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Coordination–Insertion Copolymerization of Fundamental Polar Monomers

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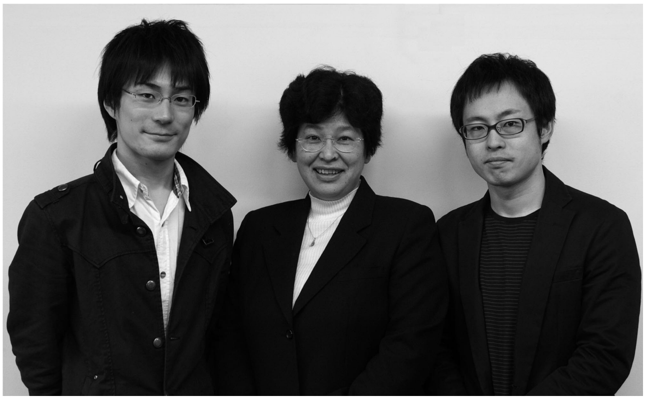
Contents

1. Introduction and Scope of Review

In the past 30 years, tremendous progress in the controlled polymerization using homogeneous, single-site catalysts has led to the development of novel materials having appealing properties and wide-ranging applications. In particular, numerous polyethylene or polypropylene compounds have been synthesized by metal-catalyzed coordination–insertion polymerization. On the other hand, organometallic catalysts



Akifumi Nakamura (left) was born in 1984 in Kanagawa, Japan. He received his B.S. degree in 2007 and M.S. degree in 2009 from the University of Tokyo under the guidance of Professor Kyoko Nozaki. During that time he joined Professor Keiji Morokuma's group at Kyoto University as a visiting student. In 2009, he started his Ph.D. study at the University of Tokyo under the guidance of Professor Kyoko Nozaki. He is also a research fellow of the Japan Society for the Promotion of Science. His research interests include synthetic organic chemistry, organometallic chemistry, computational chemistry, and polymer chemistry.

Shingo Ito (right) was born in 1981 in Nagoya, Japan. He received his B.S. degree in 2003, M.S. degree in 2005, and Ph.D. degree in 2008 from the University of Tokyo under the guidance of Professor Eiichi Nakamura. During that time he joined Professor Scott E. Denmark's group at the University of Illinois and Professor Masaharu Nakamura's group at Kyoto University as a predoctoral researcher. In 2008, he became an assistant professor at the Department of Chemistry and Biotechnology, Graduate School of Engineering, the University of Tokyo. He received the Sanyo Chemical Industries Award in Synthetic Organic Chemistry, Japan (2008). His research interests include synthetic organic chemistry, organometallic chemistry, and polymer chemistry.

Kyoko Nozaki (center) received her B.Sc. degree in 1986 and Ph.D. degree in 1991 from Kyoto University under the guidance of Professor Kiitiro Utimoto. During her Ph.D. study, she joined Professor Clayton H. Heathcock's group at the University of California at Berkeley as an exchange student. In 1991, she started her research career as an instructor at Kyoto University, became an associate professor in 1999, and then moved to the University of Tokyo as an associate professor in 2002. Since 2003, she has been a full professor at the University of Tokyo. Her accomplishments include the Chemical Society of Japan Award for Young Chemists (1998), the Organometallic Chemistry directed towards Organic Synthesis (OMCOS) prize in organometallic chemistry (2003), the SPSJ Wiley Award (2004), the Japan IBM Science Award (2005), the Mukaiyama Award (2008), the Saruhashi Prize (2008), and the Mitsui Chemicals Catalysis Science Award (2009). She is on the Editorial Board of *ChemCatChem* and on the Editorial Advisory Boards of the *Journal of the American Chemical Society*, *Organometallics*, and the *Journal of Polymer Science, Part A: Polymer Chemistry.* Her research interest is focused on development of homogeneous catalysts for polymer synthesis and organic synthesis.

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capable of incorporating comonomers with polar functions into such nonpolar polymers via the coordination−insertion mechanism have remained a significant challenge in polymer synthesis.[1] Currently, commercial processes for the incorporation of polar monomers mainly require radical polymerization, thus limiting the range of materials available.[2] Therefore, there is a strong requirement for novel catalysts capable of copolymerizing polar monomers with nonpolar monomers via controlled coordination−insertion polymerization processes that would yield polymers with novel architectures and properties.

Polar vinyl monomers such as methyl acrylate (MA), methyl methacrylate (MMA), vinyl acetate (VAc), acrylonitrile (AN), vinyl halides, and vinyl ethers are the main compounds that can be used for overcoming the challenges posed by coordination−insertion polymerization because they are readily available and widely used for manufacturing of the polymers. However, until recently, most studies on the metal-catalyzed coordination−insertion polymerization did not employ such fundamental polar vinyl monomers. Instead, the monomers employed thus far have often been ones possessing polar functional groups apart from the olefinic locus of insertion.[1,3] For example, conventional SHOP (Shell higher olefin process) [P−O]Ni catalysts[4] can copolymerize ethylene with monomers having at least two methylene spacers between the olefinic double bond and the functional group.[5] Although Grubbs et al. synthesized a family of [N−O]Ni catalysts capable of copolymerizing ethylene with functionalized norbornenes,[6] these catalysts could not incorporate fundamental polar vinyl monomers.[6d,f]

In the mid-1990s, a major breakthrough was achieved by Brookhart et al., who reported a series of olefin polymerization and copolymerization catalysts by cationic Pd(II) α-diimine complexes.[7] These catalysts were remarkably active for the copolymerization of nonpolar olefins with polar vinyl monomers such as acrylates,[8] methyl vinyl ketones,[8] and silyl vinyl ethers[9] to yield highly branched copolymers. Nonetheless, other common monomers such as vinyl acetate, acrylonitrile, and vinyl chloride could not be copolymerized by these catalytic systems. In 2002, another significant breakthrough in the copolymerization of fundamental polar monomers was reported by Drent, Pugh, et al., who reported a promising system in which a neutral Pd(II) catalyst generated in situ from phosphonium−sulfonate produced highly linear copolymers of ethylene with MA.[10] Subsequently, many studies have intensively focused on the unique characteristics of these catalysts. Many fundamental polar vinyl monomers such as acrylates,[10−13] vinyl acetate,[14] acrylonitrile,[15] vinyl fluoride,[16] vinyl ethers,[17] and other important comonomers[18,19] have thus far been found to be applicable to copolymerization with ethylene.

Another fundamental polar monomer is carbon monoxide (CO), which can be used for the coordination copolymerization with olefins to form ketone functionality. Since the first discovery of the metal-catalyzed copolymerization of ethylene and carbon monoxide in 1951,[20] a variety of palladium catalysts with bidentate ligands have been developed for the effective copolymerization of olefins with CO. The concept of catalyst design and the corresponding examples were comprehensively studied by Drent and Budzelaar in 1996.[21] Further developments including the control of stereochemistry and investigations on the physical and chemical properties of the copolymers have been abundantly reviewed.[22−24] Recent progress in this chemistry has provided novel types of CO polymerization: the nonalternating copolymerization of ethylene with CO,[25−28] the alternating copolymerization of polar vinyl monomers with CO,[29,30] and the alternating copolymerization of imines with CO to yield poly-α-peptides.[31]

This review describes the transition-metal-catalyzed coordination−insertion copolymerization of fundamental polar vinyl monomers with nonpolar olefins and the copolymerization of olefins and imines with carbon monoxide. In the context of this review, we define "fundamental polar vinyl monomers" as olefin molecules whose C−C double bond is directly substituted by polar functional groups. Examples of such compounds include methyl acrylate (MA), methyl methacrylate (MMA), vinyl acetate (VAc), acrylonitrile (AN), vinyl halide, and vinyl ethers, and these are presented as $H_2C{=}CHX$ or $H_2C{=}CMeX$. Thus, olefins possessing a certain functionality through some methylene spacers from an olefin moiety are not included.

The term "coordination−insertion polymerization" refers to *the polymerization realized by the migratory insertion of a coordinated olefin into a metal−alkyl bond via a four-membered transition state* in the case of vinyl monomers[32] and *the polymerization realized by the migratory insertion of a coordinated carbon monoxide into a metal−alkyl bond via a three-membered transition state* in the case of carbon monoxide. In this review, other polymerization mechanisms such as radical, cationic, and anionic including group transfer (or coordination−conjugate addition) polymerization are excluded even in the case that the copolymerization involves migratory insertion of nonpolar olefins.

Finally, it should be noted that homopolymerization of polar vinyl monomers is not discussed in this review. Although many transition-metal-catalyzed homopolymerization reactions of polar vinyl monomers have thus far been reported, most of them lack sufficient data to prove that the polymerization proceeded via the coordination−insertion mechanism. In fact, no concrete methods are available for differentiating coordination−insertion polymerization from other polymerization mechanisms. For example, Yamamoto et al. reported the first "coordination polymerization of polar vinyl monomers" in 1967 followed by a series of reports on Ni, Fe, Co, Ni, Rh, and Cu catalysts.[33,34] A quarter of a century later, however, some researchers reinvestigated the polymerization of AN and proposed mechanisms that differed from each other, as well as from that proposed by Yamamoto.[35] This remains an unresolved issue, and therefore, it serves as a good example of difficulties involved in elucidating the mechanism of the homopolymerization of polar vinyl monomers.

2. Copolymerization of Polar Vinyl Monomers with Nonpolar Olefins

In this section, we first discuss the significance of incorporating functional groups into polyolefins as a methodology for creating functional polymeric materials (section 2.1). Next, the characteristics of two representative ligands, α-diimines and phosphine−sulfonates, are introduced, especially from the aspect of group-10 metal catalysts for ethylene homopolymerization (section 2.2). Details for fundamental polar monomers are described in section 2.3, and their activity for the copolymerization with ethylene and α-olefin are discussed in the order of acrylates, methacrylates, vinyl acetate, acrylonitrile, vinyl halides, vinyl ethers, and miscellaneous comonomers from section 2.4 onward.

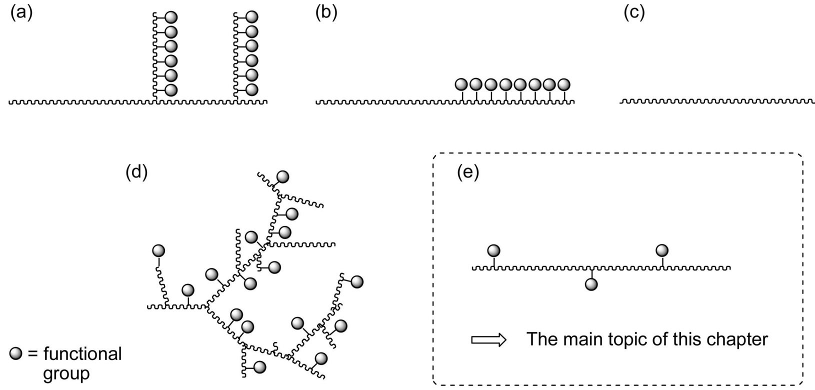


Figure 1. Classification of functional polyolefins.

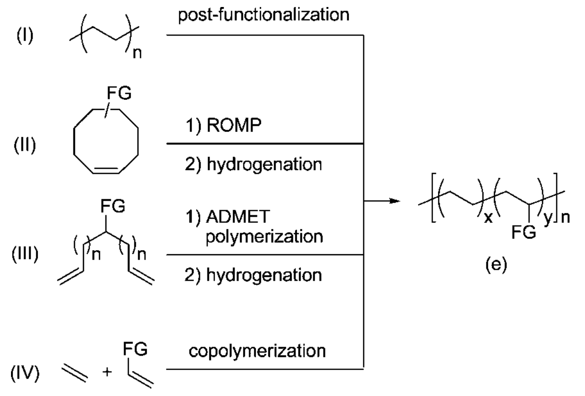
2.1. Insights into Incorporation of Functional Groups in Polyolefins

The functionalization of polyolefins has attracted considerable attention from both academic and industrial communities.[36−39] The polyolefins without any functionality often suffer from the problems associated with insufficient surface properties such as adhesion, dyeability, printability, and compatibility. On the ther hand, the incorporation of polar functional groups into polyolefins improves such properties, leading to expanding the range of applications. For example, polypropylenes modified with less than 1% of maleic anhydride can make the polymers exhibit better surface properties, enough for application to compatibilizing agents.[40] Thus, the incorporation of polar functional groups into polyolefins is a powerful method to synthesize functional polymeric materials.

Functionalized polyolefins can be classified as shown in Figure 1.[38] A variety of methodologies have been developed for the synthesis of (Figure 1a) graft copolymers,[41] (Figure 1b) block copolymers,[41,42] and (Figure 1c) chain-end-functionalized polyolefin[43] in which the functional groups are localized. On the other hand, polyolefins having randomly distributed functional groups, such as Figure 1d and 1e, provide different properties as compared to Figure 1a−c. Radical copolymerization is a promising method for obtaining functionalized branched polyolefins shown as Figure 1d.[2,44] However, fundamental polar vinyl monomers are often much more susceptible to radical intermediates than nonpolar olefins, and thus, the resulting copolymers tend to possess a high content of polar moieties. In addition, the precise control of microstructures by means of radical polymerization is generally difficult as compared to coordination polymerization. Free radical polymerization can only provide branched copolymers but not linear functionalized polyethylenes of type shown in Figure 1e.

The physical properties of polymers heavily depend on polymer chain structure. High-density polyethylene (HDPE), which is mainly produced by early-transition-metal-catalyzed polymerization, has essentially linear structures composed of long chains to have high strength, good chemical resistance, high T_m (∼135 °C), and almost no brittle behavior at low temperatures. HDPEs have found a variety of applications such as the manufacture of films, houseware, bottles, and containers.[45−48] Thus, surface modification of HDPEs will further expand the range of applications. Therefore, the synthesis of functionalized HDPE shown as Figure 1e has been extensively investigated by using many approaches shown in Scheme 1. The traditional method used for synthesizing the architecture in Figure 1e is the physical or chemical modification of preformed polyethylenes (i.e., postpolymerization approach I in Scheme 1).[49] For example, the incorporation of 1−2% of oxygen atom to HDPE induced the change of water contact angle from 89° to ca. 70°.[50] Such functionalization of polyethylenes, however, generally requires harsh reaction conditions due to the inert nature of the C−H bonds of the polymers[51] and suffers from cross-linking of multiple chains induced by radical recombination. Ring-opening metathesis polymerization (ROMP) of functionalized cyclooctenes and the subsequent hydrogenation (II)[52] and acyclic diene metathesis (ADMET) polymerization of symmetrically substituted α,ω-dienes followed by hydrogenation (III)[53] are alternative strategies for obtaining the functionalized linear polyethylene. However, specific monomers are required for these reaction procedures which involve multiple steps. In contrast, the direct copolymerization of ethylene with polar vinyl monomers (IV) is a straightforward approach for synthesizing linear functionalized polyethylenes.

Scheme 1. Synthetic Methods for Functionalized HDPE (e)



Because of the above-mentioned reasons, the development of transition-metal-catalyzed copolymerization of functionalized monomers with nonpolar olefins is eagerly desired for realizing the random incorporation of polar groups with precise control of polar/nonpolar ratios and polymer microstructures.[54] Nonetheless, early-transition-metal Ziegler−Natta,[55,56] metallocene,[57] constrained geometry complexes (CGC),[58] and postmetallocene-type complexes[59,60] are prone to be poisoned by functional groups such as Brønsted acids and oxygen and nitrogen functionalities.[1] Because of this problem, polar comonomers require either bulky substituents around the polar moiety or protection–deprotection sequences.[1] Another important factor in this process is the relative reactivity of the monomers. Since electron-withdrawing or -donating groups directly attached to the vinyl moiety significantly affect the energy of frontier orbitals, methylene spacers between a C−C double bond and polar groups are essential for coordination−insertion copolymerization. However, the cost of these special monomers would preclude possibilities of commercialization.

An alternative strategy for the direct copolymerization of polar monomers with nonpolar olefins is the manipulation of late-transition-metal catalysts.[1,7,59c,d,61,62] Their reduced oxophilicity and tolerance to other functionalities of these catalysts enable us to utilize functional monomers without protection. Thus far, several promising late-transition-metal catalysts, especially palladium complexes, have been developed and utilized for the copolymerization of fundamental polar vinyl monomers with nonpolar monomers.

2.2. Catalysts Discussed in This Review and Their Features as Ethylene Homopolymerization Catalysts

Two major types of catalysts have played key roles in the copolymerization of fundamental polar vinyl monomers with nonpolar olefins. One is Pd and Ni complexes with α-diimine ligands, and the other is Pd phosphine−sulfonate catalysts. To understand the details of the copolymerization, we first describe these complexes and their characteristics as ethylene homopolymerization catalysts. Then, the mechanism of the polymerization catalyzed by the two systems is compared. Other catalysts which can incorporate polar monomers are discussed individually from section 2.4 onward.

2.2.1. α-Diimine

One of the key catalytic systems described in this review is Pd and Ni complexes with α-diimine ligands **1**. The synthesis and detailed characteristics of this system have been described in great detail by Brookhart in 2000,[7,63] and therefore, they are not covered here. The α-diimine ligands described in this review are shown in Figure 2.

A general feature of the α-diimine catalysts is to produce branched polyethylenes due to chain walking.[64] During chain propagation, β-agostic metal−alkyl intermediates (**A1**) can undergo a series of β-H elimination and reinsertion into the metal−hydride bond of **A3** in the opposite direction (Scheme 2). When ethylene is incorporated after this isomerization, a methyl branch can be formed. Longer chain walks (isomerizations) introduce longer branches. In addition, chain transfer in the α-diimine system is so slow that high-molecular-weight polyethylene can be formed. In the case of Pd catalysts, since olefin exchange proceeds via an associative pathway, the steric bulk in the axial sites of the square plane of these α-diimine complexes is a critical requirement for retarding the chain transfer.[7,65]

The copolymerization of nonpolar olefins with methyl acrylate,[8] methyl vinyl ketone,[8] and silyl vinyl ethers[9] catalyzed by Pd α-diimine catalysts has already been reported. The functional groups are generally located at the end of the branches due to chain walking after insertion of these polar monomers. The copolymerization of ethylene with methyl acrylate catalyzed by Ni α-diimine complexes has also been reported.[60,66] The details of these systems are described in section 2.4 onward.

2.2.2. Phosphine−Sulfonate

Pd complexes bearing a phosphine−sulfonate ligand play an important role in the polymerization of polar vinyl monomers. The typical structure of the ligands reported to be effective for palladium-catalyzed coordination−insertion polymerization is $Ar_2P(C_6H_4\text{-}o\text{-}SO_3^-)$. Complexes of phosphines with sulfonated aromatic substituents such as $P(C_6H_4\text{-}m\text{-}SO_3Na)_3$ have long been used as water-soluble phosphine ligands for organic syntheses.[67] In contrast, the synthetic applications of its ortho-substituted ligand have been limited.[68,69]

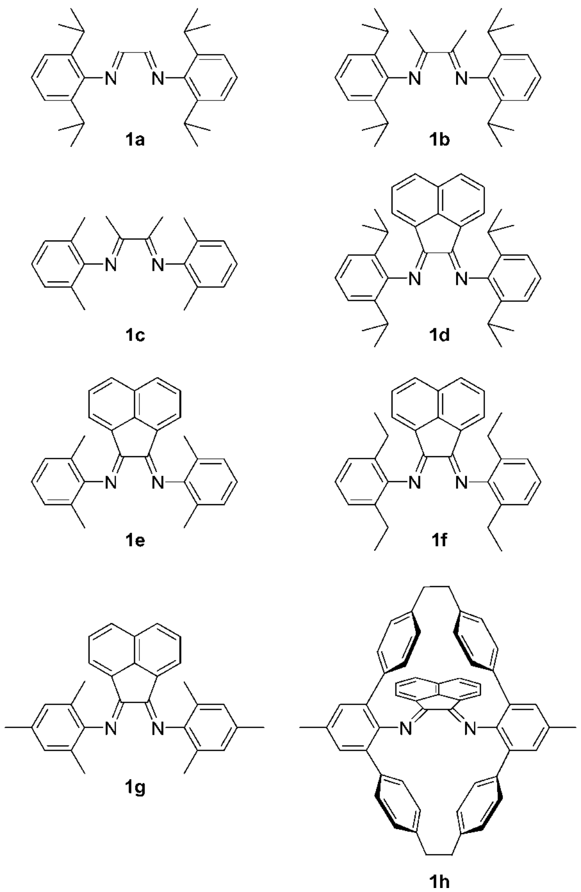


Figure 2. Series of α-diimine ligands discussed in this review.

In 1987, Murray at the Union Carbide Corp. first applied late-transition-metal complexes bearing phosphine−sulfonate ligands to ethylene oligomerization.[70] Since 1988, researchers at chemical companies including Shell (Drent, Van Leeuwen et al.),[10b,25b,71] Rohm and Haas (Goodall et al.),[72] and others[73] have filed several patents for polymerization processes using phosphine−sulfonate ligands. Immediately after the first academic reports in 2002,[10a,25a] these catalysts attracted considerable attention from a wide range of research groups.

A family of phosphinoarylsulfonate ligands (**2**) has been synthesized by the reaction of ortho-lithiated benzenesulfonate derivatives with diorganophosphine chloride or diarylmethoxyphosphine (Table 1).[25,26] The in-situ-generated [P−O]Li can be converted to [P−O]M complexes by transmetalation with Pd or Ni precursors and to [P−O]H ligands by protonation with acids. The structure of these [P−O]H ligands was confirmed by X-ray crystallography.[14,74,75] With regard to the pK_a of $ArSO_3H$ and Ar_3P^+H (≤ 2.7),[76] the proton should be located on the phosphorus atom rather than the oxygen atom. In fact, P−H coupling can be observed in the ^{31}P NMR spectra of some ligands.[26] Phosphinoalkylsulfonate ligands (**3**) were prepared by reaction of phosphide with appropriate bromoalkylphosphonate derivatives followed by protonation and isolated as zwitterions (Scheme 3).[68e,70,71a] Both [**2**]H and [**3**]H are generally stable in water and air.

Scheme 2. Mechanism for Ethylene Polymerization and Polymer Branch Formation with Pd and Ni α-Diimine Complexes

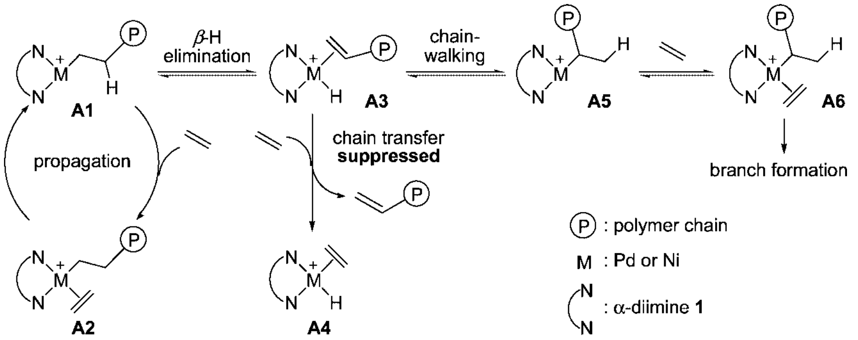
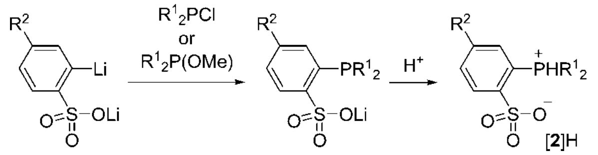
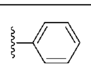
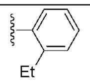
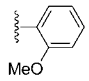
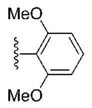
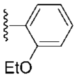
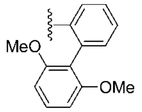
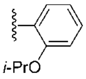
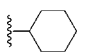
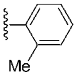


Table 1. Series of Phosphinoarylsulfonate Ligands (2) Reported in the Academic Articles and Their Synthesis[a]



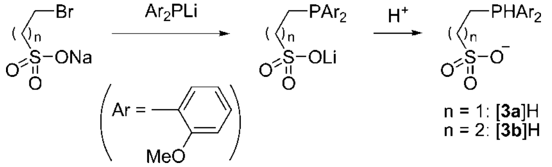
R_1	R_2	Ligand number	Ref.	R_1	R_2	Ligand number	Ref.
	H	**2a**	26,68d		Me	**2i**	77
	Mc	**2b**	16				
	H	**2c**	25a		H	**2j**	74
	Me	**2d**	17,77				
	H	**2e**	25a		H	**2k**	12
	H	**2f**	25a		H	**2l**	14
					Me	**2m**	90
	H	**2g**	26				
	Me	**2h**	26				

[a] For other ligands, see refs 70, 72, and 73a.

