J|A|C|S
ARTICLES

Mechanistic Studies on Ni(dppe)Cl_2-Catalyzed Chain-Growth Polymerizations: Evidence for Rate-Determining Reductive Elimination

Erica L. Lanni and Anne J. McNeil*

Department of Chemistry and Macromolecular Science and Engineering Program, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109-1055

Received May 23, 2009; Revised Manuscript Received October 1, 2009; E-mail: ajmcneil@umich.edu

Abstract: The mechanisms for Ni(dppe)Cl_2-catalyzed chain-growth polymerization of 4-bromo-2,5-bis(hexyloxy)phenylmagnesium chloride and 5-bromo-4-hexylthiophen-2-ylmagnesium chloride were investigated. Rate studies utilizing IR spectroscopy and gas chromatography revealed that both polymerizations exhibit a first-order dependence on the catalyst concentration but a zeroth-order dependence on the monomer concentration. ^{31}P NMR spectroscopic studies of the reactive organometallic intermediates suggest that the resting states are unsymmetrical Ni^{II}−biaryl and Ni^{II}−bithiophene complexes. In combination, the data implicate reductive elimination as the rate-determining step for both monomers. Additionally, LiCl was found to have no effect on the rate-determining step or molecular weight distribution in the arene polymerization.

Introduction

Organic π-conjugated polymers are the active components of numerous emerging technologies, including thin-film solar cells[1] and light-emitting diodes.[2] The predominant cross-coupling-based polymerization methods[3] used to synthesize these materials (e.g., the Sonogashira,[4] Kumada,[5] Stille,[6] Suzuki,[7] Heck,[8] and Negishi[9] couplings) typically proceed through *step-growth* mechanisms, leading to broad molecular weight distributions and limited control over the copolymer microstructure. In 2004, Yokozawa[10] and McCullough[11] simultaneously reported *chain-growth* syntheses of poly(3-hexylthiophene) utilizing Ni-catalyzed cross-coupling reactions. Yokozawa[12] and McCullough[13] independently proposed a novel mechanistic pathway for this polymerization in which the key step is formation of an associated Ni^0−arene π complex after reductive elimination. Subsequent intracomplex oxidative addition was suggested to occur faster than dissociation, leading to successive monomer additions at the chain end. Although Ni^0−arene π complexes are known,[14] this mechanistic hypothesis remains speculative.

If broadly applicable, this chain-growth method has the potential to provide access to polymers with controlled molecular weights,[15] narrow molecular weight distributions, and well-defined microstructures.[16] This method has since been modified to polymerize a small set of other monomers in solution[17] and

---

(1) (a) Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv. Mater.* **2009**, *21*, 1323–1338. (b) Hoppe, H.; Sariciftci, N. S. In *Photoresponsive Polymers II*; Marder, S. R., Lee, K.-S., Eds.; Advances in Polymer Science, Vol. 214; Springer-Verlag: Berlin, 2008; pp 1−86. (c) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77. (d) Coakley, K. M.; McGehee, M. D. *Chem. Mater.* **2004**, *16*, 4533–4542.

(2) (a) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897–1091. (b) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281–2305. (c) Kulkarni, A. P.; Tonzola, C. J.; Babel, A.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4556–4573.

(3) (a) Cheng, Y.-J.; Luh, T.-Y. *J. Organomet. Chem.* **2004**, *689*, 4137–4148. (b) Babudri, F.; Farinola, G. M.; Naso, F. *J. Mater. Chem.* **2004**, *14*, 11–34. (c) Yamamoto, T. *J. Organomet. Chem.* **2002**, *653*, 195–199.

(4) (a) Sanechika, K.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 752–755. (b) For a recent review, see: Bunz, U. H. F. *Macromol. Rapid Commun.* **2009**, *30*, 772–805.

(5) (a) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091–2097. (b) For a recent review, see: Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 753–765.

(6) (a) Bao, Z.; Chan, W.; Yu, L. *Chem. Mater.* **1993**, *5*, 2–3. (b) Also see: Bao, Z.; Chan, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426–12435.

(7) (a) Rehahn, M.; Schlüter, A. D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060–1062. (b) For a recent review, see: Sakamoto, J.; Rehahn, M.; Wegner, G.; Schlüter, A. D. *Macromol. Rapid Commun.* **2009**, *30*, 653–687.

(8) (a) Heitz, W.; Brügging, W.; Freund, L.; Gailberger, M.; Greiner, A.; Jung, H.; Kampschulte, U.; Niessner, N.; Osan, F.; Schmidt, H.-W.; Wicker, M. *Makromol. Chem.* **1988**, *189*, 119–127. (b) For a recent review, see: Lee, Y.; Liang, Y.; Yu, L. *Synlett* **2006**, 2879–2893.

(9) (a) Yamamoto, T.; Osakada, K.; Wakabayashi, T.; Yamamoto, A. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 671–674. (b) Also see: Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233–244.

(10) (a) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169–1171. (b) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromol. Rapid Commun.* **2004**, *25*, 1663–1666.

(11) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526–3528.

(12) (a) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547. (b) Adachi, I.; Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Macromolecules* **2006**, *39*, 7793–7795. (c) Yokoyama, A.; Yokozawa, T. *Macromolecules* **2007**, *40*, 4093–4101. (d) Yokozawa, T.; Yokoyama, A. *Chem. Rev.* [Online early access]. DOI: 10.1021/cr900041c. Published Online: Sept 16, 2009. (e) Also see ref 5b.

(13) (a) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649–8656. (b) Osaka, I.; McCullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202–1214.

