

## Unexpected Kinetics in the Polymerization of Ethene by $\text{Cp}_2^*\text{ZrCl}_2/\text{MAO}$

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A sterically hindered metallocene catalyst,  $\text{Cp}_2^*\text{ZrCl}_2$  activated with methylaluminoxane (MAO), is found to polymerize ethene at temperatures up to  $60^\circ$  with a good propagation rate constant but low number of active sites, and with negligible  $\beta$ -hydride elimination or  $\beta$ -hydride transfer to monomer. Moreover, transmetalation to Al is found to be effectively irreversible for alkyl groups larger than Me. With the major mechanisms for chain transfer and termination suppressed, one might expect a living polymerization. The bulk polymerization of ethene was indeed found to be *quasi*-living even when performed at well above room temperature, and furthermore provided rate constants which agreed remarkably well with those from the mass-spectrometric study.

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**Introduction.** – We had recently reported a microkinetic analysis of the polymerization of ethene by a methylaluminoxane (MAO)-activated  $\text{Cp}_2\text{ZrCl}_2$  catalyst system for which the analytical tool was electrospray-ionization mass spectrometry (ESI-MS) [1]. The approach was based on the quantitative, covalent trapping of intermediate metal-bound oligomers with a reactive quencher (*N,N'*-dicyclohexylcarbodiimide, DCC) yielding a distribution of cationically tagged chains readily detectable with ESI-MS. By using a custom-made computer program based on a genetic algorithm, the distributions could be fitted to a kinetic scheme from which *pseudo*-first-order rates for initiation, propagation, chain-transfer to monomer (or Zr), and chain-transfer to Al were extracted [2]. Absolute concentrations for the reactive species trapped quantitatively by DCC were determined by calibration of the MS peak intensities against the cation peak for rhodamine 6G dye, spiked in at a known concentration as the tetrafluoroborate salt immediately before measurement. In a subsequent work, we showed that pre-quenching with a tertiary amine, more specifically  $\text{Et}_3\text{N}$ , allowed an experimentally observable distinction between Zr-bound and Al-bound chains [3]. We now report the application of this ESI-MS-based methodology to the sterically much more hindered  $\text{Cp}_2^*\text{ZrCl}_2/\text{MAO}$  catalyst system, which gives an unexpected explanation for the latter's long-known poor bulk polymerization activity [4]. Importantly, the rate constants determined by MS were confirmed by independent measurements based on bulk polymerization rates, which proves the predictive power of the ESI-MS assay.

**Results and Discussion.** – A series of ethene polymerization experiments were carried out with  $\text{Cp}_2^*\text{ZrCl}_2/\text{MAO}$  at 25, 40, and  $60^\circ$  using the same microkinetic approach described above for  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  (see *Exper. Part*). Kinetic parameters and active chains counting for these runs are shown in *Table 1*. An activation energy of

Table 1. Polymerization Conditions for Runs Quenched with DCC and Analyzed by ESI-MS, along with the Rates and Rate Constants for Propagation, as well as the Rates for Chain Transfer

Run	T [K]	[C <sub>2</sub> H <sub>4</sub> ] [M]	$r_p \times 10^2$ [s <sup>-1</sup> ]	$r_{tm} \times 10^3$ [s <sup>-1</sup> ]	$k_p$ [mol l <sup>-1</sup> s <sup>-1</sup> ]	[Zr] [μM]
1	298	0.13	9.9 ± 0.7	1.3 ± 0.7	0.76 ± 0.05	0.009 ± 0.002
2	313	0.08	7.3 ± 0.5	2.6 ± 0.5	0.91 ± 0.06	0.011 ± 0.003
3	333	0.05	7.8 ± 0.5	5.9 ± 0.8	1.5 ± 0.1	0.013 ± 0.002

4.0 kcal/mol was calculated for propagation. Surprisingly, no ‘even chains’ were found in the experiment at 25°, which were barely detectable also at 60° (see Fig. 1). Moreover, the fit of the DCC-trapped oligomers showed, for Al-bound chains, a monotonically decreasing distribution unlike what we had previously seen with Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO. The distribution for Al-bound chains, deconvoluted by the microkinetic fitting, was confirmed experimentally with the Et<sub>3</sub>N prequenching, giving Al-bound chains that could be fit to a *Schutz–Flory* distribution. The ESI-MS results indicate that chain transfer to monomer is suppressed, and chain transfer to Al is slow and irreversible. This behavior is in striking contrast with the one found for Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO under comparable process conditions, and shows that, unlike what was recently reported [5], the distributions of trapped oligomers do reflect the changes in process conditions and catalyst used, and are not just a consequence of their solubility.

