

## Review

# Polymers synthesized via catalyst-transfer polymerization and their applications



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## ABSTRACT

Catalyst-transfer polymerization has enabled synthesizing conjugated polymers with unmatched control over both polymer sequence and end-group identity. These attributes provide access to complex materials, including conjugated–conjugated and conjugated–nonconjugated block copolymers, gradient copolymers, nonlinear copolymers, and hybrid materials. This review discusses these materials, highlighting their syntheses as well as their applications.

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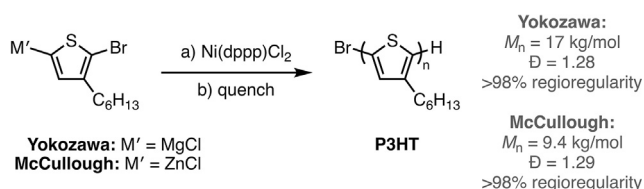
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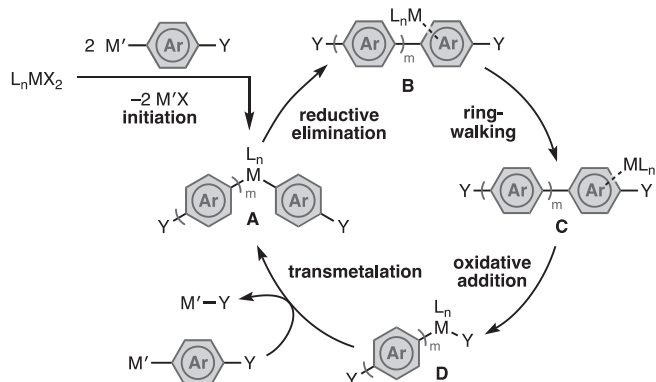
## 1. Introduction

New synthetic methods have been instrumental in enabling access to valuable compounds and materials. For example, Merrifield revolutionized biochemistry and related fields by developing solid-phase peptide synthesis, which provided practical routes to large quantities of synthetic peptides [1]. Ziegler–Natta catalysts transformed the field of polymers by providing access to high-density polyethylene and stereoregular polypropylene, ubiquitous materials that are now manufactured industrially using these catalysts [2]. Similarly, the field of conjugated polymers has benefited enormously from synthetic advances. While early routes towards semiconducting polymers like polythiophene and its derivatives were dominated by oxidative (electro)chemical methods [3], the advent of transition metal-catalyzed cross coupling greatly expanded the range of accessible conjugated polymers [4,5]. These cross-coupling methods were thought to be uniformly step-growth in nature, offering minimal control over polymer sequence and end-group, until two landmark reports from McCullough and Yokozawa in 2004 changed that perception. The authors independently observed that a method published over a decade earlier for synthesizing poly(3-hexylthiophene) (P3HT) [6] proceeded in a living, chain-growth fashion to produce materials with narrow dispersities ( $\bar{D} \leq 1.3$ ), high regioregularities, and controllable molecular weights (Scheme 1) [7,8]. Subsequent publications from the aforementioned groups and many others have demonstrated that this method, termed catalyst-transfer polymerization (CTP), is effective for polymerizing a range of (hetero)aromatic monomers, with the best results obtained for electron-rich substrates [9–16].

While the synthetic advantages of CTP quickly became apparent, the mechanistic rationale for the chain-growth behavior was initially unclear. Various scenarios were proposed, but the accumulated evidence implicates the mechanistic pathway depicted in Scheme 2 [10,17]. Initiation commonly involves a M(II) precatalyst [e.g.,  $L_nMX_2$  or  $L_nMX(RL)$  where  $RL$  = reactive ligand] that undergoes one or two transmetalations with an AB-type organometallic monomer to afford complex **A** ( $m = 1$ ). Carbon–carbon reductive elimination forms  $\pi$ -complex **B**. Rather than dissoci-



Scheme 1. Initial reports of catalyst-transfer polymerization.



Scheme 2. Catalyst-transfer polymerization mechanism.

ating, the catalyst remains bound to the growing polymer chain and engages in ring-walking to the chain-end followed by intramolecular oxidative addition, ultimately yielding M(II) complex **D** ( $m = 2$ ). The catalyst can continue to enchain monomer units by iterative transmetalation, reductive elimination, ring-walking, and intramolecular oxidative addition. In many cases, chain transfer does not occur to a significant extent, and termination only occurs on exposure to a quenching agent, such as acid or a monofunctional transmetalating agent (e.g., MeMgBr).

The chain-growth mechanism of CTP provides unmatched ability to produce narrowly disperse conjugated polymers with control over length, sequence, and end-group identity. As such, CTP has been used to prepare structures that would be difficult or impossible to access using other contemporary synthetic techniques. The resulting polymers have a wide array of uses, including in optoelectronics, magnetic materials, sensors, hybrid organic–inorganic materials, and imaging agents. In this review, we focus on papers published since 2012 [18], and highlight those that include materials with interesting applications and that we believe could not have been made without CTP. Our intention is that the reader will appreciate how these applications result directly from the structural complexity and diversity afforded by CTP.

## 2. Applications enabled by controlling polymer sequence and length

The study of sequence-controlled polymers (SCPs) has become an emerging subfield within materials science, as the effects of polymer sequence on macroscopic properties are becoming increasingly appreciated. Although there is some debate surrounding the definition of “sequence control,” a recent review suggests that any “macromolecule in which monomer sequence is controlled to some degree” [19] can be considered a sequence-controlled polymer. Compared to other methods for synthesizing conjugated polymers, CTP offers the greatest control over copolymer architecture. Block copolymers are the most common SCPs synthesized via CTP, and several examples of gradient copolymers have been reported (Chart 1). Random and statistical copolymers have also been accessed using CTP; however, these materials are not technically SCPs because the sequence is governed primarily by statistics [20]. Alternating copolymers have been synthesized via CTP using AB-type monomers that include both repeat units [21–24], although these scaffolds are also accessible using conventional step-growth methods. This section will focus on SCPs where the living, chain-growth nature of CTP was essential for their syntheses.

### 2.1. Block copolymers with the same arene backbone

The most common method of synthesizing conjugated–conjugated block copolymers using CTP initially resembles a

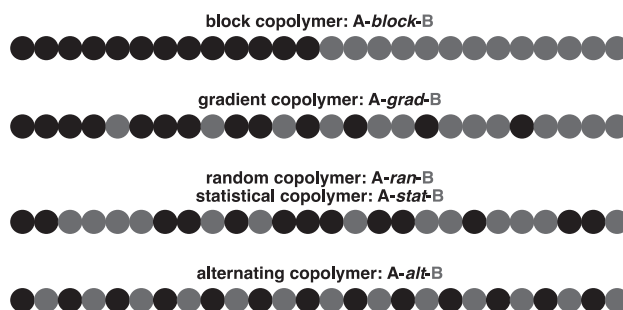


Chart 1. Copolymer structures with block, gradient, random/statistical, or alternating sequences.

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