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Effect of regioregularity and role of heteroatom on the chiral behavior of oligo(heteroalkylthiophene)s

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ABSTRACT

Novel optically active oligothiophenes bearing electron-donating chiral side chains have been prepared by synthetical methods suitable to achieve regioregular head-to-tail and head-to-head/tail-to-tail derivatives. In particular, the chiral (*S*)-(2-methyl)butyl moiety, was linked at position 3 of the thiophene ring through heteroatoms, such as S or O, to evaluate its effect on the macromolecular aggregation and, consequently, on the chiroptical properties of the material in the solid state. The materials have been fully characterized and investigated by optical and chiroptical methods upon aggregation both from the solution and as cast films. Compared to the related head-to-tail and head-to-head/tail-to-tail poly(3-alkyl)thiophene derivatives, with the same optically active moiety directly linked to the ring and possessing higher polymerization degree, the chiroptical properties of the newly synthesized oligomers were significant, or even better, and provided insight into the role of intra-interchain interactions between the heteroatom and the thienyl sulfur atom.

KEYWORDS

Regioregular oligothiophenes, electron-donating chiral side chains, optical activity, circular dichroism, solvatochromism.

1. Introduction

Chiral conjugated polymers, due to the combination of chirality with electrical conductivity, are potentially useful in many areas such as polarization-sensitive electrooptical devices, polarized photo- and electroluminescence or chiral enantioselective sensors [1,2], and therefore they have long been the object of intense research work.

Chiral polythiophenes, in particular, were initially prepared by chemical or electrochemical oxidation of monomers with a chiral substituent covalently attached to the 3-position of the thiophene ring [2]. The first chiral poly3-alkyl thiophene (P3AT) bearing the optically active moiety in the side chain, obtained by electrochemical polymerization, was investigated since 1988 by Lemaire [3]. In early investigations, however, the optically active derivatives were frequently mixtures of regioisomers involving steric interactions, as in the case of head-to-head (HH) couplings, determining a decrease of conjugation length as well as lower chiroptical properties. A decisive breakthrough in the research was represented by the possibility to prepare regioregular derivatives starting from monomeric 3-alkylthiophene through the development of regiospecific polymerization routes, such as those of Mc Cullough [4] and Chen and Rieke [5], that allowed to achieve the desired regioregular head-to-tail (HT) couplings, giving access to a wide range of chiral P3ATs with markedly enhanced chiroptical properties. Circular dichroism (CD) studies allowed to demonstrate that in HT P3ATs the aggregation involves essentially planar polymer chains that have a helical interchain order, rather than an intramolecular helical conformation. In particular, HT poly{3-[(*S*)-(2-methylbutyl)]thiophene} (PMBT) was deeply investigated and was found to display chiral anisotropy factor *g* values as high as 1.0 10^{-2} at 612 nm [6] and a high degree of crystallinity (65%) [7,8] upon aggregation from the solution by gradual addition of a weak solvent. During the ordering process a kind of sergeants-and-soldiers principle acts, in which the longest chains determine the chirality of the aggregated form, i.e. the aggregation of π-conjugated polymers is a multichain event even in the case of very dilute solutions [9]. Indeed, HT PMBT in the solid state consists mainly of stacks of nearly co-planar extended chains [10].

More recently, we reported the synthesis of the regioregular head-to-head/tail-to-tail (HH/TT) isomeric homologue of PMBT, obtained by polymerization of the bithiophenic monomer 3,3'-bis[(*S*)-(2-methylbutyl)]thiophene [11]. As evidenced by CD, the polymer displays both in solution and in the solid state chain sections having helical structure, as a consequence of steric interactions between side chain alkyl groups, that disfavor coplanarity of thiophene rings and therefore the obtainment of supramolecular chiral aggregates upon aggregation from the solution. For this reason, the introduction of a heteroatom, such as sulfur or oxygen, between the thiophene ring and the chiral alkyl group should provide a reduction of the steric hindrance and promote conformations suitable to produce improved rings coplanarity with a longer extent of conjugation in the main chain, even in HH/TT regioregular polymeric derivatives. In addition, it is widely reported [12-15+X+Y] that the presence of intramolecular interactions between the thienyl sulfur atom and the pendant sulfur or oxygen atom located in the adjacent moiety, appears to provide a strong contribution to planarity of the backboneHowever, if compared to chiral P3ATs, relatively less research concerning optically active 3-sulfanyl or 3-alkoxy thiophene polymeric derivatives can be found in the literature [2]. In particular, the presence of more than one single phase upon aggregation was reported for 4,4'-bis [*(S)*-2-methylbutylsulfanyl] 2,2'-bithiophene polymerized in the presence of ferric chloride, providing the corresponding TT/HH regioregular polythiophene. This resulted optically active when the random and optically inactive monomolecular phase present in good solvents, was first converted into a chiral monomolecular (or loosely aggregated) phase and then into one or more associate phases upon treatment with poor solvent or obtained as cast film [16].

Chiral HT and HH/TT poly(3-alkoxythiophene)s bearing the optically active 3,7-dimethyloctyloxy moiety in the side chain, as spin-coated films or upon aggregation from the solution, exhibited CD spectra characterized by large bisignate Cotton effects and high *g* factors values, originated by the formation of coplanar strands stacked in a chiral way [14,15]. Similar results were also obtained with diblock copolymers constituted by 3-alkyl- and 3-alkoxy polythiophene blocks bearing the (*S*) and/or (*R*)-3,7-dimethyloctyl moiety linked directly to the ring and/or through the oxygen atom, upon addition of poor solvent to the chloroform solution, giving rise to aggregation as helical supramolecular structures again characterized by high *g* values [17].

In this context, we have considered of interest the preparation of optically active oligomeric polythiophene derivatives bearing a chiral 3-sulfanyl or 3-alkoxy moiety in the side chain, and possessing known regioregularity, in order to investigate and assess by chiroptical methods their behavior upon aggregation from the solution and in the solid state as cast films. The same (*S*)-(2-methyl)butyl moiety was used as the chiral component, with the aim to obtain results comparable to those reported for the above mentioned optically active P3ATs [6,11] and better elucidate the effect of the sulfur and oxygen spacers on aggregation process and functional properties. The synthetic routes to monomers **TSR*Br$_2$**, **TOR*Br$_2$** and **T2SR***, **T2OR*** as precursors to the derivatives **PTSR***, **PTOR*** and **PT2SR***, **PT2OR***, respectively, are reported in Scheme 1.

2. Experimental

2.1. Materials

All commercial reagents and solvents were purchased from Sigma-Aldrich and used as received unless otherwise stated. *N*-Bromosuccinimide (NBS) was recrystallized from hot water and pyridine (Fluka) was freshly distilled before use. Anhydrous solvents were prepared following literature procedures [18] and stored over molecular sieves. All manipulations involving air- or moisture-sensitive reagents were performed under nitrogen in dried glassware.

2.2. Methods and Characterizations

Microwave (MW) irradiation was performed in a Milestone Microsynth Labstation operating at 2450 MHz and equipped with pressure and temperature sensors.

The ^{1}H-NMR spectra were recorded with a Varian Mercury 400 (400 MHz) spectrometer at room temperature in $CDCl_3$ solutions, using tetramethylsilane as internal reference. Chemical shifts are given in ppm.

Molecular mass and dispersity index of the oligomers were determined at room temperature by gel permeation chromatography (GPC) in THF solution on a HPLC Lab Flow 2000 apparatus equipped with a Rheodyne 7725i injector, a Phenomenex Phenogel mixed bed 5μ MXL type column and an RI K-2301 KNAUER detector. Calibration curves were obtained by using monodisperse polystyrene standards. Before measuring, the materials were dissolved in THF (ca. 1 mg/ml) and filtered over a 0.2 micron pore size filter.

The decomposition temperature (T_d) of the oligomers was determined in the 20÷800°C temperature range on a TGA TA Instruments Q600 apparatus operating at a heating rate of 20°C/min under nitrogen atmosphere. A DSC TA Instruments Q2000 operating under nitrogen in the –50÷200°C temperature range at a heating rate of 10°C/min was used to determine the glass transition temperature (T_g) of the oligomers.

UV-Vis and photoluminescence (PL) spectra were carried out on a Perkin Elmer Lambda 20 and Perkin Elmer LS50B spectrophotometer, respectively, at 25°C on $10^{-3}/10^{-4}$ M $CHCl_3$ solutions in 1 cm quartz cells. Thin film measurements were made on samples cast from chlorobenzene solutions on quartz slides by drop-casting.

IR spectra were carried out on Ge disks using a Perkin-Elmer 1750 or a Spectrum One spectrophotometer.

HRMS (ESI) spectra were recorded on a Waters XEVO Q-TOF instrument.

Optical activities were measured on $CHCl_3$ solutions with a Perkin Elmer 341 digital polarimeter, equipped with a Toshiba sodium bulb, using a cell path length of 0.1 cm. Specific rotation values at the sodium D line are expressed as degree dm^{-1} g^{-1} dL.

The circular dichroism (CD) spectra were recorded at room temperature on $CHCl_3$ or $CHCl_3/CH_3CN$ solutions by a Jasco 810 dichrograph; $\Delta\varepsilon$ values, expressed as L mol^{-1} cm^{-1}, were calculated by the following equation: $\Delta\varepsilon = [\Theta]/3300$, where the molar ellipticity Θ is in degree cm^2 $dmol^{-1}$.

2.3. Synthetic methods

2.3.1. (+)-2,5-Dibromo-3-[(S)-(2-methylbutyl)sulphanyl]thiophene (**TSR*Br₂**)

To a two-necked flask containing a solution of **TSR*** (0.246 g, 1.3 mmol) in 7.0 mL of CH_2Cl_2, NBS (0.518 g, 2.9 mmol) was added portion wise under stirring and protection from light. The mixture was heated at 45°C and maintained at this temperature for 24h. After cooling and washing of the organic layer with water, the crude product was purified by column chromatography on silica gel with cyclohexane to obtain 0.419 g (92% yield, $[\alpha]_D^{25}$=+14.1 c=0.5 in $CHCl_3$) of **TSR*Br$_2$** as a colorless oil.

HR-MS ESI + $[M+1]^+$ = found 342.8823, state formula $C_9H_{13}Br_2S_2$, theoretical 342.8825.

^{1}H-NMR: δ 6.90 (s, 1H, 4-H), 2.83 (dd, 1H, CH_αS), 2.67 (dd, 1H, CH_βS), 1.62-1.46 (m, 2H, C*H*CH_3 and C$H_\alpha$$CH_3$), 1.31-1.19 (m, 1H, C$H_\beta$$CH_3$), 1.01 (d, 3H, CHC$H_3$), 0.89 (t, 3H, CH_2CH_3).

