

# Recent Advances in Controlled Production of Long-Chain Branched Polyolefins

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Polyolefins, composed of carbon and hydrogen atoms, dominate global polymer production. This stems from the wide range of physical and mechanical properties that various polyolefins can cover. Their versatile properties are largely tuned by chain microstructure, including molar mass distribution, comonomer content, and long-chain branching (LCB). Specifically, LCB imparts unique characteristics, notably enhances processability crucial for downstream applications. Tailoring LCB structural features has encouraged academic and industrial efforts, chronicle in this review from a chemistry standpoint. While encompassing post-reaction modification based traditional methods like peroxide grafting, ionizing beam irradiation, and coupling reactions, the main focus is given to catalyst-centric strategies and innovative polymerization schemes. The advent of single-site catalysts—metallocenes and late transition metals catalysts—amplifies interest in tailored chemical methods, but the progress in LCB formation flourishes via tandem catalytic systems and bimetallic catalysts under controlled reaction conditions. Specifically, the breakthrough in coordinative chain transfer polymerization unveils a novel avenue for controlled LCB synthesis by sequential chain propagation, transfer, liberation, and enchainment. This short review highlights recent approaches for the production of LCB polyolefins that can provide a roadmap crucial for researchers in academia and industry, steering their efforts toward further advancements in the production of tailored polyolefin.

## 1. Introduction

Chain microstructure is a multi-dimensional key factor in determining the properties of any polymer product. In polyolefins, specifically, chain microstructure is mainly described by distributions of the molar mass, comonomer content, and chain branching.<sup>[1]</sup> The structure of chain branching also includes the branch length, their frequency, and distribution. Based on the length of branches, branched polyolefins are classified as long-chain and short-chain branched (SCB) polyolefins. These two types of branches are not only introduced into the polymer backbone in different ways but also induce substantially different changes in the final properties.<sup>[2,3]</sup> Moreover, characterization methods for detecting their nature and fraction are totally different.<sup>[4,5]</sup> Therefore, it is crucial to identify the effect of branch length on polyolefins' properties.

SCBs can be introduced into the polymer backbone either through direct copolymerization of ethylene and  $\alpha$ -olefin comonomers in a traditional early transition metal-based coordination copolymerization or formed following a specific mechanism called "chain-walking" enabled in the polymerization of ethylene in the presence of Ni/Pd-based late-transition metal catalysts.<sup>[6]</sup> The control over the short-chain branch's structure and frequency is possible in both methods by changing the  $\alpha$ -olefin type and concentration, in the former, and manipulating the structure of the catalyst, in the latter.<sup>[7]</sup> There are circumstances where the parallel formation of SCBs besides long chain branches (LCBs) is inevitable and it is necessary to distinguish them.<sup>[8]</sup> Theoretically, a long chain branch needs to have a molar mass greater than at least one entanglement length,  $M_e$ , which for polyethylene is known to be  $\approx 140$  carbons.<sup>[9,10]</sup> Only beyond this length, the presence of LCBs can induce a perceptible rheological response and cause a difference in properties. Specifically, a dramatic deviation in rheological behavior at the terminal zone, like zero-shear viscosity, from those of linear polymers is observed upon the introduction of a trace of LCBs.<sup>[11]</sup> These deviations are indirectly used to quantify the LCB content from the various rheological properties like dynamic storage and loss moduli,  $G'$  and  $G''$ , and the loss angle,  $\delta$ .<sup>[8,12–14]</sup> The alternative direct method of LCB quantification in polyolefins based on NMR spectroscopy, unfortunately,

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DOI: 10.1002/marc.202300746

fails to distinguish between branches longer than six carbons.<sup>[15]</sup> Another alternative technique is based on coupling size exclusion chromatography with multi-angle laser light scattering, which indirectly determines the LCB content by comparing the radius of gyration of each polymer fraction to that of a linear reference chain having the same molar mass.<sup>[16]</sup> The drawback is the need for considering a standard form factor and lack of sensitivity. Another drawback associated with the latter two methods is the necessity of using toxic solvents at high temperatures to dissolve polyolefins, therefore, indirect methods based on rheology are usually preferred.<sup>[3,17]</sup>

Unlike SCBs, long branches are able to form lamellar crystals of their own and traditionally have fewer effects on physical, thermal, and mechanical properties. This is of course due to the significantly lower fractions at which LCBs naturally appear in polyolefins compared to those of SCBs, otherwise, LCBs could similarly undermine the crystallinity and the associated thermal and mechanical properties. A good example is LDPE where LCB is frequently produced by chain transfer, along with SCB formed by back-biting, resulting in mechanical properties much lower than a linear low-density polyethylene (LLDPE) with comparable SCB content. In some reports, LCBs are even accounted for the subtle increase in crystallinity due to their assistance in entanglement-induced nucleation process.<sup>[18]</sup> Nevertheless, LCBs induce drastic effects on the properties of a polymer melt, that is, shear thinning, melt strength, and melt elasticity, which are closely related to its processability.

From an industrial point of view, LCB polymers offer superior processability and are, therefore, practically desirable. Good processability means low energy or power consumption in fabricating articles from polyolefin resins by extrusion, injection, or film-blowing process, which include enhanced melt strength, polyethylene (LLDPE) film grades with low-density polyethylene (LDPE) is a common approach to overcome the unfavorable processability of LLDPE in the film blowing process.

These examples highlight the importance of controlled synthesis of LCB polyolefins, specifically polyethylenes as the major member of polyolefins. LDPE was the first LCB polyethylene that was produced by free radical polymerization (FRP) at high reaction temperature and pressure with the least control on branch content and topology. After discovering coordination polymerization strategies for the synthesis of polyolefins at milder reaction conditions, academic and industrial researchers have been focused on the controlled synthesis of branched polyolefins.<sup>[19,20]</sup>

In this review, we aim to survey the main developments in the synthesis of polyolefins with controlled LCB structures with a focus on the latest chemical advances. We first briefly review traditional methods that generally include post-reactor modifications and then proceed to in situ techniques, including single and multiple catalytic systems. In sharp contrast to the traditional methods, novel catalyst-based synthetic approaches offer control over not only the length and number but also the “distribution” of LCBs, which provides a perspective for better control of material properties in LCB polymers. Specifically, we highlight very new emerged strategies based on the coordinative chain transfer polymerization (CCTP).<sup>[21]</sup> Although there are valuable review papers on producing LCB polyolefins by traditional mechanical methods or conventional catalytic systems,<sup>[8,22,23]</sup> this review will mainly focus on mechanisms of the recently developed catalyst-centered

approaches. We believe this review can pave the way for expanding the controlled synthesis of not only LCB polyolefins but even inspire the synthesis of polyolefins with novel and more tailored microstructures.

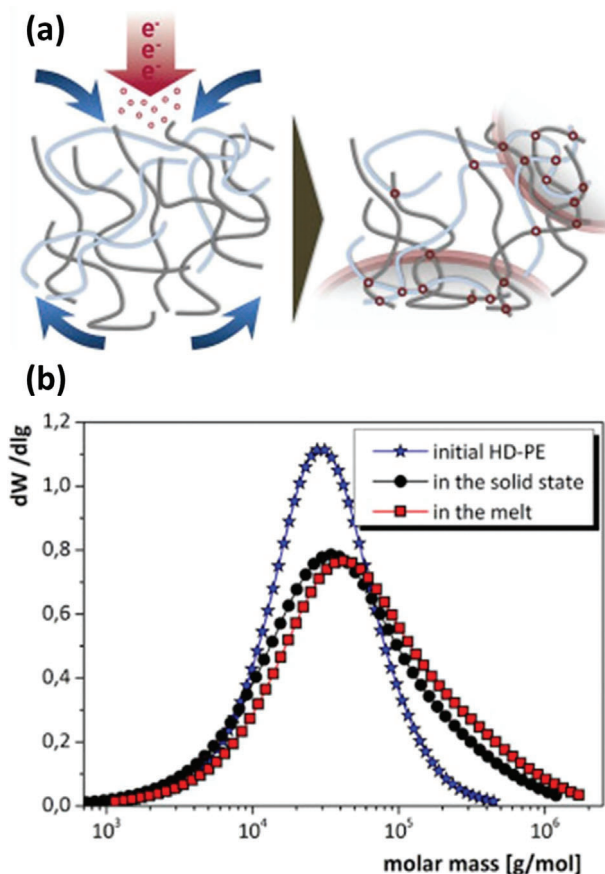
## 2. Post-Reaction Modification Methods

LDPE, the first grade of LCB polyolefin, was produced by Imperial Chemical Industries in 1938 using FRP under harsh reaction conditions (160–310 °C, 300–1300 atm). In this method, the intra- and intermolecular radical chain transfer reactions during polymerization introduce LCB and SCBs. These chain transfer reactions are fast and rather uncontrollable due to the high activity of radicals.<sup>[24]</sup> Therefore, this conventional polyethylene grade contains a significant degree of both long and short branches and a broad molar mass distribution (MMD). Although the broadening of MMD is traditionally exploited to produce high-performance high-density polyethylene (HDPE) grades (also benefiting from the inverse comonomer content distribution, CCD), in the case of LDPE the copresence of SCBs and LCBs contribute to lower mechanical properties. Nevertheless, LDPE is still produced and supports the main market of LCB polyolefins. The high temperature/pressure FRP is applicable just for the synthesis of LCB polyethylene and not to other olefins such as propylene, due to the high instability of radicals with allyl substitute, which results in excessive chain transfer reactions that limits chain growth. Therefore, scientists have been motivated to develop new methods based on post reaction modification of raw materials to access LCB polyolefins.

