

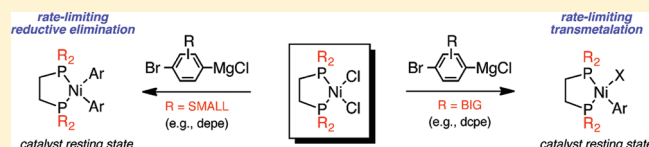
Ligand-Based Steric Effects in Ni-Catalyzed Chain-Growth Polymerizations Using Bis(dialkylphosphino)ethanes

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S Supporting Information

ABSTRACT: The role of ligand-based steric effects was investigated in the polymerization of 4-bromo-2,5-bis(hexyloxy)phenylmagnesium chloride. Three different Ni(L-L)Cl₂ catalysts were synthesized using commercially available bis(dialkylphosphino)ethane ligands with varying steric properties. One of these catalysts (Ni(depe)Cl₂) outperformed the others for this polymerization. The polymer characterization data were consistent with a chain-growth mechanism. Rate and spectroscopic studies revealed a rate-limiting reductive elimination for both initiation and propagation with Ni(depe)Cl₂. In contrast, less hindered Ni(dmpe)Cl₂ and more hindered Ni(dcpe)Cl₂ were ineffective polymerization catalysts; NMR spectroscopic studies indicated that competing decomposition and uncontrolled pathways intervene. For other monomers, Ni(depe)Cl₂ performed similar to the conventional catalysts. Copolymerization studies revealed that block copolymers could be effectively prepared. Overall, these studies indicate that altering the ligand-based steric properties can have a significant impact on the chain-growth polymerization.



INTRODUCTION

In 2004, McCullough¹ and Yokozawa² reported a chain-growth method for synthesizing π -conjugated polymers that gained attention because previously inaccessible materials, like all-conjugated block³ and gradient⁴ copolymers, could now be prepared. In the intervening years, however, it has become evident that the original chain-growth method is limited to a relatively narrow scope of monomers.^{5,6} Furthermore, the mechanistic underpinnings of this limitation remain unclear today. In addition, only a limited number of copolymers have been prepared because of inefficiencies in the cross-propagation step;⁷ these results also lack a clear mechanistic explanation.^{8,9} To advance this field, a mechanistic understanding of the key factors controlling the competition between the desired chain-growth pathway^{10–12} and the detrimental side-reactions is needed. We recently reported that the ligand scaffold had a substantial influence on the chain-growth polymerization mechanism.^{11,12} Specifically, we showed that the syntheses of both poly(*p*-(2,5-bis(hexyloxy)phenylene) and poly(3-hexylthiophene) proceed through different rate-limiting steps when different ligands (diphenylphosphinoethane (dppe)¹¹ and diphenylphosphinopropane (dppp)¹²) were used. Therefore, we hypothesized that alternative ligand scaffolds might provide catalysts with a broader substrate scope and facile cross-propagation abilities.

To account for the unexpected chain-growth nature of the cross-coupling polymerization, a Ni⁰–arene π -complex¹³ (III in Scheme 2) has been proposed as a key intermediate.^{10–12} We further postulated that the detrimental, competing reaction pathways stem from a breakdown of this key intermediate. Therefore, we selected bis(dialkylphosphino)ethane ligands for this study because we anticipated that their increased electron-donating

ability (relative to dppe and dppp)¹⁴ would increase the polymer-binding affinities to nickel (intermediate III)¹⁵ and minimize the competing reaction pathways. To probe the influence of steric effects on the polymerization, we selected a series of bis(dialkylphosphino)ethane ligands with different alkyl substituents.¹⁶

Herein, we report that poly(*p*-(2,5-bis(hexyloxy)phenylene) can be prepared via chain-growth polymerization using one of these catalysts, Ni(depe)Cl₂. Mechanistic studies were consistent with a rate-determining reductive elimination. Steric effects played a significant role in the polymerization, with the most hindered phosphine leading to low molecular weight oligomers. On the other hand, the least hindered phosphine led to significant amounts of decomposition. In addition, we identified previously uncharacterized intermediates in the initiation process. Ni(depe)Cl₂ was also an effective chain-growth catalyst for synthesizing poly(3-hexylthiophene) and poly(*N*-hexylpyrrole). Despite the improved polymerization behavior for certain monomers, the copolymerization abilities were similar to the conventional catalysts. Overall, these results highlight the important mechanistic role of ligands in Ni-catalyzed chain-growth polymerizations^{11,12} and indicate that future studies should continue to focus on optimizing the ligand scaffold.

RESULTS AND DISCUSSION

Catalyst Design and Synthesis. Nickel complexes 1–3 were synthesized from commercially available NiCl₂ · (H₂O)₆ and the

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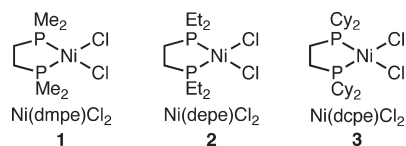
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Table 1. Polymerization Results for Monomer 4a Using Selected Ni Catalysts at 60 °C^a

catalyst	conv (%)	<i>M_n</i> (kDa)	PDI
Ni(dmpe)Cl ₂ (1)	32	1.6	1.51
Ni(depe)Cl ₂ (2)	94	9.5	2.12
Ni(dcpe)Cl ₂ (3)	25	0.8	1.02
Ni(dppe)Cl ₂	95	8.6	2.42
Ni(dppp)Cl ₂	94	5.0	3.59

^a The conversions were measured by gas chromatography relative to an internal standard. Number-average molecular weights (*M_n*) and polydispersity indices (PDIs) were determined by gel permeation chromatography relative to PS standards. The polymerizations were quenched with 5 M HCl/MeOH after 1 h ([Ni] = 0.0015 M; [4a] = 0.10 M).

