

Electronic Supporting Information

A two-stage flow strategy for the synthesis of isobutyl-modified methylaluminumoxane

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S1. Materials and chemicals

S1.1 3D printing materials

A clear-type resin (FLGPCL04) with a print resolution of 100 μm was purchased from Formlabs and used in this study. Corrosion resistance of this resin was measured and summarized in our previous work^[1], indicating sufficient chemical compatibility.

S1.2 MMAO synthesis

All manipulations involving air- or moisture-sensitive compounds are carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen glove box. Prior to experiments, toluene is dried over 4 Å molecular sieves, and further purified by a solvent purification system (PS-400-5-SD, Innovative Technology, USA). Distilled deionized water is degassed by freeze-pump-thaw cycling. Trimethylaluminum (TMA, 2.0 M in toluene), toluene (99.5%), iron acetylacetonate ($\text{Fe}(\text{acac})_3$, 99%), 2,6-diacetylpyridine (97%), and 4-methoxy-2-methylaniline (98%) were purchased from J&K Chemical Corp. (Shanghai, China). Triisobutylaluminium (TIBA, 1.0 mol/L in toluene), ethylene diamine tetraacetic acid (EDTA), hexamethylenetetramine (99%), and toluene- d_8 were purchased from Macklin Biochemical Co. (Shanghai, China). All chemicals are used as received. Both TIBA and TMA are diluted with a certain amount of toluene to the required concentration before use.

S1.3 Polymerization experiment

Chemicals including iron acetylacetonate ($\text{Fe}(\text{acac})_3$, 99%), 2,6-diacetylpyridine (97%), and 4-methoxy-2-methylaniline (98%) were purchased from J&K Chemical Co. (Shanghai, China). Zirconocene dichloride (Cp_2ZrCl_2) was obtained from Aladdin Bio-Chemistry Co. (Shanghai, China). MMAO-3A was purchased from Nouryon and stored at -20°C . High purity nitrogen (99.999%) and polymerization-grade ethylene (99.9%) were both obtained from SINOPEC (Shanghai, China) and passed through oxygen- and moisture scrubbing columns prior to use.

S2. Experimental

S2.1 Microdroplet generator (A1 and A2)

We design a microdroplet generator that produces smaller droplets based on capillary tubes. A capillary tube with 160 μm O.D. (outer diameter) and 100 μm I.D. (inner diameter) is inserted into a 3D-printed T-junction (Fig. 2a) through nuts and ferrules. In the other end, the capillary tube is inserted into and fixed in a PFA tubing with 500 μm I.D. By design, water flows through the capillary in the centre of the tubing, while toluene flows around it outside the capillary. Growing droplets detach when the forces exerted by the co-flowing continuous phase exceed the interfacial tension. In order to analyze the droplet size and distribution, we monitor and record the process of microdroplet generation in different flowrates with a high-speed camera. An image processing program (ImageJ) is used to extract the features of microbubbles (i.e., the Sauter mean diameter d_{32}) from the recorded images. The images are processed by measuring the metrics of 50 randomly selected water droplets with a projected area S_i . Then, the equivalent diameter d_i of a circle with the same area is calculated by eqn (S1) and the Sauter mean diameter is determined using a discrete distribution by eqn (S2).

$$d_i = \sqrt{\frac{4S_i}{\pi}} \quad (S1)$$

$$d_{32} = \frac{\sum_{i=1}^n d_i^3}{\sum_{i=1}^n d_i^2} \quad (S2)$$

The formed droplets are uniform in size for each pair of flowrates, ranging from 160 to 400 μm while changing the flowrate of the continuous phase (toluene). At a water flowrate (Q_W) of 30 $\mu\text{L}/\text{min}$ and a toluene flowrate (Q_T) of 0–3.0 mL/min, the formed water droplet diameter gradually decreases as Q_T increases; however, as Q_T approaches or increases above 2.0 mL/min, the size of the water droplet formed stabilizes with an averaged value of 160 μm .^[2] Q_W is further tested between 30–120 $\mu\text{L}/\text{min}$; as Q_W increases, the droplet diameter slightly increases (Fig. S1). Thus, Q_W only has a negligible influence on the size of the water droplet formed, but it is manipulated for providing the desired amount of water to meet the target production requirement. Therefore, we pump toluene at a flowrate of 2.0–3.0 mL/min, associated with a water flowrate of 30–120 $\mu\text{L}/\text{min}$, for subsequent MMAO synthesis.

