Notes

Inversion of Optical Activity of Chiral Polythiophene Aggregates by a Change of Solvent

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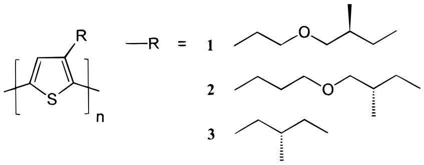
As a result of cooperative interactions, the expression of optical activity in chiral polymers can be affected by subtle changes in the macromolecular structure. In poly[(*R*)-1-deuterio-*n*-hexyl isocyanate], e.g., a cooperative interaction among many residues leads to preferential helix sense and a high specific rotation by virtue of a deuterium substitution.[1] Similarly, the odd or even position of a chiral center in the side chain of polyisocyanides has been shown to cause an alternating optical activity via an inversion of the sense of the prevailing helix.[2] Interestingly, some examples are known of a (reversible) inversion of optical activity in polymers, by changing the nature of the medium without affecting even a single stereocenter.[3] The inversion of the poly(dGC) double helix from right-handed B-DNA into left-handed Z-DNA at high-salt concentrations is probably the best known example in this respect.[4] Similar inversions have been established for poly[(*S*)-diphenyl-(1-methylpyrrolin-2-yl)methyl methacrylate] by changing the acidity of the solution and for poly(L-proline).[5,6] Although helix inversions take place in these examples, the inversion of optical rotation can also be related to the nature of the solvent (e.g., polarity, shape, polarizability) rather than conformational changes, as established for solutions of poly(propylene oxide).[7]

Recently, inversion of configuration has been reported for π-conjugated polymers carrying optically active side chains.[8] Thin films of regioregular poly{3-[2-((*S*)-2-methylbutoxy)ethyl]thiophene} were shown to give opposite optical activity depending on the cooling rate from a disordered phase at high temperature.[9] Opposite optical activity was also established for regioregular poly[3-((*S*)-3,7-dimethyloctyl)thiophene] when dissolved in chloroform−methanol mixtures of different compositions.[10] Here we show by using circular dichroism (CD) spectroscopy that regioregular optically active polythiophenes **1** and **2** aggregate from solution in chiral superstructures of opposite handedness depending on the conditions where aggregation occurs.



The optically active polymers poly{3-[2-((*S*)-2-methylbutoxy)ethyl]thiophene} (**1**) and poly{3-[3-((*S*)-2-methylbutoxy)propyl]thiophene} (**2**) were synthesized from the corresponding chiral 3-substituted thiophenes, prepared using enantiomerically pure (*S*)-(−)-2-methylbutanol. Selective bromination at the 2-position with NBS in THF, lithiation with lithium diisopropylamine at the 5-position, and transposition into the Grignard reagent with $MgBr_2{\cdot}OEt_2$ gave the reactive monomers. Polymerization was accomplished with a catalytic amount of $Ni(dppp)Cl_2$ in order to give predominant head-to-tail coupling.[11] Salts and short oligomers were removed from the reaction mixtures by Soxhlet extractions with methanol and hexane, respectively. The polymers were isolated in moderate yields by a final Soxhlet extraction with chloroform. The molecular weight (M_n) and polydispersity (D), as determined by GPC (Plgel352) in THF against polystyrene standards, is $M_n = 16.9$ and 21.3 kg/mol with $D = 1.4$ and 1.5, for **1** and **2**, respectively. The ^{1}H NMR spectra of polymers **1** and **2** show a single well-defined symmetric peak in the aromatic region, related to the protons at the 4-position. The ^{13}C NMR spectra reveal four sharp resonances for the aromatic carbon atoms of the thiophene rings. These results are consistent with a well-defined regioregular head-to-tail structure.

Polythiophenes **1** and **2** have been studied with UV/vis and CD spectroscopy. Dissolved in dichloromethane at ambient temperature, the polythiophenes exhibit an inhomogeneously broadened absorption band with $\lambda_{max} = 444$ (**1**) and 451 nm (**2**). The absorption exhibits no vibrational fine structure and is attributed to the $\pi-\pi^*$ transition of molecularly dissolved, conformationally disordered polymer chains. Under these conditions of good solubility no optical activity is observed with CD spectroscopy for the $\pi-\pi^*$ transition. The solubility can be decreased by lowering the temperature. Figure 1 shows the changes with temperature in the absorption and CD spectra of **2**, dissolved in dichloromethane. Initially, a gradual red shift of λ_{max} is observed with decreasing temperature ($\lambda_{max} = 469$ nm at 230 K). The shift to lower energy indicates an increase of effective conjugation length at lower temperatures. We ascribe this to an ever advancing degree of coplanar conformations between adjacent thiophene rings along the polymer backbone. Down to 230 K, no CD signal is observed. Between 230 and 210 K, the spectra change dramatically and at 200 K the absorption maximum has shifted to lower energy ($\lambda_{max} = 560$ nm) and a number of shoulders, characteristic of vibronic fine structure, have emerged. The 0−0 transition is found at 649 nm. The thermochromic effects occurring between 230 and 210 K are due to the transition of molecularly dissolved polymer chains to a microcrystalline phase.[12] The

