Macromolecules

Perspective

pubs.acs.org/Macromolecules

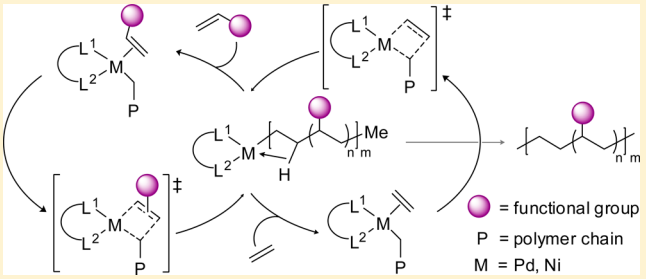
Transition-Metal-Catalyzed Functional Polyolefin Synthesis: Effecting Control through Chelating Ancillary Ligand Design and Mechanistic Insights

Brad P. Carrow[†] and Kyoko Nozaki*[,‡]

[†]Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

[‡]Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

ABSTRACT: The incorporation of polar functional groups into polyolefins can significantly alter the adhesion, barrier and surface properties, dyeability, printability, and compatibility of the resulting "functional polyolefin". Thus, the development of methods for the controlled synthesis of functional polyolefins from industrially relevant monomers holds the potential to expand the range of applications available to this already ubiquitous class of materials. In this Perspective, recent advances in transition-metal-catalyzed functional polyolefin synthesis will be reviewed. A common thread among the innovations discussed here is the perturbation of catalyst function by tailored design of the chelating ancillary ligand, aided in many cases by improved mechanistic understanding. Specific topics discussed here include rare examples of catalyst control over the regio- and stereochemistry of polar monomer insertion by phosphine−sulfonato palladium complexes (Drent-type), rate acceleration of insertion polymerization by binuclear cooperativity using salicylaldiminato nickel complexes (Grubbs-type), and formation of *linear* copolymers of ethylene and polar vinyl monomers using a cationic palladium catalyst ligated by a bisphosphine monoxide (BPMO) that contrasts the typical polymer microstructures formed by other cationic group 10 catalysts ligated by an α-diimine (Brookhart-type).



The demand for materials with defined physical properties has driven the development of new synthetic methods to prepare polymers with tailored molecular structures. A revolution in controlled polymer synthesis followed the commercialization of the Ziegler−Natta process to form high molecular weight polyethylene in the early 1950s.[1,2] Many transition-metal-catalyzed syntheses of polyolefins with defined molecular weight ranges, branching ratios, and architectures have since been developed, a number of which have been commercialized.[3−11] Despite the many advances in this field over little more than a half century, the controlled synthesis of polyolefins possessing polar functional groups in the polymer backbone remains a largely unsolved problem. Efforts to extend Ziegler−Natta-type processes to the synthesis of functional polyolefins from simple polar vinyl monomers, defined here as monomers with a polar functional group directly attached to the alkene, have been wholly unsuccessful in the absence of protecting groups.[12] The high oxophilicity of the early-transition-metal polymerization catalysts generally leads to poisoning by strong σ-coordination of the Lewis basic moiety of a polar vinyl monomer. As such, other methods have been pursued for the synthesis of functional polyolefins.

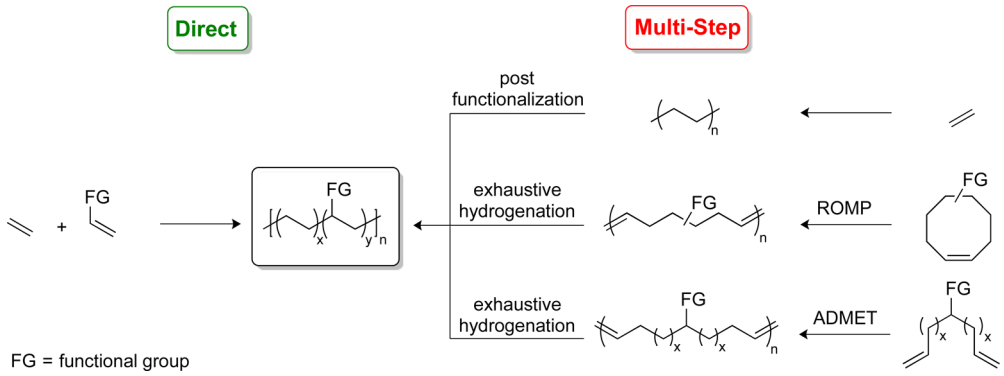
Common strategies for the preparation of functional polyolefins developed to date (Scheme 1) include post-functionalization of polyethylene,[13,14] ring-opening metathesis polymerization (ROMP) of functionalized cyclooctenes,[15−17] or acyclic diene metathesis (ADMET) of functionalized dienes.[18−21] However, these collective methods suffer from the use of cost-ineffective monomers or the requirement of multiple synthetic steps to produce the final product. Free radical processes to form functional polyolefins by polymerization of ethylene and industrial polar vinyl monomers (i.e., vinyl acetate, methyl acrylate, acrylonitrile, etc.) have been commercialized but suffer from typical issues associated with free radical polymerizations: poor control over molecular weight, branching ratios, and distribution of the polar functional groups in the polymer chain.[22] Alternatively, direct transition-metal-catalyzed insertion polymerization of ethylene and simple vinyl monomers represents a potentially ideal method for the controlled synthesis of functional polyolefins in a single step (Scheme 2).

Late-transition-metal catalysts, generally more tolerant of polar functionality compared to early-transition-metal complexes, have been developed for the insertion polymerization of ethylene with a number of polar vinyl monomers. Examples of simple polar monomers that have been successfully applied to copolymerizations with ethylene include acrylates,[23−25] acrylonitrile,[26,27] acrylamides,[28,29] acrylic acid,[30−32] vinyl acetate,[33,34]

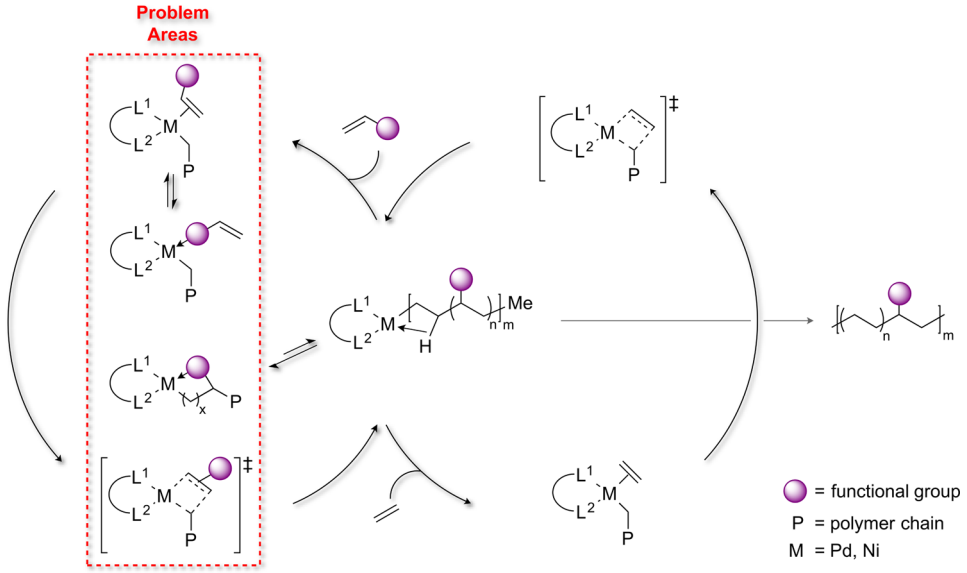
Received: January 6, 2014
Revised: March 9, 2014
Published: March 19, 2014

   dx.doi.org/10.1021/ma500034g | *Macromolecules* 2014, 47, 2541−2555

Scheme 1. General Synthetic Routes to Functional Polyolefins



Scheme 2. Generalized Catalytic Cycle of a Group 10 Metal-Catalyzed Copolymerization of Ethylene and a Functional Monomer



vinyl halides,[35,36] vinyl ethers,[34,37,38] and allyl monomers.[34,39] The majority of successful reports of polymerization of ethylene with polar vinyl monomers, however, utilize one of only two catalyst classes: cationic group 10 complexes ligated by an α-diimine (Brookhart-type) or neutral palladium complexes ligated by a phosphine–sulfonate (Drent-type).[12,40−43] Nearly a decade after these seminal advances in functional polyolefin synthesis by insertion polymerization, distinct classes of catalysts that are active for this transformation remain scarce and major challenges toward industrial application remain.

Notable obstacles toward practical insertion polymerization of polar vinyl monomers that are relevant to the topics of this Perspective include (Scheme 2) a lack of strategies to impart catalyst control over the regio- and stereochemistry of polar monomer insertion, catalyst inhibition and low overall rates of reaction due to σ-coordination of the functional group to the metal, and limited access to new types of catalysts that exhibit distinct patterns of reactivity. In this Perspective, recent advances in transition-metal-catalyzed functional polyolefin synthesis will be reviewed with an emphasis on how perturbations of the ancillary ligand of the catalyst can influence either the selectivity or the rate of migratory insertion of polar monomers (Figure 1). The scope of this Perspective is limited to catalysts that form predominantly linear polymers; recent advances in group 10 α-diimine catalysts that form branched (co)polymers have been reviewed elsewhere.[44,45]

INFLUENCING THE REGIOSELECTIVITY OF POLAR MONOMER INSERTION

The physical properties of polymers substantially depend on their microstructure, and thus control over the regioselectivity during coordination–insertion polymerization is an important consideration. What is more, the regioselectivity of polar monomer insertion can have important implications on the rate of catalysis. For example, 1,2-insertion of vinyl acetate, vinyl ethers, or vinyl halides into an alkylpalladium bond can lead to catalyst deactivation by β-elimination of the functional group (Scheme 3). In the absence of catalyst control over regioselectivity, it is therefore difficult to avoid catalyst deactivation during polymerizations of such monomers. The development of strategies to impart catalyst control of the regioselectivity of migratory insertion reactions is thus an important aspect of realizing the synthesis of tactic functional polymers and also mitigating certain catalyst deactivation pathways.

