

Palladium and Nickel Catalyzed Chain Walking Olefin Polymerization and Copolymerization

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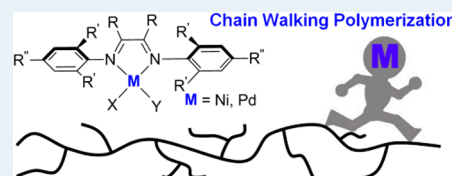
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ABSTRACT: In this perspective, recent developments on palladium and nickel mediated chain walking olefin polymerization and copolymerization with polar functionalized comonomers are described. First, the chain walking polymerization mechanism is discussed followed by its implications in olefin polymerization and copolymerization. Then, recent advances in catalyst design are provided. Special attention is paid to the influence of ligand structures on the catalytic properties. Subsequently, the applications of these chain walking polymerization catalysts in the synthesis of functionalized hyperbranched polymers and copolymers are summarized. Finally, some recent developments and perspectives on very fast and very slow chain walking polymerization catalysts are discussed.

KEYWORDS: chain walking, olefin polymerization, copolymerization, polar monomer, palladium catalysts, nickel catalysts, functionalized polyethylene



1. INTRODUCTION

The physical properties and end applications of polyolefin materials can be dramatically affected by their chain architectures and topologies.^{1,2} To this end, many strategies have been developed to modulate the polyolefin microstructures. For example, low-density polyethylene (LDPE) could be produced by radical polymerization. The intermolecular and intramolecular chain transfer reactions lead to the formation of both long chain branching and short chain branching.³ In transition metal catalyzed olefin coordination polymerization, long chain branching can be generated using Dow's constrained geometry catalysts. In this case, macromonomers were produced from ethylene polymerization and subsequently incorporated in the polymer backbone.⁴ Short chain branching can be generated from the transition metal catalyzed copolymerization of ethylene with α -olefin comonomers. Alternatively, this can be realized using only ethylene as the feedstock by combining one ethylene oligomerization catalyst and one copolymerization catalyst.⁵ In addition, Sen et al. demonstrated the synthesis of low molecular weight hyperbranched polyethylenes by combining ethylene coordination oligomerization and subsequent α -olefin cationic oligomerization.⁶

Conceptually different from the above-mentioned strategies, "chain walking" or "chain running" polymerization represents a unique approach to modulate the polyolefin microstructures. The chain walking mechanism was first presented by Fink et al. and developed by Brookhart et al.⁷ Furthermore, a chain straightening phenomenon in α -olefin polymerization was observed.^{7,8} The chain walking mechanism was proposed and validated both experimentally and theoretically.^{7–9} Here, a process involving β -hydride elimination and reinsertion with

the opposite regiochemistry is operative in addition to the common insertion, chain transfer, and termination processes. The degree of the polymer branching can be modulated via polymerization conditions and catalyst structures. Since then, tremendous efforts have been devoted to chain walking olefin polymerization and copolymerization reactions.¹⁰ This strategy has been applied for the convenient synthesis of polyethylenes with properties varied from elastomers, semicrystalline polymers, to totally amorphous hyperbranched oils (with branch-on-branch structures). Moreover, numerous copolymers with interesting microstructures have been prepared. In this perspective, we aim to provide an overall picture of this field with aspects on mechanistic details, different chain walking polymerization and copolymerization reactions, selected chain walking polymerization catalysts, the synthesis and applications of new polymeric materials, and some new research directions. We will focus on the catalysts bearing α -diimine ligands, with some brief discussions on other chain walking polymerization catalysts.

2. CHAIN WALKING POLYMERIZATION AND COPOLYMERIZATION

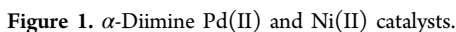
The α -diimine Pd(II) and Ni(II) catalysts (Figure 1) produce polyethylene with highly branched even branch-on-branch structures with ethylene as the only monomer. This microstructure is produced through a process known as chain walking polymerization (Scheme 1). The mechanism can be broken down into three steps after catalyst initiation: (1) chain

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The diagram illustrates the polymerization of N-vinylcarbazole (NVC) initiated by a phosphonium salt. The reaction scheme shows the following steps:

- Initiation:** A phosphonium salt (represented by a phosphonium cation and a phosphonium anion) reacts with NVC to form a phosphonium-initiated polymer chain.
- Propagation:** The phosphonium-initiated polymer chain reacts with NVC to form a growing chain end. This step is labeled "Propagation".
- Chain Transfer:** The growing chain end reacts with a phosphonium salt to form a shorter chain and a new phosphonium salt. This step is labeled "Chain transfer".
- Methyl branch:** The resulting phosphonium salt is labeled "Methyl branch" and shows a methyl group attached to the phosphonium group.
- Chain walking:** The scheme also shows a "Chain walking" process leading to longer branches.

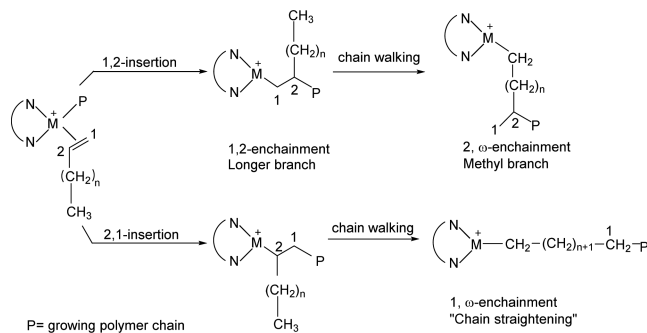
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Ni(II) catalyst can also initiate ethylene-methyl acrylate copolymerization, leading to copolymer with predominantly in chain acrylate incorporation (ca. 1%).¹³ However, very harsh polymerization conditions were used (120 °C and 1000 psi ethylene pressure). In addition, a large excess amount of tris(pentafluorophenyl)borane was required, which may serve as a Lewis acid to weaken the six membered metal chelate (Scheme 2).

The α -diimine Pd(II) catalysts are applicable for the olefin copolymerization with various polar monomers (see section 4). However, the choices of industrially relevant polar monomers (with polar groups directly attached to the olefin double bond) are rather limited with vinyl ether being a notable example. This also represents a big limitation and research challenge for this class of catalysts. Generally, vinyl ethers tend to undergo cationic polymerization or fast β -OR elimination. However, some sterically bulky and electronically deficient silyl vinyl ethers can be efficiently copolymerized with 1-hexene by α -diimine Pd(II) catalyst under a coordination–insertion mechanism.¹⁴ Most interestingly, multiple insertions of silyl vinyl ethers could be realized in the presence of excess amount of the monomer. Detailed mechanistic studies demonstrated the reasons for the successful vinyl ether copolymerization and multiple insertion reactions.¹⁵ First, cationic polymerization can be efficiently avoided using the electronically deficient silyl substituents. Second, double bond π -coordination can compete with oxygen coordination. Third, the O-chelate Pd(II) species can be readily trapped by olefins or silyl vinyl ethers. Fourth, the β -OR elimination is relatively slow comparing with chain growth rate.

2.3. Chain walking α -olefin polymerization. Chain walking α -olefin polymerization with α -diimine Pd(II) and Ni(II) catalysts affords polymers with interesting microstructures and properties.^{8,16} Chain straightening mechanism was proposed to reduce branching densities (1, ω -enchainment) and generate methyl branches (2, ω -enchainment). The total number of branches and the distribution of branches can be explained by the mechanism outlined in Scheme 3. The α -olefin

Scheme 3. Different Modes of Monomer Insertion and Enchainment in Chain Walking α -Olefin Polymerization

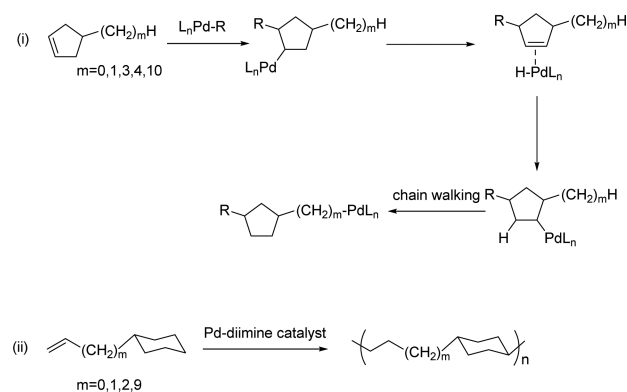


monomer can insert into the metal–carbon bond in either a 1,2- or 2,1-manner. Similar as in ethylene polymerization, chain walking of the metal along the hydrocarbon chain occurs via β -hydride elimination and reinsertion reactions. The 1, ω -enchainment is resulted from 2,1-monomer insertion followed by chain walking, and 2, ω -enchainment occurs through 1,2-monomer insertion followed by chain walking.^{8,16a} The rate of chain-walking is generally much greater than the rate of olefin insertion. Insertion occurs only into primary Pd(II)-alkyl bond

which is different from the Ni(II)-alkyl bonds where insertion can also occur at secondary metal carbon bonds. Because of this chain straightening mechanism, it is relatively difficult to prepare regio- or stereoregulated α -olefin polymers or copolymers using chain walking polymerization catalysts.

