Copolymerization of Polar Monomers with Olefins Using Transition-Metal Complexes

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I. Introduction

The evolution of olefin polymerization systems over the last 45 years has involved a prolific coupling of polymer science with organometallic chemistry.[1-4] Successes include the development of catalysts that rival the activities of enzymes and systems that yield polymers possessing structural fidelities approaching 100%.[5,6] Central to this success has been a refined understanding of reaction mechanisms and a translation of this understanding into architectural control with specifically designed catalysts. However, despite

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these successes, monumental goals still loom. Paramount among these targets is the controlled copolymerization of simple olefins with polar functional monomers. Success in this area would constitute a quantum advance in the polyolefin field.

Of the many permutations available for modifying the properties of a polymer, the incorporation of functional groups into an otherwise nonpolar material is substantial.[7,8] Polar groups exercise control over important properties such as toughness, adhesion, barrier properties, surface properties (paintability, printability, etc.), solvent resistance (or its inverse), miscibility with other polymers, and rheological properties. For example, specific targets include linear ethylene−vinyl acetate copolymers; random, linear copolymers of ethylene and acrylic acid (eq 1);[9] or propylene−vinyl alcohol copolymers possessing periodic hydroxyl groups that would fit within the polypropylene crystalline lattice without disruption. Not only would the important properties related
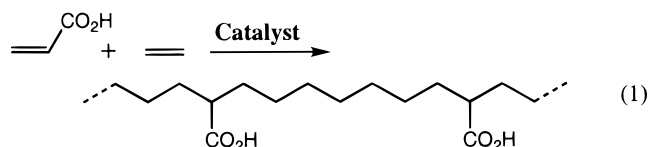
to crystallinity be maintained (modulus, strength, solvent resistance, etc.), but new properties would also be expressed.

An important feature of successful copolymerization of two monomers is the ability to control the amount and distribution of comonomer in the product polymer. Aside from monomer concentration, the other important determinant in this process is the relative reactivity of the monomer pair. This depends on the orbital energies of the monomers and their respective interaction energies with the frontier orbitals of the catalyst. All other factors equal, a monomer with good overlap of orbital energies with the catalyst will be the preferred substrate in polymerization. Electron-withdrawing or -donating groups strongly influence the energies of the HOMO and LUMO orbitals of olefins, making their chemistries far different than the reference ethylene, Figure 1.[10]

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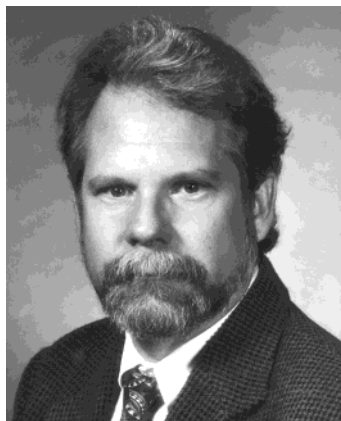
After receiving his Bachelors and Masters degrees at Cal State Northridge, Bruce Novak obtained his Ph.D. degree in Chemistry from Caltech. He then accepted a position in the chemistry department at the University of California at Berkeley. After four years he moved to the Polymer Science Department at the University of Massachusetts, Amherst. He is currently the Howard J. Schaeffer Distinguished Professor and Head of the chemistry department at North Carolina State University.

Relative to ethylene, (meth)acrylates or vinyl ethers would therefore be expected to display very different reactivities. This dissimilarity constitutes one of the substantial hurdles that needs to be overcome if economically feasible copolymerization systems are to be developed. As we will see, separating the olefin from the functional group using methylene spacers can attenuate these strong energy perturbations. Unfortunately, longer-chain functional monomers cost more and may adversely effect the degree of crystallinity and the density of the resultant polymer.

In the context of this paper, we will define a polar functional monomer as an olefin molecule that also contains a heteroatom-bearing functional group capable of interacting with the catalyst components.[11] Omitted from this review are copolymerizations of dienes and en—yne compounds, as are the extensively
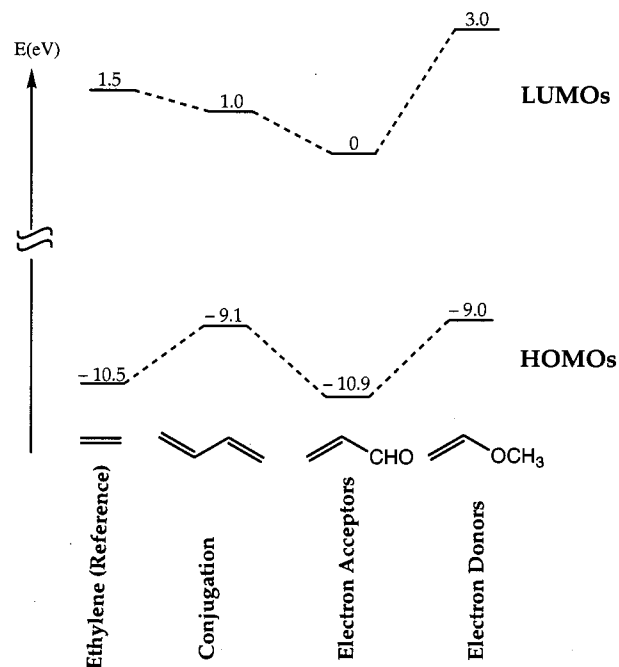

Figure 1. Orbital energy diagram showing the perturbation of the olefin π-orbital energies as a function of substituents (after ref 10).

studied copolymerizations of olefins with carbon monoxide. These copolymerizations have been reviewed in detail elsewhere.[12]

In ranking the tendency of functional groups to inhibit copolymerization, we can generalize by listing in order of increasing tolerance: Bronsted acids < oxygen functionalities < nitrogen functionalities < halogens. The latter two categories are occasionally passive enough to allow for their polymerization without protection—deprotection steps. For this reason, the direct polymerization of halogenated and amine monomers is the first copolymerization topic addressed in this review. More reactive functional groups (alcohols, acids, esters, etc.) nearly always require passivation, and these monomers are subsequently discussed in terms of the protection methodology employed. Interweaving throughout the studies on the various functional groups are the common themes of steric and proximity protection. However, prior to the discussions of copolymerization, we first discuss studies of homopolymerization of (meth)-acrylates to provide a basis for comparison and contrast. Finally, alternative late-transition-metal catalysts are discussed. Looking past fortuitous happenstance, successful strategies for functional comonomer incorporation may very well combine all of these approaches, and many of the examples reported herein do use a combination of tactics. In general, greater success can be achieved by using target monomers that have functional groups that are protected, sterically shielded, and far removed from the olefin, as well as catalysts that are based on late-transition-metal complexes.

II. Homopolymerization of (Meth)acrylates

Of the two goals, homopolymerization and copolymerization of functional monomers, the latter is the

Scheme 1
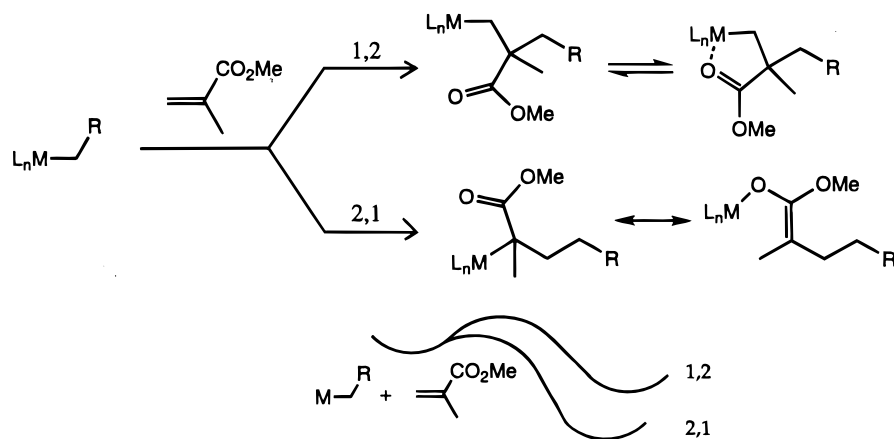
more challenging. Simple coordination of the functional group by the metal may be a problem. For example, potential olefin copolymerization could be inhibited by back chelation of the penultimate carbonyl after 1,2-insertions, a process that blocks monomer access to vacant coordination sites (Scheme 1). In homopolymerizations, the functional groups themselves may provide alternative mechanisms that facilitate propagation through intermediates unique to their structures. One example is the formation of enolate species in acrylate and methacrylate polymerizations (Scheme 1). Once the metal−oxygen enolate bond forms, however (e.g., a 2,1-insertion, Scheme 1), insertions of olefins will not occur due to the endothermicity of the insertion step (i.e., BDE_{M-O} > BDE_{M-C}) (Scheme 2).

Scheme 2
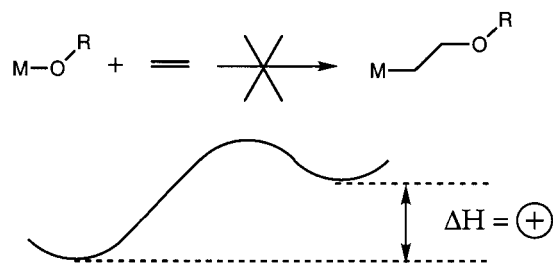
An exception to this would be a metal enolate species that was capable of rearranging from the oxygen-bound enolate to another carbon−metal-bonded intermediate. Such a system based on palladium catalysts has been discovered, and this carbon-bound intermediate does insert ethylene (vide infra).

