Measuring rate constants for active species in the polymerization of ethylene by MAO-activated metallocene catalysts by electrospray ionization mass spectrometry

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Electrospray ionization mass spectrometry (ESI-MS) of MAO-activated metallocene-catalyzed polymerizations quenched with carbodiimides provides a method for the determination of rate constants in Ziegler–Natta polymerizations.

Originally introduced as homogeneous models for heterogeneous Ziegler–Natta polyolefin catalysts, single-site catalysts, most notably metallocenes, have become interesting objects of study in their own right, both in academic and industrial laboratories.[1] Mechanistic studies have relied upon the homogeneous catalysts with well-defined active sites,[2] with the rational synthesis and modification of these complexes producing catalysts for higher value-added performance materials. The ultimate goal of predictive modeling for catalyst design requires detailed kinetics at the level of elementary reactions, for which the polyolefin catalysts present numerous technical difficulties. We report a method for the kinetic characterization of the active species in the olefin polymerization by homogeneous catalysts. The method, a combination of mass spectrometry, numerical modeling, and active chain counting, is demonstrated for a representative, MAO-activated, model metallocene, Cp_2ZrCl_2, **1**.

A toluene solution of precatalyst **1** (4 mg, 13.7 μmol) was activated by adding 100 μL MAO in toluene (Aldrich, 10% w/w solution in toluene, 165 μmol) in a tubular glass pressure reactor (20 × 2.5 cm)[3] to make a total liquid volume of 6.0 mL. The reactor was designed to circumvent the technical problems in performing kinetics on highly active polyolefin catalysts outlined by Busico.[4] The reaction was kept saturated with ethylene at a constant total pressure of 2.0 bar (MKS Baratron capacitance manometer) and held at 0 °C in a constant temperature bath. The solution was stirred magnetically at 1000–1500 rpm with a 4 cm stirring bar oriented vertically and undergoing precessional motion, which has the effect of moving the reaction solution up the walls of the reactor in a rapidly moving, thin annulus of liquid. The arrangement served to improve both heat and mass transport and is a prerequisite for reliable kinetic measurements. The reaction was quenched after a short time interval, usually 300 seconds, by rapid injection of 35 equivalents, relative to precatalyst **1**, of *N*,*N*′-dicyclohexylcarbodiimide (DCC). 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 interval separating addition of DCC, and dilution and analysis, from 1 minute to 30 minutes produced no discernible change in the mass spectrum, indicating that quenching was complete even at the shortest times. Subsequent addition of excess Brønsted acid did not affect the intensities of the amidinium cations in the ESI-MS. The procedure and conditions for analysis by electrospray ionization mass spectrometry have been previously described in our work on ethylene polymerization by the much less problematic late transition metal catalysts.[5] The odd and even oligomer chain distributions, described in that earlier work, and observed here as series of amidinium cations, were fit to the Cossee–Arlmann mechanism[6] for Ziegler–Natta polymerization, implemented as a set of coupled differential equations in PowerSim 2.5c.[7] 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 six 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. Absolute concentrations for the reactive species trapped quantitatively by DCC were determined by calibration of the mass spectrometric peak intensities against the cation peak for rhodamine 6G dye, spiked in at a known concentration immediately before measurement as the tetrafluoroborate salt.[8]

The carbodiimide quenching of an early stage polymerization reaction yields a stable, easy-to-handle solution of *C*-alkyl-*N*,*N*-dicyclohexylamidines, which electrospray as the readily-detected amidinium cations. The trapping reaction with carbodiimides has in fact been used by Sita as a synthetic route to half-sandwich metal amidate complexes.[9] From the point-of-view of experimental design, our trapping strategy resembles Chien's trapping with CH_3OT or Landis' trapping[10] with MeOD in that the traps are ultimately nothing more than electrophiles which react with alkyl metalloceniums in the same fashion, although the different electrophilic traps facilitate different analytical techniques, radiolabeling or ^2H NMR in the previous cases, and ESI-MS in the present instance. The mass spectrometrically observed distributions over different oligomers contain kinetic information which is extracted by numerical modeling. Fig. 1 shows a representative electrospray mass spectrum with the fit. As in our previous work with Pd-based catalysts, odd and even

