Research Article

Synthesis of Poly[(3-(6-(9-anthracenylmethoxy)hexyl)thiophene)-co-(3-(6-bromohexyl)thiophene)] Postfunctionalized from Poly(3-(6-bromohexyl)thiophene): A Comparative Study of the Base Polymer with Its Chlorinated Analogous

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A synthetic method based on the postfunctionalization of a reactive homopolymer precursor, which allows for the preparation of different copolymers derived from poly(3-alkylthiophene), was studied. Although these groups decrease the solubility of the resultant material, they enable controlling the degree of substitution to obtain a material with improved spectroscopic (absorption and emission) properties making them useful for the fabrication of electronic devices, for example, solar cells and light-emitting diodes. Furthermore, a comparative study of two halogenated (Cl and Br) reactive poly(3-ω-haloalkyl)thiophenes was carried out.

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1. Introduction

Among the great number of conjugated polymers, poly(3-alkylthiophene)s stand out due to their outstanding properties and potential applications. High solubility, processability, electroactivity, and stability, among others, are some of their noteworthy properties [1–5]. In addition, rechargeable batteries, electrochromic devices, chemical and optical sensors [6], positive charge carrier in organic light-emitting diodes (OLEDs) [7–10], and nonlinear optical materials [11–13], among others, are some of their most prominent applications in which they can be utilized.

All these properties call for a highly orderly polymer. The regioregularity of poly(3-alkylthiophene)s is very important and, therefore, it is necessary to know their regioregularity degree. The electrical and optical properties of polyalkylthiophenes funcionalized in their alkyl chains present great sensitivity to electrochemical or chemical perturbations [14, 15]. Due to these properties, polyalkylthiophenes functionalized in their alkyl chain have been prepared with interesting applications as chemical sensors [16].

The development of methods for the synthesis of substituted pyrrole, and particularly monomers of thiophene, has been reported using substituents such as crown-ethers [17], metalloccenes, aminoacids and peptides, and proteins and enzymes [18–21]. However, the introduction of substituent groups into the pyrrole and thiophene monomers for their subsequent polymerization has led to materials with very low electrical conductivity. This has been ascribed to steric interactions among neighboring groups that decrease the conjugation of the polymer and thus hinders the electronic transference through the main chain of pyrrole and thiophene leading to a low conductivity [22].

To overcome this drawback many workers have focussed their effort on the preparation of functionalized oligomers, for example, sexithiophenes [23], terthiophene, and
2. Experimental

All solvents and reagents utilized in this work were purchased from Aldrich and used as received. ¹H-NMR spectra were recorded on an ACP Bruker 200 Spectrometer using TMS as internal standard. FTIR spectra of the polymers were recorded on a Bruker Vector 22 FT-IR spectrophotometer using KBr pellet or films. Molecular weights were determined by gel permeation chromatography and polystyrene as standard reference on a Lab Flow 2000 HPLC chromatograph provided with a column of Phenogel and a (UVIS 200) UV-Vis detector at 263 nm. The mobile phase was toluene at a flow rate of 1.0 mL·min⁻¹. Conductivity measurements were conducted at room temperature on pellets of the polymer (24000 psi) by the four-probe method on an Elchema Electrometer CM 508. UV spectra were recorded on a Gena Specord 40 spectrophotometer.

2.1. Synthesis of [3-(6-chlorohexyl)thiophene]. 2.50 g (12 mmol) of 1-bromo-6-chlorohexane were added to 50 mL of ethyl ether containing 0.27 g of Mg turnings. The mixture was chilled to 0 °C under N₂ and constant stirring for 12 hours. The Grignard reagent prepared was added to a new solution containing 100 mL of anhydrous ethyl ether, 1.8 g (11 mmol) of 3-bromothiophene, and 0.4 mmol of Ni(dppp)Cl₂ as catalyst. The mixture was boiled for 12 hours under N₂. After cooling at room temperature, 40 mL HCl and 50 mL H₂O were added, and the organic phase was separated using a separator funnel. The organic phase was dried (Na₂SO₄) and the solvent was evaporated at low pressure.

