Synthesis by oxidative polymerization of optically active, regioregular polythiophene from quinquethiophene monomer bearing chiral and n-dodecyl groups as substituents

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Abstract: The synthesis and characterization of an optically active quinquethiophene monomer 3,3''''-didodecyl-4',3'''-di[(S)-(+)-2-methylbutyl]-2,2':5',2'':5'',2''':5''',2''''-quinquethiophene [(S)-(+)-DDDMBQT], bearing at the C-β positions of thiophene rings both linear C12 alkyl chain and chiral, enantiomerically pure, alkyl group is described. The polymerization of [(S)-(+)-DDDMBQT] by oxidative mechanism has been optimized in terms of yield of soluble polymer with high molecular weight.

The obtained polymeric derivative displays enhanced conjugation extension with respect to similar poly(3-alkylthiophene)s reported in the literature and optical activity in the spectral region related to the chromophore absorptions when in the microaggregate state, indicative of the presence of supramolecular chiral conformations.

Introduction

It is well known that head-to-tail regioregularity in poly(monoalkyl)thiophenes (PAT)s allows achievement of better performances in terms of optical and electrical properties related to the extension of conjugation of the aromatic rings, the coplanarity of thiophene rings being actually favoured by the absence of head-to-head dyads involving unfavourable steric interactions between the side chain substituents [1]. To achieve this structural requirement it is necessary to perform the polymerization of alkylthiophene in the presence of highly demanding catalysts and reaction conditions, or, alternatively, to start from symmetrically substituted oligothiophenic monomers inherently suitable to give the corresponding (PAT)s under simple and economic conditions, such as, e.g., the chemical oxidative method of widespread use with iron(III) trichloride [2].

This latter procedure was indeed previously followed by us with the aim to prepare optically active regioregular (PAT)s bearing in the side chain a chiral alkyl group of one prevailing configuration [3] or both the chiral group and a n-hexyl moiety [4], in order to improve solubility and filmability of the polymer, starting, respectively, from a symmetrical ter- or quinquethiophene monomer [(*S*)-(+)-DMBTT] or [(*S*)-(+)-DHDMBQT], respectively (Scheme 1).

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The absence of optical activity is displayed in CHCl$_3$ solution by these derivatives in the spectral region related to the π-π* electronic transition of the conjugated aromatic system, as observed by circular dichroism (CD) measurements, indicative of conformational freedom of the macromolecular chains preventing the presence of ordered chiral structures. However, when a poor solvent (MeOH) is added to the CHCl$_3$ solution, the presence of the side-chain chiral substituent induces an asymmetric perturbation of the above transitions, and dichroic absorptions are observed, thus indicating the formation of a microaggregate state of the macromolecules with a prevailing helical handedness.

(S)-(+)-DMBTT

R = C$_6$H$_{13}$ **(S)-(+)-DHDMBQT**
R = C$_{12}$H$_{25}$ **(S)-(+)-DDDMBQT**

R* =
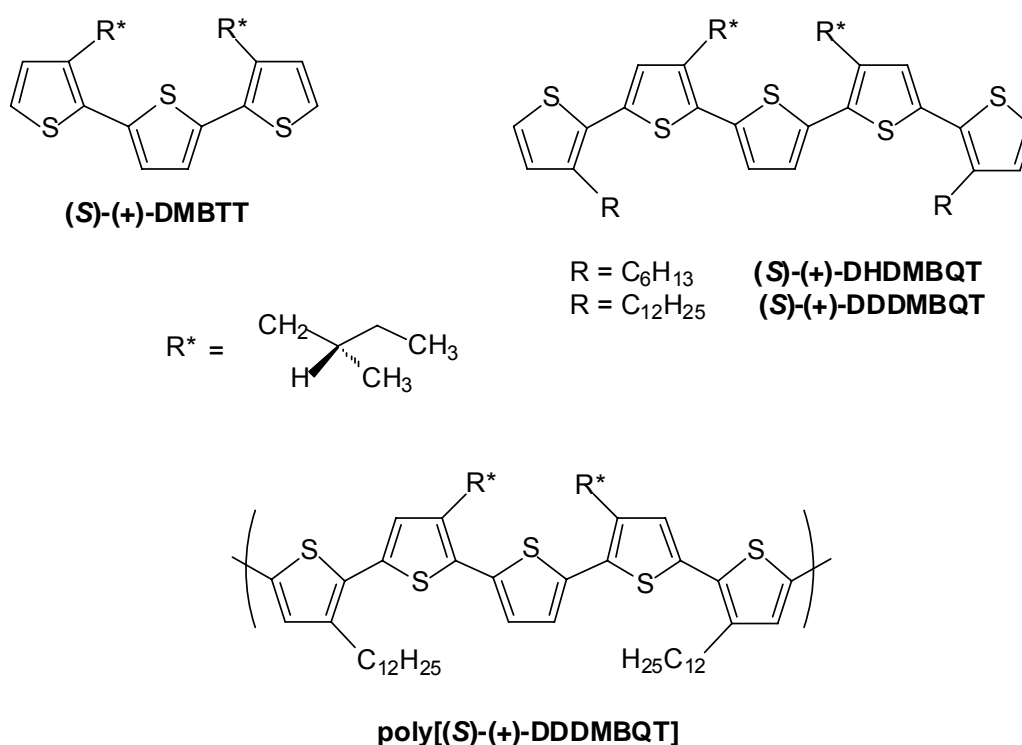
poly[(S)-(+)-DDDMBQT]

Scheme 1. Synthesis of poly(monoalkyl)thiophene from the quinquethiophene monomer [(S)-(+)-DDDMBQT].

