Chain transfer to aluminium in MAO-activated metallocene-catalyzed polymerization reactions

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Chemical trapping of metal-bound oligomeric chains during the MAO-activated, metallocene-catalyzed polymerization of ethylene identify the two observed chain-bearing species to be alkylzirconocenium species and higher alkyl aluminiums, consistent with a proposed mechanism.

The role of methylalumoxane (MAO) in the Ziegler–Natta polymerization of olefins with either heterogeneous or homogeneous transition-metal catalysts has been subject of much investigation.[1] The very large molar excesses of MAO, often several hundred-fold relative to catalyst, scavenges adventitious water and impurities, but, more importantly, alkylates and ionizes the transition-metal center to prepare the active site for coordinative insertion of ethylene or higher olefins. MAO's role subsequent to the activation step is unclear. In an earlier Communication,[2] we reported the *in situ* electrophilic trapping of growing metal-bound alkyl chains by reaction with *N*,*N*′-dicyclohexylcarbodiimide (DCC) which produced two separate but overlapping distributions of trapped oligomeric chains observable by means of electrospray ionization mass spectrometry (ESI-MS). We report here further chemical quenching studies which identify the "fast" species in the previous report as higher alkylalumoxanes; the "slow" species are the alkylzirconoceniums conventionally presumed to be the propagating species in Ziegler–Natta polymerization. Moreover, we propose a mechanism, consistent with the shape of the distributions, which indicates that, even at the relatively low Al : Zr ratios of this study, transmetalation to aluminium is at least as fast as propagation on zirconium. The result implies for many real processes, where the Al : Zr is much higher, that MAO-activated Ziegler–Natta polymerization may be better regarded as a transition-metal-promoted "*Aufbau*" reaction on aluminium.

A toluene solution of precatalyst Cp_2ZrCl_2, **1** (4 mg, 13.7 μmol) was added to a rapidly stirred, thermostatted solution of 100 μL MAO in toluene (Aldrich, 10% w/w solution in toluene, 165 μmol) presaturated with ethylene and held at a constant 2 bar in a tubular glass pressure reactor (20 × 2.5 cm)[3] to make a total liquid volume of 6.0 mL. The reactor and control studies are described in our previous report.[2] In a typical experiment at room temperature, the reaction was quenched after a short time interval, usually 90 s, by rapid injection of 35 equivalents relative to precatalyst **1**, of triethylamine.[4] After a time interval ranging from a few seconds to many minutes, there is a second injection of 35 equivalents of DCC.[5] Two drops of the quenched solution were diluted in 30 mL CH_2Cl_2 and electrosprayed. The quench time was set early enough so that neither precipitation of polymer nor significant increase in viscosity appears. Moreover, variation of the time intervals up to addition of triethylamine, to addition of DCC, and to dilution and analysis, were done and checked for differences in the resulting mass spectrum. The procedure and conditions for analysis by electrospray ionization mass spectrometry have been previously described for both early and late transition-metal catalysts.[6] The oligomer chain distributions, described in the earlier works, and observed here as series of amidinium cations, reflect the distribution of trappable metal-bound alkyl chains at the time of quenching. Free oligomers do not acquire the amidinium head group and are hence invisible under the chosen ESI-MS conditions.

A control experiment in which the quench with triethylamine is omitted produces the expected bimodal oligomer distribution, shown in the upper panel of Fig. 1, as was reported in our previous Communication. Repetition of the same experiment, but with the triethylamine quench prior to the DCC quench, produces a mass spectrum, shown in the lower panel of Fig. 1, in which only one of the two distributions of oligomeric trapping products is observed. Deconvolution of the bimodal distribution in the control experiment, and comparison to the amine-quenched monomodal distribution reveals that what we had termed the "fast" component is identical within experimental error with the single remaining distribution in the amine-quenched case. Moreover, that remaining distribution does not change when the time between the two quenches is varied up to many minutes. It should be noted that, unsurprisingly, ethylene consumption ceases immediately upon addition of triethylamine. In another control experiment, pretreatment of the MAO with a known selective quencher of trimethylaluminium (TMA), 2,6-di(*tert*-butyl)phenol,[7] following procedures described by Carlini *et al.*[8] and by Rytter and coworkers,[9] does not change the "fast" distribution, with or without triethylamine, indicating that the distribution does not derive from reactions of TMA. A final pair of control experiments help identify the carriers of the two distributions. In the first one, MAO alone in toluene is treated sequentially with triethylamine and DCC, and worked up as usual. The ESI-MS shows that aluminium-bound methyl groups in MAO are quantitatively and rapidly trapped as methylamidines even in the presence of tertiary amines. In the second,[10] chloride was abstracted from $Cp_2Zr(CH_3)Cl$ by K(BArF), BArF = tetrakis(3,5-bistrifluoromethylphenyl)borate, to produce the putative alkylzirconocenium intermediate in Ziegler–Natta polymerization, which was then treated with DCC with and without a prior triethylamine quench. ESI-MS after workup showed complete trapping of the $[Cp_2ZrCH_3]^+$ by DCC