Zirconocenes and lanthanocenes active for olefin polymerization do, in fact, carry out well-controlled homopolymerizations of (meth)acrylic monomers, but polymerization takes place by an enolate mechanism in which the conjugated carbonyl group plays a crucial role in stabilizing the active center. Both monometallic and bimetallic mechanisms have been documented. Collins and co-workers developed a zirconocene group-transfer polymerization (GTP) technique for the polymerization of methyl methacrylate (MMA) which utilizes a neutral zirconocene enolate as an initiator and the conjugate zirconocene cation as a catalyst (Scheme 3).[13,14]

Each monomer addition step interconverts the two organometallic components. The poly(methyl methacrylate) (PMMA) obtained is predominantly syndiotactic, although isotactic PMMA has been obtained by using chiral indenyl zirconocenes in combination with non-zirconocene Lewis acids.[15] No reports of attempted ethylene or α-olefin copolymerizations have been described.

A second (meth)acrylate polymerization system based on neutral lanthanocenes, particularly $(C_5Me_5)_2SmR$ (R = alkyl, hydride) complexes, has been developed by Yasuda et al.[16−21] In this case, the large and highly electropositive organosamarium center can serve simultaneously as both the initiator (insertion) and catalyst (monomer activation) components of the GTP and a second Lewis acid equivalent is not needed (eq 2).
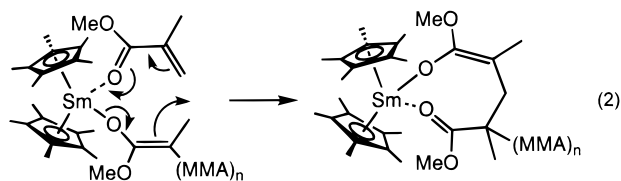
The PMMA produced by samarocene GTP is monodisperse and predominantly syndiotactic (up to >96% rr at lower temperatures) and the polymerizations are very rapid, although extremely sensitive to water and air. Acrylates are also polymerized by these catalysts in a well-defined manner, as are lactones.[22] A number of well-defined (meth)acrylic block copolymers and special-architecture macromolecules have been prepared with these catalysts.[18−21,23,24]

Smooth, but one-way, mechanistic crossover from olefin polymerization to group-transfer polymerization is possible with lanthanocene catalysts, since insertion of an acrylate into the propagating metal alkyl to form an enolate is energetically favorable. Block copolymers of ethylene with MMA, methyl acrylate, ethyl acrylate, or lactones have been prepared by sequential monomer addition to lanthanide catalysts and exhibit superior dyeing capabilities.[25] However, the reverse order of monomer addition, i.e., (meth)acrylate followed by ethylene, does not give diblocks since the conversion of an enolate (or alkoxide) to an alkyl is not favored. Therefore, although

Scheme 3
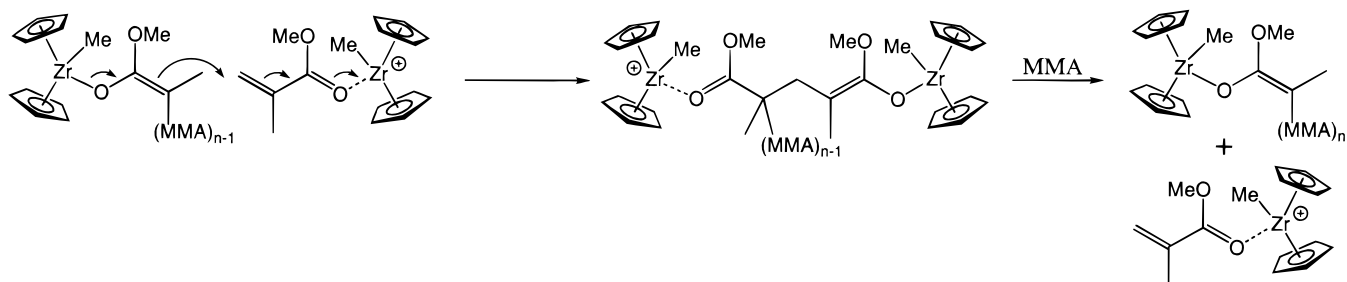
catalyst systems showing excellent behavior for both olefins and polar monomers do exist, the additional criterion of energetically compatible mechanisms must be satisfied in order for true (i.e., random) copolymerization of these two types of monomers to occur.

III. Direct Copolymerization of Functional Monomers with Group IV Catalysts

A cautionary note should preface this section. Many transition-metal catalysis require the use of Lewis-acidic cocatalysts such as MAO or aluminum alkyls. It is highly likely that polar monomers (e.g., esters, alcohols, etc.) introduced into these catalyst mixtures are complexed by the Lewis-acidic cocatalysts. This acid−base pairing makes the cocatalyst a "protecting" group and creates difficulty in rigorously classifying polymerizations into "protected" and "nonprotected" categories. We have made certain classifications based on procedures and mechanistic understandings, but any aluminum-containing "direct" polymerization method should be viewed with a critical eye to the presence of aluminum−heteroatom interactions.

a. Weakly-Interacting, Main-Group-Functionalized Monomers

Reports of polymerization of functional monomers containing heteroatoms that do not strongly interact with the group IV catalyst components (e.g., Si, Sn, and Pb) are not extensive, probably due to the limited property and chemical advantages conferred. Natta and co-workers have polymerized allylsilane and allyltrimethylsilane in good yield with titanium-based catalysts.[26,27] Poly(allylsilane) is soluble in hot heptane and has a crystalline structure (T_m = 127−128 °C), although is it cross-linked through reaction of the Si−H bonds in the presence of oxygen or water. Longi et al. prepared copolymers of propylene and allylsilane and exploited this reactivity for the synthesis of polyolefins containing Si−O−Si crosslinks.[28] Poly(allyltrimethylsilane) was obtained with a high molecular weight in a somewhat inhomogeneous form;[26,27] insoluble fractions obtained after extraction showed extremely high melting points (T_m = 350−360 °C) and were assigned to an isotactic structure based on X-ray data. Other researchers have reported similar polymerizations of silylated monomers, including polymerization of a silsesqui-

oxane-functionalized decene with a zirconocene/MAO catalyst.[29−31] Ziegler−Natta-based polymerizations of tin- and lead-containing olefins have also been carried out.[32]

b. Halogen-Containing Monomers

Halogen-containing monomers may be directly homopolymerized or copolymerized with olefins using Ziegler−Natta and metallocene catalysts; however, a number of restrictions apply. Monomers with activated (secondary or tertiary) C−X bonds or substituents close enough to alter the electronic character of the double bond are problematic (e.g., vinyl chloride). The side reactions impeding polymerization (nucleophilic substitution, elimination, and isomerization) typically involve reaction of the monomer's activated halogen atom with an alkylaluminum-containing cocatalyst, rather than with the group IV catalyst itself. The behavior of halogenated monomers toward borane activators has not been reported. Finally, once vinyl chloride undergoes insertion into a metal−alkyl bond, a β-chloro alkyl species is produced that can be highly prone to β-halo elimination, yielding a metal halide complex and the corresponding alkene.

As part of a study involving the polymerization of halogenated monomers, Clark and Powell probed the reactions between alkyl halides and Ziegler−Natta catalyst components. They found that the stability of haloolefins to side reactions increased with the size of the halogen atom (Cl < Br < I), the strength of the C−X bond (tertiary < secondary < primary), and the distance of the halogen from the double bond.[33] For these reasons, most of the existing work involving halogenated monomers has been carried out using only straight-chain, ω-substituted-α-olefins. Clark and Powell[33] also found that utilizing less Lewis-acidic cocatalysts (R$_3$Al versus R$_2$AlCl or RAlCl$_2$) and carrying out the catalyst activation step in the presence of an excess of the polymerizable olefin also disfavors side reactions. Additionally, Bacskai[34] has reported the use of Lewis-base additives such as pyridine to improve catalyst performance for halogenated monomer polymerization.

A variety of ω-halo-α-olefin homo- and copolymers have been prepared with Ziegler catalysts. Clark and Powell prepared homopolymers of 4-iodo-1-butene, 5-iodo-1-pentene, and 11-chloro-, 11-bromo-, and 11-iodo-1-undecene using TiCl$_3$/AlEt$_2$Cl in hydrocarbon solvents at 20−40 °C.[33] High yields were obtained only with the Br- and I-containing undecenes; poly-

merization of 4-bromo-1-butene and 5-bromo-1-pentene was unsuccessful. Copolymers of 4-methyl-1-pentene with 4-iodo-1-butene, 5-chloro- and 5-bromo-1-pentene, and 11-chloro-, 11-bromo-, and 11-iodo-1-undecene were similarly prepared incorporating 13–33 wt % of haloolefin monomer. For the copolymerizations, although yields were highest for the undecene, no behavioral differences were seen between the Cl-, Br-, and I-substituted monomers.