The behaviour shown by the above (PAT)s bearing chiral substituents may give the possibility of obtaining materials undergoing conformational changes induced by the interaction with chemicals, which can be revealed by chiroptical techniques such as the CD. Indeed, the presence of large CD signals in chiral (PAT)s in the microaggregate state has been repeatedly reported in the literature [5-7], the regioregularity of enchainment of the thiophene units being an important factor affecting favourably the optical activity of these materials.

Since processability, in addition to regioregularity, is a relevant requirement for the application of these materials in the areas of microelectronics, electrode materials, optoelectronic and sensors [8-10], we report here the synthesis of a PAT characterized by relevant chiroptical properties as well as by increased lengthness of the alkyl substituent with respect to poly[(S)-(+)-DHDMBQT], starting from the novel optically active, symmetrically substituted, quinquethiophene monomer [(S)-(+)-DDDMBQT] (Scheme 1).

The polymerization conditions of this monomer in the presence of iron(III) trichloride have been optimized in order to obtain the highest yield of soluble poly[(+)-DDDMBQT] fraction. The molecular, structural and chiroptical properties of the polymeric material obtained have been assessed.

Results and discussion

Synthesis and characterization of the monomer [(S)-(+)-DDDMBQT]

Monomer [(*S*)-(+)-DDDMBQT] was prepared [11] by reaction of the Grignard reagent (**II**) of 2-iodo-3-n-dodecylthiophene (**I**) [obtained in turn in good yield (88%) from 3-n-dodecylthiophene and I$_2$/H$_5$IO$_6$] with 5,5"-dibromo-3,3"-di[(*S*)-(+)-2-methylbutyl]-2,2':5',2"-terthiophene (**III**) [4], in the presence of Ni(dppp)Cl$_2$, as reported in Scheme 2. The monomer, having the same optical purity as the starting substrate (*S*)-(+)-DMBTT, was obtained in acceptable yield (53%) after column chromatography purification (see Experimental) and its structure confirmed by IR and ^{1}H-NMR spectrometry.
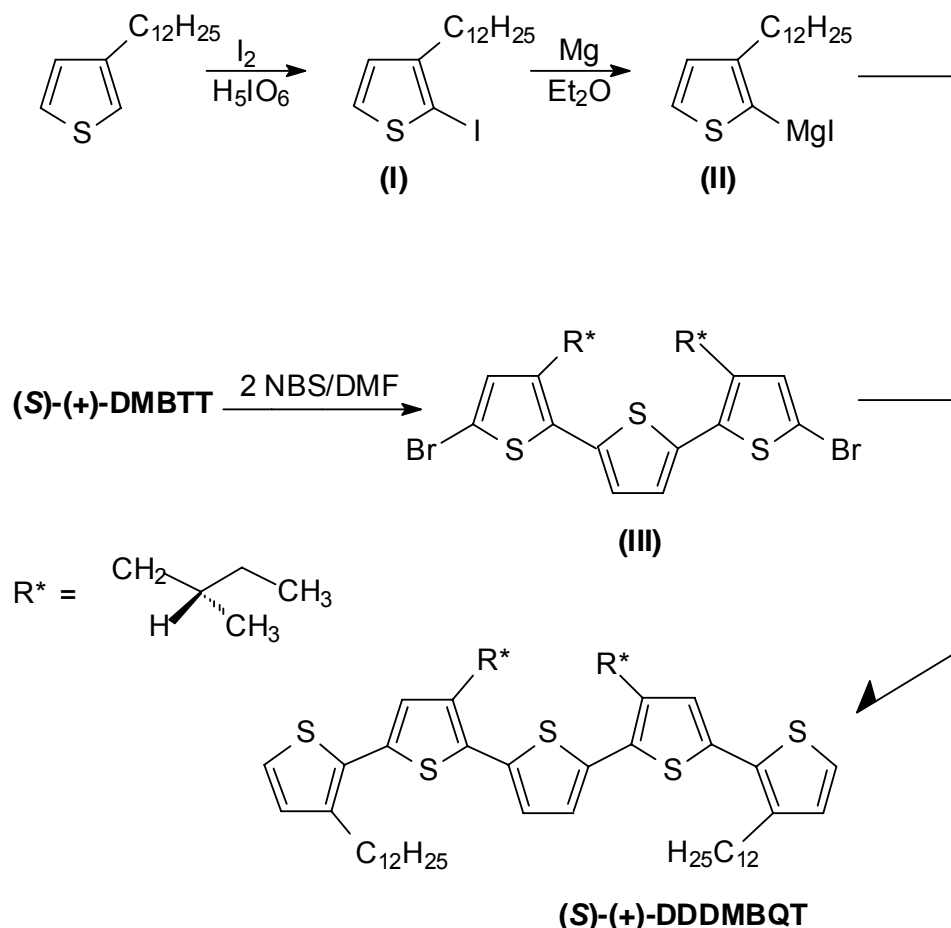
Scheme 2. Synthesis of [(*S*)-(+)-DDDMBQT].

