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# Palladium-Catalyzed Copolymerization of Ethene with Acrolein Dimethyl Acetal: Catalyst Action and Deactivation

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The incorporation of polar heteroatom-containing functionalities into (intrinsically apolar) polyolefins by the copolymerization of simple olefins with functional olefinic comonomers is of substantial interest as a potential route to polyolefin materials with improved dyeability, wettability, or permeability properties.[1] A main obstacle is the poor compatibility of Lewis acidic polymerization catalysts with Lewis basic heteroatom-containing functionalities, leading to a significant decrease in catalyst performance or even rapid catalyst deactivation. The advent of (relatively soft Lewis acidic) late transition-metal-based catalysts, in particular cationic (α-diimine)-Pd-based systems,[2] has provided encouraging results such as the successful (if rather slow) copolymerization of ethene and methyl acrylate to give branched copolymers.[3] Nevertheless, many issues still need to be resolved to estimate the full potential for catalytic routes to functional polyolefins.

A recent paper described the copolymerization of ethene with olefins containing $\omega$-ether functionalities using cationic (α-diimine)-Pd-catalysts.[4] This was only successful when the ether functionality was separated from the olefinic group by a spacer containing a quaternary carbon atom. This led to the conclusion that "chain walking" of the metal center to the ether group, followed by $\beta$-alkoxide transfer to the metal, is the likely catalyst deactivation pathway. Here we describe the successful copolymerization of ethene with acrolein dimethyl acetal (ADMA) using a cationic (α-diimine)Pd-catalyst and show that, in this case, catalyst deactivation occurs by the formation of inert cationic ($\eta^3$-allyl)palladium species via alcohol elimination, rather than by $\beta$-alkoxide transfer to the metal.

Reaction of (DAD)Pd(Me)Cl (**1**; DAD = ArN═CMe−CMe═NAr; Ar = 2,6-diisopropylphenyl)[2a] with ADMA and $NaBAr^f_4$ ($BAr^f_4$ = B[3,5-$(CF_3)_2C_6H_3]_4$) in $CH_2Cl_2$ yielded the five-membered chelate complex [(DAD)Pd($CH_2CHMeCH(OMe)_2$][$BAr^f_4$] (**2**). The complex was identified by $^1$H and $^{13}$C NMR spectroscopy,[5] elemental analysis, and a single-crystal X-ray structure determination.[6] The chelate fragment on Pd is highly disordered, as the crystal packing in these (DAD)Pd compounds is strongly dominated by the aryl groups of the ligand. Nevertheless, it can be seen that 1,2-insertion of ADMA into the Pd−Me bond has taken place, and that one of the acetal OMe groups is coordinated to the metal. The compound is air-stable and thermally stable in solution at least up to 50 °C. Complex **2** catalyzes the copolymerization of ethene and ADMA at ambient temperature (results are listed in Table 1). It is seen that addition of ADMA comonomer significantly slows down the polymerization rate, but that copolymers with up to 2.0 mol % (6.9 wt %) comonomer can be obtained. A catalyst deactivation process is present, leading to full deactivation within 20 h (see below for details).

The branched PE-co-ADMA copolymers contain two main types of acetal groups, as seen by $^1$H and $^{13}$C NMR spectroscopy.[7] These correspond to $CH(OMe)_2$ groups attached to either a primary carbon or a secondary carbon (in 1:1 to 1:0.8 ratio for lowest to highest comonomer content) revealed by the presence of either a triplet or a doublet resonance for the acetal CH proton, indicating, respectively, comonomer incorporation on a chain/branch end or within a chain/branch. Increasing the comonomer concentration leads not only to increased comonomer incorporation but also to a lowering of the polymerization rate and of the polymer molecular weight.

