The Ni-catalyzed Polymerization of Poly(3-alkoxythiophene)s a

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The Ni-catalyzed polymerization of poly(3-alkoxythiophene)s (P3AOTs) was studied and compared with the controlled chain-growth polymerization of poly(3-alkylthiophene)s (P3ATs). By varying the ratio of the initial monomer concentration to the initiator concentration, no linear dependence of the molar mass was observed, revealing that the polymerization does not proceed via a controlled mechanism. This was also confirmed by analyzing the end-groups of the polymer with MALDI-TOF mass spectrometry. To acquire more information on the polymerization mechanism, the formation of the actual monomer and the polymerization reaction were studied into more detail. These experiments proved that the polymerization proceeds via a chain-growth mechanism, although not in a controlled way.

^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.macros.wiley-vch.de>, or from the author.

Introduction

Poly(3-alkylthiophene)s (P3ATs) are a class of conjugated polymers that has been intensively studied over the past decades. The discovery by McCullough and Yokozawa of the chain-growth polymerization mechanism of P3ATs has led to a renewed interest in the synthesis of these polymers.^[1] This chain-growth mechanism is made possible by the ‘ring-walking process’ of the Ni-catalyst, whereby the Ni(0) species is transferred intramolecularly along a polymer chain to its end where it oxidatively inserts in the C-Br bond.^[2] Due to this mechanism, all polymer chains are equipped with the same end-groups, being a bromine and a hydrogen atom (after quenching with acid). It also allows control of the molar mass by adjusting the feed ratio of the monomer to the Ni-catalyst, and the formation of block copolymers by successive monomer addition.^[3]

The versatility of the quasi-controlled chain-growth polycondensation has also been demonstrated by the use of other monomers, polymerized with Ni- as well as Pd-catalysts. In this way, polyfluorenes^[4], poly(para-phenylenes)^[5] and polypyrroles^[3d] have been successfully prepared.

If the polythiophene backbone is substituted with an alkoxy instead of an alkyl side-chain, a polymer with different characteristics is obtained. Regioregular HT-coupled poly(3-alkoxythiophene)s (P3AOTs) are electronically different and show a significantly higher λ_{max} compared to P3ATs.^[6] Their Faraday rotation is much larger (Verdet constant up to $3 \times 10^6 \text{ T}^{-1} \text{ m}^{-1}$)^[7] and their magnetic properties differ^[8]. Although their properties are interesting, the polymerization behavior of P3AOTs has never been studied in detail.

An important finding in this respect is that starting the polymerization of P3AOT with an *o*-tolyl nickel initiator complex results in polymers which mainly bear *o*-tolyl/hydrogen end-groups – as would be formed by a controlled chain-growth mechanism – but also *o*-tolyl/bromine and even small amounts of Br/Br, Br/H and H/H end-groups.^[9] Although most

polymers were equipped with the initiator unit, the appearance of the other end-groups reveals that the polymerization of P3AOTs does not proceed completely in the same way as P3ATs.

Therefore, this paper provides a more detailed study of the synthesis of P3AOTs and investigates whether their polymerization also proceeds via a chain-growth mechanism, as is the case for P3ATs, or whether the alkoxy-substituent alters the polymerization behavior of the polythiophene, turning the mechanism invalid for these polymers.

Experimental Section

Reagents and Instrumentation

All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka and Avocado. Reagent grade solvents were dried and purified by distillation.

Gel permeation chromatography (GPC) measurements were done with a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in tetrahydrofuran (THF) as eluent toward polystyrene standards. ^1H nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz. Mass spectrometry analyses were carried out by MALDI-ToF. MALDI mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 J/m^2 delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight mass analysis were performed in the reflectron mode at a resolution of about 10000. The matrix, trans-2-[3-(4-t-Butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), was prepared as 20 mg/mL solution in chloroform. The matrix solution (1 μL) was applied to a stainless steel target and air dried. Polymer samples were dissolved in chloroform to obtain 1mg/mL solutions. 1 μL aliquots of these solutions were applied onto the target area already bearing the matrix crystals, and then air dried. For the recording of the single-stage MALDI-MS spectra, the quadrupole (rf-only mode) was set to pass ions from 750 to 7000 Th, and all ions were transmitted into the pusher region of the

time-of-flight analyzer where they were mass analyzed with 1 s integration time. Data were acquired in continuum mode until acceptable averaged data were obtained.