In particular, the IR spectrum displays two bands at 3105 and 3065 cm^{-1} related to C$_\alpha$-H and C$_\beta$-H stretching vibrations, respectively, typical of 3-alkyl substituted thiophene rings, [12] as well as the presence of an out-of-plane bending signal at 794 cm^{-1}, attributed to the β hydrogens of the 2,5-disubstituted thiophene central ring [13].

The ^{1}H-NMR spectrum in CDCl$_3$ solution exhibits in the aromatic region [Fig. 1(a)] the expected pattern, consisting of two doublets centered at 7.16 and 6.93 ppm, related to the *a* and *b* protons, respectively, and two singlets at 6.91 and 7.08 ppm, related to the *c* and *d* protons, respectively.
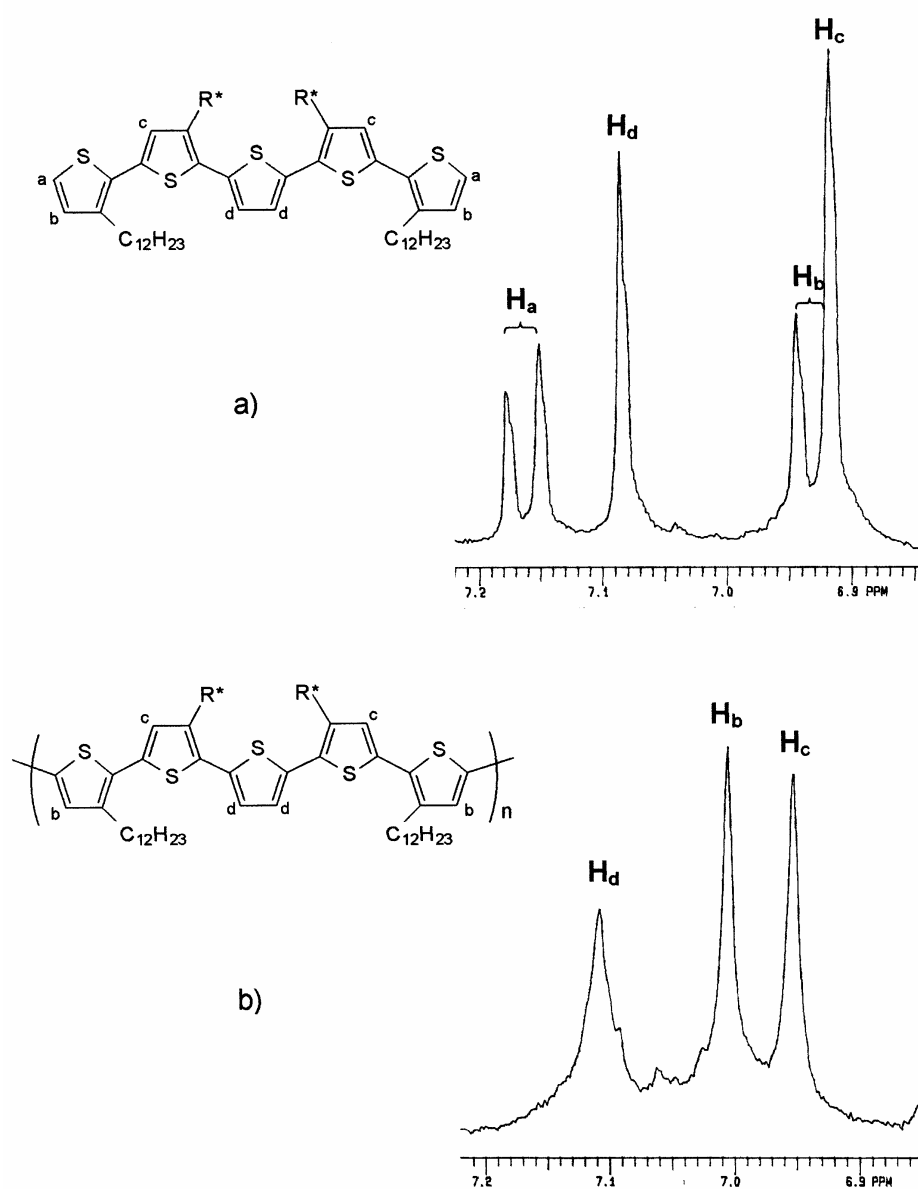

Fig. 1. ^{1}H-NMR aromatic protons resonances of [(*S*)-(+)-DDDMBQT] (a) and poly[(*S*)-(+)-DDDMBQT] (b).

