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Kumada Catalyst-Transfer Polycondensation of Thiophene-Based Oligomers: Robustness of a Chain-Growth Mechanism

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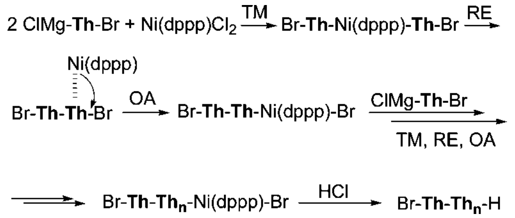
ABSTRACT: Polymerization of conjugated oligomers is an efficient approach for band gap engineering of conjugated polymers. On the other hand, a recently discovered chain-growth Ni-catalyzed Kumada polycondensation of monothiophenes becomes an important tool in engineering of macromolecular architectures. In this paper we evaluate the feasibility for chain-growth polycondensation of model monomers comprising one, two, or three thiophene rings. We found that Ph−Ni(PPh$_3$)$_2$−Br-mediated polycondensations of HT-coupled bi- and terthiophenes lead predominantly to Ph-terminated polymers indicating the chain-growth polymerization mechanism. Although an increase of the monomer molecular length somewhat decreases the fraction of the Ph-terminated products as a result of increased probability of a chain-termination and chain-transfer reactions, chain-growth elementary steps remain dominating even for lengthy monomers. Such results reflect that in the key polycondensation step the Ni catalyst undergoes selective intramolecular "ring walking" along conjugated systems comprising two or even three thiophene rings. The chain-growth performance is sensitive to the substitution pattern of the polymerized oligomers. The best results were obtained with the monomers having alkyl substituents in an ortho (respective to the growing site) position possibly due to higher stabilities of intermediate ortho-substituted aryl−nickel complexes, and this knowledge might be helpful for proper design of conjugated oligomers polymerizable on the chain-growth manner.

Introduction

A Ni-catalyzed Kumada cross-coupling reaction is one of the most efficient tools for construction of carbon−carbon bonds.[1] This method is widely used in the synthesis of small-sized aromatic molecules as well as for preparation of conjugated oligomers and polymers.[2] A potential of this reaction has been greatly extended due to an outstanding discovery of Yokozawa[3] and McCullough[4] groups. They found that the Kumada polycondensation into regioregular poly(3-alkylthiophenes) (P3ATs) follows a chain-growth but not a step-growth mechanism as it was believed for years. The chain-growth mechanism occurring as a "one-by-one" addition of monomers to a growing end is always desired in polymer chemistry since it opens straightforward access to well-defined and narrowly distributed polymers and block copolymers of various architectures.[5] The ability to prepare polymers with desired architecture is especially important in the case of conjugated polymers, whose properties are greatly dependent on nano-, micro-, and macroscales organization.[6] Despite the great promise that chain-growth Kumada polycondensation in the synthesis of a new generation conjugated polymers gives, some aspects of the mechanism as well as the scope and limitation of the reaction are not yet properly explored.

Progress toward an understanding of the Kumada polycondensation mechanism was recently achieved. It is now generally accepted that polymerization proceeds by extension of tail-to-tail dimers formed in the first step from Ni(dppp)Cl$_2$ (dppp = propane-1,3-diylbis(diphenylphosphane)) or similar catalyst precursors and two Grignard-type monomer molecules. As for the parent Kumada cross-coupling reaction, the catalytic cycle of the polycondensation involves transmetalation (TM), reductive elimination (RE), and oxidative addition (OA) elementary steps (Scheme 1). McCullough et. al suggested that the Ni(0) species formed at the reductive elimination step associates with the nearest thiophene ring, forming an associated pair, then "moves" toward a growing polymer chain end, and finally inserts into the terminal C−Br bond.[4] Thus, the unique propensity of Ni(0) species to transfer intramolecularly via a "ring walking" process[7] is responsible for the observed chain-growth nature of the polycondensation.[8]

Scheme 1. Mechanism of Chain-Growth Polycondensation into Polythiophenes According to Yokozawa et al.[3] and McCullough et al.[4]



Recently we found a way to initiate the polycondensation from added initiators (e.g., Ph−Ni(PPh$_3$)$_2$−Br) prepared by oxidative addition of tetrakis(triphenylphosphine)nickel(0), Ni(PPh$_3$)$_4$, to aromatic halides.[9] We found that polycondensation performed at 0 °C results in regioregular head-to-tail poly(3-hexylthiophene), P3HT, and involves the chain-growth mechanism. Relying upon this method, we developed surface-initiated polycondensation to graft P3HT from surface-immobilized poly(4-bromostyrene).[9]

On the other hand, copolymerization is a very fruitful approach for molecular engineering of conjugated polymers with tailored properties.[10] Indeed, involvement into the polycondensation of lengthy monomers comprising more than one aromatic ring, possibly of a different nature (e.g., electron donor and acceptor), is a powerful tool to tune the electronic, optical, or other properties of the resulting polymer.[11] The ability to prepare conjugated oligomers by the chain-growth polymerization route is strongly desired since it would provide the possibility for simultaneous engineering of the band gap and macromolecular architecture of conjugated polymers. Although the Kumada polycondensation of bithiophenes was recently reported, the

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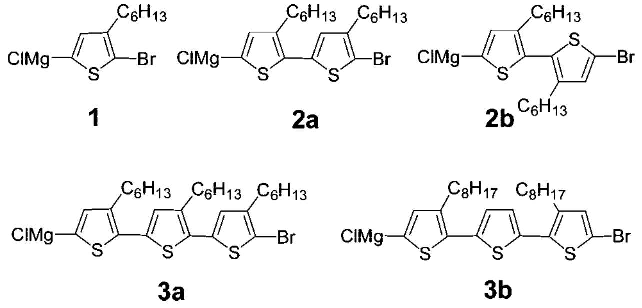
Chart 1



mechanism of this reaction was not addressed.[12] In the present work we aim to verify whether the chain-growth mechanism is also preserved in the Kumada polycondensation of monomers comprising two or even three thiophene rings.

