

Palladium-catalyzed synthesis of oligo(alkylthiophenes)

Jwanro Hassan, Emmanuelle Schulz, Christel Gozzi, Marc Lemaire*

*Laboratoire de Catalyse et Synthèse Organique, UMR 5622, UCBL, CPE, 43 Bd du 11 Novembre 1918,
69622 Villeurbanne Cedex, France*

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Abstract

A new palladium-catalyzed polymerization of 2-bromo-3-octylthiophene is described giving rise to oligo(3-octylthiophenes) with good yields. A study was carried out in order to optimize the polymer regioregularity (reaching 90%) and to increase the molecular weight (up to dodecamers). A mechanism is proposed with a coordination between palladium and sulfur, in a modified Heck mechanism.

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1. Introduction

The search and development for new ordered materials is an important field of interest for synthetic chemists. Poly(3-alkylthiophenes) have been particularly studied, as the most significant class of conjugated polymers [1]. They are thermodynamically stable and have been used as materials for many applications, such as light-emitting devices [2,3] and thin film transistors [4]. The physical properties depend on the nature and the regioregularity of the polymers. Polythiophenes were synthesized either by oxidative electrochemical or chemical polymerization or by organometallic couplings [5]. Sugimoto et al. [6] have developed a chemical polymerization implying the monomer oxidation by iron trichloride, leading to high-molecular-weight polymers. Nevertheless, this method requires an over stoichiometric amount of iron trichloride and generates a large quantity of

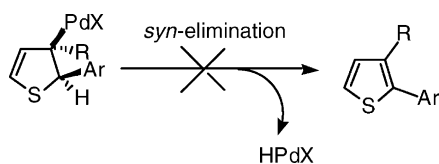
effluents. McCullough et al. [7] have reported the synthesis of regioregular polythiophenes.

By using a Kumada–Corriu coupling, the homopolymerization of 2-bromo-5-(bromomagnesio)-3-alkylthiophenes was carried out in the presence of a catalytic amount of Ni(II). Rieke and co-workers [8] have also used a catalytic amount of Ni(II) in the polymerization of 2-bromo-3-alkyl-5-(iodozincio)-thiophenes. Iraqi and Barker [9] performed a Stille coupling for the polymerization of 2-iodo-3-alkyl-5-tri-*n*-butylstannyl-thiophenes. More recently, this reaction has been optimized by Lère-porte et al. [10], higher-molecular-weight polymers were obtained. Bidan and Guillerez [11] have synthesized regioregular polythiophenes using the Suzuki coupling for the polymerization of 2-iodo-3-alkyl-5-thienyl-boronic esters. Regioregular and high-molecular-weight polymers were thus obtained by the above-described coupling methods. The main drawbacks of these syntheses are the use of organometallic reagents which are often dangerous and/or toxic, and the requirement of monomers with high purity to allow the preparation of regular polymers.

* Corresponding author. Tel.: +33-4-7243-1407;

fax: +33-4-7243-1408.

E-mail address: marc.lemaire@univ-lyon1.fr (M. Lemaire).

Fig. 1. *Syn*-elimination.

We have successfully performed the direct arylation of thiophenes in position 2 or 5, using an Heck-type reaction [12–14] with a mixture of $\text{Pd}(\text{OAc})_2$, $n\text{-Bu}_4\text{NBr}$ and a base as catalytic system. We have then applied this method to the polymerization of 2-iodo-3-alkylthiophenes [15–17]. The obtained polymers are regioregular and possess an iodide at the end chain. The mechanism of this palladium-catalyzed coupling reaction is still not well defined. $\text{Pd}(\text{OAc})_2$ is indeed known for its strong oxidizing character [18] and it has thus to be reduced in situ to the active complex $\text{Pd}(0)$. The first oxidative addition of the aryl halide leads to a complex of $\text{Pd}(\text{II})$. Taking into account the aromatic character of the substrate and the *cis* addition between the palladium and the aryl group, a classical subsequent β -elimination is here not achievable to deliver an arylated product Fig. 1.

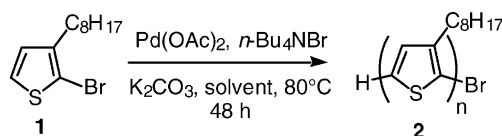


Fig. 3. Heck-type polymerization of 2-bromo-3-octylthiophene.