2.3.2. 2-Bromo-3-[(S)-(2-methylbutyl)sulphanyl]thiophene (**TSR*Br**)

A solution of NBS (0.497 g, 2.8 mmol) in 4.0 mL of DMF was added dropwise at 0°C in 1h, under stirring and in the dark, to a solution of **TSR*** (0.520 g, 2.8 mmol) in 4.0 mL of DMF. The reaction mixture was stirred for 24h protected from the light, then diluted with water and finally extracted with Et_2O. After drying over Na_2SO_4 and solvent evaporation at reduced pressure, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate 19:1 v/v as eluent, to give 0.723 g (98% yield) of **TSR*Br** as a colorless liquid.

^{1}H-NMR: δ 7.24 (d, 1H, 5-H), 6.92 (d, 1H, 4-H), 2.87 (dd, 1H, CH_αS), 2.68 (dd, 1H, CH_βS), 1.60-1.42 (m, 2H, C*H*CH_3 and C$H_\alpha$$CH_3$), 1.32-1.20 (m, 1H, C$H_\beta$$CH_3$), 1.00 (d, 3H, CHC$H_3$), 0.89 (t, 3H, CH_2CH_3).

2.3.3. (+)-3,3'-Bis[(S)-(2-methylbutyl)sulphanyl]-2,2'-bithiophene (**T2SR***)

A mixture of **TSR*Br** (0.342 g, 1.3 mmol), bis(pinacolato)diboron (0.197 g, 0.8 mmol), Pd(dppf)Cl_2 (0.053 g, 5% mol) and $NaHCO_3$ (0.325 g, 3.9 mmol) in THF/water 2:1 (3.0 mL) was irradiated by MW at 90°C for 40 min. The reaction mixture was then cooled to room temperature, diluted with dichloromethane and washed with water; the solvent was evaporated under reduced pressure and the product purified by flash chromatography with cyclohexane as eluent to afford 0.433 g (90% yield, $[\alpha]_D^{25}$=+17.3 c=0.3 in $CHCl_3$) of **T2SR*** as a yellowish oil.

HR-MS ESI + $[M+1]^+$ = found 371.0993, state formula $C_{18}H_{27}S_4$, theoretical 371.0995.

^{1}H-NMR: δ 7.36 (d, 2H, 5-H), 7.08 (d, 2H, 4-H), 2.80 (dd, 2H, CH_αS), 2.62 (dd, 2H, CH_βS), 1.60-1.38 (m, 4H, C*H*CH_3 and C$H_\alpha$$CH_3$), 1.24-1.10 (m, 2H, C$H_\beta$$CH_3$), 0.92 (d, 6H, CHC$H_3$), 0.83 (t, 6H, CH_2CH_3).

2.3.4. *(+)-3-[(S)-(2-Methylbutoxy)]thiophene* (**TOR***)

To a solution of 3-methoxythiophene (Alfa Aesar) (0.760 g, 6.7 mmol) in 8.4 mL of toluene, (*S*)-(–)-2-methyl-1-butanol (1.4 mL, 13.3 mmol) and *p*-toluenesulfonic acid monohydrate (0.189 g, 1.0 mmol) were sequentially added under stirring and inert atmosphere. After 24h at reflux, the mixture was cooled to room temperature, poured into 100 mL of water and then extracted with CH_2Cl_2. The organic phase was washed with water, dried over Na_2SO_4 and concentrated by evaporation under reduced pressure. The crude product was purified by column chromatography on silica gel with cyclohexane/CH_2Cl_2 80:20 v/v as eluent to afford 0.764 g (67% yield, $[\alpha]_D^{25}$=+8.7 c=0.4 in $CHCl_3$) of **TOR*** as a yellow liquid.

HR-MS ESI + $[M+1]^+$ = found 171.0842, state formula $C_9H_{15}OS$ theoretical 171.0843.

^{1}H-NMR: δ 7.15 (dd, 1H, 5-H), 6.76 (dd, 1H, 4-H), 6.22 (dd, 1H, 2-H), 3.81 (dd, 1H, CH_αO), 3.73 (dd, 1H, CH_βO), 1.94-1.88 (m, 1H, C*H*CH_3), 1.62-1.50 (m, 1H, C$H_\alpha$$CH_3$), 1.36-1.20 (m, 1H, C$H_\beta$$CH_3$), 1.01 (d, 3H, CHC$H_3$), 0.94 (t, 3H, CH_2CH_3).

2.3.5. *(+)-2,5-Dibromo-3-[(S)-2-methylbutoxy]thiophene* (**TOR*Br2**)

The same procedure described for **TSR*Br2** was followed starting from **TOR*** (0.199 g, 1.2 mmol) and NBS (0.464 g, 2.6 mmol) in CH_2Cl_2 to give 0.328 g (54% yield, $[\alpha]_D^{25}$=+4.0 c=0.6 in $CHCl_3$) of pure **TOR*Br2** as a colorless oil.

HR-MS ESI + $[M+1]^+$ = found 326.9052, state formula $C_9H_{13}Br_2OS$, theoretical 326.9053.

^{1}H-NMR: δ 6.76 (s, 1H, 4-H), 3.85 (dd, 1H, CH_αO), 3.77 (dd, 1H, CH_βO), 1.90-1.76 (m, 1H, C*H*CH_3), 1.60-1.48 (m, 1H, C$H_\alpha$$CH_3$), 1.32-1.18 (m, 1H, C$H_\beta$$CH_3$), 1.01 (d, 3H, C$H_3$CH), 0.94 (t, 3H, C$H_3$$CH_2$).

2.3.6. *2-Bromo-3-[(S)-2-methylbutoxy]thiophene* (**TOR*Br**)

The same procedure described for **TSR*Br** was followed starting from **TOR*** (0.565 g, 3.3 mmol) and NBS (0.591 g, 3.3 mmol) in DMF obtaining 0.740 g (90% yield) of pure **TOR*Br** as a light brown oil.

HR-MS ESI + $[M+1]^+$ = found 248.9947, state formula $C_9H_{14}BrOS$, theoretical 248.9948.

^{1}H-NMR: δ 7.18 (d, 1H, 5-H), 6.73 (d, 1H, 4-H), 3.89 (dd, 1H, CH_αO), 3.81 (dd, 1H, CH_βO), 1.88-1.78 (m, 1H, C*H*CH_3), 1.62-1.50 (m, 1H, C$H_\alpha CH_3$), 1.32-1.20 (m, 1H, C$H_\beta CH_3$), 1.01 (d, 3H, CH_3CH), 0.95 (t, 3H, CH_3CH_2).

2.3.7. *(+)-3,3'-Bis[(S)-(2-methylbutoxy)-2,2'-bithiophene* (**T2OR***)

A solution of *n*-butyl lithium in hexane 2.5 M (0.4 mL, 1.0 mmol) was added dropwise under inert atmosphere at –70°C to a solution of **TOR*Br** (0.215 g, 0.9 mmol) in dry THF (3 mL). After 30 min $Fe(acac)_3$ (Alfa Aesar) (0.494 g, 1.4 mmol) was added to the reaction mixture and the mixture allowed to reach room temperature under stirring overnight before quenching with water. The aqueous phase was extracted with Et_2O and the combined organic phases washed with brine. After drying over Na_2SO_4 and removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica with hexane as eluent to afford 0.050 g (16% yield, $[\alpha]_D^{25}$=42.7 c=0.4 in $CHCl_3$) of **T2OR*** as a dark green oil constituted by a 60:40 mixture of HH and HT regioisomers.

HR-MS ESI + $[M+Na]^+$ = found 361.1270, state formula $C_{18}H_{26}NaO_2S_2$, theoretical 361.1271.

^{1}H-NMR: δ 7.07 (d, 2H, 5-H and 5'-H, **HH**), 7.02 (d, 1H, 5-H, **HT**), 6.88 (d, 1H, 3'-H, **HT**), 6.83 (d, 2H, 4-H and 4'-H, **HH**), 6.81 (d, 1H, 4-H, **HT**), 6.10 (d, 1H, 5'-H, **HT**), 4.01 and 3.94 (m, 4H, 3- and 3'-OCH_α and -OCH_β, **HH**), 4.01 and 3.94 (m, 2H, 3-OCH_α and 3-OCH_β, **HT**), 3.81 and 3.73 (m, 2H, 4'-OCH_α and 4'-OCH_β, **HT**), 2.00-1.80 (m, 4H, C*H*CH_3), 1.70-1.50 (m, 4H, C$H_\alpha CH_3$), 1.44-1.18 (m, 4H, C$H_\beta CH_3$), 1.12-1.06 (m, 12H, CHCH_3), 1.02-0.90 (m, 12H, CH_2CH_3).

2.3.8. *Oligo{3-[(S)-(2-methylbutyl)sulphanyl]thiophene}* (**PTSR***)

To a three-necked flask containing **TSR*Br$_2$** (0.313 g, 0.9 mmol), dry 2-methyltetrahydrofuran (5 mL) and 2M hexylmagnesium bromide in Et_2O (0.5 mL, 1.0 mmol) were sequentially added under stirring and nitrogen atmosphere. The solution was heated to reflux in the dark for 1h. Then, Ni(dppp)Cl_2 (0.024 g, 5 mol%) was added and the mixture left under stirring and reflux overnight. After cooling, chloroform was added and the mixture washed with water, followed by drying over Na_2SO_4. The organic phase was concentrated to small volume and finally treated with hot MeOH to afford 0.121 g (73% yield) of **PTSR*** as a dark red solid.

^{1}H-NMR: δ 7.38 (s, 1H, backbone 4-H), 3.00-2.60 (m, 2H, C*H$_2$*S), 1.80-1.15 (m, 3H, CH_3C*H* and CH_3C*H$_2$*), 1.10-0.95 (m, 3H, C*H$_3$*CH), 0.95-0.78 (t, 3H, C*H$_3$*CH_2).

2.3.9. *Oligo{3-[(S)-(2-methylbutoxy)]thiophene}* (**PTOR***)

To a three-necked flask containing **TOR*Br$_2$** (0.296 g, 0.9 mmol), dry THF (5 mL) and 2M hexylmagnesium bromide in Et_2O (0.5 mL, 1.0 mmol) were sequentially added under stirring and nitrogen atmosphere. The solution was heated to reflux in the dark for 1h. Then, Ni(dppp)Cl_2 (0.024 g, 5 mol%) was added and the mixture left under stirring and reflux for 1h. After cooling, chloroform was added and the mixture washed with water, followed by drying over Na_2SO_4. The organic phase was concentrated to small volume and finally treated with hot MeOH to afford 0.079 g (53% yield) of pure **PTOR*** as a dark blue powder.