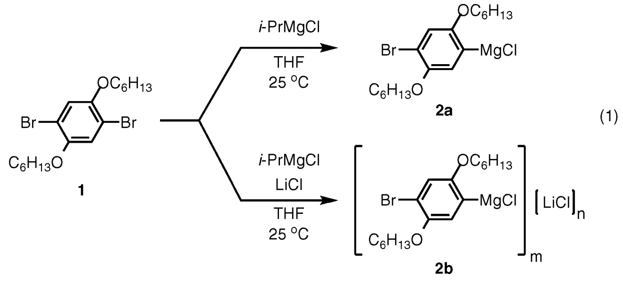
10.1021/ja904197q CCC: $40.75

on surfaces,[18] including 2,5-bis(hexyloxy)phenylene,[19] 9,9-dioctylfluorene,[20] 2,3-dihexylthienopyrazine,[21] *N*-octylcarbazole,[20b] 3-alkoxythiophene,[22] and *N*-hexylpyrrole.[23] However, without mechanistic data, each monomer has required empirical development of unique reaction conditions to achieve chain growth. Preliminary attempts at preparing simple block copolymers have highlighted the challenges involved when each monomer requires highly specific conditions.[23,24] For example, Yokozawa reported that the sequence of monomer addition had a significant effect on the molecular weight distribution in the synthesis of poly(2,5-bis(hexyloxy)benzene-*b*-*N*-hexylpyrrole).[23] He suggested that the excess 1,2-bis(diphenylphosphino)ethane (dppe) ligand, which is required for chain-growth polymerization of the pyrrole, interfered with the phenylene polymerization. However, the mechanistic influences of the ligand and other additives that are reported to promote chain growth have not been explored. In order to rationally expand this methodology to other monomers and copolymerizations, a detailed understanding of the reaction mechanism, particularly the roles of ligand, monomer, and additives, is essential.

To date, the few mechanistic studies that have been performed on these Ni-catalyzed chain-growth polymerizations have focused solely on thiophenes.[12,13,25,26] Most notably, rate studies by McCullough on the polymerization of thiophene catalyzed by $\mathrm{Ni(dppp)Cl_2}$ [dppp = 1,3-bis(diphenylphosphino)propane] found that the reaction is first-order in monomer, suggesting rate-determining transmetalation.[13a] Given the narrow substrate scope, we sought to elucidate the mechanistic influences of both the monomer and the ligand structure. Herein we report the results of rate and spectroscopic studies of the polymerization of 2,5-bis(hexyloxy)phenylene and 3-hexylthiophene using $\mathrm{Ni(dppe)Cl_2}$, a frequent alternative to $\mathrm{Ni(dppp)Cl_2}$.[12b,19,23] We provide strong evidence for rate-determining reductive elimination and identify $\mathrm{Ni^{II}}$–biaryl and $\mathrm{Ni^{II}}$–bithiophene complexes as the catalyst resting states. Furthermore, we show that LiCl, an additive reported to be beneficial in controlled polymerizations of 2,5-bis(hexyloxy)phenylene,[19] has no effect on the rate-determining step or the molecular weight distribution under our reaction conditions. These results, combined with the rate data previously reported by McCullough for $\mathrm{Ni(dppp)Cl_2}$-catalyzed polymerization,[13a] suggest that the ligand structure has a strong influence on the polymerization mechanism.

Results

Grignard Metathesis. Monomer **2a** was generated in situ from **1** via Grignard metathesis (GRIM) with *i*-PrMgCl (eq 1):[27] In the presence of 1 equiv of LiCl, rate studies demonstrated that the reaction is 4 times faster than in the absence of salt [see the Supporting Information (SI)]. Furthermore, a peak shift was observed in the aromatic region of the product's no-D NMR spectrum depending on the presence and absence of LiCl (Figure 1A). These results suggest that a mixed aggregate (**2b**) between LiCl and the ArMgCl is formed.[28] The aggregation state (e.g., 1:1 mixed dimer vs 2:2 mixed tetramer) for this species was not determined, but Knochel has suggested that related aryl



(1)

---

(14) (a) Yoshikai, N.; Matsuda, H.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 15258–15259. (b) Johnson, S. A.; Huff, C. W.; Mustafa, F.; Saliba, M. *J. Am. Chem. Soc.* **2008**, *130*, 17278–17280. (c) Ateşin, T. A.; Li, T.; Lachaize, S.; García, J. J.; Jones, W. D. *Organometallics* **2008**, *27*, 3811–3817. (d) García, J. J.; Brunkan, N. M.; Jones, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 9547–9555. (e) Braun, T.; Cronin, L.; Higgitt, C. L.; McGrady, J. E.; Perutz, R. N.; Reinhold, M. *New J. Chem.* **2001**, *25*, 19–21. (f) Bach, I.; Pörschke, K.-R.; Goddard, R.; Kopiske, C.; Krüger, C.; Rufińska, A.; Seevogel, K. *Organometallics* **1996**, *15*, 4959–4966. (g) Stanger, A.; Shazar, A. *J. Organomet. Chem.* **1993**, *458*, 233–236. (h) Boese, R.; Stanger, A.; Stellberg, P.; Shazar, A. *Angew. Chem., Int. Ed.* **1993**, *32*, 1475–1477. (i) Stanger, A.; Vollhardt, K. P. C. *Organometallics* **1992**, *11*, 317–320. (j) Stanger, A.; Boese, R. *J. Organomet. Chem.* **1992**, *430*, 235–243. (k) Scott, F.; Krüger, C.; Betz, P. *J. Organomet. Chem.* **1990**, *387*, 113–121. (l) Choe, S.-B.; Klabunde, K. J. *J. Organomet. Chem.* **1989**, *359*, 409–418. (m) Benn, R.; Mynott, R.; Topalović, I.; Scott, F. *Organometallics* **1989**, *8*, 2299–2305. (n) Brezinski, M. M.; Klabunde, K. J. *Organometallics* **1983**, *2*, 1116–1123. (o) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1977**, *16*, 884–891. (p) Jonas, K. *J. Organomet. Chem.* **1974**, *78*, 273–279.

(15) Hiorns, R. C.; Bettignies, R.; Leroy, J.; Bailly, S.; Firon, M.; Sentein, C.; Khoukh, A.; Preud'homme, H.; Dagron-Lartigau, C. *Adv. Funct. Mater.* **2006**, *16*, 2263–2273.

