# **Macromolecules**

# One-Step Simple Preparation of Catalytic Initiators for Catalyst-Transfer Kumada Polymerization: Synthesis of Defect-Free Polythiophenes

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**Supporting Information** 

**ABSTRACT:** Externally initiated living catalyst-transfer polymerization based on Ni(II)-catalyzed Kumada coupling of aromatic halogen-substituted Grignard monomers is an established and highly efficient method for the controlled preparation of conjugated polymers such as polythiophenes and poly(*p*-phenylenes). In this contribution, we report a simple preparation of external catalytic initiators for such a



polymerization based on oxidative addition between a readily available Ni(0) complex  $Ni(dppp)_2$  (where dppp is 1,3bis(diphenylphosphino)propane) and various aryl halides. As a direct challenge to previous reports and established opinion that such a reaction would be impossible, this clean and efficient oxidative addition enables simple preparation of highly reactive catalytic initiators for the catalyst-transfer polymerization. In particular, we demonstrated that polymerization of 5-halo-2thienylmagnesium monomers initiated by these catalysts produced highly regioregular, defect-free polythiophenes and block copolymers with high molecular weight and low polydispersity. We also found that the polymers prepared using this catalytic system showed a uniform end-group composition with one end terminated with an aryl group from the catalytic initiator and the other end with Br. The bromine termination could potentially allow further synthetic manipulations with the polymers. Overall, this convenient and advantageous method for the preparation of external catalytic initiators provides a simple and straightforward approach to controlled synthesis of polythiophenes and other conjugated polymers.

# ■ INTRODUCTION

Organic semiconducting polymers have emerged as materials of choice for electronic and optoelectronic applications (such as thin-film transistors, photovoltaic cells, and polymer lightemitting diodes)<sup>1</sup> and chemo- and biosensing devices.<sup>2</sup> Among semiconducting polymers, polythiophenes (PTs) hold a special place due to their excellent thermal and environmental stability, high conductivity in doped form, and possibility to adjust their optical and electronic characteristics by structural modifications.<sup>3</sup> The pressing need to fine-tune the polymers' properties to meet the requirements of particular applications necessitates searching for simple and efficient synthetic methods to prepare PTs and their copolymers, as well as other classes of semiconducting polymers, in a controlled manner and with precisely defined molecular composition. Living catalysttransfer polymerization based on Ni-catalyzed Kumada coupling of 5-bromo-2-thienylmagnesium monomers became a well-established method for preparing PTs and their block copolymers<sup>4</sup> following the milestone discovery by McCullough<sup>5</sup> and Yokozawa<sup>6</sup> that this process occurs in a living chain-growth fashion. Over the recent years it has been a subject of detailed mechanistic studies, which revealed that the polymerization proceeds through a catalytic cycle mechanism involving a series of consecutive transmetalation-oxidative addition-reductive elimination steps in a manner similar to elementary steps in a typical transition-metal-catalyzed reaction, with strong dependence of the mechanism on the structure of catalyst.<sup>7</sup>

Participation of an associative Ni(0)-arene  $\pi$ -complex as a key intermediate was proposed to explain the "living" character of the polymerization; however, this intermediate has not been experimentally observed in the polymerization (although recent results by McNeil showed strong, albeit indirect, evidence in favor of participation of a Ni(0)-arene intermediate in the polymerization process<sup>8</sup>). Typically, in order to stay within the "living" regime, the polymerization has to be carried out at ambient temperature, and due to lower reactivity of the conventionally used Ni(II) catalysts (e.g., Ni(dppp)Cl<sub>2</sub>, where dppp is 1,3-bis(diphenylphosphino)propane), this generally yields polymers with low to moderate molecular weights and insufficient regioregularity.<sup>9</sup> Furthermore, there is a prominent possibility of the occurrence of transfer of the propagating Ni(II) reactive center to another chain during polymerization<sup>7c</sup> or chain termination by disproportionation;<sup>10</sup> therefore, the polymerization sometimes is described as quasi-"living".5b Achieving truly "living" polymerization thus depends upon the availability of highly reactive universal catalytic systems. An important milestone was introduction, by Kiriy<sup>11</sup> and Luscombe,<sup>12</sup> of externally initiated catalyst-transfer polymerization where stable aryl-Ni(II) initiating complexes, e.g. square-planar complex 1, could be used to carry out Kumada

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Scheme 1. Various Routes To Prepare External Catalytic Initiator in Catalyst-Transfer Polymerization (X = Cl, Br) and Its Use To Prepare PT by Kumada Polymerization of Grignard Monomer 3



polymerization of Grignard monomer 3 to form PT polymers and block copolymers with well-defined molecular composition (Scheme 1). Since initial reports, new more efficient catalysts for externally initiated polymerization have been developed, and this approach has been extended toward other classes of important semiconducting polymers such as poly(*p*-phenylene)s,<sup>13</sup> polyfluorenes,<sup>14</sup> poly(*p*-phenylene ethynylene)-s,<sup>15</sup> alternating copolymers,<sup>16</sup> and block copolymers<sup>17</sup> as well as some complex polymer architectures.<sup>18</sup> In another important development, externally initiated catalyst-transfer polymerization was used with surface-immobilized external initiators to prepare surface-attached brushes and thin films of semiconducting polymers.<sup>19</sup> Thus, it looks obvious that externally initiated catalyst-transfer polymerization is superior in preparation of highly regioregular PTs as well as other classes of semiconducting polymers in a controlled manner. In all known cases, the best external catalytic initiators were square-planar Ni(II) complexes stabilized by bidentate phosphine ligands (such as complex 1), whereas using monodentate ligands (such as PPh<sub>3</sub>) proved to yield catalytic initiators with poor performance.<sup>11a,20</sup>