### 2.1. Ionizing Beam Irradiation

High energy irradiation is used at low temperatures (below 100 °C or even at ambient temperature) and atmospheric pressure in the solid and in the melt state. Electron-beam and gamma irradiations are the most prevalent technologies used. Electron-beam irradiation of raw polymeric material results not only in transforming the structure from linear to LCB but also changes other molecular characteristics like molar mass and its distribution and consequently the intrinsic viscosity. Accordingly, Boldt et al. reported that irradiation of HDPE in the solid state by increasing the irradiation dosage gradually enhances the polydispersity index, PDI, from 1.7 to 3.1, as shown in **Figure 1**. Irradiation in the solid state did not change the morphology, as it alters the chain topology mainly in the amorphous state, while irradiation in the melt state could also affect the crystallizable segments. Despite the former decreased the crystallization temperature due to branching and degradation, the latter led to higher crystallization temperatures with increased doses due to in situ self-nucleation.<sup>[25]</sup> Similarly, Entezam et al. have reported the same trend of increasing the PDI of LLDPE from 3.49 to 5.94 upon irradiation in the solid state.<sup>[26]</sup> This approach has been used to induce LCBs in HDPE,<sup>[25]</sup> LLDPE,<sup>[26]</sup> polypropylene (PP),<sup>[27]</sup> and isotactic poly(1-butene) (iPB-1).<sup>[28]</sup>

During the interaction of high energy electrons with polypropylene chains, proton abstraction and scission of polymer chain via  $\beta$ -scission prevail due to the presence of loose hydrogen linked to a tertiary carbon atom in the backbone. The produced



**Figure 1.** a) Schematic representation of the inhomogeneous crosslinking and LCB formation upon electron beam irradiation treatment. b) The corresponding broadening of the MMD. Reproduced with permission from Ref. [25] Copyright 2016 Elsevier.

radicals have a relatively long lifetime at the utilized low temperatures, particularly at room temperature;<sup>[25,27]</sup> therefore, they have the chance to recombine and saturate with heteroatoms available in the atmosphere. In the case of polyethylene, radicals are produced upon proton abstraction from the backbone and C–C bond scission, however, due to the higher activity of primary radicals, long-chain branching and even crosslinking are dominant. As such, the extent of the structural modifications depends on the polymer structure, on top of the intensity and time of irradiation,<sup>[26,29]</sup> temperature, as well as the atmosphere.

Although irradiation is easy to implement and relatively cost-effective, some drawbacks with this method include serious side reactions such as crosslinking, oxidation (if irradiated in the air), and chain scission (degradation) parallel to the long-chain branching, which limits the extent of grafting reaction. Moreover, due to the random nature of irradiation-induced reactions, tuning branching attributes including content, length, and distribution of LCBs is rather uncontrollable and not well defined.

## 2.2. Coupling Reactions

In coupling reaction, polyolefins with specific functional end-groups are prepared and then grafted onto other polyolefins that

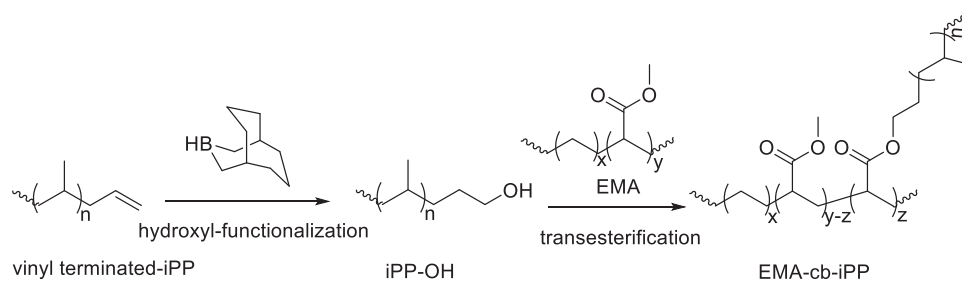
contain a complementary coupling function. Click reactions such as azide–alkyne and thiol–ene reactions,<sup>[30]</sup> are more effective compared to the traditional transesterification or Diels–Alder reactions. Accordingly, various LCB structures like a three-arm star, comb-shaped, or dendrimer are producible, according to the pre-designed structure of components.<sup>[31–33]</sup> Following this approach, Brant et al. applied the transesterification reaction for grafting hydroxyl-terminated i-PP onto commercially available ethylene/methyl acrylate copolymer to obtain comb polyolefin block copolymers, as shown in **Figure 2**.<sup>[34]</sup>

The reactive copolymer approach in which a comonomer that is protected during the coordination copolymerization but becomes active afterward is very useful to prepare the polyolefin backbone with a controlled number of functional groups for further attachment of the complementary telechelic polyolefins.<sup>[35,36]</sup> For instance, Jandaghian et al. copolymerized 1-hexene and p-methylstyrene in the presence of a generic Brookhart-type catalyst. The loose methylenic protons could be selectively functionalized by maleic anhydride under very mild reaction conditions.<sup>[37]</sup> On the other side, the end-functionalized telechelic polyolefins are frequently produced by CCTP.<sup>[38]</sup> Very similar to the reversible addition–fractionation transfer polymerization, where the chain transfer segment, which is attached to the polymer terminal group, can be transformed into useful functions, the chain transfer agent (CTA) used in CCTP, can be simply transformed into a myriad of functional groups,<sup>[38,39]</sup> to be used for attaching the polymer chain as a LCB on functional polyolefin backbones.

## 2.3. Peroxide Grafting

Peroxide grafting is another strategy for producing LCBs on linear polyolefins. i-PP has beneficial physical properties such as low density, high melting point, and chemical resistance but lacks the high melt strength that is necessary in applications such as thermoforming, film blowing, blow molding, extrusion coating, and foaming. Therefore, despite the chain scission is dominant in the peroxide grafting of PP, there is a research trend for reversing the scission reaction and stitching the radicals via reactive monomers.<sup>[40]</sup>

Grafting in a melt state, also known as reactive extrusion includes the linear polymer, free radical initiator (usually peroxides), and potentially a multifunctional monomer serving as the branching point all mixed in an extruder. Decomposed peroxide radicals form macro-radicals on the polymer backbone, which may attack the other chains or the multifunctional monomer on the double bond and subsequently result in LCB formation, as shown in **Figure 3**.<sup>[40–43]</sup> In the case of i-PP, the selectivity for self-grafting of PP macroradicals is relatively low and most of the microradicals undergo a  $\beta$ -scission reaction, resulting in a decrease of the chain length. To overcome this limitation multifunctional grafting monomers can greatly help capturing radicals and forming LCBs.<sup>[44]</sup> Grafting monomers are usually acrylates and maleics such as triallyl trimesate (TAM) and trimethylpropane triacrylate (TMPTA), which contain multiple reactive carbon–carbon double bonds. The use of grafting monomers can promote the formation of the branched structure, but side reactions cannot be well controlled, which results in prevailing  $\beta$ -chain scission reaction and limits the grafting degree. Control-



**Figure 2.** Conversion of the terminal vinyl group into OH via oxidative hydroboration followed by synthesis of EMA-co-iPP comb block copolymer via transesterification. Reproduced with permission from Ref. [34] Copyright 2020 American Chemical Society.

ling parameters in such a reactive extrusion are mixing efficiency, shear rate, temperature, residence time, and more importantly, choice of the reactive multifunctional monomer.<sup>[41,45]</sup>

Although the reactive extrusion process offers very short reaction times, little or no use of solvents, simple product isolation, and relatively low investment,<sup>[41]</sup> like electron-beam irradiation, the main drawback is undesirable side reactions that take place along with branching, including  $\beta$ -scission of macroradicals, crosslinking, and possible homopolymerization of the multifunctional monomer, which may compromise the LCB formation.

Chemical modification via grafting in the solid state is also reported for producing branched i-PP. The reagents, including the peroxide and the multifunctional monomer, are dissolved in a solvent that would not dissolve the polymer and the mixture is added to the PP powder in the solid state. Therefore, the reaction takes place only on the surface of polymer particles. According to Picchioni et al., an impregnated PP is deprived upon solvent evaporation, which is sealed under a nitrogen atmosphere and let to react at 130 °C for 3.5 h. Characterization of the modified i-PP by gel permeation chromatography and rheological measurements revealed an increase in the molar mass averages, relative to the reference sample, along with a low gel content, and a higher melt elasticity, indicative of LCB formation.<sup>[46]</sup>

The above-mentioned post reactor technologies, belonging to the class of traditional methods, are still frequently used in industry due to the ease of the process, efficiency, and economic advantages. The significance of post polymerization modification technologies becomes more apparent when we remember that FRP cannot produce branched polyolefins except LDPE. Therefore, some valuable polyolefins like PP and iPB-1 mainly rely on such methods for improved melt strength. Nevertheless, because of the radical mechanisms involved in post reactor treatments, control over branching microstructure is rather inefficient; hence, in the best scenario polymers with complex structures and broad-

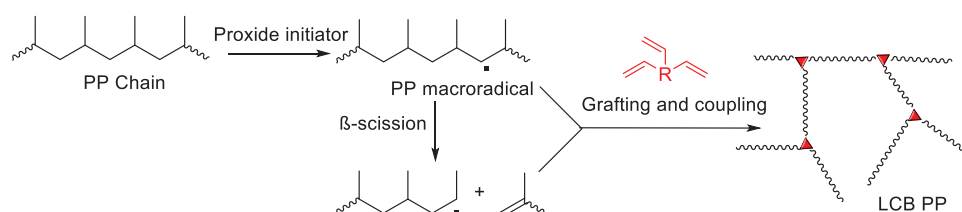
ened MMD are prepared. To address this gap and to more precisely control the microstructure of LCB polyolefins, in situ reactions are developed.

### 3. In Situ Formation of LCB Polyolefins

The in situ formation of LCB in polyolefins requires the manipulation of the polymerization reaction, therefore, unlike post-reaction modification methods require further investment and include more complications. However, they can provide a larger control over LCB attributes including the length, frequency, and distribution, with less interference with other chain architecture attributes like MMD and SCB compared to the traditional post-reaction methods. Therefore, they become superior when the precise control of the chain microstructure and the corresponding material properties is desired.

#### 3.1. Direct Copolymerization with Difunctional Comonomers

A straight forward and traditional in situ approach for the synthesis of LCB polyolefins is the copolymerization with difunctional comonomers. In the case of using nonconjugated  $\alpha,\omega$ -diene comonomers, pendant vinyl moieties are created that are further incorporated into growing chains. The pendant dienes create H-shape links connecting two linear segments. However, with increasing the diene concentration, H-type branching could easily lead to the undesirable crosslinking of the polymer and gel formation regardless of the catalyst type.<sup>[47]</sup> To avoid gel formation, a difunctional branching "T" reagent, p-(3-butenyl)styrene has been introduced in the presence of hydrogen to limit LCBs to T-type branching topology instead of H-type.<sup>[48,49]</sup> T-reagent serves as both comonomer and chain transfer agent. Copolymerization of the but-3-ene group of the p-(3-butenyl)styrene via 1,2-insertion results in the formation of a copolymer with pendant



**Figure 3.** Schematic demonstration of chain scission by H-abstraction and  $\beta$ -chain scission reactions and formation of LCB structures in i-PP using peroxide initiator and reactive multifunctional monomers in melt.