We propose the formation of the aryl–aryl bond to arise from a coordination of the $\text{ArPd}(\text{II})\text{X}$ complex with the sulfur atom, followed by a migration of the aryl group to the thiophene. The aromaticity of the system is re-established by an electronic rearrangement in the cycle and the elimination of HPdX , Fig. 2.

The regeneration of $\text{Pd}(0)$ can be performed by the base and the quaternary ammonium salt, as in the case of the Heck reaction [19]. Although iododerivatives give rise to interesting results in terms of regioregularity, the access of these monomers is costly and dangerous. 2-Iodoalkylthiophenes are indeed obtained in good yield and satisfactory purity by using mercury derivatives of thiophene.

We present here the Heck-type polymerization of 2-bromo-3-octylthiophene **1** using $\text{Pd}(\text{OAc})_2$ as the catalyst. Bromo-derivatives could be easily obtained in good yield and purity by using bromine as bromi-

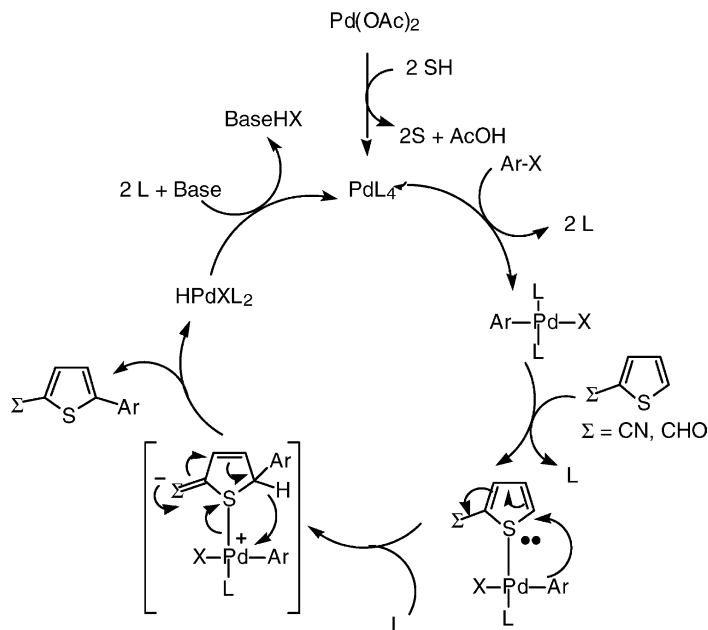


Fig. 2. Postulated mechanism for the arylation of 2-substituted thiophenes by iodobenzene.

nating agent. The reaction conditions were modified in order to improve the polymer regioregularity and the molecular-weight Fig. 3.

2. Characterization of the polymers

The regioregularity of the obtained polymers could be determined by NMR study. The NMR

^1H spectrum of the polymer synthesized by our method was compared to a commercial regioregular oligo(octylthiophene) (Aldrich, $M_n = 54,000$, synthesized according to the Rieke method [8]). The resonance of the isolated aromatic proton in the 4-position of thiophene has been undoubtedly assigned for the four possible triad sequences that arise from the different alignment of the monomer. The singlet at δ : 6.98 ppm is assigned to the 4-position of the central