We a priori expected that the chain-growth mechanism would be less favored for lengthy monomers since in this case the path for the intramolecular transfer of Ni(0) species will be enlarged, which, in principle, would favor other reaction pathways.[13] With this idea in mind, mono-, bis-, and trithiophenic monomers, 2-bromo-5-chloromagnesio-3-hexylthiophene (**1**), 5′-bromo-3,4′-dihexyl-5-chloromagnesio-[2,2′]bithiophene (**2a**), 5-bromo-3,3′-dihexyl-5′-chloromagnesio-[2,2′]bithiophene (**2b**), 5″-bromo-3,4′,4″-trihexyl-5-chloromagnesio-[2,2′;5′,2″]terthiophene (**3a**), and 5-bromo-5″-chloromagnesio-3,3″-dioctyl-[2,2′;5′,2″]terthiophene (**3b**) (Chart 1), were prepared and their polymerizations induced by the Ph−Ni(PPh$_3$)$_2$−Br initiator investigated.

Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at 500.13 MHz for ^{1}H using CDCl$_3$ as solvent. The spectra were referenced on the solvent peak (δ ^{1}H = 7.26 ppm).

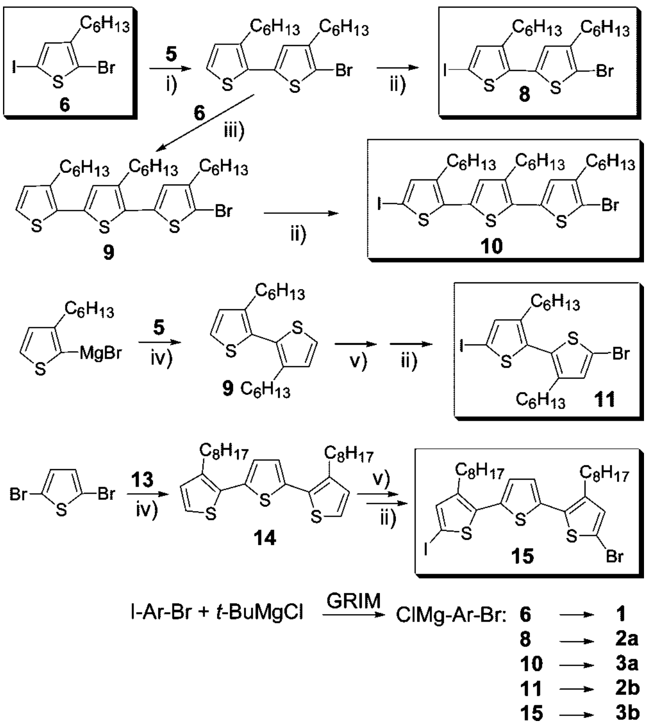
GPC measurements were carried out on Agilent 1100 Series (Agilent, USA) normal-temperature size exclusion chromatograph, equipped with a refractive index detector and one column PL Gel MIXED-B (Polymer Laboratories, U.K.); the eluent was chloroform, and the flow rate was 1 mL/min. Number-average molecular weights (M_n) and polydispersity indexes (PDI) of the obtained polymers were determined based on calibration with polystyrene standards obtained from Polymer Standards Service (PSS, Germany).

MALDI-TOF mass spectra were recorded on a Bruker Daltonics biflex IV mass spectrometer. Experiments were done with an accelerating potential of 20 kV in the reflectron mode collecting positive ions. Samples for measurements were prepared in chloroform by mixing of 5 μL of polymer solution (1 g/L) with 50 μL of matrix (dithranol) solution (1 g/L). A total of 1 μL of this mixture was deposited on the plate, and after evaporation of the solvent, measurements were performed under high vacuum. To produce the final spectrum, mass spectra from 100 to 200 shots were accumulated. PEG was used as the external standard.

Materials. 2-Bromo-3-hexylthiophene, 2,5-dibromothiophene, 2-bromo-3-octylthiophene, *tert*-butylmagnesium chloride (^{t}BuMgCl, 2.0 M solution in tetrahydrofuran, THF), Ni(PPh$_3$)$_4$, NidpppCl$_2$, bromobenzene (Ph-Br), *o*-bromotoluene (*o*-Tol-Br), *N*-bromosuccinimide (NBS), *N*-iodosuccinimide (NIS), *n*-butyllithium (*n*-BuLi), tri(isopropyl)borate, pinacol, dithranol, magnesium powder, chloroform, dichloromethane, hexane, diethyl ether, anhydrous MgSO$_4$, and ZnCl$_2$ as well as dry THF (stabilizer free) were purchased from Aldrich and used as received.

Synthesis of Monomers. The monomers **1**, **2a**, **2b**, **3a**, and **3b** were prepared by adaptations of known methods to oligothiophenes that included a combination of halogenation with *N*-halogenosuccinimides and metal-catalyzed cross-coupling reactions (Kumada, Negishi, or Suzuki, Scheme 2).[3,14,15]

Scheme 2. Synthesis of Precursors to Monomers Used in This Work[a]



[a] Key: (i); thiophene boronic ester **5,** Pd(PPh$_3$)$_4$, NaHCO$_3$ reflux, 24 h; (ii) NIS, CHCl$_3$−CH$_3$COOH (50/50 v/v), 0°C, overnight; (iii) THF, *n*-BuLi, −80 °C, 1h, then ZnCl$_2$, **6**, Pd(PPh$_3$)$_4$, RT, 24 h; (iv) 2-bromo-3-hexylthiophene, diethyl ether, Mg, Ni(dppp)Cl$_2$, room temperature, 3 h; (v) NBS, CHCl$_3$−CH$_3$COOH (50/50 v/v), 0°C, overnight.