^{1}H-NMR: δ 7.02-6.80 (bm, 1H, backbone 4-H), 4.10-3.90 (m, 2H, C*H$_2$*O), 2.08-1.90 (m, 1H, CH_3C*H*), 1.78-0.86 (m, 8H, C*H$_3$*CH, C*H$_3$*CH_2 and CH_3C*H$_2$*).

2.3.10. *Oligo{3,3'-bis[(S)-(2-methylbutyl)sulphanyl]-2,2'-bithiophene}* (**PT2SR***)

To a solution of **T2SR*** (0.075g, 0.2 mmol) in anhydrous $CHCl_3$ (8.1 mL), $FeCl_3$ (0.131 g, 0.8 mmol) was added under a weak stream of nitrogen at room temperature. The suspension was left under stirring for 24h, turning from greenish to dark blue color. Then, 50 mL of THF and 100 mL of $CHCl_3$ were added, the mixture washed several times with 2% v/v aqueous HCl up to complete elimination of the iron (III) ion (negative essay with NH_4SCN) and finally with water to neutrality. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure and finally treated with MeOH to afford 0.071 g (97% yield) of **PT2SR*** as a brownish waxy solid.

^{1}H-NMR: δ 7.38 (d, 1H, terminal 5-H), 7.22-7.12 (ms, 2H, backbone 4-H and 4'-H), 7.08 (d, 1H, terminal 4-H), 2.96-2.82 (m, 2H, C*H$_α$*S), 2.76-2.62 (m, 2H, C*H$_β$*S), 1.70-1.40 (m, 2H, CH_3C*H*), 1.34-1.10 (m, 2H, C*H$_α$*CH_3), 1.04-0.98 (m, 2H, C*H$_β$*CH_3), 0.98-0.92 (m, 6H, C*H$_3$*CH), 0.92-0.78 (m, 6H, CH_2C*H$_3$*).

2.3.11. Oligo{3,3'-bis[(S)-(2-methylbutoxy)-2,2'-bithiophene} (**PT2OR***)

The same procedure described for **PT2SR*** was followed starting from the HH and HT mixture of regioisomers labeled as **T2OR*** (0.050 g, 0.1 mmol) and $FeCl_3$ (0.065 g, 0.4 mmol) in $CHCl_3$ to obtain 0.032 g (95% yield) of **PT2OR*** as a black solid.

^{1}H-NMR: δ 7.18-7.08 (m, 2H, backbone 4-H and 3'-H, **HH**), 7.08-6.92 and 6.92-6.68 (m, 2H, backbone 4-H and 3'-H, **HH** and backbone 4-H and 4'-H, **HT**), 4.2-3.6 (m, 4H, OCH_2), 2.0-1.8 (m, 2H, $CHCH_3$), 1.7-1.5 (m, 2H, $CH_\alpha CH_3$), 1.4-1.2 (m, 2H, $CH_\beta CH_3$), 1.1-1.0 (m, 6H, $CHCH_3$), 1.0-0.9 (m, 6H, CH_2CH_3).

3. Results and discussion

3.1. Synthesis

The mono- and bithiophene monomers **TSR*Br₂**, **TOR*Br₂** and **T2SR***, **T2OR*** (Scheme 1) used for the preparation of the corresponding oligomeric derivatives were obtained respectively from the starting materials **TSR*** and **TOR***.

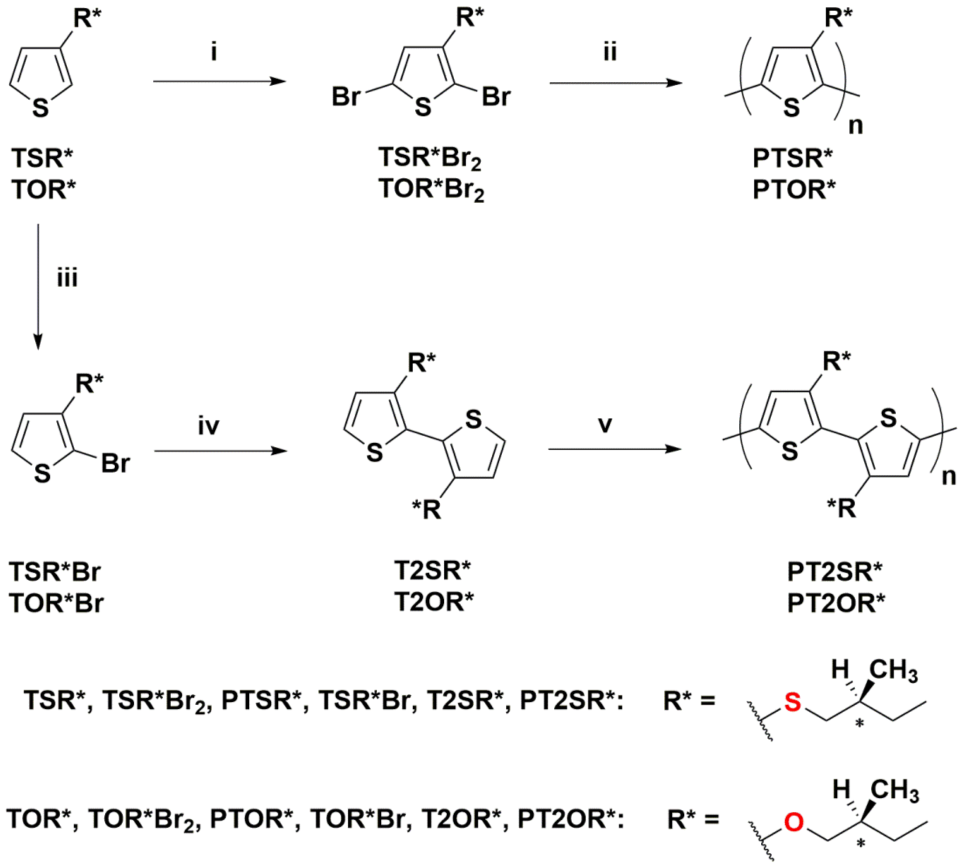
The synthesis of (+)-3-[(*S*)-(2-methylbutyl)sulphanyl]thiophene (**TSR***) [19] was carried out following the method reported for the related 3-S-hexyl thiophene [12] by nucleophilic reaction of 3-mercaptothiophene [12] with (+)-(*S*)-1-bromo-2-methylbutane, prepared in turn by reaction with LiBr [20] of the *p*-toluensulfonate ester of enantiomerically pure (–)-(*S*)-2-methyl-1-butanol, obtained through a modified literature procedure [21] (see SI for details).

(+)-3-[(*S*)-(2-Methylbutoxy)]thiophene (**TOR***) was obtained by transetherification of commercial 3-methoxythiophene with (–)-(*S*)-2-methyl-1-butanol, according to the procedure reported by Xu for the related 3-O-hexyl thiophene derivative [22].

Treatment of **TSR*** and **TOR*** with N-bromosuccinimide according to established procedures [23,24] allowed to obtain the related 2,5-dibromo derivatives **TSR*Br$_2$** (*dextrorotatory* enantiomeric isomer of the previously reported compound [25]) and **TOR*Br$_2$**, as well as the 2-bromo derivatives **TSR*Br** [19] and **TOR*Br**, subsequently used for the preparation of the HH bithiophene monomers **T2SR*** and **T2OR***.

In particular, (+)-3,3'-bis[(*S*)-(2-methylbutyl)sulphanyl]-2,2'-bithiophene **T2SR*** was obtained in high yield following the synthetic protocol based on microwave-assisted Suzuki-Miyaura reaction recently adopted for similar, optically inactive, derivatives [26]. By contrast, the preparation of the related oxyalkyl disubstituted bithiophene monomer **T2OR*** through this route was unsatisfactory. Moreover, despite the expected higher reactivity due to the presence of oxygen directly connected to the thiophene ring, the synthesis by oxidative coupling with BuLi/$CuCl_2$ [26] was also inconclusive. However, (+)-3,3'-bis[(*S*)-(2-methylbutoxy)-2,2'-bithiophene **T2OR*** could be obtained from **TOR*Br** with BuLi in the presence of $Fe(acac)_3$ according to the method adopted for similar derivatives [27], although mixed with 40% of the HT regioisomer, as established by ^{1}H-NMR spectroscopy (see Experimental and Figure S2B).

Scheme 1. Synthetic route to optically active heteroalkyl thiophene monomers and oligomers[a].



[a]Reagents and conditions: (i) 2 equiv of NBS, CH_2Cl_2, reflux; (ii) 1 equiv of hexylmagnesiumbromide in Et_2O, Ni(dppp)Cl_2, 2-MeTHF, reflux; (iii) 1 equiv of NBS, DMF, 0°C; (iv) 0.5 equiv of bis(pinacolato)diboron, Pd(dppf)Cl_2, $NaHCO_3$, THF/H_2O 2/1, MW, 90°C for **T2SR***; *n*-butyllithium in hexane, $Fe(acac)_3$, THF for **T2OR***; (v) 4 equiv of $FeCl_3$, $CHCl_3$ room temp.

The optically active mono- and bithiophene monomers were then polymerized, respectively, by regiospecific organometallic coupling to the corresponding HT derivatives and by simple oxidative coupling with $FeCl_3$, leading to HH/TT derivatives in consequence of the chemical equivalence of the bithiophenic reactive sites.

The GRIM (Grignard Metathesis) procedure [28,29], involving a magnesium/bromine exchange after the initial treatment with a Grignard reagent, was adopted for the polymerization of **TSR*Br$_2$** and **TOR*Br$_2$**, in order to obtain highly regioregular HT-derivatives, due to the selectivity of the sterically hindered catalyst Ni(dppp)Cl_2 that does not promote HH or TT couplings. However, similarly to what obtained by Goldoni et al. [24] in the polymerization of 3-(butylthio)thiophene, in our case the polymerization of **TSR*Br$_2$**, carried out under the same reaction conditions, gave a low molecular mass product probably due to unfavorable interactions between the catalyst and the thioethereal moiety. Consequently, the polymerization of **TOR*Br$_2$** was performed with the aim ~~in order~~ to ~~have~~ obtain a macromolecular derivative with comparable polymerization degree.