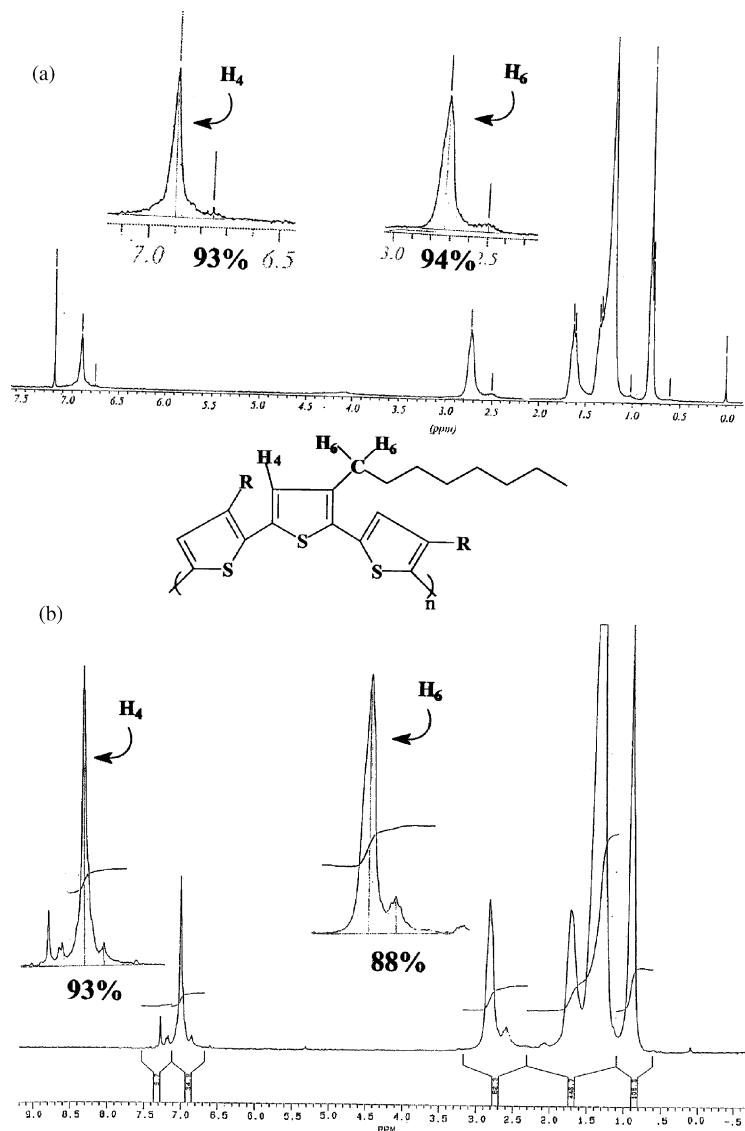


Fig. 4. ^1H NMR spectrum of poly(3-octylthiophenes): (a) commercial polymer; (b) polymer synthesized by our method.

thiophene ring of a HT–HT configurational triad of 3-octylthiophene rings. The other small signals in the aromatic region can, in part, be assigned to irregular coupled thiophenes or to aromatic protons at the chain ends Fig. 4.

The regioregularity of the polymers is both evaluated by the ratio of the integrals of these signals, and of the peaks around 2.8 and 2.6 ppm, representing the allylic methylene groups [20,21]. These analyses prove that our method leads to polymers with a regioregularity of approximately 90% (Fig. 4). Absorption spectra on these polymers in chloroform have been measured and show maximum absorptions at $\lambda_{\text{max}} = 438$ nm. As comparison, 449 nm is the value reported for higher molecular mass polymers due to extent of electronic delocalisation [22]. The MALDI-TOF analyses furthermore indicate that the precipitate is a mixture of the expected polymer and debrominated and dibrominated compounds. This result can be explained by Ullmann-type couplings, by reduction of the C–Br bond or by oxidative coupling. In fact, during our palladium-catalyzed polymerization, several secondary pathways can compete with the main reaction. Some of them lead to a lengthening of the chain, but in an irregular way.

3. Solvent effect

Different solvents, such as DMF, THF, toluene and *N*-methyl-2-pyrrolidinone were tested. DMF and THF appeared to be the best solvents for the palladium-catalyzed polymerization (entries 5 and 6, Table 1) as far as regioregularity, chain length and yield are concerned.

Several parameters should be taken into account to explain these results but the solubility of the formed polymer in the different reaction medium appeared obviously to be primordial. We assume furthermore

Table 1
Solvent effect

Entry	Solvent	UV (DP) (nm)	Regioregularity NMR (%)	DP MALDI-TOF	Yield (%)
1	Toluene	427 (9)	78	12	67
2	Dioxane	405 (6)	40	–	82
3	1-Methyl-2-pyrrolidinone	429 (9–10)	70	–	65
4	Chloroform	412 (7)	70	–	61
5	THF	440 (12)	88	8	75
6	DMF	438 (11–12)	90	12	82

Table 2
Influence of the temperature

Entry	Temperature (°C)	Regioregularity NMR (%)	UV (DP) (nm)	Yield (%)
1	80	90	429 (9–10)	78
2	150	50	407 (6)	63

that the reductive properties of the solvent are involved in the observed regioregularity.

