Synthesis, characterization and polymerization of thiophene units anchored with an imine-type mesogen group

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Summary

Thiophene structures anchored in position 3 of the ring were synthesized using spacers of different lengths (6,8,10, and 12 carbon atoms linked to a 2-((4-octyl-phenylimino)methyl)phenol) group. The thermal studies of the units demonstrated that they possess liquid-crystal properties and their optical study indicated that all the compounds present a nematic phase. Further chemical polymerization of these units was performed by oxidation of the respective monomers using iron(III) chloride. The resulting polymers proved to be insoluble and therefore their characterization was only possible by XPS and FT-IR techniques. In addition, as the polymers have no melting point because they decompose at temperatures over 200 °C, it was not possible to determine if they were effectively liquid-crystals. Finally, the iodine-doped polymers displayed conductivities of about 10^{-7} S cm^{-1}, *i.e.*, semiconductor-like conductivity.

Introduction

Scientific investigation within the ambit of the development of new materials has increased a big deal since in the 70s doped (poly)acetylene was describes as the first conducting polymer [1], which disclosed a completely new field, not only within organic chemistry but also in physics and engineering, concerning to the application of these new materials to the fabrication of different devices, *e.g.*, photocells, diodes, displays, and so on. Among the early conductive polymers, (poly)thiophenes, due to their conducting properties and stability at room conditions, have been widely studied [2,3,4,5]. The polymerization process of these units may be obtained by two different well established routes, *i.e.*, chemical, that usually yields oligomeric units that can be further doped with an oxidizing agent [6,7], and electrochemical that, compared to the former, is a cleaner process because of the polymer film is obtained by straight deposition upon the electrode. Besides, this method allows doping control of the polymer in situ [8,9]. The problem lies

in that both methods lead to insoluble products, hard to characterize. On the other hand, another exciting area of research in the development of electronic devices nowadays is the synthesis of compounds with liquid-crystal (LC) properties. Among the LCs, the thermotropics, that reach a mesophase at a determined temperature, are the most employed. Several groups that may confer LC properties to a molecule, as a rule structures that combine rigid and flexible sectors such as biphenyls [10,11] and imines [12,13], have been described in the literature. Roncali et al. [14] synthesized a thiophene unit with a mesogen group, as depicted in Fig. 1, that displayed thermotropic LC properties, wherein an isotropic and nematic phase was identified at 79 ºC and 39 ºC, respectively. This work disclosed a novel line of research in relation to the characteristics of a mesogen compound. Accordingly, in the present work we report the synthesis of new thiophene units bearing a group with liquid-crystal properties, such as imine, anchored by means of spacers of different lengths to generate new structures through a synthetic route described elsewhere [15], as shown in Fig. 2. Polymerization of the respective units in order to establish their properties will be attempted too.
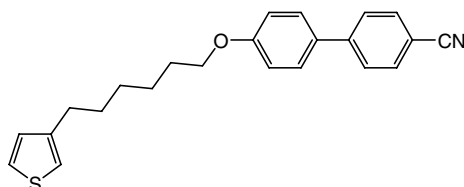
Figure 1. 4-cyano-4'-[8-(3-thienyl)oxi]biphenyl