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Synthesis of poly[(S)-(+)-DDDMBQT]

The polymerization of [(S)-(+)-DDDMBQT] was initially carried out following the well known oxidative method [2] with iron(III) trichloride in $CHCl_3$, instead of CCl_4, as suggested [11] in order to favor a higher molecular weight of the polymeric product when its solubility is sufficiently good. Under the conditions adopted (monomer concentration $6 \cdot 10^{-2}$ M, molar ratio $FeCl_3$/monomer 4:1, at room temperature for 15 hrs), the polymer was obtained in quantitative yield, free from unreacted monomer as well as insoluble fraction, with only negligible amounts of oligomeric fraction, thus allowing consideration of the reaction not yet optimized, as far as the maximum obtainable molecular weight of the soluble fraction is concerned.
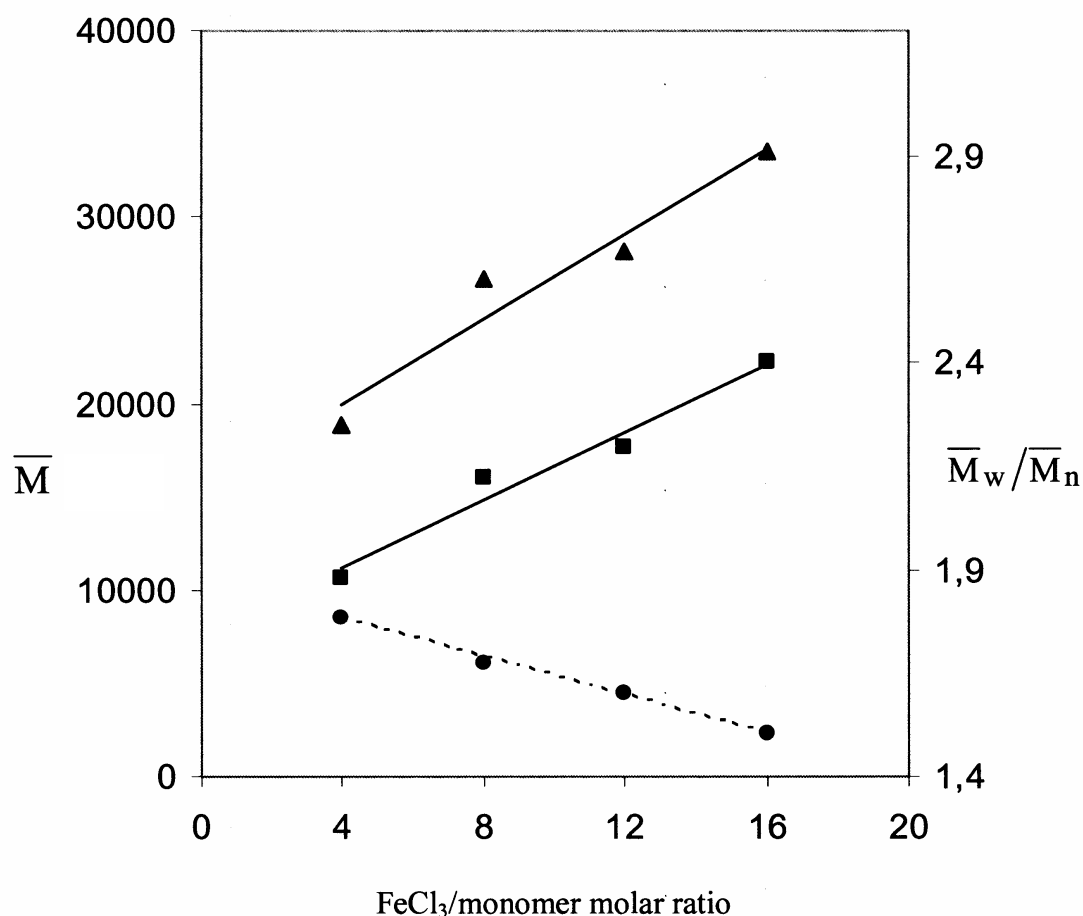

Fig. 2. Variation of $\overline{M}_w$ (▲), $\overline{M}_n$ (■) and $\overline{M}_w/\overline{M}_n$ (●) with the $FeCl_3$/monomer molar ratio in the synthesis of poly(DDDMBQT).

The increase of the reaction duration from 15 to 25 hrs, however, produced a product with essentially the same characteristics as those found in the preceding run. This result suggested that in both the cases the polymerization reaction had involved only the monomer, without significant participation of the oligomeric species present in the reacting mixture, in contrast with literature reports concerning the polymerization mechanism, which underline the participation of monomeric or oligomeric radical, or cationic-radical, species to the growing chain [14]. Since one possible explanation of this finding could be originated by the decay, or unavailability, of the active sites of

the catalyst during the process due to the consumption of FeCl$_3$, the polymerization of [(S)-(+)-DDDMBQT] was repeated starting from the initial FeCl$_3$/monomer 4:1 molar ratio and the increase of the molecular mass of the polymeric product followed upon further additions to the reaction mixture of equal aliquots of catalyst so as to obtain in subsequent steps the molar ratios 8:1, 12:1 and 16:1 (Figure 2).

As graphically shown in Figure 2, the results obtained indicate that a strong increase of the molecular mass of the polymeric product is obtained by using an excess of catalyst, which appears to be able to involve in the propagation to an increasing extent the oligomers present in the mixture, thus allowing to achieve a still soluble product and reduced polydispersity.