Starting from 2-bromo-3-hexylthiophene (**4**), by lithiation with *n*-butyllithium (*n*-BuLi) and reaction with tri(isopropyl)borate and pinacol the corresponding 3-hexylthiophene-2-boronic ester (**5**) has been synthesized. Selective halogenation of **4** with NIS leads to 2-bromo-3-hexyl-5-iodothiophene (**6**). Suzuki cross-coupling of **5** and **6** yields 5-bromo-4,3′-dihexyl-2,2′-bithiophene (**7**). **7** was either iodinated by NIS into 5′-bromo-3,4′-dihexyl-5-iodo-[2,2′]bithiophenyl (**8**), which was used as the precursor for the monomer **2a**, or converted to the corresponding zincate via lithiation with *n*-BuLi and metal−metal exchange by zinc chloride. Then in the Negishi reaction under palladium catalyst it was selectively cross-coupled with **6** to give head-to-tail-coupled isomerically pure 5-bromo-4,3′,3″-trihexyl-[2,2′;5′,2″]terthiophene (**9**).[14] Finally, it was iodinated by NIS to produce 5″-bromo-3,4′,4″-trihexyl-5-iodo-[2,2′;5′,2″]terthiophene (**10**), the precursor for monomer **3a**. Symmetric, head-to-head-coupled 3,3′-dihexyl-[2,2′]bithiophene (**11**) was synthesized by Ni(dppp)Cl$_2$-catalyzed Kumada cross-coupling of **4** and 5-bromomagnesio-3-hexylthiophene prepared from **4** and Mg powder.[15] **11** was sequentially brominated and then iodinated into 5-bromo-3,3′-dihexyl-5′-iodo-[2,2′]bithiophene (**12**) using NBS and NIS, respectively. The Kumada coupling reaction between commercially available 2,5-dibromothiophene and Grignard reagent prepared from 2-bromo-3-octylthiophene (**13**) and Mg powder afforded 3,3″-dioctyl-2,2′,5′,2″-terthiophene (**14**). It was sequentially brominated and then iodinated into 5-bromo-5″-iodo-3,3″-dioctyl-[2,2′;5′,2″]terthiophene (**15**) using NBS and NIS, respectively. All monomer precursors **6**, **8**, **10**, **12**, and **15** and intermediates **4**, **5**, **7**, **9**, **11**, **13**, and **14** were carefully purified by column chromatography.

General Polymerization Procedure. Monomer precursors (**6**, **8**, **10**, **12**, and **15**) (were converted into monomers **1**, **2a**, **2b**, **3a**, and **3b** by a Grignard metathesis reaction (GRIM).[16] To this end, 1 mmol of **6**, **8**, **10**, **12**, or **15** was placed in a round-bottomed flask equipped with a magnet stirrer bar, and the atmosphere was replaced with argon. Dry THF (20 mL) was added via a syringe, and the mixture was cooled to 0 °C. Afterward, *tert*-butylmagnesium chloride (2.0 M solution in THF, 0.50 mL, 1.05 mmol) was added via a syringe, and the mixture was stirred at 0 °C for 1 h. A solution of the Ph−Ni(PPh$_3$)$_2$−Br initiator (15 mg, 2.5 mol %, for monomer **1**, 30 mg, 5 mol %, for monomers **2a** and **2b**, and 45 mg, 7.5 mol %, for **3a** and **3b** in 1 mL of toluene) was added via a syringe at 0 °C, and then the mixture was stirred for 3 h at 0 °C. The reaction mixture was quenched by 5 M hydrochloric acid,[17] and the products were extracted with chloroform. The organic layer was washed with water, dried over anhydrous MgSO$_4$, and concentrated under reduced pressure. These crude reaction mixtures, containing the rest of the hydrolyzed monomers besides polymeric materials, were analyzed by ^{1}H NMR in order to determine a conversion degree. Finally, methanol was added to the residues, and the insoluble materials were collected by filtration and washed with methanol to give pure **poly1**, **poly2a**, **poly3a**, and **poly3b** as a purple solids or **poly2b** as a yellow solid. The solids were also analyzed by ^{1}H NMR and MALDI-TOF.

Results and Discussion

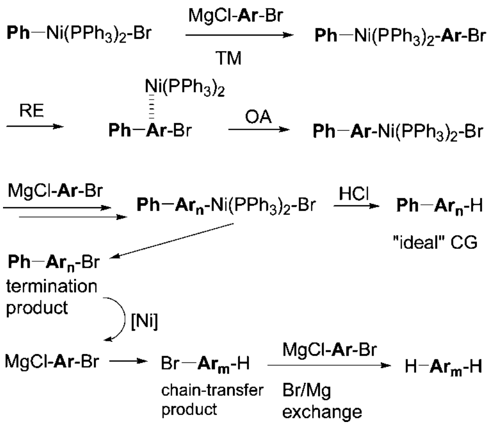
Criteria for Evaluation of the Polymerization Mechanisms. In general, chain-growth polymerizations having an ideal "living" performance differ considerably from purely step-growth polymerizations by many parameters[5] and therefore can be easily distinguished from each other. Thus, step-growth polycondensations result in high molecular weight (MW) polymers only at monomer conversions approaching 100%, and therefore, a coexistence of a high molecular weight polymer product with a significant fraction of monomers is a clear sign of chain-growth polymerization. On the other hand, a low polydispersity index (PDI) approaching 1, a straight-line dependence of the polymerization degree (DP) on the monomer conversion, and the possibility to control MW by a monomer-to-initiator ratio are criteria for the "living" chain-growth polymerizations. However, in many cases chain-growth polymerizations are not "living" due to undesired side reactions (e.g., a chain termination or/and chain transfer) and determination of the polymerization mechanism becomes less straightforward.

Polymer end group analysis is a powerful tool in investigations of polymerization mechanisms, and it was previously applied to understand the initiating step and some aspects of the propagation and termination steps of the Kumada polycondensation.[3,4,18,19] However, for the polymers formed by Ni(dppp)Cl$_2$-mediated Kumada polycondensation, the formed starting and end groups (H and Br) are not too specific to address the delicate peculiarities of the mechanism. In addition, the Br termination is easily convertable into a H one if some ^{t}BuMgCl is unintentionally left after the monomer preparation (GRIM) procedure[3b] that additionally complicates interpretation of results.

Recently we developed a method to perform the chain-growth Kumada polycondensation by starting from externally added initiators prepared at a separate step by oxidative addition of Ni(PPh$_3$)$_4$ to aryl halides.[9] Besides the synthetic advantages the developed polymerization is a useful analytical approach since it allows distinguishing the product forming by the "ideal" chain-growth mechanism from chain-termination and chain-transfer products (Scheme 3).

