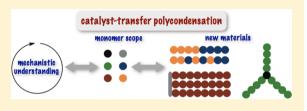
Macromolecules

Conjugated Polymer Synthesis via Catalyst-Transfer Polycondensation (CTP): Mechanism, Scope, and Applications

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ABSTRACT: The recent discovery of a living, controlled chaingrowth method for synthesizing π -conjugated polymers has ignited the field and led to the development of many new materials. This Perspective focuses on the mechanistic underpinnings of the synthetic transformation, highlighting the controversial hypotheses and supporting data. A critical analysis of the literature revealed that the monomer scope remains largely limited to electron-rich monomers at



this time. Last, a brief overview of some exciting new materials accessed via this method is provided.

INTRODUCTION

While most organic polymers are colorless insulators, a subset of polymers with a π -conjugated backbone can absorb/emit light as well as conduct charge. These polymers are utilized as the active layer in many optical and electronic devices. Their commercial impact is expected to be significant, as it has been estimated that the conductive polymers market will reach 1.6 billion dollars in the US by 2017.2 This growth can largely be traced back to the Nobel Prize-winning discovery by Shirakawa, MacDiarmid, and Heeger that the simplest conjugated polymer, poly(acetylene), is conductive in the oxidized state.^{3,4}

For decades the synthetic routes to soluble π -conjugated polymers were dominated by transition-metal-catalyzed stepgrowth polymerizations, and as a result, little control could be exerted over the resulting polymer sequence. This landscape changed dramatically in 2004, when McCullough⁵ and Yokozawa⁶ independently identified a living, chain-growth method (now referred to as catalyst-transfer polycondensation (CTP)) for synthesizing poly(3-hexylthiophene) (Scheme 1). These initial reports sparked a flurry of activity in the field, and more than 150 papers using CTP have been published since 2004. The majority of these papers focused on (i) gaining a mechanistic understanding of the chain-growth process, (ii) polymerizing other monomers, and (iii) synthesizing previously inaccessible materials, including gradient copolymers and surface-initiated polymers. This Perspective will highlight the most significant advances in each of these areas, with a focus on the mechanistic studies, and discuss the current limitations.

CTP MECHANISM

Evidence for a Chain-growth Mechanism. The first reports of poly(thiophene) synthesis using Ni catalysts and difunctional halo/Grignard monomers were by Yamamoto⁸ and Lin⁹ in 1980. A remarkable 24 years lapsed between these reports and the discovery that the mechanism is chain growth. 5,6,10 This time lag can be attributed to the fact that the analogous small molecule reaction mechanism would

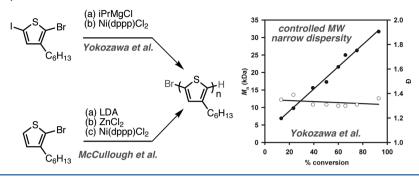
predict a step-growth polymerization. Evidence of a living, 11 chain-growth polymerization provided by both McCullough⁵ and Yokozawa⁶ included (i) linear correlations between the number-average molecular weight (M_n) and monomer conversion, (ii) the ability to control the M_n based on the monomer/catalyst ratio, (iii) the creation of simple block copolymers via sequential monomer addition, and (iv) a single set of polymer end groups (H/Br) observed by MALDI-TOF mass spectrometry.

Chain Propagation via an Associative Complex. An early indication that the cross-coupling mechanism might be different for difunctional molecules was provided by Kumada and co-workers in 1976; they observed an unexpected doublesubstitution reaction even with an excess of dichlorobenzene (Scheme 2). 12,13 This result suggested that after an initial crosscoupling the Ni selectively reacts with the initial product a second time before consuming additional starting material. At the time, Kumada and co-workers simply stated that the second reaction is "mechanistically different" than the first, without proposing a specific pathway. In 2004, McCullough and coworkers also observed a preferential double-substitution reaction with a dibromothiophene (Scheme 2).5 On the basis of these observations, McCullough proposed that the polymerization proceeds through a "nondiffusive associated pair" 14 between the Ni catalyst and the polymer, with a concomitant intramolecular oxidative addition.⁵ Yokozawa suggested several potential mechanisms, including enhanced reactivity of the polymeric end group (relative to monomer) as well as polymer coordination to Ni via either a π -bond or the nonbonding electron pair on sulfur. The majority of researchers in the field eventually gravitated toward a mechanism that proceeds through a Ni-polymer π -complex, which enables the active catalyst to stay associated with the growing polymer chain and facilitates chain propagation via an intramolecular oxidative