Bacskai synthesized copolymers of propylene and 4-methyl-1-pentene with ω-halo-1-butene (X = Br), -1-pentene (X = Cl, Br), -1-octene (X = Cl, Br), and -1-undecene (X = Cl) with halomonomer incorporations of up to 7% utilizing TiCl$_3$/Et$_2$AlCl (conditions: heptane solvent, 50 psi propylene, 50–70 °C).[34] The yields of copolymer are lower than yields obtained for homopolypropylene, although they can be equalized and comonomer incorporations can be increased by the addition of 1–2 equiv of pyridine or a similar Lewis base to the polymerization mixture. A terpolymer of ethylene, propylene, and 8-bromo-1-octene having 22% halomonomer incorporation was also prepared with this method. The copolymers are crystalline and display lower melting points and increased solubilities compared to polypropylene. However, they are inhomogeneous with respect to halide incorporation, and no characterization of tacticity or cross-linking was carried out.

Galimberti and co-workers synthesized ethylene/propylene/4-iodo-1-butene terpolymers with a V(acac)$_3$/AlEt$_2$X catalyst (X = Cl, I).[35] The copolymers prepared were amorphous, having at least 35 wt % propylene content, and possessed a bimodal molecular weight distribution of high polymer (MW > 500 000) and oligomers. The preparation of crystalline copolymers of propylene with linear ω-haloolefins using TiCl$_3$/Et$_3$Al has also been reported by Hoechst.[36]

Recently, metallocene catalysts have been used to prepare polymers containing ω-chloroolefins. Deffieux and co-workers used a *rac*-Et(Ind)$_2$ZrCl$_2$/MAO catalyst (conditions: 20 °C, 95:5 heptane:CH$_2$Cl$_2$ solvent) to synthesize poly(11-chloro-1-undecene) and random copolymers of 11-chloro-1-undecene with 1-hexene.[37] The polymerization is well-behaved as evidenced by molecular weight data (PDI ≈ 2) and dehydrochlorination side reactions are absent, although the use of toluene as the solvent results in the Friedel–Crafts conversion of some ω-chloride side chains to ω-tolyl groups. In contrast, 5-chloro-1-pentene is not polymerized, presumably due to formation of a stable seven-membered ring by Zr complexation of the chloride atom of the inserted monomer unit. Well-defined terpolymers of ethylene, propylene, and 11-chloro-1-undecene were similarly prepared having up to 2 mol % incorporation of the halogenated monomer (M_n = 40 000 to 60 000; PDI = 1.7–2.0).

Although ω-fluoroolefins were not included in the above investigations, Overberger and co-workers studied the polymerization of linear and branched α-olefins containing the trifluoromethyl group with various Ziegler–Natta systems.[38,39] 5,5,5-Trifluoro-1-pentene and 4-trifluoromethyl-1-pentene were polymerized in high conversion with VCl$_3$/*i*-Bu$_3$Al or TiCl$_3$/AlEt$_2$Cl (conditions: heptane, 70–100 °C), while 4,4,4-trifluoro-1-butene and 3-trifluoromethyl-1-butene gave low conversions to solid polymer, and 3,3,3-trifluoropropylene produced only an oil. Monomers containing a fluorine atom or a $-$CF$_3$ group bound directly to the double bond also failed to polymerize. Spectroscopic experiments indicated that the double bonds of the butene monomers are electron-poor and do not coordinate to the catalyst center, while the pentene monomers have electronic properties and behavior similar to their nonfluorinated analogues. The homopolymers are crystalline, free of cross-links, and possess higher melting points than the analogous nonfluorinated polymers. The polypentenes possessed higher solubilities than the polybutenes (in HMPA), as did the polymers of linear monomers versus those of the branched monomers. All of the butene and pentene monomers were successfully copolymerized with their nonfluorinated analogues, although conversions were significantly lowered when the mole fraction of fluorinated monomer in the feed was high.

Attempts to polymerize monomers besides linear ω-haloolefins and trifluoromethyl-substituted olefins with Ziegler–Natta catalysts have proved generally unsuccessful. Allyl halides, 7-chloro-1-octene, and 3-chlorocyclohexene give no or low molecular weight polymer due to dehydrohalogenation.[33,34,40,41] Bacskai has also noted that 6-chloro- and 6-bromo-1-hexene are not polymerized and suggests that monomer dehydrohalogenation is accelerated in this case by a double-bond-assisted, six-membered ring intermediate. A few scattered reports exist describing Ziegler–Natta polymerization of vinyl chloride,[42–45] perfluorinated monomers,[46] chloroprene,[47] and halostyrenes.[48]
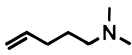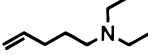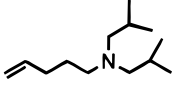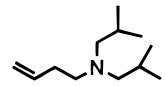
c. Olefinic Monomers Possessing "Inaccessible" Esters

Certain ester monomers can be polymerized by group IV catalysts without protection, if their structures rigorously prevent simultaneous interaction of the double bond and the ester group with the metal center. Amiard and co-workers successfully copolymerized methyl 5-norbornen-2-yl ester with ethylene, propylene, 1-butene, and dicyclopentadiene using vanadium-based Ziegler–Natta catalysts, although functional monomer incorporations were rather low (1–3%). The dicyclopentadiene-containing copolymer was vulcanized to give an elastomer showing 300% elongation at break.[49] The vast majority of olefinic esters, as well as other oxygen-containing functionalities, are best copolymerized using protection–deprotection strategies (vide infra).

d. Olefinic Monomers Possessing Free Amines

Direct polymerizations of primary and secondary amines have not been successfully carried out, with one exception. Shell has claimed the copolymerization of *N*-phenyl-10-undecenamine with 1-hexene (9–13 wt % comonomer incorporation) with TiCl$_3$ in the presence of excess Et$_2$AlCl.[50] The polymers obtained have properties similar to the tertiary aminoolefin/1-hexene copolymers discussed below.

Table 1. Amine Monomers and Their Respective Activities Polymerized with Cp*₂ZrMe₂/Borate Catalyst[51]

Activities $(h \cdot c[M])^{-1}$	9	155	619	151

Tertiary amine-functionalized olefins are not difficult to polymerize and copolymerize with group IV catalysts, provided that sufficient steric hindrance is present around the nitrogen atom. Amines of sufficient bulkiness, including diisopropyl and diphenyl derivatives, can be polymerized without the necessity of protection by Lewis-acid complexation. Smaller monomers (such as dimethyl and diethylamines) can be polymerized if 1 equiv of a proper alkylaluminum protecting group is used (vide infra). However, if the amine functionality is too near to the double bond, the additional steric bulk provided by the aluminum species may actually inhibit monomer coordination and polymerization.

A detailed survey of olefin amine polymerizations was carried out by Waymouth et al. using a variety of zirconocene and Ziegler−Natta catalysts.[51,52] 5-(N,N-Dimethylamino)- and 5-(N,N-diethylamino)-1-pentene showed low activities for zirconocene polymerization as compared to the bulkier diisopropylamino and diphenylamino derivatives (Table 1; activity for 5-(N,N-diphenylamino)-1-pentene = 111 $(h \cdot c[M])^{-1}$). Evaluation of the activity trends in light of pK_a and steric considerations indicates that the bulkiness of the amine substituents is more important in determining compatibility with the catalysts than electronic factors. A smaller monomer, 4-(N,N-diisopropylamino)-1-butene, also had a lower activity than the analogous pentene derivative, and diallylphenylamine was not polymerized at all. A similar trend was observed with Ziegler catalysts by Giannini et al. for diisopropylamines having 1,2,3,5, or 9 methylene spacers between the double bond and the amine.[53,54] Both studies suggest that a minimum of three carbons between the functional groups is generally necessary to achieve well-controlled polymerization behavior.

Zirconocene/borane catalysts were found to give the highest activities for 5-(N,N-diisopropylamino)-1-pentene. Zirconocenes in conjunction with excess MAO gave lower activities but were still 40 times as efficient as heterogeneous TiCl₃/(i-Bu)₃Al, which produced high MW polymer despite low activity. The less successful results obtained with the MAO systems suggest that, in contrast to protecting the monomer and rendering it more metallocene-tolerable, an aluminum−amine complexed functionality may actually be less desirable. By choosing zirconocenes with different symmetries, isotactic, syndiotactic, and atactic poly(olefin amines) were prepared; the stereoregularity of the polymers was actually higher than that observed with poly(1-hexene) prepared as a control. T_ms of the tactic polymers (M_n > 9 500) were between 109 and 115 °C, while the atactic polymer displayed no melt transition. Poly(5-(N,N-diisopropylamino)-1-pentene) can be quaternized to the corresponding poly(amminium chloride), which is water soluble.[52]

Waymouth et al. also prepared atactic and isotactic copolymers of 5-(N,N-diisopropylamino)-1-pentene with 1-hexene and 4-methyl-1-pentene.[55] Using an Et(tetrahydroindenyl)₂ZrMe⁺-based catalyst, copolymerization of the amino monomer with 1-hexene was almost ideal ($r_1 r_2 = 0.99$), allowing polymers with a wide range of compositions to be prepared. The functional monomer was preferred when the olefin comonomer was 4-methyl-1-pentene ($r_1 \approx 3$), an interesting finding in light of the lower activities found for amine homopolymerization as compared to the α-olefin monomers. Hexene polymerization inhibition studies with a saturated analogue, 1-N,N-diisopropylaminopentane, revealed that the double bond of the functional monomer plays an important role in disfavoring insertion of the α-olefin comonomer. Both intermolecular coordination of a free amine group with the metallocene center and intramolecular coordination of the amine group from the last inserted monomer unit are thought to contribute to this behavior.

