

## Random Catalyst Walking along Polymerized Poly(3-hexylthiophene) Chains in Kumada Catalyst-Transfer Polycondensation

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**Abstract:** A “walking” process of Ni catalysts during Kumada catalyst-transfer polycondensation along polymerizing poly(3-hexylthiophene), P3HT, chains was investigated. To simplify polymer end group identifications, a compound Br–C<sub>6</sub>H<sub>4</sub>–Ni(dppe)–Br was prepared and used as an externally addable initiator. Normally, aryl moieties present in initiators incorporate into the structure of the resulting P3HT as the starting groups. We demonstrate that due to the presence of the C-Br group located in the *para*-position to the Ni substituent of the initiator, two different polymeric products are formed. One of them is the “normal” product, that is, P3HT with a *para*-bromophenyl end group, whereas another one has the phenyl ring inside the P3HT chain. The content of the product with the internal phenyl ring increases with the increase of the polymerization degree. Control experiments demonstrated that no intermolecular catalyst transfer takes place in the conditions used. Such results suggest that catalytic Ni(0) species are able to walk along the polymerizing chain containing many tens of thiophene rings up to the opposite end and can initiate polymerization there. Numerical analysis of a random hopping model was undertaken, which revealed that a combination of a random catalyst walking along the chain and a “sticking effect” at the end groups is operative in Kumada catalyst-transfer polycondensation.

### Introduction

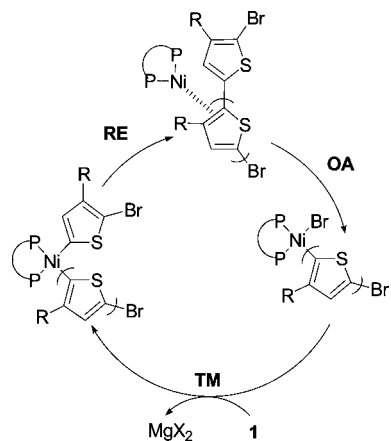
Ni-catalyzed chain-growth Kumada polycondensation<sup>1–18</sup> nowadays emerges into a powerful synthetic route to well-defined conjugated polymers,<sup>1,2</sup> block copolymers,<sup>9–13</sup> and other polymer architectures.<sup>3–8</sup> Interest in Ni-catalyzed Kumada polycondensation was greatly renewed after the discovery of a

chain-growth catalyst-transfer polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene (**1**) into regioregular poly(3-alkylthiophene)s (P3ATs).<sup>1,2</sup> This process is of great practical importance because it paves the way to earlier inaccessible materials useful for various optoelectronic applications.<sup>15</sup> This reaction is also interesting from a theoretical point of view<sup>16</sup> since it exemplifies a new way for the transformation of polycondensations that normally have step-growth character into more attractive chain-growth polymerizations.<sup>17–19</sup>

It is now generally accepted that under “classical” McCullough/Yokozawa conditions, Grignard methathesis (GRIM) polymerization or Kumada catalyst-transfer polycondensation

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**Scheme 1.** State-of-the-Art Vision of the Mechanism of Chain-Growth KCTP<sup>16</sup>

(KCTP) can be initiated by catalytic species formed from 1 equiv of  $\text{Ni(dppf)Cl}_2$  [dppf = ethane-1,3-diylbis(diphenylphosphane)],  $\text{Ni(dppp)Cl}_2$  [dppp = propane-1,3-diylbis(diphenylphosphane)], or similar catalyst precursors and 2 equiv of Grignard type monomer molecules. Alternatively, KCTP can be initiated by externally added  $\text{Ar-Ni(L)}_2\text{-X}$  initiators, synthesized in an independent step.<sup>3–9,20–22</sup> Preparation of the externally addable initiators involves a two-step reaction of aryl halides ( $\text{Ar-X}$ ) with diethylbipyridylnickel [ $\text{Et}_2\text{Ni}(\text{bipy})$ ] followed by addition of dppp or dppf to replace bipy.<sup>7</sup> An advantage of this approach is that it allows initiation of the polymerization from pre-designed functions positioned at desired locations, such as from surfaces leading to P3AT brushes<sup>7,8</sup> or from bifunctional initiators allowing preparation of rod-coil block copolymers.<sup>9</sup>

A chain-propagation catalytic cycle of KCTP (or GRIM polymerization) involves transmetalation (TM), reductive elimination (RE), and oxidative addition (OA) elementary steps (Scheme 1).<sup>1,2,16</sup> The chain-growth mechanism is provided by the fact that within the chain-propagation cycles, the Ni(0) catalytic species eliminated upon the RE step do not dissociate from the chain and do not react with another monomer molecules or other halides but, instead, undergo the *intramolecular* OA into a C–Br bond present in the same chain. It is noteworthy that Ni(0) species do not exchange their host chains and that the intramolecular transfer proceeds at the level of each individual growing chain,<sup>23</sup> as it was proved previously.<sup>3</sup> If so, during polymerization, Ni(0) species should “walk”<sup>24,25</sup> over a distance at least equal to the length of one monomer unit. The ring-walking (RW) process is one of the most intriguing and not yet understood aspects of the KCTP mechanism. Understanding of this process is desirable for successful involvement in the chain-growth polymerization of other monomer units, including those that comprise several aromatic rings. It could be a priori expected that the chain-growth mechanism is less

favored for lengthy monomers since in this case the distance for the RW is enlarged, which, in principle, would favor other reaction pathways.