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Scheme 1. CTP Discovery and Data



Scheme 2. Preferential Double-Substitution Reaction

Kumada et al. (1976)

$$\begin{array}{c} \textbf{CI} & \textbf{C}_4\textbf{H}_9\textbf{M}gBr \\ & (1 \text{ equiv}) \\ & \textbf{Ni(dppe)CI}_2 \end{array} \quad \begin{array}{c} \textbf{C}_4\textbf{H}_9 \\ & 96\% \end{array} \quad \begin{array}{c} \textbf{C}_4\textbf{H}_9 \end{array} \quad + \quad \begin{array}{c} \textbf{CI} \\ & \textbf{C}_4\textbf{H}_9 \end{array}$$

McCullough et al. (2004)

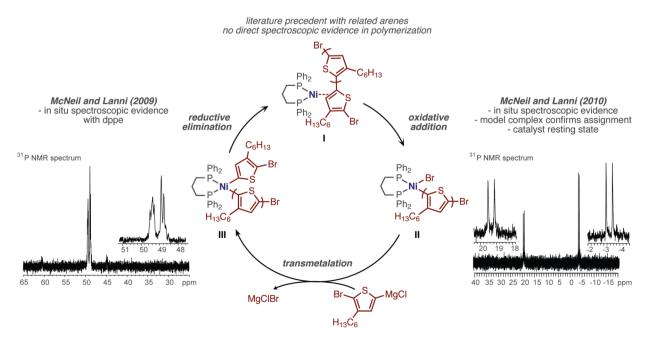
addition (Scheme 3). The proposed mechanism seemed plausible because both arene- and alkene-based π -complexes with Ni have precedent in the literature, ¹⁵ and several have been observed (or hypothesized) as intermediates in oxidative addition reactions. ¹⁶ Moreover, recent ¹³C kinetic isotope effect measurements revealed that haloarene π -complexation to Ni(0)

is the first irreversible step in small molecule cross-coupling reactions. 17

Support for Proposed Mechanism. McNeil and Lanni reported the first comprehensive mechanistic studies in 2009 and 2010.¹⁸ Rate and spectroscopic studies were performed on the polymerizations of 4-bromo-2,5-bis(hexyloxy)phenylmagnesium chloride and 5-bromo-4-hexylthiophen-2vlmagnesium chloride mediated by both Ni(dppe)Cl₂ and Ni(dppp)Cl₂. These studies revealed that for both monomers the turnover-limiting step changes from transmetalation (with dppp (1,2-bis(diphenylphosphino)propane)) to reductive elimination (with dppe (1,2-bis(diphenylphosphino)ethane) as the ligand bite angle is altered. These studies also provided in-situ spectroscopic evidence for intermediates II and III in the proposed catalytic cycle (Scheme 3). The proposed Nipolymer π -complex (I) was not observed because oxidative addition is not turnover-limiting with these monomer/catalyst combinations. Nevertheless, this work lent credence to the proposed mechanism and, importantly, eliminated other mechanistic possibilities including a Ni(I)/Ni(III) pathway championed by Kochi and Tsou. 19

To date, there has not been any definitive evidence of a Ni–polymer π -complex forming during the polymerization.²⁰ However, several studies have shown that unactivated dihaloarene precursors, when present, are not significantly

