

Supporting Information for:

Living Cationic Polymerization of Vinyl Ethers Using a Strong Lewis Acid without Stabilizing Additives: Effective Interaction of Monomers with Growing Ends and/or SnCl₄

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Experimental

Isobutyl vinyl ether (IBVE) was distilled twice over calcium hydride. Toluene was dried by passage through solvent purification columns just before polymerization. EtAlCl₂ (solution in hexane), SnCl₄ (solution in heptane), and TiCl₄ (solution in toluene) were used as received. For FeCl₃ and GaCl₃, stock solutions in diethyl ether and hexane were prepared from commercial anhydrous FeCl₃, GaCl₃, respectively. IBVE-HCl adduct was prepared from the addition reaction of IBVE with HCl.¹ Polymerization was carried out under dry nitrogen in a baked glass tube. Recovery of the product polymers was conducted as already reported.² The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C using three polystyrene gel columns. The number-average molecular weight (M_n) and M_w/M_n were calculated from the chromatographs based on polystyrene calibration.

Effect of Lewis Acid

To investigate the effect of Lewis acids, polymerization of IBVE in the absence of any external additive was also studied using various other Lewis acids (EtAlCl₂, TiCl₄, FeCl₃, and GaCl₃). The polymerization was carried out in toluene at 0, -30, and -78 °C ([IBVE]₀ = 0.76 M, [IBVE-HCl]₀ = 4.0 mM, [Lewis acid]₀ = 5.0 mM). All Lewis acids induced extremely rapid polymerization at any temperature. The resulting polymers were invariably uncontrolled at -30 °C in stark contrast to the polymers prepared with SnCl₄. Figure S1 shows the MWDs of the polymers obtained using various Lewis acids. SnCl₄ gave polymers with narrow MWDs at each temperature, especially very narrow ($M_w/M_n < 1.1$) at below -30 °C (Figure S1-C). On the other hand, the product polymers had uncontrolled molecular weight and broad MWDs even at lower temperatures when EtAlCl₂ or TiCl₄ was used (Figure S1-A and D). With FeCl₃ or GaCl₃, the polymers with relatively narrow MWDs were obtained at -78 °C (Figure S1-B and E). However, the polymers obtained using FeCl₃ had broader MWDs than those using SnCl₄, and GaCl₃ generated polymers with molecular weight much higher than the calculated values. Thus, living cationic polymerization in the absence of additives at low temperatures was specific to the SnCl₄-based initiating system.

Recently, we demonstrated specific properties of the SnCl₄ initiating system by comparing to the Et_xAlCl_{3-x} system from viewpoints of computational chemistry; SnCl₄ has lower bond dissociation energy of various polar compounds, and led to lower ionization energy of C-Cl bond than Et_xAlCl_{3-x}.³ These results are consistent with the order of Lewis acid activity determined from various reactions; for example, FeCl₃ > SnCl₄ > TiCl₄ > AlCl₃ (chlorine ion affinity), AlCl₃ > TiCl₄ > SnCl₄ (interaction with dibutyl ether), AlCl₃ > GaCl₃ > FeCl₃ > SnCl₄ (isomerization and disproportionation; namely side reactions).⁴⁻⁶ Therefore, SnCl₄ has presumably a greater tendency to achieve living cationic polymerization than other Lewis acids.

