

Transition Metal-Catalyzed Ternary Polymerization of Olefins

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Abstract

Polyolefins are widely used polymers, with an annual global production of hundreds of millions of tons. Because they are the simplest hydrocarbon polymers, their intrinsic non-polar properties limit further applications. Coordination–insertion copolymerization of an olefin with other monomers, mediated by transition metal catalysts, is the most efficient way to synthesize polar and multi-functionalized polyolefins with enhanced material performance. Previous reviews have primarily focused on the structural design of a specific catalyst or on binary copolymerization of an olefin with a particular comonomer. However, the transition-metal-catalyzed ternary coordination–insertion polymerization of olefin monomers remains scarce. In this contribution, early transition-metal catalysts, such as Ti, Zr, Hf, and V, are employed for the terpolymerization of all-hydrocarbon or non-polar monomers to access advanced polyolefin materials with high performance. By contrast, late transition metal catalysts based on Ni and Pd, as well as rare-earth metal catalysts ligated by Sc and Y, enable the terpolymerization of olefins with a variety of heteroatom-containing monomers. Their strong tolerance empowers the development of polyolefins with multiple functionalities, thereby distinguishing these systems. The catalyst structure, catalytic process, and mechanism studies are summarized, along with the microstructure and functionality of the polymerization products, by classifying the types of termonomers employed.

Keywords: coordination-insertion polymerization; transition metal catalyst; non-polar olefins; polar functionalized monomers; terpolymers

1. Introduction

Polyolefins, such as polyethylene and propylene, are widely used polymeric materials with massive global production [1]. However, these conventional hydrocarbon materials also exhibit significant shortcomings and lack functional diversity due to their simple molecular structures and intrinsic nonpolar nature [2]. To address these shortcomings, several technologies have been developed to achieve multi-functionalization and enhance the performance of polyolefin materials. For instance, free-radical polymerization is a standard method for preparing olefin copolymers from ethylene and other olefin monomers [3]. Commercially available products include ethylene-ethyl vinyl acetate copolymer (EVA) and ethylene-vinyl alcohol copolymer (EVOH). Nevertheless, free radical polymerization has limitations, including limited types of comonomers, poor control over polymer microstructures, and the need for harsh conditions, such as high temperature and high pressure. Alternatively, post-modification of polymers enables the introduction of various functionalized groups and additives into polyolefins, thereby significantly broadening the



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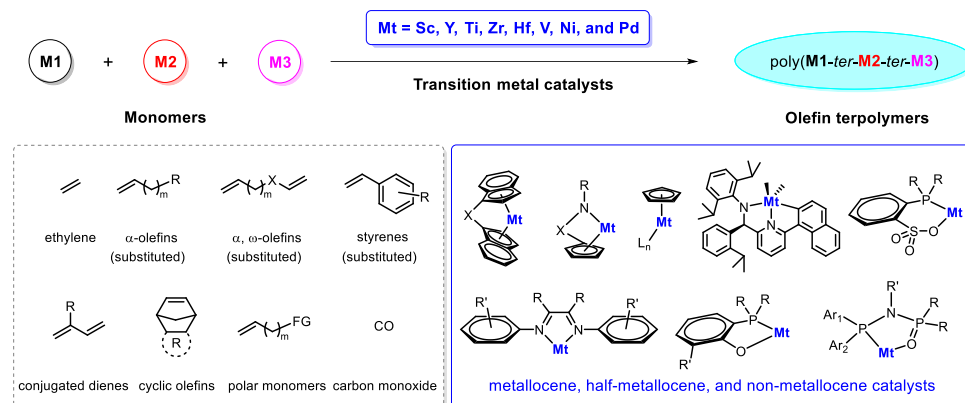
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range of polar groups and enhancing multi-functionality [4]. Despite this advantage, the reactive pathway may lead to side reactions on the polymer chain, such as chain scission and crosslinking. Additionally, compatibility issues between the additives and the polymer matrix arise from differences in their interfacial properties. This may lead to agglomeration and migration of functional components during the use of polymer materials, resulting in short-lived functional modification.

Coordination–insertion polymerization has been a predominant approach for producing bulk polyolefin products, such as high-density polyethylene and isotactic polypropylene [5–7]. Using organometallic catalysts, researchers have controlled the microstructure. This included controlling molecular weight, distribution, branching degree, and thermal properties such as glass transition temperature (T_g) and melting point (T_m) [8]. Ziegler–Natta catalysts, developed in the 1950s and awarded the Nobel Prize in Chemistry in 1963, enabled the polymerization of ethylene, propylene, and α -olefins. These catalysts were successfully industrialized and now dominate industrial polyolefin production [9,10]. Subsequently, well-defined metallocene catalysts demonstrated high catalytic activity, improved thermal stability, and greater control over polymer microstructure [11,12]. Researchers then replace the traditional cyclopentadienyl ligands and early transition metals. This led to the development of robust late-transition-metal and non-metallocene catalysts, such as salicylaldimine and α -diimine catalysts [13,14]. One key advantage of these well-defined transition-metal catalysts is their ability to copolymerize olefins with other monomers. This produces commercially available copolymers, including the ethylene-propylene copolymers, polyolefin elastomers, and cyclic olefin copolymers. Thus, coordination–insertion copolymerization of an olefin and another monomer allows easy control of the copolymer microstructures and material properties. This can be achieved by modifying the comonomer structures, contents, sequence distributions, and the transition-metal catalysts employed [15,16]. As a result, coordination–insertion polymerization is regarded as the most promising approach for developing advanced polyolefin materials.

A vast majority of the current review studies on the preparation of polyolefin materials via coordination polymerization focus on the development of new catalyst structures and the improvement of catalytic activity, copolymerization capacity, thermal stability, polar tolerance and other properties, or on the binary random/block polymerization of bulk olefins such as ethylene and propylene with specific comonomers to develop high-performance and multi-functional polyolefin materials [17–33]. Review of the ternary polymerization of various olefins catalyzed by transition-metal catalysts is scarce. Possible reasons include that, compared with olefin homopolymerization and binary polymerization, ternary polymerization places greater demands on catalytic performance, requiring more rigorous screening of the catalyst structure employed. Moreover, additional side reactions may occur during ternary polymerization. The complicated single-site active centers can exhibit markedly different reactivity toward a given comonomer, making it challenging to regulate the coordination–insertion polymerization process, polymer microstructures, and material properties as intended. Nevertheless, several excellent catalytic systems based on early transition metals (Ti, Zr, Hf, V, etc.) have been reported to achieve terpolymerization and to synthesize advanced polyolefin materials with high performance. Late transition-metal catalysts based on Ni and Pd, and rare-earth metal catalysts ligated by Sc and Y, can catalyze the terpolymerization of olefins with different polar, heteroatom-containing monomers due to their strong tolerance, enabling the development of polyolefins with multiple functions and facilitating post-modification strategies for the polymer products. In the present review and as shown in Figure 1, the catalytic processes, including structure–activity relationships and mechanisms of catalysts, as well as the microstructure and functionality, such as polarity, stimuli-responsiveness, self-healing, and degradability of

the polymerization products, have been discussed by classifying the types of comonomers used in the terpolymerizations. This review covers the literature from 2011 up to the end of 2025.



✓ Catalytic activity, molecular weight, termonomer content and sequence, mechanism, terpolymer microstructure and performance, ...

Figure 1. Catalytic systems for transition metal-catalyzed ternary polymerization of olefins.

2. Ternary Polymerization of All-Hydrocarbon/Non-Polar Olefins

Early transition-metal-based homogeneous single-site catalysts exhibit several key features, including extremely high catalytic activity, the ability to copolymerize a wide range of all-hydrocarbon olefin monomers, and the capacity to synthesize copolymers with controllable molecular weight, polymer dispersion index, and uniform composition. Moreover, some of them exhibit living character, making them ideal candidates for the synthesis of copolymers with tailored polymer microstructures. Therefore, the terpolymerizations of non-polar olefin monomers are mainly carried out by well-defined early transition metal catalysts, including metallocene and non-metallocene catalysts. The monomers applied in this section, as shown in Figure 2, include not only bulk products such as ethylene, propylene, and α -olefins, but also conjugated and non-conjugated dienes, styrene, and cyclic allyl compounds, cyclic olefins, as well as the olefins substituted with unsaturated bonds and conjugated aromatic groups.

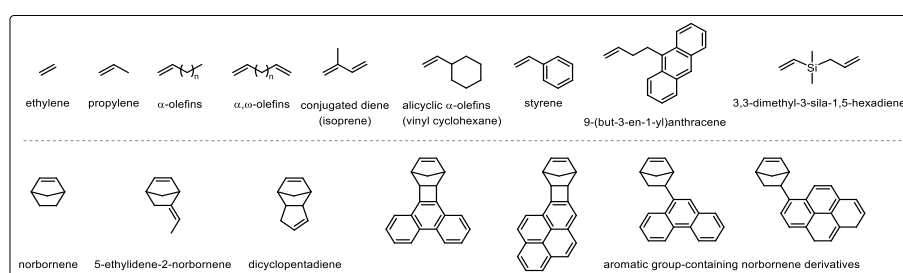
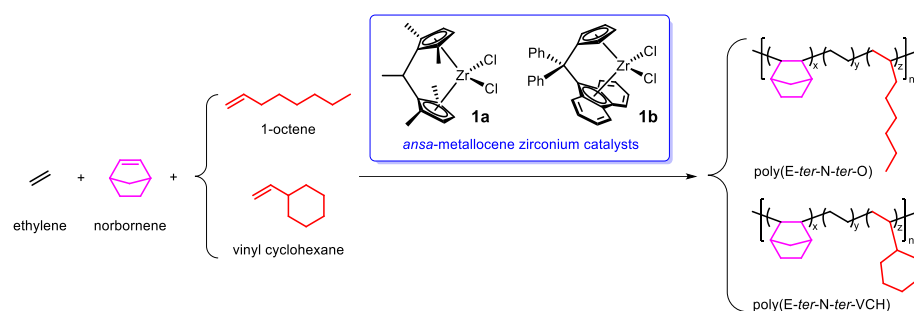


Figure 2. All-hydrocarbon/non-polar monomers are used in the terpolymerizations.