Scheme 3. Mechanism Proposed for Chain Growth



Scheme 4. Indirect Evidence for Associative Intermediate

consumed during polymerization, consistent with an associative intermediate.²¹ Compelling indirect evidence of an associative intermediate was recently provided by McNeil and Bryan using competition experiments (Scheme 4).²² Even though a high concentration of a more reactive competitive agent was utilized, the major products were from the intramolecular pathway. These small molecule results were compared to the polymerizations under the same conditions, which revealed similar trends among the catalysts. Combined, these studies convincingly demonstrate that there is an associative intermediate with a subsequent intramolecular oxidative addition in the chaingrowth polymerization. Whether this associative intermediate involves a η^2 -, η^4 -, or η^6 - π -coordination to Ni(0), which undergoes oxidative addition via a two-electron pathway, or a caged radical pair that goes through a one-electron pathway has not been distinguished at this time. Nevertheless, few definitive examples of the latter pathway exist, ^{19a} whereas Ni(0) π complexes have precedent. 15,16

Limitation: Chain Walking. Immediately following the initial reports, McCullough and co-workers made an unusual observation when end-capping their polymers: some Grignard reagents (e.g., CH_2 =CHMgBr) led to monocapped polymers while others (e.g., PhMgCl) led to dicapped polymers (Scheme 5).²³ They hypothesized that, following reductive elimination, the alkene- and alkyne-based end groups formed irreversible π -complexes with Ni(0), thereby preventing further reaction. At the time, the dicapped polymer was presumed to form via an intermolecular reaction, though one could imagine the Ni(0) migrating to the other chain end in an intramolecular fashion via a series of π -complexes (i.e., chain walking).

Scheme 5. Evidence for Ni(0) Chain Walking

McCullough et al. (2005)

PhMgBr

Ph

$$C_{6}H_{13}$$

Ph

 $C_{6}H_{13}$

Rii(dppp)Cl₂
 $C_{6}H_{13}$

Ph

 $C_{6}H_{13}$

Riiriy et al. (2010)

 $C_{6}H_{13}$
 $C_{6}H_{13}$
 $C_{6}H_{13}$

In 2010, Kiriy and co-workers provided compelling evidence of a chain walking process during CTP: propagation from both ends of the polymer was observed when using a bromoben-zene-functionalized Ni precatalyst (Scheme 5). Because the Ni(0) walking along the polymer chain was not completely random, they concluded that the chemically distinct repeat units (e.g., thiophene versus phenyl) have different π -binding affinities for Ni(0). In 2011, Koeckelberghs and co-workers provided further support for bidirectional propagation by showing that the tail-to-tail dyad of thiophene, which formed during initiation, became incorporated within the polythiophene structure during propagation.

The importance of chain walking in copolymerizations cannot be overstated. Using the conventional $L_n NiX_2$ precatalysts allows propagation to occur at both chain ends. Thus, if sequence control is desired (e.g., in a diblock or gradient copolymer synthesis), Ni precatalysts with unfunctionalized reactive ligands must be utilized (vide infra). In retrospect, the chain walking phenomenon explains the directional dependence observed in block copolymerizations when the monomers have different π -binding affinities; that is, other competing pathways such as chain transfer and chain termination can intervene before the desired intramolecular oxidative addition occurs at the chain end.

Limitation: Chain Transfer and Chain Termination. The presence of certain end groups on the synthesized polymers (e.g., Br/Br and H/H starting from a L, NiX, precatalyst) is indicative of competing reactions leading to chain transfer and/or chain termination. One such reaction involves the polymer being displaced from the Ni(0) by another molecule (e.g., solvent, monomer, oligomers, etc.) in the π -complex. To date, this chain-transfer pathway has been considered relatively insignificant because numerous studies have shown that potentially reactive species, such as 2,5dibromo-3-hexylthiophene, do not get consumed during CTP.²¹ An alternative reaction is disproportionation, wherein two Ni(II) catalysts swap ligands, generating L_nNiX₂ and L, Ni(polymer), (Scheme 6). The latter complex undergoes reductive elimination to generate Ni(0) and a polymer with twice the expected molecular weight. In 2004, Yokozawa and co-workers suspected disproportionation occurred when neutral H₂O was used as the quenching reagent because the gel permeation chromatograms (GPC) were bimodal, and the $M_{\rm p}$ of the first eluting peak was approximately twice that of the second peak. 6b,27 Quenching with 5 M HCl resulted in unimodal chromatograms, suggesting that protonation was faster than this competing pathway. Quenching with strong acid

Scheme 6. Disproportionation Pathway

Yokozawa et al. (2004)

computational support - Locklin et al. (2012)

is now standard within the field. Though experimental evidence of disproportionation has been circumstantial, ²⁸ Locklin and co-workers recently provided computational support for this pathway using simplified model compounds. ²⁹ Overall, chain transfer or chain termination reactions are indicative of nonliving polymerizations, and if present, factors like the copolymer sequence can no longer be controlled.