In conventional methods, preparation of the external catalytic initiators with bidentate ligands requires a relatively complicated synthetic procedure. In an earlier procedure developed by Luscombe,<sup>12</sup> oxidative addition of an aryl halide to a commercially available Ni(0) complex Ni(PPh<sub>3</sub>)<sub>4</sub> resulted in a square-planar intermediate 2 (Scheme 1, route A). This was followed by ligand exchange between the intermediate 2 and dppp to form catalyst 1. This indirect method is relatively complex and low yielding and results in contamination of the target polymerization catalytic initiator 1 with an undesired monodentate ligand PPh<sub>3</sub>. Because external catalytic initiators containing monodentate ligands are inferior catalysts in the chain-growth Kumada polymerization, contamination with such ligands leads to less efficient polymerization, with the resulting PT polymers having relatively low molecular weight. Furthermore, monodentate ligands may facilitate disproportionation and subsequent aryl-aryl homocoupling of the catalytic initiator. Senkovskyy et al. recently developed an alternative procedure which includes reaction of Ni(dppp)Cl<sub>2</sub> with sterically crowded Grignard reagents (Scheme 1, route B).<sup>21</sup> This method is convenient in producing external catalytic initiator 1 but also suffers from the possibility of aryl-aryl homocoupling and therefore is limited to sterically crowded

aryl moieties (and also requires relatively complex work-up and purification procedure). So far, the best approach available for the preparation of catalytic initiator **1** was developed by Kiriy.<sup>11b</sup> It starts with the reaction between an aryl halide and Et<sub>2</sub>Ni(bipy) (where bipy is 2,2'-bipyridyl), and the intermediate complex is further converted to **1** via ligand exchange (Scheme 1, route C). This method enabled preparation of an uncontaminated and reactive external catalytic initiator, which was used to prepare highly regioregular defect-free poly(3hexylthiophene) (P3HT) via controlled chain-growth polymerization.<sup>22</sup> However, Et<sub>2</sub>Ni(bipy) is not easily available, unstable, and hard to handle (due to its high reactivity with moisture and oxygen), and the overall preparation still requires a more complex two-step procedure.

Obviously, the simplest direct approach to prepare uncontaminated catalytic initiators like complex 1 would be to employ oxidative addition of Ni(0) complexes with bidentate ligands (e.g.,  $Ni(dppp)_2$ ) to aryl halides (Scheme 1, route D)). This, however, has never been accomplished because Ni(0)complexes with bidentate phosphine ligands were considered either unreactive toward aryl halides or yielding complex mixtures of various byproducts.<sup>20,21,23</sup> In our search for a simpler method enabling preparation of pure and efficient external catalytic initiator like 1, we decided to investigate more closely direct oxidative addition of an easily available<sup>24</sup> and stable Ni(dppp)<sub>2</sub> to aryl halides as, if successful, this would produce external catalytic initiators in a highly yielding simple route and uncontaminated with monodentate ligand or any other undesirable byproducts. Indeed, generating Ni(II) external initiators by this direct method resulted in a highly efficient catalytic system for Kumada "living" polymerization, allowing simple preparation of defect-free PT polymers and block copolymers with high molecular weight in short reaction times. In this article, we describe preparation by this novel method and properties of the resulting external catalytic initiators, and their application in chain-growth living polymerization, as well as some unexpected mechanistic consequences of using these catalytic initiators.

#### RESULTS AND DISCUSSION

**Reaction of Aryl Halides with Ni(dppp)**<sub>2</sub>. In spite of the earlier reports and established consensus that Ni(0) complexes containing bidentate phosphine ligands do not react with aryl halides,<sup>23</sup> we decided to investigate the reaction between 5-

bromo-2,2'-bithiophene 4 and  $Ni(dppp)_2$  (Scheme 2A). Although not commercially available,  $Ni(dppp)_2$  can be easily

Scheme 2. Preparation of External Catalytic Initiators 5 and 7 by Direct Oxidative Addition of Ni(dppp)<sub>2</sub> to Aryl Bromides as Well as by the Ligand-Exchange Route



prepared in large scale using a simple literature procedure<sup>24</sup> and can be stored for a long time. The choice of bithienyl (rather than more typical phenyl or substituted phenyl) as an aryl species was prompted by the anticipated higher reactivity of the bithiophene-based catalytic initiator in chain-growth Kumada polymerization. For the reaction, an equimolar mixture of 4 and  $Ni(dppp)_2$  was stirred in THF or toluene at 50 °C. The reaction was monitored by <sup>31</sup>P NMR where  $Ni(dppp)_2$  could be easily identified by a characteristic singlet at 12.8 ppm. In THF solvent, over a short period of time the formation of two doublets at approximately 19 and -3 ppm ( $J_{P-P} = 66$  Hz) typical of the square-planar Ni(II) complex 5 was observed, and after 24-48 h reaction time the transformation was approximately 80% complete (Figure 1A). The transformation of bromide 4 to complex 5 was very clean, with essentially no byproducts present in the reaction mixture (as was judged by <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy).