The successful use of ligand design to impart catalyst control over the regioselectivity of insertions of acrylates, a class of polar vinyl monomers that routinely affords high selectivity for

dx.doi.org/10.1021/ma500034g | Macromolecules 2014, 47, 2541−2555

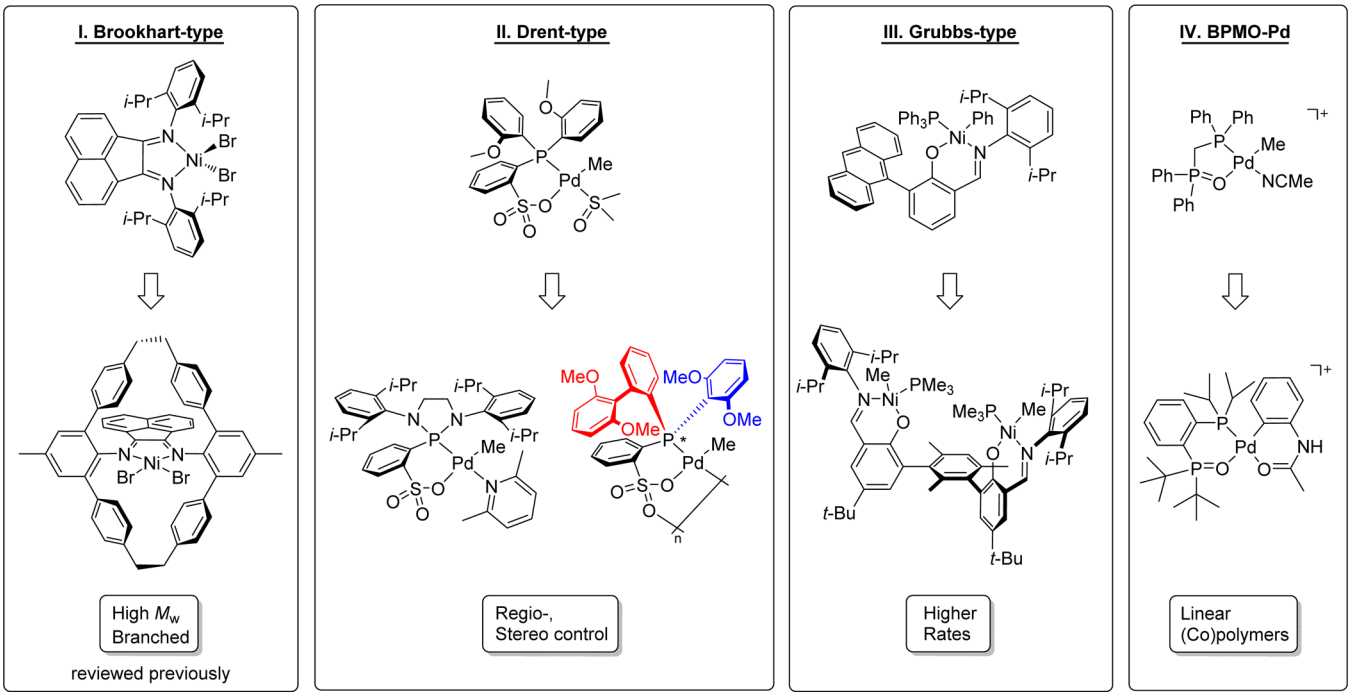
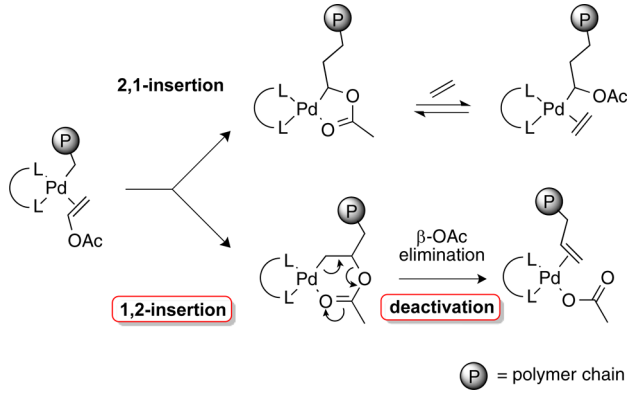


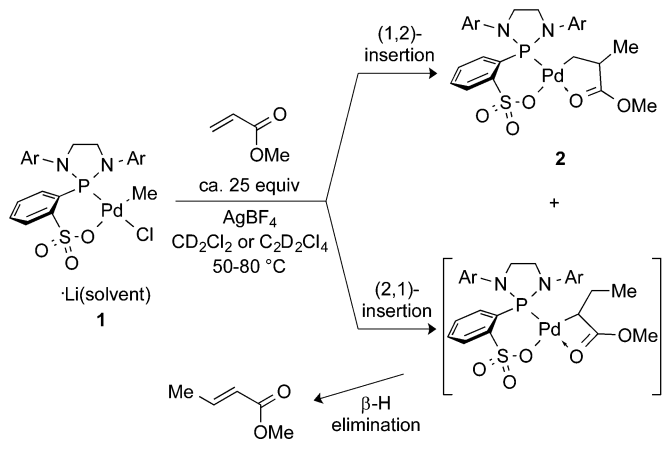
Figure 1. Overview of recent advances in ancillary ligand design for group 10 polymerization catalysts.

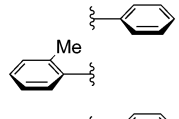
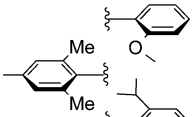
Scheme 3. Illustrative Example of How the Regioselectivity of Vinyl Acetate Insertion Can Lead to Chain Termination or Further Propagation during Insertion Polymerization



(2,1)-insertion regardless of the nature of the catalyst, was recently reported by Caporaso, Mecking, and Göttker-Schnetmann.[46,47] In these studies, the stoichiometric insertion of methyl acrylate into a series of diazaphospholidine–sulfonato methylpalladium complexes, after abstraction of chloride by silver salt, afforded a mixture of palladium and organic products (Scheme 4). A stable five-membered chelate complex (**2**) was obtained after (1,2)-insertion of methyl acrylate, whereas the product formed from (2,1)-insertion was unstable and decomposed by β-H elimination yielding methyl crotonate as the organic product. The ratio of **2** to methyl crotonate, determined by ^{1}H NMR spectroscopy, was used to quantify the regioselectivity for the insertion of methyl acrylate into **1**. These data clearly show that increased steric bulk about the phosphine portion of the metal complex correlates to higher selectivity for the (1,2)-insertion of methyl acrylate. The highest selectivity for (1,2)-insertion of methyl acrylate (>95%)

Scheme 4. Observed Influence of *N*-Aryl Substituents on the Regioselectivity of Methyl Acrylate Insertion into the Palladium–Methyl Bond of Diazaphospholidine–Sulfonato Palladium Complexes



Ar	(1,2)-insertion : (2:1)-insertion
	<5 % : **>95 %**
	50 % : 50 %
	50 % : 50 %
	93 % : 7 %
	>95 % : <5 %
	>95 % : <5 %

dx.doi.org/10.1021/ma500034g | *Macromolecules* 2014, 47, 2541–2555

was observed in the cases of the very bulky complexes with 2,6-diisopropylphenyl or 2,6-di(*p*-tolyl)phenyl *N*-aryl substituents. The high selectivity for (1,2)-insertion of methyl acrylate is exceptional and unusual—a notable manifestation of catalyst control over the migratory insertion of alkenes that lack a directing group.

Insight into the origin of the ligand steric effect was obtained through DFT calculations. Previous theoretical investigations have established that migratory insertion of alkenes into a phosphine–sulfonato alkylpalladium complex proceeds through an intermediate in which the alkene and the phosphine group are located in a *cis* orientation.[48,49] Thus, (2,1)-migratory insertion of methyl acrylate into **1** (Ar = 2,6-diisopropylphenyl) is unfavorable due to steric repulsion between the phosphorus substituents and the ester group of the monomer. Conversely, (1,2)-insertion from the same *cis* complex orients the functional group of the monomer away from the bulky diazaphospholidine moiety. In the absence of substantial steric bulk at phosphorus (i.e., Ar = phenyl in **1**), however, the typical substrate-controlled (2,1)-insertion dominates (>95%).

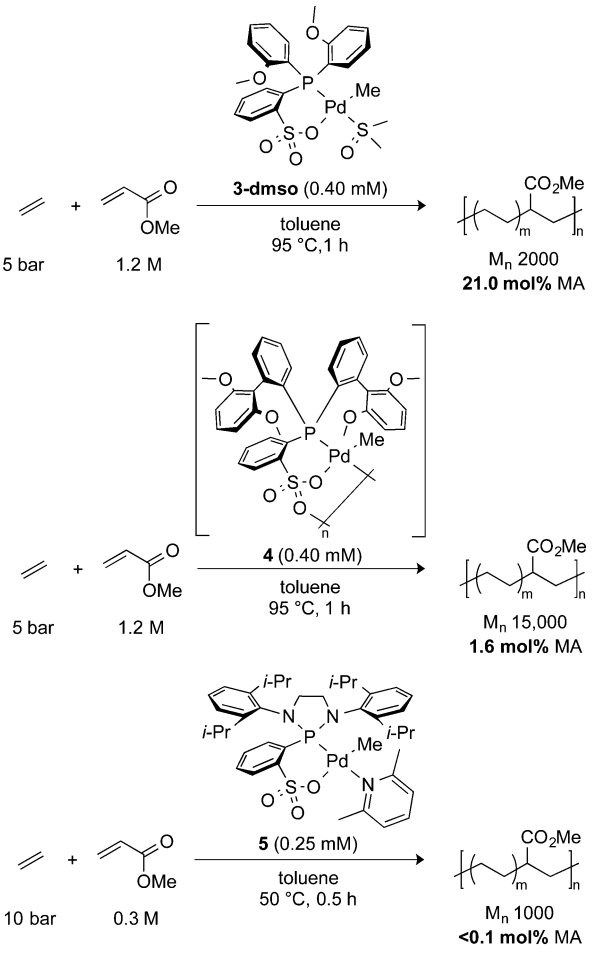
Increasing the steric bulk at phosphorus as a strategy of catalyst controlled (1,2)-insertion of monosubstituted alkenes is not without drawbacks. A marked impact on enchainment of methyl acrylate during copolymerizations with ethylene was observed using phosphine–sulfonato palladium complexes with extremely bulky phosphorus substituents. A typical copolymerization between methyl acrylate and ethylene catalyzed by the *o*-anisyl-substituted phosphine–sulfonato palladium complex **3-dmso** is shown in Scheme 5 (top), producing a random copolymer with 21 mol % incorporation of the polar monomer.[50] The use of the more bulky derivatives **4**, formed *in situ* by silver-mediated abstraction of chloride from the corresponding (methyl)(chloro)palladium complex,[50] and diazaphospholidine–sulfonato palladium complex **5** (Scheme 5) produced copolymers with substantially reduced incorporation ratios. This trend was corroborated theoretically; the relative activation energy difference ($\Delta\Delta E$) between insertion of methyl acrylate versus ethylene was calculated to be +18 kJ/mol for **3** and +31 kJ/mol for **4**. Thus, enhancement of the steric bulk at phosphorus in phosphine–sulfonato palladium catalysts can be exploited to override the intrinsic preference of electron-deficient alkenes to insert in a (2,1) fashion, but this strategy leads to a higher insertion barrier that has a deleterious effect on the enchainment of polar monomers in copolymerizations with ethylene.

TOWARD STEREOSELECTIVE FUNCTIONAL POLYOLEFIN SYNTHESIS

Coordination–insertion polymerization has been adapted into numerous stereoselective chain growth processes to generate tactic polymers, perhaps best exemplified by the industrial production of isotactic polypropylene using metallocene catalysts.[11] While nonpolar alkenes have been utilized in these reactions that produce stereoregular (co)polymers by an insertion mechanism, a general strategy for the stereoselective insertion polymerization of polar monomers is lacking.

Among the late-transition-metal polymerization catalysts, phosphine–sulfonato palladium complexes stand out as holding the potential to facilitate stereoselective synthesis of polymers from polar vinyl monomers. While electrophilic cationic group 10 catalysts ligated by a α-diimine generally undergo facile β-hydrogen elimination/reinsertion during polymerization,[51] the neutral phosphine–sulfonato palladium complexes suffer

Scheme 5. Copolymerization of Ethylene and Methyl Acrylate Using a Diazaphospholidine–Sulfonato Palladium (bottom) or Phosphine–Sulfonato Palladium (top, middle) Catalysts



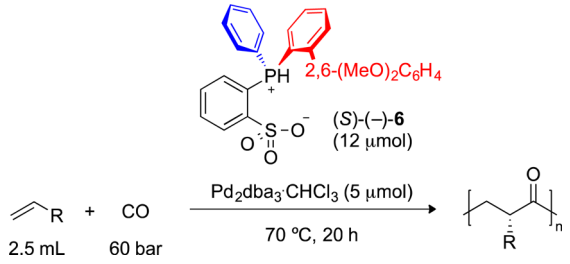
negligible chain walking and afford consistently linear polymers. This feature of phosphine–sulfonato palladium catalysts is attractive for efforts to effect stereoselective insertions of prochiral monomers because chain walking could scramble any stereogenic centers installed along the polymer backbone.