2.4. Chain walking polymerization of cyclo-olefins and dienes. The α -diimine Pd(II) catalysts are effective for the polymerization of cyclo-olefins, dienes and trienes.^{10g,j,17} The polymerization proceeds in a selective manner to give polymers containing five- or six-membered rings in every repeating unit. For example, 4-alkyl-cyclopentenes undergo smooth isomerization polymerization in the presence of α -diimine Pd(II) complex to afford polymers composed of alternating 1,3-*trans*-cyclopentane group and oligo-methylene group (Scheme 4i).^{17a,b} The mechanism of 4-alkyl-cyclo-

Scheme 4. (i) 4-Alkyl-cyclopentenes Isomerization Polymerization, and (ii) Alkenyl-cyclohexanes Isomerization Polymerization Catalyzed by α -Diimine Pd(II) Catalysts

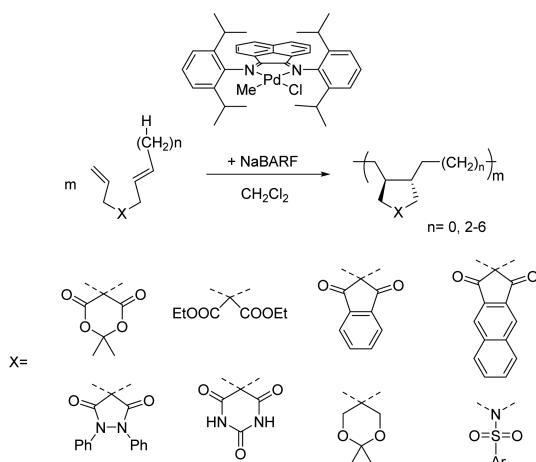


pentenes polymerization involves coordination and insertion of the monomer into the Pd(II) species and chain walking of the Pd center to the terminal alkyl groups. The length of the spacer between adjacent cyclopentane groups of the polymer is determined by the length of the alkyl group in the monomer. In a similar fashion, alkenyl cyclohexanes undergo isomerization polymerization by α -diimine Pd(II) catalysts (Scheme 4ii).^{17c} The intervals between the six-membered rings are determined by the spacer length between the vinyl and cyclohexyl group in the monomer.

Takeuchi et al. reported that 1, 6-dienes with both terminal and internal C=C bonds underwent cyclo-polymerization.^{10j,17d} The chain walking process affords polymers with $(CH_2)_n$ spacers of the desired length between the functionalized five-membered rings (Scheme 5). The insertion of the vinyl group ($-CH=CH_2$) into Pd(II)-polymer bond, followed by intramolecular insertion of the vinylene ($-CH=CH-$) group, yields a five-membered ring. The secondary Pd(II)-alkyl intermediate can be isomerized to primary Pd(II)-alkyl species by chain walking process. The coordination and insertion reactions of another monomer occur after the isomerization/chain-walking process.

3. CHAIN WALKING POLYMERIZATION CATALYSTS

In contrast to early transition metals, late transition metals are more prone to chain walking process because of their high tendency toward β -hydride elimination and reinsertion. Since Brookhart's seminal work in 1995, numerous late transition metal catalysts with chain walking capabilities have been

Scheme 5. Cyclopolymerization of 1,6-Dienes by α -Diimine Pd(II) Catalysts

reported. As it turned out, the chain walking feature is quite common among most late transition metal olefin polymerization catalysts. An interesting aspect is that the two major exceptions (late transition metal catalyst systems that do not undergo fast chain walking) are both based on phosphine containing ligands.¹⁸ For example, the SHOP catalysts with phosphanylenolato ligand have been widely used as highly efficient ethylene oligomerization catalysts for the generation of linear α -olefins.¹⁹ Recently, various Pd(II) catalysts bearing phosphine-sulfonate and other derivative ligands have been widely reported for the production of highly linear polyethylene and functionalized linear copolymers.²⁰

In this section, we will discuss two classes of late transition metal chain walking polymerization catalysts: (1) Pd(II) and Ni(II) catalysts bearing various α -diimine ligands (2) Pd(II) and Ni(II) catalysts bearing other nitrogen-containing ligands.

3.1. Pd(II) and Ni(II) catalysts with α -diimine ligands.

For α -diimine ligands, bulky *ortho*-aryl substituents were shown to suppress the associative chain transfer process by sterically blocking the access of monomers to the metal axial positions.^{7c,10b} This is essential to achieve high polymerization activity and high polymer molecular weight. In addition, the destabilization of the ground state species from steric effect contributes to the high catalytic activities. The degree of branching and branching distribution can be regulated by the competition between chain propagation and chain walking, which are intrinsically associated with ligand structures.

There are some apparent differences between the Ni(II) and the Pd(II) systems. The Ni(II) catalysts are highly active with turnover frequencies of up to $3 \times 10^6/\text{h}$ at 35°C , rivaling many early transition metal catalysts.^{7c,10b,21} The β -hydride elimination is less favored in the Ni(II) catalysts compared to the Pd(II) catalysts. As a result, the Ni(II) catalysts generate polymers with low to moderate branching density, consisting of mostly methyl groups. The microstructures can be varied from highly linear to highly branched by varying the polymerization conditions, resulting in highly crystalline or totally amorphous polymers.²¹ In contrast, the Pd(II) catalysts are usually far less active, generating polymers with branching numbers of between 90 and 125 per 1000 carbon atoms.^{10a} These polymers are generally hyperbranched even dendritic, with randomly distributed branches including Me, Et, ⁱPr, *n*-Bu, *sec*-Bu and long chain branches. It is highly difficult to control the polymerization process and the properties of the resulting (co)polymers by varying polymerization conditions. For example, the catalytic activity, the molecular weight, the branching density and the distribution of short-chain branches are relatively independent of ethylene pressure.^{10a,b,22}

The structure of the α -diimine ligand has an enormous effect on the polymerization processes. Since Brookhart's initial report, numerous modifications on the α -diimine ligands have been made, including steric tuning, electronic perturbation,