X = 4, 6, 8, 10
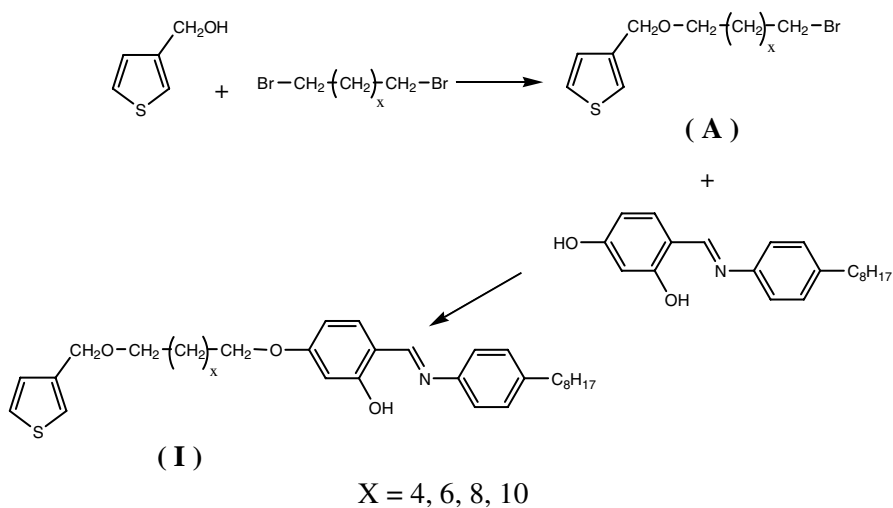
Simbology

compounds	X=4	X=6	X=8	X=10
A	A-6	A-8	A-10	A-12
I	I-6	I-8	I-10	I-12

Figure 2. Synthetic route to prepare the monomeric units

Experimental

Materials

Except for iron(III) chloride, purchased from Merck and vacuum dried at 100 ºC, all chemicals employed in the present work were from Aldrich and were used without further purification.

Instruments

The thermal properties of the materials were determined by differential scanning calorimetry (DSC) using a Mettler-Toledo, Model 821, Differential Scanning Calorimeter with a heating rate of 5 ºC min^{-1}, under nitrogen atmosphere. Identification of the phases was performed by Polarized Light Microscopy on an Olympus Model BH-2 Polarizing Microscope equipped with a Linkan, Model THMS 600; Hot Stage Unit controlled by a Linkam TMS 91 system.

Synthesis of alkylthiophenes (A)

18 mmol of 3-thiophenomethanol and 42 mmol of the dibromated alkyl were dissolved in 200 mL THF, followed by the addition of 89 mmol of KOH aqueous solution, 6 mmol tetrabutylammonium bromide, and a small amount of KI as catalyst. The resulting solution was refluxed for 48 h and the solvent removed by distillation. 200 mL of chloroform was poured and after the separation of the two layers, the organic phase was left to dry over anhydrous $CaCl_2$. After solvent evaporation, the resulting material was purified by column chromatography using hexane and subsequently a chloroform/hexane mixture, where the chloroform ratio gradually increases, as eluent. The yields of the obtained oily yellow products were as follows: 75 % for A-6; 70 % for A-8; 65 % for A-10, and 60 % for A-12.

Synthesis of 4-[(4-octylphenylimino)-methyl]-benzene-1,3-diol

To 50 mL ethanol 2.2 g (0.01 mol) 4-octylaniline and 1.4 g (0.01 mol) 2,4-dihydroxybenzaldehyde and a small amount hydroquinone (catalyst) were added and the mixture was refluxed for 4 h. The resulting solution was then poured into 200 mL of water. The obtained precipitate was filtrated and purified by re-crystallization with methanol to yield a yellow solid (75 % yield).

Synthesis of alkylthiophenes substituted with a 2-((4-octylphenylimino)methyl)phenol group (I)

2 g (7,2·10^{-3} mol) 4-[(4-octylphenylimino)-methyl]-benzene-1,3-diol and 2.4 g (7,2·10^{-3} mol) of compound (A) were mixed in 50 mL anhydrous acetone. A stoichiometric amount of anhydrous potassium carbonate was added and the mixture refluxed for 24 h. The resulting product was then purified by column chromatography using chloroform/ethyl acetate: 1/1 as eluent to yield a yellow solid (47 % yield). All compound were characterized by ^{1}H-NMR: **I-6** 1.29 (19H, m); 1.78 (4H, m); 3.46 (2H, t, J=6.6 Hz); 3.97(4H, m); 4.51 (2H, s); 6.47 (2H, d, J=8.7 Hz); 6.92 (2H, d, J=8.7); 7.37 (6H, m); 8.51 (1H, s).   **I-8** :1.27 (23H, m); 1.74 (4H, m); 3.47 (2H, t, J=6.7 Hz); 4.01(4H, m); 4.52 (2H, s); 6.52 (2H, d, J=8.6 Hz); 6.90 (2H,

