Advances in synthetic methods for the preparation of poly(3-hexylthiophene) (P3HT)

Published version:

DOI:10.2174/1570178615666180322150512

Advances in Synthetic Methos for the Preparation of Poyl(3-hexylthiophene) (P3HT)

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Abstract: Synthetic methods for the poly(3-hexylthiophene) polymers (P3HT) preparation were reviewed. Different protocols were reported such as electropolymerization, oxidative method (mainly by $FeCl_3$), Ni-catalyzed methods (McCullough, Rieke, GRIM), Pd- catalyzed methods such as Suzuki and Stille coupling and, the more recent, Direct Arylation Polymerization (DArP). The present reviews focuses on the synthetic protocols and their relationship to the final key-structural polymer characteristic like regioregularity and molecular weight control which are of importance in the final properties and application of P3HT. An extended literature review was performed covering also very recent advancements. The use of NHC palladium of Nickel catalysts, disclosed the door to the preparation of "quasi" living polymers for most of the Ni and Pd catalyzed reactions, enabling a fine tuning of both regioregularity and molecular weight.

Keywords: P3HT, Conductive polymers, Organic Synthesis, Organic Materials, Nickel catalyzed reactions, Palladium catalyzed reactions.

Outline

1. INTRODUCTION

Highly conjugated polymers have shown very interesting electrical properties since the first report in 1977.[1]

Different from the classical insulating polymers, they have been characterized by the ability to conduct electricity and then were often referred to as conductive polymers. Their impact on technology was enormous (e.g in Organic Light-Emitting Diodes, OLED and Organic PhotoVoltaics, OPV) [2] and, still, they play a great role in hot research topics for both fundamental and industrial purposes.[3] Just to mention a few applications, Field Effect Transistors (FET and the Organic-based ones, OFET),[4-5] OPV,[6-7] and Perovskite Solar Cells (PSC)[8] used P3HT as a valuable active material which, in most cases, became a reference standard. To celebrate and recognize the discovery of their properties, the 2000 Nobel prize was awarded to the first discoverers: Alan J. Heeger, Alan. G. MacDiarmid and Hideki Shirakawa.[9] Polyacetylene, an insulator polymer, undergoes properties change after exposure to chlorine, bromine or iodine becoming highly conductive. In analogy to the inorganic semiconductors, this modification was called “doping”.[1] several classes of conjugated, conductive polymers were designed and produced over the years (fig. 1). Polythiophene (PT), as obtained from synthesis, showed interesting electrical properties, but was characterized by dramatic low solubility in all solvents already for ten monomer length chain. To overcome this issue, the interest was shifted towards modified thiophene-based polymers such as the poly(3-alkylthiophenes) and, in particular, the poly(3-hexylthiophene) (P3HT). P3HT found broad applicability thanks to the high solubility in several organic solvents, high thermal stability, easy processing ability and doping and reasonable photochemical stability.[10] The electron-rich conjugated ring in thiophene has a lower aromatic stabilization energy than benzene (being a bit closer to a diene), improving the electron mobility along the polymer chain while conferring, however, a pronounced aromatic character to the polymer, which assures the thermal stability. Polypyrroles and polyfurans are characterized by a lower aromaticity when compared to the thiophene analog (aromaticity order: benzene > thiophene > furan > pyrrole), but also by a higher chemical reactivity (i.e. decomposition) of the polymer. The state-of-art of the P3HT synthesis has now highlighted a large number of different tools that can be exploited to tune the preparative work towards different monomers and polymers having the desired characteristics.[3, 10-11]

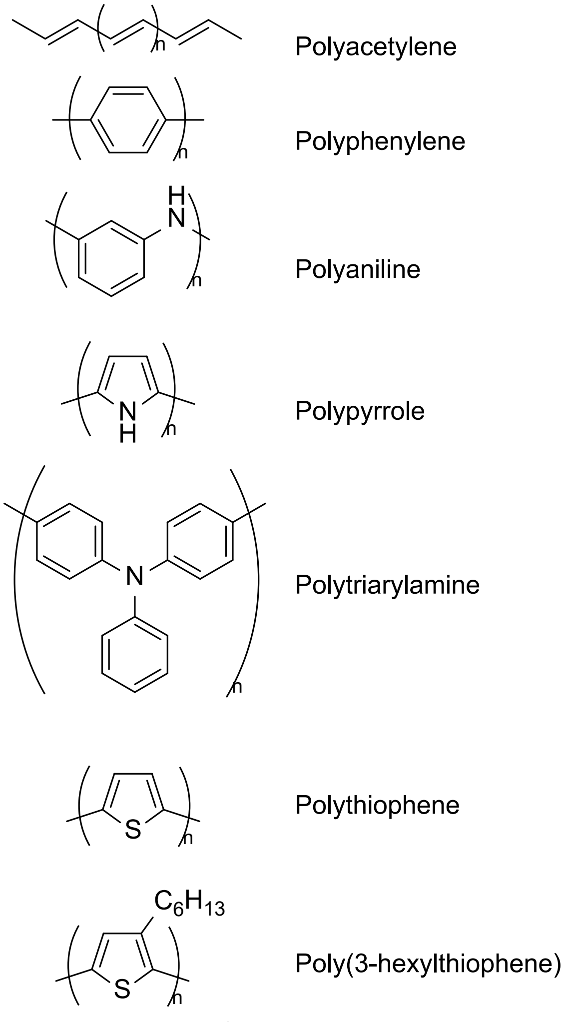


Figure 1. Examples of conductive polymers.

2. P3HT GENERAL ASPECTS

The purpose of this review, far from being an exhaustive account of literature, is to discuss the recent advances in the P3HT synthetic procedures (Fig. 1). The reaction conditions and modifications are discussed in relationship to the structural characterization of the final P3HT polymers, analyzing the pathway for a better control on the polymer molecular weight, polydispersity and regioregularity. In the last years, the P3HT was applied more or less in a ubiquitous way[11-15] and clear relationships among the performances (conductivity, charge mobility, etc.) and the structural features emerged.[15-16] The charge mobility, as an example, was found to be dependent on the molecular weight.[5] Despite the intrinsic nature of the polymer, careful synthetic and purification controls are crucial and compulsory to obtain tailored materials.[17-18] The huge efforts and the high level of the research produced very interesting findings.[14, 19]

2.1. Regioregularity

The P3HT can be produced by different methods (see below) providing polymers with largely different properties related to the polymer structure. The 3-hexylthiophene is asymmetrical and can dimerize providing the head to tail (HT), head to head (HH) and tail to tail (TT) dimers (Fig.2).

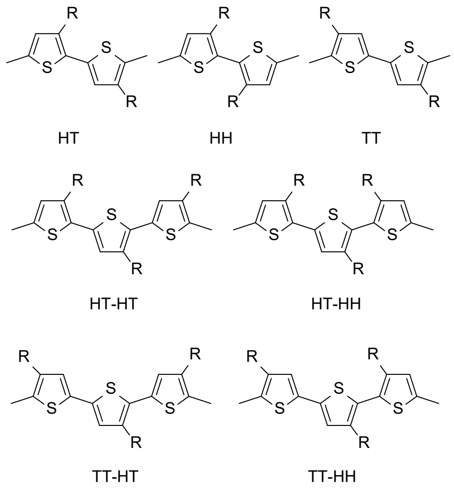


Figure 2. Different linkages for dyads and triads.

The presence, the content and the distribution of the different mode of linkage in the final polymer chain are the most important structural aspect in the definition of the polymer final properties. A full HT polymer is extremely regioregular and can easily pack and form crystalline, well-ordered, domains (Fig. 3). The possible interdigitation of the chains of different polymer molecules was commonly accepted in the past, but it was demonstrated that for P3HT the interdigitation does not occur.[20]

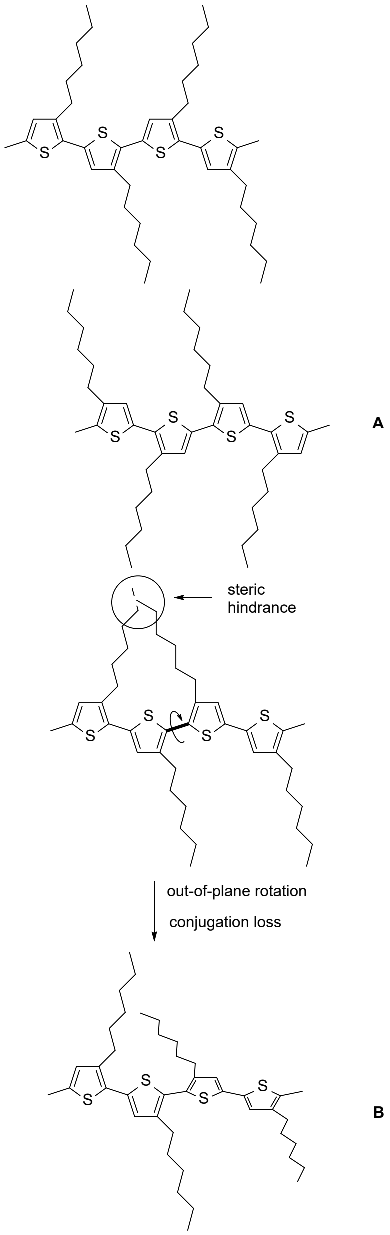
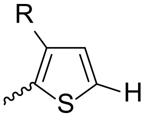
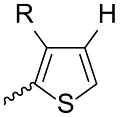
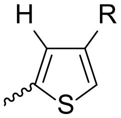
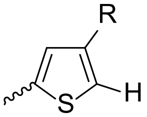
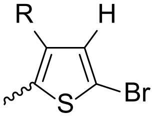
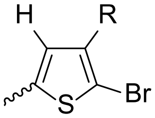


Figure 3. A) Arrangement of regioregular P3HT in solid state; B) Effect of a regioirregularity: the steric hindrance among chains causes two rings to displace each other from the planar arrangement, interrupting the conjugation length.

The low crystallinity of the polymer is determined by the different presence and content of the TT or HH dimeric linkages (i.e. absence of regularity), which is reflected by steric hindrance between hexyl chains when HH linkage is present (Fig.3).

Table 1. NMR assignments of different dyads, triads, terminations and defects in P3HT.[21] Reprinted with permissions from Trznadel et al. [21] Copyright (1992-1994) American Chemical Society.

Proton	D (ppm) [m, J(Hz)	triplet	ref
Diads			
H-T	-	*2.79*	[22-24]
H-H	-	2.56	[22, 25-26]
Triads			
HT-HT	*6.98* s		[22-24, 27]
TT-HT	7.00 s		[23]
HT-HH	7.02 s		[23]
TT-HH	7.05 s		[22-23, 25-26]
Terminal protons			
	7.16 [d, 5.3]		[27-29]
	6.93 [d, 5.3]		[27-29]
	*7.00* [d, 1.2]	*2.7*-2.8	[25, 28-29]
	*6.90* [d, 1.2]	*2.7*-2.8	[25, 27-29]
	6.94 s	2.5-*2.7*	[23]
	*6.82* s	2.5-*2.7*	[23]

Note: the most relevant peaks are shown in *italic*.

