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# Toward One-pot Olefin/Thiophene Block Copolymers using an in situ Ligand Exchange

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**ABSTRACT**

Block copolymers containing both conducting and insulating segments are of interest due to their enhanced electrical properties arising from their increased crystallization. Yet few methods exist for generating these copolymers because the reaction conditions for synthesizing each block are often incompatible. Herein, efforts towards identifying a one-pot, living polymerization method for synthesizing block copolymers of 1-pentene and 3-hexylthiophene is described. An in situ ligand exchange enables the optimal catalyst to be utilized for synthesizing each block. Even under these conditions, however, only homopolymers are observed. Computational studies modeling the ligand exchange reveal that the added stabilizing ligands likely inhibit propagation of the second block. These results suggest an ancillary ligand-based 'goldilocks' effect wherein catalysts which are stable yet still reactive are required.

**KEYWORDS:** polymerization; ligand exchange; block copolymer; mechanistic studies

## INTRODUCTION

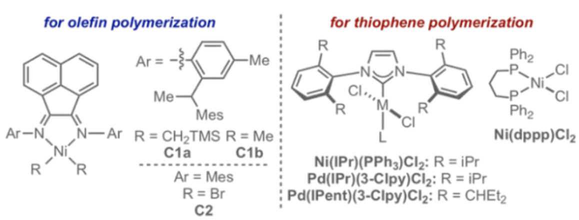
Block copolymers containing both insulating and conducting segments have not been widely explored due in part to their challenging syntheses, which often proceed via multiple reactions involving different catalysts and purifications, as well as post-polymerization modifications.[1,2,3,4] Nevertheless, these copolymers exhibit interesting properties, including improved charge mobility in organic field effect transistors due to their more crystalline solid-state organization.[1,2] A more streamlined approach to insulating/conducting block copolymers could take advantage of the fact that both olefin and thiophene monomers can undergo living, chain-growth polymerizations via structurally similar intermediates, albeit by different mechanisms.[5,6,7,8,9,10,11]

On the basis of these similarities, we previously attempted to generate 1-pentene/3-hexylthiophene block copolymers in one pot using diimine-ligated Ni precatalysts that were known to polymerize olefins via an insertion and chain-walking mechanism[10,11] and thiophene via catalyst-transfer polymerization

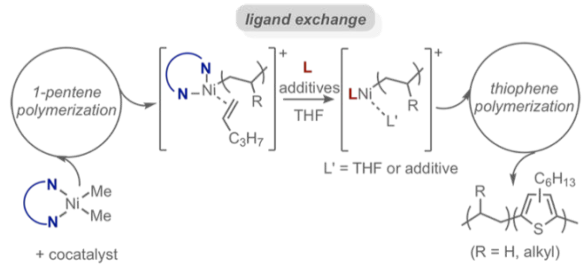
(CTP) (Chart 1).[12,13,14,15,16,17] Although precatalyst **C1a** was efficient in both homopolymerizations, attempted copolymerization led mostly to homopolymer formation.[18] Computational studies suggested that the copolymerization may have failed due to a high $sp^3/sp^2$ reductive elimination barrier during mechanism-switching.

Herein, we took a different approach toward a one-pot 1-pentene/3-hexylthiophene copolymerization involving an in situ ligand exchange, which is commonly used in catalysis.[19,20] The rationale is that this approach enables the optimal catalyst to be utilized for enchaining each block. Our proposed copolymerization would first involve a diimine-ligated precatalyst to generate a poly(olefin) macroinitiator. A subsequent ligand exchange would render the metal-center ready for $sp^3/sp^2$ reductive elimination and ultimately thiophene polymerization (Scheme 1).

