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Influence of solvent used on oxidative polymerization of Poly(3-hexylthiophene) in their chemical properties

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Abstract

The aim of the study is to utilize the simplicity of oxidative polymerization with ferric chloride to originates poly(3-hexylthiophene) of lower molecular weight. So, the chloroform, in general used as solvent in this synthesis, was switched by dichloromethane. The obtained polymers were characterized by infrared spectroscopy (FTIR), ultra-violet visible spectroscopy (UV-Vis), gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) were used to evaluate the structure, conjugation length, molecular weight and regioregularity with the goal of comparing these properties with those of poly (3-hexylthiophene) synthesized in chloroform. Despite large difference observed in molecular weight of polymers obtained by chloroform and dichloromethane, no significant differences were observed of these polymers in regioregularity and conjugation length.

Keywords: *ferric chloride, oxidative coupling, poly(3-alkylthiophene), poly(3-hexylthiophene).*

1. Introduction

Conjugated polymers are largely studied due to the combination of characteristics similar to semiconductors (electrical and optical properties) and low weight and processability of common polymers. Between these polymers, polythiophenes are one of the most studied polymer due to possibility of attach different functional groups into their backbone to originates different properties^[1]. The insertion of alkyl chain on position 3 of thiophene ring brings to this polymer the possibility of being melted and solubilized^[2]. These polymers can be applied in fabrication of electroluminescent devices, as light emission diode (LED), Field Effect Transistors (FET)^[1], Polymer solar cells^[3].

There are many synthetic methods for polymerization of 3-alkylthiophene by chemical synthesis, for instance Rieke, McCullough and GRIM methods^[4-6]. The differential of these methods is that the obtaining polymers have low molecular weight and high content of regioregularity. On the other hand, these methods need more than one step of reaction and special conditions of synthesis, such as temperature maintained lower than -5 °C or higher than 60 °C. The chemical synthesis with ferric chloride (FeCl₃), although do not leads to high regioregularity polymers, is probably the most used chemical method of synthesis due to its simplicity and possibility of be applied in large scale. Almost all the polymerizations reactions of poly(3-alkylthiophene) by chemical oxidation with FeCl₃ uses chloroform as solvent. This polymerization originates polymers with regioregularity about 70-80% and high molecular weight in relation to other methods^[7]. In some applications, like those that need electron conduction, since the same regioregularity is maintained, polymers with lower molecular weight present the higher electron conduction.

The decrease of electron conduction, with the enhanced of molecular weight, was attributed in some studies to the decrease of cristallinity of these polymers^[8-10].

The aim of this work is to utilize the simplicity of oxidative synthesis with FeCl₃ to synthesize poly(3-hexylthiophene) (PHT) with low molecular weight. For this purpose, this synthesis will use dichloromethane as the reaction medium, since this is a solvent in which the PHT presents low solubility. Although in literature there are reports of synthesis of poly(3-alkylthiophenes) using FeCl₃ and dichloromethane as solvent^[11], no description was made about which polymer of this class were polymerized and none characterization was made to compare the characteristics of the polymer obtained in dichloromethane in relation the same polymer obtained in conventional method (with chloroform). There is a variation on time of polymerization of polymers synthesized in dichloromethane, to ensure the characteristics observed between the poly(3-hexylthiophenes) synthesized in different solvents are related only to difference of solubility of the solvent used in polymerization, and no to the differences in reaction media. Was observed a large difference in relation to molecular weight of poly(3-hexylthiophene) synthesized in different solvents. No relevant differences were observed in relation to the conjugation length and regioregularity.

2. Materials and Methods

2.1 Experimental

3-hexylthiophene 99% of purity from sigma-aldrich and anhydrous ferric chloride (FeCl₃) from BDH GPR, was used as received. Halogenated solvents chloroform

and dichloromethane (both P.A. from Vetec) was dried over phosphorus pentoxide (P_2O_5) under reflux, and then was used immediately after distilled. Acetone (P.A. Dinâmica) was used as received.