The differences between the two systems can be traced to the quite different steric neighborhoods around Zr-atoms in the two complexes. The Me groups on the two cyclopentadienyl ligands, in fact, tend to stay away from each other, especially in the back of the catalyst where they are closer, producing an increment in the Cp–Zr–Cp bending angle (134° vs. 129° of Cp<sub>2</sub>ZrCl<sub>2</sub>) and, consequently, bringing nearer the Me groups in the front region, where the catalysis takes place [6]. Hence, the space around the ancillary ligands becomes more crowded (coordination gap aperture [7] of 55° vs. 92° of Cp<sub>2</sub>ZrCl<sub>2</sub>), resulting in different catalyst/cocatalyst interactions and in unfavorable steric contacts that raise the energies of both β-H elimination and β-H transfer transition states. In particular, comparing the extracted rate constants to those obtained for Cp<sub>2</sub>ZrCl<sub>2</sub> [8], one finds that: *i*) activation energies for propagation are roughly the same for the two catalysts; *ii*) rate constants for propagation are larger for the Cp\* system at each considered temperature; *iii*) concentration of chains on Zr, which, taking into account the presence of an irreversible chain transfer to Al, is also the total amount of ‘active’ chains, is up to one order of magnitude lower at the time of quenching. This indicates that Cp<sub>2</sub>\*ZrCl<sub>2</sub> is not intrinsically a low-activity catalyst, as is often reported in the literature, but rather a precursor less efficiently activated, at least with MAO. For low Al/Zr ratios, a close-to-living polymerization of ethene should, therefore, be possible at temperatures up to 60°. To confirm these data and, at the same time, to verify the general ability of the methodology to predict polymer properties without actually synthesizing them, a series of polyethylene samples were prepared in bulk polymerization experiments. Thus, Cp<sub>2</sub>\*ZrCl<sub>2</sub> and 12 equiv. of MAO were aged in toluene for 20 min at the desired temperature. The resulting solution was pressurized with ethene at a constant total pressure and then reacted for the specified period of time before quenching and precipitation of the polymer from acidified MeOH. In

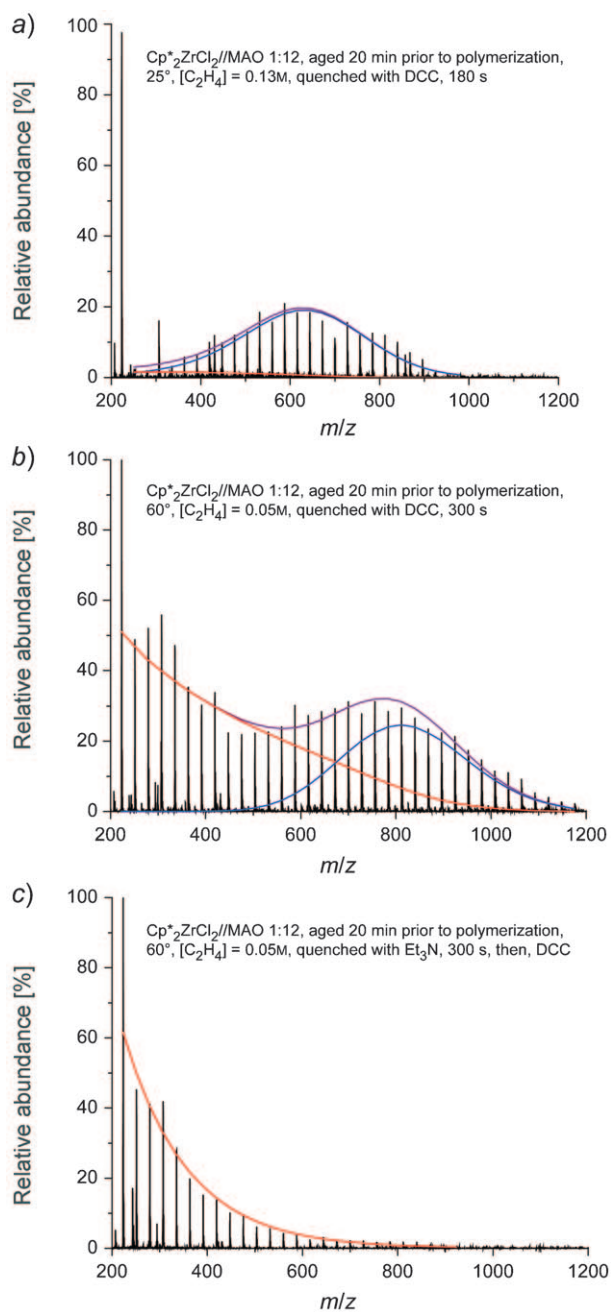


Fig. 1. ESI-MS of the amidinium cations produced by reactive quenching of a MAO-activated polymerization of ethene with  $\text{Cp}^*_2\text{ZrCl}_2$ , showing Zr-bound 'odd' chains (blue), a monotonically-decreasing distribution of Al-bound 'odd' chains (red), the composite spectrum (violet), and no 'even' chains

