

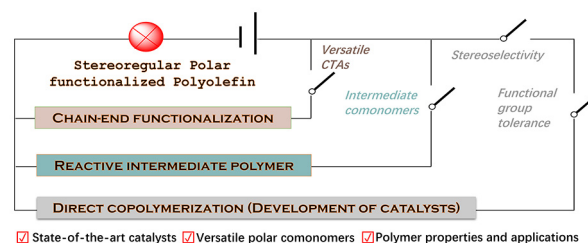
# Stereoselective Copolymerization of Olefin with Polar Monomers to Access Stereoregular Functionalized Polyolefins

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**Abstract** Introducing polar functionalities to polyolefins such as polyethylene and polypropylene is highly desirable for improving physical properties of the otherwise non-polar material. The synthesis of stereoregular functionalized polyolefins, however, has been a relatively underdeveloped area compared to that of functionalized polyethylene because of the lack of suitable catalysts that tolerate polar groups while possessing stereoselectivity. This review summarizes recent advances concerning the access to stereoregular functionalized polyolefins, including synthetic strategies such as post-functionalization, chain transfer and direct copolymerization methods. The focus of the review lies in the copolymerization approach, in which various polar comonomers and versatile stereoselective polymerization catalysts based on both early and late transition metals are involved. Polymer properties and potential applications for these materials are simply discussed.

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**Key words:** polypropylene, isotactic, stereoregularity, functionalized polyolefins, stereoselective polymerization, poly( $\alpha$ -olefin)s

## 1. Introduction

The importance of stereochemistry has been clearly seen in the painful experience related to small-molecule drug thalidomide.<sup>1</sup> Regarding physical properties, chirality generally does not matter much for small molecules, but stereoregularity for polymers often leads to huge differences. In this aspect, the effect of geometric isomerism in polyisoprene (i.e., natural rubber versus gutta percha) constitutes a well-known comparison. Thus, precise control of stereochemistry has long been an important goal pursued by synthetic polymer chemists for accessing polymers with tailor-made properties.<sup>2</sup> The development of stereoselective polymerization of monomers such as acrylates,<sup>3</sup> lactides,<sup>4</sup> vinyl ethers,<sup>5</sup> and carbenes<sup>6</sup> also reflects the crucial role of stereochemistry in polymer synthesis.

In 1954, heterogeneous early transition metal catalysts were used by Natta to prepare crystalline isotactic polypropylene (iPP) with mechanical properties far superior to the amorphous, atactic PP, laying the foundation for iPP to become one of the largest commodity polymers. The development of homogeneous single-site catalysts, especially metallocene catalysts, has greatly facilitated the synthesis of polyolefin with more uniform stereochemistry, composition and molecular weight.<sup>7</sup>

To accommodate wider applications of polyolefins including iPP, additional polar functional groups are needed to improve printability, dyeability, and adhesion to other materials (e.g., metal and wood).<sup>8</sup> For polyethylene, this issue has been partly solved by high-pressure radical copolymerization of ethylene and polar monomers such as vinyl acetate, which unfortunately is not practical for propylene due to the dominant chain transfer tendency in the radical process. The post-functionalization method has been widely used to access functionalized stereoregular poly( $\alpha$ -olefin)s under harsh reaction conditions, which suffers from many side reactions. Although some new efficient post-functionalization methods have been developed later,<sup>9</sup> obstacles are still to be circumvented for practical application. It is thus desirable to establish a coordination polymerization method

## Biosketches



Hongliang Mu was born in Baicheng, China, in 1984. He received his bachelor's degree (2006) in materials science and technology from Jilin University (Changchun, China) and Ph.D. (2013) in polymer chemistry and physics from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (CAS), under the supervision of Prof. Yue-sheng Li. He is currently an associate professor in Changchun Institute of Applied Chemistry, China. His research interests focus on the development of transition metal olefin polymerization catalysts, the preparation of functionalized polyolefin, and synthesis of high-performance polyolefin elastomers.



Zhongbao Jian was born in 1984. He graduated from Sichuan Normal University with a Chemistry bachelor's degree in 2007, and received his Ph.D. in polymer chemistry and physics from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences in 2013, advised by Prof. Dr. Dongmei Cui. From 2013 to 2017, he worked as a postdoctoral researcher (Alexander von Humboldt fellow) at the University of Konstanz (Prof. Dr. Stefan Mecking) and the University of Münster (Prof. Dr. Gerhard Erker) in Germany. He joined Changchun Institute of Applied Chemistry for an independent research career since July 2017. He is now a full professor in Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. His research interest is the development of olefin polymerization catalysts, synthesis and application of high-performance polyolefin materials. He is the recipient of Thieme Chemistry Journals Award (2022), NSFC for Excellent Young Scholars (2021), Youth Science and Technology Award of Jilin Province (2021), and Polymer Young Scholar Award of Chinese Chemical Society (2019).

that can be carried out under mild conditions and allows control over the (co)polymer structure. In this connection, significant progress has been made recently in functionalization of polyethylene, with several newly developed catalysts, and an expansion of polar monomers used for copolymerization.<sup>10</sup> For the functionalization of poly( $\alpha$ -olefins), however, the pace is slowed down by two intertwined factors, namely stereoselectivity and functionality tolerance. Only when  $\alpha$ -olefin polymers have a certain stereoregularity can the materials exhibit adequate strength, while the catalysts with high stereoselectivity are usually sensitive to polar groups,<sup>11</sup> which greatly limits the applicable polar monomers. On the other hand, late transition metals are known for better tolerance toward polar functionalities, but generally fail to control the stereoselectivity.

