Synthesis of Highly Regioregular Poly[3-(4-alkoxyphenyl)-thiophene]s by Oxidative Catalysis using Copper Complexes

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ABSTRACT: A novel, easy, and cost-effective synthetic procedure is reported for the production of very highly regioregular poly[3-(4-alkoxyphenyl)thiophene]s by means of oxidative coupling. Four copper complexes were synthesized and used as catalysts to obtain polymers with higher regioregularity compared to the previous oxidative coupling methodologies reported in the literature and similar to that obtained by McCullough and Rieke methods in the synthesis of poly-3alkylthiophenes. The regioregularity of the synthesized polymers was investigated by UV-Visible characterization on polymer thin films and ¹H NMR analysis. The remarkable

INTRODUCTION Organic electronics have attracted much interest in the last decade owing to particular characteristics of π -conjugated polymeric and molecular compounds which join optical and electrical properties of semiconductors with chemical-physical features and easy processability of organic materials. Hence, these types of materials have been the object of intensive research especially in the fields of field-effect transistors,^{1–4} photovoltaics,^{5–9} and light-emitting devices.^{10–17} Among the conjugated polymers, poly(3-alkylthiophenes) have been widely studied for potential applications.¹⁸⁻²³ A key factor to obtain poly-3-substituted thiophenes with good electrical performance resides in their regioregularity.²⁴ In fact, the electron-transport characteristics of these materials are strongly dependent on their regioregularity as only head-totail connection sequences allow energy stable planar conformation of the backbone which, in turn, provides a wide delocalization of the π electron density. Different preparation methodologies are described in the literature, based on metalcatalyzed crosscoupling of the thiophene monomers: the most popular procedures are based on the oxidation of the potentialities of these polymers have emerged from field-effect transistor mobility measurements operated on devices with bottom-contact configuration and hexamethyldisilazane-treated SiO₂ gate dielectric, showing a well-defined p-type field-effect response and maximum mobility values in air higher than 10^{-4} cm² V⁻¹ s⁻¹. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 4351–4360

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3-substituted thiophene monomer by Br_2 at the 2- and 5-positions, followed by reaction of the dihalogenated product with finely powdered electropositive metals (Rieke²⁵ metals) or Grignard²⁶ reagents to afford the desired polymer. These synthetic procedures lead to highly regioregular polymers (>98%) obtained in good yields, but they are usually expensive, multistep, and require inert atmosphere. Another approach to the preparation of regioregular 3-substituted polythiophenes is the polymerization of thiophene monomers through an oxidative coupling method. In this regard, Leclerc and coworkers²¹ and Andersson et al.²³ described a procedure based on the use of FeCl₃ as oxidant agent in wide excess. Recently, the synthesis of regioregular poly[3-(4-alkylphenyl)thiophene]s²⁷ and poly[3-(4-alkoxyphenyl)thiophene]s²⁸ by the oxidation of the corresponding thiophene monomers catalyzed by vanadyl complex $(VO(acac)_2)^{29}$ has been reported. These synthetic procedures can be considered very simple and inexpensive, nevertheless they afford materials with lower regioregularity (around 90%) as compared to the crosscoupling methods cited above.

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In this respect, it seemed interesting to investigate a new synthetic approach to make poly[3-(4-alkoxyphenyl)thiophene]s with as good regioregularity as the McCullough and Rieke methods through a simple and inexpensive method based on oxidative catalysis. The interest in this kind of polymers lies in their potential electronic properties deriving from the higher stability to the oxidation induced by the phenyl ring functionalization, as a consequence of the highest occupied molecular orbital (HOMO) level stabilization. This property is highly desirable in the field of organic fieldeffect transistors (FETs) as well as in that of organic photovoltaics, where the HOMO stability of the donor polymer greatly influences the open circuit voltage, one of the critical parameters for improving efficiency. Starting from our previous studies,²⁸⁻³⁰ we therefore developed a novel synthetic procedure to prepare poly[3-(4-octyloxyphenyl)thiophene]s (PT8) with high regioregularity. On the basis of the literature evidence about the regiospecific polymerization of naphthalene derivatives by copper catalysts,³¹ we have first investigated the behavior of $Cu(acac)_2$, by analogy with $VO(acac)_2$, obtaining a regioirregular PT8. Instead, highly regioregular PT8s were obtained by changing the chemical environment of the metal by complexation with salicylaldehydic and salicylaldimine ligands. The same results were not achievable with the analogous vanadyl complexes of the same ligands. The molecular structure of PT8 is shown in Figure 1. The synthesized polymers were fully characterized through UV-Visible spectroscopy and their regioregularity degree was deeply investigated using ¹H-NMR analysis.