2-Bromo-4-((*S*)-3,7-dimethyloctyloxy)thiophene (**1**) was synthesized according to literature procedures.^[6]; (bis(diphenylphosphino)-2-methyl-4-trimethylsilylacetylenenickel bromide was prepared analogously as described in reference 9.

General polymerization procedure

Freshly prepared lithium diisopropylamide [prepared by the addition of *n*-BuLi (2.5 M in hexanes; 1.50 mmol; 0.60 mL) to diisopropylamine (1.80 mmol; 0.182 g) and THF (0.8 mL)] (1.50 mmol in THF (1.5 mL)) was added to a solution of **1** (1.00 mmol, 0.319 g) in dry THF (1.2 mL) at -78 °C. After stirring for 30 min at -78 °C, the solution was added to a suspension of MgBr₂ (1.50 mmol, 0.275 g) in dry THF (3 mL) and stirred for another 30 min at RT. In case Ni(dppp)Cl₂ was used as initiator, the Grignard reagent was then transferred to a suspension of Ni(dppp)Cl₂ (0.015 mmol, 8.13 mg) in dry THF (4 mL). After reacting overnight, the polymer was precipitated in methanol and filtered off. For the externally initiated polymerization, dppp (0.133 mmol, 54.9 mg) was added to a solution of the nickel complex (66,5 mmol, 56.6 mg) in dry THF (10 mL), stirred for 30 min and then, the Grignard reagent was transferred. After reacting for 2 h, the polymer was precipitated in methanol and filtered off.

Quenching procedure

Prior to cannulation to MgBr₂ (for quenching the Li-salt) or addition to the Ni-catalyst (for quenching of the monomer), a small aliquot was removed from the reaction mixture with a syringe and quenched in deuterated water. The sample was extracted with diethylether and the organic layer was dried over MgSO₄. After removing the solvent by rotary evaporation, the obtained product was analyzed by ¹H NMR spectroscopy.

Results and Discussion

Molar mass versus [M]₀/[In]

From a synthetic point of view, it has been shown that the Ni(dppp)Cl₂ initiated polymerization of HT-P3AOT requires the formation of only one isomer of the monomer to obtain a regioregular polymer, since both isomers of the alkoxy-substituted monomer are consumed by the catalyst.^[6] As a consequence, the Grignard metathesis method (GRIM), starting from the dibromothiophene derivative - as is used for the chain-growth polymerization of HT-P3AT - cannot be employed for the polymerization of HT-P3AOT, since this method produces both isomers.^[10] Also a selective GRIM on 2-iodo-5-bromo-3-alkoxythiophene, even if *i*PrMgCl·LiCl was employed, was unsuccessful in our hands. Instead, the monomer formation requires the use of a ‘modified McCullough procedure’, employing 2-bromo-4-alkoxythiophene (**Scheme 1**), in which the most stable isomer is formed and which therefore leads to a regioregular HT-P3AOT with superior properties compared to the irregular counterpart.^[6-8]

To verify the chain-growth nature of the polymerization of P3AOT, the correlation between the molar mass of the polymer and the ratio of the initial monomer concentration to the initiator concentration was studied. All polymerizations were carried out at room temperature, varying the amount of Ni-catalyst, but keeping the initial concentration of **1** constant. After 1.5 h, the obtained polymers were precipitated in methanol and the collected polymer samples were analyzed by GPC without further fractionation. The polydispersities of all the samples were between 1.5 and 1.7. The $\overline{M}_n$ versus $[M]_0/[In]$ plot shows a nonlinear dependence of $\overline{M}_n$, which initially increases but levels off at higher feed ratios of monomer (**Figure 1**). The experiment was repeated, which gave essentially the same result. According to a controlled chain-growth mechanism, a linear plot is expected, whereby the molar mass is determined by the feed ratio of monomer to catalyst. The negative deviation from linearity, however, points at transfer reactions during the polymerization.