In 2011, Tritto and coworkers reported the ternary polymerization of ethylene and norbornene with linear 1-octene or sterically demanding vinyl cyclohexene (VCH) to prepare modified cyclic olefin copolymers (COCs), poly(E-ter-N-ter-O) and poly(E-ter-N-ter-VCH), respectively, with metallocene zirconium catalysts **1a** and **1b** (Scheme 1) [34]. It was found that although the incorporation of a third monomer leads to a decrease in the polymer molecular weight ($16\text{--}163\text{ kg mol}^{-1}$) compared to the ethylene-norbornene copolymers ($160\text{--}784\text{ kg mol}^{-1}$), the glass transition temperature (T_g) values can be adjusted within the range of $74\text{--}162\text{ }^\circ\text{C}$ when the termonomer contents change from 1 to 5 mol%.

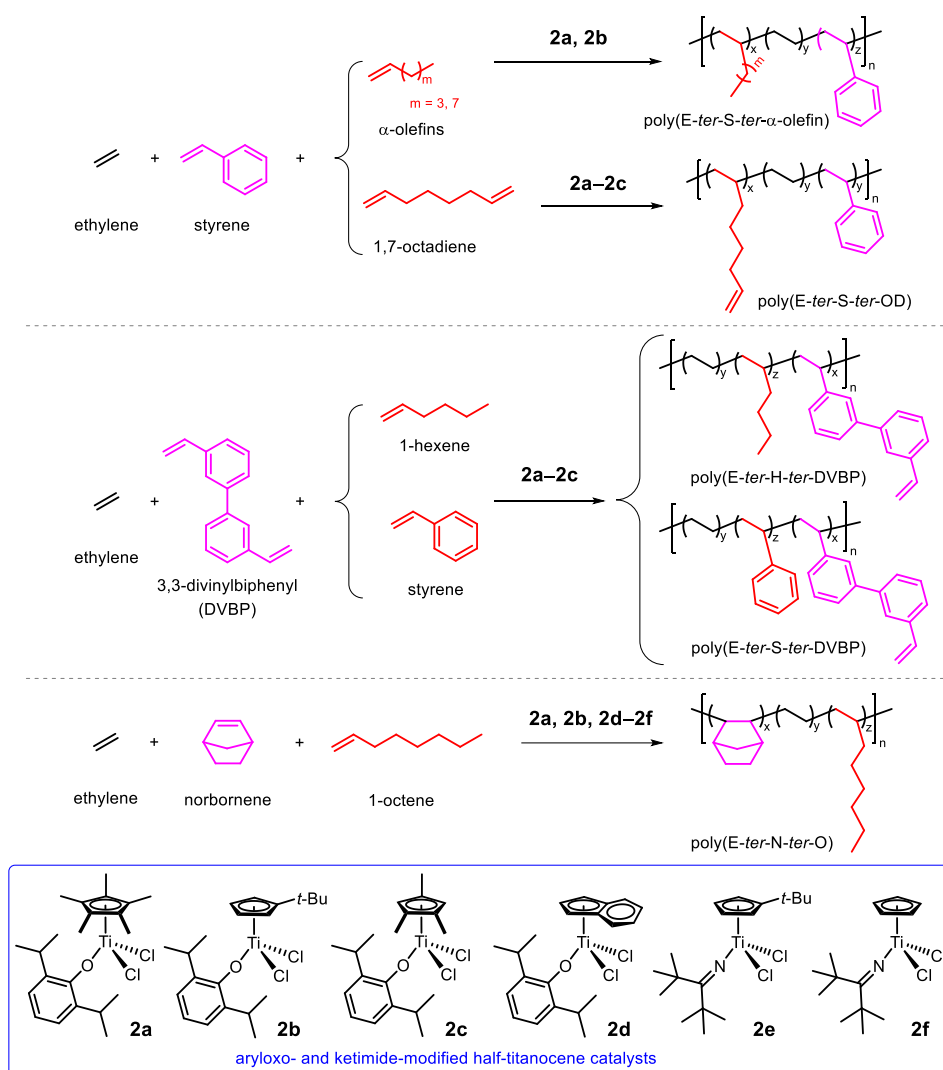


Scheme 1. Terpolymerization of ethylene, norbornene, with 1-octene and vinyl cyclohexene catalyzed by **1a** and **1b**.

Since 2013, Nomura's group has reported a series of studies on ternary ethylene copolymerization using different aryloxo- and ketimide-modified half-titanocene catalysts (Scheme 2). The survey of the ethylene and styrene with α -olefins catalyzed by **2a** and **2b** revealed that the kind of cocatalysts used in the terpolymerization exert significant influence on the catalytic activity, in which the borate cocatalyst system generally give higher activity than the MAO system while the two systems maintaining similar molecular weight ($M_n = 199\text{--}537 \text{ kg mol}^{-1}$), PDI (1.95–2.51), and comonomers incorporations [35]. Polymer microstructure analysis indicates the absence of styrene-*co*- α -olefin repeat units due to steric hindrance conflict between the two monomers. The terpolymerization of ethylene and styrene with *p*-methylstyrene (*p*-MS) catalyzed by **2a** and **2b** and the terpolymerization of ethylene and styrene with 1,7-octadiene (OD) catalyzed by **2a–2c** also give negligible signals of the styrene-*co*-*p*-MS and styrene-*co*-OD units, because of the same reason, to produce amorphous terpolymers, in which the pendant olefinic double bonds, without cyclization during the polymerization, can seek further functionalization [36]. The terpolymerization of ethylene and DVB with 1-hexene or styrene was also achieved using **2a–2c**, yielding poly(E-*ter*-DVB-*ter*-1-hexene) and poly(E-*ter*-DVB-*ter*-St) with DVBP contents of 1.7–6.5 mol%. The residual olefinic double bonds of the DVBP monomer were partially initiated to graft polystyrene chains via an anionic process [37]. Both the aryloxo-modified (**2a**, **2b**, and **2d**) and ketimide-modified half-titanocene catalysts (**2e** and **2f**) can terpolymerize ethylene and norbornene with 1-octene to produce COCs with high 1-octene contents (up to 13.5 mol%), high molecular weights (M_n of up to 442 kg mol^{-1}), and tunable T_g values (23–153 °C) [38]. Note that the activity and the molecular weight of the terpolymer obtained by **2e** and **2f** are higher than those of **2a**, **2b**, and **2d**, due to their less β -H elimination reaction. Catalyst **2f** was reported as the most active catalyst (with an activity of up to $97,700 \text{ kg mol}^{-1} \text{ h}^{-1}$) among the transition metal catalysts in preparing the poly(E-*ter*-N-*ter*-1-hexene).

Ethylene and propylene copolymer is known as an industrially important synthetic rubber (EPR) with excellent chemical and environmental resistance due to its saturated structure. The introduction of a third cyclic unit or cross-linkable group, such as norbornene and 5-ethylidene-2-norbornene (5E2N), can further improve its physical and mechanical properties. Shiono and coworkers demonstrated the terpolymerization of ethylene and propylene with norbornene or 5E2N catalyzed by *ansa*-dimethylsilylene(fluorenyl)(amido)dimethyltitanium catalyst **3a** to produce a terpolymer with precisely controllable polymer microstructure (Scheme 3) [39]. The catalytic system was found, for the first time, to exhibit higher reactivity toward propylene than toward ethylene due to its more open η^3 -coordination site compared to other η^5 -coordinated constrained geometry catalysts (CGC), thereby making it easier to control E content in the terpolymer. There is no N-*co*-P sequence in the terpolymers due to the predominant insertion of E. The T_g values of the terpolymer increase linearly (25–198 °C) with the N

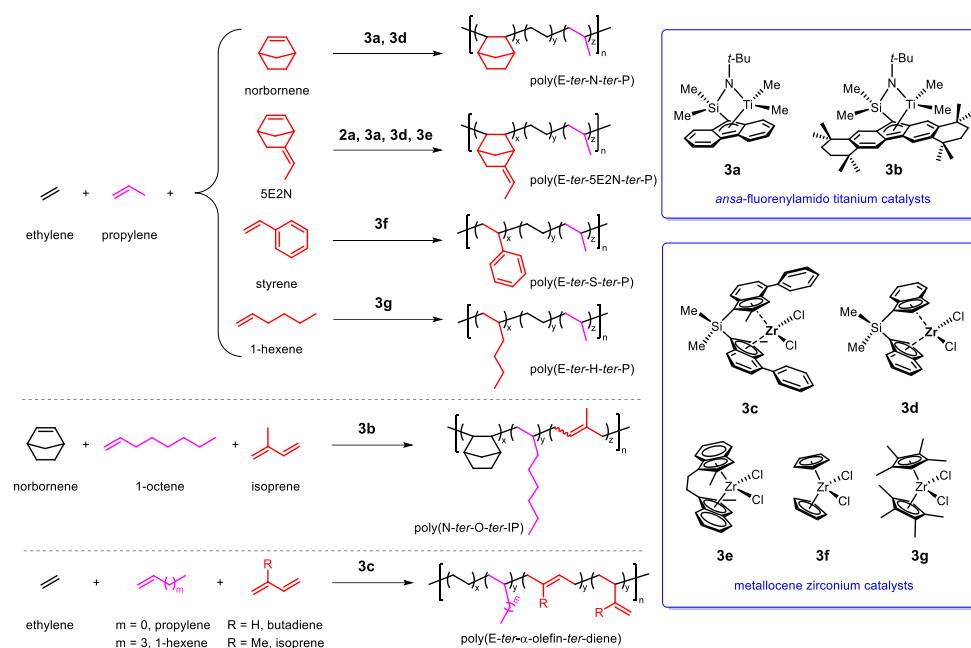
content (9–58 mol%) regardless of the E/P content. Catalyst **3d** facilitates the synthesis of poly(E-*ter*-P-*ter*-N) with low N content (1.1–9.1 mol%) to reveal the terpolymer microstructures, which were equipped with an isotactic polypropylene segment, a discrete ethylene unit, and a unique ethylene-norbornene sequence, respectively [40].



Scheme 2. Terpolymerization behaviors of catalysts **2a–2f**.