The poly α-olefin/aminoolefin copolymers had lowered T_ms as compared to their homopolyolefin analogues (223 °C for poly-4-methyl-1-pentene, 159−186 °C for copolymers, 115 °C for the polyamine) but showed greatly increased decomposition temperatures. With just 2.5 mol % amino comonomer present, the decomposition temperature of poly(4-methyl-1-pentene) was raised by 43 °C. This enhancement is thought to be a result of the antioxidant capabilities of the tertiary amine functionality. The copolymers can also be quaternized to give alcohol- and water-soluble polyolefins.

As previously mentioned, Giannini and co-workers have carried out studies of aminolefin polymerization with aluminum-activated TiCl₃/trialkylaluminum catalysts.[53,54] Homopolymers of several hindered amines were obtained in high yield, although catalyst activities were not as high as for the analogous polymerizations of similar unfunctionalized α-olefins. 5-N,N-Diisopropylamino-1-pentene and 5-N,N-diisobutyl-amino-1-pentene were polymerized to give crystalline polyaminoolefins, while the larger monomers 7-N,N-diisopropylamino-1-heptene and 11-N,N-diisopropylamino-1-undecene gave amorphous polymers. Secondary amines, even if highly hindered (i.e., 5-N-tert-butylamino-1-pentene), caused catalyst deactivation; less hindered tertiary amines (5-N,N-dimethyl-, -diethyl-, and -di-n-butylamino-1-pentene) were only polymerized in low yield to give oils. Monomers with less than three methylene units between the amine and double bond gave either no polymer (3-N,N-

diisopropylamino-1-pentene) or lowered (4-*N,N*-di-isopropylamino-1-butene) yields. The best results were obtained when the alkylaluminum cocatalyst also had a bulky, branched structure; this feature helps to prevent formation of aluminum−nitrogen complexes, which are undesirable for the already sterically protected monomers.

IV. Protecting Group Chemistry

The reactivity of most functional groups toward the metal catalysts requires that protection−deprotection strategies be employed.[56] For compatibility with metallocene and Ziegler−Natta catalysts, the most commonly employed protecting groups are based on aluminum, boron, and silicon. Aluminum offers an advantage because of its ubiquitous existence in polymerization formulations.[57]

a. Amine Monomers

In contrast to the diisopropyl and similarly bulky amine monomers, which actually need to remain free from complexing agents for successful polymerization, Giannini found that a preprotection with 1 equiv of Et_2AlCl allowed the smaller dimethyl, diethyl, and di-*n*-butyl derivatives of 5-amino-1-pentene to be polymerized (amorphous polymers, yields 60−90%).[53,54] Precomplexed 3-*N,N*-dimethyl- and -diethylamino-1-propylene did not polymerize, however. Langer and Haynes report a similar behavioral difference for copolymerizations involving branched versus unbranched ω-aminoolefins.[58] *N,N*-Diisopropyl-7-octenylamine and *N,N*-diisopropyl-5-hexenylamine were successfully copolymerized with propylene or 1-butene using activated $TiCl_3/Et_3Al/HMPA$. No relative loss of catalyst activity was noted, regardless of whether an excess of trialkylaluminum was present to complex the amine. In contrast, *N,N*-diethyl-4-pentenylamine caused extensive catalyst deactivation if an excess of Et_3Al was not present in the polymerization system. Films and fibers of these copolymers showed excellent dyeabilities.

A different preprotection strategy has been used to prepare ethylene copolymers containing *primary* amine groups. Mülhaupt and co-workers copolymerized the protected monomer *N,N*-bis(trimethylsilyl)-1-amino-10-undecene using a zirconocene/MAO initiating system.[59] The protecting TMS groups were cleaved during workup with aqueous HCl followed by a sodium hydroxide wash. Even at 16 000 equivalents of MAO per zirconium, a marked decrease in activity was seen at higher concentrations of comonomer in the feed. Nevertheless, 6−19 wt % amine-containing polymers were obtained which showed useful molding capabilities. The copolymers, even at low nitrogen incorporation, were insoluble in solvents normally used to dissolve LLDPE and showed decreased T_ms (101−116 °C) and crystallinities compared to the parent polyolefin. The copolymers were reacted with maleic anhydride-functionalized polystyrenes in film form, giving interchain imide bonds that improved interfacial adhesion and compatibility.

Amiard copolymerized 2-(5-norbornen-2-yl)pyridine with ethylene using $VOCl_3/Et_2AlCl$; precomplexation

of the monomer with $EtAlCl_2$ was employed. The resultant copolymer was crystalline and contained 2.4 wt % of the amine monomer.[49]

The homo- and copolymerization of 4-vinylpyridine (4VP) by $TiCl_3\cdot$(alkyl aluminum) catalysts has been investigated.[60] 4VP was studied both free and precomplexed with $Al(i\text{-}Bu)_3$ or $Al(i\text{-}Bu)_2Cl$. Even in the case of "free" 4VP, large excesses of Al or Zn alkyls were used as cocatalysts. Marked differences were found for the different forms. With unusually large catalyst loadings, the precomplexed 4VP could be obtained in high yields (ca. 90%) but the molecular weights were very low (ca. 1 000 to 3 500). Higher molecular weights could be obtained using the free 4VP (ca. 10^4), but the yields dropped precipitously to 7−30%. Copolymerization of 4VP with other olefins proved to be problematic. For example, the polymer obtained from the "copolymerization" of the aluminum complex of 4VP and (*S*)-4-methyl-1-hexene was fractionated into two polymers: homo-poly(4VP) and homo poly[(*S*)-4-methyl-1-hexene]. No true copolymer was formed. Similar results were obtained using the free 4VP. The poly(4VP) in all cases had an atactic microstructure despite the fact that the catalyst employed yields highly isotactic polyolefins. Clearly, one has to wonder about the possibility of radical polymerization rather than a true coordination−insertion mechanism.

Motivated by the fact that polyolefins are stabilized using piperidine derivatives that can leach with time, the copolymerization of α-olefins with polymerizable piperidine derivatives was investigated. Hindered vinyl piperidines (e.g., **Pip-I**) can complex with aluminum compounds and incorporate into copolymers with propylene using commercial $TiCl_4/MgCl_2$ Ziegler−Natta catalysts.[61]
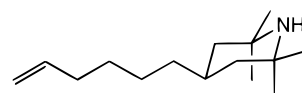
Pip-I

Precomplexing **Pip-I** with triethylaluminum (heated for 1 h at 70 °C in heptane) proved to be more effective than not precomplexing. Under identical polymerization conditions, the catalyst activity for propylene drops from 2.4 kg pg PP/g of cat to 1.8 and 1.2 kg of PP/g of cat, respectively, in the complexed and uncomplexed **Pip-I** copolymerizations. The mole ratios of propylene to **Pip-I** used were from approximately 150/1 to 20/1.

b. Monomers Possessing Oxygen-Containing Functional Groups

Oxygen-containing groups are among the most studied functionalities for copolymerization with ethylene and α-olefins. Alcohol-, acid-, and ester-containing copolymers are of interest as precursors for potential polyolefin elastomers, since both ionic (via deprotonation of alcohols or acids) and chemical (via transesterification) cross-links may be introduced. Often, oxygenated functionalities are precomplexed with an aluminum-based Lewis acid, such as Et_2AlCl, for successful polymerization (deprotection

to the free oxygenated functionality is accomplished by acid wash upon termination of polymerization). The widespread use of aluminum complexes in Ziegler–Natta catalyst formulations makes them a favored choice element for functional group protection. In addition to the use of chemical protection strategies, the proper steric protection of the active site from the oxygenated functionality is also required.

The most comprehensive study of oxygenated functional group trends has been carried out by Aaltonen and co-workers, using zirconocene catalysts in the presence of excess MAO as a monomer protecting reagent.[62,63] The trends obtained for catalyst poisoning demonstrate that functional groups capable of forming stable, protected aluminates (alcohols and to some extent carboxylic acids) are less deactivating than "weaker" (less acidic and/or less polar) groups such as esters and ketones. Steric protection was also found to be important for maintaining catalyst activity, as noted by studying methyl and *tert*-butyl ester monomers and primary, secondary, and tertiary alkenols. Also, although longer chain monomers showed higher incorporation levels for olefin copolymerization, monomers of a sufficient spacer length showed similar deactivation behavior independent of functionality (10-undecen-1-ol vs 10-undecenoic acid).

i. Esters

The polymerization of straight-chain ω-ester olefins with Ziegler–Natta catalysts has been extensively studied by Purgett and Vogl. Aluminum-activated TiCl$_3$ ("TiCl$_3$ AA") was used in conjunction with 4 equiv of an aluminum cocatalyst (*i*-Bu$_2$AlCl or Et$_2$AlCl) in toluene or hexane at 25–65 °C to homopolymerize a series of R$_2$AlCl-precomplexed esters with varying lengths and substitutions.[64] More sterically hindered ester groups were needed for high conversion to polymer. While 2,6-dimethylphenyl and 2,6-diphenylphenyl 10-undecenoate were polymerized in high yield (>75%), phenyl 10-undecenoate gave only a moderate yield (54%) and conversions of the analogous methyl, *tert*-butyl, 2-ethyl-1-hexyl, and trifluoroethyl esters were low (2–20%). Similarly, a minimum distance between the ester and olefin functionalities was necessary: 2,6-dimethylphenyl 8-nonenoate was polymerized similarly to the analogous 10-undecenoate monomer, and 7-octenoic acid esters can be polymerized,[65] while 2,6-dimethylphenyl 5-hexenoate and 2,6-dimethylphenyl 3-butenoate gave no conversion. On the basis of NMR data showing the degree of electronic influence of the ester substituent on the double bond, Purgett and Vogl conclude that a spacer of between 3 and 6 methylene units is necessary between the two functionalities for polymerization to occur.[64,66] This value is consistent with restrictions observed by others for other types of monomers (for relatively less polar silicon substituents, one CH$_2$ group is necessary; for dialkylamines, two).