Recently, we demonstrated a “robustness” of the chain-growth mechanism in examples of KCTP of thiophene-based oligomers comprising two and three thiophene rings.<sup>5</sup> In all cases, the chain-growth mechanism was a dominating polymerization pathway with a selectivity of the intramolecular catalyst-transfer elementary step (versus the intermolecular diffusion step) of  $\sim 99\%$  for polymerization of the dithiophene and of  $\sim 97\%$  for polymerization of terthiophenes. This means that Ni species are able to undergo selective RW and intramolecular transfer over distances, larger than 1 nm. The observed selectivity of the intramolecular transfer over the intermolecular diffusion pathway is likely due to a strong propensity of the Ni(0) species to form intramolecular complexes with conjugated systems. The latter is caused by unsaturated coordination of the Ni(0) center formed at the RE step in the absence of appropriate stabilizing ligands.<sup>25</sup>

However, important details of the RW remain unknown. It is, for example, not clear whether (1) the movement of Ni is unidirectional toward the nearest C–Br bond (“unidirectional RW”) or, instead, (2) it freely “walks” back and forth along the growing chain via a set of intermediate  $\eta^2$  ( $\eta^4$  or  $\eta^6$ ) complexes until it finds a C–Br bond to undergo the OA (“random RW”).<sup>25</sup> If the variant 1 is realized and if, to provide the chain-growth propagation, the Ni catalyst should necessarily always move in a *correct* direction toward the nearest C–Br bond, then the extension of the KCTP scope onto lengthy or strongly polarized monomers may be problematic. In principle, the directionality of the catalyst walking toward the terminal thiophene ring would be provided by the orientation effect of the electron-deficient C–Br group; however, it should decay quickly with the increase of the monomer unit length. On the other hand, a complex substitution of monomer units with electron-donating and -withdrawing groups would also mask the orientation effect of the terminal C–Br bond. From these regards, the random “RW” (the variant 2) seems to be more promising mechanism. Indeed, if during the polymerization of **1** into P3HT Ni catalysts walk randomly along the polymerizing chains and, nevertheless, they do not dissociate from the chain and provide a near living chain propagation (that is defacto observed<sup>1–18</sup>), then the binding propensity of Ni(0) species toward  $\pi$ -conjugated systems is indeed huge. If so, the chain-growth polymerization of lengthy and complex monomers should be possible since anyway upon polymerization of even short monomer **1** the Ni catalysts overcome distances much larger than the monomer length.

A detailed revealing of the structure of polymeric products of GRIM polymerization of **1** catalyzed by  $\text{Ni(dppp)Cl}_2$  would, in principle, shed light on the RW process. Preparation of the initiator in GRIM polymerization involves two consecutive TM steps between  $\text{Ni(dppp)Cl}_2$  and two monomer molecules leading to symmetrical adduct **2** (Scheme 2). In the next step, the Ni catalyst undergoes RE and then oxidatively adds either to the left-hand or to the right-hand thieryl rings with an equal probability leading to **3**. If the polymerization of **1** initiated by **3** involves the unidirectional RW, then the chain should extend only in a one direction predetermined by the initial catalyst choice (made at the very first OA step). The polymerization in this case should lead to P3HT in which the tail-to-tail (TT) defect is the starting group. If, instead, GRIM polymerization involves the random RW, then both ends of the initiator **3** should be reactive and the chain extends in both directions, leading to

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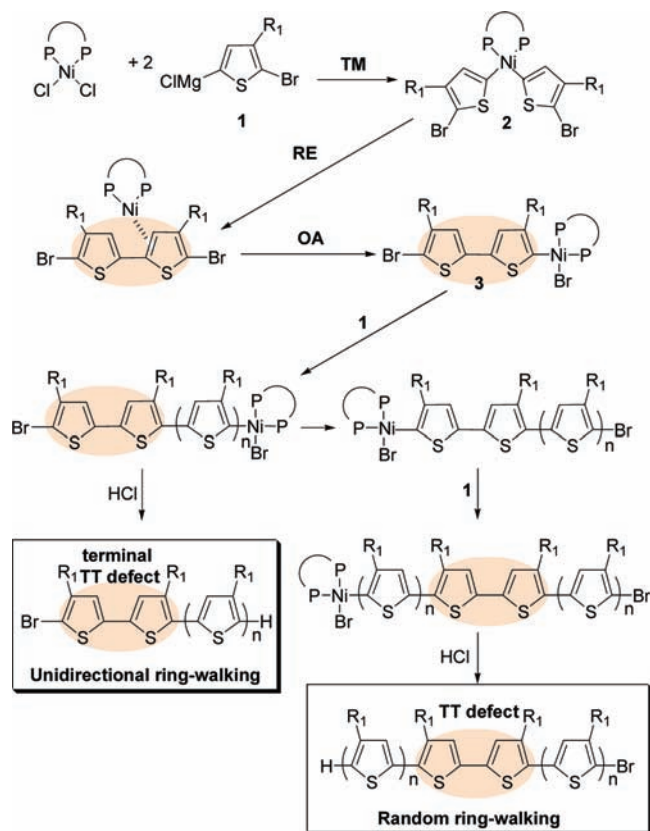
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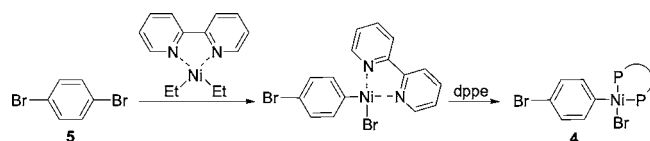
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**Scheme 2.** Possible Mechanisms of Unidirectional and Random Catalyst Walking Taking Place upon GRIM Polymerization Resulting in Different Positions of the TT Defect<sup>1,2</sup>



**Scheme 3.** Synthesis of the Initiator



P3HT with the TT defect located inside the chain. Hence, one would determine the character of the RW, if the position of the initiator residue in the structure of the final polymeric product would be detectable. Unfortunately, identification of the exact position of the above-mentioned TT defect in the P3HT structure is highly challenging.

