Stereomutation in optically active regioregular polythiophenes

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Stereomutation in Optically Active Regioregular Polythiophenes**

By *Michiel M. Bouman* and *E. W. Meijer**

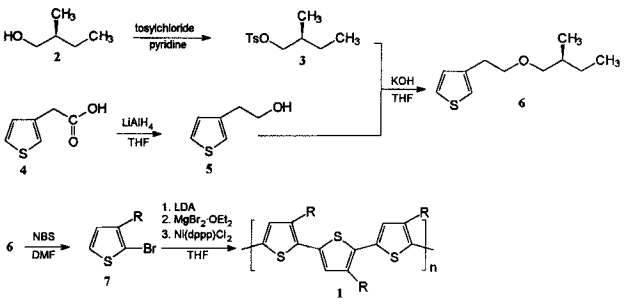
Inversion of main-chain chirality in optically active polymers without changing the configuration of stereocenters is a phenomenon seldom observed. Although most polymers adopt helical conformations in solution and/or in the solid state,[1] optical activity from main-chain chirality can only be observed when the polymers are prepared in an enantioselective way.

An interesting class of optically active polymers is based on the enantioselective induction of main-chain chirality by the presence of enantiomerically pure side chains. A very elegant example has been reported by Green et al.; the induced main-chain chirality in poly((R)-1-deuterio-*n*-hexylisocyanate) originates from the subtle difference between deuterium and hydrogen in the chiral side chain.[2] Based on numerous studies on polymers like the poly(L-glutamate) family, it is now generally accepted that significant main-chain chirality is only induced when the polymer is brought into a micro-aggregrated well-ordered form.[3]

Although various examples are reported in which the main-chain chirality, and hence ordering and conformation, is influenced by the concentration of the polymer, the solvent used or by other external stimuli, reversible stereomutation is limited to biopolymers, like poly-L-proline,[4–6] polynucleotides[7–10] and the Bilrubin-Albuminium complex.[11] The circular dichroism spectrum of the latter in an aqueous solution inverts on the addition of one drop of chloroform.[11]

Only one example of stereomutation of a synthetic polymer is known: optically active poly[(S)-diphenyl(1-methylpyrrolidin-2-yl)methylmethacrylate] changes the screw sense of its main chain on changing the pH.[12] The most thoroughly studied examples of inversion of chirality in synthetic materials are found in the area of cholesteric liquid crystalline materials. A cholesteric phase is obtained by chiral dopants in a nematic liquid crystal. Temperature and concentration of the dopant influences the pitch-length and can even change the sense of the cholesteric helix.[13–17]

Recently, chiral π-conjugated polymers have attracted general interest. All these polymers, except polyanilines,[18] belong to the class of chiral polymers in which the main-chain chirality is induced by the presence of enantiomerically pure side groups.[19–26] We have shown that regioregularity in this type of polymers increases the degree of induced chirality tremendously and that the optical activity is only present in an ordered microcrystalline associated form, as demonstrated for chiral 3-substituted polythiophenes.[27] In this paper, we show that stereomutation in thin films of optically active regioregular 3-substituted polythiophene **1** (Scheme 1) can be observed and modulated via the thermal history of the material, and discuss the use of these materials for reversible optical recording.



Scheme 1. Synthesis of the optically active polythiophene **1**.

Poly{3-[2-((S)-2-methylbutoxy)ethyl] thiophene} **1** (M_n = 16900 g mol^{-1}; D = 1.4) was synthesized using the McCullough method[28,29] starting from 2-bromo-3-[2-((S)-2-methylbutoxy)ethyl]thiophene (**7**). The latter was synthesized from commercially available optically pure (S)-2-methylbutanol (**2**) and 3-thiophene acetic acid (**4**) by modification of standard procedures. Regioregularity of **1** with respect to head-to-tail coupling is better than 98%, as detected by ^{1}H- and ^{13}C-NMR spectroscopy. Absorption and circular dichroism spectra are obtained for spincoated films of **1** on glass plates (Fig. 1). All three absorption bands

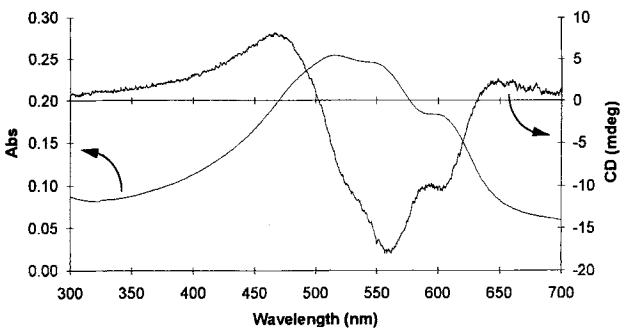


Fig. 1. CD and UV spectra of **1** in the solid state.

