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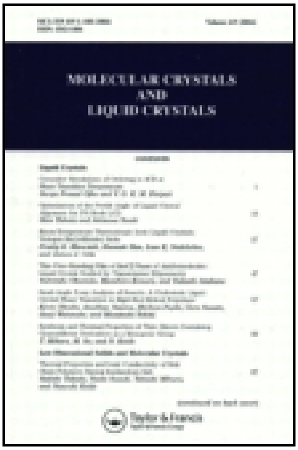

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Thiophene Oligomers: Synthesis and Characterization

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Thiophene Oligomers: Synthesis and Characterization

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The series of thiophene oligomers from bithienyl to α-sexithienyl has been synthesized according to the methods reported in the literature and some variation introduced by us. UV-visible, FT-IR, ^{13}C-nmr and mass spectra of thiophene oligomers have been recorded and also cyclic voltammograms. Results are compared with data available in literature and are discussed in terms of conjugation length and coplanarity.

Keywords: thiophene oligomers, 2,5-thienylene oligomers, ^{13}C-nmr, FT-IR, spectroscopy

INTRODUCTION

The synthesis and study of thiophene oligomers have attracted for several years much attention due their biological activity against microorganisms[1,2] and recently as model compounds or monomers to produce polymer which are able to conduct the electricity. The monomers have been electro[3] and chemically polymerized.[4]

Studies based on the electropolymerization of bithiophene and α-terthienyl, have shown for instance that these two monomers would give less conjugated and poor electrically conducting polythiophene as compared with the same polymer obtained from thiophene (3 b)c)g)). It has also been reported that by direct action of iron (III) perchlorate on bithiophene, a higher conducting polythiophene is produced as compared with the polythiophene obtained from oxidation of thiophene with the same salt (4a).

Two main factors have motivated the use of these compounds as starting monomers in the polymerization of thienyl oligomers. One is the lower polymerization potential found in bithiophene and α-terthienyl (3a)e)) and the second, the poly(bithiophene) or poly(α-terthienyl) are expected to have less non α,α′-bonding than poly(thiophene) (3 g). The same reasoning is applicable to the higher oligomers in the series of thiophene, with the advantage that the larger the thiophene ring number in the monomeric unit, the higher the probability of obtaining purely α,α′-coupling by polymerization.

We report here the synthesis, purification and spectroscopic characterization of thiophene oligomers from bithienyl to α-sexithienyl(UV-visible,FT-IR, ^{13}C-NMR spectra). In addition the mass spectra, and cyclic voltammograms of each oligomer has also been recorded. The results are examined and discussed in terms of conjugation length and coplanarity.

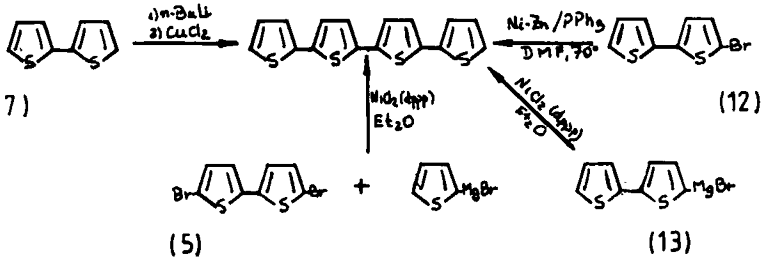
EXPERIMENTAL

Oligomeric 2,5-thienylenes were synthesized following the cross-coupling Grignard reaction reported by Kumada[5] and other methods found in the literature.[6–13] We introduced some variation in the Grignard reactions, making use of different monobromo or dibromothienylene by us synthesized to get α-quinquethienyl and α-sexithienyl. A modification in the procedure of purification was also made in order to obtain as pure as possible the series of oligomers.