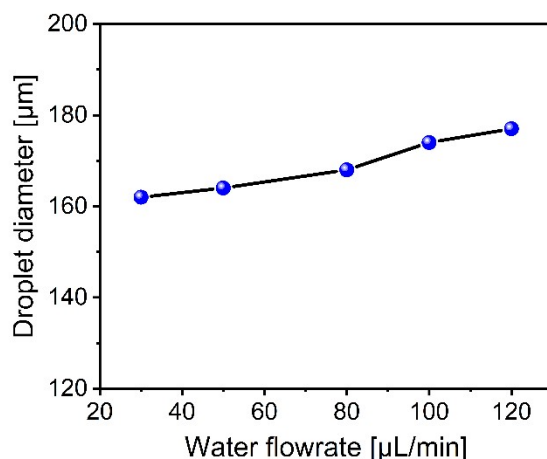


Fig. S1 Performance of water microdroplet formation under toluene flowrate of 2.0 mL/min and water flowrate of 30–120 µL/min.

S2.2 Micromixer (B) and microreactor (C1)

The formed water droplets in toluene blend with the TIBA/toluene solution in a 3D-printed passive micromixer B (Fig. 2b), with an I.D. of 3.0 mm. 0.8 mol/L TIBA in toluene is delivered at a flowrate of 6.0 mL/min, and the molar ratio between water and TIBA is fixed at 0.75. Due to the small amount of water, with a water/toluene volume ratio below 0.1, the reaction behaves as a pseudo-single-phase reaction in the beginning. The microliter-level reactor size limits the extremely exothermic hydrolysis of TIBA to a low volume in order to mitigate risks of a thermal runaway. As the reaction proceeds, isobutane is formed and its volume quickly exceeds that of the liquid stream. To efficiently handle this multiphase system, the reactive flow subsequently goes through a coiled PFA tubing (I.D. 1.59 mm, O.D. 3.18 mm), which is placed inside a compact and 3D printed substrate (Fig. 2c). This substrate in a plastic resin reduces any interactions of heat exchange between the hot zone and its neighboring cold zone, and allows for imaging analysis via high-speed camera or thermal camera. The reactor length is 0.47 m to ensure enough reaction time. Benefiting from the superior heat transfer characteristics of the reactor, the reaction is performed at 20 °C safely. Reaction analysis shows the yield of IBAO is >98%. We measure the co-catalytic activities of IBAO, obtaining 3977 kg·(mol Fe)⁻¹·h⁻¹ for ethylene oligomerization, using L-Fe(acac)₃ as the main catalyst, at Al/Fe of 1000; and obtaining 330 kg·(mol Zr)⁻¹·h⁻¹ for ethylene polymerization, using Cp₂ZrCl₂ as the main catalyst, at Al/Zr of 500. In this step, IBAO is obtained at high yield and high co-catalytic activities.

S2.3 Micromixer (E)

The formed IBAO reacts with TMA/toluene to generate a coordination complex. Mixer E is employed to perform this reaction. During the study, we manipulate the molar ratio between TMA and TIBA (i.e., TMA/TIBA) from 0.5 to 2.33, and therefore the amount of TMA is based on TMA/TIBA and TIBA concentration of 0.8 mol/L. Instead of simple contacting structures such as T-, Y-, and co-flow mixers, Mixer E (I.D. 4.0 mm) has a split-and-recombination (SAR) structure, which consists of a network of divided and then recombined spaces. The detailed dimensions of the mixer are presented in Fig. S2. Each SAR mixing unit encompasses a unique array of four blades (Fig. 2d), each of which has a thickness of 0.3 mm and a width of 1.0 mm, thus dividing the fluids into four microscale portions. To guarantee enough reaction time, we use three mixing units with a void factor of 0.92 and a rotation angle of 90°. The total reaction volume is 0.25 mL. This mixer is effective to handle the reaction because the diffusional distances are reduced exponentially in multiple SAR iterations. Once the formed IBAO/TMA complex flows into mixer F, water droplets in toluene (through A2) are fed and the total flowrate of the reactive flow is controlled at ~10.7 mL/min.