2.2 Polymer synthesis

The synthesis was carried out at room temperature under nitrogen atmosphere in oven dried glassware. Polymers were obtained by oxidative coupling with anhydrous ferric chloride in dry chloroform or dichloromethane as follow. A 3-hexylthiophene (12 mmol) was added in solution into a dispersion of ferric chloride (48 mmol) with 150 mL of solvent. After 16 hours (or 40 hours), the polymer was precipitated by methanol. The obtained polymer was the dissolved in chloroform and re-precipitated in methanol to be purified. The obtained polymer was dried in a vacuum oven.

2.3 Characterization

FTIR spectra in the middle IR region in the range $4000\text{--}400\text{ cm}^{-1}$ (128 scans at resolution 4 cm^{-1}) were obtained on a Bruker ISF66 spectrometer by KBr pellet (pressed discs with 5000 kg/cm^2 during 10 min) in a proportion of 0.7 mg of sample and 100 mg KBr. NMR spectra were recorded on a VARIAN UNMRS 400 MHz in $CDCl_3$. The aromatic region of poly(3-hexylthiophene) in 1H NMR spectra, were deconvoluted using a Varian VnmrJ software and relatively integrated in order to measure the regioregularity of these polymers. UV-Vis spectra were recorded in Perkin Elmer Lambda 650 in THF solution. GPC was performed on a Viscotek TDA 032 equipped with light scattering and refractometer index detectors and a column of Fluorinated divinylbenzene gel. The samples were prepared with concentrations ranging from 0.5 to 2 mg/mL of THF.

3. Results and Discussion

Differences were observed in relation to reaction media of polymers obtained with different solvents. On chloroform synthesis, a dark black color was observed with presence of insoluble particles of $FeCl_3$, while a dark green color is observed in dichloromethane synthesis and no observation of $FeCl_3$ particles was made. Then, it could be seen that ferric chloride is partially solubilized in ferric chloride in concentration used (0.04 g/mL).

The polymerization yield after soxhlet extraction in acetone to removal of oligomers was of 73% for poly(3-hexylthiophenes) synthesized in dichloromethane for 16 hours (PHTdcm16); 83% and 88% for poly(3-hexylthiophenes) synthesized in dichloromethane for 40 hours (PHTdcm40) and poly(3-hexylthiophenes) synthesized in chloroform for 16 hours (PHTcl), respectively.

3.1 Infrared absorption

In Figure 1 are presented the infrared spectra of PHTcl; PHTdcm16 and PHTdcm40 polymers. In all spectra are present bands at 3055 cm^{-1} related to the stretching vibrations of C-H aromatic bonds, peaks near 2920 and 2850 cm^{-1} relative to symmetric and asymmetric vibrations of C-H linkages in alkylic chains, respectively. Near to 1510 and 1458 cm^{-1} , the symmetric and asymmetric vibrations of thiophene rings (C=C bond)

are present in all polymers^[12]. In 824 , 823 and 824 cm^{-1} the thiophene ring C-H out-of-plane bend modes of PHTcl, PHTdcm16 and PHTdcm40 can be observed, respectively. According to Zerbi et al.^[13], a correlation between these band and backbone planarity can be made, being the bands at higher wave numbers (around 835 cm^{-1}) related to a more twisted conformation, while the lower wave number (near 820 cm^{-1}) is related to a more planar conformation. Once we could not find a significant difference in these bands, we can infer that the two solvents used under the adopted conditions in this study, did not influence in planarity for the obtained polymers.

3.2 Molecular weight

In Table 1, the molecular weights of polymers are presented. It can be seen that the polymer synthesized in chloroform has higher molecular weight than polymers synthesized in dichloromethane, even when a large time of polymerization was applied. Differences were observed with relation to polydispersity, presenting the polymers synthesized in dichloromethane lower dispersion than polymer synthesized in chloroform.