Methods to produce isotactic γ-polyketones from carbon monoxide and nonpolar olefins (e.g., propylene or styrene) by alternating insertion polymerization have been developed.[52−55] Copolymerizations of CO and alkenes possessing remote functional groups have also been reported.[56,57] However, examples of even unselective polymerization of CO with polar vinyl monomers are few.[58−61,56,57] The Nozaki group recently reported a rare example of stereoselective, alternating insertion polymerization of carbon monoxide and vinyl acetate or methyl acrylate to produce new types of chiral γ-polyketones.[62] Several achiral and P-chiral phosphine–sulfonato palladium catalysts were initially surveyed for activity and selectivity in the alternating polymerization of carbon monoxide with vinyl acetate, methyl acrylate, or styrene. Among the catalysts investigated, head-to-tail regioselectivity was highest using a phosphine–sulfonate ligand containing one phenyl and one 2′,6′-dimethoxy(1,1′-biphenyl)-2-yl substituent on phosphorus (**6**). Enantio-enriched ligand (*S*)-(−)-**6**, obtained from separation of the racemic **6** by chiral HPLC, was subsequently used for asymmetric polymerizations (Table

dx.doi.org/10.1021/ma500034g | *Macromolecules* 2014, 47, 2541−2555

1). The head-to-tail ratios of CO/styrene and CO/methyl acrylate copolymers formed using a combination of $Pd_2(dba)_3$·

Table 1. Asymmetric Copolymerization of Carbon Monoxide with Vinyl Acetate, Methyl Acrylate, or Styrene Using a *P*-Chiral Phosphine−Sulfonato Palladium Catalyst



entry	R	TOF[a]	$[\Phi]_D$	M_n[b]	M_w/M_n[b]	head-to-tail[b] (%)
1	OAc	7.4	−8.5[c]	20 000	1.8	90
2	CO_2Me	4.7	+4.4[d]	10 000	1.2	>99
3	Ph	3.8	+463[e]	12 000	1.1	>99

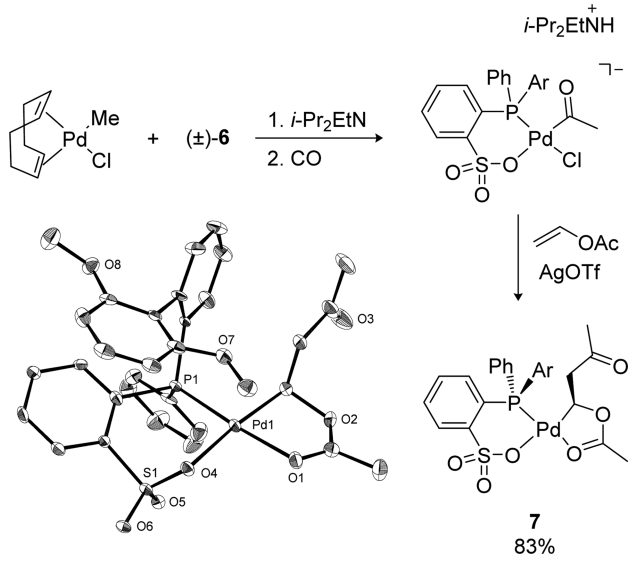
[a]In mol (mol Pd)$^{-1}$ h^{-1}. [b]Determined by NMR analysis. [c]22 °C, c = 0.32 in $CHCl_3$. [d]26 °C, c = 0.32 in $CHCl_3$. [e]24 °C, c = 0.053 in $CHCl_3$.

$CHCl_3$ (dba = *trans, trans*-dibenzylideneacetone) and (*S*)-(−)-**6** were >99%. However, the polyketone obtained from the reaction of CO and vinyl acetate catalyzed by the same catalyst mixture was also regioregular (ca. 90% head-to-tail), even though vinyl acetate often yields mixtures of (2,1)- and (1,2)-insertion products.[63] The polyketones formed by the catalyst derived from (*S*)-(−)-**6** exhibited optical rotation, consistent with stereoselective migratory insertion of the alkene monomers during the alternating copolymerization. Additionally, ^{13}C NMR analyses of the polymers formed by the Pd/**6** catalyst indicate that only γ-polyketone structures were formed; polyspiroketal resonances were not observed.

The migratory insertion of carbon monoxide and vinyl acetate into the palladium−methyl bond of a phosphine−sulfonato palladium complex derived from **6** was also performed in a stoichiometric experiment. The resulting insertion product **7** was isolated and fully characterized by multinuclear NMR spectroscopy and X-ray crystallography (Scheme 6). The structure of **7**, which was formed in 83% isolated yield, is consistent with 2,1-insertion of vinyl acetate into the palladium−acyl bond followed by coordination of the ester oxygen to palladium to form a stable five-membered chelate. From these data, a model for stereoinduction in the asymmetric copolymerization of CO and vinyl acetate was proposed (Scheme 7) in which vinyl acetate binds to palladium such that the acetate group resides on the same side as the smaller phosphine substituent. This monomer orientation is consistent with the observed regio- and relative stereochemistry observed in the isolated **7**.[48,49]

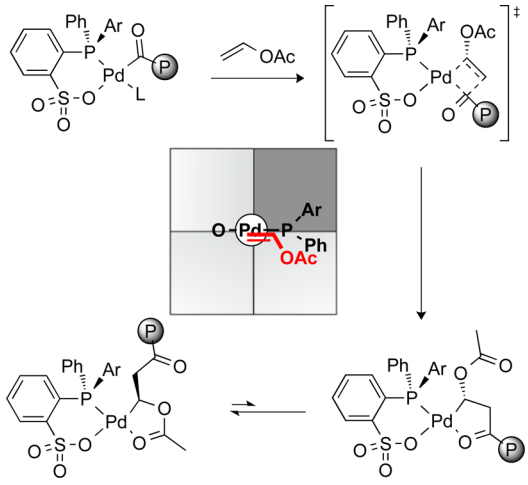
Separately, the groups of Caporaso and Mecking undertook a detailed experimental and theoretical study of a series of phosphine−sulfonato ligands and their corresponding palladium complexes (Figure 2) to elucidate the molecular dynamics of these complexes that might facilitate or impede the stereoselective insertion of polar vinyl monomers.[64] Facial selectivity during insertion of a prochiral monomer into a chiral phosphine−sulfonato palladium complex represents a promising strategy for the synthesis of tactic functional polymers by an insertion process.

Scheme 6. Synthesis and Single-Crystal X-ray Structure of 7[a]



[a]Thermal ellipsoids are shown at 50% probability, and hydrogen atoms are omitted for clarity. Ar = 2′,6′-dimethoxy(1,1′-biphenyl)-2-yl.

Scheme 7. Proposed Mechanism Accounting for the Asymmetric Induction during Copolymerization of Vinyl Acetate and Carbon Monoxide by a *P*-Chiral Phosphine-Sulfonato Palladium Catalyst and a Quadrant Analysis Consistent with the Observed Relative Stereochemistry in 7[a]



[a]Ar = 2′,6′-dimethoxy(1,1′-biphenyl)-2-yl.

The reaction of phosphine−sulfonato methylpalladium complexes **9a−g** with methyl acrylate following abstraction of chloride by silver(I) salt was monitored by multinuclear NMR spectroscopy at room temperature. In most cases a stable chelate complex was formed upon insertion of two acrylate monomers (Scheme 8). Multiple insertions of acrylates into palladium complexes of **8a** have previously been observed and characterized.[65] The structures and relative stereochemistry of complexes **11a−d**, **11f**, and **11g** were examined in solution by ^1H, ^1H TOCSY, and $^1H-^1H$ COSY NMR spectroscopic analyses, and from these data it was determined that consecutive insertions of methyl acrylate occurred with diastereoselectivity that ranged from 1:1 to 3:1 favoring the isomer with opposite configuration at each stereogenic carbon.

dx.doi.org/10.1021/ma500034g | *Macromolecules* 2014, 47, 2541−2555

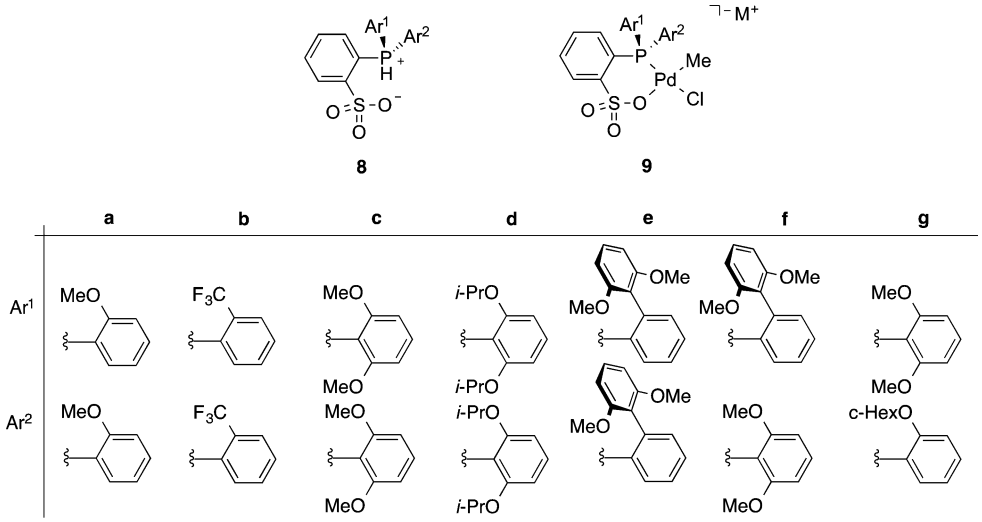
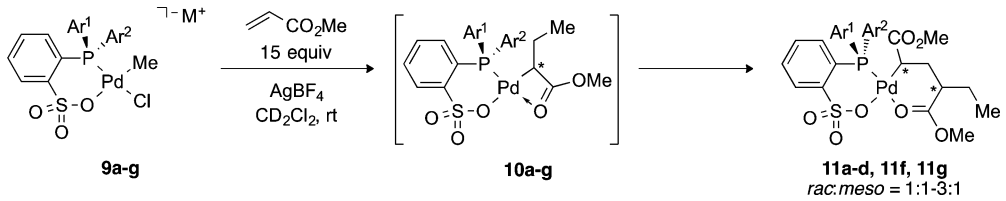


Figure 2. Phosphine–sulfonate ligands (**8a–8g**) and corresponding $\{[P,O]Pd(Me)(Cl)\text{-}(\mu\text{-}M)\}_n$ (M = Li, Na) complexes (**9a–9g**) investigated by Caporaso and Mecking.

Scheme 8. Stoichiometric Reaction of Methyl Acrylate with a Series of Phosphine–Sulfonato Methylpalladium Complexes To Probe the Stereoselectivity of Insertion as a Function of the Arylphosphine Substituents[a]

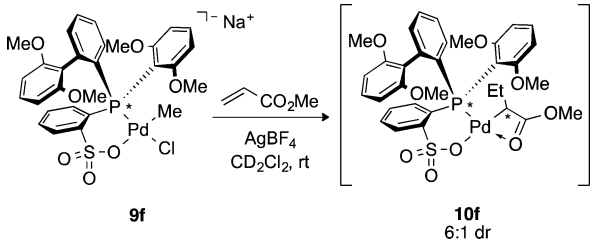


[a]The authors' use of *racemic* and *meso* designations refers to a hypothetical growing polymer chain in which the adjacent stereogenic carbon centers have the opposite or same configuration, respectively.

