

Droplet Spray Ionization from a Glass Microscope Slide: Real-Time Monitoring of Ethylene Polymerization

Jie Jiang,^{*,†} Hong Zhang,[‡] Ming Li,[§] Maria T. Dulay,^{||} Andrew J. Ingram,^{||} Na Li,[†] Hong You,[‡] and Richard N. Zare^{*,||}

[†]School of Marine Science and Technology, Harbin Institute of Technology at Weihai, Weihai, Shandong 264209, P. R. China

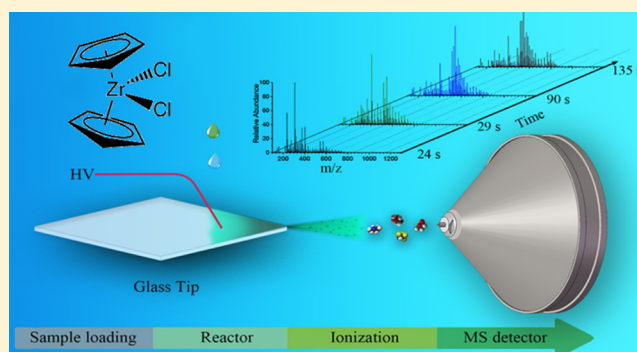
[‡]State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin, Heilongjiang 150040, P. R. China

[§]Division of Chemical Metrology and Analytical Science, National Institute of Metrology, Beijing, 100013, P. R. China

^{||}Department of Chemistry, Stanford University, Stanford, California 94305, United States

S Supporting Information

ABSTRACT: Ambient ionization mass spectrometry is achieved in a simple manner by loading a sample solution onto a corner of a microscope cover glass positioned in front of the inlet to a mass spectrometer and applying a high voltage to the sample. The resulting stream of charged droplets is stable, has no contamination from the substrate platform, and can be used repeatedly. The utility of droplet spray for in situ analysis and real-time monitoring of chemical reactions was demonstrated by the bis(cyclopentadienyl)zirconium dichloride (zirconocene dichloride)/methylaluminoxane, $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, homogeneously catalyzed polymerization of ethylene in various solutions. Reaction times ranged from seconds to minutes, and catalytically active species and polymeric products of ethylene were acquired and identified by tandem mass spectrometry.



Mass spectrometric ionization methods that operate at room temperature and atmospheric pressure and require minimal or no sample preparation have received much attention.^{1,2} Among these ambient ionization techniques, the introduction of paper spray seems highly appealing because of its simplicity and ease of use.^{3–7} Ions of analyte are generated by applying a high voltage to a paper triangle wetted with a small volume of solution. However, the use of paper has several disadvantages. It can lead to unwanted contamination of the sample loaded on the paper and it cannot be used repeatedly. We present an easy way to overcome these two limitations. It is based on replacing the paper platform for spray ionization with a glass microscope slide and is functionally similar to a recently reported method for extraction and detection of soluble paint additives on coated steel panels.⁸ The power of this approach is illustrated by monitoring in real time the homogeneous polymerization of ethylene by a single-site metallocene catalyst (a Ziegler–Natta catalyst).

We first demonstrated the versatility of the droplet spray method using pure methanol solvent. There are important factors for determining the ease of use of an ionization source. The effect of sample volumes and the deformation of substrates were characterized. Different volumes of methanol were used in these versatility tests. When a high voltage was applied, the spray mist was easily recorded by an optical camera under

strong illumination (see Figure 1a inset). A microscope cover glass, similar to a laboratory glass container, can hold from 5 μL to as much as 60 μL of liquid with a steady total ion current (see Figure S2), and no deformation of the glass slide was observed before or after an experiment. It is not difficult to optimize the signal for steady droplet spray. As long as the corner of the slide is positioned within an area of approximately $5 \times 15 \times 3$ mm (x, y, z) in front of the instrument's inlet, adjusting the tip to obtain a good signal is straightforward.