4. Influence of the temperature

The Heck-type polymerization was carried out at different temperatures in DMF (entry 1, Table 2) and dimethylacetamide (DMA) (entry 2, Table 2) as solvents. A decrease of maximum absorption (λ_{max}) was observed at higher temperatures.

We propose that the increase of the temperature favors a number of side-reactions, such as the carbon–halogen bond reduction, the Ullmann reaction and the oxidative coupling. These side-reactions limit both the polymerization and decrease the polymer regioregularity.

5. Influence of the phase-transfer agent nature

The quaternary ammonium salt plays a role not only as phase transfer agent but probably also as stabilizer of the active palladium species [19], especially because the use of triphenylphosphine was avoided. Among a number of quaternary ammonium salts tested, tetrabutylammonium bromide (entry 1, Table 3) led to more regioregular polymers than other salts (entries 2 and 3). This particular behavior is not easily explainable, but hydrophobic and steric hindrance effects can be invoked.

Table 3
Influence of the phase-transfer agent nature

Entry	Ammonium salt	Regioregularity NMR (%)	UV (DP) (nm)	Yield (%)
1	<i>n</i> -Bu ₄ NBr	90	438 (11–12)	82
2	(C ₂ H ₅) ₄ NBr	67	417 (7)	87
3	(C ₂ H ₅) ₃ (PhCH ₂)NBr	72	418 (7)	80

Table 4
Influence of the base

Entry	Base	Regioregularity NMR (%)	UV (nm)	Yield (%)
1	K ₂ CO ₃	90	438 (11–12)	82
2	NaOAc	10	347 (2–3)	52
3	KHCO ₃	65	415 (7)	74

6. Influence of the base

We noticed for the direct arylation of thiophene [12–14] that potassium carbonate was the most efficient and selective base for this Heck-type reaction. Indeed, the presence of a base is necessary to generate the zerovalent palladium catalyst. A similar behavior was observed for the polymerization reaction since potassium carbonate gave a better result than NaOAc and KHCO₃ (entries 2 and 3, Table 4). With NaOAc as the base, only dimers and trimers were obtained (entry 2). Indeed, probably due to the more difficult elimination step, a stronger base is required in order to obtain fast and efficient polymerization.

7. Polymer debromination

The MALDI-TOF spectroscopy indicates that polymers obtained by Heck-type reaction are a mixture of brominated and debrominated polymers. Therefore, the polydispersity appears to be relatively broad. In order to obtain polymers with a lower polydispersity and because many potential applications do not require the presence of halogen atoms, we studied the debromination reaction using zinc/AcOH in a mixture of THF and water at 110 °C [23]. Oligo(3-octylthiophene) **3a**, prepared in DMF as solvent, (entry 1, Table 5) have a polydispersity of 1.4. After the debromination, the polydispersity was improved to 1.2. The PDI

Table 5
Polymers debromination

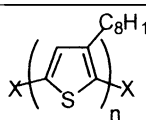
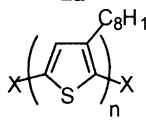
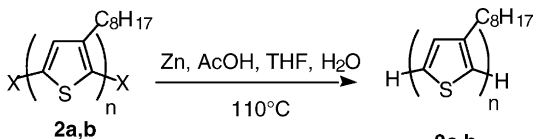
	Regioregularity						
	NMR (%)	Yield (%)	<i>M</i> _n	<i>M</i> _w	IP	DP	
1		81 3a,b	81 3a,b	2185	2637	1.2	12
	X = H, Br n = 12 2a						
2		66 3a,b	86 3a,b	2139	2387	1.2	12
	X = H, Br n = 12 2b						
							

Fig. 5. Debromination reaction.

decreased from 1.5 to 1.2 for polymer **3b** prepared in THF (entry 2, Table 5). The elemental analyses proved furthermore that bromine is present only as traces Fig. 5.