The end-groups of the P3AOTs were analyzed by Matrix-assisted Laser Desorption Ionization time-of-flight mass spectrometry (MALDI-TOF MS) (see Supporting Information). If the

polymerization proceeds via a controlled chain-growth mechanism similar to that of P3ATs, the polymer would bear a bromine atom (arising from the beginning of each polymer chain) on one end and a hydrogen atom (arising from the quenching of the Ni-complex) at the other end. The MALDI-TOF mass spectrum of a P3AOT obtained after a polymerization time of 30 min is dominated by H/Br terminated polymer chains, but also minor peaks originating from Br/Br and H/H terminated polymers are present (see Figure S1). Increasing the polymerization time to 2 h significantly influences the MALDI-TOF mass spectra, as the major peaks then arise from H/H terminated polymers while the peaks from the H/Br terminated polymers have lower intensities and those with Br/Br end-groups become almost invisible. Moreover, the molar mass does not increase (see Figure S2). The MALDI-TOF mass spectrum recorded after 4 h of polymerization is virtually identical to that observed after 2 h of polymerization. The fact that no increase in the molar mass is observed after 30 minutes, was also confirmed by GPC. It must however be noted that GPC, calibrated toward PS standards, typically overestimates the molar mass of polymers which adopt a rigid rod-like conformation, as is the case for P3AOT. Therefore, the absolute values determined by GPC must be put into perspective, which also (partly) explains the deviation between the GPC and MALDI-TOF values. The fact that the molar mass reaches its maximum after a polymerization time of 30 minutes also confirms that the $\overline{M}_n$'s in Figure 1 are not affected by a possible incomplete polymerization reaction, as those experiments were stopped after 1.5 h. Both the nonlinear dependence of $\overline{M}_n$ versus $[M]_0/[In]$ and the appearance of different end-groups in the MALDI-TOF mass spectra demonstrate that the polymerization of P3AOTs does not proceed via a controlled mechanism, in contrast with P3ATs. In order to get more information regarding the polymerization, the actual polymerization procedure was studied in more detail.

Detailed investigation of the polymerization reaction

The polymerization reaction of P3AOT can be divided in three different parts (Scheme 1). In a first step, the actual monomer is prepared, which is done by treating **1** with freshly prepared LDA (lithium diisopropylamide) and subsequently with MgBr₂. The as-formed Grignard reagent (**3**) is then added to the Ni-catalyst in order to induce the polymerization. All these different steps were investigated in more detail.

Formation of the lithiated species

The first step in the polymerization procedure involves the formation of the Li-compound (**2**), which is performed by the addition of LDA to **1**. The generation of this Li-compound was verified by withdrawing a small amount of the reaction mixture and quenching it with D₂O. The reaction was repeated several times. ¹H NMR spectroscopy confirmed that, during the lithiation, only one isomer – 2-lithio-5-bromo-3-alkoxythiophene and not 5-lithio-2-bromo-3-alkoxythiophene – was present. Importantly, the ¹H NMR spectrum also revealed the presence of a variable but considerable amount (10-27%) of unreacted **1**. Due to this incomplete monomer formation, some test reactions were performed in order to achieve a fully lithiated monomer. Variation of the monomer concentration and the reaction temperature (Table 1) did not result in any improvements on the yield and no clear trend was observed in the amount of lithiated species. However, stirring the Li-compound at room temperature for a prolonged period of time results in a gradual degradation. Since higher temperatures do not improve the reaction yield, all subsequent reactions with LDA were performed at -78 °C for 30 min. In a next experiment, the amount of LDA was varied. If more equivalents were used, more of the Li-compound was formed, but a full conversion was never achieved. Moreover, by adding three or more equivalents, an increasing amount of 2,5-dilithiated monomer, was formed. Since this molecule can interfere with the actual polymerization, its formation should be avoided (see also further).

All these experiments demonstrate that the deprotonation of **1** with LDA is not a quantitative reaction due to the poor acidity of **1**. In order to test this hypothesis, LHMDs (lithium bis(trimethylsilyl)amide), a weaker and more sterically demanding base, was used. This resulted in no reaction at all, showing that the acidity of **1** indeed is too low to allow deprotonation by LHMDs and thus confirming the hypothesis.

Formation of the Grignard reagent

After the formation of the Li-compound, this species is transformed into a Grignard reagent by transmetalation with MgBr_2 . For this reaction, the conditions of entry 5, Table 1 were used. In a first trial, commercial $\text{MgBr}_2 \cdot \text{OEt}_2$ powder was added to **2** to perform this reaction. However, this yielded only very small amounts of deuterated **1** after quenching with D_2O , implying that also water was added to the reaction mixture. Next, freshly prepared MgBr_2 , generated from the reaction between Mg and 1,2-dibromoethane, was employed, which significantly increased the yield. The transmetalation, which is accompanied by the disappearance of the MgBr_2 precipitate, was complete within a few minutes. The reaction was repeated several times and a variable amount (36-60%, calculated starting from **1**) of the Grignard reagent was formed, showing that still some minor traces of protons must be present during the reaction, albeit much less than with the use of $\text{MgBr}_2 \cdot \text{OEt}_2$.