This finding therefore indicates that a large excess of iron(III) trichloride is required to obtain soluble poly(DDDMBQT) of enhanced average molecular weight. As with the usually adopted FeCl$_3$/monomer ratio, the polymerization of oligothiophenic monomers gives the corresponding polymers with molecular mass remarkably lower with respect to monothiophenic monomers [15, 16]. The here reported procedure allows to overcome this drawback.

Characterization of poly[(S)-(+)-DDDMBQT]

Relevant data for poly[(S)-(+)-DDDMBQT] are reported in Table 1. It can be noted that the thermal stability of this polymer is remarkably higher than those of related poly[(S)-(+)-DHDMBQT] (339 °C) [4] and poly[DMBTT] (305 °C) [17]. By contrast, the T_g value decreases with respect to poly[DMBTT] (49 °C) [17] and poly[(S)-(+)-DHDMBQT] (36 °C) [4], in agreement with the increase of steric hindrance of the side-chain alkyl substituents favouring a better mobility of the macromolecules.

Tab. 1. Characterization data for poly[(S)-(+)-DDDMBQT].

Sample	Yield (%)	$\overline{M}_w$ [a]	$\overline{M}_n$ [a]	$\overline{M}_w/\overline{M}_n$	T_d [b] (°C)	T_g (°C)
Poly[(S)-(+)-DDDMBQT]	~100	33 000	22 200	1.50	391	14

a) Determined by SEC.
b) Determined after a weight loss of 2%.

In the IR spectrum of poly[(S)-(+)-DDDMBQT] the band at 3105 cm^{-1}, related to the C$_\alpha$-H stretching of the monomer, is absent, thus confirming that the polymerization reaction has occurred at the C$_\alpha$ position of thiophene ring. In addition, only two bands, attributed to the out-of-plane bending vibrations of aromatic rings, are present at 826 and 792 cm^{-1}: the former, absent in the monomer, is typical of the C$_\beta$-H bond of 2,3,5-trisubstituted thiophene rings [18], the latter, present also in the monomer at 794 cm^{-1}, is attributed to the C$_\beta$-H bonds of 2,5-disubstituted thiophene rings [19]. A further consideration can be made concerning the CH$_2$ rocking vibration located at 722 cm^{-1}, having a reduced intensity with respect to the corresponding band at the same frequency in the monomer. This apparent contradiction has been explained [4] considering that the absorption intensity in the monomer is enhanced due to overlapping with an out-of-plane bending vibration of the C$_\alpha$-H bond occurring at the same frequency. Finally, the presence in the IR spectrum of poly[(S)-(+)-DDDMBQT] of a strong band at 1504 cm^{-1}, related to the asymmetrical stretching of the C=C bonds of the thiophene rings, more intense than the corresponding band related to

the symmetrical stretching vibration at 1462 cm^{-1}, is indicative of extended electronic conjugation among the thiophene rings located in the main chain [21].

The ^{1}H-NMR spectrum is in accordance with the proposed structure, as it displays in the aromatic region three main resonances at 6.96, 7.01, and 7.11 ppm, related to the *c, b* and *d* protons, respectively, located in each repeating unit [Fig. 1 (b)]. The absence in the spectrum of doublets of low intensity connected to the *a* and *b* protons linked to thiophene terminal groups at 7.16 and 6.93 ppm confirms the occurrence of the polymerization reaction at the α carbons, as well as that the average molecular weight of poly[(*S*)-(+)-DDDMBQT] is sufficiently high so as to prevent the observation of the thiophene end rings.

The UV spectrum of poly[(*S*)-(+)-DDDMBQT] in dilute solution of a good solvent (CHCl$_3$) [Fig. 3(a)] displays an absorption maximum at 456 nm (ε = 42900 L mol^{-1} cm^{-1}) related to the π-π* electronic transition of the conjugated aromatic system, close to the maximum wavelength values found for poly[(*S*)-(+)-DMBTT] [3] and poly[(*S*)-(+)-DHDMBQT] [4]. This value is appreciably higher than those reported for optically active regioregular poly(3-alkylthiophene)s [20-22]. The larger conjugation extension exhibited by poly[(*S*)-(+)-DDDMBQT] is probably originated by its lower substitution degree as well as the different distribution and steric hindrance of the alkyl substituents along the main chain, favouring a more extended coplanarity of the thiophene rings.
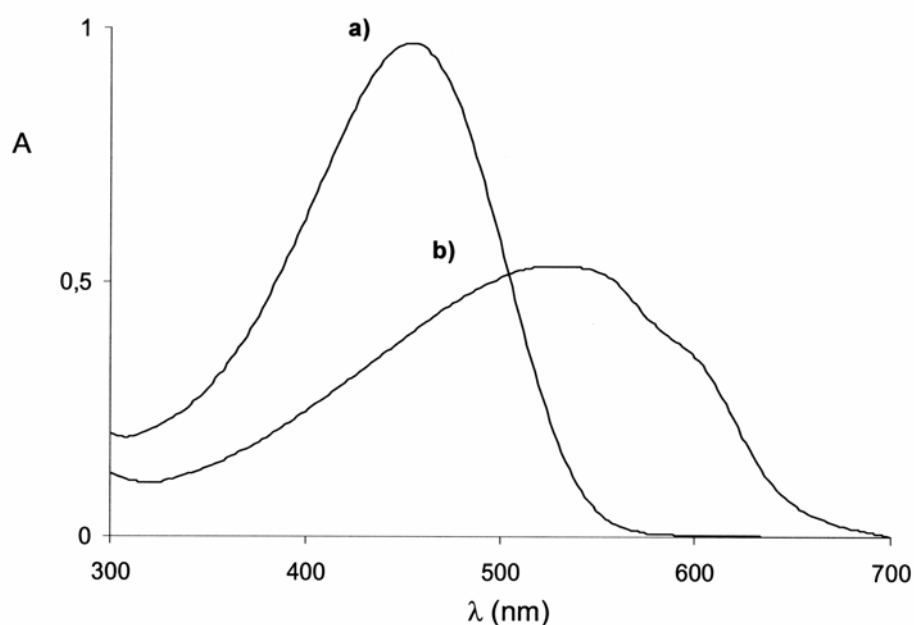