A second insertion of methyl acrylate into **10e** was not observed. It should be noted that more than two diastereomers could be observed after some of the insertion reactions, but these additional isomers differed not by the stereochemistry in the ester enolate fragment of the molecules but by the conformation of the phosphine–sulfonato ligand about palladium (vide infra). The similar ratios of *racemic* and *meso* isomers observed in these reactions indicates poor catalyst control of the stereoselectivity of methyl acrylate insertion by these phosphine–sulfonato palladium complexes.

The stereochemistry of the first insertion of methyl acrylate could also be evaluated in solution by quantifying the diastereomeric ratio of compounds that contain a *P*-chiral phosphine sulfonate ligand (Scheme 9). The ratio could not be determined unambiguously for **10g** due to the presence of multiple insertion products that could not be clearly assigned, but complex **10f** was formed in a ca. 6:1 ratio of diastereomers. Thus, the first insertion of the methyl acrylate into complex **9f** occurs with a higher selectivity (6:1) than does the second insertion of methyl acrylate (3:1 *rac*/*meso* in **11f**).

Scheme 9. Observation of the Relative Stereoselectivity of 10f Formed from Insertion of Methyl Acrylate into 9f That Contains a *P*-Chiral Phosphine–Sulfonate Ligand



The molecular dynamics of these complexes were also investigated by a combination of variable temperature NMR spectroscopy and DFT calculations to better understand the molecular motions of phosphine–sulfonato complexes **9a–g** that could potentially give rise to site stereocontrol during migratory insertion. First, examination of available X-ray crystallographic data for arylphosphine–sulfonate ligands established that this class of compounds generally adopts one of two diastereomeric conformations (exo_2, exo_3) that differ by the preference of two or three of the *ortho* aryl substituents to orient toward the phosphorus atom, respectively (Figure 3). Thus, these ligands exhibit a helical twist that gives rise to stereoisomers (*P*, *M*). Rotations about the phosphorus–carbon bonds at a rate faster than monomer insertion, however, would erode any site stereocontrol afforded by the axial chirality in these complexes. The energy barrier of rotation determined by line-shape analysis in solution for ligands **8a–g** and complexes **9a–g** by variable temperature NMR resulted in an estimated range of free energy of activation ($\Delta G_{T_c}^{\ddagger}$) of 44–64 kJ/mol at the coalescence temperature (T_c).

A second dynamic motion of these phosphine–sulfonato palladium complexes is a ring flip of the six-membered metal–ligand chelate (Figure 4). Within the temperature range of −90 to 130 °C the ring flip could not be observed by NMR

dx.doi.org/10.1021/ma500034g | *Macromolecules* 2014, 47, 2541–2555

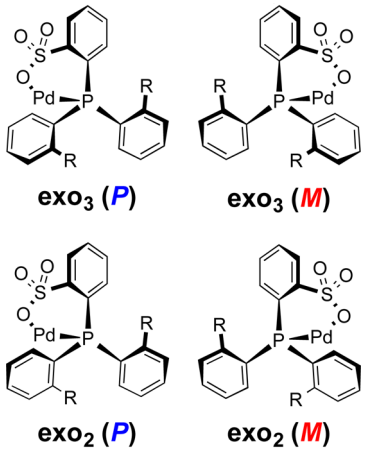


Figure 3. Diastereomers (exo_3, exo_2) and axial chirality (*P*, *M*) of Ar_3ZX motifs experimentally observed in isolated phosphine–sulfonato palladium complexes.

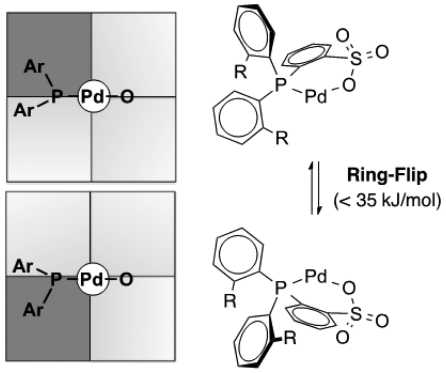
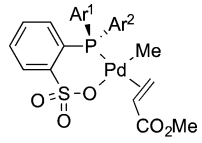


Figure 4. Quadrant analysis of square-planar phosphine–sulfonato palladium complexes during a ring-flip motion of the six-membered metal–ligand chelate. Darker color quadrants indicate more steric crowding.

spectroscopy and consequently was concluded to occur with a barrier of <35 kJ/mol. Because insertion of polar monomers such as acrylates into phosphine–sulfonato alkylpalladium complexes typically occur over a matter of minutes at 60–90 °C, it was concluded that insertion occurs qualitatively slower than either of these two fluxional motions of the metal complexes. Consequently, site stereocontrol is unlikely in the absence of an alternate, persistent element of chirality in the catalyst.

The relative transition state energies of methyl acrylate insertion, ring flip, and aryl rotation in complexes **12a**, **12c**, **12e**, and **12f** determined by DFT calculations are summarized in Table 2. In all cases, the ring flip and aryl rotations are predicted to occur with lower barriers than insertion of methyl acrylate, which is consistent with the poor diastereoselectivity observed experimentally for consecutive acrylate insertion into phosphine–sulfonato palladium complexes that lack a permanent stereocenter at phosphorus (e.g., **9a–e** in Figure 2). Additionally, the barrier to insertion of *re*-methyl acrylate into complex (*R*)-**12f** was estimated to be 11 kJ/mol lower in energy compared to insertion from the *si*-methyl acrylate complex. The energy difference between the second *re*- or *si*-methyl acrylate insertion was reduced to only 3 kJ/mol, which correlated to the empirical stereoselectivities of 6:1 and 3:1

Table 2. Calculated Relative Transition State Energies (kJ/mol) for Insertion of Methyl Acrylate into 12, Ring Flip, and Aryl Rotation



12

compd	$TS_{insertion}$	$TS_{ring\ flip}$	$TS_{aryl\ rotation}$
12a	0	−49	−34
12c	0	−51	
12e	0	−49	−14
12f	0	−18	−5

observed for the first and second insertion of methyl acrylate into **9f**, respectively.

An origin of the reduced stereoselectivity of consecutive methyl acrylate insertions was attributed to the influence of the growing chain end. The close proximity (ca. 3.5 Å) of a methoxy group of the ligand with *re*-methyl acrylate monomer accounts for the reduced enantiomorphic site control for the second insertion. The conformation of the methoxy group arises from a reorientation of the biaryl phosphine substituent after the first methyl acrylate insertion to alleviate steric interaction with the chain end. From these observations, the authors conclude that the good enantiomorphic site stereocontrol observed for the insertion of methyl acrylate into the palladium–methyl bond of **9f** is counteracted by a mismatched chain end stereocontrol during subsequent methyl acrylate insertions into the ester enolate palladium complex **10f**.

Several perspectives on strategies to effect stereoselective insertion of polar monomers using phosphine–sulfonato palladium catalysts were offered from this study. First, the fluxional behavior of these complexes (e.g., ring flip and aryl rotation) occur at rates that are faster than typical insertions of polar monomers, which necessitates the presence of a permanent stereocenter on the ligand (i.e., *P*-chiral phosphine) to facilitate appreciable enantiomorphic site stereocontrol. The use of extreme bulk at phosphorus in the phosphine–sulfonate ligand was shown to increase the stereoselectivity and/or (1,2)-regioselectivity of migratory insertion of polar monomers, but in so doing the activation barrier of insertion of the polar monomer was also raised. Thus, it becomes necessary to strike a balance of steric bulk in the catalyst that affords acceptable stereoselectivity, regioselectivity, and rate. Additionally, the development of new chelating (P,O) ligand motifs that retard the fluxional behavior of the metal–ligand complex would also have a beneficial impact on efforts to synthesize tactic functional polyolefins by insertion polymerization.

BIMETALLIC COOPERATIVITY IN INSERTION POLYMERIZATION OF POLAR MONOMERS

Cooperativity effects in bimetallic group 4 constrained geometry or aryloxy–iminato-type polymerization catalysts have been shown to enhance both catalyst activity and the resulting polymer architecture of polyethylene and poly(ethylene-*co*-(α-olefin)) materials.[66,67] Recently, Grubbs-type salicylaldiminato nickel catalysts have been adapted into several bimetallic frameworks, and some of these binuclear analogues exhibit cooperative effects in ethylene homopolymerizations and copolymerizations of ethylene with comonomers possess-

dx.doi.org/10.1021/ma500034g | *Macromolecules* 2014, 47, 2541–2555

ing remote functional groups (Figure 5).[68−81] These bimetallic nickel compounds were shown to increase, versus mononuclear analogues, the turnover frequency of ethylene polymerization, comonomer enchainment, chain branching, and selectivity for methyl branching. However, copolymerizations of ethylene and polar monomers using salicylaldiminato group 10 catalysts had been restricted to comonomers in which the polar functional group is spatially restricted from interacting with the catalyst after migratory insertion (i.e., functionalized norbornenes). Note that the only example of copolymerization of ethylene with a simple polar vinyl monomer (e.g., methyl acrylate or methyl methacrylate) using a binuclear salicylaldiminato nickel catalyst reported to date has been withdrawn due to irreproducibility of these copolymerizations.[82,83]

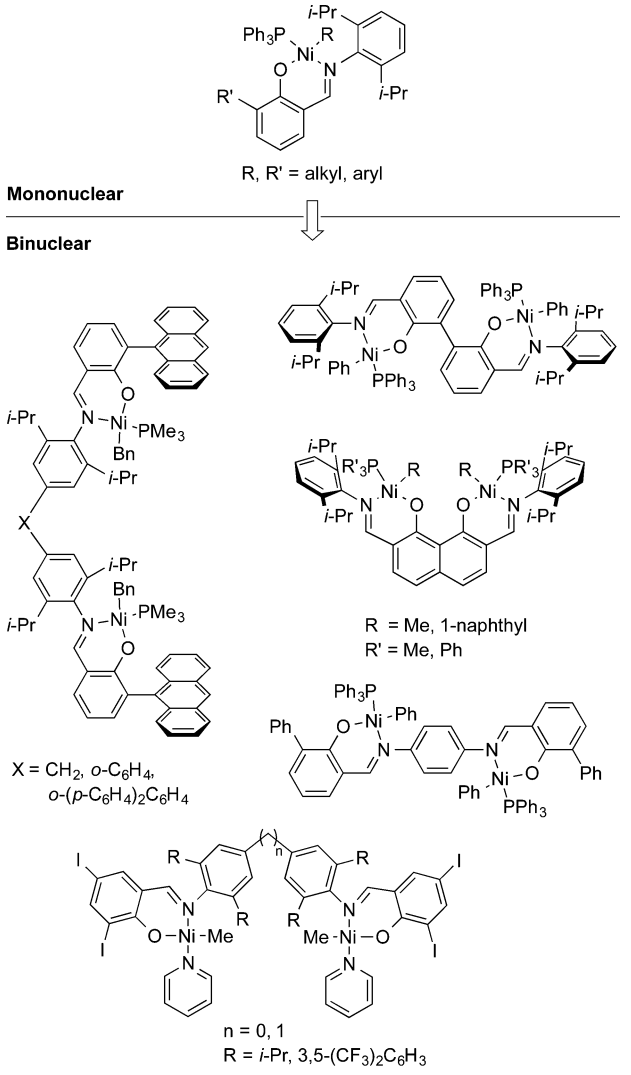
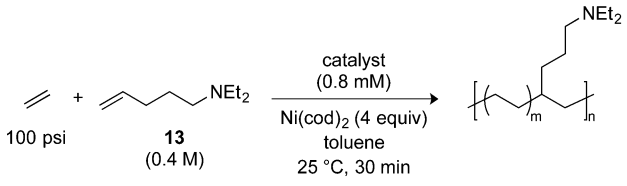


Figure 5. Representative structures of a mononuclear Grubbs-type salicylaldiminato nickel catalyst and selected binuclear derivatives.

