

Supporting information available for

**Cationic Polymerization of Vinyl Monomers using Halogen Bonding Organocatalysts with Varied Activity**

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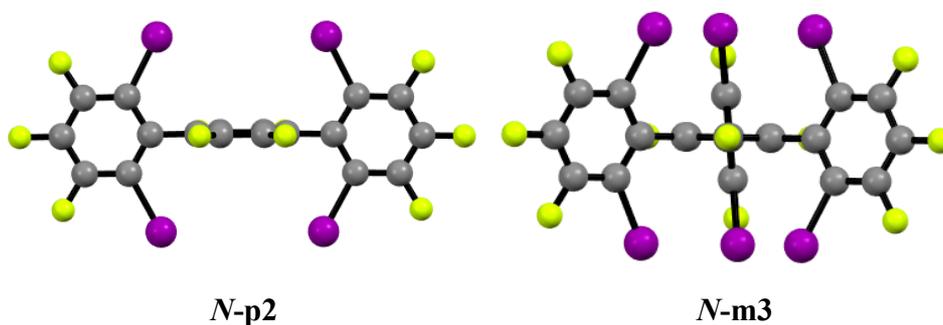
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## S1. Materials and instruments

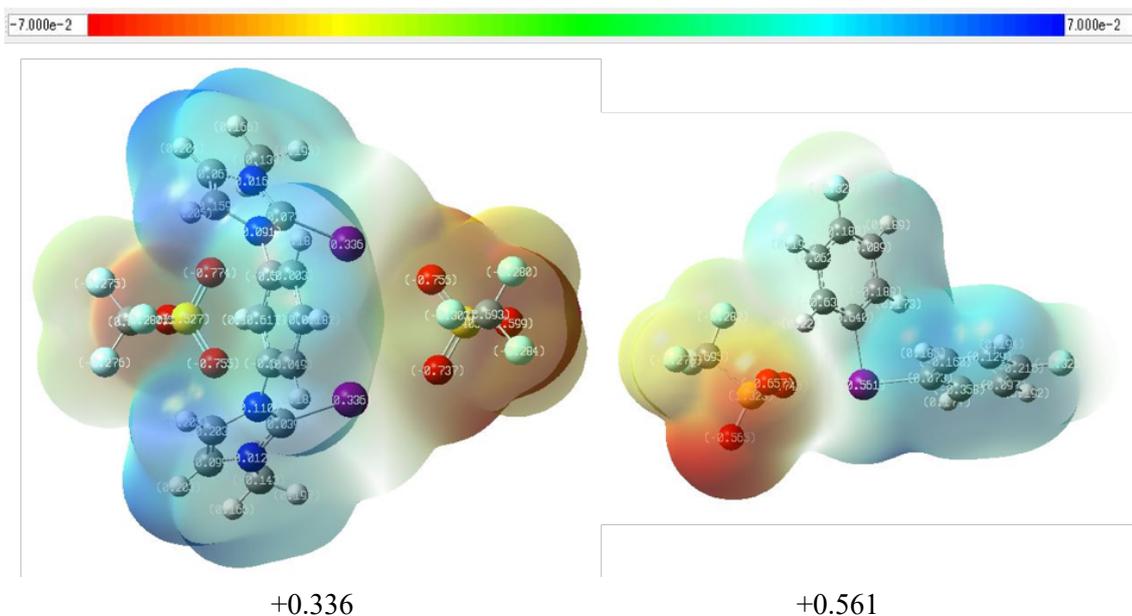
All reactions were performed under dry nitrogen atmosphere. All monomers and solvents were dried following to the general methods, distilled, and stored under dry nitrogen atmosphere. Other reagents were purchased from commercial suppliers and used without purification. The HCl adduct of IBVE (IBVE-HCl) was prepared by the addition reaction of distilled IBVE with dry HCl gas in hexane according to the literature.<sup>1</sup> The residual free HCl was completely removed by a dry nitrogen gas purge, and the concentration was determined by the titration technique using <sup>1</sup>H-nuclear magnetic resonance (NMR) spectrum. The HCl adduct of pMOS (pMOS-HCl) was likewise prepared in CCl<sub>4</sub>. The halogen bonding organocatalyst *N*-**p2**,<sup>2</sup> *N*-**m3**,<sup>2</sup> *I*-OTf,<sup>3</sup> *I*-BPh<sub>4</sub>,<sup>3</sup> and *I*-Br<sup>F</sup><sub>4</sub><sup>4</sup> were synthesized according to the previous methods.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker Avance III HD 400 FT-NMR spectrometer. Melting points (Mp) were determined on a Yanagimoto micro melting point apparatus (model MP-500D) and are uncorrected. Elemental analyses (EA) were performed on a Elementar vario EL cube. Gel permeation chromatographic (GPC) analyses were carried out with a Shodex 104 system using tandem LF-404 columns (THF as eluent, flow rate=1.0 mL/min, 40 °C) equipped with refractive index (RI) and ultraviolet (UV) detectors. Number-averaged molecular weight (*M<sub>n</sub>*) and molecular weight distribution (*M<sub>w</sub>*/*M<sub>n</sub>*) were determined on the basis of a calibration curve made from standard polystyrene samples and ethylbenzene.