Pd complexes bearing a phosphine–sulfonate ligand (Table 2) can be prepared by addition of general catalyst precursors such as PdMeCl(cod)[11] (cod = 1,5-cyclooctadiene) and $PdMe_2$(tmeda)[77] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) with phosphonium–sulfonate salts. When a Pd(0) source such as $Pd(dba)_2$ (dba = dibenzylideneacetone) is mixed with a phosphonium–sulfonate salt, a Pd(II) hydride complex, [P–O]Pd–H, should be formed, given that formation of similar metal–H species was reported in the case of SHOP catalysts.[4a] Although direct observation of the Pd–H species has not yet been reported, Pd–H bond formation was supported by the end-group analyses of some polymers obtained by in-situ-generated catalysts.[10]

One of the key characteristics of Pd phosphine–sulfonate polymerization catalysts is the ability to produce highly linear polyethylenes without any activators[78] or noncoordinating counterions.[12,13,77,79–81] Under typical reaction conditions, polymerization catalyzed by Pd phosphine–sulfonate systems proceeds with an activity of 10^{-1}–10^{2} gmmol^{-1} h^{-1} bar^{-1}, and the resulting polyethylene has molecular weights of 10^3–10^5 and highly linear structures with less than 1–10 branches per 1000 carbons. Bulky substituents on the phosphorus atom have a favorable effect on the productivity and molecular weight. Thus far, Pd complexes with 2-[bis(2′,6′-dimethoxy-biphenyl-2-yl)phosphanyl]benzenesulfonate ligand (**2k**) give the highest activity (98.5 gmmol^{-1} h^{-1} bar^{-1}) and molecular weight (M_n = 227 000).[12] Given that the Pd complexes with ligand **2i** (ethyl groups) afforded a similar activity and molecular weight as compared to that obtained by Pd complexes with **2d** (methoxy groups), it is suggested that the Pd---OMe interaction is not important in ethylene homopolymerization.[79]

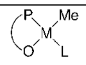
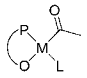
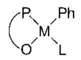
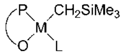
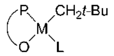
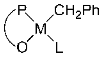
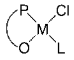
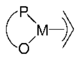
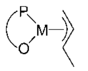
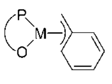
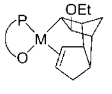
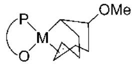
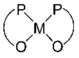
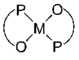
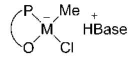
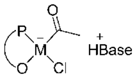
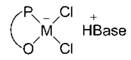
Scheme 3. Synthesis of Phosphinoalkylsulfonate Ligands (3) Reported in the Academic Articles[28,68e a]



[a] For other ligands, see refs 70 and 71a.

The mechanism of ethylene homopolymerization catalyzed by the Pd phosphine–sulfonate system was first theoretically investigated by Ziegler.[82] Subsequently Nozaki and Morokuma et al. obtained a further understanding of the polym-

Table 2. Isolated Palladium and Nickel Complexes Bearing a Series of Phosphine–Sulfonate Ligands[a]

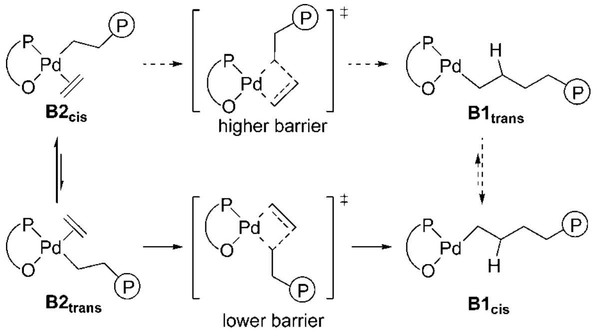
	Metal	P–O Ligand	L	Base	Ref.
 [P–O]MMeL	Pd	**2a**	pyridine		79
		2c	pyridine		13,27
			2,6-lutidine		15
			dmso		13
			tmeda		13
			none (dimer)		28
		2d	pyridine		12,17
			pyridazine		77
			tmeda		12
			PPh_3		77
		2k	pyridine		12
			tmeda		12
			dmso		13
		2l	2,6-lutidine		14
			dmso		14
			tmeda		14
		3a	none or solvent		28
	Ni	**2c**	pyridine		91
			4-(non-5-yl)pyridine		91
			dmso		13
 [P–O]MCOMeL	Pd	**2c**	pyridine		27
 [P–O]MPhL	Ni	**2a**	PPh_3		89
		2c	PPh_3		89
		2g	PPh_3		89
 [P–O]M(CH_2SiMe_3)L	Pd	**2d**	pyridine		77
			none (dimer)		77
 [P–O]M(CH_2t-Bu)L	Pd	**2d**	pyridine		77
			none (dimer)		77
 [P O]M(η^1-CH_2Ph)L	Pd	**2d**	pyridine		
 [P–O]MClL	Pd	**2c**	2,6-lutidine		79
 [P–O]M(η^3-allyl)	Pd	**2c**			74
	Ni	**2a**			92
		2c			92
 [P–O]M(η^3-crotyl)	Pd	**2c**			74
 [P O]M(η^3-CH_2Ph)	Ni	**2d**			90
		2m			90
 [P–O]M(CP-OEt)	Pd	**2c**			26
		2h			26
 [P O]M(Codyl*)	Pd	**2c**			28
		3a			28
 [P–O]M[P–O]	Pd	**2a**			26,68d
		2c			26,28
		2g			26
		2h			26
		3a			28
 [P–O]M[O–P]	Ni	**2a**			89
		2c			89
		2g			89
		2h			89
 {[P–O]MMeCl}(HBase)	Pd	**2a**		Et_3N	11
				i-Pr_2NEt	11
		2c		i-Pr_2NEt	11
		2l		i-Pr_2NEt	14
 {[P–O]M(COMe)Cl}(HBase)	Pd	**2c**		i-Pr_2NEt	30
 {[P O]MCl_2}(HBase)	Pd	**2c**		i-Pr_2NEt	79

[a] For other complexes, see refs 28–30 and 79. dmso = dimethyl sulfoxide, tmeda = N,N,N',N'-tetramethylethylenediamine, CP-OEt = 5η^1-6-ethoxy-*exo*-5,6-dihydrodicyclopentadiene, Codyl* = 2-methoxycyclooct-5-enyl.

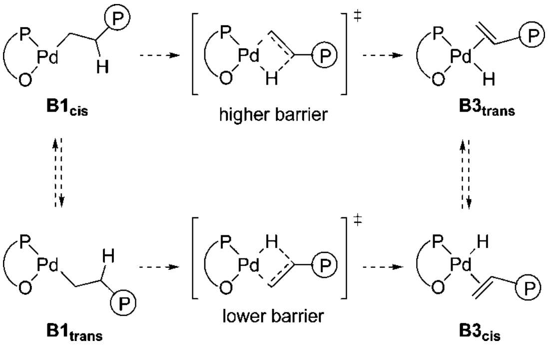
erization mechanism through investigations using DFT calculations.[79] Here, the essential part of the study is summarized below in order to clarify how Pd phosphine–sulfonate complexes catalyze the ethylene polymerization to afford highly linear polyethylenes.

Because of the unsymmetrical nature of phosphine–sulfonate ligands, both cis and trans isomers should be considered in their square planar metal complexes.[79,82–85] In Schemes 4 and 5, the isomers of the alkyl group or hydride located at the cis position of the phosphorus atom are described as "cis" and vice versa. It has been confirmed by X-ray crystallographic analyses that the alkyl chain is located cis to the phosphorus atom in the more stable isomer.[11–15,26,27,77,79] This is because the strong trans influence of the phosphorus atom does not favor the existence of an alkyl chain trans to the phosphorus atom. In contrast, ethylene insertion occurs with a lower barrier from the isomer **B2$_{trans}$**. In this case, the migrating ability of the alkyl chain is enhanced due to the strong trans effect of the phosphorus atom leading to facile migratory insertion of ethylene. It should be noted that the olefin can accept a strong back-donation from Pd because of the charge of the metal center and the nature of the sulfonate located at the trans position (i.e., weak σ-donor and weak π-acceptor).

Scheme 4. Ethylene Insertion Catalyzed by Pd Phosphine−Sulfonate Complexes



Scheme 5. *β*-H Elimination Catalyzed by Pd Phosphine−Sulfonate Complexes



Similarly, β-H elimination from the alkylpalladium complexes could proceed from both **B1**$_{\text{cis}}$ and **B1**$_{\text{trans}}$ isomers (Scheme 5).[79] The trans isomer, **B1**$_{\text{trans}}$, is much more susceptible to β-H elimination reaction than **B1**$_{\text{cis}}$. The transition state of β-H elimination from **B1**$_{\text{trans}}$ is lower in energy than that of ethylene insertion from **B2**$_{\text{trans}}$. Nevertheless, it was found that all routes to reach **B1**$_{\text{trans}}$ require as high energy as ethylene insertion. On the other hand, the β-H elimination pathway from **B1**$_{\text{cis}}$ requires as high energy as the ethylene insertion from **B2**$_{\text{trans}}$. Thus, the barriers for (i) ethylene insertion from **B2**$_{\text{trans}}$, (ii) β-H elimination from **B1**$_{\text{cis}}$, and (iii) the routes to **B1**$_{\text{trans}}$ are comparable in energy. This result suggests that insertion of ethylene (i) should be the most favorable route *in the presence of ethylene* because a high concentration of ethylene accelerates only route i.[79]

As summarized in Scheme 6, Pd phosphine−sulfonate systems produce linear polyethylene because β-H elimination is suppressed *under the ethylene pressure*.[79] It should be noted that this catalytic system can cause β-H elimination *in the absence of ethylene*. If **B3**$_{\text{trans}}$ or **B3**$_{\text{cis}}$ once form by β-H elimination, the subsequent chain transfer and branch formation are suggested to take place with reasonable energy barriers.[79] In fact, this is consistent with experimental results by Jordan et al., who observed that [P−O]PdCH$_2$(*t*-Bu) induced the isomerization of α-olefin in the absence of ethylene.[77]

The characteristic features of the phosphine−sulfonate ligand in a square planar Pd(II) complex are shown in Figure 3. (i) The ligand is anionic, and therefore, the charge on the metal center is less positive when compared to its analogs with neutral ligands. (ii) The sulfonate is a weak σ-donor, and this stabilizes the electron-donating ligand at its trans site. (iii) The sulfonate is a weak π-acceptor, and this causes strong back-donation from the metal to the ligand at its trans site.

The Pd phosphine−sulfonate catalyst was found to be applicable to the copolymerization of ethylene with various comonomers,[86] including acrylates,[10−13,72,73d] vinyl acetate,[14] acrylonitrile,[15] vinyl fluoride,[16] vinyl ethers,[17] vinyl ketones,[19] *N*-vinyl-2-pyrrolidinone,[18,72f] acrylamides,[18,72f] *N*-vinylcarbazole,[72f] *N*-vinylphthalimide,[72f] and functionalized norbornene derivatives.[71d,73b,74] In some reports, copolymerization by Pd phosphine−sulfonate catalysts was performed in an aqueous emulsion.[74,87,88]

Ni phosphine−sulfonate complexes have also been synthesized and applied to ethylene homopolymerization to afford linear polyethylenes (1−18 branches per 1000 carbons).[13,89−92] In contrast to the Pd catalysts, however, Ni phosphine−sulfonate complexes have not yet been reported to be active for the copolymerization of fundamental polar monomers.

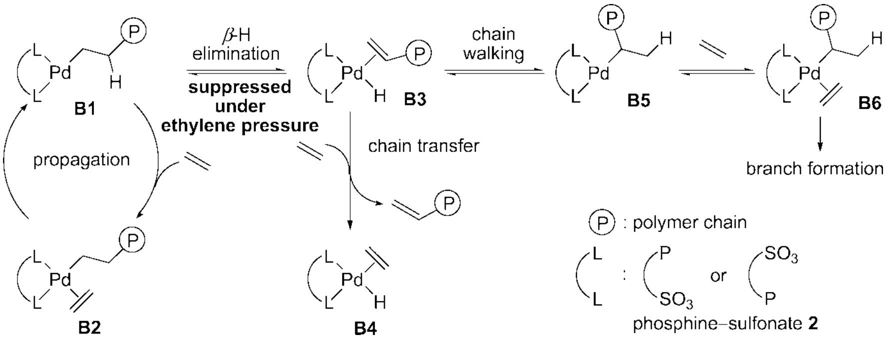
The unique characteristics of the Pd phosphine−sulfonate system also appeared in olefin/CO copolymerization, as discussed in section 3. This catalyst copolymerizes ethylene with CO in a nonalternating fashion.[25−28] The alternating copolymerization of vinyl acetate,[29] methyl acrylate,[30] or acetylene[71c] with carbon monoxide has been also reported.

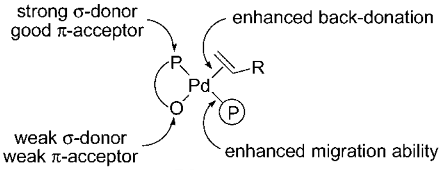
2.3. General Aspects on the Coordination−Insertion Polymerization of Polar Vinyl Monomers

Fundamental polar vinyl monomers are expected to exhibit reactivities different from that of ethylene because electron-withdrawing or -donating groups are directly attached to the olefin moiety. The functional groups strongly influence the energies of the frontier molecular orbitals of the monomers, as indicated by the calculated orbital energy diagrams shown in Figure 4.[93] Their characteristics are discussed individually in the next section.

A prerequisite for the incorporation of vinyl monomers by coordination−insertion polymerization is π-coordination

Scheme 6. Mechanism for Ethylene Polymerization and Linear Polyethylene Formation with Pd Phosphine−Sulfonate Complexes





B2$_{trans}$

Figure 3. Nature of Pd phosphine−sulfonate olefin complex.

of an olefin double bond to a metal center. As far as electron-deficient metals are concerned, the energy of π(C=C), generally the HOMO level of the monomer, becomes an important factor in estimating the stability of the metal−olefin bond because electron donation from the C=C π bond to the empty d_σ orbital on the metal center is generally more dominant than back-donation from the metal d_π orbital to the empty C=C π^* bond.[95−97] As exemplified by Pd(II) α-diimine complexes, the more electron deficient the monomer is (i.e., the lower the π-orbital of olefins is), the weaker the bonding to the metal is.[95] This preference is opposite to that of electron-rich metals, where back-donation from the metal to the olefin's C=C π^* orbital dominates for formation of metal−olefin complexes.[98,99]

In the case of polar vinyl monomers, competitive heteroatom σ-coordination over olefin π-coordination would constitute a serious problem (Figure 5).[96,100] AN prefers *N*-coordination to form the most stable σ-complex among the polar monomers, and MA and VAc follow. Vinyl chloride forms the weakest bond to the cationic Pd center via its chlorine atom among the monomers compared by Ziegler et al.[96] The influence of the charge of metal centers on the preference of a π-complex over a σ-complex has been also studied for these monomers by using the α-diimine catalysts (Figure 6).[96] In going from a positive to a negative charge, the relative preference switched from σ-complexation to π-complexation, due to the increased back-donation from the electron-rich Pd center to the olefin. The strong preference of σ-coordination over π-coordination in the case of electron-deficient metals may be a major obstacle to successful polymerization. However, this is just a matter of pre-equilibrium. Eventually, AN insertion does take place when the activation energy for AN insertion is reasonably low, even if the *N*-coordination predominates over π-complexation (see section 2.7).

The rate of migratory insertion of polar vinyl monomers depends on the character of transition-metal complexes. In the case of Pd α-diimine complexes, the rate of olefin insertion increased with the electron-withdrawing effect of the substituent on the olefin.[95,101] This tendency is opposite to that observed in $(^t\mathrm{Bu_3SiO})_3\mathrm{TaH_2}$, where the insertion rate decreased for electron-deficient monomers (it should be noted that coordination of the monomers was not observed experimentally and could not be confirmed by DFT calculation).[102] The influence of electron-withdrawing or -donating substituents on the olefin moiety has been extensively investigated using para-substituted styrene derivatives.[97−99] These reports suggested that the direction of insertion (2,1- or 1,2-mode) has a strong influence on the insertion rate.[97,98]

The origin of regioselectivity (2,1- or 1,2-mode) in the insertion of polar vinyl monomers has not yet been fully clarified (Figure 7). Thus far, with regard to insertion into Pd−alkyl bonds, electron-deficient monomers such as MA, VAc, and AN favor 2,1-insertion and electron-rich monomers such as vinyl ethers prefer 1,2-insertion (vide infra). Intrinsically, monosubstituted ethenes prefer 2,1-insertion due to the steric repulsion between a migrating alkyl group and the substituent on the olefin.[95] This theory has been also accepted in the Mizoroki−Heck reaction, where the regioselectivity originates from the 2,1- vs 1,2-olefin insertion to an organopalladium intermediate.[103] In addition, the energies required for the distortion of the monomers in insertion TS favor 2,1-insertion.[96,104] The steric repulsion between the ligand and the substituent on an olefin can affect the regioselectivity.[54c,104] The electronic effect (LUMO orbital ($2p_z$) coefficients of the sp^2 carbons and charge difference between the two sp^2 carbons) induced by substituents also modifies the selectivity (Figure 7).[95] Electron-rich vinyl ethers and propylene override the inherent 2,1-insertion preference to undergo 1,2-insertion due to their substantial electronic difference of two sp^2 carbons.[95] In contrast, electron-deficient monomers have similar coefficients and charges on the two sp^2 carbons, while the slight difference can strengthen 2,1-selectivity.[95,105] Although it is expected from the calculations that VC prefers 2,1-inser-

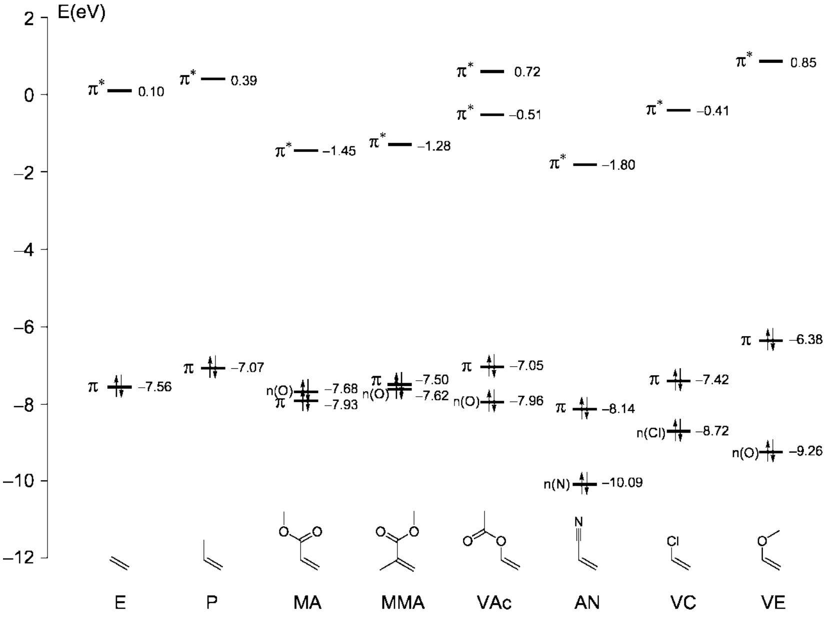


Figure 4. Key molecular orbitals of the monomers described in this article as calculated by the B3LYP/6-311G(d,p) method.[93,94]

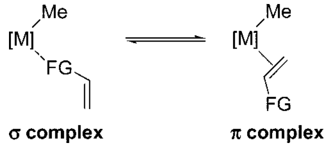


Figure 5. σ-Coordination and π-coordination of polar vinyl monomers to a metal center.

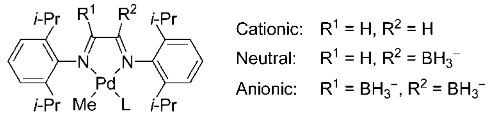


Figure 6. Cationic, neutral, and anionic Pd(II) diimine catalysts investigated by the DFT calculations by Ziegler et al.[96]

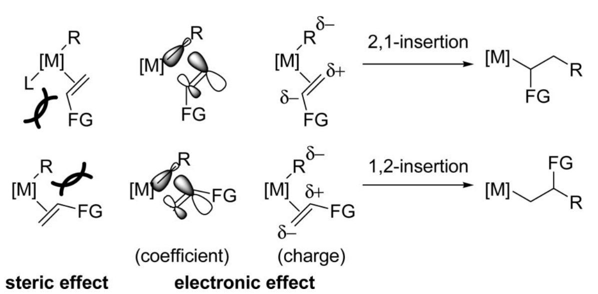


Figure 7. Origin of the regioselectivity in the insertion of polar vinyl monomers into metal−alkyl bonds.

tion,[100] the actual direction of VC insertion into M−alkyl bonds has not yet been clarified (see section 2.8). The general regioselectivity of the insertion of polar vinyl monomers into Pd−H[106] and Pd−acyl bonds (see section 3.2) has not yet been well characterized.

There are several critical problems after the migratory insertion of polar monomers. (i) The resulting alkylmetal complexes can form strong chelates or aggregates via the intra- or intermolecular coordination of polar groups to the metal center, which would prevent further coordination of the monomers. (ii) The polar substituents on the alkyl group of the intermediate, $L_nMCH(FG)CH_2R$, can dramatically change the reactivity of the subsequent insertion. (iii) For VAc, vinyl halides, and vinyl ethers, β-heteroatom elimination is also problematic if the polar groups (−OAc, −X (X = F, Cl, Br, I), −OR, respectively) are located at the β-position from the metal center. These problems are discussed in detail in the next sections.

We conclude this section with a few remarks about the polymerization mechanism. Again, the term "coordination−insertion polymerization" of vinyl monomers refers to the polymerization realized by migratory insertion of a coordinated olefin into a metal−alkyl bond via a four-membered transition state.[32] Given that fundamental polar vinyl monomers are susceptible to radical and either anionic or cationic intermediates, it is necessary to show sufficient supporting experimental data to confirm the coordination−insertion mechanism. A usual test for the participation of radical mechanisms is the addition of radical-trapping agents under the assumption that they will slow or stop the radical reactions. Nevertheless, the reliability of commonly used radical traps shown in Figure 8 has been questioned recently. Phenol derivatives such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) and 4-methoxyphenol have been suggested to accelerate radical polymerization.[107] Stable radical traps such as galvinoxyl, TEMPO, and DPPH are found to retard the initiation step by reacting with a Pd−H bond.[108] In addition, such radical traps also react with metal activators such as MAO.[109] Thus, it is necessary to show other independent experimental results in addition to the radical-trapping experiments before coming to a definitive mechanistic conclusion. For example, detailed analyses of the resulting copolymers, including chain-end analysis and regio- and stereochemical analysis, as well as the comparisons with the polymer structures obtained from other methods (i.e., radical, anionic, and cationic polymerization) are necessary. Moreover, it is preferable to isolate catalytically active intermediates and confirm the plausible mechanisms step by step. Kinetic and thermodynamic investigations as well as the theoretical calculations will strongly validate the proposed mechanism.[110]

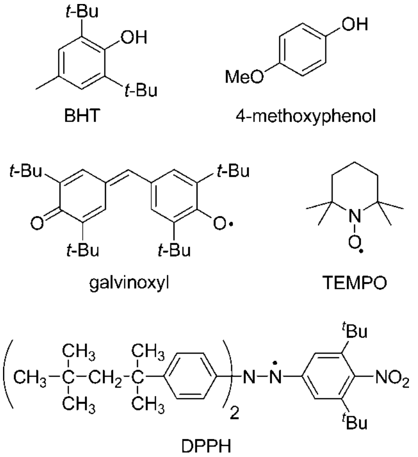


Figure 8. Common reagents used for radical trap.

2.4. Acrylates

Acrylic esters such as methyl acrylate (MA) are one of the most important monomers in polymer chemistry.[111,112] The combination of durability, clarity, and the ability to tailor molecules relatively easily to specific applications have made acrylic ester polymers a prime candidate for numerous and diverse applications such as the manufacture of coatings, textiles, adhesives, and so on. Polyacrylates[111−113] can be produced by radical processes[44] and anionic processes including group transfer polymerization (GTP).[111] This section deals with the coordination−insertion copolymerization of nonpolar olefins with MA catalyzed by well-defined metal complexes. Although significant progress on the living/controlled radical copolymerization of ethylene with MA has been reported recently, the resulting copolymers contain MA units with the range of 50−100%.[114] On the other hand, thus far, the development of the coordination−insertion polymerization process has enabled us to obtain copolymers with less than 50% MA units in a controlled manner.

2.4.1. Early-Transition-Metal Catalysts

Few studies have dealt with the copolymerization of acrylate monomers with nonpolar olefins using early-transition-metal complexes.[1,102,115,116] This could be attributed to the high oxophilicity of the early transition metals. Thus, the 2,1-insertion of acrylates into early metal−alkyl or metal−hydride bonds produces *O*-enolate or oxa-π-allyl-η^3-complexes rather than *C*-enolate complexes. Once the metal−oxygen enolate bond is formed, further insertion of olefins would not occur due to the endothermicity of the insertion step.

