

*Electronic Supplementary Information*

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**Microsystem Controlled Cationic Polymerization of Vinyl Ethers Initiated by CF<sub>3</sub>SO<sub>3</sub>H**

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**General.** <sup>1</sup>H NMR (600 MHz) spectra were recorded on a JEOL ECA-600 spectrometer in CDCl<sub>3</sub> and the chemical shifts are reported in parts per million (δ) from the signal of tetramethylsilane.

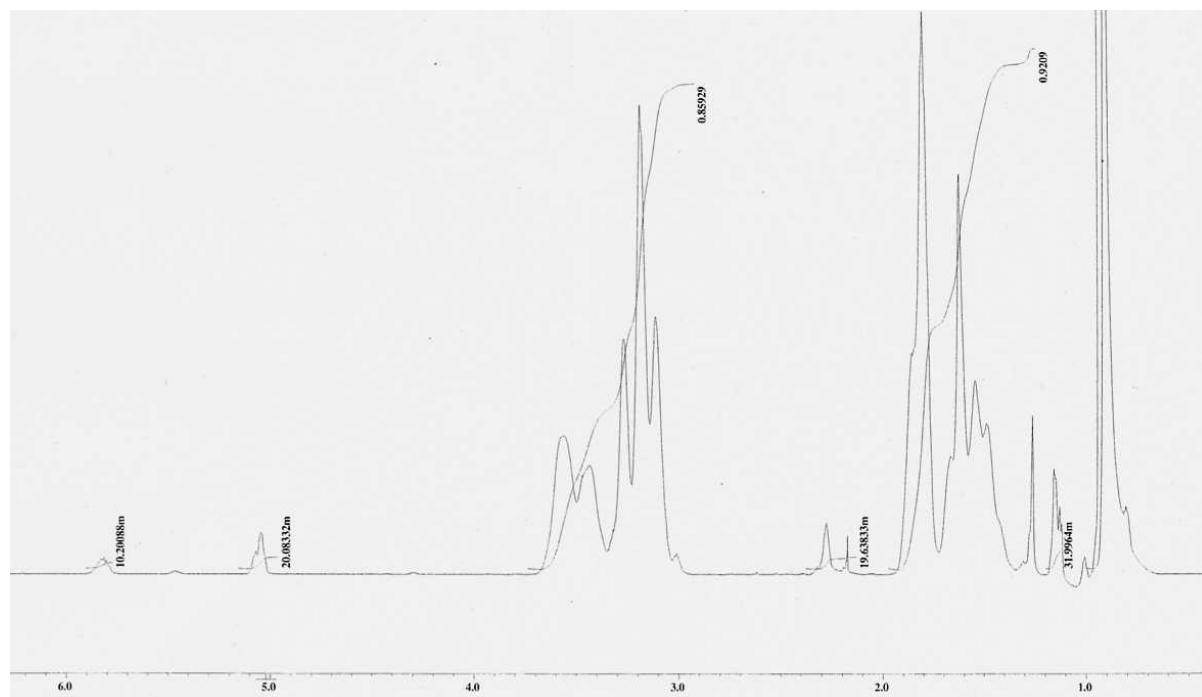
**Materials.** Dichloroethane was purchased from Aldrich as a dehydrated solvent and was dried over molecular sieves 4A before use. *n*-Butyl vinyl ether, isobutyl vinyl ether, and ethyl vinyl ethers were distilled before use.

**Molecular Weight and Molecular Weight Distribution.** The molecular weight (*M<sub>n</sub>*) and molecular weight distribution (*M<sub>w</sub>*/*M<sub>n</sub>*) were determined in THF at 40 °C with a Shodex GPC-101 equipped with two LF-804L columns (Shodex) and an RI detector using a polystyrene (polySt) standard sample for calibration.