Fig. 3. UV-vis spectra of poly[(*S*)-(+)-DDDMBQT] 2.3·10^{-5} M in chloroform (a) and chloroform/methanol 40/60 v/v solution (b).

As expected in dilute solution [23,24] no vibronic bands are observed in the spectrum, as a consequence of the conformational freedom of the macromolecular chains originated by the flexibility of the alkyl substituents. Upon addition of a poor solvent, such as methanol, at a chloroform/methanol composition of 40/60 v/v (after which precipitation occurs), the absorption maximum gradually shifts to higher wavelength, with flattened maxima at 524 nm and near 550 nm, with a concomitant

remarkable hypochromism (ε = 23000 L mol^{-1} cm^{-1}), and a vibronic band also present at around 580 nm. The observed solvatochromism is attributed to the transition of the macromolecules from a disordered random coil conformation to an ordered π-stacked structure originated by self-assembling of the polythiophene chains with interchain π-π* interactions [25,26].
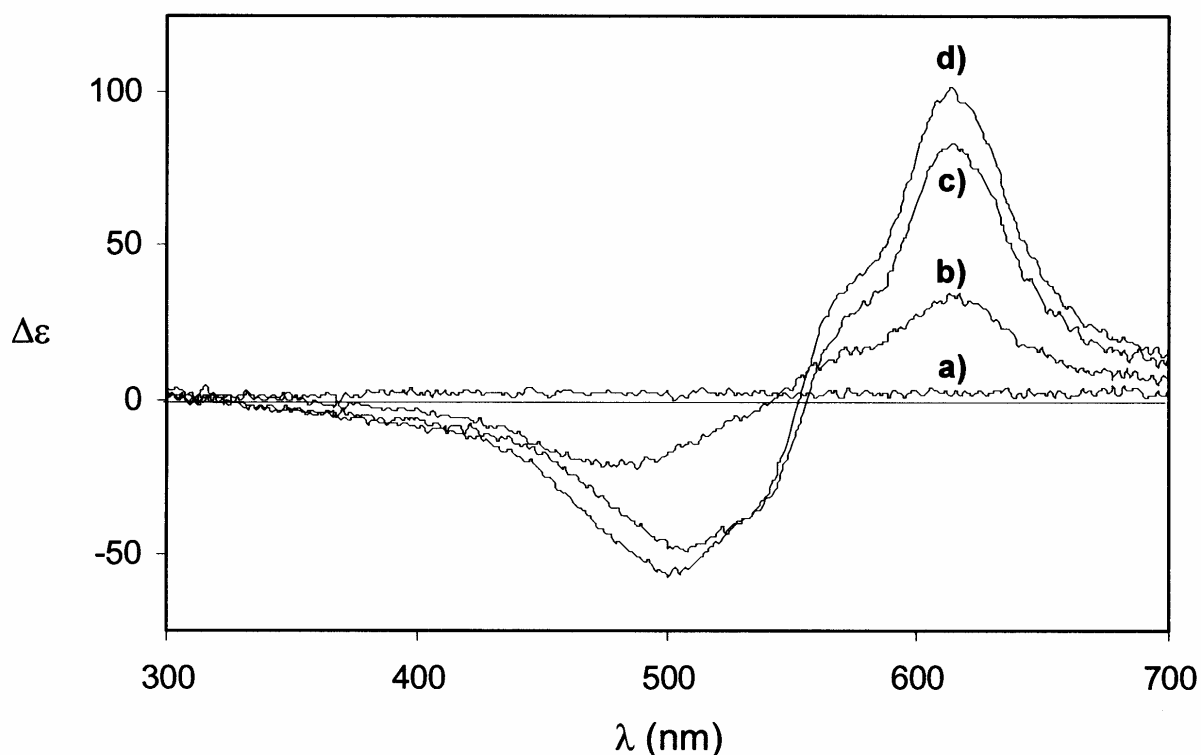

Fig. 4. CD spectra of poly[(*S*)-(+)-DDDMBQT] in chloroform (a) and in chloroform/methanol 50/50 (b), 45/55 (c), 40/60 (d) v/v solution.

