

Trials and Tribulations of Designing Multitasking Catalysts for Olefin/Thiophene Block Copolymerizations

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ABSTRACT

Block copolymers containing both insulating and conducting segments have been shown to exhibit improved charge transport properties and air stability. Nevertheless, their syntheses are challenging, relying on multiple post-polymerization functionalization reactions and purifications. A simpler approach would be to synthesize the block copolymer in one pot using the same catalyst to enchain both monomers via distinct mechanisms. Such multitasking polymerization catalysts are rare, however, due to the challenges of finding a single catalyst that can mediate living, chain-growth polymerizations for each monomer under similar conditions. Herein, a diimine-ligated Ni catalyst is evaluated and optimized to produce block copolymer containing both 1-pentene and 3-hexylthiophene. The reaction mixture also contains both homopolymers, suggesting catalyst dissociation during and/or after the switch in mechanisms. Experimental and theoretical studies reveal a high energy switching step coupled with infrequent catalyst dissociation as the culprits for the low yield of copolymer. Combined, these studies highlight the challenges of identifying multitasking catalysts, and suggest that further tuning the reaction conditions (e.g., ancillary ligand structure and/or metal) is warranted for this specific copolymerization.

KEYWORDS: poly(olefin), poly(3-hexylthiophene), nickel, catalysis, diimine

INTRODUCTION

Block copolymers have had an outsized impact on materials science, with applications including templating nanostructures^{1,2} and thermally stabilizing polymer blends.^{3,4,5,6} Synthesizing block copolymers is facile when the comonomers are similar because they can be enchain sequentially in the same flask via the same mechanism (Scheme 1A). In contrast, synthesizing block copolymers from dissimilar monomers is significantly more challenging.

Most approaches require multiple synthetic and purification steps to isolate the desired copolymer from unreacted polymer precursors.

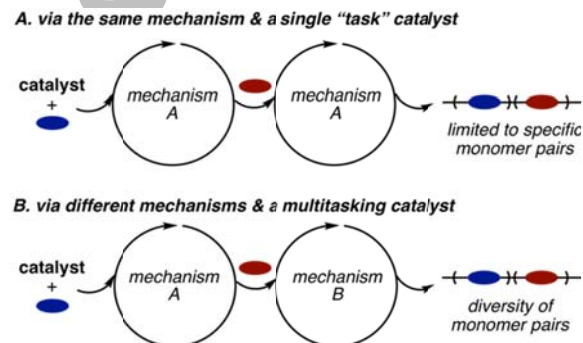
An alternative strategy involves using “switchable catalysts” that rely on an external stimulus to alter their reactivity.⁷ This approach requires installing stimuli-responsive functional groups on the catalyst, which usually adds synthetic steps and can generate compatibility issues. Moreover, this method has so far only

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been demonstrated with monomers enchainment via the same mechanism.

SCHEME 1. One-pot approaches for synthesizing block copolymers.



Another strategy would be to identify a single "multitasking" catalyst that can mediate sequential, mechanistically distinct polymerizations (Scheme 1B). Deming and Novak reported an early example of a multitasking polymerization catalyst in 1991.⁸ A single, cationic Ni(II) species was used to sequentially polymerize butadiene via a coordination/insertion mechanism, followed by isocyanide via a coordination/nucleophilic addition mechanism. This work was later extended to other co-monomer pairs using similar Ni precatalysts.^{9,10,11,12,13,14,15,16,17,18,19} In each example, the same active catalyst mediates mechanistically distinct polymerizations to generate a block copolymer.

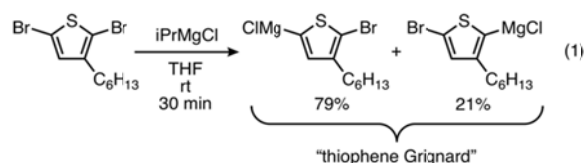
Motivated by these studies, we sought to identify a single multitasking catalyst for copolymerizing olefins with thiophene to generate insulating/conductive block copolymers. Similar materials have been made with multi-step processes.²⁰ For example, Stingelin-Stutzmann showed that even with 10 wt% thiophene in the copolymer, the resulting materials exhibited higher charge mobility, strength and flexibility than poly(3-hexylthiophene) (P3HT).²¹ Similarly, Chen and co-workers showed that a thiophene/syndiotactic polypropylene block copolymer exhibited higher charge mobilities and air-stability than P3HT alone.²²

While both Ni and Pd catalysts have been used for poly(olefin) and poly(thiophene) syntheses, we focused on Ni because it out-performs Pd in the latter case.²³ Diimines were selected as the ancillary ligands for our multitasking catalyst based on their wide use in poly(olefin) synthesis,^{24,25,26} with recent applications in conjugated polymer synthesis.^{27,28,29,30,31} Both olefin and thiophene enchainment mechanisms involve a Ni(II) intermediate, suggesting that switching from one mechanism to the other may be possible.