The HT linkages percentage contained in the polymer is referred to as regioregularity. A polymer containing only HT bonds, can be defined as strictly regioregular (rrP3HT). HH and TT linkages along the chain decrease the polymer regioregularity degree which is reflected by a proportional modification of the overall polymer properties. Along to the HT, HH and TT dyads, also triads can be considered: HT-HT; HT-HH; TT-HT (Fig. 2). Every synthetic method provides different regioregularity and modification of the same method can improve or reduce the regioregularity,[12, 24, 30-34] obtaining highly crystalline or more amorphous P3HT.

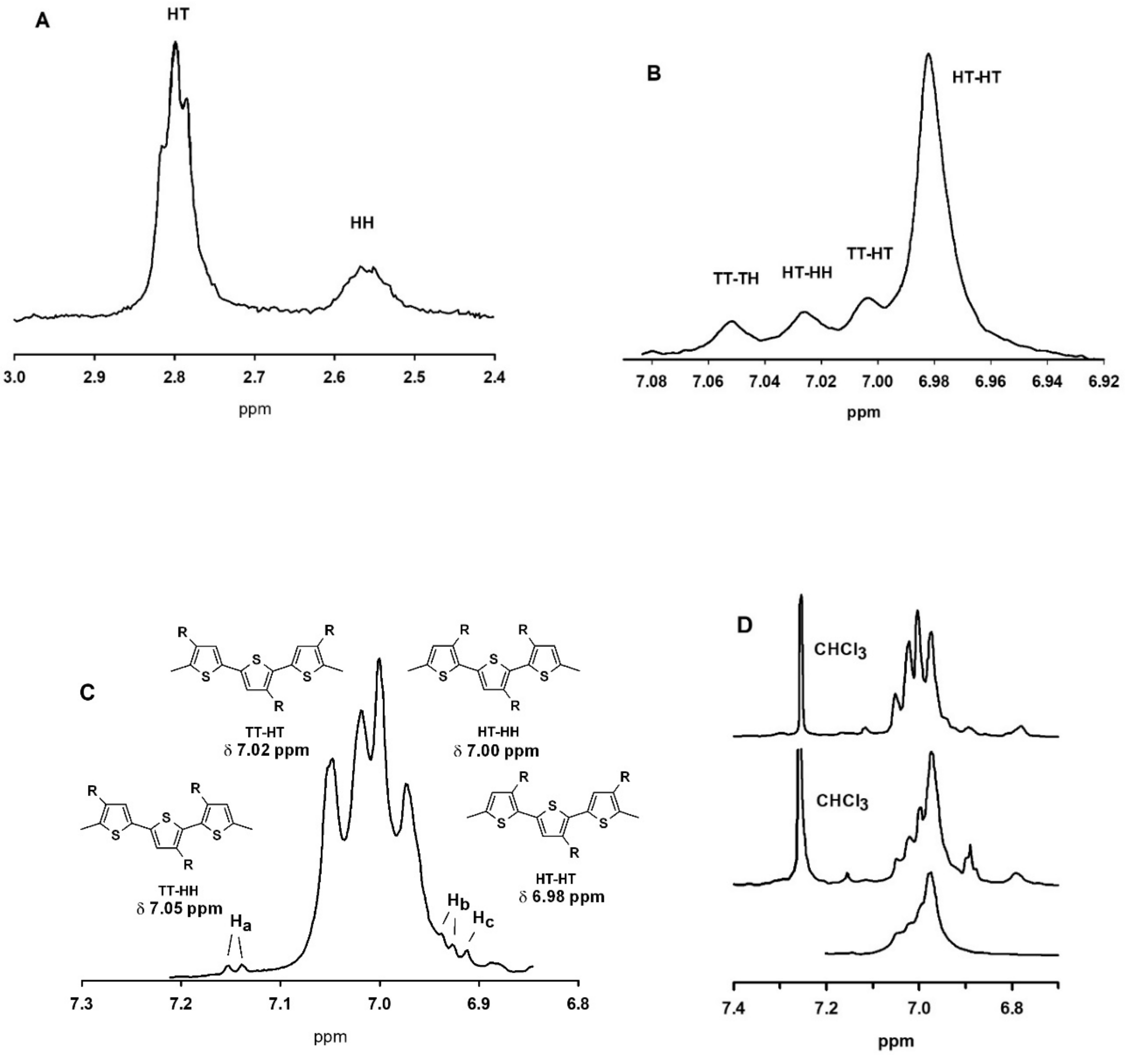


Figure 4. Examples of ^{1}H-NMR spectra useful to determine the P3HT regioregularity (see the text for discussion).[23, 25, 35-36] Adapted with permission from: A) Amou et al.[35] Copyright © 1999 John Wiley & Sons, Inc. Adapted with permission from: B) Barbarella et al.,[23] C) Chen et al.,[36] D) Mao et al.[25]. Copyright (1992-1994) American Chemical Society.

The regioregularity is usually determined by analyzing the 2.9-2.40 ppm ^{1}H-NMR region (Fig. 4, **A**).[21, 30] The first CH_2 linked to the thiophene ring resonates at 2.80 ppm if HT dimers and at 2.54 ppm in the case of HH or TT linkages. (Table 1). The integral ratio of the regular versus the irregular linkage provides percentage of the polymer regioregularity.[24, 37] The analysis of triads assigned the aromatic different peaks, which can be used to compare different samples, at 6.98, 7.00, 7.02, 7.05 to the HT-HT, TT-HT; HT-HH and TT-HH triads, respectively (Fig. 4, **B**, **C** and **D**, and Table 1).[21, 23, 25] The appearance of few smaller peaks indicates polymers of low to moderate molecular weight (<20 kDa), until they are detectable, and refers to terminal hydrogens (Table 1).[21, 38] Finally, ^{1}H-NMR could evidence the branching defects on P3HT showing a CH_2 resonating at 2.4-2.2 ppm range, due to the attack of a 3HT monomer to the β-position of a thiophene along the main chain. [39]

2.2. Molecular Weight

The P3HT polymers show different properties, not only as a function of the regioregularity, but also of the molecular weight. Some properties, like the spectroscopic one, can be related and affected to the increase or decrease of the molecular weight.[7, 21, 40] The UV-Vis absorption is usually red-shifted for larger molecular weights. Fractionation of moderately regioregular P3HT showed that increasing the molecular weight increases the regioregularity, the conductivity and red-shifts the UV-Vis absorption band.[41] Moreover IR investigation found that longer conjugation length is present in P3HT with higher molecular weight. The morphology and crystalline state of regioregular P3HTs is influenced by the molecular weight.[37] Drop casted films are characterized by higher level of organization and crystallinity in comparison to spin casted one. The molecular weight influences also the behavior of P3HT:PCBM (poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester) mixtures in OPV BHJ solar cells.[7] The higher molecular weight reduces consistently the PCBM segregation (separation from the mixture) after annealing, and provides higher photovoltaic performances (PCE). Higher polymer molecular weight was also reported to increase the charge mobility in P3HT:PCBM mixtures.[42] The molecular weight of fractions, obtained from a large batch of a Rieke P3HT polymer, correlated well with their influence on BHJ solar cells parameters.[40] Recently, in perovskite solar cells an increase of P3HT molecular weight increased the PCE, up to 16.2%.[8] Finally, the increase in the molecular weight was also reported to improve the Field Effect charge mobility in three P3HT with different synthetic origin. [5]

2.3. Spectroscopic Properties

UV-Vis spectra, measured in $CHCl_3$ or THF solution, of P3HT are indicative of regioregularity and are usually characterized by a large absorption band, with no fine structure. As a general characterization, moving from a regiorandom, to a moderate and finally to a highly regioregular P3HT the absorbance peak shifts from 428 to 436 to 450 nm respectively and sometimes even above.[11, 27] A 69 and a 80 % regioregular P3HT present the absorbance maxima at 434 and 440 nm respectively.[25] Different synthetic method can increase the regioregularity and the molecular weight which would be characterized by a red-shifted UV-Vis absorption maximum, as a result of a lower π-π^* transition energy. This increased average conjugation length,[11, 43-45] is defined as the number of aromatic rings lying in a coplanar arrangement. The larger is the number of the coplanar rings, larger is the bathochromic effect on the absorption spectrum. High molecular weight P3HT solutions usually appear clear and orange at high temperature while purple and turbid when cooled down. The UV-Vis spectrum changes in the same remarkable way from large undefined band with no fine structure at high temperature to a strongly red-shifted and well-defined band at lower temperature.[46-47] The evolution of the P3HT aggregation in solution to form fibrils was measured by scattering techniques.[48] These features can also be recognized in P3HT solid film characterize by a large red-shifted (up to 100 nm) and fine structured band,[27] showing, in the 500-600 nm region, three peaks of variable relative intensity as a function of the film thickness, and indicative of the morphological order/disorder of the solid film. The thinner the film, the larger the red shift (Table2).[49-50] IR spectra can give information on the conjugation length.[11, 27] The ratio of the 1460 cm^{-1} (symmetric C=C stretching) and at 1510 cm^{-1} (asymmetric C=C stretching) peaks, decreases when the conjugation length increases. The regiorandom P3HT gives a value of about 12-15 while rrP3HT are characterized by values around 6-9.[27]

Table 2. UV-Vis spectra on solid films of P3HT coming from different synthetic methods.[11, 27, 51-52]

Polym.	λ_{max} in solid state [nm]			
	McCullough "thick film" rr >98%[a] HT[51]	McCullough "thin film" rr >98%[a] HT[52]	Rieke "thin film" rr>98%[a] HT[27]	$FeCl_3$ rr 70%[a] HT[51]
P3HT	504*	525	526	480
	550	555*	556*	
	600	610	608	

*) The more intense peak is shown. [a] regioregularity.

3. SYNTHETIC METHODS

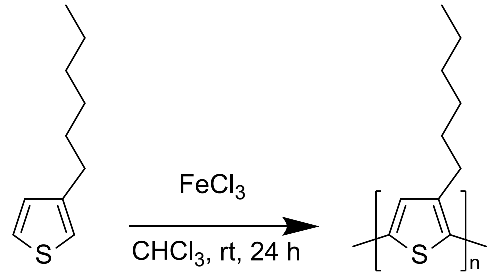
Several methods were reported for the P3HT preparation. The electrochemical polymerization[30, 53-56] is probably one of the most elegant among all, but presents some limitation. The reaction scale is limited due to the relevant amount of monomer required for the electrolysis and because of the oxidation/degradation of P3HT on the electrodes at the synthetic working potential. This is known as "the polythiophene paradox".[57] The electrochemically prepared P3HT is interesting despite the lower regioregularity, depicted as blue shifted absorption band, in comparison to the one obtained by classical synthetic pathways.[56] Recently the electrochemical protocol was improved by using a microflow reaction which allowed a better P3HT molecular weight control.[55] Since the difficulties to apply this method on large scale production, this review will mainly focus on metal catalyzed reactions.

3.1. Metal-assisted Polymerizations

The most used strategies for the production of P_3HT are all based on metal promoted reactions such the oxidative method mainly based on $FeCl_3$ or the Ni-catalyzed methods (McCullough, Rieke, Grignard Metathesis) or, finally, the Pd-catalyzed methods (Suzuki, Stille, Direct Arylation Polymerization).