The titanium catalyst **2a** and zirconium catalysts **3d** and **3e** are also efficient for the terpolymerization of ethylene, propylene, and 5E2N. The type of cocatalyst used in the catalytic system of **2a** significantly affects the active species generated, thereby influencing activity, molecular weight, and polymer properties. In this regard, both the use of modified methylaluminoxane (MMAO) and the combination of triisobutylaluminum (TIBA) with $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ have been reported to yield high activity (up to $62 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$) [41]. Methylaluminoxane-activated **3d** exhibited higher activity ($2740\text{--}4150 \text{ kg mol}^{-1} \text{ h}^{-1}$) than that of the borate-activated catalyst ($1700\text{--}2750 \text{ kg mol}^{-1} \text{ h}^{-1}$), while the two systems maintained similar molecular weights within the range of $261\text{--}671 \text{ kg mol}^{-1}$ [42]. Similarly, the structure of the isobutylaluminum aryloxide activator also significantly affects the behavior of catalyst **3e**, in which a bulky substituent on the para position of the aryloxide motif can increase molecular weight but at the cost of reduced activity and termonomer content [43]. Al-Harthi and coworkers also reported the synthesis of poly(E-*ter*-P-*ter*-St) and poly(E-*ter*-P-*ter*-H) catalyzed by metallocene zirconium catalysts **3f** and **3g**, respectively. The introduction of styrene as the termonomer increased activity by two times compared

to the copolymerization of ethylene and propylene, while the introduction of 1-hexene also increased the productivity of the terpolymerization. The thermal properties and thermal degradation behavior of these terpolymers have been studied intensively [44,45].

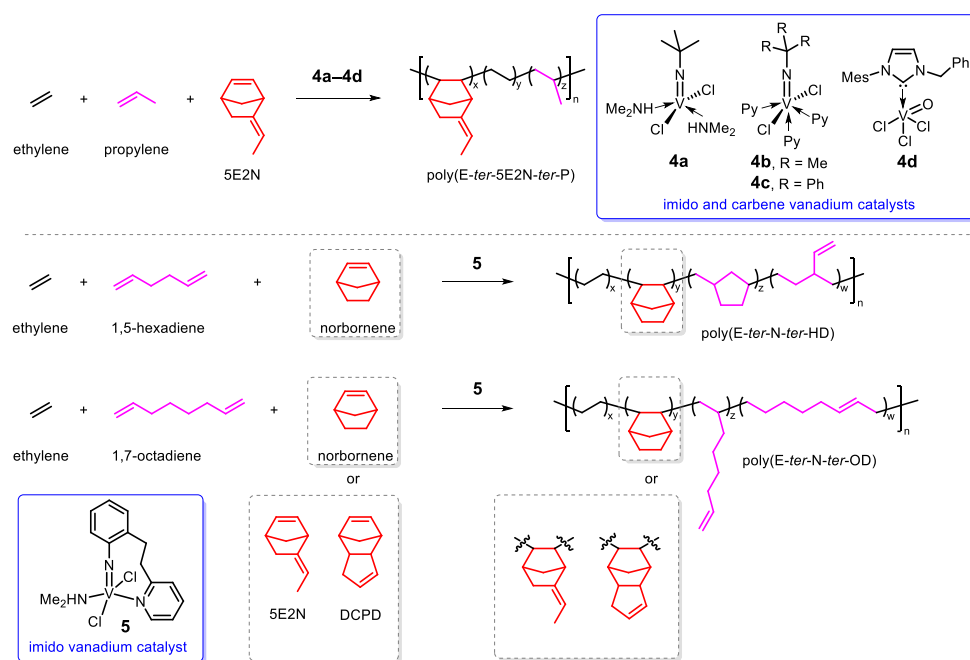


Scheme 3. Terpolymerization behaviors of catalysts **2a** and **3a–3g**.

The metallocene titanium and zirconium catalysts also qualified for terpolymerization with conjugated dienes, such as 1,3-butadiene and isoprene. Shiono's group also reported an active *ansa*-fluorenylamido titanium catalyst **3b** for the efficient terpolymerization of norbornene and 1-octene with isoprene (IP) to produce terpolymers with high isoprene incorporation up to 7 mol% and mainly 1,4-insertion [46]. The activity is higher than that reported for catalysts in similar reactions, and the products exhibit reasonable T_g values (168–185 °C) and a narrow PDI (1.5–2.1). Metallocene zirconium catalyst **3c** promotes the terpolymerization of ethylene, propylene/1-hexene, and dienes. Introducing propylene or 1-hexene into the copolymerization of ethylene and dienes reactivates a stable π -allyl species formed by the 1,4-insertion of diene, which is significantly important for its high activity and high molecular weight [47].

The vanadium complexes bearing different imido substituents and coligands, upon activation with Et_2AlCl and using ETA as the reoxidant, were also efficient catalysts for the synthesis of EPDM via the terpolymerization of ethylene, propylene, and 5E2N (Scheme 4). Both **4b** and **4c** are more active than **4a** in the same terpolymerization, producing high-ethylene EPDM ($\text{E} > 80 \text{ mol}\%$) with high molecular weight and unimodal, reasonably narrow PDI (1.9–2.0) [48]. The terpolymer products were confirmed to be a mixture of gradient terpolymers with multiblocks, in which the comonomers are segmented because a continuous ethylene supply was used in a semibatch process. N-heterocyclic carbene (NHC)-based vanadium catalyst **4d** promoted the synthesis of ultra-high-molecular-weight EPDM ($M_w = 384\text{--}1580 \text{ kg mol}^{-1}$) with activity ($80\text{--}265 \text{ kg mol}^{-1} \text{ h}^{-1}$), narrow PDI (2.0–3.2), and controllable 5E2N content within 1.4–12.5 mol% when the terpolymerizations were conducted at -4°C . The produced terpolymers then undergo post-modification via the reactive $\text{C}=\text{C}$ double bond to introduce a polar epoxy group (up to 11.2 mol%), which can be equivalently transferred to a carbonyl group, thereby demonstrating enhanced hydrophilicity [49].

A chelated vanadium catalyst **5** to catalyze the terpolymerizations of ethylene and 1,5-hexadiene (HD) with different cyclic olefin monomers, including norbornene, 5E2N, and DCPD [50]. Poly(E-*ter*-N-*ter*-HD) with isolated cyclic units in-chain, and pendant unsaturated double bonds were prepared. As a result, 1,2- and 2,1-insertion of 1,5-hexadiene were achieved, with molecular weight (M_w) up to 200 kg mol^{-1} and adjustable T_g values from -29°C to 4°C . Interestingly, the terpolymerizations of ethylene and 1,7-octadiene (OD) with cyclic olefin monomers afford Poly(E-*ter*-N-*ter*-OD) with terminal unsaturated long branches and internal unsaturated linear main chains. The unsaturated terpolymer can also be functionalized by post-modification of the terminal C=C bond, such as via thiolene addition.

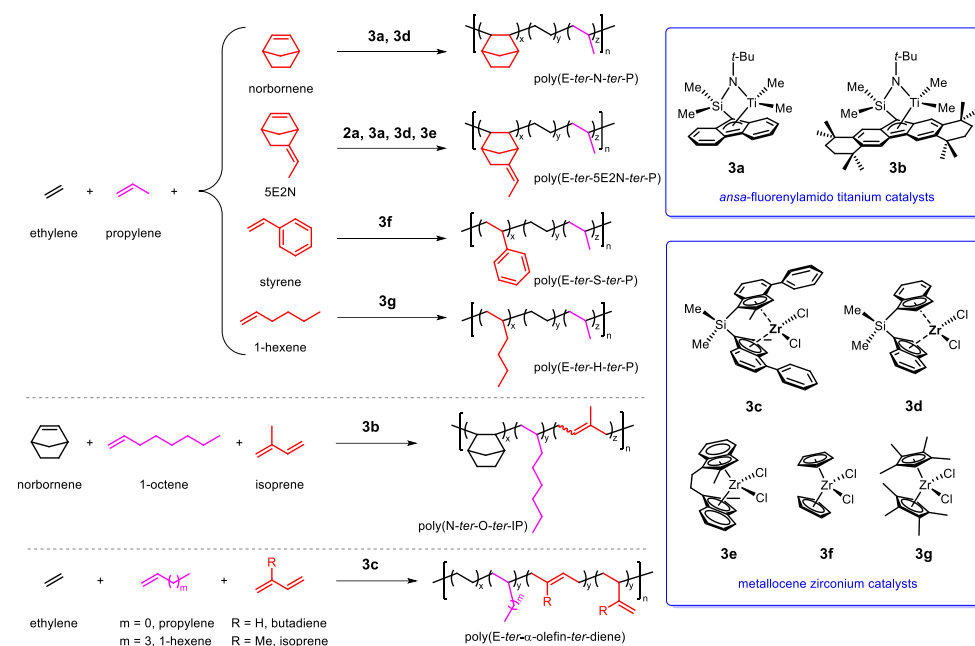


Scheme 4. Terpolymerization of ethylene, α -olefins, and cyclic olefins by **4a–4d** and **5**.

Half-sandwich scandium catalyst **6a** enabled, for the first time, the cycloterpolymerization of ethylene and styrene with α , ω -olefins to form terpolymers containing both saturated cyclic units and aromatic rings, which were also defined by the α , ω -olefin monomer structures employed (Scheme 5) [51,52]. Poly(E-*ter*-S-*ter*-HPD) obtained from **6a** features, six- and five-member rings (HPD content: 8–52 mol%), as well as a syndiotactic polystyrene block (15–83 mol%), exhibits a high T_m of approximately 250°C . No HPD-St sequence was formed during the terpolymerization because of the bulkiness of the two monomers. A five-member ring structure in the main chain (12–26 mol%) together with a small amount of vinyl branch (ca. 1.0 mol%) was observed in Poly(E-*ter*-S-*ter*-HD), which also contains 49–66 mol% of ethylene and 7–38 mol% of styrene. The terpolymers exhibit two sets of T_m values at 100 – 119°C and 206 – 241°C , which can be attributed to the polyethylene and syndiotactic polystyrene blocks, respectively.

Ternary coordination copolymerization of ethylene, styrene, and 1,3-butadiene was first achieved using a thioanisole-modified CGC yttrium catalyst **6b**. Owing to its unique structure, this catalyst effectively couples high activity and stereoselectivity in styrene polymerization with good copolymerization capacity with ethylene and 1,3-butadiene. The resulting poly(E-*ter*-S-*ter*-BD) features a high BD content (54.6–85.2 mol%), with mainly 1,4-units (ca. 80%), as well as comparable contents of ethylene segments (12.8–27.9 mol%) and syndiotactic styrene sequences (1.5–27.7 mol%). This is attributed to the higher reactivity of BD relative to the other two monomers. The multiblock microstructure of the terpolymer

affords it microphase separation and excellent compatibility when blended with other rubber materials, such as SBR, leading to enhanced tensile strength, elongation at break, and rolling resistance [53].



