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On-line monitoring of Brookhart polymerization by electrospray ionization mass spectrometry

Leonardo Silva Santos¹ and Jürgen O. Metzger^{2*}

¹Instituto de Química de Recursos Naturales, Universidad de Talca, P.O. Box 747, Talca, Chile ²Institut für Reine und Angewandte Chemie der Universität, Carl von Ossietzky Universität, P.O. Box 2503, 26111 Oldenburg, Germany

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For the first time, an electrospray ionization (ESI) mass spectrometer coupled on-line with a microreactor permitted the fast screening of polymerization growth of alkenes in the liquid phase mediated by palladium Brookhart catalyst and allowed the direct mass spectrometric identification of alkyl chains still bonded to Pd. The method also allowed us to intercept the catalytically active cationic intermediates of the Brookhart polymerization of alkenes, and to prove on-line their catalytic activity through ion/molecule reactions. The technique is fast and sensitive, requires no sample preparation and manipulation, and is therefore suitable for the fast screening of catalyst/polymer growth by MS identification, with potential applications in areas such as new catalyst development, polymer chemistry, and product quality monitoring in manufacturing. Copyright © 2008 John Wiley & Sons, Ltd.

In the 1990s Brookhart and coworkers developed a class of diimine nickel and palladium catalysts that polymerized ethene to high molecular weight polyethene.^{1–4} An attractive feature of diimine-Pd(II) catalysts is their potential to afford living polymerization of ethene and 1-alkenes. These catalysts were unique because they produced highly branched polyethene rather than linear polyethene, particularly for Pd (100 branches/1000 C),⁵ suggesting a 'chain walking' mechanism. The overall mechanism of polymerization consists of three main processes following initiation: (1) chain propagation, (2) metal migration along the polymer chain ('chain walking'), and (3) chain transfer, as depicted in Scheme 1.^{6–10} Chen and coworkers¹¹ reported an ingenious high-throughput screening method for Brookhart polymerization using electrospray ionization mass spectrometry (ESI-MS), which is selective for ionic species.

The analytical technique described herein for on-line polymerization screening applies a microreactor, where the polymerization reactions are ongoing, coupled to the ion source and direct on-line positive ion ESI-MS analysis. ESI^{12,13} is an interesting 'ion-fishing' technique, since either positive or negative ions formed in solution are gently transferred directly to the gas phase.¹⁴ Due to a variety of outstanding features and advantages ESI-MS (and its tandem version ESI-MS/MS) is rapidly becoming the most suitable

tool for the fast screening of intermediates directly from solution,^{15–21} giving exceptional gains in chemical information for solution mechanistic studies in chemistry and biochemistry,²² and in high-throughput screening of homogeneous catalysis reactions.²³ We reported recently on studies of homogeneously catalyzed Ziegler-Natta polymerization of ethene by ESI-MS.²⁴

In this article, we report our study of Brookhart polymerization of ethane and of 1-butene with the homogeneous catalyst diimine Pd(Me)Cl (1), with methylaluminoxane (MAO) or silver trifluoromethanesulfonate (AgOTf) as co-catalysts, using a microreactor coupled directly to the ESI source of a quadrupole time-of-flight (Q-TOF) mass spectrometer, focusing on the direct detection and mass spectrometric characterization of the transient cationic and catalytically active species involved, and on the direct demonstration of their catalytic activity.

EXPERIMENTAL

All manipulations of air- and/or water-sensitive compounds were performed using standard high-vacuum Schlenk techniques. High-pure argon was purchased from White-Martins (Bremen, Germany). Toluene and diethyl ether were distilled under argon from sodium/benzophenone ketyl. CH₂Cl₂ was distilled under argon from CaH₂. Ethene (99.99%), 1-butene (>99%), PdCl₂(cod), 2,3-butadienone, 2,6-diisopropylaniline, formic acid, MeOH (HPLC grade), ethanol (HPLC grade), AgOTf, and MAO (methylaluminoxane solution, 10 wt. % in toluene) were purchased from Aldrich (Steinheim, Germany) and used without further purification.

^{*}*Correspondence to*: J. O. Metzger, Institut für Reine und Angewandte Chemie der Universität, Carl von Ossietzky Universität, Oldenburg, Germany.

