Convenient Route To Initiate Kumada Catalyst-Transfer Polycondensation Using Ni(dppe)Cl₂ or Ni(dppp)Cl₂ and Sterically Hindered Grignard Compounds

Volodymyr Senkovskyy,*,†,‡ Michael Sommer,*,†,‡ Roman Tkachov,† Hartmut Komber,† Wilhelm T. S. Huck,‡ and Anton Kiriy*,†

Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany, and Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K. V.S. and M.S. contributed equally to the work

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Conjugated polymers (CPs) attract considerable attention as promising materials for solar cells, field effect transistors, light-emitting diodes, etc. However, the properties of existing CPs that are prepared predominantly by conventional step-growth polycondensations are still far from optimal. For industrial-scale applications, CPs with controllable molecular weight (MW), MW distribution, chain-end functionality, minimum amounts of defects, and as a result, controlled and reproducible optoelectronic properties are required. In addition, new CP architectures are needed that predictably self-assemble into desirable nanomorphologies, thus solving a longstanding problem with improper morphologies of active layers in optoelectronic devices. Nowadays, chain-growth Kumada catalyst transfer polycondensations (KCTP), also referred to as Grignard metathesis polymerization (GRIM), has become a powerful tool for the synthesis of well-defined polymers, all-conjugated block copolymers and polymer brushes. However, despite impressive progress, several important challenges still remain. Although a number of model thiophene-based conjugated block copolymers were already synthesized via the sequential polymerization of different monomers, examples of all-conjugated block copolymers composed of two substantially different blocks remain scarce. While some effort has been made in synthesizing various types of donor–acceptor block copolymers, all-conjugated block copolymers composed of state-of-the-art electron-donor and electron-acceptor conjugated blocks have not been synthesized to date. Such architectures are potentially promising materials for interface engineering in organic solar cells, especially when considering that power conversion efficiencies of all-polymer blend photovoltaics are currently lagging behind polymer/fullerene derivative-based devices. Difficulties in preparing such block copolymers originate from the synthetic requirements that the two different blocks should be formed with the aid of the same catalyst, under approximately the same polymerization conditions and without a sacrifice in the chain-growth polymerization performance. One way to solve this problem is to optimize the polymerization conditions and catalysts that are suitable to grow both blocks. An alternative strategy implies that two blocks are polymerized in two steps under optimal conditions for polymerization of each block. Here, the most challenging step is to selectively prepare functional Ni-initiators in high yield (frequently called as externally added initiators) that are properly attached to molecules or objects, from which polymerization of conjugated polymer can finally be performed. In usual GRIM polymerizations the Ni-initiator is formed in situ from the first two monomer molecules that react with Ni(dppe)Cl₂ or Ni(dppp)Cl₂ under GRIM polymerization conditions. A failure of attempts to apply a similar strategy in the preparation of externally added initiators from Ni(L)Cl₂ and Phenylmagnesiumbromide (5): Highly Efficient Method for the Preparation of Initiators from Aryl Halides and Ni(bipy)₄Cl₂ followed by Ligand Exchange Using the Previously Reported Method

Scheme 1. (A) In Situ Formation of Ni Initiators from Commercially Available Ni(L)Cl₂ (Ni(dppe)Cl₂ or Ni(dppp)Cl₂) under GRIM Polymerization Conditions; (B) Failure of Attempts To Apply a Similar Strategy in the Preparation of Externally Added Initiators from Ni(L)Cl₂ and Phenylmagnesiumbromide (5); (C) Highly Efficient Method for the Preparation of Initiators from Aryl Halides and Ni(bipy)₄Cl₂ Followed by Ligand Exchange Using the Previously Reported Method

*Corresponding author. Telephone: +49-351-4658-294, E-mail: (V.S.) senkovskyy@ipfd.d; (A.K.) kiriy@ipfd.d; (M.S.) ms928@cam.ac.uk.

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functionalized Ni-initiators can be prepared in a similar way via monotransmetalation of Ni(L)Cl₂ and readily available Grignard reagents, e.g., 5 (Scheme 1B). One should, however, take into account that product 6 forming in the first transmetalation step may undergo further transmetalation with 5 leading to 7 and finally to homocoupling product 8 and free Ni(0) species. Unfortunately, this unwanted pathway indeed dominates when Ph⁻MgBr is used as the Grignard reagent, as was demonstrated in our previous work. Although a small amount of the potential initiator 6 was detected in the reaction mixture, the selectivity toward that species was generally low even at a high excess of Ni(L)Cl₂. The main reason for the low selectivity is the much better solubility of 6 compared to Ni(dppe)Cl₂, so that effectively 6 is always present in the reaction mixture in excess and reacts faster with 5.