3.1.1. Oxidative polymerization ($FeCl_3$ and other oxidants)

The first heterocycles (thiophene, pyrrole and furan) oxidative polymerization, $FeCl_3$ (Scheme 1) mediated, was introduced by Sugimoto and Yoshino to produce conductive polymers.[58] This simple and relatively cheap method became immediately popular, and was extended to other modified thiophenes, expanding the polythiophene class. The $FeCl_3$ oxidation is relatively easy and suitable for large scale production, giving access to high molecular weights. Several other oxidants were explored, such as $MoCl_2$, $RuCl_2$[58] vanadium acetylacetonate,[59] ammonium persulfate[60] or $FeCl_3$.[61] Recently, the combined use of palladium(II) acetate, copper(II) acetate and trifluoroacetic acid, in presence of oxygen was reported, despite lower regioregularity and blue-shifted absorption and emission spectra at 338 and 534 nm respectively.[62]



Scheme 1. Oxidative polymerization of 3-hexylthiophene.

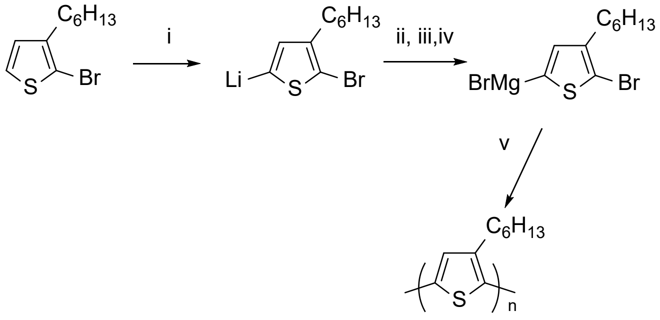
A comparison on 3-alkylthiophenes obtained by $FeCl_3$ oxidative polymerization or electropolymerization,[30] evidenced similar degree of regioregularity (80%) and molecular weight. In 1994, Andersson et al. produced a (PTOPT) by $FeCl_3$ in high yield (around 80%) and very high regioregularity (around 94%).[31] The original method[58] requires the addition of the 3HT to the $FeCl_3$ suspension, providing regioregularity ranging from 50 to 70%. Andersson et al performed the reverse addition of reactants,[31] ensuring a low Fe^{3+}/3HT ratio, low Fe^{3+}/Fe^{2+} ratio and oxidation potential in solution. In those conditions the regioregularity of the polymer was improved as confirmed in later results.[12] The addition of 3HT to $FeCl_3$ suspension at room temperature provided a 58% regioregular polymer, while reversing the addition order, the regioregularity rose up to 70%.[30] The effects of the oxidant/3HT molar ratio, the solvent (chloroform, hexane, dichloromethane) and oxidant concentration were also systematically investigated.[63] Standard $FeCl_3$/3HT ratio of 4:1 gives high molecular weight polythiophenes.[30-31] Lowering the ratio to 1:1 provided a yield of 30% and an average molecular weight of 100 kDa, while a 2:1 ratio was characterized by 57% yield. Higher temperature remarkably lowers the polymer molecular weight. The polymerization was reported to occur better on solid $FeCl_3$ crystals, while homogeneous solution provided poor results. The use of amylenes stabilized chloroform is recommended while ethanol is reported to inhibit the reaction lowering both the yield and the molecular weights. Shimizu et al. prepared P3HT by modifying 3HT and $FeCl_3$ concentrations. Higher 3HT concentration provided higher molecular weight (4.0-69KDa) and low PDI (below 2).[64] Lower temperature (-45°C) maximized the regioregularity (91%) in chloroform with 3HT concentration of 0.02 M for 3 days.[35] Facchinatto et al.[65] reported that both longer addition times and lower temperature in hexane or acetone were beneficial to higher the molecular masses (M_w=318 kDa and M_n=68 kDa, 81% regioregularity). Pratt et al. proposed the use of $CoCl_2$ to improve the P3HT oxidative synthesis by $FeCl_3$ increasing both the regioregularity and the molecular weight.[32] The use of $CoCl_2$ and other additives in the reaction elucidated the cationic and radical polymerization mechanisms. $CoCl_2$ selectively inhibits the radical mechanism acting as radical scavenger increasing the molecular weight (near 1000 KDa) and the regioregularity, even when the 3HT was added to the $FeCl_3$ slurry.[66] A comparison of P3HTs obtained by classical way or by microwaves irradiation showed a positive effect of microwaves on all characteristics (yield, regioregularity, structure and properties), also for the final devices.[67-68] Well performing materials were obtained by refrigerating the reaction during the microwave irradiation, preventing the low regioregularity caused by high temperature. Interestingly, Liu et al.[36] used a P3HT obtained by $FeCl_3$ oxidation and fractionated it by selective precipitation caused by stepwise addition of methanol to the toluene solution, at 8°C. It was reported that earlier fractions were characterized by higher regioregularity and molecular weight along with long conjugation and higher conductivity.

3.1.2. Polymerization by Ni Catalysis

The Ni-catalyzed P3HT synthesis, by McCullough,[33] Rieke[36] and GRIM[34] methods, are the most interesting and performing ones. In comparison the Pd-catalyzed reactions results are slightly lower.

3.1.2.1. McCullough Method

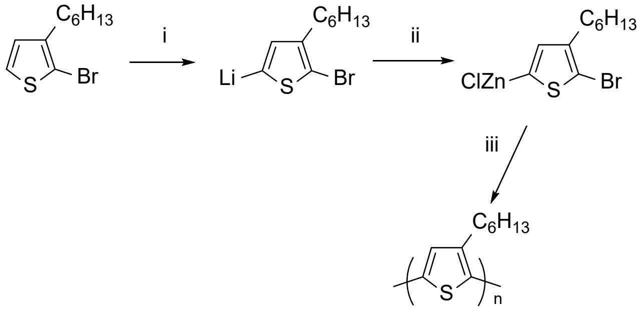
The first highly regioregular P3HT was prepared by McCullough in 1993 (Scheme 2).[24, 33] 2-bromo-3-hexylthiophene was deprotonated with LDA at -78°C, and reacted with $BrMgr_2 \cdot Et_2O$, giving the 2-bromo-5-bromomagnesio-3-hexylthiophene. The reaction regioselectivity was really high (98%). Exploiting the in situ catalysis of $Ni(dppp)Cl_2$ on the Grignard reagent, highly regioregular P3HTs (98-100%) were obtained in moderate to good yields (44 to 66%). The reason of this extraordinary selectivity was mainly ascribed to the stabilizing effect of the alkyl chain for oxidative addition on the C-Br bond in ortho position. Moreover, the steric hindrance hampers the formation of a Nickel complex bearing two thiophenes having the hexyl chain in ortho to the Ni-C bond.[69-70]



i) LDA, THF, -40°C; ii) $MgBr_2.OEt_2$, -60°C; iii) -40°C; iv) -10°C;
v) $Ni(dppp)Cl_2$, from -5 to 25°C.

Scheme 2. McCullough original synthetic method.[33] Adapted from McCullough et al.[33] with permission from The Royal Society of Chemistry.

The initiation and propagation high efficiencies was due to the presence of the alkyl substituents on 3-position (ortho position to the halogen), which prompted higher conversion and molecular weight and narrowed the polydispersity with respect to the oligomers with no substituents ortho to the bromine.[70-71] Due to the strong similarity, the mechanistic aspects are discussed later (see GRIM method section 3.1.2.3). Replacing the poorly soluble $MgBr_2 \cdot Et_2O$ with the highly soluble $ZnCl_2$ accelerated the reaction (Scheme 3).[72] Similar method evolution is also found in the Rieke method (see next paragraph). The obtained regioregular P3HTs (rrP3HT) showed very high conductivities with respect to the regioirregular materials, such as those obtained by the oxidative method. Final method evolution is reported as GRIM method (see below)[34] which is currently the most used one since it does not require strong based or cryogenic temperatures.

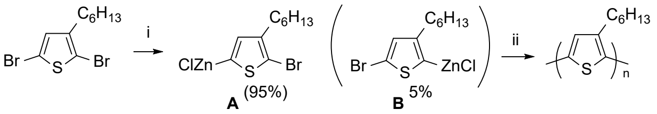


i) LDA, THF, -40°C; ii) $ZnCl_2$, iii) -40°C; iv) -10°C;
v) $Ni(dppp)Cl_2$, 0°C.

Scheme 3. McCullough $ZnCl_2$ modified synthetic method.[72] Reprinted and adapted with permission from Liu et al.[72]. Copyright (2002) American Chemical Society.

3.1.2.2. Rieke Method

Just after the McCullough method publication, Rieke et al.[36] treated the 2,5-dibromothiophene with an activated Zn ("Rieke Zinc") at -78°C, giving the two possible intermediates (A and B) in a ratio 90:10. The mixture was then reacted with $Ni(dppe)Cl_2$ at 0°C to 25°C (Scheme 4), obtaining P3HTs with 75% yield and excellent regioregularity (97-100%).



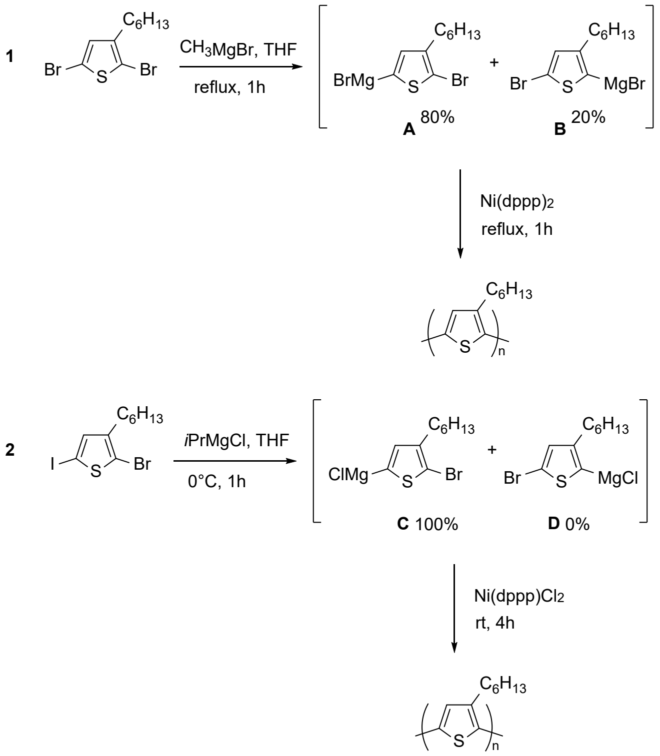
i) Zn*, THF, -78°C to rt, 4h; ii) $Ni(dppp)Cl_2$, 0°C.

Scheme 4. Rieke Method: two possible zincate intermediates were obtained: 2-bromo-5-(bromozincio)-3-hexylthiophene (**A**) and 5-bromo-2-(bromozincio)-3-hexylthiophene (**B**).[73] Adapted with permission from Kudret et al.[73] Copyright © 2013 John Wiley & Sons, Inc.