Table 1. Ethylene Polymerizations by Various α -Diimine Ni(II) Catalysts

Catalyst	T ($^\circ\text{C}$)	Cocatalyst/Ni	P (psi)	TOF ^a ($\times 10^{-3} \text{ h}^{-1}$)	M_n^b ($\times 10^{-3}$)	PDI ^b	B ^c /1000C	T_m^d ($^\circ\text{C}$)	ref.
L1a-NiBr ₂	25	MAO ^e , 500	145	50	n/a	n/a	n/a	133	24a
L1a-Ni(acac) ⁺ B(C ₆ F ₅) ₄ ⁻	60	AlMe ₃ , 500	145	854	89	3.5	3	129	24b
L1b-Ni(acac) ⁺ B(C ₆ F ₅) ₄ ⁻	60	AlMe ₃ , 500	145	140	283	1.8	21	109	24b
L1c-NiBr ₂	25	MAO, 500	145	235	3460	1.3	n/a	130	24a
L2-Ni(η^3 -allyl) ⁺ BAF ^{-f}	120	B(C ₆ F ₅) ₄ , 20	600	8.9	28	2.3	70	66	25
L3-Ni(η^3 -allyl) ⁺ BAF ⁻	150	B(C ₆ F ₅) ₄ , 20	600	43	7.2	3.2	60	90	25
L4a-NiBr ₂	70	MMAO ^g , 3000	200	1307	619	1.43	89	n/a	26a
L4a-NiBr ₂	90	MMAO, 3000	200	1007	462	1.64	96	n/a	26a
L4a-Ni(acac) ⁺ B(C ₆ F ₅) ₄ ⁻	115	Al(<i>i</i> -Bu) ₃ , 1500	200	33	131	1.50	117	n/a	26e
L4b-Ni(acac) ⁺ B(C ₆ F ₅) ₄ ⁻	105	Al(<i>i</i> -Bu) ₃ , 1500	200	12	159	2.30	33.2	81, 122	26e
L6-NiBr ₂	35	AlMe ₂ Cl, 3000	200	588	56.5	2.20	3.6	131	28
Ancenaphthyl-NiBr ₂ ^h	35	MAO, 2000	200	2400	337	1.80	24	110	21
L8-NiBr ₂	35	MAO, 2000	200	900	766	1.70	28	96	21
L9-NiBr ₂	35	MAO, 2000	200	1600	844	1.70	39	100	21
L10a-NiBr ₂	80	MAO, 600	8	13	123	2.00	129	- ⁱ	30a
L13b-NiBr ₂	50	AlEt ₂ Cl, 500	147	194	127	2.31	n/a	73	35a
L14-NiBr ₂	30	MAO, 500	147	54	105	2.20	9	131	35b
L15-NiBr ₂	r.t.	MMAO, 100	74	38	85	2.50	85	n/a	36
L16-Ni ₂ Br ₄	20	MAO, 500	132	179	112	3.37	15	n/a	37

^aTurnover frequency, which is calculated as the moles of monomer per mole of Ni(II) per hour. ^bDetermined by GPC. ^cBranching density, branches per 1000 carbons. ^dDetermined by DSC. ^eMethylaluminoxane. ^fBAF = 3,5-(CF₃)₂C₆H₃. ^gModified methylaluminoxane. ^hArN = C(An)-C(An) = NArNiBr₂(Ar = 2,6-CH(CH₃)₂-C₆H₃). ⁱAmorphous.

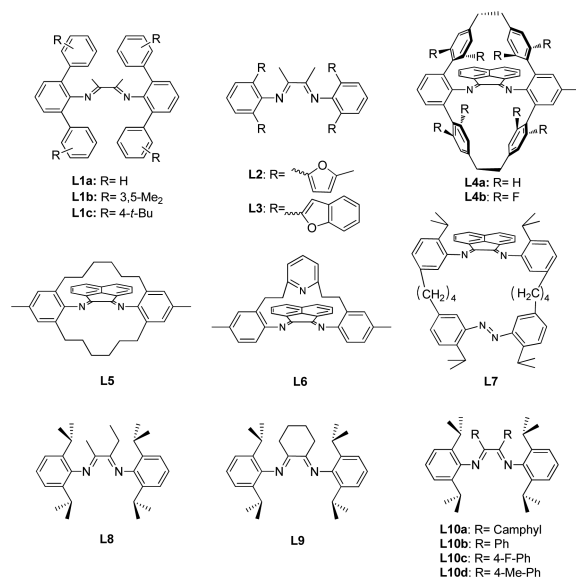
Table 2. Ethylene Polymerizations and Copolymerization with MA by Various α -Diimine Pd(II) Catalysts

catalyst	T (°C)	mono	[comon.] (M)	P _E (psi)	TON ^a / [C ₂ H ₄]	Incorp. ^b (%)	M _n ^c ($\times 10^{-3}$)	PDI ^c	B ^d / 1000C	ref.
L4a-Pd(CH ₂) ₃ C(O)OCH ₃ ⁺ BAF ^{-e}	35	E	-	88	8100	-	12.9	1.68	106	26c
L4a-Pd(CH ₂) ₃ C(O)OCH ₃ ⁺ BAF ⁻	35	E/MA	4.0	88	60	21.8	6.7	1.18	153	26c
L4b-PdMe(NCAr) ⁺ BAF ⁻	35	E	-	88	9540	-	269	1.60	53.2	26e
L6-PdMeCl ^f	25	E	-	88	1872	-	731	2.20	2.5	28
L10a-Pd(CH ₂) ₃ C(O)OCH ₃ ⁺ BAF ⁻	35	E	-	400	4264	-	28.8	1.55	86	30b
L10a-Pd(CH ₂) ₃ C(O)OCH ₃ ⁺ BAF ⁻	70	E	-	400	1276	-	15.1	1.79	91	30b
L10a-Pd(CH ₂) ₃ C(O)OCH ₃ ⁺ BAF ⁻	35	E/MA	0.5	15	396	1.2	12.0	1.59	84	30b
L17-PdMeCl ^g	40	E	-	147	16100	-	17.0	4.10	72	38
L17-PdMeCl ^g	40	E/MA	2.2	147	234	6.6	8.1	4.70	40	38

^aTurnover number, moles of monomer incorporated per mol of catalyst. ^bMA incorporation, determined by ¹H NMR. ^cDetermined by GPC. ^dBranching density, branches per 1000 carbons. ^eBAF = 3,5-(CF₃)₂C₆H₃. ^f100 equiv of AlMe₂Cl as cocatalyst. ^g1.2 equiv of NaBAF as cocatalyst.

ligand backbone adjustment, and so on. In this section, only some notable examples are discussed. Influences of the catalyst structures and the polymerization conditions on α -diimine Ni(II) and Pd(II) catalyzed olefin (co)polymerization are summarized in Tables 1 and 2.

First of all, the substituents on the aryl *ortho*-positions can be adjusted. Sterically bulky substituents are required to obtain high activity, stability and polymer molecular weight.^{23–30} For example, Rieger et al. prepared a series of Ni(II) catalysts bearing *meta*-substituted terphenyl-based α -diimine ligands L1a–1c (Figure 2).²⁴ These catalysts showed high activity

Figure 2. Modified α -diimine ligands for Pd(II) and Ni(II) catalysts.

and stability in ethylene polymerization. The most interesting feature of these catalysts is that they can maintain good activity and stability in the presence of hydrogen, which also serves as an effective chain transfer reagent to reduce the polymer molecular weight. Specifically for the Ni(II) catalyst based on L1a, polyethylene with very low branching density (ca. 4/1000C) could be obtained. Ionkin et al. reported some Ni(II) catalysts bearing ligands L2 and L3 containing *ortho*-difuryl moiety.²⁵ These catalysts could maintain reasonable activity even at 150 °C, generating polyethylene with high molecular weight. In addition, the polymer branching density is relatively low (7–70/1000C).

Guan et al. designed a macrocyclic ligand L4a by connecting the aryl substituents of 2,6-diarylphenylimino moieties using ethylene tether.²⁶ Both the cyclophane-based Ni(II) and Pd(II) catalysts showed significantly higher thermal stability than the acyclic analogs. These catalysts also generated polymers with significantly high branching density compared to the acyclic counterparts, suggesting faster chain walking process.^{26a} The cyclophane-based Ni(II) catalyst promoted living polymerization of propylene even at 50–75 °C. This type of catalyst enhances both the 2,1-insertion of propylene and the chain walking reaction. The branching density of the generated polypropylene is slightly above 100/1000C, which is only half of the value comparing with conventional α -diimine Ni(II) catalyst.^{26b} The cyclophane-based α -diimine Pd(II) catalysts showed higher methyl acrylate incorporation in ethylene-methyl acrylate copolymerization than the acyclic analogs.^{26c} This was attributed to the much slower associative monomer exchange based on detailed mechanistic studies.^{26d} The Pd(II) catalyst bearing a fluorinated cyclophane ligand L4b was also investigated.^{26e} It afforded polymer with comparatively low branching density and high molecular weight. Based on NMR analysis, strong coupling between the fluorine atoms and the catalyst provided evidence for a direct interaction between the fluorine atom and the metal center, resulting in a significant reduction in chain walking rate. Pd(II) and Ni(II) complexes bearing a similar macrocyclic of ligand L5, containing two C6 alkyl bridges, exhibited very low activities in ethylene polymerization.²⁷

Guan et al. also designed a ligand framework with potential hemilabile donating group (L6).²⁸ Interestingly, both the Pd(II) and the Ni(II) catalysts showed no activity in ethylene polymerization unless excess amount of AlMe₂Cl was added to the catalyst system. With the addition of AlMe₂Cl, moderate activities were observed, affording polyethylene with high molecular weight and low branching density. The real active species and the operative mechanism were not fully understood in this system. In addition, whether the high molecular weight and low branching density could be maintained in ethylene-polar monomer copolymerization was not studied.