2.4.2. Cationic Palladium α-Diimine Catalysts

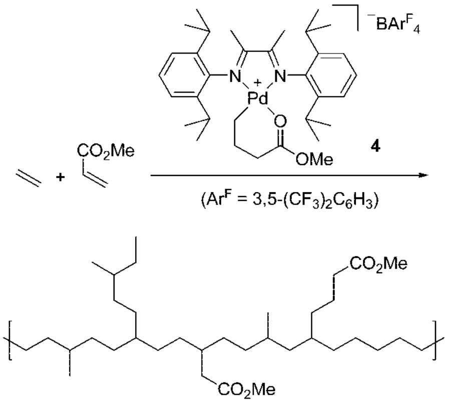
In 1996, Brookhart et al. found that a series of cationic Pd α-diimine (Figure 2, **1a**−**1d**) complexes (Versipol) catalyzed the copolymerization of ethylene and MA.[7,8] The copolymers were typically amorphous, highly branched materials possessing ca. 100 branches per 1000 carbon atoms (Scheme 7). The ester groups were evenly distributed over all molecular weights of the monomodal distribution, and they were predominantly located at the end of the branches because of the tendency of the Pd(II) complex **4** to undergo chain walking[64] during polymerization. The productivity (up to 6.0 $\mathrm{g\,mmol^{-1}\,h^{-1}\,bar^{-1}}$) of the copolymerization of ethylene and MA was greatly reduced relative to that of ethylene homopolymerizations (ca. 24 $\mathrm{g\,mmol^{-1}\,h^{-1}\,bar^{-1}}$).[8] The low ester incorporation ratio (2−12%)[8] and the results of control experiments[117,118] suggested that copolymerization proceeded through the coordination−insertion mechanism rather than radical or anionic polymerization, which produce MA-rich copolymer.

Other acrylic monomers, $CH_2{=}CHCO_2R$ (where R = H, Me, Et, *t*-Bu, CH_2CH_2OH, $CH_2CH_2(CF_2)_9CF_3$, $OCH_2(CF_2)_6CF_3$, $(CH_2)_2SiCl_3$, or CH_2Ph),[7,119] were successfully used for copolymerization with ethylene catalyzed by Pd α-diimine complexes. Instead of ethylene, α-olefins such as propylene and 1-hexene can also be used for copolymerization with MA.[8b]

In Pd α-diimine complex-catalyzed copolymerization of ethylene and MA, the MA incorporation ratio increased with increasing concentration of MA in the reaction solution; however, the copolymer molar masses and productivities significantly decreased.[8,118] Although the migratory insertion of electron-deficient MA occurs much more rapidly than insertion of nonpolar olefins into a Pd−alkyl bond,[95,101] this effect is overridden by the low binding affinity of MA to the electrophilic cationic metal center ($K_{\mathrm{MA/ethylene}} = 3 \times 10^{-4}$ at 35 °C). Svensson et al. elucidated that σ-donation from the C−C double bond of an olefin to a metal center is a more dominant interaction than π-back-donation from the metal center to the olefin in the case of the electron-deficient cationic Pd α-diimine complex.[95] Thus, the methoxycarbonyl group of MA lowers the HOMO level, leading to a low coordination ability to the cationic Pd center. The Gibbs energy diagram for insertion of comonomers is shown in Figure 9. According to the Curtin−Hammet kinetics, ethylene insertion was more favorable than MA insertion.[8]

The variation of the diimine backbone substituents R (**1a**−**1c**, ArN=C(R)−C(R)=NAr) did not significantly affect the percentage of acrylate incorporation in the copolymer, although it influenced the productivities and molecular weights. Decreasing the steric bulk of the substituents or incorporating more electron-donating substituents on the aryl moieties resulted in an increase in the relative acrylate incorporation, presumably through enhancement of the binding affinity of MA to the catalyst center.[7] It should be noted that double or multiple insertion of MA has not been detected in ethylene/MA copolymers produced by Pd α-diimine catalytic systems. In fact, Pd α-diimine catalysts are inactive to the homopolymerization of MA: The exposure of Pd α-diimine complexes to an excess amount of MA in the absence of nonpolar olefins leads to decomposition of the catalyst and formation of a small amount of dimeric compounds.[8] Recently, Guan et al. reported another approach to increase the acrylate incorporation by using a Pd complex bearing cyclophane α-diimine ligand (**1h**).[120] They showed that the catalyst incorporated MA with 20% greater efficiency. NMR studies indicated that shielding the axial binding sites by **1h** significantly reduced the associative exchange of comonomers. Additionally, kinetic data revealed that the difference between the insertion barriers for ethylene and MA is similar to the original Pd catalyst with **1d**, suggesting that rapid pre-equilibrium between the ethylene adduct and the MA adduct is hindered to enhance the incorporation of MA.

Scheme 7. Copolymerization of Ethylene with Methyl Acrylate Catalyzed by Cationic Pd α-Diimine Catalysts



The mechanism of the copolymerization of ethylene and MA catalyzed by Pd α-diimine complexes was confirmed by low-temperature NMR experiments[8] as well as theoretical calculations[100,104,121] (Scheme 8). The complex **C2**, which is formed by the reaction of complex **C1** with MA, undergoes migratory insertion of MA into the Pd−alkyl bond in a 2,1-mode with >95% regioselectivity to form a four-membered chelate **C4** (in the case of *tert*-butyl acrylate, 1,2-insertion also occurs). The complex **C4** is believed to have a *C*-enolate structure as opposed to an *O*-enolate structure (**C5**).[100] The subsequent rapid β-H elimination and reinsertion leads to formation of the most stable six-membered chelate **C7** via a five-membered chelate **C6**. In fact, MA insertion into the Pd−Me bond of {[**1a**]PdMe(OEt$_2$)}(BAr$^F_4$) (Ar^F = 3,5-(CF$_3$)$_2$C$_6$H$_3$) and rearrangements to the analogous structures of **C6** and **C7** were observed at −60 and −20 °C, respectively.[8,122] Theoretical calculations have suggested that ethylene can be further incorporated not from the intermediates **C4** or **C6** but from **C7** because the overall barriers of ethylene insertion become a minimum when the reaction proceeds from **C7** through a two-step chelate-opening mechanism (Scheme 9).[104,121] Both ethylene insertion and further β-H elimination/reinsertion can occur from **C7**, leading to formation of a branched polyethylene with an ester group at the branch end. The intramolecular ester moiety strongly favors the chelate complex **C7** rather than the alkyl olefin species **C8** even under high ethylene pressure. Accordingly, the productivity of the copolymerization of ethylene and MA is generally lower than that of ethylene hompolymerization.

2.4.3. Neutral Palladium Phosphine−Sulfonate Catalysts

In 2002, Pugh et al. reported that neutral catalysts generated in situ from Pd(dba)$_2$ or Pd(OAc)$_2$ and phosphonium−sulfonate, [**2c**]H, produced highly linear ethylene/alkyl acrylate copolymers with in-chain acrylate incorporation.[10] The structure of the copolymer was unambiguously determined by NMR analyses, in which the

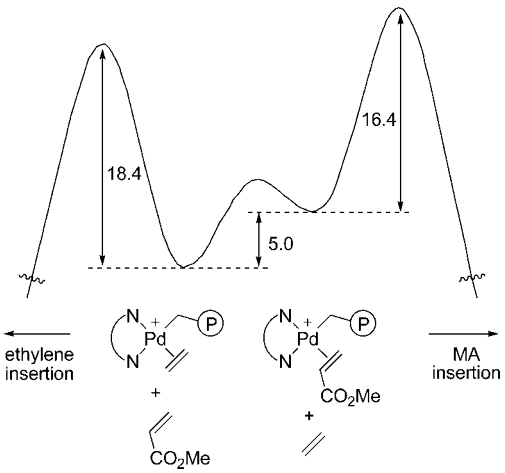
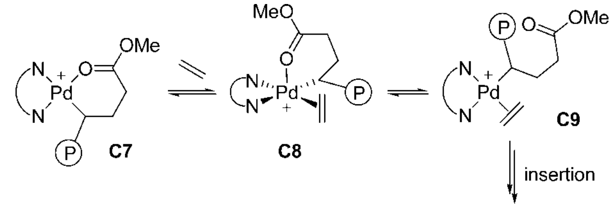


Figure 9. Gibbs free energy (35 °C, kcal/mol) diagram calculated from Brookhart's kinetic experiments ([N–N] = **1a**).[8]

number of Me branches on the backbone of the copolymer was very low (ca. 1 Me per 1000 carbons) and the incorporation ratio of MA was ca. 10%. No double acrylate insertions were observed even in the copolymer produced under a high concentration of MA.

The neutral and anionic palladium complexes bearing a phosphine–sulfonate ligand (listed in Table 2) were examined for the copolymerization of ethylene with MA to afford linear ethylene/MA copolymers.[11–13] In a manner similar to that in the Pd α-diimine system, the incorporation rate was increased at the expense of the catalytic activity when the concentration of MA was increased. The bulky substituents on the phosphorus atom led to an increase in both the productivity and the molecular weight of the copolymer. Especially when the ligand **2k** was used, the highest molecular weight (M_n = 41 200) was realized.[12] The catalytic copolymerization of ethylene and MA could occur in an aqueous emulsion to afford colloidally stable ethylene/MA copolymer latexes.[87,88] Other acrylic monomers such as isopropyl,[10] *n*-butyl,[10,12] *tert*-butyl,[10] benzyl acrylate,[12] and isobornyl acrylate[72b] could be used as a comonomer.

Scheme 9. Chelate-Opening Mechanism for Ethylene Coordination to Complex C7, Proposed by Ziegler et al.[104,121]



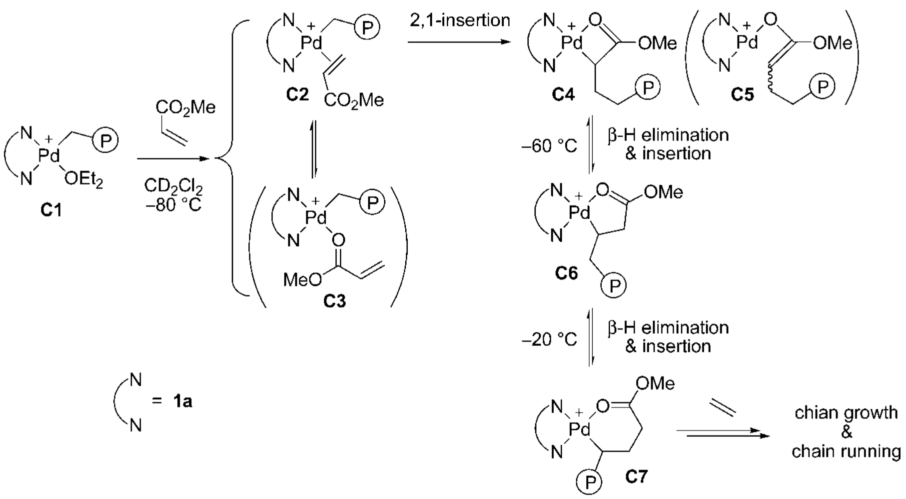
Recently, Mecking et al. demonstrated that [**2c**]PdMe(dmso) exhibited the highest productivity (26 g mol^{-1} h^{-1} bar^{-1}) for copolymerization of ethylene and MA to afford the copolymer with a MA incorporation ratio of 52%, Scheme 10.[13] It should be noted that other Pd catalysts bearing a phosphine–sulfonate ligand gave a MA incorporation of up to 17%.[10–12] NMR studies showed that there exist consecutive acrylate units in the linear polymer chain. Actually, the homooligomerization of MA can be performed, and it is suggested to proceed via the coordination–insertion mechanism.

The mechanism of the copolymerization of ethylene with MA catalyzed by Pd phosphine–sulfonate systems has been investigated experimentally and theoretically. Mecking et al. found that the 2,1-insertion of methyl acrylate into the Pd–Me bond of [**2c**]PdMe(dmso) (**5**) affords Pd *C*-enolate complex [**2c**]PdCH(CO_2Me)Et(dmso) (**6**) at room temperature (Scheme 11).[13] Whereas the corresponding *C*-enolate of the cationic Pd α-diimine complexes rapidly isomerizes at −60 °C,[8] the intermediate **6** containing the fourth ligand was particularly stable. Given that Ziegler et al. performed calculatations to show that a five-membered chelate (**7**) is the most stable structure in the absence of any additional ligand,[82] the fourth ligand may play an essential role in stabilizing intermediate **6** rather than the five- or six-membered chelate structures. The analysis of the polymer structures revealed that the subsequent ethylene insertion occurred not into the palladium–alkyl bond of either **7** or **8** but into that of **6**.

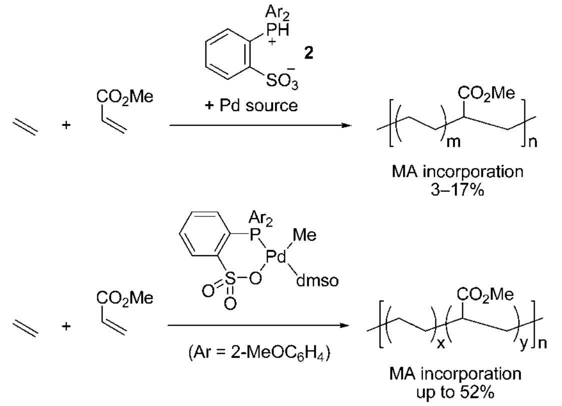
2.4.4. Other Palladium Catalysts

Thus far, Pd catalysts with a variety of ligands have been tested for copolymerization of MA with nonpolar olefins.[123–125] Nonetheless, successful coordination–insertion polymerization has been limited to the two catalytic systems mentioned above, namely, Pd α-diimine and Pd phosphine–sulfonate systems. For example, copolymerization of norbornene with MA by a series of Pd catalysts [Me(L)Pd(μ-Cl)]$_2$ (L = PPh_3, PCy_3, PMe_3, pyridine) to give MA-rich copolymers was

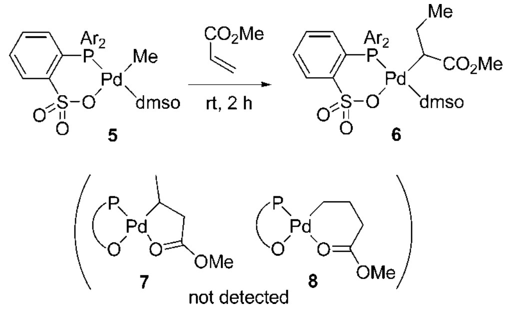
Scheme 8. Methyl Acrylate Insertion and Rearrangements Catalyzed by Pd α-Diimine Complexes



Scheme 10. Copolymerization of Ethylene with MA Catalyzed by the Pd Phosphine−Sulfonate System



Scheme 11. Insertion of MA into [2c]PdCH(CO$_2$Me)Et(dmso) (5)

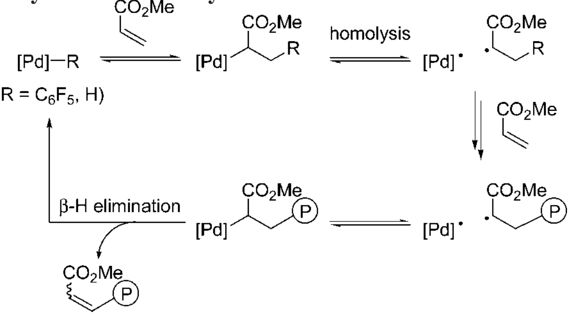


reported in 2000,[124] but 8 years later, it was found that copolymerization by a similar catalyst, [{(η^3-allyl)Pd(PCy$_3$)}$_2$(μ-Cl)][PF$_6$], proceeded via a radical pathway.[125] The reactivity of Pd complexes bearing a series of [N−N] and [N−O] ligands toward copolymerization of ethylene with MA has been investigated by using DFT calculations, although no experimental support has been reported.[96,126]

Sen and Espinet proposed that after insertion of MA, ethylene insertion into the resulting Pd species such as **C4**, **C6**, and **C7** (Scheme 8) is retarded by stable chelation. The lower nucleophilic nature of the α-carbon of PdCH(CO$_2$Me)R also attenuates the activity of the subsequent ethylene insertion.[54c] When the ethylene insertion is sluggish, homolytic cleavage of the Pd−C bond occurs to initiate radical polymerization of MA. For example, a neutral palladium complex, [Pd(C$_6$F$_5$)Br(NCMe)$_2$], was found to promote the homopolymerization of acrylates and copolymerization of 1-hexene with MA to afford copolymers with a high MA incorporation ratio.[127,128] These polymerizations occurred by a free radical mechanism initiated by the homolysis of the Pd−carbon bond after the 2,1-insertion of MA, and the mechanism for terminating the polymerization was β-H elimination (Scheme 12).

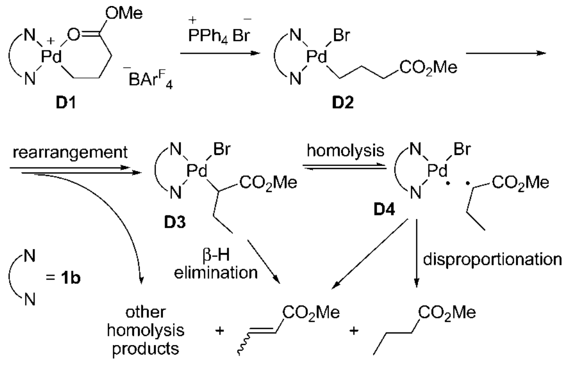
This type of homolysis can be also observed in the Pd α-diimine complexes when the catalyst is neutralized by bromide ions (Scheme 13).[129] When one equivalent of tetraphenylphosphonium bromide was added to the cationic six-membered chelate bearing **1b** as a ligand (**D1**), complete and rapid conversion to the neutral complex (**D2**) was observed. Interestingly, rearrangements occurred in the opposite direction to those in the cationic Pd α-diimine system in the absence of the fourth ligand (Scheme 7). This can be attributed to the fact that the neutral palladium complexes prefer to have an ester group at the α-position (**D3**), while cationic complexes prefer the γ-position due to formation of an intramolecular chelate structure (**D1**). Alternatively, it may be interpreted that the α-position is preferable when the fourth ligand exists (see also Scheme 11). In both cases, the chain walking of Pd between the α-position and the γ-position occurs with low energy barriers such that the palladium atom finally ends up in the most stable position. It should be noted that various products arising from the homolysis of Pd−alkyl bonds, such as methyl crotonate and methyl butyrate, were produced during the course of the reactions.

Scheme 12. Radical Polymerization of MA Initiated by the Homolysis of a Pd−Alkyl Bond[a]



[a] The initiator is [Pd(C$_6$F$_5$)Br(NCMe)$_2$].

Scheme 13. Proposed Reaction Pathways Following the Disruption of the Six-Membered Chelate

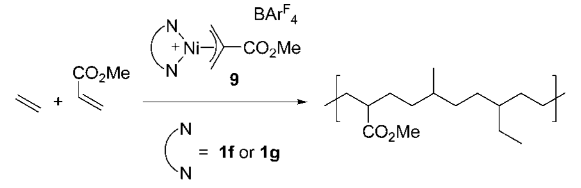


2.4.5. Nickel Catalysts

As discussed above, major advances in the copolymerization of nonpolar olefins with MA have been achieved by the use of Pd catalysts. On the other hand, most attempts to copolymerize ethylene using MA by Ni catalysts were unsuccessful.[5,6d,f,7,130] For example, Ni α-diimine catalysts exhibited low activities and low incorporation of MA.[7,130] In this context, Michalak and Ziegler investigated the differences between Pd and Ni catalysts for copolymerization of ethylene and MA as well as other polar vinyl monomers using DFT calculations.[121,126,133] They have shown that Ni α-diimine catalysts are capable of MA insertion and the subsequent ethylene insertion. The most important difference between Pd and Ni is an initial poisoning of the catalyst by the *O*-binding mode (such as **C3**) of MA in the latter case due to the higher oxophilicity.[131] Thus, they suggested the Ni α-diimine system may catalyze the copolymerization of ethylene with MA under harsh conditions as shown below.

In 2002, Johnson et al. reported the copolymerization of ethylene with MA using Ni α-diimine catalyst **9** using **1f** or **1g** as a ligand with or without a cocatalyst (Scheme 14).[60,66] The key enabling factor was the use of high temperatures

Scheme 14. Copolymerization of Ethylene with MA Catalyzed by Ni α-Diimine Complex



(120 °C) and high pressures (340 bar). It should be noted that the Pd α-diimine-catalyzed ethylene/MA copolymerization can be typically carried out at low ethylene pressures and low temperatures (e.g., 1 bar ethylene and ambient temperature) because higher ethylene pressures and temperatures result in low acrylate incorporation and decomposition of the catalyst. In the case of the Ni α-diimine catalyst, the harsh conditions appeared to contribute to dissociation of the carbonyl coordination of MA from the electrophilic Ni center. In contrast to the analogous Pd diimine catalysts that provide highly branched structures (100 Me per 1000 carbons) with ester groups at the end of the branches, the copolymer obtained with **9** ranged from moderately linear (30 Me per 1000 carbons) to highly branched with predominantly in-chain acrylate incorporation (ca. 1%).[60,66]

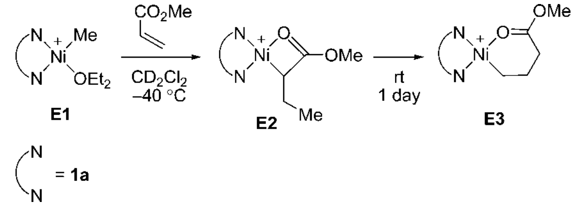
Low-temperature NMR studies showed that MA insertion into the Ni−Me bond occurs rapidly at −40 °C. A four-membered chelate complex **E2** slowly rearranges at room temperature to a six-membered chelate complex **E3** within the course of 1 day, Scheme 15. This is indicative of a strong Ni−carbonyl interaction as, in comparison, the rearrangement of the analogous Pd four-membered chelate complex occurs at −60 °C. Theoretical calculations also supported this difference between Pd and Ni α-diimine catalysts. The barrier of isomerization from four-membered chelate to five-membered chelate is higher in the case of Ni than in the case of Pd.[132]

Since the *O*-binding of MA to the nickel center would be a problem due to the high oxophilicity, the use of anionic ligands would enhance the preference to a π-olefin complex of MA to accelerate the coordination−insertion copolymerization.[121,133] Johnson et al. also synthesized a series of Ni catalysts bearing anionic [P−O] and [P−N] ligands as shown in Figure 10.[60,134,135] Upon activation with Lewis acids such as $B(C_6F_5)_3$, these nickel phosphine-based catalysts were found to be active for copolymerization of ethylene with hexyl acrylate. The obtained copolymers had low alkyl branching (ca. 10 Me per 1000 carbons) with low molecular weights (M_n = ca. 10^3, $M_w/M_n = 1.8-10$). The ester groups of these polymers were directly connected to the polymer backbone or located in end groups of the polymer main chain rather than being located at the end of the side chains, although the ester incorporation ratio was quite low (ca. 0.5%). It is noteworthy that LiCl-coordinated catalysts **10c−e** were more productive than catalyst **10b**.

Recently, Cámpora et al. utilized a Ni catalyst with [N−O] ligand (**11**), 2-iminopyridine *N*-oxides (PymNox), for copolymerization of ethylene with MA in the presence of MMAO.[136] Although the molecular weight (M_n = 1900) and acrylate incorporation ratio (ca. 0.7%) are rather low, ester groups are incorporated in chain ($-CO_2Me$) as well as at one methylene branch ($-CH_2CO_2Me$). Longer branches ending in methoxycarbonyl groups are apparently absent.

The attempted use of other neutral [P−O]Ni[5] and [N−O]Ni[6d,f,137,138] catalysts for copolymerization of MA with ethylene have been reported. Grubbs[6f] and Mecking[137] investigated the reactions of neutral Ni salicylaldimine catalysts **12** and **13** with MA to reveal that no polymerization of MA or ethylene was observed, although the first insertion of MA into a Ni−Ph or Ni−H bond was confirmed. After insertion of MA, β-H elimination or the hydrolysis of the Ni−alkyl bond occurred (Scheme 16).