Since we faced severe problems in the preparation of initiators from Ni(L)Cl₂ and Grignard precursors via the transmetalation route as shown in Scheme 1B, we switched our attention to an alternative approach based on the oxidative addition of Ni(0) complexes to aryl halides. Unfortunately, Ni(0) complexes with two bidentate phosphorus ligands (e.g., Ni(dppp)₂ or Ni(dppe)₂) are inert toward aryl halides, and in situ generated Ni(dppp) or Ni(dppe) species supported by single ligands are too reactive to selectively give the desirable adducts. We therefore developed a method for the preparation of initiators via oxidative addition of Ni(0) carrying monodentate ligands (Ni(PPh₃)₄) to aryl halides Ar⁻X and reported the first surface-initiated polymerization of poly(3-hexylthiophene) (P3HT). This process, however, suffers from two major drawbacks. First, initiators are formed in relatively low yields due to undesirable homocoupling side-reactions. Second, the chain-growth performance of the Ni(PPh₃)₄-catalyzed polymerization is much worse compared to Ni complexes with bidentate phosphorus ligands. While the latter problem can be circumvented using a ligand-exchange strategy, the former is difficult to overcome and this strongly limits the applicability of the approach.

Recently, we developed a much more universal method which is tolerant to many functional groups and that allows a high-yield preparation of a large variety of initiators from differently substituted aryl halides (e.g., 9, Scheme 1C). The method proceeds via intermediate bipyridyl (bipy)-supported complexes (e.g., 10) formed from aryl halides and Ni(bipy)Et₂, which are further converted into dppe or dppe-based initiators via ligand-exchange (e.g., 6). However, Ni(bipy)Et₂ is not commercially available and highly reactive toward moisture and oxygen making it difficult to handle (a glovebox is usually required).

Very recently, we studied the reactivity of alkyl-substituted thiophene monomers, such as 2-bromo-5-chloromagnesio-3,4-dihexylthiophene (11), and found that monomers having the alkyl substituent in the ortho-position to the chloromagnesium group do not polymerize if Ni(dppe)Cl₂ or Ni(dppp)Cl₂ catalysts are used (Scheme 2). A closer look at the reaction products by in situ ³¹P NMR measurements revealed that these monomers participate in the first transmetalation step (TM1) with Ni(dppe)Cl₂ forming 12, but are not reactive toward the consecutive second transmetalation step (TM2). Therefore, intermediate 13, in which two alkyl substituents are directed toward the Ni center, is not formed, presumably because of steric hindrance occurring upon the attack of the second monomer onto 12. We assumed such a behavior, which is unwanted if one aims to polymerize 11, to be useful for the preparation of Ni-initiators starting from Ni(L)Cl₂.

To verify this idea, Grignard compounds 15 and 19 were prepared from o-bromotoluene 14 and 2-bromo-3-hexylthiophene 18, respectively, and magnesium turnings (Scheme 3). These were then reacted with Ni(dppe)Cl₂ and Ni(dppp)Cl₂ at 0°C in THF-d₈ and the reactions were followed by in situ ³¹P NMR. In each case the first spectrum taken about 3 min after mixing (Figure 1) shows the major signals of the expected product of monotransmetalation 16 and 20, respectively, represented by the corresponding bromo- and chloro-derivatives.

The formation of the bromo-derivatives results from the exchange of the chloride atom from Ni(L)Cl₂ by bromide, which comes from MgBrCl (TM1 byproduct). Complete conversion of the chloro compound to the bromo-derivative was realized by the addition of a small amount of MgBr₂-Et₂O solution in THF-d₈, thus proving the signal assignment. Trace amounts of Ni(dppe)₂ and Ni(dppp)₂ side-products (1–2%) were also detected in the reaction mixtures. The composition of the reaction mixture remained constant for more than 30 min as long as no excess of the Grignard compound was used. Further evidence for the Cl←Br exchange and the ³¹P NMR assignments is provided by the additional synthesis of complex 20 starting from 18 via Scheme 1C, which results in the direct formation of the bromo-complex. The identity with the complex formed from 19 and Ni(dppe)Cl₂ was confirmed by ³¹P NMR (Supporting Information, Figure S2).