To circumvent the identification problem, in the present work, we prepared  $\text{Br-C}_6\text{H}_4\text{-Ni(dppe)-Br}$  (**4**), which has an easily recognizable (by  $^1\text{H}$  NMR) *para*-substituted phenyl ring, and used it as initiator for the polymerization of **1**. The structure of the products formed and the course of polymerization were investigated experimentally and theoretically, which allowed us to deduce that during the KCTP, catalytic Ni(0) species are able to walk along the polymerizing chain containing many tens of thienyl rings up to the opposite end and can initiate polymerization there.

## Results and Discussion

The initiator **4** was cleanly obtained using a recently developed procedure in our lab<sup>7–9</sup> by reacting **5** with  $\text{Et}_2\text{Ni}(\text{bipy})$  followed by ligand exchange with an excess of dppe (Scheme 3). Only one bromine atom in **5** was reactive toward  $\text{Et}_2\text{Ni}(\text{bipy})$ , which was confirmed by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy (for experimental details and NMR spectra, see Supporting Informa-

tion). In this work, the dppe-based Ni initiator was used because of its higher solubility (than solubility of dppp-based initiators), which simplified handling of the complex and NMR characterizations. We demonstrate here that the use of dppe-supported initiators does not necessarily cause worsening of the polymerization control if they are introduced in a dissolved state.<sup>16</sup>  $\text{Ni}(\text{dppe})\text{Cl}_2$  and  $\text{Ni}(\text{dppp})\text{Cl}_2$  are poorly soluble in THF; therefore, their addition into the reaction mixture in the solid state does not provide the chain initiation simultaneously by all Ni species added. Even though  $\text{Ni}(\text{dppe})\text{Cl}_2$  has a better solubility than  $\text{Ni}(\text{dppp})\text{Cl}_2$ , this problem is more pronounced for polymerizations induced by the former initiator since the polymerization rate is much higher with  $\text{Ni}(\text{dppe})\text{Cl}_2$ .<sup>26</sup> However, as the initiator **4** is soluble in THF, efficient initiation is provided, which leads to narrowly distributed polythiophenes with a near complete incorporation of *para*-bromophenyl group into the P3HT structure (see MALDI-TOF data, Figure S4 of the Supporting Information).

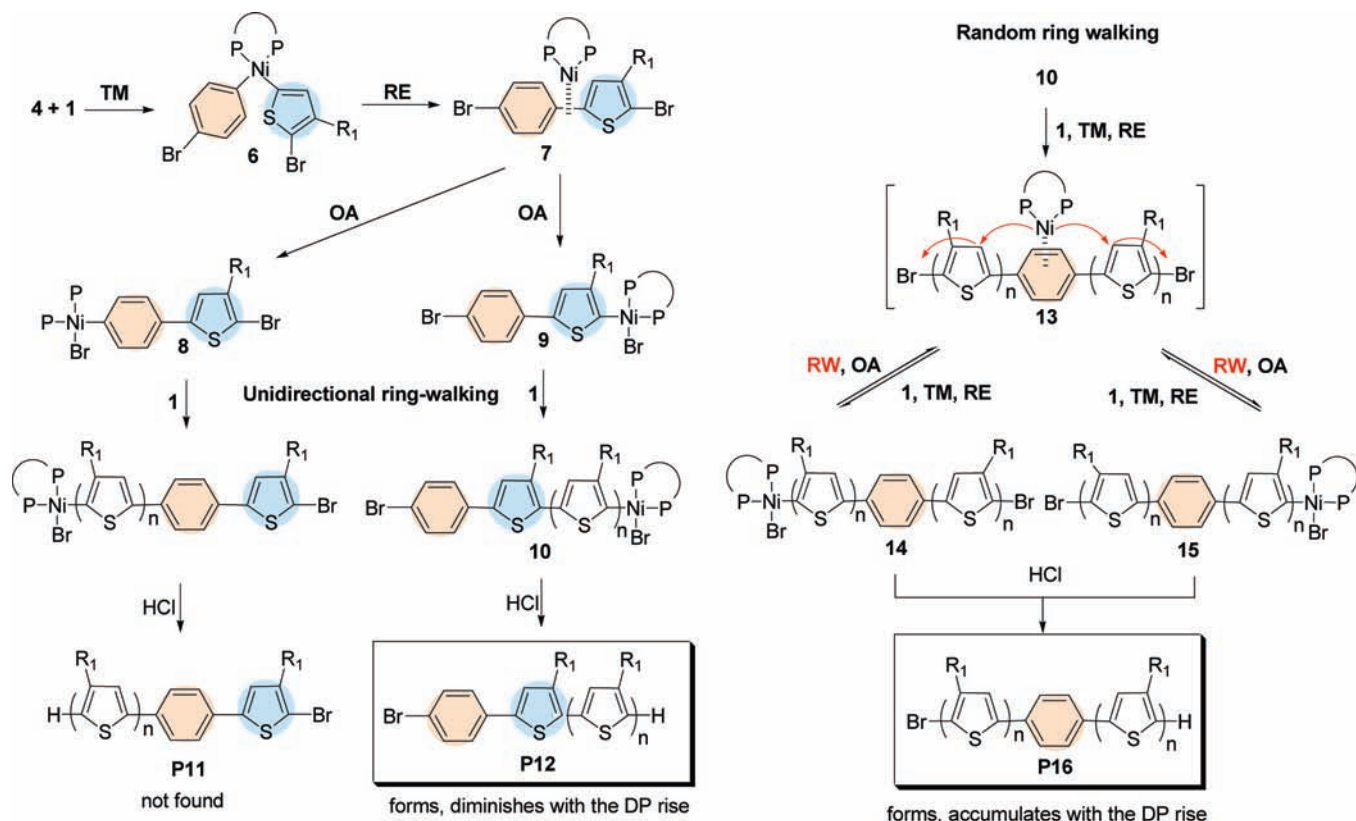
Scheme 4 depicts possible transformations that may occur upon mixing of **1** and **4**. In the first step, **1** reacts with **4** (TM step) giving nonsymmetrical adduct **6** that undergoes RE, leading to **7** in which the eliminated Ni(0) species is associated with either benzene or thienyl rings. Afterward, **7** may undergo OA, reacting with the C–Br bonds of either phenyl or thienyl rings, forming **8** or **9**, respectively, in the ratio corresponding to the relative reactivity of the C–Br bonds. Let us further consider two chain-propagation scenarios, one of them corresponding to the unidirectional catalyst walking and another one corresponding to the random RW mechanism. Upon the unidirectional RW, the chain should be polymerized either from the thienyl or from benzene rings, resulting in **P11** or **P12**, which have 2-bromo-3-hexyl-thien-5-yl or *para*-bromophenyl starting groups, respectively. The opposite terminal groups for both **P11** and **P12** should be H atoms attached to the 2-position of the thiophene ring due to termination by HCl. An alternative random catalyst walking assumes the extension of the initiator **4** in both directions via intermediates **6–10** and **13–15** with the assistance of the same Ni catalytic species that freely move (walk) along the polymerized chain from one end to the opposite leading to **P16** in which the 1,4-connected phenyl ring is located inside the chain. One can also assume that these two RW pathways (unidirectional and random) may both contribute to a real polymerization process in a certain degree.