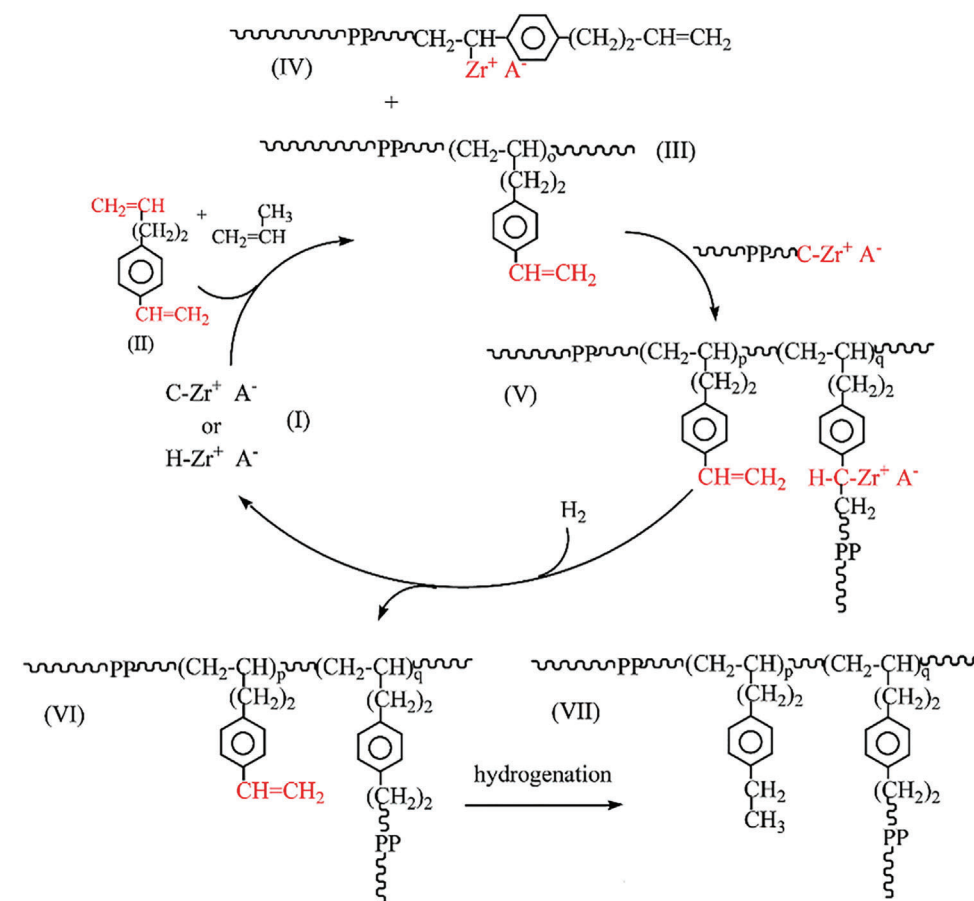


Figure 4. Schematic of using of T-agent to produce LCB PP. Reproduced with permission from Ref. [49] Copyright 2007 American Chemical Society.

styrene functionality. In contrast, the incorporation of the styrene group of p-(3-butenyl)styrene via 2,1-insertion results in a dormant catalyst site hindered by the bulky aromatic benzyl ring. Hydrogen can retrieve the dormant catalyst site via the subsequent chain-transfer reaction to produce a macromer with the  $\alpha$ -olefin-like but-3-ene at the chain end. Theoretically, branches in LCB PP can be formed when a growing polymer chain either incorporates the but-3-ene chain end of a macromer or transfers to the pendant styrene of the copolymer as shown in Figure 4.

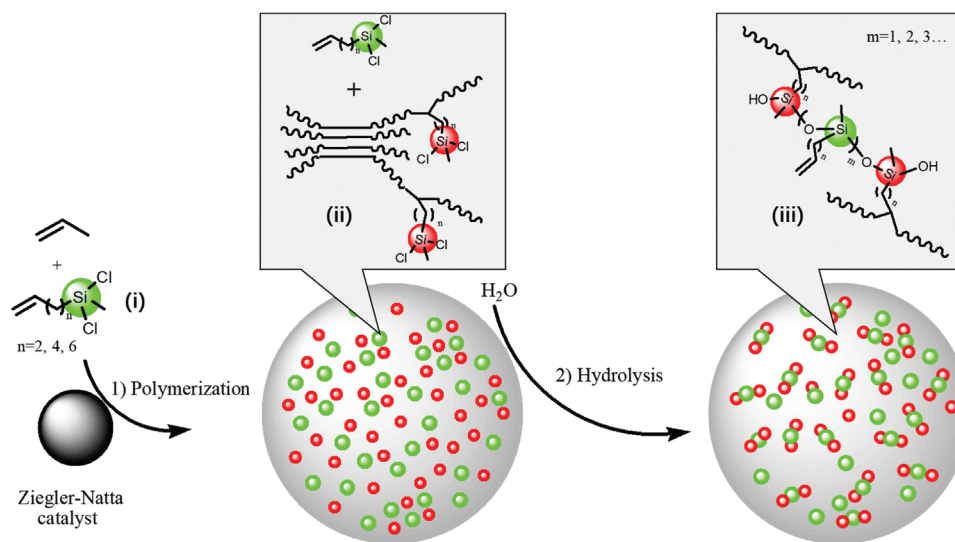
Rheological studies show that melt rheological properties of the Ziegler–Natta-catalyzed propylene/ $\alpha,\omega$ -diene copolymers resemble those of metallocene-catalyzed LCB homopolymers. The number of LCB structures per 1000 carbons, as determined from  $^{13}\text{C}$  NMR spectra, was reported to vary in the range of 0.7–1.15 when 1,9-Decadiene comonomer was added between 160 and 320 mmol. More affirmation for LCB formation was obtained from the van Gurp–Palmen (vGP) plot of  $\delta$  versus  $G^*$ , which demonstrated a gradual reduction of  $\delta$  at low  $G^*$  region from  $80^\circ$  to  $20^\circ$  for linear and LCB PP, respectively.<sup>[50]</sup>

Beside advances in  $\alpha,\omega$ -dienes copolymerization using metallocene<sup>[47]</sup> and post-metallocene catalysts,<sup>[51]</sup> the production of LCB PP and PE via  $\alpha,\omega$ -dienes copolymerization using Ziegler–Natta catalysts ( $\text{MgCl}_2/\text{TiCl}_4$ ) has received great attention, due to the commercial dominance of Ziegler–Natta catalysts in PP and PE industry.<sup>[50,52]</sup> In this regard,

there are several reports on using a variety of  $\alpha,\omega$ -diolefin like di-*n*-hexyldiethoxysilane, di-5-hexenyldiethoxysilane, di-5-hexenyldimethylsilane<sup>[53]</sup> and 1,9-decadiene.<sup>[50,52]</sup> Besides  $\alpha,\omega$ -dienes, Dong, and coworkers have reported on the incorporation of  $\omega$ -olefins difunctional comonomer, like  $\omega$ -alkenylmethylchlorosilane using Ziegler–Natta<sup>[53,54]</sup> and metallocene<sup>[55]</sup> catalytic systems for the synthesis of LCB PP. In this approach, the  $\omega$ -alkenylmethylchlorosilane copolymerization is followed by the addition of water to the reactor to direct a hydrolysis reaction. Water inside polymer granules initiates a joint hydrolysis reaction by the remaining pristine  $\omega$ -alkenylmethylchlorosilane and extends the macromolecular alkylmethylchlorosilane species (PP-g-alkylmethylchlorosilane), binding PP chains together via the formation of dialkylsiloxane oligomers and finally produces the H-shape LCB structure, as shown in Figure 5.

### 3.2. Single Catalytic Systems

The LCB formation mechanism in coordination polymerization is based on the incorporation of macromers in metal-catalyzed olefin polymerization that has been demonstrated to be more controllable than what is achievable in radical (co)polymerization by inter- or intra-macromolecular radical chain transfer. There-



**Figure 5.**  $\omega$ -Alkenylmethylchlorosilane-assisted propylene polymerization with Ziegler–Natta catalysts to LCB-PP Reproduced with permission from Ref. [54] Copyright 2020 Elsevier.

fore, the manipulation of single-site catalytic systems toward controlled incorporation of LCBs has been an active field of research.

### 3.2.1. Metallocene Catalysts

The discovery of single-site metallocene catalysts enabled the synthesis of polyolefins with new tailored structures and properties that were not possible with multi-site Ziegler–Natta and Phillips catalysts, which could produce polyethylene chains with either linear structure or with a small amount of LCB, respectively.

