

# ORGANOCATALYSTS IN SOLVING CHALLENGES IN POLYMER SYNTHESIS

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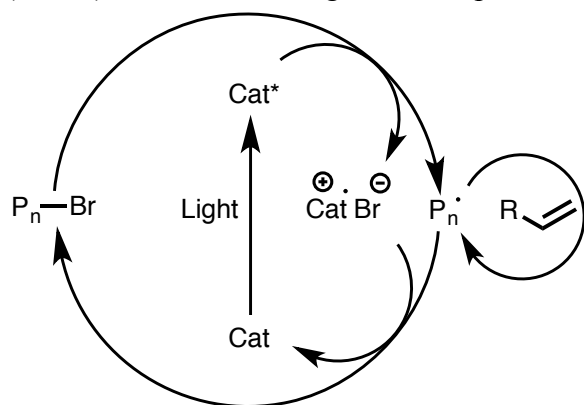
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## INTRODUCTION

Polymeric materials are ubiquitous in our daily life and play a major role in scientific discoveries for constructing next generation smart materials, bioelectronics, novel drug carriers and so on.<sup>1</sup> Numerous polymerizations methods have been developed to access functional polymeric materials, with metal-catalyzed polymerizations proven one of the most successful. However, some inherent limitations include metal contamination hinders the application of polymers synthesized in these methods. This report summarizes the development of metal-free atom transfer radical polymerization (ATRP) and the recent advance of H-bonding catalyzed ring-opening polymerization (ROP) to discern the potential of using organocatalysts to overcome challenges associated with metal catalyzed polymerization reactions.

## PHOTOINDUCED METAL FREE ATRP

ATRP is one of the most studied methods for control radical polymerization (CRP). The broad scope and versatility makes ATRP the most utilized methods to convert vinyl monomers to a plethora of polymers for a board range of applications.<sup>2</sup> One major drawback of traditional copper-catalyzed ATRP is the inevitable contamination with toxic and colorful metal residue, which has hindered the application of polymers synthesized by this method in biomedical and electronic fields.<sup>3</sup> Early attempts such as introducing sacrificial reducing agents<sup>5</sup> and using photoredox catalysts<sup>6</sup> have been utilized to enhance catalyst reactivity and allow low catalyst loading. However, a complete metal-free ATRP system remains absent. Inspired by the success of photomediated iridium catalyzed ATRP, perylene and phenothiazine were first identified as organic photocatalysts for metal-free ATRP to polymerize methyl methacrylate (MMA) due to their strong reduction potential at photoexcited state (-1.68 and -2.1 V vs SCE respectively).



**Scheme 1.** Proposed mechanism for metal-free photo-mediated ATRP (Cat = catalyst, P<sub>n</sub> = polymer chain).

Kinetic studies for both cases suggested a controlled polymerization process and polymerization only processes in the presence of light. The structure-activity relationship and reaction mechanism of phenothiazine and its derivatives were then extensively studied by different groups to direct the development of more efficient catalyst system.<sup>8-11</sup>

Currently, the most efficient system consists of highly conjugated phenoxazine, which polymerizes

MMA in a highly controlled fashion ( $DP_n > 200$ ,  $\bar{D} = 1.1-1.3$ ) with almost quantitative initiator efficiency ( $> 97\%$ ).<sup>11</sup> The proposed oxidative quenching mechanism for perylene and phenothiazine catalyzed ATRP is shown in Scheme 1. The scope of metal-free ATRP was quickly expanded to polymerize styrene, acrylonitrile, amine containing methacrylate (impossible to polymerize with Ir mediated ATRP), biomass-derived vinyl monomer to construct different homopolymers and block copolymers.<sup>3,4, 11, 13</sup>

### **ANIONIC UREA/ THIOUREA CATALYZED ROP**

Polyesters including polylactic acid (PLA) are of great interest due to their biodegradable and biocompatible nature for food packaging, plastic substitutes, and biomedical applications. In 2013, the global demand for PLA was 714.2 kilotons, and this number is expected to reach 2000 kilotons by 2020. The major production method for PLA is through ROP of lactides, which is often catalyzed by tin (II) 2-ethylhexanoate ( $Sn(Oct)_2$ ). Two major disadvantages associated with tin-catalyzed ROP are the inevitable tin contamination and poor control over polymerization ( $\bar{D} > 1.5$ ).<sup>15</sup> To overcome these challenges, a monofunctional H-bonding organocatalyst system that utilizes thiourea as hydrogen bond donor to activate carbonyl and amine base to activate alcohol initiator was shown to catalyze ROP of PLA with high selectivity ( $DP_n = 215$ ,  $\bar{D} = 1.05$ ) yet slow reaction rate ( $> 5$  days).<sup>16</sup> One of the most active catalysts for ROP of PLA, triazabicyclodecene (TBD), was shown to exhibit high rate of polymerization ( $DP_n = 500$ , 1 min reaction time) through a bifunctional mechanism where TBD activates both initiator and monomer.<sup>15</sup> However, due to the strong basicity of TBD, transesterification and polymer degradation was observed with extended reaction time.<sup>16</sup> Recently, anionic urea/thiourea systems were reported to produce PLA with both high reactivity ( $DP_n = 200$ , 6 seconds) and high selectivity (no transesterification after 30 hours). Further study indicates the size of the counter ion governs the high selectivity while the electronics of the catalyst system governs the reactivity of the catalyst.<sup>17,18</sup> Both the rate and control of polymerization of the current systems are great improvements compared with those of the tin-catalyzed system.

### **SUMMARY AND OUTLOOK**

In this report, the competitive performance of organocatalysts for ATRP and ROP is highlighted to show the capability of organic molecules as metal catalyst substituents. These organocatalysts are particularly relevant for applications requiring polymers with no metal contamination. More studies are required on the development of more stable catalyst systems (e.g., air and moisture) and achieve high molecular weight polymers ( $> 100$  kDa) to truly impact the polymer synthesis on an industrial scale.

Organocatalysts were traditionally known for catalyzing enantioselective transformations. Since the physical properties such as glass transition temperature, crystallinity, and packing structure of polymeric materials largely depend on the tacticity of the polymer, one future interest is the use of organocatalysts to achieve stereoregulation during the polymerization process.

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