A Journal of the Gesellschaft Deutscher Chemiker
Angewandte Chemie
International Edition
www.angewandte.org

Accepted Article

Title: Early Transition Metal Catalysis for Olefin-Polar Monomer Copolymerization

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To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.202000060
Angew. Chem. 10.1002/ange.202000060

Link to VoR: http://dx.doi.org/10.1002/anie.202000060
http://dx.doi.org/10.1002/ange.202000060

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Angewandte Chemie International Edition
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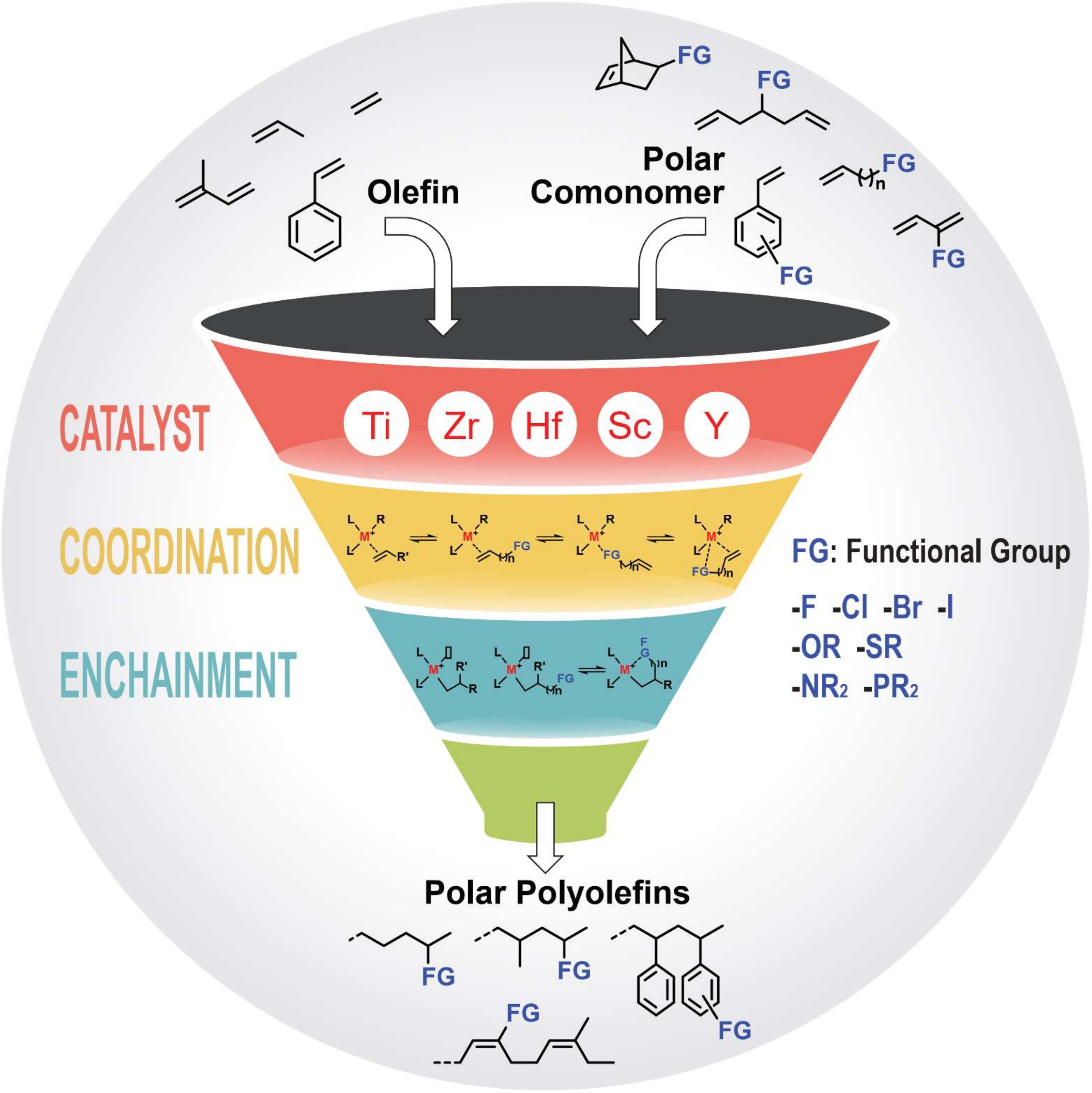
MINIREVIEW

Early Transition Metal Catalysis for Olefin-Polar Monomer Copolymerization

Jiazhen Chen, Yanshan Gao,* and Tobin J. Marks*



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Abstract: Introducing polar functional groups into widely used polyolefins can enhance polymer surface, rheological, mixing, and other properties, potentiallly upgrading polyolefins for advanced, value-added applications. The metal catalyst-mediated copolymerization of non-polar olefins with polar comonomers represents the seemingly most straightforward, atom- and energy-efficient approach for synthesizing polar functionalized polyolefins. However, electrophilic early transition metal (groups 3 and 4)-catalyzed processes which have achieved remarkable success in conventional olefin polymerizations, encounter severe limitations here, associated with the Lewis basicity of the polar co-monomers. In recent years, however, new catalytic systems have been developed and successful strategies have emerged. In this minireview, we summarize the recent progress in early transition metal polymerization catalyst development, categorized by the catalytic metal complex and polar comonomer identity. Furthermore, we discuss advances in the mechnistic understanding of these polymerizations, focusing on critical challenges and strategies that mitigate them.

1. Introduction

Polyolefins such as polyethylene and polypropylene are the most widely used polymeric materials worldwide.[1] Polymerizations of simple monomers such as ethylene and propylene can generate polymers with vastly different structures and thus, very different materials properties to meet the requirements of numerous applications. Control over the polymer microstructure largely derives from the transition metal catalyst design characteristics and the coordinative polymerization process it enables.