The isomerism in stereoselective polymerization should include the geometric stereoregularity (*cis* and *trans*) involved in the polymerization of monomers like isoprene, as well as the optical isomerism (tacticity) caused by the presence of chiral carbons in polymers like PP, which is the focus of this mini-review. Differences in tacticity will bring about different polymer microstructures, morphologies, and polymorphisms, which ultimately reflect on the physical and mechanical properties of the material.<sup>2,12</sup> For vinyl polymers, the main tactic configuration types are isotactic, syndiotactic and atactic, which can be expressed as shown in the Figure 1, where the substituents R are all located on the same side as isotactic, and the spacing of the substituents is syndiotactic, and the random distribution of R is called atactic. For poly( $\alpha$ -olefin) materials, the mechanical properties of atactic polymers are not good, and isotactic or syndiotac-

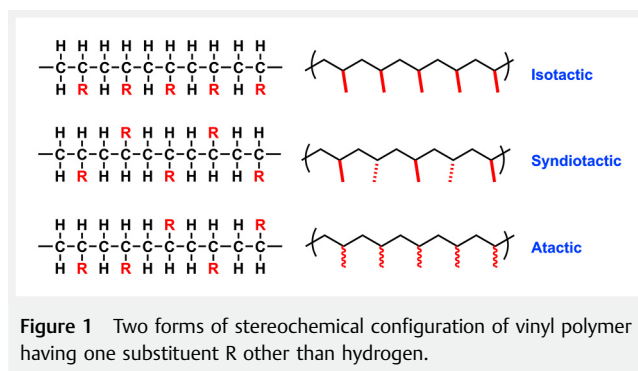


Figure 1 Two forms of stereochemical configuration of vinyl polymer having one substituent R other than hydrogen.

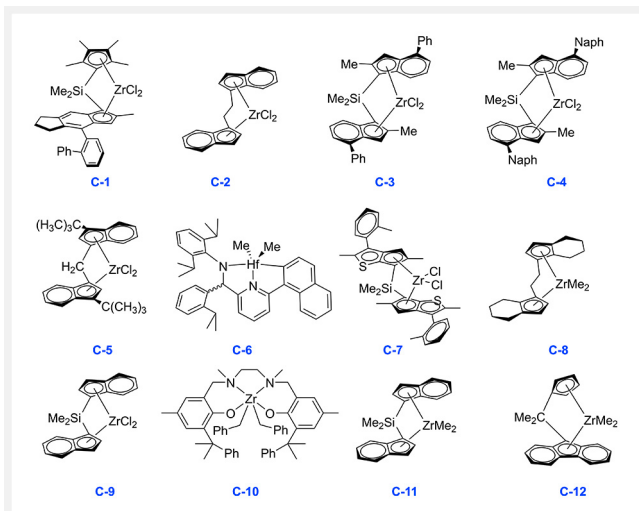
tic polymers obtained with the introduction of polar functional groups by using a proper polymerization catalyst are expected to provide materials with better performance and wider application. The review aims to selectively highlight the results to date on the copolymerization of  $\alpha$ -olefins with polar monomers to prepare functionalized stereoregular polyolefins, which covers different catalyst systems, polar monomers used and the polymer properties and applications.

## 2. Reactive-Intermediate-Polymer Approach to Stereoregular Functionalized Polypropylene

Traditional Ziegler–Natta (Z–N) catalysts are based on strongly oxophilic early transition metals, which are sensi-

tive to Lewis-basic polar functional groups, and some special strategies are thus required to achieve direct copolymerization. The situation for single-site catalysts in this regard is relatively alleviated, since polar functional groups can be hindered from interacting with the active site through careful ligand modification with respect to steric hindrance and/or electronic effects.

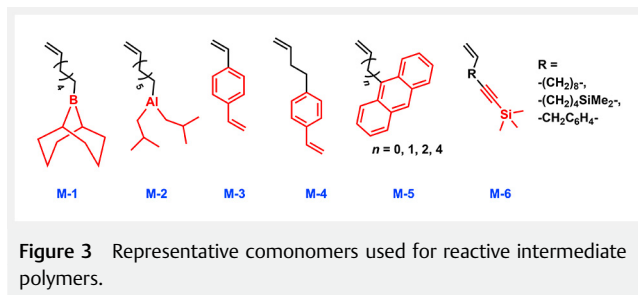
In addition to catalyst modification, an alternative perspective is to design polar monomers. For example, the large steric hindrance around the polar functional group prevents itself from approaching the metal center. Alternatively, convertible yet less poisoning functional groups can be utilized as latent reactive sites for post-functionalization, i.e., “reactive intermediate polymer” strategy.<sup>13</sup> Although additional synthetic effort and transformation steps are needed for this method, it allows the utilization of state-of-the-art early transition metal polymerization catalysts (see Figure 2). This method has thus been rigorously studied, and functional groups that meet such conditions include borane, unsaturated bonds, halogen, etc.<sup>14</sup>



**Figure 2** Selective early transition metal catalysts used for stereoselective copolymerization of olefin with polar monomers.

Borane groups have a low poisoning effect on Z–N catalysts or metallocene catalysts that can realize the stereoregular polymerization of propylene. Therefore, copolymerization of propylene with monomers containing borane groups (e.g., Figure 3, **M-1**) is a feasible route to borane-functionalized polymers. Related comonomers can be readily obtained by the B–H addition to the C=C double bond, and the pendant borane groups can be oxidized to generate free radicals or hydroxyl groups, which can be taken advantage of for subsequent grafting by free-radical<sup>15</sup> or ring-opening polymerization.<sup>16</sup>

Alkenyl-aluminum comonomer **M-2** has also been recently reported to be copolymerized by a C<sub>1</sub>-symmetric zir-



**Figure 3** Representative comonomers used for reactive intermediate polymers.

conocene catalyst (**C-1**) to give a functionalized isotactic copolymer with high activities up to  $2.5 \times 10^8 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ . By treating with CO<sub>2</sub> or O<sub>2</sub> in a one-pot process, ionomers with small amounts of ion clusters and improved processability can be obtained.<sup>17</sup>

Isospecific copolymerization of propylene and 1,4-divinylbenzene (**M-3**) can be achieved by using a MgCl<sub>2</sub>-supported Z–N catalyst. The resultant copolymer containing pendant styrene groups (0.65 mol%) can be used as an intermediate polymer for post-functionalization via atom transfer radical polymerization or anionic polymerization routes.<sup>14c</sup> Interestingly, conventional C<sub>2</sub>-symmetric *ansa*-metallocene catalysts such as *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> (**C-2**) and *rac*-Me<sub>2</sub>Si(2-Me-4-Ph-Ind)<sub>2</sub>ZrCl<sub>2</sub> (**C-3**) are unable to copolymerize propylene and styrene derivatives due to their conflicting regioselectivity, which can be dealt with by using a bulky catalyst (*rac*-CH<sub>2</sub>(3-<sup>t</sup>Bu-1-Ind)<sub>2</sub>ZrCl<sub>2</sub>) (**C-5**) that reverses the regioselectivity of styrene insertion.<sup>18</sup> The pyridylamino hafnium catalyst (**C-6**) is an efficient non-metallocene catalyst for the isospecific polymerization of propylene, during which the styrene moiety of monomer *p*-(3-but-1-enyl)styrene (**M-4**) can be preserved to give *i*PP (*mmmm* > 0.99) with pendant styrene groups for further transformations.<sup>19</sup>