Limitation: Slow Initiation. The molecular weight dispersities (Đ) for most of these chain-growth polymerizations are significantly greater than the ideal 1.0. While chain transfer and chain termination are contributing factors, another source of broad D is the slow rate of precatalyst initiation relative to propagation. Slow initiation has been documented in several CTPs.³⁰ One notable example is that the "minor" thiophene regioisomer ((5-bromo-3-hexylthiophen-2-yl)magnesium chloride) exhibits negligible initiation rates with Ni(dppe)Cl2 due to steric effects, which can be overcome using Ni(dppe)PhCl.^{30c} In 2011, McNeil and co-workers first observed a product of initiation (L_nNi(aryl)₂—generated via reaction of monomer with L_nNiCl₂) persisting well into the polymerization, bringing slow initiation to center stage.²⁸ In 2012, the relative reaction rates were measured, revealing that initiation is approximately 20× slower than propagation for a conventional metal/ligand combination (Ni/dppe). 30b In this case, selectively accelerating initiation was challenging because rate studies revealed that the turnover-limiting step for both initiation and propagation was reductive elimination (Scheme 7). Thus, modifying the

Scheme 7. Reactive Ligands Selectively Accelerate Initiation

ancillary ligand (e.g., the bidentate phosphine) will have a similar effect on both reaction rates. The solution involved modifying the reactive ligand (i.e., Ar in Scheme 7) to selectively accelerate the reductive elimination during initiation and leave the propagation rate unchanged. Because the same ancillary ligand was used, these studies provided a direct measure of the impact of initiation; the slowest initiators gave a D=2.13 while the fastest initiator resulted in a D=1.12 at the same conversion. Therefore, the impact of initiation on the polymer D should not be underestimated.

Catalyst Design: Ancillary Ligands. While a handful of monodentate phosphines,³¹ carbenes,^{21a} and diimines³² have been used in CTP, the vast majority of polymerizations use bidentate phosphines.³³ The steric and electronic properties of these phosphines can be tuned by modifying the substituents on phosphorus. McNeil and co-workers examined the impact of

ligand steric properties and found that the chain-growth pathway was easily derailed when the ligand steric contribution was too little (e.g., with 1,2-bis(dimethylphosphino)ethane) or too much (e.g., with (1,2-bis(dicyclohexylphosphino)ethane), which was attributed to catalyst decomposition and π -complex disruption, respectively. In terms of ligand electronic properties, electron-rich ligands were expected to promote π -complex formation through donation of electron density from the metal into the arene LUMO. Indeed, McNeil and coworkers have demonstrated that the electron-rich ligands consistently outperform the electron-poor analogues (Scheme 8). 22,28,30b Nevertheless, because most of these polymerizations

Scheme 8. Electron-Rich Ancillary Ligands Promote Chain Growth

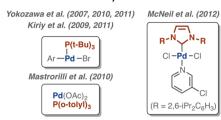
proceed through a turnover-limiting reductive elimination, the increased electron density slows down the propagation rate, and as a consequence, quenching by adventitious moisture can be problematic.

Catalyst Design: Reactive Ligands. Because the $L_n NiCl_2$ salts are largely insoluble in THF at the concentrations required for polymerization, many researchers began utilizing $L_n Ni(Ar)X$ as soluble alternatives. These so-called reactive ligands have many additional advantages, such as providing specific endcapping groups on polymers, ensuring unidirectional propagation for sequence control, ensuring polymers to grow off of surfaces. Reactive ligands can also be used to modify initiation rates.