As noted above, introducing functional groups into polyolefins can impart beneficial properties, including adhesion, toughness, electrical conductivity, miscibility, and rheological properties.[2] The wide variety of potential polar monomers and readily available conventional monomers (ethylene, propylene, styrene, isoprene, etc.) in principal offer the opportunity to create polar polyolefins with vastly different microstructures and properties. Here, the direct copolymerization of olefins with polar monomers would seem to provide the most straightforward and atom-economic methodology for introducing polar functionality into polyolefins. Therefore, developing early transition metal catalysts for polar monomer copolymerization has become a topic of intense research.[3]

Despite the aforementioned attractions, polar monomer copolymerizations face challenges arising from the strong interactions between typical Lewis-acidic cationic metal centers and Lewis-basic polar functional groups. Furthermore, if the C=C bond is directly attached to the polar group, the olefinic orbital energies and electronic structure will be significantly altered.[4] These factors present a substantial impediment to vinyl polar monomer enchainment. Nevertheless, late transition metal (Ni, Pd) catalysts have made remarkable progress in addressing these issues, reflecting the lower acidity and oxophilicity than early metal catalysts.[4-5] However, the late metal catalysts exhibit significant limitations, including modest activity and thermal stability, overall poor control over enchainment regio- and stereochemistry, modest M_ns due to competing chain transfer, and limited catalyst performance tunability.[4-5] While groups 3 and 4 catalysts have achieved remarkable success in conventional olefin polymerizations, their efficacy for polar monomers has remained limited, and effective strategies require further refinement.

In this minireview, we summarize recent advances in homogenous catalyst development with emphasis on advances in mechanistic understanding of early transition metal-catalyzed olefin + polar comonomer polymerizations and on the novel resulting polar polyolefin properties. Due to length constraints, the focus here is exclusively on ethylene and propylene. The reader is referred to other literature[6] for recent styrenic and diene work. Lewis basic polar comonomers containing nitrogen, phosphorus, oxygen, sulfur, and halogens are discussed here but not those with significantly less Lewis basic character such as boranes, silanes, or reactive aromatics which were topics of previous reviews.[7] Similarly, lanthanide,[8] middle-transition metal ((V,[9] Fe, Co), and conventional heterogeneous catalysts are beyond the scope of this discussion. While this minireview emphasizes research not covered in previous reviews, some work predating the 2012 Rieger review [7a] is introduced to clarify new insights. Regarding organization, we first discuss the importance and potential impact of transition metal-catalyzed polar monomer copolymerizations, then key parameters used to evaluate catalytic systems, and current issues. We next summarize recent progress in that area, categorized by catalyst and olefin identity. We then summarize advances in mechanistic understanding which relate to polymerization activity and comonomer selectivity. The concluding section deals with generalizations and perspectives.

2. Group 4 Transition Metal Catalysts

2.1. Ethylene copolymerization with polar monomers

Group 4 (Ti, Zr, Hf) d^0 organotransition metal catalysts play a pivotal role in tailoring polyethylene product properties, such as number average molecular mass (M_n), polydispersity (Đ), rheology, branch architecture/density, and block sequence.[10] They have been long-sought candidates for polar monomer copolymerization catalysis.[7] To counter Lewis basic functional group deactivation effects, excess Lewis acidic "masking" reagents such as MAO or AlR_3 have been employed. Nevertheless, few catalytic systems exhibit both high activity and high polar monomer enchainment selectivity.

Imuta[11] reported the one-pot synthesis of hydroxyl-capped polyethylenes mediated by an *ansa*-metallocene having indenyl and fluorenyl π-ligands (**Zr-1**; Figure 1). Excess AlR_3 was used to convert the comonomer hydroxyl to $-OAlR_2$ groups. Alkenols such as 10-undecen-1-ol with long $(CH_2)_n$ spacers can then be enchained.

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Interestingly, allyl alcohol (n = 1) is only introduced at the chain ends with TEA ($AlEt_3$) or TMA ($AlMe_3$) masking reagents. In contrast, TIBA (triisobutylaluminum) or TOA (trioctylaluminum) enable allyl alcohol enchainment at all polyolefin sites. These polymers have 0.2 -1.1 mol% alkenol content with M_w = 10,000 - 60,600 kg/mol at activities of 40 - 120 kg·mol^{-1}·h^{-1}·atm^{-1}.

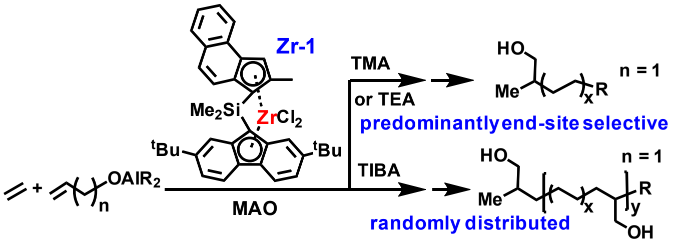

Figure 1. Ethylene + R_3Al-masked ω-alkenol copolymerizations using a **Zr-1** –based catalyst.

Fujita[12] reported that bis(phenoxyiminate)Ti complex **Ti-1**, upon activation with dried methylaluminoxane (dMAO), catalyzes ethylene + 5-hexene-1-yl-acetate copolymerizations with activities up to 515 kg·mol^{-1}·h^{-1}·atm^{-1} and comonomer contents up to 3.2 mol% (Figure 2). Theoretical analysis suggests that more electron-donating ligands create a less electrophilic Ti center which enhances catalytic activity. Tang[13] activated a series of Ti complexes (**Ti-2a**, **Ti-2b**, **Ti-3**) bearing tridentate [ONX] ligands, with modified methylaluminoxane (MMAO), to afford efficient catalysts for copolymerizations of ethylene with ω-alkenols, ω-alkenoic acids, and diphenyl(undec-10-enyl)phosphine. The highest activity was 1.3 x 10^5 kg·mol^{-1}·h^{-1}·atm^{-1} with 0.6 - 11.2 mol% comonomer content. The electronic and steric properties of the ligand pendant substituents strongly influence the copolymerization process. Li[14] then expanded the comonomer scope to 5-norbornene-2-methanol using **Ti-5**, and Hu[15] compared metal and temperature effects on comonomer incorporation for **Ti-4** vs. **Zr-2**. Note that the aluminoxanes used above also plays the role of a masking reagent. Many masked alkenol polar monomer polymerizations are summarized in published reviews.[7]