Scheme 15. Insertion of MA into {[1a]NiMe(OEt$_2$)}(BAr$^F_4$) and Subsequent Isomerization



2.4.6. Other Late-Transition-Metal Catalysts

Other metals were also investigated for copolymerization of ethylene with MA.[139,140] Stibrany et al. reported that the combination of Cu bisbenzimidazole complexes (**14**) and MAO catalyzed copolymerization of ethylene with MA and *tert*-butyl acrylate.[60,140] The resulting copolymers exhibited in-chain incorporation of ester groups in a linear copolymer backbone with high levels of acrylate incorporation (45−100%). These catalytic systems also catalyzed the homopolymerization of ethylene to produce linear polyethylenes with no detectable branches under mild conditions. Considering that highly linear polyethylene is difficult to obtain by using

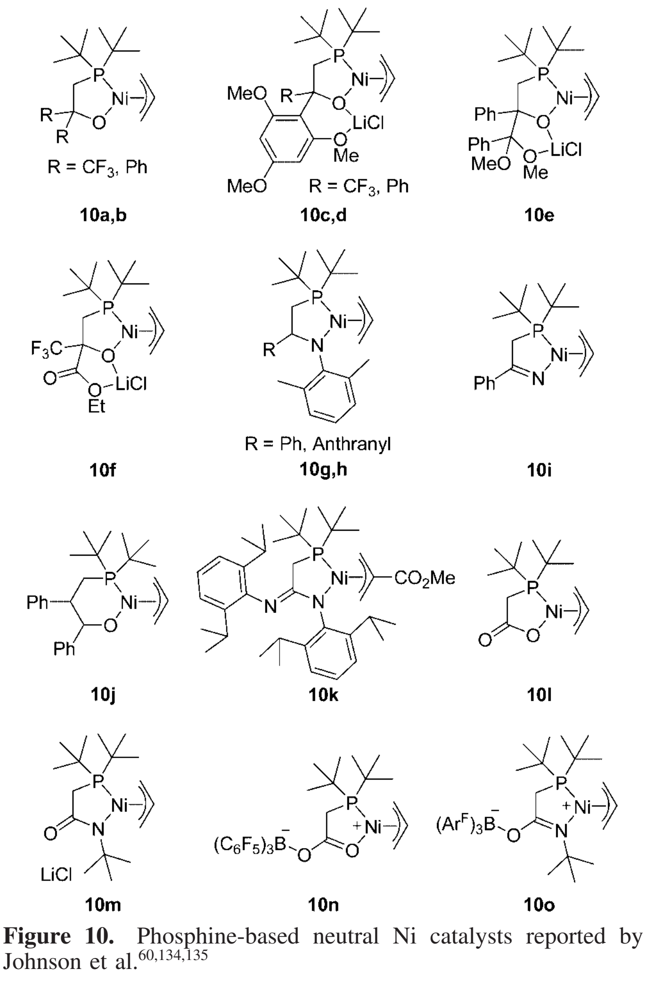
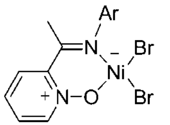


Figure 10. Phosphine-based neutral Ni catalysts reported by Johnson et al.[60,134,135]

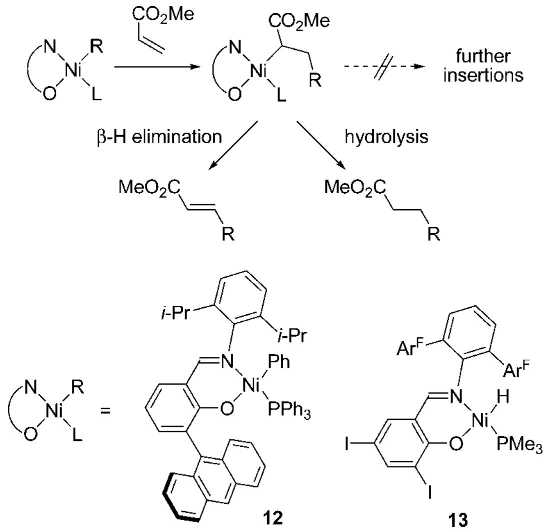


11

(Ar = 2,6-i-$Pr_2C_6H_3$)

Figure 11. Ni catalyst bearing a 2-iminopyridine *N*-oxides (PymNox) ligand.

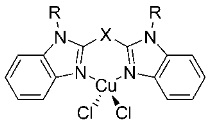
Scheme 16. Reactions of MA with Neutral Ni Salicylaldimine Complexes



radical polymerization, the authors concluded the homopolymerization and copolymerization proceeded via the coordination—insertion mechanism, although the real active species were not conclusively identified. On the other hand, Foley et al. recently reported that when Cu(II) catalysts bearing [N—N] or [N—O] ligands were treated with MAO, ligand transfer reactions from Cu to Al occurred to yield the corresponding Al complexes, which may initiate and catalyze the copolymerization.[141]

2.5. Methacrylates

Homopolymers of methacrylates[111,142,143] are known to exhibit properties that differ from those of the corresponding polyacrylates, since the presence of the methyl group on the α-carbon restricts the freedom of movement of the polymer backbone. In addition, the active α-proton of the carbonyl group does not exist in polymethacrylate. Thus, polymethacrylates possess high rigidity, high resistance to redox, water, and acid/base, and high thermal stability.[111,142] Although there have been numerous reports on the homo- and copolymerization of methyl methacrylate (MMA) and related monomers, most reactions proceeded via an anionic pathway[144] including GTP (group-transfer polymerization)[1,145−147] and radical[44,148] pathways in the presence of metal catalysts. MMA is considered to be among the most challenging monomers for coordination—insertion polymerization since the coordination ability of 1,1-disubstituted ethenes to a metal center is significantly decreased as compared to that of monosubstituted ethenes.

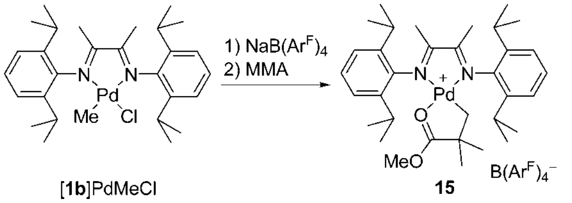


R = Me, Et, n-Bu, etc.
X = CHOH, CH_2, 2,2'-biphenyl, C_2F_4, etc.

14

Figure 12. Copper catalysts bearing bisbenzimidazole ligands.

Scheme 17. Reactions of MMA with the Pd Catalyst Bearing Ligand 1b

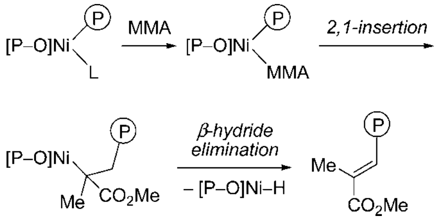


Late-transition-metal catalysts bearing nitrogen-containing neutral ligands have been extensively investigated for the copolymerization of MMA. The α-diimine complexes of group 10 metals such as nickel and palladium, known to be one of the very few catalysts capable of the coordination—insertion copolymerization of ethylene and MA (vide supra),[8] could be a powerful candidate as a catalyst for MMA copolymerization. Marques et al. studied the copolymerization of ethylene and MMA catalyzed by Ni(II) α-diimine complexes and MAO in which trialkylaluminum was employed as a protection agent.[149] Sen et al. observed that the palladium complex [**1b**]PdMeCl underwent 1,2-insertion of MMA in the presence of $NaB(Ar^F)_4$ to yield a stable five-membered cyclic chelate complex **15** presumably because the complex **15** has no substituents on the α-carbon and no *β*-hydrogens (Scheme 17).[54c,150] The regiochemistry of the insertion was found to be the opposite of that observed in the reaction with MA (i.e., 2,1-insertion). The kinetic analyses revealed that the enthalpy ($\Delta H^{\ddagger}$) for MMA insertion was 4 kcal/mol higher than that of MA insertion, which could be the main reason why incorporation of MMA into the polyethylene chain has failed when Pd(II) α-diimine catalysts were employed for the copolymerization. Other [N—N][60,140c] and [N—N—N][139] ligands have also been investigated for the copper- and iron-catalyzed copolymerization of ethylene and MMA, respectively.

In 2001, Gibson et al. reported the use of nickel catalysts with [P—O] ligands (**16**) to produce ethylene/MMA copolymers with low molecular weights (M_n = 2600−3800).[151] NMR and IR analyses revealed the presence of MMA units at the chain ends of the individual polymer. It was suggested that the chain-end MMA was formed via a mechanism involving the 2,1-insertion of MMA into the growing polyethylene and subsequent *β*-H elimination exclusively from the CH_2 group rather than the CH_3 group (Scheme 18). The regiochemistry of *β*-H elimination was totally opposite to the trend observed in the reaction of $[Pd(C_6F_5)Br(NCMe)_2]$ with MMA.[54c,127]

Copolymerization of ethylene and MMA with the in-chain incorporation of MMA has recently been investigated by using [N—O] bidentate ligands.[138,152−154] Carlini et al. performed the copolymerization of ethylene and MMA by nickel salicylaldiminate complexes **17** activated with MAO to yield ethylene/MMA copolymers with high contents of MMA counits (61−81%),[152] which indicates the intermediacy of radical-related processes.[114] On the other hand, copolymerization by $Ni(cod)_2$ and ligands **18**,[152] **19**,[152b] and **20**[152b] afforded ethylene/MMA copolymers with 3−7% MMA incorporation, although the mechanism of the copolymerization is still unclear.

Scheme 18. Reactions of MMA with the Ni Catalyst 16



Li et al. reported that the neutral nickel complexes bearing β-ketoiminato ligand **21** efficiently initiated and catalyzed the copolymerization of ethylene and MMA in the presence of MMAO with an activity of 0.12−2.65 gmmol^{-1} h^{-1} bar^{-1} (Scheme 19).[153] The copolymers were characterized by molecular weights of M_n = 2480−7700 and up to 16.7% of MMA incorporation into the moderately branched polyethylene chain. Chain-end analysis revealed the presence of $CH_3CH{=}CH-$ and $CH_2{=}CH-$ groups as chain ends and the absence of $PhCH_2CH_2-$ and methyl enoate end groups, suggesting that the polymerization was initiated by ethylene insertion into Ni−H species and terminated with β-H elimination after ethylene insertion. All the experimental data by the NMR analyses and control experiments support the coordination−insertion mechanism rather than radical pathways.

2.6. Vinyl Acetate

Vinyl acetate (VAc) is an industrially important monomer to produce poly(vinyl acetate) (PVAc), vinyl acetate copolymers, and poly(vinyl alcohol) (PVA),[47,155,156] which have been used for manufacturing a variety of functional polymeric materials such as water-based paints, adhesives, and paper coatings.[157−160] Conventionally, the homopolymers and copolymers of VAc have been produced by radical polymerization.[159,161,162] On the other hand, coordination polymerization of VAc has been less investigated because of the difficulty of metal-catalyzed coordination−insertion polymerization and copolymerization of VAc. Some reports have described the transition-metal-catalyzed copolymerization of vinyl acetate with olefins; however, the polymerization mechanism has not been clarified.[149,163]

In a series of seminal work, Brookhart et al. thoroughly investigated the reactions of VAc with Pd and Ni α-diimine complexes bearing **1e** to provide significant insights into the difficulty in coordination−insertion copolymerization of VAc with ethylene.[164] The results of their study are summarized in Schemes 20 (for Pd) and 21 (for Ni), in which the difficulty can be attributed to the following four steps: (1) coordination of VAc to a metal center, (2) insertion of VAc into a M—C bond, (3) subsequent ethylene coordination and insertion, and (4) β-OAc elimination.

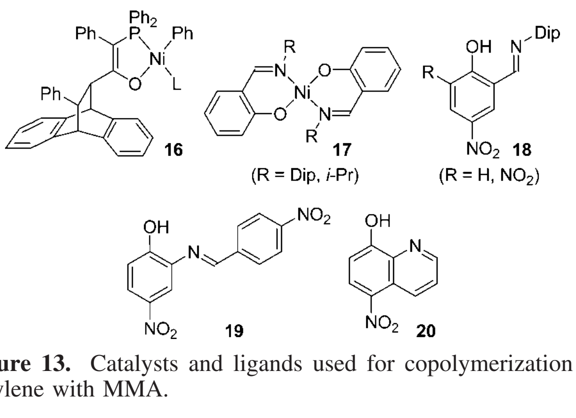
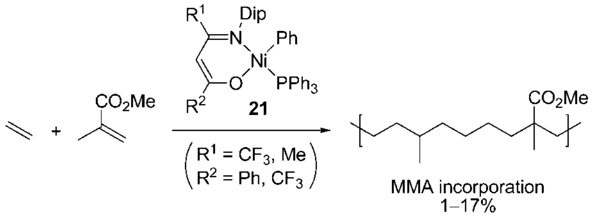


Figure 13. Catalysts and ligands used for copolymerization of ethylene with MMA.

Scheme 19. Copolymerization of Ethylene with MMA by the Ni Catalyst 21



First, VAc has a much lower coordination ability to a cationic Pd complex bearing **1e** as compared to that of ethylene ($K_{\text{VAc/ethylene}}$= 0.015 at 25 °C).[164] According to the comparison of frontier orbitals in Figure 4,[93,94,96,126] the π-orbital of C═C (HOMO) of VAc is higher than that of ethylene, which would facilitate coordination to a metal center. Therefore, it can be concluded that the lower coordination ability of VAc is mainly attributed to the steric effect. In addition, *O*-coordination of VAc may be a problem. In fact, the *O*-coordination complex (**G2**) was observed in the case of the Ni α-diimine complex (Scheme 21).[164]

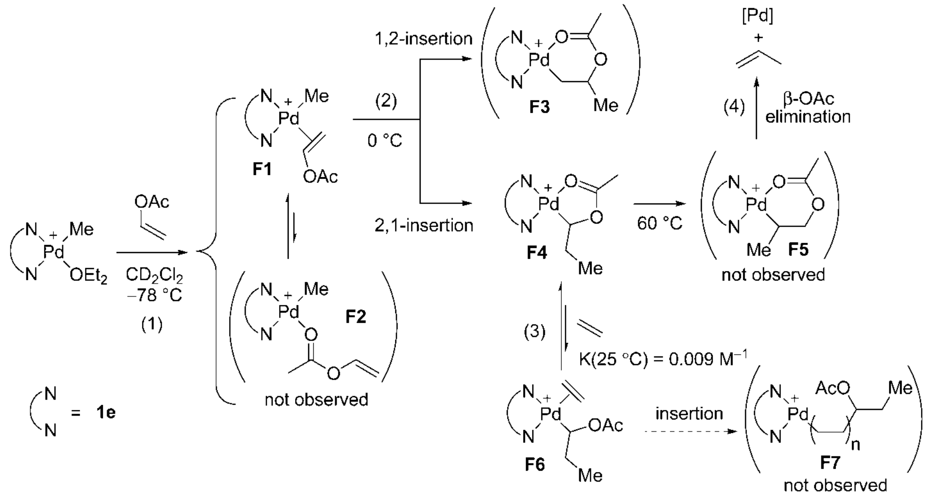
Second, the rate of VAc insertion into M—alkyl bonds is slightly slower relative to ethylene. Insertion of VAc into a Pd—Me bond proceeded in a 2,1-fashion, while both 2,1- and 1,2-insertion into a Ni—Me bond were observed. In all cases, insertion of VAc was slower than that of ethylene,[63c,164] although no clear explanation has yet been provided.[165]

The sluggish coordination and insertion of ethylene after insertion of VAc appears to be a critical problem for polymerization by Pd α-diimine catalysts. After the 2,1-insertion of VAc into a Pd—Me bond, the acetoxy group forms a stable internal five-membered chelate structure (**F4**).[166] When the isolated complex **F4** was used as an initiator of the homopolymerization of ethylene, only a small amount of PE was obtained without detectable VAc at its chain end.[164] The equilibrium between the strong chelate **F4** and ethylene adduct **F6** strongly favored the former (K = 0.009 M^{-1}).[164] Furthermore, Goddard et al. estimated the subsequent ethylene insertion barrier from **F6** to be as high as $\Delta E^{\ddagger}$ = 25.1 kcal/mol,[100] which could be attributed to the electron-withdrawing character of the acetoxy group on a sp^3 α-carbon.[167]

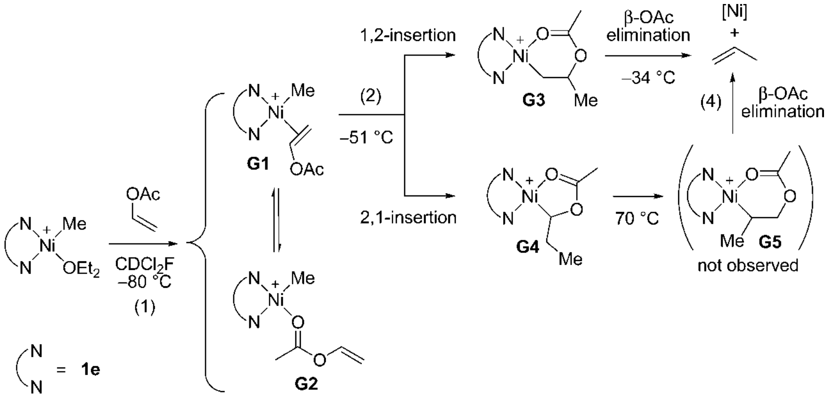
Finally, the acetoxy group at the β position causes β-OAc elimination, leading to decomposition of the catalyst due to the stability of the resulting Pd−OAc bond. Theoretical calculations proposed that there exist two possible TSs for β-OAc elimination:[168] one is a four-membered ring TS, and the other is a more favorable six-membered ring TS (Scheme 22).[169] It was elucidated that the β-OAc elimination is thermodynamically more favored than β-H elimination, while the β-H elimination is kinetically more favored. The five-membered ring intermediate **F4**, formed via the 2,1-insertion of VAc into the Pd—Me bond of **F1**, decomposed at 60 °C to release propylene. This reaction can be recognized as isomerization from **F4** to **F5** followed by β-OAc elimination. In a similar manner, after 2,1-insertion of VAc into the Ni—Me bond of **G1**, the resulting complex **G4** decomposed at 70 °C to afford propylene. The 1,2-insertion product **G3** also underwent β-OAc elimination at −34 °C without isomerization.

Reaction of a neutral Ni salicylaldiminate complex (**13**) with VAc was extensively investigated by Mecking et al.[137]

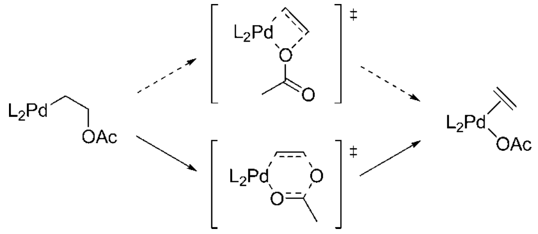
Scheme 20. Reactions of VAc with Pd α-Diimine Complexes



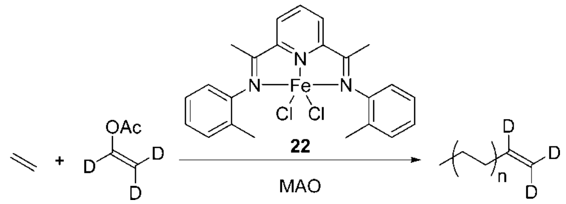
Scheme 21. Reactions of VAc with Ni α-Diimine Complexes



Scheme 22. Two Plausible Transition States for β-OAc Elimination



Scheme 23. Attempted Copolymerization of Ethylene and Vinyl Acetate by a Fe Complex Bearing a [N−N−N]-Tridentate Ligand

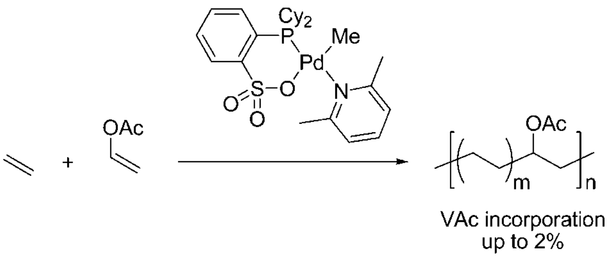


The observed reactivity of **13** with VAc was found to be similar to that of the cationic Ni α-diimine complexes. Insertion of VAc into a Ni−R bond proceeded in both the 2,1- and the 1,2-modes and the subsequent β-OAc elimination occurred to decompose the catalyst.

An iron complex with a 2,6-bis(imino)pyridine ligand (**22**) was examined for the copolymerization of ethylene with VAc.[139,170] Boone et al. confirmed that insertion of VAc followed by acetoxy elimination took place to yield an olefin terminus during the copolymerization (Scheme 23).[170] In the presence of deuterated VAc, $D_2C{=}CDOAc$, the product was the oligomer of ethylene in which the deuterium atoms were located only at the olefin terminus, and no acetoxy functionality was detected. Supported by DFT calculations, this reaction was believed to proceed either by favorable 2,1-insertion of VAc into the Fe−alkyl bond followed by rearrangement and β-OAc elimination or by 1,2-insertion of VAc and the following β-OAc elimination. The remaining Fe(II) acetate did not exhibit any catalytic activity for the copolymerization because it cannot be efficiently reactivated by MAO.

Very recently, Nozaki et al. found that the Pd complexes bearing alkylphosphine−sulfonate ligands catalyzed the copolymerization of ethylene with vinyl acetate (Scheme 24).[14] When a mixture of $Pd(dba)_2$ and [**2l**]H or isolated complexes [(**2l**)PdMeL] (L = 2,6-lutidine, DMSO) was exposed to VAc and ethylene (30 bar) in toluene at 80 °C for 15 h copolymers with a VAc incorporation ratio of 0.5−1.9% and M_n of 5000−10 000 were obtained. The alkylphosphine ligand **2l** exhibited higher catalytic activity than arylphosphine **2c**, and the copolymerization by isolated complex [(**2l**)PdMeL] (L = 2,6-lutidine, dmso) proceeded with higher catalytic activity than that by in-situ-generated catalysts (i.e., $Pd(dba)_2$ and [**2l**]H). Characterization of the products by NMR analysis revealed that the polymers are undoubtedly VAc/ethylene copolymers rather than a mixture of homopolymers. The structure of the copolymer was proven to have highly linear polyethylene backbones without a

Scheme 24. Copolymerization of Ethylene and Vinyl Acetate Catalyzed by Pd Phosphine−Sulfonate Complex (2l)PdMe(2,6-lutidine)



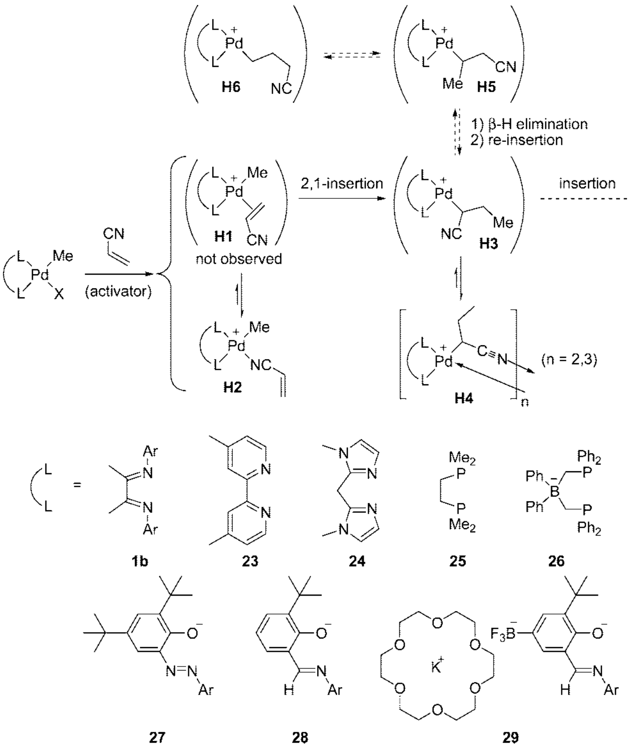
detectable branching unit (<1 branch/10^3 C). The acetoxy groups were linked to the main chain as well as to initiating and terminating chain ends. The present study provides the first example of the coordination−insertion copolymerization of vinyl acetate and ethylene.[14]

2.7. Acrylonitrile

Introduction of acrylonitrile (AN) into polymers can cause drastic change in their physical and chemical properties, as exemplified by unique features of various acrylonitrile (AN) polymers such as polyacrylonitrile (PAN), acrylic fibers, and nitrile rubbers.[171,172] For example, hydrogenated nitrile butadiene rubbers (HNBRs), which have analogous structures to ethylene/AN copolymers with branched structures, exhibit excellent oil, heat, and chemical resistance. Polyacrylonitrile (PAN) is currently prepared by anionic or radical polymerization,[173] and ethylene/AN branched copolymers[174] and HNBRs[172] are produced by the radical processes.

Despite its synthetic importance, acrylonitrile has been recognized as a challenging monomer for coordination−insertion copolymerization. For example, Jordan[175] and Baird[176] independently investigated the reaction of cationic Pd α-diimine complex [(**1b**)PdMeL]$^+$ with AN to observe formation of *N*-bounded AN complex **H2** (Scheme 25). The subsequent 2,1-insertion of AN[177] via **H1** produces α-cyanoalkylpalladium complex **H3**, which did not undergo isomerization via chain walking to give **H5** and **H6**.[178] The complex **H3** readily aggregates via bridging nitrile groups to give complexes **H4**, which are too stable for the next monomer to coordinate to the Pd center. In fact, addition of AN suppressed not only the copolymerization of ethylene and AN but also the homopolymerization of ethylene.[176] Although Pd complexes with other bidentate ligands including [N−N],[175] [P−P],[179] and [N−O][180] ligands have been examined, the obtained results were similar to those observed in the case of the Brookhart α-diimine catalyst, [(**1b**)PdMeL]$^+$. Thus, a major obstacle to coordination−insertion copolymerization of AN by Pd catalysts is formation of *N*-bounded AN complex **H2** and catalytically inactive aggregate **H4**. Low nucleophilicity of the α-carbon in **H3** arising from a cyano group is also considered to be unfavorable for the ethylene insertion. It should be noted that in the presence of $B(C_6F_5)_3$ coordination of ethylene to the palladium complex **H4** with CH_2(*N*-methylimidazol-2-yl)$_2$ ligand **24** was observed.[175] Nevertheless, the subsequent ethylene insertion did not occur because the strong electron-withdrawing nature of the α-CN−$B(C_6F_5)$ substituent inhibits the migratory insertion.

