

Accelerating Ni(II) precatalyst initiation using reactive ligands and its impact on chain-growth polymerizations†

Cite this: *Dalton Trans.*, 2013, **42**, 4218

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Nickel(II) complexes with varying reactive ligands, which were designed to selectively accelerate the initiation rate without influencing the propagation rate in the chain-growth polymerization of π -conjugated monomers, were investigated. Precatalysts with electronically varied reacting groups led to faster initiation rates and narrower molecular weight distributions. Computational studies revealed that the reductive elimination rates are largely modulated by the ability of the two reacting arenes to stabilize the increasing electron density on the catalyst during reductive elimination. Overall, these studies provide insight into a key mechanistic step of cross-coupling reactions (reductive elimination) and highlight the importance of initiation in controlled chain-growth polymerizations.

Received 15th November 2012,
Accepted 12th December 2012

DOI: 10.1039/c2dt32735j

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Introduction

Organic π -conjugated polymers are used in energy-related applications such as photovoltaics (PVs),¹ light-emitting diodes (LEDs)² and field effect transistors (FETs).³ In all of these applications, the device performance can be substantially influenced by the polymer molecular weight and copolymer sequence, as well as the molecular weight distribution. For example, Kowalewski and coworkers observed improved charge carrier mobilities with higher molecular weight poly(3-hexylthiophene) in thin-film FETs.⁴ In another example, Galvin and co-workers observed higher LED efficiencies when poly((2,5-bis(octyloxy)-1,4-phenylene vinylene)s with narrower molecular weight distributions were utilized.⁵ Because device performance is dependent on molecular weight, copolymer sequence and polydispersity, synthesizing π -conjugated polymers with control over these variables is important. The recently developed Ni- and Pd-catalyzed chain-growth polymerization methods^{6–8} have enabled unprecedented control over polymer molecular weight and copolymer sequence.^{9–12} Nevertheless, the current methods exhibit sluggish precatalyst initiation (compared to propagation), as well as chain-transfer

and chain-termination processes, all of which impact the polymer molecular weight, copolymer sequence and polydispersity. As a result, the continued development of new catalysts is needed.

We¹³ and others¹⁴ have investigated the impact of ancillary ligand structure on the Ni-catalyzed chain-growth polymerizations. We recently reported that catalysts ligated by electron-donating phosphines led to polymers with lower polydispersity indexes (PDIs) than catalysts containing electron-withdrawing phosphines.^{13a} These results were attributed to the impact of increased electron-density in promoting the formation and reactivity of a key intermediate (*i.e.*, Ni(0)-polymer π -complex).¹⁵ During these studies we observed a surprisingly slow precatalyst initiation relative to propagation ($k_{rel} \sim 20$), even for the conventional catalyst containing 1,2-bis(diphenylphosphino)ethane (dppe) as the ligand.^{13a} Slow precatalyst initiation leads to broader sequence and molecular weight distributions in chain-growth polymerizations. Further studies revealed that the turnover-limiting step for both initiation and propagation is the same. As a consequence, the ancillary ligand cannot be used to selectively accelerate the initiation. An alternative is to use a reactive ligand (*e.g.*, a functionalized arene) to increase the precatalyst initiation rate without influencing the propagation rate.

We report herein the synthesis of four new Ni precatalysts with electronically varied reactive ligands and their impact on the initiation rate. Our precatalyst design was inspired by Shekhar and Hartwig's study of reductive elimination rates in (L-L)Pt(Ar)(Ar') complexes.¹⁶ The fastest rates were observed when the two reactive arenes were the most electronically differentiated. These rate differences were attributed to the

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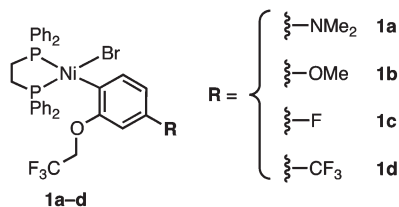
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†Electronic supplementary information (ESI) available: Experimental details; rate and spectroscopic data; MALDI-TOF MS data; computational details. See DOI: 10.1039/c2dt32735j

increased electrophilicity and nucleophilicity of the two reacting arenes. We applied the same rationale to design a series of precatalysts with varying reactive ligands. Using this approach, we demonstrate herein that precatalyst initiation can be selectively accelerated over propagation, and that faster initiations produce polymer samples with narrower molecular weight distributions. Combined, these results highlight the important role of initiation in chain-growth polymerizations. Because the fastest rates were obtained when the reactive ligand was the most electronically differentiated from the monomer, we originally attributed this effect to the nucleophilicity/electrophilicity of the reacting arenes. However, computational studies revealed no correlation between the free energy barriers and atomic charges at the reacting carbons. Instead, a strong correlation was observed between the free energy barriers and the change in charge delocalization onto the reactive ligands during the turnover-limiting step. As a consequence, the fastest rates are predicted to occur when the reactive ligand is substituted with resonance-based electron-withdrawing groups. Overall, these results demonstrate that a simple approach for improving chain-growth polymerizations of π -conjugated monomers is to modify the reactive ligand's electronic properties.