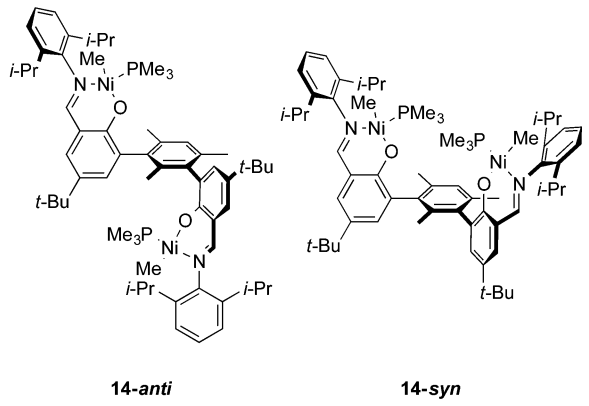
Recently, Agapie has demonstrated that binuclear salicylaldiminato nickel catalysts **14** and **15**, in which the metal complexes are connected through a substituted phenylene linker, mediate the polymerization of ethylene and amino-functionalized alkenes to form random copolymers.[84] The authors previously noted that polymerizations of ethylene and 1-hexene catalyzed by their binuclear nickel catalysts were inhibited in the presence of amine additives but not prohibitively so.[80,81] As such, investigations into polymerization of ethylene and amino-functionalized alkenes followed. The atropisomers of dinuclear complex **14** with a *syn* or *anti* disposition of the two metal centers about the phenylene linker are stable and isolable. It was subsequently shown that complex **14-*syn*** mediated the reaction of ethylene with *N,N*-diethyl 4-penten-1-amine in the presence of bis(1,5-cyclooctadiene)-nickel(0) as a phosphine scavenger with a higher turnover frequency (by a factor of ca. 5) compared to the atropisomer **14-*anti*** (Scheme 10). Intramolecular cooperativity is prohibited in the later complex; thus, these experiments provide convincing evidence that, all other things equal, the spacial proximity of the two metal centers plays a pivotal role in the observed increase in activity.

A survey of the polymerization of ethylene with a series of tertiary amino olefins using two dinuclear nickel catalysts is summarized in Table 3. In all cases, the dinuclear catalyst **14-*syn*** produced copolymer with higher activity compared to **15-*syn***. The number of methylenes between the alkene and the tertiary amine did not significantly influence the degree of amino olefin enchainment, but a positive correlation between the catalyst activity and the spacer length in the amino olefin is evident. Little or no enchainment of *N*-allyl dipropylamine

Scheme 10. Comparison of Atropisomers of 14 as Catalysts for the Copolymerization of Ethylene and *N,N*-Diethyl-4-penten-1-amine[a]



catalyst	activity (kg mol^{-1} h^{-1})	incorp. **13** (mol %)
14-*anti*	8	0.7
14-*syn*	45	0.3

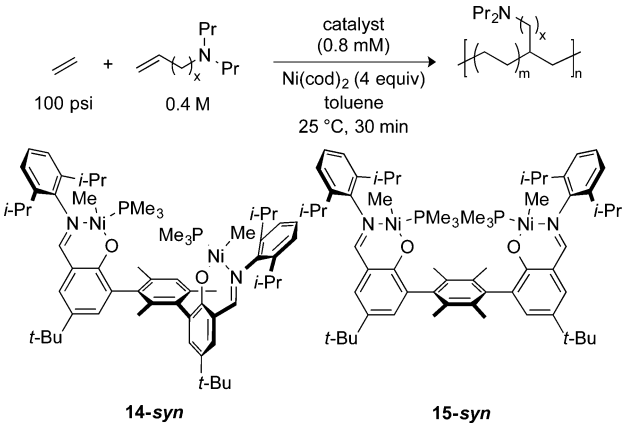


14-*anti* **14-*syn***

[a]cod = 1,5-cyclooctadiene.

dx.doi.org/10.1021/ma500034g | *Macromolecules* 2014, 47, 2541−2555

Table 3. Copolymerization of Ethylene and ω-Aminoalkenes Catalyzed by Binuclear Salicylaldiminato−Nickel Complexes[a]



14-*syn* 15-*syn*

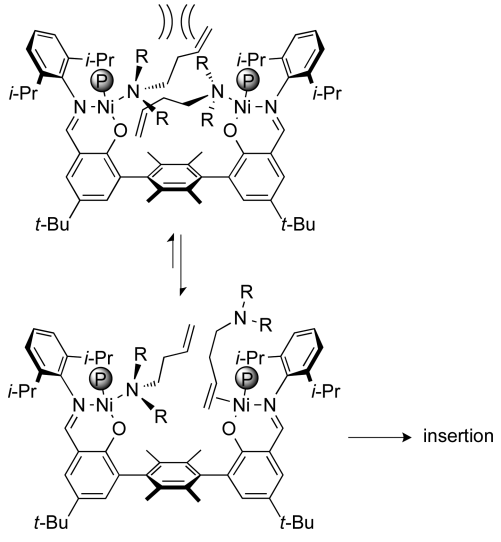
	15-*syn*		14-*syn*	
x	av activity[b]	incorp (mol %)	av activity[b]	incorp (mol %)
1	8	0.0	21	0.1
2	5	0.4	11	0.4
3	16	0.5	45	0.3
4	16	0.7	54	0.3
5	15	0.8	78	0.3
6	13	0.7	100	0.3

[a]cod = 1,5-cyclooctadiene. [b]In kg (mol Ni)$^{-1}$ h^{-1}.

(0.0−0.1 mol %) was observed using **14-*syn*** or **15-*syn*** as catalyst.

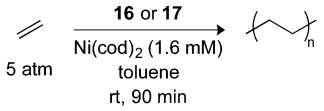
The origin of the bimetallic cooperativity is proposed as a shift in the equilibrium between the inactive complex with an *N*-bound amino olefin and the active complex that is π-bound (Scheme 11). The isomerization is thought to become favorable in the binuclear framework to alleviate steric congestion, given that alkenes in d^8 group 10 η^2-olefin complexes typically orient perpendicular to the metal square plane. The resulting π-complex would thus move one of the bulky tertiary amine groups away from the adjacent metal center and in so doing facilitate enchainment of the amino olefin.

Scheme 11. Proposed Cooperative Mechanism of Polar Monomer Enchainment Using Bimetallic Salicylaldiminato−Nickel Complexes

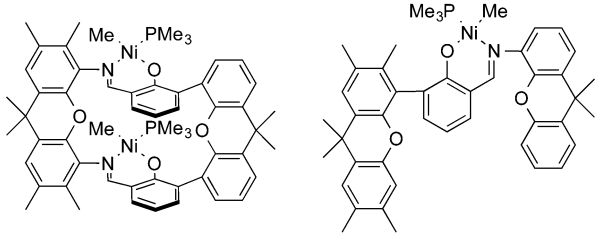


Osakada and Takeuchi have reported a dinuclear salicylaldiminato−nickel catalyst that is geometrically distinct from other dinuclear nickel complexes reported to date.[85] Whereas the two nickel centers are typically oriented in an edge-to-edge fashion, binuclear complex **16** exists in a "stacked" orientation whereby the square plane of one nickel complex is directly above the other (Scheme 12). This unique structural arrangement results in a very close proximity (ca. 4.7 Å) of the two nickel atoms. Similar to previously observed trends of reactivity of dinuclear salicylaldiminato nickel catalysts, the activity for polymerization of ethylene using **16** with Ni(cod)$_2$ as cocatalyst was higher compared to the mononuclear analogue **17** (Scheme 12). However, the branching ratio in polyethylene formed by dinuclear **16** was lower than for the mononuclear **17**, contrary to trends seen in other binuclear nickel catalysts.[66] Complex **16** was also used as a catalyst for the copolymerization of ethylene and unsaturated esters (Table 4). A moderately branched copolymer was obtained from the reaction of ethylene and

Scheme 12. Polymerization of Ethylene by a Mononuclear or Stacked Dinuclear Salicylaldiminato−Nickel Catalyst[a]



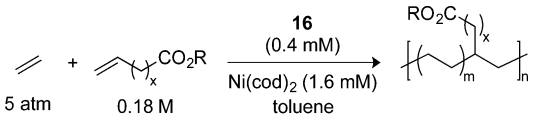
catalyst	activity (kg mol^{-1} h^{-1})	Me branches per 1000 C	M_n (M_w/M_n)
16 (0.4 mM)	11	59	2700 (4.5)
17 (0.8 mM)	1.9	95	940 (1.8)



16 **17**

[a]cod = 1,5-cyclooctadiene.

Table 4. Copolymerization of Ethylene and Ester Functionalized Monomers Catalyzed by Osakada and Takeuchi's Binuclear Salicylaldiminato−Nickel Catalyst 16[a]



x	R	av activity[b]	Me branches per 1000 C	M_n	M_w/M_n	incorp (mol %)
0	Me					
1	*t*-Bu	0.10	35	nd[c]	nd[c]	1.4
2	Et	0.25	32	2700[d]	6.5[d]	0.4

[a]cod = 1,5-cyclooctadiene. [b]In kg (mol Ni)$^{-1}$ h^{-1}. [c]Not determined. [d]Bimodal molecular weight distribution.

dx.doi.org/10.1021/ma500034g | *Macromolecules* 2014, 47, 2541−2555

ethyl 4-pentenoate or *tert*-butyl 3-butenoate in the presence of **16** and $Ni(cod)_2$, but no reaction was observed in the presence of methyl acrylate.

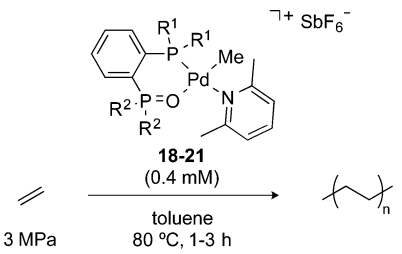
While complex **16** represents a novel structural motif in binuclear salicylaldiminato nickel polymerization catalysts, this broader family of catalysts remains inactive for insertion polymerization of any polar vinyl monomer. Nevertheless, the use of bimetallic cooperativity to mitigate catalyst inhibition through destabilization of σ-coordination/chelation of a functional group to the metal center represents a significant conceptual advance toward practical functional polyolefin synthesis.