The polymerization of (+)-3,3'-bis[(*S*)-(2-methylbutyl)sulphanyl]-2,2'-bithiophene (**T2SR***) and (+)-3,3'-bis[(*S*)-(2-methylbutoxy)-2,2'-bithiophene (**T2OR***) to the corresponding **PT2SR*** and **PT2OR*** oligomeric derivatives was carried out following the simple and well established oxidative coupling with iron(III) trichloride. The symmetrical structure and chemical equivalence of the coupling positions in the HH bithiophenic monomer allows to obtain a completely regioregular derivative that displays only HH/TT junctions between the thiophene rings, despite the use of a non regiospecific method. **T2OR***, actually a mixture of the HH and HT regioisomers (60:40 molar ratio), was anyhow submitted to oxidative coupling with $FeCl_3$, in order to obtain a product (**PT2OR***) at least partially comparable to the related sulphanyl derivative **PT2SR***.

All the macromolecular samples were characterized for molecular mass, thermal and spectral properties. As reported in Table 1, the average polymerization degrees of **PTSR*** and **PTOR*** resulted of comparable magnitude. The average molecular mass of **PT2SR*** appears significantly lower with respect to the HT derivative, being substantially constituted by bithiophenic tetramers, as confirmed also by the ^{1}H-NMR spectrum (see below). The related polymeric derivative with TT/HH regioregularity, obtained under the same conditions as **PT2SR*** by polymerization of the TT monomer (+)-4,4'-bis[(*S*)-(2-methylbutyl)sulphanyl]-2,2'-bithiophene [16], displayed a M_n value of 17000 g/mol reasonably in consequence of deeper fractionation of the crude polymeric product with respect to **PT2SR***, as inferred by the 59% reaction yield (*vs.* our 97%) reported in the above paper. By contrast, **PT2OR***, obtained with yield similar to **PT2SR***, displayed higher DP value, which is to be related to a positive role towards polymerization played by the alkoxy group, although the presence of a fraction with lower molecular weight, i.e. approximately bithiophenic dimers, was also detected by GPC.

Table 1. Yields and characterization data of macromolecular derivatives.

Sample	*Yield (%)*[a]	*M_n (g/mol)*[b]	*Đ*[c]	*DP*[d]	*T_g (°C)*[e]	*T_d (°C)*[f]
PTSR*	73	2600	1.8	14	0	288
PTOR*	53	3600	2.0	21	5	263
PT2SR*	97	1500	1.2	8	–26	139
PT2OR*	95	700, 3400	1.1, 1.3	4; 20	–16	114

[a] Weight of product/weight monomer x 100; [b] Number average molar mass determined by GPC in THF; [c] Dispersity; [d] Average polymerization degree expressed as monothiophenic repeating units; [e] Glass transition temperature determined by DSC (second heating cycle); [f] Decomposition temperature determined by TGA.

3.2. IR and ^{1}H-NMR characterizations

The IR spectrum of **PTSR*** displays the expected absorptions characteristic of 2,5-coupled 3-substituted polythiophenes: aromatic C-H stretching at 3071 cm^{-1} and one out-of-plane deformation of aromatic C-H at 803 cm^{-1} due to the trisubstituted ring. The alkyl chain gives stretching vibrations in the region 2963-2854 cm^{-1} and deformation modes below 1475 cm^{-1}.

In **PT2SR*** the alkylsulfanyl chain gives rise to C-H stretching vibrations in the region 2963-2846 cm^{-1} and to deformation modes around 1478, 1458, 1434 (S-CH_2) and 1378 cm^{-1}. The aromatic C-H stretching and out-of-plane deformation are found at 3079 and 814 cm^{-1}, respectively.

The alkoxy pendants of **PTOR*** give C-H stretching at 2959-2850 cm^{-1} (CH_2 and CH_3). Ring vibrational modes are seen at 1523, 1446 and 1350 cm^{-1}. The band at 1068 cm^{-1} is assigned to C(ring)-O-C stretch. The vibrational band at 802 cm^{-1} is attributable to C-H_β out-of-plane deformation mode of thiophene rings. Similarly, **PT2OR*** gives the corresponding absorptions at 2966-2850, 1523, 1398, 1353 cm^{-1}. The C(ring)-O-C stretch. appears at 1064 cm^{-1} and the C-H_β out-of-plane deformation mode of thiophene rings at 802 cm^{-1}.

The chemical structure and regioregularity degree of **PTSR*** and **PTOR*** were evaluated by ^{1}H-NMR spectroscopy in $CDCl_3$. The spectrum of **PTSR*** (Figure S3A) displays a major singlet at 7.38 ppm that is assigned to 4-H of the backbone, in accordance to the chem. shift value reported for HT poly(3-butylsulphanylthiophene) obtained by similar regiospecific Kobayashi procedure [24], along with other low intensity resonances, attributed to the terminal protons of oligomeric chains, and to minor HH/TT connections at around 7.2 ppm, lowering the HT regioregularity degree to about the 90%, as measured by ^{1}H-NMR. By contrast, the spectrum of **PTOR*** displays a broad resonance of the backbone 4-H proton at 7.02-6.80 ppm (Figure S3B), upfielded with respect to the corresponding proton of **PTSR***, as a consequence of increased electron density induced by the oxygen atom directly linked to thiophene ring. No accurate evaluation of the regioregularity degree can be made for **PTOR***, as the resonances of the 4-H proton related to the four possible triad sequences (HT/HT, TT/HT, HT/HH and TT/HH), reported as ranging in the intervals 7.04-6.84 ppm [30] or 6.95-6.83 ppm [31] for various poly(3-alkoxythiophene)s obtained under non regiospecific conditions, are clearly overlapped. However, as the maximum intensity of the 4-H resonance of **PTOR*** is centered at 6.90 ppm, very close to the 6.91 ppm value reported for highly regioregular HT linkage in poly(3-decyloxythiophene) obtained by the same GRIM method [32], we can conclude that **PTOR*** is characterized by highly predominant HT regioregularity.

The expected structure for **PT2SR*** is confirmed by the ^{1}H-NMR spectrum (Figure S4A) that displays at 7.2 ppm the resonance of the 4-H proton of the backbone, as well as the presence of intense signals related to terminal groups, as evidenced by the GPC measurements indicating a low molecular mass of this sample. As expected, the spectrum of **PT2SR*** appears identical to that reported for the above mentioned poly{4,4'-bis[(*S*)-(2-methylbutyl)sulphanyl]-2,2'-bithiophene} possessing TT/HH regioregularity [16]. On the other hand, the clear presence of signals related to the 4-H and 5-H hydrogens of terminal thiophene rings, in addition to the low molecular weight value determined by GPC (Table 1), confirms that the polymerization of **T2SR*** actually occurred to a limited extent, yielding a tetrameric derivative constituted by bithiophenic co-units.

The ^{1}H-NMR spectrum of **PT2OR*** (Figure S4B) confirms the obtainment of a material having a substantially regiorandom structure, with the presence of three broad signals centered at 7.13, 6.97 (main) and 6.83 ppm, related respectively to the presence of prevalently HH/TT oligomers and to HH/TT/HT and HT/HT junctions [30,31,33].

3.3. Thermal properties

As shown in Table 1, both **PTSR*** and **PTOR*** display similar thermal behavior, with a slightly higher value of the glass transition temperature and a lower decomposition temperature for **PTOR*** with respect to **PTSR***. The values for the glass transition temperature of the bithiophene derivatives **PT2SR*** and **PT2OR*** appear lower with respect to their counterparts **PTSR*** and

PTOR*, attributable to their lower molecular mass and reduced planarity of the backbone caused by the presence of HH junctions. The alkoxy derivatives **PTOR*** and **PT2OR*** exhibit a slightly higher rigidity than **PTSR*** and **PT2SR***, respectively, ascribable to larger conjugation extent in the backbone induced by the electron donor alkoxy group that increases the polarity of the aromatic system, favoring a relatively more compact arrangement of the macromolecules in the solid state.

Both **PT2SR*** and **PT2OR*** show remarkably lower thermal stability with respect to the related HT regioregular samples (Figure S5), to be again attributed to higher flexibility of the main chain, the oxygen containing derivatives **PTOR*** and **PT2OR*** resulting more unstable upon heating with respect to **PTSR*** and **PT2SR***, respectively.

The absence of endothermic peaks related to melting, and the presence of glass transitions only in the DSC thermograms (Figure S6), suggests an overall amorphous character in the solid state of all the oligomeric derivatives.

3.4. Optical properties

The UV-Vis spectra of the monomers (Table 2 and Figure 1A) display, as expected, a remarkable red shift of the absorption maxima of the alkoxy derivatives with respect to the related sulphanyl compounds, this effect being more evident in the bithiophene compounds (52 nm *vs.* 35 nm), and is attributed to higher coplanarity between the thiophene rings induced by the O atom as compared to S. Accordingly, the aromatic conjugation originated by connecting two thiophene rings in the bithiophenic monomers, is higher in the alkoxy derivatives (28 nm when passing from **TOR*** to **T2OR***) with respect to the sulphanyl derivatives (11 nm when passing from **TSR*** to **T2SR***). However, it has to be noted that a significant electron donating ability is also displayed by the sulphanyl monomers compared to the related 3-alkylthiophene and 3,3’-dialkyl bithiophene derivatives, exhibiting maximum absorptions at lower wavelengths, 241 nm [34] and 248 nm [11], respectively.

The UV-Vis spectra of the macromolecular derivatives in solution (Table 2 and Figure 1B) show absorption maxima related to the π-π* electronic transition of the backbone aromatic system. The HT regioregular derivatives confirm the electron-releasing mesomeric effect of oxygen directly linked to the thiophene ring, displaying a stronger red shift of the maximum wavelength passing from **TOR*** to **PTOR*** (274 nm) with respect to the shift shown passing from **TSR*** to **PTSR*** (218 nm). In addition to its lower polymerization degree, it is possible that steric effects of the bulky thioalkyl moiety distorting the main chain are also contributing to reduce the bathochromic shift in **PTSR*** with respect to **PTOR*** [35]. The maximum absorption wavelengths of **PTOR*** (574 nm in solution, 580 nm as film), appear blue shifted compared to those observed for the optically active HT poly(3-alkoxythiophene) containing the 3,7-dimethyloctyloxy moiety and characterized by a much higher PD value of 57 (602 nm in solution, 635 nm as film) [14]. However, the absorption maxima in $CHCl_3$ solution of HT poly(3-hexyloxythiophene) (580 nm) [35] and HT poly(3-decyloxythiophene) (565 nm) [32] having also high PD (71 and 45, respectively), are of similar magnitude to that of **PTOR*** thus suggesting high regioregularity and sufficiently extended aromatic conjugation in **PTOR*** despite its oligomeric structure. The same consideration also holds for **PTSR***, absorbing in $CHCl_3$ at a wavelength (483 nm) not much different from the absorption maximum of HT poly[(3-butylthio)thiophene] (502 nm) [25] and at similar wavelength as HT poly[(3-hexylthio)thiophene] (485 nm) [35], despite its much lower polymerization degree (14 *vs.* 22 and 76, respectively).