LCBs were usually present in polyolefins made by the Phillips catalyst. However, the amount of LCBs was insignificant, ranging between 0 and 100 branches per million carbon atoms, and at the high end of the LCB range the fraction of branched chains could be as high as 25%.<sup>[9]</sup> This nonlinear architecture has a major influence on polymer molding characteristics. As a result, HDPEs produced by Phillips catalyst were more favored than Zeigler–Natta catalyst in processing methods like blow molding, pipe, and other extrusion-based techniques. Before the discovery of metallocene catalyst, Phillips catalysts account for 40–50% of all HDPE produced. Unlike the single-site metallocene catalyst, Phillips catalysts lead to significantly broad MMD (PDI of typically from 6 to 20), however, they form LCBs following the same reactions of macromer formation and re-insertion.<sup>[56,57]</sup>

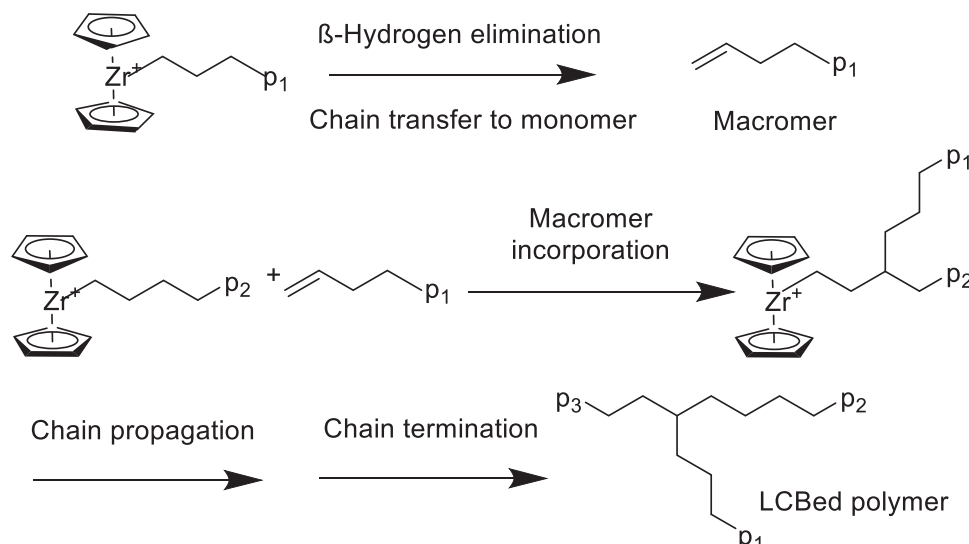
Studies on metallocene systems including unbridged-, ansa-metallocene, and constrained geometry catalyst (CGC) have shown that they are intrinsically able to produce polyethylene with low levels of LCBs. The LCB formation mechanism, generally accepted for all metallocene catalysts is the in situ production of vinyl-terminated macromers via  $\beta$ -H elimination, chain transfer to the monomer, or chain transfer to the catalyst and then incorporating the macromer into the same or another growing chain, as shown in Figure 6.<sup>[20,17]</sup> The incorporation of long-chain macromers is in competition with short-chain monomers and due to the larger steric hindrance, low levels of LCBs will be generated reasonably. Nevertheless, their incorporation frequency

can be relatively enhanced by adding a bridge behind ligands, or simply removing one ligand, as in half-sandwich CGCs.<sup>[16]</sup> However, desirable rheological and physical properties can be altered even at such low levels of Long-chain branching.<sup>[58]</sup>

CGC catalysts emerged in 1990 and were soon employed industrially by Dow chemical for introducing narrow-distributed PE grades like INSITE.<sup>[19]</sup> CGCs were the first single-site catalyst reported to produce LCB polyethylene. Although the traditional metallocene catalysts can intrinsically incorporate low levels of LCB, ansa-metallocene catalysts can incorporate more LCBs due to their wider coordination face, and half-metallocene catalysts can even incorporate more extents of LCB.<sup>[22]</sup> This is attributed to the open geometry and less sterically hindered coordination face of CGCs, which allows sterically demanding macromers to approach the active center. In general, long-chain branched PE homo- or copolymers with LCB degrees in the range of 0.01–3.0 carbons/1000 carbons, and narrow distributed molar mass with PDIs of 1.5–2.5 are reported.<sup>[22]</sup> However, the lower molar mass of CGC-catalyzed PEs compared to those produced by traditional metallocene catalysts hinders their applications.

### 3.2.2. Non-Metallocene Catalytic Systems

To enhance the control over the extent of LCB, Britovsek et al. have reported on designing other group 4 complexes as non-metallocene polymerization catalysts.<sup>[59]</sup> The series of group 4 bidentate and tridentate bi-aryl complexes, as shown in Figure 7, contain  $\eta^1$ -phenyl donors with orthogonal planar steric requirements that in comparison with  $\eta^5$ -Cp ligands in metallocene analog is expected to allow easier access to the metal center and consequently enhance long- and short-chain branch formation. The flow activation energy ( $E_a$ ) determined from time–temperature superposition of rheological measurements was only the tool used for proving the presence of LCBs, considering the fact that LCB polymers show higher  $E_a$  values compared to linear ones. While  $E_a$  values up to 28 kJ mol<sup>-1</sup> are typically reported for linear



**Figure 6.** The LCB formation mechanism of Zr-based metallocene catalysts. Reproduced with permission from Ref. [17] Copyright 2013 Springer.

HDPE, the  $E_a$  values of 40–60 kJ mol<sup>-1</sup> were indicative of LCB formation in samples obtained with 1-Ti(NMe<sub>2</sub>)<sub>2</sub> and 1-Zr(NMe<sub>2</sub>)<sub>2</sub> catalysts. The authors have already shown that 1-Ti(NMe<sub>2</sub>)<sub>2</sub> catalyst had a high affinity to incorporate 1-hexene in copolymerization with ethylene, which could be a hint for the preferable incorporation of even longer macromers by this class of non-metallocene catalysts.<sup>[10]</sup> However, further studies are required to understand and master their branch formation mechanism.

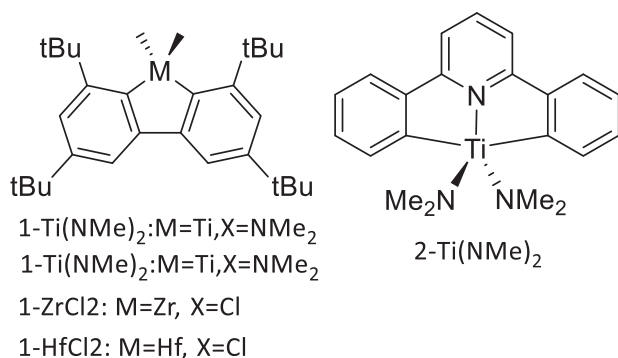
### 3.2.3. Late Transition Metal (Ni/Pd) Based Catalysts

The development of diimine nickel and palladium catalysts in the mid-90s by Brookhart and coworkers was the major breakthrough in coordination polymerization. This family of catalysts is well-known for their high potential in producing branched polyolefins with a variety of microstructures, from linear low-branched to highly branched or hyperbranched with a branch-on-branch structure. The widely accepted mechanism for branch formation is the “chain-walking mechanism”; the sequential  $\beta$ -

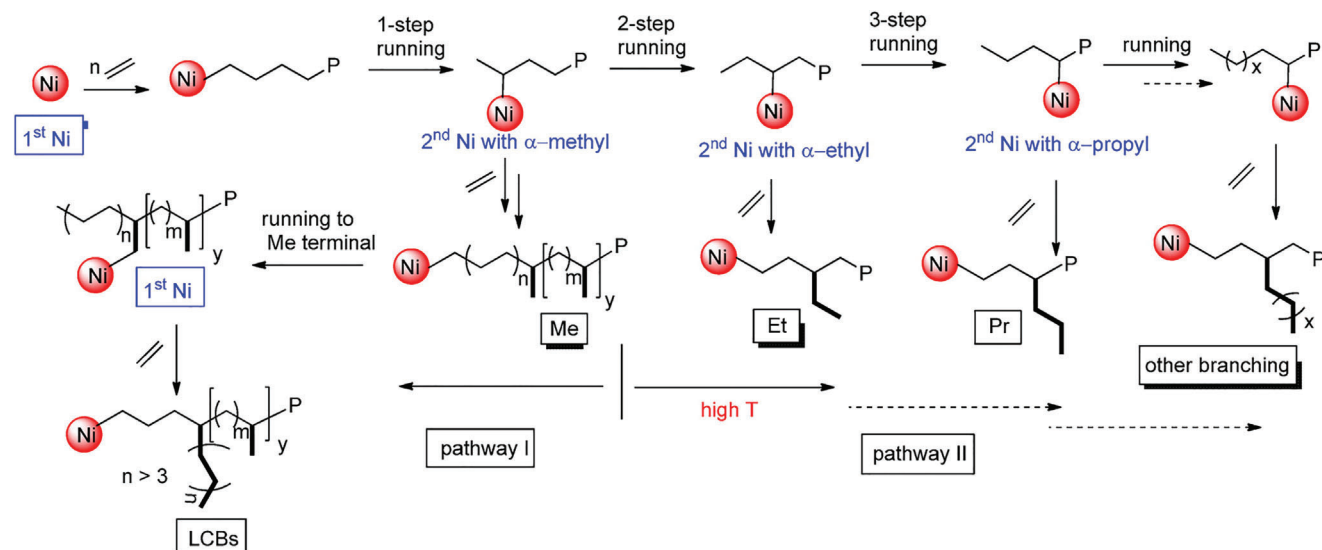
hydride elimination and reinsertion process results in the migration of the metal center along the hydrocarbon chain.<sup>[60]</sup> Modification of electronic and steric attributes of ligands, as well as tailoring polymerization temperature and pressure are the most effective approaches for controlling their branch formation. Attempts in this regard are continuing<sup>[61–64]</sup> and comprehensive reviews have been published.<sup>[6,65,66]</sup>

The branch length is determined by the competition between  $\beta$ -hydride elimination and monomer insertion. As such, the formation of LCBs in this catalyst system, with the observed specific branch length and frequency,<sup>[67,68]</sup> questioned the common chain-walking mechanism to be responsible for LCB formation.<sup>[69]</sup> Moreover, it is widely reported that branched PEs with remarkable amounts of LCBs ( $\geq C6$ ) produced via diamine Ni or Pd catalysts, contain minor amounts of methyl branches (C1) and no or traces of ethyl, propyl, butyl, and amyl branches (C2–C5). These further rule out the accountability of the chain-walking mechanism for LCB formation, which requires the formation of short branches as a prerequisite for the formation of longer ones.

Some studies attributed LCB formation to copolymerization of ethylene with macromers produced via  $\beta$ -hydride elimination<sup>[70]</sup> or intra- and intermolecular C–H activation,<sup>[71]</sup> and at the simultaneous formation of SCBs was rationalized by 2,1-insertion of macromers<sup>[70]</sup> or chain-walking for short branches as small as a methyl.<sup>[69,71]</sup> In contrast, some other studies refuse chain-walking<sup>[71]</sup> or macromer incorporation<sup>[71,72]</sup> based on their experimental results or computer simulation of LCB formation, while proposing no other mechanism. An elucidative recent study by Gao et al.<sup>[73]</sup> presents a new mechanistic model for LCB formation, attributing the methyl branch formation to a one-step chain-walking followed by ethylene insertion, whilst LCB formation was assigned to ethylene insertion into the primary Ni-alkyl species that originated from nickel migration to the methyl terminal. This is encouraged due to the restricted ethylene insertion into the secondary Ni-alkyl species with an  $\alpha$ -ethyl or a bulkier alkyl, as shown by Pathway I in **Figure 8**. This is different from the



**Figure 7.** Structure of group 4 non-metallocene complexes with bidentate and tridentate biaryl ligands 1 and 2. Reproduced with permission from Ref. [59] Copyright 2020 Wiley.