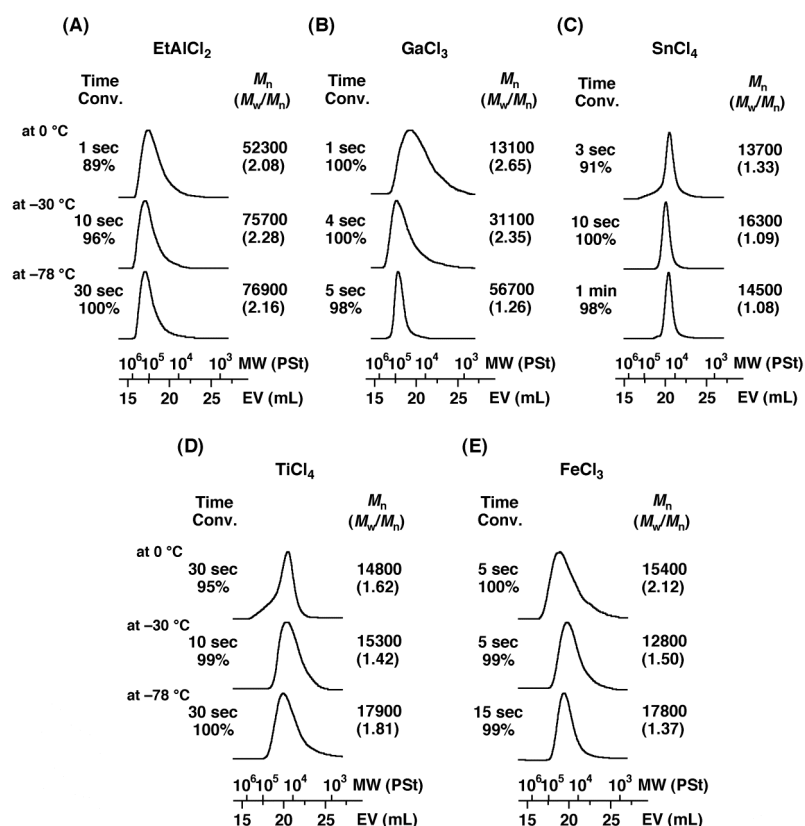


Figure S1. MWD curves for poly(IBVE) obtained using various Lewis acid systems in toluene at 0 (top), -30 (middle), and -78 °C (bottom): [IBVE]₀ = 0.76 M, [IBVE-HCl]₀ = 4.0 mM, [Lewis acid]₀ = 5.0 mM.

Cationic Polymerization of Various Vinyl Ethers Using SnCl₄ and Postulated Mechanism for the Mono-mer-Stabilized Living Cationic Polymerization

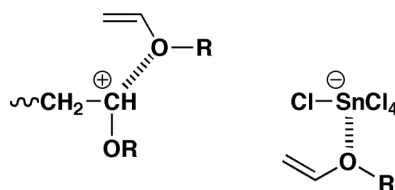
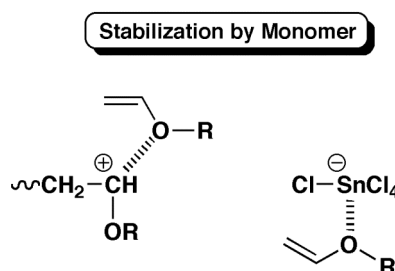
Cationic polymerization of other vinyl ethers except IBVE using the IBVE-HCl/SnCl₄ initiating system was next examined in toluene at -30 °C ([monomer]₀ = 0.80 M, [IBVE-HCl]₀ = 4.0 mM, [SnCl₄]₀ = 5.0 mM). The polymerization of ethyl vinyl ether (EVE) and *n*-butyl vinyl ether (NBVE) proceeded with living nature, being complete within 5 sec; the M_n of the obtained polymers almost agreed with the calculated values, and the MWDs were narrow ($M_w/M_n \sim 1.1$; Table S1, runs 1, 3). For the polymerization of CEVE, fast polymerization also proceeded at -30 °C (conversion = 100% in 15 sec). The GPC curve of the polymer was slightly broad with a shoulder in a higher molecular weight region ($M_n = 18,000$, $M_w/M_n = 1.28$; Table S1, run 4). The amount of this byproduct decreased with decreasing temperature, and the polymer obtained at -78 °C had a unimodal and quite narrow MWD ($M_n = 17,700$, $M_w/M_n = 1.07$; Table S1, run 6). On the other hand, the polymerization of EOVE with a pendant oxyethylene group was much slower when SnCl₄ was employed (77% in 3 h; Table S1, run 7). The strong interaction of the oxyethylene group with SnCl₄ at a low temperature likely suppressed the activity of SnCl₄.

