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Controlled Chain-Growth Kumada Catalyst Transfer Polycondensation of a Conjugated Alternating Copolymer

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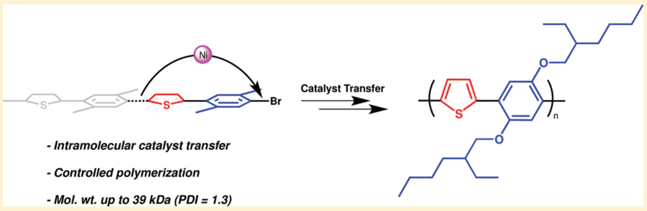
Supporting Information

ABSTRACT: The Ni-catalyzed Kumada catalyst transfer polycondensation of a novel biaryl monomer, 2-(4-bromo-2,5-bis(2-ethylhexyloxy)phenyl)-5-chloromagnesiothiophene (**2**), afforded the respective π-conjugated alternating copolymer poly(thiophene-*alt*-*p*-phenylene) (PTPP). Under optimized conditions, the polystyrene-equivalent number-average molecular weight (M_n) of the copolymers prepared using this method were varied between 6.4 and 39 kDa by adjusting the initial monomer-to-catalyst ratios and, in all cases, the resulting materials exhibited narrow polydispersity indices (PDIs $\leq$ 1.33). Moreover, the M_n of the copolymers produced were found to increase linearly with monomer conversion. The ability of PTPP to be utilized as a macroinitiator for further copolymerization was confirmed through a series of chain extension experiments as well as block copolymerizations involving 2-bromo-5-chloromagnesio-3-hexylthiophene. MALDI-MS analysis showed that the major population of the PTPP prepared using the aforementioned method contained H/Br end groups, as would be expected for efficient catalyst transfer during the polymerization with minimal occurrence of chain termination. Collectively, these results were consistent with a controlled polymerization reaction and constituted the first such example in which a conjugated polymer with an alternating repeat unit was produced via a chain-growth process.



INTRODUCTION

McCullough's[1] and Yokozawa's[2] seminal reports on the chain-growth polymerization of 3-hexylthiophene have enabled the corresponding polymer, P3HT, to become one of the most prevalent conjugated polymers (CPs) in the literature. Despite the synthetic versatility and impressive electronic properties of P3HT, significant research efforts are now being directed toward the synthesis of new CPs that feature properties tailored toward specific applications. For example, in the field of organic photovoltaics, a growing number of CPs have been shown to outperform P3HT when incorporated into solar cells,[3,4] generally owing to the former's broad absorption overlap with the solar spectrum and better energy matching with commonly used electron acceptors (e.g., phenyl-C61-butyric acid methyl ester; PCBM). Many of these new, high performance CPs are effectively "donor–acceptor" (D–A) polymers, designed to feature reduced optical bandgaps (and hence broader absorptions that extend into the red) by virtue of incorporating electron-donating and -withdrawing components into the polymer main chain.[5] Structurally, nearly all of these types of CPs take the form of an alternating copolymer comprised of donor and acceptor groups (e.g., -[D-A]-_n) and are generally synthesized by metal-catalyzed step-growth polycondensations. As such, these methods do not permit rigorous control over polymer molecular weight or polydispersity (M_w/M_n) and oftentimes afford ill-defined materials. A controlled, chain-growth synthesis of donor–acceptor CPs would not only allow for precise control over the aforementioned polymerization metrics but could also enable the preparation of more advanced macromolecular structures such as block copolymers and surface-grafted polymers. Moreover, the successful preparation of such well-defined structures could potentially facilitate greater control over the polymer morphology, which is another important parameter that governs the performance of organic electronic devices.[6,7]

We reasoned that such controlled polymerizations may be achieved by applying the Ni-catalyzed Kumada catalyst transfer polycondensation (CTP) to monomers that feature "built in" alternating repeat units. Recently, during the course of our investigations, Huck and co-workers reported a synthesis of the alternating copolymer poly(9,9′-dioctylfluorene-*alt*-benzothiadiazole) (PF8BT) using Pd-catalyzed Suzuki CTP.[8] While the chain-growth nature of the aforementioned polymerization was elegantly demonstrated, only polymers having moderate molecular weights (up to ca. 10 kDa or 19 repeat units) were isolated and efforts toward controlling the polymerization (e.g., establishing a linear relationship between polymer molecular weight and monomer conversion) appeared to be underway. We chose to continue our pursuit of Ni-catalyzed Kumada CTPs because they offer, as a complementary methodology, several potential advantages over analogous Suzuki-type polycondensations. For instance, Kumada CTPs do not require