The CD spectrum of poly[(*S*)-(+)-DDDMBQT] in CHCl$_3$ solution does not show any significant dichroic band in the spectral region of chromophore absorption [Fig. 4(a)], as expected on the basis of the optical inactivity of the π−π* electronic transition due to the conformational freedom of the macromolecular chains favoring the presence of disordered structures in solution. The addition of methanol, however, produces in the CD spectrum the appearance of strong bisignate, vibronically structured, bands [Fig. 4(b)], associated with the main chain absorptions, consisting of more intense positive signals at 613 and 576 (shoulder) nm and a less intense negative signals at 533 (shoulder) and 502 nm, with a cross-over point at 554 nm, in correspondence to the UV maximum. The dichroic bands appear with increasing amplitude upon increasing the volume of added methanol, before precipitation of the solute takes place, and clearly indicate a progressive microaggregation of the macromolecules, involving a chirally ordered structure, with a chiral anisotropy factor *g* ($\Delta\varepsilon/\varepsilon$) at 613 nm of 4.4·10^{-3}, lower than the one previously found for poly[(*S*)-(+)-DMBTT] [3] and of the same order of magnitude as other chiral poly(3-alkylthiophene)s [26, 27]. This behavior is

attributed to exciton coupling of nearly coplanar polythiophene chains closely arranged according to a helical packing of one prevailing handedness, the positive sign of Cotton effects suggesting the presence of a right-handed helix sense [28]. Similarly to poly[(S)-(+)-DHDMBQT], poly[(S)-(+)-DDDMBQT] in chloroform/methanol solution appears to follow the empirical Sol-Rel, Sed-Rod alternation rule, established by Gray and McDonnell [29] for some cholesteric liquid crystalline compounds, in agreement with the behavior of a series of regioregular chiral poly(3,4-dialkoxythiophene)s bearing the same chiral center at varying distance from the rigid backbone [30].

t is worth noting that the CD spectrum of poly[(S)-(+)-DDDMBQT], similar to poly[(S)-(+)-DHDMBQT] [4], is of opposite sign with respect to that one previously reported of poly[(S)-(+)-DMBTT] in chloroform/methanol 71/29 v/v solution [3], as well as of poly[3-((S)-2-methylbutyl)thiophene] in chloroform/methanol 86/14 v/v solution [31], although both absolute configuration and distance from the backbone of the side-chain chiral moiety are exactly the same in these polymers. This implies that the presence of side-chain C6 or C12 achiral alkyl groups is responsible for the change of the CD sign, originating stacks of polythiophene chains with opposite handedness with respect to polythiophene chains bearing in the side chain the chiral group only.

It is also of interest that the intensity of the CD absorption related to the band at 614 nm in poly[(S)-(+)-DDDMBQT] appears remarkably increased with respect to the same absorption displayed by poly[(S)-(+)-DHDMBQT] [4], the reverse being observed for the band located at 576 nm. It can be suggested that the signal at 614 is enhanced by overlapping with a positive dichroic absorption related to the vibronic band around 580 nm (Fig. 3). As the presence of vibronic absorptions is attributed to increased rigidity and reduced mobility of the macromolecules [23, 24] with concomitant insurgence of intra- and interchain interactions involving also the side-chain substituents [32]. Therefore it appears that when the C12 group in poly[(S)-(+)-DDDMBQT] replaces the C6 group of poly[(S)-(+)-DHDMBQT], the above interactions are more relevant, giving a substantial contribution to the overall chirality of the system.

Further investigations concerning the properties of these monomers and polymers both in solution and in the solid state are presently in progress.

Conclusions

A novel optically active, C12 substituted, quinquethiophene monomer, has been synthesized in quantitative yield. Due to its symmetrical structure, it can be used to obtain the corresponding regioregular polythiophene by oxidative iron(III) chloride polymerization.

The polymerization conditions of this monomer have been optimized in order to obtain a soluble polymer with high molecular mass and low polydispersity. However, a considerable excess of catalyst is required to achieve the highest polymerization degree with the absence of insoluble fraction.

Poly[(S)-(+)-DDDMBQT] displays enhanced solubility and processability, due to the lower T_g value, higher average molecular weight and more extended aromatic conjugation with respect to the previously prepared poly[(S)-(+)-DMBTT], lacking of C12 groups linked to the main chain.

The polymer exhibits high optical activity in solution when in the microaggregated form, in the presence of an appropriate amount of a poor solvent. The CD spectrum appears of opposite sign when compared to poly[(S)-(+)-DMBTT], although the configuration of the asymmetric center is the same in both the derivatives, thus suggesting that the helix sense of the supramolecular structures formed upon aggregation of the macromolecules does not only depend on the nature of the side chain chiral moiety, nor the solvent type and composition, but also on the constitutional sequence of the repeating units in the polymer, when chiral as well as achiral side chain substituents are present.

Experimental part

2-Iodo-3-*n*-dodecylthiophene (**I**) was prepared according to Suzuki [33] from 3-*n*-dodecylthiophene, obtained in turn from 3-bromothiophene as reported [34].

3,3""-Didodecyl-4',3"'-di[(S)-(+)-2-methylbutyl]-2,2':5',2":5",2"':5"',2""-quinquethiophene (S)-(+)-DDDMBQT (Scheme 2).