PT8 spin-coated films were used as active layers of p-type FET devices based on SiO₂ gate dielectric. Preliminary measurements show that the electrical response of these devices is also quite stable in air and charge carrier mobility was found to be higher than 10^{-4} cm² V⁻¹ s⁻¹.

EXPERIMENTAL

Materials

All reagents were purchased from Sigma Aldrich and used without further purification.

Physicochemical Characterization

Thermogravimetric analyses (TGAs) were performed on a TA SDT2960 instrument and the experiments were run under air flow at a scanning rate of 20 K/min. Temperature-controlled optical microscopy analysis was performed with a



FIGURE 1 Molecular structure of poly[3-(4-octyloxyphenyl)thiophene] (PT8).

Zeiss Axioscop polarizing microscope equipped with a Mettler FP90 heating stage. ¹H-NMR spectra were recorded with a Varian VXR 200 MHz and Varian Inova 500 MHz spectrometers. Proton chemical shifts were referenced to the residual solvent signal (CDCl₃, δ = 7.26; 1,1,2,2-tetrachloroethane, $\delta = 6.0$). The following abbreviations are used in describing the NMR multiplicities: s, singlet; d, doublet; t, triplet; and m, multiplet. UV-Visible measurements were performed at room temperature with a Jasco V-560 spectrophotometer. X-Ray powder diffraction spectra were recorded with a Philips PW 1830 Generator with a Geiger counter and Nifiltered Cu Ka radiation. The synthesized polymers were drop cast as thin films for XRD analysis from 1,2-dichlorobenzene solutions (2 wt %) at room temperature for 2 days and following annealing at 150 °C for 30 min in N2 atmosphere. PT8 thin films were also used as active layer in bottom-contact bottom-gate transistors: in this case, the polymers were spin-coated onto transistor substrates from hot 1,2-dichlorobenzene solutions (0.5 wt %, filtered through a 0.2-µm Whatman filter) at 700 rpm for 1 min and then annealed for 30 min at 150 $^\circ\text{C}$ in N_2 atmosphere. Before deposition, transistors Si⁺⁺/SiO₂/Au substrates were functionalized with hexamethyldisilazane (HMDS) according to the procedure described in ref. 32. All electrical measurements were performed in darkness, by using a Janis Cryogenic Probe-Station connected to a Keithley 2612A Dual-Channel system source-meter instrument. The molecular masses and their distributions were obtained on an Agilent PL GPC 220 apparatus with polystyrene samples as references and 1,2,4trichlorobenzene as eluent.

Synthesis

Monomer 3-(4-octiloxyphenyl)thiophene was prepared as described in ref. 33. To give the article a simpler readability, the synthesis of poly[3-(4-octyloxyphenyl)thiophene] with $VO(acac)_2$ is also reported, as optimized in our previous study.²⁸

Poly[3-(4-octyloxyphenyl)thiophene]-VO(acac)₂

VO(acac)₂ (0.082 g, 0.31 mmol), anhydrous 1,2-dichloroethane (1.2 ml), trifluoroacetic anhydride (TFA) (1.2 mL, 8.64 mmol), and trifluoromethanesulfonic acid (TFMSA; 5 μ L, 0.056 mmol) were introduced into a round-bottom flask (1 L),under a slight oxygen flow, and the resulting mixture was stirred at room temperature for 10 min. The monomer 3-(4-octiloxyphenyl)thiophene (1.07 g, 4.13 mmol) was added along with a further amount of TFA (0.5 mL, 3.59 mmol), and 1,2-dichloroethane (6.5 mL). The obtained mixture was stirred under an oxygen atmosphere (pressure, \sim 1 atm) for 17 h at room temperature. The resulting polymer was recovered by precipitation from methanol (250 mL) containing HCl (25 mL, 37% w/w). The crude product was extracted with acetone by a Soxhlet-extraction apparatus. Yield: 40%.