at λ = 512, 540 and 592 nm, assigned to vibronic bands of the π–π^* transition, show a bisignated Cotton effect. The g-value ($\Delta\varepsilon/\varepsilon$) found for the solid films is, depending on sample preparation, $-2\times10^{-3} < g < -1\times10^{-3}$ at λ = 600 nm, a factor of 10 to 20 lower than the g-values found for associated **1** in poor solvents.[27]

The well-known thermochromism of 3-substituted polythiophenes is observed for **1** as well. However, in this case the change in absorption spectrum (the film changes from deep purple to orange) at temperatures around 160 °C, which is the melting point of the polymer as measured by DSC, is accompanied by a complete loss of optical activity in the

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$\pi-\pi^*$ transition band (Fig. 2). Slow cooling of the polymer film yields a reversible thermochromism, while the optical activity in the three absorption bands is recovered. Crystallization upon cooling is observed at 140 °C, both with DSC as well as in the optical spectra. Apart for some hysteresis, the thermal process is reversible in all its optical features.

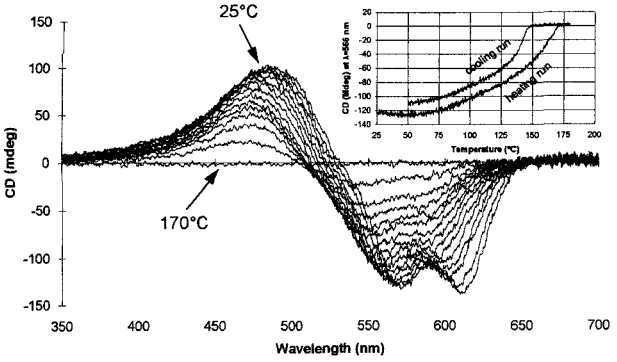

Fig. 2. Temperature dependence of the CD spectra of **1** in the solid state. The inset shows the hysteresis in a heating–cooling cycle with a heating/cooling rate of 10 °C/min.

Much to our surprise, we detected a complete stereomutation of the main chain by the appearance of a mirror image CD spectrum, when polymer **1** is cooled very fast from the disordered melt into the crystalline state by pouring the sample into a water bath at 0 °C (Fig. 3). Heating this inverted sample again to 200 °C and cooling it down slowly furnishes the original result. By adjusting the cooling rate, it is even possible to obtain an associated purple polymer with no optical activity in its $\pi-\pi^*$ transitions at $\lambda = 512$, 540 and 592 nm. Heating and slow cooling of this optically inactive film reestablishes the thermodynamically most stable optically active form. Despite the large differences in circular dichroism spectra for all the room-temperature structures, no significant differences in the absorption spectra are found.

The films with opposite chirality as detected with ORD/CD show a corresponding difference in optical rotation of the reflectivity of light of $\lambda = 680$ nm as well. Differences of the order of 0.2° are found. These values are comparable

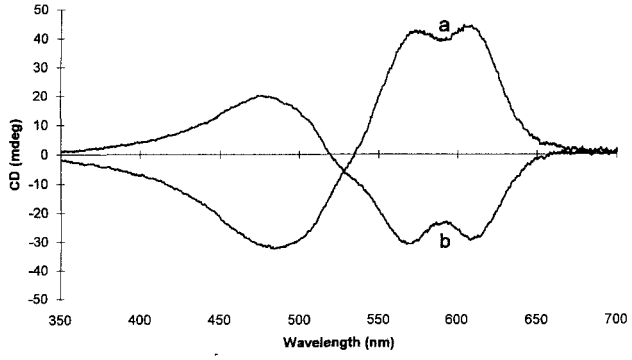

Fig. 3. CD spectra of **1** showing complete stereomutation of the main chain when the polymer is cooled very fast: a) Fast-cooled polymer film. b) Slow-cooled polymer film.

with the Kerr rotations in reflection that are the basis for MO-recording (MO = magneto-optic) using complicated magnetic multilayers.[30]

In order to use this stereomutation of solid films of **1** for optical recording, we have investigated multiple cycles of heating and cooling. However, these multiple cycles of heating to 200 °C and slow or fast cooling to 20 °C show that the polythiophene samples deteriorate rapidly in air (Fig. 4). Therefore, we are now investigating other π-conjugated polymers that are more stable and will show the same stereomutation. We are aiming at using the residual absorption at 800 nm of thin films of these π-conjugated polymers to modulate the reflectivity. Low intensity for reading and high intensity for writing with a threshold for switching, due to the phase transition, completes the proposal for a simple polymer alternative for the reversible MO-recording based on chirality.