Anthracene-containing  $\alpha$ -olefins **M-5** of various chain lengths can be used in copolymerization with propylene ( $> 2 \times 10^6 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ ). The anthracene group is compatible with hafnium catalyst **C-6**, leading to copolymers with versatile properties after subsequent Diels–Alder or other functionalization reactions. Metallocene catalyst **C-2** achieves similar catalytic activity and comonomer incorporation but affords polymers with greatly decreased molecular weight ( $< 1.8 \times 10^4$ ).<sup>20</sup>

The alkyne group is an important intermediate for functionalization reactions through the click reaction. However, transition metal catalysts cannot tolerate the acidity of the alkyne group, necessitating the protection by trimethylsilyl group when related compounds are used as comonomers. For example, **M-6** can be copolymerized with propylene using the bulky C<sub>2</sub>-symmetric zirconium catalyst **C-7** to give highly isotactic PP (*mmmm* > 0.94) with activities up to  $6.0 \times 10^6 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ . Subsequent deprotection and click reaction can be carried out in a one-pot process, introducing

polar functional groups such as -COOH or -OH, or grafting polyethylene glycol groups of different molecular weights.<sup>21</sup>

The reactive-intermediate-polymer method is important for the synthesis of functionalized stereoregular polyolefins, which allows the use of state-of-the-art metallocene catalysts developed many years ago. While versatile subsequent functionalization is available by using this method, the merits, however, are at least partly overshadowed by the additional synthetic steps and high cost.

### 3. Preparation of Stereoregular Functionalized Polypropylene by Chain-End Functionalization

In addition to the above-mentioned random copolymerization method to introduce intermediate functional groups, an alternative approach for polyolefin functionalization is to prepare end-group-functionalized copolymers followed by block-grafting reactions. An interesting example is the stereoselective polymerization of  $\alpha$ -olefin by the  $V(acac)_3/Et_2AlCl$  system, in which the metal-carbon bond can be easily converted for subsequent polymerization reactions to give block copolymers on the basis of this end-functionalized syndiotactic PP (sPP).<sup>22</sup> Of course, such a system is very special, and other examples to generate chain-end-functionalized polymers require exquisite control over chain transfer reactions. For example, through the screening of catalysts and the control of polymerization conditions, *i*PP materials dominated by unsaturated end groups can be obtained, enabling further functionalization and chain extensions.<sup>23</sup>

A more practical approach to access end-functionalized polyolefins relies on the help of chain transfer agents (CTAs) during  $\alpha$ -olefin polymerization. As compared to that for ethylene polymerization, the difficulty in exploring matching CTAs is accentuated by the lack of catalysts for stereoregular  $\alpha$ -olefins polymerization.

Dialkylboranes containing B-H bonds, such as 9-borabicyclo[3.3.1]-nonane, are known efficient CTAs for metallocene-catalyzed propylene polymerization, resulting in borane-terminated *i*PP, which facilitates the introduction of hydroxy groups or radicals for chain extension reactions (Figure 4a).<sup>24</sup>

In propylene polymerization promoted by Z-N or metallocene catalysts, alkyl aluminum or alkyl zinc also plays a role of CTAs. The resultant end-capped *i*PP can be readily converted to hydroxyl-functionalized polymers and block copolymers (Figure 4b).<sup>25</sup> By using a  $C_2$  symmetric isoselective zirconocene catalyst **C-4**, *i*PP terminated by aluminum alkyl can be obtained under suitable conditions,<sup>26</sup> which is useful for further grafting reactions.

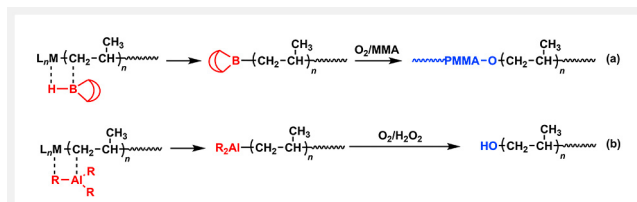


Figure 4 Chain transfer in the presence of CTA during stereoselective propylene polymerization and subsequent functionalization.

*para*-Substituted styrene derivatives in combination with hydrogen play a role of CTA for metallocene-mediated polymerizations. The styryl-capped *i*PP thus obtained directly reacts with caprolactone to give a PP-*b*-PCL block copolymer, which is a good compatibilizer for PP and PCL (polycaprolactone),<sup>27</sup> and also finds applications in PP/clay nanocomposites.<sup>28</sup> Similarly, the consecutive chain transfer to norbornadiene/hydrogen gives unsaturated end groups, which after further transformation can initiate free-radical polymerizations.<sup>29</sup> Under the induction of norbornene, selective  $\beta$ -methyl elimination may also occur to afford sPP with unsaturated end groups.<sup>30</sup> Using the monomer 1,3-diisopropenylbenzene, isospecific propylene polymerization can be achieved to afford a polymer with both ends being unsaturated. Based on this, triblock amphiphilic copolymers with *i*PP in the middle can be prepared after functionalization.<sup>31</sup>

The development of efficient CTA is crucial for the synthesis of end-group-functionalized polyolefins and subsequent chain extension reactions, and the simultaneous explorations of new catalysts will definitely be fruitful.