To demonstrate the utility of droplet spray for in situ analysis and real-time monitoring, the reaction of bis(cyclopentadienyl)zirconium dichloride (zirconocene dichloride)/methylaluminoxane, $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, homogeneously catalyzed polymerization of ethylene was monitored. This highly efficient homogeneously catalyzed system,^{9,10} $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, which features narrow polydispersity and easy operation, enables the single-site polymerization of ethylene. Although this reaction system is quite complicated and still under debate, this catalytic mixture has been the subject of much inquiry,^{10–13} including a few in-depth mass spectrometry studies.^{14–18} The generally accepted mechanism is shown in Scheme 1. The ligand-

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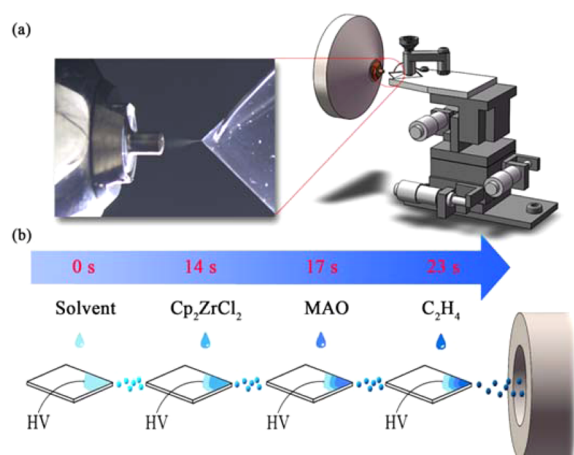
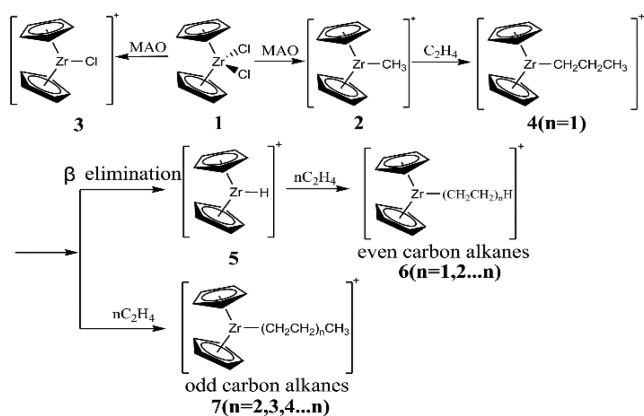


Figure 1. Experimental setup. (a) Illustration of the droplet spray. The angle between the MS inlet and the tip-end was 10° ; the tip-end was 10 mm from the MS inlet for acetonitrile and 5 mm from the MS inlet for THF and PhF. (b) Monitoring of the Cp_2ZrCl_2 /MAO homogeneously catalyzed polymerization of ethylene in PhF; 10 μL of PhF solvent, 10 μL of Cp_2ZrCl_2 (3.4×10^{-4} mol/L), 10 μL of MAO (4.12×10^{-4} mol/L), and 20 μL of saturated ethylene solution in PhF were pipetted sequentially onto the corner of the microscope slide adjacent to the MS inlet at 0, 14, 17, and 23 s. Data were recorded continuously during these additions of reagents.

Scheme 1. Proposed Mechanism for Ethylene Polymerization by Cp_2ZrCl_2 /MAO



exchange reaction of **1** with MAO, in excess, rapidly leads to the catalytically active species **2**. The first reactive intermediate **4** of the polymerization process is formed by the coordination and insertion of ethylene into the Zr-Me bond of **2**. The polymerization of ethylene then proceeds by the conventional Cossee-Arlmann mechanism where repeated insertions of ethylene generate odd carbon-number compounds, **6**. Beta-hydride elimination and further insertion yields the even carbon-number compounds, **7**. Chain transfer of polymer units to Al also occurs during this reaction which regenerates **2** for the further production of odd carbon-number compounds, **6**.^{15,19}