## S2. Theoretical calculation<sup>5</sup>



**Figure S1.** Optimized ground state structures obtained by the DFT calculation using a long-range correlated  $\omega$ B97XD density functional combined with a DGDZVP basis set for iodine and a 6-311G(d,p) basis set for the other atoms. Grey: carbon, Yellow: fluorine, Purple: iodine.

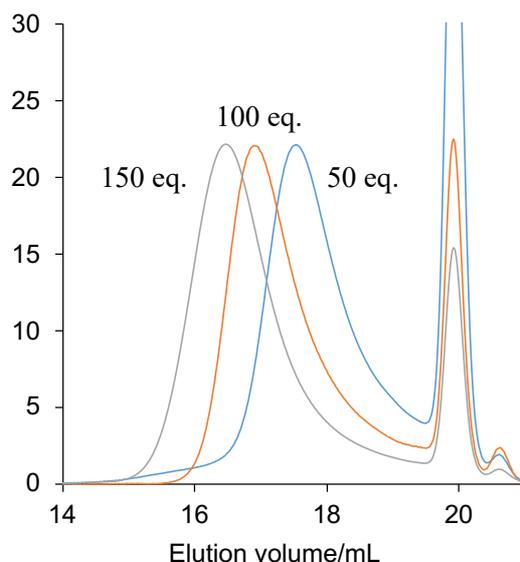


**Figure S2.** The electrostatic potential (ESP) energy surface was calculated using the molecular geometry optimized at  $\omega$ B97XD/6-31+G(d,p) level of theory for all atoms except iodine, for which DGDZVP basis set was used. The maximum values of electrostatic potential energy surface (isovalue: MO = 0.02, density = 0.0004) were indicated above. Blue colors represent positive potential (the darker the color the more positive), green, yellow, and red represent an increasing negative potential (in that order). The Mulliken charge on the iodine is also indicated. In order to save the computational cost, the calculation of *I-OTf* was performed by replacing the octyl group with the methyl group.