The method found useful applications[36, 74-75] but it was rarely used[73, 76-77] (see the reported reference, for a list) because of the McCullough and GRIM method (see below). The charge mobility of McCullough and Rieke P3HT increased with the molecular weight and is independent on the termination group (H or Br).[5] A recent work reviewed the (Zn*) preparation systems, and pointed out some reproducibility issues in the preparation and behavior, giving also advices for substantial improvement. The presence of benzothiophene (3%) in the preparation was essential to obtain the active Zn*,[73] by preventing the Zn particles agglomeration and obtaining a very fine powder. Due to this paper "Rieke Zinc" could see its "new age" in the near future, even for P3HT polymerization.

3.1.2.3. GRIgnard Methatesis Method (GRIM)

The so called GRIM method, based on a Grignard Metathesis reaction, is an evolution of the McCullough method. The Kumada reaction,[78-79] which couples a Grignard reagent with an alkyl or aryl halide, is the base of the GRIM method. Cheap Grignard reagent (i.e. iPrMgCl or t-BuMgCl), are used for a metathesis on an aryl halide monomer[34] before a Ni catalyzed reaction couples the monomers. The polymerization can be successfully performed using aryl monomers bearing two halides (i.e. two bromines or one bromine and one iodine) being more selective on the iodo/bromo monomer.



Scheme 5. GRIM Method. 1) original method;[34] 2) method modification with 2-bromo-3-hexyl-5-iodothiophene.[70] Reprinted and adapted with permission from: 1) Loewe et al.,[34] Copyright © 1999 John Wiley & Sons, Inc.; 2) Boyd et al.,[70]. Copyright (2009) American Chemical Society.

In the first GRIM reaction, the CH_3MgBr metathesis involved the 5-position of the monomer (Scheme 5, reaction 1).[34] The polymerization occurred with Ni(dppp)Cl_2 at reflux for about 3h, and was applied to other alkylthiophenes, giving highly regular polymers.[80] The metathesis on the bromine atoms was regioselective (5-Br: 2-Br 8:2) and the coupling showed complete HT selectivity (>99%). McCullough and coworkers analyzed the mechanism of the GRIM method.[34, 69, 81] The formation of two isomers (see A and B in Scheme 5, reaction 1) took place systematically providing A to B ratio in the range 80-88 to 20-12, with A being always favored over B independently on the temperature, time or Grignard reagent. The Grignard metathesis occurs usually in 30 minutes with complete selectivity for the iodine (Scheme 5, reaction 2) starting from the 2-bromo-3-hexyl-5-iodothiophene.[69] The 2,5-diiodo-3-dodecylthiophene monomer gave metathesis but no polymer,[69] since the CH_3I formed during the metathesis, coupled rapidly with the Grignard thienyl compounds. However, the 2-bromo-3-hexyl-5-iodothiophene became the key monomer combining the higher metathesis reactivity of the iodine, the lower reactivity of the bromine, avoiding unwanted reactions, and nearly complete selectivity. (Scheme 5, reaction 2, C:D 100:0). The GRIM mechanism was also analyzed in term of kinetic preference for the formation of different couplings: HT, HH and TT.[81] It was shown that more conjugated oligomers react faster with Ni catalyst than the monomers. The reaction providing HT couplings is highly favored over the other reactions (Fig. 5). HH and TT couplings are occurring occasionally, even if the formation of the Grignard intermediate does not show the same regioselectivity. Based on these evidences a general mechanism was proposed by McCullough (Scheme 6).The oxidative addition on the C-Br bond of a grown chain, without observing chain transfer, was justified by the formation of an associated pair, after the reductive elimination, which keeps the catalyst close to the growing chain until the oxidative addition takes place.[82]

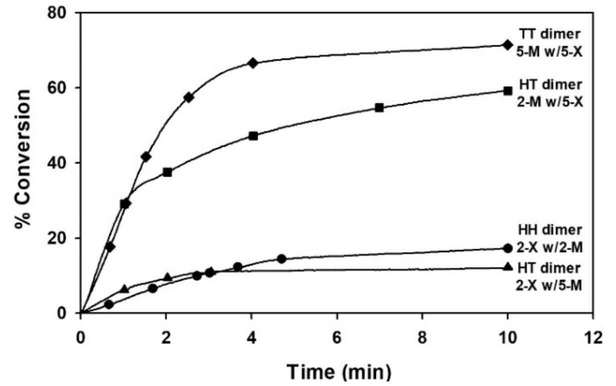
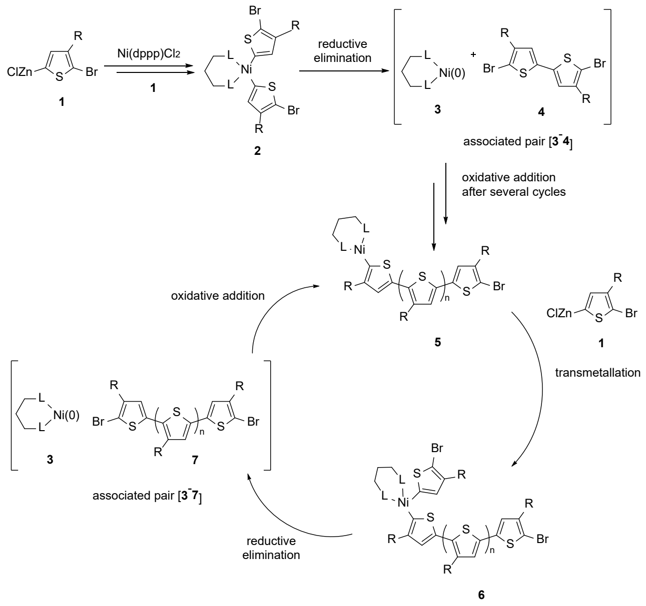
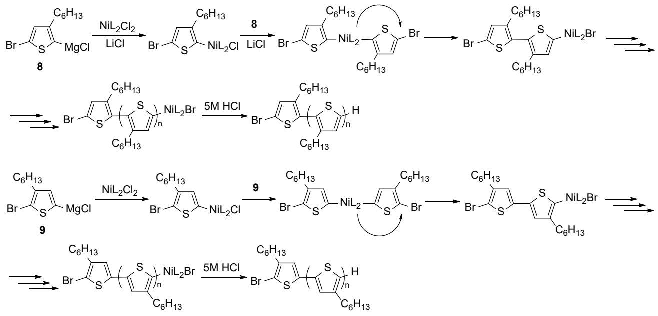


Figure 5. Kinetic experimental data supporting the selectivity for different dimerization couplings.[69] Reprinted with permission from Loewe et al.[69]. Copyright (2001) American Chemical Society

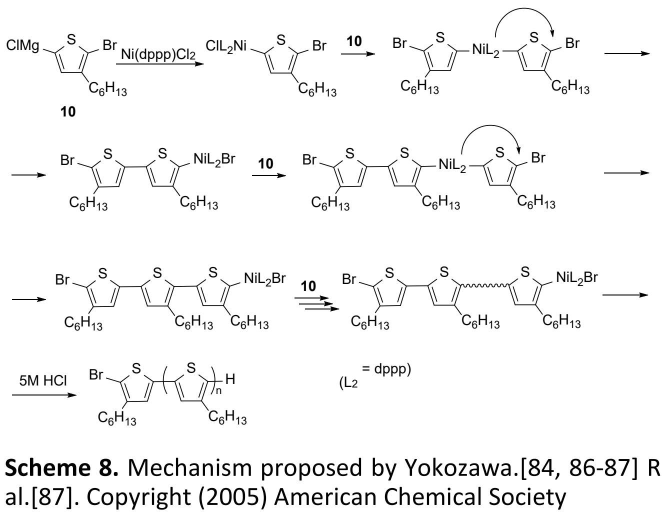


Scheme 6. Mechanism proposed by McCullough.[82] Reprinted and adapted with permission from Sheina et al.[82]. Copyright (2004) American Chemical Society

When the reaction was performed in refluxing THF, several terminal groups like H/Ph or Ph/Br as well as desulphurization of the terminal thiophene were found.[69] These issues were solved by performing the reaction at room temperature. These problems were solved by performing the reaction at room temperature. The catalyst effect is important to obtain regioregular polymers. If the ligand is highly demanding by a steric point of view, computational[83] and experimental[84] results have shown that only HT and TT adducts are favored with Ni complex catalysis. The “reverse” monomer, 5-bromo-2-chloromagnesio-3-hexylthiophene does not polymerize. Nevertheless, by using LiCl on that substrate, Wu et al. made the reaction occur very fast (Scheme 7).[85]



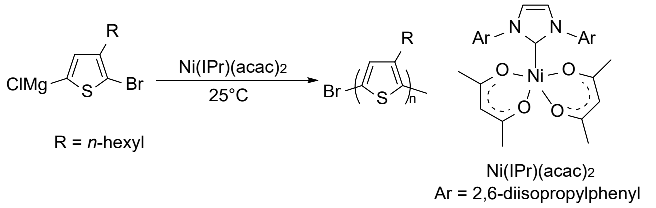
Scheme 7. The polymerization of the “reverse” (**8**) and “normal” (**9**) monomer.[85] Reprinted and adapted with permission from Wu et al.[85]. Copyright (2011) American Chemical Society



Scheme 8. Mechanism proposed by Yokozawa.[84, 86-87] Reprinted and adapted with permission from Miyakoshi et al.[87]. Copyright (2005) American Chemical Society

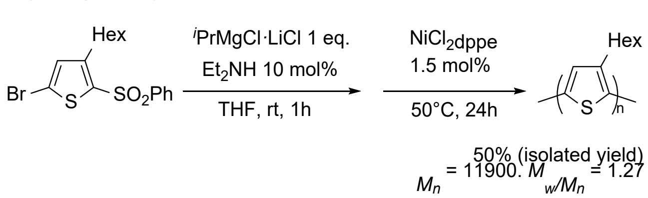
A different mechanism was proposed by Yokozawa (Scheme 8),[84] suggesting that, after the reductive elimination, the catalyst can firmly attach to the growing chain and move along it, until the new oxidative addition occurs. This was in disagreement with the previous apparent evidences of a step-growth mechanism.

