CHIRAL POLYTHIOPHENES

Francesco Tassinari
Dipartimento di Scienze Chimiche e Geologiche
Università di Modena e Reggio Emilia
francesco.tassinari@unimore.it

Chiral polythiophenes properties are strictly related to the conformation that the polymer chains adopt: these polymers can organize in helical structures both in solution and in the solid state. This self assembly can be controlled with different means, making them a very interesting material for a wide range of applications

Politiofeni chirali
Le proprietà dei politiofeni chirali sono strettamente correlate alla conformazione adottata dalle catene del polimero: questi possono infatti organizzarsi, sia in soluzione che allo stato solido, in strutture elicoidali. Questo processo di *self-assembly* può essere controllato attraverso vari metodi, rendendo questi politiofeni dei materiali estremamente interessanti per un ampio raggio di applicazioni.

Conductive Polymers (CPs), electrically conducting organic polymers have been pioneered by MacDiarmid, Shirakawa and Heeger with the synthesis of polyacetylenes in the late '70s[1].
In 1985, Baughman and co-workers synthetized the first Chiral Conductive Polymers (CCPs)[2], electrically conducting organic polymers showing some form of chirality in their structure.
The field has grown larger with time, and today many other polymers have been developed and studied that show not only a high electrical conductivity but also peculiar redox and pH switching capabilities, thus opening a whole new frontline of possible applications.
Conducting organic polymers that possess chirality present some unique opportunities when used as chiral substrates or as chiral electrode materials: they can be used in electrochemical chiral sensing or electrochemical asymmetric synthesis. Their properties can be easily modified via attachment of functional groups to the polymer backbone and their ability to be processed as particles, membranes of micro- and nano-dimensional fibres open up possibilities to the design and development of specific molecular recognition/purification systems.
The first chiral polythiophenes (CPTs) were prepared by Lemaire and co-workers in 1988 via electrochemical polymerization[3]. Macromolecular chirality was induced by the presence of enantiomeric (S)- and (R)-2-phenylbutyl groups in the side chain, bonded to the thiophene ring through a propyloxy spacer to decrease steric hindrance in the polymerization (Fig. 1).

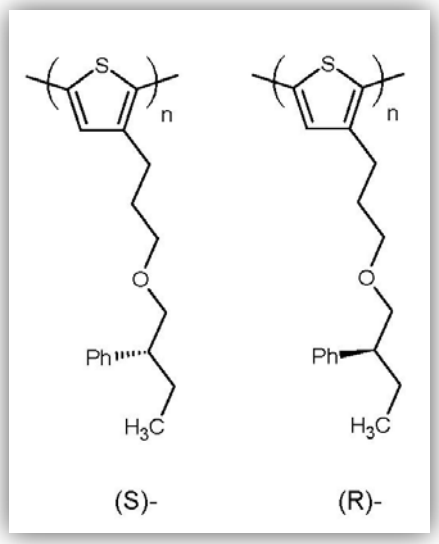


Fig. 1

The neutral, undoped films of these polymers exhibited large optical rotations compared to the corresponding monomers. This high optical activity was interpreted in therms of the adoption of a one-handed helical conformation by the polythiophene main chains, induced by the presence of the chiral substituents. Cyclic voltammograms of the (S)-polymer films in the presence of (+)- and (-)-camphorsulfonic acid (HCSA) revealed chiral discrimination by the polymer modified electrode, in that greater current density was observed during oxidation/reduction in the presence of (+)-CSA^- anions (50% higher than with (-)-CSA^-). The opposite enantioselectivity was found using (R)-polymer films.

Transoid or cisoid helical chains were proposed as possibles structures from theoretical calculations[4], whereas studies conducted by Meijer and coworkers[5] brought strong evidence that the origin of the optical activity in chiral substituted polythiophenes is actually due to the formation of supramolecular aggregates (Fig. 2). The visible region optical activity, associated with the polythiophene π,π^* absorption, generally occurs in aggregated states of the polymers, such as in films or in "poor" solvents. These aggregates are believed to be intermolecular helical packing of predominantly planar polythiophene chains.