Indeed, the "ideal" chain-growth product must possess the Ph starting group that transfers from the Ph−Ni(PPh$_3$)$_2$−Br initiator and the H end atom forming upon hydrolysis of the propagating Ar−Ni (PPh$_3$)$_2$−Br end. Ph/Br termination products are formed by the Ph−Ni(PPh$_3$)$_2$−Br-initiated chain-growth polycondensation if these chains were terminated already during polymerization (before polymerization mixtures were subjected to hydrolysis). In contrast, the absence of the Ph moiety in the product structure (i.e., H/Br P3HT) is an indication of the chain-transfer (reinitiation) reaction. As the NMR spectra of various terminated polythiophenes were carefully assigned previously,[3,4,18−20] the relative amounts of Ph, Br, and H terminations can be easily determined by integration of ^{1}H NMR spectra. The relative content of differently terminated P3HTs can be also estimated by MALDI-TOF; however, one has to keep in mind that this method frequently underestimates the real MW due to the higher volatility of polymers with lower MW.[21] In this work we used the approach based on end group analysis and relyed predominantly on NMR data for determination of the mechanism of the Ph−Ni(PPh$_3$)$_4$−Br-mediated Kumada polycondensation of various length monomers. However, MALDI-TOF measurements were also performed, and these data were in a good qualitative (and frequently in a quantitative) agreement with the NMR data.

Scheme 3. Kumada Catalyst-Transfer Polycondensation Initiated by Ph−Ni(PPh$_3$)$_2$−Br

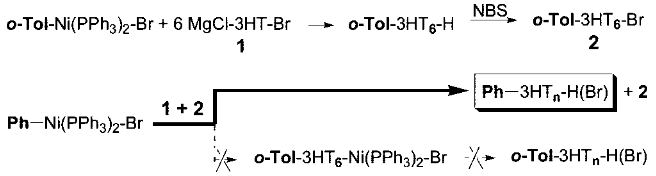


It must be emphasized that the Ph starting group in the polymerization product would be an unambiguous indication of the chain-growth polycondensation initiated by Ph−Ni(PPh$_3$)$_2$−Br only if the Ph moiety cannot be introduced into polymer structure by some other reaction pathway, such as via extension of Ph/Br oligomers formed upon the chain-transfer reaction. To this end, it was important to verify whether the above-considered catalyst-transfer process indeed proceeds intramolecularly on the single-chain level as it was earlier postulated.[3b] If, instead, the Ni(0) catalyst transfers intermolecularly, the growing polymer chains would freely exchange the Ni(0) catalyst (somewhat reminiscent a degenerative transfer mechanism in radical polymerizations),[22] then the end-group analysis will fail to address details of polycondensation mechanisms since the information about the starting groups will be scrambled.

To verify whether the catalyst indeed transfers intramolecularly, we conducted the polycondensation of **1** generated by GRIM[16] of stoichoimetric amounts of ^{t}BuMgCl and **6** in the presence of a 3-fold molar excess of *o*-Tol-Br (with respect to catalyst), which was added to the reaction mixture right after addition of the Ph−Ni(PPh$_3$)$_2$−Br to **1**. If the catalyst transfers intermolecularly, then *o*-Tol-Br molecules can serve as traps for the Ni(0) species, leading to *o*-Tol-terminated **poly1**. However, no *o*-Tol end groups were found in the reaction products, and **Ph/H-poly1** was formed predominantly.

To more accurately model the real reaction conditions, the Ph−Ni(PPh$_3$)$_2$−Br-initiated polycondensation of **1** was performed in the presence of a 3-fold molar excess of *o*-Tol/Br-terminated HT oligo(3-hexylthiophene), *o*-Tol-(3HT)$_6$-H, having DP = 6 and PDI = 1.2. *o*-Tol−(3HT)$_6$−Br (**2** in Scheme 4) was synthesized by the *o*-Tol−Ni(PPh$_3$)$_2$−Br-initiated polycondensation of **1** at a monomer-to-initiator ratio of 6 followed by bromination of *o*-Tol−(3HT)$_6$−H by NBS. **2** is readily soluble in acetone, and therefore, if it remains intact during polycondensation of **1**, it would be easily separated from higher

Scheme 4. Kumada Catalyst-Transfer Polycondensation of 1 Initiated by Ph−Ni(PPh$_3$)$_2$−Br in the Presence of *o*-Tol−(3HT)$_6$−Br



MW polymers by Soxlet extraction with acetone. Therefore, the presence of the *o*-Tol terminations in high MW P3HT fractions would be an indication of the intermolecular transfer process. However, in this experiment the *o*-Tol-terminated product was found only in the acetone fraction and not in the dichloromethane and chloroform fractions. This experiment unambiguously confirms the earlier postulated intramolecular character of the reductive elimination/oxidative addition steps, and thus, the presence of the Ph starting group in the polymerization product is indeed a clear indication of the product formed by the chain-growth mechanism.

Polycondensation of the Monothiophene 1. It was previously reported that polycondensation of the monothiophene **1** initiated by Ph−Ni(PPh$_3$)$_2$−Br performed at 0 °C leads exclusively to head-to-tail P3HT and involves a near perfect chain-growth mechanism till DP $\approx$ 30, resulting in Ph/H-terminated P3HT as the dominant product.[9] PDI for the polycondensations mediated by Ph−Ni(PPh$_3$)$_2$−Br typically varied from 1.4 to 1.8 for the unfractionated product (crude reaction mixtures were washed only with methanol). However, the polycondensation is no longer controlled at DPs higher than 30 due to the termination and chain-transfer processes as follows from the deviation of the DP vs conversion plot from a straight line and the appearance of the Ph/Br and H/Br products. The exact nature of the side reactions remains unclear; however, the limited solubility of P3HT with a DP higher than 30 at low temperatures seems to be an important factor that causes the side reactions. We found that lowering the monomer concentration has little positive effect on the solubility and reaction course. However, polycondensation of 2-bromo-5-chloromagnesio-3-dodecylthiophene, which affords a more soluble poly(3-dodecylthiophene), allows better control over the MW (up to DP = 40−50).