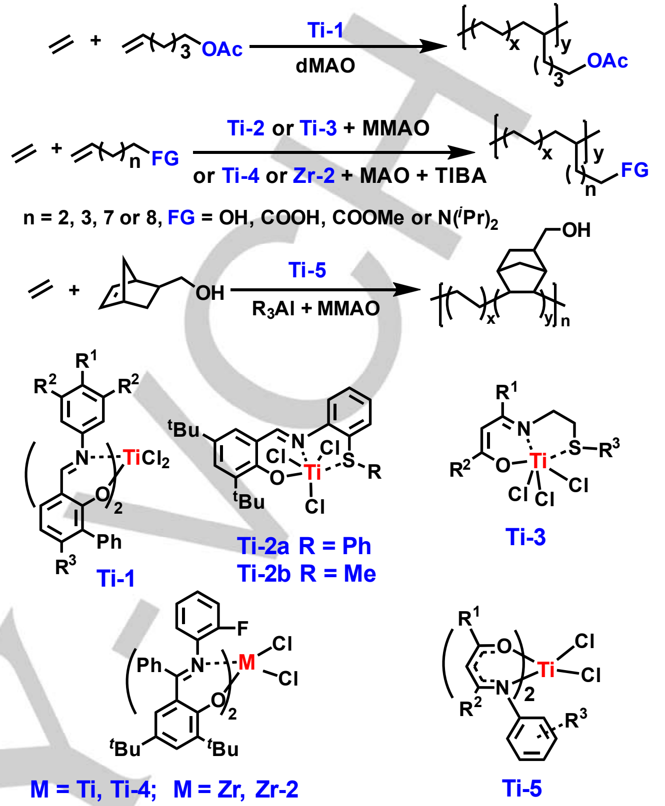

Figure 2. Examples of ethylene + masked polar monomer copolymerizations using bis(phenoxyiminate)Ti/Zr –based catalysts.

Note that the aforementioned examples generally use stoichiometric excesses of Lewis acidic Al alkyl/alkoxide masking reagents, which compromise atom efficiency and increases cost. Furthermore, masking reagents can potentially act as alkylation and/or chain transfer agents, compromising product M_n and hampering rigorous elucidation of reaction mechanism. Motivated by the advantages of masking reagent-free copolymerizations and inspired by Waymouth's work,[16] Marks and coworkers[15] examined a series of group 4 metallocene complexes for ethylene + amino-olefin (CH_2=$CH(CH_2)_nNR_2$, AO) copolymerizations (Figure 3). Group 4 metal precatalysts were activated with 1 equiv. $B(C_6F_5)_3$ (BN) or $(Ph_3C)^+B(C_6F_5)_4^-$ (BT). Precatalyst screening shows that indenyl-based Zr complexes outperform cyclopentadienyl Zr complexes in achieving both high activity and high comonomer incorporation. Comonomer enchainment levels up to 5.5 mol% are achieved with activities up to 3400 kg·mol^{-1}·h^{-1}·atm^{-1} at 0.1 M [AO]. Interestingly, Me_2Si-bridged **Zr-3** incorporates more comonomer than unbridged **Zr-4** under identical conditions, likely reflecting a more sterically open coordination sphere. Contracting the AO chain length dramatically depresses activity, while introducing exogenous N^nPr_3 affects polymerization activity and AO incorporation level only marginally.

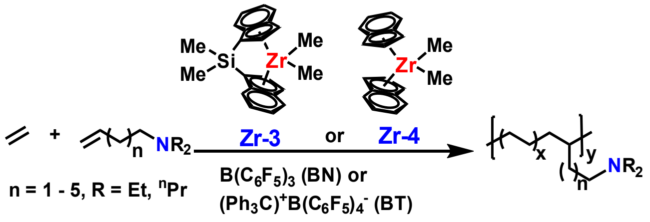

Figure 3. Ethylene + masking reagent-free amino-olefin copolymerizations using **Zr-3** or **Zr-4** –based catalysts.

In addition to ethylene + polar monomer copolymerization, Marks and coworkers[17] reported ethylene + 4-halo styrene copolymerizations using BT-activated mono- and binuclear Ti complexes (Figure 4). Up to 29.8 mol% of 4-fluorostyrene is incorporated with activities up to 1.31 x 10^4 kg·mol^{-1}·h^{-1}·atm^{-1}. Binuclear catalyst **Ti-7** incorporates significantly more functionalized styrene than mononuclear analogue **Ti-6**. The increased comonomer enchainment nuclearity effect follows the same trend as the styrenic ipso carbon π-electron density (F > Cl > Br > H). Note that the corresponding Zr catalysts are inactive for ethylene + styrene copolymerizations.

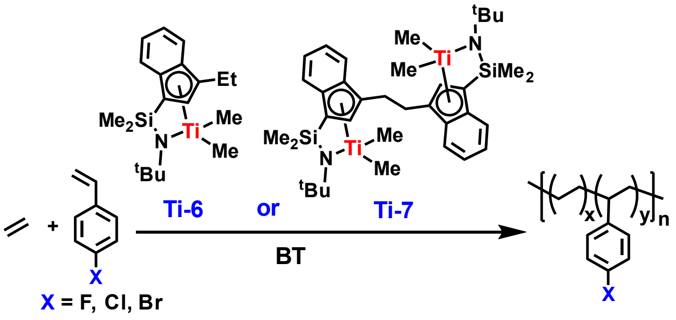

Figure 4. Ethylene + polar styrene copolymerizations using **Ti-6** and **Ti-7** –based catalysts.

2.2. Propylene copolymerizations with polar monomers

Group 4 metal catalysts catalyze propylene polymerization with high activity and precise control over tacticity and regiochemistry,[18] unlike late transition metal catalysts where chain walking processes compromise such control.[19] In contrast to conventional iPPs, functionalized iPPs should deliver widespread applications.