¹H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d₂, δ ppm): 0.89 (m, 3H), 1.31 (m, 10H), 1.78 (m, 2H), 3.96 (m, 2H), 6.89 (m, 3H), 7.28 (d, 2H, J = 8 Hz). ELEM. ANAL. calcd for

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 $(C_{18}H_{22}OS)_n$: C 75.45, H 7.74, S 11.19; found: C 73.80, H 7.64, S 10.80.

Poly[3-(4-octyloxyphenyl)thiophene]-Cu1

Complex Cu1 (0.213 g, 0.26 mmol), 1,2-dichlobenzene (3.5 mL), TFA (2 mL, 14.4 mmol), and TFMSA (13 μ L, 0.147 mmol) were introduced into a round-bottom flask (1 L), under a slight oxygen flow, and the resulting mixture was stirred at room temperature for 10 min. The monomer 3-(4-octiloxyphenyl)thiophene (1 g, 3.47 mmol) was added along with a further amount of TFA (0.8 mL, 5.75 mmol), and 1,2-dichlorobenzene (3 mL). The obtained mixture was stirred under an oxygen atmosphere (pressure, ~1 atm) for 48 h at 80 °C. The resulting polymer was recovered by precipitation from methanol (150 mL) containing HCl (15 mL, 37% w/w). The crude product was extracted with acetone by a Soxhlet-extraction apparatus. Yield: 30%.

¹H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d₂, δ ppm): 0.90 (m, 3H), 1.32 (m, 10H), 1.80 (m, 2H), 3.97 (m, 2H), 6.90 (m, 3H), 7.29 (d, 2H, J = 10 Hz). ELEM. ANAL. calcd for (C₁₈H₂₂OS)_n: C 75.45, H 7.74, S 11.19; found: C 74.49, H 7.61, S 10.95.

Poly[3-(4-octyloxyphenyl)thiophene]-Cu2

The polymer was prepared by the same procedure described for PT8-Cu1 except that Cu2 was used as catalyst. Yield: 32%.

¹H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d₂, δ ppm): 0.89 (m, 3H), 1.31 (m, 10H), 1.80 (m, 2H), 3.96 (m, 2H), 6.90 (m, 3H), 7.28 (d, 2H, J = 10 Hz). ELEM. ANAL. calcd for (C₁₈H₂₂OS)_n: C 75.45, H 7.74, S 11.19; found: C 74.48, H 7.55, S 10.94.

Poly[3-(4-octyloxyphenyl)thiophene]-Cu3

The polymer was prepared by the same procedure described for PT8-Cu1 except that Cu3 was used as catalyst. Yield: 36%.

¹H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d₂, δ ppm): 0.90 (m, 3H), 1.31 (m, 10H), 1.79 (m, 2H), 3.97 (m, 2H), 6.89 (m, 3H), 7.30 (d, 2H, J = 10 Hz). ELEM. ANAL. calcd for $(C_{18}H_{22}OS)_n$: C 75.45, H 7.74, S 11.19; found: C 74.47, H 7.64, S 10.85.

Poly[3-(4-octyloxyphenyl)thiophene]-Cu4

Complex Cu4 (0.255 g, 260.0 mmol), 1,2-dichlobenzene (1 mL), TFA (2 mL, 14.4 mmol), and TFMSA (4.2 μ L, 0.047 mmol) were introduced into a round-bottom flask (1 L), under a slight oxygen flow, and the resulting mixture was stirred at room temperature for 10 min. The monomer 3-(4-octiloxyphenyl)thiophene (1 g, 3.47 mmol) was added along with a further amount of TFA (0.8 mL, 5.75 mmol), and 1,2-dichlorobenzene (5.5 mL). The obtained mixture was stirred under an oxygen atmosphere (pressure, \sim 1 atm) for 96 h at 80 °C. The resulting polymer was recovered by precipitation from methanol (150 mL) containing HCl (15 mL, 37% w/w).

The crude product was extracted with acetone by a Soxhletextraction apparatus. Yield: 23%.

¹H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d₂, δ ppm): 0.90 (t, 3H, J = 0.90), 1.31 (m, 10H), 1.77 (m, 2H), 3.99 (m, 2H), 6.90 (m, 3H), 7.29 (d, 2H, J = 10 Hz). Anal. calcd for (C₁₈H₂₂OS)_n: C 75.45, H 7.74, S 11.19; found: C 74.65, H 7.58, S 10.91.