### 4. Stereoselective Copolymerization of Propylene and Polar Monomers by Early Transition Metal Catalysts

Most of the catalysts applied to the direct stereoselective copolymerization of propylene and polar monomers are metallocene or non-metallocene catalysts based on early transition metals, while the polar monomers generally have several methylene spacers between the double bond and the polar functional group. The copolymerization of propylene and  $\alpha$ -olefin **M-7** bearing the alkoxyamine group (Figure 5) can be achieved using the  $C_2$ -symmetric metallocene catalyst **C-8** in combination with a borate cocatalyst. The pendant functional groups in the resultant polymer are responsible for the initiation of controlled radical polymerization, which opens the possibility for subsequent grafting reactions, but no data on the polymer tacticity are known.<sup>32</sup> The **C-9**/MAO system is used to copolymerize propylene with allyl alcohol and allyl amine to generate functionalized *i*PP

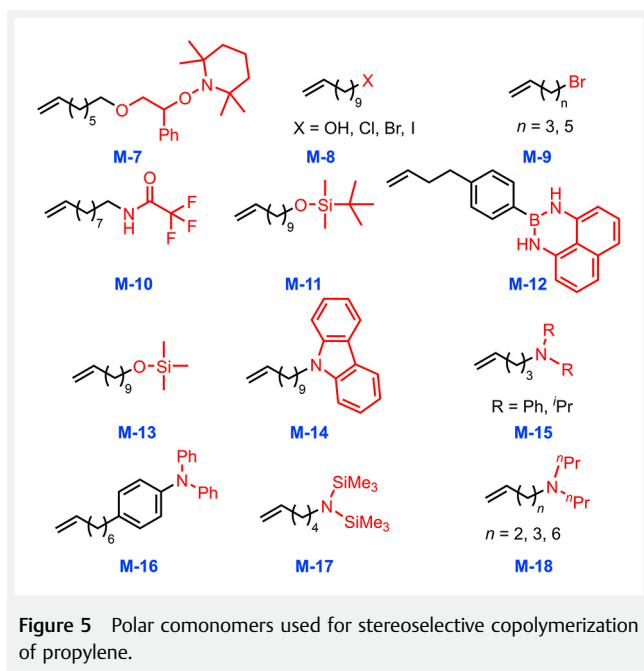


Figure 5 Polar comonomers used for stereoselective copolymerization of propylene.

(*mmmm* = 0.81–0.84). Masking of polar groups with aluminum alkyls is needed considering the proximity of the polar groups to the C=C double bond. Even so, the incorporation of these allyl polar monomers is extremely low (<0.1 mol%).<sup>33</sup> The types of catalyst and masking agent used also have an important influence on the distribution of the polar comonomer units in the polymer chain, which can also be exploited to prepare chain-end-functionalized *i*PP.<sup>34</sup>

Catalyst **C-2** is able to catalyze the copolymerization of propylene and various long-chain polar  $\alpha$ -olefins **M-8** to **M-10**. Of course, the hydroxy group in the comonomer needs to be exposed to alkyl aluminum for protection prior to use. Long-chain polar monomer **M-10** bearing the trifluoroacetamide functional group can be used to generate amine-functionalized *i*PP after simple transformation. The catalytic performance using this polar monomer is similar to that using TIBA-protected long-chain alcohol. The type of aluminum alkyl also has an important influence on the catalytic performance. *tert*-Butyldimethylsilane protection for long-chain alcohol (**M-11**) allows much higher incorporation but a lower polymer molecular weight compared to TIBA.<sup>35</sup>

Boronic acid groups protected by diaminonaphthalene and pinacol ester can be introduced to *i*PP through copolymerization under the catalysis of non-metallocene [N,N,O,O]-zirconium catalyst **C-10**. Diaminonaphthalene protection (**M-12**) leads to a better catalytic activity ( $2.3 \times 10^4 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ ) and minimal impact on isotacticity of the resulting polymer (*mmmm* = 0.90 vs. 0.91 for *i*PP). Dehydrotrimerization of the boronic acids causes in situ cross-

linking, which further improves the strength of the copolymer (yield strength up to  $28.8 \pm 1.3 \text{ MPa}$ ).<sup>36</sup>

Metallocene catalyst **C-3** enables the copolymerization of propylene with 10-undecen-1-oxytrimethylsilane (**M-13**) to give OH-functionalized PP after deprotection, following which *i*PP containing bulky phenol groups is accessed via Steglich esterification. The formed polymeric antioxidant tends to co-crystallize with PP, which is conducive to the introduction of a high concentration of antioxidant groups, effectively improving the thermal oxidation resistance of the PP-based material.<sup>37</sup>

For long-chain monomers containing halogens, 5-bromo-1-pentene (**M-9**,  $n = 3$ ) with less methylene spacers leads to catalyst (**C-2**) deactivation, while 11-chloro-1-undecene (**M-8**, X = Cl) smoothly copolymerizes with propylene to form copolymers with 22 mol% incorporation.<sup>35</sup> 11-Bromo-1-undecene (**M-8**, X = Br) can be used for stereoselective copolymerization, and the resultant copolymer can be coupled with the lithium salt derived from butyllithium-initiated styrene polymerization to afford a graft copolymer of *i*PP and polystyrene (PS) (PP-*g*-PS).<sup>38</sup>

Dow's pyridylamino hafnium catalyst **C-6** for the preparation of olefin block copolymers via chain shuttling polymerization has a very high isoselectivity for propylene polymerization, giving high-molecular-weight polymers. This catalyst has thus been used for the copolymerization of propylene with various polar comonomers.  $\omega$ -Halo- $\alpha$ -alkenes of different chain lengths have been tried and the iodo-alkenes have the least detrimental effect on catalyst performance. High isoselectivity (*mmmm* > 0.99) and a copolymer molecular weight of 134,000 (for 11-iodoundecene, (**M-8**, X = I)) have been achieved (~11.7 mol%). The resultant functionalized copolymer could be conveniently used for subsequent functionalization and grafting reactions.<sup>39</sup> Compared with metallocene catalyst **C-2** bearing a wider coordination space, the hafnium catalyst is less active (typically  $10^5 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ ) but produces polymers with much higher molecular weights (> 100,000).<sup>40</sup>

