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Direct arylation polymerization: A guide to optimal conditions for effective conjugated polymers

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ABSTRACT

The rapid increase in the breadth and scope of transformations that involve metal-promoted activation of C—H bonds is fundamentally changing the field of synthetic chemistry. Direct arylation polymerization is a newly established synthetic protocol for atom economical, effective, and affordable preparation of conjugated polymers, which continue to be incredibly advantageous as operative materials for a diverse and continually evolving array of applications. This route toward conjugated polymers for high performance materials is particularly appealing because it circumvents the preparation of organometallic derivatives and the associated cryogenic air- and water-free reactions. Although a broad range of monomers are now readily polymerizable, direct arylation polymerization is known to produce defects in the chemical structure, which have a strong impact on the optical, electronic, and thermal properties of conjugated polymers. Fundamental understanding of the underlying considerations when employing different reaction protocols is required to truly enable a broad reaching platform.

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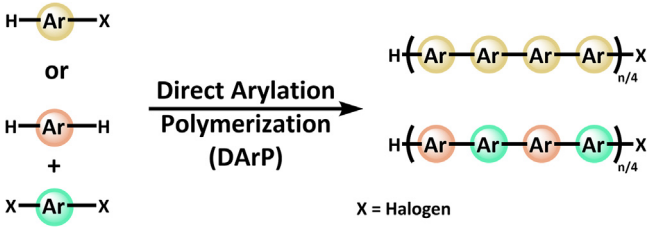
1. Introduction

Conjugated polymers are operative materials for a diverse range of applications, including photovoltaics [1], field-effect transistors [2], light-emitting diodes [3], sensors [4,5], electrochromic devices [6,7], bioimaging materials [8,9], drug delivery [10], and as photosensitizers in photodynamic therapy [11]. They have steadily improved since their discovery in the 1970s [12] through strategic and rational design modifications of the polymer backbone [13], utilization of side-chains and other functional groups [14,15], and evaluation of unique structural motifs and application-based design enhancements [16,17]. Coupled with their distinct advantages of being lightweight, solution processable, and compatible with flexible substrates, polymers have inspired high throughput industrial-scale and low-cost flexible roll-to-roll printed plastic optoelectronic devices [18–20] with recyclable components [21]. With the steady development of increasingly finely-tuned aromatic backbones, the demand for convenient, reliable, and efficient methods of generating these materials also grows.

For high performance conjugated polymers with well-defined structures from a broad array of substrates, a transition metal-catalyzed cross-coupling polycondensation is typically utilized, such as Migita-Kosugi-Stille [22], Suzuki-Miyaura [23,24], Kumada-Corriu [25], Negishi [26], Murahashi [27], and Yamamoto (reductive coupling) [28] methods, which necessitate the functionalization of one coupling site with a halogen (often brominated or iodinated) and another coupling site with an organotin, organoboron, organomagnesium, organozinc, organolithium, or organohalide species respectively (Scheme 1). While these methods have steadily developed (and continue to develop) into a powerful arsenal of protocols in the toolkit of synthetic chemistry, the past fifteen years have witnessed the emergence of metal-promoted C—H activation toward C—C bonds from an aryl halide, thus requiring the pre-activation of only one coupling partner, which has proven to be incredibly attractive for improving atom economy, providing targets in fewer synthetic steps, generating more benign byproducts, and decreasing the overall cost of transformations. Although C—H activation methods have been known for over half a century [29], they have only recently been explored for the synthesis of π-conjugated polymers, with some pertinent reviews having been written on the topic [30–48]. A deeper discussion of the implications, considerations, and strategies for achieving well-defined polymers is necessary for the broad applicability of this method, which would include not only selective and reactive methods but also evaluation of the structure-function relationships of the resulting materials.

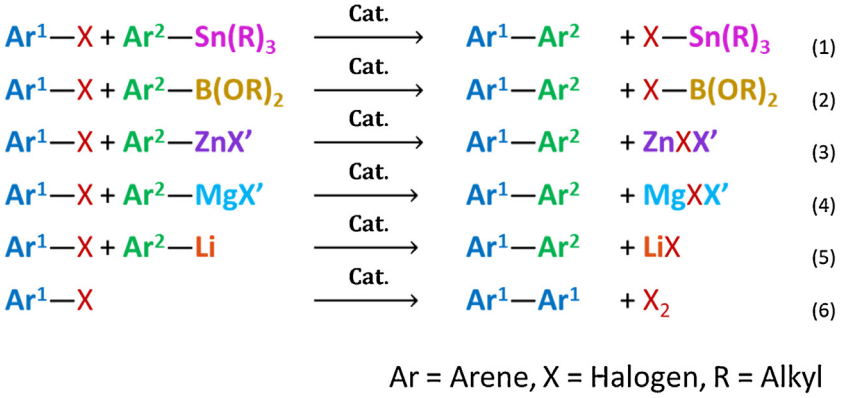
In this Review, recent advances directed toward the optimization of the direct arylation polymerization protocol are critically discussed in the context of how they have motivated the development and refinement of conditions. Specifically, how they have analyzed and minimized unselective side reactions and expanded substrate scope. Additionally, an evaluation of this protocol as a viable method toward practical applications as it correlates to defect-content will be undertaken. Fully understanding the reactivity and limitations of the method, as well as evaluating the quality of the resulting polymers, can encourage and motivate future improvements and utility, with the goal of direct arylation polymerization becoming a superlative cross-coupling method for the broad generation of exceptional polymers.



Scheme 2. Homopolymerization of a single arene or heteroarene (Ar) monomer or alternating copolymerization of two monomers toward π-conjugated polymers via DArP.

2. Development of Direct Arylation Polymerization: Considerations for Well-Defined Conjugated Polymers

Reactions that can substitute one preactivated species with a simple arene have become highly prevalent, often broadly referred to as C—H (bond) activation and C—H (bond) functionalization but also others. To describe these processes succinctly, avoid unnecessarily broad terminology, and emphasize the arene being functionalized rather than the bond being transformed, the term "catalytic direct arylation" has emerged to label reactions with both arenes and heteroarenes [49]. When applied to the generation of polymers through consecutive direct arylation reactions, this method should simply be referred to as direct arylation polymerization (Scheme 2). This method is often abbreviated as DArP or DARP [40,50–52], which fittingly emphasizes the arene, typically abbreviated "Ar" (even when referring to a heteroarene) and provides a suitable cadence. It is also sometimes abbreviated more succinctly as DAP [53,54]. In an effort to emphasize the distinction between arenes in general and heteroarenes, as well as broaden the terminology, this method is sometimes also referred to as direct (hetero)arylation polymerization (DHAP) [55]. Regardless, the advantages of such a method that can directly activate C—H bonds without the need for pre-functionalization beforehand



Scheme 1. Some traditional C—C forming reactions toward aryl-aryl (Ar-Ar) bonds for conjugated materials, which include (1) Stille, (2) Suzuki, (3) Negishi, (4) Kumada, (5) Murahashi, and (6) Yamamoto (reductive coupling).

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