d, J=8.6); 7.35 (6H, m); 8.47 (1H, s). **I-10** :1.25 (27H, m); 1.72 (4H, m); 3.46 (2H, t, J=6.6 Hz); 3.98(4H, m); 4.48 (2H, s); 6.51 (2H, d, J=8.7 Hz); 6.88 (2H, d, J=8.7); 7.32 (6H, m); 8.48 (1H, s). **I-12:**1.22 (31H, m); 1.72 (4H, m); 3.48 (2H, t, J=6.6 Hz); 3.97(4H, m); 4.49 (2H, s); 6.46 (2H, d, J=8.7 Hz); 6.91 (2H, d, J=8.6); 7.31 (6H, m); 8.50 (1H, s), and FTIR: (−OH) 3230 stretching; (−C=N−) 1670 stretching ; (Phenyl) 1611 skeletal vibration. Mp (ºC): I-6 100.2; I-8 84.8; I-10 89.1; I-12 91.0

Polymerization and doping

Chemical polymerization of the monomers (maintaining the conjugation of the system) was accomplished *via* dehydrogenation-condensation using $FeCl_3$ as oxidizing agent according to the following procedure. Pulverized $FeCl_3$ (anhydrous) was introduced into a two neck round bottom flask under nitrogen. The flask was then connected to a vacuum line and heated to 100 ºC under strong stirring. After cooling, anhydrous chloroform is added under inert atmosphere to obtain a *ca.* 0.4 M solution. A 0.1 M solution of the monomer in chloroform was then added drop-wise under constant stirring. A suspension, reddish at the start that later turns completely black, was obtained. The stirred solution was allowed to stand for 24 h at room temperature. The resulting solution was then poured into 200 mL methanol affording a black precipitate that was thoroughly washed with hot methanol to remove excess of $FeCl_3$, and with chloroform to eliminate the remaining monomer. The resulting product was vacuum dried at 40 ºC for 12 h.

Doping of the polymers was accomplished by exposing the compounds to iodine vapor for five days in a closed container. The doped material was then allowed to stand in a desiccator, weighing eventually, until constant weight.

Results and Discussion

Thermal Study

The results depicted below are referred only to series **I** because these are molecules bearing the mesogen group. In order to determine the likely existence of mesophases, a thermal study of the synthesized products was carried out, giving rise to thermograms of Fig. 3.

In thermogram I-6, two peaks can be clearly observed in the heating curve at 100 and 147 ºC corresponding to melting of the compound and to transition from a liquid crystalline phase to an isotropic one, respectively. This behavior makes this compound different from the rest of the family. In addition, the intensity of both peaks is similar, i.e., both processes should display alike enthalpy. On cooling both peaks can be observed at 77.47 and 117.13 ºC, respectively, indicating that the product is enantiotropic. Compound I-8 displays just one peak at 84 ºC and no mesophase peak was found. On cooling, a peak at 72.13 ºC can be observed, corresponding to transition between an isotropic liquid and a liquid-crystalline phase, i.e., the compound is monotropic. Finally, the crystallization peak was observed from 15.47 ºC, which is awkward considering the gap between melting and crystallization of the product.