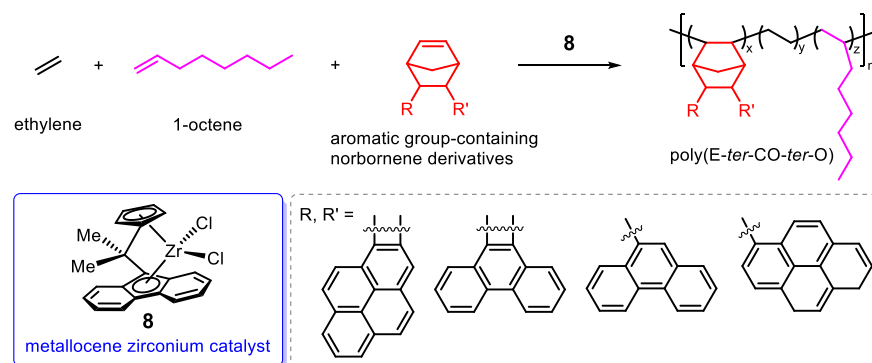
Scheme 5. Terpolymerization behaviors of scandium catalysts **6a**, **6b**, **7a** and **7b**.

Cyclopentadienyl scandium catalysts **7a** and **7b** are highly active ($1270\text{--}1860\text{ kg mol}^{-1}\text{ h}^{-1}\text{ bar}^{-1}$) in the terpolymerization of ethylene, norbornene and DCPD to generate poly(E-ter-N-ter-DCPD) with moderate molecular weight ($M_n = 49\text{--}136\text{ kg mol}^{-1}$), narrow PDI (1.7–2.3), and adjustable cyclic monomer contents from 47.4 to 59.8 mol%, in which the NB contents are 17.7–42.4 mol% and the DCPD contents are 8.8–38.6 mol%, respectively [54]. It is extraordinary that the highest cyclic monomer content exceeds 50 mol%, suggesting the existence of a continuous NB-DCPD sequence that has never been observed in a similar rare earth metal-catalyzed binary and ternary copolymerization systems. The high cyclic monomer content gives the terpolymers high T_g values up to $163\text{ }^\circ\text{C}$, while cleavage of the unsaturated $\text{C}=\text{C}$ bond of the DCPD unit and the introduction of an OH group further increase the T_g to $202\text{ }^\circ\text{C}$, with an improved hydrophilicity of the material.

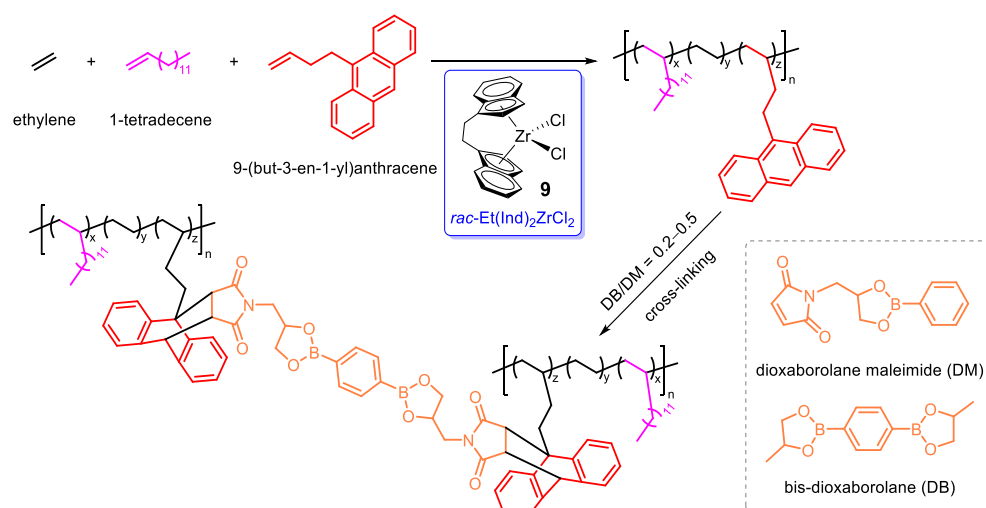
Assuming that the installation of aromatic groups would increase the polymer's refractive index and that the introduction of long branches could improve the melt processing, Jian and coworkers conducted the terpolymerization of ethylene, 1-octene, and high refractive index norbornene-based monomers (Scheme 6) [55]. The metallocene zirconium catalyst **8** exhibited high activity (above $1000\text{ kg mol}^{-1}\text{ h}^{-1}$) and excellent copolymerization ability. Indeed, the obtained terpolymers exhibit higher refractive indices (1.627–1.675) at 589 nm than the commercially available COCs, whereas their T_g values ($63\text{--}184\text{ }^\circ\text{C}$) are comparable to those of the latter. The detailed polymer microstructure, together with the thermal, optical, and mechanical properties, has been studied.

Polyolefin elastomers (POEs) composed of crystalline polyethylene segments (the hard block) and randomly distributed higher α -olefin sequences (the soft block) exhibit good mechanical strength and elasticity and are more attractive than natural and synthetic rubber materials due to their thermoplasticity and reprocessability. Recently, Li and coworkers reported a terpolymerization of ethylene, 1-tetradecene, and 9-(but-3-en-1-yl)anthracene (BA) catalyzed by *rac*-Et(Ind) $_2$ ZrCl $_2$ catalyst **9** with the activity maintained above $8000\text{ kg mol}^{-1}\text{ h}^{-1}$ (Scheme 7) [56]. The obtained poly(E-ter-1-tetradecene-ter-BA)

was first grafted with dioxaborolane maleimide (DM) through D-A reaction. It was then cross-linked in the presence of bis-dioxaborolane (DB) to form reversible cross-linking through internal boronic ester bonds between the pendant anthracene groups, in which the crosslinking density can be adjusted by varying the BA contents (0.7–2.4 mol%) of the terpolymers and also changing the DM/DB ratio (0.2–0.5), respectively. These POE vitrimers have been shown to achieve a good balance between overall mechanical properties and processing performance, including processability and heat and chemical resistance.



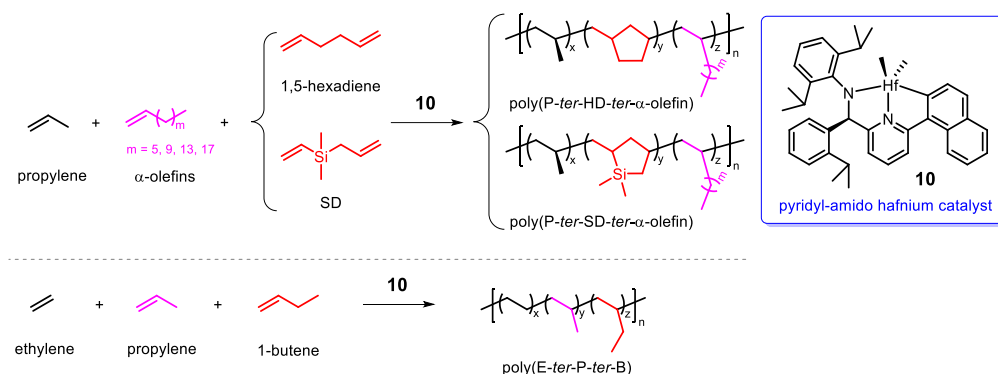
Scheme 6. Terpolymerization of ethylene, 1-octene, and high-refractive-index norbornene-based monomers catalyzed by **8**.



Scheme 7. Synthesis of cross-linkable polyolefin elastomers catalyzed by **9**.

The same group also conducted the terpolymerization of propylene, α -olefins, and α , ω -olefins with pyridyl-amido hafnium catalyst **10** to synthesize a new kind of propylene-based thermoplastic elastomer (TPE) containing a five-membered cyclic structure and long-chain branches in one pot (Scheme 8) [57]. Catalyst **10** exhibited high efficiency in producing terpolymers by varying both the type and concentration of the two comonomers in the feed. The products generally feature high melting points ($T_m = 75.4$ – 126.2 °C) and low glass transition temperatures ($T_g = -13.7$ – 0.9 °C), along with high molecular weight and a narrow PDI. Poly(P-ter-HD-ter-DO) exhibits excellent mechanical properties. It shows a tensile strength of 26 MPa, a high elongation at break of 1360%, an outstanding toughness of 153 MJ m^{-3} , and a remarkably high elastic strain recovery of up to 94%, representing the best performance among all current propylene- and α -olefin-containing elastomers. This work demonstrates the possibility of synthesizing high-performance elastomer materials by rationally adjusting the contents and sequences of crystalline segments, cyclic structures, and long branches, thereby effectively addressing the trade-off between tensile strength

and elastic recovery. More recently, catalyst **10** was also used to synthesize a terpolymer from ethylene, propylene, and 1-butene. The enhanced mechanical properties, compared to those of ethylene-propylene and propylene-butene copolymers, demonstrate the synergistic effect of the introduced termonomers in developing advanced polypropylene-based materials [58].

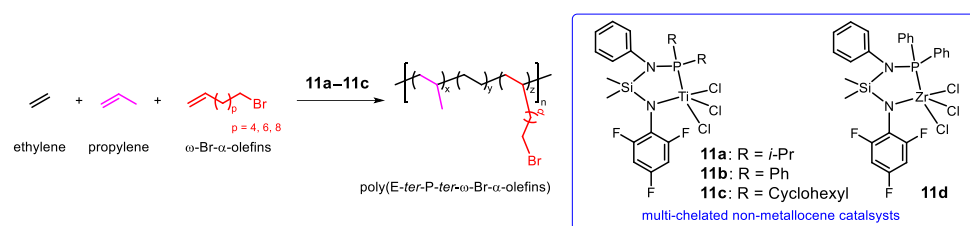


Scheme 8. Terpolymerization of ethylene, α -olefins, and α, ω -olefins catalyzed by **10**.