In 2005, the ”quasi-living” nature of the P3HT polymers prepared by GRIM method was demonstrated.[88] As already proposed, the first reaction produces a TT dimer, which undergoes an HT oxidative addition by the Ni complex with a “ring walking” phenomenon (Scheme 8), and adds monomers by a HT step-by-step mechanism. The higher stability of ortho-substituted Aryls in Aryl-Ni(II) complexes, due to interaction of π-aryl electrons with d orbitals of Ni, [89] facilitate an immediate attack of Ni to the bromine in ortho to the alkyl substituent on the growing chain by “ring walking”, after each C-C coupling.[70] In the same conditions, the “reversed” monomer, i.e. the 5-bromo-2-chloromagnesio-3-hexylthiophene, did not produce any polymer at all.[70] The “quasi-living” nature of the polymerization mechanism was demonstrated by adding 2-bromo-5-bromomagnesio-3-dodecylthiophene in a P3HT batch obtaining the poly(3-hexylthiophene)-co- poly(3-dodecylthiophene) (P3HT-co-P3DT) copolymer.[88] It was also demonstrated that reasonable monomer dilution facilitates longer polymer chain formation by limiting the aggregation phenomena of high molecular weight growing polymers.[90] The P3HT molecular weight increased together with the monomer concentration in solution while keeping constant the Ni complex one, explaining the low polydispersity of the GRIM method.[90] The molecular weight was constant after 20 minutes of reaction, but the monomer conversion continued over 2 hours evidencing a catalyst transfer mechanism taking place.[90] Moreover, after the reaction quenching with HCl/MeOH, MALDI-TOF analysis evidenced the present also of dibrominated species in addition to the expected H/Br terminated polymers.[90] Quite recently, McCullough studied the effect of the metal centers (Ni, Pd, Pt) on the 3HT polymerization.[91] Nickel produced the best high quality polymers, palladium the low regioregular P3HT while platinum yielded lower molecular weight polymers. The success of the GRIM reactions, with Ni(dppp)Cl_2 and some related catalysts, hampered the development and use of novel catalysts, with some exceptions.[92] Some NHC based Ni catalysts[93] were proposed. Among them, Ni(IPr)$(acac)_2$ gave excellent performances making the synthesis fast and simple to be performed providing high yields (>75%) and complete regioregularity control (Scheme 9).[93] The polymerization took less than 2 hour to completion giving polymers with molecular weights ranging from 416 to 4.9 kDa according to the Ni catalyst content 0.05-8%. This is one of the most significant improvements in the recent years, facilitating the P3HT production, with tailored molecular weight and complete regioregularity.[93] To the best of our knowledge, this is also the highest molecular weight, fully characterized P3HT obtained so far.



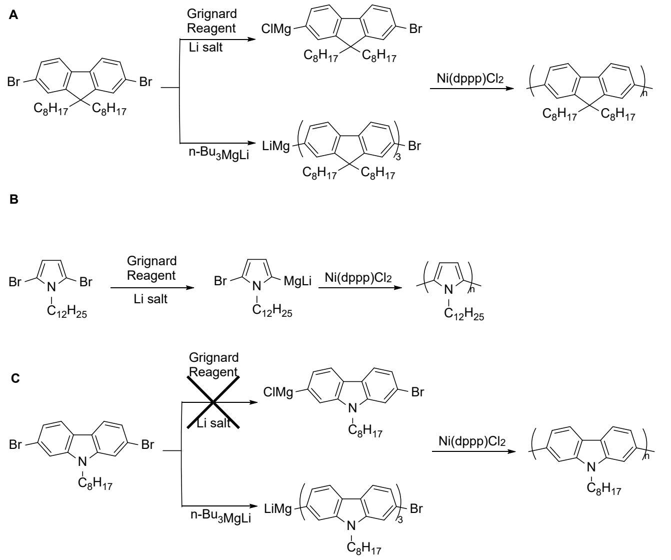
Scheme 9. A novel Ni catalyst helped to improve the method towards very high molecular weights.[93] Reproduced from Shi et al.[93] with permission from The Royal Society of Chemistry.

Very recently, other substrates as 3-hexyl-2-(phenylsulfonyl)thiophene were polymerized by the GRIM method (Scheme 10).[94] The first step is the transfer of iPrMgCl·LiCl on the position 5 of the thiophene by a trimethylamine-mediated deprotonation occurring in 1 hour at room temperature. The coupling was then performed in THF with $NiCl_2$(dppe) at 50°C for 24 h, giving a 12 kDa molecular weight polymer with low polydispersity and almost complete regioregularity.[94]



Scheme 10. A novel way to use the GRIM method onto 3-hexyl-2-(phenylsulfonyl)thiophene.[94] Reprinted and adapted with permission from Tamba et al.[94] Copyright (2014) American Chemical Society

A very recent paper prosed to use of the bioderived 2-methyltetrahydrofuran (2-Me-THF) as a green solvent instead of the commonly used chloroform, toluene and THF.[95] The proposed solvent behaves similarly to THF and was also exploited driving the reaction in flow conditions in very short time. Despite a slight lower regioregularity (93%) this flow synthetic method is extremely fast (1-10 minutes of contact time) and allows very high throughput.[95] The GRIM method was also applied to prepare P3HT with controlled and modulated regioregularity (64-98%) by precise control on the feeding of H-H dimer Grignard reactant, thus relating the structure to electronic, thermal and mechanical properties, as for flexible Organic PhotoVoltaic (OPV) solar cells, since the high crystallinity can produce brittle polymer films.[96] The GRIM protocol was made more tolerant to several functional groups by performing the metathesis step with zincate.[86] The zincate-thiophene compound tolerates well free alcohol groups on the side chain showing high regioregularity for P3HT (99%).The GRIM method was proved robust enough to be applied to other substrates such polyfluorenes,[97] thiophenes, pyrroles, fluorenes and carbazoles[98-99] becoming a universal method in the production of various conjugated polymers (Scheme 11).



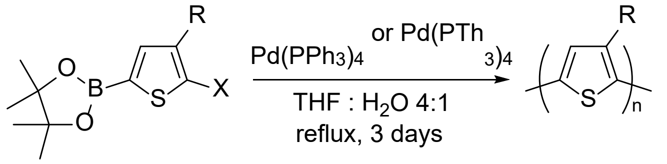
Scheme 11. Application of GRIM method to other heterocycles than thiophenes.[98-99] Reprinted and adapted with permission from Stefan et al.[98-99] Copyright (2009) American Chemical Society

3.1.3. Polymerizations by Pd Catalysis

The P3HT could also be prepared by Pd catalysis, [100-101] adapting the Suzuki[102] and the Stille[101] reactions to the polymerization, with the Stille appearing more robust.[100-101] While being less toxic and more green, the Suzuki reaction suffers of protodeboronation side-reaction which stops the polymer chain growth, [99] resulting in low molecular weight.

3.1.3.1. Suzuki Reaction Polymerization

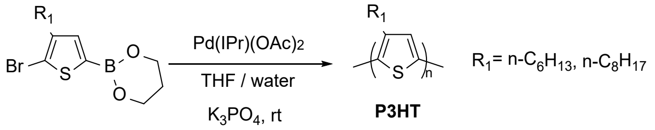
The first P3AT polymerization obtained by the Suzuki method was reported for the synthesis of poly(3-octylthiophene) (P3OT). Guillierez et al. polymerized the [1′,3-(2,2′dimethylpropylene)]-2-iodo-3-octylthienylboronate with Pd(OAc)$_2$ in THF/EtOH/H$_2$O,[103] obtaining a high quality polymer (regioregularity 96-97 %, Mn= 27 kDa; Mw= 40 kDa; PDI = 1.5). After this initial success, the Suzuki method was applied to some P3AT, investigating the catalysts effect and obtaining good regioregularities, from 92 to 98% and molecular weights around 9-17 kDa.[104]



Scheme 12. Example of Suzuki synthesis of P3AT.[105] Adapted with permission from Li et al.[105] Copyright © 2008 John Wiley & Sons, Inc.

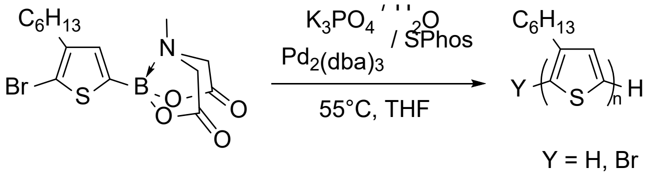
The Suzuki method was often used to couple different monomers in copolymers[106-107] but the first P3HT prepared by Suzuki reaction was reported only in 2008 by Li et al. polymerizing the 3-hexyl-5-iodothiophene-2-boronic pinacol ester,[104] with Pd(PTh$_3$)$_4$ (palladium tetrakis(tris(2-thienyl)phosphine)) instead of Pd(PPh$_3$)$_4$ (Scheme 12). The novel catalyst showed an impressive improvement of yield when thiophene monomer were coupled by Suzuki reaction (regioregularity 97-98%, yields 62-72%, molecular weight 5-26 kDa).[105] The P3HT was obtained in good yields and specifics (regioregularity 99%, M_n = 5400 g mol^{-1} and PDI = 1.3), by using Bu$_3$P-Pd(Ph)Br as catalyst.[108] Varying the monomer/catalyst ratio till about 58 increased the polymer molecular weight. Higher ratios provided lower molecular weight polymers suggesting that side-reactions (catalyst chain transfer) competed. This was an excellent result despite the reaction still need to be optimized to produce high molecular mass polymers.

In 2014 Sui et al. reported that $Pd(IPr)(OAc)_2$ can polymerize 2-bromo-5-(1,3,2-dioxaborinane)-3-hexylthiophene (Scheme 13) to P3HT in quantitative yield with 99% regioregularity and molecular weight ranging from 9.5 to 63.8 kDa.[109] The molecular weight was easily controlled by defining the starting monomer/catalyst ratio, since it was a catalyst-transfer condensation polymerization reaction (CTCP).



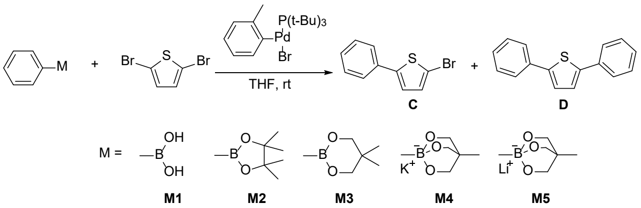
Scheme 13. Use of the NHC $Pd(IPr)(OAc)_2$ catalyst for P3HT polymerization.[109] Reproduced from Sui et al. [109] with permission from The Royal Society of Chemistry.

In 2015, PH3T 8-18 kDa molecular weight polymers were obtained almost in quantitative yield and high (97-98%) regioregularity by using a MIDA protected 2-bromo-3-hexylthiophene-5-boronic acid, $Pd_2(dba)_3$ and SPhos as ligand (Scheme 14).[110] This was a further improvement in the Suzuki reaction application to P3HT synthesis.



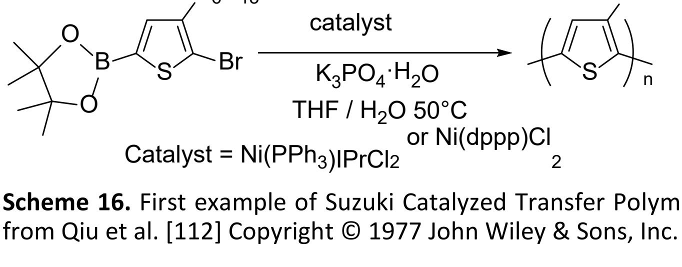
Scheme 14. Reaction with MIDA boronates.[110] Reprinted and adapted with permission from Carrillo et al. [110] Copyright (2015) American Chemical Society

In Suzuki-Miyaura reactions, water is well-known to promote the dehalogenation and the protodeboronation which are detrimental for the polymerization. At the same time water promotes the intramolecular catalyst transfer and affords low PDI polymers.[111] Large distribution of molecular masses was obtained performing the reaction in anhydrous THF due to intermolecular transfer which could be limited, but not eliminated, adding a small amount of water (Scheme 15, best case C:D 8:92 with M3).