In the case of toluene solvent, stirring the reaction mixture for 48 h at 50 °C resulted in substantial decrease of the initial <sup>31</sup>P NMR singlet of Ni(dppp)<sub>2</sub> (when compared to the signal intensity of an external reference 80% H<sub>3</sub>PO<sub>4</sub>), but no new signals were observed (Figure 1B). When, however, the reaction mixture was concentrated in vacuo and the residual product redissolved in THF, in the <sup>31</sup>P NMR spectrum we observed the same pair of doublets characteristic of the squareplanar complex 5. On the basis of the intensity decrease of the signal of  $Ni(dppp)_2$ , we could estimate similar conversion to the complex 5 as in the case of using THF solvent. Thus, independent of the solvent, the reaction between 5-bromo-2,2'bithiophene 4 and Ni(dppp)<sub>2</sub> cleanly produced Ni(II) catalytic initiator 5. Probably, the absence of NMR signals from 5 in toluene could be explained by deviation from the square-planar coordination of Ni(II) in the diamagnetic complex 5 due to steric repulsion between bithienyl and Br substituents, resulting



**Figure 1.** (A) <sup>31</sup>P NMR spectrum of the reaction between bithienyl bromide 4 and Ni(dppp)<sub>2</sub> in THF at 50 °C after 24 h. (B) <sup>31</sup>P NMR spectrum of the same reaction at 50 °C in toluene (the NMR trace of the reaction mixture after 48 h reaction time was shifted for better clarity and does not correspond to the chemical shift scale at the bottom of the figure). For the reaction in toluene the spectra were acquired with 80%  $H_3PO_4$  external reference for signal intensity calibration.

in the formation of a less planar structure with increased paramagnetic character (indeed, the extreme case of such deviation would be formation of a paramagnetic tetrahedral Ni(II) complex). We found similar distortion of the square-planar geometry in a single-crystal X-ray structure of a related compound Ni(dppp)Br<sub>2</sub> (Figure S1 in the Supporting Information) which was obtained as a product of Ni(dppp)<sub>2</sub>-promoted homocoupling of two molecules of 4 (*vide infra*). In good agreement with its somewhat paramagnetic character, Ni(dppp)Br<sub>2</sub> did not show any signals in its <sup>31</sup>P NMR spectrum. In contrast to toluene solvent, the square-planar geometry of Ni(II) center can be better stabilized in THF due to strong ability of THF molecules to coordinate at the outer-sphere axial positions of the Ni(II) complex.

One remarkable feature of the reaction between bromide 4 and  $Ni(dppp)_2$  was the absence of quaterthiophene 6 which would be a product of aryl-aryl homocoupling between two molecules of 4. Indeed, aryl-aryl homocoupling is a very common reaction of aryl halides occurring in the presence of equimolar amount of a Ni(0) complex.<sup>25</sup> Independent of whether the reaction between 4 and  $Ni(dppp)_2$  was carried out in THF or toluene, analysis of the final reaction mixture by UV/vis spectroscopy (since quaterthiophene shows a distinct absorption band at 386 nm<sup>26</sup>) revealed formation of less than 1% of 6 (Figure S2). Although no quaterthiophene was found when the reaction was carried out at 50  $^\circ C$  for 48 h, a substantial amount of quaterthiophene 6 was formed when the reaction in toluene was carried out at 70 °C for 7 days. In addition to quaterthiophene, in such conditions we observed formation of a significant amount of dark-red crystalline precipitate of Ni(dppp)Br<sub>2</sub> (which was identified by singlecrystal X-ray analysis). Formation of both quaterthiophene and Ni(dppp)Br<sub>2</sub> was consistent with disproportionation between

two molecules of **5** followed by aryl-aryl homocoupling (Scheme 3).<sup>10</sup> Thus, it appears that aryl-aryl homocoupling

Scheme 3. Suggested Mechanism of Aryl–Aryl Homocoupling through Disproportionation between Two Molecules of Catalytic Initiator 5



was negligible at 50  $^{\circ}$ C but became a substantial reaction pathway at 70  $^{\circ}$ C—an interesting example of temperature control of the reaction course.

For comparison purposes, we also attempted to prepare the Ni(II) complex 5 following the ligand exchange route developed by Luscombe (Scheme 2A).<sup>12</sup> The product mixture was characterized by <sup>1</sup>H and <sup>31</sup>P NMR. Although the ligandexchange route did result in the formation of 5, we also observed a significant amount of quaterthiophene 6, indicating the readily occurring homocoupling between two sterically unhindered bithienyl moieties. The abundance of the homocoupling product (standing in contrast with the absence of such a product in the case of direct reaction between 4 and  $Ni(dppp)_2$ ) can probably be explained by facilitation of the coupling by Ni(PPh<sub>3</sub>)<sub>4</sub>—a Ni(0) complex with a monodentate spectator ligand. Another typically related product-Ni(dppp)- $X_2$  (where X is a halogen from the initial aryl halide)—was also observed, thus pointing to disproportionation as the main homocoupling route. Since  $Ni(dppp)X_2$  can catalyze nonexternally initiated Kumada polymerization, some loss of the "living" character (and lower molecular weight and worse regioregularity) would be a likely consequence of using the catalytic initiator prepared by this ligand-exchange procedure. In addition, the ligand exchange procedure resulted in significant presence of monodentate ligand PPh<sub>3</sub> in the final product (up to 50% even after multiple reprecipitation attempts) which could have a detrimental effect on the chain-growth polymerization. Therefore, preparation of 5 by direct reaction between aryl halide 4 and  $Ni(dppp)_2$  has a clear advantage over the traditional schemes based on ligand exchange, and this advantage was critical in its performance in Kumada polymerization discussed below.