3. Ternary Polymerization of Olefins with a Polar Monomer

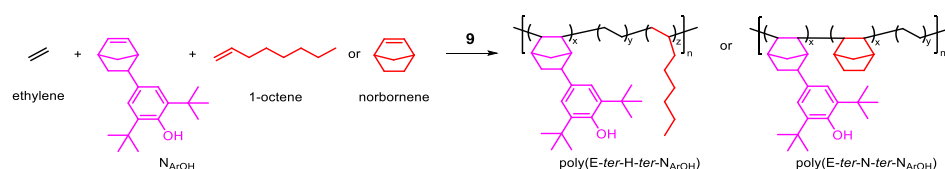
The introduction of a tiny amount of polar functional groups into the non-polar polyolefin backbone can significantly improve adhesion, dye retention, printability, compatibility, and other material properties. The direct coordination copolymerization of an olefin with polar monomers is the simplest and most effective method for synthesizing polar-functionalized polyolefins. Early transition-metal catalysts, such as Ti, Zr, and Hf, are easily poisoned by polar functional groups because of their inherent oxygen affinity. Nevertheless, with appropriate synthetic strategies, a few early transition-metal catalysts have enabled the direct copolymerization of ethylene with polar monomers, and these studies have been summarized in previous reviews. This review first focuses on the terpolymerization of polar monomers catalyzed by early transition-metal catalysts. In contrast, late transition-metal catalysts, such as Ni and Pd, with high electron saturation, exhibit strong tolerance toward heteroatoms and can catalyze the direct copolymerization of olefins and polar monomers without the need for protective masking reagents. Recently, numerous catalysts designed rationally, polar monomers with innovative structures, and polyolefin materials with new functions have been explored. The late-transition-metal-catalyzed terpolymerization of olefins with polar heteroatoms, carbon monoxide, and functional groups is also summarized here, which is of great significance for the precise preparation of advanced polyolefin materials.

Multi-chelated non-metallocene titanium catalysts **11a–11c** were synthesized and applied to the terpolymerization of ethylene, propylene, and ω -Br- α -olefins (Scheme 9) [59]. Catalyst **11a** is more active than **11b** and **11c** under consistent conditions, with the highest activity of $621 \text{ kg mol}^{-1} \text{ h}^{-1}$ observed in the terpolymerization with 11-bromo-1-undecylene. Both catalytic activity and molecular weight increase with the number of methylene groups between the olefin double bond and the Br atom, suggesting a weaker poisoning effect and less backbiting. Polar incorporation can be controlled within the range of 1.02–2.49 mol% by varying the types and concentrations of polar monomers in the feed. Zirconium catalyst **11d** was active for the terpolymerization of ethylene, propylene, and higher α -olefins (1-hexene, 1-octene, and 1-decene) with activities up to $10^4 \text{ kg mol}^{-1} \text{ h}^{-1}$ and α -olefin incorporations within the range of 1.2–16.3 mol%, respectively. Although this efficiency has been reported, the terpolymerization involving a polar monomer has not yet been described with the same catalyst [60].



Scheme 9. Terpolymerization of ethylene, propylene, and ω -Br- α -olefins catalyzed by **11a–11c**.

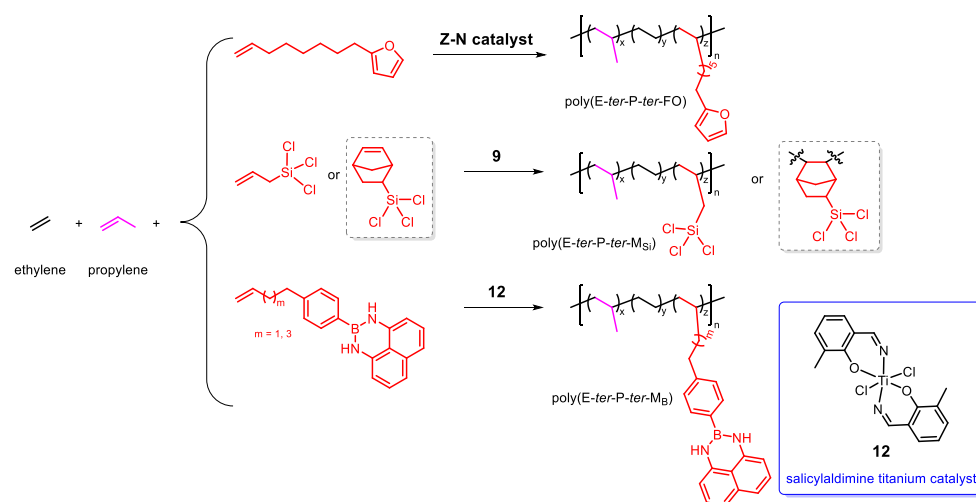
The addition of antioxidant stabilizers, such as BHT, to polyolefins can improve stability. However, the stabilizer may be lost from the polymer matrix due to weak interactions. Losio and coworkers studied the terpolymerizations of ethylene and BHT-containing cyclic olefins with 1-hexene and norbornene, respectively, catalyzed by **9**, to synthesize BHT-based terpolymers with BHT contents below 1 mol% (Scheme 10) [61]. The polymer products are used as macromolecular antioxidants, blended with commercially available LLDPE and COC materials, and exhibit good solubility in common solvents, excellent compatibility due to structural similarity, and long-term thermal stability without releasing molecular antioxidant groups.



Scheme 10. Synthesis of antioxidant polyolefins catalyzed by **9**.

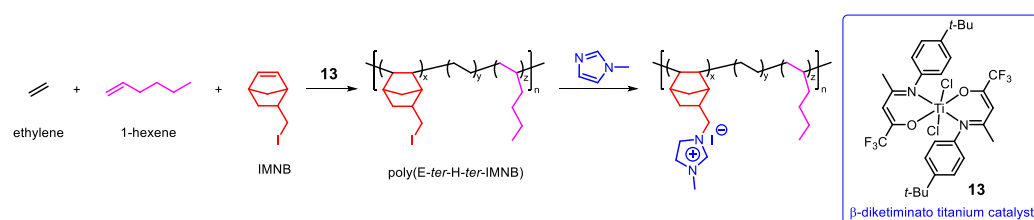
Li and coworkers introduced polar functionalized groups into EPR chains through the terpolymerization of ethylene and propylene with α -olefin- and norbornene-based polar monomers (Scheme 11) [62,63]. Poly(E-ter-P-ter-FO) was synthesized using a typical Z-N catalyst with moderate activity ($260\text{--}390\text{ kg mol}^{-1}\text{ h}^{-1}$) and adjustable FO contents of 1.1–9.7 mol%. It subsequently undergoes a Diels–Alder reaction between the furan groups and the bismaleimide, forming crosslinks in the terpolymer. The products exhibit thermoreversible behavior, undergoing de-crosslinking above $110\text{ }^{\circ}\text{C}$ and below $85\text{ }^{\circ}\text{C}$. Chlorosilane- (0.71–4.68 mol%) and methoxysilane-functionalized (0.11–0.45 mol%) terpolymers were polymerized by metallocene catalyst **9** with a high activity of $3910\text{--}4940\text{ kg mol}^{-1}\text{ h}^{-1}$. This catalyst was used to prepare EPR/SiO₂ composites in situ by adding a SiO₂-dispersed solution during polymerization. The installation of trichlorosilane groups significantly enhanced the compatibility of the polymer and SiO₂ particles. The SiO₂ content in the polymer reached up to 85 wt%, with uniform dispersion, a level that is difficult to achieve via physical blending. Both techniques reinforce EPR's mechanical properties, such as strength and modulus.

In 2024, Tanaka and Shiono reported the synthesis of a reversible cross-linking EPR material through the terpolymerization of ethylene, propylene, and an alkenylboronic acid comonomer, catalyzed by salicylaldehyde titanium catalysts **12**. The resulting terpolymers have M_n of $137\text{--}491\text{ kg mol}^{-1}$ and incorporate 0.10–0.74 mol% of the boron-containing monomer. The terpolymers undergo post-modification with acidified methanol and heating at $80\text{ }^{\circ}\text{C}$ to form cross-linked structures, yielding improved mechanical properties compared with conventionally sulfur-vulcanized EPDM. De-crosslinking is achieved by alcoholysis with a chelating reagent, such as N-methyl diethanolamine, affording the terpolymer good solubility in common solvents [64].



Scheme 11. Terpolymerization of ethylene and propylene with substituted α -olefins/cyclic olefins catalyzed by Z-N catalyst, 9, and 12.

Li and coworkers conducted terpolymerization of ethylene, 1-hexene, and 5-iodomethyl-2-norbornene with a β -diketiminato titanium catalyst **13**, which exhibited high activity ($6890\text{--}8210\text{ kg mol}^{-1}\text{ h}^{-1}\text{ MPa}^{-1}$) and strong tolerance toward iodine (Scheme 12) [65]. The IMNB and HE contents can be regulated within 3.6–7.4 mol% and 14.7–21.2 mol%, respectively. At the same time, the T_m of the terpolymer decreased from $66.4\text{ }^{\circ}\text{C}$ to $50.1\text{ }^{\circ}\text{C}$, and the T_m was not determined when the total comonomer content reached 27.9 mol%. The poly(E-ter-H-ter-IMNB) was then converted into polymeric ionomers by reacting with N-methylimidazole, followed by ion exchange with various anionic salts. Due to the existence of a dual-cross-linking network and the effect of different counter anion types, these thermoplastic elastomers demonstrate excellent mechanical properties, including stress-at-break values of (5.4–13.7 MPa), strain-at-break values of (432–624%), and elastic recovery of up to 96%, respectively.

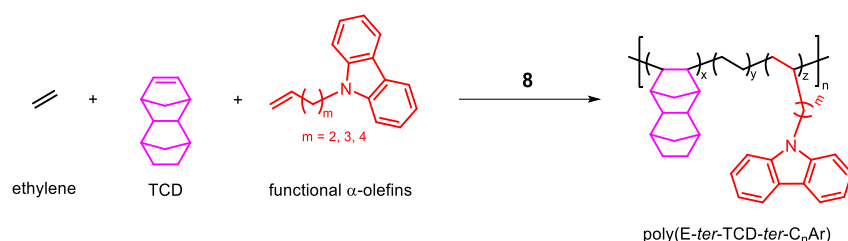


Scheme 12. Synthesis of polymeric ionomers by catalyst **13**.