In addition to halogen, **C-6** also has good tolerance to nitrogen-containing monomer 11-carbazole-1-undecene (**M-14**), yielding functionalized PP (M<sub>w</sub> ~700,000) with incorporation higher than 1.2 mol% and high activities of up to  $4.1 \times 10^6 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ . The obtained carbazole-functionalized *i*PP shows significantly improved mechanical, optical and thermal properties. In contrast, the activity and incorporation for the copolymerization promoted by metallocene **C-2** is slightly inferior, and the molecular weight is an order of magnitude lower.<sup>41</sup> Other nitrogen-containing monomers **M-15** and **M-16** can also be copolymerized with propylene to give high-molecular-weight functionalized *i*PP with activities generally higher than  $10^6 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ .<sup>42</sup> The poisoning effect on the catalyst is stronger when the nitrogen atom is protected by smaller substituents (no activity when R = Me and Et), which is consistent with the situation in pre-

vious work where bulky silane protection (**M-17**) was needed.<sup>43</sup>

Recently, it was found that the dimethyl metallocene catalysts *rac*-[Me<sub>2</sub>Si(indenyl)<sub>2</sub>]ZrMe<sub>2</sub> (**C-11**) and [Me<sub>2</sub>C(Cp)(fluorenyl)]ZrMe<sub>2</sub> (**C-12**) could promote the copolymerization of propylene and amino-olefin monomers **M-18** in the absence of any alkyl aluminum. The good tolerance is reflected in the high catalytic activity (up to  $5.4 \times 10^6 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ ) and satisfactory comonomer incorporation (0.4–4.0 mol%). More interestingly, such monomers or free amines are found to significantly improve stereoselectivity, a phenomenon that is potentially useful to increase the content of polar monomers while maintaining a high polymer melting point (high stereoregularity).<sup>44</sup>

One of the important applications of the stereoselective copolymerization of propylene with polar monomer is in the synthesis of PP ionomers. Polyethylene ionomers are commercially available as established polymer products, and these polymers prepared by free-radical polymerization methods exhibit excellent mechanical properties. In contrast, the development of PP ionomers has been sluggish. It has been reported that PP ionomers can be prepared by reactive extrusion grafting followed by titrating with metal salts, during which a serious decrease in polymer molecular weight is expected due to harsh reaction conditions.<sup>45</sup> To obtain highly crystalline *i*PP ionomers, the Z–N catalyst has been used for the copolymerization of propylene and 10-undecenoate pretreated with diethylaluminum chloride, followed by acidification and neutralization, which results in low incorporation and broad molecular weight distribution.<sup>46</sup> Through Z–N catalyzed copolymerization of propylene with branched diene, 7-methyl-1,6-octadiene, the resultant *i*PP with pendant double bonds, can be converted to the target ionomer through sulfonation.<sup>47</sup> Metallocene catalyst **C-3/d**-MAO is efficient for the copolymerization of propylene and **M-17**, giving the *i*PP ionomer after treatment with HCl and neutralization before exposure to air (Figure 6a), and its mechanical properties are significantly higher than those of the raw PP material and commercial ethylene-acrylate ionomer DuPont Surlyn<sup>®</sup>.<sup>43</sup> Iodine-functionalized *i*PP synthesized using the aforementioned pyri-

dylamino hafnium catalyst can also undergo a quaternization reaction with triethylamine or *N*-methylimidazole to form *i*PP-based ionomers, and the properties of this material can be further optimized by anion exchange (Figure 6b).<sup>48</sup>

## 5. Stereoselective Copolymerization of Propylene with Polar Monomers by Late Transition Metal Catalysts

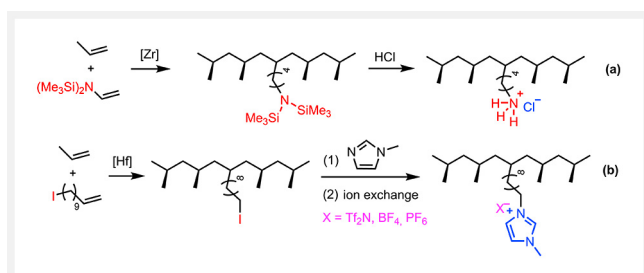
Compared with the copolymerization of ethylene and polar monomers, propylene stereoselective copolymerization is an underdeveloped field. The presence of polar monomers excludes many early transition metal systems that stand out in stereoregular polymerization, while the requirement in stereoselectivity for propylene polymerization eliminates many late transition metal catalysts that are tolerant toward polar functionalities.

As for the limited late transition metal catalysts used in stereospecific olefin polymerization, Nozaki and coworkers have summarized them in a recent review article.<sup>49</sup> While Brookhart's  $\alpha$ -diimine palladium catalysts enable the copolymerization of propylene and maleic anhydride (MA), the resultant copolymers are amorphous due to lack of stereoregularity,<sup>50</sup> which still perplexes polymer chemists even after several major upgrades for  $\alpha$ -diimine catalysts. Control of stereoselectivity for propylene homopolymerization using nickel  $\alpha$ -diimine catalyst is only possible under special polymerization conditions, rendering the copolymerization inexecutable.<sup>51</sup>

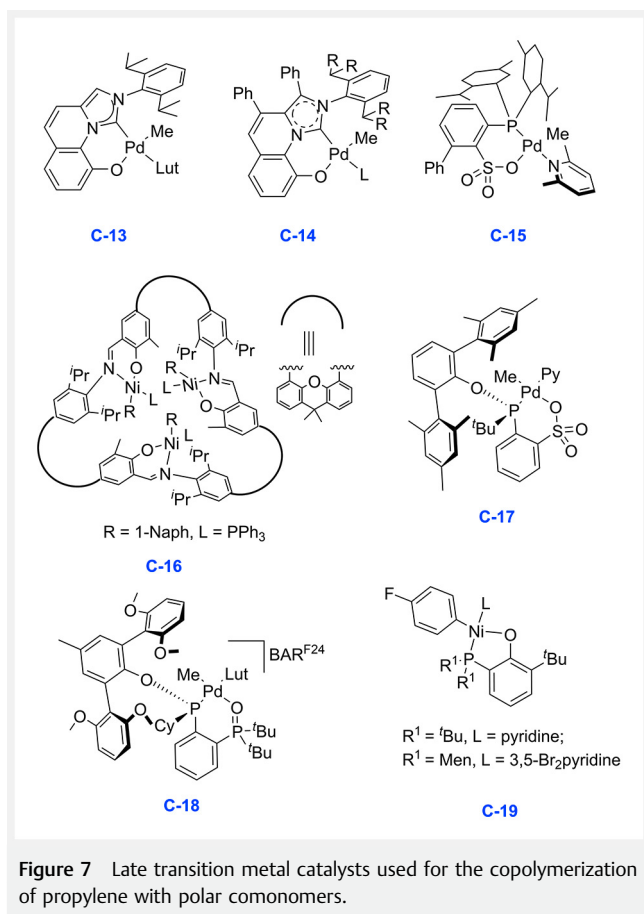
Carbene-phenolate palladium catalysts (**C-13**, Figure 7) are able to promote the regioselective copolymerization of propylene and polar monomers such as MA and allyl polar monomers with low catalytic activity (up to  $5.4 \times 10^3 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ ) and incorporation (<2.0 mol%).<sup>52</sup> A similar system based on abnormal carbene palladium (**C-14**) incorporates a higher amount of polar monomers (3.1 mol% allyl acetate). However, no polymer stereoselectivity has been reported for these two catalysts.<sup>53</sup>