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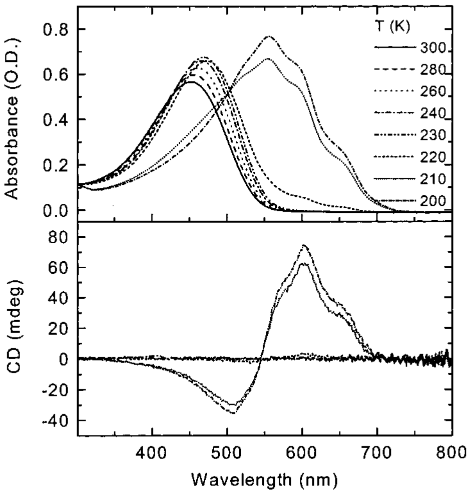

Figure 1. Temperature dependence of UV/vis and CD spectra of **2** in dichloromethane. Temperatures are given in the inset; the spectra are not corrected for volume changes of the solvent.

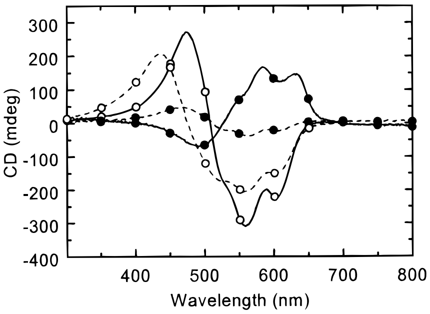

Figure 2. CD spectra of **1** (solid line) and **3** (dashed line) in dichloromethane at 170 K (solid circles) and in 1-decanol at 293 K (open circles). The spectra are normalized to unit absorbance at $\lambda_{\max}$.

abrupt changes in the absorption are accompanied by the appearance of a bisignate CD spectrum associated with the $\pi-\pi^*$ absorption band, exhibiting a positive Cotton effect at high wavelength and a negative Cotton effect at low wavelength. This CD couplet is characteristic of exciton coupling between polymer chains in a (right-handed) helical orientation.[13] Cooling of **2** in dichloromethane from 200 to 170 K does not result in significant changes in the UV/vis or CD spectra.

The UV/vis (not shown) and CD spectra of **1** in dichloromethane at 170 K are similar to those of **2**; see Figure 2. A measure for the induced optical activity is obtained from the chiral anisotropy factor g ($=\Delta\epsilon/\epsilon$). The largest g values are found close to the lowest-energy vibronic feature: $g = +0.0071$ (638 nm) for **1** and $g = +0.0045$ (669 nm) for **2**.

Much to our surprise we found that the sign of the CD couplet is inverted when primary alcohols are used as a solvent instead of dichloromethane. Figure 3 shows changes in the optical absorption between 293 and 343 K of **2**, as an example, dissolved in 1-nonanol. Since 1-nonanol is a poor solvent for **2**, an aggregated phase forms already at room temperature (293 K: $\lambda_{\max} = 485$ nm). This aggregated phase can reversibly be transformed into a molecularly dissolved chain at higher temperatures (343 K: $\lambda_{\max} = 444$ nm). The spectra shown in Figure 3 demonstrate that at ambient temperature the *CD spectrum of **2** in 1-nonanol exhibits a bisignate Cotton effect for the $\pi-\pi^*$ transition of opposite sign as compared to the CD spectrum recorded at 200 K in dichloromethane* ($g = -0.0031$ at 602 nm). The room-temperature CD spectrum of the aggregated phase of **1** formed in 1-decanol exhibits the same inversion of optical activity ($g = -0.0154$ at 618 nm); see Figure 2.

