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Synthesis and polymerization of 3,3″-di[(*S*)-(+)-2-methylbutyl]-2,2′:5′,2″-terthiophene: a new monomer precursor to chiral regioregular poly(thiophene)

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3,3″-Di[(*S*)-(+)-2-methylbutyl]-2,2′:5′,2″-terthiophene, having two equivalent reactive positions, allows the synthesis of the corresponding optically active poly(thiophene) with regioregular enchainment by using an aspecific oxidative polymerization method.

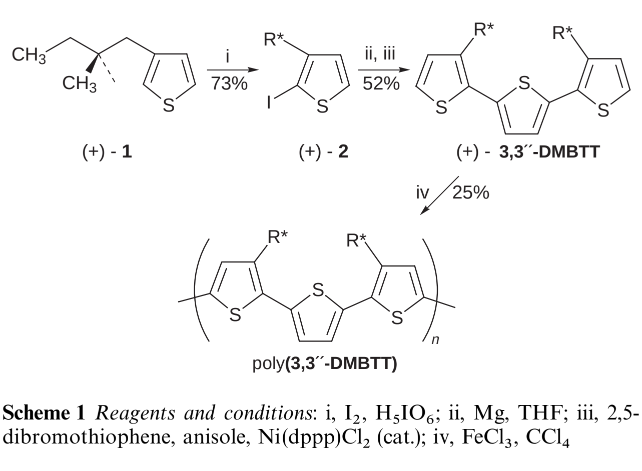
Much effort has been devoted in the recent years to the investigation of optically active polythiophenes characterized by the presence of a chiral moiety linked to the 3-position of the aromatic ring. In addition to their potential technological applications as materials for enantioselective electrodes and membranes,[1–4] chiral poly(thiophene)s offer the possibility of studying the structural changes accompanying the transition from the disordered state in solution to the ordered micro-aggregate or solid state by following the variation of their chiroptical properties by circular dichroism (CD).[5–8] A crucial role in obtaining remarkable chiroptical properties is however played by a highly predominant or exclusive presence in the macromolecular backbone of regioregular head-to-tail sequences of the 3-substituted thiophene repeating units, as the lack of this structural requirement strongly reduces the possibility of the existence of extended co-planar structures characterized by a large extent of aromatic conjugation. Synthetic methods to produce highly regioregular poly(thiophene)s have been developed[9–11] and McCullough's procedure, in particular, has been applied to the preparation of highly regioregular optically active 3-alkyl substituted poly(thiophene)s,[5–8] exhibiting much enhanced optical activity as compared to the corresponding regiorandom derivatives when the macromolecules are in the micro-aggregate or solid (film) state. A possible way to avoid the need for using regiospecific synthetic methods is given by the preparation of symmetrical monomers inherently unable to afford regiorandom polymeric derivatives even in the presence of an aspecific polymerization mechanism. Whereas symmetrically 3,3′- or 4,4′-disubstituted 2,2′-bithiophenes give polymers containing regularly spaced head-to-head (50%) and tail-to-tail (50%) coupled repeating units, symmetrically 3,3″- and 3′,4′-disubstituted 2,2′:5′,2″-terthiophenes have been reported[12–18] to produce the corresponding polythiophenes characterized by a regioregular enchainment free from head-to-head connections, provided that two identical ring substituents are present. However, no optically active terthiophene monomer precursor to a regioregular optically active polymer is mentioned in the literature. We report here the possibility of synthesizing poly(thiophene)s, characterized by relevant chiroptical properties, from the optically active 3,3″-di[(*S*)-(+)-2-methylbutyl]-2,2′:5′2″-terthiophene monomer [(+)-**3,3″-DMBTT**] (Scheme 1) having two identical reactive sites and hence polymerizable using chemical oxidative methods, such as $FeCl_3$ oxidation, which is easy to use and suitable to large scale production.

Monomer (+)-**3,3″-DMBTT** was prepared from 3-[(*S*)-(+)-2-methylbutyl]thiophene (+)-**1**, itself derived from optically pure (*S*)-(−)-2-methylbutan-1-ol, according to the reported procedure[3] which involves a bromination step to (*S*)-(+)-1-bromo-2-methylbutane followed by Grignard reaction and coupling with 3-bromothiophene in the presence of 1,3-diphenylphosphinopropanenickel dichloride [Ni(dppp)Cl_2]. The 3-alkylthiophene (+)-**1** was then submitted to iodination using the method of Suzuki,[19] thus obtaining a mixture of the 2-iodo and 2,5-diiodo derivatives. Iodination, instead of bromination, of (+)-**1** was adopted due to the expected higher reactivity of the iodinated derivative in the subsequent preparation of the Grignard reagent. The pure mono-iodinated product, 2-iodo-3-[(*S*)-(+)-2-methylbutyl]thiophene (+)-**2**, $[\alpha]_D^{25}+3.95$ (*c* 2.1, $CHCl_3$), was obtained in good yield by fractional distillation *in vacuo*, then allowed to react with magnesium in THF, and finally coupled with 2,5-dibromothiophene in the presence of Ni(dppp)Cl_2 and anisole to give (+)-**3,3″-DMBTT**, according to Kobayashi's procedure.[20]