particular, a series of polyethylene samples were prepared in bulk polymerization experiments at 60°,  $[C_2H_4] = 0.05$  mol/l, with increasing polymerization times ( $t$ ) in the range 5–20 min. The results of the GPC characterization of the produced polymers are reported in Table 2. The 60° data are typical of what Keii *et al.* defined as a ‘quasi-living’ kinetic regime [9][10], *i.e.*, of a polymerization process in which chain transfer is not truly negligible but is slow in the time scale of the experiment. Indeed, the asymptotic plot of  $M_n$  vs.  $t$  (Fig. 2), which extrapolates to a limiting  $M_n$  value of  $1.4 \times 10^4$  Da, is almost linear in the whole range of reaction times. The plot in Fig. 2 can be linearized in terms of the following Keii’s Equation:

$$\frac{1}{P_n} = \frac{M_0}{M_n} = \frac{f_t}{k_p[M]} + \frac{1}{k_p[M]t}$$

where  $P_n$  is the number-average degree of polymerization,  $M_0$  the molar mass of the monomer,  $[M]$  the monomer concentration,  $k_p$  the kinetic constant of chain propagation, and  $f_t$  the frequency of chain transfer.

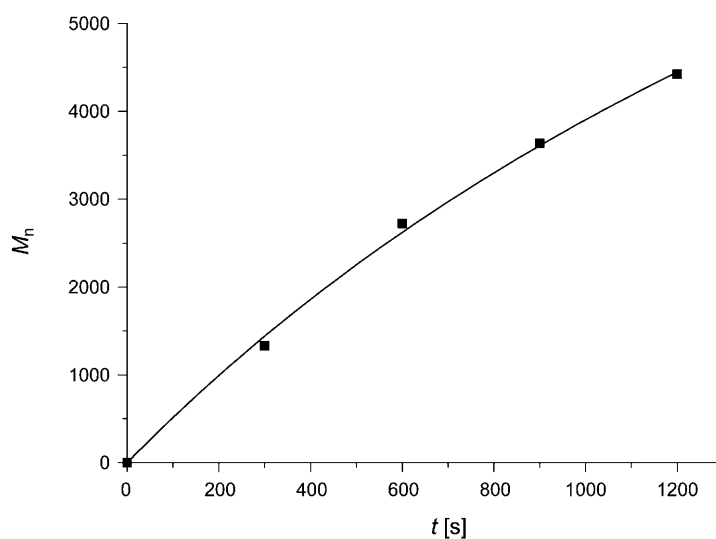


Fig. 2. Number-average molecular mass ( $M_n$ ) vs. polymerization time  $t$  for ethene homopolymers prepared at 60° in the presence of  $Cp_2^*ZrCl_2/MAO$  with a fit according to the Equation

Table 2. GPC Analysis of Polyethylene Produced in Bulk Polymerizations by  $Cp_2^*ZrCl_2/MAO$  at 60°

Run	$t$ [s]	$M_n$ [kDa]	$P_n$	$M_w/M_n$
4	300	1.3	46	1.4
5	600	2.7	96	1.5
6	900	3.6	129	1.5
7	1200	4.4	157	1.7

