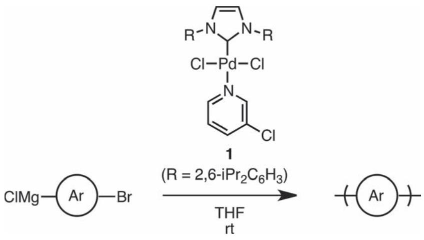
Chain-Growth Polymerization of Aryl Grignards Initiated by a Stabilized NHC-Pd Precatalyst

Zachary J. Bryan, Mitchell L. Smith, Anne J. McNeil*

An N-heterocyclic carbene-ligated palladium catalyst was discovered to mediate living, chain-growth polymerizations of both phenylene- and thiophene-based monomers. Polymerization of a fluorene-based monomer, on the other hand, did not proceed through a living, chain-growth pathway. Excitingly, block copolymerizations of phenylene and thiophene proceeded via a chain-growth pathway, regardless of the order of monomer addition. Although some chain termination was observed during these copolymerizations, this pathway could be minimized when the second monomer was added shortly after consumption of the first monomer. These results suggest that the catalyst resting-state at the end of polymerization is unstable. As a result, modifications to the NHC-scaffold or the 3-chloropyridine ligand will be necessary to generate an improved catalyst.



1. Introduction

The recent discovery of chain-growth methods for synthesizing π-conjugated polymers[1] has generated significant interest because copolymers with specific sequences and potentially advantageous properties can now be targeted.[2] For example, all-conjugated block[3] and gradient[4] copolymers as well as surface-grafted[5] and end-functionalized[6] polymers have been prepared. These chain-growth methods largely consist of cross-coupling reactions between difunctionalized arenes (e.g., Br/MgX) using Ni catalysts ligated by chelating phosphines.[7] One current limitation is the narrow scope of monomers that are capable of undergoing chain-growth homo- and copolymerizations. As a consequence, there is an ongoing search for a more universal catalyst.

One approach is to modify the steric and electronic properties of the ligand. In 2011, we reported on a series of bis(dialkylphosphino)ethane-based ligands and demonstrated that unhindered ligands led to facile catalyst decomposition while hindered ligands interfered with the chain-growth pathway.[8] More recently, we examined the influence of ligand electronic properties and found that electron-rich ligands promoted the chain-growth pathway.[9] We hypothesized that this electronic effect was due, in part, to stabilization of the key intermediate (i.e., a Ni(0)-polymer π-complex). Combined, these results suggest that electron-donating ligands with moderate steric properties are ideal for chain-growth polymerizations. Because N-heterocyclic carbenes (NHCs) are stronger σ-donors than phosphines,[10,11] and their steric properties are easily modified, we anticipated that they would be ideal ligands for the chain-growth polymerizations.[12]

An alternative approach for developing new catalysts is to change the nature of the metal species. Pd catalysts have recently emerged as an alternative to Ni in the chain-growth polymerizations.[13–15] For example, using (t-Bu$_3$P)Pd(Ph)Br as the catalyst, both Suzuki-Miyaura[13] and Suzuki-Heck[14] conditions have led to chain-growth polymerizations. Excitingly, the scope of monomers is broad and even includes *n*-type monomers, which have been rare in the Ni-catalyzed processes.[16] Nevertheless,

Z. J. Bryan, M. L. Smith, Asst. Prof. A. J. McNeil
Department of Chemistry and Macromolecular Science and Engineering Program, University of Michigan,
930 North University Avenue, Ann Arbor, MI 48109-1055, USA
E-mail: ajmcneil@umich.edu

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these methods need further improvement. For example, in most cases, the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis of the resulting polymers revealed a significant amount of polymers with Ph/Br end-groups. These end-groups indicate that either the catalyst fails to undergo an intramolecular oxidative addition into the growing polymer chain or the propagating species is unstable, leading to premature reductive elimination of polymer-Br.