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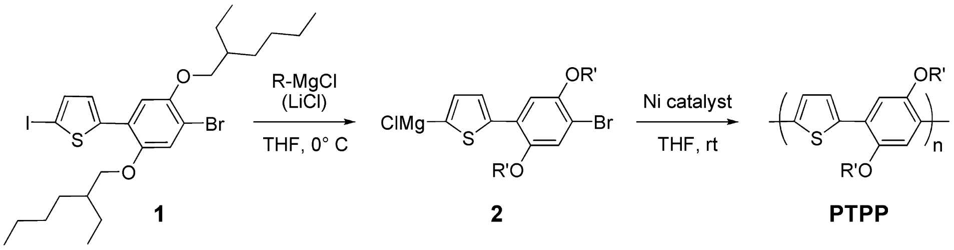
Scheme 1. Synthesis of PTPP[a]



[a] R = *t*-butyl or *i*-propyl. R′ = 2-ethylhexyl.

the use of specially synthesized catalysts or *ex-situ* initiation. Furthermore, despite the evidence that a chain-growth mechanism is operative in the Kumada CTP of monomers having relatively large molecular lengths (e.g., fluorenes, carbazoles, oligothiophenes, etc.), control over such polymerizations largely remains an unsolved problem, presumably due to inefficient catalyst transfer across the length of the monomer.[9−15] Here, we report the first controlled, chain-growth synthesis of a π-conjugated alternating copolymer, poly(thiophene-*alt*-*p*-phenylene) (PTPP), via the Kumada catalyst transfer polycondensation of a novel bicyclic monomer.

■ RESULTS AND DISCUSSION

We elected to incorporate thiophene and dialkoxybenzene into a single monomer unit because the Kumada catalyst transfer polymerizations of both thiophenes[1,2] and dialkoxybenzenes[16] have already been independently established.[17] Premonomer **1** was prepared in two steps by the Suzuki coupling of 2-thiopheneboronic acid and 1,4-dibromo-2,5-di(2-ethylhexyloxy)benzene followed by iodination with *N*-iodosuccinimide in 57% overall yield (see the Supporting Information for additional details). As summarized in Scheme 1, treatment of **1** with 1.0 equiv of ^{i}PrMgCl at 0 °C in THF resulted in the fast, quantitative conversion to **2**, as deduced by ^{1}H NMR spectroscopic analysis of the reaction mixture after quenching with HCl(aq). The reaction was complete within 20 min, and metalation occurred selectively at the α-position of the thiophene, leaving the aryl bromide intact, also evidenced by ^{1}H NMR spectroscopy of the corresponding quenched product, which revealed signals that were identical to that of 2-(4-bromo-2,5-bis(2-ethylhexyloxy)phenyl)thiophene (i.e., the precursor to **1**).

Polymerization was carried out at 23 °C by the addition of a Ni catalyst (3 mol %) to the THF solution of **2** and monitored by gel permeation chromatography (GPC) over time until the respective polymer molecular weight ceased to increase. Two Ni catalysts, Ni(dppp)Cl_2 and Ni(dppe)Cl_2 (dppp = 1,3-bis(diphenylphosphino)propane; dppe = 1,2-bis(diphenylphosphino)ethane), were investigated for the polymerization of **2**, as they have been shown to be suitable catalysts for the homopolymerization of 2,5-dibromo-3-alkylthiophenes as well as 2,5-dibromo-1,4-dialkoxybenzenes.[2,16,18] As summarized in Table 1, both of the aforementioned catalysts afforded polymeric products. When Ni(dppe)Cl_2 was used as the catalyst, a relatively high number-average molecular weight (M_n) polymer was obtained; however, the resulting polymer also exhibited a broad polydispersity index (PDI) (Table 1, entry 1). In contrast, when Ni(dppp)Cl_2 was used, the PDI of the resultant polymer was much narrower, but only materials with relatively low M_ns were obtained (entry 2).