It is noteworthy that the position of the phenyl ring in the structure of the polymerization product would be a clear indication of a certain RW mechanism only if the polymerization cannot be restarted intermolecularly from the *para*-bromophenyl group of the polymer **P12** to form **P16**. We demonstrated previously that no intermolecular catalyst transfer occurs for the polymerizations catalyzed by Ni supported by monodentate phosphorus ligands.<sup>5</sup> In the present work, we performed similar control experiments using  $\text{Ni}(\text{dppp})\text{Cl}_2$  and  $\text{Ni}(\text{dppe})\text{Cl}_2$  catalysts. In particular, polymerizations of **1** initiated by  $\text{Ni}(\text{dppp})\text{Cl}_2$  and  $\text{Ni}(\text{dppe})\text{Cl}_2$  were conducted in the presence of a large excess of either 1,4-dibromobenzene **5**, bromobenzene, or 2,5-dibromothiophene. We found that these additives did not affect the normal polymerization course and that P3HT with low polydispersities in a 1.1–1.2 range were obtained. No polymerization products with phenyl (or unsubstituted thienyl) end functions

(26) Alternatively, narrowing of polydispersities can be achieved via a preinitiation approach, as described in ref 16, according to which some portion of the monomer is mixed with  $\text{Ni}(\text{dppe})\text{Cl}_2$  to give soluble “living” short oligomers that are used as initiators.



Scheme 4. Unidirectional versus Random Catalyst Walking upon KCTP



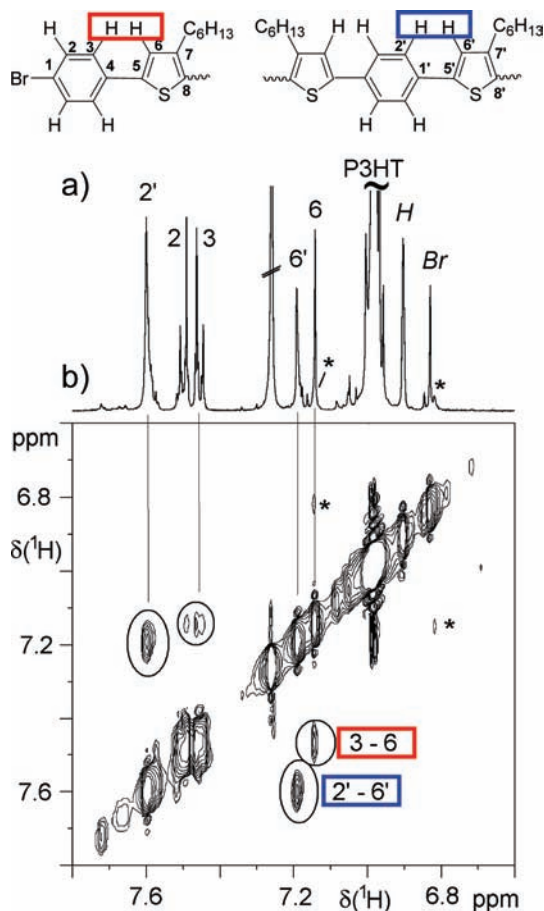
were formed in these experiments; hence, the intermolecular catalyst-transfer pathway can be ruled out in the particular conditions. On the other hand, experiments discussed below strongly suggest that the polymerization involves the intramolecular catalyst-transfer mechanism, in full agreement with previous observations.<sup>1–22</sup>

In the next step, polymerizations of **1** initiated by **4** were conducted at room temperature (RT) at different monomer-to-initiator (feed) ratios of 3, 7, 20, 40, and 150. To follow the polymerization course, several samples at different polymerization times (corresponding to different conversions of **1**) were withdrawn from the polymerization mixture. P3HT with a polydispersity index in a 1.1–1.2 range (determined for nonfractionated crude products washed with water and methanol only) and controllable (by the feed ratio and monomer conversion) molecular weight (MW) were obtained, reflecting a near “living” polymerization performance. Somewhat increased polydispersities (~1.4) were observed when the MW of the resulting polymer exceeded 30000 g/mol value, presumably because of a limited solubility of a high MW P3HT-promoted chain termination and reinitiation (Figure S5 of the Supporting Information). A typical <sup>1</sup>H NMR spectrum of the reaction mixture quenched with HCl and washed with methanol is shown in Figure 1. Whereas the characteristic signals of terminal thiophene units ( $H_{Br}$  and  $H_H$ ) were well-known from the literature,<sup>1–7</sup> the additional AB spin system (signals  $H_2$  and  $H_3$ ) is due to the *para*-bromo phenyl starting group in **P12**, and the singlet ( $H_2'$ ) represents the phenyl units on both sides substituted by P3HT in **P16**. The rotating frame Overhauser effect spectroscopy (ROESY) spectrum allows us to assign the neighboring proton of the P3HT chain ( $H_6$  and  $H_6'$ , respectively) and thus to prove the terminal and internal positions, respectively, of these phenyl moieties. The fraction of both substitution pattern was