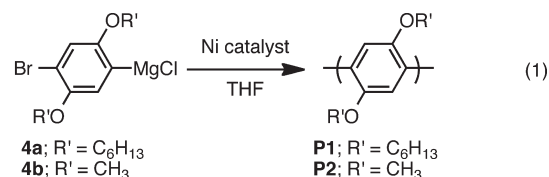
corresponding bis(dialkylphosphino)ethane.¹⁷ With the exception of 1, the ligand complexation reactions resulted in quantitative conversion in one step. The resulting Ni complexes were precipitated from EtOH to give analytically pure compounds (Supporting Information).



The steric properties of ligands are generally defined by the Tolman cone angle,¹⁸ which is based on molecular models and describes the opening of a cone that encompasses the metal and the outermost atoms of a ligand. An alternative measure of steric properties is the solid angle,¹⁹ which is based on experimental data and describes the size of a shadow that the ligand creates on a sphere if the metal is a point-source of light. Weigand and co-workers²⁰ recently reported an extension of this model by performing a comprehensive analysis of 900 crystal structures of Pt complexes with bidentate phosphines. In this work they calculated a “generalized equivalent cone angle” which we will use in this paper. The generalized equivalent cone angles for the ligands used in this study are bis(dimethylphosphino)ethane (dmpe, 155°), bis(diethylphosphino)ethane (depe, 175°), and bis(dicyclohexylphosphino)ethane (dcpe, 191°). For chelating phosphines, the natural bite angle²¹ is another parameter that can influence the steric properties.²² We intentionally selected three phosphine ligands with similar bite angles (~85°) for this study because we previously showed that changes in ligand bite angles altered the polymerization mechanism.^{11,12} Overall, these ligands provide large variation in the steric crowding near the metal center, and thus the influence of steric properties on the polymerization can be elucidated.

Catalyst Screening: Polymerization of Monomer 4a. Monomer 4a²³ was selected for catalyst screening because it is known to undergo a robust chain-growth polymerization with both Ni(dppp)Cl₂ and Ni(dppe)Cl₂.^{6e,11,12} Thus, polymerization of 4a using catalysts 1–3 was first attempted at room temperature (eq 1). The results were quite surprising; complex 2 was the only catalyst capable of producing polymer at room temperature (Supporting Information, Table S3). At elevated temperatures (60 °C), all three catalysts were active in the polymerization of 4a (Table 1). Under these reaction conditions, Ni(depe)Cl₂ (2) provided polymer samples with narrower distributions of

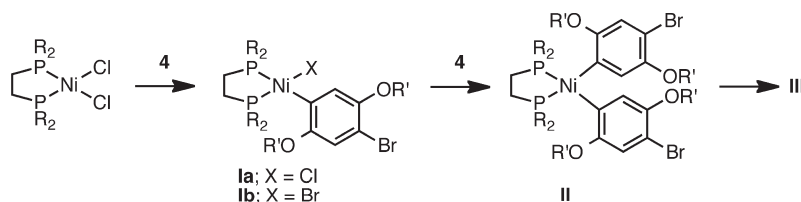
molecular weights than the conventional catalysts, Ni(dppe)Cl₂ and Ni(dppp)Cl₂. In contrast, the more hindered Ni(dcpe)Cl₂ (3) and the less hindered Ni(dmpe)Cl₂ (1) were largely unreactive and provided low molecular weight oligomers. Despite the relatively broad polydispersity index obtained with catalyst 2 (2.12), a close inspection of the gel permeation chromatogram revealed a predominant polymer peak with narrow polydispersity (~1.18) and a “tail” in the low molecular weight region (Supporting Information, Figure S13).²⁴ These results suggested that the polymerization might be predominantly chain growth, with either a slow initiation or an early termination reaction being responsible for the low molecular weight oligomers. Therefore, ³¹P NMR spectroscopic studies were conducted to understand the origin of the minor amount of low molecular weight species with catalyst 2 and the limited reactivity of catalysts 1 and 3.