(16) For syntheses of end-functionalized polymers via this method, see: (a) Urien, M.; Erothu, H.; Cloutet, E.; Hiorns, R. C.; Vignau, L.; Cramail, H. *Macromolecules* **2008**, *41*, 7033–7040. (b) Hiorns, R. C.; Khoukh, A.; Gourdet, B.; Dagron-Lartigau, C. *Polym. Int.* **2006**, *55*, 608–620. (c) Jeffries-EL, M.; Sauvé, G.; McCullough, R. D. *Macromolecules* **2005**, *38*, 10346–10352. (d) Iovu, M. C.; Jeffries-EL, M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D. *Polymer* **2005**, *46*, 8582–8586. (e) Jeffries-EL, M.; Sauvé, G.; McCullough, R. D. *Adv. Mater.* **2004**, *16*, 1017–1019. For examples of controlled microstructure polymers via this method, see: (f) Wu, P.-T.; Ren, G.; Li, C.; Mezzenga, R.; Jenekhe, S. A. *Macromolecules* **2009**, *42*, 2317–2320. (g) Ouhib, F.; Khoukh, A.; Ledeuil, J.-B.; Martinez, H.; Desbrières, J.; Dagron-Lartigau, C. *Macromolecules* **2008**, *41*, 9736–9743. (h) Ohshimizu, K.; Ueda, M. *Macromolecules* **2008**, *41*, 5289–5294. (i) Zhang, Y.; Tajima, K.; Hirota, K.; Hashimoto, K. *J. Am. Chem. Soc.* **2008**, *130*, 7812–7813.

(17) For polymerization of thiophene derivatives via this method, see: (a) Benanti, T. L.; Kalaydjian, A.; Venkataraman, D. *Macromolecules* **2008**, *41*, 8312–8315. (b) Li, Y.; Xue, L.; Xia, H.; Xu, B.; Wen, S.; Tian, W. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3970–3984. (c) Ouhib, F.; Dkhissi, A.; Iratçabal, P.; Hiorns, R. C.; Khoukh, A.; Desbrières, J.; Pouchan, C.; Dagron-Lartigau, C. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 7505–7516. (d) Vallat, P.; Lamps, J.-P.; Schosseler, F.; Rawiso, M.; Catala, J.-M. *Macromolecules* **2007**, *40*, 2600–2602.

(18) (a) Sontag, S. K.; Marshall, N.; Locklin, J. *Chem. Commun.* **2009**, 3354–3356. (b) Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Horecha, M.; Stamm, M.; Uhrich, C.; Riede, M.; Leo, K.; Kiriy, A. *J. Am. Chem. Soc.* **2009**, *131*, 153–161. (c) Beryozkina, T.; Boyko, K.; Khanduyeva, N.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Simon, F.; Stamm, M.; Kiriy, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2695–2698. (d) Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Bocharova, V.; Simon, F.; Nitschke, M.; Stamm, M.; Grötzschel, R.; Kiriy, A. *Macromolecules* **2008**, *41*, 7383–7389. (e) Senkovskyy, V.; Khanduyeva, N.; Komber, H.; Oertel, U.; Stamm, M.; Kuckling, D.; Kiriy, A. *J. Am. Chem. Soc.* **2007**, *129*, 6626–6632.

(19) Miyakoshi, R.; Shimono, K.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2006**, *128*, 16012–16013.

(20) (a) Huang, L.; Wu, S.; Qu, Y.; Geng, Y.; Wang, F. *Macromolecules* **2008**, *41*, 8944–8947. (b) Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough, R. D. *Macromolecules* **2009**, *42*, 30–32.

(21) Wen, L.; Duck, B. C.; Dastoor, P. C.; Rasmussen, S. C. *Macromolecules* **2008**, *41*, 4576–4578.

(22) (a) Sheina, E. E.; Khersonsky, S. M.; Jones, E. G.; McCullough, R. D. *Chem. Mater.* **2005**, *17*, 3317–3319. (b) Also see ref 12b.

(23) Yokoyama, A.; Kato, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2008**, *41*, 7271–7273.

(24) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Chem. Lett.* **2008**, *37*, 1022–1023.

(25) Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriy, A. *Macromolecules* **2008**, *41*, 7817–7823.

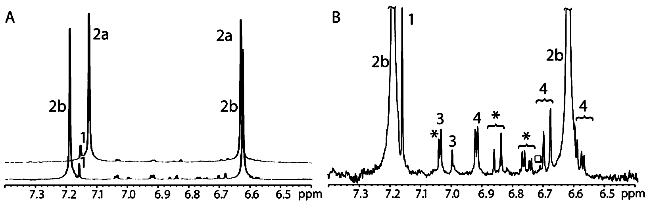
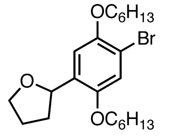
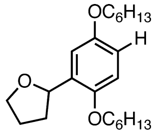


Figure 1. ^{1}H NMR spectra of (A) **2a** and **2b** and (B) **2b** with byproducts [(*) quenched monomer; (□) 1,4-bis(hexyloxy)benzene].

Grignards form 1:1 mixed dimers with LiCl in THF.[27f] Though **2a** or **2b** are the major products, several minor products (<10%) were frequently observed in the aromatic region of the no-D ^{1}H NMR spectrum (Figure 1B). These products were identified by independent synthesis and coinjection into the NMR sample (see the SI). THF adducts **3** and **4** were unexpected; however, a related coupling reaction between electron-rich aryl Grignards and THF has previously been reported and was suggested to proceed through a radical pathway.[29] Importantly, these byproducts were not consumed during the polymerization; however, monomers **2a** and **2b** were titrated immediately prior to each kinetic run to account for their formation (see the SI).

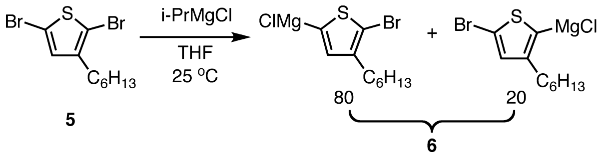


3



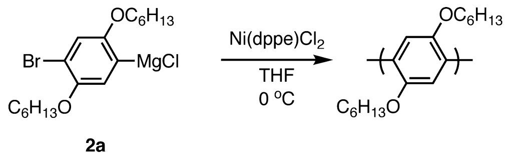
4

Monomer **6** was generated in situ from **5** via GRIM with *i*-PrMgCl (eq 2). ^{1}H NMR spectroscopic analysis revealed an 80:20 ratio of regioisomers. Unlike the case of monomers **2a** and **2b**, no byproducts were observed after the GRIM reaction.



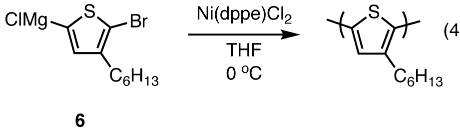
(2)

Rate Studies. Rate studies were carried out to ascertain the rate-determining step in the Ni(dppe)Cl$_2$-catalyzed chain-growth polymerizations of **2a** and **6** (eqs 3 and 4). Polymerization of **2a** was monitored by in situ IR spectroscopy, while GC analysis of aliquots was used to monitor the polymerization of **6** relative to an internal standard. Because of the insolubility of Ni(dppe)Cl$_2$, we found it convenient to initiate this precatalyst with 5−7 equiv of monomer before starting the rate studies (see the SI for details);[30] preinitiation also avoided any potential complications resulting from sluggish Ni(dppe)Cl$_2$ reduction.