To better understand electronic nature of the catalytic initiator 5, we carried out electrochemical studies. Cyclic voltammograms (CVs) in THF solutions of complex 5 (prepared by direct reaction between bromide 4 and Ni(dppp)<sub>2</sub>

as well as by the ligand exchange procedure as outlined in Scheme 2A),  $Ni(dppp)_2$ , and  $Ni(dppp)Br_2$  are shown in Figure 2. The Ni(0) complex exhibited two reversible one-electron



Figure 2. Cyclic voltammograms of catalytic initiator 5 and related reference compounds. Data were acquired in THF solutions at 0.1 V  $\rm s^{-1}$  scan rate.

waves at  $E_{1/2}$  0.08 and -0.66 V vs Ag/Ag<sup>+</sup> electrode. These waves could be assigned to Ni(I/0) and Ni(II/1) couples, respectively. Both samples of complex **5** exhibited almost superimposable CV traces, with reversible waves at  $E_{1/2}$  -0.71 V (directly prepared) or  $E_{1/2}$  -0.76 V (prepared by ligand exchange) corresponding to Ni(II/I) couple, but practically no Ni(I/0) wave. Indeed, the position of the Ni(II/1) redox wave was similar to a redox peak of the reference complex Ni(dppp)Br<sub>2</sub> ( $E_{1/2}$  -0.71 V). This result indicated that, independent of the preparation procedure, complex **5** was a Ni(II) species with a square-planar metal configuration.

Although a solution of 5 prepared by the reaction between 4 and Ni(dppp)<sub>2</sub> at 50 °C could be immediately used for initiation of Kumada polymerization (as it contained ~80% of 5, along with 1 equiv of released dppp ligand, small amounts of unreacted 4 and Ni(dppp)<sub>2</sub>, and trace dppp oxide), we also found useful to purify the catalyst by precipitation into hexanes. The precipitation could help to remove unreacted 5-bromo-2,2'-bithiophene 4 and only partially help in removing free dppp ligand and unreacted Ni(dppp)<sub>2</sub>; however, the latter two impurities could not interfere with subsequent Kumada polymerization (as Ni(dppp)<sub>2</sub> does not catalyze such a polymerization, vide infra). After precipitation, the collected solid could be dried *in vacuo* and stored in a refrigerator at -30°C for a few months with no detectable decrease in catalytic activity. When needed, the solid could be redissolved in THF to yield a solution of the catalyst 5. We found that both solid and solutions of 5 were not particularly air-sensitive and could be handled with reasonable precaution normally used with transition-metal-catalyzed reactions.

To check for the generality of the direct oxidative addition of Ni(dppp)<sub>2</sub> to aryl halides, we investigated reaction between chloro- and bromobenzene and Ni(dppp)<sub>2</sub> in THF (Scheme 2B). In the case of bromobenzene, after 48 h of stirring the reaction mixture at 40 °C, we found the characteristic pair of doublets in the <sup>31</sup>P NMR spectrum at 22 and -3 ppm ( $J_{P-P} = 46 \text{ Hz}$ ) which could be attributed to the complex 7 with square-planar configuration of the Ni(II) center (Figure S3). The reaction was a little slower as compared to the case of 5-bromo-

#### Scheme 4. Preparation of Various Polythiophenes by Externally Initiated Kumada Polymerization<sup>a</sup>



<sup>a</sup>The polymers chains were mainly Br-terminated, although fractions of H-terminated chains were also observed in some cases.

2,2'-bithiophene 4, as only approximately 40% conversion to 7 was observed. Nevertheless, the reaction was clean and resulted in no aryl-aryl homocoupling despite the lack of steric hindrance of the unsubstituted phenyl (quenching the reaction mixture with aqueous HCl and subsequent chromatography analysis revealed less than 1% of the homocoupling product biphenyl). Upon precipitation of the reaction mixture in hexanes the isolated solid product showed approximately 75% of the catalyst 7 by <sup>31</sup>P NMR (with the rest mainly being unreacted Ni(dppp)<sub>2</sub> and free dppp ligand). In contrast, chlorobenzene produced no detectable product 7, and only starting materials were detected in the reaction mixture. Thus, we concluded that, in contrast to previous literature reports, oxidative addition between Ni(0) complex Ni(dppp)<sub>2</sub> and aryl bromides (as well as iodides but not chlorides) is a general reaction. Unlike previous approaches to catalytic initiators for catalyst-transfer Kumada polymerization, this method does not produce aryl-aryl homocoupling products even with sterically unhindered aryl groups, nor does it result in contamination with any other undesired byproducts. Since formation of bithiophene-based catalyst 5 was a clean and high-yielding process, in addition to high reactivity of the catalyst 5 in Kumada polymerization, this made it a natural choice for further polymerization studies.

Kunada Catalyst-Transfer Polymerization Catalyzed by Complexes 5 and 7. The most important application of aryl–Ni(II) complexes like 5 is using them as external catalytic initiators in chain-growth catalyst-transfer Kumada polymerization of 5-bromo-2-thienylmagnesium monomers to prepare polythiophenes. Therefore, we studied 5 as a catalytic initiator for polymerization of 5-bromo-4-hexyl-2-thienylmagnesium chloride (3). Typically, the Grignard monomer 3 is prepared by reaction between 1 equiv of a sterically hindered Grignard reagent (e.g., isopropylmagnesium chloride) and 1 equiv of 2,5dibromo-3-hexylthiophene. We found experimentally (and this finding was in agreement with previous literature data<sup>27</sup>) that using exactly a 1:1 ratio of dibromothiophene to *i*-PrMgCl did not result in complete conversion to 3 even after prolonged reaction time. Thus, as a matter of practical convenience, we found that using *i*-PrMgCl in a slight excess (1.1 equiv) enabled achieving complete conversion to 3 (actually ~75% of 3 and 25% of its polymerization-unreactive regioisomer, as was determined by <sup>1</sup>H NMR analysis after quenching the reaction mixture with water) in 1 h reaction time at 0 °C (see the Supporting Information for experimental details). The small residual amount of unreacted *i*-PrMgCl did not affect the living polymerization (vide infra), and therefore this method can be recommended as a practically convenient way to prepare Grignard monomer 3 from an easily available dibromothiophene starting material. Adding a catalytic amount of catalyst 5 (1 mol %) to a solution of 3 in THF and allowing them to react for 1 h at 35 °C, followed by precipitation of the reaction mixture into methanol, produced completely regioregular poly(3-hexylthiophene) (P3HT) P1 (Scheme 4). The percent regioregularity in poly(3-alkylthiophene)s refers to the fraction of head-to-tail (HT) coupled repeating units; thus, a 100% regioregular PT has 100% of HT coupling, whereas a polymer with low percentage of HT coupling (50-80%) would be considered regiorandom.<sup>28</sup> The percent regioregularity is normally determined by careful integration of the two signals between 2.4 and 3.0 ppm in <sup>1</sup>H NMR spectra; these signals belong to  $\alpha$ -CH<sub>2</sub> protons of the 3-alkyl chains, and a ratio of their integral intensities serves as a reliable measure of regioregularity of 3-alkyl-substituted PTs.<sup>29</sup> As can be seen