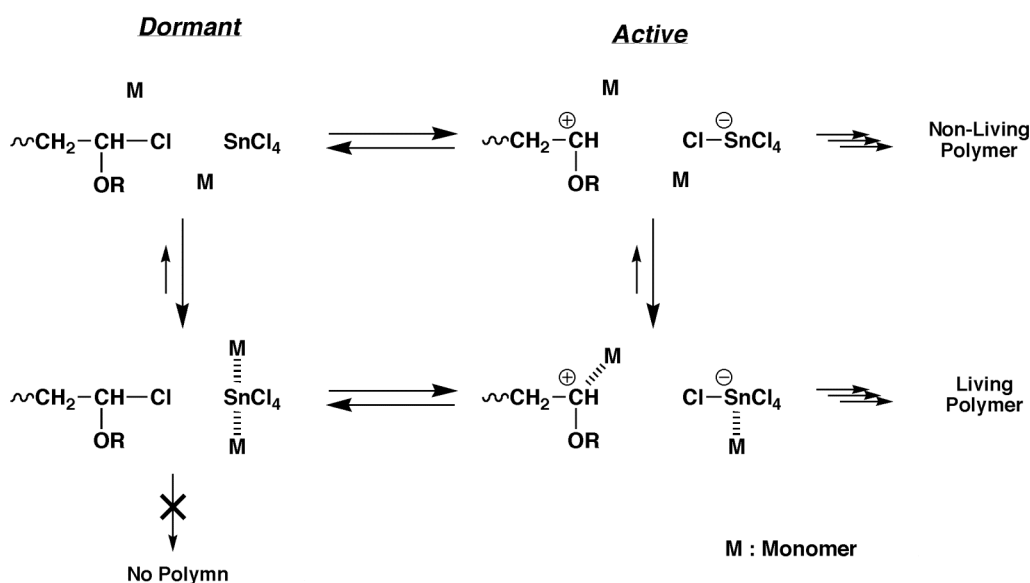
Table S1. Cationic Polymerization of Various Vinyl Ethers Using SnCl₄^a

Run	Monomer	Temp. (°C)	Time	Conv. (%)	M_n^b	M_w/M_n^b
1	EVE	-30	5 sec	100	14,300	1.11
2	IBVE	-30	10 sec	100	18,400	1.08
3	NBVE	-30	5 sec	100	18,100	1.11
4	CEVE	-30	15 sec	100	18,000	1.28
5	CEVE	-45	30 sec	97	17,500	1.15
6	CEVE	-78	1 min	97	17,700	1.07
7	EOVE	-30	3 h	77	12,500	1.30

^a [Monomer]₀ = 0.80 M, [IBVE-HCl]₀ = 4.0 mM, [SnCl₄]₀ = 5.0 mM, in toluene.^b Determined by GPC, polystyrene calibration.

The mechanism that vinyl ether monomers stabilize carbocations and Lewis acids is also supported by the polymerization behavior of CEVE. Since the electron-withdrawing chlorine atom of CEVE decreases electron densities of both the vinyl group and the ether oxygen, the stabilization of carbocations and Lewis acids was incomplete at -30 °C for living polymerization. Therefore, in order to attain livingness, cationic polymerization of CEVE required a lower temperature, where the formation of the SnCl₄-ether complex becomes stronger (Table S1, runs 4–6). Thus, both experimental results (Figure 1 and Table S1) and computational chemistry (Figure 3) suggested that vinyl ethers likely serve as a weak Lewis base to realize living cationic polymerization as shown in Schemes S1 and S2, especially at a lower temperature. It has been reported that a similar non-additive system (SnCl₄ (0.2 mM) / dichloromethane / -78 °C) yielded long-lived species.⁷ In the present study (SnCl₄ (5.0 mM) / toluene / -30 °C), more stable growing ends were obtained due to low polar solvent where the dormant species are more stable and dominant than in polar solvent. The favorable conditions for the dormant species permitted living polymerization at higher temperature and higher SnCl₄ concentration.

**Scheme S1.** Postulated stabilization mechanisms of carbocations for the cationic polymerization of vinyl ethers.



Scheme S2. Postulated mechanism for the monomer-stabilized living cationic polymerization of vinyl ethers using SnCl_4 without additives.

Cationic Polymerization in the Presence of Model Ether Compounds

Cationic polymerization of IBVE was examined in the presence of model ether compounds, *n*-butyl ethyl ether ($[\text{IBVE}]_0 = 0.76 \text{ M}$, $[\text{IBVE-HCl}]_0 = 4.0 \text{ mM}$, $[\text{SnCl}_4]_0 = 5.0 \text{ mM}$, $[\textit{n}$ -butyl ethyl ether] = 0.76 M , in toluene at 0°C). The polymerization proceeded with non-living nature, producing bimodal polymers at 0°C , and a polymer with an appreciable higher molecular weight byproducts even at -30°C . These results suggest that some of the model ether molecules interact with the growing carbocations but not stabilize them enough, interfering with the monomer-cation interaction. This interference is likely to lead to non-living cationic polymerization of isobutyl vinyl ether even at -30°C .

References

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