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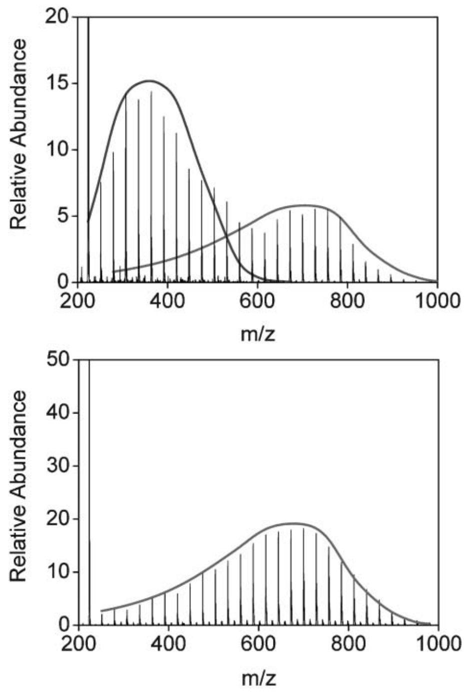
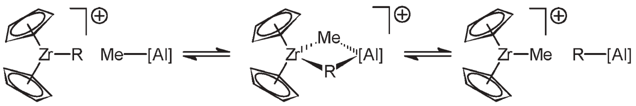


Fig. 1 ESI-MS of the quenched polymerization of ethylene by MAO-activated Cp_2ZrCl_2. The control experiment in the upper panel shows the two distributions of amidinium cations produced from two different metal-bound oligomeric chains trapped by DCC. The lower panel shows the single distribution produced by treatment of the reaction mixture with triethylamine prior to DCC quenching. The two distributions at high masses for both panels are essentially identical. The two sets of lines in the upper panel show the deconvolution of the distributions using methods from ref. 2.

when triethylamine is absent. In the presence of triethylamine, no methylamidinium cations are observed in the mass spectrum.

The rather simple series of experiments have nevertheless a difficult-to-avoid conclusion. The "slow" species behaves as one would expect for the proposed active species in metallocene-catalyzed Ziegler–Natta polymerizations. The alkylzirconocenium cation, and its ion pairs and dimers to the extent that they are kinetically indistinguishable, have been observed *in situ* by various spectroscopic techniques by many groups.[11] The cationic active species have also been the subject of increasingly sophisticated quantum chemical studies[12] which confirm the results of model studies as well as general expectations from industrial practice. One would expect that a tertiary amine would bind strongly to the zirconocenium cation. We have performed DFT calculations at the B3LYP level of theory, with the DZVP basis set on Zr and 6-31+G** on all other atoms, and found very substantial binding energies of $\sim$40 kcal mol^{-1}. Accordingly, it is reasonable, and moreover consistent with our control experiment on amine-quenched $[Cp_2ZrCH_3]^+$, that triethylamine would bind strongly enough, not only to quench propagation, but also to prevent alkylation of the DCC. Oligomer chains on zirconium centers therefore do not appear as the corresponding amidinium cations in the mass spectrum after an amine quench. On the other hand, we demonstrate that the methyl groups on MAO are still trappable with DCC, even in the presence of large amounts of triethylamine, which leaves higher alkylalumoxanes as the only reasonable precursors to the "fast" distribution observed in the experiment. Higher alkylalumoxanes have been characterized crystallographically by Barron and co-workers,[13] and the compact cage structures could plausibly tolerate tertiary amines. One should note that the labels, "slow" and "fast," from the previous Communication are used here only as designations.

We propose the following mechanism for the transmetalation. The doubly-bridged intermediate allows a near-thermoneutral alkyl exchange between zirconium and aluminium centers.



Reversible zirconium to aluminium chain transfer is implied in a report by Przybyla and Fink,[14] in which chain transfer between two different metallocenes is mediated by aluminium species. Very similar mechanisms have been proposed for several analogous cases involving a main group metal and either a transition metal, a rare earth, or an actinide.[15] A close analogy is furthermore the recent report by Gibson and co-workers involving an iron catalyst with an alkylzinc.[16] While the end product of the reaction is a polyolefin, the reaction has been called a transition metal-promoted *Aufbau* reaction.[17] One could suggest that the difference lies in the relative rates for propagation on the transition-metal center versus transfer to the main group metal. In the case that the former is much faster, one has a slightly modified Cossee–Arlmann mechanism[18] for metallocene-catalyzed Ziegler–Natta polymerization in which multiple addition steps occur on the zirconium with only occasional transfer to aluminium. If, on the other hand, transmetalation, *i.e.* chain transfer to aluminium, were to be much faster than propagation, then the chain goes back to aluminium after each monomer unit is added.