The critical reaction parameter for successful polymerization was found to be precomplexation of the

ester monomer with one or more equivalents of a dialkylaluminum chloride. When free 2,6-dimethylphenyl 10-undecenoate was added to the TiCl$_3$/AlEt$_2$Cl catalyst, only 5% conversion to polymer was observed. Pretreatment of the monomer with AlEt$_2$Cl, in contrast, raised the polymer yield to above 89%. Varying the exact precomplexation procedure did not significantly affect polymer yield, with the exception that carrying out complexation/polymerization at 60–65 °C gave polymers with substantially less solubility or lower molecular weight than polymers prepared at 25 °C due to side reactions (possibly cross-linking via Friedel–Crafts alkylation of the phenyl groups). The toluene-soluble homopolyesters are tough, rubbery materials; the use of over 4 equiv of aluminum cocatalyst or the use of other Ziegler catalysts (TiCl$_4$, ZrCl$_4$) gives lower molecular weight, tacky polymers or oligomers, respectively.

Purgett and Vogl prepared high-yield copolymers of 2,6-dimethylphenyl 10-undecenoate with 1-dodecene, 1-octene, 1-hexene, propylene, and ethylene using similar methodologies.[67] The copolymers are tough and rubbery, with intrinsic viscosities of 2.8–5.7 dL/g and ester comonomer incorporations of up to 18 mol %. Ester incorporations for the propylene and ethylene polymers were lowest (3–5%) due to the greater differences in relative monomer reactivity. Terpolymers with ethylene and propylene were also synthesized,[68] although rigorous fractionation experiments to confirm homogeneous composition were not carried out. Use of TiCl$_3$/AlEt$_2$Cl as the catalyst gave a crystalline, elastic material with 6 mol % ester monomer incorporation; a VOCl$_3$/AlEt$_2$Cl catalyst produced an amorphous terpolymer with higher ester comonomer incorporation.

Other researchers have reported the Ziegler–Natta-catalyzed synthesis of long-chain ω-ester olefin/α-olefin copolymers using precomplexation techniques. Hoechst carried out copolymerizations of 2,6-dimethylphenyl, phenyl, and ethyl 10-undecenoate with propylene and ethylene to give moldable materials; copolymers incorporating methyl acrylate as the ester component are also claimed.[69] Methyl 10-undecenoate copolymers with 1-octene having varying degrees of crystallinity have been prepared,[70,71] as have vulcanizable ethylene/propylene/allyl 17-octadecenoate copolymers.[72] Shell patented *n*-butyl 10-undecenoate homopolymers, as well as block/random copolymers with propylene, 1-hexene, and 4-methyl-1-pentene, for potential dyeable film and fiber applications.[50]

The polymerization of ω-ester monomers with metallocene catalysts has been investigated by Aaltonen, Hakala, and co-workers.[62,63] Methyl 9-decenoate and *tert*-butyl 10-decenoate are copolymerized with propylene using Et(Ind)$_2$ZrCl$_2$ or ethylene using (*n*-BuCp)$_2$ZrCl$_2$ (4000 equiv MAO, 30 °C, 2.5–3 bar olefin, toluene solvent, preaddition of MAO to the ester monomer). In all cases, loss of catalyst activity was seen, although the *tert*-butyl ester caused less catalyst deactivation than the methyl ester. The resultant propylene copolymers are well-defined ($M_w \approx 30\,000$, PDI 1.8–1.9, T_m 133–139 °C) and the ethylene copolymers less so ($M_w \approx 139\,000$, PDI 3.8,

1.1% comonomer incorporation). This difference is at least partly attributed to behavioral differences between bridged and nonbridged zirconocenes.

ii. Alcohols

Alkenols may be polymerized by group IV catalysts using a mixture of both steric and protective strategies. Aaltonen and co-workers reported the copolymerization of a variety of alkenols with ethylene and propylene using zirconocene/MAO catalysts.[62,63,73,74] It is assumed that the monomers are present as aluminates. Although separately pretreating the alcoholic monomers with MAO prior to polymerization did not improve comonomer conversion of incorporation (ethylene uptake was improved), the polymerization procedure involves mixing of the polar comonomer with MAO prior to zirconocene addition, and higher total levels of MAO (ca. 10 000 equiv per Zr) were found to have a more favorable effect on conversion.

The copolymerization behavior of both straight-chain ω-alkenols (10-undecen-1-ol, 5-hexen-1-ol) and branched alcohols (1,1-dimethyl-2-propen-1-ol, 2,2-dimethyl-3-(1,1-dimethylethyl)-11-dodecen-3-ol, 2-methyl-3-butenol, 12-tridecen-2-ol) was investigated. Straight-chain monomers were found to have a more detrimental effect on catalyst activity, as measured by the lowering of activity and polymer molecular weight in propylene copolymerization, than the branched alcohols. However, while tertiary alkenols did not cause loss of catalyst activity, they were not incorporated into the polymer at all. Surprisingly, the secondary alcohol 12-tridecen-2-ol showed better incorporation than the ω-alkenols. Increased spacer length between the double bond and the $-OH$ group was also found to improve copolymerization; incorporation of 10-undecen-1-ol into an ethylene copolymer was 3 times as high (9.9%) as that of 5-hexen-1-ol (3.3%). An unrelated report by Wilén et al. describes successful propylene copolymerization of an extremely bulky alcohol, 6-*tert*-butyl-2-(1,1-dimethylhept-6-enyl)-4-methylphenol, using similar metallocene/MAO catalysts.[75]

When nonbridged zirconocenes were used for copolymerization, reduced polymer molecular weights and broadened MWD distributions as compared to olefin homopolymerization were observed, presumably due to additional active catalyst sites formed from reactions between the alcohol and the metallocene. Stereorigid bridged indenyl zirconocenes exhibited better tolerance, producing narrow-MWD copolymers with higher comonomer conversions and incorporations. The identity of the bridge was also important: ethylene-bridged catalysts tolerated the comonomers better in terms of activity, while silylene-bridged catalysts gave better conversion and comonomer incorporation. In all cases, significant catalyst deactivation begins to occur as the concentration of polar comonomer in the feed is increased.

Ethylene or propylene random copolymers containing 10-undecen-1-ol, 5-hexen-1-ol, or 12-tridecen-2-ol were synthesized using bridged zirconocenes/MAO in toluene at 60–80 °C. The propylene copolymers contained 0.6–2.7 wt % of the comonomers; incorpo-

rations were higher (up to 13.4 wt %) for the ethylene-based copolymers. The melting points of the ethylene copolymers (126–136 °C) decreased with increased comonomer; all showed increased melt flow indices compared to polyethylene, indicating improved processability.

Ziegler–Natta polymerizations of aluminate-protected alcohols have also been reported. Shell patented a synthesis of film-forming poly(10-undecen-1-ol) prepared with $TiCl_3/Et_2AlCl$ in which the monomer is utilized as aluminum tris(10-undecenoxide).[50]

A recent study reported the terpolymerization of hexen-1-ol, 10-undecen-1-ol and 10-undecen-oic acid with ethylene and propylene.[76] The catalysts employed were bis-indenyl zirconocenes. Again, the monomers were complexed with trimethylaluminum (TMA). Several mixing strategies were employed, and the comparisons indicate that complexing with TMA is far more effective than complexing using MAO. The target terpolymers could be prepared but at the price of substantial decreases in catalyst activity.

The copolymerization of propylene and allyl alcohol has been reported using $TiCl_3$/ethyl aluminum sesquichloride catalyst.[77] The resulting polymer contained about 4 wt % of the allyl alcohol and an isotactic fraction of about 98%. Catalyst activities, however, were very low (ca. 320 g of PP/g of Ti·h· atm) (eq 3).

$$\text{eq (3)}$$
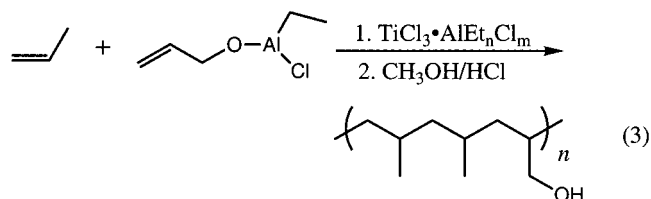
Protection of the alcohol group with a silyl ether, easily cleaved after polymerization, is an alternate strategy. Giannini and co-workers polymerized the trimethylsilyl ether derivatives of 5-hydroxy-1-pentene and 11-hydroxy-1-undecene using aluminum-activated $TiCl_3$ in conjunction with certain aluminum alkyl cocatalysts (branched alkyl groups are necessary to shield the aluminum from interaction with the silyl ether).[53,54] The resultant homopolymers are obtained in 20–25% yield after hydrolysis to the polyalcohols with acidified methanol and are crystalline and isotactic with melting points much higher than the corresponding poly-α-olefins (poly-10-undecen-1-ol, $T_m = 134$ °C; poly-4-penten-1-ol, decomposes at 300 °C). The smaller monomer allyloxytrimethylsilane was not polymerized and in fact inhibits the polymerization of ethylene and propylene, presumably through a side reaction with the aluminum cocatalyst in which an aluminum silyl ether and cyclopropene are formed (in contrast, allyldialkylamines do not inhibit olefin polymerization).[54]