As for compound I-10 DSC, an intense peak was observed at 89 ºC during the heating, corresponding to melting, and no mesophase peaks were found at higher temperatures.
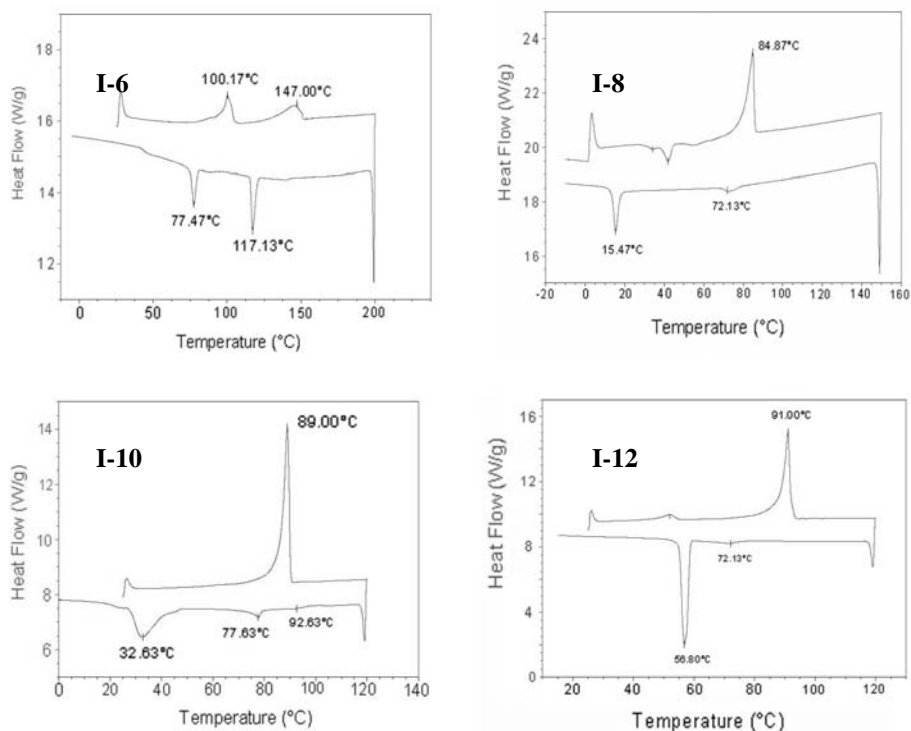
Figure 3. DSC thermogram of the monomers recorded at a heating rate 5 ºC min^{-1} under N_2

Nevertheless, the cooling curve shows a peak at 77.63 ºC corresponding to transition from an isotropic liquid to a liquid crystalline phase (mesotropic compound). A further peak due to sample crystallization can be observed at 32.6 ºC. Finally, compound I-12 displays a melting peak at 91 ºC and, as before, no presence of a mesophase was detected. On cooling, a small peak, corresponding to a mesophase, was found that would be produced at a temperature lower than that corresponding to melting of the product, which is also monotropic. Finally, a strong peak was observed at 56.8 ºC, corresponding to crystallization of the compound.

Polarized light microscopy studies

An optical polarized light microscope, equipped with a controlled temperature plate, was employed to identify mesophase texture. All compounds displayed a nematic mesophase characterized by a typical Schlieren texture and consequently the compounds were all monotropic, *i.e*., the mesophase can be observed just on cooling. The only exception was compound I-6 that presented a mesophase both during heating and on cooling, Fig. 4.

To understand this behavior it is essential to take into account the structure of the compounds, emphasizing the balance between the necessary flexibility and stiffness for liquid crystallinity: family I possesses, besides of the spacer group common to the other compounds, an additional alkyl chain of eight carbon atoms in the benzene ring that would lend the necessary degree of disorder for a mesophase formation. This was not so for the rest of the surveyed products.
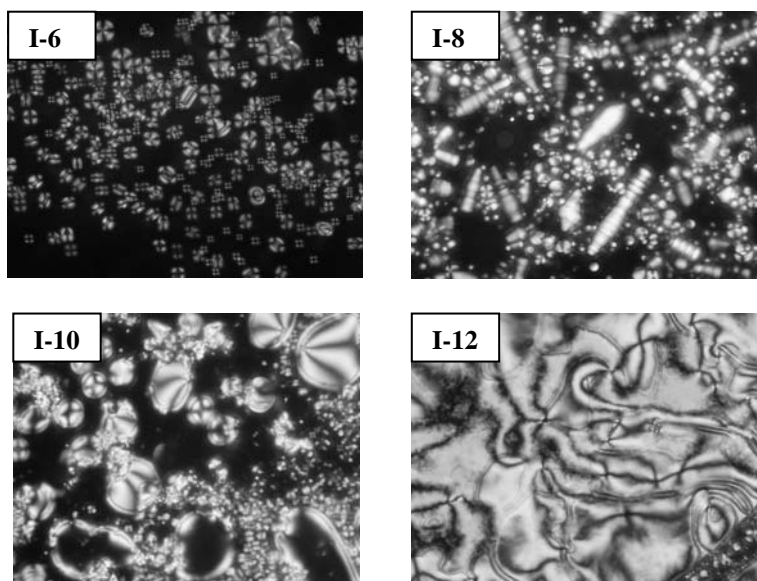
Figure 4. Photograph of the obtained mesophases, enlargement 200 X, for compounds

Polymerization

Monomers were chemically polymerized and the respective solids, isolated after reacting for 24 h, vacuum dried for 48 h yielding in *ca.* 70 % a brown powder as final product.

