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Combination of olefin insertion polymerization and olefin metathesis to extend the topology and composition of polyolefins

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Since Ziegler, Hogan and Banks' seminal discoveries for the catalytic polymerization of olefins, many generations of catalysts have been reported [1–5]. These include the transition from the original heterogeneous catalysts (Ziegler and Phillips) to homogeneous catalysts combining metallocene, post-metallocene and late transition metal-based catalysts. The development of new catalysts has enabled a higher control over polyolefin architecture and composition. Despite the tremendous achievements made in the last few decades, the chemical tunability offered by catalytic olefin polymerization remains limited. Therefore, alternative strategies have been developed to further expand the chemical and topological control achieved by current methods and ultimately to advance the material properties of the polymers. A strategy combining insertion polymerization and olefin metathesis has emerged as an alternative way to introduce chemical functionalities to polyolefins. The orthogonal reactivity of these two reactions while sharing the same substrate (olefin) provides a unique avenue to expanding the topology and composition of polyolefins (Figure 1).

Three approaches, distinguished by the order at which the olefin insertion polymerization and olefin metathesis are performed, have been developed. The first approach consists of performing the insertion polymerization first to yield a polyolefin, followed by an olefin metathesis post-polymerization functionalization to introduce functional groups to the polymer. The original report using this method employed a polyolefin containing pendant olefinic groups (co-polymerization of ethylene or propylene with α, ω-diene). A 2nd generation Grubbs catalyst then enabled these pendant olefin groups to react with an array of olefinic substrates (Figure 2(a)) [6]. The advantage of performing the post-polymerization functionalization with Grubbs olefin metathesis catalyst is its high chemical compatibility [7]. This functional group tolerance enables the introduction of polar groups into the polyolefin that could not have been incorporated during the olefin polymerization. One potential side reaction of performing the cross-metathesis reaction on polymeric substrates containing pendant olefinic groups is the cross-linking of the polymer (cross-metathesis of two polymeric olefin groups and release of ethylene). However, upon the appropriate choice of reaction conditions (excess of a cross-coupling partner), the molecular weight distribution of the functionalized polyolefin remained similar to the one of the original polyolefins. The benefit of introducing functional groups into the polyolefin was highlighted by the decrease in surface tension of the functionalized polyolefin over its original form [6,8].

This cascade post-polymerization reaction was also implemented for polyolefins that contain only a single terminal olefin end-group to access semi-telechelic polyolefins (Figure 2(b)). This strategy is built on the chain termination (through transfer to monomer or β-X elimination) of catalytic olefin polymerization that invariably results in the formation of an olefinic group at the end of the polyolefin

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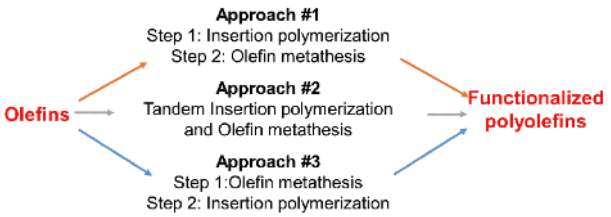

Figure 1 Combination of olefin insertion polymerization and olefin metathesis for the synthesis of functionalized polyolefins (color online).