**CHART 1** Precatalysts for olefin or thiophene living, chain-growth polymerizations examined herein.




**SCHEME 1** Proposed ligand-exchange reaction to generate block copolymers.




## EXPERIMENTAL

### Standard Copolymerization Conditions.

Precatalyst **C1b** (8.2 mg, 0.011 mmol) was dissolved in 1-pentene (0.40 mL) and placed in the freezer (–30 °C) for 2 min. Then, while both **C1b** and tris(pentafluorophenyl)borane (BCF) were still cold, BCF (0.0072 M in 1-pentene, 3.06 mL, 0.0221 mmol, 2.00 equiv) was added to the stirring catalyst, which were stirred for 3 min at rt. Overall [Ni] = 0.0032 M in 1-pentene. Then, THF (10.42 mL) was added to stall the polymerization. Overall [Ni] = 0.0008 M in 1-pentene/THF (total volume = 13.88 mL). An aliquot (2.0 mL) was removed from the glovebox and immediately quenched with MeOH (5 mL) for size-exclusion chromatography (SEC) analysis. To the remaining macroinitiator solution (0.0095 mmol Ni remain), pyridine (0.10 M in THF, 114 µL, 0.0114 mmol, 1.20 equiv) and IPr (0.010 M in THF, 1.14 mL, 0.0114 mmol, 1.20 equiv) were added and stirred for 15 min at rt. Overall [Ni] = 0.00072 M in 1-pentene/THF (total volume = 13.13 mL). Three aliquots (0.00072 M Ni in THF/1-pentene, 1.50 mL each, 0.00109 mmol Ni, new 1.00 equiv) from the ligand-switched macroinitiator solution were added to Grignard thiophene monomer solutions (see solutions A–C below) and stirred for 1 h before quenching outside of the glovebox with aq. HCl (12 M, 2 mL) and working up for GC, SEC and MALDI-TOF/MS analysis. (A) thiophene monomer

(0.080 M in THF, 0.34 mL, 0.027 mmol, 25 equiv) in THF (0.89 mL). (B) thiophene monomer (0.080 M in THF, 0.68 mL, 0.055 mmol, 50 equiv) in THF (0.54 mL). (C) thiophene monomer (0.080 M in THF, 1.36 mL, 0.109 mmol, 100 equiv). See SI for SEC traces and yield data.

## RESULTS AND DISCUSSION

Our first goal was to identify an ancillary ligand that would facilitate the $sp^3/sp^2$ reductive elimination. We began by evaluating bidentate phosphines and N-heterocyclic carbenes (NHC) because they make efficient thiophene polymerization catalysts when ligated to Ni or Pd.[5] We evaluated three commonly used CTP precatalysts: $Ni(dppp)Cl_2$, $Ni(IPr)(PPh_3)Cl_2$, $Pd(IPr)(3\text{-}Clpy)Cl_2$. In addition, we evaluated a more sterically hindered precatalyst ($Pd(IPent)(3\text{-}Clpy)Cl_2$), hypothesizing that the more crowded metal center would facilitate reductive elimination. Most precatalysts reacted with both thiophene Grignard regioisomers (except $Ni(dppp)Cl_2$), albeit at different rates (see SI, Table S1). To evaluate each catalyst's ability to perform an $sp^3/sp^2$ reductive elimination, the generated poly(3-decylthiophene) macroinitiator[21] was reacted in situ with MeMgI to generate Me-terminated polythiophene (Figure 1).[22] This end-capping reaction was designed to model the challenging polyolefin/thiophene $sp^3/sp^2$ reductive elimination involved in the copolymerization. More specifically, we reasoned that the catalyst that generates the highest fraction of Me-terminated polythiophene should be the most efficient at mediating $sp^3/sp^2$ (polyolefin/thiophene) reductive elimination in the copolymerization. Excess 5,5'-dibromo-2,2'-bithiophene was concurrently added to scavenge any Ni(0) or Pd(0) generated after reductive elimination.[22] For all precatalysts, the polymer molecular weights remained approximately the same before and after the end-capping experiments (see SI, Table S2). The resulting polymers were analyzed by MALDI-TOF/MS to determine their end-group identities.