E-mail: juergen.metzger@uni-oldenburg.de

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Scheme 1. Simplified mechanism for Brookhart polymerization of ethene using diimine-Pd(II) complex 1.

Preparation of [PdClMe(cod)]^{25,26}

[PdCl₂(cod)] (1.00 g, 3.50 mmol) was charged into a 250 mL flask, and CH₂Cl₂ (68 mL) was introduced. The mixture was stirred, and Me₄Sn (0.626 mL, 1.29 equiv) was added by syringe. The mixture was refluxed until the yellow color was discharged (21 h, some decomposition to palladium metal was observed). The solution was cooled and filtered through diatomaceous earth; then the solvent was evaporated to leave a white solid. The solid was washed with diethyl ether (3 × 4.0 mL) and dried in vacuum (0.88 g, 95%).

Preparation of ligand ArN=C(Me)-C(Me)=Nar $(Ar = 2,6-C_6H_3(^iprop)_2)^{27,28}$

To a 50 mL flask containing 2,6-diisopropylaniline (5.00 g, 28.2 mmol, 5.32 mL) was added 5% of formic acid (0.053 mL) as catalyst at 0°C. A solution of 2,3-butanedione (1.21 g, 14.1 mmol, 1.23 mL) in MeOH (2.5 mL) was then added dropwise to the aniline mixture. In the course of the reaction at room temperature diazadiine precipitated in the solution. The reaction took 20 h. After this period, the crude product was washed with cold MeOH and the precipitate was dissolved in pentane. The solution was dried with Na₂SO₄ and after filtration the pentane was evaporated under reduced pressure. Recrystallization with MeOH/EtOH afforded a yellow solid in 76% yield (8.65 g). HRMS (ESI(+)-MS) for [C₂₈H₄₀N₂+H]⁺ m/z calcd. 405.3270, found 405.3272. The ¹H and ¹³C NMR results are in accordance with literature values.

Preparation of 1³

Et₂O (11.4 mL) was added to a Schlenk flask containing PdClMe(cod) (0.543 g, 2.05 mmol) and a slight excess of ArN=C(Me)-C(Me)=NAr diimine (0.836 g, 2.07 mmol). An orange precipitate began to form immediately upon mixing. The reaction mixture was stirred overnight and Et₂O and free 1,5-cyclooctadiene (cod) were then removed via filtration. The product was washed with an additional 5.0 mL of Et₂O and then dried overnight in vacuum. A pale orange powder was isolated in 95% yield (0.795 g). ¹H NMR (CD₂Cl₂, 400 MHz) δ : 0.36 (s, 3H), 1.17 (d, 6H, J 6.89), 1.20 (d, 6H, J 6.81), 1.36 (d, 6H, J 6.79), 1.40 (d, 6H, J 6.79), 2.00 (s, 3H), 2.02 (s, 3H),

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3.00 (septet, 2H, J 6.89), 3.05 (septet, 2H, J 6.81), 7.42-7.24 (m, 6H). 13 C NMR (CD₂Cl₂, 100 MHz) δ : 6.0, 20.3, 21.5, 23.4, 23.5, 23.7, 24.0, 28.7, 29.3, 123.4, 124.4, 127.3, 128.1, 138.3, 138.8, 142.2, 142.2, 170.2, 175.0. HRMS (ESI(+)-MS) for [C₂₉H₄₃N₂PdCl+H]⁺ *m*/*z* calcd. 561.2236, found 561.2230.

Dimer 7 (Fig. 1(a))

To a Schlenk flask was added **1** (0.039 g, 0.0696 mmol) followed by CH₂Cl₂ (10.0 mL). The solution was cooled to -90° C and MAO (in toluene, 10% w/v solution) was added at low temperature. A dark red solution was obtained, warmed to -10° C, and analyzed as soon as possible by ESI(+)-MS (approximately 1.0 min after mixing the reactants) that showed the dimeric species **7** of *m*/*z* 1051.5. After a few minutes the reaction mixture turned black, possibly due to formation of the dimer and decomposition. Trying to use this solution in polymerization reactions with C₂H₄ gave no products. Ion/molecule reactions in the gas phase using **7** gave no C₂H₄ insertions.