As the solubility of a polymeric chain obey the relation of the attractive force between them and the cohesive force polymer/solvent, the lower molecular weight of polymers synthesized in dichloromethane compared to polymer prepared by the same conditions in chloroform may be related to the precipitation of polymeric chains in this solvent. In other words, assuming that the polymer has low solubility in the solvent used in the synthesis (dichloromethane), as

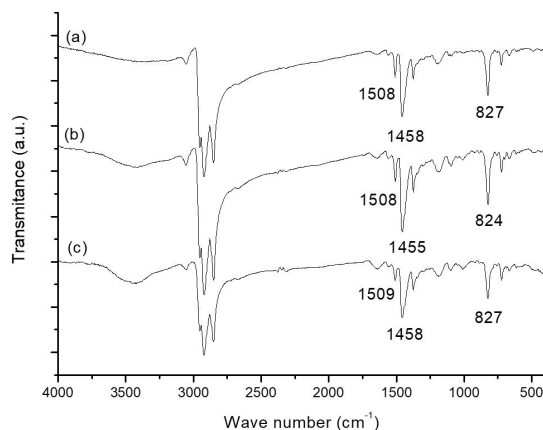


Figure 1. FTIR spectra of (a) PHTcl; (b) PHTdcm16; (c) PHTdcm40.

Table 1. Molecular Weights and polydispersity of poly(3-hexylthiophene) synthesized with chloroform for 16 hours (PHTcl) and poly(3-hexylthiophene) synthesized with dichloromethane for 16 and 40 hours, respectively (PHTdcm16 and PHTdcm40).

	Mn (KDa)	Mw (KDa)	Polidispersity
PHTcl	1300	2700	2.04
PHTdcm16	200	378	1.89
PHTdcm40	282	500	1.77

the polymerization occurs the chain reaches a size greater than the solubility capacity of the reaction medium and then precipitates. Thus, the polymers obtained under these conditions should have a smaller chain size and therefore less number of repeating units than polymers synthesized in more soluble medium.

On the other hand, increasing polymerization in dichloromethane should not result in considerable improvements in the molecular weight of originated polymer. Thus, since the molecular weight of PHTdcm16 is higher than molecular weight of PHTdcm40, more than difference in solubility in synthesis in different solvents is observed.

The answer for the unusual molecular weight of the polymers obtained in dichloromethane may be related to the polymerization mechanism. The most accepted mechanism polymerization of poly(3-hexylthiophene) in ferric chloride is radicalar^[14] in which the growth of polymeric chain occurs in two ways: insertion of on monomer per time or combination of oligomers in solution. Since chloroform and dichloromethane do not exhibit large differences in density, considerable differences in monomer diffusion in these solvents are unlikely to be observed. However, difference in polarity is observed between the two solvents used. The high polarity of dichloromethane in relation to chloroform promotes more cationic stabilization of the species, leaving the cationic species less reactive in relation to polymerization made in chloroform. This phenomenon can contribute to the low molecular weight presented by PHTdcm16 and PHTdcm40.

Another possible explanation to the variation of molecular weight is the difference of solubility of FeCl_3 in these solvents. Was observed that ferric chloride is much more soluble in dichloromethane than chloroform. According to Niemi et al.^[14], its necessary the presence of FeCl_3 crystals to polymerization happen. So, the large number of ferric chloride crystals presents on reaction made in chloroform can be the reason for the large molecular weight on this polymer.

Most studies analyzing molecular weight of poly (alkyl thiophenes) use regioregular synthesis methods, such as McCullough and Rieke^[15-17]. The polymers obtained by oxidative synthesis, using ferric chloride as oxidant agent, presents higher molecular weight and, therefore, cannot be compared with polymers synthesized by other methods.

3.3 NMR

The poly(3-alkylthiophenes) were analyzed by ^1H NMR, and can be observed in these spectra the presence of peaks related to methylenic protons in the region of 0.8-3 ppm, and aromatic proton on interval of 6.98 to 7.05 ppm (Figure 2).