Table 1. Polycondensation of 2 with Various Ni Catalysts[a]

entry	catalyst	equiv of LiCl	Grignard reagent	M_n[b]	M_w/M_n[b]
1	Ni(dppe)Cl_2	0	^{i}PrMgCl	12 000	2.03
2	Ni(dppp)Cl_2	0	^{i}PrMgCl	3 700	1.32
3	Ni(dppe)Cl_2	1.0	^{i}PrMgCl	12 000	1.74
4[c]	Ni(dppp)Cl_2	1.0	^{i}PrMgCl	14 500	1.33
5	Ni(dppe)Cl_2	1.0	^{t}BuMgCl	15 200	2.03
6	Ni(dppp)Cl_2	1.0	^{t}BuMgCl	10 500	1.53

[a] Polymerizations were carried out by treating **1** with 1.0 equiv of Grignard reagent in THF ($[\mathbf{1}]_0$ = 0.1 M) for 20 min at 0 °C, followed by warming to 23 °C and addition of the Ni catalyst ($[\mathbf{1}]_0/[\mathrm{Ni}]_0$ = 33). In all cases, the expected M_n was based on a degree of polymerization of 33 and calculated to be 13 700 Da. [b] Determined by GPC based on polystyrene standards (eluent: THF). [c] Conversion of **2** to polymer: 87%; isolated yield: 71%.

It has been shown that the addition of LiCl to Kumada CTP reactions can have beneficial effects on the chain-growth polymerization characteristics of aryl-Grignard monomers. For example, Yokozawa and co-workers reported that the addition of LiCl conferred controlled, chain-growth characteristics to the polymerization of 1-bromo-4-chloromagnesio-2,5-dihexyloxybenzene to afford poly(*p*-phenylene)s with high molecular weights and narrow PDIs (e.g., 1.18).[16] We thus performed the polymerization of **2** with the aforementioned Ni catalysts in the presence of 1.0 equiv of LiCl. As shown in Table 1, the addition of LiCl had little effect on the polymerization when Ni(dppe)Cl_2 was used as the catalyst, as the molecular weight of PTPP remained unchanged from that which was obtained from the corresponding reaction without LiCl, although a slight decrease in polydispersity was observed (entry 3). When Ni(dppp)Cl_2 was used, however, the M_n of the resulting polymer increased significantly compared to that obtained from the analogous polymerization without LiCl, while the polymer's PDI remained relatively low (entry 4). After quenching the polymerization with HCl(aq), the pure homopolymer, poly(thiophene-*alt*-*p*-phenylene) (PTPP), was isolated in 71% yield by means of precipitation from methanol, followed by collection with the aid of vacuum filtration. When the polymerization was repeated in the presence of an internal standard (1,4-dihexyloxybenzene) and monitored over time by ^{1}H NMR spectroscopy, we found that the polymerization proceeded rapidly at 23 °C, consuming 87% of **2** within 15 min (Figure S1). Substituting ^{t}BuMgCl for ^{i}PrMgCl to facilitate the Grignard metathesis reaction did not lead to any significant molecular weight increase or narrowing of the polydispersity of the respective polymers (entries 5 and 6).