Monomer (+)-**3,3″-DMBTT** purified by column chromatography (SiO_2, hexane), $[\alpha]_D^{25}+16.0$ (*c* 1.7, $CHCl_3$), was fully characterized by IR and ^1H NMR spectroscopy, mass spectrometry (*m*/*z* 388; M^+, 100%) and elemental analysis (Found: C, 67.8; H, 7.4; S, 24.8. Calc. for $C_{22}H_{28}S_3$: C, 67.99; H, 7.26; S, 24.75%). In particular, it is worth noting the presence in the IR spectrum of two bands at 3102 and 3063 cm^{-1}, related to C_α–H and C_β–H stretching, respectively, typical of 3-alkyl-substituted thiophene rings,[21] as well as the presence of an out-of-plane bending signal at 797 cm^{-1}, attributed to the 2,5-disubstituted central ring.[22,23]

The ^1H NMR spectrum in $CDCl_3$ [Fig. 1(*a*)] exhibits the expected pattern in the aromatic region, consisting of two doublets at 7.17 and 6.91 ppm, related to the *a* and *b* protons, respectively, and of one singlet at 7.05 ppm (*c* protons).

The oxidative polymerization of (+)-**3,3″-DMBTT** has been carried out following the general method of Sugimoto *et al.*,[24]



Scheme 1 *Reagents and conditions*: i, I_2, H_5IO_6; ii, Mg, THF; iii, 2,5-dibromothiophene, anisole, Ni(dppp)Cl_2 (cat.); iv, $FeCl_3$, CCl_4

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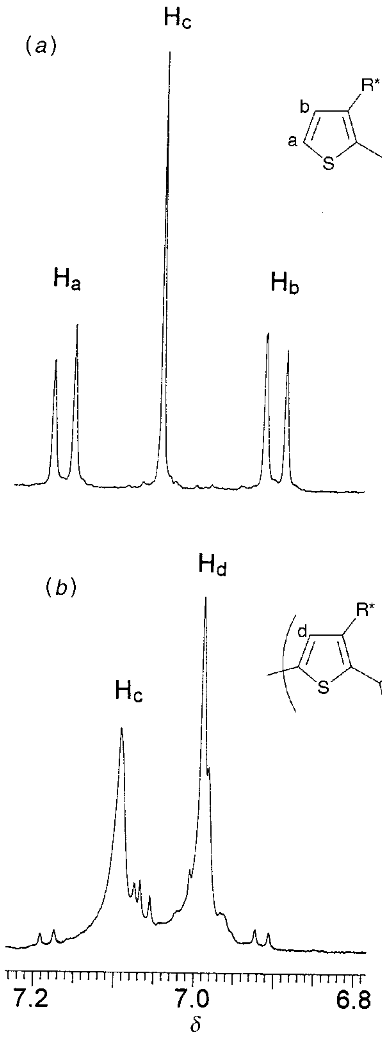

Fig. 1 ^{1}H NMR spectra in $CDCl_3$ of the aromatic region of (*a*) (+)-**3,3″-DMBTT** and (*b*) **poly(3,3″-DMBTT)**

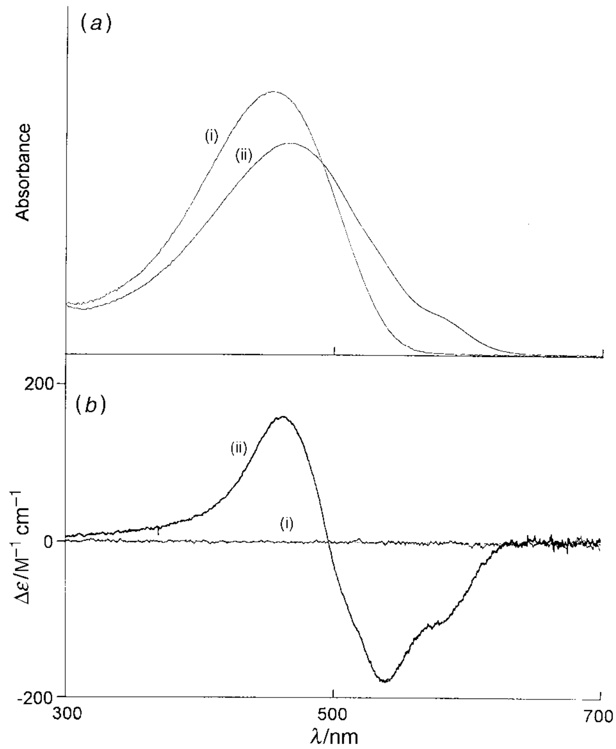

Fig. 2 (*a*) UV and (*b*) CD spectra of **poly(3,3″-DMBTT)** in (i) $CHCl_3$ and (ii) $CHCl_3$–CH_3OH (71:29)

