Reactions of Metal Catalysts with Polar Vinyl Monomers

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Introduction

The polymerization of olefins by insertion chemistry using single-site metal catalysts provides a powerful approach to the synthesis of polyolefins with exquisite control of composition and structure. The development of metal catalysts that can polymerize or copolymerize *functionalized olefins* by insertion mechanisms would significantly expand the scope of metal-catalyzed polymerization and enable the synthesis of new materials with enhanced properties. While limited success has been achieved in the copolymerization of acrylates and vinyl ketones with ethylene and propylene using Pd, Ni or Cu catalysts, general strategies for designing catalysts with functional group tolerance are lacking.[1] The most important "polar" monomers are CH_2=CHX compounds, such as vinyl chloride (VC), acrylonitrile (AN) and vinyl ethers, in which the functional group is directly bonded to the olefin. These monomers are polymerized by radical or ionic mechanisms, but control of polymer composition and structure in such reactions is limited compared to what is possible through catalyst tuning in a metal-catalyzed insertion process. Important long term polymer targets include (i) new homopolymers with enhanced properties, such as stereoregular, defect-free PVC, (ii) linear ethylene/CH_2=CHX copolymers via direct synthesis from the monomers, and (iii) new copolymers such as VC/α-olefin copolymers (plasticizer-free, flexible PVC-type materials) or styrene/VC copolymers (flame resistant polystyrene-type materials). To pursue these goals, it is necessary to develop new generations of olefin polymerization catalysts and reactions that are tolerant of functional groups. We are investigating the reactions of single-site catalysts with CH_2=CHX monomers to identify and understand the chemical issues that underlie this challenge.

Results and discussion

Vinyl Chloride. We studied the reactions of VC with Ti, Zr, Fe, Co, Ni and Pd single-site catalysts.[2,3] Two important reaction channels were observed. First, certain catalysts initiate radical VC polymerization through the action of radicals derived directly from the catalyst/activator or by autoxidation of metal alkyl species by trace oxygen. This mode was observed for Cp*$TiCl_3$/MAO, $(C_5R_5)_2ZrR^+$ in the presence of trace O_2, and neutral Pd catalysts. Radical VC polymerization can be identified by the presence of terminal and internal allylic chloride units and other "radical defects" in the PVC that arise from the characteristic chemistry of $PCH_2CHCl^\bullet$ macroradicals. However, this test must be used with caution since the defect units can be consumed by post-polymerization reactions with catalyst components such as MAO. Competing radical polymerization is not a long-term problem because it may be avoided by using non-redox-active metals and anaerobic reaction conditions. The second general reaction observed is *net* 1,2 VC insertion and β-Cl elimination of L_nMR active species to produce L_nMCl species and CH_2=CHR. This process terminates chain growth after a single VC insertion, is fast for both early and late metal L_nMR species, and is the main obstacle to insertion polymerization of VC. However, deuterium labeling experiments show that several mechanisms are operative for these reactions and provide hints to how a successful catalyst might be developed. For example, (α-diimine)PdR^+ catalysts undergo 2,1 VC insertion to produce (α-diimine)$PdCHClCH_2R^+$ species, which undergo chain walking and syn-β-Cl elimination. This result suggests that non-chain-walking late metal catalysts may be good candidates for VC copolymerization.

Chlorocarbyl metal complexes are anticipated to be key intermediates in VC insertion polymerization. Model chloromethyl-Pd species were synthesized by the reaction of diazomethane with Pd-Cl precursors.[4] Chloromethyl-Pd species insert CO, ethylene and VC, but at a slower rate than analogous methyl-Pd complexes, due to the electron-withdrawing effect of the Cl. The beta-chlorophenyl zirconocene complex Cp*$_2$Zr(2-Cl-Ph)$^+$ was generated by orthometalation of Cp*$_2$ZrMe(PhCl)$^+$.[5] This species undergoes facile β-Cl elimination to generate a transient zirconocene benzyne species Cp*$_2$Zr(C_6H_4)Cl), which in turn rearranges by benzyne insertion into a Zr-C_{Cp^*} bond to form (η^4,η^1-$C_5Me_5C_6H_4$)Cp*ZrCl$^+$. The fact that β-Cl elimination occurs readily even when a high energy Zr benzyne species is formed underscores the strong thermodynamic driving force for this process at early metal centers.