calculated from the intensities of signals ( $H_2 + H_3$ ) and  $H_2'$ , and the intensity of the  $\alpha$ -CH<sub>2</sub> group signal of the hexyl residue was related to the intensity of two phenyl protons [ $(H_2 + H_3 + H_2')/2$ ] to calculate an averaged degree of polymerization (DP). Integration of the spectra shows a near quantitative incorporation of the phenyl moiety into the structure of the resulting polymer. In the experiments conducted, the **P12** and **P16** products were formed in substantial quantities but at a variable ratio, whereas **P11** was not found among the polymeric reaction products.<sup>27</sup> For the thiophene proton in the single bromo-3HT unit in **P11**, a chemical shift of 7.03 ppm was calculated based on the chemical shift of  $H_{Br}$ , taking into account that replacement of a P3HT chain by a P3HT-C<sub>6</sub>H<sub>4</sub>- moiety results in a low-field shift of 0.20 ppm for that position (compare  $H_2'$  and  $H_{P3HT}$ ). However, no signal that could prove this group is observed. Only in very low-molecular products (DP ~ 3) was such a structure found (see Table S1 and Figure S1 of the Supporting Information).

As a typical example, we further discuss results of the experiment conducted at RT and a 1/150 feed ratio. Three samples were withdrawn in this polymerization run, at 90 s, 210 s, and 30 min, and P3HT samples with DPs of 40, 70, and 168, respectively, were obtained, as determined by NMR (these DPs agree rather well with DPs determined from GPC data, which gave DPs of 46, 90, and 186, respectively; Figure S5 of the Supporting Information). The reaction shows a clean chain-growth performance, allowing preparation of P3HT with number average molecular weight ( $M_n$ ) up to 30000 g/mol with a satisfactory integration of starting and end groups. This result

(27) Trace amounts of **P11** were found only in a fraction corresponding to DP ~ 3, demonstrating a negligible probability of the formation of **P11**.

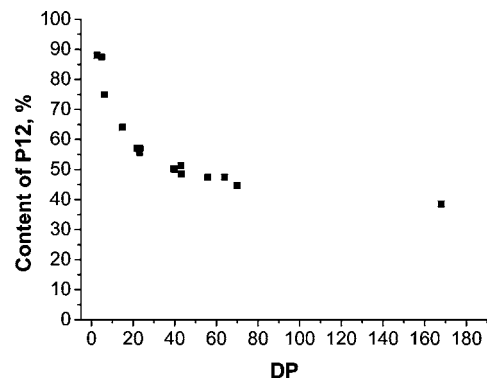


**Figure 1.** (a) <sup>1</sup>H NMR spectrum (region) of a P3HT obtained upon Kumada catalyst-transfer polymerization of **1** initiated by **4** at RT and (b) the corresponding region of the ROESY spectrum. Br and H, thiophene signals from Br and H chain termination; \*, <sup>13</sup>C satellites of the P3HT backbone signal.

further proves that each Ni species polymerizes only a single polymer chain, and no Ni exchange between the growing chains takes place in these conditions.<sup>28</sup>

The fraction of *para*-bromophenyl terminated product **P12** decays, whereas the fraction of **P16** with internal phenyl groups grows with the increase of an overall DP of P3HT (Figure 2). For instance, only ~12% of **P16** was found in products with DP ~ 3, whereas **P16** and **P12** products are present in near equal quantities at DP ~ 40. It is noteworthy that at a fixed polymerization temperature, relative yields of **P12** and **P16** products depend only on DP and are independent of the concentration of monomer **1** and the feed ratio. For example, P3HT with a DP ~ 40 was obtained as the final product in the polymerization with the set feed ratio of 40, P3HT with the same DP was isolated at incomplete conversion of **1** in the experiment with the “ordered” DP of 150, and the same content of **P16** of ~50% was obtained in both cases. In another pair of experiments, the same content of **P16** was observed in products when polymerizations were conducted at two different monomer concentrations of 0.067 and 0.016 M. Such insensitivity of the

(28) This is in a full agreement with previously reported Yokozawa et al. and McCullough et al. data (refs 1, 2, and 23) as well as with our previous papers (refs 3–9) but contradicts with the paper of Rawlins et al., who did not succeed in obtaining P3HT with  $M_n$  higher than 8000 g/mol and to control  $M_n$  by the feed ratio but, instead, observed a dependence of  $M_n$  on the monomer concentration. Achord, B. C.; Rawlins, J. W. *Macromolecules* **2009**, *42*, 8634–8639.



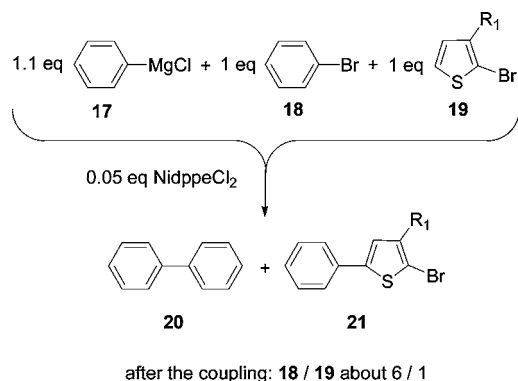
**Figure 2.** Dependence of the **P12** fraction on the polymerization degree for the polymerization of **1** initiated by **4** at RT.

polymerization course to variations in the composition of the reaction mixture (and hence, on viscosity, molecular diffusion, etc.) corroborates with the assumption that intermolecular migrations of Ni catalysts are not responsible for the formation of **P16**.