Hagihara and Shiono[20] reported propylene + allyl alcohol/amine (pretreated with AlR_3) copolymerizations using **Zr-3** + MAO/(dMAO + R_3Al) with activities up to 190 kg·mol^{-1}·h^{-1}·atm^{-1} (Figure 5). After aqueous work-up, copolymers with [*mmmm*] >80% are isolated with 0.04 – 0.64 mol% comonomer content. AlR_3-dependent comonomer enchainment was also observed for **Zr-3** catalyzed propylene + allyl amine copolymerizations. With $AlMe_3$ addition/protection, allyl amine is enchained only at the polymer chain ends. With TIBA, allyl amine units are introduced at both the chain ends and within the chain. Such observations echo Imuta's work on **Zr-1**-catalyzed ethylene + allyl alcohol copolymerizations discussed above (Figure 1).[11] Similarly, the polar monomer scope was expanded to longer α-alkenols such as 5-hexen-1-ol,[21] with the resulting polar copolymers exhibiting enhanced mechanical properties versus PP and nonpolar poly(propylene-*co*-1-hexene).[22]

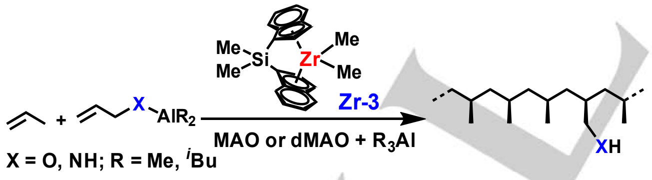

Figure 5. Ethylene + allyl amine or alcohol copolymerizations using an isospecific **Zr-3** –based catalyst

Chung[23] systematically studied the copolymerization of propylene with higher α-olefin comonomers containing silyl-protected amino groups and an isospecific metallocene catalyst (Figure 6). Optimum performance is achieved with **Zr-5**, purified dMAO, and 6-bis-(trimethylsilyl)amino-1-hexene as comonomer. The maximum comonomer incorporation is 4.8 mol% with 380 kg·mol^{-1}·h^{-1}·atm^{-1} activity. Subsequent work-up converts the silane-protected amino groups [-$N(TMS)_2$] to ionic -$NH_3^+Cl^-$ species. The resulting iPP-$NH_3^+Cl^-$ ionomers are melt-processable in air and exhibit systematic increases in mechanical properties and thermal stability with increasing $NH_3^+Cl^-$ content. Using this protecting strategy, pendant hindered phenols can also be introduced into iPP, affording greater oxidative stability and higher dielectric constants with lower loss.[24] Additionally, Eisen[25] showed that this strategy is extendable to polar monomers such as acetamides.

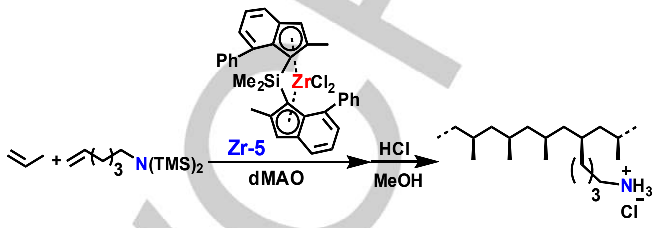

Figure 6. Propylene + $CH_2{=}CH(CH_2)_4N(TMS)_2$ copolymerization using a **Zr-5** –based catalyst

In addition to Ti and Zr catalysts, post-metallocene Hf catalysts have emerged as important single-site catalysts, exhibiting high thermal stability and isoselectivity in propylene polymerizations.[26] Thus, Li[27] used **Hf-1** + BT (2 equiv.) + TIBA (100 equiv.) to catalyze the stereospecific copolymerization of propylene with ω-halo-α-alkenes (Figure 7). High molecular mass (M_w > 100 kg·mol^{-1}) functional iPPs possessing up to 11.7 mol% iodoalkene units and Đ≈2 are obtained under mild conditions with [*mmmm*] > 99% and activities up to 860 kg·mol^{-1}·h^{-1}·atm^{-1}. Catalyst ω-halo-α-alkene deactivation scales as, Cl > Br > I. Deactivation effects are more pronounced for short chain comonomers, i.e., 4-halo-1-butene > 11-halo-1-undecene. Recently, Li[28] reported propylene + amino-olefin (AO) copolymerizations using the same catalyst system with activity up to 7440 kg·mol^{-1}·h^{-1}·atm^{-1}, M_n up to 5.90 × 10^5, high AO comonomer enchainment (up to 11.6 mol %), and tacticity ([*mmmm*] > 99%) (Figure 7). Note that steric -NR_2 bulk is critical, and catalytic activity is minimal with 100 equiv. TIBA/Hf when R = primary alkyl, suggesting severe deactivation effects.

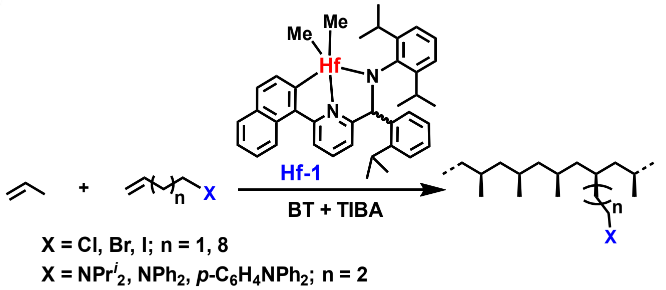

Figure 7. Isotactic propylene + polar monomer copolymerizations catalyzed by **Hf-1**

Compared to propylene + polar monomer copolymerizations with masking reagents, direct copolymerizations are rare. Waymouth and Hawker[29] described **Zr-6** + $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$ (NB)-catalyzed masking reagent-free propylene + alkoxyamine substituted olefin copolymerizations (Figure 8a). Neither comonomer content, isotacticity, nor T_m data are reported for this interesting PP copolymer. In 2019, Marks reported direct isotactic and syndiotactic PP + AO copolymerizations without masking reagents (Figure 8b).[30] Significant AO polar comonomer levels are enchained with substantial activities. Up to 91.9% [*mmmm*] (Zr-3) and 81.4% [*rrrr*] (**Zr-7**) are achieved, frequently exceeding those in the corresponding homopolymerizations. AO deactivation effects are significantly greater for the FluZrMe$_2$-derived catalysts than for the SBIZrMe$_2$-derived catalysts.

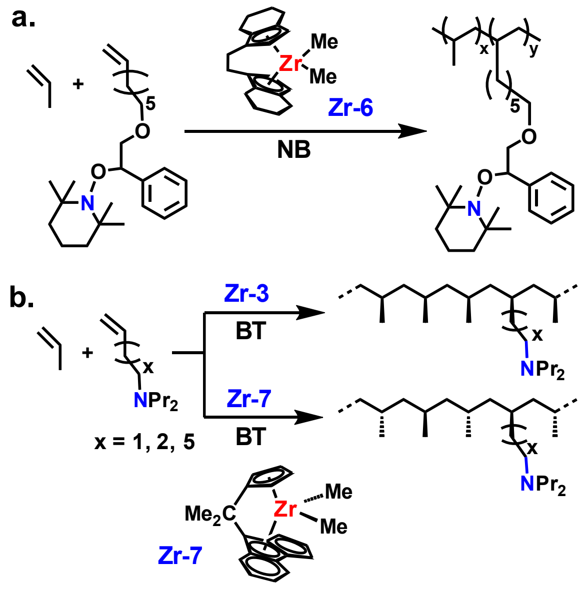

Figure 8. Propylene + polar monomer copolymerization without masking reagents.