Dimer 8 (Fig. 1(b))

The same procedure described above was used, applying the microreactor to mix **1** and MAO in CH₂Cl₂ at -10° C. A new dimeric species **8** of *m*/*z* 1087.5 was observed after reaction times of around 0.9 to a few seconds. It was noted that the quantity of MAO did not have a great influence on the dimer formation. Similar results were obtained using AgOTf as co-catalyst (4.4 equiv.).

Detection of the active species 2 (Scheme 1)

To a Schlenk flask was added **1** (0.007 g, 0.0125 mmol) followed by CH₂Cl₂ (90.0 mL) and MeCN (10.0 mL). The solution was cooled to -10° C and AgOSO₂CF₃ (0.013 g, 0.0506 mmol) was added at low temperature. A dark red solution was obtained and analyzed by ESI(+)-MS (10 s after mixing the reactants) that showed as the most abundant ion the adduct [**2**:MeCN]⁺ of *m*/*z* 566. Ion **2** of *m*/*z* 525 was also observed, and increasing the cone voltage increased the signal intensity of ion **2** and decreased the intensity of the adduct [**2**:MeCN]⁺.





Figure 1. ESI(+)-MS of (a) a solution of pre-catalyst 1 and MAO showing ion 7; (b) a reacting mixture of 1 and MAO formed in the microreactor directly coupled to the ESI source (see insert); and (c) a solution of 1 and AgOTf in $CH_2Cl_2/MeCN$. This figure is available in colour online at www.interscience.wiley.com/journal/rcm.

Polymerization reactions

To a Schlenk flask containing **1** (20.8 mg, 0.037 mmol) was added CH_2Cl_2 (5.3 mL). The solution was cooled to $-90^{\circ}C$, evacuated, and placed under ethylene atmosphere (1 atm). The cold solution was warmed to $-10^{\circ}C$ and mixed with a cold solution of MAO (0°C, 0.0445 mmol in 4.0 mL of CH_2Cl_2) in a microreactor coupled to the ESI source as depicted in Fig. 1. Growth of the polymer was observed immediately and differences in the growth were observed with time (see Fig. 2).

ESI-MS microreactor monitoring

A mixture of 1/ethene (saturated solution of C_2H_4 in toluene) was mixed with MAO (10% solution in toluene) in anhydrous and degassed toluene using a dual-syringe pump operating at different flow rates in an effective micromixer (ALLTECH, PEEK mixing tee, Rottenburg-Hailfingen, Germany) that was coupled directly to the ion source of the mass spectrometer (Fig. 1), and the solution was fed continuously into the mass spectrometer. The flow rate could be varied from 2.5 to 100 mL/min. By connecting the microreactor directly to the spray capillary, reaction times from 0.9 to 28 s could be covered.^{15–18} ESI-MS and ESI-MS/ MS analyses were conducted in a high-resolution hybrid quadrupole (Q) and orthogonal time-of-flight (TOF) mass spectrometer (Q-TOF Premier, Micromass, Manchester, UK) with a constant nebulizer temperature of 100°C. The experiments were carried out in the positive ion mode, and the cone and extractor potentials were set to 10 and 4.5 V, respectively, with a scan range of m/z 200–5000. MS/MS experiments were carried out by mass selection of a specific ion in Q1 which was then submitted to collision-induced dissociation (CID) with argon in the collision chamber. The product ion MS analysis was accomplished with the high-resolution orthogonal TOF analyzer. A similar experiment was performed with 1-butene in place of ethene.



Figure 2. ESI mass spectra of the reacting solution of ethene/1/MAO after reaction times of 0.9, 1.8 and 3.6 s showing higher intensity odd-chain **3** and lower intensity even-chain **6** product series using a microreactor (see insert Fig. 1). This figure is available in colour online at www.interscience.wiley.com/journal/rcm.



