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Synthesis, Characterization and Properties of Polythiophenes Modified with Mesogenic Group Spacers with Different Chain Lenghts

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Summary

A new family of conjugated polymers formed by 3-alkyloximethylthiophenes substituted with a biphenylcarbonitryl group was synthesized by a route involving first the coupling of a functionalized alkyl chain, from 6 to 12 carbon atoms, to 3-methanolthiophene, and then the attachment of the mesogenic group. The monomeric units were characterized by conventional techniques. Thermal studies were also carried out. The polymerization of these monomers was accomplished by chemical oxidation with $FeCl_3$, and the resulting polymers were characterized by FT-IR spectroscopy, elemental microanalysis, and XPS. Subsequently, these materials were doped with I_2 and characterized by the same above-mentioned techniques. Conductivity measurements indicate that the polymers lie within the semiconductor range. Electrochemical polymerization of these monomers was also performed. XPS analysis and theoretical calculations revealed that both the biphenyl group and the thiophene ring are simultaneously oxidized during the electrochemical synthesis of the product, giving rise to an overoxidized material.

Introduction

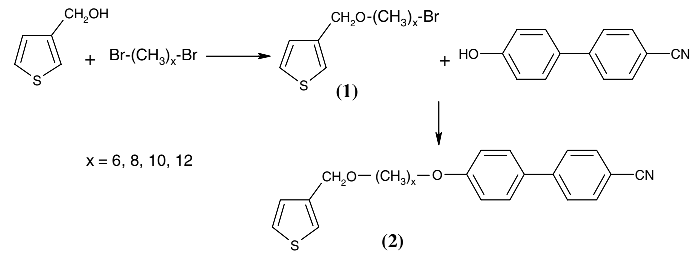
For over a decade extensive work has been accomplished to synthesize and analyze new organic materials useful in the preparation of numerous electric and/or electronic devices, such as diodes, photoluminescent cells, sensors, etc. Among these materials, conducting polymers have aroused considerable interest due to their outstanding properties. Following this trend, the latest contributions in this field have been aimed to synthesize compounds whose main polymeric chain presents a lateral functionalization, that confers them new properties, such as higher solubility and reactivity, disclosing new and exciting possibilities of applications.

Amidst these new materials, polythiophene has been extensively studied because the polymer possesses high conductivity and good stability, which accounts for its wide range of applications [1,2]. Inconvenience of working with such units is the incompatibility of its synthesis with the insertion of functional groups, because most of the reactions involved are of the Kumada-type, being the formation of Grignard's reagent the main limitation for the diversification of the structures and, therefore, of the possible materials that can be formed [3].

The main innovation in this context is functionalization with groups that are capable of modifying the electronic density of the side chain, the attachment of alkyl groups in the positions 3 and 4 of the thiophene ring, or then, ether-like groups that increase the solubility of these materials. Their low solubility is the greatest disadvantage of working with these compounds [4, 5].

A compound of thiophene with a mesogen group in position 3 of the ring (4'-(8-thiophen-3-yl-octyloxy)biphenyl-4-carbonitrile) has been recently reported wherein some mesophases could be identified. Electropolymerization was also attempted, but difficulties in the characterization of the polymeric material were found because the biphenyl group is also electroactive [6].

In this paper a novel synthetic route is reported for the preparation of thiophene units functionalized in position 3, Scheme 1. The properties of the polymers and the way these properties are affected by the length of the alkyl chain are discussed.



Scheme 1: Synthetic route of functionalized thiophenes

Experimental

3-thiophenemethanol, 1,6-dibromohexane, 1,8-dibromooctane, 1,10-dibromodecane, 1,12-dibromododecan, 4'-hydroxy-4-biphenyl-carbonitrile, and anhydrous $FeCl_3$ were supplied by Aldrich and used as received.