Both the λ_{max} values of the bithiophene derivatives **PT2SR*** and **PT2OR*** in $CHCl_3$ solution are blue-shifted compared to **PTSR*** and **PTOR*** as a consequence of their lower polymerization degree and backbone configuration, which is expected to disfavor coplanar arrangements of the conjugated aromatic rings. As expected, the λ_{max} value of **PT2SR*** appears lower than the value (469 nm) reported [16] for the polymeric TT/HH derivative poly{4,4'-bis[(*S*)-(2-methylbutyl)sulphanyl]-2,2'-bithiophene} but not much dissimilar from the chemically pure oligomer HH/TT octithiophene bearing the side chain thiohexyl moiety (434 nm in CH_2Cl_2) [20].

In addition to a weak absorption at 345 nm, ascribable to the presence of a shorter oligomeric fraction, as suggested by GPC, it is noteworthy that the λ_{max} (522 nm) of **PT2OR*** is strongly red-shifted compared to both the derivatives **PTSR*** and **PT2SR***. Indeed, despite **PT2OR*** is actually a mixture of oligomers with an overall regiorandom structure, as suggested by its lower maximum absorption wavelength with respect to regioregular HH/TT poly(3,3'-dibutoxy-2,2'-bithiophene) and TT/HH poly(4,4'-dibutoxy-2,2'-bithiophene) with similar polymerization degrees (545 and 574 nm, respectively) [33], as well as to the optically active HH/TT poly[3,3'-bis(3,7-dimethyloctyloxy)-2,2'-bithiophene] (583 nm) [15] and other regioregular mono-alkoxy substituted polythiophenes (583-588 nm) [31], it is confirmed that the oxygen atom promotes a remarkable electron delocalization, even in the absence of prevalent regioregularity and high polymerization degree. It is again to be noted that the maximum absorption values in solution of all the sulphanyl and alkoxy oligomeric derivatives are in any case red shifted with respect to the related maxima of HT (431 nm) [6] and TT/HH P3ATs (392 nm) [11] materials bearing the same chiral moiety in the side chain.

Table 2. Maximum absorption (λ_{max}) of monomers and absorption/emission (λ_{em}) wavelengths (nm) of oligomers in $CHCl_3$ solution and as films obtained from chlorobenzene solution.

		Solution				*Film*
Monomer	*λ_{max} (nm)*	*Oligomer*	*λ_{max} (nm)*	*λ_{em} (nm)*	*Stokes shifts (nm, cm^{-1})*	*λ_{max} (nm)*
TSR*	265	**PTSR***	483	601	118, 4579	509
TOR*	300	**PTOR***	574	665	91, 2250	580
T2SR*	276	**PT2SR***	416	582	166, 7333	469
T2OR*	328	**PT2OR***	522	612	90, 2834	529

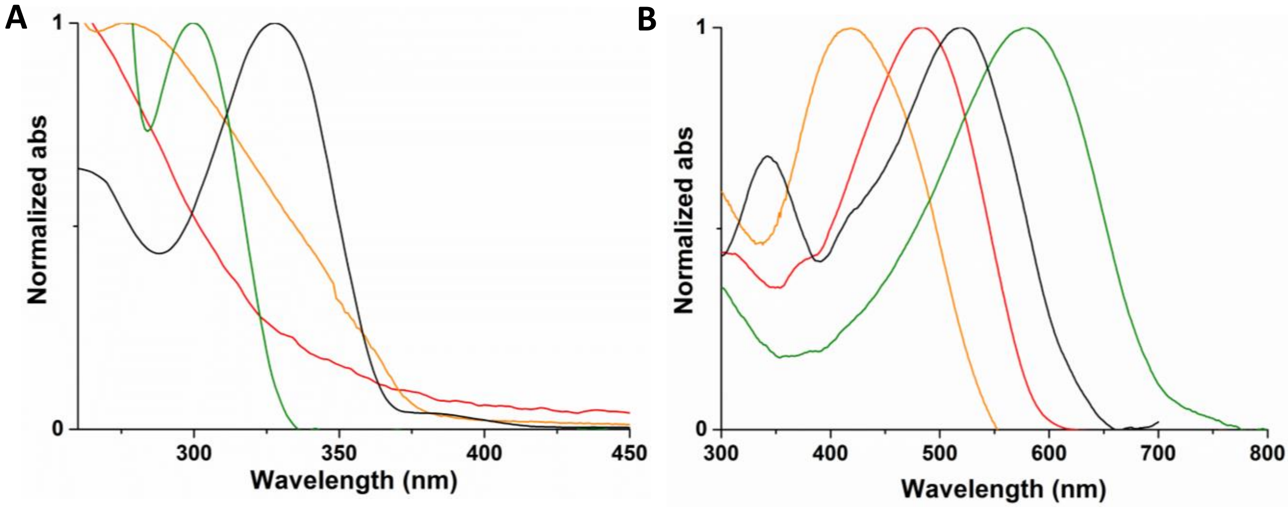


Figure 1. Normalized absorption spectra in $CHCl_3$ of monomers (A) and oligomers (B) (red line: **TSR*** and **PTSR***; green line: **TOR*** and **PTOR***; orange line: **T2SR*** and **PT2SR***; black line: **T2OR*** and **PT2OR***).

Photoluminescence (PL) spectra carried out on the macromolecular derivatives (Table 2 and Figure S7B) allowed to assess lower Stokes shift values of the alkoxy derivatives with respect to the sulphanyl derivatives, indicative of reduced energy level difference of the excited states of the formers. As deduced by the UV-Vis absorption spectra, and in agreement with the results obtained with the above mentioned optically active regioregular poly(3-alkoxythiophene)s [15], this confirms the increased extent of aromatic resonance and hence coplanarity of the thiophenic rings in **PTOR*** and **PT2OR***. Interestingly, as Stokes shift values ranging around 2000 cm^{-1} are considered typical of rigid conjugated polymers in solution [36,37], it appears that **PTOR*** and **PT2OR*** are characterized by significantly higher stiffness with respect to their sulphanyl counterparts.

Solvatochromism experiments were carried out on the chloroform solutions of the oligomers upon gradual addition of a poor solvent, such as acetonitrile, in order to promote a transition from the disordered random coil conformation to self-assembling and microaggregation of the macromolecules.

The addition of acetonitrile to the chloroform solutions of HT **PTSR*** and **PTOR*** (Figures 2A and 2C) produces a gradual decrease of light absorption with a broadening of the band related to the electronic π-π* transition, as well as a slight red-shift of the maximum wavelength (~10 nm) without particularly evident vibronic features. Upon similar treatment, **PT2OR*** (Figure 3C) behaves similarly to **PTSR*** and **PTOR*** as far as the main absorption is concerned, with the absorption at 345 nm, related to a shorter, more soluble, oligomeric fraction insensitive to the change of solvent. By contrast, HH/TT **PT2SR*** (Figure 3A) exhibits the appearance of a new band close to 470 nm at a $CHCl_3/CH_3CN$ composition of 10/90 v/v, suggesting the presence of structures possessing more extended electronic conjugation upon aggregation, regardless the presence of unfavorable HH junctions.

The UV-Vis spectra of thin films of **PTSR***, **PTOR***, **PT2SR*** and **PT2OR***, obtained by drop-casting from chlorobenzene solution, are reported in Figures 4 and the related data in Table 2. In addition to a sequence of absorption maxima similar to the solution in chloroform, all samples exhibit broader bands and appear furtherly red-shifted with respect to those of the aggregated structures obtained from solvatochromism experiments, with **PT2SR*** confirming the presence in the solid state of multiple aggregated structures.

3.5. CD Spectroscopy

The CD spectrum of **PTSR*** in pure chloroform (Figure 2B) does not display any optical activity in the spectral region related to the π-π* electronic transition of polythiophene, as expected, due to the random coil conformation of the macromolecules. By contrast, a weak CD signal is present in the spectrum of **PTOR*** (Figure 2D) at around 580 nm, in correspondence to the UV-vis absorption, suggesting an intrinsically chiral structure of short main chain sections, even in dilute solution, to be reasonably ascribed to the increased rigidity of the backbone induced by the mesomeric effect of the side chain alkoxy group. The gradual addition of the poor solvent acetonitrile produces in both **PTSR*** and **PTOR*** the appearance of bisignate dichroic signals of opposite sign, with cross-over points related to the UV-vis maxima (at around 520 nm for **PTSR*** and 580 nm for **PTOR***) (Table 3).

A bisignated CD signal is characteristic of exciton coupling between transition dipole moments of chromophores on adjacent polymer chains in the aggregate state, while for individual polymer chains with a helical conformation, the CD effect is not expected to be bisignated [6,38]. Thus, the bisignated CD spectra observed in π-conjugated oligomers with optically active pendant side chains such as **PTSR*** and **PTOR*** are due to a chiral supramolecular structure of predominantly planar macromolecules [39].

In particular, the alkoxy derivative **PTOR*** displays higher optical activity, as well as higher chiral anisotropy factor *g* ($\Delta\varepsilon/\varepsilon$) ($2 \cdot 10^{-3}$ at 651 nm) with respect to **PTSR*** ($1 \cdot 10^{-3}$ at 562 nm), which exhibits, in addition to the bisignate band, a positive CD signal as a shoulder around 630 nm. The *g* value of **PTOR*** is close to the reported value of $3 \cdot 10^{-3}$ at 568 nm found for the optically active HT poly(3-alkoxythiophene) bearing the 3,7-dimethyloctyloxy moiety in the side chain [15]. These findings can be interpreted as due to aggregation of macromolecules giving rise to supramolecular arrangements of opposite helicity both in **PTOR*** (*levo* helix sense) and, to a less extent, in **PTSR*** (*dextro* helix sense), where aggregates possessing intrinsic chiral structure are also present. Even at very low polymerization degree, the oligomer HT **PTOR*** is able to give chiral supramolecular aggregates characterized by a significant *g* value, similarly to the related HT poly{3-[(*S*)-(2-methylbutyl)]thiophene} possessing remarkably higher molecular mass [6,7].