By introducing a methyl group to the phosphine-sulfonate palladium catalyst (**C-15**), the molecular weight and regioselectivity can both be greatly improved. A large substituent at the *ortho*-position of the sulfonate group facilitates enantiomorphic site control, which is beneficial for obtaining functionalized PP materials with moderate isotacticity (*mm* = 0.55–0.59), and the incorporation of polar groups reaches 1–3 mol%.<sup>54</sup>

Macrocyclic trinuclear neutral nickel catalyst (**C-16**) homopolymerizes propylene to a isotactic polymer ( $< 1.2 \times 10^3 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ ), but no data concerning the copolymerization with polar monomers have been reported.<sup>55</sup> The new synthetic method developed by Nozaki is beneficial for rapid catalyst screening, providing a series of P-stereogenic



**Figure 6** *i*PP ionomer preparation through stereoselective copolymerization and subsequent functionalization.



phosphine-sulfonate (e.g., **C-17**) and BPMP palladium catalysts (e.g., **C-18**).<sup>56</sup> These catalysts are applicable for the copolymerization of propylene with various polar monomers including MA and polar allyl monomers containing -Cl, -CN and -OAc groups, among which the propylene/allyl acetate copolymerization shows the best isoselectivity ( $mm = 0.74$ ).

Phosphine-phenolate neutral nickel catalysts **C-19** are active for the copolymerization of propylene with *tert*-butyl allylcarbamate or but-3-en-1-ol whose polar functional group is not directly connected to a double bond, giving a functionalized PP material with moderate isotacticity ( $mm = 0.65$ ).<sup>57</sup> In situ generated BPMP nickel catalysts or a preformed  $\eta^3$ -allylnickel/MMAO system copolymerizes propylene with allyl acetate, but the activity and incorporation are low, and the obtained copolymer is stereoirregular.<sup>58</sup>

In general, stereoselective polymerization of propylene with late transition metal catalysts is scarce, the challenge of which is certainly scaled up by the involvement of polar functional groups. Future work should be centered on the improvement on stereoregularity, catalytic activity, and comonomer incorporation. Guidelines in these aspects for late transition metal catalysts are still lacking, which warrants

extensive experimental studies combined with theoretical calculations.

## 6. Stereoselective Copolymerization of $\alpha$ -Olefins with Polar Monomers

Similar to the case for propylene, most of the late transition metal catalysts fail to mediate stereoregular polymerization of  $\alpha$ -olefins under normal conditions, as well as the copolymerization of  $\alpha$ -olefin with polar monomers. Alternatively, chain walking polymerization may occur, and again a stereoregular polymer cannot be obtained.<sup>59</sup>

Metallocene catalyst **C-8** in combination with borate [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] is able to copolymerize 1-hexene or 4-methyl-1-pentene with amine-containing monomer **M-15** (R = *i*Pr) to yield isotactic functionalized poly( $\alpha$ -olefin)s, but the copolymers of 1-hexene are still amorphous. Polar monomers greatly suppress polymerization, while the polymer properties such as decomposition temperature are significantly improved with the increasing functional group content.<sup>60</sup> Metallocene **C-2** catalyzes the copolymerization of 1-hexene and halogen-containing monomer **M-8** (X = Cl) to give a copolymer with molecular weight up to 20,000, but no stereoregularity data are reported.<sup>61</sup>

Copolymerization of 1-butene and eugenol can be achieved using a Z-N catalyst supported by MgCl<sub>2</sub> to give a functionalized *i*PP with molecular weight of tens of thousands and a broad molecular weight distribution. With the increase of eugenol incorporation, the isotacticity of the copolymer decreases, but at the same time the polymer molecular weight increases. While the incorporation of polar monomer eugenol is low (~0.62 mol%), it is adequate to improve the thermal-oxidative stability of the polymer.<sup>62</sup> Eugenol, as a polar allylbenzene monomer, has been reported to copolymerize with ethylene mediated by late transition metals which have no stereoselectivity for  $\alpha$ -olefin polymerization.<sup>63</sup>

In contrast to the case for PP, PS of atactic type (*a*PS) has better commercial applications than its syndio- and isotactic counterparts. *a*PS is an amorphous polymer with high glass transition temperature (100 °C), while *i*PS has little commercial use due to its very low crystallization rate. *s*PS possesses good chemical resistance and mechanical properties, but its high melting point (> 265 °C) requires processing at very high temperatures, which may lead to polymer decomposition.<sup>64</sup> Due to the lack of polar functional groups, surface properties of PS materials are poor, which could be solved post-functionalization.<sup>65</sup> Similar to the situation of PP functionalization, direct stereoselective copolymerization of styrene and polar monomers is also challenging.

A fluorenyl yttrium catalyst containing a pyridyl group enables the highly syndiotactic copolymerization of styrene and various methoxy-substituted styrenes, and the substi-

tution pattern has an important influence on catalytic activity.<sup>66</sup>

Alternating copolymerization of styrene and allylbenzene monomers with polar functional groups can be achieved with half-metallocene rare earth metal catalysts, giving rise to copolymers with interesting co-syndiotactic stereoselectivity ( $rrrr > 0.99$ ).<sup>67</sup>

## 7. Stereoselective Homopolymerization of Polar Monomers

Homopolymers of polar vinyl monomers such as methyl methacrylate and vinyl ethers can be viewed as highly functionalized polyolefins, and stereoregularity certainly imparts additional properties to these polyolefin materials. The stereoselective polymerization of most polar vinyl monomers containing oxygen, nitrogen or phosphorous atoms have been rigorously summarized in review articles.<sup>68</sup>