(3)

2a



(4)

6

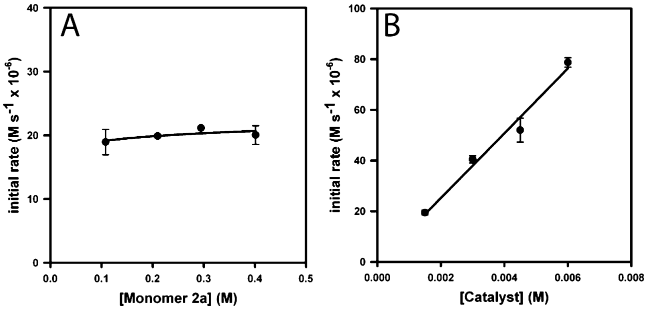


Figure 2. (A) Plot of initial rate vs [monomer] for the polymerization of **2a** in THF at 0 °C ([Ni(dppe)Cl$_2$] = 0.0015 M). The curve depicts an unweighted least-squares fit to the expression initial rate = a[monomer]^n that gave $a = 22 \pm 1$ and $n = 0.06 \pm 0.04$. (B) Plot of initial rate vs [catalyst] for the polymerization of **2a** in THF at 0 °C ([**2a**] = 0.20 M). The curve depicts an unweighted least-squares fit to the expression initial rate = a[catalyst]^n that gave $a = (1.3 \pm 0.1) \times 10^4$ and $n = 1.01 \pm 0.01$.

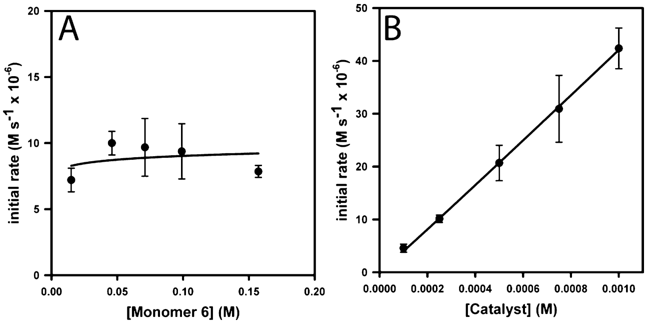


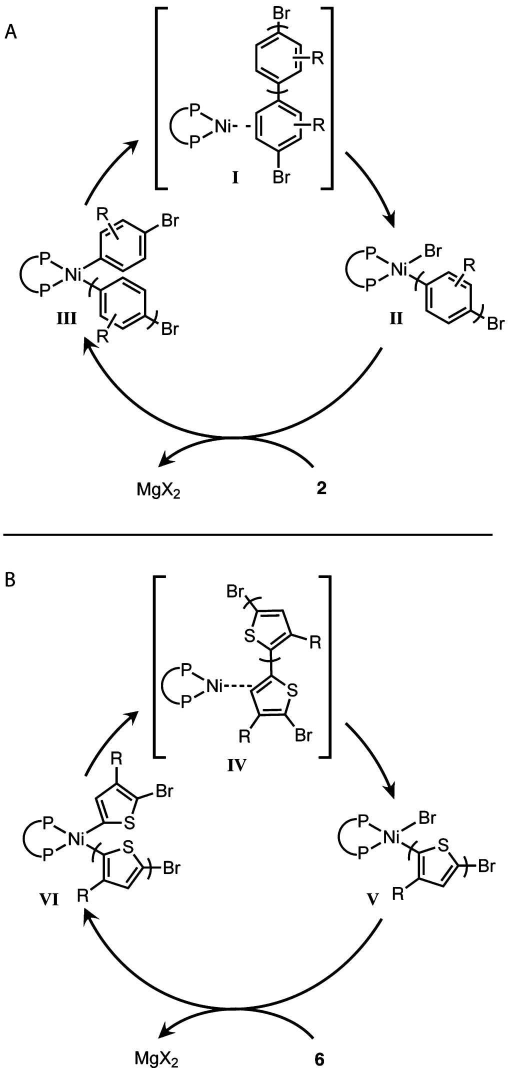
Figure 3. (A) Plot of initial rate vs [monomer] for the polymerization of **6** in THF at 0 °C ([Ni(dppe)Cl$_2$] = 0.00025 M). The curve depicts an unweighted least-squares fit to the expression initial rate = a[monomer]^n that gave $a = 10 \pm 3$ and $n = 0.05 \pm 0.09$. (B) Plot of initial rate vs [catalyst] for the polymerization of **6** in THF at 0 °C ([**6**] = 0.10 M). The curve depicts an unweighted least-squares fit to the expression initial rate = a[catalyst]^n that gave $a = (4.9 \pm 0.8) \times 10^4$ and $n = 1.02 \pm 0.02$.

For the polymerization of monomer **2a** with Ni(dppe)Cl$_2$, a plot of the initial rate versus [monomer] showed a zeroth-order dependence, while a plot of initial rate versus [catalyst] displayed a first-order dependence (Figure 2A,B). Similarly, for the polymerization of **6** by Ni(dppe)Cl$_2$, the reaction was zeroth-order in monomer and first-order in catalyst (Figure 3A,B). These data eliminate transmetalation as a plausible rate-determining step because it would exhibit a first-order dependence on [monomer]. However, these rate studies were not able to distinguish between rate-limiting reductive elimination and intracomplex oxidative addition because both cases would exhibit zero- and first-order dependencies with respect to [monomer] and [catalyst], respectively. We used NMR spectroscopic studies to characterize the catalyst structure in the resting state to differentiate between these two steps.

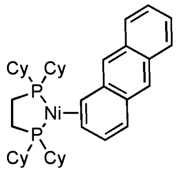
Spectroscopic Studies. ^{31}P NMR spectroscopic studies were used to identify the catalyst resting state in the chain-growth polymerizations of **2a** and **6**. These studies were performed on samples with higher catalyst concentrations than in the polymerizations in order to obtain sufficient signal (see the SI). According to the proposed catalytic cycles (Scheme 1), the resting states would be complexes **I** and **IV** if oxidative addition were rate-limiting and complexes **III** and **VI** if reductive elimination were rate-limiting.