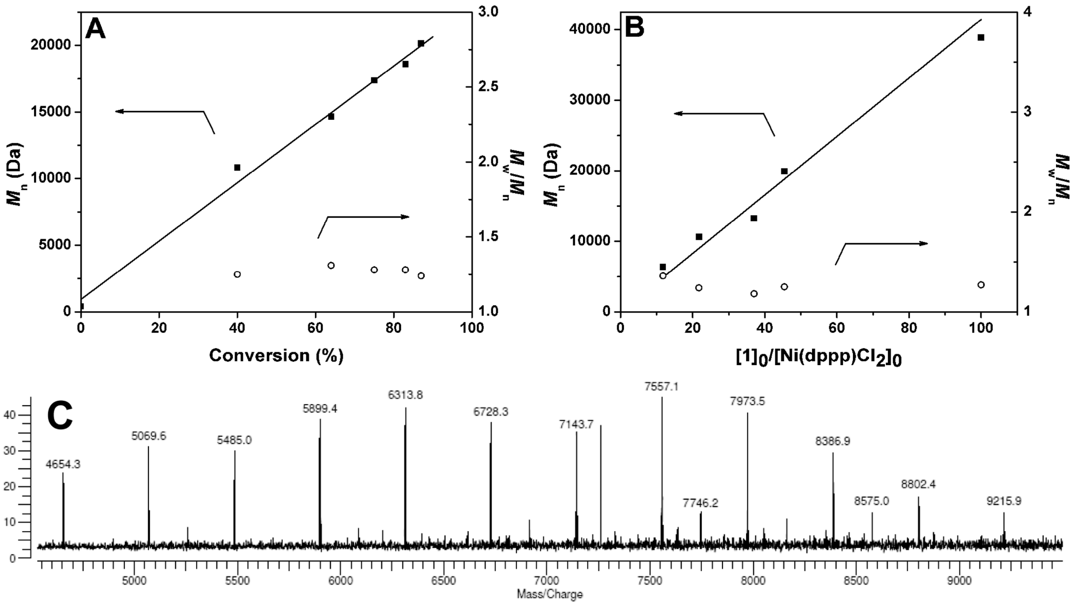
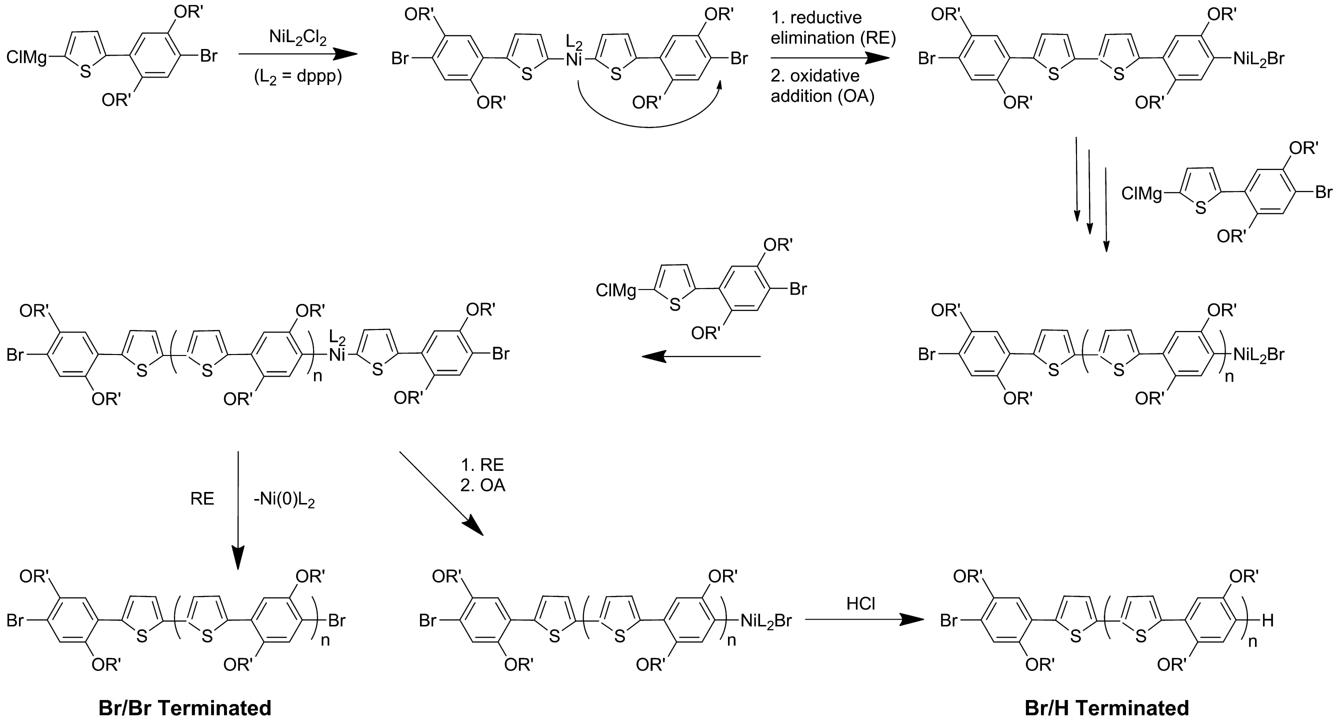


Figure 1. (A) M_n and M_w/M_n of PTPP plotted as a function of monomer conversion ($[\mathbf{1}]_0/[Ni(dppp)Cl_2]_0 = 56$); see text for further details. (B) M_n and M_w/M_n of PTPP plotted as a function of $Ni(dppp)Cl_2$ loading (conversion of **2** to polymer: 78−85%). Solid line indicates the theoretically expected M_n at a given $Ni(dppp)Cl_2$ loading. (C) MALDI mass spectrum of PTPP (M_n = 10 800 Da, M_w/M_n = 1.25, as determined by GPC). The peak at $m/z \sim 7257$ reflects electronic noise. For all polymerizations, $[\mathbf{1}]_0$ = 0.10 M.