A BRUKER, ACP200, NMR Spectrometer, with Superconductor Magnet and Fourier Transform, was utilized to obtain ^{1}H-NMR spectra. FTIR spectra were measured at KBr pellets in a BRUKER, Vector 22 Spectrophotometer. XPS analyses were recorded with a Leybold LHS-12 Spectrometer at Nantes-CNRS University, Nantes, France. Elemental analysis was carried out on a CE Instruments, Model EA 1108 Elemental Analyzer, configured to perform the simultaneous determination of carbon, hydrogen, nitrogen and sulfur percentages. A DSC822 Star High Performance Differential Scanning Calorimeter, Mettler Toledo Star System within the range 25-200 ºC, scanning rate 5 ºC/min, was used for the calorimetric measurements. Conductivity measurements were carried out at room temperature, on polymer-powder pressed pellets, by the four-probe method in a Elchema Electrometer CM 508.

The electrochemical work was accomplished using a conventional three-compartment cell. Polycrystalline platinum (0.07 cm^2 geometric area), was used as working electrode. All potentials quoted in this work are referred to Ag/AgCl electrode in tetramethylammonium chloride to match the potential of a SCE at room temperature [7]. The auxiliary electrode was a helical platinum wire of large area.

Synthesis of alkylthiophenes (1)

$1.8\cdot10^{-2}$ moles of 3-methanolthiophene and $4.2\cdot10^{-2}$ moles of the dibrominated alkyl is dissolved in 200 mL of tetrahydrofurane (THF), and then aqueous KOH solution of tetrabutylammonium bromide, and KI was added as catalyst, and the resulting solution was refluxed for 48 h. THF was then evaporated and 200 mL of chloroform was added and the immiscible mix was poured in a separator funnel. The organic phase was dried over anhydrous $CaCl_2$, the solvent evaporate, and finally, the product was purified in a chromatographic column using hexane/chloroform (1:1) as eluent. The product was obtained as a yellow oil with a yield of 75% (CN-6), 75% (CN-8), 65% (CN-10), and 60% (CN-12).

Addition of a biphenyl centre (2)

1.0 g ($5\cdot10^{-3}$ mole) of 4-carbonitrile-4'-hydroxibiphenyl was dissolved in 50 mL of dimethylformamide (DMF) and mixed with 1.0 g of anhydrous K_2CO_3, and the compound (1) ($5\cdot 10^{-3}$ mole) is added slowly and the mixture is heated to 80 ºC for 24 h. After cooling, 200 mL of water is poured into the mix, filtered and the precipitate was dried, washed with ethyl ether and finally recrystallized from methanol. The product is obtained as a white powder, with a yield CN-6 (46%), CN-8 (52%), CN-10 (50%), and CN-12 (51%). The characterization of these products was accomplished by ^{1}H-NMR, FTIR and microanalysis:

^{1}H-NMR

CN-6: 1.35 (4H, m); 1.62 (4H, m); 3.43 (2H,t, J=6.5 Hz); 4.01 (2H, t, J=6.5 Hz); 4.52 (2H, s); 7.01 (2H, d, J=8.71 Hz); 7.26 (3H, m); 7.55 (2H, d, J=8.72); 7.71 (4H, m).
CN-8: 1.37 (8H, m); 1.60 (4H, m); 3.47 (2H,t, J=6.5 Hz); 4.01 (2H, t, J=6.5 Hz); 4.51 (2H, s); 7.00 (2H, d, J=8.75 Hz); 7.28 (3H, m); 7.53 (2H, d, J=8.78); 7.68 (4H, m).
CN-10: 1.31 (12H, m); 1.58 (4H, m); 3.47 (2H,t, J=6.5 Hz); 4.06 (2H, t, J=6.5 Hz); 4.49 (2H, s); 7.02 (2H, d, J=8.76 Hz); 7.27 (3H, m); 7.51 (2H, d, J=8.78); 7.70 (4H, m).
CN-12: 1.28 (16H, m); 1.55 (4H, m); 3.43 (2H,t, J = 6.5 Hz); 4.05 (2H, t, J = 6.5 Hz); 4.53 (2H, s); 7.04 (2H, d, J=8.77 Hz); 7.29 (3H, m); 7.53 (2H, d, J = 8.77); 7.68 (4H, m).

FTIR

ν (cm^{-1}): 2231 (CN stretching); 2925, 2857 (CH_2 stretching); 1603 (arom. ring); 1293 (aryl-O stretching); 1037 (alkyl-O stretching).