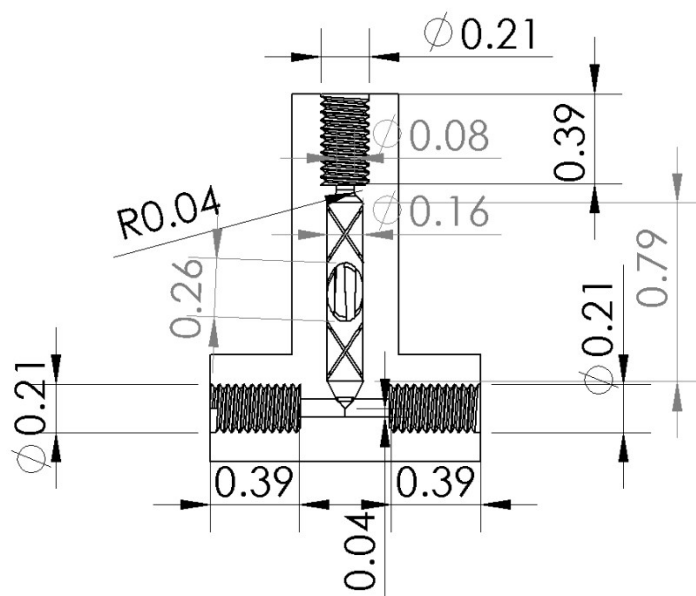


Fig. S2 Detailed dimensions of the SAR mixer (E) in inches.

S2.4 Micromixer (F) and microreactor (C2)

For the synthesis of *i*Bu-MMAO, mixer F (I.D. 3.0 mm) offers first-stage reagents blending, wherein the water droplets in toluene reacts with the TMA/IBAO/toluene solution. Compared with the 1st-stage hydrolysis to form IBAO, this reaction appears more exothermic and more

difficult to control. In this synthesis, we adjust the molar ratio between water and TMA from 0.5 to 1 and TMA/TIBA from 0.5 to 2.33. During the reaction, methane/isobutane is formed in a large volume and a segmented flow pattern is observed in the tubular reactor. The gas/liquid volume ratio increases to ~10-15. Visible solid by-product aluminum hydroxide forms especially at high TMA/TIBA due to the excessive hydrolysis of TMA. The solids may gradually deposit on the wall, which can ultimately lead to channel clogging. Therefore, the reactor (C2), with a volume of ~2.2 mL, is coiled (Fig. 2c) such that the rotating velocity streamlines drive the deposited solid to fall off the inner wall of reactor. The reactor length is 1.12 m to ensure enough reaction time and provide good mixing to mitigate the impacts of the formed gas/solid on the synthetic process. The reaction system is stable and no clogging is observed for a 12-hour continuous synthesis test.

S2.5 Separation

After the entire reaction, we obtain the crude reaction mixtures that contain methane, isobutane, solid by-products ($\text{Al}(\text{OH})_3$), and toluene solution of *i*Bu-MMAO and a small amount of unreacted TMA. The products in toluene directly flow into an in-house gas-liquid-solid separation unit (illustrated in Fig. S3), which is 3D printed with one inlet and two outlets for gases and liquids, respectively. In the middle of this unit, we place and seal a sheet of sand core filter layer with an average pore diameter of 15–40 μm to filter out the fine precipitates aided by a vacuum pump. When the product mixture flows in, methane/isobutane is immediately removed from the top right outlet and volumetrically measured for reaction analysis. The pressure gradient drives the solution containing MMAO flowing smoothly through the pores in the sand core, which is drained from the bottom outlet, while the solids remain on the sand core. In order to evaluate the solids, the particle size is measured using a laser diffraction size analyzer (Malvern Mastersizer 2000, UK). The mean particle diameter is determined by the equivalent diameter of equal volume sphere. The measured mean particle size is 232 μm , which is much smaller than the characteristic dimension of the coiled reactor (I.D. 1.59 mm), suggesting that this reactor is suitable for long-term processing of MMAO synthesis. Finally, we obtain a clear toluene solution containing the *i*Bu-MMAO product and unreacted TMA for reaction analysis.