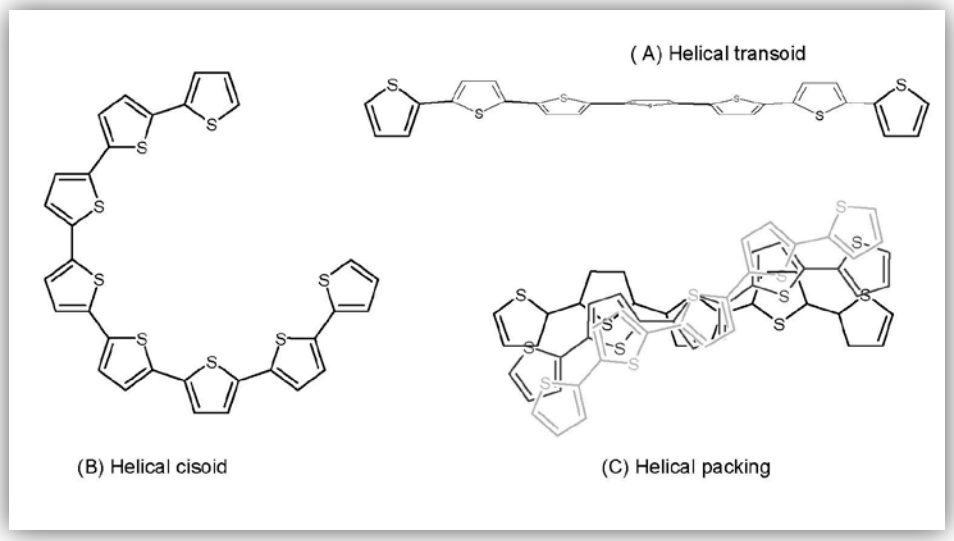


Fig. 2

In literature there are different examples of CPTs, such as the one reported by Inganas and co-workers[6], where the optical activity is present even in the absence of the aggregates. This particular CPT bears a chiral serine aminoacid bonded to the thiophene ring via an ether linkage (Fig. 3), and its CD, UV-visible and fluorescence emission spectra show a high pH dependence, indicative of major conformational changes. At the pH corresponding to the isoelectric point of the serine aminoacid, the polythiophene chains are separated and adopt a non planar helical conformation, while increasing the pH leads to a more planar conformation of the backbone and aggregation of the polymer chains occurs. The CD spectra of the polymers bearing the two different serine enantiomers are mirror imaged, showing that the chirality of the polythiophene side chains is reflected in the conformation of the polymer backbone.

The connection between the macromolecular conformation and the properties of these materials is intriguing and can be exploited in different applications such as chiral sensors or organic electronics. Different studies have already been conducted on the pH and redox switching of different CCPs, and their solvatochromism and thermochromism is also well known.

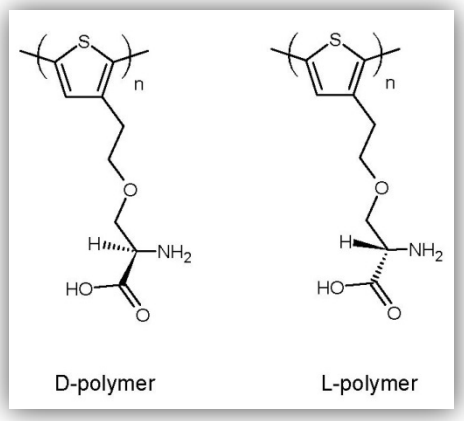
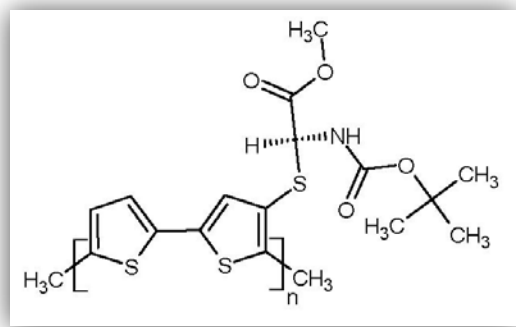


Fig. 3



I am currently studying the effect of an external electric field on the conformational structure of a CPT bearing a chiral protected cysteine aminoacid directly bonded to the thiophene ring (Fig. 4)[7]. The purpose of the research is to better understand the processes behind the formation of the chiral structures in the solid state of the CPTs and to see if it is possible to easily control and tune the properties of the films made with these particular polymers.

Fig. 4

REFERENCES

[1] H. Shirakawa *et al., J. Chem. Soc. Chem. Commun.,* 1977, 578.
[2]R.L. Elsenbaumer *et al., Mol. Cryst. Liq. Cryst.*, 1985, **118**, 111.
[3]M. Lemaire *et al., J. Chem. Soc. Chem. Commun.,* 1988*,* 658.
[4]C.X. Cui, M. Kertesz, *Phys. Rev. B*, 1989, **40,** 9661.
[5]B. Langeveld-Voss *et al., J. Mol. Struct.,* 2000*,* **521,** 285.
[6]M. Andersson *et al., Polym. Commun.*, 1991, **32**, 546.
[7]A. Mucci *et al., Macromol. Rapid Commun.*, 2003, **9**, 547.