In the next experiment, a “livingness” of the polymerization was tested. In this experiment, 3 equiv of the monomer **1** was polymerized in the presence of **4** for a few minutes, and afterward, the first sample was withdrawn; the rest of the reaction mixture was kept overnight under argon at RT, and then, the second sample was withdrawn; finally, 20 equiv of **1** was added to the reaction mixture, which was allowed to polymerize for a further 10 min, giving the third sample. The first and the second samples had the same DP (~3, <sup>1</sup>H NMR data) and the same composition (**P16**/**P12** ratio of 12/88). Importantly, the addition of a new portion of **1** resulted in a clean extension of the 3-mer into the 28-mer with a negligible amount of reinitiated H/Br-terminated P3HT. Furthermore, the ratio between **P12** and **P16** in this product was exactly the same as in other experiments, in which polymerization was conducted in a single run without a storage of the “living” prepolymer. This result further demonstrates the livingness of the polymerization initiated by externally added initiator **4**.

It is important for interpretation of the results to understand that the formation of *para*-bromophenyl terminated product **P12** requires that *all* chain-propagation steps occur in the same direction (corresponding to the right-hand side direction in Scheme 4) from intermediate **6** and via **9** without activation of the *para*-bromophenyl group. On the other hand, even a *single* activation of the *para*-bromophenyl group followed by at least one chain-propagation step from this end will result in **P16**. In other words, **P16** should be formed with a much higher probability if the reactivity of the two C–Br bonds located in phenyl and thieryl rings would be equal. However, **P12** is a major product in most polymerization runs (with DP up to 40), suggesting that the activation of the *para*-bromophenyl group is a much less efficient process than the activation of the C–Br bond of the thieryl ring. To verify this hypothesis, a competition Kumada coupling experiment was conducted in which 1.1 equiv of *para*-phenyl-magnesium chloride (**17**) was reacted with 1 equiv of phenylbromide (**18**) and 1 equiv of 2-bromo-3-hexylthiophene (**19**) in the presence of 0.05 equiv of NidpCl<sub>2</sub> for 10 min (Scheme 5). Analysis of the reaction mixture by gas chromatography with a mass spectrometer detector revealed a largely preferential consumption of **19** (the ratio between unreacted **18** and **19** of ~1/6 was detected). The obtained results clearly show a higher reactivity of the thiophenic bromide than

**Scheme 5.** Competitive Kumada Cross-Coupling Experiment Demonstrating a Higher Reactivity of Thienyl Bromide **19** than of Phenylbromide **18**

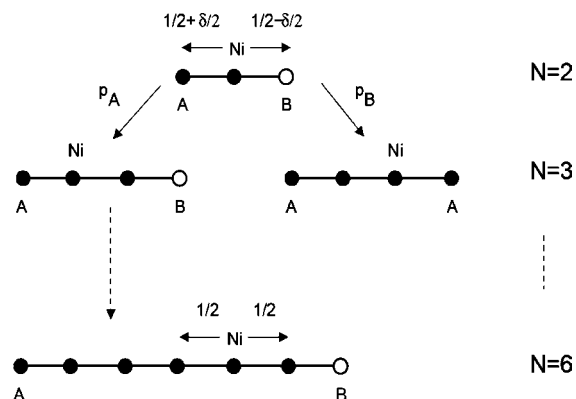


of the bromobenzene in Kumada cross-coupling reaction that qualitatively corroborates with the postulated higher reactivity of the thienyl than the *para*-bromobenzene ends in KCTP. The higher reactivity of the thiophene derivatives in Kumada coupling could be either due to a higher reactivity at the OA step of the C–Br bond as a result of activation of this bond by electron-withdrawing sulfur atom, due to a higher complexation ability of the thienyl ring than of the phenyl one with Ni species,<sup>29</sup> or due to a combination of these factors.

In a view of this, the obtained results can be best explained in terms of walking of the Ni catalyst along the polymerizing chain with a preferential OA to C–Br of the thienyl end. In the first OA step, the intermediate **7** is mainly transformed into **9**, whereas the amount of **8** (product of OA into the C–Br of the phenyl ring) is low after the first monomer addition step. Extrapolation of the curve in Figure 2 to DP = 1 shows that only about 4–5% of **P16** is formed, corresponding to only 4–5% of Ni species undergoing OA into C–Br of the phenyl ring at the first polymerization step. The major pathway implies the consecutive addition of monomer **1** to the intermediate **9**, resulting in **10**, “a living” precursor of **P12** (Scheme 4). However, the experimental observation is that the product **P16** with an internal phenyl ring progressively accumulates with the DP rise and a substantial increase of **P16** fraction is still observed at relatively high DPs. Such results together with the fact that **P16** is not forming via intermolecular reinitiation from the *para*-bromophenyl end group (see control experiments) unambiguously suggest that at least some number of catalytic Ni(0) species walks along the polymerizing chain up to the opposite end over distances of several tens of nanometers. At each polymerization step, some (relatively minor) portion of such Ni(0) species that reached the opposite end oxidatively adds to the *para*-bromophenyl end group, forming intermediates **13** and **14**, which initiate polymerization into **P16** in which the phenyl ring is located inside the chain. At the same time, the extension of the  $\pi$ -conjugation system gradually decreases the probability for Ni species to reach the opposite terminus that reduces the rate of OA into the *para*-bromophenyl end group that is qualitatively consistent with the proposed random walk polymerization model.

If, however, both ends of the initiator are identical, such as in the classical GRIM polymerization initiated by Ni(dpppe)Cl<sub>2</sub>

**Scheme 6.** Schematic Picture of the Various Steps Involved in the Chain-Hopping and Reaction Process



(Scheme 2), then both ends should propagate equally, leading to P3HT with the TT defect located inside the P3HT chain but not being only the terminal group, as represented in some articles.<sup>1</sup>

**Numerical Analysis.** The obtained data reveal that the Ni catalyst walks randomly during KCTP; however, these data do not exclude a possible contribution from a unidirectional catalyst walking. To get deeper inside the walking process, the experimental data were used to test the random walker model (random hopping of the catalyst) quantitatively. The model is defined as follows: At the beginning of the process, the Ni catalyst is initially placed between the two different end groups, which we call A and B for simplicity (which correspond to the bromothiophenyl and *para*-bromophenyl ends, respectively; Scheme 6).