During the polymerization of **2a**, the ^{31}P NMR spectrum revealed two proximate, broad doublets (J_{PP} = 11 Hz; Figure

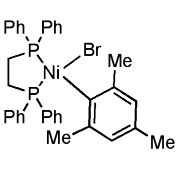
Scheme 1. Proposed Mechanism for the Chain-Growth Polymerizations of **2** and **6**



4A). The coupling constant is consistent with a Ni^{II} species,[14d] and the small $\Delta\delta$ is suggestive of complex **III** (with two similar phosphorus nuclei). We synthesized a model Ni^0−anthracene π complex (**7**) for comparison (Figure 4B). This π complex exhibited a relatively large coupling constant (J_{PP} = 68 Hz) compared to the observed resting state. On the basis of this data, we have assigned the catalyst resting state as complex **III**.



7

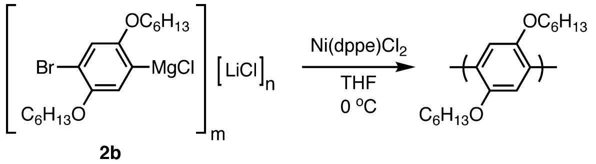


8

During the polymerization of **6**, the ^{31}P NMR spectrum also revealed two proximate signals (J_{PP} = 24 Hz; Figure 4C), which we have assigned to complex **VI** by analogy to **2a**. However, the spectrum clearly shows additional, related species. Since both regioisomers of **6** are consumed at these low [monomer]/[catalyst] ratios (see the SI), we have tentatively attributed these peaks to regioisomeric Ni^0−bithiophene complexes. These results, combined with the first-order rate dependence on [catalyst] and zeroth-order rate dependence on [monomer], support reductive elimination as the rate-determining step in the chain-growth polymerizations of **2a** and **6**.

Interestingly, different Ni complexes were observed in the ^{31}P NMR spectra when the polymerizations of **2a** and **6** were complete. After **2a** was consumed, two doublets appeared, which we hypothesized were from complex **II** (J_{PP} = 25 Hz; Figure 5A). We synthesized a related Ni^{II} model complex (**8**), which showed a similar spectrum (J_{PP} = 15 Hz; Figure 5B), supporting this assignment. After **6** was consumed, the ^{31}P NMR spectrum also showed two new doublets (J_{PP} = 36 Hz; Figure 5C), which we hypothesized were from complex **V**. The proximate, lower intensity doublets were again attributed to regioisomeric Ni^{II} complexes, since both regioisomers of **6** were consumed under these conditions. These results are consistent with the proposed catalytic cycle, since the reaction should stall at complexes **II** and **V** when the monomers are consumed. It should be noted that complexes **III** and **VI** could not be isolated because of this facile conversion to **II** and **V** once polymerization was complete.[32]

Role of LiCl. Yokozawa reported that LiCl accelerated the Ni(dppe)Cl_2-catalyzed polymerization of **2b** (eq 5) and led to a narrower molecular weight distribution (PDI).[19] We anticipated that to produce such a rate acceleration, the LiCl must not only aggregate with the monomer but also change the rate-determining step, since (1) the polymerization rate was shown to be independent of [monomer] for **2a** and (2) transmetalation with either **2a** or aggregate **2b** should result in the same Ni^{II}−biaryl complex. Instead, initial rate measurements on the polymerization of **2b** gave zeroth- and first-order dependencies in [monomer] and [catalyst], respectively (Figure 6A,B). Moreover, the absolute initial rates were nearly identical to the rates without LiCl (Figure 2A,B), indicating that LiCl has no effect on the rate. Initial rates were also measured for polymerizations with *excess* LiCl to determine whether rate acceleration could be caused by nonaggregated salt. As evident in Figure 7A, the rate remained unchanged with more than 1 equiv of LiCl. Further evidence came from temperature-dependent rate data, which provided nearly identical activation parameters (Figure 7B). In the presence of LiCl, the activation enthalpy and entropy were $\Delta H^‡ = 18.4 \pm 0.7$ kcal/mol and $\Delta S^‡ = 0 \pm 3$ cal mol^{-1} K^{-1}, respectively, while in the absence of LiCl, the values were $\Delta H^‡ = 18 \pm 1$ kcal/mol and $\Delta S^‡ = -3 \pm 5$ cal mol^{-1} K^{-1}. Finally, ^{31}P NMR spectroscopic studies of the catalyst resting state



(5)

---

(26) (a) Lamps, J.-P.; Catala, J.-M. *Macromolecules* **2009**, *42*, 7282–7284. (b) Mao, Y.; Wang, Y.; Lucht, B. L. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5538–5547.

(27) (a) Shi, L.; Chu, Y.; Knochel, P.; Mayr, H. *Org. Lett.* **2009**, *11*, 3502–3505. (b) Shi, L.; Chu, Y.; Knochel, P.; Mayr, H. *J. Org. Chem.* **2009**, *74*, 2760–2764. (c) Shi, L.; Chu, Y.; Knochel, P.; Mayr, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 202–204. (d) Krasovskiy, A.; Straub, B. F.; Knochel, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 159–162. (e) Hauk, D.; Lang, S.; Murso, A. *Org. Process Res. Dev.* **2006**, *10*, 733–738. (f) Krasovskiy, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3333–3336. (g) Knochel, P.; Dohle, W.; Gommermann, N.; Kneisel, F. F.; Kopp, F.; Korn, T.; Sapountzis, I.; Vu, V. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 4302–4320. (h) Boymond, L.; Rottländer, M.; Cahiez, G.; Knochel, P. *Angew. Chem., Int. Ed.* **1998**, *37*, 1701–1703.