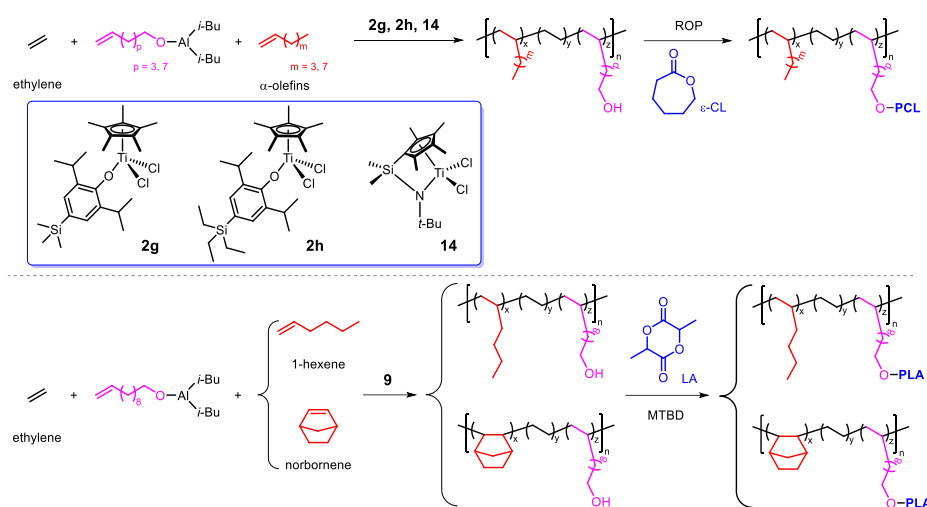
A high-refractive-index carbazole group was incorporated into the COC polymer chain through the terpolymerization of ethylene, TCD, and C_nAr to develop COT with enhanced properties by metallocene catalyst **8** (Scheme 13) [66]. The catalytic activity remained in the order of $105\text{ kg}^{-1}\text{ mol}^{-1}\text{ h}^{-1}$ under varying total monomer concentration, comonomer ratio, and methylene length between the olefin double bond and the carbazole group. The high TCD content of 26.3–35.8 mol% resulted in high T_g values ($115\text{--}167\text{ }^{\circ}\text{C}$) for the terpolymer. The effective incorporation of the carbazole-based monomer improved the refractive index to 1.550–1.569 and maintained excellent transparency (93–95% transmittance), making it a promising optical material.

Nomura and coworkers developed aryloxo-modified half-titanocene catalysts **2g** and **2h** with SiMe₃ and SiEt₃ *para*-substituents for the terpolymerization of ethylene and α -olefins with 1-alkenes bearing a terminal hydroxy group (protected by aluminumalkyl) (Scheme 14) [67]. Both catalysts **2g** and **2h** outperform the other half-titanocene catalysts and

the CGC-titanium catalyst in terms of catalytic activity, thermal stability, tolerance to polar monomers, and molecular weight, owing to the stabilizing effect of silicon-containing substituents on the active species. This work demonstrates the first synthesis of high-molecular-weight (M_n of up to 141 kg mol^{-1}) OH-functionalized ethylene copolymers with adjustable OH contents (3.0–2.5 mol%) by the Group 4 transition metal catalysts. Poly(ethylene-*ter*-DC-*ter*-(DC-OH)-*graft*-poly(CL)) with high molecular weights ($243\text{--}274 \text{ kg mol}^{-1}$) and narrow PDI (1.70–1.77) was then prepared through the ring-opening polymerization (ROP) of ϵ -caprolactone (CL) from the pendant OH groups. Li and coworkers also reported the synthesis of graft copolymers by combining the coordination terpolymerization of ethylene, 10-undecen-1-ol, and 1-hexene/norbornene, followed by the ROP of L-lactide (L-LA) initiated by a MTBD catalyst from the terminal hydroxyl groups [68]. The OH contents of the obtained LLDPE_{OH} and COC_{OH} products, in the first stage, were 4.5–5.4 mol%, and the PLA contents in the graft copolymers were controlled at 63–89 mol%, with the PLA blocks bearing molecular weights of 2–3 kg mol^{-1} . The products serve as efficient toughening agents for commercial PLA, and the polymer blends exhibited improved strength and toughness while maintaining other excellent material properties, such as good transparency.

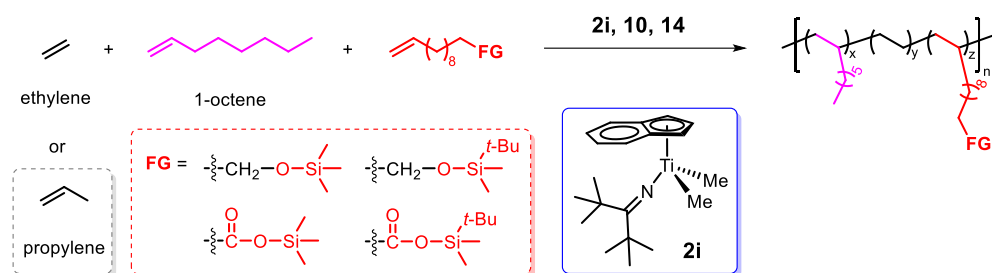


Scheme 13. Terpolymerization of ethylene, TCD, and functional α -olefins catalyzed by **8**.



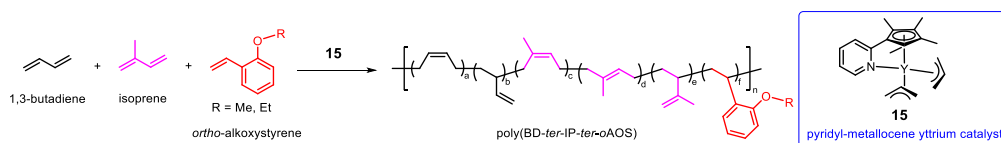
Scheme 14. Synthesis of polyolefin graft polymers with PCL and PLA by catalysts **2g**, **2h**, **9**, and **14**.

To synthesize polar-functionalized POEs with higher molecular weights and controllable incorporation of polar groups, Chen and coworkers developed a silane protection strategy, superior to the conventional protective aluminum reagent, for the terpolymerization of ethylene/propylene and 1-octene with Si- and O-containing polar monomers (Scheme 15) [69]. Catalyst **2i** is more effective in the nominated terpolymerizations than catalysts **10** and **14**; the highest activity of **2i** reached $10,800 \text{ kg mol}^{-1} \text{ h}^{-1}$, yielding terpolymers with molecular weights up to 438 kg mol^{-1} and reasonable incorporation of the polar monomer at 0.7–2.7 mol%. Both the activity and molecular weight are higher than those of the terpolymers obtained by a similar terpolymerization using polar monomers protected with triisobutylaluminum, demonstrating great potential for practical production.



Scheme 15. Synthesis of polar-functionalized POEs catalyzed by **2i**, **10**, and **14**.

With the prospect that rare earth metals present good tolerance toward polar functional groups, pyridyl-metallocene yttrium catalyst **15** was selected for the heteroatom-assisted tercopolymerization of polar *ortho*-alkoxystyrene (*o*AOS), isoprene (IP), and butadiene (BD) by Cui and coworkers (Scheme 16) [70]. This is the first report of successful synthesis of polar functionalized poly(*o*AOS-*ter*-IP-*ter*-BD)s with high *o*AOS contents (5.6–62.5 mol%), high molecular weight ($M_n = 94$ –250 kg mol^{−1}), and relatively narrow PDI (1.1–1.4). Polymer microstructure analysis and kinetic studies revealed that these terpolymers have high syndio- and *cis*-1,4-regioregularity, including gradient poly(*o*MOS-*ter*-IP-*ter*-BD) and random poly(*o*EOS-*ter*-IP-*ter*-BD), respectively, due to the different steric hindrance effects of the two monomers.

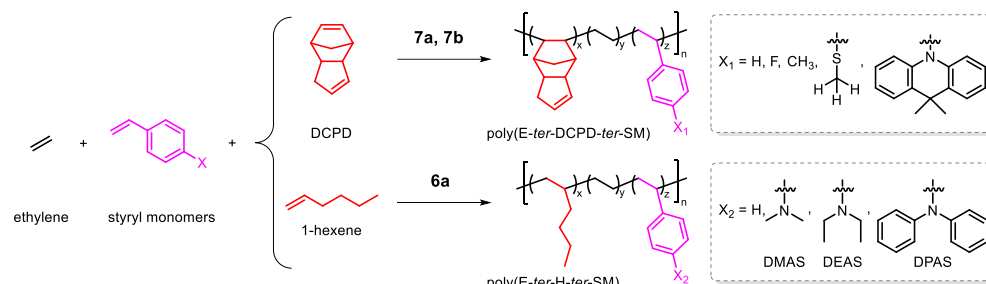


Scheme 16. Terpolymerization of 1,3-butadiene, isoprene, and *ortho*-alkoxystyrene catalyzed by **15**.