The conclusion that the "fast" distribution is due to higher alkylalumoxanes comes from the chemical quenching results. Fitting of the distributions to a mechanism produces a set of rate constants particular to that mechanism; a plausible mechanism should produce an acceptable fit. A minimal model would ignore chain transfer to monomer, which is adequate for the room temperature experimental runs in our study. More restrictive in a minimal model would be an assumption that the rate constant for transmetalation be largely independent of chain length. Work presently underway seeks to extract the best possible rate constants from the distributions under the minimal and somewhat less minimal models. The results will be reported in a later contribution, but even the minimal model does successfully reproduce the general bimodal distribution of trapped oligomers. It is important to realize that the kinetic model would predict that the bimodal distribution of trapped oligomers arises because the DCC quenching was done at a time early enough so that there were still methyl groups on the aluminium. The longer chain lengths of the (non-methyl) alkylalumoxanes relative to the alkylzirconoceniums comes because each transmetalation involves an exchange of alkyl residues which sends the zirconium-centered chains back to methyl until the methyl groups on aluminium are exhausted. At later times, the zirconium-centered and aluminium-centered distributions should converge. As mentioned above, the detailed quantitative fitting is still underway, but the qualitative result is already evident that the rate of transmetalation exceeds the propagation rate under the conditions chosen for the reaction. With the low Al : Zr ratio of 12 : 1, one can surmise that the balance of transmetalation versus propagation is even more in favor of transmetalation at the 100 : 1–1000 : 1 ratios encountered in industrial reactors. Higher ethylene pressures can compensate to a degree, but, assuming first-order dependences of the two processes on the concentrations of Al and ethylene, respectively, the *ratio* of transmetalation to propagation for Al : Zr = 500 and a pressure of ethylene of 100 bar would be similar to that in the present experiment.

The difference between a Cossee–Arlmann mechanism modified with a slight extent of chain transfer to aluminium and a metallocene-promoted *Aufbau* reaction would most likely be visible in stereoselective polymerizations of propylene and other higher α-olefins. The highly isotactic or syndiotactic polymer produced by the C_2 or C_s/C_1 symmetric single-site catalysts requires that the growing chain remain bound to the transition-metal center and incorporate multiple monomer units sequentially without chain transfer to another metal. The *Aufbau* reaction with transmetalation after each insertion of monomer is much less likely to display high stereoselectivity. Given that the rate constants for transmetalation and propagation have been reported by Gibson and co-workers[16] to depend differently on steric or electronic substituent effects, as had been already suggested by Lieber and Brintzinger on the basis of polymer end-group analyses,[19] the shift from faster propagation to faster transmetalation could occur at different Al : Zr ratios for different catalysts. Moreover, a pressure-dependent stereoselectivity, as reported by Busico *et al.*,[20] will likely be a general phenomenon for which the relative rate constants will be decisive. Lastly, Rieger and co-workers[21] have proposed reversible chain transfer to aluminium as the origin of stereoerrors in stereoselective polymerizations by comparing results in bulk polymerizations with different cocatalysts. We expect, accordingly, that the elementary rate constants in a suitable kinetic model would constitute important parameters in the design and optimization of stereoselective polymerization catalysts.

A final observation prompts a further conjecture. When the DCC-quenching experiment is repeated with $Cp_2Zr(CH_3)_2$ as precatalyst and stoichiometric $B(Ar_F)_3$ as activator, the reaction at the same temperature and same ethylene pressure produces much more, and much longer, chains, even for very short (DCC) quench times. For example, at 10 s quench times, precipitation of polymer is already visible, which was not seen in the MAO-activated case even at much longer times. The result suggests that the reversible chain transfer to aluminium, where propagation does not occur,[22] affects the overall kinetics by introducing a pre-equilibrium that slows the observed rate of polymerization. Higher Al : Zr ratios would mean slower propagation rates, which are counter-balanced by a higher fraction of activated Zr sites. The two effects working in opposite directions may be the origin of a bell-shaped dependence of catalyst productivity on the Al : Zr ratio. Quantitative characterization of the individual processes should lead to predictive modeling of the optimum Al : Zr ratio for maximum productivity.

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