RESULTS AND DISCUSSION

The molecular structure of the Cu(II) complexes is shown in Figure 2. Their chemical synthesis was performed by following a procedure described in the literature.³³

The scheme in Figure 3 shows the synthetic pathway for the preparation of Cu(II) complexes. The first step shows the preparation of ligand 3 through the reaction of 2,4-dihydroxybenzaldehyde with 4-(octyloxy)benzoic acid in the presence of N,N'-dicyclohexylcarbodiimide in tetrahydrofuran. This reaction leads to a mixture of two isomers with the esterification occurring at positions 2 (by-product) and 4 (the prevalent and desired product, ligand 3) of 2,4-dihydroxybenzaldehyde. Ligand 3 can be isolated by exclusive complexation of copper(II).

The complexes Cu4 and Cu1 were prepared by reacting **3** with $Cu(CH_3COO)_2$, respectively, in the presence or absence of 1-hexylamine. The complexes Cu2 and Cu3 were instead obtained by reaction of $Cu(CH_3COO)_2$ with 2,4-dihydroxybenzaldehyde or 2-hydroxybenzaldehyde, respectively. The complexes stoichiometry was confirmed by TGA performed in air atmosphere. The theoretical and experimental values of CuO residue are lised in Table 1 and are in good agreement.

The molecular structure of Cu4 was solved by X-ray analysis on single crystal obtained by slow evaporation from an *o*dichlorobenzene solution (for more details, refer to Supporting Information material). The effect of the four copper complexes in the polymerization catalysis of 4-octiloxyphenylthiophene



FIGURE 2 Molecular structure of Cu(II) complexes.





was investigated. In a previous study,²⁸ the same material was prepared using VO(acac)₂ as oxidation catalyst (VO procedure in the following). This reaction was accomplished in dichloroethane at room temperature with an oxygen atmosphere, TFMSA, and TFA as cocatalysts. In the same conditions, the replacement of VO(acac)₂ with the copper complexes here reported afforded no polymerization at all. Following the hypothesis that the copper complexes were less active catalysts than vanadyl complexes, the polymerization was performed at higher temperatures. The higher boiling point 1,2dichlorobenzene was used as solvent to have a higher range of accessible temperatures. Three reaction temperatures were tested (60, 80, and 100 °C) and in this case polymerization did occur. In particular, polymers with noteworthy and wellstructured red-shifted UV-Visible spectra on thin film were obtained, as compared to the VO procedure. The UV-Visible characterization will be described in detail in the next paragraph. The intermediate temperature of 80 °C was chosen as the optimal one affording the higher yield in regioregular polymers. The general synthesis scheme is shown in Figure 4.

The effects of the reaction time and concentration of TFMSA and TFA on the reaction yield were also investigated. It was found that greater amounts of TFMSA and TFA were required as compared to the VO procedure to achieve reasonable yields. The optimal reaction times were determined from a balance between yields and regioregularities of the polymers. Shorter reaction times than 48 h for PT8-Cu1, PT8-Cu2, and PT8-Cu3 led to poor yields, whereas longer times caused a drop in the regioregularity. For PT8-Cu4, a reaction time of 96 h was found to be optimal. All the poly-

TABLE 1	TGA of	Cu(II)	Complexes
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Cu1 (wt %)	Cu2 (wt %)	Cu3 (wt %)	Cu4 (w %)
9.9 ^a	23.5 ^a	26.0 ^a	8.2 ^a
10.2 ^b	23.8 ^b	26.3 ^b	8.4 ^b

^a Theoretical value.

^b Experimental values.

mers were obtained in yields ranging between 23 and 36%. On the basis of experimental conditions, we can assume that the Cu(II) complexes have lower activity as compared to VO(acac)₂, because higher temperatures, longer times, and greater amounts of catalyst, TFMSA, and TFA were needed to achieve comparable yields. The lower reaction rate can, in turn, have a good effect on the polymer regioregularity. Regarding the polymerization mechanism, we could advance some hypotheses also, considering the model proposed for the VO procedure. Here, the role of TFMSA is to promote the disproportionation of V(IV) in V(III) and V(V); V(V) is the actual oxidant of the thiophene monomer turning again in V(IV). On the other side, V(III) is reoxidized to V(IV) by molecular oxygen closing the catalytic cycle. In the case of copper catalysts (Cu procedure), apparently there is no need of acidic conditions because Cu(II) should not give dismutation reaction. However, we observed that without TFMSA the polymerization reaction did not occur at all: the acid is therefore needed but its role should be different than the case of VO procedure. We hypothesize that a higher amount of TFMSA in the Cu procedure should determine the rupture of a Cu-O bond by means of protonation of the ligand phenate group and a consequent creation of a free coordination position. Considering the molar ratio copper complex/TFMSA to be 3:1, we can argue that on the average less than one free coordination position per copper complex is created in this way. This free coordination is presumably occupied by the triflate anion which is known to increase the Lewis acidity of copper complexes. This effect can in turn promote the interaction between Cu and the sulfur atom of thiophene monomers; experimental evidence of this kind of interaction