We performed the reaction of Cp_2ZrCl_2 with MAO to determine whether our new ionization source could produce stable mass spectra and capture the proposed catalytically active species in a toluene solution. A mixture of Cp_2ZrCl_2 /MAO (1:1 v/v) in toluene was pipetted onto the corner adjacent to the MS inlet to form the spray droplets. Because of poor ion intensity by direct analysis of the catalytically active species in

toluene, the mixture was diluted 4-fold with acetonitrile to enable the acquisition of stable mass spectra¹⁶ containing four cationic species: ion **2** (m/z 235), ion **3** (m/z 255), 2·MeCN (m/z 276), and 3·MeCN (m/z 296) (see Figure 2a). These or

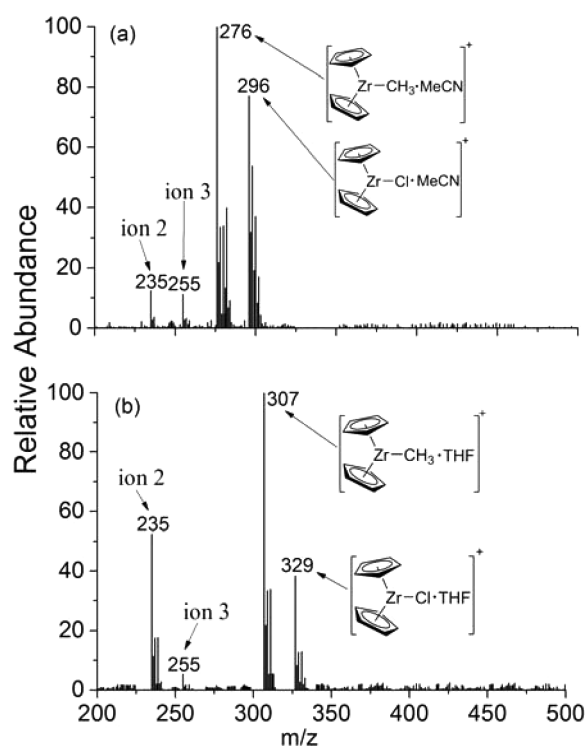


Figure 2. Full-scan positive-mode droplet spray mass spectra of catalytically active species in different solvents: (a) acetonitrile/toluene and (b) THF.

similar species have been observed by ESI-MS previously^{14–18} and were easily identified by CID (see Figure S3) and by their isotopic patterns. Cp_2ZrCl_2 /MAO mixtures are known to be air-sensitive, and Cp_2ZrOH , m/z 237, overlaps with **2** (m/z 235) and distorts its isotope profile. The signal for the $[M + 2]$ isotopomer of **2** was consistently enhanced by this artifact, which has been observed before.¹⁸ It is not clear whether this compound was formed by hydrolysis in solution or in the gas phase, and it is somewhat surprising that these sensitive ions can be observed at all by this open air technique. The clear and steady mass spectra demonstrated that a signal from the sample could be consistently acquired via the droplet spray.

The reaction between Cp_2ZrCl_2 and MAO in toluene is extremely rapid. The time scale of ESI monitoring is often limited by solution transfer and the need to dilute solutions prior to analysis, which results in a delay between the reaction and the detection of reactive intermediates (i.e., a dead time). In contrast, separately pipetting Cp_2ZrCl_2 and MAO onto the corner of a glass slide is a feasible method for in situ analysis and real-time monitoring of the reaction process at approximately subsecond dead times.

To probe the characteristics of droplet spray for in situ analysis and real-time monitoring of chemical reactions, a Cp_2ZrCl_2 /MAO catalyzed ethylene polymerization in acetonitrile on a glass slide was attempted. When acetonitrile was used as a cosolvent, 10 μL of acetonitrile/toluene (4:1 v/v), 10 μL of Cp_2ZrCl_2 , 10 μL of MAO, and 20 μL of saturated ethylene solution in acetonitrile/toluene were sequentially loaded onto a