By applying the Equation to the data of Table 2 (Fig. 3), the best fitting values of  $k_p = 3.4 \text{ mol l}^{-1} \text{ s}^{-1}$  and  $f_t = 1.0 \times 10^{-3} \text{ s}^{-1}$  are obtained. Considering both the conceptual and practical differences between the ESI-MS assay and the bulk polymerizations, it is gratifying to note how the absolute  $k_p$  values derived from the two, independent methods differ by only a factor of two. Also, the small value found for  $f_t$  mirrors the fact that ‘even chains’ are essentially absent in the mass spectra. This provides further evidence that the ESI-MS assay is representative of the actual polymerization process. The  $M_w/M_n$  ratios increase proportionally to  $t$  from 1.4 to 1.7, presumably because of an increasing contribution from Al-bound chains as the polymerization progresses. The rather high polydispersities for  $\text{Cp}_2^*\text{ZrCl}_2/\text{MAO}$  polymerizations in the early literature presumably derive from the very high Al/Zr ratios needed to achieve an adequate level of activation in those studies [4]. Since the rate for transmetalation is directly proportional to the amount of Al in solution, it is likely that, with such a high concentrations of chain-transfer agent, molecular mass distributions result significantly broadened. On the basis of these results, one would expect Al-free catalyst formulations based on the  $\text{Cp}_2^*\text{ZrR}_2$  system to yield not only higher activities but also much lower polydispersities, enabling a truly ‘living’ polymerization of ethene at well above room temperatures. Experiments in this direction are currently underway in our laboratories.

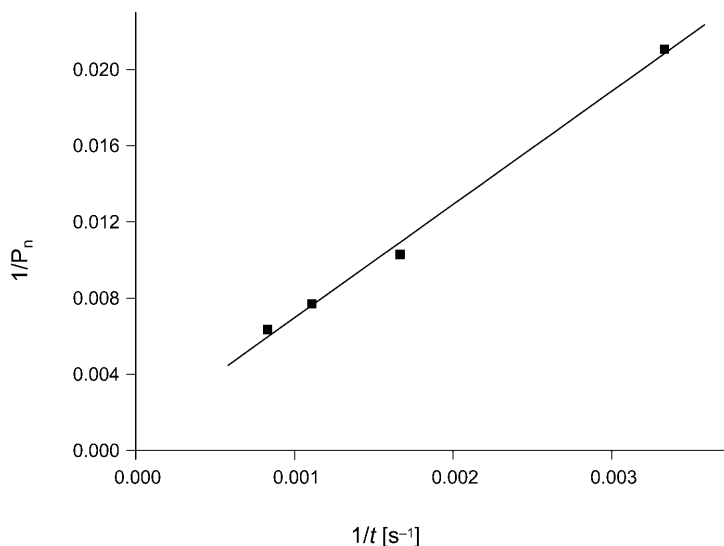


Fig. 3. Plot of the inverse of the number-average degree of polymerization ( $P_n$ ) vs. inverse of the polymerization time  $t$  for ethene homopolymers prepared with  $\text{Cp}_2^*\text{ZrCl}_2/\text{MAO}$  at  $60^\circ$

**Conclusions.** – The present work shows that the system  $\text{Cp}_2^*\text{ZrCl}_2/\text{MAO}$ , which had been long thought a poor catalyst, is not intrinsically poor, but rather simply suffers from a low level of activation. Moreover, while the propagation rate constant is not impacted by the steric bulk,  $\beta$ -H chain transfer and elimination reactions are strongly suppressed, leading to a *quasi*-living behavior. Importantly, the rates extracted from the

mass spectra of the DCC-trapped oligomer distributions resulted to agree remarkably well with those obtained from bulk polymerization experiments, confirming the validity of the ESI-MS methodology.

### Experimental Part

*General.* All manipulations of air- and/or H<sub>2</sub>O-sensitive compounds were performed under Ar with either standard *Schlenk* techniques or in an *MBraun LabMaster 150* glove box, unless otherwise specified. Toluene (*Fluka*, >99.7%) and Et<sub>3</sub>N (*Acros Organics*, 99%) were distilled from Na and CaH<sub>2</sub>, resp., before use. CH<sub>2</sub>Cl<sub>2</sub> (*J. T. Baker*, >99.5%), ethene (*PanGas*, N35 grade, >99.95%), MeOH (*Fluka*, >99.8%), HCl fuming (*Fluka*, 37% (w/w) in H<sub>2</sub>O), 1,2,4-trichlorobenzene (*Fluka*, ≥99%), methylaluminoxane (MAO; *Sigma Aldrich*, 10% (w/w) in toluene), bis(cyclopentadienyl)zirconium dichloride (*Fluka*, 97%), bis(pentamethylcyclopentadienyl)zirconium dichloride (*Acros Organics*, 97%), DCC (*Fluka*, ca. 99%), and rhodamine 6G tetrafluoroborate (*Acros Organics*, laser grade) were used as received.