3. Group 3 Catalysts

Group 3 Sc, Y, and lanthanide cyclopentadienyl monoalkyl and monohydride complexes are active polymerization catalysts without cocatalysts.[31] However, polymerization studies have been largely limited to ethylene or activated polar monomers as in acrylate, lactone polymerization via ring opening processes, whereas low activity is observed for higher olefins, slowing development of polar monomer copolymerizations with these catalysts.[32] Only after the synthesis of group 3 dialkyl species was their potential unleashed.[33] Treatment of these dialkyls with equimolar borate/borane activators such as NB or BT generates cationic monoalkyls, which exhibit far higher polymerization activity and broader reactivity with higher olefins such as α-olefins, styrenes, 1,3-conjugated dienes, and cyclic olefins.[32a, 34]

Tritto and Okuda[35] showed that half-sandwich **Sc-3** catalyzes ethylene copolymerization with R$_2$Al-protected hydroxy-norbornene on **BT** activation. Comonomer enchainment levels reach 13 mol% with activities up to 2340 kg·mol^{-1}·h^{-1}·atm^{-1}. Adding norbornene to the copolymerization yields terpolymers (Figure 9).

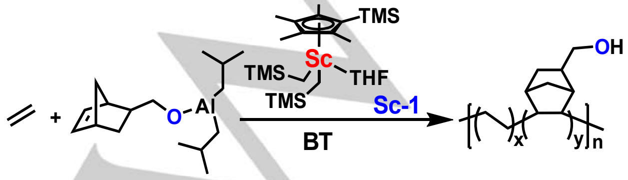

Figure 9. Ethylene + R$_2$Al-protected hydroxy-norbornene copolymerization using a **Sc-1** –derived catalyst and the product obtained after hydrolytic work-up.

In 2017, Hou[36] reported that ethylene copolymerization with heteroatom-functionalized α-olefins (e.g., ArS-, ArO-, Ar$_2$P-) is achieved in the absence of masking reagents (Figure 10a). Copolymers with 2.6 - 73.5 mol% comonomer content and Đ ≈ 2 were prepared with activities up to 103 kg·mol^{-1}·h^{-1}·atm^{-1}. Experimental and computational studies reveal that interaction between the α-olefin heteroatom and the catalyst center plays a critical role in polymerization activity and stereoselection. In 2019, Hou[37] reported ethylene + anisyl-substituted propylene copolymerizations using **Sc-3** (Figure 10b). Copolymerization proceeds in a controlled fashion, affording multi-block copolymers composed of relatively long alternating ethylene-*alt*-anisylpropylene sequences and short ethylene-ethylene units. The copolymers with T$_g$ values below 25°C have high elastic moduli, impressive toughness, and remarkable self-healing while those with T$_g$ near or above 25°C exhibit excellent shape-memory properties.

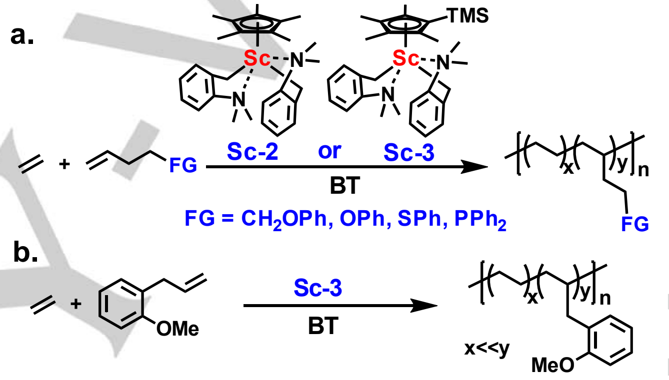

Figure 10. Polar monomer copolymerizations using **Sc-2** or **Sc-3** –based catalysts.

In 2017, Marks[38] showed that mono- (**Sc-1**) and binuclear (**Sc-4a** and **Sc-4b**) organo-Sc complexes with cocatalyst **BT** are active for ethylene + amino-olefin (AO) copolymerizations in the absence of masking reagents (Figure 11). Activity up to 420 kg·mol^{-1}·h^{-1}·atm^{-1} and AO incorporation up to 12.5% at 0.2 M [AO] is achieved. A systematic investigation of AO linker length effects reveals that AO selectivity increases with shorter linker lengths while activity is insensitive. Switching from -N^{n}Pr$_2$ to less hindered -NEt$_2$ groups depresses activity but affords higher comonomer incorporation. Adding N^{n}Pr$_3$ (0.1 M) to **Sc-3**-catalyzed ethylene + 1-hexene (0.1 M) copolymerizations lowers comonomer incorporation from 4.8 mol% to 0.1 mol%. However, introducing N^{n}Pr$_3$ (0.1 M) to ethylene + N(1-butenyl)^{n}Pr$_2$ appreciably increases AO incorporation from 2.0 mol% to 3.5 mol%. These results raise the intriguing possibility that exogenous amines can be utilized to modulate comonomer incorporation. Furthermore, binuclear catalysts **Sc-4a** and **Sc-4b** exhibit enhanced functional-group tolerance and enchain more long chain AO than mononuclear **Sc-1**.

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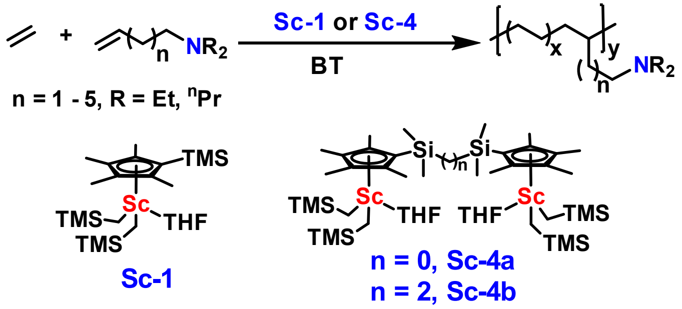

Figure 11. Ethylene + amino-olefin copolymerization using **Sc-1** or **Sc-4** –based catalysts.