Scheme 25. Reaction of AN with Pd Complexes Bearing Several Bidentate Ligands



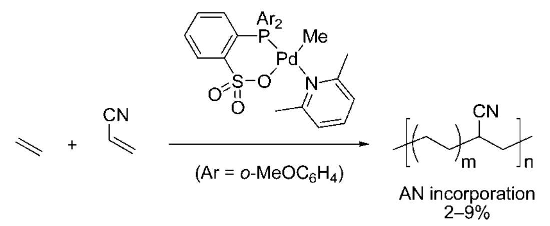
The problems described above were suggested to be solved by increasing the net charge of metal catalysts because of the following. (i) The equilibrium between **H1** and **H2** would be shifted to **H1**: Experimental[179,180] and theoretical studies[96,100,105,181−184] revealed that AN prefers *N*-coordination to cationic transition-metal complexes, but the preference decreases in the case of neutral or anionic metal complexes due to the stronger π-back-donation from an electron-rich metal center to the olefin. (ii) Insertion of AN would be enhanced: The more electron rich the metal center becomes, the faster AN inserts into a Pd−alkyl bond.[179,180]

In 2007, Nozaki et al. found that the Pd phosphine−sulfonate complex, (**2c**)PdMe(2,6-lutidine), catalyzed the copolymerization of ethylene with AN with an activity of up to 13 g mmol^{-1} h^{-1} bar^{-1} to afford ethylene-rich linear copolymers of M_n up to 12 300 with an AN incorporation ratio of 2−9% (Scheme 26).[15] NMR analyses revealed that the copolymer has no branching architectures with AN units found in the polyethylene backbone as well as initiating and terminating chain ends. Thus, the melting temperature of the copolymer was higher than those produced by radical methods. The end-group analyses suggested that chain propagation is initiated by ethylene insertion into a Pd−Me bond or insertion of ethylene or AN into a Pd−H bond and that chain transfer reactions occur via β-H elimination more often after insertion of AN than ethylene.

2.8. Vinyl Halides

The polymerization of vinyl halides[185−188] is an important issue in polymer science, since incorporation of halogens into polymers influences many fundamental properties, such as chemical resistance, thermostability, gas permeability, and adhesion properties.[45,189,190] Therefore, it is important to develop novel synthetic methods that enable the generation of halogen-containing polymers with a large range of halogen contents and distribution. Conventionally, halogenated polyolefins have been prepared by the halogenation of polyethylene or its analogs[45,190,191] or by the dehalogenation of

Scheme 26. Copolymerization of Ethylene and Acrylonitrile Catalyzed by Pd Phosphine−Sulfonate Complex (2c)PdMe(2,6-lutidine)



homopolymers of vinyl halides,[190,192] both of which generally result in polyolefins having poorly defined structures. Although direct synthesis via the radical copolymerization of ethylene and vinyl halides is also possible,[193] the range of halogen contents and distribution is rather limited because the precise control of the radical species remains difficult.[194] Recently, ring-opening metathesis polymerization (ROMP) of halogen-substituted cyclooctenes[52] and acyclic diene metathesis (ADMET) polymerization of halogen-substituted dienes[53] followed by hydrogenation have been developed to synthesize halogen-containing polyethylenes.

The coordination copolymerization of ethylene and vinyl halides using early-transition-metal catalysts is problematic due to the side reactions arising from the activated halogen atom, such as β-halogen elimination.[1] This behavior could be explained by the difference of the bond dissociation energies of metal−halogen bonds relative to metal−carbon bonds: For early transition metals, the difference is quite large, leading to predominant β-halogen elimination.[102,195] In fact, most studies on the homopolymerization of VC in the presence of early-transition-metal single-site catalysts such as Cp*TiX$_3$ (Cp* = pentamethylcyclopentadienyl; X = Cl, OMe, OPh),[196,197] Zr(IV) metallocene complexes,[196,198] and (t-Bu$_3$SiO)$_3$TaH$_2$[102a] have been unsuccessful. In most cases, the main pathway was found to be insertion of VC into metal−alkyl bonds followed by rapid β-Cl elimination to yield a metal−Cl species.[199] Similarly, vinyl fluoride (VF) and related monomers underwent insertion into a metal−H bond of Cp$_2$ZrHCl[200] or Cp$_2$ZrH$_2$[201] (Cp = cyclopentadienyl) followed by rapid β-fluoride elimination to afford the Zr−F species.

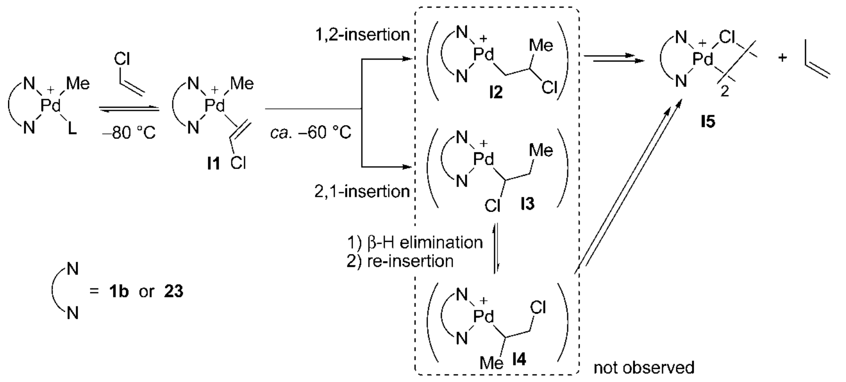
In contrast, late-transition-metal catalysts would be more promising for the coordination−insertion polymerization of vinyl halide. The β-halogen elimination of late transition metals is expected to be less favorable than that of early transition metals due to the smaller difference between the M−X and M−C bond strengths.[202] In fact, there have been some examples of late-transition-metal−alkyl complexes containing β-halogens, including iron,[203] iridium, [204] and platinum complexes,[205] as well as some metal−perfluoroalkyl complexes. [206]

The polymerization of VC with late-transition-metal complexes has been extensively investigated. Jordan et al. examined the reactions of a cationic Pd−bipyridine complex, (**23**)PdMe$^+$, with various olefins to reveal that VC coordinates more weakly to a cationic palladium center than propylene and ethylene due to the electron-withdarwing effect of chloro group.[207] The olefin insertion rate of (**23**)PdMe(olefin)$^+$ was found to vary in the order of VC > ethylene > propylene, which is consistent with the observations that the insertion rate of Pd α-diimine complexes, (**1b**)PdMe(olefin)$^+$, was in the order of vinyl bromide > ethylene > propylene.[101] The VC complexes of bipyridine or α-diimine ligands are converted to β-chloroethylpalldium species **I2** or **I4** via either 1,2-insertion of VC or 2,1-insertion of VC followed by β-H elimination and reinsertion, respectively. Rapid β-Cl elimination proceeds from **I2** or **I4** to **I5** and propylene (Scheme 27). It should be noted that the actual direction of VC insertion (1,2-insertion vs 2,1-insertion) remains unclear,[100,206a,208] although insertion of VC into a palladium−acyl bond of Pd bipyridine complexes or diphosphine complexes proceeded in the 2,1-mode.[209]

The same phenomenon was observed when Fe or Co diiminopyridine complexes/MAO catalysts (**22**, **30**, **31**)[170,207] and [P−O]Ni complexes (**32**)[207] were employed (Figure 14). Boone et al. demonstrated that the copolymerization of ethylene and deuterium-labeled VC in the presence of **22** afforded low-molecular-weight ethylene oligomers containing deuterium at the olefin terminus with no Cl functionality incorporated (Scheme 28).[170] This result also supports the reaction mechanism involving the insertion/β-chloride elimination pathway.

Recently, Jordan et al. reported the coordination−insertion copolymerization of ethylene and vinyl fluoride by using palladium phosphine−sulfonate complexes as a catalyst (Scheme 29).[16] The use of vinyl fluoride as a comonomer is essential for successful copolymerization, since it is less susceptible to radical polymerization[193b,c] and to β-elimination[169] than other vinyl halides. Thus, the copolymerization of ethylene and vinyl fluoride catalyzed by (**2b**, **2d**, **2i**)PdMe(pyridine) efficiently proceeded with an activity of 0.12−0.89 gmmol^{-1} h^{-1} bar^{-1} under a total pressure of 43.5 bar at 80 °C. The obtained copolymers possessed highly linear polyethylene structures with molecular weights of M_n = 4500−14 500 with low incorporation of vinyl fluoride (0.09−0.45%). At the same total pressure of ethylene and VF, increasing the proportion of VF resulted in an increase

Scheme 27. Reactions of VC with Cationic [N−N]Pd Complexes



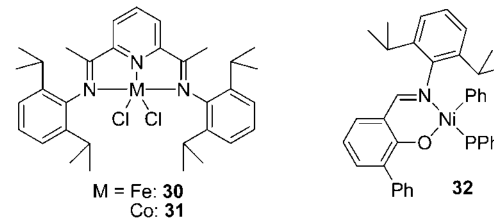
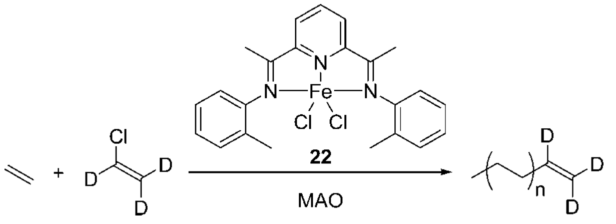
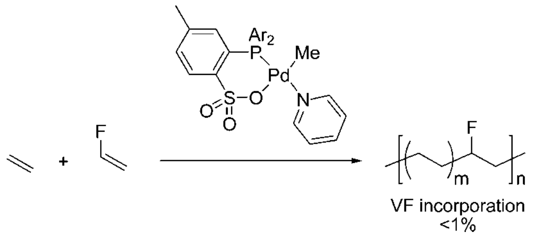


Figure 14. Catalysts used for the attempted copolymerization of ethylene with vinyl chloride.

Scheme 28. Copolymerization Study of Ethylene with Deuterated Vinyl Chloride Using Tridentate Fe Complex



Scheme 29. Copolymerization of Ethylene with Vinyl Fluoride Catalyzed by Pd Phosphine−Sulfonate Complexes (2b, 2d, 2i)PdMe(pyridine)



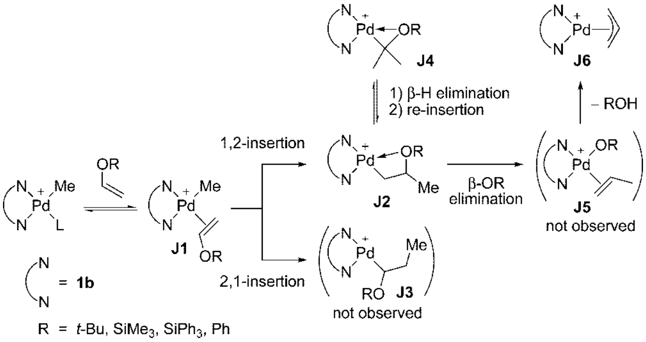
in the VF incorporation level and a decrease in copolymer yield and molecular weight. The low level of VF incorporation could be attributed to the weak coordinating ability to Pd(II) species as compared to ethylene. On the basis of NMR analyses and control experiments, the authors concluded that the reaction proceeded via the coordination−insertion mechanism.

2.9. Vinyl Ethers

Vinyl ethers (VE) are among the most attractive comonomers for the synthesis of functionalized polyolefins[210,211] because their structures and properties can be finely tuned by varying the OR group. However, the coordination−insertion polymerization of VE is difficult due to some severe limitations. First, vinyl ethers are susceptible to cationic polymerization in the presence of electrophilic metal catalysts.[212] Second, the insertion barriers of VE are generally high due to the electron-donating property of the OR group,[95] although the initial π-coordination of VE to an electrophilic metal must be favorable.[213] Third, the intermediate after the VE insertion, $L_nMCH_2CH(OR)R'$, would be easily decomposed via β-OR elimination.[102,169,214]

To clarify the reactivity of vinyl ethers toward the coordination and insertion, the stoichiometric reactions of [(**1b**)PdMe][B(C_6F_5)$_4$] with vinyl ethers were investigated by Jordan et al. (Scheme 30).[9] Complex [(**1b**)PdMe]$^+$ reacted with vinyl ethers to form π-coordination complexes **J1**. After the following insertion of vinyl ethers, a mixture of 1,2-insertion products **J2** and the isomerized products **J4** was observed in a state of equilibrium, which is consistent with the calculation results that vinyl ethers prefer 1,2-insertion to 2,1-insertion.[95] No evidence for formation of 2,1-insertion products **J3** was obtained. Complex **J2** gradually decomposed at room temperature to yield Pd η^3-allyl complex **J6** and releasing ROH.

Scheme 30. Reactions of Vinyl Ethers with Cationic [N−N]Pd Complexes



The cationic palladium α-diimine complex, [(**1b**)PdMe][B(C_6F_5)$_4$], was found to catalyze the copolymerization of 1-hexene and $CH_2{=}CHOSiPh_3$ to yield copolymers with moderate levels of VE incorporation (up to 20%).[9] The key to the success is the use of $CH_2{=}CHOSiPh_3$, which is inactive toward cationic homopolymerization in the presence of [(**1b**)PdMe][B(C_6F_5)$_4$]. Another key feature of the monomer is slow β-$OSiPh_3$ elimination from $L_nMCH_2CH(OR)R'$ species generated by VE insertion. Trimethylsilyl vinyl ether, $CH_2{=}CHOSiMe_3$, could also be copolymerized with 1-hexene with VE incorporation up to 11%, although a substantial amount of VE homopolymer was obtained by cationic polymerization. The obtained copolymers possessed highly branched structures (90−100 branches per 1000 carbons) with comonomer units located mostly at the branched ends. For example, the major comonomer units of the poly(1-hexene-*co*-$CH_2{=}CHOSiPh_3$) were found to be $CH_3CH(OSiPh_3)CH_2-$ (85%) and $Ph_3SiOCH_2CH_2-$ (6%). It was proposed that polymerization proceeded via a normal insertion/chain-walking mechanism, which was often observed in the Pd α-diimine catalytic systems.[7,8,64] It should be noted that the multiple insertion of $CH_2{=}CHOSiPh_3$ into the Pd−Me bond of in-situ-generated [(**1b**)PdMe][B(C_6F_5)$_4$] complex was observed.[215]

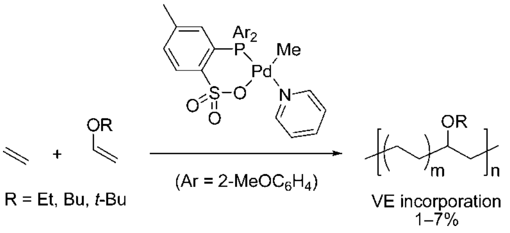
Significant progress in the coordination−insertion copolymerization of olefin and vinyl ethers was realized by the use of phosphine−sulfonate ligands.[17] The neutral palladium catalyst (**2d**)PdMe(pyridine) successfully copolymerized ethylene and vinyl ethers such as $CH_2{=}CHOR$ ($R = t$-Bu, Et, Bu, Ph) with an activity of 0.01−0.05 gmmol^{-1} h^{-1} bar^{-1} in toluene at 60−100 °C to give highly linear polyethylene containing 1−7% of VE (M_n = 900−4800) (Scheme 31). NMR analyses revealed that the copolymer contains in-chain VE units ($-CH_2CH(OR)CH_2-$) as well as chain-end units ($CH_3CH(OR)CH_2-$). The ethylene/VE copolymers can be converted to the corresponding HO- or Br-substituted polyethylene by functional-group transformation.

2.10. Other Monomers

In addition to the substrates mentioned above, other fundamental polar vinyl monomers have been investigated for copolymerization with nonpolar olefins. In this section, the polymerization studies of the monomers shown in Figure 15 are reviewed.

While attempts to copolymerize vinyl ketone (**33**) and acrolein (**34**) with ethylene by early-transition-metal catalysts

Scheme 31. Copolymerization of Ethylene with Vinyl Ethers Catalyzed by Pd Phosphine−Sulfonate Complex (2d)PdMe(pyridine)



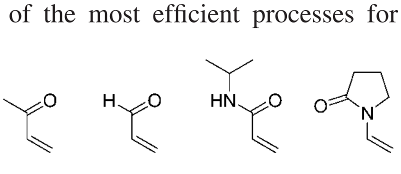
have been unsuccessful,[102a,116] late-transition-metal catalysts, especially Pd, were found to be effective for such copolymerization: Methyl vinyl ketone (**33**) can be copolymerized with ethylene by Pd complexes bearing α-diimine ligand **1b**[8a] or phosphine−sulfonate ligand **2c**.[19] Although the copolymerization of **34** has not yet been reported, its acetal derivative (i.e., acrolein dimethyl acetal) successfully underwent copolymerization with ethylene in the presence of Pd α-diimine complex with ligand **1b**.[216]

Polymerization of *N*-isopropylacrylamide (NIPAM, **35**)[217,218] and *N*-vinylpyrrolidone (NVP, **36**)[219,220] with ethylene can be obtained by using Pd phosphine−sulfonate catalysts to give highly linear copolymers, which exhibited a lower melting point than HDPE without any functionality.[18,72f] Copolymerization of other nitrogen-containing monomers such as *N*,*N*-dimethylacrylamide, *N*-vinylphthalimide (**37**), and *N*-vinylcarbazole (**38**) with ethylene by Pd phosphine−sulfonate catalysts has also been reported in the patent literature.[72f] Copolymerization of acrylamides with ethylene has been also studied by using Ni α-diimine catalysts.[149]

Early transition metals effectively copolymerize vinylsilanes (**39**) with ethylene. Jordan et al. investigated the coordination[213] and insertion[221] behavior of vinylsilanes by using zirconium complexes to suggest a possibility for coordination−insertion polymerization. In 2008, Nomura et al. discovered that nonbridged half titanocenes such as **40** and **41** (Figure 16) catalyze the copolymerization of trimethylvinylsilane and triethylvinylsilane with ethylene in the presence of MAO as a cocatalyst.[222] The obtained copolymer possessed highly linear structures with vinylsilane units incorporated in chain.

3. Recent Advances in Copolymerization Including Carbon Monoxide

Carbon monoxide (CO) is a cheap and readily available “fundamental polar monomer” which can be used for the production of functional polymeric materials. Late-transition-metal-catalyzed alternating copolymerization of olefins with CO is one of the most efficient processes for producing γ-polyketones.[21−24] The perfect alternating nature of the γ-polyketone provides unique chemical and physical properties, including impermeability to hydrocarbons, strong rigidity, and high impact strength. Thus far, some olefin/CO copolymers have been produced industrially, for example, Carilon by Shell and Ketonex by BP.[223] In the following section, we describe recent developments of the coordination−insertion polymerization of olefins with CO to generate new types of polymeric materials: nonalternating copolymerization of olefins with CO in section 3.1 and copolymerization of functionalized olefins with CO in section 3.2. The alternating copolymerization of imines with CO is also of great interest because it provides novel methods for the synthesis of α-polypeptides. The development of the alternating copolymerization of imines with CO is described in section 3.3. Since the completely alternating copolymerization of nonpolar olefins with CO has already been widely reviewed,[21−24] it is not covered in this review.


33 34 35 36

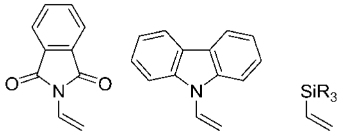

37 38 39

Figure 15. Other fundamental polar vinyl monomers.

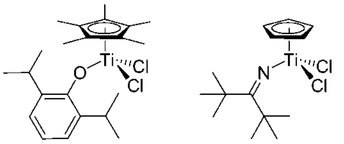

40 41

Figure 16. Titanium catalysts used for copolymerization of ethylene with trimethylvinylsilane and triethylvinylsilane.

3.1. Nonalternating Copolymerization of Ethylene with Carbon Monoxide

The transition-metal-catalyzed alternating copolymerization of ethylene with carbon monoxide has been widely investigated to produce a variety of γ-polyketones.[21−24] However, the resultant alternating γ-polyketone generally suffers from low processability due to its insolubility in common solvents and very high T_m (~260 °C), both of which are attributed to high crystallinity induced by dipolar interactions between carbonyl groups.[24f] Incorporation of a small amount of propylene in addition to ethylene is one solution to obtain a melt processable alternating ethylene/CO copolymer.[224] The problem of processability can be also avoided by reducing the CO content in the copolymer by producing nonalternating copolymers. Conventionally, the radical[225,226] process has been employed for the synthesis of such nonalternating copolymers; however, they generally provide branched polymers.

Despite numerous reports on the transition-metal-mediated copolymerization of ethylene and CO,[21−24] most of them afforded strictly alternating copolymers (Scheme 32). The alternating nature can be attributed to (i) formation of five-membered cationic palladacycle **K1**, which kinetically favors CO insertion over ethylene insertion to form six-membered chelate complex **K2**,[227,228] and (ii) thermodynamically disfavored double insertion of CO.[229] Nonalternating copolymers could be obtained if the ethylene is incorporated into the five-membered chelate complex **K1**. Until recently, however, there was no catalyst that provides nonalternating ethylene/CO copolymers. Even under high ethylene/CO ratio conditions, copolymerization produces exclusively error-free γ-polyketone until all the carbon monoxide is consumed.[21]

In 2002, Drent and Pugh et al. reported the first example of nonperfectly alternating copolymerization of ethylene with carbon monoxide via the coordination−insertion mechanism.[25] They showed that a mixture of $Pd(OAc)_2$ and a

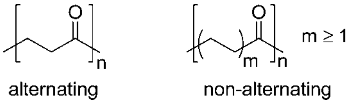


Figure 17. Alternating and nonalternating ethylene/CO copolymers.

phosphine–sulfonate ligand (**2c**, **2e**, **2f**) produced ethylene/CO nonalternating copolymers with CO contents of 42–49%. Since this discovery, many investigations have been performed based on phosphine–sulfonate ligands.[26–28,83,84] The Pd complexes bearing a phosphinoarylsulfonate (**2**) and a phosphinoalkylsulfonate (**3**) shown in Figure 18 were found to be active for nonalternating copolymerization in which the former complexes are more active than the latter ones.[28] The complexes (**2c**)Pd(CP-OEt) and (**2c**)Pd(Codyl*) exhibited catalytic activities as high as 100–600 gmmol^{-1} h^{-1} and molecular weights (M_n) of around 150 000.[26,28] It should be noted that polyethylene-block-poly(ethylene-*alt*-CO) can be also obtained because the Pd phosphine–sulfonate catalysts produce linear polyethylenes.[27]

The incorporation ratio of ethylene can be controlled by changing the reaction conditions. For example, the multiple insertion of ethylene is enhanced with an increase in the ethylene/CO ratio, although the catalytic activity is reduced.[25–27] Moreover, introduction of a bulkier *o*-alkoxy group or *o*-methyl group on the aryl substituent led to a significant increase in the amount of ethylene incorporation into the copolymer. Thus, it has been possible to produce nonalternating copolymers with as little as 10 mol % CO incorporation.[27] It should be noted that the multiple ethylene insertion decreased significantly when the ratio of the ligand and Pd was 2:1. Rieger et al. reported that the dimeric bisphosphine–sulfonate catalyst [P–O]Pd[P–O][26,28,68d] produced only a pure form of the alternating copolymers.[26]

The origin of the multiple ethylene units was investigated through experimental[28] and theoretical[83,84] studies (Scheme 33). Formation of multiple ethylene units can be understood as a result of ethylene insertion into the five-membered palladacycle **L1**. This insertion is facilitated because of the following two reasons. (i) The relative stability of chelate complexes **L1** over $\mathbf{L2}_{cis}$, $\mathbf{L2}_{trans}$, $\mathbf{L3}_{cis}$, and $\mathbf{L3}_{trans}$ is lower than those of the corresponding cationic complexes, since the back-donation from palladium to ethylene or CO is likely to be enhanced in the case of neutral Pd phosphine–sulfonate complexes.[83,84] Thus, opening the chelate structure of **L1** by ethylene becomes easier[28] as compared to the analogous cationic Pd systems.[230] (ii) The decarbonylation from Pd–acyl complexes bearing a phosphine–sulfonate ligand (**L4**) is more favorable than that from cationic Pd–acyl complexes bearing a dppp (**42**) ligand.[83,84] The facile decarbonylation could be attributed to the instability of the six-membered chelate structure (**L4**) arising from the relatively weak Pd–O chelate bond trans to the phosphorus atom. This is also supported by experimental results that formation of **L4** was not observed by NMR analyses.[28] Introduction of bulky substituents on the phosphorus atom of phosphine–sulfonate ligands also weaken the chelate structure of **L4** to promote decarbonylation followed by multiple ethylene insertion.[25] Regarding these two reasons, the concentrations of ethylene adducts $\mathbf{L2}_{cis}$ and $\mathbf{L2}_{trans}$ should be higher than those of the corresponding cationic complexes. As a result, ethylene insertion is facilitated because of the higher concentration of precursor $\mathbf{L2}_{trans}$.[231]

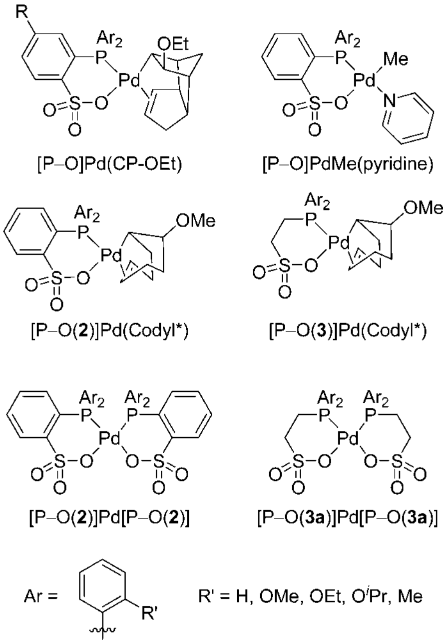
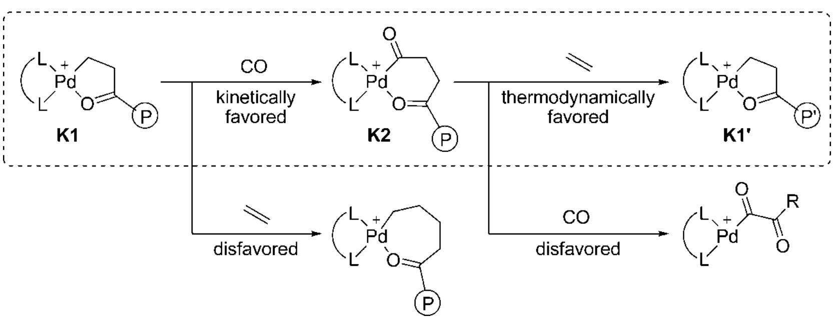


Figure 18. Catalysts employed for the nonalternating copolymerization of ethylene with carbon monoxide. CP-OEt = 5η^1-6-ethoxy-*exo*-5,6-dihydrodicyclopentadiene, Codyl* = 2-methoxy-cyclooct-5-enyl.