Waymouth et al. used a variety of zirconocene/borane catalysts to polymerize 5-*tert*-butyldimethylsiloxy-1-pentene and to cyclopolymerize the protected dienes 4-trimethylsilyloxy-1,6-heptadiene and 4-*tert*-butyldimethylsiloxy-1,6-heptadiene (conditions: −25 to 24 °C, with higher molecular weights resulting at

lower temperatures, 0.5 equiv of borane, toluene solvent).[52] Although in all cases activities were lower for the silylated monomers than for 1-hexene, monomer conversions of up to 98% were achieved and at least 100 turnovers were possible for both types of monomer. Significant differences in tolerance to the silyl functionalities were observed with variances in the zirconocene structure: $(C_5Me_5)_2ZrMe^+$ catalysts are deactivated to a lesser degree than chiral, bridged $Et(tetrahydroindenyl)_2ZrMe^+$ catalysts; the bridged catalysts tolerate 4-*tert*-butyldimethylsiloxy-1,6-heptadiene but are poisoned by the less hindered 4-trimethylsilyloxy-1,6-heptadiene and 5-*tert*-butyldimethylsiloxy-1-pentene. Similarly, allyloxy-*tert*-butyldimethylsilane, allyloxytrimethylsilane, and the less sterically protected monomer 5-trimethylsilyloxy-1-pentene did not polymerize with either catalyst. The polymers are isotactic and can be cleanly converted with HCl to the corresponding polyalcohols, which are soluble in polar solvents (DMSO, DMF, pyridine) or water.[52]

A series of patents were issued to DuPont in the mid-1970s that covered the terpolymerization of ethylene, propylene, and functional monomers. The catalyst employed was a soluble $VCl_4/AlEt_2Cl$ in combination with hexachloropropene as a catalyst activator. The functional comonomers studied included 2-hydroxy-5-norbornene, 2-hydroxymethyl-5-norbornene, allylsulfonyl chloride, 2-allylphenol, and 5-norbornene-2-acetic acid.[78,79] Large excesses of $AlEt_2Cl$ were used not only in order to activate the catalyst, but also to complex and passivate the polar functional groups.

iii. Ketones

Since the ketone functionality undergoes weaker interaction with an aluminum-based protecting agent, the strategies described above for alcohols have not been successfully studied to any extent. Aaltonen attempted the copolymerization of 2,2-dimethyl-11-dodecen-3-one with propylene using zirconocene/MAO catalyst but found that the ketone comonomer completely suppressed polymerization.[63]

iv. Ethers

Ether monomers also undergo only weak complexation to aluminum cocatalysts for protection purposes and have not been extensively studied, although the phenoxy group is fairly well tolerated by Ziegler catalysts. Shell has reported homopolymerization of 7-phenoxy-1-heptene and 4-allylanisole with $TiCl_3/Et_2AlCl$. The 1-heptene polymer is produced in 94% yield, is hydrocarbon-soluble, and can be used as a precursor to sulfonated and nitrated materials. The anisole polymer is formed in a much lower yield (15%).[50] Copolymers of both monomers with 4-methyl-1-pentene were also prepared; a copolymer of propylene with of 7-phenoxy-1-heptene was synthesized, requiring only a minimum amount of extra aluminum alkyl for protection. In contrast, Waymouth et al. reported the failure of diallyl ether to polymerize with zirconocene/borane initiating systems.[52]

v. Carboxylic Acids and Carboxylates

Carboxylic acids may also be polymerized utilizing precomplexation strategies, although successful reports of this technique are less common than those involving esters or alcohols. Copolymers of 10-undecenoic acid with 1-hexene and 4-methyl-1-pentene were prepared by Shell with $TiCl_3/Et_2AlCl$ using the acid monomer in a protected form, aluminum tris-(10-undecenoate). The copolymers contain appreciable anhydride and carboxylate groups, in addition to liberated acid functionalities, after acid workup.[50] Propylene copolymerizations of protected ω-acid derivatives such as ethylchloroaluminum 10-undecenoate with similar initiating systems have been carried out by Landoll and Breslow and others.[77,80–84] Landoll and Breslow report that the analogous copolymerization of ethylchloroaluminum acrylate with propylene was unsuccessful; a similar study by Matsumura and Fukumoto gave copolymers containing a large fraction of acrylate-rich copolymer, presumably resulting from competing, non-Ziegler processes.[85]

Aaltonen and co-workers carried out the zirconocene/MAO copolymerization of 10-undecenoic acid with propylene (0.7–2.4 wt % comonomer incorporation) and ethylene (2.1 wt % comonomer).[62,63] The deactivation of the metallocene catalyst with the acid monomer was twice as severe as when 10-undecen-1-ol was used as the comonomer.

Deprotection of poly(olefin esters) prepared by precomplexation techniques is easily accomplished as a route into olefin/acid and olefin/carboxylate polymers. The 2,6-dimethylphenyl 10-undecenoate homopolymers and copolymers with ethylene and propylene prepared by Purgett and Vogl can be converted in high yield to the sodium carboxylate analogues by base-catalyzed hydrolysis (dioxane solvent, 85 °C). These ionomers in turn can be treated with acetic acid to quantitatively generate carboxylic acid-containing polyolefins.[64,68,86] Both the terpolymer salts and acids showed broader and higher glass transitions as compared to the parent polymer esters; the polysalts also exhibited a high melt transition at 250–270 °C corresponding to the melting of ionic carboxylate domains.

As described above, the copolymerization of (meth)-acrylate esters with olefins has proven to be most difficult because of both the potential for enolate formation and the polarization of the olefin. A few literature reports claiming copolymerization of acrylics with olefins exist, although details are few. For example, Hoechst claimed the synthesis of ethylene and propylene copolymers incorporating methyl acrylate with $TiCl_4/Et_2AlCl$.[69] All other factors being equal, (meth)acrylate salts would be attractive alternative monomers because they will not form enolate anions, eliminating one of these two main obstacles. Polarization of the double bond (the HOMO–LUMO energies) can be modulated by choice of the coordinating "counterion" (i.e., build in covalent character between the (meth)acrylate anion and the counterion). Additionally, coordinating counterions (or sufficiently tight ion pairs) must be used because the free (meth)acrylate anions are far too nucleophilic

and would be expected to strongly coordinate with group IV cation catalysts.

One method of circumventing the potential limitation is to introduce a degenerate exchange process between protected (meth)acrylate and its counterion where the counterion is itself a metallocene cation (eq 4).
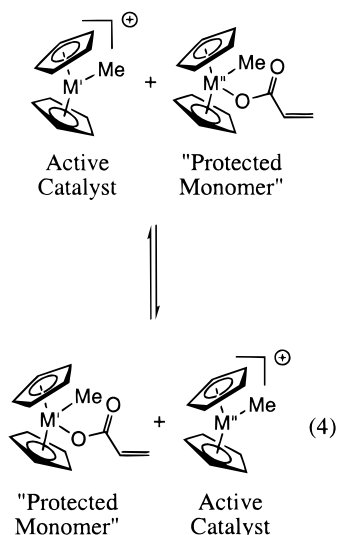
To this end, several (meth)acrylate salts were examined by Novak with respect to their polymerization behavior. Two promising candidates are the Ti(III) complexes **Tim** and **Tia** shown below.[87]

The copolymerization of **Tim** and **Tia** with ethylene has been examined using metallocene catalyst systems. Of the two protected carboxylates, **Tia** appears to be preferred in terms of its incorporation into the copolymer (eq 5).
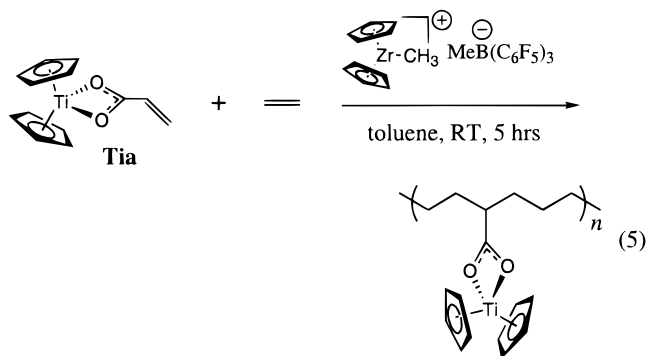
The results in Table 2 show the copolymerization behavior of **Tia** and **Tim** with ethylene. Data from control experiments are also shown in Table 2. Yields of the copolymerizations are reported as percentages relative to the appropriate control. These

Table 2. Copolymerization of Ethylene and Tim and Tia Using [Cp$_2$TiCH$_3$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ in Toluene at Room Temperature

comonomer (mM, % feed)	ethylene (atm)	polymer yield (mg)	relative yield	C=O intensity (au)
none	5	469	100	
Tim (8, 0.5%)	5	388	83	~0
Tim (32, 2%)	5	461	98	44
Tim (60, 37%)	2	367	78	18
Tia (8, 0.5%)	5	466	99	~0
Tia (32, 2%)	5	467	99	40
none	2	243	100	
Tia (32, 2%)	2	136	55	71

experiments show that activity remains high in the presence of both **Tia** and **Tim**.