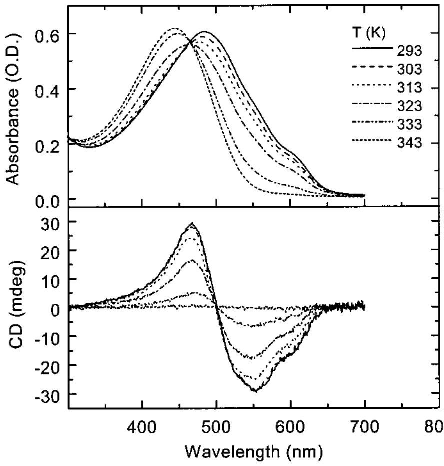

Figure 3. Temperature dependence of UV/vis and CD spectra of **2** in 1-nonanol. Temperatures are given in the inset; the spectra are not corrected for volume changes of the solvent.

For polymers **1** and **2** a transition from the disordered polymer chain in chloroform solution to an aggregated and ordered phase can also be achieved at ambient temperature via the slow addition of a nonsolvent like methanol to a solution of the polymers in a good solvent like chloroform. The amount of methanol required to reach maximum aggregation is different for **1** and **2** ($CHCl_3/CH_3OH$ (v/v): ~40:60 for **1** and ~20:80 for **2**). The UV/vis and CD spectra of the aggregated solutions are significantly red-shifted and exhibit a CD signal of the same sign (**1** $CHCl_3/CH_3OH$ (v/v) 39:61, $g = -0.0217$ at 611 nm; **2** $CHCl_3/CH_3OH$ (v/v) 22:78, $g = -0.0036$ at 602 nm) as obtained in 1-decanol for (**1**) and 1-nonanol for (**2**).

The unexpected inversion of the CD couplet by a change of solvent indicates that the handedness of the optically active superstructures is different in dichloromethane and 1-decanol (**1**) or 1-nonanol (**2**). The possibility that an electronic effect induced by the solvent is responsible for the observed effect was discarded on the basis of a study of regioregular poly-[3-((*S*)-2-methylbutyl)thiophene] (**3**, $M_n = 6.2$ kg/mol, $D = 1.7$) synthesized following a procedure similar to that of **1** and **2**. In contrast to the inversion observed for **1** and **2**, the signs of the bisignate CD spectra of **3** in the aggregated phase are identical for all the conditions studied so far (1-decanol 293 K, $g = -0.0106$ at 616 nm; dichloromethane 170 K, $g = -0.0022$ at 629 nm; $CHCl_3/CH_3OH$ (v/v) ~59/41 293 K, $g = -0.0023$ at 603 nm).

We propose that the interaction of the optically active side chains induces a helical packing of polymer chains into a chiral superstructure, which creates an optical activity associated with the electronic transition of the polymer backbone via exciton coupling. The experiments demonstrate that the handedness of the chiral organization of the polymer main chains is very sensitive to the ordering conditions and, hence, imply a small energy difference between the two diastereomeric forms. A tentative explanation for the constant optical activity observed for **3** is the closer proximity of the chiral center to the main chain and the smaller overall length of the side chain, when compared with **1** and **2**.[14] This is likely to increase the energy difference between the two crystalline forms.[15] The observation of two diastereomeric forms of **1** and **2** is similar to the polymorphism recently described for crystalline regioregular poly(3-alkylthiophenes).[16] Furthermore, the stereomutation of **1** and **2** parallels the inversion of chiroptical properties observed in cholesteric phase of liquid crystals with temperature or by the addition of a chiral dopant.[17]

The results presented here will add to the emerging understanding that subtle changes in the interplay between reversible associating macromolecules and the solvents used can bring about significant differences in the stereochemical outcome of the mesoscopic morphologies.

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(14) One of the reviewers suggested that the alcohols make a hydrogen bond with the ether oxygen of **1** and **2**, affecting the aggregation and the sign of the CD effect. Although this seems a likely explanation based on our experiments, it does not explain similar inversions previously observed in poly(3-alkylthiophenes) (ref 10).

(15) An attempt to confirm this proposition by investigating regioregular poly{3-[((*S*)-2-methylbutoxy)methyl]thiophene} was not successful. Upon polymerization of 3-[((*S*)-2-methylbutoxy)methyl]thiophene following the route described for **1** and **2**, a polymer (M_n = 18.8 kg/mol, D = 1.5) with only ~85% head-to-tail coupling was obtained, as evidenced from ^{1}H and ^{13}C NMR. The lack of complete regioregularity in this case is probably related to the position of the oxygen in the side chain, as in the lithiated intermediate an energetically favored (chelating) complex is formed by exchange of bromine and lithium (See: McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608). As a result of the low regioregularity the aggregation of this polymer was very poor in 1-decanol (a small positive CD couplet was found with $g = +0.003$ at 510 nm) and further studies were abandoned.

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