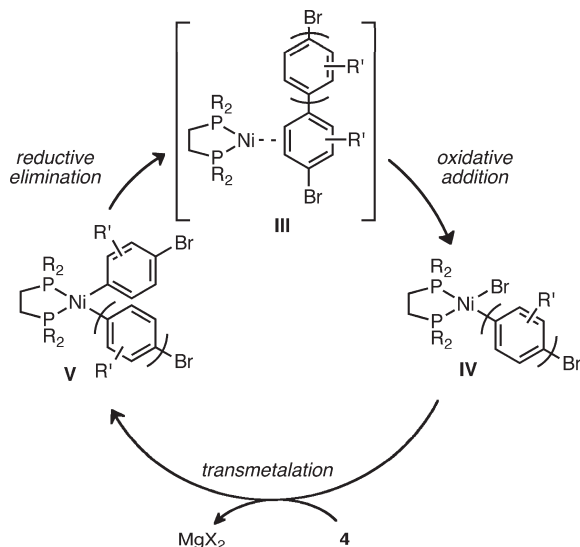
Spectroscopic Studies: General Considerations. Although the primary goal of these spectroscopic studies was to explain the reactivity trends in the polymerizations, we anticipated that these experiments might also reveal information about the initiation sequence because of the low catalyst reactivities at room temperature. Initiation is believed to occur through two consecutive transmetalation reactions,²⁵ followed by reductive elimination (Scheme 1). The resulting Ni species enters the catalytic cycle shown in Scheme 2, presumably via intermediate III. Although this sequence of intermediates has been observed the polymerization of 3-hexylthiophene,^{16a} they have not yet been observed in the polymerization of 2,5-(bishexyloxy)phenylenes.^{26,27}

Spectroscopic Studies with Ni(depe)Cl₂ (2) and Monomer 4a. Adding several equivalents of monomer 4a to Ni(depe)Cl₂ at room temperature resulted in the immediate, quantitative formation of a new species with a single resonance (55.3 ppm) in the ³¹P NMR spectrum (Figure 1A). This species was tentatively assigned as symmetric Ni^{II}–biaryl complex II_{depe}. A structurally related complex, Ni(depe)(CH₂C₆H₄-*o*-CH₃)₂, was reported to have a similar chemical shift (54.8 ppm).^{28,29} With additional turnovers, this complex gradually converted to a new species with two doublets (*J*_{PP} = 14.5 Hz) in the ³¹P NMR spectrum (Figure 1B). On the basis of our previous studies with Ni(dppe)Cl₂¹¹ and the proximity of this species to complex II_{depe}, we assigned this species as unsymmetrical biaryl complex V_{depe}. As the monomer concentration decreases with polymerization, a new species appeared with two distal doublets (*J*_{PP} = 30.6 Hz) in the ³¹P NMR spectrum (Figure 1C). We hypothesized that this species is complex IV_{depe} because the polymerization should stall at this complex in the absence of monomer. To provide support for this assignment, model complexes 6a/6b were prepared via ligand exchange between complexes 5a/5b and depe (eq 2). Interestingly, the identity of the halide ligand had a dramatic effect on the downfield resonance, with bromine-substituted complex 6b showing a 3 ppm downfield shift relative to chlorine-substituted complex 6a (Supporting Information, Figures S30 and S31). Complex 6b gave a similar chemical shift difference (Δδ = 6.7 ppm) and coupling constant (*J*_{PP} = 24.3 Hz) to the species present at the end of the polymerization, supporting the assignment of complex IV_{depe} (Figure 1D).

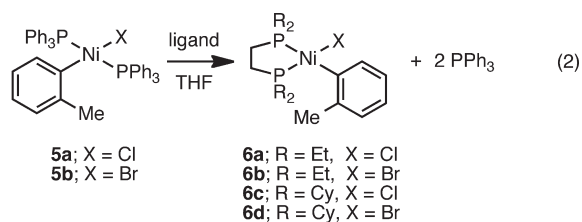
Scheme 1. Proposed Mechanism for Catalyst Initiation



Scheme 2. Proposed Mechanism for Chain-Growth Polymerization



It is notable that, at room temperature, complex II_{depe} persisted even after the monomer is completely consumed. This result indicates that reductive elimination from the symmetric biaryl species (II_{depe}) is significantly slower than the unsymmetric biaryl species (V_{depe}).³⁰ In other words, initiation is slower than propagation with $\text{Ni}(\text{depe})\text{Cl}_2$; this result could account for the low molecular weight oligomers observed in the gel permeation chromatogram. We previously¹¹ hypothesized that a slow initiation process might explain the improvements in M_n and PDI with adding LiCl, as reported by Yokozawa and co-workers^{6c} in the polymerization of **4a** with $\text{Ni}(\text{dppp})\text{Cl}_2$ and $\text{Ni}(\text{dppe})\text{Cl}_2$.



Similar spectra were observed when these experiments were repeated at 60 °C, consistent with the fact that catalyst **2** was active for polymerization of monomer **4a** at both temperatures (Supporting Information, Figure S39). The predominant species observed during polymerization at 60 °C is complex V_{depe} , which we assigned as the catalyst resting state for the polymerization. This assignment was supported by the ^1H NMR spectrum that simultaneously shows signals corresponding to the polymer and

monomer (Supporting Information, Figure S39). Once polymerization was complete, the resulting complex (IV_{depe}) was unstable and decomposes over 24 h at room temperature and 3 h at 60 °C. During decomposition, the solution became green/black and precipitation occurred. A new peak (82.6 ppm) is observed in the ^{31}P NMR spectrum, which was assigned as $\text{Ni}(\text{depe})\text{Br}_2$.³¹ These results were consistent with a transarylation reaction between 2 equiv of complex IV_{depe} to generate $\text{Ni}(\text{depe})\text{Br}_2$ and $\text{Ni}(\text{depe})\text{(polymer)}_2$, which, after reductive elimination, produced polymer and Ni^0 .³² These decomposition reactions, which are second-order in catalyst, are expected to be less prevalent under the standard polymerization conditions due to the significantly lower nickel concentrations used.³³

In summary, initiation of catalyst **2** with monomer **4a** produced complex II_{depe} , during propagation the catalyst resting state was complex V_{depe} , and once polymerization was complete the catalyst resting state was complex IV_{depe} (Scheme 3). These results suggest that reductive elimination is rate-limiting for both initiation and propagation with catalyst **2**. The rate studies described in more detail below further support this assignment.