A NEW CATALYST FAMILY FOR FUNCTIONAL POLYOLEFIN SYNTHESIS

Research efforts into the optimization of group 10 catalysts ligated by a phosphine−sulfonate, α-diimine, or salicylaldimine ligand for functional polyolefin synthesis have been extensive over the past decade, yet these existing methods still struggle against low turnover frequency, limited catalyst stability at elevated temperatures, or formation of copolymers with modest molecular weight.[40,41,43] The reactivity of many group 10 metal complexes that possess a (P,O)-type chelating ligand, other than a phosphine−sulfonate, for oligomerization or polymerization of ethylene has been established, but none have shown activity for polymerization with polar vinyl monomers other than acrylates.[86−93] New types of ancillary ligands that are weakly chelating, such as the recently reported phosphine−trifluoroborates that are selective for oligomerization of ethylene, are also dubious for applications in copolymerizations of polar vinyl monomers.[94−96] As such, there is an ongoing need for discovery and development of new catalyst families to complement ongoing efforts to mechanistically understand and optimize current classes of late metal polymerization catalysts (e.g., Brookhart-type, Grubbs-type, and Drent-type).

A promising new class of polymerization catalyst possessing a chelating (P,O)-type ligand was recently discovered by Carrow and Nozaki.[34] Cationic palladium complexes ligated by a bisphosphine monoxide (BPMO) were found to polymerize ethylene and a number of polar vinyl monomers, including historically challenging examples such as vinyl acetate, acrylonitrile, and vinyl ethers, to form linear random copolymers. Cationic group 10 complexes ligated by a BPMO have previously been shown to oligomerize ethylene.[89] However, ligands used in the prior study possessed only phenyl substituents on the phosphorus atoms in all cases. A notable observation in the work of Carrow and Nozaki was a marked effect on both the molecular weight of polyethylene and the turnover frequency as a function of the identity of the substituents on the phosphorus atoms (Table 5). The lowest polymer molecular weight and activity were observed when the phosphorus substituents of the catalyst were all phenyl (entry 1), consistent with the prior study of ethylene oligomerization using related group 10 BPMO complexes.[89] A significant increase in the average activity of ethylene homopolymerization was observed when the phosphine substituents were isopropyl rather than phenyl (entries 3 and 4). Additionally, a more pronounced effect was observed when the phosphine oxide substituents, which are more remote from the metal center than are the phosphine substituents, were *tert*-butyl rather than phenyl. In these cases, a substantial increase in polyethylene molecular weight was observed when the ligand contained *tert*-butyl substituents on the phosphine oxide (entries 2 and 4).

Table 5. Homopolymerization of Ethylene Using Cationic Bisphosphine Monoxide−Palladium Catalysts[a]



entry	catalyst	R^1	R^2	average activity[a]	M_n	M_w/M_n
1	**18**			63	800	1.8
2	**19**			36	16000	2.5
3	**20**			130	900	1.8
4	**21**			**340**	**39000**	2.3

[a]In kg (mol Pd)$^{-1}$ h^{-1}.

The polyethylene formed by these BPMO palladium catalysts was highly linear; analysis by quantitative ^{13}C NMR spectroscopy consistently showed less than ca. 6 methyl branches per 1000 methylene carbons and no higher alkyl branches. The ability to tune catalyst function by variation of the substituents near the oxygen donor atom of the BPMO is significant; many (P,O)-type chelating ligands, including phosphine−sulfonates, lack substituents near the oxygen donor atom that could be perturbed to tune the catalyst.

The correlation between the identity of the phosphine oxide substituent in the BPMO ligand and the resulting polymer molecular weight could be attributed to a steric effect, since it has been shown that group 10 metal polymerization catalysts often exhibit a positive correlation between steric crowding about the apical positions of the metal and the resulting polymer molecular weight.[97−99] While a *tert*-butyl substituent is substantially larger than a phenyl substituent, the effect of the phosphine oxide substituents in the BPMO ligand on the molecular weight of polymer formed may not be purely steric. An increase in the rate of chain transfer has been observed in (P,O)-type palladium complexes that have a weaker Pd−O bond, though it is unclear if the origin of this effect is due to changes in electron density at the metal or by facilitating hemilabile behavior in the chelating ancillary ligand.[88,100]

Comparison of single-crystal X-ray crystallographic data for a series of (P,O)Pd(Me)(Cl) compounds (Figure 6) clearly shows the palladium−methyl bond located *trans* to the *tert*-butylphosphine oxide moiety of the BPMO ligand is the longest. These data suggest the *trans* influence of the *tert*-butylphosphine oxide moiety of the BPMO ligand is larger than for any of the other neutral or anionic oxygen ligands in this series of complexes.[34,101−105] Additionally, the P−Pd−C bond angles of **22** and the phosphine−sulfonato palladium complex, the only two types of complexes in this series that can polymerize ethylene, are not distinguished from those in the other complexes. This argues against steric pressure from the phosphine ligand as a major contributor to the observed lengthening of the Pd−C bond in **22** relative to the other (P,O)Pd(Me)(Cl) complexes. Thus, the electronic properties of BPMO ligands that contain alkyl phosphine oxide substituents appear to be distinct compared to other (P,O)-type ligands, including BPMO ligands that possess aryl

dx.doi.org/10.1021/ma500034g | *Macromolecules* 2014, 47, 2541−2555

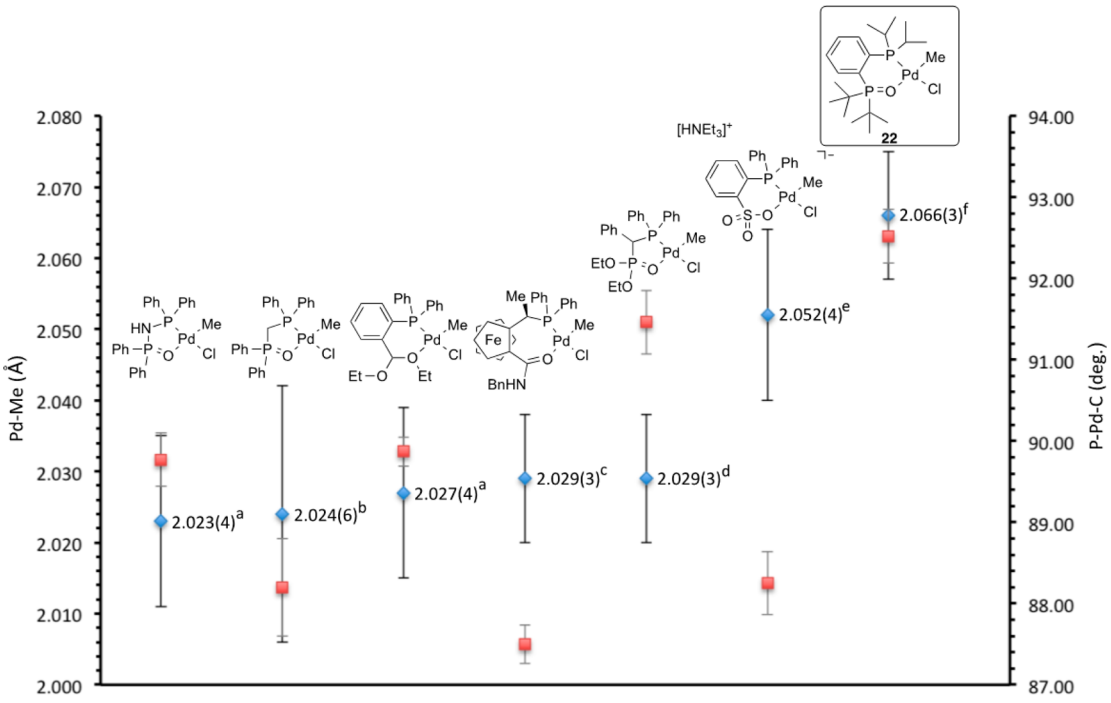


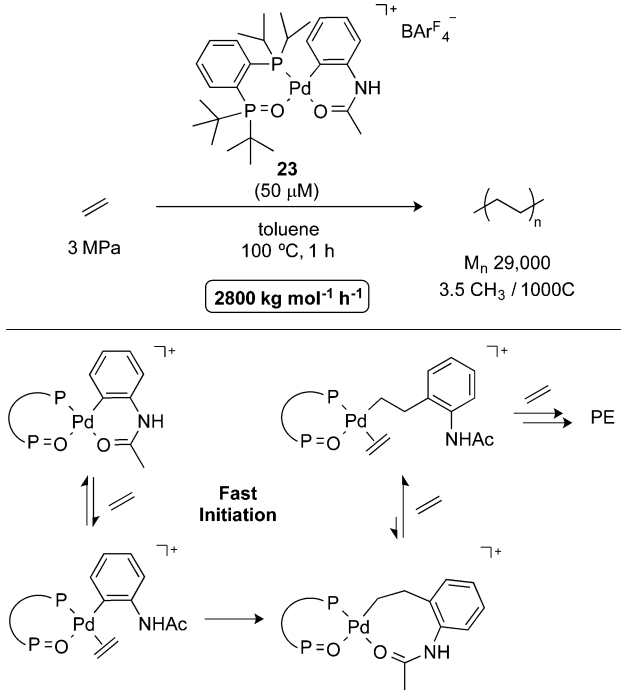
Figure 6. Pd−CH_3 bond lengths ($\pm 3\sigma$) and P−Pd−C bonds angles ($\pm 3\sigma$) determined by single-crystal X-ray crystallography for a series of (L_2)Pd(Me)(Cl) complexes with a chelating (P,O)-type ligand. [a]Ref 101. [b]Ref 102. [c]Ref 103. [d]Ref 104. [e]Ref 105. [f]Ref 34.

phosphine oxide substituents. Further studies could provide insight into how the BPMO confers such unique structural and catalytic properties to palladium compared to other types of cationic group 10 polymerization catalysts.

Single component group 10 metal polymerization precatalysts typically possess a stabilizing ligand (i.e., amine, pyridine, phosphine) that can affect the initiation and/or propagation steps by competing with monomer for coordination to the metal center.[29,106] One strategy to mitigate this kinetic impediment is the use of weakly coordinating ligands, such as dimethyl sulfoxide, that can be readily displaced by ethylene.[107] Alternatively, a palladacycle in which a dative ligand of the precatalyst is directly attached to the carbon ligand could be used, but group 10 single component polymerization catalysts containing this structural motif are infrequently utilized.[23,98,108] In the case of BPMO palladacycle **23**, the coordinating group (e.g., acetamide) is incorporated into the polymer chain upon insertion of ethylene into the palladium−phenyl bond during initiation and is subsequently removed from the proximity of the metal during propagation (Scheme 13). Complex **23** was shown to form linear polyethylene with good molecular weight at 100 °C and high average turnover frequency (ca. 10^5 h^{-1}) for a palladium catalyst, but also performed consistently better in copolymerizations of ethylene and polar monomers compared to an analogous BPMO palladium complex (**21**) containing a 2,6-lutidine spectrator ligand (vide infra).