In our hands, it appears to be impossible to achieve a full conversion to the monomer. Vallat *et al.* also observed an incomplete reaction of $^i\text{PrMgCl}$ with their monomeric thiophene species, and suggested that the source of the protons, resulting in the occurrence of protonated monomer, arose from the solvent, THF.^[11] To check if indeed a reaction occurs between the Li-compound and THF, the lithiation was performed in deuterated THF. If the solvent is responsible for the partial protonation of the Li-compound, the deactivated monomer should bear a deuterium atom instead of a hydrogen atom. However, after quenching the reaction

with water, no deuterated **1** was found in the ^1H NMR spectrum, revealing that metallation of tetrahydrofuran is not the reason for the incomplete monomer formation.

Monomer formation: conclusions

In conclusion, it is shown that the monomer formation never reaches completeness and variable amounts of the Li-compound (before transmetallation) and the actual Grignard reagent (after transmetallation) are formed. As a consequence, the monomer/catalyst ratio cannot be predicted beforehand and is always lower than **1**/Ni(dppp)Cl₂. Moreover, it turns out that, during the polymerization, an appreciable but variable amount of **1** (40-64%) is always present, which clearly does not impede the polymerization. These findings imply that the polymerization proceeds by an, albeit not controlled, chain-growth mechanism. Indeed, if the polymerization would proceed via a step-growth mechanism, the presence of such large amounts of **1**, a chain-stopper, would result in the formation of low-molar mass oligomers.

Polymerization

Different catalysts were used in order to improve the polymerization reaction. Both Ni(dppp)Cl₂ and Ni(dppe)Cl₂ are able to polymerize the alkoxythiophene monomer, although the obtained molar mass was slightly higher for the first catalyst. Extra additions of ligand (dppp or dppe) did not result in any improvement; in contrast, hardly any polymer was formed. Also the addition of LiCl to the polymerization, as has been published by Yokozawa for poly(*p*-phenylenes)^[5], gives no better results for the polymerization of P3AOTs. Varying the monomer concentration (0.12 M – 0.07 M – 0.04 M), while keeping the ratio of monomer to catalyst constant, or varying the polymerization temperature (0° C – rt – 40° C), shows no difference in molar mass, although the polymerization runs of course faster at 40° C.

As already mentioned, by the addition of three or more equivalents of LDA to **1**, an increasing amount of di-lithiated thiophene is formed. After addition of MgBr₂, this results in the

corresponding di-Grignard reagent. This was confirmed by quenching an aliquot of the reaction mixture with D₂O and analyzing it with ¹H NMR spectroscopy, which revealed the presence of 2-5-dideuterio-3-alkoxythiophene. After addition of Ni(dppp)Cl₂ to this mixture, no polymer is formed. This indicates that the di-Grignard reagent acts as a chain-stopper during the polymerization. The appearance of some amounts of di-Grignard reagent would not be such a problem if the polymerization proceeded by a step-growth mechanism, which again points at a chain-growth mechanism.

Proposed polymerization mechanism

Based on the experimental findings, it is quite clear that the polymerization of P3AOT proceeds via a chain-growth mechanism. A proposed polymerization pathway is presented in **Scheme 2**. In a first step, Ni(II)(dppp)Cl₂ reacts with **3**, forming **4a**, being the actual initiator. Alternatively, a bromoarylnickel complex (**4b**) can be prepared and purified in a separate step and added to the polymerization mixture.^[9] Then, another molecule of **3** reacts with **4**. In case of **4a**, a dimer in a head-to-head fashion is formed. Although the formation of a head-to-head coupling is difficult in case of alkylthiophenes due to the large steric hindrance of the Ni(dppp)Cl₂ catalyst,^[12-13] it is possible for alkoxythiophenes since the Van der Waals radius of an oxygen atom is much smaller in comparison with a methylene unit and therefore the steric hindrance is strongly reduced.^[14] Another possible factor stabilizing the intermediate involved in the HH-formation, is an interaction between the Ni-center and the O-atom. Polymerization consists of the addition of **3** to the Ni-complex (transmetallation), followed by a reductive elimination and transfer and insertion of the catalyst into the terminal C-Br bond. If no side-reactions would occur and the Ni(0)(dppp) remains with its 'own' polymer chain, a controlled polymerization with H/In (if an external initiator is used) or H/Br (if the polymerization is initiated by Ni(II)(dppp)Cl₂) end-groups is obtained after quenching with acid (path A). Clearly, this is not the case. In principle, two termination reactions can occur. A first possibility is a disproportionation reaction of two bromoarylnickel compounds (**5**) (path