We report herein our efforts to synthesize olefin/thiophene block copolymers using Ni-diimine precatalysts. Extensive optimization was needed to identify the appropriate reactive ligands, activator, olefin monomer, and reaction conditions for the copolymerization. Although some block copolymer was isolated, the reaction mixture contained mostly homopolymers, suggesting widespread chain termination and/or chain transfer. This result was traced to a high activation barrier for the "switch" from one mechanism of enchainment to the other, with concomitant chain transfer and/or catalyst dissociation.

EXPERIMENTAL

Activation of 2,5-dibromo-3-hexylthiophene (eq 1). In the glovebox, 2,5-dibromo-3-hexylthiophene (250 mg, 0.768 mmol, 1 equiv), n-dodecane (approx. 4 mg), and tetrahydrofuran (THF, 7.40 mL) were added sequentially to a 20 mL vial equipped with a stir bar. To this solution iPrMgCl (268 μ L, 0.537 mmol, 2.00 M in THF, 0.7 equiv) was added. The resulting thiophene Grignard solution was stirred for 30 min at rt and then titrated using salicylaldehyde phenylhydrazone.³² An aliquot of the Grignard solution (0.3 mL, 0.070 M) was quenched with aq. HCl (0.5 mL, 12 M) outside the glovebox, extracted with CHCl_3 (2 mL), dried over MgSO_4 , and analyzed by gas chromatography (GC) to show a mixture of regioisomers (79:21).



Copolymerization of 1-pentene and thiophene.

In the glovebox, precatalyst **C2** (15.7 mg, 0.0177 mmol, 1.0 equiv) and cold 1-pentene (2.00 mL, kept at $-30\text{ }^{\circ}\text{C}$) were added to a 4 mL vial while stirring. After 2 min, the mixture was filtered through a PTFE syringe filter (0.2 μm) into a 50 mL round-bottom flask equipped with a stir bar. A solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (18.0 mg, 0.0354 mmol, 2.0 equiv) in cold 1-pentene (1 mL) was added and the reaction stirred for 20 s. Then, THF (5.0 mL) and toluene (3.0 mL) were added. The flask was then held under reduced pressure for 30 min (until ~ 2 mL solvent remained).

An aliquot (0.50 mL) of the remaining solution was added to a J-Young tube and analyzed by ^1H NMR spectroscopy before quenching with MeOH (2 mL) and concentrating in vacuo. The residue was redissolved in THF (1.5 mL), passed through a PTFE syringe filter (0.2 μm), and analyzed by gel permeation chromatography (GPC) to estimate the macroinitiator molecular weight.

THF (8.0 mL) and thiophene Grignard (4.0 mL) were added to the remaining macroinitiator solution. After 2 h, the reaction was quenched with aq. HCl (10 mL, 12 M). The resulting polymer was extracted with CHCl_3 (2 x 15 mL), dried over MgSO_4 , and filtered using a Buchner funnel.

An aliquot (0.5 mL) of this solution was split into two equal portions. The first portion was diluted with CHCl_3 (2.0 mL) and analyzed by GC to determine the thiophene conversion. The second portion was concentrated in vacuo and then redissolved in THF/toluene (99:1; 1.5 mL) with mild heating, passed through a PTFE filter, and analyzed by GPC. After analysis, both portions were recombined with the mother liquor and the solvent was removed in vacuo, yielding a maroon solid (25 mg).

Block Copolymer Purification. The maroon solid was dissolved in CHCl_3 (0.5 mL) and precipitated with MeOH (15.0 mL). The mixture was spun in a centrifuge for 10 min. The supernatant was decanted and saved. The precipitate was dried under reduced pressure, yielding 15 mg of polymer. ^1H NMR spectroscopic analysis revealed that this solid resembled P3HT homopolymer.