Spectroscopic Studies with $\text{Ni}(\text{dcpe})\text{Cl}_2$ (3**) and Monomer **4a**.** Adding several equivalents of monomer **4a** to $\text{Ni}(\text{dcpe})\text{Cl}_2$ at room temperature led to the formation of two Ni complexes, each displaying a pair of doublets in the ^{31}P NMR spectrum (Figure 2A). The minor species was assigned as complex Ia_{dcpe} , the product resulting from transmetalation of 1 equiv of **4a** with $\text{Ni}(\text{dcpe})\text{Cl}_2$. The major species observed was assigned as complex Ib_{dcpe} . We hypothesized that this complex formed through a halide exchange with a bromide salt (e.g., MgBr_2) present in the reaction mixture. To support these assignments, model complexes **6c** and **6d** were synthesized in situ by adding dcpe to complex **5a** and **5b**, respectively (eq 2). As seen in Figure 2B,C, the similarities in both the chemical shift differences and coupling constants are consistent with these assignments.

After several hours at room temperature, a new species appeared, again with a pair of doublets in the ^{31}P NMR spectrum (Supporting Information, Figure S40). We tentatively assigned this complex as IV_{dcpe} . Heating the sample to 60 °C for 24 h resulted in polymerization, as evidenced by ^1H NMR spectroscopy. Notably, complex Ib_{dcpe} never completely disappeared (Figure 2D). This result indicated that either Ib_{dcpe} was being regenerated during the reaction (through competing reaction pathways) or its reactivity was lower than that of IV_{dcpe} . During polymerization, the predominant species was assigned as complex IV_{dcpe} . Similar spectra were obtained if the experiment is repeated at 60 °C (Supporting Information, Figure S41).³⁴

In summary, initiation of catalyst **3** with monomer **4a** led to complexes Ia_{dcpe} and Ib_{dcpe} , followed by their slow conversion to complex IV_{dcpe} at room temperature (Scheme 4). Once the reaction was heated to 60 °C and polymerization began, complex IV_{dcpe} remained the dominant species. These results suggested

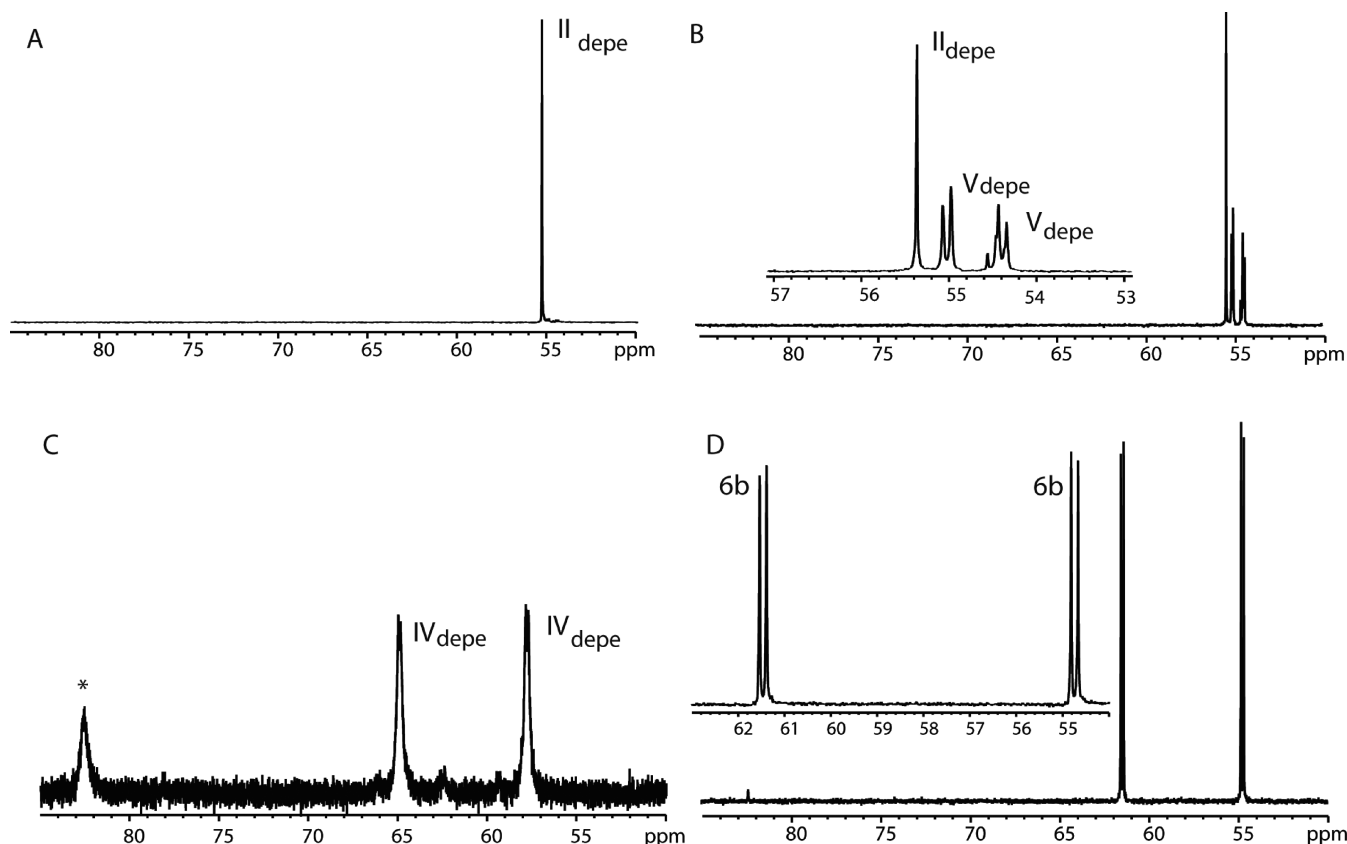
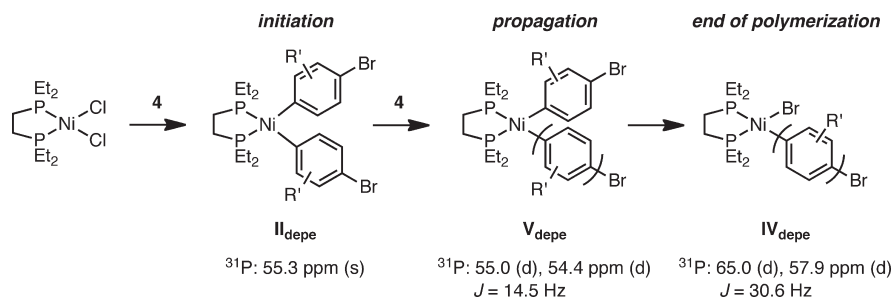