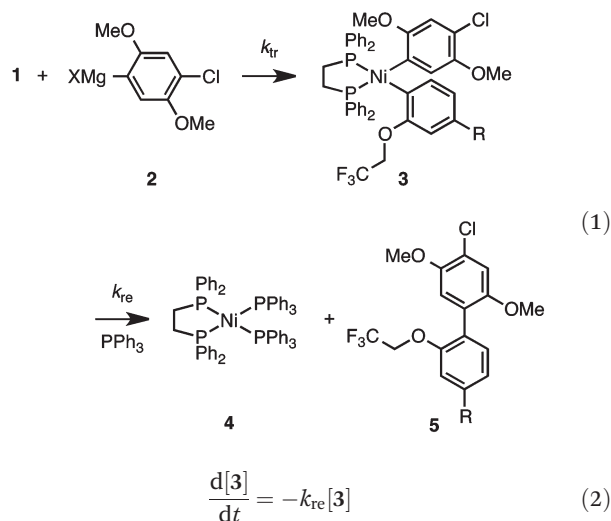
Results and discussion

To determine the reactive ligand influence on precatalyst initiation, Ni precatalysts **1a–d** were prepared (ESI[†]). The reactive ligand includes: (i) an *ortho*-trifluoroethoxy substituent for facile analysis *via* ¹⁹F NMR spectroscopy and stabilization,¹⁷ and (ii) *para*-substituents with varying electronic properties to tune the reductive elimination rate. Commercially available dppe was selected as the ancillary ligand because it mediates chain-growth polymerizations of several important π -conjugated monomers.¹⁸



Initiation involves precatalyst **1** undergoing transmetalation with monomer (*i.e.*, aryl Grignard), followed by reductive elimination (eqn (1)). To prevent polymerization in our model system, Grignard **2** was used as a substitute for monomer **6**. The key difference is that the 4-Cl substituent (in **2**) minimizes the likelihood of further propagation due to its low reactivity in oxidative addition reactions.¹⁹ Importantly, there should be minimal rate differences between the model system and the polymerization because Cl and Br have similar electronic properties. Grignard **2** was prepared by Grignard metathesis with *i*-PrMgCl and 1-bromo-4-chloro-2,5-dimethoxybenzene (ESI[†]).²⁰

A quenched sample revealed exclusive formation of regio-isomer **2**, indicating selective metathesis of the C–Br bond (ESI[†]).²¹



Initiation of precatalysts **1a–d** with stoichiometric amounts of Grignard **2** was monitored *via* ¹⁹F NMR spectroscopy at 0 °C in THF (Fig. 1A and ESI[†]). Triphenylphosphine (PPh₃) was used to trap the Ni(0) as complex **4** after reductive elimination. Control experiments revealed that excess PPh₃ has no effect on reaction rates (ESI[†]). Because transmetalation was too fast to monitor under these conditions, reductive elimination from intermediates **3a–d** was followed as a function of time (Fig. 1A/B). The data were fit to the corresponding rate equation (eqn (2)), providing the rate constants for reductive elimination (Table 1).²² As anticipated, the reactive ligand had a dramatic impact on the reductive elimination rate constants. For example, intermediate **3c** (R = F) exhibited a reductive

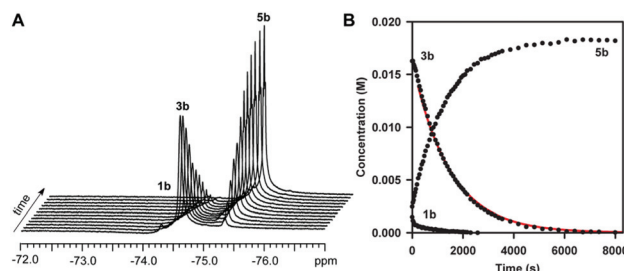


Fig. 1 (A) Representative ¹⁹F NMR spectroscopic data for the reaction depicted in eqn (1) using catalyst **1b**. (B) Representative fit of the data to eqn (2) to obtain the rate constant.