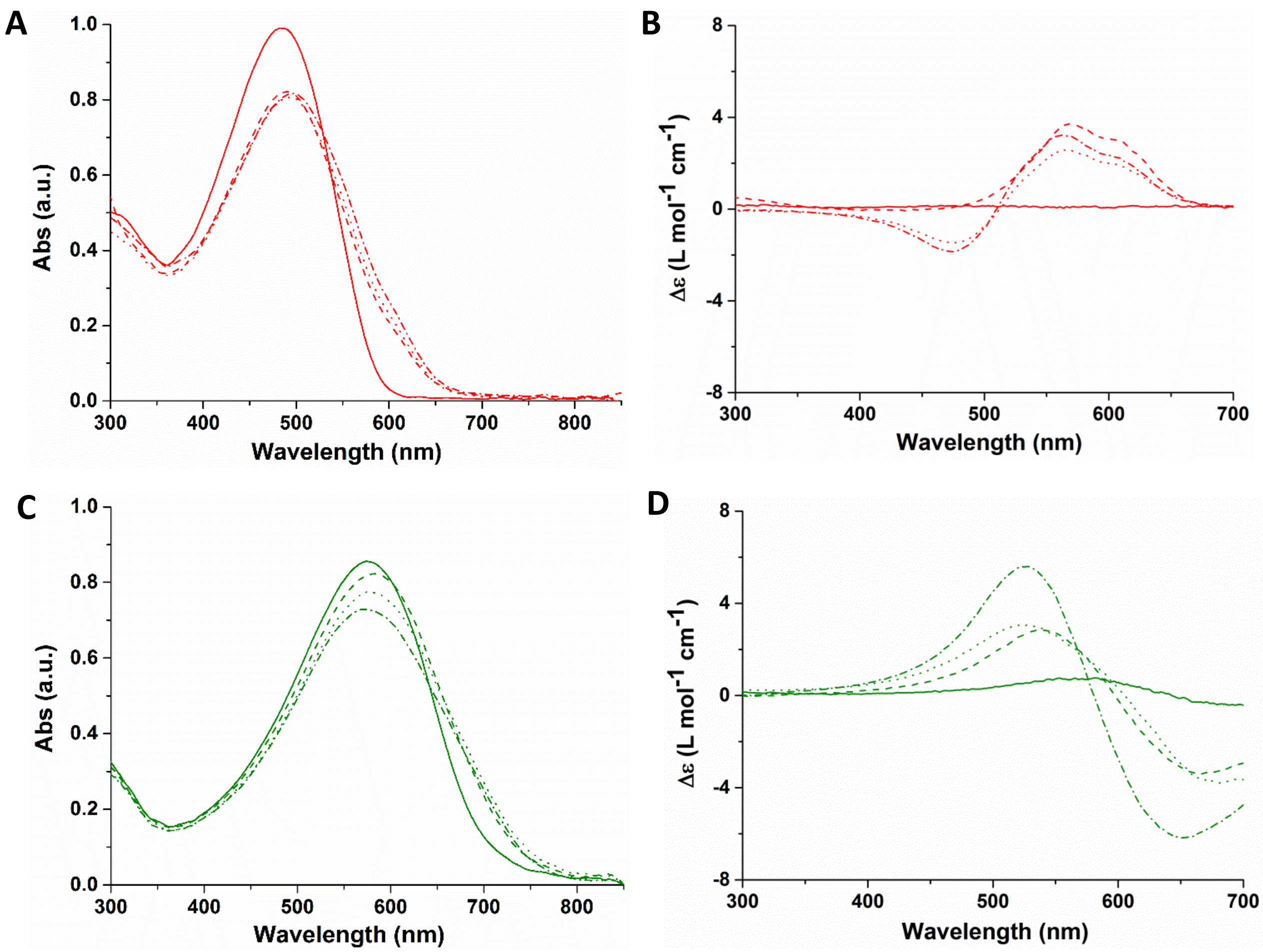


Figure 2. Absorption (A) and CD (B) spectra of **PTSR*** in $CHCl_3$ (red solid line), $CHCl_3/CH_3CN$ 40:60 (red dashed line), $CHCl_3/CH_3CN$ 30:70 (red dotted line) and $CHCl_3/CH_3CN$ 20:80 (red dashed-dotted line); absorption (C) and CD (D) spectra of **PTOR*** in $CHCl_3$ (green solid line), $CHCl_3/CH_3CN$ 60:40 (green dashed line), $CHCl_3/CH_3CN$ 40:60 (green dotted line) and $CHCl_3/CH_3CN$ 20:80 (green dashed-dotted line).

Table 3. CD spectra at 25°C of oligomers in the microaggregated state.

Sample	*Solvent* $CHCl_3:CH_3CN$ (v/v)	$\Delta\varepsilon_1$[a]	λ_1[b]	λ_0[c]	$\Delta\varepsilon_2$[a]	λ_2[b]
PTSR*	20:80	+3.21	563	512	–1.80	474
PTOR*	20:80	–6.09	650	579	+5.59	523
PT2SR*	10:90	–0.63	523	486	+0.55	458
PT2OR*	20:80	+0.15	561	-	-	-

[a] Δε expressed in L mol^{-1} cm^{-1}; [b] Wavelength (in nm) of the maximum dichroic absorption; [c] Wavelength (in nm) of the cross-over point of dichroic bands.

The CD spectrum (Figure 3B) of HH/TT sulphanyl derivative **PT2SR*** in dilute $CHCl_3$ solution shows a weak signal in the spectral region 300-400 nm, indicative of the presence of a small amount of chain sections possessing one-handed helical sense. By gradual addition of acetonitrile, a moderate but clear bisignate dichroic signal related to exciton coupling between the thiophene rings in the backbone appears in consequence of chiral supramolecular aggregation, similar and with opposite helicity, with respect to **PTSR***. Indeed, the cross-over point of CD spectrum is centered at 486 nm, corresponding to the wavelength of the shoulder displayed in the corresponding UV-vis spectrum and related to aggregates of **PT2SR*** (Figure 3A). However, the maximum optical activity (g $3 \cdot 10^{-4}$ at 522 nm) results to be lower than in **PTSR*** mainly in consequence of its lower polymerization degree, disfavoring the formation of large chiral macromolecular aggregates. In addition, a shoulder around 600 nm is present in the CD spectrum, similarly to **PTSR***, to be attributed to an optically active phase constituted by oligomeric strands of one prevailing helicity. Similar UV-vis and CD spectra were also observed upon aggregation of the above mentioned polymeric TT/HH derivative poly{4,4'-bis[(*S*)-(2-methylbutyl)sulphanyl]-2,2'-bithiophene} by addition of methanol or *n*-hexane to its chloroform solution, or by evaporation from a good solvent, and attributed to the formation of more than one single aggregate phase, depending on the experimental conditions [16].

It therefore appears that the possibility of coplanar arrangement of thiophene rings partially exists also in the case of disfavoring HH connections originated by the presence of 3,3'-disubstituted 2,2'-bithiophene co-units. The extra sulfur atom linked to each thiophene ring may in fact induce self-aggregation via S···S interactions and weak CH···S hydrogen bonding [12, 13]. The directionality of the above interactions, as well as the large polarizability of sulfur in thioether fragments, would favor the formation of highly anisotropic supramolecular systems characterized by anti-planar conformations involving reduced steric hindrance between the side chain substituents [26] even in the case of oligomeric constitution of the material.

By contrast, the CD spectrum in chloroform (Figure 3D) of the alkoxy oligomer **PT2OR***, possessing actually a regiorandom configuration, shows weak CD positive signals (g $2 \cdot 10^{-4}$ at 555 nm) with maxima related to the UV-vis main chain absorptions, indicative of intrinsic chirality of the backbone limited to short sections, insensitive to the addition of poor solvent. Thus, the absence of exciton coupling in the CD spectrum of **PT2OR***, in contrast to what observed for **PTOR***, can be attributed to the absence of regioregular sections capable to promote sufficiently extended coplanarity of the thiophene rings, so as to favor the development of chiral supramolecular structures upon aggregation of the macromolecules.