Figure 1. ^{31}P NMR spectra for the reaction of monomer **4a** with catalyst **2** showing (A) the complex formed during initiation, (B) the catalyst resting state during polymerization, (C) the catalyst resting state after polymerization, and (D) complex **6b**. The asterisk (*) indicates $\text{Ni}(\text{depe})\text{Br}_2$.

Scheme 3. Ni Complexes Observed during the Reaction of Monomer **4** with $\text{Ni}(\text{depe})\text{Cl}_2$



that transmetalation is rate-limiting for both initiation and propagation. The change in rate-determining step from catalyst **2** was not surprising given the significant increase in steric crowding near the Ni center, which is expected to both accelerate reductive elimination³⁵ and decelerate transmetalation.³⁶ In addition, these results are consistent with Kiriy et al., who demonstrated that transmetalation is highly sensitive to the steric properties of the monomer.^{16a} Moreover, the continued presence of complex **Ib_{depe}** suggests that an uncontrolled pathway was intervening; we speculate that the increased steric properties of the ligand may be facilitating the breakdown of the postulated Ni^0 –polymer π -complex.

Spectroscopic Studies with $\text{Ni}(\text{dmpe})\text{Cl}_2$ (1**) and Monomer **4a**.** Adding several equivalents of monomer **4a** to $\text{Ni}(\text{dmpe})\text{Cl}_2$ at room temperature led to the immediate formation of green

solid in the NMR sample tube, indicating decomposition.³² The ^{31}P NMR spectrum of the species remaining in solution showed a single new peak at 34.2 ppm (Figure 3A). We tentatively assigned this species as complex **II_{dmpe}** based on similarities to catalyst **2**. In addition, a structurally related complex, $\text{Ni}(\text{dmpe})(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-CH}_3)_2$, was reported to have a similar chemical shift (29.7 ppm).²⁸ Nevertheless, we wanted to further characterize this new complex because a bischelated complex ($\text{Ni}(\text{dmpe})_2\text{Cl}_2$) was preferentially formed during the synthesis of catalyst **1**. Specifically, the dmpe-to-arene stoichiometry was determined by ^1H NMR spectroscopy. To avoid overlap in the alkyl region, both *d*₈-THF and monomer **4b** were used in this experiment. Integrating the appropriate regions of the ^1H NMR spectrum provided a dmpe:monomer ratio of 1:2, which is consistent with the assignment of complex **II_{dmpe}** (Figure 3B).

