

Odd–even effect in optically active poly(3,4-dialkoxythiophene)

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Received (in Cambridge, UK) 12th March 1999, Accepted 23rd March 1999

An odd–even effect is observed in the CD spectra of a homologous series of aggregated optically active poly(3,4-dialkoxythiophene)s, suggesting a helical packing of polymer chains into chiral superstructures, similar to that of the cholesteric liquid crystalline phase.

Polythiophenes attract considerable interest for their incorporation as active elements into electronic and electro-optical devices.¹ The optical and electronic properties of polythiophenes are dependent on the chemical structure² as well as on the intrachain and interchain structural organisation.³ Control over the chemical structure has improved dramatically since synthetic routes towards well-defined substituted polythiophenes have become available.² The three-dimensional structure of the macromolecules in solution and the morphology in the solid state are influenced to a great extent by solvent and temperature.⁴

Novel insights into the organisation process of substituted polythiophenes have been obtained from well-defined polymers carrying optically active β -substituents.⁵ Although in solution or in the melt no optical activity is observed for the π - π^* transition of these chiral polythiophenes, they exhibit a strong bisignate circular dichroism (CD) effect associated with the main-chain absorption in the aggregated or solid state, consisting of a positive and a negative signal of comparable intensity. The presence of a CD effect shows that the chirality of the side chains induces optical activity in the polythiophene main chains. The parallel occurrence of aggregation and optical activity, as well as studies on bis(oligothiophene) model compounds,⁶ indicate that the bisignate CD effect originates *via* exciton coupling from adjacent polythiophene chains in chiral superstructures. The sign of the experimental CD effects in the model compounds is in accordance with the prediction from exciton theory for the relative orientation of the two oligothiophene moieties in these models.⁶ This suggests that in optically active polythiophenes, chiral packing of polythiophene chains occurs, comparable to the organisation processes in cholesteric liquid crystals. However, a complete understanding of the organisation process and the induction of chirality is lacking.

For some cholesteric liquid crystalline compounds an empirical relation between the helical ordering of the constituent molecules in the mesophase and the chirality in the flexible chain has been established by Gray and McDonnell.⁷ According to these Sol-Rel, Sed-Rod alternation rules, the rotation of plane polarised light through a helical mesophase, clockwise (+, dextro) or counterclockwise (–, laevo), depends on the absolute configuration of the chiral centre (*S* or *R*) and its distance to the rigid mesogenic core (odd or even number of atoms). By definition the dextro-rotation is produced from a left handed helix, while the laevo-rotation originates from a right handed helical organisation. The rules are also applicable to other liquid crystalline mesophases, like helicoidal smectics,⁸ and a similar odd–even alternation effect has even been observed for helical poly(isocyanides) with mesogenic substituents.⁹ Here we show that the alternation rules are applicable to aggregated optically active poly(3,4-dialkoxythiophene)s.

In order to investigate the effect of distance between the stereocentre in the side chain and the polymer main chain, a series of poly(3,4-dialkoxythiophene)s **2–7** (Fig. 1) containing

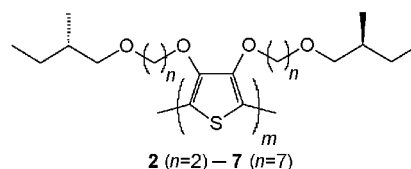


Fig. 1 Optically active poly(3,4-dialkoxythiophene)s **2–7**.

increasing lengths of alkoxy spacers has been synthesised. For the synthesis the tosylate of commercially available (*S*)-2-methylbutanol is coupled once to the spacers ethane-1,2-diol through to heptane-1,7-diol. The resulting optically active alcohols are introduced at the β -positions of thiophene by transesterification of 3,4-dimethoxythiophene.¹⁰ Polymerisation is accomplished by chemical oxidation using anhydrous iron(III) chloride.¹¹ The crude poly(3,4-dialkoxythiophene)s are dedoped by precipitation in MeOH–25% ammonia (v/v, 5/1). Further purification *via* Soxhlet extractions using MeOH–25% ammonia (v/v, 5/1) and hexane, and isolation *via* Soxhlet extraction with CHCl_3 gives pristine **2–7**. ¹H and ¹³C NMR spectroscopy reveal the desired 2,5-polymerization without any observable irregularities.[†]

Microcrystalline aggregates of **2–7** are readily formed in poor solvents, e.g. decan-1-ol and pentan-1-ol.[‡] The UV–Vis spectra of the microaggregates of **2–7** exhibit vibronic fine structure, indicative of intrachain and interchain order, with a 0–0 transition at *ca.* 610 nm, *i.e.* considerably red-shifted compared to the spectra of the polymers in good solvents (e.g. CHCl_3).^{5b,c} The CD spectra of these ordered aggregates alternate in sign with an odd or even number of atoms in the spacer (Fig. 2).§

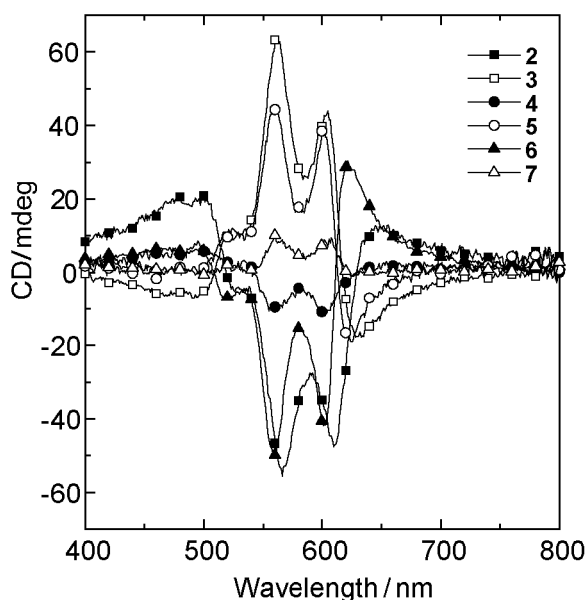


Fig. 2 CD spectra of **2–7** in decan-1-ol at room temperature. The spectra are normalised to unit absorbance at λ_{max} .