c. Amides and Imines

Shell patented the synthesis of hindered amide olefin homo- and copolymers with TiCl$_3$/Et$_2$AlCl, noting that amide monomers require precomplexation with more than one equivalent of an aluminum reagent to achieve polymerization. Poly(*N,N*-di-*n*-butyl-10-undecenamide) prepared in this manner is a very viscous liquid of high molecular weight, soluble in a wide range of solvents such as 2-propanol, ether, and toluene. Copolymers of *N,N*-di-*n*-butyl-10-undecenamide and *N,N*-diphenyl-10-undecenamide with 1-hexene, 4-methyl-1-pentene, or 1-dodecene, incorporating typically 6−10% polar comonomer, have similar physical properties.[50]

The terpolymerization of aluminum-complexed imides (e.g., *N*-vinylsuccinimide·AlEtCl$_2$) with ethylene and propylene was reported by workers at Elf Aquitaine in early 1979.[88] The catalyst employed was a soluble VCl$_4$/AlEtCl$_2$ catalyst system in dry heptane.

d. Protecting Group Chemistry Based on Boron

The combination of versatile chemistry and similarity to aluminum makes boron an attractive choice for protecting group chemistry. This has been amply demonstrated in a series of papers by Chung et al. from work initially carried out at Exxon. Patents published in 1988 disclose the use of boron-functionalized monomers in both homo- and copolymerizations using heterogeneous TiCl$_3$ (pretreated with aluminum alkyl)·AlEt$_2$Cl formulations.[89,90] Monomers were prepared by monohydroboration of dienes (1,4-pentadiene, 1,7-octadiene, etc.) with 9-borabicyclo-[3.3.1]nonane (9-BBN). Near quantitative yields of the homopolymers of 7-octenyl-9-BBN and 5-hexenyl-9-BBN could be obtained (eq 6).
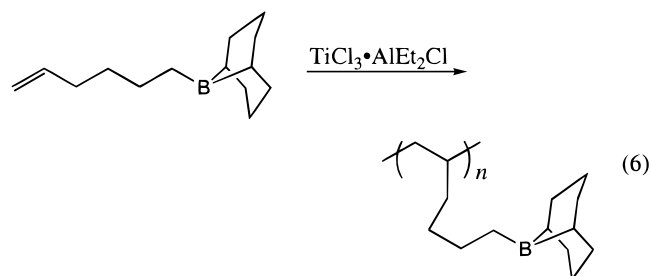
Under identical reaction conditions, no polymerization of the 4-pentenyl-9-BBN derivative was observed. It was concluded that the electron-withdrawing borane moiety must be removed from the double bond by at least three carbon atoms for normal polymerization activity to be observed. No direct rate comparisons between these boron derivatives and comparable α-olefin hydrocarbons were made. However, experiments polymerizing 1-octene with and without added triethylborane showed that the borane had no deleterious side effects on the reaction.[89,90]

The borane-containing polymers are air-sensitive, but this feature can be taken advantage of in controlled functional group transformation chemistry (vide infra). Once polymerized, the pendant borane can be converted to a number of functional groups. For example, poly(7-octenyl-9-BBN) could be quantitatively converted to the corresponding polyol by allowing the polymer to react with sodium hydroxide and hydrogen peroxide at 50 °C for 2 h. NMR and X-ray studies showed the structure to be highly isotactic. Grafted polyolefins can be prepared from these polyols by using the hydroxide group to initiate other polymerizations, for example, caprolactone ring opening.[91]

Copolymers of 1-octene and 7-octenyl-9-BBN were also reported.[89] Like the homologue poly(7-octenyl-9-BBN), these copolymers could also be cleanly converted to the alcohol derivatives under similarly mild conditions. The reported copolymer was shown to have a composition that was the same as that of the monomer feed (one to one). A later report showed that 5-hexenyl-9-BBN is slightly less reactive than 1-octene. A subsequent, more complete kinetics paper calculated reactivity ratios for these borane monomers.[92] By gel permeation chromatography, apparent molecular weights appeared to decrease with increasing borane incorporation. Whether this trend is due to a changing hydrodynamic volume of the polymer with increasing number of functional groups or to some other process such as a chain transfer to boron remains an open question.

Propylene was also copolymerized with 5-hexenyl-9-BBN using a $TiCl_3/AlEt_3$ catalyst.[93,94] In this case, the monomers have substantially different reactivity ($r_1 = 70.5$ for propylene (M_1) and $r_2 = 0.028$ for 5-hexenyl-9-BBN (M_2)),[92] resulting in a nonuniform distribution of functional groups. Although these copolymers have poor solubility vis-à-vis the homopolymers discussed above, high conversion of the boranes to alcohols can be realized.

Taking advantage of the rich chemistry offered by boranes, conversions of the borane to functional groups other than alcohols can also be accomplished. Functionalities include amines, halogens, aldehydes, and cyanides. One particularly useful transformation leads to grafts of the polyolefin and poly(methyl methacrylate) (PMMA).[91,95] Grafting onto the 9-BBN polymers can readily be accomplished by taking advantage of the air sensitivities of the alkyl borane side groups. Treating the pendent 9-BBN polymers

with oxygen in the presence of methyl methacrylate forms MMA grafts (eq 7).

(7)
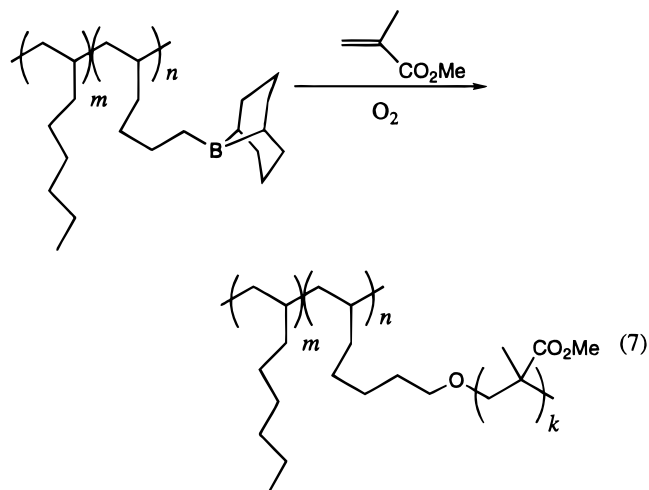
The formation of grafted copolymer is evidenced by a change in solubility, fractionation attempts, a second glass transition temperature, and gel permeation chromatography data.

e. ω-Halo-1-olefin Monomers as Protecting Groups

When ω-haloolefins are used as comonomers, the primary C−X bond may be exploited as a protecting group to be unmasked after polymerization. Ethylene/propylene/4-iodo-1-butene terpolymers synthesized by Galimberti et al. have been quantitatively dehydrohalogenated with t-BuOK/18-crown-6 to give ethylene/propylene/1,3-butadiene terpolymers in which the diene (incorporated at up to 3.6 wt %) has exclusively a 1,2-incorporation microstructure.[35] Copolymers of propylene or 4-methyl-1-pentene with 8-bromo-1-octene undergo S_N2 reactions with amines (pyridine, morpholine); copolymers prepared with chloro monomers were found to be less reactive.[34] The pyridinium derivative of the propylene/8-bromo-1-octene copolymer could be dyed permanently with Alizarin Blue. Terpolymers of ethylene, propylene, and 11-chloro-1-undecene have been quantitatively transformed at the pendant chloro group to benzoate (via $PhCO_2K$) and subsequently hydroxy (via ester cleavage) functionalities to give amphiphilic polyols; reaction of the chloro group with NaN_3 similarly gives azido-substituted terpolymers.[37]

## V. Alternative Catalysts: The Late Transition Metals

As a good approximation, there are not pronounced differences in tolerance between supported Ziegler−Natta catalysts and homogeneous catalysts based on zirconium or titanium metallocenes. Exceptions may be in the activators used (e.g., MAO vs borate), with the borates showing a wider range of compatibilities.[96]

Although catalysts based on late transition metals were investigated early in olefin polymerization studies, they failed to display the same high activities as the early metal group IV and V systems. Consequently, studies focusing on late-metal catalysts lagged behind. This apparent lapse has been more than made up for in recent years.[97] In the context of functional monomers, late-metal catalysts are thought to be among the most promising. This is due in large part to their reduced oxophilicity vis-à-vis the early metals.