The supernatant was concentrated under reduced pressure to generate a purple solid (10 mg). MeOH (10 mL) was added followed by sonication for 1 min. The resulting mixture was spun in the centrifuge for 10 min, and then the supernatant was removed and saved. This process was repeated 3 times. Hexanes (10 mL) was added to the remaining solid, followed by centrifugation (10 min). The resulting yellow supernatant was collected, passed through a PTFE syringe filter (0.2 μm), and concentrated in vacuo to yield a solid (4 mg). ^1H NMR spectroscopic analysis revealed that the solid contains a mixture of the desired copolymer and poly(1-pentene) homopolymer.

Computational Details

Quantum chemical simulations were performed on key reaction steps, with pathways and transition states optimized using the growing string method.^{33,34,35} Reported energies come from the $\omega\text{B97X-D}$ density functional³⁶ using the triple-zeta, polarized cc-pVTZ basis set,³⁷ and the SMD solvation model³⁸ with THF as the solvent.

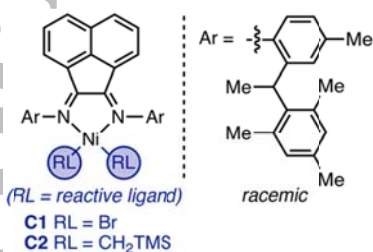
RESULTS AND DISCUSSION

Identifying Reactive Ligands

We initially selected Ni precatalyst **C1** (Chart 1), which was chosen based on its reported living, chain-growth olefin polymerization behavior^{39,40,41,42,43} as well as its ability to synthesize poly(3-hexylthiophene) (P3HT) with a targeted number-average molecular weight (M_n) and moderate dispersity (\bar{D}).^{44,45} Due to the

high sensitivity of the olefin polymerization to coordinating substrates, including thiophene and THF, we investigated synthesized the polyolefin block first, followed by polythiophene.

CHART 1. Precatalyst structures.

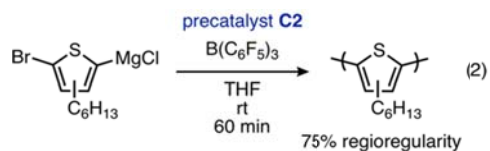


To initiate thiophene polymerization, the two reactive ligands in **C1** (i.e., Br) are displaced via two sequential transmetalations with thiophene Grignard, followed by reductive elimination to generate bithiophene. In contrast, to initiate olefin polymerization, an alkyl aluminum reagent (e.g., Et₂AlCl) is needed to perform the sequential transmetalations followed by alkyl group abstraction to generate a cationic catalyst. We hypothesized that the residual Et₂AlCl and generated alkyl aluminum species may interfere with the thiophene polymerization. Indeed, no P3HT was formed when Et₂AlCl was added to the standard thiophene polymerization conditions (Figure S6). Most likely, the Grignard and aluminum reagents formed a less reactive mixed aggregate.^{46,47} To avoid using an aluminum activator, the Br reactive ligands in precatalyst **C1** were replaced with trimethylsilylmethylene ("TMSCH₂") to yield precatalyst **C2** (Chart 1).⁴⁴

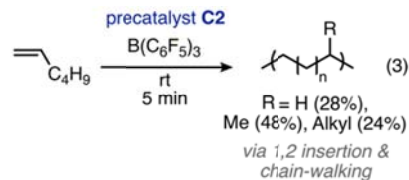
Selecting a Co-catalyst

We next sought to identify a co-catalyst that could generate a cationic Ni(II) species by abstracting one TMSCH₂ from precatalyst **C2**. Triarylboranes were evaluated based on their known ability to act as a co-catalyst for poly(olefin) synthesis⁴⁸ and their anticipated lack of reactivity with Grignard reagents. Indeed, PH3T synthesis was unaffected by the presence of tris(pentafluorophenyl)borane

(B(C₆F₅)₃) (eq 2, Figure S7). Note that, in this case, initiation involves thiophene transmetalation with a cationic Ni(II) intermediate; computational studies revealed a low activation barrier (10.2 kcal/mol) for this step (Figure S26b).

