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EDGE ARTICLE

Effect of ligand electronic properties on precatalyst initiation and propagation in Ni-catalyzed cross-coupling polymerizations†

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The role of ligand-based electronic effects was investigated in the Ni-catalyzed polymerization of 4-bromo-2,5-bis(hexyloxy)phenylmagnesium chloride. The catalyst with the most electron-donating ligand outperformed the other catalysts by providing polymers with narrower molecular weight distributions. This result is attributed to both a suppression of competing reaction pathways (*e.g.*, chain transfer and termination) as well as a relative acceleration of precatalyst initiation compared to propagation. Further studies revealed that, for all three catalysts, precatalyst initiation is slower than propagation, despite the fact that they exhibit the same rate-determining steps (*i.e.*, reductive elimination) and have similar catalyst resting states. These results suggest that better control over the polymer molecular weight, end-functionality and sequence can be obtained with electron-rich catalysts, such as those described herein.

Introduction

Ni-catalyzed cross-coupling reactions to form sp^2–sp^2 carbon–carbon bonds are widely utilized in both small molecule[1] and polymer syntheses.[2] It was recently discovered that certain difunctionalized molecules undergo Ni-catalyzed polymerization in a chain-growth fashion.[3] These methods have gained attention because previously inaccessible materials, like all-conjugated block[4] and gradient[5] copolymers, could now be prepared.[6] A new mechanism was proposed to account for this unexpected chain-growth behavior, which involves an intermediate Ni^0-polymer π-complex.[7–9] We anticipated that these polymerizations could be improved by modifying the ligand electronic properties. Specifically, we hypothesized that electron-donating ligands would facilitate chain-growth because they should promote the formation[10] and reactivity[11] of Ni^0-polymer π-complexes. We demonstrate herein that an electron-rich ligand outperforms the other ligands in the chain-growth polymerizations by providing polymers with narrower molecular weight distributions.

During these studies we observed slow initiation of the Ni(II) precatalyst. Although this transformation is often assumed to be fast relative to the cross-coupling reaction, this is not always the case.[12] Slow precatalyst initiation can impact both the yield and substrate scope in small-molecule cross-coupling reactions. For example, the development of activated M(II) precatalysts has enabled thermally unstable boronic acids to be cross-coupled in high yields.[12b] Slow precatalyst initiation can also have a significant impact on polymerizations, influencing both the molecular weight and molecular weight distributions (PDI) of the resulting polymers.[13] Despite the importance of precatalyst initiation, its rate relative to the cross-coupling reaction is often unknown. Thus, we report herein on the relative rates of precatalyst initiation and polymerization. These studies led to the surprising conclusion that precatalyst initiation is approximately 20× slower than polymerization, despite the fact that they share similar catalyst resting states and rate-limiting steps. Overall, these mechanistic studies provide a comprehensive view of ligand electronic effects in Ni-catalyzed cross-coupling polymerizations and suggest how to improve the chain-growth polymerizations by modifying the catalyst structure.

Results and discussion

Because most $(L–L)NiX_2$ precatalysts are insoluble in ethereal solvents, we prepared soluble precatalysts **1a–c** to avoid any complications from heterogeneous initiation. Key structural features of these catalysts include: (1) the *ortho*-substituted arene reactive ligand, which increases catalyst solubility and stability[14] and (2) bis(diarylphosphino) ethanes with electron-withdrawing (*p*-Cl, $\sigma_{para} = 0.24$) and electron-donating (*p*-OMe, $\sigma_{para} = -0.12$) substituents to tune reactivity.[15,16] The polymerization of monomer **2** was used to evaluate the influence of ligand electronic properties (eqn (1)).[8c,17,18]

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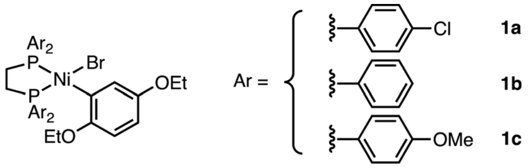
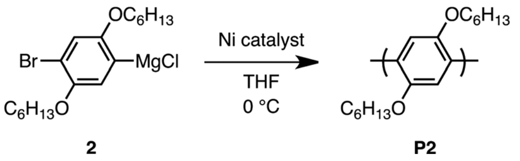




(1)