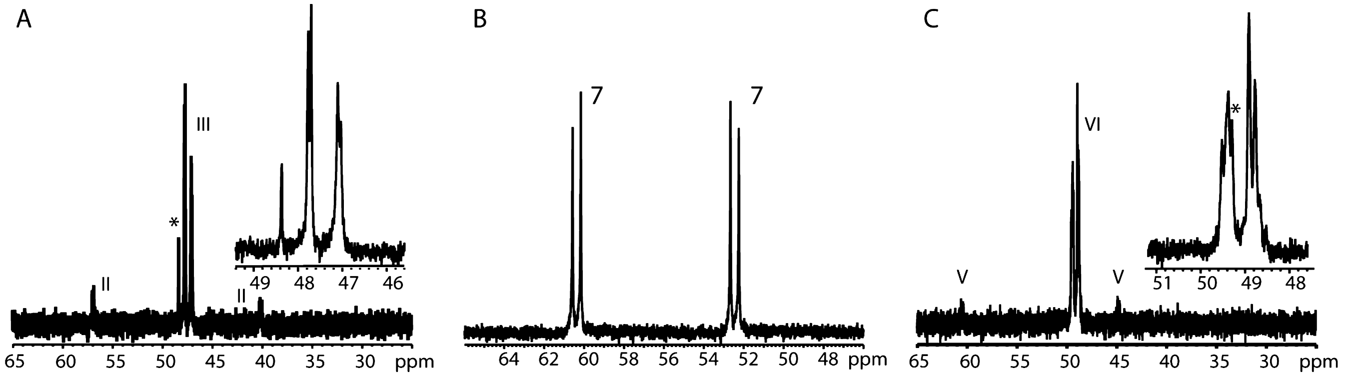


Figure 4. ^{31}P NMR spectra for (A) the resting state during polymerization of **2a**, (B) Ni^0—anthracene complex **7**, and (C) the resting state during polymerization of **6**. We have tentatively assigned the peaks labeled with * to Ni(dppe)$_2$X$_2$.[31]

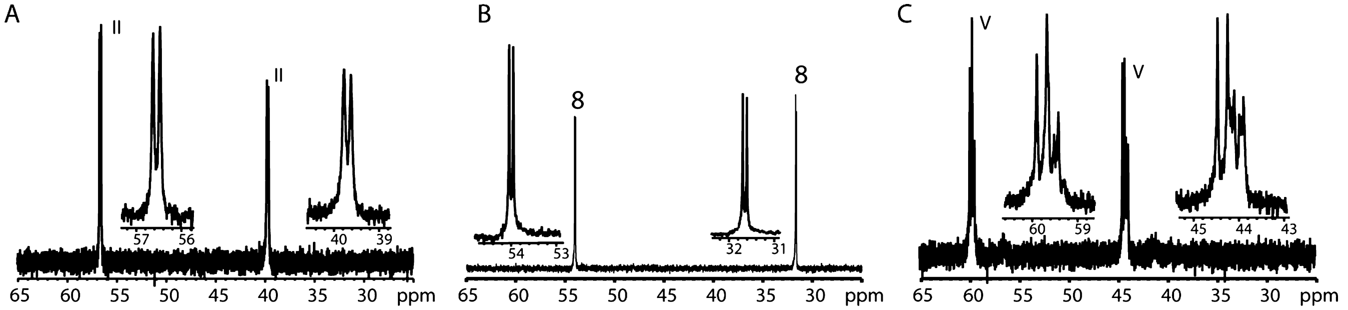


Figure 5. ^{31}P NMR spectra (A) after consumption of **2a**, (B) for complex **8**, and (C) after consumption of **6**.

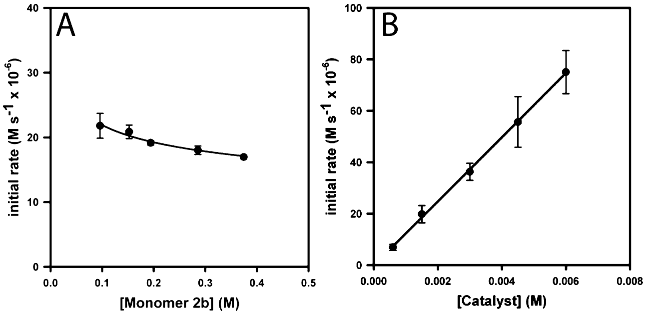


Figure 6. (A) Plot of initial rate vs [monomer] for the polymerization of **2b** in THF at 0 °C ([Ni(dppe)Cl$_2$] = 0.0015 M). The curve depicts an unweighted least-squares fit to the expression initial rate = a[monomer]^n that gave $a = 14.2 \pm 0.5$ and $n = -0.19 \pm 0.02$. (B) Plot of initial rate vs [catalyst] for the polymerization of **2b** in THF at 0 °C ([**2b**] = 0.20 M). The curve depicts an unweighted least-squares fit to the expression initial rate = a[catalyst]^n that gave $a = (1.3 \pm 0.2) \times 10^4$ and $n = 1.01 \pm 0.03$.

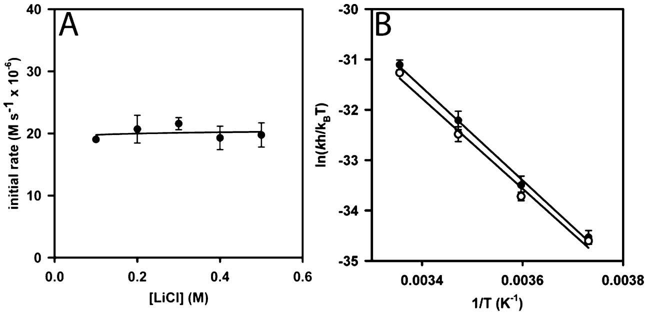


Figure 7. (A) Plot of initial rates vs [LiCl] for the Ni(dppe)Cl$_2$-catalyzed polymerization of **2b** in THF at 0 °C ([**2b**] = 0.20 M, [Ni(dppe)Cl$_2$] = 0.0015 M). The curve depicts an unweighted least-squares fit to the expression initial rate = a[LiCl]^n that gave $a = 20 \pm 1$ and $n = 0.02 \pm 0.05$. (B) Plot of $\ln(kh/k_BT)$ vs $1/T$ for the polymerization of **2a** (○) and **2b** (●) in THF ([**2a**] = [**2b**] = 0.20 M, [Ni(dppe)Cl$_2$] = 0.001 M). The curves depict unweighted least-squares fits to the formula $\ln(kh/k_BT) = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$ that provided $\Delta H^{\ddagger} = 18 \pm 1$ kcal/mol and $\Delta S^{\ddagger} = -3 \pm 5$ cal mol^{-1} K^{-1} for **2a** and $\Delta H^{\ddagger} = 18.4 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = 0 \pm 3$ cal mol^{-1} K^{-1} for **2b**.

showed two proximate doublets (J_{PP} = 9 Hz; Figure 8A), consistent with complex **III** and rate-limiting reductive elimination. Complex **II** was observed once conversion of monomer (**2b**) was complete (Figure 8B). Altogether, these data imply that there is no substantive effect of LiCl on the absolute rate and the rate-determining step.