A solution of 2-iodomagnesium-3-dodecylthiophene (**II**) (5.5 mmol) in diethylether (5 ml) was prepared from **I** (5.55 mmol) by reaction with magnesium turnings (6.17 mmol) in the presence of a catalytic amount of methyl iodide and kept under reflux for 5 hrs. To this solution, dichloro[1,3-bis(diphenylphosphino)propane]Ni(II), [Ni(dppp)Cl$_2$] (0.028 mmol) was added, followed by addition of 5,5"-dibromo-3,3"-di[(S)-(+)-2-methylbutyl]-2,2':5',2"-terthiophene (**III**) [4] (1.37 mmol) in diethylether solution (30 ml).

The mixture was heated under reflux for 20 hrs, and then poured into acid water. The organic material was extracted with diethylether and purified by chromatography (Al$_2$O$_3$, n-hexane) to give [(S)-(+)-DDDMBQT] (53%).

^{1}H-NMR: 7.16 (d, 2H, H-5, H-5""", J$_{4,5}$ = 5.1 Hz); 7.08 (s, 2H, H-3", H-4"); 6.93 (d, 2H, H-4, H-4""); 6.91 (s, 2H, H-3', H-4"'); 2.85-2.55 (m, 8H, α-CH$_2$); 1.9-1.1 (m, 46H, CH and CH$_2$); 0.9 (m, 18H, CH$_3$) ppm.

FT-IR: 3105 (v_{CH} arom. α); 3065 (v_{CH} arom. β); 2957, 2925, 2853 (v_{CH} aliph.); 1462 ($v_{C=C}$); 1377 (δ_{CH3}); 834, 794, 722, 691, 651 (δ_{CH} arom.); 722 (rocking $_{CH2}$) cm^{-1}.

Mass spectrometry: (*m/z*) 888.

$[\alpha]_D^{25}$ = +6.4 (c=1.18, CHCl$_3$).

Polymerization of [(S)-(+)-DDDMBQT]

To a 6·10^{-2} M solution of [(S)-(+)-DDDMBQT] in chloroform anhydrous iron(III) trichloride was added under nitrogen flow so as to have a molar ratio Fe/monomer 4:1. The reaction was left at room temperature for 15 hrs, then 0.1 N HCl and chloroform were added and the mixture heated to reflux under vigorous stirring up to complete decomposition of the polymer/iron chloride complex.

The chloroform solution was washed with acid water up to exhaustive extraction of the iron(III) ion (negative essay with NH$_4$SCN).

After a final purification from any unreacted monomer and low molecular weight fraction by extraction with acetone in a Soxhlet apparatus, the polymer was obtained in 98% yield with respect to the feed.

The ^{1}H-NMR spectra were recorded with a Varian Gemini 300 spectrometer at room temperature on 5-10% $CDCl_3$ solutions. Tetramethylsilane (TMS) was used as internal reference. ^{1}H-NMR spectra were performed at 300 MHz, by using the following experimental conditions: 24 000 data points, 4.5 kHz spectral width, 2.6 s acquisition time, 16 transients.

FT-IR spectra were carried out on a Perkin-Elmer 1750 spectrophotometer, equipped with an Epson Endeavour II data station. The absorption frequencies are reported in cm^{-1} with the spectra being obtained on cast thin films deposited over KBr discs.

Number-average molecular weight ($\overline{M}_n$) and polydispersity ($\overline{M}_w / \overline{M}_n$) of the polymer were determined by size exclusion chromatography (SEC) in THF solution using a HPLC Lab Flow 2000 apparatus, equipped with an injector Rheodyne 7725, a Phenogel Mixed MXL column and a UV-Vis detector Linear Instruments model UVIS-200, working at 254 nm. Calibration curves were obtained by using several monodisperse polystyrene standards.

The decomposition temperature T_d of poly[(*S*)-(+)-DDDMBQT] was determined by using a Perkin Elmer TGA-7 thermogravimetric analyser operating at a heating rate of 20°C/min under air. The glass transition temperature T_g was determined by a TA Instruments DSC 2920 apparatus operating at a heating rate of 10°C/min under nitrogen after one heating-cooling cycle.

Optical activities were measured at 25°C on $CHCl_3$ solutions with a Perkin Elmer 341 digital polarimeter, equipped with a Toshiba sodium bulb, using a cell path length of 1 dm. Specific rotation values at the sodium D line are expressed as deg dm^{-1} g^{-1} dL.

UV-Vis absorption spectra were recorded at 25°C on a Perkin-Elmer Lambda 19 spectrophotometer in the 300-700 nm spectral region on $2.3 \cdot 10^{-5}$ M $CHCl_3$ solutions, in terms of quinquethiophene co-units, by using a cell path length of 1.0 or 0.1 cm.

CD spectra of the samples were recorded at 25°C on $CHCl_3$ or $CHCl_3/CH_3OH$ solutions on a Jasco 810 dichrograph, using the same spectral regions, cell pathlengths and concentrations as for UV measurements. $\Delta\varepsilon$ values, expressed as L mol^{-1} cm^{-1}, were calculated by the following equation: $\Delta\varepsilon = [\Theta]/3300$, where the molar ellipticity $[\Theta]$ is in deg cm^2 $dmol^{-1}$.

Mass spectrometry (ms) measurements were carried out on a VG 7070E spectrometer operating at 70 eV.

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