B), resulting in Ni(II)(dppp)Br₂, Ni(0)(dppp) (which, on its turn, eventually reacts to Ni black and stable and unreactive Ni(dppp)₂) and a polymer chain with Br/Br or In/In end-groups (for initiation with Ni(II)(dppp)Cl₂ and an external initiator, respectively). Decomplexation of Ni(0)(dppp) (path C) results in a polymer chain with Br/Br or In/Br end-groups.

It is clear that end-group analysis of an externally initiated polymerization is very useful to reveal the absence/presence of the various paths. Since the ligand significantly affects the controlled nature of the polymerization – PPh₃ is inferior to dppp in this respect – we added dppp prior to monomer addition in order to allow ligand exchange. End-group analysis of this externally initiated P3AOT polymerization using 2-methyl-4-trimethylsilylacetylenepheryl as aromatic moiety revealed that In/Br is the major peak, together with small amounts of In/H and traces of Br/H (Figure 2). No In/In residues were found. This confirms again that termination takes place and that it occurs via decomplexation. A similar behavior was found for the polymerization of oligothiophenes^[2a] and fluorenes^[4b], but this contrasts with the polymerization of P3AT, for which the absence of this decomplexation gives rise to the living character of its polymerization.^[2b] It seems that P3AOTs are much more susceptible to decomplexation of the Ni-catalyst than P3ATs. This decreased stability of the Ni-complex in case of P3AOTs can tentatively be attributed to the increased electron-richness, which weakens the interaction between the Ni(0)(dppp) moiety and the conjugated polymer chain. Moreover, it has already been reported that a substituent in the ortho-position to the C-Br bond stabilizes the formed Ni-complex.^[2a,9,13,15-16] Therefore, the lack of a β-substituent in the P3AOT polymerization is a second reason for the decreased stability of the growing Ni-center in this case. However, in contrast to P3AT^[13], in which the polymerization completely failed when a reversed thiophene monomer (with substituent in meta-position) was used, a polymer is still formed, albeit in a non-controlled fashion.

When released, Ni(0)(dppp) does not insert in **1**, where it could initiate a new polymer chain. This must be concluded from the fact that hardly any polymer chain lacking an initiator

moiety was found when using an external initiator. The difficult reinsertion in an alkoxythiophene can again be correlated with its more electron-rich nature. This is also in line with the findings of Luscombe, who compared various external initiators with different functional groups for their efficiency to polymerize P3HT.^[17] It was found that the rate of oxidative addition is strongly reduced by the presence of electron donating groups, as is also the case for alkoxythiophene.

Instead of an oxidative reinsertion, Ni(0)(dppp) disproportionates, forming Ni black and Ni(0)(dppp)₂. To verify this, a ³¹P NMR spectrum was recorded of a polymerization initiated with Ni(dppp)Cl₂ (Figure S5). The presence of a singlet at 12.4 ppm confirmed the formation of Ni(dppp)₂ – even as the dominant species.

The proposed polymerization scheme also offers an explanation for the observed MALDI-TOF mass spectra. The MALDI-TOF mass spectrum of the acid-quenched polymerization obtained after 30 minutes shows mainly H/Br and Br/Br end-groups. After a polymerization time of 2 h, MALDI-TOF mass spectra showed the appearance of mainly H/H terminated polymer. Since the polymerization reaction runs very fast and is finished in less than 30 min, these peaks must arise from post-polymerization reactions. Traces of unreacted LDA - which are clearly present given that the monomer formation is not quantitative - could convert Br into H (after quenching with water), which also explains why all Br/Br terminated polymer has nearly disappeared. Although the controlled chain-growth polymerization runs very smoothly for P3AT, other groups have also reported a non-optimal behavior of the polymerization of other conjugated polymers and the appearance of multiple end-groups in their MALDI-TOF mass spectra.^[4b,18] Achord *et al.* suggested that diffusion of the Ni-catalyst also occurs in the P3AT polymerization using the GRIM method.^[19]