***Table 1.*** Ethene/ADMA Copolymerization with **2** as Catalyst

| conditions[a] | ADMA (mmol) | yield (g) | product[b] | $M_w$ (×10$^{-3}$) | PDI | ADMA (mol %)[c] |
|---|---|---|---|---|---|---|
| A | 0 | 3.50 | 13.0 | 186 | 1.5 | 0 |
| A | 4.2 | 1.21 | 4.5 | 105 | 1.7 | 0.29 |
| A | 8.4 | 0.64 | 2.4 | 52 | 2.0 | 0.32 |
| A | 17.4 | 0.44 | 1.6 | 31 | 2.3 | 0.66 |
| B | 4.2 | 1.60 | 1.2 | 50 | 1.7 | 0.72 |
| B | 8.4 | 1.50 | 1.1 | 32 | 1.7 | 1.30 |
| B | 19.1 | 1.20 | 0.9 | 16 | 1.7 | 1.67 |
| B | 26.1 | 0.52 | 0.4 | 13 | 1.6 | 2.02 |

[a] Reaction conditions A: 13.4 $\mu$mol **2**, 15 mL $CH_2Cl_2$, 5 bar ethene, ambient temperature, 20 h run time. B: 67 $\mu$mol **2**, 3 mL $CH_2Cl_2$, otherwise as A. [b] Productivity kg(PE) mol$^{-1}$ h$^{-1}$. [c] Determined by $^1$H NMR.

Upon workup of the ethene/ADMA copolymerization reaction mixtures, orange crystals of a palladium species were isolated. NMR spectroscopy,[8] elemental analysis, and a single-crystal structure determination[9] revealed the formation of the 1-methoxyallyl complex [(DAD)Pd($\eta^3$-1-MeOCHCHCH$_2$)][$BAr^f_4$] (**3**, Scheme 1). Complex **3** itself is not active in ethene homopolymerization, and its recovery in >80% yield after recrystallization indicates that its formation is the main catalyst deactivation process.

Unlike the copolymerizations with ADMA described above, the copolymerization of ethene with allyl ethyl ether (AEE), using **2** as an introduced catalyst species, could not be achieved. Instead, rapid catalyst deactivation is observed, and the cationic allyl complex [(DAD)Pd($\eta^3$-$CH_2CHCH_2$)][$BAr^f_4$] (**4**)[10] was recovered in high yield. In the reaction mixture, the formation of ethanol was observed by GC/MS analysis. As the reaction of [(DAD)PdMe-($OEt_2$)][$BAr^f_4$][2a] with 1 equiv of AEE resulted in clean formation of the stable five-membered chelate [(DAD)Pd($CH_2CHMeCH_2$-OEt)][$BAr^f_4$] (**5**),[11] the catalyst decomposition via ethanol elimination and formation of the cationic palladium allyl species apparently takes place only in the presence of excess comonomer.

A possible route to the formation of these allylic species is shown in Scheme 2. An equilibrium between the Pd−alkyl species and the hydride−olefin complex (implied in chain-transfer processes for these catalysts[12]), followed by olefin exchange by an allylic ether comonomer, can lead either to 1,2-insertion of the comonomer (reforming a chelate) or to elimination of a molecule of alcohol, producing an $\eta^3$-allylic species. This type of reaction was recently implied in the catalytic substitution of allyl alcohol with amines to give allylic amines, catalyzed by cationic palladium bis(phosphin-


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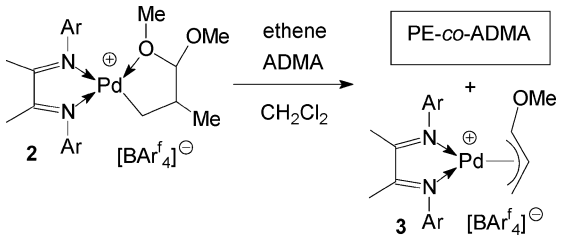
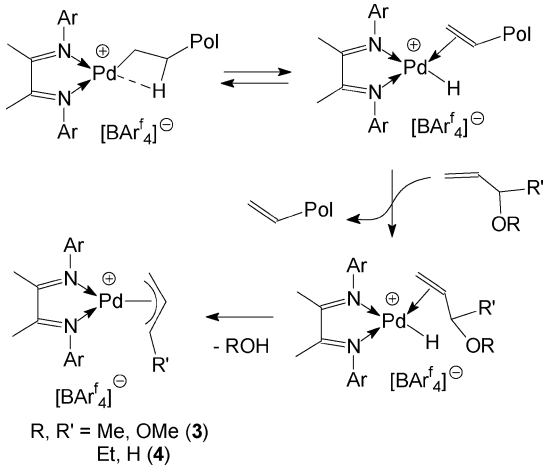
***Scheme 1***