Cationic BPMO−palladium complexes also promoted the copolymerization of ethylene and polar monomers. A summary of polymer products obtained from the reaction of ethylene and a polar monomer catalyzed by palladacycle **23** is shown in Scheme 14. The polymers formed were highly linear with less than two methyl branches per 1000 methylene carbons observed in all cases, and the polar functional group was distributed randomly throughout the polymer chain. Incorporation of the functional monomer at both the chain ends and in the main chain was observed for polar vinyl monomers; only

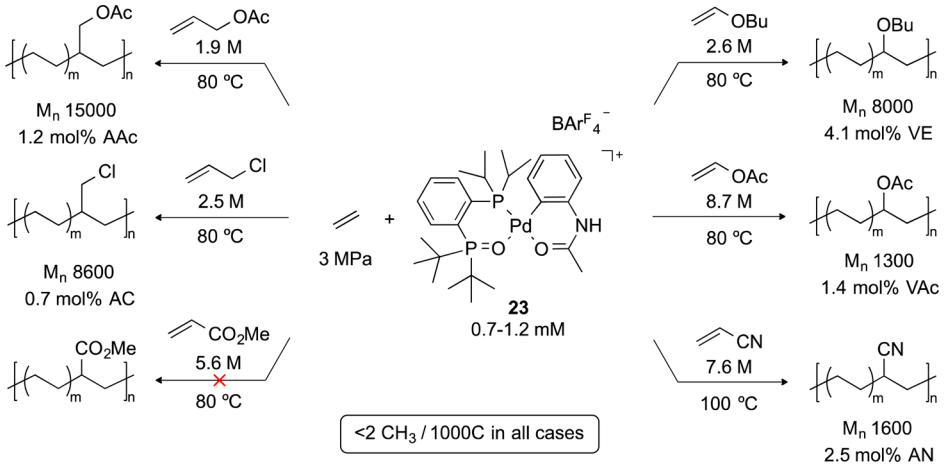
Scheme 13. Homopolymerization of Ethylene by a Single Component BPMO−Palladacycle Precatalyst and a Proposed Mechanism of Initiation



main chain incorporation of allyl monomers was observed, as determined by quantitative ^{13}C NMR spectroscopy. The enchainment of the polar monomer into these polymers ranged from 0.7 to 4.1 mol %, which was comparable to or lower than the incorporation ratios previously obtained using phosphine−sulfonato palladium catalysts under similar reaction conditions. The incorporation ratio of polar monomer (except

dx.doi.org/10.1021/ma500034g | Macromolecules 2014, 47, 2541−2555

Scheme 14. Polymerization of Ethylene and Polar Monomers Using a Cationic Bisphosphine−Monoxide Palladium Catalyst



for allyl chloride) and the average activity were higher in copolymerizations conducted with BPMO palladacycle **23** compared to **21**, which contains a 2,6-lutidine ligand. The molecular weight was also comparable or higher when **23** was used as catalyst compared to **21** in these reactions.

An anomaly in the reactivity of BPMO−palladium catalysts **21** and **23** is their inability to promote the copolymerization of ethylene and methyl acrylate. Heating either **21** or **23** in the presence of ethylene and methyl acrylate for 12−18 h at 80 °C did not afford measurable quantities of polymer. Among industrial polar monomers, acrylates are the most amenable to polymerization with ethylene by a coordination−insertion mechanism; numerous late-transition-metal complexes have been reported to promote this reaction.[41] However, few metal catalysts can promote polymerization of ethylene and polar vinyl monomers other than acrylates. Thus, the reactivity trend of cationic BPMO palladium complexes is transposed from that of other late-transition-metal catalysts. The origin of the poor reactivity of **21** or **23** toward ethylene and acrylates has not yet been clarified.

The observed reactivity of cationic BPMO−palladium complexes contrasts several trends in reactivity observed for other cationic palladium polymerization catalysts. First, cationic Brookhart catalysts afford varying degrees of chain branching depending on the ligand structure, ethylene pressure, and reaction temperature, yet the polyethylenes and random poly(ethylene-*co*-X) copolymers (X = polar monomer) formed by cationic BPMO palladium catalysts are consistently linear. Second, cationic palladium complexes ligated by an α-diimine tend to decompose during polymerizations conducted at or above ambient temperatures; even the most thermally robust examples are persistent for only ca. 15 min at 90−100 °C, though certain nickel complexes ligated by a bulky 2,6-diaryl substituted α-diimine have been reported to remain active for hours at elevated temperatures.[98,109−112] On the other hand, **21** and **23** are persistent at 80−100 °C over a period of at least several hours. Also, BPMO−palladium complexes were demonstrated to tolerate polar vinyl monomers that readily deactivate the catalyst by β-elimination of the functional group (e.g., vinyl acetate and vinyl ethers) following insertion or by strong σ-coordination rather than π-coordination of the polar vinyl monomer (e.g., acrylonitrile). All other reported cationic group 10 catalysts do not tolerate vinyl acetate, vinyl ethers, or acrylonitrile. These reactivity trends highlight the powerful influence the ancillary ligand can have on the reactivity of late transition metal polymerization catalysts and the potential reward for continued efforts to uncover new types of ligands and catalysts.

SUMMARY AND OUTLOOK

As should be evident from this Perspective, there have been a number of exciting developments in the area of functional polyolefin synthesis. A common thread among these innovations is the perturbation of catalyst function by tailored design of the chelating ancillary ligand, aided in many cases by improved mechanistic understanding of the initiation, propagation, chain transfer, and deactivation steps during (co)-polymerizations. Specific advances surveyed here include (Figure 1):

- Steric bulk at phosphorus in diazaphospholidine−sulfonato palladium complexes was used to reverse the inherent preference of electron-deficient olefins to undergo (2,1)-insertion, thus demonstrating that catalyst control over insertion regioselectivity in late-transition-metal catalysts is possible even for simple polar vinyl monomers that lack directing groups.
- Enantiomorphic site stereocontrol has for the first time been demonstrated for the insertion of simple polar vinyl monomers (e.g., methyl acrylate and vinyl acetate) in stoichiometric and catalytic reactions using *P*-chiral phosphine−sulfonato palladium complexes.
- Binuclear cooperativity in salicylaldiminato nickel catalysts was shown to facilitate increased turnover frequency for polymerization of ethylene and monomers with a remote functional group, potentially by a shift in the equilibrium between the inactive (σ-bound) and active (π-bound) states of the catalyst when coordinated by the polar monomer.
- A new class of group 10 metal catalyst, cationic palladium complexes ligated by a bisphosphine monoxide, were shown to exhibit unusual activity for the formation of linear polyethylene and random poly(ethylene-*co*-X) (X = vinyl acetate, acrylonitrile, vinyl ether, allyl chloride, allyl acetate) that contrasts the reactivity of cationic Brookhart-type catalysts.

Looking forward in this research area, challenges still remain and pressing issues in need of further development exist. To date, almost all catalysts for functional polyolefin synthesis

dx.doi.org/10.1021/ma500034g | *Macromolecules* 2014, 47, 2541−2555

using polar vinyl monomers other than acrylates are palladium complexes. Base metal catalysts, especially those of nickel, would be desirable from an industrial perspective for polymerizations of polar vinyl monomers, yet developments in this arena currently lag far behind those using palladium catalysts. Second, even state-of-the-art catalysts for functional polyolefin synthesis function with turnover frequencies several orders of magnitude below their respective activity for ethylene homopolymerization. These copolymerization activities have not yet risen to a level acceptable for industrial functional polyolefin synthesis. Furthermore, many late-transition-metal catalysts are not stable over prolonged periods of time at elevated temperature, even if initial rates are high.[97,113,114] Lastly, known catalysts for functional polyolefin synthesis fall into predominantly one of only three categories: α-diimine palladium or nickel complexes (Brookhart-type), salicylaldiminato nickel complexes (Grubbs-type), and particularly phosphine−sulfonato palladium complexes (Drent-type). Thus, substantial potential exists for innovation in functional polyolefin synthesis through continued discovery and design of fundamentally new classes of catalysts within and beyond the group 10 transition metals.

AUTHOR INFORMATION

Corresponding Author

*E-mail: nozaki@chembio.t.u-tokyo.ac.jp (K.N.).

Notes

The authors declare no competing financial interest.

Biographies

Brad P. Carrow is an Assistant Professor of Chemistry at Princeton University. His research interests revolve around transition metal catalysis in the context of polymer synthesis, sustainable organic synthesis, and inert bond activation. Previously he was a postdoctoral fellow and then an assistant professor at the University of Tokyo working under Kyoko Nozaki and completed his Ph.D. studies under John F. Hartwig at the University of Illinois at Urbana−Champaign.

Kyoko Nozaki is Professor of Chemistry and Biotechnology at The University of Tokyo. Her research interest is focused on development of homogeneous catalysts for polymer synthesis and organic synthesis. She received her Ph.D. in 1991 (Professor Kiitiro Utimoto). In 1991, she started her research career as an instructor at Kyoto University, became an associate professor in 1999, and since 2003 occupies her current position. Her accomplishments include the Chemical Society of Japan Award for Young Chemists (1998), the Organometallic Chemistry directed towards Organic Synthesis (OMCOS) prize (2003), the Japan IBM Science Award (2005), the Mukaiyama Award (2008), the Saruhashi Prize (2008), the Mitsui Chemicals Catalysis Science Award (2009), ACS 2012 Organometallic Lecturer (2012), and The Award of the Society of Polymer Science, Japan (2013). She is on the editorial board of *ChemCatChem* and on the editorial advisory boards of *Chem. Lett.*, *J. Am. Chem. Soc.*, *Organometallics*, *Inorg. Chem.*, *Chem. Sci.*, *Catal. Sci. Technol.*, *Angew. Chem.*, and *J. Polym. Sci., Part A: Polym. Chem.*

REFERENCES

(1) Boor, J. *Ziegler-Natta Catalysts and Polymerizations*; Academic Press: New York, 1979.
(2) McMillan, F. M. *The Chain Straighteners*; Oxford University Press: London, 1979.
(3) Jordan, R. F.; Stone, F. G. A.; Robert, W. *Adv. Organomet. Chem.* **1991**, *32*, 325.
(4) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1.
(5) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255.
(6) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.
(7) Huang, J.; Rempel, G. L. *Prog. Polym. Sci.* **1995**, *20*, 459.
(8) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907.
(9) Hlatky, G. G. *Coord. Chem. Rev.* **1999**, *181*, 243.
(10) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.
(11) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223.
(12) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.
(13) Boaen, N. K.; Hillmyer, M. A. *Chem. Soc. Rev.* **2005**, *34*, 267.
(14) Chung, T. C. *Functionalization of Polyolefins*; Academic Press: London, 2002.
(15) Hillmyer, M. A.; Laredo, W. R.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 6311.
(16) Lehman, S. E.; Wagener, K. B.; Baugh, L. S.; Rucker, S. P.; Schulz, D. N.; Varma-Nair, M.; Berluche, E. *Macromolecules* **2007**, *40*, 2643.
(17) Scherman, O. A.; Walker, R.; Grubbs, R. H. *Macromolecules* **2005**, *38*, 9009.
(18) Watson, M. D.; Wagener, K. B. *Macromolecules* **2000**, *33*, 3196.
(19) Watson, M. D.; Wagener, K. B. *Macromolecules* **2000**, *33*, 5411.
(20) Watson, M. D.; Wagener, K. B. *Macromolecules* **2000**, *33*, 8963.
(21) Schwendeman, J. E.; Church, A. C.; Wagener, K. B. *Adv. Synth. Catal.* **2002**, *344*, 597.