The obtained polymers are highly insoluble in all common solvents, being impossible to gather more information about the structure of these macromolecules than that obtained by FTIR and XPS analysis. According to the recorded FTIR spectra, a marked increase of the band attributed to the OH stretching can be observed for every compound. Besides, no bands were obtained in the carbonyl region, indicating that during the reaction of polymerization a fraction of the molecules underwent fragmentation by hydrolysis, affording ROH-like species. All polymers behave likewise.

It was possible to appraise that the other bands experienced no intensity change, therefore, if hydrolysis occurs, the fragments should be inside the polymer either occluded or linked to the backbone. On the other hand, a band was obtained within the 2920 cm^{-1} region due to the aryl skeleton of the thiophene ring. This band has been also observed by other authors that worked with non-substituted thiophene and under similar experimental conditions than those utilized in this work in compounds synthesized both chemical and electrochemically, precluding the assignment of these bands to likely oxidation occurring during polymerization. This fact would indicate that the wide band observed may have both contributions, being impossible to discriminate them from the analyses performed to the samples.

XPS spectra show a shift towards higher energies, 286.5 eV, relative to the C1s reference energy, 285 eV, consequently it may be inferred that these samples present low conductivity too.

Table 1 lists surface composition of the surveyed polymers in which it is noteworthy the high values found for oxygen, that can be due, on the one hand, to superficial

contamination, which is typical in this kind of samples and is usually ascribed to working conditions when the samples are exposed to the laboratory environment, and, on the other hand, to polymer over-oxidation, that would be consistent with the results obtained by FTIR analysis.

Table 1. Surface composition of polymers PI-1 to PI-12 obtained by XPS (% atomic)

Polymer	%C	%N	%S	%O
PI-6	69,2	1,2	1,6	17,5
PI-8	70,3	1,0	1,5	18,7
PI-10	73,2	1,2	1,8	20,5
PI-12	74,6	1,1	1,6	20,1

The formed polymers show no melting point but they decompose at temperatures above 200 ºC. In addition, assays performed on the microscope revealed that the compounds present no liquid crystal properties.

Monomers and polymers displayed a conductivity in the range of 10^{-9} S cm^{-1}, therefore the materials are semiconductors-like. Moreover, the polymers doped with $FeCl_3$ and I_2 showed conductivities in the range 10^{-6} and 10^{-7} S cm^{-1}, respectively, *i.e.* they fall within the range of semiconductors as well. A likely explanation for these values might be the planarity of the thiophene rings in the chain bearing bulky substituents and their over-oxidation.

Conclusions

The monomers synthesized in this work exhibit liquid crystalline properties presenting in all cases a nematic-like mesophase. This feature was not found in any of the polymers because they did not show a melting temperature but they underwent decomposition at temperature over 200 ºC instead. Chemical polymerization carried out from the synthesized monomers allowed in every case the obtention of the corresponding polymer, although side chain degradation, amounting to *ca.* 6 %, was obtained leading to a partial over-oxidation of these materials.

XPS studies confirmed the structure and the partial over-oxidation of the polymeric compounds and that undoped polymers have poor conductivity. In addition, the level of doping, usually *ca.* 5 mass %, could be also estimated which affords materials within the range of semiconductors.

Finally, regarding the obtained results, it can be inferred that when a side group is attached to the thiophene ring, aimed at the attainment of a liquid-crystal, the spacer group plays a very important role since if the stiffness of the system is too high, the necessary flexibility for the formation of a liquid crystalline phase is not reached. Therefore, if a polythiophene bearing liquid-crystal characteristics is to be synthesized, in addition to the previous considerations, the polymerization process must be controlled in order to obtain meltable chains of low molecular weight.

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