**Figure 8.** Mechanism of LCB formation by ethylene insertion into the primary Ni-alkyl species originating from nickel migration to methyl terminal of the growing chain. Reproduced with permission from Ref. [73] Copyright 2018 American Chemical Society.

commonly proposed chain-walking mechanism, which includes ethylene insertion into the secondary Ni-alkyl species (>C6) by multiple-step chain-walking reactions. This mechanism rationalizes the common presence of LCB with methyl branches while bypassing the formation of C2-C6 branches, as shown by Pathway II in Figure 8. Interestingly, in this contribution, the macromer incorporation was refused for LCB formation as the insertion of  $\alpha$ -olefins into nickel and palladium active centers should generally lead to 1, $\omega$ - or 2, $\omega$ - enchainment by chain straightening.

### 3.3. Multiple Catalytic System

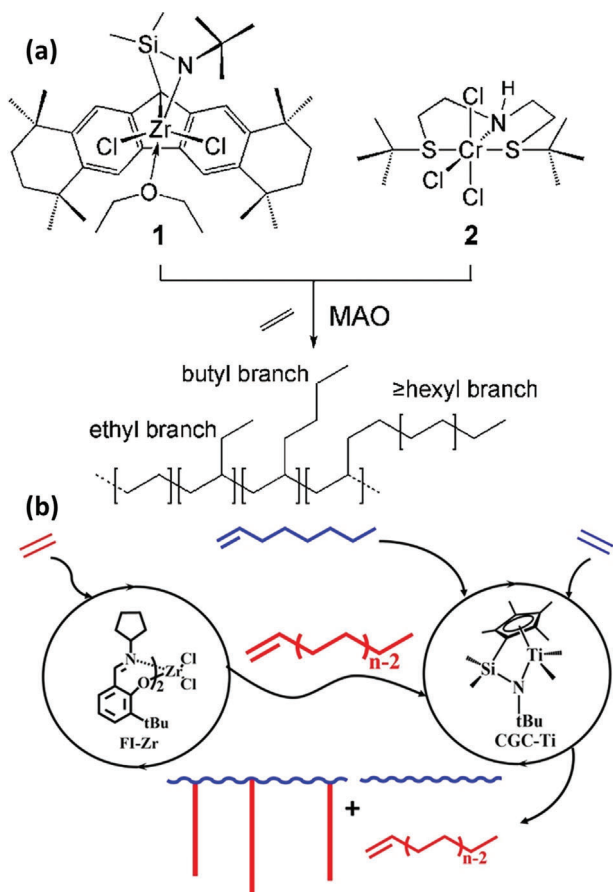
Beside single catalytic systems, where a single catalyst is in charge of producing double bonds and its re-insertion, multiple catalysts can cooperate in a loop to form macromers and re-inserting them. Although these systems have more freedom in selecting catalyst or reaction schemes, specifically designed for independent double bond formation and re-insertion, they require the close cooperation of multiple reaction lines, that is, not only they should not interfere with the parallel reactions, they should work in a harmony so that a uniform microstructure can be produced continuously. Therefore, the larger degree of control over LCB attributes comes with harder control over reaction kinetics.

#### 3.3.1. Tandem Catalytic Systems

The single catalytic systems, even those with an open geometry like CGCs, have limitations in the precise control over the branch length and frequency. Therefore, new strategies are developed based on the separate production of well-defined macromers and then incorporating them into the main polymer backbone with a copolymerization catalyst either in a single reactor following simultaneous or sequential tandem catalytic mechanisms or in

two reactors in series. Of course, the single reactor process has obvious advantages over the two-stage process due to the costs of plant investment and operation, however, this comes along with the complexity of employing catalysts in parallel that may have degradative interactions.

Miller and coworkers have reported on a tandem catalytic system encompassing a chromium-based oligomerization catalyst,  $[(t\text{BuSCH}_2\text{CH}_2)_2\text{NH}]\text{CrCl}_3$ , which converts ethylene to 1-hexene and 1-octene and a zirconium-based polymerization catalyst,  $\text{Me}_2\text{Si}(\eta^1\text{-C}_{29}\text{H}_{36})(\eta^1\text{-N-tBu})\text{ZrCl}_2$ , which in the present of the oligomerization catalyst yields LLDPE with short and long branches, as shown in Figure 9a.<sup>[74]</sup> In a similar study, two non-metallocene catalysts; difluoro-substituted 2,6-bis(imino) pyridyl Fe/MMAO as the oligomerization catalyst and mono  $\beta$ -diimino titanium complex/MMAO as copolymerization catalyst were used to convert ethylene as the sole monomer feed to branched polyethylene.<sup>[75]</sup> In both studies, which were conducted in a single reactor following a simultaneous approach, <sup>13</sup>C NMR spectra revealed that by increasing the molar ratio of oligomerization/polymerization catalyst, the number of ethyl, butyl, and long ( $\geq 6\text{C}$ ) branches per 1000 carbon atoms increase and the melt temperature shifts into lower temperatures as measured by DSC, accordingly. Miller and coworkers reported a variation of LCB density in the range of 14–21 LCB/1000C.<sup>[74]</sup> In a novel study in 2018, Zhang et al. reported on the preparation of comb-branched polyolefins using a tandem metallocene catalytic system, however, the oligomerization and copolymerization were not conducted simultaneously, but sequentially. In this single reactor process, at first ethylene monomers were converted to linear PE macromers using a Zr catalyst ligated with phenoxycycloalkylimine (FI-Zr) and afterward, the CGC-Ti catalyst and 1-octene solution were introduced into the reactor to start the copolymerization of ethylene, 1-octene, and the PE macromer, as shown in Figure 9b. The product is a novel type of comb-shaped polyolefin elastomer having ethylene/1-octene copolymer backbone and long-chain polyethylene branches.<sup>[76]</sup> There are numerous



**Figure 9.** Single reactor tandem catalytic systems with a) simultaneous application and b) sequential usage of catalysts. Reproduced with permission from Refs. [74, 76] Copyright 2010 and 2018 American Chemical Society.

examples of tandem catalytic systems from 1995, which were reviewed by Liu et al. in 2016.<sup>[23]</sup> The initial examples of tandem catalytic systems suffered from the degradative interaction of catalyst components, therefore, sequential processes in two reactors were employed. Still, the poisoning effects of the first catalyst remnants and the separation of unreacted macromers hinder the application of such systems.

### 3.3.2. Bimetallic Catalytic Systems

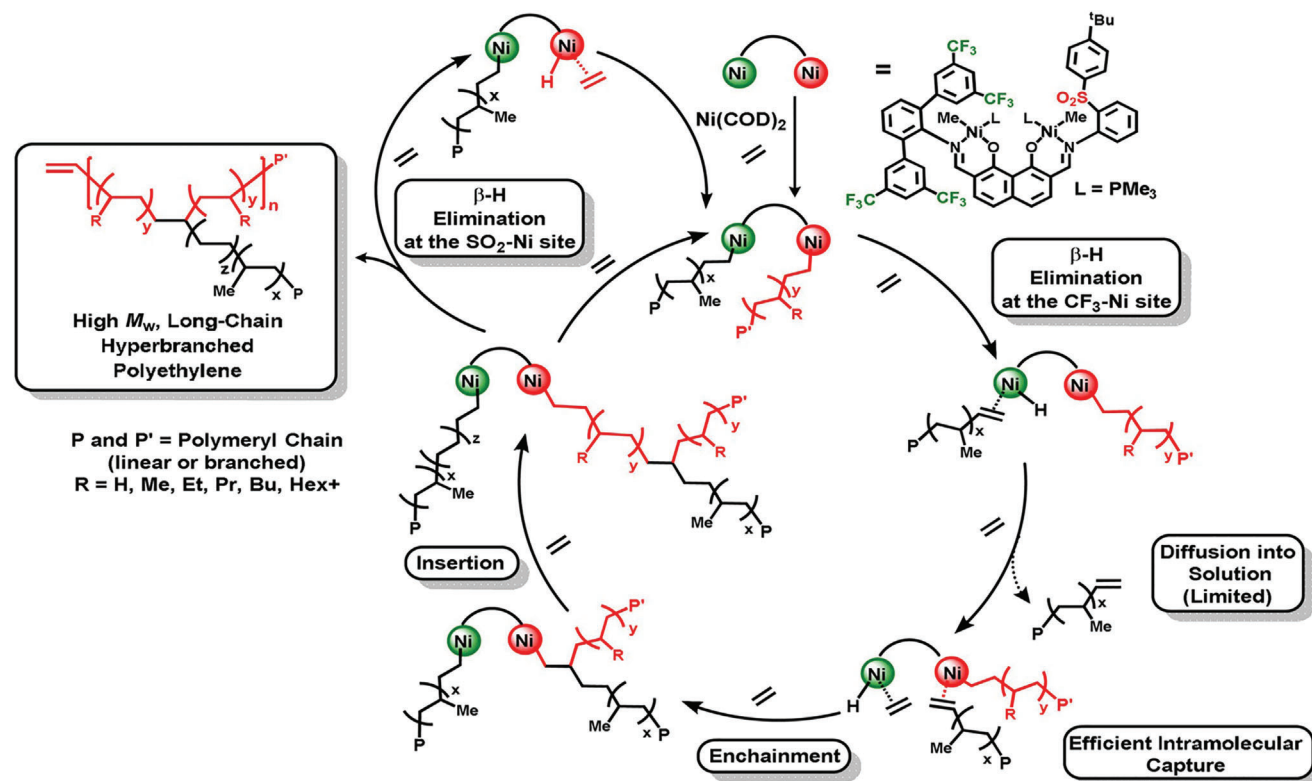
While tandem catalytic systems employ two separate catalysts together or sequentially, the emerging class of “bimetallic coordination catalysts”, introduces a method for olefin polymerization with two different reactive centers under metal–metal cooperative effects, which also has the potential to produce LCB polyolefins. In 2014, Marks and coworkers revealed that the bimetallic “constrained geometry” polymerization catalysts are able to produce polyethylene with specific microstructures. In this system, Ti metal is able to efficiently capture and enchain sizable oligomers produced at the Zr center into the propagating Ti-polymer backbone. To prove this mechanism, they showed that the heterobinuclear catalyst CGCTiZr introduces LCBs ( $\geq C_6$ ), as calculated from  $^{13}\text{C}$  NMR, in the range