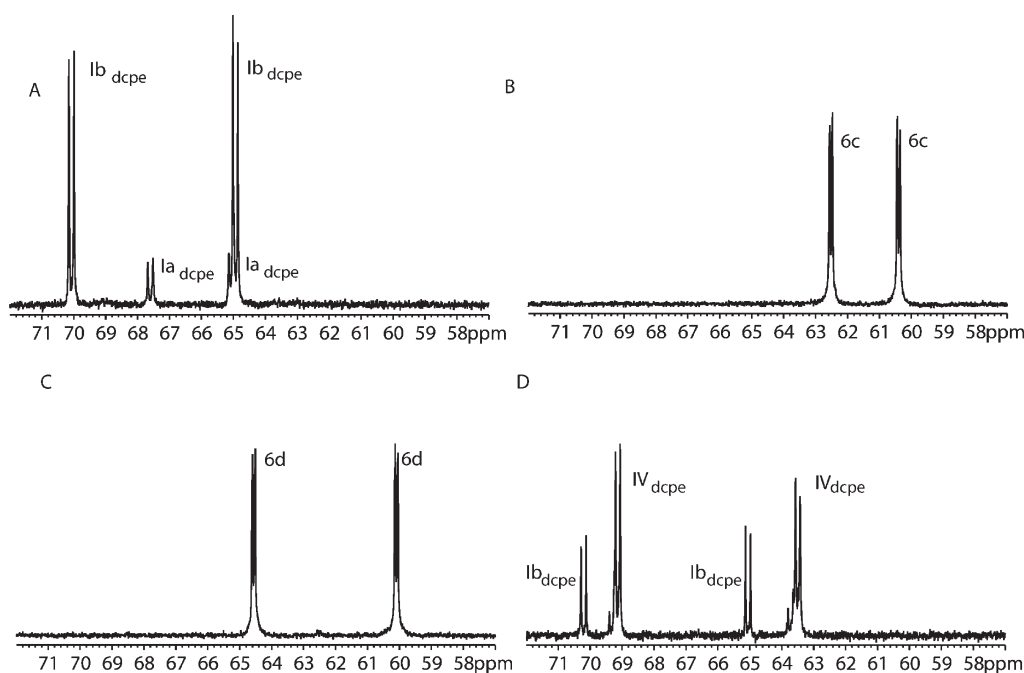
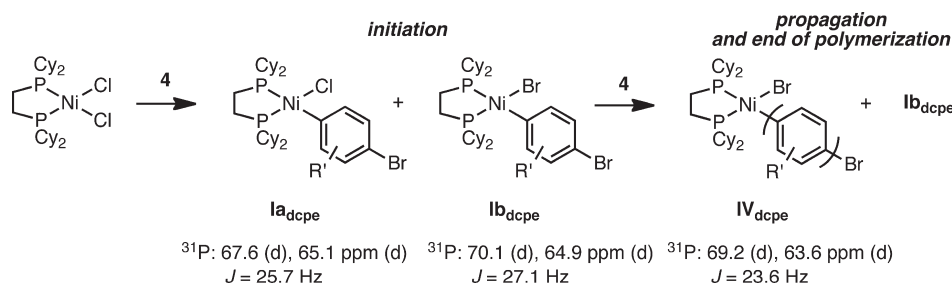


Figure 2. ^{31}P NMR spectra for the reaction of monomer **4a** with catalyst **3** showing (A) the first two complexes observed during initiation, (B) complex **6c**, (C) complex **6d**, and (D) the species observed during propagation.

Scheme 4. Ni Complexes Observed during the Reaction of Monomer **4** with $\text{Ni}(\text{dcpe})\text{Cl}_2$



Although no polymer was observed at room temperature, heating this complex to 60 °C initiated polymerization. Coincident with the onset of polymerization, a new species with proximal doublets and a narrow coupling constant ($J_{\text{PP}} = 14.8$ Hz) appeared (Figure 3C). We assigned this as complex V_{dmpe} based on analogy to catalyst **2**. Notably, complex II_{dmpe} persisted, which is consistent with an initiation process that is slower than propagation. Once polymerization was complete, several species with general structure $\text{Ni}(\text{dmpe})\text{ArBr}$ (IV_{dmpe}) were observed (Figure 3D), along with decomposition products (e.g., $\text{Ni}(\text{dmpe})\text{Cl}_2$ and $\text{Ni}(\text{dmpe})\text{Br}_2$). On the basis of the apparent decomposition reactions occurring both in the initial and final stages of polymerization, $\text{Ni}(\text{dmpe})\text{Cl}_2$ is a less suitable polymerization catalyst than $\text{Ni}(\text{depe})\text{Cl}_2$.

In summary, initiation of catalyst **1** led to formation of symmetric biaryl complex II_{dmpe} , which is inactive for polymerization at room temperature (Scheme 5). The lower reactivity of complex II_{dmpe} relative to II_{depe} is consistent with the notion that increased steric crowding accelerates reductive elimination with depe .³⁵ Heating this complex initiated polymerization, with concomitant formation of complex V_{dmpe} . These results suggest that the rate-limiting step for both initiation and propagation is

reductive elimination, similar to $\text{Ni}(\text{depe})\text{Cl}_2$. The lower reactivity of catalyst **1** can also be explained by the irreversible loss of soluble Ni via precipitation during initiation.