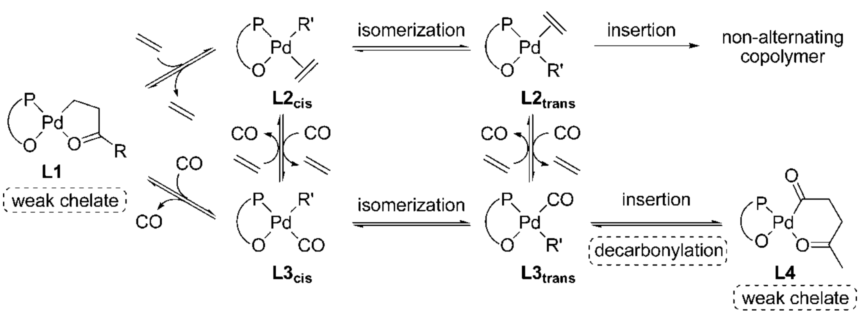
Recently, Bianchini et al. found that Pd(II) complexes bearing phosphanylferrocenecarboxylic acids (**43** and **44**) catalyzed the nonalternating copolymerization of ethylene with CO, albeit with low activities (~10 gmmol^{-1}), molecular weight (M_n up to 13 400), and ratio of adjacent ethylene units (CO content 48%) as compared to those by Pd phosphine–sulfonate catalysts.[232] It was suggested that the ligands worked as a monodentate phosphine to generate cationic Pd(II) catalysts in the presence of excess TsOH in MeOH.

The physical properties of the nonalternating ethylene/CO copolymers have been investigated. The melting points of ethylene/CO nonalternating copolymers were much lower

Scheme 32. Mechanism of the Alternating Copolymerization of Ethylene with Carbon Monoxide



Scheme 33. Plausible Explanations for Multiple Insertion of Ethylene[231]



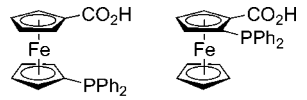
than those of perfectly alternating copolymers ($T_m \approx 260$ °C) and decreased with increasing multiple ethylene units. For example, copolymers with CO contents of 35%[26] and 10%[27] exhibited melting temperatures of 220 and 118 °C, respectively. This tendency could be attributed to the relatively weakened interactions between the polymer chains.

3.2. Copolymerization of Functionalized Olefins with Carbon Monoxide

Incorporation of additional functional groups into the alternating and nonalternating polyketones would expand the range of available materials. However, most reports on the copolymerization of olefins with CO have dealt with the olefins without any polar functionality. Recent progress in this field has enabled the synthesis of highly functionalized polyketones by the copolymerization of functionalized olefins with CO. In this section, two types of copolymerization are described: (1) copolymerization of olefins possessing a functional group at a remote position with CO and (2) copolymerization of fundamental polar vinyl monomers with CO.

There have been several reports on the copolymerization of functionalized olefins with carbon monoxide. Catalysts consisting of Pd and dppp (**42**) were found to catalyze the copolymerization of CO with various functionalized olefins such as methyl 10-undecenoate, 10-undecenoic acid, 10-undecenyl alcohol, 3-butenol,[233] and allylbenzene derivatives[234] as well as terpolymerizations of these functionalized olefins, nonpolar olefins, and CO.[233b,235] Highly functionalized olefins bearing benzo-15-crown ether, saccharide, amino acids, and steroids have been also employed for co- or terpolymerization.[236] Norbornene[237] and other bicyclic olefins[238] bearing ester groups have also been employed for copolymerization with CO catalyzed by Pd complex **45**. It should be noted that when oxabicyclic diene **46** was employed, copolymerization accompanied by the retro Diels–Alder reaction proceeded to produce poly(ketovinylene)s (Scheme 34).

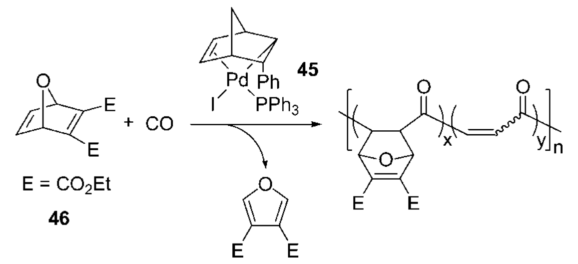
The asymmetric alternating copolymerization of olefin and CO has been achieved by using chiral ligands, (*R*,*R*)Me-DuPHOS (**47**) and (*R*,*S*)-BINAPHOS (**48**) (Figure 20). In the presence of palladium complexes bearing **47**, the functionalized olefins possessing hydroxy[239] and carboxy[239] groups as well as carbamates,[240] amides,[240] fluoroarenes,[241] and epoxides[242] (Figure 21) can be used as monomers for the asymmetric copolymerization with CO. Nozaki et al. reported that **48** was effective for olefins containing a perfluoroalkyl group[243] and *p*-chlorostyrene[244] (Figure 22).



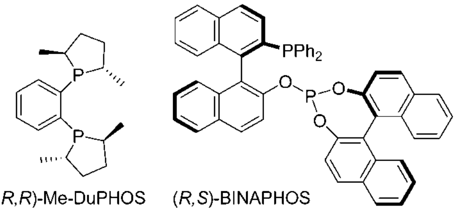
43 **44**

Figure 19. Ligands employed for the palladium-catalyzed nonalternating copolymerization of ethylene with carbon monoxide.

Scheme 34. Synthetic Route for the Perfectly Alternating Copolymer of Acetylene with CO



In contrast to the above-mentioned monomers, fundamental polar vinyl monomers whose polar group is directly attached to the olefin moiety are difficult to be copolymerized with CO.[245] Among many problems associated with metal-catalyzed copolymerization of polar vinyl monomers with CO, the most critical one is formation of chelate intermediates after insertion of vinyl monomers. It was reported that methyl acrylate,[166a,b,227a,b,246–251] methyl vinyl ketone,[247] vinyl acetate,[166a,b] vinyl chloride,[209] and ethyl vinyl ether[212a] can insert into cationic Pd–acyl bonds to give five-membered chelate intermediates with a polar group substituted at the α-position (**M1**); however, further insertion of the next monomers was not successful. The ligands employed for attempted copolymerization are summarized in Scheme 35. This could be attributed to the following three problems. (i) CO coordination may be suppressed by the strong intramolecular ketone coordination in **M1**. Jordan et al. found that the Cl-substituted complex (**M1**, FG = Cl) has a short Pd–C bond as well as a Pd–O bond.[209] This may suggest that the α-electron-withdrawing-group-substituted chelate structure is more stable than that of nonsubstituted chelate complexes, leading to a low tendency of **M1** to form a chelate-opened structure (**M2**). (ii) The low nucleophilicity of the α-carbon arising from the electron-withdrawing group in **M2** would be an obstacle for CO insertion. It is well known that



47 **48**

Figure 20. Ligands used for the asymmetric alternating copolymerization of olefin and CO.

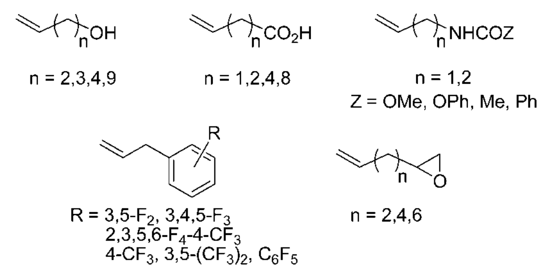


Figure 21. Functionalized olefins copolymerized with carbon monoxide by Pd complex bearing (*R*,*R*)-Me-DuPHOS **47**.

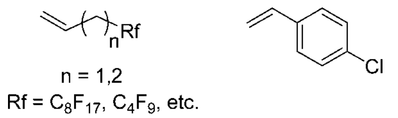
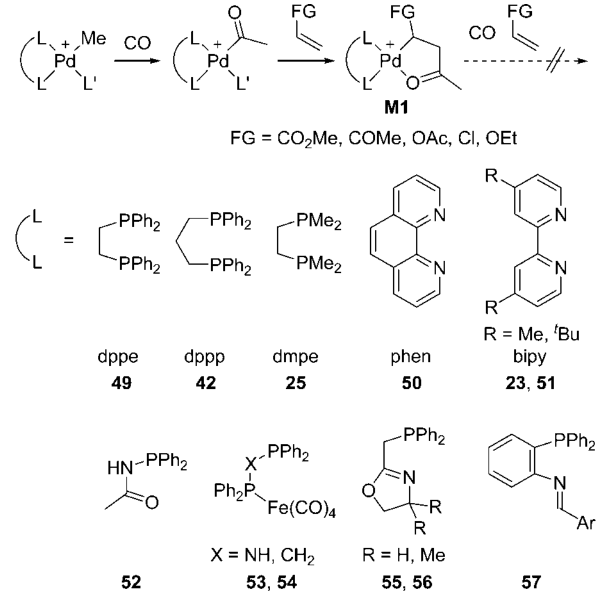


Figure 22. Functionalized olefins copolymerized with carbon monoxide by Pd complex bearing (*R*,*S*)-BINAPHOS **48**.

Scheme 35. Formation of Five-Membered Chelate Complexes by Insertion of Polar Vinyl Monomers into a Palladium−Acetyl Bond

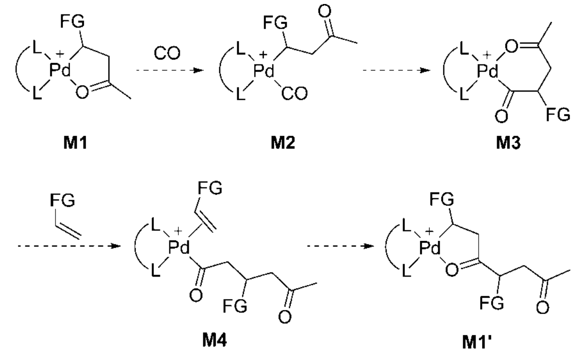


electron-withdrawing substituents retard CO insertion into M−alkyl and M−aryl bonds.[252,253] (iii) Formation of **M4** and **M1′** is retarded due to the low coordination−insertion ability of polar vinyl monomers (see also section 2.3).

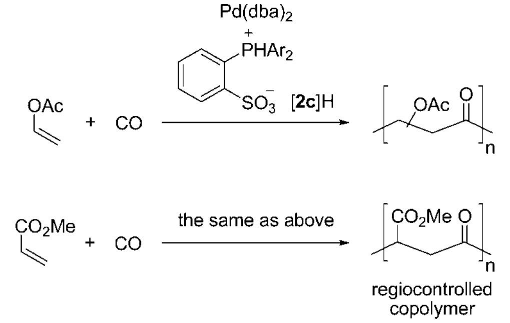
In 2007, Nozaki et al. reported that the mixture of Pd(dba)$_2$ and phosphonium−sulfonate (**2a**, **2c**) catalyzed the alternating copolymerization of vinyl acetate with CO.[29] The alternating structure of the obtained copolymers was unambiguously confirmed by NMR analyses and MALDI-TOF mass analysis. However, head-to-tail selectivity was found to be less controlled, which suggests that VAc insertion into the acyl−palladium bond may occur in both the 2,1- and 1,2-modes. The productivity was up to 3.0 gmmol^{-1} h^{-1}, and the molecular weight (M_n) was up to 38 000.

The alternating copolymerization of methyl acrylate with CO was also accomplished by using the same catalytic system.[30] The activity of MA/CO copolymerization (up to 4.4 gmmol^{-1} h^{-1}) and molecular weight (up to M_n = 30 000) of the copolymers were similar to those in the case of VAc/CO copolymerization, Scheme 37. The NMR studies revealed that the regiochemistry is strictly regulated, implying that insertion of MA into the acyl−palladium bond occurs only in the 2,1-insertion mode.

Scheme 36. Problems in the Copolymerization of Polar Vinyl Monomers with CO



Scheme 37. Alternating Copolymerization of Vinyl Acetate/CO and Methyl Acrylate/CO

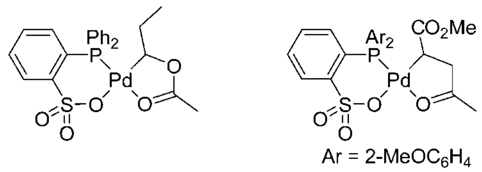


Some control experiments have suggested both copolymerizations[29,30] proceed via the coordination−insertion mechanism: (i) Chelate complexes **58** and **59**, which correspond to complex **F4** in Scheme 20 and **M1** in Schemes 35 and 36, also initiated and catalyzed the copolymerizations of VAc with CO and copolymerizations of MA with CO, respectively. The obtained copolymers had an initiating chain end arising from the catalysts, **58** and **59**, Figure 23. (ii) Addition of galvinoxyl hardly affected either the activity or the molecular weight of the obtained copolymer. (iii) The reaction initiated by AIBN afforded only poly(vinyl acetate) and poly(methyl acrylate).

3.3. Copolymerization of Imines with Carbon Monoxide

Polypeptides are the most ubiquitous biopolymers that have been used for a broad range of applications in materials, catalysis, and pharmaceuticals. For a long time, polypeptides have been synthesized from various amino acids, which requires multistep procedures for the preparation and subsequent activation using a stoichiometric amount of condensing agents to form peptide bonds.[254−256] In contrast, the alternating insertion of carbon monoxide and imines into metal−carbon bonds would provide a new general procedure for the synthesis of polypeptides. Since the reaction is analogous to olefin/CO copolymerization, the possibility for imine/CO copolymerization has been investigated by using palladium catalysts that have been widely used in olefin/CO copolymerization over the past decade.

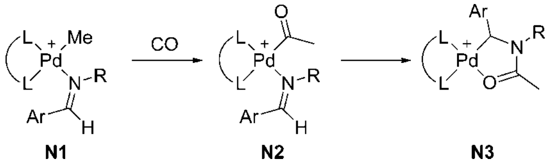
In 1998, Sen[257] and Arndtsen[258] independently reported the first observation of imine insertion into acyl palladium−carbon bonds (Scheme 38). By using diphosphine and bipyridine as ligands, they observed the coordination of the imine through its nitrogen atom (**N1**) and CO insertion into



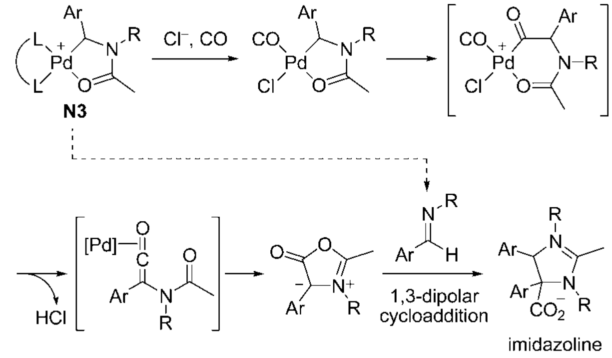
58 **59**

Figure 23. Catalysts used for copolymerization of polar vinyl monomers with CO.

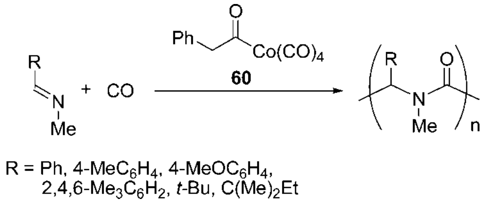
Scheme 38. Reactions of CO and Imines with a Pd—Me Complex



Scheme 39. Formation of Carboxylate-Substituted Imidazoline



Scheme 40. Alternating Copolymerization of Imines with Carbon Monoxide Catalyzed by Acylcobalt Complex 60



the Pd—Me bond to yield acylpalladium intermediate **N2**. Insertion of imine into the Pd—Me bond of **N1** did not occur. After formation of acylpalladium complex **N2**, imine insertion proceeded in a direction that can form an amide bond. The resulting complex **N3** possesses a square planar geometry with the carbonyl oxygen of the amide coordinating as a fourth ligand. Chelation of the carbonyl group is directly analogous to that observed in palladium-catalyzed olefin/CO copolymerization intermediates (**K1**). These observations are consistent with theoretical calculations, suggesting that insertion of an imine into acylpalladium proceeds through a four-membered-ring transition state that is similar to olefin insertion.[259]

Further incorporation of CO and imine to comlpex **N3** did not occur even at elevated temperature and pressure. This may be attributable to the strong chelation of the amide ligand in **N3** effectively blocking the coordination site required for coordination and insertion of CO. With the objective of breaking the strong chelate structure of **N3**, Arndtsen et al. investigated the use of chloride ions, which can coordinate to the palladium center (Scheme 39).[260] Rather unexpectedly, an imidazoline derivative was obtained in the presence of Cl anions under a CO atmosphere. It is suggested that CO was inserted into the Pd−C bond of **N3** followed by subsequent reactions including β-H elimination, cyclization, and 1,3-dipolar cycloaddition with imine that is formed from **N3**.

Other metals such as nickel[261] and manganese[262] have been investigated by Arndtsen et al. As in the case of Pd complexes, five-membered chelate complexes such as **N3** have been formed via reaction of alkylmetal complexes with CO and imines. Subsequent CO insertion into the five-membered chelate complex was observed in the case of manganese, and the resulting α-amido acyl complex was successfully characterized by X-ray crystallographic analysis. Cobalt complexes have also been investigated by Sen et al.[263] because they are one of the most frequently used metal catalysts for the carbonylative polymerization of azirizines.[264,265] However, reaction of *N*-alkylbenzaldimines with CO in the presence of $[Co(^{13}CH_3C(O))(CO)_3(P(o\text{-tol})_3)$ or $[Co_2(CO)_8]$ resulted in formation of *N*-alkylphthalimidines.[263]

In 2007, Sun et al. reported the first copolymerization of imines with CO using a Co catalyst (Scheme 40).[31] They found that an acylcobalt catalyst **60** effectively catalyzed the copolymerization of aldimines, ArCH=NMe with CO.[266] Copolymerization was performed in dioxane under 55 bar of CO pressure at 50 °C for 6 h to obtain the alternating copolymer with $M_n = 1900-4100$ in 73% yield. The alternating structure was confirmed by NMR and MS analyses. One end group is an acyl group, while the other end group is presumed to be an imidazoline skeleton similar to that obtained in Scheme 39. When *t*-BuCH=NMe was used, copolymers with high molecular weights M_n of up to 28 800 were obtained. The low polydispersity index (1.18) and linear change in the molecular weight with the monomer to catalyst ratio suggested that polymerization proceeded in a living fashion. They proposed a coordination−insertion mechanism in which imine insertion occurs via a four-centered transition state.[259] The unique properties of *N*- and *C*-disubstituted poly-α-peptides include good solubility in common organic solvents such as THF and chloroform and facile degradation by trifluoroacetic acid.[31]

4. Conclusions and Outlook

In this review, two topics regarding the transition-metal-catalyzed coordination−insertion copolymerization of fundamental polar monomers have been comprehensively reviewed: one is copolymerization of polar vinyl monomers with nonpolar olefins and the other is copolymerization of olefins and imines with carbon monoxide. The products thus obtained by the copolymerizations possess unique structures that have never been achieved by the conventional methods or required multistep synthesis.

Incorporation of a small amount of polar monomers to polyolefins endows additional physical and chemical properties depending on the polar functional groups. A variety of fundamental polar vinyl monomers, including methyl acrylate, methyl methacrylate, vinyl acetate, acrylonitrile, vinyl fluoride, and vinyl ethers, have been successfully incorporated into polyethylenes and other polyolefins. The microstructures of copolymers, including either linear or branched, can be well controlled by the appropriate choice of metal catalysts and/or ligands. Recent progress in the alternating copolymerization of olefins with carbon monoxide has enabled the synthesis of a completely novel class of materials. The nonalternating ethylene/CO copolymers may potentially find applications in the manufacture of engineering plastics or high-strength fibers. Although applications of copolymers consisting of polar vinyl monomers with CO have not yet been explored, further studies on their physical and chemical properties will lead to the development of functional polymers that exhibit truly novel properties. The chemistry has been extended to the alternating copolymerization of imines and CO to provide poly-α-peptides.

The polymeric materials obtained here are highly attractive from an industrial viewpoint; however, the catalytic activities that have thus far been achieved are not sufficient for industrialization. Therefore, one of the most important objectives is the improvement of catalytic activity for the copolymerization of fundamental polar monomers. Today's economical and environmental concerns induce another requirement for this chemistry. Despite the remarkable progress described in this review, most methods have been based on the use of palladium as a catalyst. Thus, replacement of such a precious metal by less expensive and ubiquitous metals such as iron and titanium constitutes significant future challenges. Alongside further progress regarding the catalysts, the physical and chemical properties of the new materials will be extensively investigated since the potential performance of them has not yet been completely revealed. Finally, the most challenging objective may be incorporation of polar functional groups into isotactic polypropylene. Production of isotactic polypropylene is realized by continuous 1,2- or 2,1-insertion of propylene when early-transition-metal catalysts are employed. On the other hand, propylene tends to be incorporated into a polymer chain as a $-CH_2CH_2CH_2-$ unit via β-H elimination and reinsertion (i.e., 1,3-insertion) with late-transition-metal catalysts. This 1,3-insertion should be avoided for synthesizing functionalized isotactic polypropylene. In order to achieve the goal, it may be necessary to develop a completely novel design of catalysts.

5. Abbreviations

alt	alternating
AN	acrylonitrile
Ar^F	3,5-bis(trifluoromethyl)phenyl
DFT	density functional theory
FG	functional group
HDPE	high-density polyethylene
MA	methyl acrylate
MAO	methylaluminoxane
MMA	methyl methacrylate
MMAO	modified methylaluminoxane
M_n	number-average molecular weight
M_w	weight-average molecular weight
ROMP	ring-opening metathesis polymerization
SHOP	Shell higher olefin process
T_m	melting temperature
VAc	vinyl acetate
VC	vinyl chloride
VE	vinyl ether
VF	vinyl fluoride

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7. References

(1) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.

(2) Bamford, C. H. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1986; Vol. 13, p 708.

(3) Recent examples of coordination−insertion polymerization of olefins containing functional groups with some spacers, see: (a) Imuta, J.; Kashiwa, N.; Toda, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1176. (b) Liu, W. J.; Malinoski, J. M.; Brookhart, M. *Organometallics* **2002**, *21*, 2836. (c) Chen, G.; Ma, X. S.; Guan, Z. *J. Am. Chem. Soc.* **2003**, *125*, 6697. (d) Park, S.; Takeuchi, D.; Osakada, K. *J. Am. Chem. Soc.* **2006**, *128*, 3510. (e) Li, W.; Zhang, X.; Meetsma, A.; Hessen, B. *Organometallics* **2008**, *27*, 2052. (f) Terao, H.; Ishii, S.; Mitani, M.; Tanaka, H.; Fujita, T. *J. Am. Chem. Soc.* **2008**, *130*, 17636.

(4) (a) Kuhn, P.; Sémeril, D.; Matt, D.; Chetcuti, M. J.; Lutz, P. *Dalton Trans.* **2007**, 515. (b) Skupinska, J. *Chem. Rev.* **1991**, *91*, 613.

(5) (a) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123. (b) Klabunde, U.; Mulhaupt, R.; Herskovitz, T.; Janowicz, A. H.; Calabrese, J.; Ittel, S. D. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, *25*, 1989.

(6) (a) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149. (b) Younkin, T. R.; Conner, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460. (c) Chan, M. S. W.; Deng, L.; Ziegler, T. *Organometallics* **2000**, *19*, 2741. (d) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Hwang, S.; Grubbs, R. H.; Roberts, W. P.; Litzau, J. J. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 2842. (e) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Waltman, A. W.; Grubbs, R. H. *Chem. Commun.* **2003**, 2272. (f) Waltman, A. W.; Younkin, T. R.; Grubbs, R. H. *Organometallics* **2004**, *23*, 5121.

(7) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.

(8) (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.

(9) Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *128*, 12072.

(10) (a) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744. (b) Drent, E.; Pello, D. H.; Jager, W. W. Eur. Pat. Appl. 0,589,527, Mar 30, 1994.

(11) Kochi, T.; Yoshimura, K.; Nozaki, K. *Dalton Trans.* **2006**, 25.

(12) Skupov, K. M.; Marella, P. R.; Simard, M.; Yap, G. P. A.; Allen, N.; Conner, D.; Goodall, B. L.; Claverie, J. P. *Macromol. Rapid Commun.* **2007**, *28*, 2033.