Luscombe and co-workers were the first to introduce these functionalized precatalysts in 2009.³⁸ They postulated that including an ortho methyl substituent would stabilize the precatalyst species by forcing the arene into an orientation where the π^* -orbital overlaps with the d_m orbital on Ni, which lowers the HOMO and decreases reactivity.³⁹ On the other hand, Kiriy and co-workers have had success with the unsubstituted L, Ni(Ph)X, particularly with sterically congested monomers.^{30c} Ultimately, it is important that the substituent, if included, is not too large such that it hinders transmetalation during initiation.⁴⁰ Both Luscombe and Kiriy prepared these precatalysts in situ, and as a consequence, the reaction mixtures often contained impurities, including uncoordinated Ph3P or bpy, chelating ligand, and the bis-chelated Ni(II) complex. Though less convenient, isolating and purifying the precatalysts will ensure that no other catalytic species are present during both initiation and propagation. Overall, given the many advantages of using reactive ligands, we suspect that their frequency will only increase in the future.

Catalyst Design: Palladium versus Nickel. While Ni has remained a popular metal for CTP, the past five years have witnessed a substantial growth in reports of Pd-catalyzed chaingrowth polymerizations. As highlighted in Chart 1, Pd precatalysts ligated with hindered carbenes^{21a} and bulky, monodentate phosphines^{21b,31a-g} have exhibited chain-growth behavior. Overall, the scope of these Pd-catalyzed polymer-

Chart 1. Selected Pd Precatalysts in CTP



izations has been broader than Ni⁴¹ and included Suzuki-, Stille-, and Kumada-based monomers. In addition, cross-propagation between two chemically different monomers has been demonstrated.^{21a} Nevertheless, many of these polymerizations produced polymers with low molecular weights, broad dispersities, and a multitude of end groups. Although the chaingrowth mechanisms remain to be elucidated in most cases, Pd-based CTPs represent an emerging area for this field.

Additives. To date, several additives have been shown to improve the chain-growth polymerization behavior of certain monomers. For example, lithium chloride, which is known to accelerate Grignard metathesis reactions, 42 is frequently present during polymerizations. Although Yokozawa included LiCl in the initial polymerization reported in 2004,6 it was not until 2006 that its impact on the polymerization was noted.⁴³ Since then, LiCl has been known to both accelerate and decelerate the polymerization rate, 18,27,30d increase the reactivity of sterically hindered monomers,⁴⁴ and improve the controlled,⁴⁵ chain-growth nature of the polymerization.⁴⁶ The mechanism(s) to explain these results have not been elucidated, but there are several possibilities: (1) LiCl forms mixed aggregates with the monomer and modifies its reactivity. (2) LiCl mediates a Br to Cl transformation on the Ni(II) catalyst, which facilitates transmetalation due to its smaller atomic size. Regardless of the mechanistic details, it is clear that LiCl is noninnocent, and as a consequence, its presence and concentration should be varied when optimizing polymerizations with different monomers and catalysts.

The ancillary and reactive ligand can also serve as a beneficial additive in CTP. For example, Yokozawa and co-workers found that an additional equivalent of phosphine ligand (relative to Ni) led to narrower molecular weight distributions in synthesizing poly(N-hexylpyrrole), although the mechanistic role was not elucidated. In another example, Wang and co-workers found that $Ni(dppp)(acac)_2$ was superior to $Ni(dppp)Cl_2$ for polyfluorene synthesis. The improved polymerization behavior suggests a noninnocent role of the acac ligand during propagation since both acac ligands should be displaced from the catalyst during the initiation. Further studies are needed to determine whether the acac displaces the halogen after oxidative addition, stabilizes the π -complex, or serves some other mechanistic role.

Mechanism: Summary and Outlook. The past ten years have witnessed a tremendous growth in CTP-based mechanistic studies. Beyond providing a window into the polymerization mechanism, these studies have informed the design of new catalysts and reaction conditions. While some mechanistic details remain elusive, we are optimistic about the future. Moreover, as new monomers/catalysts/conditions are introduced, new mechanistic questions will undoubtedly arise, fueling more activity in this area.

