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Insertion of Carbon Monoxide into Zr−Polymeryl Bonds: "Snapshots" of a Running Catalyst

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Two main strategies have been devised for the challenging determination of active site concentration (C^*) in catalytic olefin polymerizations: (i) analysis of the time dependence of polymer yield and number average molecular mass at very early stages under stopped-flow conditions;[1] (ii) use of a "quenching" agent (typically, ^{14}CO or CH$_3$O^{3}H) able to tag the polymer chains with a radioactive label at their growing end.[2] Unfortunately, both approaches are potentially flawed: the former, because the initial phase of a polymerization may be severely affected by induction phenomena; the latter, due to the possible incorporation of more than one radio-label per growing chain and/or to the tagging also of "dead" chains bound to the metal-alkyl cocatalyst (when used).[2]

As a matter of fact, when applied to the classical heterogeneous Ziegler−Natta catalysts,[3] the two approaches can give substantially different results (for MgCl$_2$/TiCl$_4$ supported systems,[3c−e] in particular, C^* would be 0.1−0.2 mol/mol (Ti) based on radio-tagging experiments,[4] and only 0.01−0.05 mol/mol (Ti) according to stopped-flow investigations[1]). On the other hand, the development of new classes of homogeneous polymerization catalysts with well-defined precursors[5] has provided a chance of testing such methods on less complicated systems.

In our laboratory, we have recently applied the stopped-flow approach to ethene and propene polymerization promoted by one of the most efficient *ansa*-metallocene catalysts[5a] presently available, namely *rac*-dimethylsilyl-bis(2-methyl-4-phenyl-1-indenyl)ZrCl$_2$[6] (**I**; cocatalyst, methyl-aluminoxane, MAO), and found that C^* can be (much) lower than the analytical Zr concentration, particularly when the monomer is ethene.[7] To verify this (somewhat unexpected) result and to rule out a possible idiosyncratic tendency of the stopped-flow method to underestimate C^*, we decided to make a cross-check by means of catalyst quenching with ^{14}CO (a route that appeared to be viable, based on early literature studies on the reactivity of CO with polyethylene chains growing at the active species of bis(cyclopentadienyl)MtCl$_2$/MAO with Mt = Ti[8] or Zr[9]).

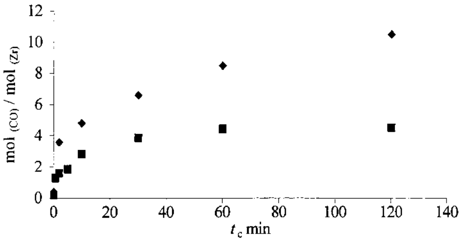

Figure 1. Incorporation of CO in growing polyethylene (◆) and polypropylene (■) chains as a function of catalyst/CO contact time (t_c) in the presence of the catalyst system **I**/MAO at 40 °C.

Radio-tagging experiments were performed at 40 °C following the procedure described by Tait et al.,[10] and the CO content in the polymers was measured and plotted as a function of catalyst/CO contact time, t_c (Figure 1). According to the literature,[4,9−11] such plots would reveal two different kinetic regimes: an initial phase of faster CO incorporation, during which the growing chains are tagged with the formation of transition metal-acyl bonds, and a subsequent one of much slower incorporation, vaguely attributed to "side reactions".[2,4,9−11] The measurement of C^* should be based on the CO content of the polymer at the completion of the former phase; this would require a few minutes for metallocene catalysts,[9,10] and up to 1 h for Ziegler−Natta ones.[4,11]

To our surprise, instead, the curves of Figure 1 for system **I**/MAO tell a different story. The high values of CO incorporation, in excess of 1 mol/mol (Zr) after 1 min already, suggest the occurrence of a copolymerization process, both with ethene and propene. Moreover, the regular asymptotic shape of the curves gives no evidence for different kinetic regimes and more simply indicates an exponential decay of catalytic activity (frequently observed for metallocene-based systems[5a]).