Nickel has a long history of dimerization and oligomerization of α-olefins.[98] Examples are many and include the SHOP process that is run on large scales commercially to convert ethylene to higher α-olefins using phosphine−oxygen chelating ligands (e.g., complex **I**) (eq 8).[99]


(8)

99% linear
98% a-olefins
$n \approx 1\text{-}20$

I
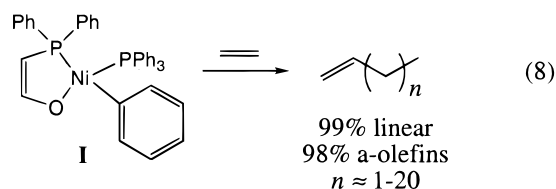
The use of nickel complexes to polymerize ethylene dates back into the early-to-mid 1950s.[100−102] Among the catalysts reported to be active for these polymerizations were allyl nickel complexes.[100] In 1985 and 1987, Ostoja Starzewski and co-workers reported the polymerization of ethylene using bis(ylide)nickel complexes (**II**) formed in situ from catalyst precursor solutions (eq 9).[103] No attempt to polymerize func-


(9)

II
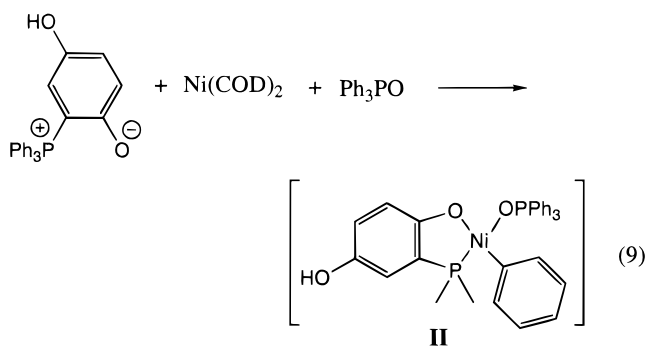
tional monomers was reported, although it should be noted that these ethylene polymerizations were run in toluene/DMF mixtures to no disadvantage.

Klabunde and Ittel reported the use of nickel complexes containing the phosphorus−oxygen chelating ligands to homo- and copolymerize ethylene with a variety of functional olefins.[104] Negative results were obtained with both vinyl acetate and methyl methacrylate, but copolymers could be obtained if monomers with at least two methylene spacers between the olefin and polar group. The functionalities successfully tolerated include ester, trimethylsilyl-protected acids, ketones, fluoro groups, and 2° amides.

Recently, Grubbs and co-workers reported the use of neutral salicylaldimine nickel complexes (e.g., complex **III**) for ethylene polymerizations.[105] A phosphine scavenger (e.g., Ni(COD)₂) is used as an activa-

III

$$\left(\begin{array}{l} \text{R = Bulky group} \\ \text{X = Electron withdrawing group} \end{array} \right)$$
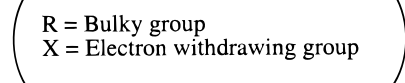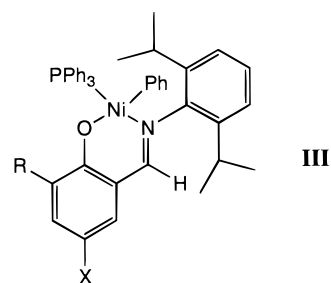
tor, if needed. This use of the salicylaldimine complexes was recently extended to the copolymerization of ethylene with functionalized norbornene monomers (5-norbornen-2-yl acetate or 5-norbornen-2-ol) (eq 10).[106]

(10)

Incorporation weight = 22%
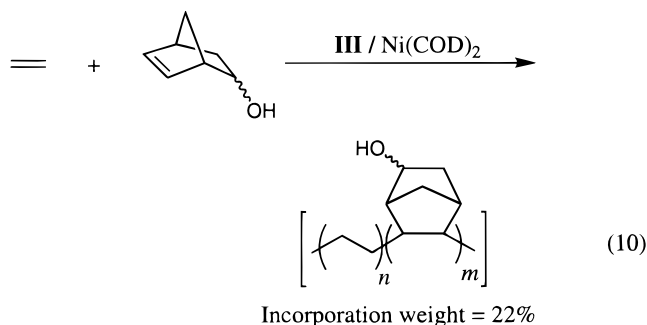
The tolerance to polar groups was tested in this system by running ethylene polymerizations in the presence of small molecule additives at a level of approximately 1500 equiv per metal center. On the basis of decreases in both molecular weight and catalyst turn over numbers, the neutral nickel catalysts displayed decreasing tolerance to functional groups in the following order ethers > ketones > esters > water > alcohols > tertiary amines.

Brookhart and co-workers recently reported tantalizing results that were close to constituting true copolymerizations of ethylene and methyl acrylate.[107,108] The catalyst employed was the palladium version of the diimine complexes that were previously reported for ethylene and α-olefin homopolymerizations (complexes **IV**).[109] The "close" qualification

Counter Ion : $B(Ar)_4^{\ominus}$, $SbF_6^{\ominus}$
Ar = 3,5-(CF₃)₂C₆H₃
M = Ni, **IVa**
     Pd, **IVb**
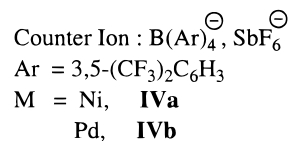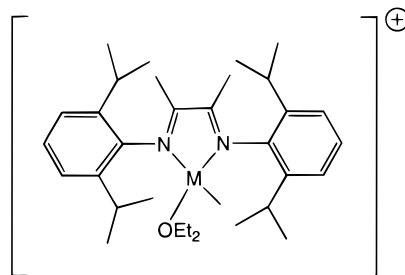
Scheme 4
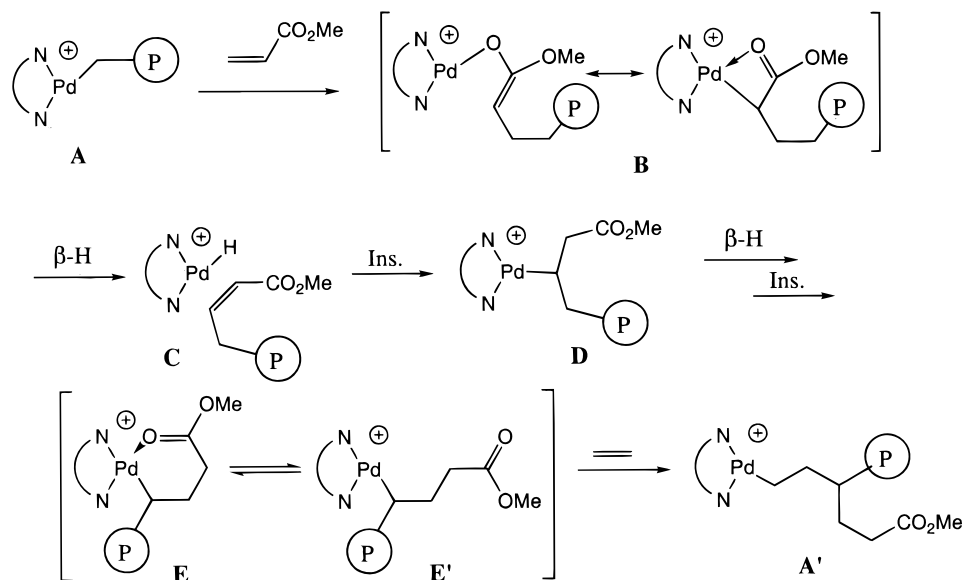
simply refers the placement of acrylate units. In general, the **IV** class of diimine catalysts yield highly branched polyethylenes, and in copolymerizations, the palladium catalyst **IVb** positions the acrylate units at the branch ends rather than randomly dispersed throughout the main chain. The branching results from sequential β-hydride elimination–hydride insertion steps that shift the palladium cation to adjacent carbons along the backbone. In addition to creating highly branched structures, this facial isomerization process prevents enolate formation from becoming a terminal sink and accounts for the acrylate units being localized at the chain ends. Acrylates are thought to insert into the palladium–carbon bond in a 2,1-fashion leading to an enolate structure, **B** (Scheme 4). Intermediate **B** does not insert olefin but rearranges at a faster rate to a six-membered chelated structure (**E**) possessing a new palladium–carbon bond. Reversible opening of this chelate to **E'** allows for coordination and insertion of another equivalent of ethylene. In effect, the catalyst "walks" away from the acrylate unit and isolates it at a chain end. This isomerization of **B** to **E** may well be the single most important reaction reported in this review. It is through this transformation that the formation of an enolate does not become a mechanistic dead-end to further olefin incorporation.

The addition of acrylates to the feed is not without some negative consequences. As the amount of acrylate is increased from 1 to 12 mol %, the catalyst turnover numbers decrease from 7710 mol of ethylene/mol of catalyst to 455 and the molecular weight drops from ca. 88 000 to 11 000. The decreased rates are thought to be due to the formation of chelated species, **E**, involving dative bonding that blocks the needed coordination site. Nevertheless, this is a substantial step forward in the metal-catalyzed copolymerization field as it is the first report of a metal-catalyzed copolymerization of ethylene and acrylate monomers that yields high molecular weight polymer.

Chien and co-workers studied Brookhart's nickel diimine analogues (e.g., **IV**) as catalysts for the copolymerization of ethylene, propylene, and trimethylaluminum protected polar monomers.[110] The comonomers reported included 5-hexen-1-ol, 10-undecen-1-ol, and 10-undecen-1-oic acid. Good yields of copolymers were obtained with some loss of catalyst activity. This last approach embodies nearly all the strategies used to date for functional olefins: olefins isolated from the polar groups, complexing the functional groups to reduce their basicity, and using catalysts based on late transition-metal complexes.

VI. Outlook

Despite a near half-century of work, the smooth incorporation of functional groups into polyolefins still remains a challenging area for further research into catalyst development. Most promising has been the resurgence in the studies on late-metal catalysts. Incorporation of (meth)acrylates into traditional polyolefins is perhaps on the horizon. Particularly interesting in this regard are catalysts that are capable of isomerizing from an enolate species, which is normally considered a thermodynamic dead-end toward further olefin insertions.

VII. References

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