FIGURE 4 Synthesis scheme of polythiophenes using Cu(II) complexes.

is reported in several literature articles.^{34,35} The oxidation of the thiophene monomers is then operated by Cu(II), reducing itself to Cu(I). The molecular oxygen could oxidize Cu(I) again to Cu(II), with production of water in acidic environment, and thus closing the catalytic cycle. Following the model proposed for the VO procedure, Cu(II) oxidizes preferentially the 2-position of the thiophene ring, on which a higher electron density is expected because of the o-substitution with 4-octiloxyphenyl group. Two tiophene radical cations formed in this way can dimerize in two different configurations, head to head (HH) or head to tail (HT). According to ref. 27, HT is a more energetically stable configuration and it is preferentially formed; moreover, HT dimers have a higher reactivity than HH dimers toward further oxidation (HT has a free 2-type position for oxidation, whereas HH features only 5-type positions available for oxidation). In VO procedure, HH dimers remain unreacted in the first part of the polymerization and start reacting when the concentration of monomers and HT dimers or oligomers becomes sufficiently low, causing a decrease of the overall regioregularity. In the case of Cu procedure, it is reasonable to expect that a higher amount of the less-stable HH dimer is formed owing to the higher reaction temperature. Nevertheless, the regioregularity of the obtained polymers remains very high even for very long reaction times; conversely, the yield is lower in the Cu procedure as compared to the VO procedure. We propose that HH dimers remain unreacted in the reaction media owing to both the not extremely high activity of the Cu(II) complexes and steric reasons: HH dimers are more distorted as compared to HT dimers²⁷ and could less easily approach the sterically hindered Cu(II) center. Interestingly, the polymerization in the Cu procedure conditions with $Cu(acac)_2$ as catalyst affords a polymer with very poor regioregularity. This evidence corroborates the hypothesis that the steric hindrance of these new copper catalysts is important for the final regioregularity of the polymer.

UV-Visible Analysis

To qualitatively assess the regionegularity of PT8 prepared by the Cu procedure, we performed a careful UV-Visible analysis on thin films obtained by spin-coating from hot 1,2-dichlorobenzene solutions. The films were annealed for 15 min at 150 °C in air. UV-Visible spectra showed no evident changes after annealing being already well structured before this process. All spectra feature absorption in the UV region below 300 nm, characteristic of the π - π * transition of phenyl substituents. It is known that UV-Visible spectra can be assumed as qualitatively diagnostic of the regioregularity of poly(3-substituted)thiophenes. McCullough et al.³⁶ reported that a redshift of λ_{max} could be found in regionegular poly(3-alkylthiophene)s (HT sequences) in comparison with regioirregular poly(3alkylthiophene)s, both in solution and in film. The redshift is particularly significant in films: spectra of HT sequences show λ_{max} values of 550–560 nm, whereas for regioirregular poly(3-alkylthiophene)s λ_{max} is about 450 nm. Moreover, a vibronic structure appears in spectra of films of HT sequences with less intense secondary peaks at 590-600 and 665-700 nm. UV-Visible spectra of PT8 synthesized by Cu(II) catalysts

are shown in Figure 5. All the spectra show a stronger redshift of λ_{max} and a more definite vibronic structure than the polymer prepared by the VO procedure. For these reasons, a higher regioregularity can be assumed as compared to the value reported for PT8-VO (ca. 90%). The spectrum of PT8-Cu1 is particularly impressive being characterized by a maximum absorption peak at 618 nm, with a shoulder at 678 nm. From a qualitatively point of view, the spectra of PT8-Cu1 and PT8-Cu4 appeared more defined, whereas the spectra of PT8-Cu2 and PT8-Cu3 featured some absorption at ~450 nm [Fig. 5(bottom)], typical of regioirregular sequences.