■ CTP: SCOPE

Electron-Rich Monomers. To date, the vast majority of reported chain-growth polymerizations involve electron-rich monomers. Among this class of compounds, thiophene derivatives are the most abundant (Chart 2).⁴⁷ For example,

Chart 2. Selected Polymers Containing Thiophene or Related Compounds Synthesized via CTP

$$\begin{array}{c} C_{6}H_{13} \\ C_{2}H_{5} \\ C_{6}H_{13} \\ C_{7}H_{13} \\ C_{8}H_{17} \\$$

carbon-, oxygen-, and sulfur-based side chains have been incorporated to modify the polymer's physical, optical, and electronic properties. Thiophene analogues—selenophene 48,49 and pyrrole 50 have also been successfully polymerized using CTP. Regioregular polymers can be prepared if (a) the monomer forms as a single regioisomer or (b) the two regioisomers are consumed at different rates due to steric interactions with the ancillary ligand on the catalyst. Although the mechanism for each of these derivatives has been assumed to be same as the one proposed for 3-hexylthiophene (see Scheme 3), the fact that each monomer/catalyst combination provides polymers varying D and end-group fidelity suggests that the impact of chain walking, chain transfer, chain termination, and initiation is different in each case. Until detailed mechanistic studies are performed on each system, this variability in polymerization results cannot be readily under-

The first non-thiophene-based monomer to undergo CTP was dialkoxyphenylene, which was reported by Yokozawa and co-workers in 2006 (Chart 3).⁴³ Although commercial

Chart 3. Selected Electron-Rich Polymers Synthesized via CTP

$$C_6H_{13}$$
 $H_{17}C_8$ C_8H_{17} $H_{25}C_{12}$ $C_{12}H_{25}$ $C_6H_{13}O$ $C_$

applications of poly(*p*-phenylene)s remain limited, this discovery was important because it suggested that the chaingrowth method could be expanded to other monomers. Moreover, this result suggested that CTP does not require sulfur coordination to Ni, as originally postulated by Yokozawa. A closely related analogue, dialkylfluorene, was next discovered to undergo CTP. Poly(fluorene)s are used commercially as the blue emitter in light-emitting diodes. The initial reports revealed that the fluorene polymerizations were less controlled, with a variety of end groups being observed,

suggesting chain transfer and chain termination reactions were prevalent. A breakthrough was reported in 2012, when Wang and co-workers used (dppp)Ni(acac)₂ to synthesize poly(9,9-dioctylfluorene) with high molecular weight and narrow \mathcal{D} . In 2012, Bielawski and co-workers utilized a monomer containing both phenylene and thiophene to synthesize an alternating copolymer. ^{26a}

Excitingly, the CTP method was recently expanded to prepare poly(fluorenylene vinylene)s (PFVs)⁵² and poly(p-phenylene ethynylene)s (PPEs),^{41a} respectively (Chart 3). Although the mechanisms remain to be elucidated, the chaingrowth behavior is not surprising considering that both alkenes and alkynes are known to form π -complexes with Ni(0).¹⁵ With further development in this area, we anticipate that these chaingrowth methods could displace the traditional synthetic routes to PPVs and PPEs.

Electron-Deficient Monomers. To date, few chain-growth polymerizations of electron-deficient monomers have been reported (Chart 4). ⁵³ Because failed results often go

Chart 4. Selected Electron-Deficient Polymers Synthesized via CTP

$$H_{13}C_{6} C_{6}H_{13}$$

$$H_{17}C_{8} C_{8}H_{17}$$

$$H_{13}C_{6} C_{6}H_{13}$$

$$OR$$

$$H_{18}C_{18}C_{18}H_{17}$$

$$H_{19}C_{18}C_{18}H_{17}$$

$$H_{19}C_{18}C_{18$$

unpublished, the rationale for this scarcity is unknown. From a mechanistic perspective, both the transmetalation and reductive elimination steps will be significantly slower with an electron-deficient monomer, which can drastically impact the initiation rate. On the other hand, the π -binding between Ni (or Pd) and an electron-deficient monomer should be strong, and oxidative addition will be accelerated, both of which would promote the chain-growth pathway and minimize the competing chain transfer reactions. The inability to polymerize most electron-deficient monomers represents a significant limitation in the field as copolymerizing these monomers with their electron-rich counterparts provides access to low band gap donor—acceptor materials, with applications in organic solar cells.