Elemental analyses

monomer	Theoretical				Experimental			
	C	**H**	**S**	**N**	**C**	**H**	**S**	**N**
CN-6	73.62	6.44	8.19	3.58	73.35	6.22	7.97	3.51
CN-8	74.43	6.97	7.64	3.34	74.15	7.05	7.70	3.29
CN-10	75.13	7.43	7.16	3.13	74.98	7.21	7.25	3.12
CN-12	75.75	7.84	6.74	2.94	75.38	7.70	6.89	3.01

Chemical Polymerization

Anhydrous $FeCl_3$ powder was placed in a two neck round-bottom flask under dry nitrogen atmosphere. The flask was connected to a vacuum line and heated at 100 ºC with strong stirring. After cooling, enough anhydrous chloroform (under nitrogen atmosphere) was added to produce a *ca.* 0.4 M solution. A 0.1 M solution of the monomer is dropped slowly under constant stirring, in chloroform. A reddish suspension, which turns completely black, is formed at the beginning. The product is let under stirring, for 24 h at room temperature. The product was placed into 200 mL of hot methanol, and the black precipitate obtained was washed with methanol and chloroform to get rid of the excess of $FeCl_3$ and to remove the remaining monomer, respectively. The resulting product was vacuum dried at 40 ºC for 12 h.

Electrochemical Polymerization

The electrochemical polymerization was performed under the following conditions: the supporting electrolyte was tetrabutylammonium hexafluorophosphate dissolved in dichloromethane. The concentration of the monomer and electrolyte was $1 \cdot 10^{-3}$ M and $1 \cdot 10^{-2}$ M, respectively. A triangular wave was utilized to sweep the potential of the working electrode between 0 and +2500 mV ($v = 50\ mV \cdot s^{-1}$).

XPS Analysis

XPS data were obtained with the magnesium source radiation (1253.6 eV) operating at 10 kV and 10 mA. The energy resolution was 1 eV at a pass energy of 50 eV. High-resolution scans with a good signal-to-noise ratio were obtained in the S2p, C1s, O1s, Id3/2 and Id5/2 regions of the spectrum.

Quantitative studies were based on the determination of the S2p, C1s, N1s, F1s, O1s, Id3/2 and Id5/2 peak areas with sensitivity factors 0.44, 0.2, 0.36, 0.61 and 0.58, respectively (the sensitivity factor of the spectrometer is provided by the manufacturer).

The deconvolution of the XPS peak into different components and the quantitative interpretation were obtained, after the subtraction of the background, by Shirley's method [8]. Fitting programs for the development of curves allow the variation of parameters such as the Gaussian/Lorentzian ratio, the full width at half maximum (FWHM), and/or the position and intensity of the contribution. These parameters were optimized by a curve fitting program to achieve the best fit.

Theoretical calculations

The theoretical calculations were carried out using a SPARTAN program version 4.0.

Results and Discussion

The synthesis of the monomer units is typically achieved through the addition of a dibromated alkyl chain to 3-methanolthiophene in a two-phase reaction. The product of the reaction was separated by means of a chromatographic column, extracting first with hexane as eluent to remove the excess of the dibromated compound, and then with chloroform. A yellow liquid was obtained as product. The yield of this intermediate was always *ca.* 65 %.

The substituted biphenyl group was then attached to the end of the chain using DMF as solvent. Potassium carbonate is also added to the solution to promote the removal of bromide as KBr.

Finally, the solution was treated with water to precipitate the product, which was filtered and washed with methanol to remove remaining reagent. As in the previous stage, the product of the reaction was separated by column chromatography utilizing a mixture chloroform-acetone as eluent. The overall yield of the reaction was rather low, approximately 50 %.

The products were characterized by conventional techniques, *i.e.*, FTIR, ^{1}H-NMR, and elemental microanalysis. Furthermore, differential scanning calorimetric studies were accomplished to verify the presence of mesophases. Two products have been isolated following the proposed synthetic pathway, namely, our target product, and a by-product generated by the coupling of two alkylbiphenyl groups giving rise to an ether in *c.a.* 10 % yield, (di-(4'-hexyloxy-biphenyl-4-carbonitrile)ether).