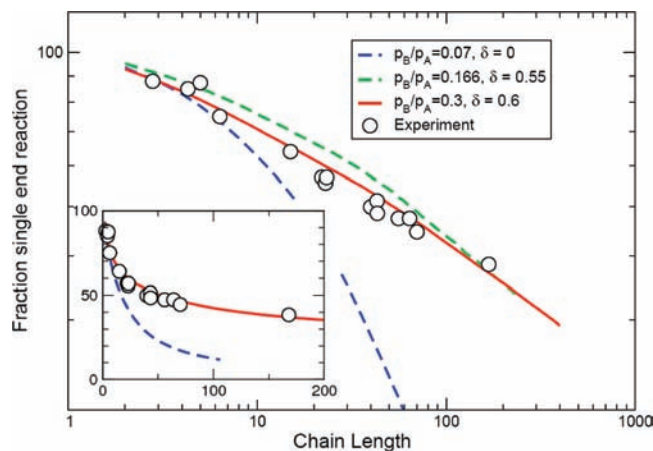
Within a given unit of time, it takes a random step with equal probability to the neighboring monomers. Whenever the catalyst reaches the end groups A or B, we assume that a monomer is added with probabilities  $p_A$  or  $p_B$ , corresponding to relative reactivities of the two different ends (equates to the OA step), which, after following TM and RE steps, results in prolongation of the chain ( $N \rightarrow N + 1$ ). Such different reactivities corroborate with the experimental finding that **8** and **9** are not formed with the same probability from **7**. In the following time step, the catalyst is set to the position next to the reactive side (equates to TM and RE steps). As discussed above, the new chain end is always of type A. In the course of time, the catalyst walks unbiased and randomly along the chain. When a given number of monomers are consumed, a given DP  $N$  is realized. The fraction of chains of type AB and length  $N$  shall be denoted by  $p_{AB}(N)$ .

The above-described process can be easily simulated. A comparison of the simulation with the experimental results (Figure 2) for the fraction of AB type chains is given in Figure 3. To obtain a best fit to the experimental results for small oligomers ( $N = 2, 3$ ), a ratio of  $p_B/p_A = 0.07$  has to be chosen (for simplicity, we assume  $p_A = 1$ ). The result for this model is displayed as the dashed blue curve in Figure 3. This curve decays too fast, actually with an asymptotic power law of  $1/N$ . The asymptotic power law decay of  $p_{AB}(N) \sim N^{-1}$  does not depend on the values of  $p_A$  and  $p_B$  and is in marked contrast to the experimental data. The best fit to the data predicts a power law decay according to  $N^{-0.23}$ .

Now, let us reconsider the case that the Ni(0) catalyst is sitting next to the reactive end group A that corresponds to the intermediate formed after each TM followed by RE steps.

(29) Arene  $\pi$ -complexation to Ni(0) is the first irreversible step in cross-coupling reactions of some aromatic halides with Grignards. Yoshikai, N.; Matsuda, H.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 15258–15259.





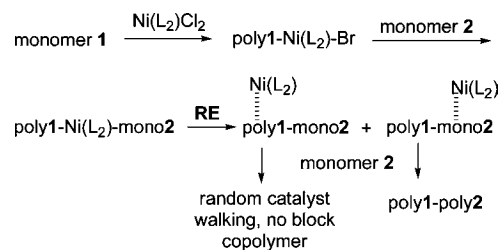
**Figure 3.** Number fraction of AB type chains ( $p_{AB}$ ) as a function of the chain length  $N$ . The experimental data are compared with the result of a random walk simulation using various parameters as discussed in the text. The inset shows the data in linear coordinates.

Because the chemical environment left and right to the catalyst is not equivalent, it is not evident that the hopping rate is symmetrical in this position. Indeed, it can be assumed that an electronegative bromine atom present at the end group induces polarization of the aromatic system so that complexation of the Ni(0) species with a more electronegative bromothiophenyl end group becomes more favored than complexation with any other (internal) thiophene rings [we suppose that Ni(0) has a higher affinity to more electronegative groups since in the next step it undergoes an energetically favored oxidation by the C–Br bond]. In our model, a preferential hopping of Ni(0) to the bromothiophenyl end group is described by a “stickiness”  $\delta$  of the catalysts to A, which gives rise to a probability to jump on A of  $1/2 + \delta/2$  and a probability to jump in the opposite direction (i.e., into the nonterminal thiophene ring when  $DP > 2$ ) of  $1/2 - \delta/2$ ; see Scheme 6.<sup>30</sup> We hasten to note that the stickiness does only apply to the site next to A and not to any other site in the chain; thus, the walk is still globally unbiased and random. Using a finite value of  $\delta$  implies a higher value of  $p_B/p_A$ , since the stickiness enlarges the fraction of AB type chains at a given ratio of  $p_B/p_A$ . Interestingly, the value of  $\delta$  is directly related with the asymptotic decay of  $p_{AB}(N)$  (Supporting Information), which gives access to  $\delta$  without considering other parameters of the model. The best fit to experimental data was obtained for  $\delta = 0.6$  and  $p_B/p_A \sim 0.3$  as displayed by the solid red curve in Figure 3. The fit using  $p_B/p_A = 1/6$  (0.166), that is, the value obtained from the competition Kumada cross-coupling, also gave quite satisfactory agreement with the experimental data (green curve in Figure 3).