Since these polymers present asymmetric structure, the enchainment of 3-alkylthiophenes can originate three different configurations during polymerization. These configurations originate four different triads, which are HT-HT (head to tail - head to tail); HT-TT (head to tail - tail to tail); HT-HH (head to tail - head to head); TT-HH (tail to tail - head to head), as can be seen on Figure 3. Due to differences on chemical environments observed by NMR, these triads are presented on aromatic proton interval (between 6.98 and 7.05), and each triad present a difference of approximately 0.02 ppm between chemical

shift. So, the regioregularity of poly(3-alkylthiophenes) was obtained by integration of each of these peaks^[18,19]. These regioregularity can be obtained by alkylc protons and ^{13}C integration too, but these protons are less sensitive than aromatic ones, and in carbon spectra, the aromatic carbons for 100% regioregularity polymer originate 4 signals, while for less regioregular polymers, 12 different peaks can be observed^[2]. The percentage of the four triade present on PHTcl, PHTdcm16 and PHTdcm40 can be observed on Table 2.

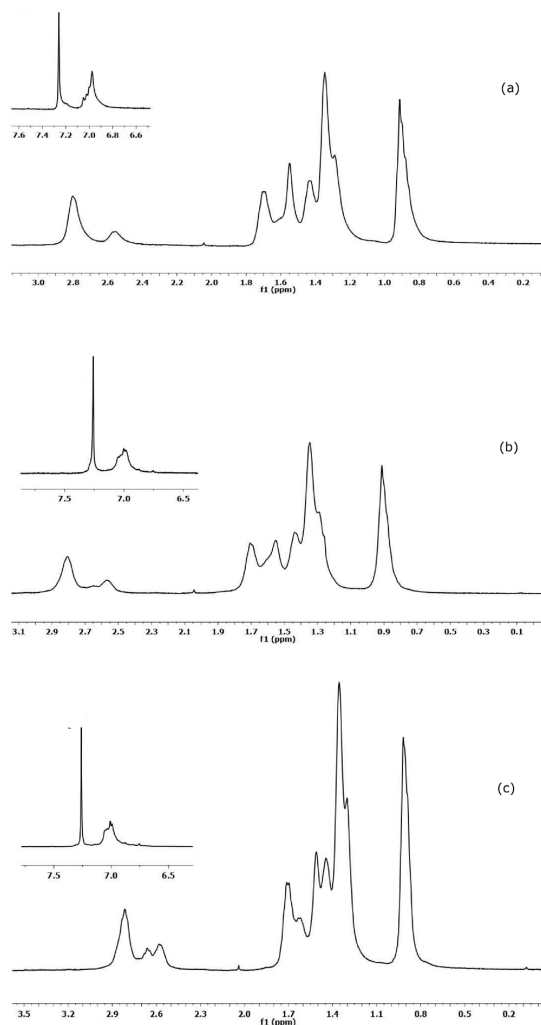


Figure 2. ^1H -NMR spectra of (a) PHTcl; (b) PHTdcm16; (c) PHTdcm40 with expanded area corresponding to the region of aromatic hydrogens.

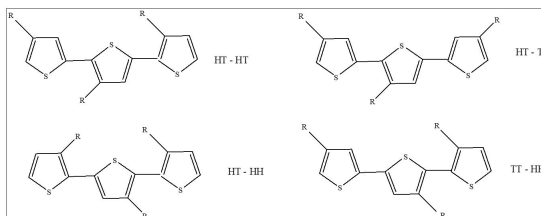


Figure 3. Scheme of possible poly(3-alkylthiophene) triads HT-HT, HT-TT, HT-HH and TT-HH.

The differences presented by HT-HT linkages between the PHTcl and PHTdcm16 are not very significant. So, can be inferred that the differences between reactional media, ferric chloride solubility and solvent polarity, do not affect the considerably the regioregularity of obtained polymers. Otherwise, PHTdcm 40 presents a very low percentage of HT-HT linkages, and no explanation was found to this.