CO/1-alkene copolymerization (in alternated fashion) is efficiently promoted by coordination catalysts based on late transition metals,[12] whereas—to our knowledge—it has never been documented for early transition metal ones. Therefore, we thought it worthwhile to confirm our interpretation by using ^{13}CO instead of ^{14}CO and characterizing the reaction products by means of ^{13}C{^{1}H} 1-D and ^{1}H/^{13}C 2-D NMR. To increase the fraction of chains containing ^{13}CO, the polymerization runs were conducted under stopped-flow conditions.[1,7,8] A specially devised microreactor, in sequence to the polymerization one, allowed us to achieve catalyst/^{13}CO contact times down to 10 s, prior to treatment of the reaction phase with acidified methanol.

The ^{13}C NMR spectra of ^{13}CO-terminated polyethylene samples show, in addition to the resonance of the polymethylenic chains ($\delta = 30.0$ ppm downfield of TMS), one or more clear peaks in the carbonyl region at $\delta \approx 210$ ppm, typical of $-CH_2-CO-CH_2-$ structures.[13] Further resonances in the range of $\delta = 90-120$ ppm most probably arise from ^{13}C-enriched hemiketalic and ketalic species deriving from the cyclization of $-(CO-CH_2-CH_2)_n-$ sequences, possibly during sample coagulation in CH$_3$OH/H$^+$.[14]

In the case of polypropylene, the ^{13}C NMR analysis in solution of samples obtained at longer catalyst/^{13}CO contact times (t_c > 1

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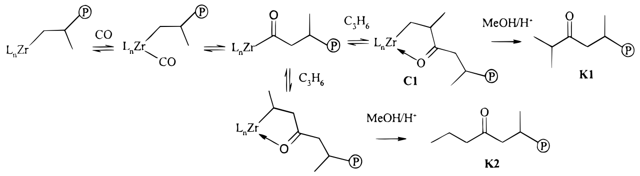
Scheme 1



min) turned out to be problematic because, at the temperature needed to dissolve them (120 °C), extensive rearrangements of carbonyl structures were observed during the accumulation process. On the other hand, the most remarkable feature of the solid-state ^{13}C CP-MAS NMR spectra of such samples is a resonance at a value of chemical shift ($\delta = 120$ ppm) typical of alternated CO/propene copolymers and assigned to a spiroketalic structure.[15] Conversely, the high resolution ^{13}C NMR spectra of samples recovered after very short contact times ($t_c < 30$ s) are simple and show, apart from the resonances of polypropylene, only one clear peak at $\delta = 214$ ppm, indicative of a single ^{13}C-enriched *mono*ketone, which from ^{1}H/^{13}C 2-D NMR spectra (vide infra) was identified as the *iso*-propyl-polymeryl-ketone **K1** of Scheme 1.[16]

In our opinion, the above observations indicate that: (i) the investigated catalyst system is able to promote the (alternated) copolymerization of CO with ethene and propene, though at a very low rate; (ii) the resting state of the catalyst in the presence of CO does *not* correspond to a growing chain with a last-inserted CO unit (as generally assumed[2,4,8−11]), but to the stable 5-membered chelate structure formed after one more olefin insertion[17] (**C1** of Scheme 1 for propene); and (iii) propene polymerization can be quenched by CO under conditions resulting (mainly) in CO monoinsertion products.

An exciting aspect of the latter result is that, from the NMR characterization of such products, one can obtain direct information on the distribution of the growing polypropylene chains among the various possible structures at the moment in which quenching by CO took place. In particular, we were interested in the possibility of revealing the presence of "dormant" chains due to regiochemical inversion of a last-added propene unit (2,1 enchainment instead of 1,2).[18] We tested this possibility for a metallocene catalyst, that is, *rac*-ethylene-bis(1-indenyl)ZrCl$_2$ (**II**), that—compared with metallocene **I**[6]—is known to be much less regioselective (and, correspondingly, much more dormant) in propene polymerization.[18b,c]