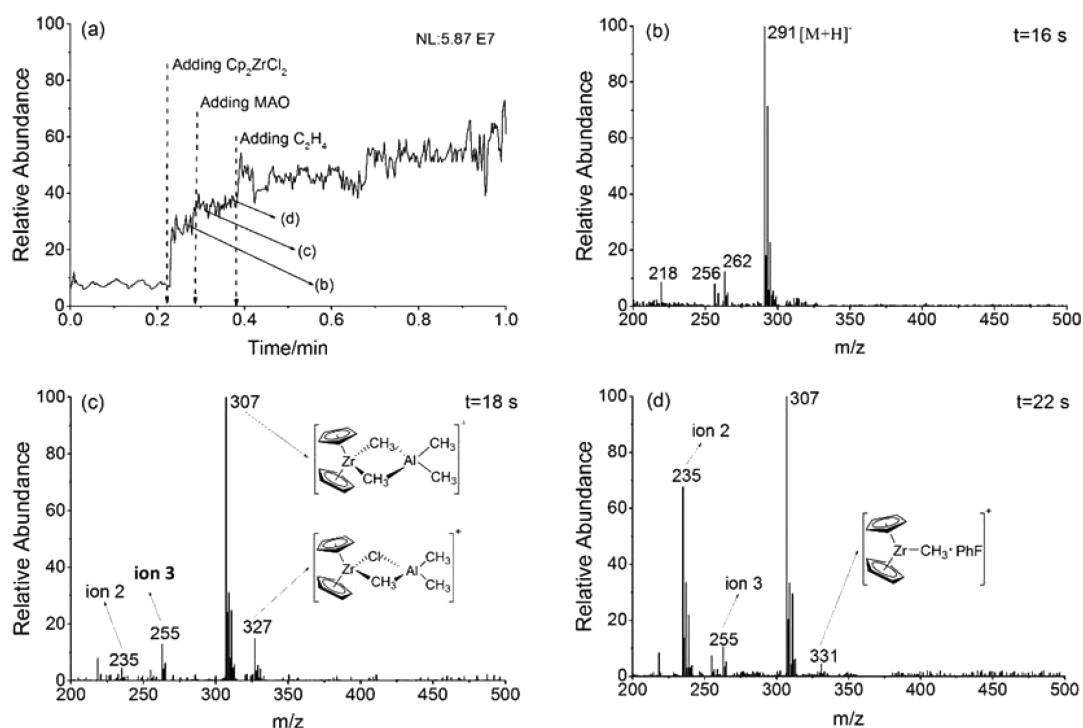


Figure 3. In situ analysis and real-time monitoring of the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ homogeneously catalyzed polymerization of ethylene in PhF. PhF (0 s), Cp_2ZrCl_2 (14 s), MAO (17 s), and C_2H_4 -saturated PhF (23 s) were pipetted onto the corner of the microscope cover glass adjacent to the MS inlet. (a) The total ion current (TIC) of the ethylene polymerization reaction from 0 s to 1 min. Mass spectra for catalyst formation at (b) 16 s, (c) 18 s, and (d) 22 s.