In the spectra obtained by ^{1}H-NMR, the signals corresponding to both the aromatic and alyphatic parts of the molecule are clearly observed. In addition, a singlet-type signal, corresponding to the methyl group of the 3-thiophene methanol, is clearly displayed. Triplets assigned to the two ether-type bonds of the molecule are exhibited too.

The FTIR spectra exhibit the characteristic bands of the different groups of the molecule, *e.g.*, cyan group, aliphatic chain, phenyl groups, and the thiophene ring, to be identified.

Figure 1 shows the spectra obtained by DSC analysis. The data of the peaks are listed in Table 1. Peaks at temperature above the melting point are observed for monomers CN-6 and CN-8 suggesting the presence of a mesophase in these compounds. Monomer CN-8 also displays a peak below the crystallization point. Compounds CN-10 and CN-12 do not exhibit other peaks, except those corresponding to the melting and crystallization temperatures, respectively. These evidences indicate that above 10 carbon atoms in the alkyl chain, the system is unable to sustain an order in the melted state, therefore, is unable to generate the mesophase observed in alkyl molecules of the same family bearing a shorter chain. Consequently, for these molecules, the ideal equilibrium between rigidity and flexibility would be the use of spacers ranging from 6 to 8 carbon atoms.

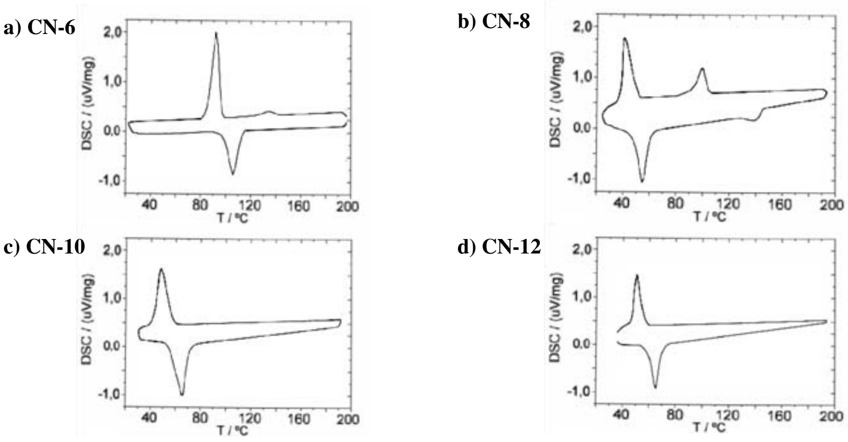

a) CN-6
b) CN-8
c) CN-10
d) CN-12

Figure 1: DSC spectra of the obtained compounds at a scan running of 5 °C /min

The monomers were chemically polymerized via dehydrogenation-condensation employing $FeCl_3$ as oxidising agent under N_2 inert atmosphere and anhydrous chloroform as solvent. The mixture is stirred for 24 h and the precipitate formed is filtered and washed with methanol and chloroform to remove Fe(III) chloride and to eliminate the low molar mass units, respectively. Subsequently, the product was dried under vacuum for 48 h.

The advantage of the proposed method is the absence of intermediates during the polymerization, and the high yield. Table 2 contains the values of yield obtained for each of the synthesized polymers.

Table 1: Melting, cristallization and mesophase temperatures of monomeric units

compound	melting point / °C	crystallization temperature / °C	mesophase temperature / °C
CN-6	118	97	138
CN-8	57	41	142, 102
CN-10	66	49	----------
CN-12	65	50	----------

Table 2: Surface composition obtained by XPS and yield obtained in the chemical synthesis of the polymers

Polymer	%C	%N	%S	%O	yield %
PCN-6	67.1	2.6	4.7	15.1	80
PCN-8	68.3	2.8	4.8	15.7	78
PCN-10	70.5	3.0	5.0	15.5	84
PCN-12	71.6	3.1	5.0	15.9	76

The disadvantage of the polymers obtained through the proposed route lies in their low solubility in most of the common solvents, which may be ascribed to the high molecular weight of their chains, or to a slight degree of cross-linking. The analyses of these materials are thus restricted to their electric and thermal properties, being unable to provide additional information about the structure of the macromolecule than that obtained by IR and XPS spectrometry.