Spectroscopic Studies: Summary. Combined, the ^{31}P NMR spectroscopic studies described above provide evidence for each intermediate depicted in the initiation sequence (Scheme 1) as well as two of the three intermediates in the chain-growth polymerization (Scheme 2). A summary of the results is provided in Table 2. The lower reactivity of catalyst **1** compared to catalyst **2** can be explained by its decomposition as well as decreased steric properties. On the other hand, the lower reactivity of catalyst **3** compared to catalyst **2** can be explained by a change in rate-determining step to transmetalation and a corresponding reduction in rate due to the increased steric crowding at the metal center. Furthermore, the spectroscopic studies implicated an uncontrolled mechanism for catalyst **3**. Finally, the low molecular weight tail observed in the polymerizations with $\text{Ni}(\text{depe})\text{Cl}_2$ apparently stem from a slow initiation process relative to propagation.³⁰

Evidence for Chain-Growth Polymerization of Monomer **4a with $\text{Ni}(\text{depe})\text{Cl}_2$ (**2**).** Additional studies were undertaken to determine whether the polymerization of monomer **4a** using

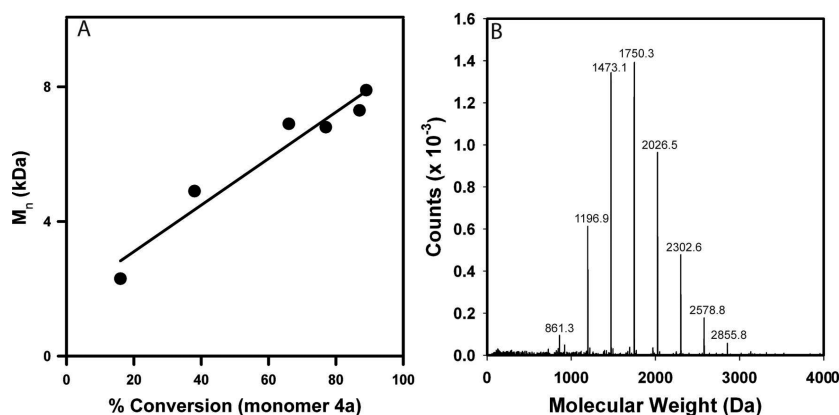


Figure 4. (A) Plot of M_n (●) versus conversion for the polymerization of **4a** using complex **2** at 60 °C ($[\text{Ni}] = 0.0015 \text{ M}$; $[\text{4a}] = 0.10 \text{ M}$). (B) MALDI-TOF-MS data obtained from the polymerization of **4a** using complex **6a** at 60 °C ($[\text{Ni}] = 0.0015 \text{ M}$; $[\text{4a}] = 0.010 \text{ M}$).

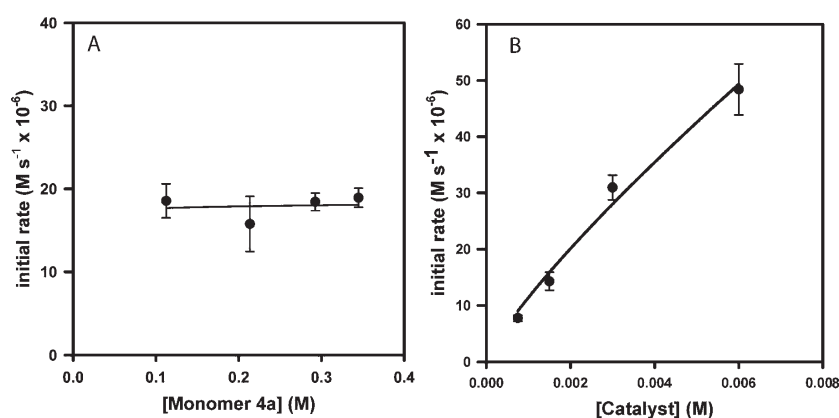


Figure 5. (A) Plot of the initial rate versus $[\text{monomer}]$ for the polymerization of **4a** in THF at 50 °C ($[\text{2}] = 0.0015 \text{ M}$). The curve depicts an unweighted least-squares fit to the expression $\text{initial rate} = a[\text{monomer}]^n$ that gave $a = 18 \pm 3$ and $n = -0.02 \pm 0.01$. (B) Plot of the initial rate versus $[\text{catalyst}]$ for the polymerization of **4a** in THF at 50 °C ($[\text{4a}] = 0.30 \text{ M}$). The curve depicts an unweighted least-squares fit to the expression $\text{initial rate} = a[\text{catalyst}]^n$ that gave $a = (3 \pm 1) \times 10^3$ and $n = 0.82 \pm 0.09$.

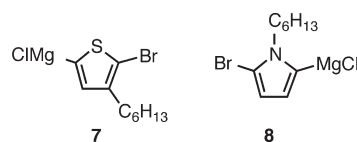
Supporting Information Figures S42–S44). Combined, these data suggest that *depe* is an effective ligand and leads to living, chain-growth polymerizations of monomer **4a**. Nevertheless, the spectroscopic studies indicated that the resulting chain end is not stable indefinitely. Thus, polymerizations must be intentionally terminated (i.e., quenched) to obtain specific molecular weights.

Rate Studies for Polymerization of Monomer 4a with Ni(*depe*)Cl₂ (2). To determine the influence of *depe* ligand on the polymerization mechanism, rate studies were performed for the Ni(*depe*)Cl₂-catalyzed polymerization of **4a**. The initial rates of polymerization were monitored by in situ IR analysis. As seen in Figure 5, the Ni(*depe*)Cl₂-catalyzed polymerization of **4a** showed a zero-order dependence on $[\text{monomer}]$ and a first-order dependence on $[\text{catalyst}]$. These results were consistent with reductive elimination as the rate-determining step because this reaction does not involve the monomer (see Scheme 2). The ³¹P NMR spectroscopic studies discussed above indicate that the catalyst resting state was complex **V_{depe}**, also consistent with a rate-limiting reductive elimination.