Table 1: Conductivity of doped and undoped polymers (III), (IV), (V).

| Polymer | Undoped (ms) | Doped (ms) *
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>(III)</td>
<td>4.0 × 10⁻¹¹</td>
<td>1.4 × 10⁻⁶</td>
</tr>
<tr>
<td>(IV)</td>
<td>2.0 × 10⁻⁹</td>
<td>1.0 × 10⁻⁴</td>
</tr>
<tr>
<td>(V)</td>
<td>6.0 × 10⁻¹⁰</td>
<td>2.0 × 10⁻³</td>
</tr>
</tbody>
</table>

* I₂ was utilized as doping agent.
The residue was purified by column chromatography on silica-gel (hexane). The product was a colorless liquid, yield 1.49 g (67%), bp. 172 °C, at 0.1 mm Hg. $^1$H-NMR (CDCl$_3$, 200 MHz) $\delta$ 1.28 – 1.48 (4H, m), 1.61 (2H, m), 1.82 (2H, m), 2.60 (2H, t, $J = 8$ Hz), 3.55 (2H, t, $J = 7$ Hz), 6.89 (2H, m), 7.18 (2H, m); $^{13}$C-NMR (CDCl$_3$, 200 MHz) $\delta$ 26.7, 28.3, 30.1, 30.3, 32.4, 45.1, 119.9, 125.1, 128.2, 142.9. FTIR (film, cm$^{-1}$): 3089, 2931, 2856, 1541, 1460, 1438, 1410, 1258, 834, 826, 759, 644. Calculated elemental analysis for C$_{10}$H$_{15}$ClS: C, 59.24; H, 7.46; S, 15.81. Found: C, 59.21; H, 7.42; S, 15.78.

2.2. Description of 3-(6-bromohexyl)thiophene synthesis. As mentioned above, the method utilized was that of Iraqi [33] with 60% yield, based upon 3-bromothiophene. Spectra of the product are as follows. $^1$H-NMR (CDCl$_3$, 200 MHz) $\delta$ 1.28-1.48 (4H, m), 1.62 (2H, m), 1.82 (2H, m), 2.60 (2H, t, $J = 8$ Hz), 3.35 (2H, t, $J = 7$ Hz), 6.86-6.92 (2H, m), 7.10-7.24 (1H, m); $^{13}$C-NMR (CDCl$_3$, 200 MHz) $\delta$ 27.9, 28.3, 30.1, 30.3, 32.7, 33.9, 119.9, 122.1, 128.3, 142.8. FTIR (film, cm$^{-1}$): 3103, 3053, 3004, 2931, 2856, 1537, 1460, 1438, 1410, 1258.
2.4. Synthesis of poly[3-(6-bromohexyl)thiophene]. The preparation of this compound was that described by Lanzi et al. [34]. 1.60 g (9.6 mmol) of anhydrous FeCl₃ dissolved in 10 mL CH₃NO₂ was slowly poured during 20 minutes into a solution of 0.6 g (2.4 mmol) of 3-(6-bromohexyl)thiophene in 30 mL CCl₄. The mixture was stirred for 6 hours at room temperature and then vacuum filtered. The solid was Soxhlet extracted with methanol and dried at 60 °C. The product was a red solid, yield 1.4 g (61%). The spectral data were ¹H-RMN (CDCl₃, 200 MHz) δ 1.30-1.95 (8H, m), 2.50-2.90 (2H, m), 3.40 (2H, m), 6.92, 6.98, 7.01, 7.08 (1H, 4s); ¹³C-RMN (CDCl₃, 200 MHz) δ 28.0, 28.6, 29.3, 30.3, 32.7, 33.9, 128.7, 130.6, 133.7, 139.6. FTIR (KBr, cm⁻¹): 3054, 2932, 2856, 1661, 1514, 1461, 1440, 832, 728, 648, 562.

2.5. Synthesis of poly[(3-(6-(9-anthracenylmethoxy)hexyl)thiophene)-co-(3-(6-bromohexyl)thiophene)]. To a solution of 0.4 g (1.6 mmol) of poly[3-(6-bromohexyl)thiophene] in 30 mL of anhydrous THF, 0.036 g (0.16 mmol) of sodium 9-anthracenyl methoxy (previously prepared from 9-anthracenyl methanol and NaH in THF) was added. This solution was stirred for 24 hours at 60 °C in the presence of 0.026 g (0.16 mmol) of KI. After cooling at room temperature, 30 mL methanol was added and the solid was filtered and Soxhlet extracted with methanol. The product, a red solid, was dried at 60 °C yielding 0.45 g. FTIR (KBr, cm⁻¹): 3100 (sp² C-H stretching), 2934 y 2858 (sp³ C-H stretching), 1647 y 1442 (C=C aromatic stretching), 1380 (symmetric in-plane C=C stretching of thiophene ring), 1250 and 1060 (ArC-O-C-al, symmetric stretching), 835 (2,3,5-trisubstituted thiophene C-H out-of-plane bending vibration), 690 (methylene groups rocking vibration), Figure 4.

3. Results and Discussion

Using the monomers 3-(6-clorohexyl)thiophene and 3-(6-bromohexyl)thiophene as starting materials, the respective polymers were prepared. With the purpose of comparing the prepared compounds, similar reaction conditions, oxidizing agent, monomer concentration, and time of reaction were utilized. Thus, we expected polymers with analogous characteristics, however the obtained products showed different molar mass and regioregularity, Schemes 1 and 2.