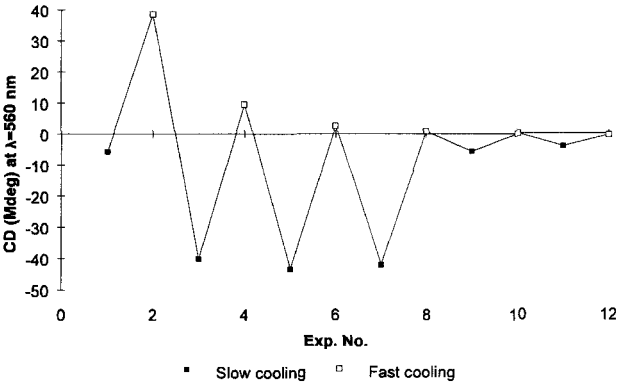

Fig. 4. Switching between states of different chirality by adjusting the cooling rate.

The thermochromism observed is easily explained by the transition between a disordered state without main-chain chirality and the thermodynamically most stable ordered, associated state with main-chain chirality. The pronounced exciton coupling observed for the latter is the result of the Davydov splitting of all the vibrational bands of the excited state S_1.[31, 32] This Davydov splitting is either the result of an intramolecular helical conformation of the backbone or the result of an intermolecular chiral orientation of predominantly co-planar, but probably chiral, polymer chains with a kind of supercoiling in the microcrystalline phase. Theory concerning exciton coupling[32, 33] does not unambiguously distinguish between both modes.[34]

A more careful examination of the optical spectra recorded during the heating and cooling cycles (Fig. 2) indicates that an optically active form of the polythiophene without the presence of vibronic bands is present as well. However, details on the nature of this in-between structure are not available. The significance of polymer association and hence cooperativity for a large increase in optical activity of chiral polythiophenes is similar to the results reported for chiral polydiacetylenes.[35]

Apparently, we are able to freeze-in a metastable chiral associated form of **1**, that exhibits the mirror-image main-

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chain chirality. It should be noted that the configuration of the side chain is not altered during this process. Therefore, the two chiral forms obtained by slow and fast cooling, respectively, possess a diastereomeric relation. In the case of the formation of an optically inactive form, it is unclear to us whether we have prepared an achiral polymer film with a zigzag conformation, or a diastereomeric mixture of the two forms presented above. However, by adjusting the appropriate rate of cooling we can switch the film between chiral forms of opposite chirality. The cause of this inversion is speculative at this stage, but the conformation of the chiral side groups, which induces the chirality in the main chain, is playing an important role.

The effect of two different conformations on the crystallization of low-molecular weight organics and their polymorphism is well documented.[36] Slow cooling will give the thermodynamically most stable form, while using fast cooling the kinetically favored metastable form will associate and is frozen-in. Although a number of chiral polymers, including π-conjugated structures, have been investigated, the results presented here represent the first example of inversion of chirality using metastable associates. It is worthwhile noting that the importance of metastable microscopic crystalline aggregates in the observation of optical activity in polymers has been discussed already in 1964 by Tolbolsky.[3, 37] Research to gain detailed insight into the remarkable phenomenon of stereomutation is in progress.

Experimental

GPC measurements were performed on a Waters 590 GPC, using THF as solvent and a PL gel $10^3 + 500 + 10^2$ column, calibrated with polystyrene standards. NMR spectra were recorded on a Bruker AM 400 operating at 400.13 MHz for proton and 100.62 MHz for carbon spectra, using $CDCl_3$ as solvent and TMS as internal reference. UV-vis spectra were recorded on a Perkin-Elmer Lambda 3B spectrophotometer and CD spectra were recorded on a Jasco J-600 spectrophotometer.