Aida et al. studied a cyclophane-type α -diimine Pd(II) catalyst bearing ligand L7.²⁹ The *trans*-azobenzene unit can be photochemically converted to *cis* configuration. Interestingly, the *trans* catalyst showed much better activity and stereoselectivity than the *cis* catalyst in the cyclo-polymerization of diallylmalonate monomer (Scheme 5).

Alternatively, the substituents on the α -diimine ligand backbone can be adjusted. Greater steric bulkiness on the

backbone generally enhances the catalyst stability and activity. Brookhart et al. reported that Ni(II) catalysts bearing ligands **L8** and **L9** with alkyl substituents on the backbone led to polymers with higher molecular weight and narrower molecular weight distributions than the catalysts bearing planar aromatic acenaphthyl backbone.²¹

Recently, Wu et al. studied a series of α -diimine Ni(II) and Pd(II) catalysts with various backbone structures such as camphyl (**L10a**), phenyl (**L10b**), 4-fluorophenyl (**L10c**), 4-methylphenyl (**L10d**) and methyl.³⁰ The Ni(II) complex bearing camphor quinone-derived ligand **L10a** showed moderate activities at up to 80 °C. The Pd(II) complex bearing this ligand was also highly robust, demonstrating good activities at up to 70 °C.

The ligand electronic effect was also shown to affect the polymerization properties in α -diimine catalyst system (**L11a**–**L11g**, Figure 3).³¹ In α -diimine Pd(II) catalyzed ethylene

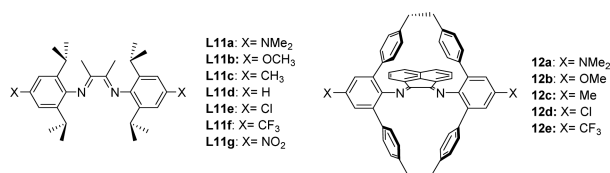


Figure 3. Ligand electronic effects in α -diimine Pd(II) and Ni(II) catalysts.

polymerization, electron-donating substituents led to higher polymer molecular weight and more linear topology. In ethylene-methyl acrylate copolymerization, electro-donating substituents led to higher methyl acrylate incorporation. Also, more stable catalysts could be generated using electro-donating substituents. Putting these results together, it was concluded that the catalysts were more resistant to chain transfer with electro-donating substituents. Guan et al. also examined the ligand electronic effect (**L12a**–**L12e**) on a family of cyclophane-based Ni(II) and Pd(II) catalysts.³² The Ni(II) catalysts exhibited little variation in activity or thermal stability. However, the electronic effects in the Pd(II) system were significant. In contrast to the previously studied acyclic α -diimine Pd(II) catalysts,^{31a} the catalysts with electron-withdrawing substituents generated polymers with higher molecular weight, indicating a different operative mechanism in the Pd(II)-cyclophane system.

The investigation of metal–metal cooperative effect on olefin polymerization and copolymerization has attracted a lot of attention.³³ However, very few examples of dinuclear α -diimine Ni(II) or Pd(II) complexes were reported. Schumann group³⁴ and Sun group^{35a} reported the ethylene polymerization studies of some methylene bridged α -diimine (**L13a** and **L13b**, Figure 4) dinuclear Ni(II) complexes. Our group³⁶ and Sun group^{35b} reported the synthesis and studies of a series of dinuclear Ni(II) complexes based on conjugated α -diimine ligands **L14** and **L15**. These dinuclear species generally demonstrated higher stability and activity in ethylene polymerization comparing with the mononuclear analogues, generating polyethylene with narrow polydispersity.

Very recently, we described the synthesis and ethylene polymerization studies of a series of xanthene bridged dinuclear α -diimine Ni(II) complexes bearing ligands **L16**.³⁷ In addition to the higher stability and higher catalytic activity, polyethylenes with much lower branching density (up to three

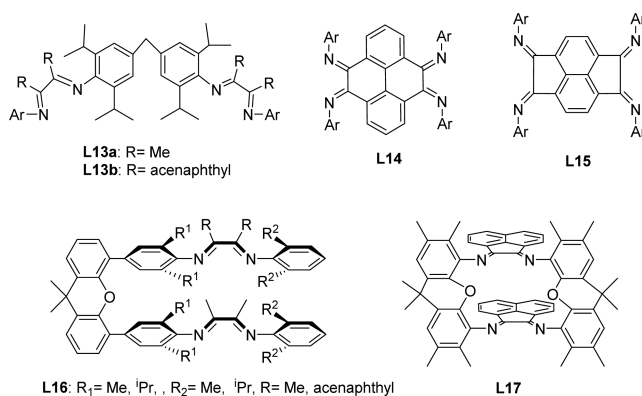


Figure 4. Some previously reported dinuclear α -diimine ligands.

times) were produced by these dinuclear complexes comparing with mononuclear analogues. It was hypothesized that metal–metal cooperativity effect might be able to slow down the β -hydride elimination and correspondingly the chain walking process. Recently, Takeuchi et al. showed that a dinuclear α -diimine Pd(II) complex bearing ligand **L17** with a double-decker structure catalyzed ethylene-methyl acrylate copolymerization to yield branched copolymers with some acrylate units located in the polymer main chain.³⁸ This is totally different from conventional α -diimine Pd(II) catalysts, which produce copolymer with almost all of the acrylate units at the end of the branches.^{7d,e,12} A potential metal–metal cooperativity effect was proposed to be responsible for this interesting effect. These results clearly demonstrated the great potentials of dinuclear α -diimine Ni(II) and Pd(II) catalysts in controlling the olefin polymerization and copolymerization processes.

In addition, various α -diimine Pd(II) catalysts could be generated from the insertion of different acrylate monomers into the Pd–C bond (Figure 5).^{7,10a,39} This enables the

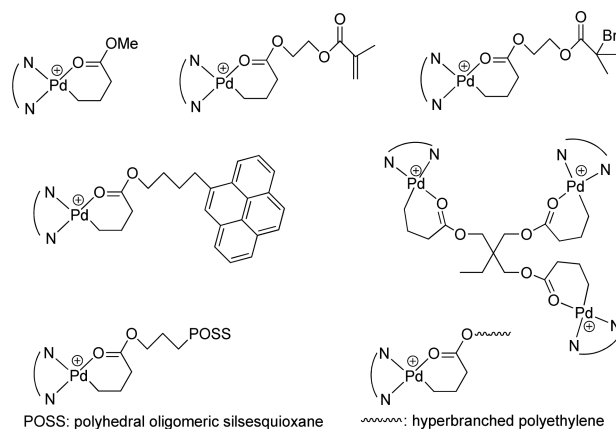


Figure 5. Various α -diimine Pd(II) catalysts from the insertion of different acrylate monomers into the Pd–C bond.

convenient synthesis of functionalized polyethylenes of various complex architectures, such as star, hyperbranched-on-hyperbranched, block, telechelic, etc. The applications of these catalysts in the synthesis of functionalized polymers and copolymers will be discussed in detail in section 4.

3.2. Chain walking polymerization catalysts with other nitrogen-containing ligands. In this section, we will briefly discuss some of the notable examples of chain walking polymerization catalysts with nitrogen-containing

bidentate ligands (Figure 6). In literature, there are a large amount of dinuclear late transition metal olefin polymerization catalysts, which are not included in this perspective.³³

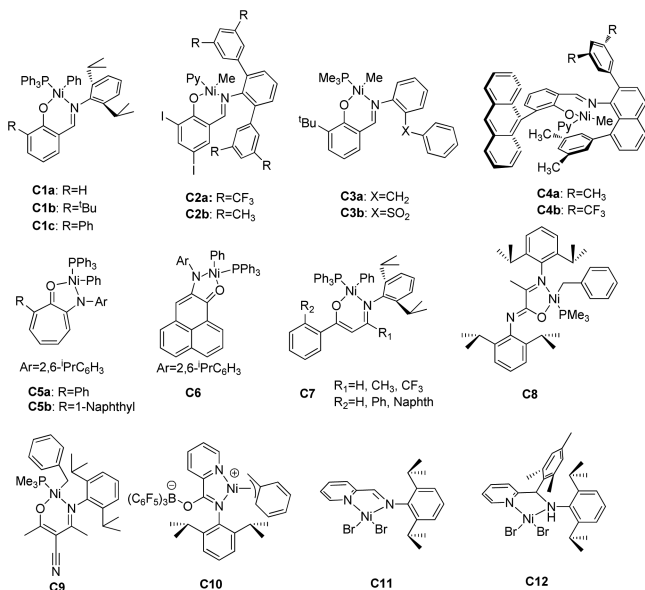


Figure 6. Selected examples of chain walking polymerization catalysts with nitrogen-containing ligands.