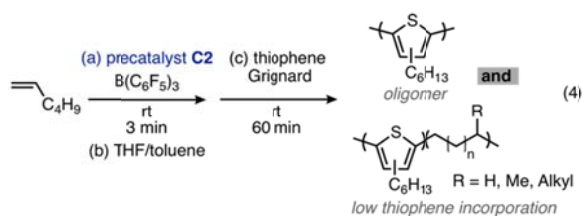


In addition, this precatalyst/co-catalyst combination led to poly(1-hexene) with narrow dispersities and molecular weights that tracked linearly with time, suggesting a living, chain-growth polymerization (Figure S9). The olefin polymerization mechanism involves predominantly 1,2-insertion, followed by chain-walking to generate mostly linear polyolefin (eq 3, Figure S8). Under these conditions, however, neat olefin was necessary because borane-activated catalysts have lower reactivity than aluminum-activated catalysts.



First Copolymerization

Olefin enchainment begins when the borane co-catalyst is added to a solution containing precatalyst **C2** and 1-hexene (eq 4). After a few minutes, an aliquot of THF is added to stall the polymerization and to target a lower molecular weight macroinitiator. THF should bind to the open coordination site on Ni(II), inhibiting further olefin binding and insertion. Indeed, a control experiment confirmed that adding THF prevents further olefin incorporation (Figure S12). The thiophene monomer was subsequently added to the reaction mixture and the polymerization continued for 60 min.



Gel permeation chromatography (GPC) was used to monitor block copolymer formation (Figure 1A). Almost no change in number-average molecular weight of the macroinitiator was observed, suggesting minimal thiophene addition into the chains. Nevertheless, the UV and RI traces exhibit similar peak shapes, suggesting that some thiophene units were incorporated. Additionally, a new polymer peak with a lower molecular weight was observed, which is consistent with shorter thiophene homopolymers. Thiophene conversion in the block copolymerization was significantly lower than observed in thiophene homopolymerization (c.f., 11% versus 70%), suggesting that not all catalysts were actively enchaining monomer. Combined, these results suggest low thiophene incorporation in the block copolymer with a subsequent chain-transfer or chain-termination event releasing catalysts capable of synthesizing P3HT, albeit slowly.

To understand these results, we considered the differences between the copolymerization and thiophene homopolymerization. The most significant change is the presence of unreacted olefin during the copolymerization. Based on this observation, we suspected that olefin competitively displaces the polymer from Ni(0).⁴⁹ This hypothesis is based on studies by McCullough^{50,51} and Pickel,⁵² where added olefin attenuated catalyst reactivity during P3HT synthesis. To probe this hypothesis, the relative binding energies for 1-hexene and thiophene to diimine-ligated Ni(0) were calculated and found to be similar ($\Delta G = 0.6$ kcal/mol; eq 5), suggesting that olefin can displace the copolymer from Ni(0) under the reaction conditions. This hypothesis is further supported by our data showing that even 1

equiv. of 1-hexene (relative to thiophene Grignard) inhibits thiophene homopolymerization with pre-catalyst **C2** (Figure 1B).

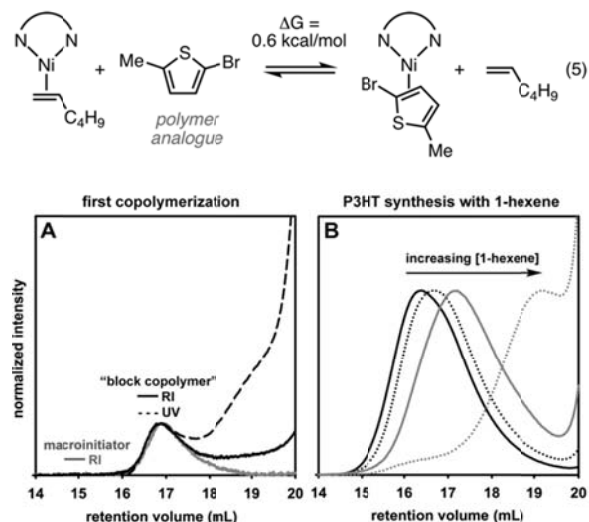
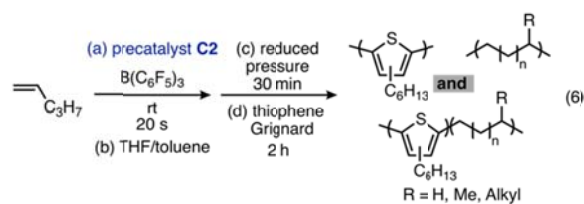


FIGURE 1. Gel permeation chromatograms for (A) 1-hexene and thiophene Grignard copolymerization, and (B) thiophene homopolymerization in the presence of 1-hexene (SI).