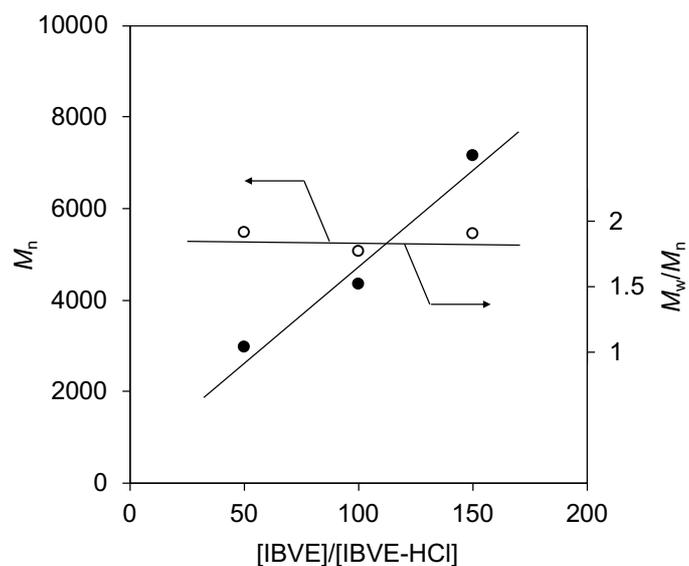
### S3. Experimental

#### Typical polymerization procedure (Table 1, Entry 7)

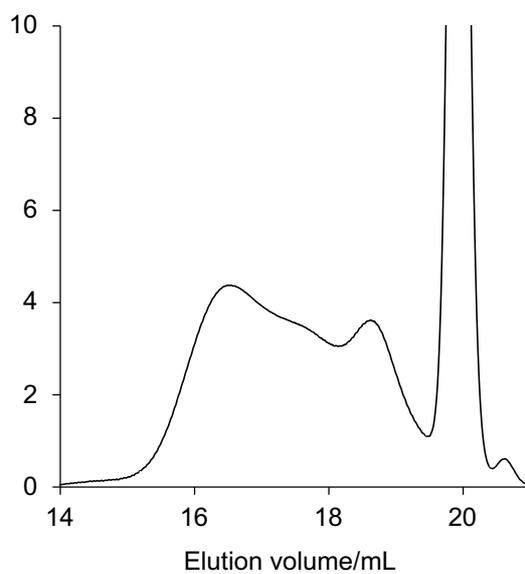
All flasks equipped with three-way stopcocks were baked with a heating gun at 400 °C before use. In flask A, a 0.98 M hexane solution of IBVE-HCl (0.2 mL) was diluted with CH<sub>2</sub>Cl<sub>2</sub> (1.8 mL) and cooled to -10 °C (initiator solution A). In a flask B, *N-m3* (51 mg, 40 μmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2.0 mL) and cooled to -10 °C (catalyst solution B). In a flask C, a solution of IBVE (501 mg, 5.01 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3.35 mL) was cooled to -10 °C (monomer solution C). A monomer solution C (0.4 mL) was transferred to flask D, and an initiator solution A (0.1 mL) and a catalyst solution B (0.5 mL) were added at 25 °C with stirring. After 2 h, the polymerization was quenched by adding 2 M NH<sub>3</sub> solution in CH<sub>3</sub>OH (0.2 mL). The solution was diluted with hexane and washed with water. Organic solvents were removed by the rotary evaporator, and the residue was dried in-vacuo. The polymer yields were determined by gravimetry.



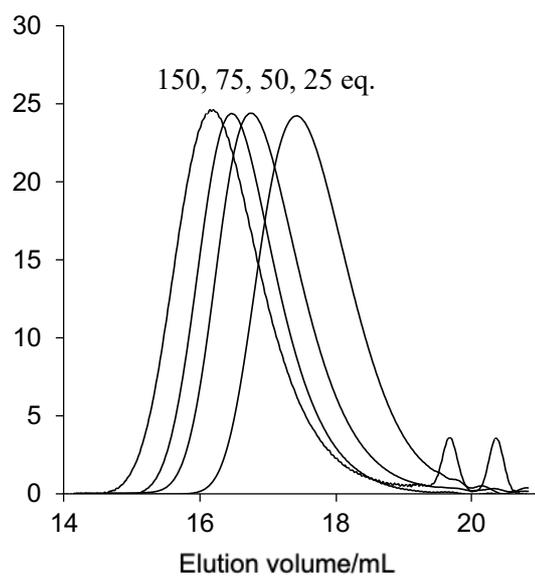
**Figure S3.** GPC profile of polymers obtained in the polymerization of IBVE by using IBVE-HCl and *N-m3* as initiator and catalyst, respectively, in dichloromethane at 25 °C.



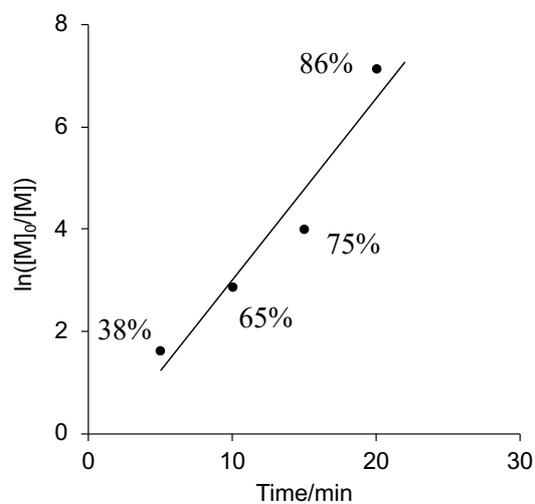
**Figure S4.** Number averaged molecular weight (closed circle) and molecular weight distribution (open circle) as a function of monomer feed ratio in the polymerization of IBVE using *N-m3* as an organocatalyst in dichloromethane at 25 °C.



**Figure S5.** GPC profile of polymer obtained in the polymerization of IBVE by using IVBE-HCl and *N-m3* as initiator and catalyst, respectively, in toluene at 25 °C.



**Figure S6.** GPC profile of polymers obtained in the polymerization of pMOS by using pMOS-HCl and *I-OTf* as initiator and catalyst, respectively, in dichloromethane at 25 °C.



**Figure S7.**  $\ln([M]_0/[M])$  versus time plot in the polymerization of pMOS. The numbers in the graph indicate the monomer conversion.

## S4. References

- 1) H. Katayama, M. Kamigaito, M. Sawamoto, and T. Higashimura, *Macromolecules* **1995**, *28*, 3747–3755.
- 2) F. Kniep, S. H. Jungbauer, Q. Zhang, S. M. Walter, S. Schindler, I. Schnapperelle, E. Herdtweck and S. M. Huber, *Angew. Chem. Int. Ed.* **2013**, *52*, 7028–7032.
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