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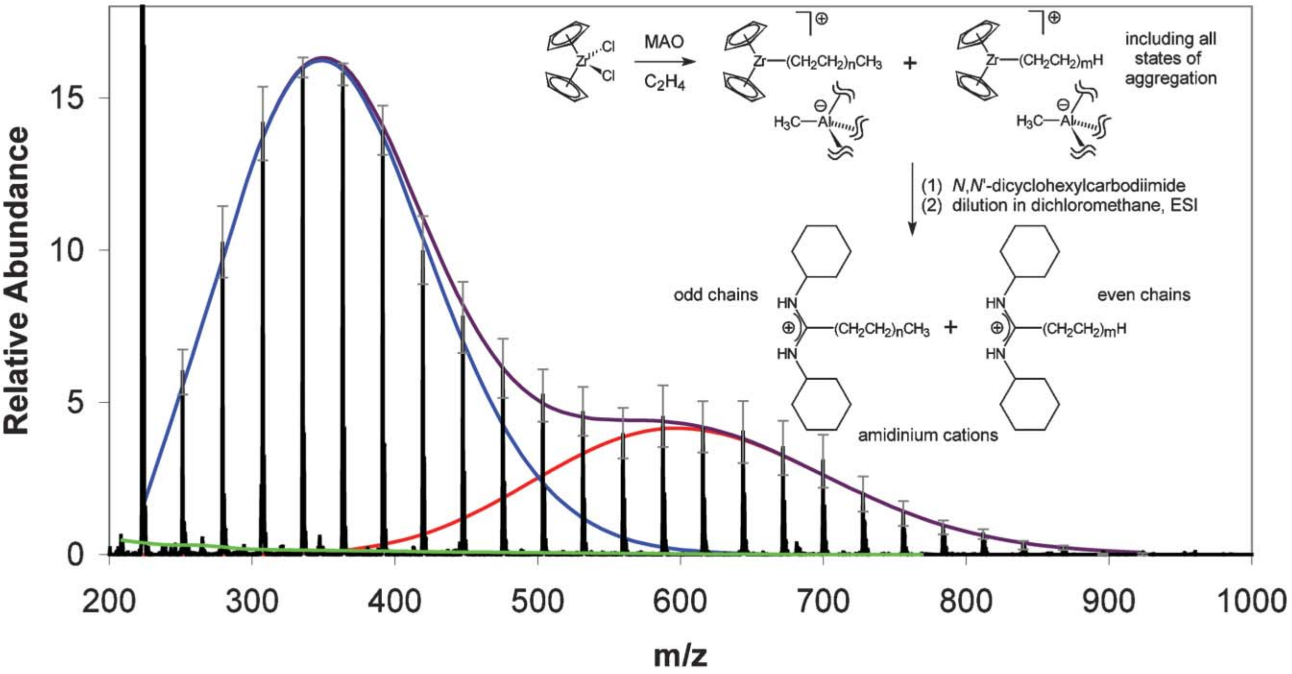

Fig. 1 ESI-MS of the amidinium cations produced by workup of a MAO-activated polymerization of ethylene by Cp_2ZrCl_2, quenched at short time with *N*,*N'*-dicyclohexylcarbodiimide (DCC). The peak intensities are averaged from six independent measurements and show 1σ error bars. The blue and red fits to the two odd distributions sum to make the violet composite odd distribution. The fit to the even distribution is shown in green.

chains are visible. The odd chains are oligomer chains, which at the time of quenching, had not yet undergone chain transfer by associative or dissociative loss of an α-olefin. The even chains have undergone chain transfer at least once.

Calibration of the integrated peak intensities by comparison to the rhodamine 6G standard gives the absolute number of active chains, which when compared to the precatalyst concentration, yields the efficiency of activation, which with the low Al : Zr ratio, is extremely low, as would be expected, (see Table 1). One should note that the number of active chains includes those chains on aluminium which exchange rapidly on the timescale of propagation. The modeling of the distributions produces phenomenological initiation, propagation, and chain transfer rates for two observed active species. To convert the rates to rate constants, accounting for the fraction of the total pressure attributable to toluene vapor,[11] the solution-phase ethylene concentration was computed[12] to be 0.40 M. Assuming propagation and chain transfer to be both first-order in active catalyst and ethylene, the phenomenological rates can be converted into elementary rate constants which include the transfer of chains between Al and Zr as a preequilibrium within the rate constant. These are collected together in Table 1. Comparing the second-order rate constants to those previously reported for related systems on the basis of bulk rates or extrapolation of low-temperature NMR kinetics, as well as expectations based on quantum chemical calculations,[13,14] one sees good agreement in the general order-of-magnitude, which is encouraging considering that the methodologies are so different.

Older work has proposed the intermediacy of more than one active species. Observations of bimodal molecular weight distributions in the finished polymer, however, are difficult to interpret at the molecular level. There are other possible effects, *e.g.* slow, reversible chain transfer to aluminium, reinitiation of "dead" chains, viscosity changes, or temperature effects due to poor thermalization of growing particles, that could complicate final polymer distributions. In the present work, integration of the equations corresponding to the Cossee–Arlmann mechanism can produce oligomer distributions at short-time quenching with only certain prescribed shapes. The allowed distributions for one single active species are not necessarily symmetric, but they are not bimodal. Our consistent observation of deviations from the expected shapes for a single species over a large number of experiments under varying conditions is most clearly explained by the intervention of a second propagating species which is formed concurrently with the first, and which does not interconvert quickly with it. The present experiment, with very early quenching of the polymerization reaction, sees the metal-bound alkyl groups,