To be sure that any changes in the polymerization course (i.e., PDI, distribution of products) originate from the certain varied parameter, we investigated to what extent the polymerization could be affected by unintended variations of the reaction conditions. We assumed that the unintended deviations of the ^{t}BuMgCl-to-**6** ratio from stoichimetric 1/1 at the GRIM stage is both a highly probable[23] and a potentially important factor that would affect the reaction course. Table 1 (entries 1−4) shows MWs, PDIs (GPC data), and relative content (calculated by ^{1}H NMR) of differently terminated P3HT products (further designated as **poly1**) obtained at ^{t}BuMgCl/**6** ratios varied in a large range from 0.75 to 1.5. As it was for Ni(dppp)Cl$_2$-mediated polycondensation, the best results with Ph−Ni(PPh$_3$)$_2$−Br catalyst we obtained with a ^{t}BuMgCl/**6** ratio close to stoichometric 1:1.[4] We, however, found that a slight excess of ^{t}BuMgCl ($\sim$1.05) is needed in order to obtain the best reaction performance. In these conditions the "ideal" chain-growth product (**Ph/H-poly1**) with DP $\approx$ 35 constitutes at least 95% and has PDI $\approx$ 1.45 (Table 1, entry 4). Since **Ph/H-poly1** is a largely dominating product the assignment and integration of the ^{1}H NMR spectrum (Figures 1a and S4, Supporting Information) is unequivocal.[24] In the aromatic area of the ^{1}H NMR spectra, besides signals of internal thienyl rings (6.98 ppm), signals of the starting Ph group (7.59, doublet; 7.38, triplet; 7.29, multiplet), a proton of the first thienyl ring adjacent to the Ph group (7.16, singlet), and a signal of a terminal proton (6.90, singlet) are observed. They integrate well with each other, and virtually no other terminations are seen. An increase of the ^{t}BuMgCl excess to 1.5 moderately decreases the fraction of the desired Ph termination product (Table 1, entry 3). As seen from Figure 1b, a new signal at 6.825 corresponding to the Br termination appears and the integral of the signal of the last thienyl ring (at 6.90 plus 6.825 for H and Br terminations, respectively) now becomes larger than the integral of the first ring (at 7.16). The observed misbalance is due to formation of some amount of the chain-transfer **Br/H-poly1** product. In this case analysis of the mixture is no longer straightforward and it is difficult to calculate precisely the relative content of Ph/H, Ph/Br, H/Br, and H/H products assuming that all of them are present in the mixture. However, it is possible to estimate the overall content of both Ph-terminated products (Ph/H and Ph/Br) in the mixture as follows. Let the proton unit for the Ph-terminated **poly1** be the integral of the signal corresponding to the proton of the first thienyl ring attached to the Ph moiety (at 7.16). To calculate the proton unit of the **Br/H-poly1** we subtract one unit (corresponding to the integral of the end hydrogen of the Ph-terminated **poly1**) from the integral at 6.8−6.92 and divide it by a factor of 2, since there are two end protons in **Br/H poly1** appearing at 6.8−6.92. According to such calculations the content of **Ph-poly1** in the mixture is $\sim$76%, whereas it is $\sim$24% for **Br/H-poly1**. These values are in good agreement with MALDI-TOF data (not shown for this experiment).

The decrease of the ^{t}BuMgCl/**6** ratio to 0.75 further decreases the content of the Ph-terminated product **Ph-poly1** down to $\sim$ 60% along with an increase of the content of the chain-transfer product. However, the observed effect is not dramatic taking into account the potentially high reactivity of **6** toward Ni(0) complexes. Indeed, due to the presence of electron-withdrawing moieties the reactivity of C−I and C−Br bonds must be much higher in the oxidative addition reaction of Ni(0) than the reactivity of the strongly deactivated reaction by the electron-donating magnesium moiety on the C−Br bond in **1**. The fact that even in the presence of significant amounts of reactive traps for Ni(0) (7-fold excess of **6** relative to the Ni(0) initiator) the polycondensation involves predominantly the chain-growth mechanism illustrates the great propensity of the Ni(0) species to transfer intramolecularly.

Polycondensation of Oligothiophenes. In the next experiments the Ph−Ni(PPh$_3$)$_2$−Br-mediated polycondensations of differently substituted bi- and terthiophenes were examined and compared with the polycondensation of the monothiopene **1**. The monomers **2a** and **3a** are higher homologs of the monomer **1**; therefore, the series **1** → **2a** → **3a** allows monitoring solely the influence of monomer length on the catalyst-transfer process unaffected by other factors. The peculiarity of the structure of bi- and terthiophenes **2b** and **3b** is that they have no substituents adjacent to the bromine atom, whereas the chloromagnesium group in these monomers has the same surroundings as in **1**. Thus, polycondensation of **2b** and **3b** would give information about the influence of the substitution pattern on the polycondensation mechanism.

Because of the limited and MW-dependent solubility of polythiophenes and rather significant influence of aggregation processes on termination reactions, monomer-to-initiator ratios were set to obtain polymers **poly1**, **poly2a**, **poly2b**, **poly3a**, and **poly3b**, all having $\sim$40 thienyl rings (assuming the "ideal" chain-growth mechanism and full conversion of the monomers). We kept the same mass concentrations of the monomers and conducted all polycondensations at the same temperature (0 °C) and polymerization time (3 h) that corresponded to incomplete conversions of monomers (from 68% to 89%). As in these experiments, in fact, there were always different molar con-