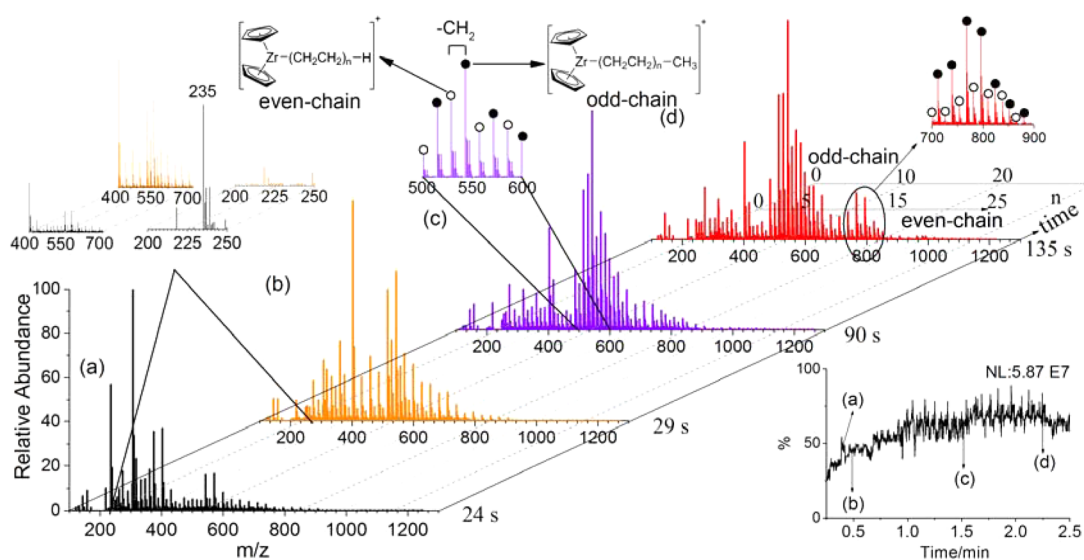


Figure 4. In situ analysis and real-time monitoring of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyzed polymerization of ethylene. Reagent additions were the same as in Figure 3. The mass spectra were obtained after adding C_2H_4 -saturated PhF at 23 s. The TIC (inset) of this reaction was recorded over the range of 0.25 to 2.5 min. The mass spectra are displayed at reaction times of (a) 24 s, (b) 29 s, (c) 90 s, and (d) 135 s.

glass slide at 0, 14, 17, and 23 s, respectively. Upon application of a high voltage, spray droplets and steady signals were obtained from the sample. The catalytically active species, **2**, was easily identified (Figure 2a). As expected, no polymeric products of ethylene in acetonitrile/toluene were observed. The free coordination site of catalytically active intermediates is likely blocked by acetonitrile.^{16,20,21}

Because THF and PhF exhibited minimal interference with the acquisition of stable signals, these low-polarity solvents were also investigated as replacements for toluene. The reaction

progress of $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ homogeneously catalyzed polymerization of ethylene was monitored in THF and PhF, as well as acetonitrile spray solvent. However, the signals typically disappeared more rapidly than they did in acetonitrile, presumably because of solvent volatility. As shown in Figure 2b, in the case of THF as the solvent, the mass spectrum showed minimal interference and was dominated by the ions **2** and **3** and adduct ions **2**-THF and **3**-THF, which were further evaluated by CID (see Figure S4). The increase of the signal intensity of ion **2** over time provides excellent evidence that ion

2 persists in THF. In contrast, the peak intensity of the polymeric products of ethylene was low and the polymerization rate dramatically decreased (not shown), presumably because of the competition between the THF ligand and ethylene for the Zr coordination sites.^{16,21} Although the use of THF as solvent for this reaction effectively demonstrates the viability of real-time monitoring using droplet spray, coordination of the THF ligand to the ion 2 prevents detection of polymerization intermediates and supports that the coordinating nature of acetonitrile and THF preclude observation of these species.

The use of noncoordinating PhF as the solvent for the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ homogeneously catalyzed polymerization of ethylene might allow desirable and reliable mass spectra with minimal interference with the reaction and the detection of relevant reaction intermediates. Furthermore, in very nice recent studies of zirconocene activation with MAO,^{17,18} PhF was used as the solvent to monitor the reaction of Cp_2ZrCl_2 with MAO by ESI-MS and study the chemistry of these intermediates in solution. Therefore, the utility of droplet spray for in situ analysis and real-time monitoring was demonstrated in PhF (see Figure 1b). When a high voltage (3.5 kV) was applied to the corner of the microscope slide loaded sequentially with PhF (0 s), Cp_2ZrCl_2 (14 s), MAO (17 s), and ethylene-saturated PhF (23 s), acceptable mass spectra with minimal interference from 0 s to minutes were obtained (see Figures 3 and 4).