We selected NHC-ligated Pd precatalyst **1**[17,18] based on a recent report by Larrosa and co-workers,[19] who observed an unexpected difunctionalization of 1,4-dibromobenzene when one equivalent of PhMgCl was used. A diffusion-controlled oxidative addition was invoked to rationalize this selectivity.[20] This mechanism is similar to that proposed for the Ni-catalyzed chain-growth polymerizations (see Scheme 2),[21,22] suggesting that this Pd precatalyst might also mediate chain-growth polymerization of aryl monomers. In addition, Organ and co-workers[17c] demonstrated that this precatalyst could facilitate cross-coupling reactions between two hindered arenes, suggesting that precatalyst **1** will readily polymerize the *ortho*-functionalized monomers typically used to make soluble π-conjugated polymers. Finally, these pyridine-stabilized Pd precatalysts have additional advantages in that they are air- and moisture-stable as well as commercially available.

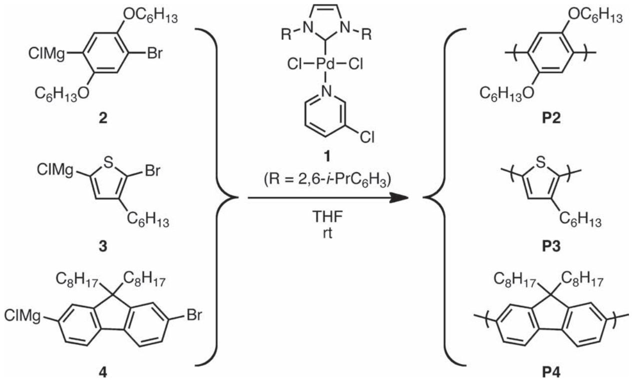
We report herein the homo- and copolymerizations of (4-bromo-2,5-bis(hexyloxy)phenyl)magnesium chloride (**2**), (5-bromo-4-hexylthiophen-2-yl)magnesium chloride (**3**), and (7-bromo-9,9-dioctyl-fluoren-2-yl)magnesium chloride (**4**) mediated by Pd precatalyst **1** (Scheme 1). A chain-growth homopolymerization was observed for both monomers **2** and **3**, with linear increases in the number-average molecular weight ($\overline{M}_n$) with conversion as well as narrow molecular weight distributions (PDI). Block copolymerizations gave the expected chain extension when the second monomer was added soon after complete consumption of the first monomer. In contrast, polymerization of monomer **4** was neither living nor perfectly chain-growth. Overall, these studies indicate that further modifications to the catalyst scaffold, either by selecting an alternative NHC ligand or by varying the steric and electronic properties of the stabilizing ligand (i.e., 3-chloropyridine),[23] are needed to further improve the chain-growth polymerizations.

2. Experimental Section

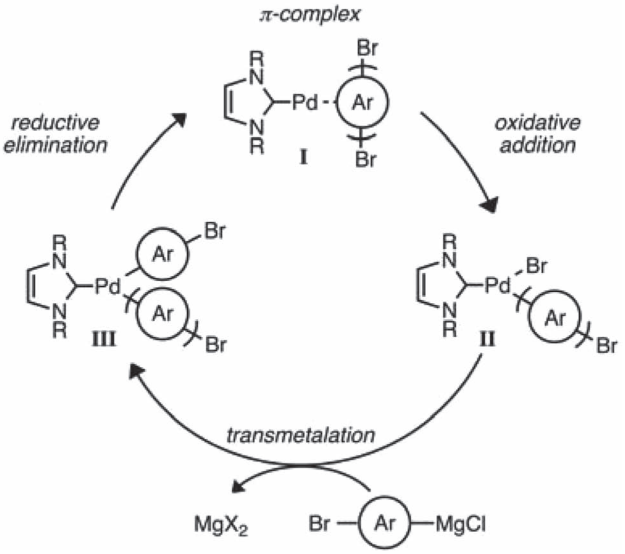
2.1. Monomer Preparation

Monomers **2**, **3**, and **4** were generated in situ via Grignard metathesis of the dibromo precursors using *i*-PrMgCl (see Supporting Information).[24,25]

Anne McNeil received her B.S. degree in Chemistry from the College of William and Mary where she carried out undergraduate research with Professor Robert Hinkle. She then pursued graduate studies at Cornell University working with Professor David Collum. Following postdoctoral work at the Massachusetts Institute of Technology with Professor Timothy Swager, she joined the faculty at the University of Michigan in 2007 as an Assistant Professor of Chemistry and Macromolecular Science and Engineering. She has been recognized with a number of awards, including a Presidential Early Career Award in Science and Engineering, a Beckman Young Investigator Award, a Sloan Research Fellowship, an Office of Naval Research Young Investigator Award, and an NSF CAREER Award. Research in the McNeil group focuses on the design and synthesis of novel organic materials.