Comparing plots of PDI versus conversion for the polymerizations of **2a** and **2b** revealed that in contrast to the report by Yokozawa,[19] LiCl had no significant effect on the PDI of the resulting polymers (Figure 9A,B). In this case, however, a subtle difference between the two reports may be playing an important role. In chain-growth polymerizations, the relative rate of initiation versus propagation influences the molecular weight distribution.[33] We avoided this relative rate issue by preinitiating the Ni(dppe)Cl$_2$ with 5−7 equiv of monomer before beginning the rate studies. In contrast, Yokozawa initiated his catalyst in situ, where the influence of LiCl on the initiation rate may be significant. This hypothesis is supported by the identification of a monomer−LiCl mixed aggregate (**2b**) that would be involved in initiation.

Discussion

Despite the general utility of Ni-catalyzed cross-coupling reactions[34] in both small-molecule[35] and polymer syntheses,[3,5,9,36] the operative mechanisms are still highly debated.[37] Moreover, the extrapolation of small-molecule-based mechanistic studies to polymerizations is not straightforward. Yokozawa[12] and McCullough[13] independently proposed a new mechanistic

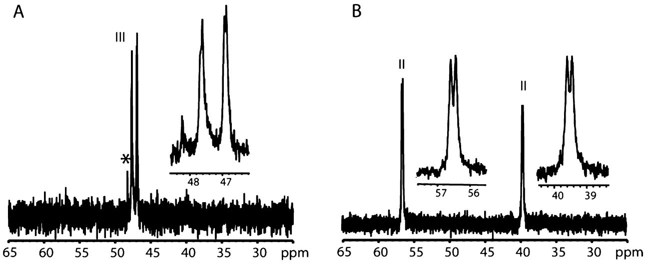


Figure 8. ^{31}P NMR spectra for (A) the resting state during polymerization of **2b** and (B) after consumption of **2b**. We have tentatively assigned the peak labeled with * to Ni(dppe)$_2$X$_2$.[31]

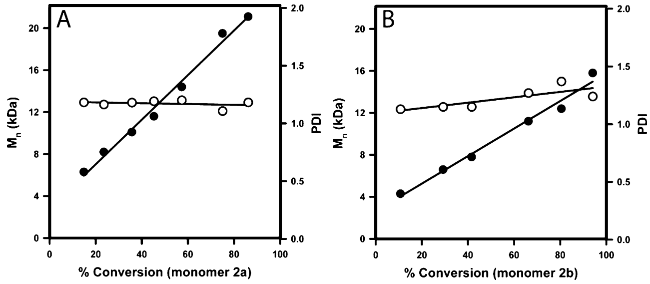


Figure 9. M_n (●) and PDI (○) vs conversion for the Ni(dppe)Cl$_2$-catalyzed polymerizations of (A) **2a** and (B) **2b** in THF at 0 °C ([**2a**] = 0.10 M; [**2b**] = 0.20 M; [Ni(dppe)Cl$_2$] = 0.0015 M).

pathway for this polymerization in which the key step is the formation of an associated Ni^0−arene *π* complex (e.g., complexes **I** and **IV**). Subsequent intracomplex oxidative addition leads to chain growth. Although Ni^0−arene *π* complexes have precedent,[14] their role in the polymerization mechanism remains uncertain. Both the potential of this method to provide access to novel well-defined polymers and its current limitations motivated us to explore the mechanism in more detail, particularly the influence of the ligand, monomer, and additives, with the aim of generating improved catalysts.

Mechanism. Through a combination of rate and spectroscopic studies, we have found evidence supporting a rate-determining *reductive elimination* for the polymerization of monomers **2a**, **2b**, and **6** using Ni(dppe)Cl$_2$. Interestingly, the monomer structure (arene vs thiophene) had no influence on the rate-determining step of the catalytic cycle. Notably, McCullough found evidence for a rate-determining *transmetalation* in the polymerization of **6** using a different catalyst, Ni(dppp)Cl$_2$.[13a] In combination, these results point to a significant mechanistic influence of the ligand on the polymerization and suggest that alternative ligand structures may lead to catalysts with improved reactivities.[38,39] Finally, though LiCl formed a mixed aggregate with the arene monomer, our rate and spectroscopic studies showed that this additive has no effect on either the polymerization rate or mechanism. Nevertheless, the role of LiCl in the initiation step may be significant, and future studies are needed to address this issue.

Chain Growth via Ni^0 *π* Complexes? The structure[40] and reactivity[41] of Ni^0−*olefin* *π* complexes has been widely documented. For example, van der Boom recently demonstrated that alkene coordination to Ni^0 is kinetically preferred over oxidative addition of aryl−I and aryl−Br bonds.[42] In addition, they only observed products resulting from intracomplex oxidative addition after alkene coordination. Far fewer studies for Ni^0−arene *π* complexes have been reported; recent theoretical and kinetic isotope effect studies by Nakamura have suggested that arene *π* complexation to Ni^0 is the first irreversible step in cross-coupling reactions of *o*-chloro- and *o*-bromotoluene with Grignards.[14a] Evidence of an intermediate Ni^0-arene *π* complex in the chain-growth polymerization has only been circumstantial: (1) Kiriy indirectly probed the existence of a *π* complex by examining whether the chain-growth mechanism depends on monomer size.[25] A decrease in chain-growth behavior was observed for terthiophene relative to thiophene, suggesting that detrimental chain-transfer and termination processes become more prevalent with larger distances between the C−C bond-forming site and the reactive end group. (2) McCullough observed an unexpected double-substitution reaction to generate thiophene trimers when a 2:1

---

(28) For an X-ray crystal structure of a related mixed aggregate, see: Buttrus, N. H.; Eaborn, C.; El-Kheli, M. N. A.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C.; Tavakkoli, K. *J. Chem. Soc., Dalton Trans.* **1988**, 381–391.

(29) Inoue, A.; Shinokubo, H.; Oshima, K. *Synlett* **1999**, 1582–1584.