Scheme 15. Test reaction to demonstrate the intramolecular catalyst transfer.[111] Adapted with permission from Kosaka et al.[111] Copyright © 1977 John Wiley & Sons, Inc.

Finally, despite not being a Pd-catalyzed reaction it is worth to mention here the very recently reported first Ni-catalyzed Suzuki catalyzed transfer polymerization reaction (CTP),[112] in which a NHC based catalyst ($Ni(PPh_3)IPrCl_2$) gave high molecular weights (up to 74 kDa). This was probably due to hydrolysis of the Ni complex to $Ni(OH)_2$ in presence of water, which reduces consistently the catalyst concentration, lowering the number of started chains (Scheme 16). The $Ni(dppp)Cl_2$ complex, however did not suffer from hydrolysis in presence of water and gave easily controlled polymerization with very narrow distribution (18.8 KDa molecular weight and 1.08 PDI at 2% catalyst loading).

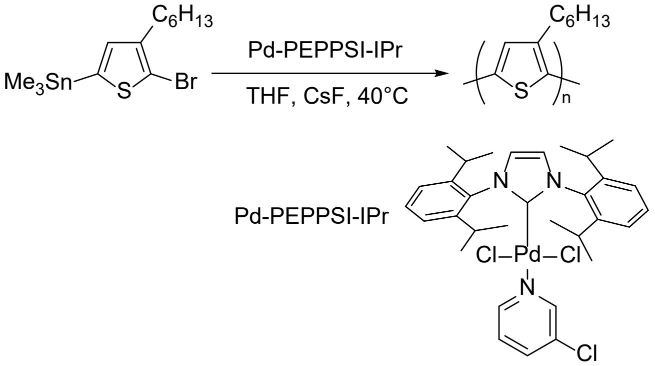


Scheme 16. First example of Suzuki Catalyzed Transfer Polymerization by Ni-catalysis.[112] Adapted with permission from Qiu et al. [112] Copyright © 1977 John Wiley & Sons, Inc.

3.1.3.2. Stille Reaction Polymerization

The Stille reaction requires the coupling of an aryl halide with arylstannanes.[100] The protocol is known to be quite robust since the arylstannanes are normally stable, making it advantageous over the Suzuki reaction, as reported above (see 3.1.3.1). [113]

The first polymerization of 3HT was published by Iraqi et al., by reacting 2-iodo-3-hexyl-5-(tri-n-butylstannyl)thiophene with $Pd(PPh_3)_4$.[101] The reaction was performed refluxing various solvents, giving the best results with toluene and 1,2-dichloroethane (regioregularity >96%, molecular weights M_n = 7-8 kDa and M_w = 10-14 kDa, respectively). Nevertheless the reaction was much slower than the McCullough and Rieke ones. The P3HT molecular weight could be limited by the solubility of the growing chain in toluene.[101] Interestingly, the addition of $Pd(PPh_3)_4$ to a P3HT oligomers (degree of polymerization, DP, of about 14) produced longer P3HT with a DP of about 28. This enabled the production of longer telechelic polymers and/or copolymers characterized by a red-shifted absorption from 424 to 439 nm from low to high mass polymers.[101]

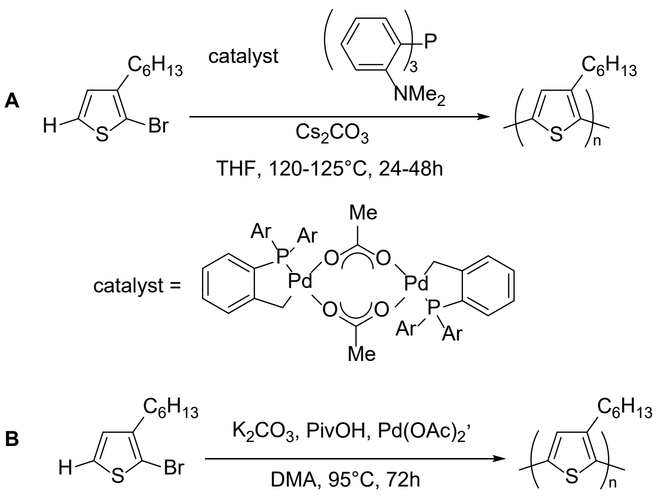


Scheme 17. Stille Catalyst-Transfer Polymerization of P3HT by using a NHC Pd catalyst (Pd-PEPPSI-IPr).[114] Adapted with permission from Qiu et al.[114] Copyright © 2015 John Wiley & Sons, Inc.

Burkhart et al. prepared a sample of P3HT by the Stille method ($Pd(PPh_3)_4$, DMF, 95°C, 48h), [115] which was highly useful for organic electronics and solar cells, and became a reference to optimize the Direct Arylation protocol(see later).[116] A simple way to introduce modifications on P3HT was reported by Li et al.[117] showing how the residual hydrogen could be halogenated to activate the substitution with aromatic groups by Suzuki, Stille or Heck couplings. As happened for Kumada, GRIM, Suzuki, Negishi methods[93, 109, 114, 118-122] a Stille Catalyst-Transfer Condensation Polymerization (CTCP) was set-up by the Pd NHC catalysts.[114] The use of the Pd-PEPPSI-IPr catalyst (Scheme 17) improved the Stille protocol by exploiting the catalyst property of "ring walking".[114] The molecular weights were modulated by the monomer/catalyst ratio, as for GRIM[89] and Suzuki[106] reactions (Mn = 7-73 kDa, Mw = 8-111 kDa and PDI = 1.14-1.53).

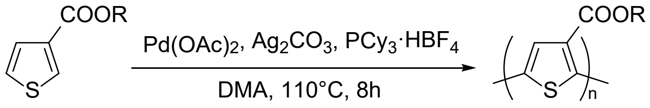
3.1.3.3. Direct Arylation Polymerization (DArP)

A great innovation in the cross-coupling reactions was the aromatic C-H activation by Pd catalysts,[123-126] since no pre-functionalization of aryls with halogens, boronic acids or stannyl moieties, was required. The protocol was appointed as a green chemistry method. [124] The Direct Arylation Polymerization (DArP) was developed in parallel by Fagnou[127-129] and Ozawa[130-132] and is still evolving (Scheme 18). Until now, full control on the cross coupling regioselectivity and on the different ring position activation was not reported. The Ozawa conditions use a Pd catalyst, tri(o-anisyl)phosphine, Cs_2CO_3, in THF or Toluene at 110-120°C. [130-132] The Fagnou conditions, on the contrary, are based on cheap materials, $Pd(OAc)_2$ with or without phosphine ligands, K_2CO_3, a carboxylic acid additive, in N,N-dimethylacetamide (DMA), at 95-100°C.[127-129] A first DArP reaction involving a thiophene-based monomer was a copolymerization between a 3,4-dimethylthiophene or 3,3',4,4'-tetramethylbithiophene and a dibromoaryl monomer in DMA at 100°C in presence of $Pd(OAc)_2$, with $PCy_3{\cdot}HBF_4$ as ligand giving high yield (82%) and molecular weight (36 kDa).[133]



Scheme 18. Methods of Ozawa[130] (**A**) and Fagnou[127] (**B**). A) Adapted with permission from Wang et al.[130] Copyright (2010) American Chemical Society; B) Adapted with permission from Lafrance et al.[127] Copyright (2006) American Chemical Society.

The synthesis of P3HT and some copolymers of 3HT, thiophene (T) and benzothiadiazole (BTD) of diketopyrrolopyrrole (DPP) was immediately tried[128] but provided lower yields and regioregularity in comparison to the Stille products. Ozawa et al. reported a synthesis of P3HT and its end capping, using a particular ligand $P(C_6H_4\text{-o-}NMe_2)_3$, which ensured excellent results for both yields and regioregularity (>98%).[134] A modification of the general DArP protocol gave access to a series of hyperbranched 3HT-based polymers.[39] Rudenko et al. optimized the P3HT synthesis, using $Pd(OAc)_2$, K_2CO_3, neodecanoic acid in DMA at 70°C to improve the polymer quality, (yield 60%, regioregularity up to 93.5%).[135-136] The sterically hindered neodecanoic acid was able to activate the C-H bond, but not the □-hydrogen of the thiophene, thus limiting the branching of the final polymer. Hayashi et al. used Pd/C as a catalyst, under a phosphine-free condition, obtaining a 16 KDa molecular weight and 91% yield of a completely linear P3HT without branching.[137] A study of solvent effect showed the mesitylene as a solvent of choice, since its C-H bonds are not reacting.[138] The reactivity of solvents C-H was also reduced by the presence of one or more chlorine atoms. Electron deficient thiophenes were better polymerized using toluene while DMA was best solvent for the electron rich ones.[139] Rudenko et al. defined the effect of the different amide solvents, and of the carboxylic acid additive structure.[140-141] An evolution of the DArP was proposed, the Oxi-DArP.[142] The method works by using a catalyst ($Pd(OAc)_2$) and an oxidizing metal salt ($Cu(OAc)_2$ or Ag_2CO_3), on a 3-thiophenecarboxylic ester (3EHT) (Scheme 19). The ester group acts as directing group, and promotes the activation of C-H bonds. By using a phosphine ligand, medium to high yield (24-82%) and a regioregularity of 88% were obtained. The reaction was tried also on 3HT but the results were, so far, poor.



Scheme 19. Oxi-DArP reaction to prepare poly((3-alkyoxycarboxy)thiophenes).[142] Reproduced from Gobalasingham et al.[142] with permission from The Royal Society of Chemistry.

4. CONCLUSIONS

P3HT synthetic methods are here reported, along with their effect on the structural characteristics which tunes specific properties allowing different applications. Several methods, like McCullough, Rieke and GRIM now allow for a precise control of the regioregularity and the molecular weight. Stille and Suzuki couplings have shown remarkable advances and, in the near future, will provide comparable control on the polymer properties. Recently, advances have been reported for all the methods, in particular for the one using NHC palladium or nickel catalysis, generating true "living" polymers which enables a fine tuning of the molecular weight. The simpler and cheaper oxidative methods produced less regioregular materials, sometimes, of very high molecular weight, which are highly appreciated in the applicative field.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of the Università di Torino (Ricerca Locale ex-60%, Bandi 2016 e 2017).

REFERENCES

[1] Chiang, C. K.; Fincher, C. R.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; Gau, S. C.; MacDiarmid, A. G., *Phys. Rev. Lett.* **1977,** *39* (17), 1098-1101.

[2] Chizu, S.; Yoshiaki, T.; Takeshi, Y.; Makoto, K.; Shuji, D., *Sci. Technol. Adv.Mater.* **2014**, *15 (3)*, 034203.

[3] Osaka, I.; McCullough, R. D., *Acc. Chem. Res.* **2008,** *41* (9), 1202-1214.

[4] Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M., *Nature* **1999**, *401 (6754)*, 685-688.

[5] Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J. M. J., *Adv. Mater.* **2003**, *15* (18), 1519-1522.

[6] Holliday, S.; Ashraf, R. S.; Wadsworth, A.; Baran, D.; Yousaf, S. A.; Nielsen, C. B.; Tan, C. H.; Dimitrov, S. D.; Shang, Z.; Gasparini, N.; Alamoudi, M.; Laquai, F.; Brabec, C. J.; Salleo, A.; Durrant, J. R.; McCulloch, I., *Nat. Commun.* **2016**, *7*, 11585.