Scheme 1. Syntheses of π-conjugated polymers **P2**-**P4** mediated by Pd precatalyst **1**.



Scheme 2. Proposed mechanism for the observed chain-growth behavior.

2.2. General Procedure for Homopolymerizations

A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv.), and THF (7.5 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **2** (2.25 mL, 1.01 mmol) was then added via syringe and stirred for 90 min at room temperature (rt). The reaction was then quenched with aq. HCl (5 M, 10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The resulting white solid was then washed with MeOH and dried under vacuum. (209 mg, 75% yield) $\overline{M}_n = 28.2$ kDa, PDI = 1.19.

2.3. General Procedure for Block Copolymerizations

A 25 mL Schlenk flask was equipped with a stir bar, precatalyst **1** (10.2 mg, 0.0150 mmol, 1 equiv.), and THF (5.0 mL) in a glovebox under an N_2 atmosphere. The flask was then equipped with a septum (secured with copper wire), removed from the glovebox, and put under an N_2 atmosphere. Monomer **2** (1.8 mL, 0.50 mmol) was then added via syringe and stirred for 180 min at rt. After 180 min, an aliquot (0.5 mL) was withdrawn via syringe and immediately quenched with aq. HCl (12 M, 1 mL). The mixture was extracted with $CHCl_3$ (3 × 1 mL) with mild heating and the combined aliquots were dried over $MgSO_4$, filtered, and analyzed by GPC ($\overline{M}_n = 9.2$ kDa, PDI = 1.24). Monomer **3** (3.2 mL, 0.90 mmol) was then added via syringe and stirred for 60 min at rt. After 60 min, the reaction was quenched with aq. HCl (5 M, 10 mL) and extracted with $CHCl_3$ (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and the solvent was removed in vacuo. The resulting purple solid was then dissolved in a minimum amount of $CHCl_3$ and precipitated into MeOH. The precipitate was collected and dried under vacuum (223 mg, 78% yield). $\overline{M}_n = 17.8$ kDa, PDI = 1.32.

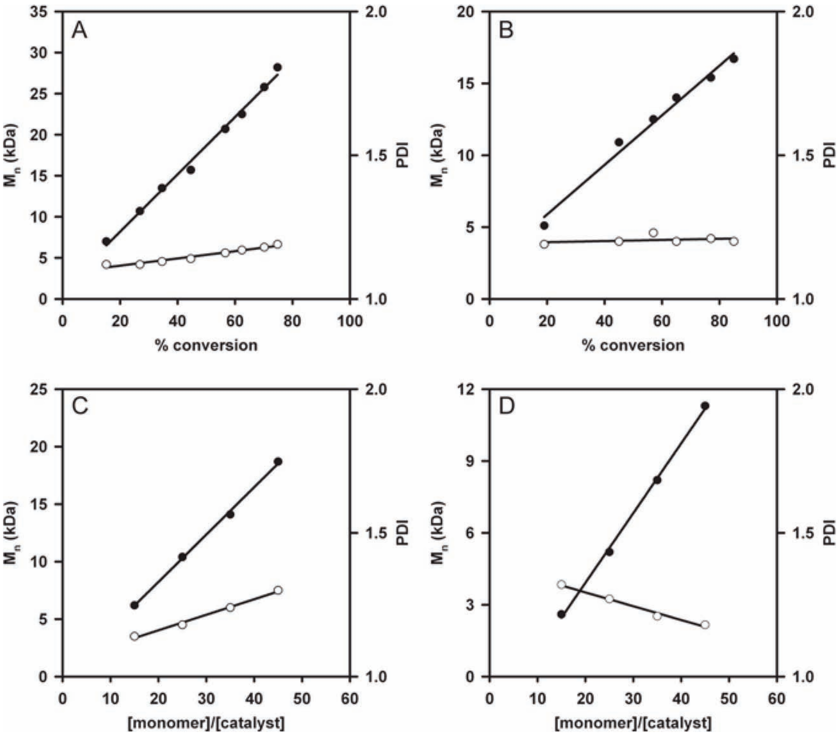


Figure 1. Plots of $\overline{M}_n$ (●) and PDI (○) versus conversion for the polymerization of monomers (A) **2** and (B) **3** using precatalyst **1** ([**1**] = 1.5 × 10^{-3} M; [**2**] = 77 × 10^{-3} M; [**3**] = 98 × 10^{-3} M; 25 °C; THF). Plots of $\overline{M}_n$ (●) and PDI (○) versus [monomer]/[catalyst] ratio for polymerization of monomers (C) **2** and (D) **3** using precatalyst **1** (25 °C, THF).