The regioregularity of poly[3-(6-clorohexyl)thiophene] and poly[3-(6-bromohexyl)thiophene] was determined by ¹H-NMR spectroscopy [35]. To this end, however, the relative ratio of the areas ascribed to CH₃ adjacent to the thiophene ring has to be determined, Figure 2.

Comparison of the results obtained for polymers (III) and (IV) shows that when Cl is used at the end of the alkyl chain, as monomer unit, a polymer with lower average molar mass and regioregularity than that of the brominated analogous is produced. This has been attributed to the smaller size of the halogen, Cl, which increases the probability of approaching of the monomer units, due to a lower steric interaction amidst them. On the other hand, when Br is employed as halogen at the end of the alkyl chain
the steric interaction of the monomers increases owing to
the greater size of the halogen, decreasing the probability
of forming 2,2' head-to-head (H-H) bonds and increasing
the probability of forming 2,5' head-to-tail (H-T) bonds.
This becomes evident by the difference in regioregularity of
polymers (III) and (IV), Table 2.

Synthesis of polymers (III) and (IV) was carried out
in a similar way producing compounds with similar sol-
ubility in organic solvents, such as THF, CHCl₃, ethyl ether,
and CCl₄. FT-IR spectra are also similar for
these compounds, however UV-Vis spectra in CHCl₃ show
different absorption maxima, 412 and 43 nm, respectively,
Figure 3. This difference suggests that the conjugation in
the main chain of thiophene is greater in polymer (IV).
This finding agrees well with the average molecular weight,
Mₘ根据不同, determined for polymers (III) and (IV): the brominated
derivative (IV) shows a higher average molecular weight, Mₘ, 40000.

Polymer (IV) was employed as starting material for the
synthesis of copolymer (V) because of its greater regioregu-
larity, HT. The degree of substitution of terminal bromine
atoms of the alkyl chain is conducted by controlling the
added amount of sodium 9-anthracenyl metoxide. The low
nucleophilicity of the substituent chromophore group makes
the use of KI and sodium salt of 9-anthracenyl methanol
necessary. When 20 or 30% of the substituent (sodium
9-anthracenyl metoxide), with respect to the number of
moles of polymer (IV), was employed in the preparation
of the copolymer, a sparingly soluble product was obtained;
however, when 10% of the substituent was used in the post-
functionalization, a material with higher solubility than in
the previous cases was produced.

Copolymer (V) is only fairly soluble in common organic
solvents, hindering the determination of its average molar mass,
polydispersity, and NMR spectrum. Nevertheless,
its UV-Vis, photoluminescent and FT-IR spectra allow its
characterization and determination of some of its interesting
properties. Figure 4 depicts an FT-IR spectrum of copolymer
(V).

The copolymer (V) presents a very strong absorption
in the UV-Vis spectrum with a maximum at 433 nm,
Figure 5; however, when excited at that wavelength its
photoluminescent spectrum shows a maximum at 654 nm
with a low fluorescent intensity, Figure 6, allowing to
assume that a high percentage of the relaxation process
occurs through a triplet state, indicating that the copolymer
possesses suitable properties to be utilized in solar cells.

Table 1 lists the conductivities of doped and undoped
polymers (III), (IV), and (V). The conductivities can be
related to the respective regioregularities. Polymer (IV)
displays a greater conductivity than polymer (III), which is
consistent with the fact that the conductivity is greater for
highly ordered systems, enhancing thus the coplanarity of
thiophene rings in the doped state.

On the other hand, it is likely that the observed
conductivity of the copolymer in the doped state being due
to the presence of aromatic anthracene rings as substituent,
which allows for the conduction to be accomplished by
overlapping of π systems orbitals. This is consistent with the
higher conductivity found for copolymer (V).

The optical band gap of these polymers was estimated
by UV-Vis and was found to be: (CHCl₃) 530 nm, 2.33 eV
for polymer (III), 506 nm, 2.45 eV for polymer (IV), and
539 nm, 2.30 eV for copolymer (V), this presents a lower
band gap than its base polymer.

The decrease in the band gap in conductive polymers
occurs when the number of monomer units of thiophene
increases in the polymeric chain. However, in the present case
it has been ascribed to a higher order and stiffness conferred
by the substituent group, which is responsible for many of its
properties.

4. Conclusions

The synthesis of two novel polymers derived from thiophene
has been described along with their characterization and
determination of the average molar mass, regioregularity,
conducting properties, and optical bandgap. The low sol-
ubility of copolymer (V) hinders its characterization by
techniques such as FT-IR, and absorption and emission
spectroscopy. The latter techniques are very important since
our interest is focussed on the use of the copolymer to
fabricate electronic devices, for example, solar cells, light
emitting diodes, and so on.
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