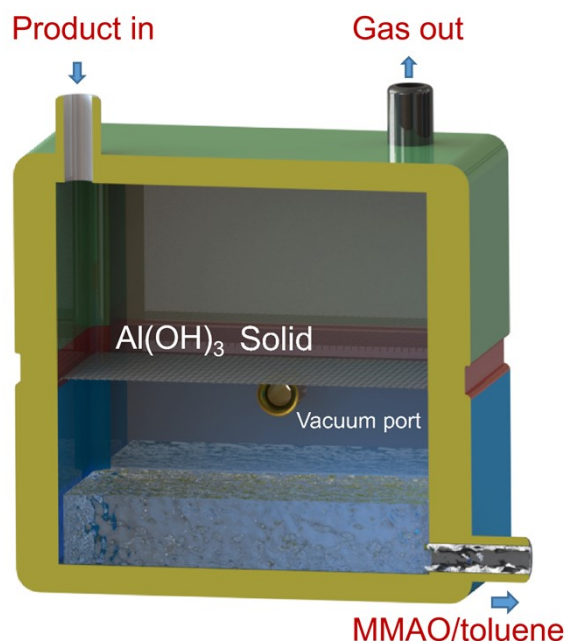


Fig. S3 Cross-section view of the gas-liquid-solid separation unit, with one inlet for raw product solution (top left), one gas outlet for methane/isobutane removal (top right), one outlet for MMAO/toluene solution (bottom right), a sand core filter layer to collect the solids (in the middle), and a vacuum port (in the back) connected to a vacuum pump.

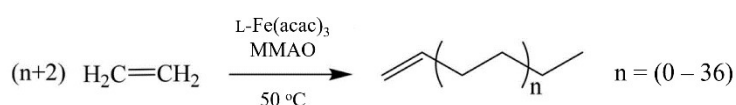
S2.6 Reaction analysis

After reaction, with an IBAO yield above 98%, we calculate the reaction conversion and MMAO yield based on the 2nd-stage hydrolysis (eqn (4)-(5)), i.e., using the molar flowrate of *i*Bu-MMAO in the product solution. We use a titration method to determine the total aluminum content in the as-synthesized MMAO. The clear MMAO solution is weighed into a Schlenk flask under nitrogen and decomposed by slow addition of water. Methane/isobutane is formed when the reaction begins. We use a flow integrating instrument connected to the Schlenk flask outlet to measure the volume of gasses, which is converted into moles using the ideal gas equation of state. The acidity of the solution is adjusted to pH of 3.0 with aqueous sulfuric acid (10% v/v). A certain amount of EDTA is added, and then the solution is refluxed for 3 min. Hexamethylenetetramine (ca. 2 mg) are added until the pH increases to 6.0. The mixture is immediately titrated with an aqueous ZnSO₄ solution (0.02 M) using xylenol orange as an indicator (yellow-red). The unreacted alkylaluminumoxanes are quantified by a UV-Vis approach, as previously demonstrated elsewhere^[2]. Therefore, the molar amount of MMAO is calculated based on the conservation of aluminum element.