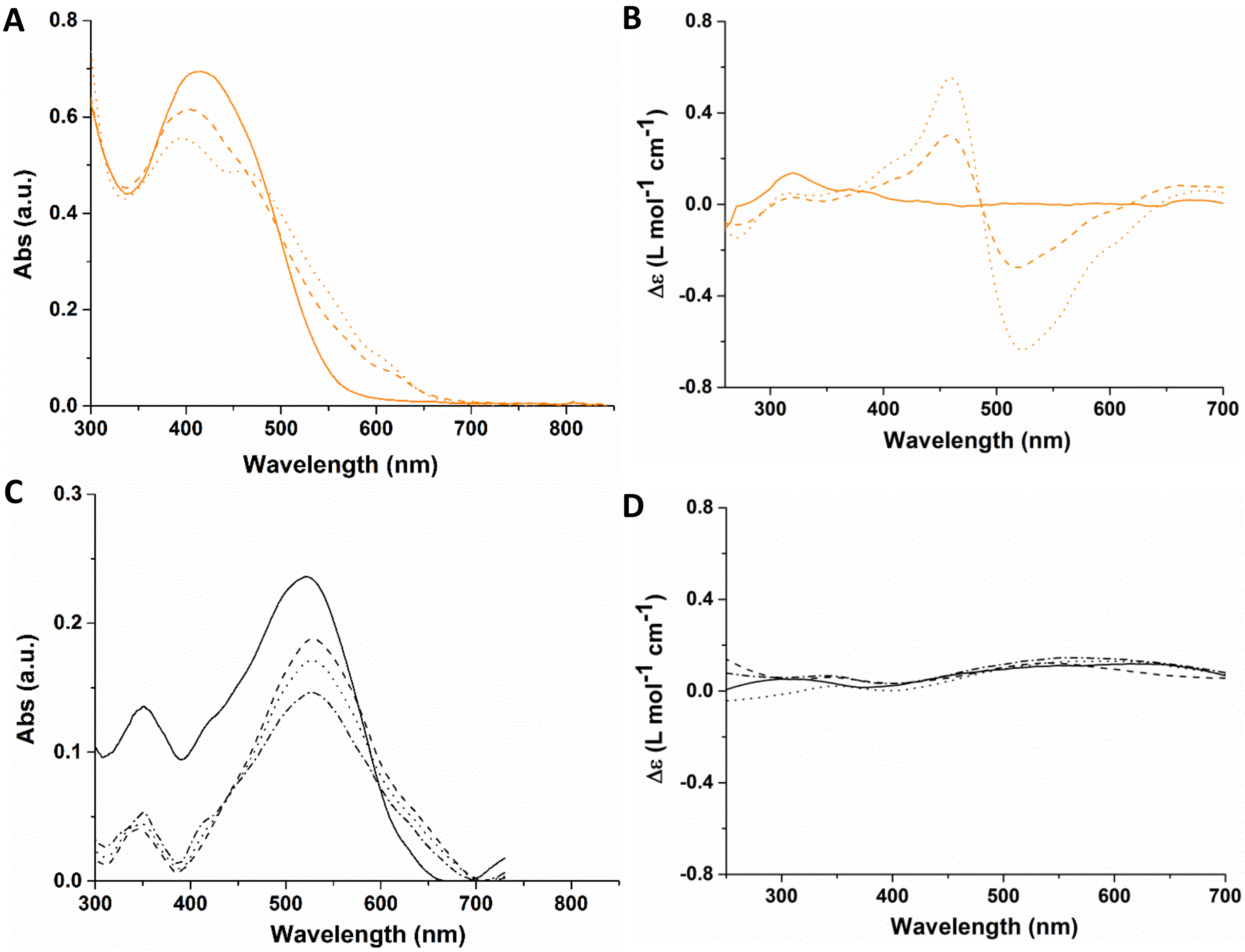


Figure 3. Absorption (A) and CD (B) spectra of **PT2SR*** in $CHCl_3$ (orange solid line), $CHCl_3/CH_3CN$ 30:70 (orange dotted line) and $CHCl_3/CH_3CN$ 10:90 (orange dashed line); absorption (C) and CD (D) spectra of **PT2OR*** in $CHCl_3$ (black solid line), $CHCl_3/CH_3CN$ 60:40 (black dashed line), $CHCl_3/CH_3CN$ 40:60 (black dotted line) and $CHCl_3/CH_3CN$ 20:80 (black dashed-dotted line).

It appears, however, that experimental procedure of aggregation and molecular structure of the material significantly affect the chiral behavior of the samples. In fact, when thin films of **PTSR*** and **PTOR*** are produced by slow evaporation of dilute chlorobenzene solutions, the resulting CD spectra differ from those obtained from solvatochromism experiments.

In particular, **PTSR*** (Figure 4B), **PTOR*** (Figure 4D) and **PT2OR*** (Figure 4G) actually display low optical activity with respect to that given by addition of acetonitrile to the chloroform solution. By contrast, the CD spectrum of a thin film of **PT2SR*** resulting from slow evaporation of dilute chlorobenzene solutions (Figure 4F), is similar to those given by the microaggregates formed upon acetonitrile addition to the chloroform solution, likely in consequence of its more homogeneous molecular composition (Table 1) with respect to the other derivatives. Thus, low dispersity value and regioregularity degree appear as relevant factors affecting the ordering process of the macromolecules from the solution to the solid state.

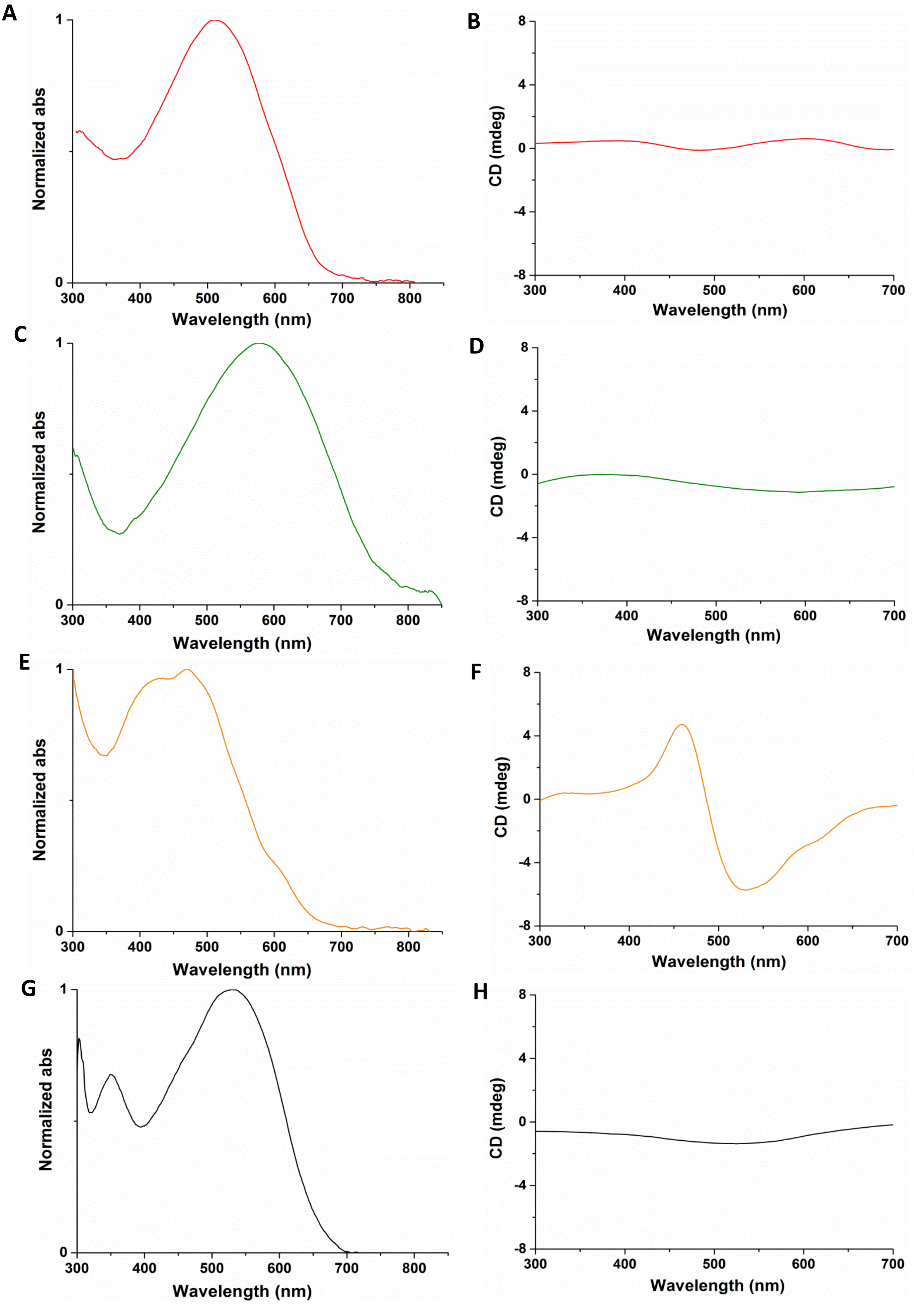

A
B
C
D
E
F
G
H
Normalized abs
CD (mdeg)
Wavelength (nm)
300
400
500
600
700
800
8
4
0
-4
-8
1
0

Figure 4. Absorption and CD spectra of **PTSR*** (A-B), **PTOR*** (C-D), **PT2SR*** (E-F) and **PT2OR*** (G-H) as films cast from chlorobenzene.

In conclusion, both the HT oligomeric derivatives **PTSR*** and **PTOR*** are able to display a behavior similar to HT poly{3-[(*S*)-(2-methylbutyl)]thiophene}, with formation of chiral supramolecular aggregates upon aggregation from the solution, although with lower optical activity originated by their low polymerization degree. Indeed, it is confirmed that the S or O heteroatom interposed between the chiral residue and the thiophene ring favors coplanarity of aromatic rings in the backbone, due to attractive interactions between the thienyl sulfur and the S or the O atom connecting the side chain.

Notwithstanding its unfavorable regioregularity, even the behavior of the HH/TT sulphanyl derivative **PT2SR*** appears substantially analogous to that of **PTSR*** and displays in the microaggregated state a relevant amount of chains with supramolecular chirality with respect to macromolecular strands possessing a prevailing one-handed helical sense. In comparison to the previously investigated optically active HH/TT poly(3-alkylthiophene) bearing the same (*S*)-(2-methyl)butyl chiral residue directly linked to the thiophene ring, which is characterized by the presence of helical intrachain conformations disfavoring the formation of chiral supramolecular structures [11], **PT2SR*** appears more prone to produce helical interchain order even at a much lower polymerization degree (8 *vs.* 172 in terms of one thiophenic repeating unit). This can be attributed to the presence of the thioalkyl sulfur atom that promotes a more coplanar arrangement of thiophene rings with respect to the HH/TT optically active P3AT derivative.

4. Conclusions

HT and HH/TT optically active large-size oligothiophenes bearing the (*S*)-(2-methyl)butyl residue linked at position 3 of the thiophene ring through sulfur or oxygen atom have been prepared with the aim to compare their chiroptical properties to those of the related HT and HH/TT P3AT derivatives possessing the same chiral moiety. Compared to the polymers, both the sulphanyl and alkoxy oligomers display red-shifted absorption maxima indicative of enhanced aromatic conjugation in the backbone due to the electron releasing properties of the heteroatom. Upon aggregation from the solution by means of poor solvent addition, both the HT oligomers, exhibit chiroptical properties, in consequence of the formation of supramolecular chiral aggregates, similarly to the related HT P3AT derivative possessing higher molecular mass. In addition, the HT 3-sulphanyl derivative displays the presence of individual chains possessing helical conformation. The HH/TT 3-sulphanyl derivative behaves similarly to its HT counterpart, although with lower chiral anisotropy, showing however a greater tendency to give chiral supramolecular aggregates than the related optically active HH/TT P3AT polymeric derivative. ~~Differently~~ By contrast, the HH/TT 3-alkoxy oligomer, actually constituted by macromolecules with a mixture of HH/TT and HT connections, appears unable to produce relevant chiroptical properties upon aggregation and exhibits only the presence of short sections possessing chiral conformation in the aggregated state. It is also to be noted that these materials do not display relevant chiroptical properties as cast films obtained by direct evaporation from the solution, thus suggesting, as previously observed, that the aggregation of these π-conjugated materials is a stepwise event which requires to start from very dilute solutions and gradually add a weak solvent in order to the process may take place with significant formation of chiral aggregates. To this respect high regioregularity degree and low dispersity values appear to be favorable parameters positively affecting the film formation from the solution. In addition to favor the extent of conjugation in the main chain, of interest for application to polarization-sensitive devices in photovoltaic cells and oLEDs, the presence of oxygen or sulfur as connecting atom between the thiophene ring and the chiral alkyl side chain allows to achieve supramolecular chiral aggregations not dissimilar, or better, with respect to those obtained with the related chiral P3ATs even in the case of low polymerization degree.