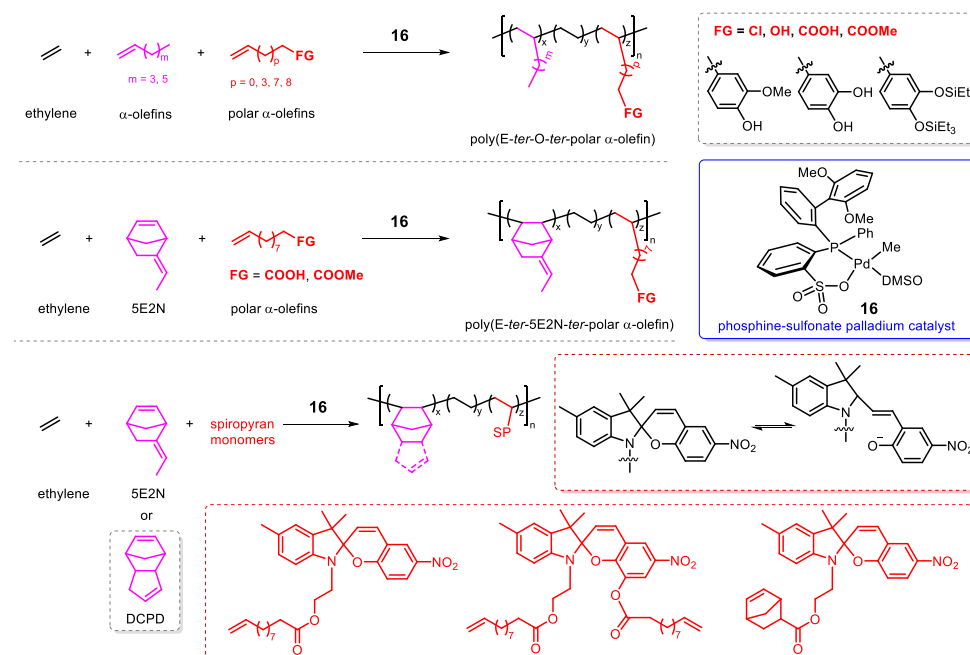
The same group recently reported the terpolymerization of ethylene and DCPD with differently substituted styrene to synthesize a new type of COC material, followed by post-modification of the remaining unsaturated double bonds (Scheme 17) [71]. Both scandium complexes **7a** and **7b** yield styryl-monomer-rich terpolymers upon installation of an electron-donating substituent. At the same time, higher DCPD contents (26.6–28.4 mol%) than that of the styryl monomer (7.0–13.0 mol%) can be observed when an electron-withdrawing substituted monomer, such as styrene-F and styrene-*p*-(9,9-dimethyl-9,10-dihydroacridinyl), is used. The terpolymer microstructures depend on the comonomer concentration, in which the high DCPD and styryl monomer concentration afford a high- T_g -terpolymer with DCPD-(E)_y-DCPD and discrete styrene-F sequences, while a low comonomer concentration gives styrene-F-(E)_x-styrene-F units that contribute to low T_g values. Catalyst **6a** is also active for the terpolymerization of ethylene (E) and 1-hexene (H) with styrene (St) or styrene derivatives (DMAS, DEAS, and DPAS). Both the activities of E-H-DMAS terpolymerization (1720–2550 kg mol^{−1} h^{−1}) and E-H-DEAS terpolymerization (1404–2280 kg mol^{−1} h^{−1}) are lower than those of E-H-St terpolymerization (3684–4780 kg mol^{−1} h^{−1}) due to the interaction of the amine group with the central metal. At the same time, a higher activity (5020–5730 kg mol^{−1} h^{−1}) was observed in the terpolymerization of ethylene, 1-hexene, and DPAS. Similarly, there is no continuous H-H, St-St, or St-H sequence in the terpolymer, indicating a uniform and random dispersion of the different monomers [72].

Late transition metal catalysts based on nickel and palladium have great potential for the direct synthesis of polar functionalized polyolefins due to their strong tolerance toward polar substituents. Phosphine sulfonate palladium catalyst stands out due to its high catalytic activity, good copolymerization capacity with a broad scope of olefin monomers, and the ability to produce linear polyethylene with polar functional groups inserted in the main chain. Chen and coworkers reported a series of terpolymerizations involving ethy-

lene, α -olefins, cyclic olefins, polar, and multifunctional monomers using the nominated catalyst (Scheme 18) [73–76]. Catalyst 16 terpolymerized ethylene, 1-octene, and long-chain-branch α -olefin with terminal COOH/COOMe/Cl groups with moderate activity of ca. $100 \text{ kg mol}^{-1} \text{ h}^{-1}$ to produce terpolymers with molecular weights of $22\text{--}133 \text{ kg mol}^{-1}$ and polar monomer incorporation of $0.7\text{--}1.4 \text{ mol}\%$, respectively. The terpolymers exhibited enhanced tensile properties and surface polarity. The same catalyst was then used for the synthesis of terpolymers from ethylene, ENB, and COOH/COOMe-substituted 1-decene with significantly improved ENB content ($5.7\text{--}22.3 \text{ mol}\%$), polar monomer incorporation (up to $2.6 \text{ mol}\%$), and terpolymer molecular weight (up to $1760 \text{ kg mol}^{-1} \text{ h}^{-1}$). The introduction of long branches (with terminal polar groups) and cyclic structures (with unsaturated) reduces the crystallinity of polyethylene, and the addition of iron ions in the polymeric matrix forms iron-carboxylate interactions that can be regulated under UV light, affording polar-functionalized, cross-linkable, self-healing, and photoresponsive materials. The terpolymerization of ethylene with 1-hexene and bioresourced catechol-functionalized monomers, incorporating various metal ions, yielded polyolefin products with improved mechanical properties and dynamic behavior that enable self-healing. Similarly, the installation of spiropyran (SP) on the polyolefin chain through the terpolymerization of ethylene, DCPD/ENB, and SP-based termonomer with different patterns (alkyl chain, double olefin bonds, and cyclic structure) generated light, heat, and force-responsive materials via the stimulus-responsive function of the intramolecular SP group.



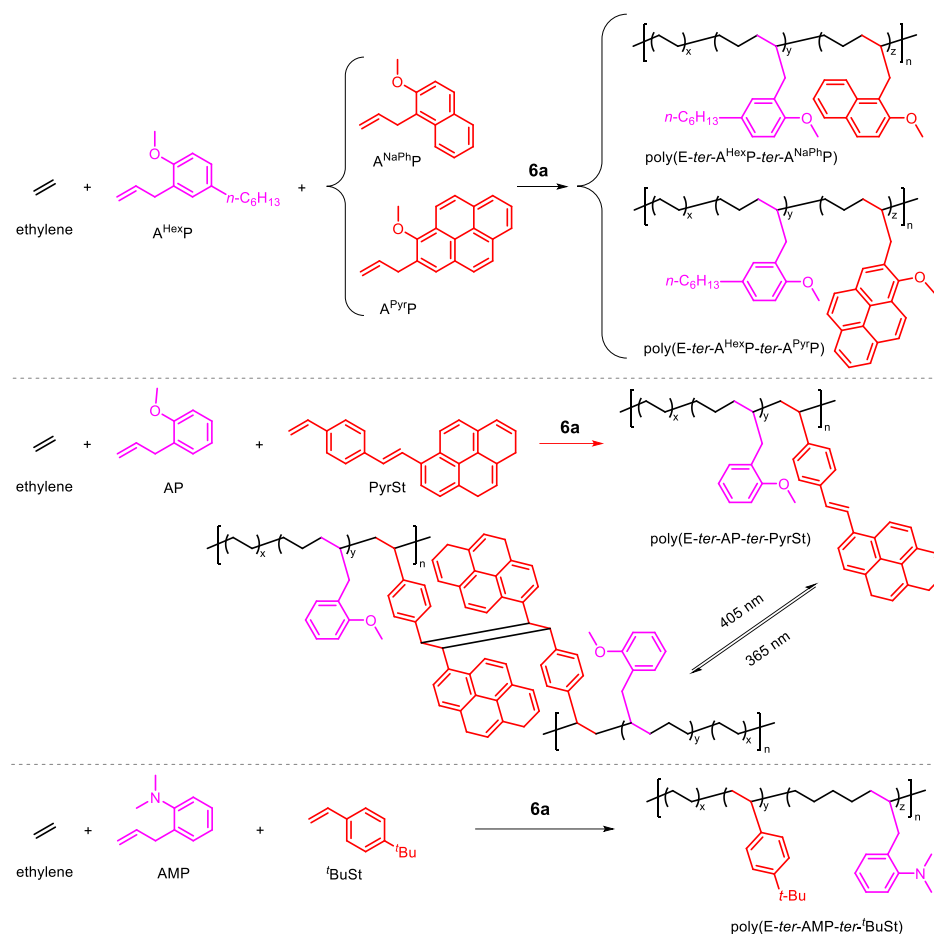
Scheme 17. Terpolymerization of ethylene, DCPD, and styryl monomers catalyzed by **6a**, **7a**, and **7b**.



Scheme 18. Terpolymerization behaviors of the late transition metal catalyst **16**.

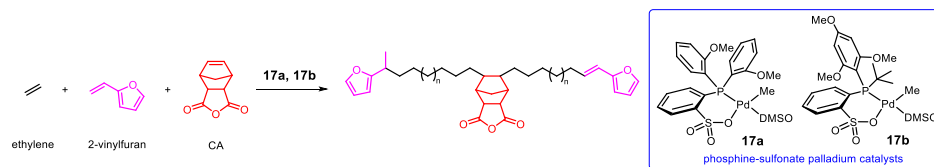
4. Ternary Polymerization of an Olefin with Two Polar/Functionalized Monomers

The first example of the effective terpolymerization of a non-polar olefin with two different polar functionalized olefin monomers was achieved by Hou and coworkers with the use of half-sandwich scandium catalyst **6a** (Scheme 19) [77]. This affords a series of terpolymers with precisely controllable sequence distribution, excellent strength and elasticity, and, most importantly, self-healing functionality. The terpolymerization of ethylene with two substitute allyl benzene monomers, the A^{HexP} and $A^{\text{NaPhP}}/A^{\text{PyrP}}$, affords multi-block poly(E-*ter*- A^{HexP} -*ter*- $A^{\text{NaPhP}}/A^{\text{PyrP}}$) with a short crystalline polyethylene block, a soft block containing alternating E- A^{HexP} sequence, and a hard block with alternating E- $A^{\text{NaPhP}}/A^{\text{PyrP}}$ sequence, respectively. Similarly, the terpolymer obtained from ethylene, AP, and 4-[2-(1-pyrenyl)ethyl]styrene (Pyr) comprises multiple blocks with a short polyethylene chain, an E-*alt*-AP sequence, and discrete Pyr units, demonstrating excellent tensile and fluorescent properties [78]. Moreover, the unsaturated C=C double bond between the styrene and pyrene moieties in the product can undergo a photoinitiated [2 + 2] cycloaddition to form a reversible cross-link. When AMP, equipped with a slightly bulky NMe_2 group on the ortho position, was used as the polar monomer, the terpolymerization of ethylene, 4-*tert*-butylstyrene, and AMP generates a distinguishing multi-block terpolymer with continuous polyethylene segments, continuous polystyrene segments, and alternating sequences consisting of AMP and two ethylene units [79]. Mechanism studies revealed that the self-healing of the above terpolymers originates from a nanophase-separated structure comprising crystalline or amorphous (high T_g) hard segments dispersed in a flexible, low- T_g matrix.