[7] Nicolet, C.; Deribew, D.; Renaud, C.; Fleury, G.; Brochon, C.; Cloutet, E.; Vignau, L.; Wantz, G.; Cramail, H.; Geoghegan, M.; Hadziioannou, G., *J. Phys. Chem. B* **2011**, *115 (44)*, 12717-12727.

[8] Nia, N. Y.; Matteocci, F.; Cina, L.; Di Carlo, A., *ChemSusChem* **2017**, *10 (19)*, 3854-3860.

[9] Plastic that conducts electricity. https://www.nobelprize.org/nobel_prizes/chemistry/laureates/2000/press.html (accessed 10th Nov 2017).

[10] Sista, P.; Luscombe, C. K., *Adv. Polym. Sci.* **2014,** *265* (P3HT Revisited--From Molecular Scale to Solar Cell Devices), 1-38.

[11] McCullough, R. D., *Adv. Mater.* **1998,** *10* (2), 93-116.

[12] Sivaraman, P.; Mishra, S. P.; Bhattacharya, A. R.; Thakur, A.; Shashidhara, K.; Samui, A. B., *Electrochim. Acta* **2012,** *69*, 134-138.

[13] Gustafson, M. P.; Clark, N.; Winther-Jensen, B.; MacFarlane, D. R., *Electrochim. Acta* **2014,** *140*, 309-313.

[14] Kleinschmidt, A. T.; Root, S. E.; Lipomi, D. J., *J. Mater. Chem. A* **2017**, *5* (23), 11396-11400.

[15] Scheinert, S.; Paasch, G., *Phys. Status Solidi A* **2004,** *201* (6), 1263-1301.

[16] Lee, J.; Kwon, J.; Lim, J.; Lee, C., *Mol. Cryst. Liq. Cryst.* **2010**, *519*, 179-186.

[17] Shimomura, M.; Kaga, M.; Nakayama, N.; Miyauchi, S., *Synth. Met.* **1995**, *69* (1-3), 313-314.

[18] Bannock, J. H.; Treat, N. D.; Chabinyc, M.; Stingelin, N.; Heeney, M.; de Mello, J. C., *Sci. Rep.* **2016**, *6*, 23651.

[19] Hedley, G. J.; Ruseckas, A.; Samuel, I. D. W., *Chem. Rev.* **2017**, *117* (2), 796-837.

[20] Kline, R. J.; DeLongchamp, D. M.; Fischer, D. A.; Lin, E. K.; Richter, L. J.; Chabinyc, M. L.; Toney, M. F.; Heeney, M.; McCulloch, I., *Macromolecules* **2007**, *40 (22)*, 7960-7965.

[21] Trznadel, M.; Pron, A.; Zagorska, M.; Chrzaszcz, R.; Pielichowski, J., *Macromolecules* **1998**, *31* (15), 5051-5058.

[22] Sato, M.; Morii, H., *Macromolecules* **1991**, *24* (5), 1196-1200.

[23] Barbarella, G.; Bongini, A.; Zambianchi, M., *Macromolecules* **1994**, *27* (11), 3039-3045.

[24] McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L., *J. Org. Chem.* **1993**, *58* (4), 904-912.

[25] Mao, H.; Xu, B.; Holdcroft, S., *Macromolecules* **1993**, *26* (5), 1163-1169.

[26] Maior, R. M. S.; Hinkelmann, K.; Eckert, H.; Wudl, F., *Macromolecules* **1990**, *23* (5), 1268-1279.

[27] Chen, T.-A.; Wu, X.; Rieke, R. D., *J. Am. Chem. Soc.* **1995**, *117* (1), 233-244.

[28] Mao, H.; Holdcroft, S., *Macromolecules* **1992**, *25* (2), 554-558.

[29] Bidan, G.; De Nicola, A.; Enée, V.; Guillerez, S., *Chem. Mater.* **1998**, *10* (4), 1052-1058.

[30] Leclerc, M.; Martinez Diaz, F.; Wegner, G., *Makromol. Chem.* **1989**, *190* (12), 3105-3116.

[31] Andersson, M. R.; Selse, D.; Berggren, M.; Jaervinen, H.; Hjertberg, T.; Inganaes, O.; Wennerstroem, O.; Oesterholm, J. E., *Macromolecules* **1994**, *27* (22), 6503-6506.

[32] Pratt, C. M.; Foot, P. J. S.; Davis, R., *Polym. Polym. Compos.* **2016**, *24* (3), 185-190.

[33] McCullough, R. D.; Lowe, R. D., *J. Chem. Soc. Chem. Commun.* **1992**, 70-72.

[34] Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D., *Adv. Mater.* **1999**, *11* (3), 250-253.

[35] Amou, S.; Haba, O.; Shirato, K.; Hayakawa, T.; Ueda, M.; Takeuchi, K.; Asai, M., *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37* (13), 1943-1948.

[36] Chen, T. A.; Rieke, R. D., *J. Amer. Chem. Soc.* **1992**, *114* (25), 10087-10088.

[37] Elsenbaumer, R. L.; Jen, K. Y.; Oboodi, R., *Synth. Met.* **1986**, *15* (2-3), 169-174.

[38] Dissanayake, D. S.; Sheina, E.; Biewer, M. C.; McCullough, R. D.; Stefan, M. C., *J. Polym. Sci. Part A: Polym. Chem.* **2017**, *55* (1), 79-82.

[39] Okamoto, K.; Housekeeper, J. B.; Michael, F. E.; Luscombe, C. K., *Polym. Chem.* **2013**, *4* (12), 3499-3506.

[40] Spoltore, D.; Vangerven, T.; Verstappen, P.; Piersimoni, F.; Bertho, S.; Vandewal, K.; Van den Brande, N.; Defour, M.; Van Mele, B.; De Sio, A.; Parisi, J.; Lutsen, L.; Vanderzande, D.; Maes, W.; Manca, J. V., *Org. Electron.* **2015**, *21*, 160-170.

[41] Liu, Y.; Oshima, K.; Yamauchi, T.; Shimomura, M.; Miyauchi, S., *J. Appl. Polym. Sci.* **2000**, *77* (14), 3069-3076.

[42] Schilinsky, P.; Asawapirom, U.; Scherf, U.; Biele, M.; Brabec, C. J., *Chem. Mater.* **2005**, *17* (8), 2175-2180.

[43] Izumi, T.; Kobashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T., *J. Am. Chem. Soc.* **2003**, *125* (18), 5286-5287.

[44] Meier, H.; Stalmach, U.; Kolshorn, H., *Acta Polym.* **1997**, *48* (9), 379-384.

[45] Ten Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W., *J. Am. Chem. Soc.* **1991**, *113* (15), 5887-5889.

[46] Berson, S.; De Bettignies, R.; Bailly, S.; Guillerez, S., *Adv. Funct. Mater.* **2007**, *17* (8), 1377-1384.

[47] Samitsu, S.; Shimomura, T.; Heike, S.; Hashizume, T.; Ito, K., *Macromolecules* **2008**, *41* (21), 8000-8010.

[48] Huang, Y.; Cheng, H.; Han, C. C., *Macromolecules* **2011**, *44* (12), 5020-5026.

[49] Roncali, J.; Yassar, A.; Garnier, F., *J. Chem. Soc., Chem. Commun.* **1988**, 581-582.

[50] Yassar, A.; Roncali, J.; Garnier, F., *Macromolecules* **1989**, *22* (2), 804-809.

[51] McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M., *J. Am. Chem. Soc.* **1993**, *115* (11), 4910-4911.

[52] McCullough, R. D.; Williams, S. P.; Jayaraman, M.; Reddinger, J.; Miller, L.; Tristram-Nagle, S., "Synthesis and Physical Properties of Self-Orienting, Head-To-Tail Polythiophenes." In: *Electrical, Optical, and Magnetic Properties of Organic Solid State Materials*, Dalton, L.; Lee, C., Eds. Materials Research Society: Pittsburgh PA, **1994**; Vol. *328*, pp 215-220.

[53] Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K., *Chem. Express* **1986**, *1*, 635-638.

[54] Sato, M.; Tanaka, S.; Kaeriyama, K., *J. Chem. Soc., Chem. Commun.* **1986**, 873-874.

[55] Mizuno, M.; Tateno, H.; Matsumura, Y.; Atobe, M., *React. Chem. Eng.* **2017**, *2* (5), 642-645.

[56] Patel, R. J.; Tighe, T. B.; Ivanov, I. N.; Hickner, M. A., *J. Polym. Sci., Part B: Polym. Phys.* **2011**, *49* (17), 1269-1275.

[57] Krische, B.; Zagorska, M., *Synth. Met.* **1989**, *28* (1-2), 263-268.

[58] Katsumi, Y.; Shigenori, H.; Ryu-ichi, S., *Jpn. J. Appl. Phys.* **1984**, *23* (12A), L899-L900.

[59] Takagi, K.; Torii, C.; Yamashita, Y., *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47* (12), 3034-3044.