**A Typical Procedure for the Polymerization Using Microsystem:** A microsystem consisting of a T-shaped micromixer **M1** (inner diameter: 250 μm) and a microtube reactor **R1** (SUS316, inner diameter: 500 μm, length: 50 cm) was used. Tube pre-cooling units **C1** and **C2** (inner diameter 1.0 mm, length 2 m) were connected to the inlets of **M1**. The whole system was cooled in the cooling bath at -25 °C. Thus, a solution of isobutyl vinyl ether (IBVE) in 1,2-dichloroethane (0.2 M, 6.0 mL/min) and that of TfOH in 1,2-dichloroethane (0.02 M, 6.0 mL/min) were introduced to **M1** through **C1** by syringe pumping technique. The outlet solution from **R1** was introduced to a solution of saturated potassium carbonate in methanol to quench the polymerization. The mixture was poured into water. The organic phase was separated and the aqueous phase was extracted with hexane or tetrahydrofuran. The combined organic phase was dried over sodium carbonate. After filtration, the solvent was removed under reduced pressure to obtain the polymer product (almost quantitative yield).

**Typical Procedure for the Allyltrimethylsilane Trapping :** A microsystem consisting of two T-shaped micromixers **M1** and **M2** (inner diameter: 250 μm) and two microtube reactors **R1** and **R2** (inner diameter: 500 μm) was used. The length of **R1** was 20 cm. The length of **R2** was 50 cm. Tube pre-cooling units **C1**, **C2**, and **C3** (inner diameter 1.0 mm, length 2 m) were connected to the inlets of **M1** and the inlet of **M2**. The whole system was cooled in the cooling bath at -25 °C. Thus, a solution of IBVE in 1,2-dichloroethane (0.2 M, 6.0 mL/min) and that of TfOH in 1,2-dichloroethane (0.02 M, 6.0 mL/min) were introduced to **M1** through **C1** and **C2**, respectively by syringe pumping technique. A solution of allyltrimethylsilane in 1,2-dichloroethane (0.3 M, 4.0 mL/min) was introduced to **M2** through **C3**. The outlet solution from **R2** was taken into a flask and the mixture was stirred at 0 °C for 1 h. The solution was added to a solution of saturated potassium carbonate in methanol and the resulting mixture was poured into water. The organic phase was separated and the aqueous phase was extracted with hexane or tetrahydrofuran. The combined organic phase

was dried over sodium carbonate. After filtration, the solvent was removed under reduced pressure to obtain the polymer product.



**Figure 1.** 600MHz  $^1\text{H}$  NMR spectrum of the polymer obtained by quenching with allyltrimethylsilane.

**Typical Procedure for the Block Co-polymerization:** A microsystem (Figure 7) consisting of two T-shaped micromixers **M1** and **M2** (inner diameter: 250  $\mu\text{m}$ ) and two microtube reactors **R1** and **R2** (inner diameter: 500  $\mu\text{m}$ ) was used. The length of **R1** was 20 cm. The length of **R2** was 50 cm. Tube pre-cooling units **C1** and **C2**, and **C3** (inner diameter 1.0 mm, length 2 m) were connected to the inlets of **M1** and the inlet of **M2**, respectively. The whole system was cooled in the cooling bath at  $-25\text{ }^\circ\text{C}$ . Thus, a solution of IBVE in 1,2-dichloroethane (0.2 M, 6.0 mL/min) and that of TfOH in 1,2-dichloroethane (0.02 M, 6.0 mL/min) were introduced to **M1** through **C1** and **C2**, respectively by syringe pumping technique. A solution of the second monomer (NBVE or EVE, 0.3 M, 4.0 mL/min) was introduced to **M2** through **C2**. The outlet solution from **R2** was introduced to a solution of saturated potassium carbonate in methanol to quench the polymerization. The resulting mixture was poured into water. The organic phase was separated and the aqueous phase was extracted with hexane or tetrahydrofuran. The combined organic phase was dried over sodium carbonate. After filtration the solvent was removed under reduced pressure to obtain the polymer product.

**Typical Procedure for the Polymerization using Batch System:** The polymerization was carried out in a glass flask (100 mL). To a solution of isobutyl vinyl ether (200 mg, 2 mmol) in dry dichloroethane (19 mL) at  $-25\text{ }^\circ\text{C}$  under argon atmosphere, 0.2 mmol of TfOH (0.2 mol/L, 1 mL) were added with stirring vigorously by magnetic stirrer. After 10 sec the reaction was quenched with a saturated potassium carbonate in methanol (5 mL). The resulting mixture was poured into water. The organic phase was separated and the aqueous phase was extracted with hexane or tetrahydrofuran. The combined organic phase was dried over sodium

carbonate. After filtration, the solvent was removed under reduced pressure to obtain the polymer product.