Scheme 2. Proposed Mechanistic Pathways Leading to the Formation of H/Br end-Capped PTPP



Elegant mechanistic studies by McNeil and co-workers revealed that the role of LiCl in the controlled formation of poly(*p*-phenylene) and P3HT depends on the catalyst used. In $Ni(dppe)Cl_2$-catalyzed polymerizations, LiCl was found to have no effect on the polymerization rate, whereas in $Ni(dppp)Cl_2$-catalyzed polymerizations a rate dependence on LiCl was observed.[18,19] Our results were consistent with these observations: the addition of LiCl had a significant effect on the polymerization of **2** when $Ni(dppp)Cl_2$ was used as the catalyst, affording PTPP with a high molecular weight and low polydispersity, and little effect when $Ni(dppe)Cl_2$ was used. We therefore presume that the polymerization of **2**, as catalyzed by $Ni(dppp)Cl_2$, exhibits a rate dependence on [LiCl], which may serve to explain the rapid kinetics of polymerization observed in the presence of LiCl.

The M_n of the PTPP obtained using $Ni(dppp)Cl_2$ as the catalyst in the presence of 1.0 equiv LiCl (M_n = 14 500 Da, M_w/M_n = 1.33) was close to the theoretically expected value of

13 700 Da, assuming both quantitative initiation and conversion of monomer to polymer. These results suggested to us that the polymerization was proceeding via a chain-growth mechanism. To probe whether the polymerization was controlled, the molecular weight of the polymer formed in the reaction was monitored as a function of monomer conversion. Briefly, a polymerization reaction was set up under the aforementioned conditions (i.e., catalyst = Ni(dppp)-Cl_2, 1.0 equiv LiCl, 23 °C in THF) at an initial monomer-to-catalyst ratio of 56 in the presence of an internal standard (1,4-dihexyloxybenzene); aliquots were then removed at regular intervals, quenched with aqueous HCl, and poured into excess methanol. After collection of the precipitated solids via filtration, the isolated polymers and filtrates were analyzed by GPC and ^{1}H NMR spectroscopy, respectively. As shown in Figure 1A, a linear dependence of the M_n versus the percent conversion of monomer over the course of the polymerization was observed. Moreover, the PDIs of the isolated polymers remained at or below 1.3 over the course of the polymerization reaction. When the polymerization of **2** was performed using varying initial catalyst loadings, the M_n increased proportionally with the initial monomer-to-catalyst ratio ($[\mathbf{1}]_0/[\mathrm{Ni(dppp)Cl_2}]_0$) while PDIs remained relatively low (Figure 1B), indicating that the molecular weight of PTPP was successfully controlled over a wide M_n range (i.e., 6.4−39 kDa). Furthermore, the experimentally determined M_ns were in good agreement with the theoretically expected values at all of the initial catalyst loadings explored. Taken together, these results suggested to us that the polymerization followed a controlled chain-growth mechanism. It is also worth noting that PTPP, even at high molecular weights, maintained excellent solubility in THF (ca. 80 mg mL^{-1}), presumably due to the presence of the branched alkoxy side chains in every repeat unit.

End-group analysis using matrix-assisted laser desorption ionization (MALDI) mass spectrometry has been shown to provide important insight into polymerization mechanisms.[2,8,20] We therefore obtained MALDI mass spectra of a sample of PTPP (isolated after quenching the polymerization with HCl). As shown in Figure 1C, we observed a major population of signals that corresponded to H_2O adducts of H/Br end-capped PTPP, as calculated by the formula 414.3*n* (mass of *n* repeat units) + 1 (H) + 79.9 (Br) + 18 (H_2O).[21] The presence of H/Br end-capped polymers, along with a negligible population of polymers bearing Br/Br or H/H end groups, is a hallmark of efficient catalyst transfer in self-initiated catalyst transfer polycondensation reactions.[2,20] Collectively, these results suggested to us that nearly every polymer grew via catalyst transfer to the end of the polymer chain, as opposed to the catalyst freely diffusing through the reaction mixture to initiate a new polymerization or transferring to another chain. Therefore, we concluded that the polymerization proceeded through a chain-growth mechanism with minimal chain termination (Scheme 2).