Ion/molecule reactions

To probe directly that ions 2, 3, 4 and 6 are catalytically active species we studied the gas-phase reaction of the monoisotopic ions (selected in the quadrupole, Q1) with ethene in the collision cell of the Q-TOF and carried out mass analysis of the product ions using the TOF analyzer. The argon in the collision cell was changed for highly pure C₂H₄ (99.99%). The ethene pressure used was between 3×10^{-3} and 2×10^{-2} mbar.²⁹ Under low-energy collisions (1.1–2.0 eV) in the collision cell, the mass-selected and relatively cold cations (which were quenched by low-energy collisions with the neutral species) reacted with C2H4 yielding the cationic addition product ions.³⁰ The T-wave collision cell in the Q-TOF Premier enabled us to observe several product ions.³¹ The product-ion mass spectrum was acquired under multiple collision conditions that caused typical beam attenuations of 50-70% in the collision cell so as to increase the reaction yields and to promote the collisional quenching of both the reactant and the product ions. Reactant ions should therefore display no or negligible amounts of excess internal energy.³² A similar experiment was performed using 1-butene rather than ethene.

RESULTS AND DISCUSSION

Proof-of-principle reactions

As a first test we performed the reaction of pre-catalyst 1 with MAO trying to intercept the proposed active species 2 in CH₂Cl₂ as solvent. At low temperature, a dark red solution was obtained and was analyzed approximately 1 min after mixing the reagents by ESI(+)-MS. In that solution, a dimeric ion $[L2Pd-(\mu CH2)-Pd(Me)L2]^+$ (7) of m/z 1051.5 was observed (Fig. 1(a)). Cation 7 was described and characterized by ESI-MS and X-ray structure analysis recently by Brownie et al. who claimed that it was active for ethene polymerization, affording the corresponding polymers.³³ We obtained the same ESI mass spectrum as published for ion 7; however, trying to use that stock solution for polymerization of ethene gave no polymeric products. Furthermore, no ethene insertion through ion/molecule reaction was observed using this dimer as an isolated species in the gas phase.

We also used a microreactor coupled directly to the ESI source^{15–18} to study the reaction of the pre-catalyst **1** and MAO (Fig. 1(b)). Interestingly, a new dimeric product $[L_2Pd-(CH_3)-Pd(CH_3)(\mu Cl)L_2]^+$ (**8**) of *m*/*z* 1087.5 was observed. Similar results were achieved when AgOTf was used as co-catalyst. Finally, using AgOTf as co-catalyst and MeCN as co-solvent (10:1, CH₂Cl₂/MeCN), we could intercept ion **2** from the reaction solution. The adduct ion³³ [**2**·MeCN]⁺ of *m*/*z* 566 was the most abundant ion in the spectrum (Fig. 1(c)). Ion **2** was also observed, and increasing the cone voltage increased the signal intensity of ion **2** and decreased the intensity of ion [**2**·MeCN]⁺ thus giving evidence that ion **2** was formed by in-source decay of [**2**·MeCN]⁺.

The next step was the polymerization of ethene by mixing a solution of MAO and a solution of **1** saturated with C_2H_4 , both in CH₂Cl₂, using a microreactor coupled to the ESI source (Fig. 1). The outstanding feature of this device is that



Figure 3. ESI mass spectra of the reacting solution of 1-butene/1/MAO after (a) 5.2 s, (b) 2.7 s, (c) 1.8 s, and (d) 1.3 s reaction time showing odd-chain preferentially.

reaction times of around 0.9s to a few minutes can be covered. Differences in the growth of polymer with time were observed. The spectra in Fig. 2 show two series of ions: the odd-chain species **3** as the main polymerization pathway and the even-chain species **6** derived from ethene insertion in Pd-H species **4**. Remarkably, even ions could already be observed at the shortest reaction time of 0.9s, and the ratios of odd ions **3** to even ions **6** of 3.2, 2.6 and 2.7 were almost independent of the reaction time at 0.9, 1.8 and 3.6s. Performing the same experiment but using AgOTf instead of MAO, almost exclusively the odd-chain species and some even-chain species of very low intensity were detected. A similar experiment with MAO using 1-butene as the



Figure 4. ESI(+)-MS/MS of the ions (a) 2 (m/z 525), (b) [2.MeCN]⁺ (m/z 566), (c) 3 (n = 1, m/z 553), and (d) 3 (n = 3, m/z 609).