Grubbs et al. described the ethylene polymerization studies of several nickel catalysts **C1a–C1c** bearing salicylaldimine ligands.⁴⁰ Bulky substituents on the 3-position of the salicylaldiminato ring could increase the catalytic activity and decrease the polymer branching density. Using these catalysts, high molecular weight polymer with about 10–50 branches per 1000 carbons could be obtained. Similar with the α -diimine Ni(II) system, branching density can be controlled by different polymerization temperatures and pressures. In addition, these complexes were shown to be tolerant toward polar additives and capable of copolymerizing ethylene with polar functionalized norbornene monomers.

Mecking et al. showed that the substituents at the terphenyl 3,5-positions can dramatically influence the catalytic properties of the Ni(II) complexes, despite their spatial remoteness from the metal center.⁴¹ The CF₃ containing catalyst **C2a** generated high molecular weight semicrystalline polyethylene with low branching densities ($M_w = 9.7 \times 10^4$, Branching = 10/1000 C, $T_m = 123$ °C). In contrast, the CH₃ containing catalyst **C2b** generated low molecular weight amorphous polyethylene with high branching densities ($M_w = 2.3 \times 10^3$, Branching = 76/1000 C, no T_m). A remote ligand electronic effect was proposed to be responsible for this interesting effect. Recently, the potential involvement of weak (ligand)C–F...H–C(polymer) interactions was proposed by Marks et al. in a very similar system.⁴²

Marks et al. showed that a weakly coordinating SO₂ moiety can greatly increase catalytic activity, polymer molecular weight and branching density comparing with the CH₂ counterpart in Ni(II) catalyzed ethylene polymerization (**C3**).⁴³ The possible stabilization of the 14-electron metal intermediate from the SO₂ group was hypothesized.

Brookhart et al. studied the ethylene polymerization properties of neutral Ni(II) catalysts **C4**.⁴⁴ These catalysts produced ultrahigh-molecular-weight polyethylenes (M_w up to 3.0×10^6 g/mol) with low to moderate branching densities in

the range of 4–31 branches per 1000 carbon atoms. The same group also studied a series of neutral nickel catalysts **C5** and **C6**.⁴⁵ Interestingly, catalysts **C5** were much more active than **C6**. With catalyst **C5**, the polymer branching numbers were relatively insensitive to polymerization conditions (35–45 branches per 1000 carbon atoms), which was different from the α -diimine Ni(II) system.

Li et al. described the ethylene polymerization studies using a series of neutral nickel complexes **C7** bearing β -ketoiminato chelate ligands.⁴⁶ The variations of the R₁ and R₂ groups exhibited a remarkable effect on polymer microstructure, allowing access to polyethylenes with branching numbers varying from 18 to 103 branches per 1000 carbon atoms.

Bazan et al. synthesized a series of α -iminocarboxamidato Ni(II) catalysts **C8**, β -iminocarboxamidato Ni(II) catalysts (**C9**) and pyridinecarboxamidato Ni(II) catalysts (**C10**).⁴⁷ These catalysts showed similar performance in ethylene polymerization, affording branched polyethylene with 33 to 106 branches per 1000 carbon atoms.

Ni(II) Catalysts **C11** with imino-pyridine ligands usually showed very low activity in ethylene polymerization and afforded branched polyethylene with low molecular weight.⁴⁸ However, Wu et al. recently reported that pyridine-amine based Ni(II) catalysts (**C12**) were capable of producing polyethylenes with narrow molecular weight distributions in a living fashion. Highly branched polymers with branching numbers ranging from 76 to 105 per 1000 carbon atoms can be obtained through fast chain walking process.⁴⁹ Even at 0 °C, the branch-on-branch microstructures can be observed.

4. FUNCTIONALIZED HYPERBRANCHED COPOLYMERS PREPARED VIA CHAIN WALKING (CO)POLYMERIZATION

Polar functionalized polyolefins are valuable materials because of their unique properties. Since Brookhart's seminal work on α -diimine Pd(II) catalysts, significant progresses have been made in late transition-metal catalyzed olefin-polar monomer copolymerization.⁵⁰ In this section, we will discuss some of the notable examples of functionalized hyperbranched copolymers prepared using α -diimine Pd(II) catalysts. Two key features of these catalysts should be mentioned to better understand their behaviors in the copolymerization reactions. First, the chain-walking mechanism makes the topology of the copolymers adjustable through polymerization conditions. Low ethylene pressure favors the formation of hyperbranched copolymers with long chain and branch-on-branch structures, while high ethylene pressure favors the formation of relatively linear copolymers with short chain structures (Figure 7). In either case, most of the polar groups are located at the end of branches. Second, these catalysts can polymerize ethylene in a living fashion at below 5 °C and above 400 psi ethylene pressure.²² As a result, mono- and diend-functionalized polyethylene and some block copolymers with unusual microstructures can be prepared.⁵¹ These features enabled the synthesis of novel materials with complex architectures. These materials can be mainly separated into two categories: functionalized copolymers from direct chain walking copolymerization, and functionalized copolymers from the combination of chain walking polymerization with other polymerization techniques.

4.1. Functionalized copolymers from direct chain walking copolymerization. Figure 7 summarizes some of the reported comonomers that can be incorporated in

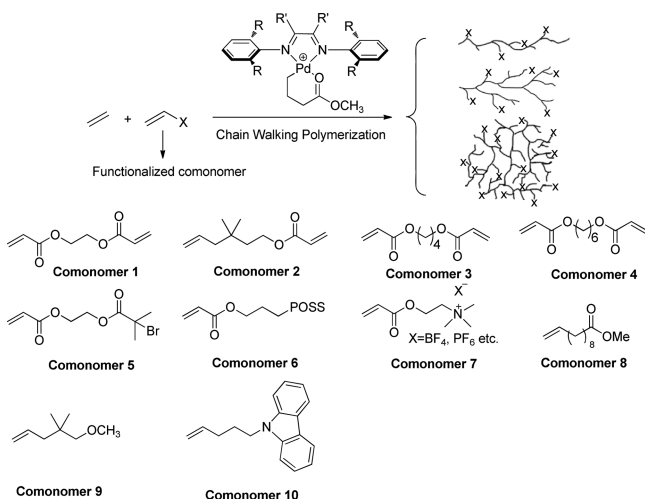


Figure 7. Functionalized comonomers and the corresponding copolymers.

hyperbranched polyethylene with high comonomer incorporation. Ye's group has done a lot of work in this field.^{10f,i} They synthesized hyperbranched polyethylenes tethered with polymerizable methacryloyl groups, from the copolymerization of ethylene with two hetero bifunctional **comonomer 1** and **comonomer 2**.⁵² Copolymerization of ethylene with 1,4-butanediol diacrylate (**comonomer 3**) can lead to functionalized hyperbranched polyethylene containing both cross-linked structure and pendant vinyl groups at low comonomer concentration.⁵³ Heterofunctionalized hyperbranched copolymers were generated from the ethylene copolymerization with functional **comonomer 4** and **comonomer 5**.⁵⁴ Interestingly, hyperbranched polyethylenes containing covalently tethered polyhedral oligomeric silsesquioxane (POSS) nanoparticles could be synthesized by chain walking ethylene copolymerization with a POSS containing **comonomer 6**.⁵⁵ The aggregation/interaction of the POSS nanoparticles enabled the observation of gel-like rheological behaviors. Recently, hyperbranched polyethylene ionomers containing tetralkylammonium ions and various counteranions were prepared by direct chain walking copolymerization of ethylene with ionic liquid type comonomers (**comonomer 7**).⁵⁶