using CCl_4 in place of $CHCl_3$ and lower monomer and $FeCl_3$ molar concentrations (0.025 and 0.1 M, respectively), in order to reduce, according to recently reported[18] results, the relative amount of insoluble material. Although the reaction conditions have not been yet optimized, we have observed that, indeed, no insoluble polymer fraction is produced at all, even though **poly(3,3″-DMBTT)** is reasonably expected to be not very soluble, due to the lower average density of 2-methylbutyl side chains as compared to the corresponding poly[3-(2-methylbutyl)thiophene].[3] **Poly(3,3″-DMBTT)**, purified by exhaustive extraction with CH_3OH of any unreacted monomer and low molecular weight fractions, exhibits the disappearance of the band at 3102 cm^{-1}, while the 3063 and 797 cm^{-1} signals remain unchanged, with respect to the IR spectrum of the monomeric precursor. Moreover, two bands at 818 and 833 cm^{-1}, typical of the out of plane bending of the C_β–H bond in 2,3,5-trisubstituted thiophene rings,[23] appear in the spectrum, thus confirming that the polymerization has taken place only at the C_α atom of the monomer, with no mislinkages through the β-positions occurring during the process. The ^{1}H NMR spectrum [Fig. 1(*b*)] is in accordance with the proposed structure, as it displays two main resonances at 7.10 and 6.99 ppm, related to the *c* and *d* protons, respectively, located along the main chain. Less intense signals are also observable in the spectrum, due to the hydrogen atoms of terthiophenic end groups. Calculations based on the integrated areas of these last resonances allow the assessment that the mean molecular weight of the macromolecular chains is around 5000 g mol^{-1}, corresponding roughly to a polymerization degree $\bar{x}_n$ of 13, expressed as terthiophene co-units. This value appears to be in good agreement with the $\bar{M}_n$ value of 4300 g mol^{-1} ($\bar{x}_n = 11$), determined by gel permeation chromatography using monodisperse polystyrene samples as standard references. Optimization of the polymerization reaction aimed at obtaining both better yields and higher values of $\bar{M}_n$ in the soluble fraction of **poly(3,3″-DMBTT)** is currently under study.

The UV spectrum of **poly(3,3″-DMBTT)** in $CHCl_3$ (Fig. 2) displays an absorption maximum at 454 nm, related to the π–π* electronic transition of the conjugated aromatic system, similar or even higher than the maximum wavelength values reported in the literature[4,5,7,8] for optically active regioregular head-to-tail poly(3-alkylthiophene)s, thus suggesting an enhanced extent of conjugation, probably attributable to improved coplanarity of the thiophene rings along the main chain. A solvatochromic effect is also evidenced in the UV spectrum upon addition of increasing amounts of methanol (poor solvent), which promotes the aggregation of the macromolecules. A progressive appreciable red-shift of the maximum absorbance, accompanied by the appearance of vibronic bands and shoulders, up to a λ_{max} of 467 nm is observed, corresponding to a $CHCl_3$–CH_3OH ratio of about 70:30 (v/v). Upon further addition of CH_3OH, precipitation of the solute takes place. This behaviour indicates an increase of conjugation length attributable to an increase of the conformational order in the micro-aggregate state. In this state, also, the polymer main chain becomes optically active, as revealed by its CD spectrum (Fig. 2), as a consequence of chirality transmitted by the alkyl side-chain to the conjugated backbone.

The CD spectrum of the micro-aggregated macromolecules displays strong dichroic signals which correspond closely to the UV absorbances, originated by the presence of chiral conformations assumed by the macromolecules when the crystallization begins to take place, with a remarkable value of the chiral anisotropy factor *g* ($\Delta\varepsilon/\varepsilon$) of -3×10^{-2} at 578 nm, close to the values reported for regioregular poly(3-alkylthiophene)s.[8] By contrast, the CD spectrum of **poly(3,3″-DMBTT)** in pure $CHCl_3$, which favours the presence of disordered random coil conformations of the macromolecules, does not display any optical activity (Fig. 2), due to the absence of chirally ordered structures in the polymer in solution.

It can therefore be concluded that although **poly(3,3″-DMBTT)** has a lower content of chiral alkyl substituents per thiophene ring with respect to regioregular poly(3-alkylthiophene)s, it behaves similarly, or better, as regards extent of conjugation and chiroptical properties. Interestingly, it could be synthesized also by electrochemical oxidative coupling of (+)-**3,3″-DMBTT**, thus directly yielding a thin chiral polymeric film on the electrode surface, which would be particularly useful for electrochemical characterizations and applications.

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