Cui and Maron[39] investigated ethylene + polar styrene copolymerizations using Sc catalyst **Sc-5** (Figure 12a). Comonomer incorporation is in the range 26.4 mol% - 50.7 mol% with TOFs up to 16.7 x 10^3 h^{-1}, significantly higher than for ethylene homopolymerization, highlighting positive polar styrene monomer effects. Methoxystyrene heteroatom chelation to the Sc/lanthanide center does not deactivate the catalyst but surprisingly lowers the methoxystyrene insertion barrier relative to those styrene derivatives lacking a methoxy group.[6a, 40] Furthermore, switching to N-heterocyclic carbene-tethered catalyst **Sc-6** affords pseudo- or ideal alternating ethylene + polar styrene copolymerizations with activities up to 80 kg·mol^{-1}·h^{-1}·atm^{-1}.[41] Studies were then extended to other polar styrenes (Figure 12b). Note that 2 - 20 equiv of TIBA relative to catalyst were used in all experiments.

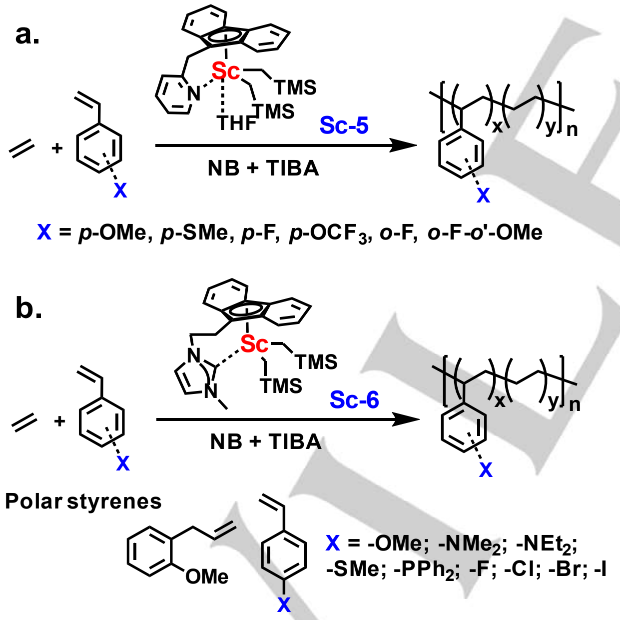

Figure 12. Ethylene + polar styrene copolymerization using **Sc-5** and **Sc-6** –based catalysts

Hou[42] also reported the regio-, diastereoselective, and stereoregular cyclopolymerization of ether- and thioether-functionalized 1,6-heptadienes + ethylene with **Sc-3** (Figure 13). Thus, polymerization of 4-benzyloxy-1,6-heptadiene selectively affords the polymer composed of 1,2,4-*cis*-substituted-ethylene-cyclopentane (ECP) microstructures arrayed in an isospecific fashion (95% *mmm*). In contrast, the thioether analogue affords 1,2-trans-1,4-cis-ECP units having high syndiotacticity (95% *rrr*).

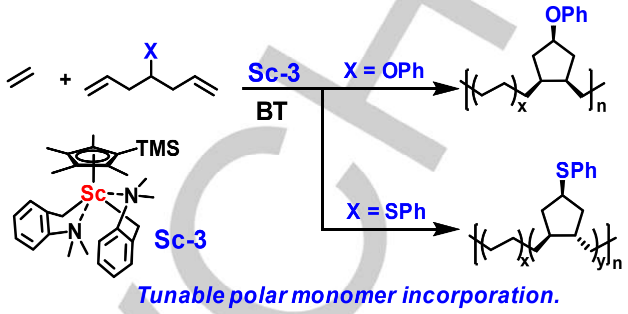

Figure 13. Ethylene + polar diene copolymerizations using the **Sc-3** –based catalyst.

4. Mechanistic Generalizations

Many important advances in early transition metal-catalyzed polar monomer copolymerization were discussed above. The polar monomer Lewis basic heteroatoms significantly challenge early transition metal catalysts. Introducing polar monomers renders the competitive coordination equilibria involving monomer, solvent, counteranion, etc. even more intricate, and perturbs monomer/-polar monomer enchainment. Nevertheless, recent developments in understanding catalyst deactivation/poisoning and polar monomer enchainment reveal promising strategies.

As supported by DFT analysis,[43] non-polar olefin polymerizations involve two key steps, monomer olefin coordination/-activation and insertion/enchainment. Introducing polar comonomers renders both processes more complex than for non-polar monomers (Figure 14). For coordination, non-insertive functional group binding such as in **C** and **E** is possible, as is insertive olefin coordination such as **A**, **B**, and **D**. If the equilibrium between non-insertive and insertive coordination strongly favors the former, the effect can be catalyst deactivation/poisoning by competitive basic group binding to the metal electrophile. Depending on whether the polar monomer undergoes insertion or not, functional group coordination can be intermolecular (before insertion) or intramolecular (after insertion, "back-biting"; see **4.1.** below). The corresponding insertion processes with respect to **A**, **B**, and **D**, the rates and concentrations of these olefinic coordinating species will determine overall polar monomer selectivity. Note that for late transition metal catalysis, β-X elimination processes may also deactivate the catalyst.[44]

4.1. Catalyst poisoning/deactivation

Intermolecular coordination (C-type). In principle, intermolecular functional group σ-coordination (**C**, Figure 14) is in competition with olefin π-coordination (**B**, Figure 14).[45] When the former predominates, it prevents olefin coordination and insertion, and may even suppress non-polar olefin coordination, thus deactivating the catalyst. To shift the equilibrium away from functional group σ-coordination, two effective strategies are: *i)*. Polar group modification to increase steric bulk and/or decrease the

Lewis basicity. *ii)*. Ligand modification to alter the metal center electronic and steric environment.