8. Conclusion

A Heck-type polymerization method enabled us to synthesize relatively regioregular oligomers with good yields. The side-reactions are the limiting factor for the polymerization. However, this method presents numerous advantages compared to reported methods,

since catalytic amount of palladium is used without additional organometallic products. We assume that this method is one of the rare methods which can be economically used at a bulk level. We have proved that the polymerization can be controlled by various parameters, such as the nature of the base and the nature of the phase transfer agent. The role of the quaternary ammonium salt is still not clearly defined. We have proposed a mechanism for the Heck-type polymerization based on the coordination between the sulfur atom and the ArPd(II)X complex. Work is in progress to find a better catalytic system in order to obtain high-molecular-weight polymers.

9. Experimental section

9.1. Equipment

The NMR spectra were run in chloroform on a Bruker AC 200 MHz. The polymer absorption spectra were obtained in chloroform on a HP 8453 UV-Vis spectroscopy. MALDI-TOF spectra were obtained on a Perkin-Elmer—Voyager-DE STR, laser N_2 : 337 nm, matrix: DHB (2,5-dihydroxybenzoic acid).

9.2. General procedure for Heck-type polymerization

To a solution of 2-bromo-3-octyl-thiophene (5 mmol in 6 ml DMF) was added under nitrogen potassium carbonate (12.5 mmol) and tetrabutylammonium bromide (5 mmol). The mixture was heated to 80 °C under stirring and palladium acetate (0.25 mmol) was added. The mixture was stirred at 80 °C for 48 h. The precipitate was then filtered out, washed with water and methanol, and finally dissolved in chloroform. This solution was washed again with water. The organic layer was dried over MgSO_4 . Solvent was removed by rotatory evaporation to give a deep red residue.

9.3. Characterization of the polymers

- 2-Bromo-3-octylthiophene (**2**): Prepared according to [7]; yield: 85%; b.p.: 91 °C (3×10^{-2} bar); ^1H NMR (200 MHz, CDCl_3) δ : (ppm): 7.36 (d, 1H5,

$J = 5.5$ Hz); 6.73 (d, 1H4, $J = 5.5$ Hz); 2.53 (t, 2H6, $J = 4$ Hz); 1.4–1.2 (m, 12H7–12); 0.87 (t, 3H13, $J = 6.4$ Hz); ^{13}C (50 MHz, CDCl_3) δ : (ppm): 141 (C3); 130.9 (C4); 128.7 (C5), 109.3 (C2); 32.5 (C11); 32.4 (C7); 30.3 (C9); 30.0 (C10); 29.9 (C8); 23.2 (C6); 23.1 (C12); 14.0 (C13). MS m/z (%): 276 (35) [$M + 2$]; 274 (20) [M^+]; 238 (22); 236 (85); 234 (100); 202 (8); 201 (45); 199 (75); 178 (18); 177 (80); 175 (75); 164 (45); 155 (75).

- Polymer prepared in DMF **2a**: Elemental analysis. Calculated: C: 72.7; H: 9.1; S: 16.1; Br: 2; Exp.: C: 71.9; H: 9.1; S: 13.38; Br: 1.36 MALDI-TOF: M_n : 2327; M_w : 2629; PDI: 1.14; DP: 12.
- Polymer prepared in THF **2b**: Elemental analysis. Calculated: C: 72; H: 9; S: 16; Br: 2.8; Exp.: C: 71.32; H: 9.31; S: 12.48; Br: 0.74 MALDI-TOF: M_n : 1525; M_w : 2314; PDI: 1.51; DP: 8.
- Debrominated polymer **3**: Prepared according to [20]. ^1H (200 MHz, CDCl_3) δ : (ppm): 7.2–6.9 (m, nH5, nH4); 2.9–2.7 (t, nH6, $J = 4$ Hz); 1.8–1.1 (m, nH7–12); 0.9 (t, nH13, $J = 6.4$ Hz).
- Debrominated polymer **3a** (entry 1, Table 5): Elemental analysis. Calculated: C: 74.3; H: 9.2; S: 16.5; Br: 0; Exp.: C: 76.96; H: 10.88; S: 11.88; Br: 0.75 MALDI-TOF: M_n : 2185; M_w : 2637; PDI: 1.20; DP: 12.
- Debrominated polymer **3b** (entry 2, Table 5): Elemental analysis. Calculated: C: 74.2; H: 9.4; S: 16.5; Br: 0; Exp.: C: 69.94; H: 8.92; S: 13.22; Br: 1.81 MALDI-TOF: M_n : 2139; M_w : 2387; PI: 1.11; DP: 12.

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