Acrylonitrile. We studied the reactions of Pd-based catalysts with acrylonitrile (AN) and olefin/AN mixtures.[6] Cationic "L_2PdMe^+" active species form N-bound AN adducts that rearrange to the C=C π-bound isomers and undergo 2,1 insertion to yield $L_2Pd\{CH(CN)Et\}^+$ species These alpha-cyano alkyls form $[L_2Pd\{CH(CN)Et\}]_n^{n+}$ (n = 1-3) aggregates in which the Pd units are linked by PdCHEtCN---Pd bridges. Further AN or olefin insertion is strongly inhibited by the tendency of $L_2Pd\{CH(CN)CH_2R\}^+$ species to aggregate, which competes with monomer coordination, and by the low insertion reactivity of $L_2Pd\{CH(CN)CH_2R\}(substrate)^+$ species, which results from the presence of the electron-withdrawing alpha cyano group. The influence of the CN substituent on insertion reactivity was probed by studies with the model substrate CO. The reaction of (bim)$Pd\{CH(CN)Et\}^+$ (bim = CH_2(*N*-Me-imidazol-2-yl)$_2$) with CO results in initial formation of the CO adduct (bim)$Pd\{CH(CN)Et\}(CO)^+$ followed by slow reversible insertion to generate (bim)$Pd\{C(=O)CH(CN)Et\}(CO)^+$. For comparison, (bim)$Pd(Me)(CO)^+$ inserts CO much more rapidly to yield (bim)$Pd\{C(=O)Me\}(CO)^+$ quantitatively and irreversibly. Thus the α-CN group clearly inhibits but does not prevent the CO insertion.

At high temperature, AN acts as a chain transfer agent in Pd-catalyzed ethylene polymerizations via 2,1-insertion into L_nMR followed by β-H elimination, to produce PE–CH_2CH_2CH=CHCN end groups (PE = polyethylene chain) and L_2PdH^+ species that start new chains. The main obstacle to incorporation of AN in insertion polymerization processes is the slow insertion reactivity of $L_nM\{CH(CN)CH_2R\}$ (monomer) species.

We also studied two catalyst that were claimed to polymerize AN by insertion mechanisms: Cy_3PCuMe and $(bipy)_2FeEt_2$.[7] The complex Cy_3PCuMe undergoes reversible ligand redistribution at low temperature in solution to form the tight ion-pair $[Cu(PCy_3)_2][CuMe_2]$. The structure of the ion pair was assigned based on (i) the stoichiometry of the Cy_3PCuMe = $[Cu(PCy_3)_2][CuMe_2]$ equilibrium, (ii) the observation of a triplet for the PCy_3 C1 ^{13}C NMR resonance due to virtual coupling to two ^{31}P nuclei, and (iii) reverse synthesis of Cy_3PCuMe by combining separately generated $Cu(PCy_3)_2^+$ and $CuMe_2^-$ ions. Cy_3PCuMe, free PCy_3, and $(bipy)_2FeEt_2$ each initiate AN polymerization. In each case, the poly-AN contains branches that are characteristic of an anionic polymerization mechanism. The principal end groups in the poly-AN produced by Cy_3PCuMe are $Cy_3P^+CH_2CR(CN)$- and $CH_3CH_2CH(CN)$-, which indicates that initiation occurs by both PCy_3 and Me^- addition to AN monomer. The major initiator in AN polymerization by Cy_3PCuMe is PCy_3, which is liberated by dissociation from Cy_3PCuMe . The poly-AN produced by $(bipy)_2FeEt_2$ contains $CH_3CH(CN)CH_2CH(CN)$- chain ends, consistent with initiation by hydride addition to AN. A transient iron hydride complex is proposed to initiate AN polymerization by in this case.

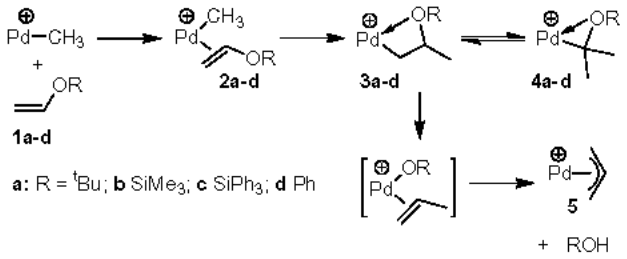
Vinyl-ethers. Vinyl-ethers (CH_2=CHOR) are attractive potential polar comonomers for olefin polymerization because their steric and electronic properties can be tuned by variation of the OR group. However, (i) vinyl ethers are susceptible to cationic polymerization by electrophilic metal catalysts [8,9,10], (ii) insertion barriers for $L_nMR'(CH_2$=CHOR) species are predicted to be high due to the electron donation by the OR group [11], and (iii) $L_nMCH_2CH(OR)R'$ species generated by insertion may undergo β-OR elimination, which would terminate chain growth. [12]

We found that cationic CH_2=CHOR polymerization can be completely suppressed by control of reaction conditions, tailoring of the vinyl ether structure, and proper selection of catalyst.