The regioregularity values obtained for PHTcl and PHTdcm16 are high in relation to values obtained in literatures for the same variables, as temperature of polymerization^[20,21]. According to Amou et al.^[22], the decrease of monomer concentration in polymerization, increase the regioregularity. With a concentration of 1 mol monomer/L of solvent, the HT content is of 76% and this value increase to 88% when concentration decrease to 0.05 mol monomer/L. As the concentration of monomer used in our study is lower, 0.05 mol/L, then other studies, 0.066 mol/L^[21,23], this is the possible explanation for higher regioregularity obtained.

3.4 UV-vis absorption

The UV-vis absorption spectra in conjugated polymers, can give a measurement of the transition $\pi - \pi^*$, and consequently, the conjugation length of the poly(3-alkylthiophenes). This conjugation length depends mainly to regioregularity of polymer. In Figure 4 is observed UV-Vis absorption spectra of polymers synthesized in chloroform and dichloromethane. Higher wave length absorption is observed to PHTcl. Although only a little difference in percentage of HT-HT triads is observed between the PHTcl and PHTdcm16, the larger wave number absorption of PHTcl is relative to higher molecular weight presented by

Table 2. Regioregularity of poly(3-hexylthiophene) synthesized in chloroform for 16 hours (PHTcl) and poly(3-hexylthiophene) synthesized with dichloromethane for 16 and 40 hours, respectively (PHTdcm16 and PHTdcm40).

	HT-HT (%)	HT-TT (%)	HT-HH (%)	TT-HH (%)
PHTcl	76.6	5.6	10.4	7.4
PHTdcm16	71.6	0.7	-	27.7
PHTdcm40	43.4	22.6	-	34.0

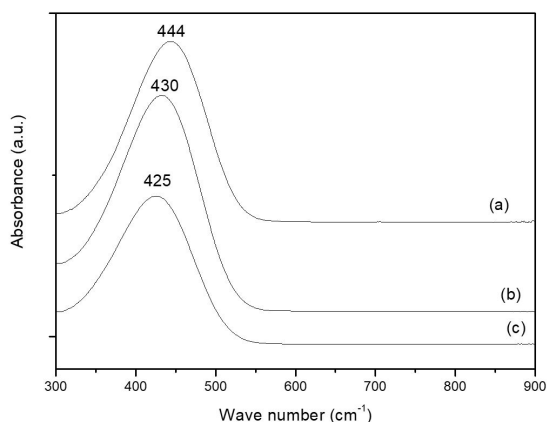


Figure 4. UV-vis absorption spectra of (a) PHTcl; (b) PHTdcm16; (c) PHTdcm40.

this polymer. According to Jeffries-El and McCullough^[6], the conjugation length of poly(3-alkylthiophenes) increase with the molecular weights. The values of maximum absorption for poly(3-hexylthiophenes) are in accordance with the literature. For PHT for example, McCullough and Lowe^[24] observed a maximum absorption of 436 nm for polymer obtained by oxidation with FeCl_3 .

In observations made by infrared spectra, polymeric chains of PHTcl is more planar than PHTdcm16 and PHTdcm40 chains. These results corroborate the observed by UV-Vis.

4. Conclusions

Poly(3-hexylthiophene) was successful synthesized by oxidative polymerization with anhydrous ferric chloride, using dichloromethane as solvent. A large difference of molecular weight is observed by this polymer in relation to poly(3-hexylthiophene) synthesized by the same conditions, but using chloroform as solvent. Polymers synthesized in dichloromethane presents considerable lower molecular weight in relation to polymer synthesized in chloroform, and this diminution is observed in polydispersity too. This decrease can be related to differences in solvent polarity or solubility of ferric chloride. Despite the observed differences in molecular weight, no considerable variation is observed in the regioregularity of these polymers. The UV-Vis analyses show that PHTcl presents higher conjugation length than PHTdcm16 and PHTdcm40, which is expected because of the higher molecular weight found for PHTcl.

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