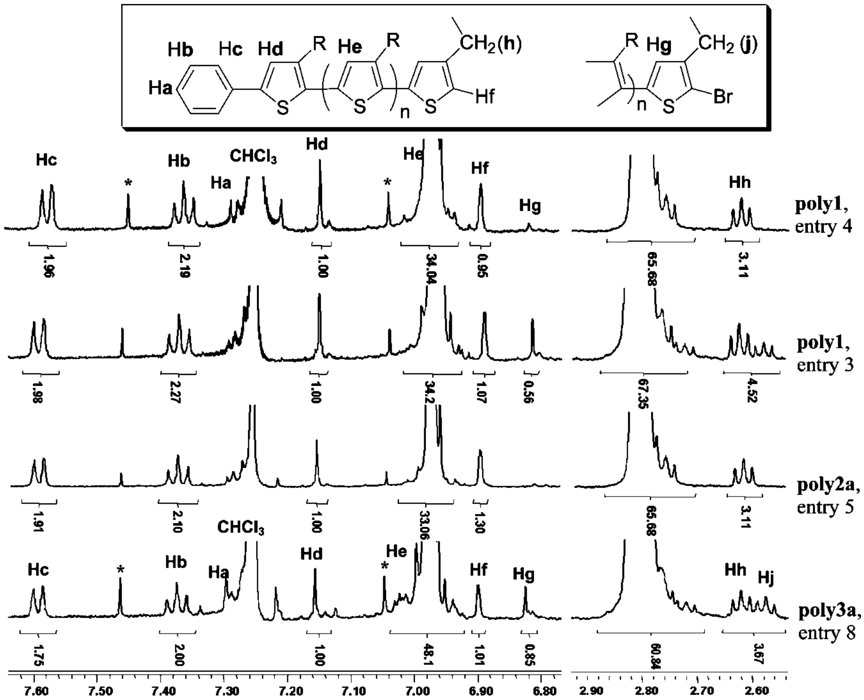
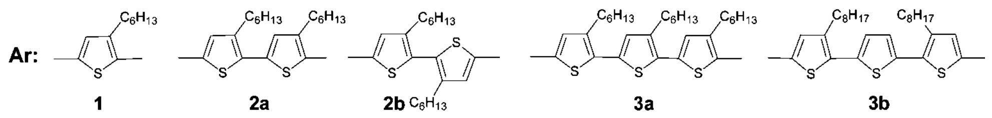


Figure 1. Regions of the ^{1}H NMR spectra showing signals of the starting Ph group and the end Br and H groups as well as of the α-methylene protons for polymers corresponding to entries 4, 3, 5, and 8 in Table 1 (asterisk (*) indicates ^{13}C satellites).

Table 1. Results of the Ph−Ni(PPh$_3$)$_2$−Br-Initiated Kumada Polycondensation

$$\text{Ph-Ni(PPh}_3)_2\text{-Br} \xrightarrow{\text{MgCl-Ar-Br}} \text{Ph-Ar}_n\text{-H} + \text{Br-Ar}_m\text{-H}$$



entry	monomer	monomer precursor/ ^{t}BuMgCl ratio	conversion, %[a]	Mn/DP[b]	PDI	Ph/H and Ph/Br, %[a]	Br/H and H/H, %[a]
1	**1**	0.75	67	3000/18	2.47	60	40
2	**1**	0.9	71	4300/26	2.45	72	28
3	**1**	1.5	65	3800/23	2.27	76	24
4	**1**	1.05	89	6100/37	1.45	95	5
5	**2a**	1.05	87	5300/15	1.67	87	13
6	**3a**	1.05	85	5700/12	1.74	69	31
7	**2b**	1.05	72	3300/10	1.91	45	55
8	**3b**	1.05	68	4200/9	2.0	31	69

[a] ^{1}H NMR data. [b] GPC data.

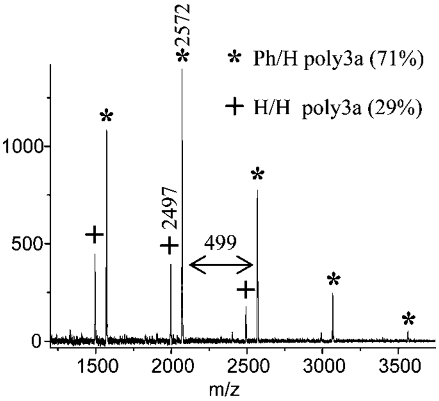
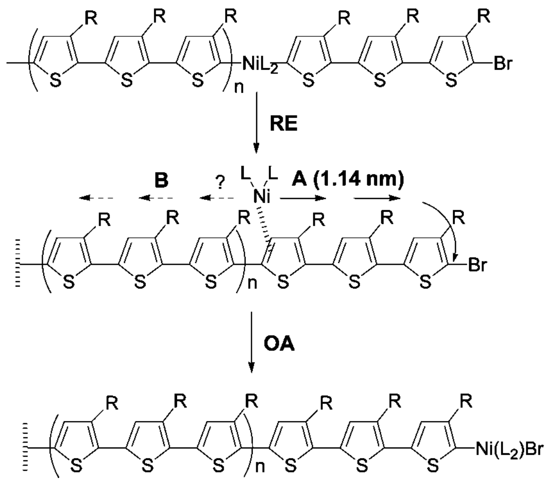


Figure 2. MALDI-TOF spectra of **poly3a** treated with ^{t}BuMgCl in order to reduce Br end atoms.[28]

centrations of monomers and different monomer-to-initiator ratios, we did not compare the rates of polymerizations but rather looked at the polymerization mechanism (chain growth vs step growth).

Table 1 (entries 5−8) shows MWs, PDIs, and the relative content of differently terminated reaction products obtained upon Ph−Ni(PPh$_3$)$_2$−Br-mediated polycondensation of monomers **2a**, **2b**, **3a**, and **3b** extracted from ^{1}H NMR (Figures 1c, 1d, and S58 (see Supporting Information)) and GPC data. In all cases formed polymeric products had higher MWs than might be expected for the step-growth polycondensation mechanism for given conversions of monomers (see Supporting Information).[25] Furthermore, the Ph-terminated polymers constitute the main fractions in the polymerization mixtures in the series **1** → **2a** → **3a** and substantial fractions in the **2b** → **3b** series. For example, the fraction of Ph-terminated polymers obtained upon polycondensation of the tertiophene **3a** is equal to 69% according to ^{1}H NMR results (Figure 1d). MALDI-TOF gives essentially the same content of the **Ph-poly3a** (71%, Figure 2).[26] As discussed above, the presence of the Ph end group in polymer chains means that these chains were formed by the chain-growth polycondensation. However, a quite broad MW distribution and the presence of substantial amounts of Ph-free products (Table 1) reflects the existence of chain-termination and chain-transfer processes. For both series of experiments (**1** → **2a** → **3a** and