As shown in Figure 3b at 16 s, the signal at m/z 291, corresponding to $[\text{Cp}_2\text{ZrCl}_2 + \text{H}]^+$, is clearly evident, although it had not been previously reported in the conventional ESI-MS studies of this system.^{14,16,18} The dominant ion at m/z 307 (Figure 3c,d), consistent with the heterodinuclear cation $[\text{Cp}_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$, which can also be written as $2 \cdot \text{AlMe}_3$, compared well with the results of earlier studies.¹⁸ In the range of 17 to 23 s, corresponding to the $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ period, the increasing signal intensity of the peak at m/z 235 with time (see Figure 3c,d) was in good agreement with previous results¹⁸ and provided compelling evidence that the catalytically active species did not cause an interference and existed steadily in PhF. Interestingly, beyond the detection of catalytically active species, droplet spray is also applicable to capture the process of formation of ion 2. The signal intensity of 2 increased over time at the expense of the ion at m/z 327, which corresponds to $[\text{Cp}_2\text{Zr}(\mu\text{-Me})(\mu\text{-Cl})\text{AlMe}_2]^+$. Ample precedent exists for observation of this intermediate in detailed kinetic and spectroscopic studies;^{11,13,18} however, to our knowledge, this work represents the first time this compound has been reported by MS. This successful real-time detection of this species offers direct and powerful evidence to support the mechanism of ligand exchange during the formation of 2.¹⁸

When ethylene-saturated PhF was subsequently pipetted onto the cover glass at 23 s, a distinct mass spectrum corresponding to two series of ions, the odd-chain transfer species 7 and the even-chain transfer species 6, identified by MS/MS experiments (see Figure S5), was clearly observed (see Figure 4). An ion at m/z 361, tentatively assigned as the zirconium hydride, 5, was also detected at very low intensity. Figure 4a,b illustrates the dramatic decrease in the intensities of the signals associated with ion 2 and increase in those associated with the polymeric products (see their insets); these results match well with previous results,¹⁶ indicating that the formation of the polymeric products was at the expense of ion 2. The intensity ratio of the odd-chain and even-chain polymerization products (see Figure 4c inset) supports the

hypothesis that the insertion of ethylene into the Zr-CH₃ bond is an ethylene polymerization pathway, as proposed in previous studies^{14,16,22} and supported by ion–molecule reactions.¹⁶ Interestingly, the ratios of the odd-chain transfer species 7 to the even-chain transfer species 6 were 3.53, 1.84, and 1.4 at reaction times of 24, 29, and 90 s, respectively (see Figure 4a–c). The intensity of the even-chain species 6 never surpasses the intensity of the odd-chain species 7, consistent with the results of previous investigations.^{12,14,15}

We observe a dramatic increase in intensity with time of polymeric products at m/z 400 to 500, especially the odd-chain polymeric product at m/z 403, corresponding the addition of six ethylene subunits to ion 2 and the even-chain polymeric product at m/z 361, corresponding to the addition of five ethylene subunits to ion 5 (see Figure 4a,b). Over time, these peak intensities dramatically decreased and the intensity of polymeric products with narrow polydispersity from m/z 400 to 700 (see Figure 4b,c) increased. The narrow polydispersity of the polymeric products is expected;¹⁹ however, time-resolved reaction monitoring of this process was not performed and this dramatic change of polymeric products from m/z 400 to 500 was not observed in previous studies using ESI-MS.^{15,16}

Beyond monitoring significant real-time changes in reactions on the time scale of seconds, droplet spray is also applicable to longer real-time monitoring of reactions (see Figure 4c,d), limited by the volatility of the deposited sample. Figure 4d shows monitoring by droplet spray for the duration of minutes. Notably, a comparison of the mass spectra in Figure 4c,d shows the outstanding feature (see Figure 4d inset) that the peak intensity in the range of m/z 700 to 800 is dramatically increased. The reasons for this phenomenon are not fully understood at present.

A distinct feature of droplet spray directly coupling to MS without a solution transfer capillary is that very low dead times are accessible, on the order of less than a second. This feature makes droplet spray a potential candidate for real-time monitoring of key reaction intermediates. The present system does have a time-varying concentration caused by solvent evaporation, and it is not currently clear whether the sequentially deposited solutions fully mix on the glass slide, although it is expected that nearly complete mixing does occur. This possible evaporation drawback could be overcome by surrounding the spray platform in the proper gas-phase environment.