Initial rates (0–10% conversion) were monitored *via in situ* IR spectroscopy, following loss of monomer **2** as a function of time (ESI†). All three precatalysts (**1a–c**) exhibited polymerization rates with a zero-order dependence on [monomer] and approximately first-order dependence on [catalyst] (Fig. 1A/B).[19] These rate data are consistent with either a turnover-limiting reductive elimination or intramolecular oxidative addition (*via* a Ni^0-polymer π-complex). To distinguish between these two scenarios, ^{31}P NMR spectroscopic studies were used to elucidate the catalyst resting state (ESI†). The observed pair of proximate doublets with narrow coupling constant was consistent with a (L–L)Ni(aryl)$_2$ species (**8**) as the resting-state (ESI†).[8c] Combined, these rate and spectroscopic results are consistent with a turnover-limiting reductive elimination for all three catalysts. The electron-poor ligand gave the fastest rates of reductive elimination (Hammett ρ value = +3.2 ± 0.4). This result is also consistent with a turnover-limiting reductive elimination because it involves a formal reduction of Ni(II) to Ni(0), which should be accelerated when the electron-density at the metal center is decreased.[20]

During these studies, a significant induction period was observed, which varied based on both the catalyst and monomer concentrations. We suspected that this was due to slow precatalyst initiation because a similar slow initiation was observed for (L–L)NiCl$_2$ using bis(dialkylphosphino)ethane-based ligands.[8a,21] To measure the precatalyst initiation rates, model complexes **3a–c** were prepared. The key structural feature is a *para*-F substituent, which enabled *in situ* monitoring *via* ^{19}F NMR spectroscopy. To observe a single turnover, (2-methoxyphenyl)magnesium bromide (**4**) was used instead of monomer **2** (eqn (2)).[22]

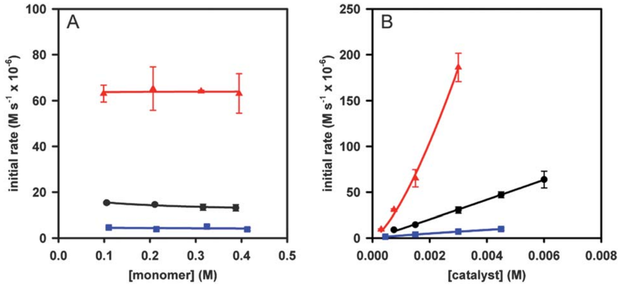
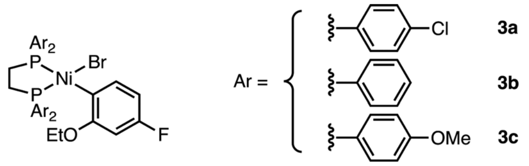
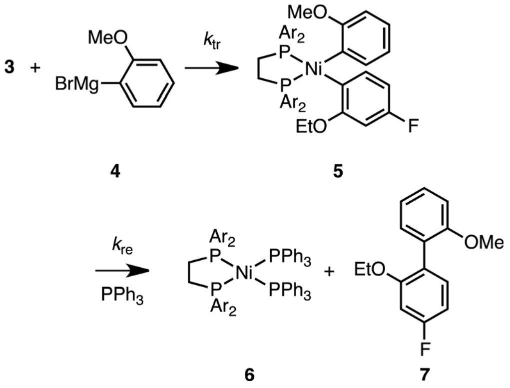


Fig. 1 Plot of the initial rate *versus* (A) [monomer] and (B) [catalyst] for the polymerization of **2** in THF at 0 °C using catalysts **1a** (▲), **1b** (●) and **1c** (■).





(2)

The loss of precatalyst **3**, formation and loss of intermediate **5**, and formation of product **7** were followed as a function of time (Fig. 2A). The fact that all three species (**3**, **5** and **7**) were readily observed suggests that the relative rates of transmetalation and reductive elimination were similar. As a result, the effects of ligand electronic properties on both steps could be determined. By fitting the data for all three species to the rate equations (eqn (3)–(5)), the rate constants for both transmetalation (k_{tr}) and reductive elimination (k_{re}) were obtained (ESI†, Fig. 2B and Table 1).[23]

$$\frac{\mathrm{d}[\mathbf{3}]}{\mathrm{d}t} = -k_{\mathrm{tr}}[\mathbf{3}][\mathbf{4}] \tag{3}$$

$$\frac{\mathrm{d}[\mathbf{5}]}{\mathrm{d}t} = k_{\mathrm{tr}}[\mathbf{3}][\mathbf{4}] - k_{\mathrm{re}}[\mathbf{5}] \tag{4}$$

$$\frac{\mathrm{d}[\mathbf{7}]}{\mathrm{d}t} = k_{\mathrm{re}}[\mathbf{5}] \tag{5}$$