Overall, the Ni precatalysts outperformed Pd, generating 97–99% Me-terminated polymers. The highest fraction of Me-terminated polymers (99%) was generated from $Ni(IPr)(PPh_3)Cl_2$,[23] while the Pd analogue gave only 89% of Me-terminated polymers. With $Ni(dppp)Cl_2$ only 97% of polymers were Me-terminated (3% remaining Br/H). The sterically hindered precatalyst, $Pd(IPent)(3\text{-}Clpy)Cl_2$, generated polymers with a relatively broad dispersity (Đ = 1.76) and the lowest fraction of Me-terminated polymers (88 %). These results could be attributed to sluggish turnover caused by the increased steric bulk or unproductive pathways that generate inactive species.

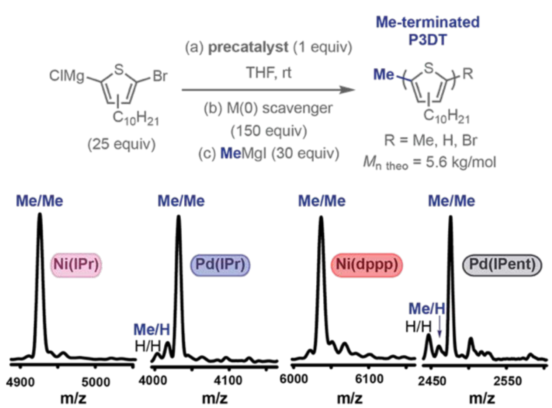



**FIGURE 1** (Top) Reaction conditions for 3-decylthiophene polymerization followed by end-capping with methyl Grignard. (Bottom) MALDI-TOF/MS data for the experiment

described above. (The full MALDI-TOF/MS spectra can be found in the SI Figures S8–S11).

Having identified an optimized metal (Ni) and ancillary ligand (IPr) for facilitating $sp^3/sp^2$ reductive elimination, the next goal was to elucidate reaction conditions for efficient ligand exchange. A similar model system was used, except that the initial precatalyst is now a diimine-ligated Ni, which will be replaced with IPr during the ligand exchange (Figure 2). A thiophene polymerization followed by end-capping with methyl Grignard and the M(0) scavenger will be used. If ligand exchange is quantitative, we would expect to observe similar Me end-capping efficiencies as before.

Precatalyst **C2** was used for these preliminary studies because it is synthetically easier to access than **C1**, which is a more effective olefin polymerization catalyst. Treating precatalyst **C2** with IPr before initiating thiophene polymerization and subsequent end-capping generated no detectable Me-terminated polymers (Figure 2).[24] Furthermore, as evidenced by SEC, the resulting materials exhibited broad dispersity and variable end-group identities, suggesting that multiple catalytic species were formed. Combined, these results indicate that displacing the diimine ancillary ligand with IPr alone will not be sufficient. One significant difference between initiating with IPr-treated **C2** versus the commercial precatalyst is the presence of a stabilizing ligand (L = $PPh_3$). When **C2** was pre-mixed with both IPr and $PPh_3$, polymers with an extremely broad dispersity (Đ = 17.1) were generated, suggesting again that several Ni species capable of polymerizing thiophene were generated (e.g., $(PPh_3)_2NiBr_2$).

To avoid generating multiple catalytic species, we next evaluated a different stabilizing ligand. Pyridine and its derivatives have precedent as stabilizing ligands for IPr-ligated precatalysts.[25,26] Adding both IPr and pyridine to **C2** prior to initiating thiophene polymerization and subsequent end-capping resulted in 90% Me-terminated polymers and a narrow dispersity, suggesting successful ligand exchange, thiophene polymerization, and $sp^3/sp^2$ reductive elimination (Figure 2).