An integrated platform for droplet spray mass spectrometry was developed using readily available, inexpensive, and convenient microscope cover glasses as the substrate for launching a charged droplet spray by the application of an electric field. With this device, we successfully demonstrated the in situ analysis and real-time monitoring of chemical reactions. The reaction intermediates of ethylene polymerization by zirconocene/MAO mixtures were rapidly obtained. This simple, economical, and flexible methodology has the potential for being coupled to portable and miniature mass spectrometers. The successful use of a microscope cover glass opens new areas for the application of sampling and ionization under ambient conditions. Eliminating the need for a sample transport capillary, droplet spray opens a new avenue for the in situ analysis and real-time monitoring of chemical reactions at subsecond dead times.

MATERIALS AND METHODS

Chemicals and Reagents. All HPLC-grade organic solvents including toluene, methanol, acetonitrile, tetrahydrofuran (THF), and fluorobenzene (PhF) were purchased from Sigma-Aldrich (Darmstadt, Germany). Ethylene gas of purity >99.99% was purchased from Jinghua Industry Co. (Hangzhou, China). The microscope cover glasses used in this study were purchased from Thermo Electron Corp. (Waltham, MA). The bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) and methylalumoxane (MAO) were acquired from Aike Co. (Chengdu, China).

Sample Preparation. Compatible organic solvents were purified by being refluxed over Na/K alloy under a nitrogen atmosphere before analysis. Ethylene, MAO, and Cp_2ZrCl_2 were prepared without further treatment. Cp_2ZrCl_2 (17.2 μmol , 5 mg) and 14 μL of MAO (10% solution in toluene) were, respectively, dissolved in 5 mL of PhF solution for future dilution. Before the online real-time monitoring experiments, ethylene was injected into a PhF solution at pressure of 1 MPa for 15 min. All solutions were prepared on the day of use. Extra precautionary measures should be taken against the toxicity of ethylene and the flammability of toluene, THF, and PhF. Also, care needs to be taken in handling MAO and Na/K because these compounds are pyrophoric.

Droplet Spray Ionization. Prior to sample loading, a microscope cover glass (18 \times 18 \times 0.15 mm) with four identical right-angle corners was placed onto a three-dimensional disposable (20 \times 15 \times 20 mm) custom-built platform (see Figure S1). The sample solution was loaded onto the corner adjacent to the MS inlet. A metal wire fixed on the platform with a high voltage from the MS was applied to the sample solution at the corner to form charged droplets. The end of the tip was positioned parallel and 10 mm from the MS inlet for acetonitrile and 5 mm from the MS inlet for THF and PhF. The angle formed between the MS inlet and tip-end was 10°.

Mass Spectrometry Experiments. Initial experiments were begun at Stanford University, but the vast majority of this study is based on work done at Harbin Institute of Technology. Mass spectra were acquired on a LTQ/Orbitrap mass spectrometer (Thermo Fisher Scientific, Waltham, MA). Full-scan positive (+) ion spectra were obtained over an m/z range from 100 to 2000 for catalytically active species and polymeric products of ethylene. High time-resolution data were acquired in the linear ion trap. Spectra and analysis were carried out using the Xcalibur software package (version 2.0.7, Thermo Fisher Scientific, US). To form the spray droplets, a high voltage was adjusted in the range of 3.0–5.0 kV, and an optimal ion signal for acetonitrile was obtained at 4.5 kV; clear spectra were obtained for THF and PhF when a high voltage of 3.5 kV was applied to the corner. The other basic conditions for data acquisition were as follows: tube lens voltage, 110 V; capillary temperature, 275 °C; and capillary voltage, 35 V. The ion maximum injection time of the linear ion trap was 10 ms. The identification of reactive intermediates was confirmed by collision-induced dissociation (CID) in LTQ mass spectrometry using the default parameters. A standard LTQ Velos ESI positive-ion calibration solution (Thermo Fisher Scientific, Waltham, MA) was used for the calibration of positive ionization before each experiment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.5b02390.

Illustration of the droplet spray ionization; total ion chromatogram in methanol via droplet spray ionization; positive-mode droplet spray tandem mass spectra (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: jiejiang@hitwh.edu.cn. Fax: +(86)-631-5685-359.

*E-mail: zare@stanford.edu. Fax: +(1)-650-725-0259.

Notes

The authors declare no competing financial interest.

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