It is tempting to interpret the sign of the CD effect of these poly(3,4-dialkoxythiophene)s in terms of supermolecular helicity. Exciton theory and model studies predict that, for the $\pi-\pi^*$ transition of helically ordered aggregates of poly(3,4-dialkoxythiophene)s, a positive CD signal at the high wavelength implies a right-handed organisation of the chains in the aggregates, *i.e.* laevo in liquid crystal terminology. When the CD signal at the 0-0 transition (*ca.* 610 nm) is taken to represent the sign of the low-energy component of the couplet, it is found that 2–7 follow the Sol-Rel, Sed-Rod alternation rules that were originally developed for cholesteric liquid crystals. Polymer 6, for example, has an *S* configuration at the stereocentre, 10 atoms (even) from the rigid part to the stereocentre, and is organised according to a left-handed helix (dextro) because of a negative CD signal at 605 nm.

While the CD spectra of 2–7 are indeed reminiscent of exciton coupling, the spectra fail to represent the characteristic exciton couplet, consisting of two peaks of equal intensity and opposite sign,⁶ and integration of the CD spectrum over the $\pi-\pi^*$ band does not yield zero. These are clear indications that the CD spectra do not represent simple exciton couplets. Therefore, the explanation of the CD effect in terms of an interaction between chains in a helical fashion, providing the exciton coupled CD (bisignate), has to be augmented with a helical conformation for the individual polymer chains resulting in an intrinsic CD (monosignate).

The CD spectra of 2–7 in Fig. 2 are normalised to unit absorbance and clearly differ in intensity. Similar to a decreasing pitch observed in liquid crystals with increasing distance between the stereocentre and mesogenic core,⁷ it can be expected that the influence of the optical activity in the side chain on the chiral organisation within the aggregates decreases with the number of atoms in the spacer. However it was extremely difficult to verify this expectation, because the magnitude of the CD effect is influenced by batch-dependent characteristics like the molecular weight and polydispersity,¹² and on subtle changes in sample preparation conditions, *i.e.* polymer concentration, temperature, and time of aggregation.[¶]

In conclusion, we have shown that in a homologous series of poly(3,4-dialkoxythiophene)s 2–7 with increasing lengths of spacers in β -substituents, the sign of the induced optical activity in the $\pi-\pi^*$ transition alternates with the parity of the number of atoms in the spacer when the polymers are in an aggregated phase. This effect is similar to alternation effects observed in helical liquid crystals and suggests that the CD effect associated with the $\pi-\pi^*$ transition arises from a similar chiral organisation of the polythiophene main chains. When the CD signal at the first vibronic transition is used to predict the sense of helicity *via* exciton theory, it is found that the alternation of CD signal in polythiophenes is consistent with the Sol-Rel, Sed-Rod alternation rules that were originally developed for cholesteric liquid crystals.^{||}

We would like to thank the EU for support for E. R. L. (Marie Curie Fellowship) and Philips Research BMWLV.

Notes and references

† The polymerisation conditions were varied for the amount of oxidising agent (2–4 equiv.) and the reaction time (4–16 h) but have not been

optimised for each monomer. The final polymers differ significantly in molecular weight M_n and polydispersity D as determined by SEC measurements in THF, relative to polystyrene standards. M_n (D) varies between 10 kg mol⁻¹ (3.3) for 2 and 62 kg mol⁻¹ (4.7) for 5. The work-up procedure of 4 repeatedly gave problems in the dedoping step and results presented for 4 should be regarded as tentative.

‡ Microaggregate formation in decan-1-ol was achieved by adding a small quantity of the polymer to decan-1-ol, warming until the polymers dissolved completely, and slow cooling to room temperature. Solutions in pentan-1-ol were prepared by adding a drop of a concentrated solution of 2–7 in CHCl₃ to pentan-1-ol.

§ Similar CD spectra with alternating sign have been obtained for thin films of polymers 3 and 5–7 on glass substrates when spin coated from CHCl₃ solution. For polymer 3 this involved an annealing step at 150 °C for 2 h to reach the thermodynamically most stable form of aggregation, while 4 did not show good film formation.

¶ The shape and sign of the CD spectra are usually not affected by these parameters.

|| Poly{3,4-bis[(*S*)-2-methylbutoxy]thiophene}^{5b,c} also follows the Sol-Rel, Sed-Rod alternation rules (*S*, odd, CD at 610 nm is positive and hence laevo), whereas poly{2,5-bis[(*S*)-2-methylbutoxy]-1,4-phenylenevinylene} shows an opposite behaviour (*S*, odd, CD at 575 nm is negative and hence dextro).¹³

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Communication 9/01960J