Figure 3. (A) GPC elution traces for P3HT polymers P1 prepared by varying the amount of catalytic initiator 5 added to a solution of Grignard monomer 3. Solid traces correspond to samples prepared by quenching the reaction mixture with methanol; dash trace: quenched with 5 M HCl. (B) Experimental and calculated dependence of number-average molecular weight ( $M_n$ ) of P1 from the reciprocal molar fraction of catalytic initiator 5 (solid line represents linear fit of experimental data,  $R^2$  0.954; dash line: calculated dependence).  $M_n$ 's were determined by GPC relative to polystyrene standards.

Table 1. Characterization of Polythiophenes Prepared by Externally Initiated Catalyst-Transfer Kumada Polymerization<sup>*a,b*</sup>

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entry	polymer	catalyst, mol %	yield, %	M <sub>n</sub> (calcd), kDa	<i>M</i> <sub>n</sub> (GPC), <sup><i>c</i></sup> kDa	$M_{ m w}/M_{ m n}$	% HT <sup>a</sup>
1	P1 $(P3HT)^e$	5 (0.3)	76	55.3	60.0	1.47	100
2	<b>P1</b> (P3HT) <sup>e</sup>	5 (0.5)	71	33.2	45.3	1.43	100
3	<b>P1</b> (P3HT) <sup>e</sup>	5 (1.0)	74	16.6	26.7	1.53	100
4	<b>P1</b> (P3HT) <sup><i>f</i></sup>	5 (1.0)	75	16.6	24.0	1.54	100
5	P1 $(P3HT)^e$	5 (3.0)	77	5.5	10.1	1.72	100
6	$P2^{e}$	5 (1.0)	69	40.8	41.0	1.41	100
7	$P3^{e}$	5 (1.0)	72	40.8	41.0	1.46	100
8	<b>P4</b> (P3HT) <sup>e</sup>	7 (1.0)	66	16.6	27.0	1.25	100
9	<b>P4</b> (P3HT) <sup>f</sup>	7 (1.0)	73	16.6	24.0	1.16	100
10	<b>P5</b> (P3HT) <sup>e</sup>	5 (1.0)	55	16.6	16.9	2.00	100
11	P6 $(P3HT)^e$	7 (1.0)	40	16.6	14.0	1.75	100

<sup>*a*</sup>Data were obtained for crude polymer samples, without additional purification. <sup>*b*</sup>The Grignard monomers used for polymerization were prepared by reacting 1.1 equiv of *i*-PrMgCl with 1 equiv of the corresponding dibromothiophene at 0 °C for 1 h, except entries 10 and 11, where 1 equiv of *i*-PrMgCl was used. <sup>*c*</sup>Relative to polystyrene standards. <sup>*d*</sup>Determined by <sup>1</sup>H NMR. <sup>*c*</sup>Reaction was quenched with methanol. <sup>*f*</sup>Reaction was quenched with 5 M HCl.



Figure 4. (A) Number-average molecular weight  $(M_n)$  and polydispersity index (PDI) of polymer P1 as a function of the monomer 3 percent conversion (solid line: calculated data). (B)  $M_n$  of P1 as a function of polymerization time. Polymerization was carried out with 0.25 mol % of 5;  $M_n$  and PDI  $(M_w/M_n)$  were determined by GPC relative to polystyrene standards, and percent conversion was determined by <sup>1</sup>H NMR.

from the <sup>1</sup>H NMR spectrum of **P1** in the Supporting Information, there was only one peak in this region (a triplet at 2.80 ppm) which corresponded to HT junction, and the essential absence of other peaks reflected 100% regioregularity of **P1**. The 100% regioregularity of **P1** was also confirmed by the single aromatic peak at 6.98 ppm corresponding to HT

junction and the absence of lower-field signals in the aromatic region corresponding to other junction types.<sup>22</sup>

In multiple experiments, we consistently prepared P3HT P1 with number-average molecular weight  $(M_n)$  ranging from 10 to 80 kDa, depending on the molar fraction of catalyst 5. In all the cases, obtained P3HT polymers were essentially defect-free