(13) Guironnet, D.; Roesle, P.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 422.

(14) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, in press (DOI: 10.1021/ja9050839).

(15) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948.

(16) Weng, W.; Shen, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 15450.

(17) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 8946.

(18) Skupov, K. M.; Piche, L.; Claverie, J. P. *Macromolecules* **2008**, *41*, 2309.

(19) Borkar, S.; Newsham, D. K.; Sen, A. *Organometallics* **2008**, *27*, 3331.

(20) Reppe, W.; Magin, A. U.S. Patent 2,577,208, Dec 4, 1951. A patent literature reporting the first copolymerization of ethylene with CO was submitted in 1941 and published in 1953, see: Ballauf, F.; Bayer, O.; Leichmann, L. DE 863, 711, Jan 19, 1953.

(21) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.

(22) Bianchini, C.; Meli, A. *Coord. Chem. Rev.* **2002**, *225*, 35.

(23) *Catalytic Synthesis of Alkene-Carbon Monoxide Copolymers and Cooligomers*; Sen, A., Ed.; Kluwer Academic Publishers: Dordrecht, 2003.

(24) García Suárez, E. J.; Godard, C.; Ruiz, A.; Claver, C. *Eur. J. Inorg. Chem.* **2007**, 2582. (b) Bianchini, C.; Meli, A.; Oberhauser, W. *Dalton Trans.* **2003**, 2627. (c) Robertson, R. A. M.; Cole-Hamilton, D. J. *Coord. Chem. Rev.* **2002**, *225*, 67. (d) Nozaki, K.; Hiyama, T. *J. Organomet. Chem.* **1999**, *576*, 248. (e) Abu-Surrah, A. S.; Rieger, B. *Top. Catal.* **1999**, *7*, 165. (f) Sommazzi, A.; Garbassi, F. *Prog. Polym. Sci.* **1997**, *22*, 1547–1605. (g) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303.

(25) (a) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 964. (b) Drent, E.; Pello, D. H. L. Eur. Pat. Appl. 0,632,084, Jan 4, 1995.

(26) Hearley, A. K.; Nowack, R. J.; Rieger, B. *Organometallics* **2005**, *24*, 2755.

(27) Newsham, D. K.; Borkar, S.; Sen, A.; Conner, D. M.; Goodall, B. L. *Organometallics* **2007**, *26*, 3636.

(28) Bettucci, L.; Bianchini, C.; Claver, C.; Suarez, E. J. G.; Ruiz, A.; Meli, A.; Oberhauser, W. *Dalton Trans.* **2007**, 5590.

(29) Kochi, T.; Nakamura, A.; Ida, H.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 7770.

(30) Nakamura, A.; Munakata, K.; Kochi, T.; Nozaki, K. *J. Am. Chem. Soc.* **2008**, *130*, 8128.

(31) Sun, H.; Zhang, J.; Liu, Q.; Yu, L.; Zhao, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 6068.

(32) (a) Cossee, P. *J. Catal.* **1964**, *3*, 80. (b) Arlman, E. J.; Cossee, P. *J. Catal.* **1964**, *3*, 99.

(33) Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1967**, *89*, 5989.

(34) (a) Yamamoto, A.; Yamamoto, T. *J. Polym. Sci., Macromol. Rev.* **1978**, *13*, 161. (b) Yamamoto, A. *J. Organomet. Chem.* **1986**, *300*, 347. (c) Yamamoto, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1027, and references cited therein.

(35) (a) Schaper, F.; Foley, S. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2004**, *126*, 2114. (b) Yang, P.; Chan, B. C. K.; Baird, M. C. *Organometallics* **2004**, *23*, 2752.

(36) Chung, T. C. *Functionalization of Polyolefins*; Academic Press: London, 2002.

(37) *Functional Polymers: Modern Synthetic Methods and Novel Structures*; Patil, A. O., Schulz, D. N., Novak, B. M., Eds.; ACS Symposium Series 704; American Chemical Society: Washington, DC, 1998.

(38) Dong, J. Y.; Hu, Y. L. *Coord. Chem. Rev.* **2006**, *250*, 47.

(39) (a) Padwa, A. R. *Prog. Polym. Sci.* **1989**, *14*, 811. (b) Patil, A. O. *Chem. Innovation* **2000**, *30*, 19. (c) Yanjarappa, M. J.; Sivaram, S. *Prog. Polym. Sci.* **2002**, *27*, 1347. (d) Nomura, K.; Kitiyanan, B. *Curr. Org. Synth.* **2008**, *5*, 217.

(40) For example, see: Novák, I.; Borsig, E.; Hrèková, L.; Fiedlerová, A.; Kleinová, A.; Pollák, V. *Polym. Eng. Sci.* **2007**, *47*, 1207.

(41) Chung, T. C. *Prog. Polym. Sci.* **2002**, *27*, 39.

(42) Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714.

(43) Amin, S. B.; Marks, T. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 2006.

(44) (a) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (b) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689.

(45) Beach, D. L.; Kissin, Y. V. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1986; Vol. 6, p 383.

(46) (a) Kissin, Y. V. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I., Howe-Grant, M., Eds.; Wiley-Interscience: New York, 1996; Vol. 17, p 702. (b) Kotz, J. *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, 1996; Vol. 8, pp 5953, 6424.

(47) Whiteley, K. S.; Heggs, T. G.; Koch, H.; Mawer, R. L. Immel, W. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. 28, p 393.

(48) For spectral analysis of polyethylene microstructures, see: Galland, G. B.; de Souza, R. F.; Mauler, R. S.; Nunes, F. F. *Macromolecules* **1999**, *32*, 1620.

(49) Boaen, N. K.; Hillmyer, M. A. *Chem. Soc. Rev.* **2005**, *34*, 267.

(50) Wu, S.; Zhang, J.; Xu, X. *Polym. Int.* **2003**, *52*, 1527.

(51) Recently, catalytic functionalization methods have been also reported. For example, see: Bae, C.; Hartwig, J. F.; Harris, N. K. B.; Long, R. O.; Anderson, K. S.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2005**, *127*, 767. See also ref 49.

(52) (a) Lehman, S. E., Jr.; Wagener, K. B.; Baugh, L. S.; Rucker, S. P.; Schulz, D. N.; Varma-Nair, M.; Berluche, E. *Macromolecules* **2007**, *40*, 2643. (b) Yang, H.; Islam, M.; Budde, C.; Rowan, S. J. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2107. (c) Hillmyer, M. A.; Laredo, W. R; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311.

(53) (a) Boz, E.; Ghiviriga, I.; Nemeth, A. J.; Jeon, K.; Alamo, R. G.; Wagener, K. B. *Macromolecules* **2008**, *41*, 25. (b) Boz, E.; Nemeth, A. J.; Ghiviriga, I.; Jeon, K.; Alamo, R. G.; Wagener, K. B. *Macromolecules* **2007**, *40*, 6545. (c) Boz, E.; Nemeth, A. J.; Alamo, R. G.; Wagener, K. B. *Adv. Synth. Catal.* **2007**, *349*, 137. (d) Boz, E.; Wagener, K. B.; Ghosal, A.; Fu, R. Q.; Alamo, R. G. *Macromolecules* **2006**, *39*, 4437.

(54) (a) Berkefeld, A.; Mecking, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 2538. (b) Nozaki, K.; Magro, A. A. N. *Chim. Oggi* **2008**, *26*, 54. (c) Sen, A.; Borkar, S. *J. Organomet. Chem.* **2007**, *692*, 3291.

(55) (a) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, *67*, 426. (b) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, *67*, 541. (c) Natta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708.

(56) (a) *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H. H., Eds.; Springer: Berlin, 1995. (b) Mülhaupt, R. *Macromol. Chem. Phys.* **2003**, *204*, 289.

(57) (a) Alt, H. G.; Koppl, A. *Chem. Rev.* **2000**, *100*, 1205. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (c) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413. (d) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (e) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(58) (a) Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, *250*, 2691. (b) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587.

(59) (a) Matsugi, T.; Fujita, T. *Chem. Soc. Rev.* **2008**, *37*, 1264. (b) Mitani, M.; Saito, J.; Ishii, S. I.; Nakayama, Y.; Makio, H.; Matsukawa, N.; Matsui, S.; Mohri, J. I.; Furuyama, R.; Terao, H.; Bando, H.; Tanaka, H.; Fujita, T. *Chem. Rec.* **2004**, *4*, 137. (c) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (d) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

(60) *Beyond Metallocenes: Next-Generation Polymerization Catalysts*; Patil, A. O., Hlatky, G. G., Eds.; ACS Symposium Series 857; American Chemical Society: Washington, DC, 2003.

(61) Goodall, B. L. *Late Transition Metal Polymerization Catalysis*; Rieger, B., Baugh, L. S., Katcker, S., Striegler, S., Eds.; Wiley-VCH: Weinheim, 2003.

(62) (a) Gibson, V. C.; Redshaw, C.; Solan, G. A. *Chem. Rev.* **2007**, *107*, 1745. (b) Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 534. (c) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325.

(63) For mechanistic investigations published after 2000, see: (a) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. (b) Shultz, L. H.; Tempel, D. J.; Brookhart, M. *J. Am. Chem. Soc.* **2001**, *123*, 11539. (c) Leatherman, M. D.; Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 3068.

(64) (a) Guan, Z. *Chem.—Eur. J.* **2002**, *8*, 3087. (b) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059.

(65) For Ni catalysts, dissociative and β-hydride transfer pathways were proposed; see refs 7 and 63c.

(66) (a) Johnson, L.; Bennett, A.; Dobbs, K.; Hauptman, E.; Ionkin, A.; Ittel, S.; McCord, E.; McLain, S.; Radzewich, C.; Yin, Z.; Wang, L.; Wang, Y.; Brookhart, M. *Polym. Mater. Sci. Eng.* **2002**, *86*, 319. (b) McLain, S. J.; Sweetman, K. J.; Johnson, L. K.; McCord, E. *Polym. Mater. Sci. Eng.* **2002**, *86*, 320.

(67) Bitterer, F.; Herd, O.; Hessler, A.; Kühnel, M.; Rettig, K.; Stelzer, O.; Sheldrick, W. S.; Nagel, S.; Rösch, N. *Inorg. Chem.* **1996**, *35*, 4103, and references cited therein.

(68) (a) Mirza, A. R.; Anson, M. S.; Hellgardt, K.; Leese, M. P.; Thompson, D. F.; Tonks, L.; Williams, J. M. J. *Org. Process Res. Dev.* **1998**, *2*, 325. (b) Canipelle, M.; Caron, L.; Christine, C.; Tilloy, S.; Monflier, E. *Carbohydr. Res.* **2002**, *337*, 281. (c) Saoud, M.; Romerosa, A.; Carpio, S. M.; Gonsalvi, L.; Peruzzini, M. *Eur. J. Inorg. Chem.* **2003**, 1614. (d) Schultz, T.; Pfaltz, A. *Synthesis* **2005**, 1005. (e) García Suárez, E. J.; Ruiz, A.; Castillón, S.; Oberhauser, W.; Bianchini, C.; Claver, C. *Dalton Trans.* **2007**, 2859. (f) Bettucci, L.; Bianchini, C.; Meli, A.; Oberhauser, W. *J. Mol. Catal. A: Chem.* **2008**, *291*, 57.

(69) Phosphine—phosphinate ligands were also synthesized recently, see: Reisinger, C. M.; Nowack, R. J.; Volkmer, D.; Rieger, B. *Dalton Trans.* **2007**, 272.

(70) Murray, R. E. U.S. Patent 4,689,437, Aug 25, 1987.

(71) (a) van Doorn, J. A.; Drent, E.; van Leeuwen, P. W. N. M.; Meijboon, N.; van Oort, A. B.; Wife, R. L. Eur. Pat. Appl. 0,280,380, Aug 31, 1988. (b) Bradford, A. M.; van Leeuwen, P. W. N. M.; Wullink-Schelvis, A. M. WO Patent Application 9324553, Dec 9, 1993. (c) Drent, E.; Pello, D. H. L. Eur. Pat. Appl. 0,731,126, Sep 11, 1996. (d) Drent, E.; Sjardijn, W.; Suykerbuyk, J.; Wanninger, K. WO 0,006,615, Feb 10, 2000.

(72) (a) Shen, H.; Goodall, B. L. U.S. Patent 2006, 270,811, Nov 30, 2006. (b) Allen, N. T.; Goodall, B. L.; Mcintosh, L. H. U.S. Patent 2007, 049,712, Mar 1, 2007. (c) Allen, N. T.; Goodall, B. L.; McIntosh, L. H. Eur. Pat. Appl. 1,760,086, Mar 7, 2007. (d) Allen, N. T.; Goodall, B. L.; Kirk, T. C.; McIntosh, L. H. Can. Pat. Appl. 2,556,356, Feb 28, 2007. (e) Acholla, F. V.; Goodall, B. L.; Mcintosh, L. H.; Shen, H. U.S. Patent 2008, 207,789, Aug 28, 2008. (f) Conner, D. M.; Goodall, B. L.; McIntosh, L. H. U.S. Patent 2008, 207,854, Aug 28, 2008. (g) Conner, D. M.; Goodall, B. L.; McIntosh, L. H. U.S. Patent 2008, 207,855, Aug 28, 2008. (h) Goodall, B. L.; Kirk, T. C.; McIntosh, L. H. U.S. Patent 2008, 207,856, Aug 28, 2008.

(73) (a) Brandvold, T. A. U.S. Patent 5,760,286, Jun 2, 1998. (b) Takagi, M. Jpn. Kokai Tokkyo Koho 2003, 292,539, Oct 15, 2003. (c) Takagi, M.; Ono, K. Jpn. Kokai Tokkyo Koho 2003, 268,028, Sep 25, 2003. (d) Nozaki, K.; Kochi, T.; Ida, H. Jpn. Kokai Tokkyo Koho 2007, 046,032, Feb 22, 2007.

(74) Liu, S.; Borkar, S.; Newsham, D.; Yennawar, H.; Sen, A. *Organometallics* **2007**, *26*, 210.

(75) For the first example of X-ray analysis of *o*-TPPMS in an oxide form, see: Kathó, Á.; Bényei, A. C.; Joó, F.; Sági, M. *Adv. Synth. Catal.* **2002**, *344*, 278.

(76) Pestovsky, O.; Shuff, A.; Bakac, A. *Organometallics* **2006**, *25*, 2894.

(77) Vela, J.; Lief, G. R.; Shen, Z.; Jordan, R. F. *Organometallics* **2007**, *26*, 6624.

(78) For reviews of the activators used for the synthesis of polyolefins, see: (a) Anselment, T. M. J.; Vagin, S. I.; Rieger, B. *Dalton Trans.* **2008**, 4537. (b) Po, R.; Fiocca, L.; Cardi, N.; Simone, F.; Cardaci, M. A.; Spera, S.; Salvalaggio, M. *Polym. Bull.* **2006**, *56*, 101. (c) Chen, E. Y. X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

(79) Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K. Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14088.

(80) A few examples of Pd catalysts that are capable of producing linear polyethylenes require activators such as MAO, see: (a) Tsuji, S.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1999**, *18*, 4758. (b) Li, K.; Darkwa, J.; Guzei, I. A.; Mapolie, S. F. *J. Organomet. Chem.* **2002**, *660*, 108. (c) Mohlala, M. S.; Guzei, I. A.; Darkwa, J.; Mapolie, S. F. *J. Mol. Catal. A: Chem.* **2005**, *241*, 93. (d) Chen, R.; Mapolie, S. F. *J. Mol. Catal. A: Chem.* **2003**, *193*, 33.

(81) Among the late transition metal catalysts, the first-row transition metal such as Ni, Fe, and Co were used to obtain linear polyethylenes; see refs 4, 6, and 62a.

(82) Haras, A.; Anderson, G. D. W.; Michalak, A.; Rieger, B.; Ziegler, T. *Organometallics* **2006**, *25*, 4491.

(83) Haras, A.; Michalak, A.; Rieger, B.; Ziegler, T. *J. Am. Chem. Soc.* **2005**, *127*, 8765.

(84) Haras, A.; Michalak, A.; Rieger, B.; Ziegler, T. *Organometallics* **2006**, *25*, 946.

(85) The cis/trans isomerization can proceed via a pentacoordinated structure similar to that involved in the Berry's pseudorotation, in which the second oxygen atom of the sulfonate group is involved as an associative ligand; see ref 79.

(86) For the copolymerization of ethylene with nonpolar olefins such as vinylcyclohexane and styrene derivatives, see refs 19 and 77.

(87) Claverie, J. P.; Goodall, B. L.; Skupov, K. M.; Marella, P. R.; Hobbs, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2007**, *48*, 191.

(88) Skupov, K. M.; Marella, P. R.; Hobbs, J. L.; McIntosh, L. H.; Goodall, B. L.; Claverie, J. P. *Macromolecules* **2006**, *39*, 4279.

(89) Nowack, R. J.; Hearley, A. K.; Rieger, B. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2775.

(90) Zhou, X.; Bontemps, S.; Jordan, R. F. *Organometallics* **2008**, *27*, 4821.

(91) Guironnet, D.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. *Chem. Commun.* **2008**, 4965.

(92) Noda, S.; Kochi, T.; Nozaki, K. *Organometallics* **2009**, *28*, 656.

(93) Nakamura, A.; Chung, L. W.; Morokuma, K.; Nozaki, K. Unpublished results. It should be noted that these values are sensitive to the computational methods and basis sets. See also ref 96.

(94) Both LUMO and LUMO+1 orbitals of vinyl acetate comprise contributions from C=C and C=O. The LUMO is polarlized toward C=O and LUMO+1 toward the C=C bond. See also ref 126.

(95) von Schenck, H.; Strömberg, S.; Zetterberg, K.; Ludwig, M.; Åkermark, B.; Svensson, M. *Organometallics* **2001**, *20*, 2813.

(96) Szabo, M. J.; Jordan, R. F.; Michalak, A.; Piers, W. E.; Weiss, T.; Yang, S. Y.; Ziegler, T. *Organometallics* **2004**, *23*, 5565.

(97) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436, and references cited therein.

(98) (a) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670. (b) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134.

(99) Halpern, J.; Okamoto, T. *Inorg. Chim. Acta* **1984**, *89*, L53.

(100) Philipp, D. M.; Muller, R. P.; Goddard, W. A., III; Storer, J.; McAdon, M.; Mullins, M. *J. Am. Chem. Soc.* **2002**, *124*, 10198.

(101) Kang, M.; Sen, A.; Zakharov, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 12080.

(102) (a) Strazisar, S. A.; Wolczanski, P. T. *J. Am. Chem. Soc.* **2001**, *123*, 4728. (b) Cundari, T. R.; Taylor, C. D. *Organometallics* **2003**, *22*, 4047.

(103) (a) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146. (b) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009.

(104) Michalak, A.; Ziegler, T. *J. Am. Chem. Soc.* **2001**, *123*, 12266.

(105) Deubel, D. V.; Ziegler, T. *Organometallics* **2002**, *21*, 4432.

(106) (a) Yu, J.; Spencer, J. B. *J. Am. Chem. Soc.* **1997**, *119*, 5257. For an example of 1,2-insertion of MA into the Pd–H bond, see: (b) Drent, E.; Budzelaar, P. H. M. *J. Organomet. Chem.* **2000**, *594*, 211. Drent, E.; Budzelaar, P. H. M. *J. Organomet. Chem.* **2000**, *594*, 211.

(107) Haddleton, D. M.; Clark, A. J.; Crossman, M. C.; Duncalf, D. J.; Heming, A. M.; Morsley, S. R.; Shooter, A. J. *Chem. Commun.* **1997**, 1173.

(108) Albéniz, A. C.; Espinet, P.; López-Fernández, R.; Sen, A. *J. Am. Chem. Soc.* **2002**, *124*, 11278.

(109) Nagel, M.; Paxton, W. F.; Sen, A.; Zakharov, L.; Rheingold, A. L. *Macromolecules* **2004**, *37*, 9305.

(110) There are many reports of the copolymerization of fundamental polar monomers without sufficient supporting experimental data to confirm the coordination–insertion mechanism. In this review, however, all examples that are considered to be the coordination–insertion copolymerization of fundamental polar monomers are described.

(111) Kine, B. B.; Novak, R. B. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1986; Vol. 1, p 234.

(112) Kissin, Y. V. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I., Howe-Grant, M., Eds.; Wiley-Interscience: New York, 1996; Vol. 1, p 314.

(113) For spectral analysis of poly(methyl acrylate) microstructures, see: (a) Kawamura, T.; Toshima, N.; Matsuzaki, K. *Macromol. Chem. Phys.* **1995**, *196*, 3415. (b) Brar, A. S.; Kumar, R.; Kaur, M. *Appl. Spectrosc.* **2002**, *56*, 1380.

(114) Liu, S.; Sen, A. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6175.

(115) Cunningham, I. D.; Fassihi, K. *J. Mol. Catal. A: Chem.* **2005**, *232*, 187, and references cited therein.

(116) Sun, H. S.; Burlakov, V. V.; Spannenberg, A.; Baumann, W.; Arndt, P.; Rosenthal, U. *Organometallics* **2002**, *21*, 3360.

(117) Tian, G.; Boone, H. W.; Novak, B. M. *Macromolecules* **2001**, *34*, 7656.

(118) Heinemann, J.; Mülhaupt, R.; Brinkmann, P.; Luinstra, G. *Macromol. Chem. Phys.* **1999**, *200*, 384.

(119) Meneghetti, S. P.; Kress, J.; Lutz, P. J. *Macromol. Chem. Phys.* **2000**, *201*, 1823.

(120) Popeney, C. S.; Camacho, D. H.; Guan, Z. *J. Am. Chem. Soc.* **2007**, *129*, 10062.

(121) Michalak, A.; Ziegler, T. *Organometallics* **2003**, *22*, 2660.

(122) Polyolefins possessing MA units at the chain end can be prepared by using this phenomenon, see: Gottfried, A. C.; Brookhart, M. *Macromolecules* **2003**, *36*, 3085.

(123) For example, see: (a) Tian, G.; Boone, H. W.; Novak, B. M. *Macromolecules* **2001**, *34*, 7656. (b) Kang, M.; Sen, A. *Organometallics* **2005**, *24*, 3508.

(124) (a) Hennis, A. D.; Hilt, D. C.; Kacker, S.; Sen, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 412. (b) Hennis, A. D.; Sen, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41*, 1383.

(125) Szuromi, E.; Shen, H.; Goodall, B. L.; Jordan, R. F. *Organometallics* **2008**, *27*, 402.

(126) Michalak, A.; Ziegler, T. *Organometallics* **2001**, *20*, 1521.

(127) Elia, C.; Elyashiv-Barad, S.; Sen, A.; López-Fernández, R.; Albéniz, A. C.; Espinet, P. *Organometallics* **2002**, *21*, 4249.

(128) Albéniz, A. C.; Espinet, P.; López-Fernández, R. *Organometallics* **2003**, *22*, 4206.

(129) Nagel, M.; Sen, A. *Organometallics* **2006**, *25*, 4722.

(130) Suzuki, Y.; Hayashi, T. Jpn. Kokai Tokkyo Koho 11292918, Oct 26, 1999.

(131) Ziegler et al. explained that the difference mainly arises from a steric reason rather than the orbital interaction to the metal center as far as a comparison between the two binding modes (*O*-bound or π-bound) of these Ni and Pd α-diimine complexes is concerned; see ref 126.

(132) Mitoraj, M.; Michalak, A. *J. Mol. Model.* **2005**, *11*, 341.

(133) Michalak, A.; Ziegler, T. *Organometallics* **2003**, *22*, 2069.

(134) Wang, L.; Hauptman, E.; Johnson, L. K.; Marshall, W. J.; McCord, E. F.; Wang, Y.; Ittel, S. D.; Radzewich, C. E.; Kunitsky, K.; Ionkin, A. S. *Polym. Mater. Sci. Eng.* **2002**, *86*, 322.

(135) (a) Wang, L.; Hauptman, E.; Johnson, L. K.; McCord, E. F.; Wang, Y.; Ittel, S. D. WO 0,192,342, Dec 6, 2001. (b) Wang, L.; Johnson, L. K.; Ionkin, A. S. WO 0,192,348, Dec 6, 2001.

(136) Brasse, M.; Cámpora, J.; Palma, P.; Alvarez, E.; Cruz, V.; Ramos, J.; Reyes, M. L. *Organometallics* **2008**, *27*, 4711.

(137) Berkefeld, A.; Drexler, M.; Möller, H. M.; Mecking, S. *J. Am. Chem. Soc.* **2009**, *131*, 12613.

(138) Rodriguez, B. A.; Delferro, M.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5902.

(139) Britovsek, G. J. P.; Gibson, V. C.; Spitzmesser, S. K.; Tellmann, K. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 1159.

(140) (a) Stibrany, R. T.; Schulz, D. N.; Kacker, S.; Patil, A. O.; Baugh, L. S.; Rucker, S. P.; Zushma, S.; Berluche, E.; Sissano, J. A. *Polym. Mater. Sci. Eng.* **2002**, *86*, 325. (b) Stibrany, R. T.; Schulz, D. N.; Kacker, S.; Patil, A. O.; Baugh, L. S.; Rucker, S. P.; Zushma, S.; Berluche, E.; Sissano, J. A. *Macromolecules* **2003**, *36*, 8584. (c) Baugh, L. S.; Sissano, J. A.; Kacker, S.; Berluche, E.; Stibrany, R. T.; Schulz, D. N.; Rucker, S. P. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1817.