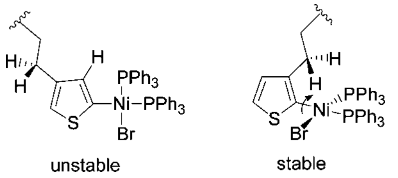
Scheme 5. Intramolecular Catalyst Transfer of 3a



2b → **3b**) the enlargement of the monomeric system results in worse polycondensation performance (higher PDI and lower content of Ph-terminated polymers) as a result of increased occurrence of chain termination and chain transfer. Nevertheless, the obtained results indicate a large domination of the chain-growth elementary steps over other pathways even in the polycondensations of lengthy monomers. Simple calculations reveal rather high selectivity of the chain-growth elementary step (compared to the chain transfer) equal to ~99% and ~97% for polycondensation of **2a** and **3a**, respectively.[27]

Thus, in the studied polycondensations the Ni catalyst undergoes selective intramolecular transfer over distances as large as 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 caused by an unsaturated coordination of the Ni (0) center formed at the reductive elimination step in the absence of appropriate stabilizing ligands. However, important details of the mechanism of this process and its kinetics remains still unknown. It is, for example, not clear whether the Ni moves unidirectionally toward the nearest C–Br bond driven by its electron deficiency (pathway **A** in Scheme 5) or it freely "walks"[7] back and forth along the growing chain via a set of intermediate η^2 complexes until it finds the C–Br bond to undergo the oxidative addition (pathway **B**). Anyway, it is the next example of an intriguing and a quite general for organometallics "ring walking" process earlier observed for some Ni,[7a] Pt,[7b] and Pd[13,7c] complexes. Understanding this process would be helpful for optimization of the polycondensation toward the "living" performance but also it would open an interesting perspective for selective aryl–halide bond activations and selective initiating of polycondensations from complex multifunctional molecules.

Chart 2



As seen from Table 1 the content of Ph-terminated products is much higher (and, hence, the chain-growth performance is much better) in the polymer series resulting in the HT-coupled polythiophenes. Thus, the increase of the monomer length from two to three thiophene rings in the HT series causes the decrease of the content of the Ph-terminated product from 87% to 69%, whereas it is from 45% to 31% in the **2b** → **3b** series. The higher content of the chain-growth polycondensation products in the HT series might be attributed to a stabilizing effect of substituents in the ortho position. It was previously proposed that the ortho substituent holds the plane of the aryl group vertical to the plane of the complex and in such a way increases its stability by lowering the energy of the highest filled orbital by bonding the d_{xy} orbitals of Ni with π^* orbitals of the aromatic ring (Chart 2).[28] On the other hand, the ortho substituents also increase the inertness of the complex by steric blocking of an axial coordinate site. It is likely that the propagating group in the **2b** → **3b** series is more prone to undesired side reactions such as a bimolecular disproportionation in the absence of such stabilization effects.

Conclusions

In this paper the feasibility of the chain-growth polycondensation of monomers comprising more than one thiophene ring (i.e., two or three) was evaluated. A Ph–Ni(PPh$_3$)$_2$–Br-mediated polycondensation of head-to-tail coupled bi- and terthiophens leads predominantly to Ph-terminated polymers indicating the chain-growth polymerization mechanism. Although an increase of the monomer length somewhat decreases the fraction of the Ph-terminated products as a result of increased probability of a chain-transfer process, the chain-growth elementary step remains dominating even for lengthy monomers, thus reflecting a "robustness" of the chain-growth polycondensation mechanism to increased monomer length. Hence, in the key polycondensation step the Ni catalyst undergoes a selective intramolecular transfer over a ~1.1 nm long conjugated system (in the case of polycondensation of terthiophenes). The chain-growth performance was found to be sensitive to the substitution pattern of the polymerized oligomers. The best results were obtained with the head-to-tail-coupled thiophenes, possibly due to the stabilizing effects of the ortho substituents, and this knowledge might be helpful for a proper design of conjugated oligomers polymerizable in a chain-growth manner. Taking into account that Ni(PPh$_3$)$_4$-based catalysts generally show worse performance for chain-growth polycondensations of monothiophenes than that of the Ni(dppp)Cl$_2$-mediated polycondensations, we believe that the later catalyst also would be superior in chain-growth polycondensations of conjugated oligomers, making this reaction a practically important tool for engineering of both the band gap and macromolecular architecture of conjugated polymers.

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Supporting Information Available: Experimental details and ^{1}H NMR characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kiso, Y.; Yamamoto, K.; Tamao, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374–4376.

(2) (a) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1470. (b) Kiriy, N.; Kiriy, A.; Bocharova, V.; Stamm, M.; Richter, S.; Plötner, M.; Fischer, W.-J.; Krebs, F. C.; Senkovska, I.; Adler, H.-J. *Chem. Mater.* **2004**, *16*, 4757–4764.

(3) (a) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169–1171. (b) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547.

(4) (a) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526–3528. (b) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649–8656.

(5) (a) *Handbook of radical polymerization*; Matyjaszewski, K., Davis, T., Eds.; Wiley-Interscience: Hoboken, 2002. (b) Ivin, K. J. ; Mol, C. J. *Olefin metathesis and metathesis polymerization*; Academic Press, London, 1997. (c) Synthesis of all-conjugated polymers by chain-

growth polycondensation: (d) Zhang, Y.; Tajima, K.; Hirota, K.; Hashimoto, K. *J. Am. Chem. Soc.* **2008**, *130*, 7812–7813. (e) Ohshimizu, K.; Ueda, M. *Macromolecules* **2008**, *41*, 5289–5294.

(6) *Handbook of Conducting Polymers*, 3rd ed.; Skotheim, T. A., Reynolds, J. R., Eds.; Taylor & Francis Group, LLC: Boca Raton, 2007.