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Appendix A. Supplementary materials

Synthesis of (+)-*(S)*-2-Methyl-1-butyl p-toluensulfonate, (+)-*(S)*-1-Bromo-2-methylbutane and 3-Mercapto-thiophene; ^{1}H NMR spectra of monomers and oligomers; TGA and DSC thermograms of oligomers and PL spectra of oligomers.

References

[1] L. Pu, The study of chiral conjugated polymers, *Acta Polymer.* 48 (1997) 116-141.

[2] L. A. P. Kane-Maguire, G. G. Wallace, Chiral conducting polymers, *Chem. Soc. Rev.* 39 (2010) 2545-2576.

[3] M. Lemaire, D. Delabuglise, R. Garreau, A. Guy, J. Roncali, Enantioselective chiral poly(thiophenes), *J. Chem. Soc. Chem. Commun.* 10 (1988) 658-661.

[4] R. D. McCullough, R. D. Lowe, M. Jayaraman, D. L. Anderson, Design, synthesis, and control of conducting polymer architectures: structurally homogeneous poly(3-alkylthiophenes), *J. Org. Chem.* 58 (1993) 904-912.

[5] T.-A. Chen, R. D. Rieke, Polyalkylthiophenes with the smallest bandgap and the highest intrinsic conductivity, *Synth. Met.* 60 (1993) 175-177.

[6] B. M. W. Langeveld-Voss, M. M. Bouman, M. P. T. Christiaans, R. A. J Janssen, E. V. Meijer, Main-chain chirality of regioregular polythiophenes, *Polym. Prepr.* 37 (1996) 499-500.

[7] M. Catellani, S. Luzzati, F. Bertini, A. Bolognesi, F. Lebon, G. Longhi, S. Abbate, A. Famulari, S. V. Meille, Solid-state optical and structural modifications induced by temperature in a chiral poly-3-alkylthiophene, *Chem. Mater.* 14 (2002) 4819-4826.

[8] P. Arosio, A. Famulari, M. Catellani, S. Luzzati, L. Torsi, S. V. Meille, First detailed determination of the molecular conformation and the crystalline packing of a chiral poly(3-akylthiophene): poly-3-*(S)*-2-methylbutylthiophene, *Macromolecules* 40 (2007) 3-5.

[9] B. M. W. Langeveld-Voss, R. J. M. Waterval, R. A. J. Janssen, E. W. Meijer, Principles of “majority rules” and “sergeants and soldiers” applied to the aggregation of optically active polythiophenes: evidence for a multichain phenomenon, *Macromolecules* 32 (1999) 227-230.

[10] F. Lebon, G. Longhi, S. Abbate, M. Catellani, S. Luzzati, A. Bolognesi, Chiral polyalkylthiophenes for organic light emitting diodes, *Mat. Res. Soc. Symp. Proc.* 708 (2002) 341-347.

[11] L. Angiolini, V. Cocchi, L. Guadagnini, A. Mignani, E. Salatelli, D. Tonelli, Optically active, regioregular, head-to-head/tail-to-tail poly(3-alkyl)thiophene by inherently regiospecific oxidative synthesis from 3,3’-dialkyl 2,2’-bithiophene monomer, *Synth. Met.* 202 (2015) 169-176.

[12] F. Di Maria, P. Olivelli, M. Gazzano, A. Zanelli, M. Biasiucci, G. Gigli, D. Gentili, P. D’Angelo, M. Cavallini, G. Barbarella, A successful chemical strategy to induce oligothiophene self-assembly into fibers with tunable shape and function, *J. Am. Chem. Soc.* 133 (2011) 8654-8661.

[13] F. Di Maria, M. Zangoli, M. Gazzano, E. Fabiano, D. Gentili, A. Zanelli, A. Fermi, G. Bergamini, D. Bonifazi, A. Perinot, M. Caironi, R. Mazzaro, V. Morandi, G. Gigli, A. Liscio, G.

Barbarella, Controlling the functional properties of oligothiophene crystalline nano/microfibers via tailoring of the self-assembling molecular precursors, *Adv. Funct. Mater.* 28 (2018) 1801946.

[14] G. Koeckelberghs, M. Vangheluwe, C. Samyn, A. Persoons, T. Verbiest, Regioregular poly-(3-alkoxythiophene)s: toward soluble, chiral conjugated polymers with a stable oxidized state, *Macromolecules* 38 (2005) 5554-5559.

[15] M. Vangheluwe, T. Verbiest, G. Koeckelberghs, Influence of the substitution pattern on the chiroptical properties of regioregular poly(3-alkoxythiophene)s, *Macromolecules* 41 (2008) 1041-1044.

[X] M Zangoli, F Di Maria, G Barbarella, Supramolecular Assembly of Thiophene-Based Oligomers into Nanostructured Fluorescent Conductive and Chiral Microfibers. ChemistryOpen 9, (2020), 499.

[Y] N. Biot, D. Bonifazi Chalcogen-bond driven molecular recognition at work. Coordination Chemistry Reviews 413, 2020, 213243

[16] D. Iarossi, A. Mucci, F. Parenti, L. Schenetti, R. Seeber, C. Zanardi, A. Forni, M. Tonelli, Synthesis and spectroscopic and electrochemical characterisation of a conducting polythiophene bearing a chiral β-bubstituent: polymerisation of (+)-4,4'-bis[*(S)*-2-methylbutylsulfanyl]-2,2'-bithiophene, *Chem. Eur. J.* 7 (2001) 676-685.

[17] K. Van den Bergh, I. Cosemans, T. Verbiest, G. Koeckelberghs, Expression of supramolecular chirality in block copoly(thiophenes)s, *Macromolecules* 43 (2010) 3794-3800.

[18] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1966.

[20] P. Kaszynski, M. Jawdosiuk, A comprehensive approach to (*S*)-(–)-2-methyl-1-butanol as a convenient precursor for synthesis of chiral liquid crystals, *Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics* 174 (1989) 21-37.

[21] F. Saito, Y. Takeoka, M. Rikukaw, K. Sanni, Synthesis of optically active regioregular poly(thiophene), *Synth. Met.* 153 (2005) 125–128.

[22] B. Xu, S. Noh, B Thompson, Fine tuning of polymer properties by incorporating strongly electron-donating 3-hexyloxythiophene units into random and semi-random copolymers, *Macromolecules* 47 (2014) 5029-5039.

[23] R. H. Mitchell, Y.H. Lai, R.V. Williams, N-bromosuccinimide-dimethylformamide: a mild, selective nuclear monobromination reagent for reactive aromatic compounds, *J. Org. Chem.* 44 (1979) 4733-4735.

[24] F. Goldoni, D. Iarossi, A. Mucci, L. Schenetti, M. Zambianchi, Synthesis and characterization of poly[3-(butylthio)thiophene]: a regioregular head-to-tail polymer, *J. Mater. Chem.* 7 (1997) 593-596.

[25] F. Tassinari, E. Libertini, F. Parenti, B. Ballarin, F. P. Di Nicola, M. Lanzi, A. Mucci, Polymers with alkylsulfanyl side chains for bulk heterojunction solar cells: toward a greener strategy, *Macromol. Chem. Phys.* 218 (2017) 1700111.

[26] E. Salatelli, M. Marinelli, M. Lanzi, A. Zanelli, S. Dell'Elce, A. Liscio, M. Gazzano, F. Di Maria, Bulk heterojunction solar cells: the role of alkyl side chain on nanoscale morphology of sulfur over-rich regioregular polythiophene/fullerene blends, *J. Phys.Chem. C.* 122 (2018) 4156-4164.

[27] F. Demanze, A. Yassar, F. Garnier, Alternating donor–acceptor substitutions in conjugated polythiophenes, *Macromolecules* 29 (1996) 4267-4273.

[28] R. S. Loewe, S. M. Khersonsky and R. D. McCullough, A simple method to prepare head-to-tail coupled, regioregular poly(3-alkylthiophenes) using grignard metathesis, *Adv. Mater.* 11 (1999) 250-253.

[29] R. S. Loewe, P. C. Ewbank, J. Liu, L. Zhai and R. D. McCullough, Regioregular, head-to-tail coupled poly(3-alkylthiophenes) made easy by the GRIM method: investigation of the reaction and the origin of regioselectivity, *Macromolecules* 34 (2001) 4324-4333.

[30] X. Hu, L. Xu, Structure and properties of 3-alkoxy substituted polythiophene synthesized at low temperature, *Polym.* 41 (2000) 9147-9154.

[31] Z.-B. Zhang, M. Fujiki, Synthesis and molecular weight dependent optical properties of mono-alkoxy substituted polythiophenes, *Polym. J.* 33 (2001) 597-601.

[32] C. Shi, Y. Yao, Y. Yang, Q. Pei, Regioregular copolymers of 3-alkoxythiophene and their photovoltaic application, *J. Am. Chem. Soc.* 128 (2006) 8980-8986.

[33] K. Faïd, R. Cloutier, M. Leclerc, Design of novel electroactive polybithiophene derivatives, *Macromolecules* 26 (1993) 2501-2507.

[34] G. Neculqueo, V. R. Fuentes, A. Lopez, R. Matute, S. O. Vasquez, F. Martinez, Electronic properties of thienylene vinylene oligomers: synthesis and theoretical study, *Struct. Chem.* 23 (2012) 1751–1760.

[35] L. Huo, Y. Zhou, Y. Li, Alkylthio-substituted polythiophene: absorption and photovoltaic properties, *Macromol. Rapid Comm.* 30 (2009) 925-931.

[36] K. Ogawa, S. C. Rasmussen, N-functionalized poly(dithieno[3,2-b:2',3'-d]pyrrole)s: highly fluorescent materials with reduced band gaps, *Macromolecules* 39 (2006) 1771-1778.

[37] G. Koeckelberghs, L. De Cremer, A. Persoons, T. Verbiest, Influence of the substituent and polymerization methodology on the properties of chiral poly(dithieno[3,2-b:2',3'-d]pyrrole)s, Macromolecules 40 (2007) 4173-4181.

[38] D. Beljonne, B. M. W. Langeveld-Voss, Z. Shuai, R. A. J. Janssen, S. C. J. Meskers, E. W. Meijer, J. L. Bredas, Exciton coupling in oligothiophenes: a combined experimental/theoretical study, *Synth. Met.* 102 (1999) 912-913.

[39] E. Peeters, A. Delmotte, R. A. J. Janssen, E. W. Meijer, Chiroptical properties of poly{2,5-bis[*(S)*-2-methylbutoxy]-1,4-phenylene vinylene}, *Adv. Mater.* 9 (1997) 493-496.