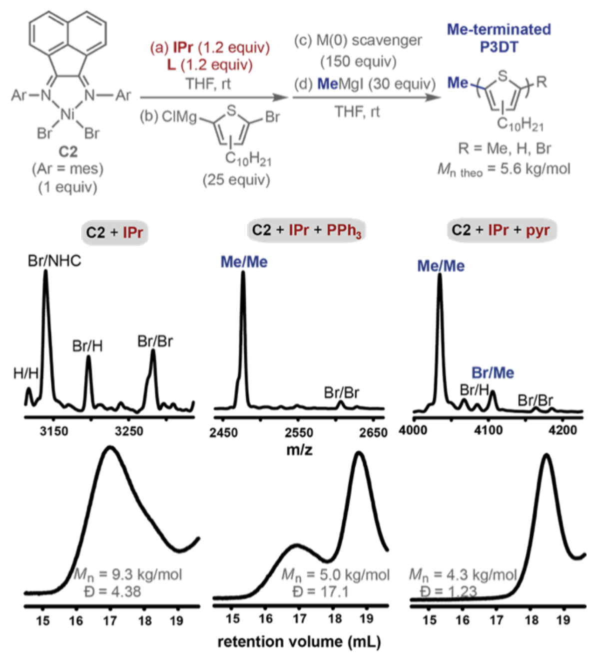



**FIGURE 2** (Top) Reaction conditions for ligand exchange followed by 3-decylthiophene polymerization, and end-capping with methyl Grignard. (Bottom) MALDI-TOF/MS data and SEC traces for the experiment described above. All $M_n$ are reported in kg/mol. (The full MALDI-TOF/MS spectra can be found in the SI Figures S14–S16).

In our previous studies, the unreacted olefin served as a competitive π-binding agent during

CTP.[18] This inhibition was not observed when IPr was the ancillary ligand (c.f., 91% Me-terminated polymers, see SI, Figure S17). In addition, the polymers generated when **C2** was pre-mixed with IPr and pyridine reach approximately the theoretical molecular weight and exhibit narrow dispersities ($M_{n(theo)}$ = 5.6 kg/mol and $M_{n(obs)}$ = 4.3–4.4 kg/mol; Đ = 1.2) These results suggest that the IPr ancillary ligand minimizes chain-transfer pathways instigated by excess olefin.[27]

Having optimized conditions for ligand exchange, we attempted copolymerization of 1-pentene and 3-hexylthiophene. We previously used a boron cocatalyst (BCF) that activates Ni(bisalkyl) complexes to polymerize olefins without disrupting CTP.[18] Precatalyst **C1b** was used for block copolymerization instead of **C2**, which typically afford polymers with a broad molecular weight distribution. Using this same co-catalyst system, precatalyst **C1b** was activated to generate a poly(1-pentene) macroinitiator in neat 1-pentene (Figure 3).[28] Then, THF was added to fill the open coordination site and stall poly(1-pentene) propagation.[18] Ligand exchange was performed by adding both pyridine and IPr. Evaluating the SEC traces for polyolefin before ($PO_i$) and after ligand exchange ($PO_{LE}$) indicated no further olefin insertion occurs after adding THF (Figure 3).

Thiophene monomer was subsequently added, producing an orange/red color indicative of poly(thiophene) enchainment. If chain-extension with thiophene monomers had occurred, an increase in the molecular weight of the poly(olefin) macroinitiator should be evident. Instead, the poly(olefin) peak maximum in the refractive index (RI) trace did not shift to higher molecular weights, suggesting that chain-extension did not occur. In addition, the UV trace shows negligible signal near the poly(olefin) peak in the RI trace, suggesting few, if any, thiophenes are added to the poly(olefin) macroinitiator. Instead, the UV trace only shows lower molecular weight poly(thiophene) (Figure 3). In a subsequent experiment, the thiophene Grignard was added prior to ligand exchange to explore whether the copolymerization failed due to premature polyolefin termination during the ligand exchange. Unfortunately, the results were similar to before, with no chain-extension of the polyolefin macroinitiator observed (see SI, Figures S26–S29).