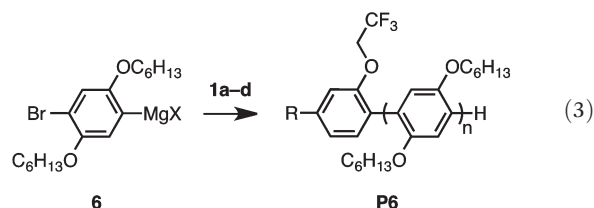
Table 1 Experimental rate constants (k_{re}) and free energy of activation (ΔG^\ddagger) for precatalyst initiation

Precatalyst	k_{re} ($\times 10^{-3}$ s ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)
1a	6.88 ± 0.06	18.6
1b	0.671 ± 0.006	19.9
1c	0.0520 ± 0.0001	21.3
1d	0.222 ± 0.002	20.5

elimination rate constant that was two orders of magnitude slower than intermediate **3a** ($R = \text{NMe}_2$). Interestingly, reductive eliminations from both electron-poor intermediate **3d** ($R = \text{CF}_3$) and electron-rich intermediate **3b** ($R = \text{OMe}$) were similar in magnitude, suggesting that the difference in reactive ligand electronic properties (compared to the monomer) is the predominant factor. The fastest rate constants were obtained when the reactive ligand contained a strongly resonance donating substituent, consistent with the notion that electrophilicity/nucleophilicity of the reactive ligands contributes to the rates. Significantly, the fastest precatalyst (**1a**) underwent initiation at a rate similar to propagation ($k_{\text{prop}} = 9.7 \times 10^{-3} \text{ s}^{-1}$).^{13a,23} This result suggests that **1a** should produce polymer samples with the narrowest molecular weight distributions. Overall, these studies revealed that the reactive ligands dramatically influence the initiation rate.

Monomer **6** was then polymerized with precatalysts **1a–d** to evaluate the impact of initiation rate on the resulting polymer samples. The polymerization was monitored *via in situ* IR spectroscopy and aliquots were periodically withdrawn and quenched to determine the number-average molecular weight (M_n) and PDI as a function of conversion by gel permeation chromatography (GPC). As evident in Fig. 2A, the fastest initiating precatalyst (**1a**) yielded polymers with the lowest PDI whereas the slowest initiating precatalyst (**1c**) yielded polymers with the highest PDI. The GPC data reveals that the broadening of the PDI is due to low molecular weight oligomers (Fig. 2B and ESI†). Because PDIs reflect slow initiations as well as chain-transfer and chain-termination events, MALDI-TOF MS analysis of the end-groups in low molecular weight oligomers was used to distinguish between these pathways. These studies revealed exclusively Ar/H end-groups for all four

precatalysts, indicating that chain-transfer or chain-termination reactions are not occurring under these conditions (ESI†). Thus, the broadening of the PDI observed with these precatalysts can be largely attributed to the different relative rates of initiation *versus* propagation. To illustrate the magnitude of this effect, Fig. 2C/D overlays the estimated concentration of unreacted precatalyst **1a/1c** with monomer **6** *versus* time for the polymerizations. These plots highlight the significance and underappreciated impact of a slow initiation on the chain-growth polymerizations. Overall, these studies reveal that selectively accelerating initiation using reactive ligands is a successful strategy for narrowing the molecular weight distributions in chain-growth polymerizations of π -conjugated monomers.



To provide a framework for generalizing this approach, the free energy barriers for reductive elimination from **3** were computed for the four substituents examined experimentally, as well as $R = \text{H}$ and 15 other *para*-substituents (see ESI† for full list). Computations were performed using Gaussian09, and employed the BP86 DFT functional²⁴ paired with the 6-311+G(d) basis set²⁵ for non-metal atoms and the SDB-cc-pVTZ basis set with the small core, fully relativistic effective core potential²⁶ for Ni. The trend in predicted activation free energies (ΔG^\ddagger) for **3a–d** are in agreement with the experimental data.²⁷