of 2.1 LCB/1000C, while in the case of CGCTi, in which no oligomers production is expected, no LCB content was recorded.<sup>[77]</sup> In another novel study, they reported on a single bimetallic (dinickel) catalyst,  $(\text{CF}_3/\text{SO}_2)\text{FI}^2\text{-Ni}_2$ , that contains two Ni centers that work cooperatively.<sup>[78]</sup> This catalytic system affords monomodal polyethylenes with LCBs using ethylene as the only feed, as depicted in **Figure 10**. The  $(\text{CF}_3)\text{FI}$  ligand fragment rapidly produces methyl-branched macromers via  $\beta\text{-H}$  elimination/reinsertion. The macromers are then efficiently enchain intra-molecularly at the Ni coordinated by the  $(\text{SO}_2)\text{FI}$  ligand fragment. Repeating this cycle yields high molar mass LCB polyethylenes up to 11 LCB/1000C, as determined by  $^{13}\text{C}$  NMR analysis. It is interesting that in comparison, the tandem monometallic  $(\text{CF}_3)\text{FI-Ni} + (\text{SO}_2)\text{FI-Ni}$  catalytic system produces a bimodal mixture under the same reaction conditions. In this dual catalytic system, a Ni olefin polymerization center produces linear high molar mass chains, whereas the other Ni polymerization center produces a highly branched low molar mass product. This highlights the synergistic role of cooperativity in the design of bimetallic coordination catalysts.

### 3.4. Tandem Coordinative Chain Transfer Polymerization

One step forward in tailoring the microstructure of LCB polyolefins is providing “living polymerization” conditions. At such conditions, not only a narrowly distributed molar mass is achievable but a precise control on branch length and density is possible. Approaches for establishing living polymerization conditions in coordination polymerization are based on either the reversible termination or the degenerative chain transfer reactions. The CCTP based on the latter mechanism has led to great possibilities for fine-tuning the microstructure and architectures of polyolefins.<sup>[79]</sup> CCTP is based on the fast and reversible transfer of growing chains from the catalytic center to a main-group metal alkyl, for example,  $\text{ZnEt}_2$ , CTA. The dormant chains on the CTA are unable to grow unless transferred back to the polymerization catalyst. This degenerative chain transfer from the living state to the dormant state homogenizes the growth of polymeric chains and produces narrower polydispersities. Compared to other approaches for living coordination polymerization based on the reversible termination, this strategy attracted more attention due to the advantages including a notable reduction in the consumption of highly expensive transition metal catalysts, by enabling the growth of several chains per catalyst complex, control over the functionality of the chain end-groups, that is determined by the CTA chemical structure.<sup>[80,81]</sup> Along with the fine control over the microstructure attributes, some challenges remain to be addressed in CCTP, including that for some special monomers the transfer efficiency of CCTP scarcely reaches 100%, and not every CTA molecule can establish a reversible transfer reaction with every active species.<sup>[82]</sup> Moreover, in reactions where stereoselectivity becomes relevant like the stereoselective polymerization of 1,4-*trans* and 1,4-*cis* of conjugated dienes both polymerization rate and 1,4-*cis* selectivity drop obviously with increasing CTA loading.<sup>[79,83]</sup>

CCTP has also enabled novel opportunities to expand the chain microstructures that can be obtained by olefins. A very delicate example is shown by Arriola et al.<sup>[84]</sup> who synthesized olefin



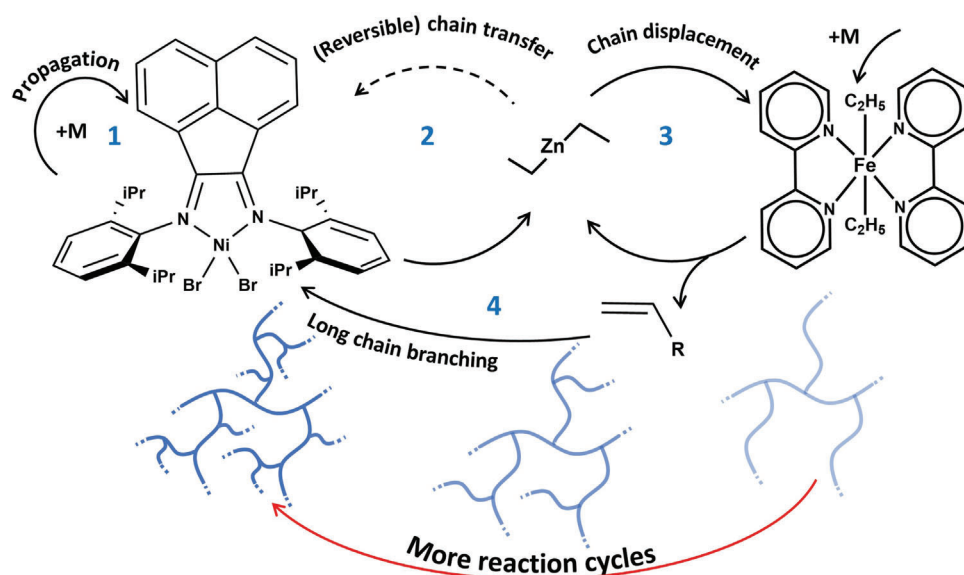
**Figure 10.** Mechanism of LCB formation using a cooperative bimetallic Ni catalyst proposed by Marks et al. Reproduced with permission from Ref. [78] Copyright 2015 American Chemical Society.

block copolymers (OBC), which led to the production of INFUSE OBCs on an industrial scale in 2010 by Dow Chemicals.<sup>[85]</sup> The reaction called “chain shuttling polymerization” is based on the copresence of two catalysts with extremely different comonomer incorporation affinities, in a CCTP copolymerization reaction. The cross-shuttling of growing chains between the two catalysts, mediated by the CTA, results in the continuous production of blocks with contrasting comonomer contents.<sup>[86–88]</sup> A very recent review by Zinck et al. provides the state of the art in coordinative chain transfer and chain shuttling polymerizations.<sup>[21]</sup>

Besides OBCs, CCTP has been widely used for the production of linear  $\alpha$ -olefins with different lengths and MMDs.<sup>[79]</sup> In this approach, growing chains on the oligomerization catalyst are frequently transferred to the chain transfer agent and a vinyl-producing catalyst, commonly named the displacement catalyst, liberates the dormant polymer chains as  $\alpha$ -olefins via  $\beta$ -hydride elimination and regenerates the CTA via ethyl/alkyl exchange. Cariou et al. used a compatible catalytic system consisting of a Bis(imino)pyridine iron,  $(\text{BiPy})_2\text{FeEt}_2$ , and  $\text{ZnEt}_2$  as the oligomerization catalyst, the displacement catalyst, and CTA, respectively, which could simultaneously produce narrowly distributed linear  $\alpha$ -olefins.<sup>[89]</sup> Later, Kempe and coworkers introduced another system consisting of Ni-based complexes, specifically,  $\text{Ni}(\text{cod})_2$  and  $\text{AlEt}_3$  as the displacement catalyst and chain transfer agent, respectively.<sup>[90–92]</sup> In general, in an ideal catalytic system for CCTP reaction for  $\alpha$ -olefins production, the oligomerization and displacement catalysts must show no or negligible poisoning effects on each other. Selecting both catalysts with the

same metal center reduces the poisoning effect due to the ligand exchange at the reaction conditions. That provided, they both should be compatible with a single CTA. Therefore, the opportunities for compatible oligomerization and displacement catalysts that provide similar metal–alkyl bond lengths are very limited. Finally, the oligomerization catalyst should have no tendency to reincorporate the in situ-produced  $\alpha$ -olefins, otherwise, a branched  $\alpha$ -olefin may form. However, the potential incorporation of the produced linear  $\alpha$ -olefins as macromer into the structure of growing chains makes this method an inspiring approach for generating LCB polyolefins.

Encouraged by this mechanism, Ahmadi et al. applied a tandem CCTP reaction to produce LCBs in ethylene and 1-hexene polymerizations.<sup>[93]</sup> In this one-pot reaction, macromers are in situ produced by an aryl-substituted  $\alpha$ -diimine nickel catalyst as the main polymerization catalyst,  $\text{ZnEt}_2$  as the CTA, and  $(\text{Bipy})_2\text{FeEt}_2$  as the displacement catalyst. Polymer chains growing on the polymerization catalyst are frequently transferred via the chain transfer agent to the displacement catalyst. Here, the transferred chains are released by  $\beta$ -H elimination as macromers with a vinyl end group ( $\text{R}-\text{CH}=\text{CH}_2$ ) and  $\text{ZnEt}_2$  is regenerated. The vinyl production performance of  $(\text{Bipy})_2\text{FeEt}_2$  in a dual catalytic one-pot system had been already investigated by Cariou et al.<sup>[89]</sup> In contrast to that work, the released macromers are consumed by the  $\alpha$ -diimine nickel polymerization catalyst and reinserted in the growing polymer structure, thanks to its open geometry and high comonomer affinity. Upon the repetition of these reaction cycles; that is, release and reinsertion of macromers,



**Figure 11.** Reaction cycles for the production of a branch-on-branch microstructure: 1) chain propagation, 2) reversible chain transfer to CTA, 3) release of macromer and regeneration of CTA, and 4) reinsertion of the macromer into growing polymer chains.