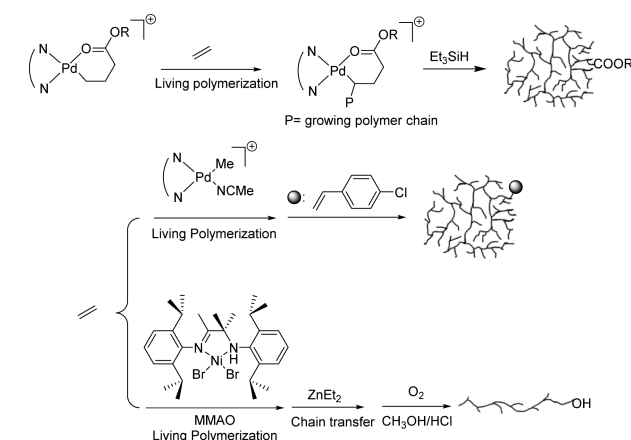
The copolymerization was relatively easy to achieve when a long spacer was put between the olefin double bond and the polar functional groups. Guan et al. reported ethylene copolymerization with the ester and ether containing polar monomers (**comonomers 8** and **9**) to synthesize functionalized copolymers with relatively linear or dendritic structures by changing ethylene pressure and comonomer concentration in a one-pot method.¹²

The nitrogen-containing functionalities can bind strongly to the metal center, thereby preventing efficient copolymerization. Interestingly, the copolymerization of ethylene with cabazole-containing comonomer (**comonomer 10**) was achieved using α -diimine Pd(II) catalysts.⁵⁷ A comonomer incorporation of 18.8 wt % could be obtained at low ethylene pressure (2 bar).

4.2. Functionalized copolymers from the combination of chain walking polymerization with other polymerization techniques. The tolerance toward polar groups and the living polymerization feature of the α -diimine Pd(II) catalysts make it possible to prepare end-functionalized polyethylenes. Starting with a polar group containing Pd(II)

catalyst (Figure 5), ethylene polymerization could lead to end-capped polyethylenes (Scheme 6). The end group can be

Scheme 6. Methods To Introduce Functional End Groups



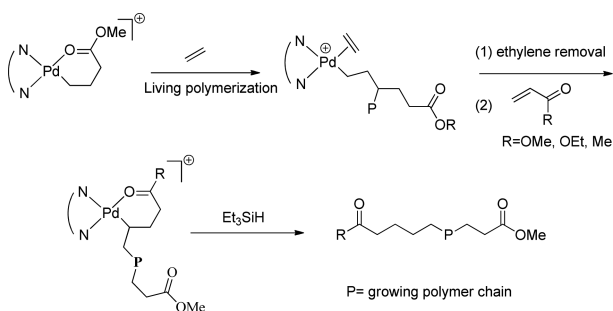
further converted to various functional groups. For example, Brookhart et al. prepared a highly branched (ca. 100 branches/1000C) polyethylene macromonomer with a methacrylate-functionalized end group by Pd(II)-mediated ethylene polymerization.^{39a} A chelating Pd(II) complex was used to catalyze ethylene polymerization, affording polyethylene chains bearing an end-capped 2-bromoisobutryl group.^{39b} Also, a fluorescent pyrene can be introduced into hyperbranched polyethylene for detection applications.^{39c} Inorganic groups may also be attached to the cationic Pd(II) center through the ester linkage. Ye et al. reported that the POSS-containing Pd(II) catalyst gave rise to polyethylene with chain end-capped with a POSS nanoparticle.^{39d} Ye group also demonstrated the synthesis of a novel trinuclear Pd-diimine complex and the synthesis of star shaped polyethylenes.^{39e}

Considering the living feature of these catalysts, different quenching method provides another strategy to introduce functional end groups.⁵¹ At the end of the polymerization, addition of quenching agents with polar functionalities can lead to end-capped polyethylenes (Scheme 6). For example, Ye et al. synthesized a series of polyethylenes containing a reactive ω -functional group by quenching the polymerization reactions with styrene derivatives such as 4-vinylbenzyl chloride.⁵⁸ Some end-functionalized polyethylenes were also produced using Ni(II) catalysts.⁵⁹ For example, Gao et al. showed that hydroxyl functionalized branched polyethylene can be prepared using ZnEt_2 as chain transfer agent and O_2 as quenching agent (Scheme 6).^{59b} The hydroxyl groups can be converted to other functional groups and initiate further polymerization to prepare block copolymers.

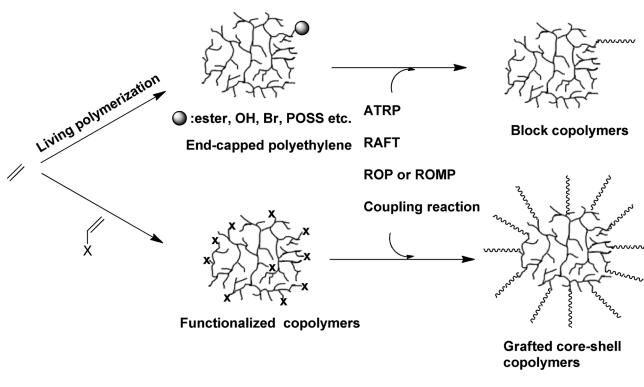
By combining these two strategies, polyethylene with functional groups at both ends can also be prepared. For example, Brookhart et al. demonstrated the synthesis of polyethylenes with acrylate units at both chain ends using the method outlined in Scheme 7.⁵¹

The above-mentioned strategies can be used to prepare polyethylene macroinitiators with one functional group (Scheme 8). Direct copolymerization of ethylene with polar monomers lead to the formation of hyperbranched copolymers with many functional groups located at chain ends. These functional groups can be readily converted to other functional groups. All of these materials provide the initiating sites to build

Scheme 7. Synthesis of Difunctional (Telechelic) Polyethylene



Scheme 8. Synthetic Strategy To Produce Polyethylene-Based Functionalized Copolymers

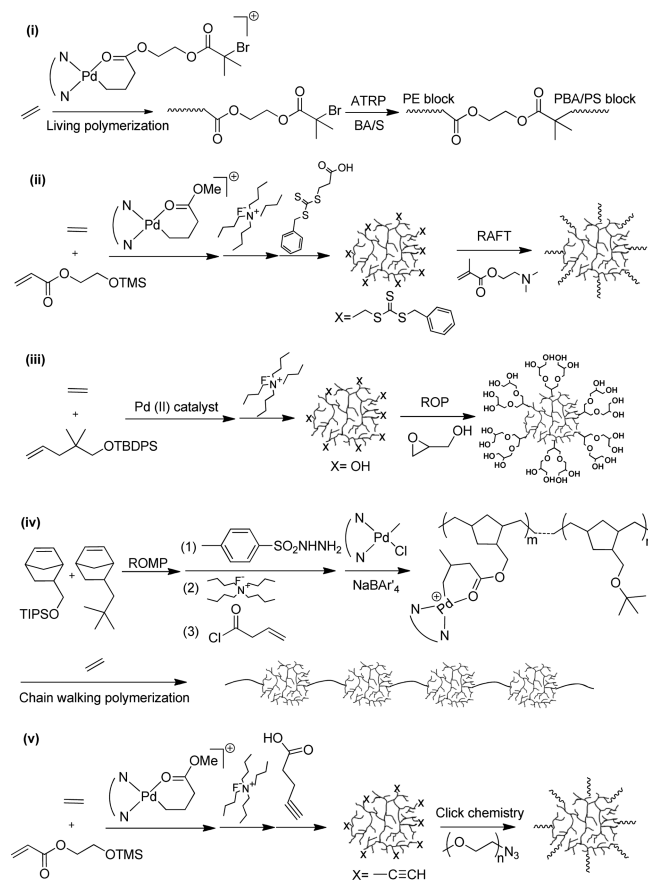


blocks or graft chains. Synthesis of block or graft copolymers can be achieved in combination with other polymerization techniques (Schemes 8 and 9).