Thus, we have obtained a quantitative analysis of the experimental data in terms of a random walker model of the catalyst, which reveals some fine details about the nature of the hopping process. In particular, we can show that a stickiness

(30) To simplify the model, we assume that the probability for Ni(0) to hop into the bromophenyl ring is also given by  $1/2 - \delta/2$ , although strictly to say, the stickiness coefficient  $\delta$  may be different here; therefore, the application of a correct value would further improve the model. We, however, intuitively suggest that a negative value of the stickiness (i.e.,  $-\delta/2$ ) correctly describes the trend since the phenyl ring should have a lower complexation ability toward Ni(0) than the thiophene ring due to favored interactions between lone electron pairs of sulfur atoms and unoccupied d orbitals in the structures of thiophene and Ni(0), respectively. Quantum mechanic calculations may elucidate quantitatively this issue, and such calculations are planned.

**Scheme 7.** Representation of KCTP-Based Block Copolymerization Performed via Sequential Addition of Two Different Monomers: It Is Favorable if Ni(L<sub>2</sub>) Species Form a Stronger Complex with the First Added Residue of the Second Monomer Rather than with Already Polymerized Polymer 1



of the catalyst to the end group is necessary to explain the decay of the fraction  $p_{AB}(N)$ . In other words, the obtained experimental data and calculations suggest that both random and unidirectional catalyst walking mechanisms are operative in KCTP in such a way that the catalyst walks randomly when it is far away from the end groups, but it experiences a “sticking” effect when it approaches the end groups (Figure S6 of the Supporting Information).<sup>31</sup>

Revealing the catalyst walking mechanism may shed light onto some not yet fully understood experimental observations. For example, detailed kinetic studies recently performed by Lamps and Catala<sup>23</sup> revealed that GRIM polymerization has two kinetic rate constants, one of them related to early, whereas the second one to later, stages of the GRIM polymerization, and the former is four times higher than the latter. This phenomenon may be explained from the positions of the catalyst walking mechanism. It is expected that chain elongation during the polymerization derives an “unproductive” random RW over large distances that should inevitably decrease the probability for the Ni catalyst to be present near the propagation-chain end, thus decreasing the rate constant. The same consideration may also explain difficulties that one meets aiming at the preparation of very high MW polymers using GRIM or KCTP.

On the other hand, a recent observation of Yokozawa et al.<sup>12</sup> related to the synthesis of all-conjugated block copolymers about the importance of the monomers addition order could also be explained in terms of the random catalyst walking mechanism. In particular, it was reported that polythiophene–polyphenylene block copolymers formed smoothly only when the polyphenylene block was polymerized first, whereas polymerization failed to give a good quality block copolymer at the reverse monomer addition order.<sup>12,14</sup> In block copolymerization, preparation of the second block is initiated by poly1–Ni(L<sub>2</sub>)–Br, which upon TM with a monomer 2 should give poly1–Ni(L<sub>2</sub>)–mono2 (Scheme 7). A subsequent RE leads to liberation of Ni(0) and its complexation with the polymerized conjugated system. We propose that polymerization of the second block proceeds smoothly if the monomer 2 and the polymer chain derived from it form stronger complexes with Ni(0) than monomer units in already prepolymerized poly1. In this case, Ni(0) preferentially complexes with the terminal monomer unit so that its unproductive RW is prohibited. This situation corresponds to a relatively high “stickiness” ( $\delta$ ) value and, consequently, to a larger contribution of unidirectional catalyst

(31) The obtained results further suggest that Ni(0) complexes associated with the  $\pi$ -conjugated systems are really existing intermediates and they play an important role in the catalyst-transfer polymerization. Works aiming at a direct detection of such Ni(0) complexes by 31P NMR are currently underway in our lab.

walking. It can be postulated that complexation of Ni(0) with phenyl rings of polyphenylene is less favored than with thienyl units; therefore, in the synthesis of polythiophene–polyphenylene block copolymer, it is essential to start polymerization from the polyphenylene block.

In conclusion, the “walking” process of the Ni catalyst during KCTP along the polymerizing poly(3-hexylthiophene), P3HT, chains was investigated. To simplify polymer end-group identifications, a compound  $\text{Br}-\text{C}_6\text{H}_4-\text{Ni}(\text{dppe})-\text{Br}$  was prepared and used as an externally added initiator. Normally, an aryl moiety present in an initiator incorporates into the structure of the resulting P3HT as the end group. We demonstrated in this work that due to the presence of C–Br group located in the *para*-position to the Ni substituent of the initiator used, two types of differently terminated polymeric products were formed. One of them is a “normal” product, P3HT with a *para*-bromophenyl end group, whereas another one has the phenyl ring inside the P3HT chain. The content of the product with the internal phenyl ring increases with the increase of the polymerization degree. Control experiments demonstrated that no intermolecular catalyst transfer takes place in the conditions used. Such results unambiguously show that catalytic Ni(0) species are able to walk along the polymerizing chain up to the

opposite end and initiate polymerization there.<sup>32</sup> Numerical analysis of a random hopping model was undertaken, which revealed that a combination of a random catalyst walking along the chain and a “sticking effect” at the end groups is operative in KCTP. The ability of Ni catalysts to walk along polymerizing chains must be taken into account when one uses KCTP for the preparation of conjugated polymers.

**Acknowledgment.** We thank Mrs. Harnisch for gas chromatographic analyses and Dr. Luxenhofer for MALDI-TOF measurements. We thank DFG for financial support (KI-1094/3-1 and KI-1094/4-1).

**Supporting Information Available:** Experimental details, <sup>1</sup>H NMR characterizations, and details of numerical analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA102210R

(32) An ability of metal catalysts to walk over  $\sigma$ -bound chains via upon ethylene polymerization was also demonstrated. Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414–6415. Möhring, M.; Fink, G. *Angew. Chem., Int. Ed.* **1985**, *24*, 1001–1002.