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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Received 15 September 2008; Revised 8 January 2009; Accepted 8 March 2009

Recommended by Bernabé L. Rivas

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 functionalized 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], metallocenes, 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

FIGURE 1: FT-IR spectrum of poly[3-(6-chlorohexyl)thiophene].

FIGURE 2: ^1H -NMR, relative areas of the signal attributed to CH_2 adjacent to the thiophene ring for poly[3-(6-chlorohexyl)thiophene] (III) and poly[3-(6-bromohexyl)thiophene] (IV).

ditiynlpyrrol [24]. As a result of the polymerization of these small oligomeric units a copolymer is obtained wherein the substituent units are separated, minimizing the steric interaction among adjacent functional groups. The resultant polymer presents a better conjugation along the heterocyclic chain and high conductivity. [25]

Various strategies exist for the preparation of this kind of polymers; the most utilized being the preparation of monomeric units already functionalized for their subsequent polymerization. However, many of these functional groups are incompatible with the polymerization process generating undesirable oxidations, along with low molecular weight of the polymer, or a total hindrance of the polymerization [26, 27]. The choice of the method of polymerization is very important if a regular material without modifications into the substituent group is sought. The most utilized method is the direct chemical oxidation using FeCl_3 [28, 29]. Nevertheless, a very efficient method for controlling the oxidation is the electropolymerization, affording substituted polymers almost without modification in the substituent groups [30]. Another very efficient way to overcome this problem is the preparation of poly-alkylthiophenes with the

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

Polymer	Undoped (ms)	Doped (ms) *
(III)	$4.0 \cdot 10^{-11}$	$1.4 \cdot 10^{-6}$
(IV)	$2.0 \cdot 10^{-9}$	$1.0 \cdot 10^{-4}$
(V)	$6.0 \cdot 10^{-10}$	$2.0 \cdot 10^{-3}$

* I_2 was utilized as doping agent

capacity of being functionalized. This is the case of poly(3-(ω -haloalkyl)thiophene), which has been successfully post-functionalized with almost quantitative conversion [31]. This allows for the combination between the properties of the conjugated polymer and the substituent group of interest.

In the present work the synthesis, characterization, properties, and the two-step preparation of its monomer unit [32], that permits a swift and facile preparation of the polymer, of poly(3-(6-bromohexyl)thiophene) are reported. In addition, a comparative study between poly(3-(6-chlorohexyl)thiophene) and poly(3-(6-bromohexyl)thiophene) was performed. The latter compound was prepared following the procedure described by Iraqi et al. [33]. Finally, poly[(3(6-(9-anthracenyl-methoxy)hexyl)thiophene)-co-(3-(6-bromohexyl)thiophene)] was synthesized by postfunctionalization of poly(3-(6-bromohexyl)thiophene), which shows the best regioregular properties of the two surveyed halogenated polymers.

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 $1.0 \text{ mL} \cdot \text{min}^{-1}$. 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 N_2 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 $\text{Ni}(\text{dppp})\text{Cl}_2$ as catalyst. The mixture was boiled for 12 hours under N_2 . After cooling at room temperature, 40 mL HCl and 50 mL H_2O were added, and the organic phase was separated using a separator funnel. The organic phase was dried (Na_2SO_4) and the solvent was evaporated at low pressure.

FIGURE 3: UV-Vis spectra in CHCl_3 for monomers (I), (II) and polymers (III), (IV).

TABLE 2: Characterization of the polymers.

Polymer	Yield%	Composition% (a)	HT % (b)	Solubility(c)	M_n (g/mol) (d) (average)	M_w/M_n (d) (average)
(III)	59	—	55	t	3.000	3.2
(IV)	61	—	73	t	40.000	2.3
(V)	—	10	73	p	-	—

(a) Molar percent of substituent, (b) head-to-tail regioregularity, in dyads, determined by ^1H -RMN spectroscopy, (c) t: Wholly soluble in common organic solvents; p: Partially soluble, (d) number average molar mass, M_n : Average polydispersity index, M_w/M_n , determined by GPC using polystyrene as standard.

FIGURE 4: FT-IR spectrum of poly[(3-(6-(9-anthracenyloxy)hexyl)thiophene)-co-(3-(6-bromohexyl)thiophene)] (V).

FIGURE 5: UV-Vis spectrum of copolymer (V) in CHCl_3 .