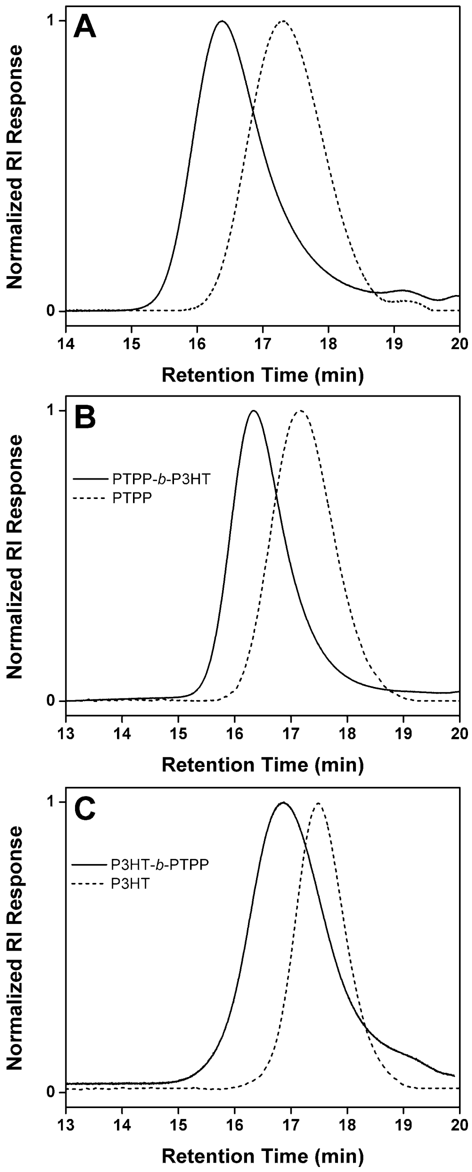
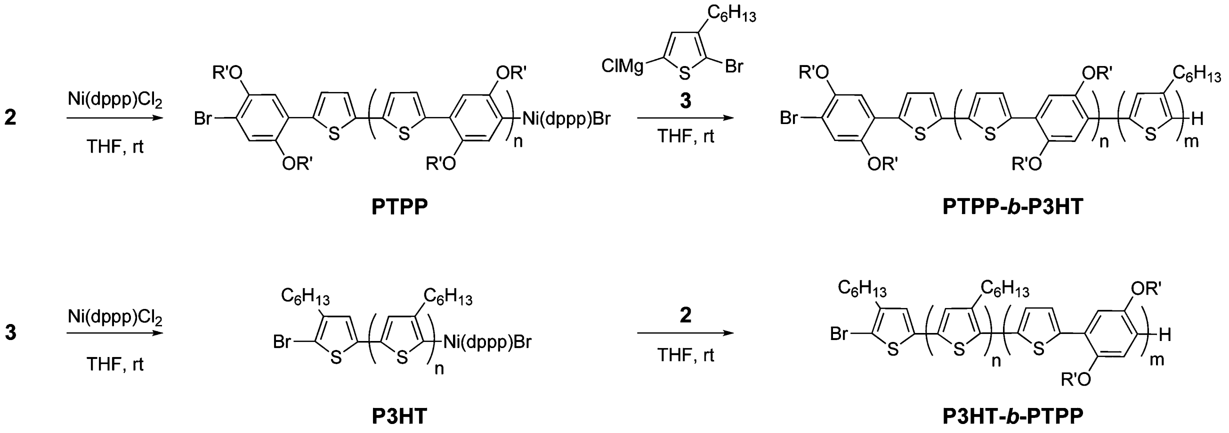