If the reductive elimination rates were purely determined by arene electrophilicity/nucleophilicity, as initially anticipated, the computed free energy barriers should correlate with the differences in atomic charges at the reacting carbons (as predicted by natural population analyses). Surprisingly, no such correlation was observed (ESI†). Instead, a modest correlation ($r^2 = 0.65$) was observed between the free energy barriers and the Hammett σ^- values,²⁸ which characterize the ability of a *para*-substituent to stabilize negative charge through direct resonance effects (Fig. 3A). The importance of charge delocalization was further supported by a strong correlation ($r^2 = 0.94$) between the barrier heights and the *change* in the charge on the two arenes on going from **3** to the transition state (Fig. 3B). This correlation indicates that the reductive elimination rates are largely modulated by the ability of the two arenes to stabilize the increasing electron density on the catalyst during reductive elimination. Importantly, the strong correlation is only observed when *both* rings are considered, indicating that there is some interplay between the delocalizing effect of the two arenes in the transition state. These results predict that the fastest initiation rates with monomer **2** (or **6**) will occur with strongly resonance-based electron-withdrawing substituents (*e.g.*, $R = \text{NO}_2$) on precatalyst **1**. These and related reactive ligands will be the subject of future studies.

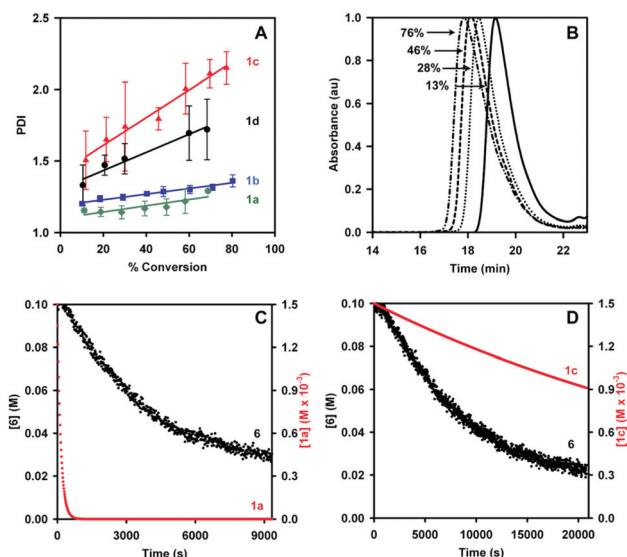


Fig. 2 (A) Plot of polydispersity index (PDI) *versus* monomer conversion for the polymerization of **6** using precatalysts **1a–d**. (B) Representative gel permeation chromatograms at varying percent conversions for the polymerization of **6** with precatalyst **1c**. (C) and (D) Plot of [monomer] and [precatalyst] *versus* time for the polymerization of **6** with precatalysts **1a** (C) and **1c** (D).

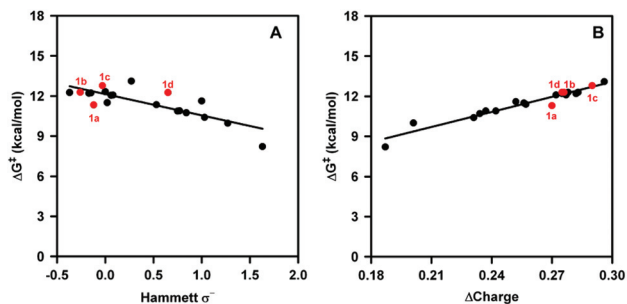


Fig. 3 Plots of computed free energy barriers (ΔG^\ddagger) for reductive elimination from **3** versus (A) Hammett σ^- values for substituent R and (B) the change in charge (ΔCharge) on the two reacting arenes going from **3** to the transition state, excluding the carbon atoms bound to Ni.

Conclusions

In summary, we have demonstrated that modifying the reactive ligand on the Ni precatalyst can be used to selectively accelerate initiation over propagation. We have shown that faster initiations lead to polymer samples with narrower molecular weight distributions, highlighting the importance of precatalyst initiation in these chain-growth polymerizations. Significantly, the PDIs obtained with precatalyst **1a** are the lowest reported for poly(2,5-bis(hexyloxy)phenylene) synthesis. Computational studies predict that the lowest activation free energies can be achieved with precatalysts containing resonance-based electron-withdrawing substituents, in contrast to our initial assumption about the nucleophilicity/electrophilicity of the reactive ligands. Although this work focuses on aryl cross-coupling reactions, the results are anticipated to be generalizable to heteroaryl cross-coupling reactions (*e.g.*, thiophenes) because the mechanism (including the turnover-limiting step) was previously shown to be similar.

Acknowledgements

We thank the National Science Foundation (CAREER CHE-0954610) and the ACS Petroleum Research Fund (ACS PRF 50645-DNI6) for support of this work, as well as the TAMU Supercomputing Center for providing computational resources. S. R. L. thanks the National Science Foundation for a predoctoral fellowship. J. W. G. B. thanks A. Pitts for fruitful discussions.

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