***Scheme 2***




idene)cyclobutene hydride complexes.[13] This process appears to be facile for AEE, thus preventing the formation of copolymer, whereas for the acetal comonomer ADMA, the allyl formation is sufficiently retarded to allow the formation of a significant amount of copolymer before catalyst deactivation.

If this deactivation mechanism is correct, it is conceivable that the catalyst lifetime may be improved by the addition of alcohol to the reaction mixture. A series of experiments using conditions A (defined in Table 1) with 4.2 mmol of ADMA and 37 equiv/Pd of methanol (0.5 mmol) showed that this does lead to improved overall productivity. Run times of 6, 12, 20, and 40 h gave polymer yields of 0.90, 1.21, 1.72, and 2.31 g, respectively. In the absence of methanol, a maximum polymer yield of 1.2 g was reached after 12 h, after which no additional polymer was formed. Although methanol addition improves overall productivity, it is clear that gradual catalyst deactivation still takes place. The addition of substantially larger amounts of methanol (500 equiv/Pd) again led to a decrease in catalyst productivity, possibly due to the occurrence of an alternative catalyst deactivation process under these conditions. The improvement is apparently obtained by retarding the allyl formation (rather than by reactivation of the allyl species once it is formed), as addition of methanol to $CH_2Cl_2$ solutions of complex **3** did not induce ethene polymerization activity.

In conclusion, we have successfully copolymerized ethene with acrolein dimethyl acetal using a palladium catalyst to give a branched polyethene copolymer with pendant acetal groups. Allyl formation via methanol elimination was found to be the dominant catalyst deactivation pathway. The lifetime of the catalyst (and with it overall copolymer production) could be improved by the addition of methanol to the reaction mixture. The identification of catalyst deactivation pathways thus provides information that can lead to approaches that improve the catalytic production of functionalized polyolefins.