Figure 2. GPC traces of polymers obtained from chain extension polymerization experiments. (A) A monomer addition experiment: PTPP-1 (dashed line) ($[\mathbf{1}]_0/[\mathrm{Ni(dppp)Cl_2}]_0$ = 20, conversion of **2** to polymer: 80%; PTPP-1: M_n = 8700 Da, M_w/M_n = 1.25); PTPP-1′ (solid line) ([remaining and added $\mathbf{1}]_0/[\mathrm{Ni(dppp)Cl_2}]_0$ = 31; conversion of **2** to polymer: 72%; PTPP-1′: M_n = 17 000 Da, M_w/M_n = 1.29). (B) A block copolymerization experiment (polymerization order: PTPP followed by P3HT). PTPP (dashed line): $[\mathbf{1}]_0/[\mathrm{Ni(dppp)Cl_2}]_0$ = 18, conversion of **2** to polymer: 86%; polymer: M_n = 11 600 Da, M_w/M_n = 1.29. PTPP-*b*-P3HT (solid line): $[\mathbf{3}]_0/[\mathrm{Ni(dppp)Cl_2}]_0$ = 51, conversion of **3** to polymer: 96%; polymer: M_n = 21 900 Da, M_w/M_n = 1.33. (C) A block copolymerization experiment (polymerization order: P3HT followed by PTPP). P3HT (dashed line): $[\mathbf{3}]_0/[\mathrm{Ni(dppp)Cl_2}]_0$ = 60; conversion of **3** to polymer: 84%; polymer: M_n = 7500 Da, M_w/M_n = 1.22. P3HT-*b*-PTPP (solid line): $[\mathbf{1}]_0/[\mathrm{Ni(dppp)Cl_2}]_0$ = 24, conversion of **2** to polymer: 67%; polymer: M_n = 9200 Da, M_w/M_n = 1.70.

To further demonstrate the controlled, chain-growth nature of the aforementioned Kumada CTPs, a series of chain extension and block copolymerization experiments were performed. First, a monomer addition experiment was conducted, wherein a fresh feed of monomer **2** was added to an unquenched, stirring solution of PTPP (PTPP-1) (initial conditions: $[\mathbf{1}]_0/[\mathrm{Ni(dppp)Cl_2}]_0$ = 20; conversion of **2** to PTPP-1: 80%; PTPP-1 M_n = 8700 Da, M_w/M_n = 1.25). As shown in Figure 2A, the GPC trace of the polymer formed at the conclusion of this reaction (PTPP-1′) was clearly shifted toward higher molecular weight ([remaining and added $\mathbf{1}]_0/[\mathrm{Ni(dppp)Cl_2}]_0$ = 31; PTPP-1′: conversion of **2** = 72%, M_n = 17 000 Da, M_w/M_n = 1.29) with respect to PTPP-1. No discernible signal attributable to the presence of unreacted PTPP-1 was observed, suggesting to us that the added feed of **2**

Scheme 3. Synthesis of Diblock Copolymers PTPP-*b*-P3HT and P3HT-*b*-PTPP[a]



[a]R′ = 2-ethylhexyl.

was successfully polymerized via chain extension from the terminus of PTPP-1.

We subsequently shifted our attention to the formation of diblock copolymers, choosing to incorporate P3HT as the second block because of its well-behaved polymerization behavior via Kumada CTP (Scheme 3).[9] As shown in Figure 2B, addition of 2-bromo-5-chloromagnesio-3-hexylthiophene[20] (**3**) to an unquenched solution of PTPP (M_n = 11 600 Da, M_w/M_n = 1.29) afforded a polymer with a monomodal GPC profile that was of higher molecular weight (M_n = 21 900 Da) than that obtained for its parent PTPP homopolymer. Furthermore, the PDI of the product remained low (M_w/M_n = 1.33), indicating that the unquenched PTPP in solution was active and effectively initiated the polymerization of **3**, which also proceeded in a chain-growth manner. The formation of a diblock copolymer, consistent with the expected structure (i.e., PTPP-*b*-P3HT), was further confirmed by ^{1}H NMR spectroscopy, which revealed signals attributable to both PTPP and P3HT (Figure S10).

Considering recent reports that have shown that the order of polymerization can affect the outcome of block copolymerizations involving Kumada CTPs,[13,22,23] we next attempted to synthesize the aforementioned diblock copolymer P3HT-*b*-PTPP by reversing the order of monomer addition. Thus, a THF solution of **2** ($[\mathbf{1}]_0/[\mathrm{Ni(dppp)Cl_2}]_0 = 24$) was added to a stirring solution of unquenched P3HT (M_n = 7500 Da, M_w/M_n = 1.22). In this case, the resulting copolymer (M_n = 9200 Da, M_w/M_n = 1.70) displayed a broader molecular weight distribution than the parent P3HT homopolymer, and the conversion of **2** remained relatively low (conversion of **2** to polymer: 67%), even after prolonged reaction periods (Figure 2C). This result suggested to us that P3HT was not an efficient macroinitiator for the polymerization of PTPP, possibly due to the strong association of the Ni catalyst with P3HT.[22,24] Nevertheless, successful chain extension polymerizations of PTPP were achieved, which provided additional support that chain-growth polymerization of **2** proceeded in a controlled fashion.