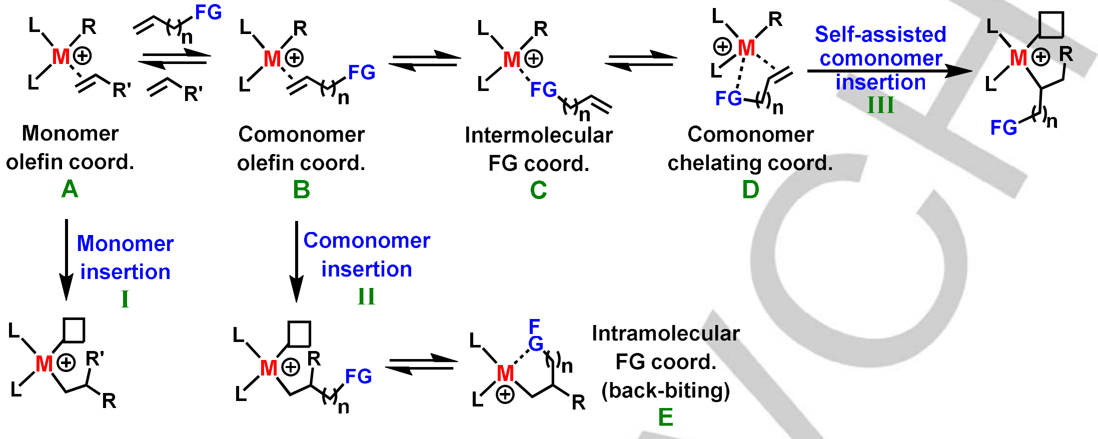

Figure 14. Pathways modulating polar monomer copolymerization in early transition metal catalysis.

Function *i)* can be achieved via bulky protecting groups or Lewis acidic masking reagents. Trialkylsilyl groups are known to hinder ether and amine coordination to Lewis acidic metal centers.[23] Bulky trialkylsilyl groups were screened to minimize deactivation,[7c] and Baird reported no clear correlation between protective group bulk and polar monomer selectivity in *rac*-$C_2H_4(Ind)_2ZrCl_2$ + MAO catalyzed ethylene + $CH_2{=}CH(CH_2)$-CH_2OR copolymerizations.[46] Lewis acidic Al reagents such as AlR_3 are another effective means to minimize deactivation. AlR_3 binds polar functional groups (e.g., Figures 2, 3, 6 and 11) or reacts with protic polar comonomers such as alcohols (e.g., Figures 1, 2 and 9) and primary/secondary amines (e.g., Figure 5). Due to the multiple roles AlR_3 can play (alkylation agent, reducing agent, chain transfer agent, aluminate formation, water scavenger), the identity and amount of AlR_3 reagent can dramatically influence polymerization pathways.

Catalyst design is another strategy to suppress/prevent deactivation effects. Among group 4 metallocenes, increasing π-ligand steric demands can typically impede polar monomer coordination. For example, "Kashiwa" (FI) polymerization catalysts[47] exhibit remarkable tolerance towards functional groups. For phenoxy-iminate group 4 catalysts, Fujita[12] showed that ligand electron-donating substituents (-^{t}Bu, -OMe) enhance catalytic activity whereas an electron-withdrawing substituent (-CF_3) lowers it (**Ti-1**, Figure 2). DFT analysis reveals that the energetic difference between olefin and carbonyl group binding is significantly lower for FI than for metallocene catalysts, implying greater polar functional group tolerance. Tang's[13] "side arm" strategy introduces an electron donating ligand on FI complexes to reduce the Ti Lewis acidity for **Ti-2** and **Ti-3** (Figure 2).

Intramolecular coordination (E-type). Here intramolecular σ-coordination of the metal center by the Lewis basic group on the inserted comonomer, forms a chelate structure (**E**, Figure 14). The chelating species may be too stable for further monomer + comonomer olefin coordination and insertion. This effect is severe in group 4 catalyzed copolymerizations with short chain comonomers since a stable 5- to 7-member chelating ring can be formed. Strategies such as functional group protection and/or catalyst structural modification can effectively suppress/prevent polar monomer binding. In principle, these could also reduce back-biting effects. Thus, Imuta[11] and Hagihara[20] showed that smaller $AlMe_3$ and $AlEt_3$ favor chain transfer while larger Al^iBu_3 promotes chain growth in Zr-catalyzed ethylene or propylene copolymerizations with allylic alcohols and amines, affording different polymer microstructures (Figures 1 and 5). Another effective strategy to suppress back-biting is using longer linker comonomers.[7c, 48]

With the diverse catalyst deactivation pathways possible, it is important to understand details of the relevant mechanisms. Thus, experimental and theoretical studies have focused on decoupling and quantifying intermolecular and intramolecular σ-coordination. Recently developed masking reagent-free catalytic systems have simplified this task, enabling more straightforward analysis. Introducing non-olefinic Lewis bases in a polar monomer copolymerization can further decouple intramolecular coordination from intermolecular coordination effects. Thus, Waymouth[49] compared activity inhibition by introducing N(1-pentenyl)^{i}Pr$_2$ vs. N(pentyl)^{i}Pr$_2$ in a **Zr-6** + borate catalyzed 1-hexene homo-polymerization and found that the AO is 3.5x more effective in inhibiting polymerization, suggesting both intramolecular and intermolecular coordination operate, but that intramolecular coordination dominates. Marks[48] investigated **Zr-3**-catalyzed ethylene + N(1-octenyl)^{n}Pr$_2$ copolymerizations (Figure 3). The activity and AO content are only marginally depressed by 0.1 M N^{n}Pr$_3$, indicating minimal intermolecular coordination. DFT computation shows that **Zr-3** prefers olefin coordination over amine coordination by ~4.5 kcal/mol.[48] In **Sc-3**-catalyzed ethylene + AO copolymerization, N^{n}Pr$_3$ and N(1-alkenyl)^{n}Pr$_2$ inhibit activity similarly, arguing that intermolecular amine coordination is the major inhibition pathway.[38] DFT analysis[43a] shows that amine coordination is preferred when AOs approach the Sc center. Furthermore, intramolecular coordinating species are disfavored by ~4.3 kcal/mol for N(1-butenyl)^{n}Pr$_2$ and ~15.5 kcal/mol for N(1-octenyl)^{n}Pr$_2$), supporting the dominance of intermolecular coordination. Thus, for competitive inter- vs. intramolecular AO coordination, Zr, Sc, and Ni catalysts show very different linker length and R group steric effects on polymerization activity and comonomer selection (Table 1).[48]