All FTIR spectra show bands due to the stretching of the OH group. Moreover, no bands are produced in the carbonyl region, which suggests that, during the polymerization reaction, some fraction of the molecules underwent fragmentation by hydrolysis, affording species of the type ROH. This behavior was observed in all the polymers synthesized in this work. Moreover, it was observed that the intensity of the other bands remains unchanged, *i.e.*, if hydrolysis occurs, these fragments are located inside the polymer, either occluded within or bound to the chain. These OH bands may also be ascribed to the occlusion of the solvent into the polymeric chain. On the other hand, an intense band was verified in the 2920 cm^{-1} range, associated to the aryl backbone of the thiophenol ring. This band has been previously reported by other authors working with unsubstituted thiophene under similar experimental conditions [9, 10], *i.e.*, anhydrous conditions, using chemical or electrochemical polymerization and, consequently, these bands cannot be ascribed to a likely oxidation occurring during the polymerization process. The wide band observed in this region may have thus the contribution of both, but, on the other hand, it is impossible to discriminate each other by the methods of analysis utilized in this investigation.

Considering the shift of the C_{1s} bands (285 eV reference), all the polymers display a shift to higher energies, accounting for the semiconductor character of these compounds. All the XPS spectra recorded for the polymers exhibit the same characteristics. The carbon spectrum shows 3 bands associated to C – C bond (286.2 eV), C – N bond of the carbonitril group (287.8 eV), and C – O bond (289.3 eV), respectively. The XPS spectrum of nitrogen displays the signal of the N – C bond of the carbonitril group at 400.1 eV. The spectrum of oxygen shows two contributions, which may be due to contamination of the surface, very common in this kind of samples. Curves for sulphur, present a typical doublet at 165 and 167 eV.

The surface composition of the polymers is listed in Table 2. Here, the percentage of all the elements, except that of oxygen, is lower in the samples as compared with the percentage of their monomer units, corroborating the slight contamination of the polymers. Usually, exposure of the samples to ambient conditions accounts for this surface contamination.

Figure 2 depicts the voltammetric pattern of the electropolymerization of CN–6 by cyclic voltammetry. This figure shows that the oxidation of the monomer takes place at *ca.* + 2.3 V. When the scan approaches this potential range, deposition of a yellow film onto the electrode surface can be clearly observed. The small increase in current on successive scans, would be an indication of a lower conductivity of the formed deposit as compared with the conductivity of thiophene itself because, under the same conditions, the increase in current during the electropolymerization of thiophene is significantly higher [11,12]. Besides, this finding is consistent with the fact that after cycling for some time, passivity of the modified electrode is attained, and a dull layer of the polymer is formed onto the platinum electrode. One factor that may explains this behaviour is that, under the polymerization conditions, the polymer undergoes overoxidation with a significant loss of conductivity, as reported by other authors in similar cases. On the other hand, if lower deposition potentials are employed to avoid overoxidation, no deposit at all is formed on the electrode. Another factor accounting for this behaviour may be the polymerization taking place simultaneously in both the thiophene and the benzene rings, affording a highly disordered material, difficult to compact. To verify this, a theoretical study of the CN - 6 monomer was carried out, using a combined method, to optimize the structure of the molecule. A semi-empiric method, *e.g.* AM1 was used, and then ab-initio (method 6-31G*) to reckon the energy of the optimized structure. The data obtained with this approach allow the optimization of the structure and to determine the geometry of the frontier orbital of this molecule, Fig. 3. This figure shows that both the HOMO and LUMO orbital are located, in an exclusive manner, above the biphenyl ring. The biphenyl ring would be preferentially oxidized prior to the oxidation of the thiophene ring and, hence, the