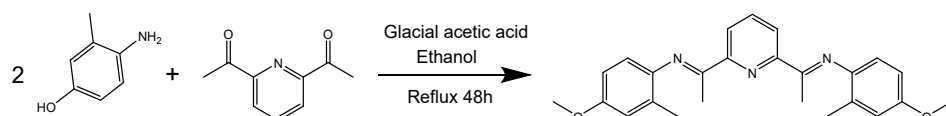
S2.7 Synthesis of catalysts

S2.7.1 Bis(imino)pyridine iron complexes

Bis(imino)pyridine iron complexes in combination with MMAO as catalysts exhibit excellent activity and linearity for α -olefin production (Scheme S1). In this system, iron acetylacetonate ($\text{Fe}(\text{acac})_3$) is mainly used as the iron source to form a homogeneous pre-catalyst with a 2,6-bis[1-(4-methoxy-2-methylphenylimino)ethyl]pyridine ligand (L), which is synthesized by reaction of 4-methoxy-2-methylaniline and 2,6-diacetylpyridine (Scheme S2). 4-methoxy-2-methylaniline is added to a solution of 2,6-diacetylpyridine in absolute ethanol. The solution is refluxed for 48 h after dropping a small amount of glacial acetic acid. Upon cooling to room temperature, the product is crystallized out from ethanol, and it is then filtered, washed with cold ethanol, and dried in a vacuum oven (60 °C) overnight. Then, the bis(imino)pyridine ligand is mixed with $\text{Fe}(\text{acac})_3$ in identical molar ratio and dissolved in toluene, obtaining a homogeneous orange-red mixture solution, abbreviated as $\text{L-Fe}(\text{acac})_3$. The concentration of the catalyst precursor in toluene, in terms of iron atoms, is 4 $\mu\text{mol/mL}$.



Scheme S1 Ethylene oligomerization using $\text{L-Fe}(\text{acac})_3$ and MMAO.



Scheme S2 Synthesis of 2,6-bis[1-(4-methoxy-2-methylphenylimino)ethyl]pyridine (L).

Ethylene oligomerization experiments are carried out in a 250 mL dried three-necked round-bottom flask which is immersed in a Magnetism Msier with an agitation speed of 800 rpm. A continuous and steady stream of ethylene is introduced into the flask under stirring. The desired amount of toluene (50 mL), MMAO, and $\text{L-Fe}(\text{acac})_3$ (2 μmol) are sequentially added into the flask, of which the amount of MMAO added is calculated based on a set Al/Fe molar ratio of 1000. The oligomerization is initiated immediately and lasts for 30 min at atmosphere pressure. Finally, the reaction is quenched by addition of the acidified ethanol solution. The product is then separated by filtration. The insoluble polyethylene wax is washed out and

dried overnight at 60 °C under reduced pressure until a constant weight is achieved. For soluble oligomers, an internal standard (n-heptane, 1.0 mL) is injected into the liquid phase. α -olefin products are quantitatively analyzed by Agilent GC 6890 equipped with an Agilent HP-5 column (5% phenylmethylsiloxane, 30 m \times 0.32 mm \times 0.25 μ m), and the temperature programming is: injection temp, 320°C; initial column temperature, 50 °C/2 min; progress rate, 20 °C /min; final column temperature, 300 °C/10 min. The yield of volatile C₄ fraction is determined by extrapolation based on the α value, which is a characteristic coefficient of the Schulz-Flory distribution, as calculated from the relative rate of chain propagation and chain termination or the ratio of the molar amounts of two subsequent oligomer fractions, C₁₄ and C₁₂ in this case. Finally, the co-catalytic activity is quantitatively analyzed by summation of the amount of the linear α -olefin products, including the soluble oligomers and insoluble polymers.

S2.7.2 Cp₂ZrCl₂

Ethylene polymerization is conducted at 70 °C in a 250 mL dried three-necked round-bottom flask equipped with a magnetic stirred bar. Then, it is immersed in a Magnetism Msier with an agitation speed of 800 rpm. Ethylene is continuously fed into the solvent under stirring. In the next, 100 mL dry toluene is introduced into the flask, followed by the addition of the desired amount of MMAO. The polymerization is initiated by addition of the catalyst Cp₂ZrCl₂ (15 μ mol), in which the Al/Zr molar ratio is kept at 500. After the required polymerization time of 1 h, the system is quenched by addition of an acidified ethanol solution. The precipitated polymer is collected by filtration and washed out with methanol. The collected polymer is dried overnight under reduced pressure at 60 °C to obtain polyethylene in white powder for analysis of the co-catalytic activity of MMAO.