(100% regioregularity) and were characterized by narrow polydispersity index, PDI  $(M_w/M_n < 2)$  even in crude samples, without any additional purification steps. The strongest evidence in favor of living chain-growth polymerization catalyzed by 5 was the fact that the molecular weight of P3HT P1 was linearly dependent on the reciprocal molar fraction of 5 taken for polymerization (Figure 3 and Table 1, entries 1-5). Experimentally (GPC) obtained number-average molecular weights  $(M_n)$  were somewhat higher than theoretically predicted  $M_n$ 's, yet experimentally obtained molecular weights fell on the straight line with the slope identical to the theoretical prediction (Figure 3B). The higher GPC molecular weights of the polymer P1 relative to the theoretically predicted weights were reproducibly obtained in all polymerization runs. In a not perfectly "living" Kumada catalyst-transfer polymerization, experimentally obtained molecular weights would be lower than the theoretically predicted ones. The lower molecular weights originate from occasional chain transfer occurring through catalytic metal center migration from a growing polymer chain to a monomer in solution, which initiates a new polymer chain. The increased molecular weight, in this sense, reflects an exceptionally "living" character of the polymerization catalyzed by 5. An apparent "increase" could be related to a known overestimation of the molecular weights by polystyrene-calibrated GPC which becomes particularly significant at lower molecular weights (but turns into underestimation at particularly high molecular weights).<sup>30</sup> This may introduce a systematic error which can explain why both experimentally found and theoretically calculated M<sub>n</sub> data sets fell on parallel straight lines in the  $M_n$  vs  $1/[5]_0$  plot (Figure 3B).

Linear dependence of the **P1**'s number-average molecular weight  $M_n$  on Grignard monomer **3** conversion (Figure 4A) also reflected the living chain-growth mechanism of polymerization. Furthermore, the polymerization was indeed rapid and efficient; it was practically complete in 20 min after addition of **5** to the Grignard monomer (Figure 4B).

We found some tendency for the polymers to undergo disproportionation upon quenching of the polymerization reaction mixture with methanol, which resulted in pronounced higher molecular weight shoulders in GPC traces (Figure 3A). The intensity of these shoulders increased proportionally to the catalyst **5** loading, which was likely related to the larger number of initiating sites increasing the propensity for the disproportionation to occur. This phenomenon has been observed previously<sup>27,31</sup> and is seemingly facilitated by quenching the polymerization reaction mixture with methanol. Indeed, we found that quenching the polymerization mixture with 5 M HCl (instead of methanol) produced **P1** with almost the same molecular weight and polydispersity but without the higher molecular weight shoulder (Figure 3A and Table 1, entries 3 and 4).

One of the essential characteristics of a truly living polymerization is the possibility to prepare block copolymers by sequential addition of different monomers to the reaction mixture and allowing them enough time to react completely. By adding Grignard monomers **3** and **8** to a solution of the external catalytic initiator **5** (1 mol %) at 35 °C, we prepared two completely regioregular (~100% HT coupling within each block) block copolymers **P2** and **P3** with high molecular weights and in short polymerization times (Scheme 4 and Table 1, entries 6 and 7). The GPC traces for both block copolymers showed essentially monomodal narrow distribution

of molecular weights (Figure S4 in the Supporting Information) which was consistent with living character of the polymerization where all the initially formed reactive chains were active through the entire polymerization process. In preparation of block copolymers by chain-growth polymerization, it is critical to ensure complete consumption of the first monomer before addition of the second monomer (otherwise the second block would become a random copolymer of both monomers). The requirement of complete consumption of the first monomer (particularly at a high conversion when the reaction slows down) requires a polymerization reaction to be highly efficient. Catalytic initiator 5 prepared by direct reaction between 4 and  $Ni(dppp)_2$  perfectly satisfies this requirement. Indeed, the homogeneous molecular composition of both blocks in P2 and P3 was unambiguously supported by clean and sharp <sup>1</sup>H NMR peaks corresponding to aromatic hydrogens.<sup>32</sup> Beyond serving as a demonstration of living character of this polymerization and its synthetic versatility in controlled preparation of conjugated copolymers, the block copolymers P2 and P3 will be further converted into temperature-responsive poly(N-isopropylacrylamide)-grafted amphiphilic PTs for our ongoing studies of energy migration in conjugated polymers.<sup>33</sup>

We also tested phenyl-Ni(II) catalytic initiator 7 in polymerization of the Grignard monomer 3. As expected, this produced highly regioregular Ph-terminated P3HT **P4** in a living chain-growth polymerization (Scheme 4 and Table 1, entries 8 and 9). Therefore, the choice of an actual catalyst for polymerization (and aryl halide as a starting material for the catalyst) is mostly dictated by the terminal group which needs to be incorporated, whereas catalytic reactivity is not strongly dependent on the aryl halide choice.

To determine if the small excess of *i*-PrMgCl used in preparation of Grignard monomers 3 and 8 (Scheme 4) could affect the living polymerization, we also studied externally initiated (with 1 mol % of catalytic initiators 5 or 7) polymerization of Grignard monomer 3 prepared using exactly 1 equiv of *i*-PrMgCl. The total yield of the polymers obtained in this way (polymers P5 and P6 in Table 1) was lower, and they were characterized by somewhat smaller molecular weights and broader polydispersities (relative to the same polymers derived from Grignard monomer 3 prepared with 1.1 equiv of *i*-PrMgCl), which was consistent with the presence of unreacted 2,5-dibromo-3-hexylthiophene which probably acted as a chain transfer reagent in the polymerization. Thus, using a small excess of *i*-PrMgCl to prepare Grignard monomers for polymerization deems practically convenient and results in robust living polymerization. On the other hand, using large excess of i-PrMgCl (e.g., 2 equiv) to generate Grignard monomer 3 yielded P3HT polymers with low molecular weights (around 4 kDa when 1 mol % of 5 or 7 was used). Clearly, the large excess of unreacted *i*-PrMgCl was detrimental for living polymerization.