3. Results and Discussion

3.1. Homopolymerizations

The homopolymerizations of **2** and **3** mediated by precatalyst **1** showed linear increases in the number-average molecular weight ($\overline{M}_n$) with conversion and narrow molecular weight distributions (PDI) (Figure 1A and B). Both results are consistent with a chain-growth mechanism. Further support was provided by examining the relationship between the [monomer]/[catalyst] ratio and the $\overline{M}_n$ (Figure 1C and D). The observed linear relationship suggests that each Pd precatalyst initiates a single-polymer chain.

Low-molecular-weight polymers were subjected to MALDI-TOF MS analysis after quenching, which revealed predominantly polymers with H/Br end-groups. These end-groups reveal that the catalyst is located at the polymer chain end, as evidenced by its replacement with a proton during the acidic quench. To support the living nature of these polymerizations, a second aliquot of the same monomer was added immediately after consumption of the first aliquot. The observed increases in $\overline{M}_n$ with only minor broadening of the PDIs indicates that most polymer chains remain living under these conditions (Supporting Information).

The regioregularity of the poly(3-hexylthiophene) will depend on the relative reactivities of the regioisomers of monomer **3** (approximately an 80:20 mixture, major isomer is shown in Scheme 1). By monitoring their relative conversions, we observed that the major regioisomer is predominantly consumed within the first 50% conversion (Supporting Information). As the concentration of the major regioisomer decreased, the minor regioisomer was consumed. As a consequence, the poly(3-hexylthiophene) regioregularity was low (80%). The increased reactivity of the major regioisomer has been attributed to the lack of a substituent *ortho* to the reactive carbon, which leads to a faster transmetalation onto the catalyst compared with the minor regioisomer.[26] Though not explored herein, if the I/Br functionalized precursor is used to regioselectively generate **3**, a highly regioregular poly(3-hexylthiophene) is expected using this method.[27,28]

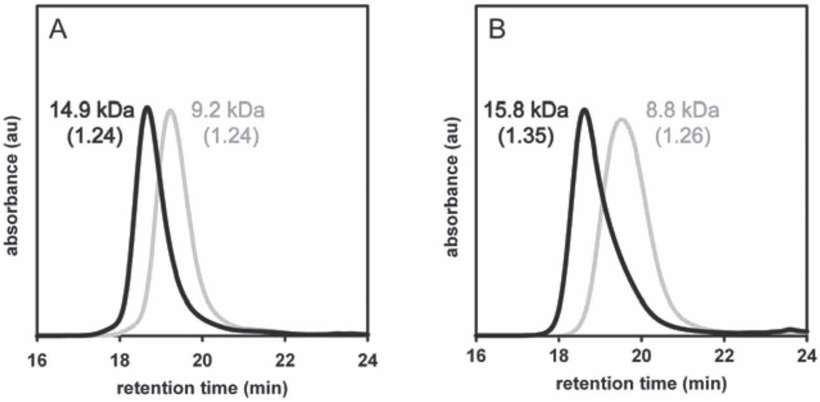


Figure 2. Gel permeation chromatograms (GPC) for block copolymerizations using Pd precatalyst **1** to generate (A) **P2**-*block*-**P3** and (B) **P3**-*block*-**P2**. The gray line represents the GPC curve immediately before second monomer addition. The black line represents the GPC curves after copolymerization is complete.