(7) (a) Zenkina, O. V.; Karton, A.; Freeman, D.; Shimon, L. J. W.; Martin, J. M. L.; van der Boom, M. E. *Inorg. Chem.* **2008**, *47*, 5114–5121. (b) Strawser, D.; Karton, A.; Zenkina, O. V.; Iron, M. A.; Shimon, L. J. W.; Martin, J. M. L.; van der Boom, M. E. *J. Am. Chem. Soc.* **2005**, *127*, 9322–9322. (c) Zenkina, O.; Altman, M.; Leitus, G.; Shimon, L. J. W.; Cohen, R.; van der Boom, M. E. *Organometallics* **2007**, *26*, 4528–4534. (d) Burdeniuk, J.; Milstein, D. *J. Organomet. Chem.* **1993**, *451*, 213–220.

(8) Tentatively, Yokozawa et al. proposed that the reactivity of the terminal C−Br bond at the oxidative addition step is higher than the reactivity of the C−Br bond of the monomer (due to a deactivating influence of the electron-donating magnesiumchloride group) that favors the preferential intramolecular transfer of the Ni(0): see ref 3a.

(9) Senkovskyy, V.; Khanduyeva, N.; Komber, H.; Oertel, U.; Stamm, M.; Kuckling, D.; Kiriy, A. *J. Am. Chem. Soc.* **2007**, *129*, 6626–6632.

(10) Roncali, J. *Macromol. Rapid Commun.* **2007**, *28*, 1761–1775, and references herein.

(11) (a) Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.; Neagu-Plesu, R.; Belletete, M.; Durocher, G.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2008**, *130*, 732–742. (b) Mullekom, H. A. M. v.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mater. Sci. Eng., R* **2001**, *32*, 1–40.

(12) (a) Hong, X. M.; Tyson, C. J.; Collard, D. M. *Macromolecules* **2000**, *33*, 3502–3504. (b) Sheina, E. E.; McCullough, R. D. *Polym. Prepr.* **2004**, *45*, 800–801.

(13) It was previously demonstrated for related Suzuki chain-growth polycondensation having a similar catalyst-transfer mechanism that Pd(0) catalytic species are able to transfer intramolecularly over a 1 nm long fluorene moiety: (a) Calhorda, M. J.; Brown, J. M.; Cooley, N. A. *Organometallics* **1991**, *10*, 1431–1438. (b) Dong, C.-G.; Hu, Q.-S. *J. Am. Chem. Soc.* **2005**, *127*, 10006–10007. (c) Sinclair, D. J.; Sherburn, M. S. *J. Org. Chem.* **2005**, *70*, 3730–3733. (d) Weber, S. K.; Scherf, U. *Org. Lett.* **2006**, *8*, 4039–4041. (e) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236–7237.

(14) Cremer, J.; Mena-Osteritz, E.; Pschierer, N. G.; Müllen, K.; Bäuerle, P. *Org. Biomol. Chem.* **2005**, *3*, 985–995.

(15) Chaloner, P. A.; Gunatunga, S. R.; Hitchcock, P. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1597–1604.

(16) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250–253.

(17) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromol. Rapid Commun.* **2004**, *25*, 1663–1666.

(18) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324–4333.

(19) Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777–5785.

(20) Chen, T.; Wu, X.; Rieke, R. *J. Am. Chem. Soc.* **1995**, *117*, 233–244.

(21) (a) Montaudo, G.; Scamporrino, E.; Vitalizi, D.; Mineo, P. *Rapid Commun. Mass Spectrom.* **1998**, *10*, 1551. (b) Montaudo, G.; Samperi, F.; Montaudo, M. S. *Prog. Polym. Sci.* **2006**, *31*, 277–278.

(22) Matyjaszewski, K.; Gaynor, S.; Wang, J.-S. *Macromolecules* **1995**, *28*, 2093–2095.

(23) An unintended mismatch between the relative amounts of **6** and ^{t}BuMgCl during the GRIM procedure is quite probable because of difficulties to dose precisely small portions of ^{t}BuMgCl solution and a high sensitivity of ^{t}BuMgCl to the moisture and air.

(24) Assignment and evaluations of ^{1}H NMR spectra were performed as described for the experiment corresponding to entry 3, Table 1 (see also Supporting Information).

(25) For given conversions of the monomers (Table 1) DP values must not exceed 10 if the polycondensation proceeds via the step-growth mechanism. For example, at 90% conversion DP $= 1/1 - 0.9 = 10$ is expected: (a) Carothers, W. H. *J. Am. Chem. Soc.* **1929**, *51*, 2548–2559. (b) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, 1953; Chapters III and VIII.

(26) Since the mass of the Br atom (80) is close to the mass of the Ph moiety (77) the polymerization mixture was treated to ^{t}BuMgCl prior to MALDI-TOF measurements according to the procedure described by McCullough et al. to reduce any existing Br end groups. ^{1}H NMR data confirmed a quantitative reduction of Br atoms, and thus, the signals with $m/z = 499 + 78$ belong to **Ph/H-poly3a**, whereas the signals with $m/z = 499 + 2$ belong to **H/H-poly3a** (Figure 2).

(27) [**Ph-poly**] = S^{DP} and S = [**Ph-poly**]$^{1/\mathrm{DP}}$, where [**Ph-poly**] is the fraction of Ph-terminated products in the polymerization mixture, S is the selectivity of the chain-growth (intramolecular catalyst transfer) elementary step, and DP is the mean polymerization degree. $S_{\textbf{Ph-poly2a}}$ = [**Ph-poly2a**]$^{1/15} = 0.87^{1/15} = 0.99$ (99%); $S_{\textbf{Ph-poly3a}}$ = [**Ph-poly3a**]$^{1/12} = 0.69^{1/12} = 0.97$ (97%); $S_{\textbf{Ph-poly2b}}$ = [**Ph-poly2b**]$^{1/10} = 0.45^{1/10} = 0.923$ (92.3%); $S_{\textbf{Ph-poly3b}}$ = [**Ph-poly3b**]$^{1/10} = 0.31^{1/9} = 0.88$ (88%).

(28) Hidai, M.; Kashiwagi, T.; Ikeuchi, T.; Uchida, Y. *J. Organomet. Chem.* **1971**, *30*, 279–282.

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