To further evaluate the possible role of residual Ni(dppp)<sub>2</sub> present in the catalyst solution, we attempted to carry polymerization of 3 catalyzed by Ni(dppp)<sub>2</sub> in the conditions similar to those used in polymerization with catalysts 5 or 7. As expected, no polymerization occurred, and even after prolonged reaction time, only a low yield (less than 5%) of short oligomers was obtained. Thus, Ni(dppp)<sub>2</sub> (which was always present as a small impurity in the reaction mixture due to incomplete reaction of the formation of 5 or 7) was not capable itself of promoting polymerization.

Scheme 5. Mechanism of Externally Initiated Kumada Catalyst-Transfer Polymerization Leading to Regioregular Poly(3-alkylthiophene)s with Ar/H and Ar/Br Terminations



**Figure 5.** Fragments of MALDI-ToF (A, B) and <sup>1</sup>H NMR (C, D) spectra showing signal assignments for P3HT **P1** prepared with 1 mol % of bithiophene initiator **5** upon quenching with methanol (A, C) and with 5 M HCl (B, D). Spectra A and C correspond to polymer in entry 3 and spectra B and D to polymer in entry 4 of Table 1. <sup>1</sup>H NMR spectra were acquired at 500 MHz in  $CDCl_3$ .

Further Details on the Mechanism of Kumada Polymerization Catalyzed by Directly Prepared Complexes 5 and 7. The mechanism of externally initiated catalyst-transfer chain-growth Kumada polymerization of Grignard monomer 3 is well established and includes a consecutive series of transmetalation, reductive elimination, and oxidative addition (Scheme 5). The Ni(0) intermediates II and IV $\pi$  formed in the reductive elimination steps remain bound to the PT chain through formation of a  $\pi$ -complex, and the Ni(0) center migrates intramolecularly to the terminus of the growing polymer chain, where it undergoes oxidative addition to the C-Br bond. Interestingly, as was convincingly demonstrated by Kiriy,<sup>34</sup> the Ni(0) migration is not exclusively unidirectional (toward the nearest C-Br polymer chain end), but the metal center can randomly walk in any direction, especially with higher molecular weight polymer chains. The mechanism of polymerization as well as structure of the intermediates should be reflected in the end-group composition of the polymer chains which can be studied by mass spectrometry (MALDI-ToF) and <sup>1</sup>H NMR end-group analysis.

We thoroughly studied the end-group composition in the P3HT polymers obtained by polymerization of Grignard monomer 3 in the presence of 1 mol % of catalytic initiators 5 and 7. To account for possible variations of end-group composition due to quenching conditions, we prepared two polymer samples for each initiator by dividing the reaction mixture on two equal portions and quenching each portion either with methanol or with 5 M HCl (which are shown as entries 4-5 and 8-9 in Table 1). For the end-group analysis, all four polymer samples were thoroughly purified by extraction in a Soxhlet apparatus successively with methanol, hexanes, and chloroform, and chloroform fractions were used in the study. With both initiators, incorporation of aryl terminal groups in all PT chains was evident from <sup>1</sup>H NMR spectra of the purified polymers which displayed distinct signals from bithienyl or phenyl end groups (shown in the Supporting Information). When the polymerization was initiated with bithiophene (biTh) catalyst 5, MALDI-ToF analysis showed predominant biTh/Br termination in the case of methanol quenching and approximately equal distributions of biTh/Br- and biTh/Hterminated chains in the case of HCl-quenched polymer (Figure 5A,B). Since MALDI-ToF data mainly reflect composition of lower molecular weight fractions, we also studied <sup>1</sup>H NMR spectra which provide better overall representation of the high molecular weight polymer samples. Figure 5C,D shows expanded fragments of <sup>1</sup>H NMR spectra corresponding to the area of signals of  $\alpha$ -CH<sub>2</sub> protons. Two small triplets around 2.6 ppm are attributed to  $\alpha$ -CH<sub>2</sub> protons of the terminal 3-hexylthien-2,5-diyl unit in regioregular P3HT.<sup>22</sup> Of these two triplets, a more downfield one corresponds to H-terminated chains whereas a more upfield signal originates from Br-terminated P3HT chains. The intensity ratio between these two signals was in a good agreement with the MALDI-ToF data, thus indicating dominating Br termination of one chain end in both polymer samples independent of the polymerization quenching method. This finding was in clear contrast with previous data on chaingrowth Kumada catalyst-transfer polymerization where almost exclusive Ar/H terminated PT chains had been observed.

The unexpected predominance of biTh/Br-terminated chains prompted us to look more closely at the reactive species existing during the polymerization. For this purpose, the polymerization of Grignard monomer **3** was carried out in an NMR tube with 18 mol % of 5 in order to obtain sufficient  $^{31}P$ NMR signal. Adding monomer 3 to the catalyst 5 caused no change in chemical shifts of the two doublets at 18 and -3 ppm characteristic of Ni(II) square-planar complex 5 but made them much sharper and better resolved. In addition, a clear signal appeared at -18 ppm characteristic of free dppp ligand, as well as a small broad signal near 17 ppm (Figure S5). This observation was in agreement with complex  $IV\sigma$  being likely the dominating species during the polymerization (Scheme 5). The persistence of square-planar Ni(II) reactive complex IV $\sigma$ during polymerization was consistent with previous experimental studies by McNeil, who observed similar Ni(II) squareplanar complex as the resting state for Ni(dppp)Cl<sub>2</sub>-catalyzed chain-growth polymerization of 3.<sup>7b</sup> The <sup>31</sup>P NMR spectrum did not change even after prolonged reaction time, but postpolymerization quenching the reaction mixture with methanol immediately resulted in disappearance of the signals.