S3. ¹H NMR spectra

S3.1 Reagents and products in *i*Bu-MMAO synthesis

In order to facilitate reaction analysis, we record the ¹H NMR spectra of all raw materials (TMA and TIBA) and products (IBAO, the IBAO/TMA complex, and *i*Bu-MMAO) from the entire synthesis. Fig. 3 in the main text shows the details of peaks and Fig. S4 presents a more complete view of datapoints.

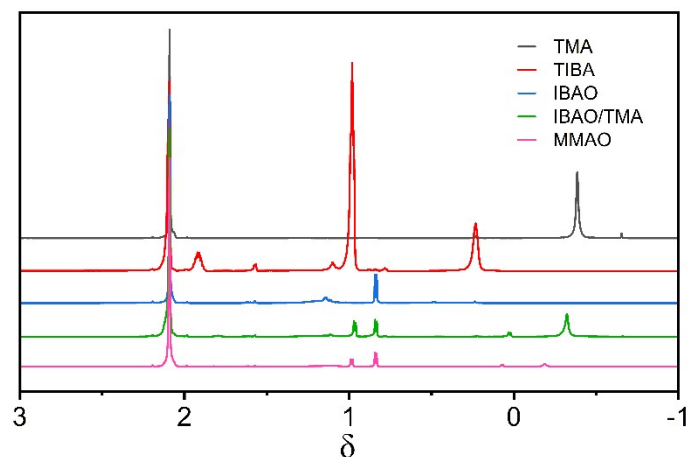


Fig.S4 The ^1H NMR spectra of all reagents and products in MMAO synthesis.

S3.2 MMAO-3A/n-heptane solution and n-heptane

To further illustrate the comparison between our synthesized MMAO/toluene sample and the commercial MMAO-3A/n-heptane sample, we obtain the ^1H NMR spectra from both the MMAO-3A/n-heptane sample and n-heptane in a sealed NMR tube at 600 MHz on an Agilent DD2 (DirectDrive2) instrument, as illustrated in Fig. S5. In MMAO-3A, the broadened peaks of $\delta \sim 1.4$ to 0.9 and $\delta \sim 0$ to -0.6 reflect the proton signal peaks of IBAO and MAO, respectively, in which the peak of IBAO is influenced by that of n-heptane. The ^1H NMR spectra indicate that the structure of MMAO-3A is similar to our sample (Fig. 3) synthesized using microreactors and flow process.

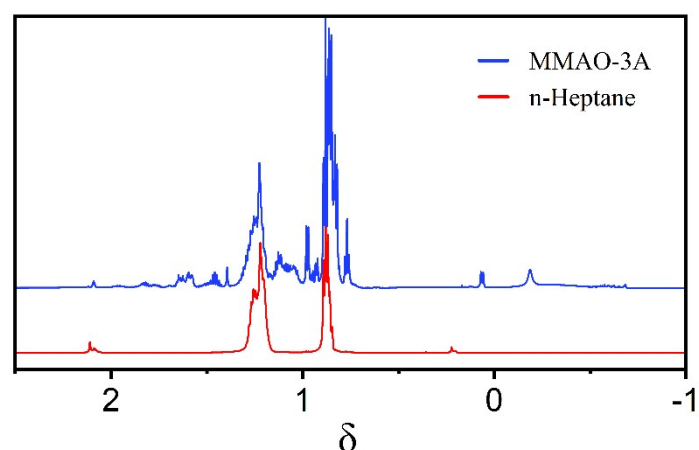


Fig. S5 The ^1H NMR spectra of MMAO-3A/n-heptane solution and n-heptane.

Reference

1. Y. Feng, H. Mu, X. Liu, Z. Huang, H. Zhang, J. Wang, Y. Yang, "Leveraging 3D Printing for the Design of High-Performance Venturi Microbubble Generators", *Ind. Eng. Chem. Res.* 2020, 59 (17), 8447-8455.
2. Y. Feng, M. Zhang, H. Zhang, J. Wang, Y. Yang, "Continuous synthesis of isobutylaluminoxanes in a compact and integrated approach", *Chem. Eng. J.* 2021, 425, 131750.