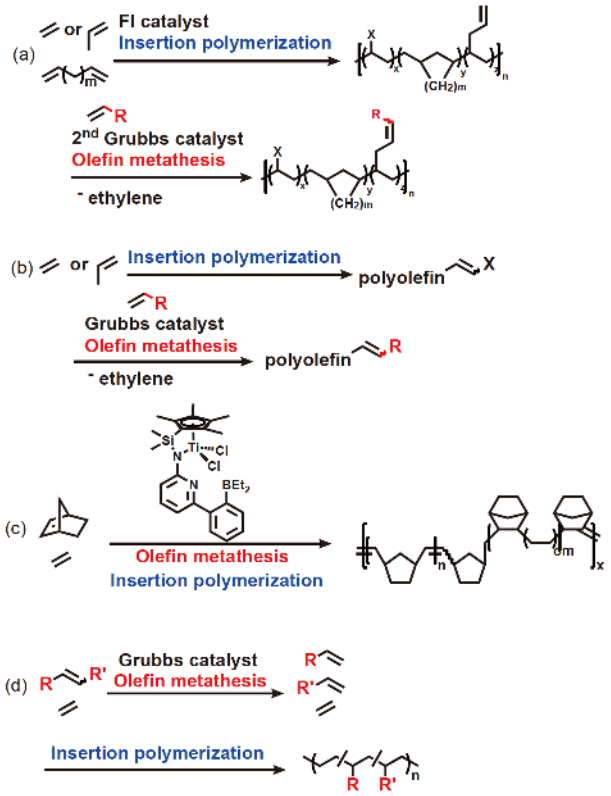

Figure 2 (a) Post-polymerization modification. (b) Post-polymerization end-functionalization. (c) Tandem copolymerization. (d) Cascade activation of olefinic comonomers (color online).

chain. A cross-metathesis reaction of this olefinic end-group with a functional acrylate has been used to quantitatively introduce functional groups at one end of polyolefins. While originally developed on amorphous polyethylene [9,10], this technique has been further developed for the post-polymerization of semi-crystalline polyethylene and polypropylene [11]. The synthetic challenge of end-functionalizing high molecular weight semi-crystalline polyolefins is two-fold. First, the polymer is only soluble in organic solvent at elevated temperature, and second, the concentration of end-groups is very low. Nonetheless, the use of slow addition of a Hoveyda-Grubbs catalyst solution enables the quantitative conversion of the polyolefin into semi-telechelic polymers that were subsequently converted into block copolymers [11]. Building on the same concept of olefinic end-group transformation of polyethylene via a cross-metathesis reaction, polyethylene-containing diblock copolymers were synthesized by coupling the polyethylene with polar polymers such as poly(methyl methacrylate) and polyesters [12]. While the product of the reaction was successful in enhancing the compatibility of the polyethylene and the polar polymer, the low reactivity of the two terminal-functionalized polymers challenges the overall yield of the cross-metathesis reaction.

The second approach consists of using a catalyst capable of simultaneously and interchangeably catalyzing the insertion polymerization and the ring-opening metathesis polymerization of cyclic monomers (Figure 2(c)) [13]. This tandem reaction is unique, as a single catalyst is used to convert a single monomer into a polymer having two distinct repeating units. A series of Group 4 catalysts containing a 6-[2-(dialklboryl)phenyl]-pyrid-2-ylamido-motif have been reported to undergo this switch in reactivity. The metal centers reversibly convert through α-H^+ addition/elimination between an under-coordinated metal center that catalyzes the insertion polymerization of olefins and a metal alkylidene that catalyzes the ring-opening metathesis polymerization of cyclic olefins. This tandem reactivity significantly increases the tunability in properties accessible with these monomers.

The third approach to combining olefin insertion polymerization and olefin metathesis consists of performing the metathesis reaction first, then following it with an olefin polymerization (Figure 2(d)). In this way the olefin metathesis can be used to convert a co-monomer with low reactivity into one with higher reactivity [14]. Thus this reaction enables a significantly higher degree of functionality to be introduced into the polymer. While this approach was only very recently developed, it opens the door to new opportunities in olefin polymerization [15]. For instance, performing the metathesis reaction prior to the copolymerization with bio-derived products that contain internal olefins would significantly enhance their incorporation, despite their originally low reactivity. Moreover, the synthesis and isolation of functional olefinic monomers to access polyolefins with specific functionalities are always challenged by the high susceptibility of terminal olefins to isomerization into less reactive internal olefins. A cascade olefin metathesis with excess ethylene prior to the copolymerization will ensure that all of the comonomers contain a terminal olefin.

In conclusion, synthetic strategies combining insertion polymerization and olefin metathesis have been gaining much attention in recent research. The complementarity of these catalytic reactions enables the synthesis of polyolefins with unique topology and composition. Three approaches have been developed over the years to harvest the strength of these catalytic reactions: insertion polymerization first, olefin metathesis first, or both reactions in tandem. All of these methods result in polymers with different and unique che-

mical structures. The continuing advances made in olefin polymerization and olefin metathesis suggest that new and exciting discoveries from combining these catalytic reactions will continue to be reported.

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Conflict of interest The authors declare that they have no conflict of interest.

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