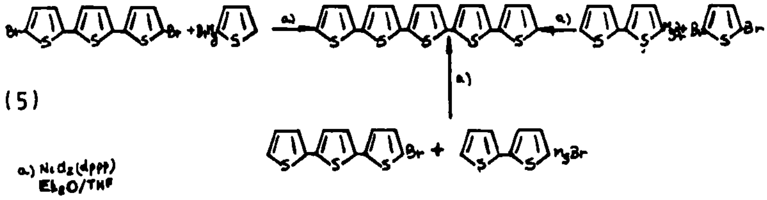
2,2′-Bithiophene(Aldrich) was distilled under vacuum and then sublimated. α-Terthienyl(Fluka) was sublimated. These two compounds were also synthesized by us and purified in the same way as with the commercial samples. No differences in melting points or spectroscopic analysis (^{13}C-NMR, FT-IR) were found between samples.

α-Quaterthienyl, α-quinquethienyl and α-sexithienyl were synthesized according to the schema below-despicted (numbers between parenthesis denotes references).

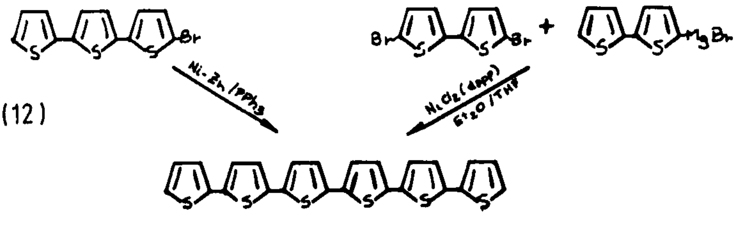
A. α-quaterthienyl.



B. α-quinquethienyl.



C. α-sexithienyl.



α-Quaterthienyl was recrystallized twice from *n*-hexane, α-quinquethienyl, after the hydrolysis process (from Grignard synthesis), was extracted with *n*-hexane in Soxhlet extractor in order to remove all the unreacted or low mono or dibromothienyl derivate (α-quinquethienyl is only slightly soluble in *n*-hexane). Then, toluene was used to extract the α-quinquethienyl from Soxhlet extractor and in this solvent twice recrystallized. Finally the produce was sublimated under high vacuum. An analogous procedure was used to purify α-sexithienyl, with the only difference that chlorobenzene was used instead of toluene in the last step. TLC of each sample gave only one spot (mixture toluol:*n*-hexane on activated silicagel). No big differences were found in the appearance of synthesized products depending on the diverse methods employed. The yields oscillate normally between 20–65% and the Grignard cross-coupling reaction[5] gave the most reproducible results with respect to yield. Solubility of oligomers in normal organic solvents diminishes as *n* (number of thiophene rings) increases. For instance, only hot chlorobenzene and N-methylpyrrolidone were found to be acceptable solvents for α-sexithienyl.

Ultraviolet-visible absorption spectra were performed on a Perkin Elmer Lambda 5 instrument. Fourier transform infrared (FT-IR) transmission spectra were recorded on a Bruker IFS 85 instrument. ^{13}C-NMR and ^{13}C-NMR MAS were recorded on a AM 270 Bruker and Bruker CXP 200 spectrometers respectively. Mass spectra were performed on a MAT 112 Finnigan instrument. Cyclic voltammogram were registered on a PAP scanning potentiostat model 362.

RESULTS AND DISCUSSION

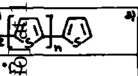
Table I resumes the results obtained from the thiophene oligomers characterization. The melting points measured for α-quinque and α-sexithienylenes are above the reported one in the literature,[1,11,12] however the UV-visible absorption spectra coincide with the values in the literature,[12] which means that probably impurities present in previous synthesized products are due to lower oligomers and not higher conjugated system or polymers. The oligomers are strongly fluorescent under the UV lamp (λ = 366 nm) which facilitates their identification by TLC.