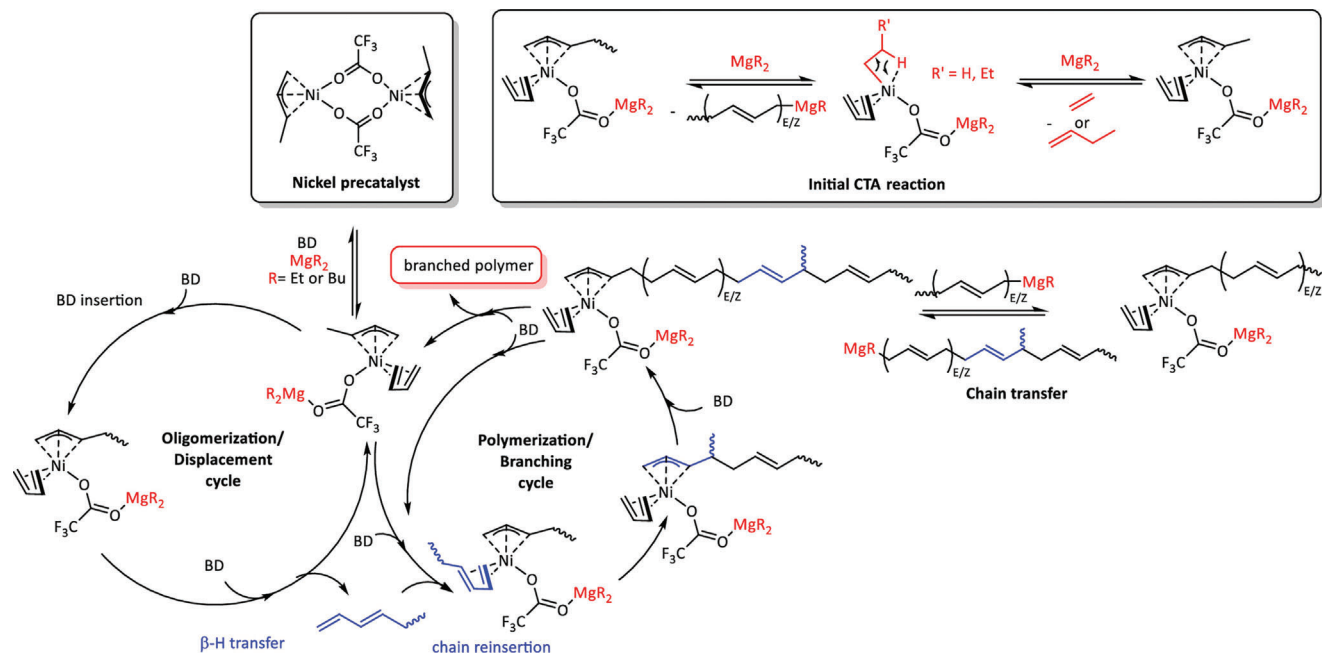
a branch-on-branch microstructure is generated, as shown in **Figure 11**.

A similar tandem CCTP polymerization reaction was developed by replacing the post-metallocene nickel catalysts with a more industrially relevant metallocene catalyst,  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ . The success of such a catalyst combination would be of great industrial relevance, as the former late transition metal  $\alpha$ -diimine nickel catalyst has limited application in the commercial production of polyolefins. The employed metallocene catalyst has a similar reactivity and high comonomer affinity due to the wide coordination face. Nevertheless, the separate polymerization of ethylene and 1-hexene showed a detrimental effect of the displacement catalyst on the activity of the metallocene catalyst, presumably because of the poisoning effect of the ligand exchange.<sup>[94,95]</sup> Therefore, looking for a compatible combination of polymerization and displacement catalysts should be sought.

Accordingly, the efficiency of a new displacement catalyst,  $\text{Ni}(\text{acac})_2$  was evaluated in a tandem CCTP reaction including the  $\alpha$ -diimine nickel polymerization catalyst and diethylaluminum chloride ( $\text{AlEt}_2\text{Cl}$ ) as the chain transfer agent.<sup>[96]</sup> As already discussed, not all metal alkyls can establish a reversible chain transfer reaction in combination with every coordination polymerization catalyst, however,  $\text{AlEt}_2\text{Cl}$  proved to function as both the CTA and the co-catalyst at the same time for the employed post-metallocene polymerization catalyst. Moreover, qualitative rheological studies showed higher  $G'$  and  $G''$  at low frequencies, and the shift of the moduli crossover to lower frequencies. At the same time, the complex viscosity,  $\eta^*$  shows a higher Newtonian viscosity at low frequencies while the Cole–Cole plot of the imaginary versus real viscosity demonstrates deviations from the semi-circle curve that is usually obtained for linear chains. All these observations suggest that the addition of  $\text{Ni}(\text{acac})_2$  to the corresponding CCTP reaction gradually leads to the formation and increase of LCBs.

In another recent study, Zinck et al. applied the same approach for the polymerization of a conjugated diene monomer and reported on the one-pot synthesis of branched polybutadiene.<sup>[97]</sup> They used an  $\pi$ -allyl nickel(II) (TFA) catalyst resulting from  $\text{Ni}(\text{COD})_2$  and trifluoroacetic acid, which functions simultaneously as the polymerization and the displacement catalysts along with  $\text{AlEt}_3$  or  $\text{Mg}^n\text{BuEt}$  as the CTA. The initiation of the chain transfer occurs via  $\beta$ -hydride elimination of the Ni-alkyl moieties and/or transfer to the monomer, which leads to the growth of additional chains. The polybutadienyl chains are terminated by the  $\beta$ -H process leading to a conjugated diene, which can be reinserted into a polybutadienyl growing chain, as described in **Figure 12**. In this study, branching was quantified by  $^{13}\text{C}$  NMR analysis after hydrogenation of the polybutadiene. The number of LCB was reported to increase from 0 to 4.7 and 9 LCB/1000C in the case of using  $\text{AlEt}_3$  as CTA, upon increasing CTA/Ni from 0 to 2.5 and 5. In the case of  $\text{Mg}^n\text{BuEt}$  3.3 LCB/1000C was reported at CTA/Ni = 5.

Beside the aforementioned attempts for producing LCB polyolefins via the one-pot tandem CCTP and displacement reaction loops, CCTP is employed by Lee and coworkers in a different approach for producing LCB polyolefins. Accordingly, pyridylamidohafnium, as the polymerization catalyst, was combined with  $(9\text{-decenyl})_2\text{Zn}$ , as the CTA, which in contrast to the conventional CTAs contains vinyl instead of alkyl side groups. In this strategy,  $(9\text{-decenyl})_2\text{Zn}$  functions not only as the chain transfer agent but also as a comonomer, and consequently, the source of LCB formation.<sup>[98]</sup> This approach consists of two separate steps including the production of dialkylzinc compounds bearing vinyl groups and applying them in a CCTP reaction as the CTA. They employed the developed catalytic system in copolymerization of ethylene/propylene and ethylene/1-octene and confirmed LCB formation by counting the number of polyolefin chains by SEC, which approved the chain-connecting mechanism, as shown in



**Figure 12.** Polymerization cycles for the production of branched polybutadiene using  $\text{Ni}(\text{COD})_2$  and TFA in the presence of  $\text{Mg}n\text{BuEt}$ , respectively as the displacement catalyst and CTA. Reproduced with permission from Ref. [97] Copyright 2023 American Chemical Society.

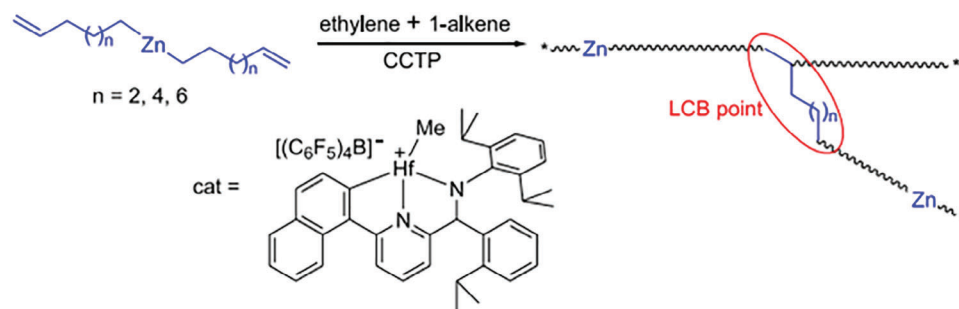
**Figure 13**, suggesting the linkage of growing PO chains. At a Zn concentration of 200 and 300  $\mu\text{mol}$ , the counted number of PO chains were 330 and 380, respectively, which is significantly less than “ $2 \times \text{Zn}$  ( $\mu\text{mol}$ )”. Moreover, the considerable shear thinning behavior of viscosity was used to qualitatively confirm the LCB formation.

This approach is based on the fact that the mechanism for introducing LCBs in a coordination polymerization using homogeneous single-site catalysts is the insertion of the polymer chains with a vinyl end group ( $\text{R}-\text{CH}=\text{CH}_2$ ) generated via the  $\beta$ -hydride elimination and chain transfer reactions. As the end groups generated in the ethylene/ $\alpha$ -olefin copolymerizations are mainly vinylidene ( $-\text{C}(\text{C})=\text{CH}_2$ ) and/or vinylene ( $-\text{C}(\text{C})=\text{CH}-$ ) groups, which are not reactive as vinyl groups, they introduced a strategy to feed dialkylzinc bearing vinyl end groups to the ethylene/ $\alpha$ -olefin copolymerization reaction environment. Thanks to the alkyl exchange between Zn-sites and no  $\beta$ -H elimination of pyridylamidohafnium catalyst, the chains growing on this cat-

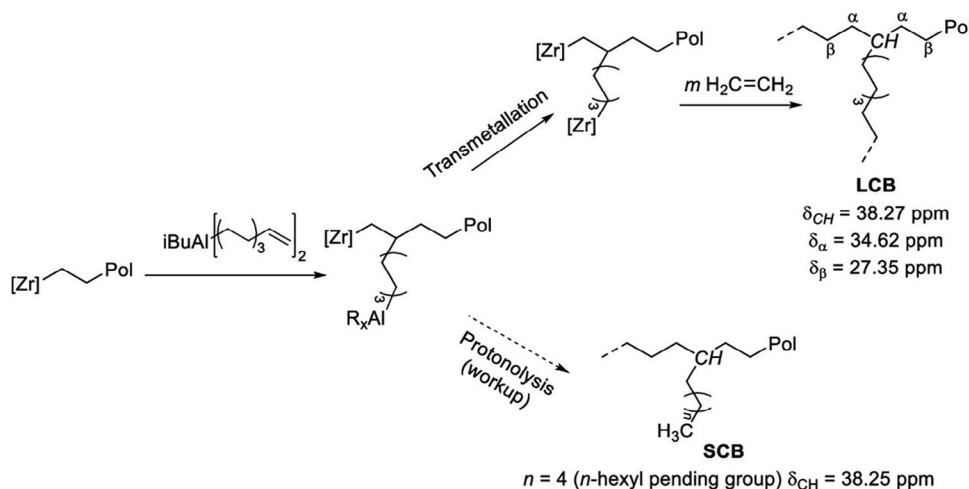
alyst reversibly transfer from the Hf center to the Zn site and gradually (polyolefinyl) $_2$  Zn species form. However, whenever an alkenyl group from the vinylic CTA takes part in chain growth as a comonomer, an LCB forms, as proposed in Figure 13.