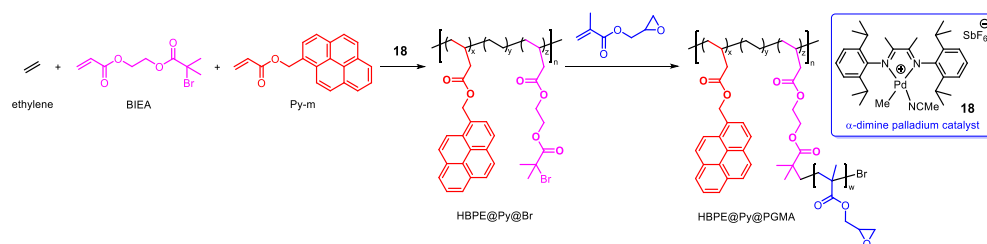
Scheme 19. Terpolymerization of a non-polar olefin with two different polar/functionalized olefin monomers catalyzed by **6a**.

Catalyst **17a** and **17b** with different substituents on the phosphine have also been used for the terpolymerization of ethylene, 2-vinylfuran, and carbic anhydride (CA) to synthesize an unusual telechelic terpolymer with CA units inserted in-chain and the VF mainly distributed at the chain ends (Scheme 20) [80]. Both experimental studies and DFT calculations have verified the detailed mechanism.



Scheme 20. Terpolymerization of ethylene, 2-vinylfuran, and CA catalyzed by **17a** and **17b**.

Xu and coworkers reported the synthesis of fluorescent polyethylene from the terpolymerization of ethylene with two substituted acrylate monomers, BIEA and Py-m, catalyzed by α -dimine palladium catalyst **18**, followed by the graft polymerization of GMA through the terminal Br atom via the atomic transfer radical polymerization (ARTP) method (Scheme 21) [81]. The obtained terpolymers, HBPE@Py@Br and HBPE@Py@PGMA, have molecular weights of 12.4 kg mol^{-1} and 47.5 kg mol^{-1} , respectively, and the Py content was fixed at 0.8 per 100 ethylene units. The installation of PGMA block onto terpolymers renders them well-dispersible in matrices such as epoxy resin, ethylene-vinyl acetate copolymer, poly(methyl methacrylate), and polystyrene, and they exhibit strong fluorescence even at extremely low pyrene concentrations (0.05–0.20 wt%) in the blending systems.



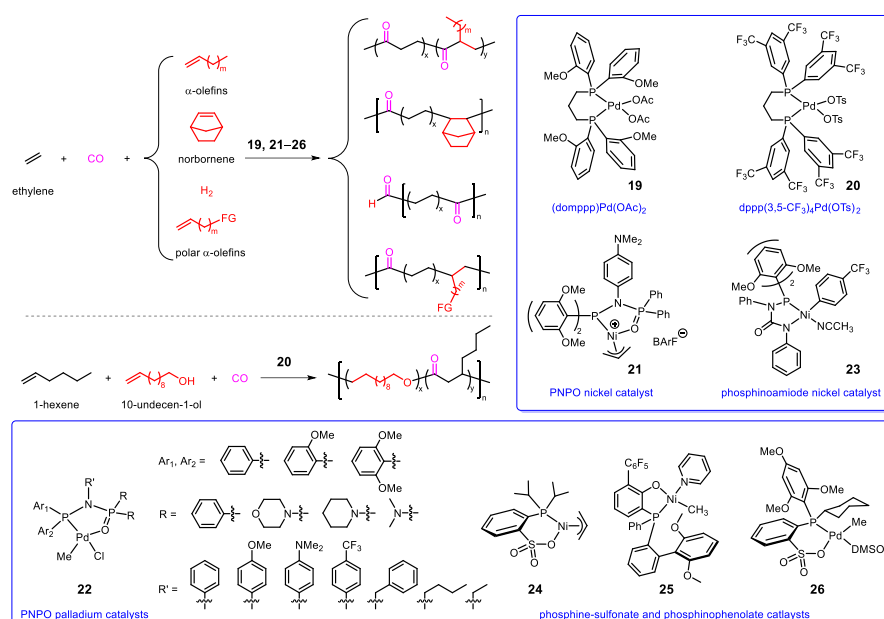
Scheme 21. Synthesis of fluorescent polyethylene by catalyst **18**.

5. Ternary Polymerization of Olefins with Carbon Monoxide

The carbonylative polymerization of ethylene with carbon monoxide (CO) has been an attractive approach, as it not only enables effective utilization of C1 resources but also offers new insights into the synthesis of aliphatic polyester (carbonyl-functionalized polyethylene) with photodegradable properties. The early attempts on the synthesis of carbonyl-functionalized polyethylene rely on free radical pathways, which gives copolymer with very high ethylene contents and high branches, exhibiting a low T_m and poor mechanical properties [82]. The subsequent development of coordination polymerization technique allowed precise control toward the CO content, sequential distribution, and copolymer branches. Since CO, similar to the polar groups, poisons the transition metal center easily, coordination copolymerization of olefins with carbon monoxide requires a catalyst with strongly tolerant transition metal catalysts. Bidentate phosphine palladium complexes, due to their strong tolerance and good copolymerization capacity, have been reported by Drent and coworker to copolymerize ethylene with CO, which produces linear and alternating polyketone and realizing industrialization [83,84].

Recently, the incorporation of a third olefin monomer, such as propylene, norbornene, or polar α -olefin monomers, has emerged to regulate polymer properties further and develop new environmentally friendly polymeric materials (Scheme 22). The (domppp)Pd(OAc)₂ catalyst **19**, in the presence of glycine betaine hydrochloride to form stable Pd nanosalts,

was applied for the terpolymerization of ethylene and CO with propylene or 1-hexene, representing the first example of antifouling polyketones (T_m value ca. 230 °C) that was synthesized without any heterogeneous seeds [85]. The $\text{dppp}(3,5\text{-CF}_3)_4\text{Pd}(\text{OTs})_2$ catalyst **20** can catalyze the terpolymerization of 1-hexene and CO with bifunctional α, ω -alkenols, such as 10-undecen-1-ol, to produce branched polyketooesters [86]. The terpolymer molecular weights can be adjusted from 1.1 to 18.9 kg mol^{−1} by varying the comonomer ratio, while maintaining very low crystallinity. The material can also become amorphous. A family of N, O, and P hybrid ligands has been developed for the synthesis of palladium and nickel catalysts used in the terpolymerization of ethylene and CO with α -olefins. PNPO catalysts exhibited a higher preference for the third olefin monomer compared to the conventional dppp-type catalysts. The PNPO nickel catalyst **21** terpolymerized ethylene and CO with propylene to give an alternating terpolymer with a productivity of 545 gPK (gNi)^{−1} with a typical propylene incorporation at 4.0 mol% [87], while the PNPO palladium catalyst **22** produced similar terpolymers with activities of 11.6–65.6 gPK mol^{−1} h^{−1} and propylene contents of 3.3–5.9 mol% [88]. Phosphinoamidate nickel catalyst **23** is efficient for the ethylene copolymerization with CO, of which the activity is up to 12,000 gPK (gNi)^{−1} [89]. However, the introduction of propylene as the third monomer significantly reduced productivity (350–5680 gPK^{−1} (gNi)^{−1}) and increased its incorporation (3.8–18.3 mol%). A remarkably high productivity of ca. 20,000 gPK (gNi)^{−1} was achieved by phosphine-sulfonate nickel catalyst **24** towards the terpolymerization of ethylene and CO with propylene, due to the installation of strong electronic-donating *i*Pr substituents on the phosphorus moiety [90]. In addition to these highly crystalline carbonyl-functionalized polyethylenes, other types of the third monomer have also been introduced into the terpolymerizations. Norbornene was introduced via terpolymerization with ethylene and CO using phosphinophenolate nickel catalyst **25**, thereby tuning the crystallinity of the terpolymers, which exhibited significantly reduced T_m values at ca. 125 °C with NB and CO contents of 0.5–3.3 mol% and 0.7–1.4 mol%, respectively [91]. Phosphine-sulfonate palladium complex **26** catalyzed the terpolymerization of ethylene and CO with various polar monomers, including acrylates, acrylic acid, vinyl ethers, vinyl acetate, and acrylonitrile, to produce photodegradable polar-functionalized polyethylenes [92]. Later, the introduction of H₂ as an inducer of chain-transfer reactions in the copolymerization of ethylene and CO, mediated by the same catalyst, affords an extraordinary aldehyde-end-capped polyethylene with in-chain ketones [93].



Scheme 22. Carbonylative polymerization of olefins with carbon monoxide catalyzed by 19–26.

6. Conclusions and Outlook

To conclude, the ternary coordination–insertion polymerization of olefin monomers catalyzed by transition-metal catalysts over the past fifteen years is summarized here. All-hydrocarbon/non-polar olefin monomers, including ethylene, propylene, (substituted) α -olefins, conjugated and non-conjugated dienes, styrene, and cyclic olefins, are terpolymerized mainly by well-defined early transition metal metallocene and non-metallocene catalysts. It achieved significant improvements in the mechanical, thermal, and other properties of the terpolymers, yielding high-performance polyolefin materials, including advanced elastomers and cycloolefin copolymers. Late transition-metal catalysts based on Ni and Pd, together with rare-earth metal catalysts bearing Sc and Y centers, generally exhibit strong tolerance toward terpolymerization with heteroatom-containing monomers. Not only polar-modified polymer products but also versatile polyolefins with antioxidant, fluorescent, stimuli-responsive, self-healing, cross-linkable, reprocessible, degradable, and other functional properties have been successfully developed.

As the most promising approach for developing advanced polyolefin materials, coordination-insertion polymerization will continue to be the subject of in-depth study. Promising research directions include the design and synthesis of novel transition-metal catalysts with high activity, high stability, strong tolerance, and, most importantly, high copolymerization ability. In addition, the dual design of unique functionalized olefin monomers, combined with new regulatory techniques for the polymerization process, will endow materials with improved performance and additional functionality. Mechanism studies of complex active species in multicomponent polymerizations will help researchers better understand the polymerization catalysis and design more effective catalytic systems and products. Moreover, combining coordination polymerization with other polymerization methods, such as post-modification via ionic polymerization, radical polymerization, and other techniques, will further push beyond the limits of coordination-insertion polymerization, enabling the development of more advanced polyolefin-based composites.

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