For example, by combining Pd(II)-mediated chain walking polymerization and atom transfer radical polymerization (ATRP), polyethylene with pendant 2-bromoisobutryl functionality can serve as a macroinitiator for the synthesis of block copolymers with hyperbranched polyethylene segment and polystyrene (PS) or poly(*n*-butyl acrylate) (PBA) segment (Scheme 9i).^{39b} Using the same strategy, a grafted copolymer of PBA and polyethylene was prepared by the combination of these two living polymerization techniques.^{39a} This strategy can also be used to graft poly(methyl methacrylate) (PMMA) arms on hyperbranched polyethylene.⁶⁰ Guan et al. prepared dendritic nanoparticles with tunable size and reactive surface functionalities by combining chain walking polymerization and Cu(I)-mediated ATRP.⁶¹

The combination of chain walking polymerization with reversible addition–fragmentation transfer polymerization (RAFT) or ring-opening polymerization (ROP) has also been realized using a variety of functional hyperbranched polyolefins. The macro-RAFT agents tethered with a thiocarbonylthio moiety were prepared from chain walking ethylene polymerization, and used to mediate RAFT polymerization of *N,N*-dimethylaminoethyl to form hyperbranched functionalized polyethylene amphiphiles (Scheme 9ii).⁶² These polymers were able to self-assemble into supramolecular polymer vesicles in aqueous solution. Guan et al. described the synthesis of a unimolecular core–shell nanocarrier derived from a hyperbranched polyethylene core and polyglycerol shell (Scheme 9iii).⁶³ This was realized through the tandem chain walking polymerization and anionic ring-opening polymerization of glycidol.

Scheme 9. Selected Examples of Functionalized Copolymers Prepared via the Combination of Chain Walking Polymerization and Other Polymerization Techniques



By combining chain walking polymerization and ring-opening metathesis polymerization (ROMP), Guan et al. reported an efficient synthesis of “necklace” polymers (Scheme 9iv).^{39f} First, a linear polymer chain containing well dispersed α -diimine Pd(II) catalysts was prepared through ROMP. The chain walking ethylene polymerization initiated from these dispersed Pd(II) catalysts led to the formation of dendritic “pearl” on the polymer chain. Large soluble nanostructures for various potential applications can be prepared using this simple and efficient approach.

Click chemistry can also be combined with chain walking polymerization. Amphiphilic copolymers with a dendritic polyethylene core and poly(ethylene oxide) (PEO) arms were prepared using azide–alkyne click chemistry on a macroinitiator generated by chain walking polymerization (Scheme 9v).⁶⁴ The quantitative conversion proved the high efficiency of this strategy. In another system, the copolymers of hyperbranched polyethylene with poly(ethyleneglycol) (PEG) were obtained by direct coupling of hetero bifunctional PEG to the hydroxyl containing polyethylene.^{39c,65} However, the coupling efficiency was limited for PEG segments with high molecular weight.

Despite these successful examples, a multistep synthetic procedure is required, which is inconvenient. Moreover, polymers with ill-defined structures are sometimes generated. Ye et al. demonstrated a ligand exchange strategy for one-pot synthesis of treelike (hyperbranched polyethylene)-*b*-polyketone block copolymers.⁶⁶ Initially, the cationic α -diimine Pd(II)

complex was capable of facilitating living ethylene polymerization. Upon the addition of an equimolar amount of 2,2'-bipyridine, the Pd(II) complex could be switched to catalyze alternating copolymerization of 4-tertbutylstyrene and CO.

The Pd(II) catalyst can be immobilized on an inorganic surface to produce hybrid materials grafted with hyperbranched polyethylene chains.⁶⁷ For example, immobilization of Pd(II) catalysts on inorganic particles was achieved from the insertion of surface acrylate groups into the Pd–C bond. In this way, the mesoporous silica hybrid materials grafted with polyethylene can be prepared and the length of polyethylene segment can be adjusted over a wide range by changing the polymerization conditions.^{67c} Similarly, Guan et al. prepared large dendritic nanoparticles using chain walking polymerization on a preformed dendritic polyethylene particle containing multiple palladium catalysts on the surface.^{39g}

5. RECENT DEVELOPMENTS AND PERSPECTIVES

The control of polymer topology through chain walking mechanism and the incorporation of polar functional groups in the polymerization process have offered great opportunities in the development of novel functional polymeric materials. Due to the unique architectures and characteristic properties, hyperbranched polymers produced using chain walking polymerization catalysts have found numerous applications as lubricants, nanocarriers, bioconjugates, catalysts support and live-cell imaging materials. These applications have been discussed in some review literatures and will not be covered in this perspective.^{10f,h,i}

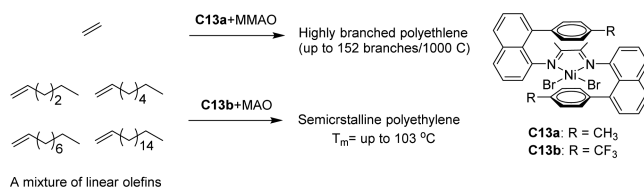
The synthesis of new functional materials and their applications will no doubt continue to be a highly attractive area for chain walking polymerization. In addition, it is very interesting and maybe more challenging to explore new chain walking polymerization catalysts. Another major challenge would be the control of the chain walking processes through new strategies other than simple ligands modulations. For example, Aida et al. showed that the polymerization properties of the α -diimine Pd(II) catalyst bearing ligand L7 can be adjusted photochemically (Figure 2).²⁹ Recently, our group studied the facile and reversible interconversion between the neutral and oxidized palladium complexes bearing ferrocene bridged phosphine-sulfonate ligands. In ethylene polymerization, the oxidized palladium complex generated polymer with lower molecular weight and higher branching density than the neutral palladium complex. This work demonstrated that the strategy of *in situ* redox control could be used to modulate the chain walking process.⁶⁸

In this section, we will discuss two extreme types of catalysts: very fast chain walking polymerization catalysts and very slow chain walking polymerization catalysts.

5.1. Fast chain walking polymerization catalysts. Fast chain walking polymerization catalysts can polymerize ethylene to generate highly branched polymers (more than 100 branches/1000C). These materials may find applications as high performance synthetic lubricants. A more interesting aspect would be the conversion of α -olefins into semicrystalline polymers via chain straightening mechanism. For example, Wu et al. reported the synthesis of poly(α -olefins) with an obvious T_m using camphyl based α -diimine Ni(II) catalysts.⁶⁹

Brookhart et al. studied a Ni(II) catalyst C13a bearing sandwich structured α -diimine ligand (Scheme 10).⁷⁰ Highly branched polyethylene (up to 152 branches/1000C) was generated in ethylene polymerization, suggesting very fast

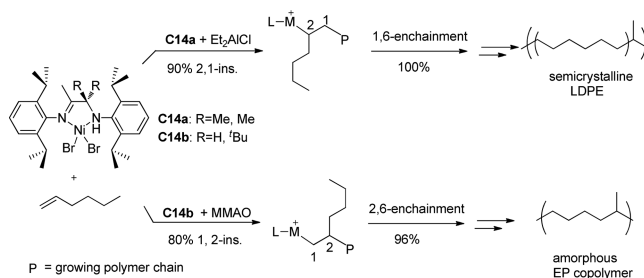
Scheme 10. Ethylene Polymerization and α -Olefins Polymerization Using Ni(II) Catalyst C13



chain walking polymerization. Recently, Coates et al. reported that Ni(II) catalyst C13b and some derivative catalysts can efficiently convert 1-decene to semicrystalline polymers (with linear fraction of up to 76% and $T_m > 100$ °C).⁷¹ Very interestingly, a mixture of α -olefins can be used, leading to similar results. Mechanistic studies showed that this was realized through highly selective 2,1-insertion followed by precise chain-walking process. In contrast, amorphous or low-melting point polymers with methyl branches are usually produced because of the 1,2-insertion and the chain walking process using traditional α -diimine Ni(II) system.^{7,8}

Using the same concept, Wu et al. described the polymerization of 1-hexene to prepare semicrystalline “polyethylene” with long methylene sequence $(-(CH_2)_n-)$, $n = 40-74$ using Ni(II) catalyst C14a bearing amine-imine ligand.⁷² 90% selectivity of 2,1-insertion was observed. In contrast, catalyst C14b with a *tert*-butyl substituent can polymerize 1-hexene in 80% selectivity of 1,2-insertion to produce amorphous polyolefin with predominant methyl branches. Different enchainment pathways (1,6-enchainment versus 2,6-enchainment) in these two systems can be briefly illustrated in Scheme 11. This class of Ni(II) catalyst can also catalyze chain walking ethylene polymerization in a living fashion above room temperature.⁷³

Scheme 11. Different Enchainment Pathways in 1-Hexene Polymerization Mediated by Ni(II) Catalysts C14a and C14b



It should be noted that the activities in both of the above-mentioned catalyst systems are low and nice selectivity can only be realized under low α -olefin concentration. Therefore, new catalysts are highly desired to improve both the activity and the selectivity.