The degree of polymerization in P3AOTs is therefore limited by the irreversible decomplexation of the Ni(0)(dppp). Since the released Ni(0)dppp does not reinsert into a ‘resting’ polymer chain, the degree of polymerization depends on the number of monomer

additions prior to decomplexation of the catalyst. This also explains the $\overline{M}_n$ versus $[M]_0/[In]$ relationship. For low $[M]_0/[In]$, a more or less linear increase in molar mass is observed, while for higher values of $[M]_0/[In]$, no difference in the molar masses is found. This shows that the degree of polymerization is limited to a certain amount of monomers that can be attached before decomplexation occurs. It should be noted that, although the nature of the monomer (alkoxythiophene) and the position of the substituent (meta), is likely to be the origin of the different behavior compared with P3AT, the presence of unreacted **1** might also play a role in the presence of termination reactions.

Conclusion

In conclusion, the mechanism of the Ni-catalyzed polymerization of P3AOT using a ‘modified McCullough’ procedure was studied. The monomer formation is not quantitative, which can be attributed to the lower acidity of the monomer compared to 3-alkylthiophenes. The polymerization proceeds via a chain-growth mechanism and can be initiated by both arylnickel(II) complexes and Ni(dppp)Cl₂ (which is in situ converted to an arylnickel(II) complex) and is possible despite the absence of an ortho-substituent. Similar to P3ATs, the chain-growth nature of the polymerization originates from a complexation of the Ni(dppp) moiety to the growing polymer chain. However, the polymerization of P3AOTs differs from P3ATs by the occurrence of irreversible decomplexation of the Ni(dppp) moiety. Reinsertion of released Ni(dppp) into a resting polymer chain or monomer does not occur. Therefore, the degree of polymerization of P3AOT is essentially governed by the number of monomer additions prior to decomplexation. Finally, during and after the polymerization, the C-Br end-groups are converted to C-H bonds (after quenching with acid or water) by the remaining organometallic species.

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Scheme 1. The polymerization of P3AOT.

Scheme 2. Proposed polymerization mechanism of P3AOT.

Figure 1. Plot of $\overline{M}_n$ versus $[M]_0/[In]$. $\overline{M}_n$ was measured by GPC in THF towards poly(styrene).

Figure 2. MALDI-TOF mass spectrum of externally initiated **3** ■ correspond to ions of P3AOT with trimethylsilyl/Br end-groups. The signals highlighted with a star correspond to fragments after a β cleavage.

Table 1. Test reactions for lithiation of **1** with LDA. The reaction time is 30 min.

Entry	[M] ₀ (M)	T (°C)	Amount of LDA (equivalents)	Conversion to 2 / dilithiated compound (%) ^a
1	0.13	-40	1.5	90 / ~0
2	0.33	-40	1.5	76 / ~0
3	0.66	-40	1.5	82 / ~0
4	0.33	0	1.5	79 / ~0
5	0.33	-78	1.5	82 / ~0
6	0.22	-78	1	82 / ~0
7	0.22	-78	3	79 / ~15
8	0.22	-78	6	68 / ~29

^a calculated from **1**

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A thorough study of the Ni-catalyzed polymerization of poly(3-alkoxythiophene)s reveals that a chain-growth mechanism is adopted, albeit not in a controlled way. MALDI-TOF MS experiments combined with a study of the monomer and the polymer formation lead to the proposed polymerization mechanism, whereby the degree of polymerization depends on the irreversible decomplexation of the Ni-catalyst.

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The Ni-catalyzed Polymerization of Poly(3-alkoxythiophene)s

Supporting Information for:

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MALDI-TOF mass spectra

Figure S1: MALDI-TOF mass spectrum after a polymerization time of 30 min. ■ and ▲ respectively correspond to ions of P3AOT with H/H, H/Br as end-groups. The highlighted signals with a star correspond to fragments after a β cleavage.

Figure S2: MALDI-TOF mass spectrum after a polymerization time of 2h. ■ and ▲ correspond respectively to ions of P3AOT with H/H, H/Br as end-groups. The highlighted signals with a star correspond to fragments after a β cleavage.

Figure S3: Typical ^1H NMR spectrum of the quenching reaction of the Li-compound.

Figure S3: Typical ^1H NMR spectrum of the quenching reaction of the Li-compound.

Figure S4: Typical ¹H NMR spectrum of the quenching reaction of the Grignard reagent.

Figure S5: ^{31}P NMR spectrum recorded in THF of a P3AOT polymerization initiated with Ni(dppp)Cl_2 after 1h.