In 2008, Rasmussen and co-workers reported polymerizing thienopyrazine monomers using the CTP method; however, the low molecular weight and relatively broad \mathcal{D} of the isolated polymers suggest the polymerization is uncontrolled and possibly nonliving. Sac In 2011 and 2012, Kiriy and co-workers suggested that the Ni-catalyzed polymerization of a naphthalene diimide monomer was chain growth, though the broad molecular weight distributions suggested several competing side reactions. The mechanism proposed involves an unusual reductive coupling step, stemming from the observed formation of a radical anion upon Zn-mediated activation of the

monomer. It will be challenging to expand this method to other monomers without a more detailed understanding of the reaction mechanism. In 2011, Kiriy and co-workers also reported the successful polymerization of a benzothiazole monomer using Pd as the catalyst. The key to their success involved sandwiching an electron-rich and solubilizing fluorene ring between two benzothiazole units. Although high molecular weight polymers were not obtained, this approach of combining an electron-rich and electron-poor monomer can lead to low band gap materials.

The first and only electron-deficient monomer to be homopolymerized in a living, controlled chain-growth fashion is based on the pyridine scaffold, which was reported in 2012 by Yokozawa and co-workers. 33c,d,53a Using a clever experiment, the authors identified chain-growth conditions by looking for selective difunctionalization in an analogous small molecule reaction, similar to the Kumada 12 and McCullough 5 experiments (see Scheme 2). Typical of many polymerizations in this field, the resulting molecular weights, *D*, and end groups varied dramatically depending on catalyst, monomer activation method, presence of LiCl, and nature (and location) of the substituents. Although poly(pyridine)s have limited commercial impact, the method used to identify the chain-growth conditions has merit and should be utilized more in the future.

Scope: Summary and Outlook. The past decade has witnessed a tremendous growth in the variety of monomers that can undergo CTP. This achievement is made even more remarkable considering that the chain-growth mechanism(s) are still being elucidated. Many of these advances have been somewhat serendipitous as catalysts, and conditions are screened for each monomer. Despite all this progress, the polymerization of electron-poor monomers remains a significant challenge. In addition, among the reported examples of CTP, there is a need for more controlled polymerizations that reproducibly give high molecular weight polymers with narrow dispersities and a single set of end groups. We suspect that the number of failed experiments exceeds the successes, and because the failed results are often unpublished, it has been difficult to identify the mechanistic bottleneck. As such, we anticipate that a greater mechanistic understanding will lead to the discovery of new catalysts and conditions and, ultimately, the synthesis of new materials.

CTP: APPLICATIONS

Block and Gradient Sequence Copolymers. Chaingrowth methods that are both living and controlled can be used to synthesize copolymers with specific sequences, including blocks and gradients. Using CTP, copolymers containing conjugated/nonconjugated blocks⁵⁵ as well as conjugated/ conjugated blocks⁵⁶ have been prepared (Chart 5). The allconjugated block copolymers are synthesized via sequential monomer addition, wherein one monomer is added after the other monomer is completely consumed. Because chain walking and chain transfer reactions can be significant with specific catalyst/comonomers combinations, one needs to carefully select the precatalyst and monomer addition order for the best results. Most of these all-conjugated block copolymers are semicrystalline and self-assemble into lamellar morphologies. These solid-state structures are of interest because they facilitate charge separation and conduction in organic solar cells.

Several diblock copolymers containing both conjugated and nonconjugated segments have been prepared using CTP. 55 The

Chart 5. Selected Block and Gradient Copolymers Synthesized via CTP

conjugated/conjugated block copolymers

conjugated/non-conjugated block copolymers

gradient copolymers

Chart 6. Selected Grafted and Branched Polymers Synthesized via CTP

nonconjugated block is usually initiated from the end group of the conjugated block in a second step. This reactive end group is installed in the first step via the reactive ligand in the initial precatalyst or as a quenching agent at the end of polymerization. Nonconjugated blocks are utilized to increase the copolymer solubility and influence the solid-state structure; however, these advantages can be offset by a decrease in conductivity due to the insulating properties of this block. In 2012, Bielawski and co-workers reported a streamlined approach that uses the same Ni catalyst for both blocks, albeit via mechanistically distinct pathways. Sola Nevertheless, this approach is limited to monomers that can be polymerized using Ni(II) or Pd(II) catalysts.