To overcome olefin inhibition, we replaced 1-hexene (bp = 63 °C) with the more volatile 1-pentene (bp = 30 °C). As a consequence, the olefin can be removed prior to adding thiophene Grignard (Figure S15), preventing competitive displacement on Ni(0).

Second Copolymerization

An apparent, significant chain extension was observed when the copolymerization was performed with 1-pentene (eq 6 and Figure 2A). This result suggests that the desired block copolymer was formed. However, the ¹H NMR spectrum of the crude reaction mixture (by precipitation in CHCl₃/MeOH) suggested the major product was P3HT homopolymer (Figure S18). After removing the P3HT and unreacted monomer, a mixture of poly(olefin) and apparent block copolymer was isolated (Figure S20).



Identifying whether or not block copolymer was synthesized was difficult due to overlapping NMR signals from the CH_2 moieties on the hexyl side chain on thiophene and poly(olefin). Nevertheless, comparing the 1H NMR spectra of independently synthesized homopolymers (P3HT and poly(olefin)) versus the copolymer mixture revealed two new resonances at 2.92 and 3.04 ppm (Figure 2B). These resonances were tentatively assigned to hydrogens on the poly(olefin) carbon directly attached to the first thiophene unit. Further evidence was provided by their NOE correlations with the aromatic- 1H resonances from poly(thiophene) (6.9–7.1 ppm) via $^1H/^1H$ NOESY (Figure S21). Combined, these data suggest successful copolymer formation.

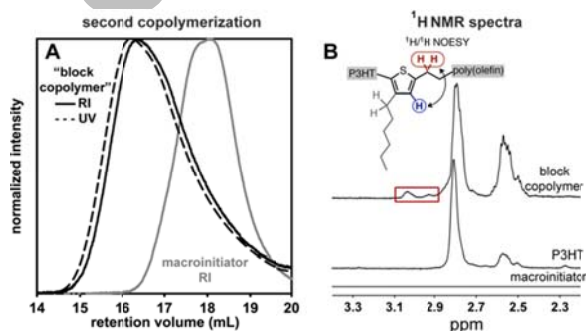


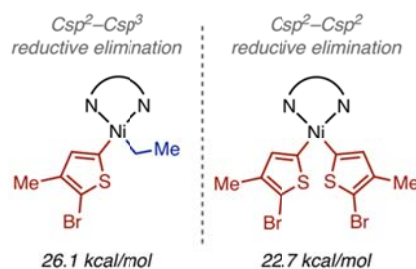
FIGURE 2. (A) Gel permeation chromatograms for 1-pentene and thiophene Grignard copolymerization. (B) 1H NMR spectral comparison of the macroinitiator, P3HT, and the isolated block copolymer.

Obtaining some block copolymer (albeit in low quantities) demonstrates that this multitasking catalyst does sequentially polymerize two dissimilar monomers via distinct mechanisms. To increase the yield, an understanding of the unproductive pathways is needed.

Identifying the Problematic Step(s)

To understand the origin(s) of the unproductive pathways, we considered the key intermediate between the two mechanistically distinct polymerizations. For the catalyst to switch enchainment mechanisms, a reductive elimination must occur between poly(olefin) (Csp^3) and a thiophene monomer (Csp^2) (Scheme 2).

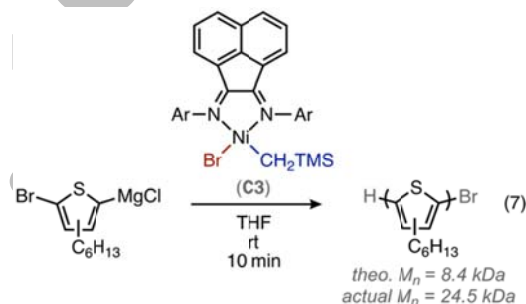
SCHEME 2. Comparison of reductive elimination barriers.



To provide insight into this step, DFT computations were used to assess the relative rates of Csp^2-Csp^3 and Csp^2-Csp^2 reductive eliminations. These computations found that the barrier for the Csp^3-Csp^2 elimination was 3.4 kcal/mol higher, and the reaction would therefore be approximately 300 times slower than bis-thiophene reductive elimination (Figure S26c).