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. ^1H -NMR (CDCl_3 , 200 MHz) δ 1.28 – 1.48 (4H, m), 1.61 (2H, m), 1.82 (2H, m), 2.60 (2H, t, $J = 8\text{ Hz}$), 3.55 (2H, t, $J = 7\text{ Hz}$), 6.89 (2H, m), 7.18 (2H, m); ^{13}C -RMN (CDCl_3 , 200 MHz) δ 26.7, 28.5, 30.1, 30.2, 32.4, 45.1, 119.9, 125.1, 128.2, 142.9. FTIR (film, cm^{-1}): 3089, 2931, 2856, 1541, 1460, 1417, 834, 826, 759, 644. Calculated elemental analysis for $\text{C}_{10}\text{H}_{15}\text{ClS}$: 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. ^1H -RMN (CDCl_3 , 200 MHz) δ 1.28-1.48 (4H, m), 1.62 (2H, m), 1.82 (2H, m), 2.60 (2H, t, $J = 8\text{ Hz}$), 3.35 (2H, t, $J = 7\text{ Hz}$), 6.86-6.92 (2H, m), 7.10-7.24 (1H, m); ^{13}C -RMN (CDCl_3 , 200 MHz) δ 27.9, 28.3, 30.1, 30.3, 32.7, 33.9, 119.9, 125.1, 128.3, 142.8. FTIR (film, cm^{-1}): 3103, 3053, 3004, 2931, 2856, 1537, 1460, 1438, 1410, 1258,

FIGURE 6: Photoluminescent and UV-vis spectra of copolymer [5] in CHCl_3 .

SCHEME 1: Synthesis of poly[3-(6-chlorohexyl)thiophene] and poly[3-(6-bromohexyl)thiophene].

1238, 1153, 1080, 860, 834, 773, 685, 635, 561. Calculated elemental analysis for $\text{C}_{10}\text{H}_{15}\text{BrS}$: C, 48.59; H, 6.12; S, 12.97. Found: C, 48.56; H, 6.09; S, 12.95.

2.3. Synthesis of poly[3-(6-chlorohexyl)thiophene]. A solution containing 1.60 g (9.6 mmol) FeCl_3 in 10 mL CH_3NO_2 was slowly poured during 20 minutes into a solution of 0.5 g (2.4 mmol) of 3-(6-chlorohexyl)thiophene in 30 mL CCl_4 . The mixture was stirred for 6 hours at room temperature and then filtered under vacuum. The solid was Soxhlet extracted with methanol and dried at 60 °C. The product was a red solid, yield 0.28 g (59%). Spectral characterizations were as follows: ^1H -RMN (CDCl_3 , 200 MHz) δ 1.30-1.85 (8H, m), 2.50-2.90 (2H, m), 3.52 (2H, m), 6.93, 6.99, 7.02, 7.09 (1H, 4s); ^{13}C -RMN (CDCl_3 , 200 MHz) δ 28.0, 28.6, 29.3, 30.3, 32.7, 34.0, 128.6, 130.6, 133.7, 139.6. FTIR (KBr, cm^{-1}): 3057 (ArCH, stretching), 2927 y 2853 (sp^3 CH stretching), 1671, 1509 y 1458 (ArC-C, stretching corresponding to combination bands of heterocycles), 1440 (C=C, symmetric stretching of the thiophene ring), 830 (C-H out-of-plane twist of thiophene 2,3,5-trisubstituted), 726 (methylene groups rocking vibration), 648 (C-Cl, stretching), Figure 1.

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 FeCl_3 dissolved in 10 mL CH_3NO_2 was slowly poured during 20 minutes into a solution of 0.6 g (2.4 mmol) of 3-(6-chlorohexyl)thiophene in 30 mL CCl_4 . 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 (CDCl_3 , 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); ^{13}C -RMN (CDCl_3 , 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 (sp^2 C-H stretching), 2934 y 2858 (sp^3 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-chlorohexyl)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-chlorohexyl)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 CH_2 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

SCHEME 2: Synthesis of poly[(3-(6-(9-anthracenyloxy)hexyl)thiophene)-co-(3-(6-bromohexyl)thiophene)].

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 solubility in organic solvents, such as THF, CHCl_3 , CH_2Cl_2 , ethyl ether, and CCl_4 . FT-IR spectra are also similar for these compounds, however UV-Vis spectra in CHCl_3 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, M_w , determined for polymers (III) and (IV): the brominated derivative (IV) shows a higher average molecular weight, M_w , 40000.

Polymer (IV) was employed as starting material for the synthesis of copolymer (V) because of its greater regioregularity, HT. The degree of substitution of terminal bromine atoms of the alkyl chain is conducted by controlling the added amount of sodium 9-anthracenyl methoxide. 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 methoxide), 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: (CHCl_3) 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 of 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 solubility 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.

Acknowledgments

The authors wish to thank Fondecyt-Chile through Grant 1050953, and Conicyt doctoral fellowship 4040121 and 23060093 TTD for financial support of this research work.

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