The reactions of (α-diimine)$PdMe^+$ with 1-2 equiv of CH_2=CHOR (**1a-d**: R = ^{t}Bu (**a**), $SiMe_3$ (**b**), $SiPh_3$ (**c**), Ph (**d**)) were investigated to probe for insertion reactivity under conditions where the vinyl ether concentration is low and cationic polymerization is slow. As shown in Figure 1, (α-diimine)$PdMe^+$ reacts with **1a-d** by C=C π-complexation to form (α-diimine)$PdMe(CH_2$=CHOR)$^+$ (**2a-d**), followed by 1,2 insertion to produce (α-diimine)$Pd(CH_2CHMeOR)^+$ (**3a-d**) and reversible isomerization to (α-diimine)$Pd(CMe_2OR)^+$ (**4a-d**) by chain-walking (i.e. via (α-diimine)$PdH(CH_2$=CMeOR)$^+$ formed by β-H

elimination). Complexes **3** and **4** interconvert rapidly on the lab time scale at 20 °C and react with MeCN to form (α-diimine)Pd($CH_2CHMeOR$)(NCMe)$^+$ (**3**·NCMe) at -40 °C. NMR data and DFT calculations show that **3** and **4** are O-chelated. No evidence for the 2,1 insertion product (α-diimine)Pd{$CH(OR)CH_2Me$}$^+$ or its chain-walk isomers was observed for **1a-d**. The **3/4** mixtures react further at 20 °C to generate (α-diimine)Pd(η^3-C_3H_5)$^+$ (**5**) and ROH, presumably by β-OR elimination of **3** to generate (α-diimine)Pd(OR)(CH_2=$CHMe$)$^+$ (not observed) and allylic C-H activation.[13] The viability of the allylic activation was established by the model reaction of [(tmeda)Pd(OPh)]$_n^{n+}$ with propylene to yield (tmeda)Pd(η^3-C_3H_5)$^+$ and HOPh quantitatively.

Figure 1. Reaction of (α-diimine)PdMe$^+$ with vinyl ethers.



The binding strength of **1a-d** to (α-diimine)PdMe$^+$ was assessed by competitive binding experiments with ethylene. The K_{eq} data (Table 1) show that **1a** binds with similar strength as ethylene but **1b-d** bind more weakly. The kinetics of key steps in Scheme 1 were measured by NMR and $t_{1/2}$ data are listed in Table 1. **2a-d** insert more slowly than does (α-diimine)PdMe(ethylene)$^+$. The conversion of **3/4** to **5** is slow, except in the case of phenyl vinyl ether, for which **3d/4d** react faster than they are formed from **2d** and hence were not directly observed.

Table 1. Reactivity of CH_2=CHOR with (α-diimine)PdMe$^+$

CH_2=CHOR	^{t}Bu	$SiMe_3$	$SiPh_3$	Ph
K_{eq} vs ethylene (-60 °C)[a]	1.2(1)	0.17(1)	< 0.01	0.04(2)
$t_{1/2}$, conv. of **2** to **3/4** (0 °C)[b]	> 1h	15 min	8.9 min	7.7 min
3/4 ratio (20 °C)	73/27	0/100	0/100	not obs
$t_{1/2}$, conv. of **3/4** to **5** (20 °C)	88 h	5.5 h	2.2 h	< 3 min

[a] K_{eq} = [**2**][CH_2=CH_2][PdMe(CH_2=CH_2)$^+$]$^{-1}$[**1**]$^{-1}$. [b] $t_{1/2}$ for insertion of PdMe(CH_2=CH_2)$^+$ at 0 °C is ca. 8 sec.

Using these results as a guide, (α-diimine)PdMe$^+$-catalyzed olefin/vinyl ether copolymerization has been achieved.

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