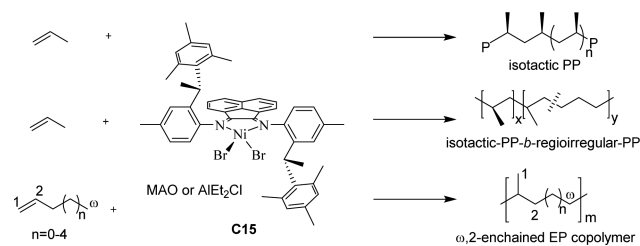
5.2. Slow chain walking polymerization catalysts. Despite the successful synthesis of various polymers and functional copolymers, the low molecular weight together with high branching densities limited their potential applications only in very specific areas. To produce semicrystalline engineering materials, new catalysts with slow chain walking capabilities are required. With such kind of catalysts, it could also be possible to copolymerize α -olefin with polar monomers in a regio and stereo controlled fashion. It should be noted that the recently emerged phosphine-sulfonate type Pd(II) catalysts

exhibited very slow chain walking feature.²⁰ However, they also suffer from some limitations. For example, they generated polymers and copolymers with low molecular weight, usually lower than those generated by α -diimine Pd(II) catalysts under similar conditions. That is a totally different research direction and is not the focus of this perspective.

Specifically, isotactic polypropylene is a highly valuable material produced on a large scale using early transition-metal catalysts. However, these catalysts are easily poisoned by hetero atoms, making it very difficult to introduce polar functionalities. In contrast, late-transition-metal catalysts can tolerate polar functional groups. However, they suffer from poor regio control in olefin polymerization mainly because of the chain straightening process. If this process can be suppressed using novel catalysts, the functionalized isotactic polypropylene may be synthesized. Recently, Nozaki et al. described the regioselective copolymerization of propylene with a series of polar monomers using palladium catalysts bearing a special N-heterocyclic-carbene ligand.⁷⁴ This is a very nice demonstration of the great potentials of late transition metal catalysts although stereo control could not be realized in that system.

Coates et al. reported living polymerization of propylene and higher α -olefins using C_2 -symmetric α -diimine Ni(II) catalyst (C15) bearing chiral *sec*-phenethyl moiety (Scheme 12).⁷⁵

Scheme 12. Polymerization of α -Olefins with Ni(II) Catalysts Catalyst C15

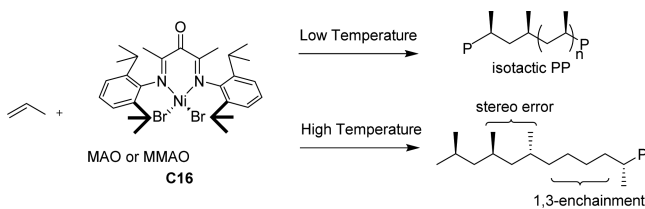


Highly *iso*-selective polypropylene can be obtained at low temperatures (e.g., $-60\text{ }^{\circ}\text{C}$). Polymerization at low, then ambient temperatures led to the formation of an isotactic-atactic regioirregular-regioirregular block copolymer. Unfortunately, the nice regio control could not be maintained in higher α -olefin polymerization. An ethylene-propylene copolymer structure were observed through $\omega,2$ -enchainment.

Bazan et al. showed that catalyst C16 can polymerize propylene in a regio- and stereocontrolled fashion at low temperatures (Scheme 13).⁷⁶ At high temperatures, atactic and regioirregular polymers were obtained. It should be noted that this system lacks chiral ligands, suggesting a chain end control mechanism.

These two catalyst systems can only realize regio and stereo control at very low temperatures, under which conditions the

Scheme 13. Propylene Polymerization with Ni(II) Catalyst C16

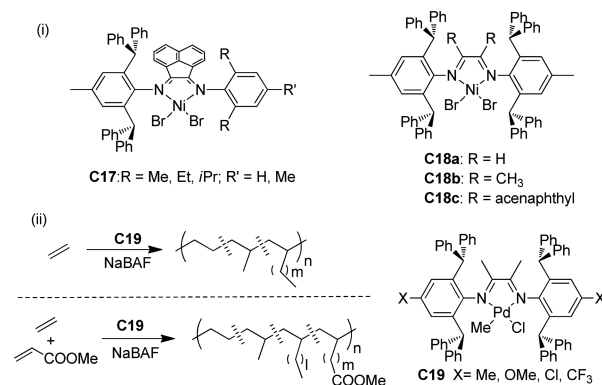


chain walking and chain straightening processes could be significantly suppressed. Nevertheless, these results suggested that the chain walking process can be slowed down to realize regio even stereo controlled α -olefin polymerization. Meanwhile, the developments of new catalysts that can maintain such nice control under high temperatures would be highly desired. Another big limitation is that these systems cannot be used for copolymerization with polar monomers because of the high oxophilicity of the Ni(II) center. Unfortunately, it is extremely difficult to suppress the chain walking process in α -diimine Pd(II) system. As a result, the α -diimine Pd(II) catalysts usually generate polymers or copolymers with more than 90 branches per 1000 carbon atoms.

Recently, dibenzhydryl-derived ligand frameworks were investigated to generate highly stable Ni(II) catalysts (C17).⁷⁷ For example, Long et al. described the synthesis of α -diimine Ni(II) complex C18, which maintained high activities at temperatures up to $100\text{ }^{\circ}\text{C}$, generating moderately branched (63–75 branches per 1000 carbons) polyethylene.⁷⁸ The enhanced thermal stability of this catalyst makes it potentially suitable for industrial gas-phase polymerization ($80\text{--}100\text{ }^{\circ}\text{C}$).

Inspired by these works, we recently reported the studies of a series of α -diimine Pd(II) complexes (C19), which turned out to be one of the most active and thermally stable α -diimine Pd(II) catalysts in ethylene polymerization (Scheme 14).⁷⁹

Scheme 14. (i) Highly Stable α -Diimine Ni(II) Catalyst Bearing a Dibenzhydryl Moiety; (ii) Ethylene Polymerization and Copolymerization with Methyl Acrylate Using α -Diimine Pd(II) Catalysts C19



Most interestingly and surprisingly, the branching density of the polyethylene generated by these complexes (23–29 branches/1000C) is much lower than those by classic Brookhart catalyst (ca. 100/1000C). The slow chain walking feature was maintained in ethylene-methyl acrylate copolymerization reactions. As a result, semicrystalline polyethylene (T_m up to $98\text{ }^{\circ}\text{C}$) and semicrystalline copolymer (T_m up to $72\text{ }^{\circ}\text{C}$) could be generated, which has proven to be very difficult to realize in previously reported α -diimine Pd(II) systems. Our work demonstrated that the chain walking process can indeed be suppressed in a α -diimine Pd(II) system through ligand modifications.

6. CONCLUSIONS

In the first section of this perspective, we discussed the chain walking polymerization mechanism, followed by chain walking ethylene polymerization and copolymerization reactions

mediated by this unique mechanism. Second, the developments of various chain walking polymerization catalysts bearing α -diimine ligands and other N containing ligands were summarized. Subsequently, the applications of these catalysts in the synthesis of novel functionalized polymers and copolymers were briefly described. Finally, some recent developments with respect to very fast and very slow chain walking polymerization catalysts were discussed.

The chain walking polymerization catalysts have greatly expanded our understanding of metal catalyzed olefin polymerization and copolymerization reactions. Despite the great successes in the synthesis of novel materials with structures that had not previously been accessible, large scale industrial applications of these catalysts have yet to be realized. The design and developments of new catalysts with high activity, high stability, and the capability of generating polymers with higher molecular weight are still highly desired. Through catalyst modifications, it is possible to finely control the polymer microstructures via a precise chain walking process. After more than 20 years of research, α -diimine Ni(II) and Pd(II) catalysts have been widely recognized as a unique class of catalysts. They and other chain walking polymerization catalysts have found applications in the synthesis of various functional materials with unique structures and properties. It is believed that new functional materials and new applications will continue to be discovered, and new catalysts with new properties will continue to be designed and prepared.

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Notes

The authors declare no competing financial interest.

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