(22) *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1985; Vol. *1*.
(23) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.
(24) Drent, E.; Pello, D. H.; Jager, W. W. EP 589, 527, March 30, 1994.
(25) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744.
(26) Kochi, T.; Noda, S.; Yoshimura, K.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 8948.
(27) Anselment, T. M. J.; Anderson, C. E.; Rieger, B.; Boeddinghaus, M. B.; Fassler, T. F. *Dalton Trans.* **2011**, *40*, 8304.
(28) Skupov, K. M.; Piche, L.; Claverie, J. P. *Macromolecules* **2008**, *41*, 2309.
(29) Friedberger, T.; Wucher, P.; Mecking, S. *J. Am. Chem. Soc.* **2011**, *134*, 1010.
(30) Rünzi, T.; Fröhlich, D.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 17690.
(31) Kryuchkov, V. A.; Daigle, J.-C.; Skupov, K. M.; Claverie, J. P.; Winnik, F. M. *J. Am. Chem. Soc.* **2010**, *132*, 15573.
(32) Daigle, J.-C.; Piche, L.; Claverie, J. P. *Macromolecules* **2011**, *44*, 1760.
(33) Ito, S.; Munakata, K.; Nakamura, A.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14606.
(34) Carrow, B. P.; Nozaki, K. *J. Am. Chem. Soc.* **2012**, *134*, 8802.
(35) Weng, W.; Shen, Z.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 15450.
(36) Leicht, H.; Göttker-Schnetmann, I.; Mecking, S. *Angew. Chem.* **2013**, *125*, 4055.
(37) Luo, S.; Jordan, R. F. *J. Am. Chem. Soc.* **2006**, *128*, 12072.
(38) Luo, S.; Vela, J.; Lief, G. R.; Jordan, R. F. *J. Am. Chem. Soc.* **2007**, *129*, 8946.
(39) Ito, S.; Kanazawa, M.; Munakata, K.; Kuroda, J.-i.; Okumura, Y.; Nozaki, K. *J. Am. Chem. Soc.* **2011**, *133*, 1232.
(40) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.
(41) Nakamura, A.; Ito, S.; Nozaki, K. *Chem. Rev.* **2009**, *109*, 5215.
(42) Goodall, B. L. *Top. Organomet. Chem.* **2009**, *26*, 159.
(43) Nakamura, A.; Anselment, T. M. J.; Claverie, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leeuwen, P. W. N. M.; Nozaki, K. *Acc. Chem. Res.* **2013**, *46*, 1438.
(44) Guan, Z.; Popeney, C. S. *Top. Organomet. Chem.* **2008**, *26*, 179.
(45) Camacho, D. H.; Guan, Z. *Chem. Commun.* **2010**, *46*, 7879.
(46) Wucher, P.; Caporaso, L.; Roesle, P.; Ragone, F.; Cavallo, L.; Mecking, S.; Göttker-Schnetmann, I. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *108*, 8955.
(47) Wucher, P.; Roesle, P.; Falivene, L.; Cavallo, L.; Caporaso, L.; Göttker-Schnetmann, I.; Mecking, S. *Organometallics* **2012**, *31*, 8505.
(48) Haras, A.; Anderson, G. D. W.; Michalak, A.; Rieger, B.; Ziegler, T. *Organometallics* **2006**, *25*, 4491.
(49) Noda, S.; Nakamura, A.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. *J. Am. Chem. Soc.* **2009**, *131*, 14088.
(50) Neuwald, B.; Falivene, L.; Caporaso, L.; Cavallo, L.; Mecking, S. *Chem.—Eur. J.* **2013**, *19*, 17773.
(51) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686.
(52) Nakano, K.; Kosaka, N.; Hiyama, T.; Nozaki, K. *Dalton Trans.* **2003**, 4039.
(53) Nozaki, K. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 215.
(54) Nozaki, K. *Pure Appl. Chem.* **2004**, *76*, 541.
(55) Nozaki, K. *Polym. J.* **2005**, *37*, 871.
(56) Kacker, S.; Jiang, Z.; Sen, A. *Macromolecules* **1996**, *29*, 5852.
(57) Lee, J. T.; Alper, H. *Chem. Commun.* **2000**, 2189.
(58) Kochi, T.; Nakamura, A.; Ida, H.; Nozaki, K. *J. Am. Chem. Soc.* **2007**, *129*, 7770.
(59) Nakamura, A.; Munakata, K.; Kochi, T.; Nozaki, K. *J. Am. Chem. Soc.* **2008**, *130*, 8128.
(60) Kageyama, T.; Ito, S.; Nozaki, K. *Chem.—Asian J.* **2011**, *6*, 690.
(61) Nakamura, A.; Munakata, K.; Ito, S.; Kochi, T.; Chung, L. W.; Morokuma, K.; Nozaki, K. *J. Am. Chem. Soc.* **2011**, *133*, 6761.
(62) Nakamura, A.; Kageyama, T.; Goto, H.; Carrow, B. P.; Ito, S.; Nozaki, K. *J. Am. Chem. Soc.* **2012**, *134*, 12366.
(63) Cabri, W.; Candiani, I. *Acc. Chem. Res.* **1995**, *28*, 2.
(64) Neuwald, B.; Caporaso, L.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2012**, *135*, 1026.
(65) Guironnet, D.; Caporaso, L.; Neuwald, B.; Göttker-Schnetmann, I.; Cavallo, L.; Mecking, S. *J. Am. Chem. Soc.* **2010**, *132*, 4418.
(66) Delferro, M.; Marks, T. J. *Chem. Rev.* **2011**, *111*, 2450.
(67) Li, H.; Marks, T. J. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15295.
(68) Zhang, D.; Jin, G.-X. *Organometallics* **2003**, *22*, 2851.
(69) Wang, C.; Friedrich, S.; Younkin, T. R.; Li, R. T.; Grubbs, R. H.; Bansleben, D. A.; Day, M. W. *Organometallics* **1998**, *17*, 3149.
(70) Younkin, T.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.
(71) Hu, T.; Tang, L.-M.; Li, X.-F.; Li, Y.-S.; Hu, N.-H. *Organometallics* **2005**, *24*, 2628.
(72) S, S.; Joe, D. J.; Na, S. J.; Park, Y.-W.; Choi, C. H.; Lee, B. Y. *Macromolecules* **2005**, *38*, 10027.
(73) Wang, W.-H.; Jin, G.-X. *Inorg. Chem. Commun.* **2006**, *9*, 548.
(74) Zhang, D.; Jin, G.-X. *Inorg. Chem. Commun.* **2006**, *9*, 1322.
(75) Na, S. J.; Joe, D. J.; S, S.; Han, W.-S.; Kang, S. O.; Lee, B. Y. *J. Organomet. Chem.* **2006**, *691*, 611.
(76) Hu, T.; Li, Y.-G.; Li, Y.-S.; Hu, N.-H. *J. Mol. Catal. A: Chem.* **2006**, *253*, 155.
(77) Chen, Q.; Yu, J.; Huang, J. *Organometallics* **2007**, *26*, 617.
(78) Wehrmann, P.; Mecking, S. *Organometallics* **2008**, *27*, 1399.
(79) Rodriguez, B. A.; Delferro, M.; Marks, T. J. *Organometallics* **2008**, *27*, 2166.
(80) Radlauer, M. R.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2012**, *134*, 1478.
(81) Radlauer, M. R.; Day, M. W.; Agapie, T. *Organometallics* **2012**, *31*, 2231.
(82) Rodriguez, B. A.; Delferro, M.; Marks, T. J. *J. Am. Chem. Soc.* **2013**, *135*, 17651.
(83) Rodriguez, B. A.; Delferro, M.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5902.
(84) Radlauer, M. R.; Buckley, A. K.; Henling, L. M.; Agapie, T. *J. Am. Chem. Soc.* **2013**, *135*, 3784.
(85) Takeuchi, D.; Chiba, Y.; Takano, S.; Osakada, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 12536.
(86) Kuhn, P.; Semeril, D.; Matt, D.; Chetcuti, M. J.; Lutz, P. *Dalton Trans.* **2007**, 515.
(87) Britovsek, G. J. P.; Keim, W.; Mecking, S.; Sainz, D.; Wagner, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1632.
(88) Mecking, S.; Keim, W. *Organometallics* **1996**, *15*, 2650.
(89) Brassat, I.; Keim, W.; Killat, S.; Möthrath, M.; Mastrorilli, P.; Nobile, C. F.; Suranna, G. P. *J. Mol. Catal. A: Chem.* **2000**, *157*, 41.
(90) Wang, L.; Hauptman, E.; Johnson, L. K.; McCord, E. F.; Wang, Y.; Ittel, S. D. WO 0192342, Dec 6, 2001.
(91) Wang, L.; Johnson, L. K.; Ionkin, A. S. WO 0192348, Dec 6, 2001.
(92) Liu, W.; Malinoski, J. M.; Brookhart, M. *Organometallics* **2002**, *21*, 2836.
(93) Malinoski, J. M.; Brookhart, M. *Organometallics* **2003**, *22*, 5324.
(94) Kim, Y.; Jordan, R. F. *Organometallics* **2011**, *30*, 4250.
(95) Gott, A. L.; Piers, W. E.; Dutton, J. L.; McDonald, R.; Parvez, M. *Organometallics* **2011**, *30*, 4236.
(96) Gutsulyak, D. V.; Gott, A. L.; Piers, W. E.; Parvez, M. *Organometallics* **2013**, *32*, 3363.
(97) Gates, D. P.; Svejda, S. A.; Oñate, E.; Killian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320.
(98) Camacho, D. H.; Salo, E. V.; Ziller, J. W.; Guan, Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 1821.
(99) 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.

(100) Cai, Z.; Shen, Z.; Zhou, X.; Jordan, R. F. *ACS Catal.* **2012**, *2*, 1187.
(101) Elsegood, M. R. J.; Smith, M. B.; Dale, S. H. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2007**, *63*, m7.
(102) Brassat, I.; Englert, U.; Keim, W.; Keitel, D. P.; Killat, S.; Suranna, G.-P.; Wang, R. *Inorg. Chim. Acta* **1998**, *280*, 150.
(103) Lamač, M.; Císařová, I.; Štěpnička, P. *Eur. J. Inorg. Chem.* **2007**, *2007*, 2274.
(104) Hamada, A.; Braunstein, P. *Organometallics* **2009**, *28*, 1688.
(105) Kochi, T.; Yoshimura, K.; Nozaki, K. *Dalton Trans.* **2006**, 25.
(106) Neuwald, B.; Ölscher, F.; Göttker-Schnetmann, I.; Mecking, S. *Organometallics* **2012**, *31*, 3128.
(107) Guironnet, D.; Roesle, P.; Rünzi, T.; Göttker-Schnetmann, I.; Mecking, S. *J. Am. Chem. Soc.* **2008**, *131*, 422.
(108) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.
(109) Rhinehart, J. L.; Brown, L. A.; Long, B. K. *J. Am. Chem. Soc.* **2013**, *135*, 16316.
(110) Schmid, M.; Eberhardt, R.; Klinga, M.; Leskelä, M.; Rieger, B. *Organometallics* **2001**, *20*, 2321.
(111) Meinhard, D.; Wegner, M.; Kipiani, G.; Hearley, A.; Reuter, P.; Fischer, S.; Marti, O.; Rieger, B. *J. Am. Chem. Soc.* **2007**, *129*, 9182.
(112) Moody, L. S.; Mackenzie, P. B.; Killian, C. M.; Lavoie, G. G.; Ponasik, J. A.; Barrett, A. G. M.; Smith, T. W.; Pearson, J. C. WO 0050470, Aug 31, 2000.
(113) Rünzi, T.; Tritschler, U.; Roesle, P.; Göttker-Schnetmann, I.; Möller, H. M.; Caporaso, L.; Poater, A.; Cavallo, L.; Mecking, S. *Organometallics* **2012**, *31*, 8388.
(114) Soshnikov, I. E.; Semikolenova, N. V.; Zakharov, V. A.; Möller, H. M.; Ölscher, F.; Osichow, A.; Göttker-Schnettmann, I.; Mecking, S.; Talsi, E. P.; Bryliakov, K. P. *Chem.—Eur. J.* **2013**, *19*, 11409.