*Cp<sub>2</sub>\*ZrCl<sub>2</sub>-Catalyzed Polymerizations Quenched with DCC.* In a typical experiment, catalyst (4 mg, 9.25 × 10<sup>-6</sup> mol) and of MAO (1.11 × 10<sup>-4</sup> mol, 67 μl, 12 equiv.) were aged in toluene (6 ml) for 20 min at the desired temp. The soln. was then pressurized with ethene at a constant total pressure of 2 bar, reacted for the specified period of time, and then the reaction was quenched with 35 equiv. (with respect to the catalyst) of DCC (3.24 × 10<sup>-4</sup> mol, 67 mg). Two drops of the resulting mixture were diluted with 30 ml of a 0.1 μM soln. of rhodamine 6G in CH<sub>2</sub>Cl<sub>2</sub> and then subjected to ESI-MS analysis, the rhodamine dye peaks serving as internal standards for the determination of abs. concentrations.

*Bulk Polymerizations with Cp<sub>2</sub>\*ZrCl<sub>2</sub>.* In a typical experiment, catalyst (4 mg, 9.25 × 10<sup>-6</sup> mol) and MAO (1.11 × 10<sup>-4</sup> mol, 67 μl, 12 equiv.) were aged in toluene (6 ml) for 20 min at 60°. The soln. was then pressurized with ethene at a constant total pressure of 2 bar, and reacted for the specified period of time before quenching the reaction with MeOH/HCl 95:5 (v/v; 3 ml). The polymers were coagulated with excess MeOH/HCl, filtered, washed with more MeOH, and vacuum-dried to constant weight.

*Polymerization Reactor.* The reactor used in all the polymerizations was a custom-designed apparatus made of a 25-mm OD Pyrex pressure tube (*Ace Glass Inc.*) fitted with a Bourdon-tube manometer on a stainless steel head fitted with high-pressure valves (*Whitey SS-43 MA-S4*, specified for up to 200 bar) and stirred with a 50-mm long, vertically-oriented, magnetic stir-bar spinning at 1500 rpm and undergoing precessional motion, which has the effect of moving the reaction soln. up the walls of the reactor in a rapidly moving, thin annulus of liquid. A thermocouple immersed in the reaction soln. ensured a constant control of the reaction isothermicity. Such an arrangement served to improve both heat and mass transport, which is a prerequisite for reliable kinetic measurements, and, in particular, to circumvent the technical problems in performing kinetics on highly active polyolefin catalysts outlined by *Busico et al.* [11]. The abs. pressure inside the reactor was measured with a *MKS Baratron* capacitance manometer, while the monomer mass-flow with a *MKS Mass-Flo*<sup>®</sup>-meter. The soln.-phase ethene concentration was computed [12] accounting for the fraction of total pressure attributable to toluene vapor [13].

*Fit of DCC-Tagged Oligomer Distributions.* Best fits of tagged oligomer distributions observed in the mass spectra were performed implementing the polymerization mechanism as a set of coupled differential equations in PowerSim 2.5c [14]. The equations were integrated numerically and fit to the experimental distributions by means of a genetic algorithm in which the elementary rates enter as variable optimization parameters. Each run was repeated several times, so that, for each oligomer peak intensity, the average and experimental variance could be determined. Uncertainty limits on the fitted rates were determined by a *Monte-Carlo* procedure, in which randomly varied combinations of rates were evaluated to determine the range for each constant for which the sum of squared deviations of the average intensities from the predicted distribution remained smaller than the sum of the experimental variances.

*ESI-MS Analysis.* ESI-MS Analyses were performed on a *Finnigan LCQ* classic mass spectrometer using the following conditions: spray voltage, 4.5 kV; sheath-gas flow rate, 20; cap. voltage, 5 V; cap. temp., 180°; tube lens voltage, 30 V; spectrum averaging, 10.

*UV/VIS Analysis.* UV/VIS Analyses of rhodamine 6G solns. and calibration solns. in CH<sub>2</sub>Cl<sub>2</sub> were recorded on a Hitachi U-2010 spectrophotometer at  $\lambda_{\max}$  521 nm, scanning in the range 600–400 nm at 100 nm/min.

*GPC Analysis.* GPC Analysis of polyethylenes were performed on a Polymer Laboratories GPC 220 equipped with a differential viscosimeter, a refractive index cell, and two 300 × 7.5 mm PLgel 10- $\mu$ m MIXED-B columns. The machine was calibrated using 1 mg/ml solns. of monodisperse fractions of atactic polystyrenes in 1,2,4-trichlorobenzene at 150°. Samples were dissolved in the same solvent at a concentration of 2 mg/ml and analyzed at the same temp. Polyethylene samples of known molecular masses and polydispersities were measured as reference.

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