The essential data of the synthesized polymers are summarized in Table 2.

¹H-NMR Analysis

¹H NMR analysis was performed on the synthesized polymers to evaluate their regioregularity by the quantitative



FIGURE 5 UV–Visible spectra of polymer films. (a) Comparison between spectra of PT8-Cu1 and PT8-VO (top); (b) comparison between spectra of PT8 synthesized with all the Cu(II)-based catalysts (bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polymer	<i>M</i> _n	M _w	PDI ^a	$T_{d} (^{\circ}C)^{b}$	λ ₁ (nm)	λ ₂ (nm)	λ ₃ (nm)
PT8-Cu1	13,900	32,200	2.3	345	578	618	678
PT8-Cu2	12,100	24,300	2.0	347	570	608	669
PT8-Cu3	12,200	24,100	2.0	344	570	608	669
PT8-Cu4	12,400	25,400	2.1	334	562	600	666
PT8-VO	15,500	29,450	1.9	300	561	601	666

TABLE 2 Chemical and Physical Properties of the Regioregular Polymers

^a PDI = M_w/M_n .

 $^{\rm b}$ Decomposition temperature taken as the temperature corresponding to a 5 % weight loss in the thermogravimetric run (20 $^\circ C/min,$ air atmosphere).

determination of the HT content. Particularly, the proton on the position 4 of the thiophene ring was investigated because it is characterized by slightly different resonance values,³⁶ depending on the configurational triad it belongs. By performing a decoupling procedure during spectrum acquisition (Fig. 6), the partial overlapping of an aromatic signal (a doublet, without decoupling) with the thiophenic singlet under investigation was avoided. Subsequently, a deconvolution procedure was applied on the thiophenic signal to separate the singlets generated by the four different configurational triads. As it is possible to verify in Figure 7, the peak of PT8-Cu1 is strongly symmetric and the minor lateral signals seem almost totally absent, as opposed to PT8-VO.

The area of each peak obtained by the deconvolution process is proportional to the fraction of a corresponding triad. These values were used to calculate the regioregularity of each polymer, defined as the percentage of HT dyads, according to a method reported in the literature.³⁷ Here, the four triads HT–HT, HT–HH, TT–HT, and TT–HH (and their fractional area) were, respectively, associated to the four peaks of thiophene proton, starting from the more intense peak (corresponding to the HT–HT triad). The fractions of



FIGURE 6 ¹H NMR spectrum of PT8-Cu1 in 1,1,2-2-tetrachloroethane-d₂.

dyads and triads are related by equations containing three independent parameters α , β , and *C*. Their values can be found by solving the system of equations for triads and used



FIGURE 7 Deconvolution process applied to thiophene singlets of PT8-Cu1 and PT8-VO. Circles: ¹H-NMR spectral data; solid line: sum of deconvolution peaks; dashed line: Lorentzian peaks from spectral deconvolution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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TABLE 3 The HT Values of PT8 Synthesized Through Cu(II)

 Complexes

PT8-Cu1 PT8- (HT %) (HT 9	Cu2 PT8-C %) (HT %	Cu3 PT8-Cu4 %) (HT %)
99.1 96.2	97.2	99.0

to calculate the fraction of HT (Supporting Information material). The results (Table 3) show a very high regioregularity for all the polymers synthesized with the Cu(II) complexes, whose HT content ranges from 96% (PT8-Cu2) to 99% (PT8-Cu1 and PT8-Cu4). These values are significantly higher than those obtained by the VO procedure and comparable to the values reached through the classical McCullough and Rieke methods for the synthesis of 3-substituted polythiophenes. Although this novel synthetic procedure was successfully applied only to poly[3-(alkoxyphneyl)thiophene]s, it results much more inexpensive and straightforward than the cited standard methods as the step of monomer dibromination is avoided, the catalysts are cheaper, easily synthesized, and not air sensitive, so that a protected environment is not required. On the basis of these results, some considerations can be derived regarding the differences between the four catalysts. The different solubilities induced by the functionalization with alkoxyphenyl moieties and/or alkyl chains do not seem to have a significant effect being all the complexes completely dissolved in the reaction medium before the monomer addition. By comparing the optimized experimental conditions, it can be evinced that the steric hindrance of bulky substituents plays the major role in the regiospecific activity. Although Cu1, Cu2, and Cu3 require the same reaction time to give a good balance between yield and regioregularity, Cu1 results the more regiospecific owing to the effect of bulky substituents. Owing to the further encumbrance produced by additional alkyl chains, Cu4 results as highly regiospecific as Cu1 although quite longer reaction times are required to reach reasonable yields.