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**Supporting Information Available:** Text giving full experimental and characterization data and crystallographic data for **2**−**5**, as well as positional and thermal parameters and bond distances and angles (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) Selected NMR data for **2**. $^1$H (500 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 4.12 (d, $J$ = 5.5 Hz, C*H*(OMe)$_2$), 3.12 (s, 3H, OMe), 2.87 (m, 2H, PdC*H*$_2$), 2.84 (s, 3H, OMe), 1.3 (m, PdCH$_2$C*H*Me), 0.74 (d, 3H, $J$ = 7.0 Hz, PdCH$_2$CH*Me*). $^{13}$C (126 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 119.48 (d, $J_{CH}$ = 172 Hz, *C*H(OMe)$_2$), 60.51 (q, $J_{CH}$ = 147 Hz, OMe), 56.55 (q, $J_{CH}$ = 145 Hz, OMe), 38.80 (t, $J_{CH}$ = 140 Hz, Pd*C*H$_2$), 38.75 (d, $J_{CH}$ = 112 Hz, PdCH$_2$*C*HMe), 14.65 (q, $J_{CH}$ = 131 Hz, PdCH$_2$CH*Me*).
(6) Crystal data for **2**: [$C_{34}H_{53}N_2O_2Pd$][$C_{32}H_{12}BF_{24}$], $M_r$ = 1491.45, monoclinic, $P2_1/n$, $a$ = 12.8098(2) Å, $b$ = 28.259(2) Å, $c$ = 19.154(1) Å, $\beta$ = 103.450(1)°, $V$ = 6743.3(7) Å$^3$, $Z$ = 4, $D_c$ = 1.469 g cm$^{-3}$, $T$ = 100(1) K, $\mu$(Mo K$\alpha$) = 0.71073 Å, $wR(F^2)$ = 0.2107 for 11 901 unique reflections, 950 parameters and 44 restraints, $R(F)$ = 0.0726 for 8207 reflections with $F_o \geq 4.0\sigma(F_o)$. A disorder model with two alternative conformations (SOF of the major fraction = 0.507(8)) and with bond restraints was used to model the CH$_2$CH(Me)CH(OMe)$_2$ fragment.
(7) $^1$H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta$ 4.33 (t, $J$ = 5.7 Hz, CH$_2$C*H*(OMe)$_2$), 4.00 (d, $J$ = 6.7 Hz, CHC*H*(OMe)$_2$), 3.33 and 3.29 (s, OMe). $^{13}$C NMR (126 Hz, $CDCl_3$, 25 °C): $\delta$ 108.9 and 104.6 (*C*H(OMe)$_2$), 54.0 and 52.5 (OMe).
(8) Selected NMR data for **3**. $^1$H (500 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 5.66 (d, $J$ = 9.6 Hz, C*H*OMe), 5.27 (m, CH$_2$C*H*CHOMe), 2.95 (m, C*HH*′CHCHOMe), 2.62 (s, 3H, OMe), 2.44 (dd, $J$ = 12.8 and 2.2 Hz, CH*H*′CHCHOMe). $^{13}$C (126 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 120.33 (d, $J_{CH}$ = 168 Hz, *C*HOMe), 98.67 (d, $J_{CH}$ = 149 Hz, CH$_2$*C*HCHOMe), 60.18 (q, $J_{CH}$ = 141 Hz, OMe), 54.50 (t, $J_{CH}$ = 156 Hz, *C*H$_2$CHCHOMe).
(9) Crystal data for **3**: [$C_{32}H_{47}N_2OPd$][$C_{32}H_{12}BF_{24}$], $M_r$ = 1445.37, monoclinic, $C2/c$, $a$ = 21.9494(9) Å, $b$ = 12.8691(5) Å, $c$ = 25.207(1) Å, $\beta$ = 115.522(1)°, $V$ = 6425.4(4) Å$^3$, $Z$ = 4, $D_c$ = 1.494 g cm$^{-3}$, $T$ = 100(1) K, $\mu$(Mo K$\alpha$) = 0.71073 Å, $wR(F^2)$ = 0.1874 for 7900 unique reflections, 597 parameters and 55 restraints, $R(F)$ = 0.0675 for 6294 reflections with $F_o \geq 4.0\sigma(F_o)$. The cation is disordered over a crystallographic inversion center.
(10) Selected NMR data for **4**. $^1$H (500 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 5.64 (m, allyl CH), 3.35 (d, 2H, $J$ = 7.0 Hz, C*H*H), 3.04 (d, 2H, $J$ = 12.8 Hz, CH*H*). $^{13}$C (126 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 121.03 (d, $J$ = 170 Hz, allyl CH), 65.78 (t, $J$ = 185 Hz, CH$_2$).
(11) Selected NMR data for **5**. $^1$H (500 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 3.53 (dd, $J$ = 7.7 and 6.0 Hz, C*H*H′OEt), 3.14 (t, $J$ = 7.6 Hz, CH*H*′OEt), 2.85 (m, 2H, OC*H*$_2$Me), 1.67 (m, 2H, PdCH$_2$), 1.29 (m, PdCH$_2$C*H*Me), 0.82 (*t*, $J$ = 7.0 Hz, OCH$_2$*Me*), 0.79 (d, $J$ = 7.0 Hz, PdCH$_2$CH*Me*). $^{13}$C (126 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 83.69 (t, $J$ = 145 Hz, *C*H$_2$OEt), 72.84 (t, $J$ = 146 Hz, OCH$_2$Me), 47.77 (t, $J$ = 150 Hz, Pd*C*H$_2$), 37.45 (d, $J$ = 161 Hz, PdCH$_2$*C*HMe), 14.62 (q, $J$ = 127 Hz, PdCH$_2$CH*Me*), 13.69 (q, $J$ = 127 Hz, OCH$_2$*Me*).
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