McNeil and Locke were the first to prepare all-conjugated gradient copolymers using CTP. To date, only thiophene/thiophene and thiophene/selenophene gradient sequence copolymers have been synthesized due to difficulties with cross-propagation among chemically distinct comonomers (Chart 5). In these examples, the comonomer reactivity ratios were close to 1, which means that the gradient sequence can only be generated via syringe pump addition of one monomer into the catalyst/comonomer mixture. Compared to the analogous block and random copolymers with similar compositions, molecular weights, and D, the gradient copolymers have unique solid-state thermal properties and

morphologies.³⁶ Moreover, the gradient copolymers have superior phase-compatibilizing properties when added to the homopolymer blend.^{36c} An emerging theme from this research is that sequence matters, and we anticipate that, as the diversity of comonomers increases, this subfield of conjugated copolymers will gain prominence.

Surface-Initiated Polymerizations. In most device configurations, conjugated polymers are deposited as thin films onto metal or oxide surfaces. This interface can have a substantial impact on the overall device performance.⁵⁷ As a consequence, an alternative approach wherein the polymerizations are initiated from the metal or glass surface has recently gained attention. To date, several conjugated polymers have been synthesized using CTP from initiators that are covalently bonded to silica, indium tin oxide, gold, or polystyrene (Chart 6).⁵⁸ In each example, a surface-bound precatalyst is first prepared by reacting Ni(0) or Pd(0) with a surface-bound aryl halide, from which the polymerization is initiated. Locklin and co-workers showed that, in practice, this approach is limited because high surface densities of catalyst lead to intermolecular disproportionation reactions.^{37b} Although film thickness can be controlled, the surface coverage is uneven, limiting its practical application. Notably, this detrimental pathway was more significant with Ni(0) than with Pd(0), 31b suggesting that future efforts should focus on Pd(0)-based initiators.

Branched Polymers. To date, only a handful of polymers with nonlinear scaffolds have also been prepared via CTP. Kiriy^{35e} and Luscombe^{35a} independently reported star-shaped poly(thiophene) synthesis using a central core molecule that is functionalized with multiple Ni initiators (Chart 6). Kiriy and co-workers used Ni(bpy)-based initiators which led to broad Đ (1.98), 35e while Luscombe and co-workers used Ni(dppp)based initiators and obtained polymers with narrow D (1.15).35a These results are consistent with the fact that Ni(dppp)Cl₂ is a superior precatalyst for the linear poly-(thiophene) synthesis.^{37e} In related work, Bo and co-workers used AB₂ monomers to generate a hyperbranched polymer with 100% degree of branching using a Pd catalyst.⁵⁹ Recently, Luscombe and co-workers reported an efficient route to hyperbranched polymers^{37a} using direct arylation (rather than a preformed organometallic group).41b

Applications: Summary and Outlook. While a number of novel polymer architectures have been accessed using CTP, the impact of these materials in real world applications (e.g., solar cells and light-emitting diodes) has been limited by the narrow scope of monomers used. Nevertheless, many of these new materials have exhibited new and exciting properties, fueling the desire for continued development in this area. With improvements in catalyst design and monomer scope, we suspect that this research area will increase in the next decade.

CONCLUSIONS

Nearly a decade has passed since the discovery of CTP by McCullough⁵ and Yokozawa.⁶ As highlighted in this Perspective, a substantial number of researchers have contributed to unveil key aspects about the chain-growth mechanism, expand the monomer scope, and synthesize new materials. Nevertheless, each of these foci needs further development for this method to make a significant impact on the greater scientific community, analogous to the living, controlled radical polymerizations like ATRP, RAFT, and NMP. Future studies should focus on broadening the scope of monomers capable of undergoing CTP by exploring alternative metals, ligands, additives, and transmetalating agents. More generally, a greater mechanistic understanding of "failed" polymerizations should guide these efforts. CTP has already enabled access to exciting, new materials (e.g., surface-grown polymers and gradient copolymers), and it has the potential to completely transform conjugated polymers from a niche material to one that is widely used by chemists, biologists, and engineers.

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