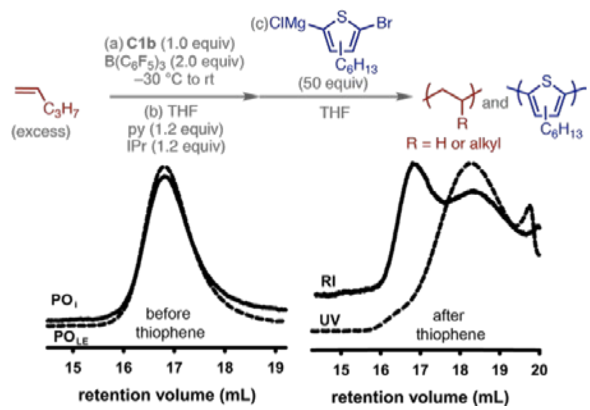
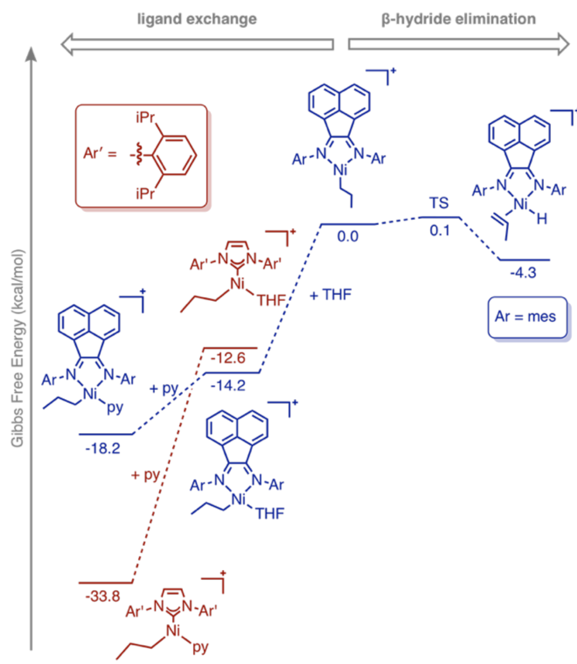



**FIGURE 3** (Top) Reaction conditions for ligand exchange during attempted copolymerization of 1-pentene with 3-hexylthiophene. (Bottom) SEC traces of the poly(olefin) macroinitiator before ($PO_i$, $M_n$ = 21.10 kg/mol) and after ligand exchange ($PO_{LE}$, $M_n$ = 21.27 kg/mol) (left), as well as after thiophene polymerization (right).

Because transmetalation reactions are less commonly performed on cationic Ni(II) complexes, we added tetrabutylammonium bromide to form a neutral Ni(II) complex. Adding the bromide salt after ligand exchange resulted in little to no thiophene incorporation into the poly(olefin) macroinitiator as well as mostly homopolymer formation, suggesting that the charged state of Ni is not contributing to the lack of thiophene incorporation (see SI, Figures S30–S33). Increasing the relative ratio of thiophene to Ni led to poly(thiophene)s with increasing molecular weight, albeit at low thiophene conversions, suggesting either slow chain termination to generate small quantities of active catalyst or some uninitiated catalyst remains after olefin polymerization (see SI, Figures S19–S21).

One potential pathway for chain termination is β-hydride elimination, which has previously been observed during olefin polymerization.[29] To investigate this potential pathway, density functional theory simulations were performed using the single-ended growing string method.[30,31] The β-hydride elimination from the cationic (diimine)Ni–alkyl intermediate is readily accessible with a negligible activation barrier ($\Delta G^{\ddagger}$ = 0.1 kcal/mol), leading to a lower energy Ni–H intermediate (–4.3 kcal/mol) that is π-coordinated to the terminal olefin (Scheme 2). Adding THF, however, forms a lower-energy THF-solvated Ni intermediate (–14.2 kcal/mol), from which β-H elimination is no longer feasible due to a lack of an open coordination site. Exchanging the diimine ancillary ligand with IPr and pyridine leads to an even more stable complex (–33.8 kcal/mol), which serves as a thermodynamic sink, potentially inhibiting thiophene incorporation.[32] Overall, these computational studies suggest that β-hydride elimination, while feasible in the unsolvated cationic complex, is unlikely to be a chain-terminating pathway during ligand exchange. Instead, these results suggest that ligand exchange stabilizes the catalyst to the point where it inhibits thiophene propagation. As such, we suspect that the low but significant conversion of thiophene to form homopolymers stems from uninitiated catalysts or undetectable catalyst impurities.