The carbonyl region of the ^{1}H/^{13}C long-range heterocorrelated NMR map of a polypropylene sample prepared with the catalyst system **II**/MAO at 60 °C and $t_c = 30$ s is shown in Figure 2. In this case, *two* main ^{13}CO monoinsertion products *in nearly equimolar amounts* were actually observed: ketone **K1** (Scheme 1) and aldehyde **A1** (Scheme 2; $\delta_{CO} = 205$ ppm). The latter must be traced to the reaction of CO with dormant polypropylene chains, forming the Zr−acyl species **Ac1** (Scheme 2) which—possibly due to steric hindrance—retains the dormant character toward propene insertion. A third carbonyl compound, present in minor amounts, was tentatively identified as ketone **K2** (Scheme 1; $\delta_{CO}= 211$ ppm), differing from **K1** for the enchainment of the last-added propene unit (2,1 instead of 1,2); this would indicate that the regioselectivity of propene insertion into a Zr-acyl bond is lower than that in homopolymerization. If so, a build-up of acyl species **Ac1** (Scheme 2) with increasing t_c might contribute to catalyst deactivation (Figure 1).

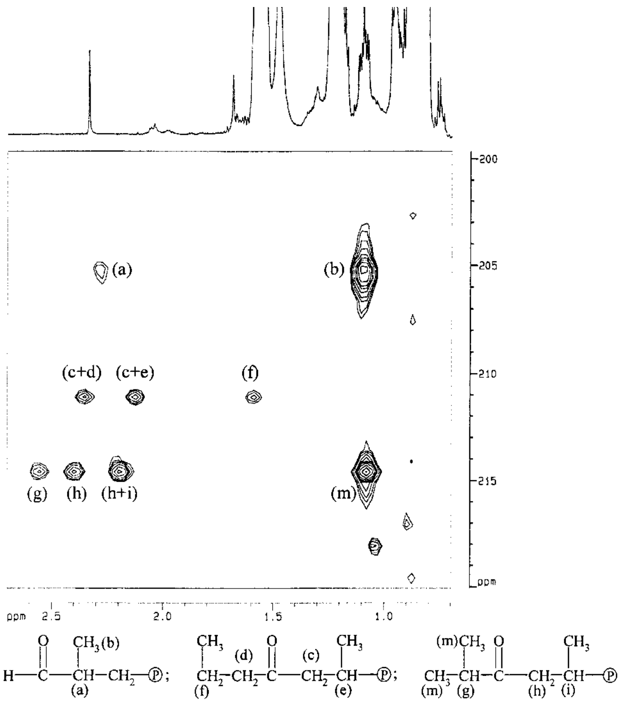
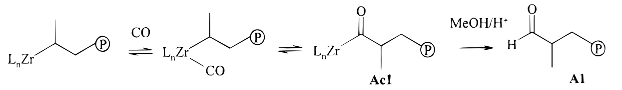


Figure 2. Carbonyl region of the ^{1}H/^{13}C long-range heterocorrelated NMR map of a polypropylene sample prepared with the catalyst system **II**/MAO at 60 °C after quenching with ^{13}CO (contact time, $t_c = 30$ s) and treatment with acidified methanol. The assignment of all observed cross-peaks is also given.

Scheme 2



In conclusion, our results provide the first clear evidence that early transition metals can promote the copolymerization of 1-alkenes with CO, although with much lower efficiency than late transition ones. In view of the above, measuring active-site concentration (C*) of coordination polymerization catalysts by means of polymer radio-tagging with ^{14}CO [2] is likely to result in grossly overestimated C* values (even though these may look plausible in some cases[4,9−11]), and the stopped-flow route[1,4,7] should always be preferred. On the other hand, termination of propene polymerization by means of ^{13}CO can be a convenient method for mapping structurally different active sites. In particular, *provided that all sites react with CO at a similar rate (which is not yet granted*), the method may allow direct estimates of the fractions of propagating and dormant chains (at variance with other approaches—like "hydro-oligomerization"[18]—that require extrapolations of the experimental data in terms of approximated kinetic models). At this moment, we are specifically addressing this point both experimentally and theoretically.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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