Table 1 Summary of quantitative data. The pseudo-first-order initiation, propagation, and chain transfer rates were extracted from the fit and are reactor-dependent. Reactor-independent second-order propagation and chain transfer rate constants are also listed. Chain transfer would be treated as β-hydrogen transfer to monomer, but the intensity of the "even" peaks in the present data (taken at $T = 0\ ^\circ C$) set is too low to extract a reliable rate constant for chain transfer

	Initiation rate (mol s^{-1})	Propagation rate (mol s^{-1})	k_{prop} (L mol^{-1} s^{-1})	Transfer rate (mol s^{-1})	k_{tr} (L mol^{-1} s^{-1})	Concentration (μM)	Activation efficiency
slow species	0.015 ± 0.007	0.021 ± 0.003	0.34 ± 0.05	NA	NA	0.10 ± 0.02	$(4.4 \pm 0.7) \times 10^{-5}$
fast species	0.029 ± 0.008	0.046 ± 0.009	2.36 ± 0.44	NA	NA	0.03 ± 0.01	$(1.5 \pm 0.3) \times 10^{-5}$
Total						0.13 ± 0.02	$(5.9 \pm 1.0) \times 10^{-5}$

trapped as amidinium cations. The quenching occurs early enough that higher olefins produced by associative or dissociative chain transfer do not rise in concentration enough be reinitiated to any significant extent. Moreover, because the carbodiimide traps alkyl groups from both the alkyl metalloceniums and alkyl aluminiums the ratio of the methyl amidinium peak to the sum of the higher alkyl amidiniums becomes a diagnostic for chain transfer to aluminium. The observed ratio of total alkyl amidinium to methyl amidinium of 1.8 ± 0.3, when MAO was in 12 : 1 excess, indicates that chain transfer to aluminium must already be fast and reversible under these conditions on the timescale of the experiment. The fact that the methyl amidinium peak is still larger than expected probably reflects the reportedly slower first insertion of ethylene in the [M]–CH_3 bond. Although it should be, in principle, possible to model that rate from the peak intensity, we did not do so because the relative contribution to the peak from the two active species cannot be separated without further experiments. Artefacts due to viscosity change, inadequate temperature control, and precipitation are also ruled out; from data in Table 1, one can show that an insignificant fraction of the dissolved ethylene is in fact polymerized prior to the quench step.

While the utility of the method will come in further studies, currently underway, in which process parameters such as temperature, ethylene concentration, catalyst loading, and Al : Zr ratio are varied, there are already some insights to be gained from the initial datasets. There have been many indications that more than one kinetically distinguishable active species arise in MAO-activated metallocenes, usually in the form of broad or bimodal polymer molecular weight distributions[15–17] or varying stereoselectivities.[18] Kinetic studies rarely operate at the level of elementary reactions, which would be the requirement for a detailed examination of the question of the number and type of active species, although there have been some cases where quantitative kinetics have been done, work by Fink[19,20] on some early titanium systems being a salient example. Very recently, Bochmann[21] and Landis[22] have reported kinetic studies on homogeneous zirconocene systems in which detailed kinetics were combined with numerical modeling. Bochmann used stopped-flow kinetics with isolation and characterization of polymer at various short time intervals. Landis counted active sites with ^{2}H NMR and followed propagation kinetics by IR measurement of the decline in olefin concentration. In subsequent work, an elementary propagation step of an active species could be directly observed by low temperature NMR, typically around -40 °C, and then extrapolated to higher temperature.[23] The ease with which the present method produces kinetic data, and the ability to distinguish even relatively small differences between related, but nevertheless distinct, active species, should facilitate mechanistic investigations over wide ranges of process parameters.

Spectroscopic studies by Bochmann[24] and kinetic work by Huang and Rempel[25] have established that even the nominally single-site metallocene catalysts actually generate multiple, equilibrating species in solution when activated by MAO. Quantum chemical calculations support the contention.[26] Whether the multiple species described in those cited studies are kinetically significant remains a topic of study, with much debate centered on ion-pair dynamics and their relationship to kinetics. While the present experiment finds two propagating species, one can only as yet speculate as to their chemical identities until more information is gathered. It is highly unlikely, however, that the two propagating species in the present report correspond to two different ion pairs with the same cationic part but different anions because the fast and reversible Zr-to-Al chain transfer seen in the data confirms rapid anion exchange.

We have described an adaptation of an ESI-MS-based kinetic method previously reported for Pd-based catalysts to the much more difficult metallocenes. The method works near ambient temperatures and can tolerate the MAO used for *in situ* activation of usual metallocenes. While the present data demonstrate proof-of-principle, the dependence of the observed species on process parameters should help define their stoichiometry as well as conditions for the preparation of polyolefins with bimodal molecular weight distributions, the control of which is an important target in catalyst design aimed at improving processibility of metallocene-based polyolefins.[27]

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