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monomer showed almost exclusively the odd-chain species and some even-chain species of very low intensity (Fig. 3).

The ions of interest were characterized by an isotopic analysis of the signal patterns and by high-accuracy measurements with external mass calibration. The experimental signal pattern is in agreement with the theoretically expected pattern and for all ions of interest a mass accuracy of <5 ppm was found. Further characterization of several ions found in these experiments was achieved through ESI-MS/MS experiments. Ion **2** showed the elimination of CH₄ (Fig. 3(a)) whereas ion **2**.CH₃CN eliminated mainly CH₃CN and some (CH₃CN+CH₄) (Fig. 4(b)). Pd-alkyl cations **3** (n = 1, 3) showed exclusively β -elimination of the respective alkene to give the Pd-hydride cation **4** at m/z 511 (Figs. 4(c) and 4(d)). Interestingly, we have not been able to observe any Pd-alkyl ethene π -complex. It was shown by NMR spectroscopy that Pd-alkyl ethene π -complexes form the resting state of the active Pd species in the catalytic cycle,^{6–10} being about 30 kcal/mol more stable than the respective Pd-alkyl cations (Scheme 1).³⁴ Possibly, the π -complexes are decomposed in the ESI process.









Figure 6. Ion/molecule reaction of precursor ions of m/z 581 (a) and 511 (b) with 1-butene.

Ion/molecule reactions

To probe directly that ion **2** is indeed the catalytically active species we performed gas-phase reaction of the isotopologue ion **2** of m/z 525 (selected in the quadrupole) in the collision cell with ethene and carried out mass analysis of the product ions using the TOF analyzer. Under low-energy collisions (1.1–2.0 eV) in the collision cell, the mass-selected and relatively cold cation **2** (quenched by low-energy collisions with the neutral) reacted with C₂H₄ yielding the cationic addition product ions **3** (n = 1–3; m/z 553, 581, and 609) in good yields (Fig. 4(a)). Additionally, ion **4** of m/z 511 was formed by CID of ions **3** (see above).

All the ions 3 as well as 4 and 6 should be catalytically active. This was proven directly by investigating the reaction of 3 (n = 2) with ethene in the gas phase showing the stepwise insertion of three molecules of ethene (Fig. 4(b)). Note that some β -hydride elimination is observed to give Pd-H 4 of m/z 511 in the ion/molecule reactions. This again gives clear evidence that ion 3 (n = 2) is a Pd-pentyl species – possibly $agostic^{6-10}$ – and not Pd-propyl **3a** (n = 1) with a π coordinated ethene. Interestingly, the similar experiment performed with 1-butene showed the insertion of only one molecule of 1-butene (Fig. 5(a)), confirming that insertion of higher 1-alkenes is slower than that of ethene and that a second insertion will only be possible after chain walking.^{1,10} The Pd-H species 4 intercepted remarkably from solution is active toward reaction with ethene. The stepwise insertion of two molecules of ethene to 4 was observed (Fig. 5(c)); however, the insertion of only one molecule of 1-butene (Fig. 6(b)) was observed, suggesting the production of even-chain species in the polymerization process from this starting species. These experiments give evidence that chain

insertion of ethene in Pd-H 4,¹ and not by direct β -hydride transfer to the monomer from the alkyl-olefin resting state. Interestingly, dimer ion 8 reacts with ethene to give ion 3 (n = 1), which can insert two further molecules of ethene (Fig. 4(e)). Possibly, dimer 8 is in solution a resting state of the catalytically active cation 2.

transfer occurs from ions 3 via β -elimination followed by

CONCLUSIONS

Our study allows new insights in the reaction mechanism of Brookhart polymerization. The experiment reported here has the advantages of high sensitivity (microgram quantities), very short assay times, direct analysis of all intermediates in the reaction mixture (active species that are being formed and consumed with time, and no quenching), new methodology to intercept highly sensitive intermediates with short life-times,³⁴ and the proving of further activity of several species trapped from solution through ion/molecule reactions with neutrals in the collision cell. This report is another example of the successful application of atmospheric pressure ionization (API) in revealing, elucidating, and helping to consolidate previously proposed reaction mechanisms.^{35–37}

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