Table 1. Amino-olefin $CH_2=CH(CH_2)_nNR_2$ comonomer catalytic activity trends for organo-Zr vs. organo-Sc and Ni catalysts[a]

	Zr	**Ni**	**Sc**
Longer linker (n) ⇒ Act.	**+**	**+**	**=**
Bulkier R on N ⇒ Act.	**=**	**+**	**+**
Longer linker (n) ⇒ Incorp.	**+**	**=**	**-**
Bulkier R on N ⇒ Incorp.	**=**	**=**	**-**

[a] Representative Zr catalyst: $\mathbf{SBIZrMe^{+}B(C_6F_5)_4^{-}}$; representative Ni catalyst: phenoxyiminate-Ni complexes;[50] representative Sc catalyst: $\mathbf{Me_3SiC_5Me_4Sc(CH_2SiMe_3)(THF)^{+}\ B(C_6F_5)_4^{-}}$.[36, 38] **+** = positive correlation; **-** = negative correlation; **=** = no significant correlation. Reprinted with permission from John Wiley & Sons, Inc.

4.2. Polar monomer enchainment

In principle, catalysts capable of enchaining non-polar olefins should be competent to enchain polar analogues. However, Lewis basic group σ-coordination (non-insertive mode, **C**, Figure 14) usually inhibits coordination/activation and subsequent enchainment of olefinic moieties (insertion mode, **B**, Figure 14). Thus, comonomer incorporation levels in polar monomer copolymerizations is typically lower than for the non-polar analogues under identical conditions. For example, Marks[48] reported that AO enchainment levels (0.4 – 5.5 mol%) are significantly lower than 1-octene enchainment levels (10.0 mol%) in **Zr-3**-catalyzed ethylene copolymerizations. Thus, the strategies discussed in Section 4.1 that shift coordination away from σ-coordination (non-insertive mode) and towards olefin coordination/activation (insertive mode) are promising.

Very recently, an intriguing comonomer enchainment pathway was reported in which functional groups play a positive role in polar monomer enchainment. Cui[6a, 39-40, 51] and Hou[36] reported that polar monomers exhibit higher activity in homopolymerizations versus the non-polar analogues. Mechanistic studies[52] suggest that functional group coordination can assist olefin coordination, activation and insertion. In some cases, functional group coordination also directs next-monomer insertion stereochemistry.[6a, 36, 40, 51] Marks proposed a self-assisted comonomer enchainment pathway based on correlations between chain length and higher AO incorporation in Sc-catalyzed ethylene + AO copolymerizations.[38] DFT computation supports this hypothesis, suggesting self-assisted enchainment is the favored enchainment pathway ($\Delta G^{\ddagger} \approx 6.0$ kcal/mol) for short chain $N(1\text{-butenyl})^{n}Pr_2$.[43a] Beyond early transition metal catalysts, similar comonomer effects are also observed for Ni catalysts.[53]

Binuclear catalysis is another promising strategy to enhance comonomer enchainment. Examples are binuclear **Ti-5**-based catalysts which incorporate up to 30% more polar styrenes than mononuclear **Ti-4** in ethylene + polar styrene copolymerizations (Figure 4).[17] Binuclear **Sc-4a** and **Sc-4b** –based catalysts also incorporate more long chain $N(1\text{-octenyl})^{n}Pr_2$ than the mononuclear **Sc-3** analogue (0.2 mol% vs. <0.1mol%) in ethylene + AO copolymerization (Figure 11).[38]

5. Conclusions and Perspectives

The past several years has witnessed exciting progress in new catalytic system designs, new polymer syntheses, and a clearer mechanistic understanding of early transition metal-catalyzed polar monomer copolymerizations. One particularly exciting breakthrough is the emergence of functional group-assisted comonomer enchainment pathways (Figure 10[36] and Figure 11,[38, 43a]). The other pivotal discovery is masking reagent-free copolymerizations catalyzed by organoscandium and organozirconium catalysts. These advances represent future opportunities in polar monomer copolymerization.

From a mechanistic viewpoint, recently developed masking-reagent-free catalysis allows more detailed and quantitative investigations of catalyst structure-polymerization performance relationships. Further computational efforts are expected to provide additional insights into such relationships and thus inform next-generation catalyst designs.[54] It will be interesting to see whether new mechanisms are discovered in this process. Whether functional group-assisted comonomer enchainment is operative in group 4 metal systems is also an intriguing question.

Early transition metal catalyzed polar monomer copolymerization was traditionally limited in scope. New opportunities are emerging as more polar and non-polar monomers are investigated, especially ones derived from sustainable sources. Note that the cost and availability of the polar monomers will become a concern with more industrial involvement and may play a crucial role for using in practical applications. Greater regio- and stereo- selective and more precise copolymer microstructure control (alternating, gradient, random) should be achievable through catalyst design. Furthermore, coupling functional monomer copolymerization with other processes such as C-H activation[52, 55], chain transfer,[56] and chain shuttling[57] should yield new copolymers with previously inaccessible properties. Note that enchaining industrially relevant vinyl polar monomers in ethylene or propylene copolymerizations is still a formidable challenge for early transition metal catalysts due to the significantly altered olefinic orbital energies and electronic structure as a consequence of the directly attached polar group.

The applications of polar copolymers will also expand as new materials are produced. Functional groups not only benefit copolymer mechanical, rheological, and surface properties, but also provide interesting new chemistry. Functional groups can sequester metal ions, bind Lewis acidic sites, form reversible or irreversible covalent bonds, and be transformed into other functional groups. Utilizing and leveraging such chemistries will surely expand the applications scope.

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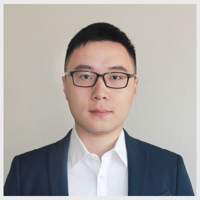

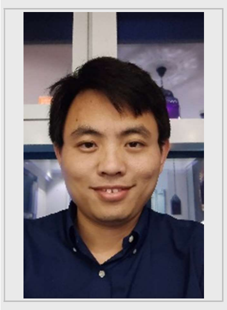

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Acknowledgement

Financial support was provided by NSF through Grant CHE-1856619. Sijia Liu is acknowledged for cover design.

Keywords: catalyst design • polymerization • olefin • polar monomer • early transition metal

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