While the stereoselective polymerization of methyl methacrylate has been well established, only a few examples of ionic or radical polymerization of methyl acrylate at low temperature have been reported. It is possible to control the stereochemistry of the first inserted MA by using an asymmetrically substituted phosphine-sulfonate palladium catalyst; however, the selectivity cannot be maintained after the insertion of the second MA due to a conflict between the enantiomeric site and the chain-end control. Increasing the steric hindrance of the substituents on phosphorus is also not helpful because of the accompanied worse regioselectivity.<sup>69</sup> The introduction of carbon monoxide spacers would weaken the chain-end control mechanism, making the stereoregularity of the polymer completely controlled by the chiral catalyst, giving stereoselective copolymers.<sup>70</sup>

For linear polar  $\alpha$ -olefins possessing O- and S-containing groups and methylene spacers of different lengths (e.g., **M-19**, Figure 8), half-sandwich rare-earth metal catalysts (e.g., **C-20**) exhibit favorable catalytic performance to give highly syndiotactic ( $rrrr > 0.95$ ) homopolymers.<sup>71</sup> Ligands

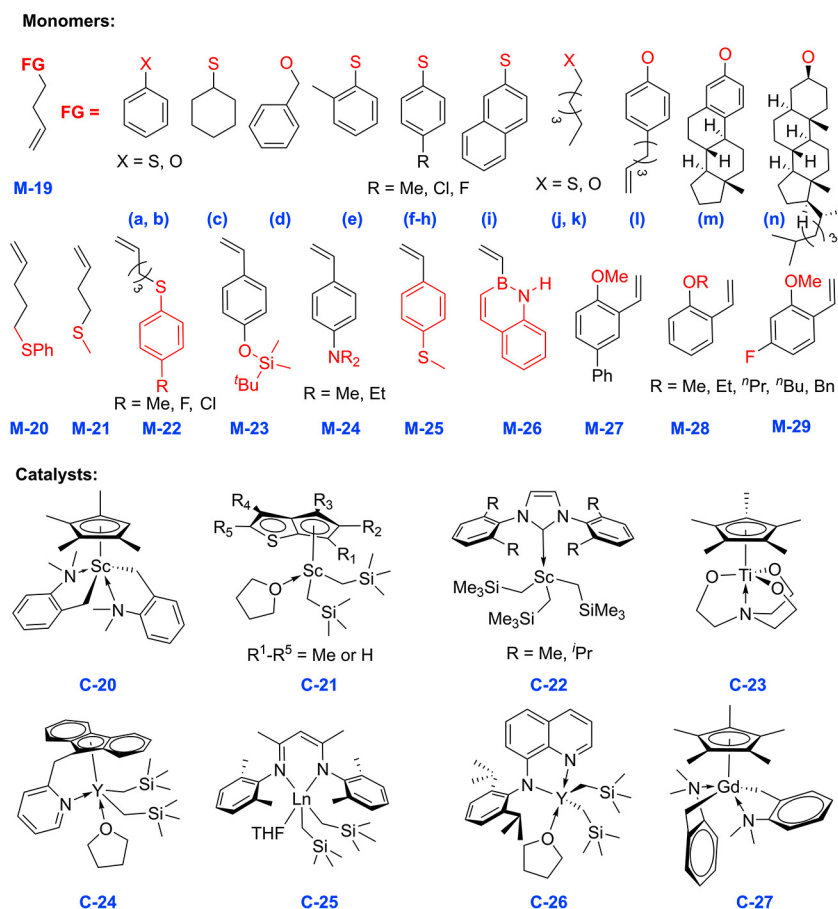


Figure 8 Polar monomers and catalysts used in stereoselective homopolymerization.



of this type of catalysts also have great influence on the catalytic performance when using different comonomers; for example, the indenyl analogue of **C-20** furnishes more polymer and leads to higher syndiotacticity when a comonomer bearing a  $\beta$ -cholestanoy substituent (**M-19 n**) and longer spacers (**M-20**) is used, respectively. The linear 4-methylthio-1-butene (**M-21**) monomer undergoes smooth highly syndiotactic polymerization under the catalysis of half-metallocene scandium **C-21**, while its non-polar analogue (1-hexene) can only be polymerized in very low activity, which is attributed to the “self-activation” between the polar groups and catalyst active centers.<sup>72</sup> Crystalline sulfur-containing poly( $\alpha$ -olefin) (**M-22**) can be accessed by using the carbene-ligated scandium complex **C-22**/borate system, during which a highly syndiotactic ( $rrrr = 0.95$ ) polymer with high melting temperature (91 °C) is obtained.<sup>73</sup>

The half-metallocene titanium catalyst **C-23** bearing the triethoxyamine ligand promotes the polymerization of silyloxy- and amine-functionalized styrene **M-23** and **M-24** to give syndiotactic polymers.<sup>74</sup> Homopolymerization of 4-methylthiostyrene **M-25** can be achieved with a very high syndioselectivity ( $rrrr > 0.99$ ) under the catalysis of half-metallocene rare earth metal catalysts **C-24**.<sup>75</sup> B–N hybrid styrenic monomer **M-27** can be converted to syndiotactic polymers by a half-titanocene catalyst. Such compounds can be oxidized under alkaline conditions to give syndiotactic polyvinyl alcohol, which avoids the limitations via cationic and free-radical pathways.<sup>76</sup> Bulky functionalized monomer 2-methoxy-5-phenylstyrene (**M-27**) can also be polymerized by catalysts **C-22** and **C-25** in syndiotactic and isotactic fashions, respectively.<sup>77</sup> For the polymerization of various alkoxy-substituted styrene monomers (**M-27** to **M-29**) catalyzed by quinolyl anilido yttrium (**C-26**), the syndiotactic selectivity is largely affected by the substituent.<sup>78</sup> Half-sandwich rare-earth catalyst **C-27** showed different properties when catalyzing the polymerization of substituted styrene monomers with methoxy groups at different positions; polymerization of *meta*- and *para*-substituted styrenes could orthogonally undergo C–H activation and C=C insertion reactions to form interesting branched structures, while *o*-OMe styrene undergoes normal coordination polymerization to yield sPS.<sup>79</sup>

By contrast, the synthesis of *i*PS is more difficult. Earlier, polymers of 2-methoxyl styrene with low isotacticity were only obtained by anionic polymerization at very low temperature.<sup>80</sup>  $\beta$ -diketiminato rare-earth-metal catalysts **C-25** were then found to generate high-molecular-weight highly isotactic ( $mmmm > 0.99$ ) polymers with this polar styrene.<sup>81</sup> The resultant polymer crystallizes faster than conventional nonpolar *i*PS, which is of interest for the industrial application of this material.