Rate Studies: Comparison of *dppe* versus *depe*. Previous mechanistic studies^{11,12} revealed that ligands with different bite angles exhibited different rate-determining steps for the polymerization of monomer **4a**. We now report that ligands with the same bite angles (*dppe* and *depe*) exhibit the same rate-

determining steps for polymerization.^{22c,37} However, the rate of polymerization was significantly slower with *depe*. Because the generalized cone angles³⁸ and bite angles^{22c,37} are similar, this result cannot be attributed to steric effects. Instead, the deceleration is likely due to the increased electron-donating ability of *depe*,¹⁴ as previous studies have shown that reductive eliminations were faster from electron-poor metal centers.^{39,40}

Monomer Scope for Ni(*depe*)Cl₂ (2). To determine whether Ni(*depe*)Cl₂ shows improved reactivity toward other monomers, the polymerization of monomers **7** and **8** were attempted. As seen in Table 3, complex **2** was an effective initiator for both monomers. Though the PDI was narrow for the poly(*N*-hexylpyrrole), the gel permeation chromatogram for the poly(3-hexylthiophene) revealed low molecular weight “tailing”, consistent with a slow initiation. Ni(*depe*)Cl₂ outperformed both Ni(*dppe*)Cl₂ or Ni(*dppp*)Cl₂ under these reaction conditions.⁴¹



Copolymerization with Ni(*depe*)Cl₂. Block copolymerization of monomers **4a** and **7** were attempted because they both

Table 3. Polymerization Results for Monomers 7 and 8 Using Selected Ni Catalysts^a

monomer	catalyst	M_n (kDa)	PDI _{total}
7	Ni(depe)Cl ₂	7.6	2.26
	Ni(dppe)Cl ₂	6.5	2.29
	Ni(dppp)Cl ₂	11	1.77
8	Ni(depe)Cl ₂	6.6	1.21
	Ni(dppe)Cl ₂	1.4	2.47
	Ni(dppp)Cl ₂	2.1	2.64

^aNumber-average molecular weights (M_n) and polydispersity indices (PDIs) were determined by GPC relative to PS standards. The polymerizations were quenched after 1 h (7) and 3 h (8) at 60 °C ([Ni] = 0.0015 M; [monomer] = 0.10 M). An equivalent of LiCl was added for polymerization of monomer 8 ([LiCl] = 0.10 M).

underwent a chain-growth homopolymerization with catalyst 2. Consistent with previous studies,⁷ the order of monomer addition influenced the molecular weight distributions. For example, polymerizing 4a followed by 7 led to an increase in molecular weight (from 5 to 14 kDa) while the PDI remained narrow (from 1.49 to 1.15). In contrast, polymerizing in the reverse order (7 followed by 4a) led to an increase in molecular weight (from 6 to 17 kDa) but with substantial broadening of the PDI (from 1.23 to 2.05). These results suggest that inefficiencies in cross-propagation, likely through termination and reinitiation reactions, were occurring. Consequently, more complex copolymerizations (e.g., gradient copolymerization⁴), which require multiple cross-propagation steps, will be problematic.

CONCLUSION

Because the ligand can tune catalyst reactivity through both steric and electronic effects, developing improved catalysts requires modifications to both aspects of the ligand scaffold. It is therefore surprising that the majority of research on these Ni-catalyzed chain-growth polymerizations has centered on two ligands (dppe and dppp). A limited number of studies have broadened the search to the structurally related diphenylphosphinoferrocene (dppf) and diphenylphosphinobutane (dppb) ligands without much success.⁴² Herein, the scope of ligands investigated was broadened to include the bis(diakylphosphino) ethane-based ligands. These phosphines were chosen because of their increased electron-donating ability (relative to dppp and dppe) and variable steric properties.

Polymerization studies indicate that ligand steric properties were critical, with the least and most hindered ligands performing poorly. Spectroscopic studies revealed that these ligands are susceptible to either decomposition (Ni(dmpe)Cl₂) or competing reaction pathways (Ni(dcpe)Cl₂). In contrast, Ni(depe)Cl₂ provided narrower PDI samples than the other catalysts for poly(2,5-bis(hexyloxy)phenylene). For polymerization of monomer 4a, a chain-growth mechanism was evident and the rate-limiting step was reductive elimination. Though the mechanism is similar to dppe,¹¹ the relative rates of polymerization were quite different. Because dppe and depe have similar generalized cone angles³⁸ and bite angles,^{22c,37} these results suggest that ligand-based electronic properties are also important; these effects are relatively unexplored, and our current efforts are elucidating their role. At this time, it remains unclear whether the increased electron-donating ability of depe was effective in stabilizing the Ni⁰–polymer π -complex and suppressing the

competing reaction pathways because the comparison, which relies on accurate PDIs, is complicated by the slow initiation. Ni(depe)Cl₂ is found to be an effective catalyst for chain-growth polymerization of 3-hexylthiophene and *N*-hexylpyrrole, and although block copolymerizations were successful, evidence of competing side reactions was observed. Overall, these results provide a foundation for development of alternative ligand scaffolds by elucidating the dependence of the chain-growth mechanism on the steric properties of the ligand.

ASSOCIATED CONTENT

S Supporting Information. Experimental details; rate and spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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