Thermal Analysis

TGA analysis was performed to evaluate the thermal stability of the four synthesized polymers. The data summarized in Table 2 highlight their thermal stability also in the presence of air. It is important to observe that the decomposition temperatures of PT8 synthesized through Cu(II) complexes range from 334 to 347 °C, indicating their thermal stability to be sensibly higher than PT8-VO, whose decomposition starts at about 300 °C.

X-ray Diffraction Analysis

X-ray powder diffraction spectra of the four PT8 polymers realized through Cu(II) complexes were recorded both in bulk and in film phase. The four different polymers showed the same behavior in this analysis (Fig. 8) and hence we reported a comparison between the XRD spectra of PT8-Cu3 in bulk and in film, as representative of all the polymers under investigation. In bulk, the XRD spectra of the PT8



FIGURE 8 X-ray powder diffraction patterns of PT8-Cu3 in bulk and in film shape.

polymers show a strong peak at low 2θ ($\sim 3^{\circ}$, corresponding to the spacing along the side chains) and a broad amorphous scattering feature, centered at $2\theta = 20^{\circ}$. Two peaks emerge over this broad reflection, at $2\theta = 19$ and 24° . According to a diffraction literature study performed on poly-3-(4-octylphenyl)thiophene,³⁸ a polymer structurally similar to the one investigated by us, the first peak can be assigned to the π - π stacking distance, that for all the polymers is around 4.8 Å (Table 4). This distance is higher than the stacking distance characterizing poly-3-alkylthiophenes (${\sim}3.8$ Å) 39 and is consistent with an arrangement of phenyl rings out of coplanarity with thiophene rings. The second peak is instead related to a repetition along the polymer chain (along the c-axis, assuming a monoclinic cell as in the case of poly-3-alkylthiophene). Polymeric films were obtained via drop-casting on glass substrates from a solution of o-dichlorobenzene and hence annealed at 150 °C in nitrogen atmosphere. In the film XRD spectra, only the low-angle reflection neatly appears (along with higher order reflection of this spacing), whereas there is a very strong decrease of the diffraction signals in the middle part of the spectra. The decrease of the intensity of the amorphous scattering feature is owing to a higher structuration of the polymers in film phase (film are made by a very slow casting procedure from an o-dichlorobenzene solution, whereas bulk polymers are obtained by a

TABLE 4 Observed Spacings from X-Ray Diffraction Patterns of the Synthesized Polymers

	<i>d</i> ₁ (Å) ^a	<i>d</i> ₁ (Å) ^b	<i>d</i> ₂ (Å) ^b	<i>d</i> ₃ (Å) ^b
PT8-Cu1	27.9	29.7	4.74	3.76
PT8-Cu2	28.3	28.1	4,75	3.74
PT8-Cu3	29.2	28.2	4,79	3,71
PT8-Cu4	29.2	28.1	4,75	3,74

^a In film phase.

^b In bulk.



brusque precipitation in methanol). Consistently with a better structuration, in film phase the reflection at low angle becomes sharper. For what concerns the absence of the diffraction peaks at 19 and 24° , assigned to the stacking distance and to a repetition distance along the polymer chain, we assume it is owing to a preferential orientation of the polymer chains with the plane of thiophene rings normal to the substrate, as typically observed for polythiophene derivatives spin-cast films.^{40,41} As a consequence of this arrangement, both the spacings are therefore barely visible or not visible at all in a XRD experiment performed, as in our case, in a reflection geometry.