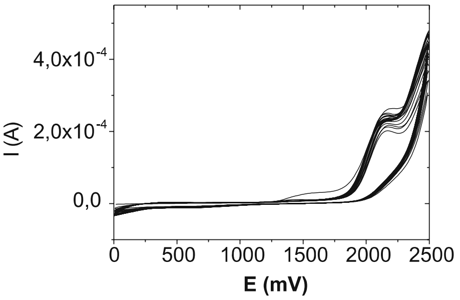


Figure 2: Voltammetric profiles obtained during the electropolymerization of CN-6

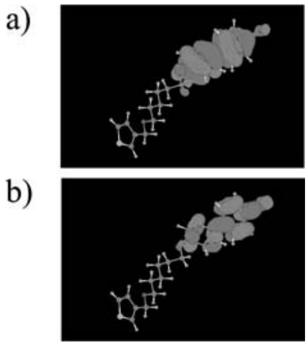


Figure 3: Frontier orbitals of CN-6: a) HOMO; b) LUMO

polymerization of this unit would be strongly inhibited, rendering the aforementioned results.

The conductivity of monomers and polymers lies close to $1.0 \cdot 10^{-9}$ $S \cdot cm^{-1}$ and, therefore, they can be considered as semi-conductors. After doping with $FeCl_3$ and I_2, their conductivity raised up to $1.0 \cdot 10^{-8}$ and $1.0 \cdot 10^{-7}$ $S \cdot cm^{-1}$, respectively. The low value of the conductivity of these materials may be attributed to the configuration and/or to the structure of the polymer chains. As the alkyl chain is bound in position 3 of the thiophene ring, a distortion of the dihedral plane of neighbouring rings of the chain along with a concomitant loss of conductivity would be expected. The conductance is lost because the quinoid structures capable of generating charges in the chain, essential for the transport of electric charge, are no longer stabilized. In addition, if bulky terminal groups are added, the interaction among these groups would increase the distortion on the chain. On the other hand, the simultaneous oxidation of the thiophene ring and the biphenyl group in the chemical polymerization process, may originate cross linking that would enhance the structural disorder of this material, decreasing thus their conducting properties.

XPS studies were performed on the doped compounds. As expected, the composition and the contribution of the species to the XPS curves were the same as those obtained previously.

The doping on the surface of the material was found to be quite low, less than 1 %. Besides, the presence of both ionic species of the dopant, I^- and I_3^-, was also detected.

Conclusions

In this work a range of monomers derived from thiophene bearing functionalized alkyl chains of variable length (6 to 12 carbon atoms) and their respective polymers have been synthesized, both chemically or electrochemically. Conductivity values allow these materials to be classified as semiconductors, however, no mesogenic properties were observed. When oxidative electropolymerization was carried out, theoretical calculations demonstrated that the monomer unit is first oxidized through its biphenyl group and, consequently, the polymerization is hindered.

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References

1. Roncali, *Chem. Rev.* **92** (1992) 711.
2. J. Roncali, *Chem. Rev.* **97** (1997) 173.
3. R. McCullough, *Adv. Mater.* **10** (1998) 93.
4. V. N. Gogte, L. G. Shah, B. D. Tilak, K. N. Gadekar and M. B. Sahasrabudhe, *Tetrahedrom* **23** (1967) 2437.
5. M. Dietrich, J. Heinze, G. Heywang and F. Jonas, *J. Electroanal. Chem.* **369** (1994) 87.
6. J. Roncali and C. Thobie-Gautier, *Adv. Mater.* (1994) 138.
7. G. A. East and M. A. del Valle, *J. Chem. Ed.* **77** (2000) 97.
8. A. Sherley, *Phys. Rev. B* **5** (1972) 4709.
9. V. Hernández, S. Hotta and J. López, *J. Chem. Phys.* **109** (1998) 2543.
10. E. Villa, C. Castiglioni, M. Galazzi and G. Zerbi, *J. Chem. Phys.* **105** (1996) 9461.
11. R. Schrebler, P. Grez, P. Cury, C. Veas, M. Merino, H. Gómez, R. Córdova and M. A. del Valle, *J. Electroanal. Chem.* **430** (1997) 735.
12. M. A. del Valle, P. Cury and R. Schrebler, *Electrochim. Acta* **48** (2002) 397.