## 8. Polymer Properties and Potential Applications

The polymer structure determines its various properties and also potential applications. Stereoregularity is undoubtedly a very important property of polymers, including polyolefins. Isotactic PP as one of the largest volume commodity polymers has tremendous applications thanks to its excellent physical and mechanical properties and processability. Brittleness and other shortcomings derived from the nonpolar nature of PP could be overcome by functionalization and/or blending modification, through which *i*PP-based polymers could be obtained with enhanced properties in ductility, aging resistance, transparency, flame retardation, anti-static properties, etc.

MA-grafted PP, commonly obtained by coextrusion of PP and MA under temperatures higher than the melting temperature of PP, is the most prominent example of functionalized PP (e.g., Mitsui's ADMER®). This material has much better printability and adhesion to polar materials, and thus finds application as a compatibilizer of PP/polyamide,<sup>82</sup> PP/EVOH (ethylene-vinyl alcohol copolymer),<sup>83</sup> PP/wood and PP blends with various inorganic additives.<sup>84</sup> PP-PCL block and graft copolymers can be used as a compatibilizer for the blend of otherwise immiscible PP and polycarbonate or used as a nanoporous membrane.<sup>85</sup> These results have recently been summarized by Duchateau et al.<sup>86</sup>

Stereoregular polymers also have very important applications in other special fields, such as polymer dielectric capacitors, in which energy density, dielectric loss and breakdown strength are all parameters that matter much for practical applications.<sup>87</sup> The most well-known example is biaxially oriented PP (BOPP), an *i*PP material with very low dielectric losses but low energy density (~2 J/cm<sup>3</sup> at electric field strengths ~600 MV/m).

The low energy density for PP is determined by its relatively low dielectric constant “ $\epsilon$ ” originated from small  $\sigma$ -electron polarization. Introduction of long alkyl chains and siloxane groups effectively improves the  $\epsilon$  of PP materials.<sup>88</sup> These groups reduce the crystallinity of the polymer and improve the mobility of the segment in the amorphous phase, thereby enhancing the dipole orientation in the electric field. The poor reversibility of this influence within the scale of capacitor application causes the sensitivity of  $\epsilon$  to temperature and frequency, and also obvious dielectric loss.

Introducing hydroxyl groups effectively eliminates the above problems by hydrogen-bond interaction, and 2 to 3 times the energy density of BOPP is achieved under the premise of low energy loss.<sup>88</sup> The beneficial influence of hydrogen bonding could be affected by bulky groups, and different comonomer sequences derived from different catalysts could also play a very crucial role in influencing dielectric properties.<sup>37</sup> Cross-linking is another way to increase

the energy density because of improved breakdown strength. In addition, the limited segment mobility also ensures the reversibility of its polarization and reduces the energy loss.<sup>89</sup>

Recently, poly(4-methyl-1-pentene) containing covalent-bonded zwitterions was reported to be excellent polymer capacitors. The motion of ions is confined by the covalent bonds, and formation of large ion clusters is prevented so that the large dipole moments can be efficiently used to increase  $\epsilon$ . In addition, ion clusters can trap charges, which reduces the electrical conductivity at high electric field, improving breakdown strength.<sup>90</sup> The breakdown strength ( $1300 \text{ MV}\cdot\text{m}^{-1}$ ) and energy density ( $35 \text{ J}\cdot\text{cm}^{-3}$ ) achieved in this work are the highest reported so far.

It is noteworthy that functionalized stereoregular polyolefins prepared by post-functionalization methods are currently used industrially despite the ill-defined polymer structure and deteriorated polymer properties, while those synthesized by copolymerization have been limited to small-scale studies in laboratories due to high cost of specially designed comonomers. Considering the well-defined structure and favorable properties of these copolymers, however, related exploration is still necessary, which could possibly be even desirable in case of emergence of efficient synthetic methods for the comonomers or high-performance copolymerization catalysts.

## 9. Conclusions and Outlook

Although atactic polymers such as PMMA and PS have found good commercial applications, stereoregularity of polymers will undoubtedly bring more potentially excellent properties, which have been seen in the polymerization of monomers such as propylene oxide and vinyl ethers, despite that these materials have not yet been commercialized on a large scale. For olefinic polymers such as PP, which has been used on a large scale, stereoregularity is particularly important, and the preparation of the corresponding polar functionalized materials is also of great industrial interest. Post-polymerization functionalization is a commercial method; its unfavorable side reactions under harsh reaction conditions tend to damage polymer properties; and this method does not allow access to polymers with well-defined structures.

For the stereoselective (co)polymerization of propylene or  $\alpha$ -olefins with polar monomers, it is challenging and highly desirable to develop suitable catalysts or regulation strategies to impose better stereoregularity control and enhance polar-functional-group tolerance. While stereoselective polymerization using early transition metal catalysts has been in use for many years, the applied comonomers are still limited to those with remote polar functional groups; even so, protecting groups and/or masking agents

are generally needed, which warrants more new and robust catalysts with high polar functional group tolerance. Late transition metal catalysts have good functional group tolerance, and related research on copolymerization of ethylene with polar monomers has recently made tremendous progress. The stereoselective polymerization, however, is progressing slowly, and the current state-of-the-art of these catalysts is definitely unable to fulfill the requirements of this topic. More communication and coalescence between the respective designing principles of early and late transition metal systems may be helpful to give birth to new efficient catalyst systems. In this connection, theoretical calculation should be given due attention, and be perfectly combined with experimental methods so that it not only explains results but also guides catalyst designing. Development of catalysts will still be a research hotspot for the preparation of stereoregular functionalized polyolefins, which will also be crucial in promoting the functionalization of other  $\alpha$ -olefin-related materials such as propylene-based elastomers.

Considering that there are already abundant varieties of non-polar stereoregular polyolefin materials, the development of efficient functionalization methods is obviously an attractive alternative from the perspective of practical application. In addition, in parallel with the continuous invention of efficient catalysts and functionalization methods, the potential application of the new functionalized stereoregular polymers should be concurrently explored. Of course, this can also be a demand-oriented designing process that can be started by the needs for certain functional polymers.

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## Conflict of Interest

The authors declare no conflict of interest.

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