(30) It should be noted that we obtained lower polymerization rates when using commercial batches of Ni(dppe)Cl$_2$ that contained impurities observable by ^{31}P NMR spectroscopy.

(31) Jarrett, P. S.; Sadler, P. J. *Inorg. Chem.* **1991**, *30*, 2098–2104.

(32) Ni^{II}−biaryl complexes with chelating phosphine ligands have previously been reported to be unstable toward isolation as a result of facile reductive elimination. For example, see: Coronas, J. M.; Muller, G.; Rocamora, M.; Miravitlles, C.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1985**, 2333–2341.

(33) Odian, G. In *Principles of Polymerization*, 4th ed.; Wiley: Hoboken, NJ, 2004; pp 422−436.

(34) (a) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374–4376. (b) Corriu, R. J. P.; Masse, J. P. *Chem. Commun.* **1972**, 144. (c) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958–1969. (d) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347–3354.

(35) (a) Takahashi, T.; Kanno, K. In *Modern Organonickel Chemistry*; Tamaru, Y., Ed.; Wiley-VCH: Weinheim, Germany, 2005; pp 41−55. (b) Phapale, V. B.; Cárdenas, D. J. *Chem. Soc. Rev.* **2009**, *38*, 1598–1607. (c) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359–1469.

(36) (a) Yamamoto, T.; Koizumi, T. *Polymer* **2007**, *48*, 5449–5472. (b) Yamamoto, T. *Synlett* **2003**, 425–450.

(37) (a) Jin, L.; Zhang, H.; Li, P.; Sowa, J. R., Jr.; Lei, A. *J. Am. Chem. Soc.* **2009**, *131*, 9892–9893. (b) Amatore, C.; Jutand, A. *Organometallics* **1988**, *7*, 2203–2214. (c) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627–2637. (d) Semmelhack, M. F.; Helquist, P.; Jones, L. D.; Keller, L.; Mendelson, L.; Ryono, L. S.; Smith, J. G.; Stauffer, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 6460–6471. (e) Smith, G.; Kochi, J. K. *J. Organomet. Chem.* **1980**, *198*, 199–214. (f) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 6319–6332. (g) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547–7560. (h) Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 1634–1635. (i) Morrell, D. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1975**, *97*, 7262–7270.

(38) For an example of the influence of the ligand (dppe vs dppp) on reductive elimination in Ni^{II} dimethyl complexes, see: Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1980**, *192*, 265–274.

(39) For examples of alternative initiators, see: (a) Doubina, N.; Ho, A.; Jen, A. K.-Y.; Luscombe, C. K. *Macromolecules* **2009**, *42*, 7670−7677. (b) Bronstein, H. A.; Luscombe, C. K. *J. Am. Chem. Soc.* **2009**, *131*, 12894–12895. (c) Also see ref 18e.

(40) (a) Massera, C.; Frenking, G. *Organometallics* **2003**, *22*, 2758–2765. (b) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *Organometallics* **1983**, *2*, 1391–1396. (c) Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780–2789. (d) Tolman, C. A.; Seidel, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 2774–2780. (e) Brauer, D. J.; Krüger, C. *J. Organomet. Chem.* **1974**, *77*, 423–438. (f) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669–2676. (g) Cheng, P.-T.; Cook, C. D.; Nyburg, S. C.; Wan, K. Y. *Inorg. Chem.* **1971**, *10*, 2210–2213. (h) Ittel, S. D. *Inorg. Chem.* **1977**, *16*, 2589–2597.

(41) For leading references, see: Johnson, J. B.; Rovis, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 840–871.

(42) Zenkina, O. V.; Karton, A.; Freeman, D.; Shimon, L. J. W.; Martin, J. M. L.; van der Boom, M. E. *Inorg. Chem.* **2008**, *47*, 5114–5121.

ratio of monomer to catalyst was used.[11] Such preferential double substitutions have also been observed in Pd-catalyzed cross-coupling reactions of small molecules[43] and polymers.[44] Interestingly, Kumada observed a similar preferential Ni-catalyzed double alkylation in 1976 when using bifunctional arenes (e.g., 1,4-dichlorobenzene) despite having a 2-fold excess of the arene reagent relative to the alkyl Grignard.[34c] He suggested that such substrates undergo a "mechanistically different" reaction but provided no further explanation.

Our observation of a rate-determining reductive elimination and McCullough's observation of a rate-determining transmetalation indicate that the Ni^0 π complex, if formed, is only a fleeting, post-rate-limiting intermediate. Moreover, our extensive spectroscopic studies identified the catalyst species both during and after polymerization, and neither was consistent with a Ni^0 π complex. As a result, the mechanistic underpinnings of the chain-growth nature of these polymerizations remain unclear, and further studies are necessary to probe both the existence and catalytic relevance of the proposed Ni^0 π complexes.

Conclusion

Rate and spectroscopic studies support a rate-limiting reductive elimination for the Ni(dppe)Cl_2-catalyzed syntheses of poly(2,5-bis(hexyloxy)phenylene) and poly(3-hexylthiophene). These results, combined with the data from McCullough[13a] using Ni(dppp)Cl_2, suggest that the ligand has a strong influence over the rate-determining step. Ni^{II}−biaryl and Ni^{II}−bithiophene complexes, though unstable to isolation, were identified as the active catalyst resting states. These studies also revealed that the role of LiCl is complex and that this additive may be unnecessary under certain reaction conditions. By addressing the mechanistic influences of monomer and catalyst structure as well as the role of additives, these results provide a strong foundation for future studies aimed at preparing novel polymers and developing improved catalysts. In addition, we are now in a position to explore the more complex yet intriguing copolymerization mechanisms.

Acknowledgment. We thank the donors of the American Chemical Society Petroleum Research Fund (47661-G7) and the University of Michigan for direct support of this work. E.L.L. thanks the NSF for a predoctoral fellowship.

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

JA904197Q

---

(43) (a) Weber, S. K.; Galbrecht, F.; Scherf, U. *Org. Lett.* **2006**, *8*, 4039–4041. (b) Sinclair, D. J.; Sherburn, M. S. *J. Org. Chem.* **2005**, *70*, 3730–3733. (c) Dong, C.-G.; Hu, Q.-S. *J. Am. Chem. Soc.* **2005**, *127*, 10006–10007.

(44) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236–7237.