The absorption and fluorescence spectra of the PTPP synthesized using the aforementioned procedures were acquired in dilute $CHCl_3$ solution and in the solid state (as thin films) (Figure S3). A slight bathochromic shift was observed in the respective absorption spectra upon concentration (λ_{max} = 467 nm → 477 nm), with a small shoulder appearing at 500 nm for the thin film. The emission spectra of PTPP in solution and as a thin film exhibited maxima at 523 and 629 nm, respectively. These results were consistent with those obtained for similar copolymers (e.g., poly(alkoxyphenylene–thienylene)s) previously reported in the literature.[15,25−28] The absorption spectra of the diblock copolymer PTPP-*b*-P3HT were also recorded in dilute $CHCl_3$ solution as well as in the solid state as a thermally annealed thin film (Figure S4). In this case, a large red shift of absorption was observed upon concentration (λ_{max} = 464 → 505 nm), likely a consequence of the $\pi-\pi$ stacking and subsequent planarization of the P3HT chains.[29,30] Moreover, vibronic structures reminiscent of P3HT homopolymer thin films were clearly visible at 560 and 605 nm. Compared to the solid state absorption of a P3HT homopolymer, however, the corresponding spectrum of PTPP-*b*-P3HT exhibited an absorption maximum at higher energies (λ_{max} = 560[31] and 505 nm for P3HT homopolymer and PTPP-*b*-P3HT, respectively). We believe that the solid state spectrum of PTPP-*b*-P3HT reflects the summed profiles of PTPP and P3HT homopolymers; thus, the blue-shifted λ_{max} of PTPP-*b*-P3HT compared to that of P3HT is a consequence of the overwhelming contribution of PTPP to the copolymer's absorption profile, rather than a morphological and/or energy transfer effect. Regardless, the absorption characteristics of PTPP-*b*-P3HT should be amenable to further fine-tuning by controlling the relative block lengths of the respective polymers, an otherwise laborious synthetic task that is effectively streamlined by the methodologies presented here, thus highlighting the potential utility of Kumada CTPs for producing conjugated alternating copolymers with tunable optical properties.

In conclusion, we have demonstrated that Kumada catalyst transfer polycondensation is a viable method for synthesizing well-defined conjugated *alt*-copolymers. We found that controlled chain-growth characteristics were conferred to the polymerization when $Ni(dppp)Cl_2$ was used as the catalyst in the presence of LiCl, a result that was consistent with efficient intramolecular catalyst transfer within the growing polymer backbone, despite the relatively large length of the repeat unit. As a benefit of this chain-growth mechanism, excellent control over copolymer molecular weight, polydispersity, and end-group composition was obtained, all of which facilitated the successful preparation of a new, well-defined block copolymer, PTPP-*b*-P3HT. These results unambiguously show, for the first time, that conjugated polymers with alternating repeating units can be synthesized in a controlled, chain-growth manner. Many low-bandgap and D−A conjugated polymers exhibit complex, alternating structures but are currently synthesized by means that do not permit the aforementioned degree of control over the polymerization. It is expected that the method presented herein will be amenable to attaining control over the synthesis of such D−A and other conjugated polymers and enable access to more complex macromolecular structures thereof.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Detailed experimental procedures and additional characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(17) Our decision to use a monomer that metalates at the thiophene as opposed to the phenyl moiety was based on the work of Yokozawa and co-workers, who demonstrated that the order of polymerization was critical to the outcome of forming block copolymers containing P3HT and poly(*p*-phenylene) (PPP) segments: successive polymerization of the phenylene monomer followed by the thiophene monomer yielded a well-defined block copolymer with narrow molecular weight distribution, while reversing the order of monomer addition resulted in polymers with broad molecular weight distributions.[22] In other words, we anticipated that if metalation occurred at the thiophene unit, the propagating end of the resulting polymer (i.e., polymer−NiLBr) would feature a terminus where Ni is connected to a phenyl group, reminiscent of a Ni-terminated PPP, and ultimately result in a controlled polymerization process. In contrast, metalation at the phenyl unit would lead to polymers with termini that are reminiscent of Ni-terminated P3HT and afford ill-defined polymers.

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