To probe the Csp^3-Csp^2 elimination experimentally, we synthesized a neutral pre-catalyst (**C3**) containing both a $TMSCH_2$ and Br reactive ligand. After transmetalation with thiophene Grignard, a Csp^2-Csp^3 reductive elimination should occur. Indeed, P3HT was observed with pre-catalyst **C3** (eq 7). Nevertheless, the isolated polymer exhibited a higher number-average molecular weight than expected based on the initial monomer/pre-catalyst ratio (Figure S23),⁵³ suggesting that not all catalysts are active. To determine whether the pre-catalyst initiation proceeded through the proposed Csp^2-Csp^3 reductive elimination, polymer end-groups were analyzed via MALDI-TOF-MS. This data showed negligible $TMSCH_2$ incorporation (Figure S24), suggesting that initiation proceeds

either through the proposed reductive elimination followed by dissociation from the chain or by disproportionation to generate Ni(0) and Ni(II), both of which are active for P3HT synthesis.



We suspect dissociation might be occurring based on our concurrent work with precatalyst **C1**,⁴⁴ where we observe some catalyst dissociation. In this case, however, the catalyst preferentially re-inserts into polymer chains rather than the monomer. This result was attributed to a statistical effect, where the polymer chain outcompetes the monomer for Ni(0) based on the greater number of π -binding sites. In contrast, in the block copolymerization described herein, catalyst re-association into a polymer is less likely to occur because the polymer chains are predominantly poly(olefin), which have no π -binding sites. Therefore, we suspect that the macroinitiator undergoes initiation followed by some propagation and ultimately dissociation. Subsequent insertion into a thiophene monomer leads to P3HT homopolymers. In addition, we believe that only a small percentage of catalysts are active at any time due to the slow Csp^2 - Csp^3 reductive elimination.

CONCLUSIONS

Combined, these studies highlight the challenges associated with identifying multitasking catalysts that can enchain different monomers via distinct mechanisms in the same pot. Even though both homopolymerizations were optimized under identical conditions, their combination in the same pot led to unanticipated challenges. Specifically, the

diimine-ligated Ni precatalyst studied herein suffered from slow “switching” between the mechanisms, and from catalyst dissociation, resulting in a mixture of poly(olefin), P3HT, and block copolymer. However, our systematic investigation into the elementary steps of this polymerization provides fundamental insight that should be leveraged when designing new multitasking catalyst systems.

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- (43) The racemic (RS, SR) ligand generates a C₂-symmetric Ni catalyst that predominantly gives ω,2-enchainment with 1-hexene, resulting in amorphous ethylene-propylene copolymers.
- (44) Precatalyst geometries not specified in Chart 1. Precatalyst **C1** is tetrahedral (as evidenced by a single-crystal x-Ray structure, see ref 39). Precatalyst **C2** is expected to be square planar based on a related diimineNi(CH₂TMS)₂ crystal structure (for ref, see: T. Schleis, T. P. Spaniol, J. Okuda, J. Heinemann, R. Mülhaupt, *J. Organomet. Chem.* **1998**, *569*, 159–167). Moreover, the ¹H NMR spectrum of precatalyst **C1** displays peak shape/positions consistent with a paramagnetic complex (Figure S3), while precatalyst **C2** displays peak shape/positions consistent with a diamagnetic complex (Figure S4).
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(53) Similar number-average molecular weights were obtained regardless of the monomer/catalyst ratio. A similar saturation in molecular weights was observed with precatalyst **C2**/ $\text{B}(\text{C}_6\text{F}_5)_3$. This “saturation” effect may be due to chain-chain aggregation, which hinders catalyst propagation and/or accelerates chain-transfer.

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GRAPHICAL ABSTRACT

Kendra D. Souther, Amanda K. Leone, Andrew K. Vitek, Edmund F. Palermo, Anne LaPointe, Geoffrey W. Coates, Paul M. Zimmerman, and Anne J. McNeil

Trials and Tribulations of Designing Multitasking Catalysts for Olefin/Thiophene Block Copolymerizations

Block copolymers containing insulating segments (derived from 1-pentene) and conducting segments (derived from 3-hexylthiophene) are synthesized in one pot using a single multitasking catalyst. Notably, this process requires different enchainment mechanisms (coordination/insertion versus cross coupling) mediated by the same precatalyst. Nevertheless, the block copolymer is the minor product due to a slow switching step between the mechanisms coupled with catalyst dissociation from the polymer chain.



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