Infrared spectra (FT-IR) absorption bands of 2,5-thienylene oligomers show clearly two main regions with characteristic peaks. The region between 1500–1400 cm^{-1} contains the C=C stretching vibration and between 900–450 cm^{-1} are situated the C—H bending (out of plane) vibrations. The absorption near to 1490 cm^{-1} (C=C asymmetric) increases in intensity from bithiophene to α-sexithienyl, while the C=C symmetric stretching absorption around 1420 cm^{-1} decreases in intensity in opposite direction. The intensity ratio of these two bands has been used by Harada *et al.*[14,15] as an approximate measure of conjugate length. The absorption around 456 cm^{-1} ascribed to a ring deformation (out of plane)[16] presents also an increasing intensity from bithiophene to α-sexithienyl and could also be used in principle as a measure of conjugation length. One of the strongest IR absorption band present in all spectra, except in bithiophene, lies between 790–798 cm and correspond to C—H bending of 2,5-bisubstituted thiophene ring.[15]

The ^{13}C-NMR analysis of oligomeric thienylenes can be centered on the two only

TABLE I

Physical and spectroscopic data of thiophene oligomers.

 a)	n = 0	n = 1	n = 2	n = 3	n = 4
°C	33 (lit.-no. 9, 33) colorless	95-96 (lit.-no. 1, 95) yellow-green	214-215 (lit.-no. 10, 211-219) chrom-yellow	258-259 (lit.-no. 3, 256-258) orange	307-309 (lit.-no. 1, 304) orange-red
ible (CHCl$_3$)	300 nm (lit.-no. 9, 305 in benzene)	354 nm (lit.-no. 9, 360)	390 (lit.-no. 9, 391	416 (lit.-no. 9, 416)	434 (lit.-no. 9, 438)
(cm^{-1}) ellet)	asym. c=c stretch. 1499 sym. c=c stretch. 1416 C-H bend. o.o.p. 827 C-H bend. 2,5-subst. -- C-H bend. 2-subst. 694 Ring def. o.o.p. 458	asym. c=c stretch. 1498 sym. c=c stretch. 1422 C-H bend. o.o.p. 831 C-H bend. 2,5-subst. 796 C-H bend. 2-subst. 688 Ring def. o.o.p. 455	asym. c=c stretch. 1495 sym. c=c stretch. 1425 C-H bend. o.o.p. 833 C-H bend. 2,5-subst. 798 C-H bend. 2-subst. 68 Ring def. o.o.p. 454	asym. c=c stretch. 1493 sym. c=c stretch. 1425 C-H bend. o.o.p. 831 C-H bend. 2,5-subst. 793 C-H bend. 2-subst. 680 Ring def. o.o.p. 457	asym. c=c stretch. 1492 sym. c=c stretch. 1425 C-H bend. o.o.p. 827 C-H bend. 2,5-subst. 792 C-H bend. 2-subst. 688 Ring def. o.o.p. 457
R (ppm)	b) C (2) 137.45 C (3) 123.77 C (4) 127.66 C (5) 124.77	b) C (2)(2") 137.07 C (2')(5') 136.14 C (4)(4") 127.10 C (5)(5") 124.42 C (3')(4') 124.25 C (3)(3") 123.64	c) C (2)(2"') 134.63 C (2')(5')(2")(5") 133.52 C (4)(4"') 127.10 C (5)(5"') 124.45 C (3')(4')(3")(4") 123.82 C (3)(3"') 123.08	d) 138.0 135.6 125.9 123.9	d) 136.4 135.1 126.3 123.9
pectrum	40,83,121,$\underline{166}$ (M$^+$, 100%) 223	57,124,203,$\underline{248}$ (M$^+$, 100%)	165,285,$\underline{330}$ (M$^+$, 100%)	206,367,$\underline{412}$ (M$^+$, 100%)	247,$\underline{494}$ (M$^+$, 100%)
lt (0.5 M LiClO$_4$ in encarbonat)	0.43	0.21	0.12	0.08	0.04

AC names: *n* = 0.2,2′-bithiophene; *n* = 1.2,2′:5′:2″-terthiophene; *n* = 2.2,2:5′,2″:5″,2″′-quarterthiophene; *n* = :5′,2″:5″,2″′:5″′,2″′:5″′,2″″-quinquethiophene; *n* = 4.2,2′:5′,2″:5″,2″′:5″′,2″″:5″″,2″″′-sexithiophene.