The persistence of the square-planar Ni(II) active species during the polymerization makes even more difficult to explain the predominant Br termination of the polymer chains. Indeed, protolysis of the Ni(II) reactive center in the intermediate IV $\sigma$ upon treatment with a protic solvent or a strong acid was supposed to deliver H-terminated polymer chains, in agreement with numerous previous studies. Thus, a major fraction of the polymer chains prior to quenching likely did not have terminal Ni(II) species but was Br-terminated. If this were the result of an active Ni center loss due to Ni(0) diffusion to another chain, this would reflect an essentially non-"living" polymerization with all its consequences such as low molecular weight and broad polydispersity of the product polymer.7c In contrast to this, in our case the polymerization was undoubtedly "living", and thus chain transfer was a negligibly minor pathway. Locklin recently suggested that disproportionation between two growing Ni(II)-terminated chains could be responsible for increased molecular weight and end-group discrepancies.<sup>10</sup> Disproportionation, however, was unlikely to be involved in our case as this would result in biTh/biTh chain termination which was not experimentally observed. A plausible explanation would be that the square-planar Ni(II) intermediate IV $\sigma$  during polymerization remained in equilibrium with a Ni(0)  $\pi$ complex IV $\pi$  where Ni(0) center migrated into the PT  $\pi$ electron conjugated chain. This would be consistent with the idea of "random walk" of the Ni(0) associated  $\pi$ -complex as was proposed by Kiriy.<sup>34</sup> The residual Ni(0) complex  $Ni(dppp)_2$  present in the catalyst solution could possibly facilitate the process of forming a migrating Ni(0)  $\pi$ -complex at the PT backbone. Indeed, experimentally observed presence of dppp signal in the <sup>31</sup>P NMR spectrum of the rection mixture during polymerization could reflect dissociation of one dppp ligand from Ni(dppp)<sub>2</sub> required for the formation of a PTbound  $\pi$ -complex. Furthermore, the broad signal at 17 ppm observed in the 31P NMR spectrum in the course of polymerization could indeed be the signal corresponding to the Ni(0)  $\pi$ -complex itself. The low intensity of this signal (and absence of a strong evidence in favor of assignment of this signal as originating from the  $\pi$ -complex) may make this explanation less credible; on the other hand, if the migration of Ni(0) center along the PT backbone was fast in the NMR time scale, the  $\pi$ -complex's NMR signal could become broad or of low intensity or even disappear. Indeed, despite being postulated as a key intermediate in catalyst-transfer chaingrowth polymerization, the Ni(0)  $\pi$ -complex has never been

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directly observed and still remains an elusive species avoiding experimental detection.  $^{35}$ 

Similar to polymerization initiated by the bithiophene catalyst 5, PTs prepared via initiation with phenyl catalyst 7 also showed predominantly Ph/Br termination both after methanol and 5 M HCl quenching (Figure S6). Thus, these results were consistent with potential intermediacy of Brterminated  $\pi$ -complex IV $\pi$  as a general reaction pathway. It is possible that unreacted excess of *i*-PrMgCl could eventually metalate the C-Br end of the complex  $IV\pi$  during the polymerization process, which upon quenching with a proton source would yield H-terminated chains.<sup>27</sup> Indeed, polymers P5 and P6 prepared with no excess of *i*-PrMgCl showed almost exclusive Ar/Br termination both after methanol and 5 M HCl quenching (Figure S7). In contrast, polymerization using Grignard monomer 3 prepared with large (2 equiv) excess of i-PrMgCl produced polymers with predominant Ph/H termination (Figure S8), thus confirming possible metalation of the C–Br terminus in the intermediate complex IV $\pi$ . At this point, we cannot offer more details on the mechanism leading to the predominant Ar/Br-terminated polymer chains. Nevertheless, the ability to obtain Br-terminated polymer chains in the course of a chain-growth catalyst-transfer polymerization (rather than typically observed H-termination) may have some practical significance as the Br site can be used for further functionalization of the polymer.

#### CONCLUSIONS

In contrast to the widely established opinion that Ni(0)complexes with bidentate phosphine ligands are inert toward aryl halides, we have developed a simple procedure for preparation of efficient catalytic initiators for catalyst-transfer Kumada polymerization by direct oxidative addition between easily available  $Ni(dppp)_2$  and aryl halides. In addition to experimental simplicity of this procedure, absence of monodentate ligands (required in conventional preparation procedures based on ligand exchange) eliminated typical side reactions (such as aryl-aryl homocoupling) and was responsible for high yield and good stability of the catalytic initiators. High reactivity of these initiators enabled highly efficient and rapid preparation of thiophene polymers and block copolymers in living chain-growth Kumada polymerization of 5-bromo-2-thienylmagnesium monomers. An interesting feature of the polymerization catalyzed by these Ni(II) initiators was that it produced PT chains with predominant Ar/Br termination (Ar = biTh or Ph). While a clear understanding of the fine mechanistic features leading to Br-termination requires further studies, it does indicate the uniqueness of the polymerization in this case as well as reflects complexity of the chain-growth catalyst-transfer mechanism where many details still remain unexplored. From a practical standpoint, our approach offers the simplest and highly efficient way to control preparation of complex PTs as well as other conjugated polymers and copolymers (we have some initial evidence that it can be used in polymerization of various aromatic monomers). Furthermore, the efficient living polymerization can be used not only for the preparation of conjugated polymers in solution but also in the preparation of surface-immobilized films of conjugated polymers by using surface-bound initiating species. This intriguing possibility is being currently investigated.

## ASSOCIATED CONTENT

#### **Supporting Information**

Detailed synthetic and experimental procedures, additional data and figures, and crystallographic data for Ni(dppp)Br<sub>2</sub> (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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