To carry out the polymerization, initiators 16 (or 20) were prepared in situ by stirring 15 (or 19) with equimolar amounts of
Ni(dppp)Cl₂ was added to the solution of (ful for photovoltaic applications. In order to test different starting groups, showing that this synthetic approach can easily be extended to more complex heterocyclic initiator precursors. A detailed investigation of the optoelectronic properties of F8TBT-P3HT and the application in organic photovoltaics will be extended to more complex heterocyclic initiator precursors. Since Br end-groups are found with F8TBT as the starting group, we can also expect Br/Br terminated P3HT, as is demonstrated particularly useful to probe the initiation efficiency and the degree of functionalization. Figure 3b shows the MALDI spectrum of 24. The major peak series corresponds to P3HT with F8TBT as the starting group and hydrogen as end-group, as exemplarily shown for the peak at 3182.7 g/mol (166.3 × 14 + 1 = 856.4 = 3185.2). The second intensive peak series arises from F8TBT/Br end-groups (166.3 × 14 + 1 + 856.4 = 3264.5, peak at 3261.9). We note that only a small fraction of polymer without the F8TBT starting group is observed, namely H/Br terminated P3HT (166.3 × 19 + 1 + 79.9 = 3240.6, peak at 3237.9), which most probably arises from conventional initiation with Ni(dppp)Cl₂. Since Br end-groups are found with F8TBT as the starting group, we can also expect Br/Br terminated P3HT, as is demonstrated for the 19-mer (19 × 166.3 + 79.9 = 3318.6, peak at 3317.1). Thus, F8TBT-P3HT 24 exhibits a high degree of F8TBT starting groups, showing that this synthetic approach can easily be extended to more complex heterocyclic initiator precursors. A detailed investigation of the optoelectronic properties of F8TBT-P3HT and the application in organic photovoltaics will be the subject of future investigations.

In conclusion, we have shown that the reactions between NiL₂Cl₂ and Grignard compounds Ar-MgBr stop after the first transmetallation step, if the aryl groups have alkyl substituent in the ortho-position to the bromomagnesium group. As such, this transmetallation reaction is a very convenient and highly selective method for the preparation of initiators for Kumada catalyst-transfer polycondensation reactions from easily available compounds. This developed
Scheme 4. Preparation of Ni Initiators with Electronic Functionality from Ni(dppp)Cl₂ and Sterically Hindered Grignard F8TBT-MgCl2 22 Followed by Polymerization of 1

Figure 3. (a) ³¹P NMR of complex F8TBT-NidpppBrCl (23). The sharp singlet arises from the formation of Ni(dppp)₂. (b) Complete MALDI-ToF spectrum of F8TBT-P3HT (24) (left) and section showing the different peak series with F8TBT/H, F8TBT/Br, Br/Br and H/Br terminated P3HT chains (right).

method allows the initiation of KCTP, and the polymerization of 2-bromo-5-chloromagnesio-3-hexylthiophene results in the corresponding aryl-terminated poly(3-hexylthiophene)s with high initiation efficiencies. Since the initiation of more complex heterocycles with electronic functionality proceeds with high yield as well, we envisage further extensions and applications in the field of multifunctional conjugated polymer architectures.

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Supporting Information Available: Text giving experimental details and characterization and figures showing NMR spectra and GPC curves. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


(8) Conjugated block copolymers can also be prepared via polymer analogous coupling, however targeted block copolymers formed by this method are usually contaminated by unreacted homopolymers so that tedious purifications are usually needed: Scherer, U.; Gutacker, A.; Koenen, N. Acc. Chem. Res. 2008, 41, 1086–1097.


(14) An attempt to use commercially available air-stable Ni(PPh₃)₂Cl₂ for preparation of externally addable initiators was undertaken, however moderate to low initiation efficiencies were achieved, most likely because of homocoupling side reactions inherent to Ni complexes having monodentate phosphorous ligands: Doubina, N.; Ho, A.; Jen, A. K.-Y.; Luscombe, C. K. Macromolecules 2009, 42, 7670.


(16) ³¹P NMR data at 0 °C in THF-d₈ (δ; Jpp): 16-dppe, 53.0 and 35.3 ppm, 17 Hz; 16-dppe-Br, 55.5 and 35.5 ppm, 18 Hz; 20-dppe, 55.1 and 38.5 ppm, 35 Hz; 20-dppe-Br, 58.4 and 42.6 ppm, 34 Hz; 16-dppp, 20.7 and −4.8 ppm, 44 Hz; 16-dppp-Br, 21.1 and −4.6 ppm, 44 Hz; 20-dppp, 17.9 and −4.2 ppm, 63 Hz; 20-dppp-Br, 19.0 and −3.6 ppm, 63 Hz.