In contrast to both monomers **2** and **3**, the polymerization of fluorene monomer **4** with precatalyst **1** is pseudo-chain-growth but not living. For example, MALDI-TOF MS analysis at low monomer conversions indicated a variety of different end-groups, suggesting that chain-transfer and/or chain-termination were occurring, even at early conversions (Supporting Information). It is interesting to note that the largest peak corresponded to polymers with iPr/H end-groups. These end-groups could arise via competitive transmetalation of iPrMgCl (leftover from the Grignard metathesis)[29] or oxidative addition of the iPrBr (formed via Grignard metathesis) into "free" $L_nPd(0)$.[17a] ^1H NMR analysis of a sample before and after polymerization (referenced to an internal standard) revealed complete consumption of iPrMgCl and no consumption of the iPrBr, consistent with the transmetalation hypothesis.

Adding a second aliquot of monomer **4** immediately following consumption of the first aliquot did not result in a significant amount of chain extension. Instead, a broadening of the molecular weight distribution was observed and new chains were initiated (Supporting Information). These results suggest that either the Pd catalyst is not efficiently transferred to the chain end during the polymerization of **4**[15] or there may be a stability issue with the catalyst at the chain end. In both cases, "free" $L_nPd(0)$ is generated and can initiate new chains. Between 5%–30% of the dibromo precursor (leftover from an incomplete Grignard metathesis) is consumed during polymerization, consistent with "free" $L_nPd(0)$ forming during polymerization (Supporting Information). As discussed below, some time-dependent catalyst stability issues are observed with both monomers **2** and **3** after complete consumption of monomer. Thus, the observed uncontrolled polymerization of monomer **4** may be due to a similar decomposition pathway.

3.2. Block Copolymerizations

Previous studies with both Pd and Ni catalysts have shown that copolymerizations can be challenging even when homopolymerizations were successful.[30] For example, the order of monomer addition can influence the results of these block copolymerizations. In contrast to these previous studies, we observed the expected increases in the polymer molecular weights regardless of the order of monomer addition in the copolymerizations of monomers **2** and **3** with Pd precatalyst **1** (Figure 2A and B). These results were obtained when the second monomer was added within 3 h after addition of the first monomer. If longer periods between monomer additions were used, some chain termination was observed. This result is most consistent with a catalyst stability issue at the end of the polymerization, once the monomer concentration is depleted.

It is important to note that there is no evidence of catalyst decomposition during the homo-polymerizations. For example, at low conversions, the MALDI-TOF MS analysis revealed predominantly H/Br end-groups, whereas Br/Br end-groups would have resulted if catalyst stability was an issue (Supporting Information). In addition, a control experiment, wherein only 50% of the dibromo precursor of **2** was activated with *i*-PrMgCl, revealed no significant consumption of the dibromo starting material, even up to 80% conversion of Grignard monomer **2** (Supporting Information). This result suggests that "free" $L_nPd(0)$ is not formed during the polymerization. The fact that the decomposition does not occur during polymerization suggests that a different catalyst resting state is present under those conditions. We[8,9,22] and others[15,21] have been probing the mechanistic details with Ni catalysts chelated by phosphine ligands, and these studies have revealed structures similar to both complexes **II** and **III** as catalyst resting states during polymerization, depending on the ligand structure.[8,9,22] At the end of these Ni-catalyzed polymerizations, structures similar to complex **II** are observed, regardless of the ligand structure. Roy and Hartwig[31] previously reported that reductive eliminations of Ar-Br can occur from LPd(Ar)Br complexes (similar to complex **II**) when sufficiently hindered ligands are used. Thus, one mechanism for decomposition could be the reductive elimination of polymer-Br from this complex. Mechanistic studies of the Pd-catalyzed polymerizations described herein are needed to address these catalyst stability issues.

4. Conclusions

NHC-ligated Pd precatalyst **1** mediates chain-growth homo- and copolymerizations of both phenylene- and thiophene-based monomers. On the other hand, polymerization of a fluorene-based monomer was problematic, with evidence of both chain-termination and reinitiation pathways occurring. In addition, the catalyst appears to be moderately unstable once monomer consumption is complete. Although not explored herein, the "throw-away" ligand (3-chloropyridine) may play a non-innocent role in the mechanism.[32] In addition, less sterically encumbered NHCs might represent a promising alternative to IPr.[31] Mechanistic studies are needed to elucidate the precise role of ligand steric and electronic properties, as well as monomer structure, on the chain-growth and competing reaction pathways. Studies aimed at addressing these issues, as well as examining the substrate scope (e.g., electron-poor monomers) for precatalyst **1** and related NHC-Pd catalysts are currently underway.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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