The electron-poor ligand led to the fastest rate constants for both transmetalation and reductive elimination. Because transmetalation (**3** → **5**) involves a formal nucleophilic substitution reaction at the metal center, it is reasonable that the electron-poor ligand, which enhances the electrophilicity of the catalyst, exhibits the highest reactivity.[24] As noted above, the electron-poor ligand is also expected to facilitate the reductive

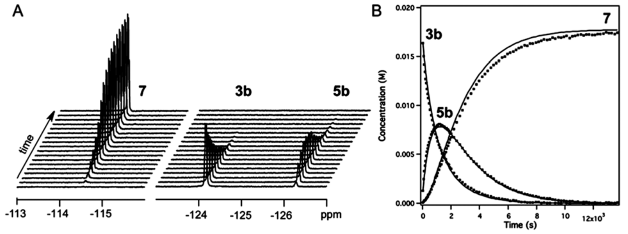


Fig. 2 (A) Representative ^{19}F NMR spectroscopic data for the reaction depicted in eqn (2) using catalyst **3b**. (B) Representative fits of the data to eqn (3)–(5) to obtain the rate constants.

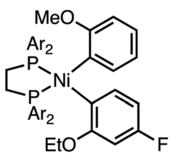
Table 1 Rate constants for precatalyst initiation and propagation

Precatalyst initiation[a]			Propagation[b]	
Catalyst	k_{tr} (M^{-1} s^{-1} × 10^{-3})	k_{re} (s^{-1} × 10^{-3})	Catalyst	k_{re} (s^{-1} × 10^{-3})
3a	140 ± 30	1.8 ± 0.2	**1a**	43 ± 6
3b	26 ± 3	0.43 ± 0.07	**1b**	9.7 ± 0.4
3c	12 ± 2	0.18 ± 0.01	**1c**	2.6 ± 0.2

[a] Reaction conditions: [**3**] = 0.02 M, [**4**] = 0.04 M, THF, −5 °C. [b] Reaction conditions: [**1**] = 0.0015 M, [**2**] = 0.2 M, THF, 0 °C.

elimination.[20] Remarkably, the magnitude of the electronic effect is similar for both transmetalation (Hammett ρ value = +2.98 ± 0.06) and reductive elimination (Hammett ρ value = +2.8 ± 0.1).

Under these stoichiometric conditions, both transmetalation and reductive elimination contribute to the overall initiation rate. In contrast, under catalytic conditions the high monomer concentration increases the transmetalation rates and reductive elimination becomes the rate-limiting step of precatalyst initiation. Thus, we can compare the rate constants for precatalyst initiation and polymerization.[25] The surprising conclusion is that propagation is significantly faster (~20×) than precatalyst initiation (Table 1). This result was unexpected because both rate-limiting steps involve the same fundamental transformation (reductive elimination) and the resting states (**5** and **8**) are similar in structure. The only difference is the substitution pattern of the reactive arenes. Previous work by Shekhar and Hartwig revealed that reductive elimination from biarylplatinum complexes is fastest when the two reactive arenes are electronically differentiated (*e.g.*, electron-rich and electron-poor).[26] Based on their results, we suspect that the difference in rates may arise from the electronic differences of the two reactive arenes in **8** (*i.e.*, polyaryl and aryl), which are more differentiated than in **5** (*i.e.*, H *versus* F). Importantly, these results are consistent with our previous work wherein the symmetric (depe)Ni(aryl)$_2$ complex, formed during precatalyst initiation of (depe)NiCl$_2$, exhibited slower rates of reductive elimination than the polymerization resting state—(depe)Ni(polyaryl)(aryl).[8a] This result demonstrates that the slow initiation observed herein is not simply a function of the model system, but is relevant to polymerizations initiated with (L–L)NiCl$_2$. Although LiCl has been reported to accelerate precatalyst initiation for thiophene-based monomers and Ni(dppp)Cl$_2$,[21] this additive effect is limited to cases where transmetalation is the rate-limiting step. When reductive elimination is rate-limiting, as it is herein, LiCl will have no effect on the initiation or propagation rates.[8c]



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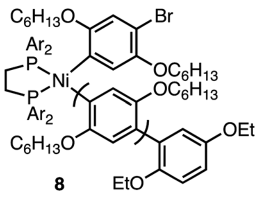

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We concluded these studies by evaluating the chain-growth behavior of catalysts **1a–c** in the polymerization of monomer **2** (eqn (1)). As noted above, we hypothesized that electron-donating ligands would improve the chain-growth polymerizations by both stabilizing the Ni^0-polymer π-complex and accelerating the subsequent oxidative addition reaction.[11] Both factors would minimize the opportunity for chain transfer and other competing reaction pathways to occur.