DCl$_3$.

MSO-d$_6$.

AS-CP ^{13}C-NMR.

α and β different kind of atoms present. The α and β carbon can also be differentiated according to the coupling they have. The α,α′-coupled carbons have at 136–137 ppm a signal and the α carbons situated on the extreme of thiophene rings show a peak around 124 ppm. Two kinds of β carbons are also distinguished: those which are on the extreme positions in thiophene rings and present a peak around 127 ppm, and carbons from the inner rings which have a peak at 123–124 ppm. A shift from the α,α′-coupling peak is observed from bithiophene to α-quaterthienyl. The signal at 137 ppm in bithiophene shifts to upfield and is observed at 133.5–135 ppm in α-quaterthienyl. The larger the conjugation, the more delocalized the π electrons about the carbon atoms and the larger the effect of electron shielding, therefore there is shifting to upfield. In chemically synthesized polythiophene, only two ^{13}C-NMR signals have been observed at 136.6 and 125.6 ppm due to the α and β carbons respectively.[17] With respect to the α-quinque and α-sexithienyl, their ^{13}C-NMR were registered in solid state (^{13}C-NMR MAS) due to their poor solubility. Four nmr signals were observed in each case between 123.9 and 138.0 ppm. The peaks under 130 ppm correspond to the carbons carrying hydrogen atoms, while the signals above 130 ppm arise from the quaternary carbons (the difference was established by the NQS technique, Non-quaternary suppression). The peaks correspond to the expected α-position (around 124 ppm) and β-position (around 135 ppm) carbons found in the chemically synthesized polythiophene.[17] The solid state ^{13}C-NMR data of α-quinque and α-sexithienyl agree in a great extent with those solution NMR spectra of lower oligomer. In solid state NMR it is known that effects like packing or defined conformation are normally present and the signals, in some cases, may be shifted from some tenths up to 10 ppm (depending mainly on the crystal structure or amorphous state). In our samples, only small differences in chemical shift were founded by comparing the solution and the solid state NMR. From the width of the signals of α-quinque and α-sexithienyl, can be assumed that both oligomers are predominantly in amorphous states, since no sharp peaks were observed.

The mass spectra from thienyl oligomers showed in every case (except α-sexithienyl) the molecular ion (M^+) as the peak base (100%) and fragments at $(M-45)^+$ were also observed in all compounds due to the species $H{-}C{\equiv}S^+$.[18] Particularly interesting is the peak at $M^+/2$, found in every oligomer; in some cases the two main peaks observed were the molecular ion M^+ and $M^+/2$. In the case of even numbered thiophene rings it is reasonable to imagine an homolytic cleavage of the molecular ion; however, it is difficult to explain the same rupture in odd oligomers.

The cyclic voltammograms of the thienyl oligomeric exhibited a clear difference between the redox potentials of each compound. The oxidation potentials shifted to less negative values as *n* increased, indicating an easier oxidation as the conjugation length increases. The oxidation potentials' values oscillate between 0.43 and 0.04 Volts (Ag/Ag^+) for bithiophene and α-sexithienyl respectively. These lower oxidation potential values with increasing *n* are in close dependence with the UV absorption values observed in respective oligomers. With a higher delocalization of pi electrons, a more stable cation-radical is obtained by electrooxidation and therefore a lower oxidation peak results from higher oligomers. The voltammogram of α-quinquethienyl showed a second peak in the vicinity of 0.26 Volts and this peak could be interpreted as a di-ion state which would be formed starting from a segment containing five rings. Only one oxidation peak was observed from bithienyl to α-quaterthienyl between 0.0 and 0.5 Volts. Heinze *et al.*[19] has noted a dependence of the redox states of oligo-*p*-phenylenes-vinylenes with the chain length of the monomeric unit. The results have been interpreted as the formation of multi-anion (di, tri, tetra, penta) as *n* (number of *p*-phenylenes-vinylen unit) increases from one to four.

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