[60] Liu, R.; Liu, Z., *Sci. Bull.* **2009**, *54* (12), 2028-2032.
[61] Jung, Y. J.; Lee, S. J.; Choi, S. W.; Kim, J. H., *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46* (17), 5968-5975.
[62] Tsuchiya, K.; Ogino, K., *Polym. J.* **2013**, *45* (3), 281-286.
[63] Hai, T. A. P.; Sugimoto, R., *J. Mol. Struct.* **2017**, *1146*, 660-668.
[64] Shimizu, H.; Yamada, M.; Wada, R.; Okabe, M., *Polym. J.* **2008**, *40* (1), 33-36.
[65] Facchinatto, W. M.; Torres, B. B. M.; Balogh, D. T., *J. Polym. Res.* **2016**, *23* (9), 1-8.
[66] Foot, P. J. S.; Davis, R.; Budd, D. Preparation of highly conductive polymers by oxidation of heterocyclic monomers in the presence of nonoxidizing transition metal compound. GB2304346A, March, 19th, 1997.
[67] Garcia-Escobar, C. H.; Nicho, M. E.; Hu, H.; Alvarado-Tenorio, G.; Altuzar, C. P.; Cadenas-Pliego, G.; Hernandez-Martinez, D., *Int. J. Polym. Sci.* **2016**, 1926972/1-1926972/9.
[68] Nicho, M. E.; García-Escobar, C. H.; Hernández-Martínez, D.; Linzaga-Elizalde, I.; Cadenas-Pliego, G., *Mater. Sci. Eng. B* **2012**, *177* (16), 1441-1445.
[69] Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D., *Macromolecules* **2001**, *34* (13), 4324-4333.
[70] Boyd, S. D.; Jen, A. K. Y.; Luscombe, C. K., *Macromolecules* **2009**, *42* (24), 9387-9389.
[71] Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriy, A., *Macromolecules* **2008**, *41* (21), 7817-7823.
[72] Liu, J.; McCullough, R. D., *Macromolecules* **2002**, *35* (27), 9882-9889.
[73] Kudret, S.; D' Haen, J.; Oosterbaan, W. D.; Lutsen, L.; Vanderzande, D.; Maes, W., *Adv. Synth. Catal.* **2013**, *355* (2-3), 569-575.
[74] Dang, M. T.; Hirsch, L.; Wantz, G., *Adv. Mater.* **2011**, *23* (31), 3597-3602.
[75] Smeets, A.; Van den Bergh, K.; De Winter, J.; Gerbaux, P.; Verbiest, T.; Koeckelberghs, G., *Macromolecules* **2009**, *42* (20), 7638-7641.
[76] Pomerantz, M.; Cheng, Y.; Kasim, R. K.; Elsenbaumer, R. L., *J. Mater. Chem.* **1999**, *9* (9), 2155-2163.
[77] Saito, F.; Takeoka, Y.; Rikukawa, M.; Sanui, K., *Synth. Met.* **2005**, *153* (1-3), 125-128.
[78] Kiso, Y.; Yamamoto, K.; Tamao, K.; Kumada, M., *J. Am. Chem. Soc.* **1972**, *94* (12), 4373-4374.
[79] Kiriy, A.; Senkovskyy, V.; Sommer, M., *Macromol. Rapid Commun.* **2011**, *32* (19), 1503-1517.
[80] Greve, D. R.; Apperloo, J. J.; Janssen, R. A. J., *Synth. Met.* **2001**, *119* (1-3), 369-370.
[81] Laird, D. W.; Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R., *Polym. Prepr.* **2001**, *42* (2), 556-557.
[82] Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D., *Macromolecules* **2004**, *37* (10), 3526-3528.
[83] Bahri-Laleh, N.; Poater, A.; Cavallo, L.; Mirmohammadi, S. A., *Dalton Trans.* **2014**, *43* (40), 15143-15150.
[84] Yokoyama, A.; Miyakoshi, R.; Yokozawa, T., *Macromolecules* **2004**, *37* (4), 1169-1171.
[85] Wu, S.; Huang, L.; Tian, H.; Geng, Y.; Wang, F., *Macromolecules* **2011**, *44* (19), 7558-7567.
[86] Higashihara, T.; Ueda, M., *Macromol. Res.* **2013**, *21* (3), 257-271.
[87] Miyakoshi, R.; Yokoyama, A.; Yokozawa, T., *J. Am. Chem. Soc.* **2005**, *127* (49), 17542-17547.
[88] Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D., *Macromolecules* **2005**, *38* (21), 8649-8656.
[89] Hidai, M.; Kashiwagi, T.; Ikeuchi, T.; Uchida, Y., *J. Organomet. Chem.* **1971**, *30* (2), 279-282.
[90] Achord, B. C.; Rawlins, J. W., *Macromolecules* **2009**, *42* (22), 8634-8639.
[91] Bhatt, M. P.; Magurudeniya, H. D.; Sista, P.; Sheina, E. E.; Jeffries-El, M.; Janesko, B. G.; McCullough, R. D.; Stefan, M. C., *J. Mater. Chem. A* **2013**, *1 (41)*, 12841-12849.
[92] Magurudeniya, H. D.; Sista, P.; Westbrook, J. K.; Ourso, T. E.; Nguyen, K.; Maher, M. C.; Alemseghed, M. G.; Biewer, M. C.; Stefan, M. C., *Macromol. Rapid Commun.* **2011**, *32* (21), 1748-1752.
[93] Shi, X.; Sui, A.; Wang, Y.; Li, Y.; Geng, Y.; Wang, F., *Chem. Commun.* **2015**, *51* (11), 2138-2140.
[94] Tamba, S.; Fuji, K.; Nakamura, K.; Mori, A., *Organometallics* **2014**, *33* (1), 12-15.
[95] Bannock, J. H.; Xu, W.; Baissas, T.; Heeney, M.; de Mello, J. C., *Eur. Polym. J.* **2016**, *80*, 240-246.
[96] Kim, J.-S.; Kim, J.-H.; Lee, W.; Yu, H.; Kim, H. J.; Song, I.; Shin, M.; Oh, J. H.; Jeong, U.; Kim, T.-S.; Kim, B. J., *Macromolecules* **2015**, *48* (13), 4339-4346.
[97] Huang, L.; Wu, S.; Qu, Y.; Geng, Y.; Wang, F., *Macromolecules* **2008**, *41* (22), 8944-8947.
[98] Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough, R. D., *Macromolecules* **2009**, *42* (1), 30-32.
[99] McCullough, R. D.; Iovu, M. C.; Osaka, I. Grignard metathesis polymerization. WO2008028166A1, March, 6th,2008.
[100] Stille, J. K., *Angew. Chem. Int. Ed.* **1986**, *25* (6), 508-524.
[101] Iraqi, A.; Barker, G. W., *J. Mater. Chem.* **1998**, *8* (1), 25-29.
[102] Suzuki, A., *J. Organomet. Chem.* **1999**, *576* (1-2), 147-168.
[103] Guillerez, S.; Bidan, G., *Synth. Met.* **1998**, *93* (2), 123-126.
[104] Liversedge, I. A.; Higgins, S. J.; Giles, M.; Heeney, M.; McCulloch, I., *Tetr. Lett.* **2006**, *47* (29), 5143-5146.
[105] Li, W.; Han, Y.; Li, B.; Liu, C.; Bo, Z., *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (13), 4556-4563.
[106] Zhang, M.; Fan, H.; Guo, X.; He, Y.; Zhang, Z.; Min, J.; Zhang, J.; Zhao, G.; Zhan, X.; Li, Y., *Macromolecules* **2010**, *43* (13), 5706-5712.
[107] Falzon, M.-F.; Zoombelt, A. P.; Wienk, M. M.; Janssen, R. A. J., *Phys. Chem. Chem. Phys.* **2011**, *13* (19), 8931-8939.
[108] Yokozawa, T.; Suzuki, R.; Nojima, M.; Ohta, Y.; Yokoyama, A., *Macromol. Rapid Commun.* **2011**, *32* (11), 801-806.
[109] Sui, A.; Shi, X.; Tian, H.; Geng, Y.; Wang, F., *Polym. Chem.* **2014**, *5* (24), 7072-7080.
[110] Carrillo, J. A.; Ingleson, M. J.; Turner, M. L., *Macromolecules* **2015**, *48* (4), 979-986.
[111] Kosaka, K.; Ohta, Y.; Yokozawa, T., *Macromol. Rapid Commun.* **2015**, *36* (4), 373-377.
[112] Qiu, Y.; Worch, J. C.; Fortney, A.; Gayathri, C.; Gil, R. R.; Noonan, K. J. T., *Macromolecules* **2016**, *49 (13)*, 4757-4762.
[113] Kinzel, T.; Zhang, Y.; Buchwald, S. L., *J. Am. Chem. Soc.* **2010**, *132* (40), 14073-14075.
[114] Qiu, Y.; Mohin, J.; Tsai, C.-H.; Tristram-Nagle, S.; Gil, R. R.; Kowalewski, T.; Noonan, K. J. T., *Macromol. Rapid Commun.* **2015**, *36* (9), 840-844.
[115] Burkhart, B.; Khlyabich, P. P.; Cakir Canak, T.; LaJoie, T. W.; Thompson, B. C., *Macromolecules* **2011**, *44* (6), 1242-1246.
[116] Rudenko, A. E.; Wiley, C. A.; Tannaci, J. F.; Thompson, B. C., *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51* (12), 2660-2668.
[117] Li, Y.; Vamvounis, G.; Yu, J.; Holdcroft, S., *Macromolecules* **2001**, *34* (10), 3130-3132.
[118] Yokozawa, T.; Yokoyama, A., *Chem. Rev.* **2009**, *109* (11), 5595-5619.
[119] Okamoto, K.; Luscombe, C. K., *Polym. Chem.* **2011**, *2* (11), 2424-2434.
[120] Yokozawa, T.; Nanashima, Y.; Kohno, H.; Suzuki, R.; Nojima, M.; Ohta, Y., *Pure Appl. Chem.* **2012**, *85* (3), 573-587.
[121] Bryan, Z. J.; McNeil, A. J., *Macromolecules* **2013**, *46* (21), 8395-8405.
[122] Ohta, Y.; Yokozawa, T., *Adv. Polym. Sci.* **2013**, *262*, 191-238.
[123] Gensch, T.; Hopkinson, M. N.; Glorius, F.; Wencel-Delord, J., *Chem. Soc. Rev.* **2016**, *45* (10), 2900-2936.

[124] Bohra, H.; Wang, M., *J. Mater. Chem. A* **2017**, *5* (23), 11550-11571.
[125] Yang, Y.; Lan, J.; You, J., *Chem. Rev.* **2017**, *117* (13), 8787-8863.
[126] Nitti, A.; Po, R.; Bianchi, G.; Pasini, D., *Molecules* **2016**, *22* (1), 21.
[127] Lafrance, M.; Fagnou, K., *J. Am. Chem. Soc.* **2006**, *128* (51), 16496-16497.
[128] Rudenko, A. E.; Wiley, C. A.; Stone, S. M.; Tannaci, J. F.; Thompson, B. C., *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50* (18), 3691-3697.
[129] Lu, W.; Kuwabara, J.; Kanbara, T., *Macromolecules* **2011**, *44* (6), 1252-1255.
[130] Wang, Q.; Takita, R.; Kikuzaki, Y.; Ozawa, F., *J. Am. Chem. Soc.* **2010**, *132* (33), 11420-11241.
[131] Wakioka, M.; Kitano, Y.; Ozawa, F., *Macromolecules* **2013**, *46* (2), 370-374.
[132] Wakioka, M.; Ichihara, N.; Kitano, Y.; Ozawa, F., *Macromolecules* **2014**, *47* (2), 626-631.
[133] Fujinami, Y.; Kuwabara, J.; Lu, W.; Hayashi, H.; Kanbara, T., *ACS Macro Lett.* **2012**, *1* (1), 67-70.
[134] Wang, Q.; Wakioka, M.; Ozawa, F., *Macromol. Rapid Commun.* **2012**, *33* (14), 1203-1207.
[135] Rudenko, A. E.; Wiley, C. A.; Tannaci, J. F.; Thompson, B. C., *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51* (12), 2660-2668.
[136] Rudenko, A. E.; Thompson, B. C., *J. Polym. Sci. Part A: Polym. Chem.* **2015**, *53* (2), 135-147.
[137] Hayashi, S.; Kojima, Y.; Koizumi, T., *Polym. Chem.* **2015**, *6* (6), 881-885.
[138] Matsidik, R.; Komber, H.; Sommer, M., *ACS Macro Lett.* **2015**, *4* (12), 1346-1350.
[139] Kuwabara, J.; Yamazaki, K.; Yamagata, T.; Tsuchida, W.; Kanbara, T., *Polym. Chem.* **2015**, *6* (6), 891-895.
[140] Rudenko, A. E.; Thompson, B. C., *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53* (21), 2494-2500.
[141] Rudenko, A. E.; Thompson, B. C., *Macromolecules* **2015**, *48* (3), 569-575.
[142] Gobalasingham, N. S.; Noh, S.; Thompson, B. C., *Polym. Chem.* **2016**, *7* (8), 1623-1631.

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