(141) Olson, J. A.; Boyd, R.; Quail, J. W.; Foley, S. R. *Organometallics* **2008**, *27*, 5333.

(142) Stickler, M.; Rhein, T. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. *28*, p 377.

(143) For spectral analysis of poly(methyl methacrylate) microstructures, see: Brar, A. S.; Singh, G.; Shankar, R. *J. Mol. Struct.* **2004**, *703*, 69, and refereces cited therein.

(144) Hatada, K.; Kitayama, K.; Ute, T. *Prog. Polym. Sci.* **1988**, *13*, 189.

(145) (a) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473. (b) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.

(146) (a) Desurmont, G.; Tanaka, M.; Li, Y.; Yasuda, H.; Tokimitsu, T.; Tone, S.; Yanagase, A. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4095. (b) Yasuda, H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1955. (c) Yasuda, H. *J. Organomet. Chem.* **2002**, *647*, 128.

(147) Jensen, T. R.; Yoon, S. C.; Dash, A. K.; Luo, L.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14482.

(148) (a) Matyjaszewski, K. *Macromol. Symp.* **1998**, *134*, 105. (b) Matyjaszewski, K. *Macromol. Symp.* **1998**, *132*, 85. (c) Sawamoto, M.; Kamigaito, M. *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 1803.

(149) (a) Marques, M. M.; Fernandes, S.; Correia, S. G.; Ascenso, J. R.; Caroço, S.; Gomes, P. T.; Mano, J.; Pereira, S. G.; Nunes, T.; Dias, A. R.; Rausch, M. D.; Chien, J. C. W. *Macromol. Chem. Phys.* **2000**, *201*, 2464. (b) Marques, M. M.; Fernandes, S.; Correia, S. G.; Caroço, S.; Gomes, P. T.; Dias, A. R.; Mano, J.; Rausch, M. D.; Chien, J. C. W. *Polym. Int.* **2001**, *50*, 579. (c) Chien, J. C. W.; Fernandes, S.; Correia, S. G.; Rausch, M. D.; Dickson, L. C.; Marques, M. M. *Polym. Int.* **2002**, *51*, 729. (d) Fernandes, S.; Ascenso, J. R.; Gomes, P. T.; Costa, S. I.; Silva, L. C.; Chien, J. C. W.; Marques, M. M. *Polym. Int.* **2005**, *54*, 249.

(150) Borkar, S.; Yennawar, H.; Sen, A. *Organometallics* **2007**, *26*, 4711.

(151) Gibson, V. C.; Tomov, A. *Chem. Commun.* **2001**, 1964.

(152) (a) Carlini, C.; Martinelli, M.; Galletti, A. M. R.; Sbrana, G. *Macromol. Chem. Phys.* **2002**, *203*, 1606. (b) Carlini, C.; de Luise, V.; Martinelli, M.; Galletti, A. M. R.; Sbrana, G. *J. Polym. Sci., A: Polym. Chem.* **2006**, *44*, 620.

(153) Li, X. F.; Li, Y. G.; Li, Y. S.; Chen, Y. X.; Hu, N. H. *Organometallics* **2005**, *24*, 2502.

(154) Galletti, A. M. R.; Carlini, C.; Giaiacopi, S.; Martinelli, M.; Sbrana, G. *J. Polym. Sci., A: Polym. Chem.* **2007**, *45*, 1134.

(155) Marten, F. L. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. *17*, p 167.

(156) Rinno, H. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. 29, p 49.

(157) Haller, W.; Onusseit, H.; Gierenz, G.; Gruber, W.; Rich, R. D.; Henke, G.; Thiele, L.; Hoffmann, H.; Dausmann, D.; Özelli, R. N.; Windhövel, U.; Sattler, H. P.; Dierichs, W.; Tauber, G.; Hirthammer, M.; Matz, C.; Holloway, M.; Melody, D.; Rust, E. U.; van Halteren, A. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. *1*, p 383.

(158) Stoye, D.; Funke, W.; Hoppe, L.; Hasselkus, J.; Curtis, L. G.; Hoehne, K.; Zech, H. J.; Heiling, P.; Yamabe, M.; Dören, K.; Schupp, H.; Küchenmeister, R.; Schmitthenner, M.; Kremer, W.; Wieczorrek, W.; Gempeler, H.; Schneider, W.; White, J. W.; Short, A. G.; Blank, W. J.; Calbo, L. J.; Plath, D.; Wagner, F.; Haller, W.; Rödder, K. M.; Streitberger, H. J.; Urbano, E.; Laible, R.; Meyer, B. D.; Bagda, E.; Waite, F. A.; Philips, M.; Köhler, K.; Simmendinger, P.; Roelle, W.; Scholz, W.; Kortmann, W.; Valet, A.; Slongo, M.; Molz, T.; Hiller, R.; Thomer, K. W.; Vogel, K.; Schernau, U.; Hüser, B.; Brandt, A.; Milne, A.; Weyers, H.; Plehn, W.; Lentze H. A. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. *24*, p 591.

(159) Daniels, W. E. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. 17, p 393.

(160) For spectral analysis of poly(vinyl acetate) microstructures, see: Katsuraya, K.; Hatanaka, K.; Matsuzaki, K.; Yamaura, K. *Macromol. Rapid Commun.* **2000**, *21*, 697.

(161) For spectra analysis of poly(ethylene-*co*-vinyl acetate) prepared by radical process, see: Su, Z. Q.; Zhao, Y.; Xu, Y.; Zhang, X.; Zhu, S.; Wang, D.; Wu, J.; Han, C. C.; Xu, D. F. *Polymer* **2004**, *45*, 3693.

(162) (a) Koumura, K.; Satoh, K.; Kamigaito, M.; Okamoto, Y. *Macromolecules* **2006**, *39*, 4054. (b) Borkar, S.; Sen, A. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3728.

(163) For example, see: GB 835,466, May 18, 1960.

(164) Williams, B. S.; Leatherman, M. D.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2005**, *127*, 5132.

(165) The influence of the acetoxy group on olefin insertion is difficult to understand. The general trend observed for nickel and palladium complexes has been that the electron-withdrawing substituents on the C−C double bond accelerate insertion. The slow insertion of VAc does not follow this trend, since the electron-withdrawing nature of the acetoxy group is suggested by the Hammett parameter ($\sigma_p = 0.31$), see: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.

(166) The chelate structures formed after 2,1-insertion of VAc were also confirmed by using imine−phosphine ligands, see: (a) Reddy, K. R.; Chen, C. L.; Liu, Y. H.; Peng, S. M.; Chen, J. T.; Liu, S. T. *Organometallics* **1999**, *18*, 2574. (b) Reddy, K. R.; Surekha, K.; Lee, G. H.; Peng, S. M.; Chen, J. T.; Liu, S. T. *Organometallics* **2001**, *20*, 1292. See also ref 29.

(167) The acetoxy group attached to sp^3 carbon centers acts as an electron-withdrawing group, since the inductive effect is dominant over the resonance effect.

(168) Another mechanism for β-OAc elimination is also proposed, see: (a) Lei, A.; Lu, X. *Org. Lett.* **2000**, *2*, 2357. (b) Zhang, Z.; Lu, X.; Xu, Z.; Zhang, Q.; Han, X. *Organometallics* **2001**, *20*, 3724.

(169) Zhao, H.; Ariafard, A.; Lin, Z. *Organometallics* **2006**, *25*, 812.

(170) Boone, H. W.; Athey, P. S.; Mullins, M. J.; Philipp, D.; Muller, R.; Goddard, W. A. *J. Am. Chem. Soc.* **2002**, *124*, 8790.

(171) Peng, F. M. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1985; Vol. 1, p 426.

(172) Kulich, D. M.; Pace, J. E.; Fritch, L. W., Jr.; Brisimitzakis, A. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; Kroschwitz, J. I., Howe-Grant, M., Eds.; Wiley: New York, 1991; Vol. *1*, p 370.

(173) For spectra analysis of the polyacrylonitrile microstructure, see: Katsuraya, K.; Hatanaka, K.; Matsuzaki, K.; Minagawa, M. *Polymer* **2001**, *42*, 6323.

(174) For spectra analysis of poly(ethylene-*co*-acrylonitrile) prepared by the radical process, see: Randall, J. C.; Ruff, C. J.; Kelchtermans, M.; Gregory, B. H. *Macromolecules* **1992**, *25*, 2624.

(175) Wu, F.; Foley, S. R.; Burns, C. T.; Jordan, R. F. *J. Am. Chem. Soc.* **2005**, *127*, 1841.

(176) Stojcevic, G.; Prokopchuk, E. M.; Baird, M. C. *J. Organomet. Chem.* **2005**, *690*, 4349.

(177) The strong tendency for the 2,1-insertion mode can be attributed to large coefficients of the terminal carbon of the HOMO and LUMO orbitals in addition to steric effects; see rer 105. See also section 2.3.

(178) Isomerization of cyanoalkylpalladium complexes has been investigated by DFT calculations; see refs 182−184.

(179) Wu, F.; Jordan, R. F. *Organometallics* **2006**, *25*, 5631.

(180) Groux, L. F.; Weiss, T.; Reddy, D. N.; Chase, P. A.; Piers, W. E.; Ziegler, T.; Parvez, M.; Benet-Buchholz, J. *J. Am. Chem. Soc.* **2005**, *127*, 1854.

(181) Deubel, D. V.; Ziegler, T. *Organometallics* **2002**, *21*, 1603.

(182) Yang, S. Y.; Szabo, M. J.; Michalak, A.; Weiss, T.; Piers, W. E.; Jordan, R. F.; Ziegler, T. *Organometallics* **2005**, *24*, 1242.

(183) Szabo, M. J.; Galea, N. M.; Michalak, A.; Yang, S. Y.; Groux, L. F.; Piers, W. E.; Ziegler, T. *Organometallics* **2005**, *24*, 2147.

(184) Szabo, M. J.; Galea, N. M.; Michalak, A.; Yang, S. Y.; Groux, L. F.; Piers, W. E.; Ziegler, T. *J. Am. Chem. Soc.* **2005**, *127*, 14692.

(185) (a) Smallwood, P. V. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. 17, p 295. (b) Bunten, M. J. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. 17, p 329. (c) Brasure, D.; Ebnesajjad, S. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. 17, p 468. (d) Newman, N. W. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. Supplement, p 822. (e) Stephenson, R. C.; Smallwood, P. V. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. Supplement, p 843. (f) Stephenson, R. C. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. Supplement, p 858. (g) Smallwood, P. V. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. Supplement, p 874.

(186) (a) Carlson, D. P.; Schmiegel, W. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. *14*, p 499. (b) Allsopp, M. W.; Vianello, G. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. 29, p 1.

(187) For spectral analysis of poly(vinyl chloride) microstructures, see: d'Antuono, P.; Botek, E.; Champagne, B.; Wieme, J.; Reyniers, M. F.; Marin, G. B.; Adriaensens, P. J.; Gelan, J. M. *J. Phys. Chem. B* **2008**, *112*, 14804.

(188) For spectral analysis of poly(vinyl fluoride) microstructures, see: Bruch, M. D.; Bovey, F. A.; Cais, R. E. *Macromolecules* **1984**, *17*, 2547.

(189) Kharitonov, A. P.; Taege, R.; Ferrier, G.; Teplyakov, V. V.; Syrtsova, D. A.; Koops, G.-H. *J. Fluorine Chem.* **2005**, *126*, 251.

(190) Boz, E.; Wagener, K. B. *Polym. Rev.* **2007**, *47*, 511.

(191) Chang, B. H.; Zeigler, R.; Hiltner, A. *Polym. Eng. Sci.* **1988**, *28*, 1167.

(192) (a) Jameison, F. A.; Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1986**, *19*, 2168. (b) Braun, D.; Mao, W.; Böhringer, B.; Garbella, R. W. *Die Angew. Makromol. Chem.* **1986**, *141*, 113. (c) Schilling, F. C.; Tonelli, A. E.; Valenciano, M. *Macromolecules* **1985**, *18*, 356. (d) Cais, R. E.; Kometani, J. M. *Macromolecules* **1982**, *15*, 954.

(193) (a) Doak, K. W. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1986; Vol. 6, p 383. (b) Burkhart, R. D.; Zutty, N. L. *J. Polym. Sci., Part A* **1963**, *1*, 1137. (c) Sianesi, D.; Caporiccio, G. *J. Polym. Sci., Part A-1* **1968**, *6*, 335.

(194) For living radical polymerization of VC, see: (a) Percec, V.; Guliashvili, T.; Ladislaw, J. S.; Wistrand, A.; Stjerndahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. *J. Am. Chem. Soc.* **2006**, *128*, 14156. (b) Percec, V.; Popov, A. V.; Ramirez-Castillo, E.; Weichold, O. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3283. (c) Percec, V.; Popov, A. V.; Ramirez-Castillo, E.; Monteiro, M.; Barbiou, B.; Weichold, O.; Asandei, A. D.; Mitchell, C. M. *J. Am. Chem. Soc.* **2002**, *124*, 4940.

(195) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

(196) Stockland, R. A., Jr.; Foley, S. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 796.

(197) (a) Endo, K.; Saitoh, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 248. (b) Endo, K.; Nomaguchi, T.; Tsuchiya, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3872.

(198) Stockland, R. A., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 6315.

(199) Poly(vinyl chloride) (PVC) was obtained in some cases; see refs 196 and 197.

(200) Watson, L. A.; Yandulov, D. V.; Caulton, K. G. *J. Am. Chem. Soc.* **2001**, *123*, 603.

(201) (a) Kraft, B. M.; Jones, W. D. *J. Am. Chem. Soc.* **2002**, *124*, 8681. (b) Clot, E.; Mégret, C.; Kraft, B. M.; Eisenstein, O.; Jones, W. D. *J. Am. Chem. Soc.* **2004**, *126*, 5647.

(202) (a) Simões, J. A. M.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. (b) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444.

(203) Schmidt, E. K. G. *J. Organomet. Chem.* **1981**, *204*, 393.

(204) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1971**, 376.

(205) (a) Fanizzi, F. P.; Maresca, L.; Pacifico, C.; Natile, G.; Lanfranchi, M.; Tiripicchio, A. *Eur. J. Inorg. Chem.* **1999**, 1351. (b) Halpern, J.; Jewsbury, R. A. *J. Organomet. Chem.* **1979**, *181*, 223.

(206) For example, see: (a) Foley, S. R.; Shen, H.; Qadeer, U. A.; Jordan, R. F. *Organometallics* **2004**, *23*, 600. (b) Hughes, R. P.; Sweetser, J. T.; Tawa, M. D.; Williamson, A.; Incarvito, C. D.; Rhatigan, B.; Rheingold, A. L.; Ross, G. *Organometallics* **2001**, *20*, 3800. (c) Hughes, R. P.; Overby, J. S.; Williamson, A.; Lam, K. C.; Concolino, T. E.; Rheingold, A. L. *Organometallics* **2000**, *19*, 5190. (d) Klabunde, K. J.; Campostrini, R. *J. Fluorine Chem.* **1989**, *42*, 93. (e) Hensley, D. W.; Stewart, R. P., Jr. *Inorg. Chem.* **1978**, *17*, 905. (f) Klabunde, K. J.; Low, J. Y. F. *J. Am. Chem. Soc.* **1974**, *96*, 7674. (g) King, R. B.; Bond, A. *J. Am. Chem. Soc.* **1974**, *96*, 1334. (h) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411.

(207) Foley, S. R.; Stockland, R. A., Jr.; Shen, H.; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 4350.

(208) Before 2002, the direction of VC insertion was suggested to be a 1,2-mode. However, 2,1-insertion followed by isomerization was proposed by theoretical and experimental studies; see refs 100 and 206a.

(209) Shen, H.; Jordan, R. F. *Organometallics* **2003**, *22*, 1878.

(210) Biswas, M.; Mazumdar, A.; Mitra, P. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. 17, p 446.

(211) Schröder, G. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. 29, p 61.

(212) (a) Chen, C. L.; Chen, Y. C.; Liu, Y. H.; Peng, S. M.; Liu, S. T. *Organometallics* **2002**, *21*, 5382. (b) Albietz, P. J., Jr.; Yang, K.; Lachicotte, R. J.; Eisenberg, R. *Organometallics* **2000**, *19*, 3543. (c) Baird, M. C. *Chem. Rev.* **2000**, *100*, 1471.

(213) Stoebenau, E. J.; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *128*, 8162.

(214) (a) Lautens, M.; Hiebert, S.; Renaud, J.-L. *J. Am. Chem. Soc.* **2001**, *123*, 6834. (b) Lautens, M.; Fagnou, K.; Hiebert, S. *Acc. Chem. Res.* **2003**, *36*, 48.

(215) Chen, C.; Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2008**, *130*, 12892.

(216) Li, W.; Zhang, X.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 12246.

(217) Buchholz, F. L. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. 27, p 711.

(218) Thomas, W. M.; Wang, D. W. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1985; Vol. 1, p 169.

(219) Hallensleben, M. L. In *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH: Weinheim, 2003; Vol. 29, p 31.

(220) Barabas. E. S. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1989; Vol. 17, p 198.

(221) Rodewald, S.; Jordan, R. F. *J. Am. Chem. Soc.* **1994**, *116*, 4491, and references cited therein.

(222) Nomura, K.; Kakinuki, K.; Fujiki, M.; Itagaki, K. *Macromolecules* **2008**, *41*, 8974.

(223) *European Plastics News*, **1995**, *Oct*57

(224) Abu-Surrah, A. S.; Wursche, R.; Rieger, B. *Macromol. Chem. Phys.* **1997**, *198*, 1197.

(225) For example, see: Brubaker, M. M.; Coffman, D. D.; Hoehn, H. H. *J. Am. Chem. Soc.* **1952**, *74*, 1509.

(226) Ionic processes were also reported. For example, see: Little, E. L., Jr. U.S. Patent 2,641,590, Jun 9, 1953.

(227) (a) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746. (b) Shultz, C. S.; Ledford, J.; DeSimone, J. M.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6351. (c) Toniolo, L.; Kulkarni, S. M.; Fatutto, D.; Chaudhari, R. V. *Ind. Eng. Chem. Res.* **2001**, *40*, 2037.

(228) (a) Margl, P.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 7337. (b) Margl, P.; Ziegler, T. *Organometallics* **1996**, *15*, 5519.

(229) Chen, J. T.; Sen, A. *J. Am. Chem. Soc.* **1984**, *106*, 1506.

(230) Mul, W. P.; Oosterbeek, H.; Beitel, G. A.; Kramer, G. J.; Drent, E. *Angew. Chem., Int. Ed.* **2000**, *39*, 1848.

(231) Similar to the case of ethylene homopolymerization mentioned in section 2.2.2, both ethylene insertion and CO insertion occur from complexes having a migrating group located trans to the phosphorous atom which have a stronger trans effect than the oxygen atom.

(232) Bianchini, C.; Meli, A.; Oberhauser, W.; Segarra, A. M.; Passaglia, E.; Lamač, M.; Štěpnička, P. *Eur. J. Inorg. Chem.* **2008**, 441.

(233) (a) Drent, E. Eur. Pat. Appl. 0,463,689, Jan 2, 1992. (b) Drent, E. Eur. Pat. Appl. 0,272,727, Jun 29, 1988.

(234) (a) Wursche, R.; Rieger, B. *Macromol. Chem. Phys.* **2000**, *201*, 2861. (b) Wursche, R.; Rieger, B. *Macromol. Chem. Phys.* **2000**, *201*, 2869.

(235) Sen, A. S.; Jiang, Z. *Macromolecules* **1993**, *26*, 911.

(236) (a) Klok, H. A.; Eibeck, P.; Schmid, M.; Abu-Surrah, A. S.; Möller, M.; Rieger, B. *Macromol. Chem. Phys.* **1997**, *198*, 2759. (b) Nieuwhof, R. P.; Marcelis, A. T. M.; Sudhölter, E. J. R.; Wursche, R.; Rieger, B. *Macromol. Chem. Phys.* **2000**, *201*, 2484. (c) Malinova, V.; Rieger, B. *Macromol. Rapid Commun.* **2005**, *26*, 945. (d) Malinova, V.; Rieger, B. *Biomacromolecules* **2006**, *7*, 2931.

(237) Liaw, D. J.; Tsai, J. S.; Sang, H. C. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1785.

(238) Safir, A. L.; Novak, B. M. *J. Am. Chem. Soc.* **1998**, *120*, 643.

(239) In the case of the copolymers of CO with olefins possessing a pendant hydroxy group, the intramolecular cyclization proceeded to form polycyclic copolymers, see: Kacker, S.; Jiang, Z.; Sen, A. *Macromolecules* **1996**, *29*, 5852.

(240) Moineau, C.; Mele, G.; Alper, H. *Can. J. Chem.* **2001**, *79*, 587.

(241) Murtuza, S.; Harkins, S. B.; Sen, A. *Macromolecules* **1999**, *32*, 8697.

(242) Lee, J. T.; Alper, H. *Chem. Commun.* **2000**, 2189.

(243) (a) Fujita, T.; Nakano, K.; Yamashita, M.; Nozaki, K. *J. Am. Chem. Soc.* **2006**, *128*, 1968. (b) Nozaki, K.; Shibahara, F.; Elzner, S.; Hiyama, T. *Can. J. Chem.* **2001**, *79*, 593.

(244) Nozaki, K.; Kawashima, Y.; Nakamoto, K.; Hiyama, T. *Polym. J.* **1999**, *31*, 1057.

(245) There are some reports of the alternating copolymerization of polar vinyl monomers with CO. However, no sufficient data are shown; see ref 233b. See also: (a) Yuan, J. C.; Chen, M. D.; Zhang, Y. H.; Lu, S. J. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2027. (b) Yuan, J. C.; Zhang, Y. H.; Chen, M. D.; Lu, S. J. *J. Mol. Catal. A: Chem.* **2001**, *174*, 63.

(246) Ozawa, F.; Hayashi, T.; Koide, H.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1991**, 1469.

(247) Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1992**, *430*, 357.

(248) Braunstein, P.; Frison, C.; Morise, X. *Angew. Chem., Int. Ed.* **2000**, *39*, 2867.

(249) Braunstein, P.; Durand, J.; Knorr, M.; Strohmann, C. *Chem. Commun.* **2001**, 211.

(250) (a) Agostinho, M.; Braunstein, P. *Chem. Commun.* **2007**, 58. (b) Agostinho, M.; Braunstein, P. C. R. *Chimie* **2007**, *10*, 666.

(251) Hamada, A.; Braunstein, P. *Organometallics* **2009**, *28*, 1688.

(252) (a) Axe, F. U.; Marynick, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 3728. (b) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1986**, *108*, 6136.

(253) It cannot be concluded that CO insertion is inhibited only by low nucleophilicity of the α-carbon, since there are some examples of CO insertion into Pd−alkyl bonds substituted by α-CN (ref 175), Cl (ref 206a), OAc (ref 164) functionality without intramolecular ketone coordination.

(254) (a) Bayer, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 113. (b) Deming, T. J. *Adv. Mater.* **1997**, *9*, 299. (c) Kricheldorf, H. R. *Angew. Chem., Int. Ed.* **2006**, *45*, 5752.

(255) Sewald, N.; Jakubke, H. D. *Peptides: Chemistry and Biology*; Wiley-VCH: Weinheim, 2002.

(256) Bodanszky, M. *Principles of Peptide Synthesis*, 2nd ed.; Springer-Verlag: Berlin, 1993.

(257) Kacker, S.; Kim, J. S.; Sen, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 1251.

(258) Dghaym, R. D.; Yaccato, K. J.; Arndtsen, B. A. *Organometallics* **1998**, *17*, 4.

(259) Cavallo, L. *J. Am. Chem. Soc.* **1999**, *121*, 4238.

(260) (a) Dghaym, R. D.; Dhawan, R.; Arndtsen, B. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 3228. Arndtsen et al. improved this reaction to establish an effective synthesis of various α-amino acid derivatives, see: (b) Arndtsen, B. A. *Chem.—Eur. J.* **2009**, *15*, 302. (c) Dhawan, R.; Dghaym, R. D.; Arndtsen, B. A. *J. Am. Chem. Soc.* **2003**, *125*, 1474.

(261) Davis, J. L.; Arndtsen, B. A. *Organometallics* **2000**, *19*, 4657.

(262) Lafrance, D.; Davis, J. L.; Dhawan, R.; Arndtsen, B. A. *Organometallics* **2001**, *20*, 1128.

(263) Funk, J. K.; Yennawar, H.; Sen, A. *Helv. Chim. Acta* **2006**, *89*, 1687.

(264) *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Cornils, B., Herrmann, W. A., Eds.; Wiley-VCH: Weinheim, 2002.

(265) Church, T. L.; Getzler, Y. D. Y. L.; Byrne, C. M.; Coates, G. W. *Chem. Commun.* **2007**, 657.

(266) The cobalt catalyst **44** was also reported as a catalyst for copolymerization of aziridines with CO to form poly-*β*-peptide, see: Jia, L.; Sun, H.; Shay, J. T.; Allgeier, A. M.; Hanton, S. D. *J. Am. Chem. Soc.* **2002**, *124*, 7282.

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