2-Bromo-3-[2-((S)-2-methylbutoxy)ethyl]thiophene (7): 3-[2-((S)-2-methylbutoxy)ethyl]thiophene (**6**) (4.96 g, 25 mmol) was dissolved in 20 ml dry dimethylformamide (DMF). To this solution a solution of 4.45 g *N*-bromosuccinimide (25 mmol) in 20 ml DMF was added under absence of light through a dropping funnel. After stirring in the dark for three days the reaction mixture was poured into ice. The water phase was extracted three times with diethylether. The combined ether extracts were washed three times with water, dried with $MgSO_4$ and evaporated. The product was distilled under vacuum which yielded 6.08 g (88%) of a slightly yellow colored oil. ^{1}H-NMR: δ 7.20 (d, $J = 5.6$ Hz, H4, 1H) 6.89 (d, $J = 5.6$ Hz, H5, 1H) 3.59 (t, $J = 6.9$ Hz, $-CH_2CH_2O-$, 2H) 3.30 (dd, $J_1 = 9.1$ Hz, $J_2 = 6.2$ Hz, $-OCHHCH(CH_3)-$, 1H) 3.21 (dd, $J_1 = 9.2$ Hz, $J_2 = 6.7$ Hz, $-OCHHCH(CH_3)-$, 1H) 2.87 (t, J = 6.9, $-CH_2CH_2O-$, 2H) 1.67–1.59 (m, $-CH_2CH(CH_3)-$, 1H) 1.46–1.39 (m, $-CH(CH_3)CHHCH_3$, 1H) 1.16–1.10 (m, $-CH(CH_3)CHHCH_3$, 1H) 0.90–0.86 (m, $2CH_3$, 6H). ^{13}C-NMR: δ 138.6 (C3) 128.7 + 125.1 (C4 + C5) 109.8 (C2) 76.3 ($-OCH_2CH(CH_3)-$) 69.9 ($-CH_2CH_2O-$) 35.0 ($-CH(CH_3)-$) 30.0 ($-CH_2CH_2O-$) 26.2 ($-CH_2CH_3$) 16.6 ($-CH(CH_3)-$) 11.3 ($-CH_2CH_3$).

Poly{3-[2-((S)-2-methylbutoxy)ethyl]thiophene} (1): 1.83 g Dry diisopropylamine (18 mmol) was dissolved in 75 ml dry THF. At room temperature 11.3 ml *n*-buthyllithium (1.6 M in hexane, 18 mmol) was added. After stirring for one hour the solution was cooled to -70 °C and 5 g (18 mmol) of **7** (18 mmol) was added. The solution was warmed slowly to -40 °C and during stirring for 40 minutes the color changed from yellow to red. At -60 °C 4.66 g magnesium bromide etherate (18 mmol) was added in one portion and the mixture was slowly warmed to 0 °C. The color changed from red to orange. 47.3 mg of catalyst [1,3-bis(diphenylphosphino)propane]nickel(II)chloride (0.5 mol%) was added and the mixture was stirred overnight at room temperature. The same amount of catalyst was added again and the reaction mixture was stirred for another night. The polymer was precipitated in hexane and washed with methanol, a 1 M HCl solution and again with methanol. It was further purified using soxhlett extractions with methanol and hexane to remove oligomers and grease and the polymer itself was extracted with chloroform yielding 0.44 g (12%) of a deep purple solid. m.p. = 160 °C. ^{1}H-NMR: δ 7.10 (s, H4, 1H), 3.70 (t, $J = 7.0$ Hz, $-CH_2CH_2O-$, 2H) 3.35 (dd, $J_1 = 9.1$ Hz, $J_2 = 6.2$ Hz, $-OCHHCH(CH_3)-$, 1H) 3.26 (dd, $J_1 = 9.2$ Hz, $J_2 = 6.7$ Hz, $-OCHHCH(CH_3)-$, 1H) 3.09 (t, $J = 6.7$ Hz, $-CH_2CH_2O-$, 2H) 1.70–1.63 (m, $-CH_2CH(CH_3)-$, 1H) 1.51–1.44 (m, $-CH(CH_3)CHHCH_3$, 1H) 1.19–1.12 (m, $-CH(CH_3)CHHCH_3$, 1H) 0.93–0.86 (m, $2CH_3$, 6H). ^{13}C-NMR: δ 136.3 + 133.4 + 131.7 + 129.3 (C2 + C3 + C4 + C5) 76.4 ($-OCH_2CH(CH_3)-$) 70.6 ($-CH_2CH_2O-$) 35.0 ($-CH(CH_3)-$) 29.9 ($-CH_2CH_2O-$) 26.3 ($-CH_2CH_3$) 16.7 ($-CH(CH_3)-$) 11.4 ($-CH_2CH_3$).

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