To quantify the LCB content from the rheology data LCB index (LCBI) as defined by Shroff and Mavridis was reported.<sup>[14,15]</sup> Accordingly, for samples prepared with 300  $\mu\text{mol}$  of (9-decenyl) $_2$  Zn and 12.5 and 15 gr 1-octene comonomer, the “ $1 + \text{LCBI}$ ” values of 0.9 and 0.71 were reported respectively, which are comparable to numbers obtained for a commercial LDPE (0.84).

After studying Zn-alkenyl reagent, in a similar study by Kirillov et al., the synthesis of LCB polyethylene in the presence of an Al-alkenyl species, namely,  $i\text{BuAl}(\text{oct-7-en-1-yl})_2$ , was reported. This species functions similarly as both the CTA and the comonomer in concerted cooperation with homogeneous  $\text{rac}(\text{EBTHI})\text{ZrCl}_2/\text{MAO}$  or its heterogeneous silica-supported counterpart, as the main polymerization catalyst.<sup>[99]</sup> Rheological properties were used to determine the ability of the Al-alkenyl



**Figure 13.** Generation of LCB by the employment of diallyl zinc as the CTA and comonomer in CCTP. Reproduced with permission from Ref. [98]. Copyright 2019 American Chemical Society.



**Figure 14.** Mechanism of short- and long-chain branching in the presence of Al-alkenyl reagent. Reproduced with permission from Ref. [99]. Copyright 2020 American Chemical Society.

reagent to form LCB. Higher  $\eta^*$  at low frequencies, stronger shear thinning behavior, and a decrease of  $\delta$  from  $80^\circ$  to  $20^\circ$  in vGP plots were assigned to the formation of LCB. After confirming LCB formation in both heterogeneous and homogeneous systems, they proposed a reaction mechanism based on density functional theory (DFT) calculations. It was suggested that LCB originates from the 1,2-insertion of the oct-7-enyl group into the Zr-polymer bond, followed by Al to Zr transmetalation. This eventually generates a growing side-chain, as shown in **Figure 14**. On the contrary, protonolysis of the intermediate species would lead to the formation of  $n$ -hexyl SCBs.

The authors attributed the enhanced LCB formation in the presence of  $i\text{BuAl}(\text{oct-7-en-1-yl})_2$  to the high copolymerization ability of the main polymerization catalyst. Therefore, they decided to study the similar tandem CCTP system by replacing the main catalyst by  $(n\text{-BuCp})_2\text{ZrCl}_2$ , an unbridged metallocene catalyst that has considerably less ability to incorporate macromers, and compare the utility of  $i\text{BuAl}(\text{oct-7-en-1-yl})_2$  in the formation of LCBs.<sup>[100]</sup> Interestingly, rheological properties including higher  $\eta^*$  at low frequencies and decrease of  $\delta$  at low modulus in vGP plots demonstrated a similar fingerprints of LCB PE produced by the relatively more sterically demanding catalyst. This suggests that regardless of the comonomer incorporation ability of the two catalysts, Al-alkenyl reagent can be incorporated in the growing chains and lead to LCB formation. This counterintuitive observation was justified by DFT calculations, explaining the mechanism of LCB formation. DFT studies propose that LCB formation starts from the insertion of the pendant alkenyl group of CTA into the Zr-polymer bond. However, this insertion is more favorable than the incorporation of a comonomer like 1-hexene due to the formation of intermediary Zr-Al heterobimetallic species as DFT calculations suggested. This is why  $(n\text{BuCp})_2\text{ZrCl}_2/\text{MAO}$  is able to copolymerize the alkenyl group of CTA but not 1-hexene comonomer.<sup>[10,100]</sup>

To further evaluate the potential of this strategy for LCB formation, Kirillov et al. studied the performance of a series of metal-alkenyl compounds including Mg-, B-, Al- and Zn-Alkenyl in combination with homogeneous  $(\text{EBTHI})\text{ZrCl}_2/\text{MAO}$  and

$(n\text{BuCp})_2\text{ZrCl}_2/\text{MAO}$  catalytic systems.<sup>[101]</sup> Extensive rheological studies including vGP plot of phase angles versus complex modulus, which demonstrated the decrease of  $\delta$  at low  $G^*$  values suggested that Al- and Zn-based reagents promote LCB formation via a two-step mechanism involving insertion of the vinylic group and  $\text{M} \rightarrow \text{Zr}$  transmetalation, whereas B-alkenyl species were found to form hydrolytically stable B-centered crosslinked polyethylene structures, and the Mg-based reagent appeared to be reluctant toward  $\text{Mg} \rightarrow \text{Zr}$  transmetalation reaction, providing only the products of vinylic group insertion, which after hydrolysis afforded SCB polyethylene.

Overall, the in situ polymerization approaches for LCB formation in polyolefins have received more attention recently both in academia and industry. This mainly stems from the higher potential of catalyst-based synthesis methods in controlling LCB attributes, including length, number, and specifically distribution, which is almost impossible to achieve in traditional post-reaction modification approaches, even with compromising other chain microstructural characteristics. Although the post-reaction modification techniques currently dominate in industry, due to the ease of implementation and cost-effectiveness, the motivation for simultaneous improved mechanical and rheological properties can shift the future of industrial methods toward in situ approaches. This will continue encouraging researchers to design novel catalytic systems and reaction schemes and advance in situ methods for LCB formation. Accordingly, **Table 1** provides an overview of the discussed methods for LCB formation and their general advantages and main shortcomings to be addressed in the next steps.

## 4. Conclusion

The quest for controlled production of LCB polyolefins initially relied on post-polymerization methods, not only lacking precise control over LCB attributes, like the number, frequency, and distribution, but interfering with other chain structure specificities like MMD. However, the emergence of single-site catalysts, like metallocenes and late transition metal catalysts, activated a shift

**Table 1.** Summary of methods developed for LCB formation in polyolefins.

Approach	Method	Polyolefin	Branch structure	Advantages	Disadvantages
Post-reaction modification	Ionizing beam irradiation	HDPE <sup>[25]</sup> LLDPE <sup>[26]</sup> PP <sup>[27]</sup> (iPB-1) <sup>[28]</sup>	Star-like, tree-like or H-shape	Easy to implement Cost-effective	Side reactions: crosslinking, oxidation, chain scission Low control of LCB attributes
	Coupling reactions	i-PP branch on Poly(ethylene-co-methyl acrylate) <sup>[34]</sup>	Comb-shaped LCB		
	Peroxide grafting	HDPE <sup>[102]</sup> i-pp <sup>[42]</sup>	Star-like, tree-like		
In situ LCB formation	Difunctional comonomers	PE <sup>[52]</sup> PP <sup>[49,50]</sup>	H-shape, T-shape	Easy to implement	Side reactions: crosslinking, gel formation
	Metallocene	PE <sup>[17]</sup>	Tree-like	Easy to implement	Low levels of LCB
	Non-metallocene	PE <sup>[59]</sup>	Tree-like	Easy to implement	Low levels of LCB
	Late transition metal catalysts	PE <sup>[73]</sup>	Tree-like	Easy to implement Ambient temperature	Parallel formation of SCB, Low Yield
	Tandem catalysts	PE branch on LLDPE <sup>[76]</sup>	Comb-shaped	More control over LCB attributes	Incompatibility of catalyst components
	Bimetallic catalysts	PE <sup>[78]</sup>	Tree-like		Need for novel catalyst design
	Tandem CCTP	PE <sup>[94,96]</sup> Poly(1-hexene) <sup>[93]</sup> Polybutadiene <sup>[97]</sup> LLDPE <sup>[98]</sup>	Tree-like		Incompatibility of catalyst components

toward in situ chemical methods. Significant progress ensued by single, tandem, and bimetallic catalytic systems operating under controlled conditions. More recently, several successful approaches are reported upon the employment of the coordinative chain transfer polymerization, for instance by intertwining the chain propagation, chain transfer to CTA, macromer liberation by a displacement catalyst, and subsequent enchainment within the growing polymer chains. The versatile nature of this catalytic system, employing diverse catalysts and transfer agents, initiated ongoing research and holds industrial promises. The superiority of synthetic methods lies in that controlling LCB attributes is not limited only to the number and length, but their distribution. LCB distribution is a key-point to overcome the compromise of interest between process-ability and mechanical properties of polyolefins. Moreover, following the recent developments in catalyst-based approaches, we can envision the synthesis of even more complex architectures, not being possible by traditional methods, like blocky structures with LCB and linear blocks. Specifically, advancements in coordination catalyst synthesis and high-throughput polymerization techniques provide an optimistic future. This can be further boosted by the application of recent advances in artificial intelligence-driven screening methods to find compatible reaction components for the development of new tandem catalytic systems not only to provide efficient control over LCB polyolefin production but to open new pathways for the synthesis of polyolefins with novel and more tailored microstructures. This convergence of cutting-edge design and synthesis approaches can provide a transformative phase in polyolefin production, unlocking new avenues for tailored polyolefins that meet evolving market demands. Therefore, regardless of the cost-effectivity and simplicity of traditional post-modification methods, the future of producing LCB polyolefins may shift toward in situ polymerization methods.

## Acknowledgements

A.D. would like to thank the Iran National Science Foundation (INSF) for financial support through the project No. 4003736. M.A. would like to thank the German Research Foundation (DFG) for the independent research grant number 491930291. Authors acknowledge DEAL 2023-2 for supporting the open-access publication.

Open access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

coordination catalysts, coordinative chain transfer polymerization, long-chain branching, polyolefins, rheology

Received: December 29, 2023

Revised: March 8, 2024

Published online: March 23, 2024

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