interaction with the biomolecule of interest. Another tantalizing possibility is to use the isomers as chiral construction elements for the assembly of bioelectronic devices.

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