Indeed, the polymerizations with all three catalysts were consistent with a chain-growth mechanism, providing linear increases in molecular weight with conversion (Fig. 3A). MALDI-TOF MS analysis of low molecular weight oligomers showed complete incorporation of Ar/H end-groups (where Ar = 2,5-diethoxybenzene, ESI†), consistent with each precatalyst initiating a single polymer chain.

Nevertheless, the polydispersity index (PDI) increased substantially with conversion for all three ligands, suggesting chain termination, chain transfer or other competing reaction pathways were occurring (Fig. 3B). Notably, the electron-rich catalyst (**1c**) gave the narrowest PDIs overall. The narrower PDI at the outset could be rationalized based on the relatively faster precatalyst initiation: propagation is merely 14× faster than initiation for **1c**. On the other hand, the increase in PDI with conversion is most readily explained by the intervention of competing reaction pathways. In principle, MALDI-TOF mass spectra acquired at later conversions would show evidence of these pathways (*i.e.*, an increase in polymers with H/H and H/Br end-groups). Unfortunately, we were unable to obtain high quality MALDI-TOF MS data for these higher molecular weight polymers. Nevertheless, the fact that the electron-donating ligand leads to the lowest PDIs suggests that it is effective in suppressing some of these competing reaction pathways, presumably *via* stabilization of the Ni(0)-polymer π-complex. The implication of these results is that further improvements in the chain-growth polymerizations may be achieved with ligands that are even more electron-donating than **1c**. Polymerizations performed at a higher monomer-to-catalyst ratio (100 : 1) gave high molecular weight polymers (29–41 kDa) in reasonable yields (54–67%) under these conditions.

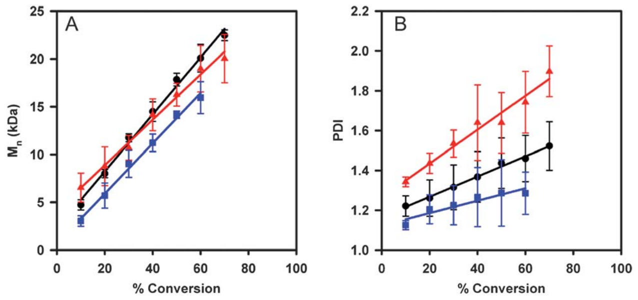

Fig. 3 Plots of (A) number-average molecular weight (M_n) and (B) polydispersity index (PDI) *versus* conversion for the polymerization of **2** in THF at 0 °C using catalysts **1a** (▲), **1b** (●) and **1c** (■).

Conclusions

In summary, we have demonstrated that ligand electronic properties have a significant impact on Ni-catalyzed chain-growth polymerizations. Specifically, the catalyst with the most electron-donating ligand gave improved chain-growth behavior compared to the conventional catalyst (Ni(dppe)Cl$_2$), due to both a suppression of chain-transfer and other competing pathways and a relative acceleration of precatalyst initiation over propagation. This new catalyst can provide access to polymers with better control over the molecular weight distribution and end-group functionality. By minimizing chain termination and transfer pathways, this catalyst will also lead to more homogeneous polymer samples in block and gradient copolymerizations.

These studies also revealed that precatalyst initiation is significantly slower than the cross-coupling polymerization. Similar results have been reported for Ni(II) and Pd(II) with boronic acids,[12b] suggesting that slow precatalyst initiation may be a more general phenomenon. Our studies revealed that, despite the different rates, both initiation and propagation proceed through the same rate-limiting step (reductive elimination) with structurally similar resting-states. As a consequence, changes to the ancillary ligand cannot be used to overcome this limitation. Instead, the reactive ligand (*i.e.*, aryl in complexes such as (L–L)Ni(aryl)X) will need to be modified to accelerate precatalyst initiation selectively.[27] Efforts toward this goal are currently underway in our laboratories.

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