Electrical Characterization

The electrical response of the fabricated PT8 transistors was investigated both in air and in vacuum by measuring the output and the transfer-curves. In particular, the transfer-curves were recorded in the saturation regime by applying a gate-source voltage $V_{\rm GS} = -50$ V and scanning the drain-source voltage $V_{\rm DS}$ from 40 to -100 V and backward. Figure 9 shows the electrical response of a PT8-Cu1 device. Very similar performances in terms of maximum current, mobility, and threshold voltage values were registered, however, for



FIGURE 9 (a) Output and (b) transfer curves in the saturation regime measured in air (filled symbols) and vacuum (open symbols) for a PT8 transistor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the PT8-Cu4 transistors. As shown in Figure 9, as the drainsource current (I_{DS}) in both output and transfer-curves increases when negative V_{GS} voltages are applied (charge accumulation phenomenon), the experimental data confirm the p-type behavior (hole-transporting) of PT8 films. The output curves exhibit a quite good linear behavior in the low $V_{\rm DS}$ region, suggesting a negligible contribution related to the contact resistance effect at the drain-source electrodes. Moreover, the presence of the saturation regions is well defined at each applied V_{GS} . Significantly, the transfer-curves highlight that the $I_{\rm DS}$ current values in air are always higher than those recorded in vacuum. In particular (inset, Fig. 9), in the off-region (for positive V_{GS} values), the I_{DS} current in air is enhanced by a factor close to 3. Consequently, on-off ratio $(I_{\rm on}/I_{\rm off})$ in air (~2 \times 10²) results to be slightly reduced in comparison with vacuum $(I_{on}/I_{off} = 3 \times 10^2)$. In coherent manner, the threshold voltage shifts toward more negative values in vacuum. For the transfer curves in Figure 9(b), specifically, $V_{\rm th}$ was estimated to be -33 in air and -36 V in vacuum. All these findings prompt for the presence of a charge-doping effect in the analyzed compounds which, owing to the found reversible character when the samples are moved from air to vacuum, cannot be associated to the residual presence of chemical impurities in the analyzed films but rather to the action of ambient agents and in particular to oxygen. This effect is similar to that reported and analyzed for other compounds belonging to the polythiophene family⁴² and should be, at least partially, attenuated by preparing the material solutions in an inert atmosphere.⁴³ Very interestingly, however, it is also to outline that the effect of the air was found to be beneficial in terms of the charge-carrier mobility values (μ). Indeed, the maximum μ mobility estimated in air (4 \times 10 $^{-4} \text{cm}^2$ V $^{-1}$ s $^{-1}$) was found to be almost the double of the corresponding value measured in vacuum.

In conclusion of this section, it should be remembered that FETs were previously fabricated also by using PT8-V0 polymers. In that case, Strontium Titanate (S_rTiO_3) gate dielectrics were employed and the maximum mobility measured was about two orders of magnitude lower than the values estimated in this study.²⁸ This significant mobility enhancement is clearly to be ascribed to the higher regioregularity of HT content obtained with the new synthetic route described here. In any case, a further improvement of the PT8 transistor electrical response, both in terms of mobility values and reduction of the hysteresis effects observed in the transfer-curves, will be pursued in future by optimizing the film-deposition procedure and/or using alternative hydrophobic treatments of the SiO₂ surface.

CONCLUSIONS

In this article, we report on a new synthetic procedure for the preparation of regioregular poly[3-(4-alkoxyphenyl)thiophene]s based on the oxidative coupling catalyzed by Cu (II) complexes. Although keeping the simplicity and the cheapness of oxidative polymerization of thiophene monomers already reported in the literature, the novel procedure afforded polymers with extremely high regioregularity, up to 99% of HT content. This approach could therefore represent an interesting alternative to the known crosscoupling procedures for the synthesis of highly regioregular 3-substituted polythiophenes (McCullough or Rieke methods) as no monomer functionalization, no protected environment are required and cheaper, easily synthesized catalysts can be used. Electrical measurements on OFET devices with bottom-gate bottom-contact configuration, with SiO₂ gate dielectric functionalized by HMDS coverage, show a well-defined p-type field-effect response, with a maximum mobility value in air of 4×10^{-4} cm² V⁻¹ s⁻¹. In conclusion, this innovative method makes available polymers with several interesting properties: (i) high ambient stability, with PT8 FETs exhibiting larger mobility values in air than in vacuum; (ii) good processability, as spin-coated transistors have been fabricated in simple, inexpensive, and fast way; (iii) remarkable and reproducible electrical properties, confirmed by field-measurements displaying well-defined p-type behavior and mobility values larger than 10^{-4} cm² V⁻¹ s⁻¹ also in bottom-contact bottom-gate transistors.

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