**SCHEME 2** Reaction pathways during ligand exchange as elucidated using density functional simulations.




## CONCLUSIONS

To summarize, the one-pot synthesis of insulating/conducting polymers, specifically poly(1-pentene)-*block*-poly(3-hexylthiophene), continues to be a challenge. Our model system was successful in elucidating a catalyst capable of facilitating an $sp^3/sp^2$ reductive elimination and in identifying conditions for an efficient ligand exchange. Nevertheless, the attempted copolymerization still failed to produce copolymers. Two key differences between the model system and the copolymerization are (i) the nature of the transmetalating group (MeMgI versus thiophene Grignard) and (ii) the nature of the reactive ligand (polythiophene versus polyolefin). We suspect that these differences most significantly impact transmetalation during the switch from polymerizing olefin to polymerizing thiophene. This hypothesis is further supported by the computational studies, which revealed substantial stabilization provided by IPr and pyridine when the poly(olefin) was the reactive ligand. Further studies should be aimed at teasing apart these differences, which may yet yield a streamlined approach for synthesizing these block copolymers.

## ACKNOWLEDGEMENTS

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[28] Note that theoretical molecular weights were not determined for the olefin macroinitiator because the polymerization was performed in neat olefin.

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**GRAPHICAL ABSTRACT**

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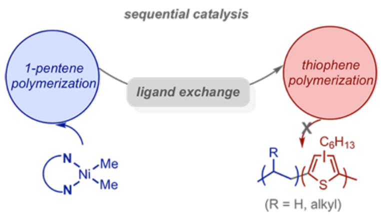

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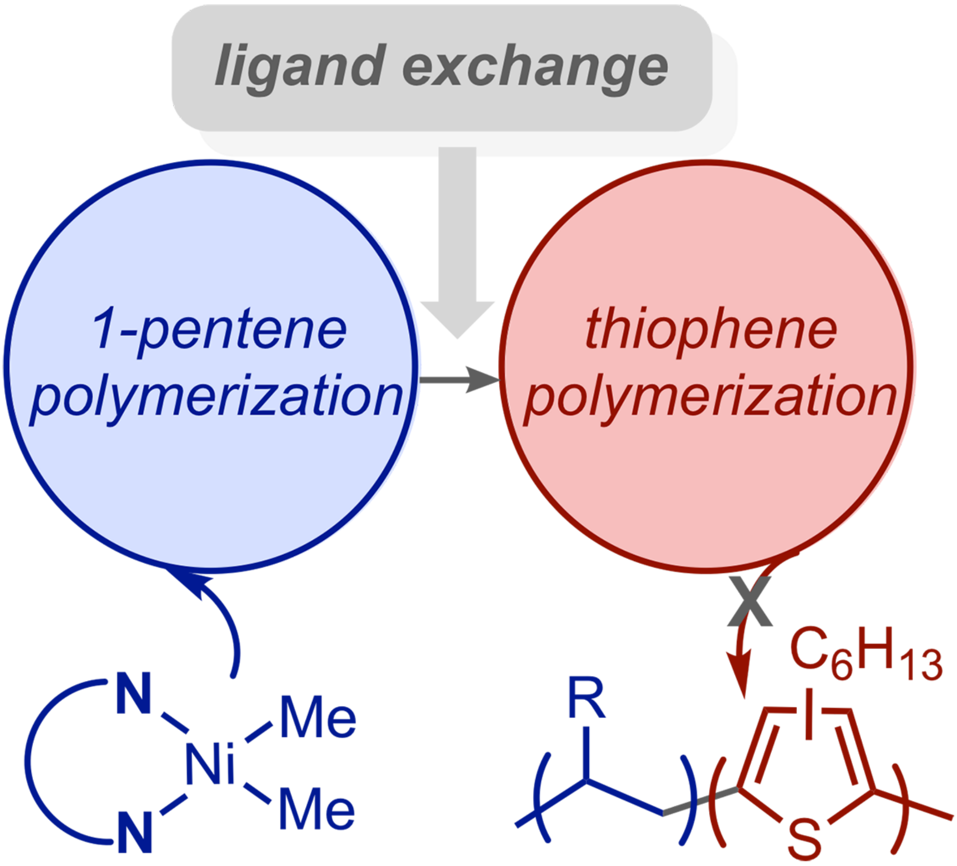


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