

## Rediscovery of a Broad Array of Lewis Acids for Living Cationic Polymerization in the Presence of an Added Base

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### Introduction

It has been a couple of decades since living cationic polymerization of vinyl ethers<sup>1</sup> or isobutene<sup>2</sup> was first reported. After the discovery, most of initiating systems were developed within a decade. However, there has apparently been a limited choice of Lewis acids (metal halides) employed in living cationic polymerization.<sup>3</sup>

We have synthesized a variety of functionalized polymers, including stimuli-responsive polymers, via living cationic polymerization in the presence of an added base.<sup>4,5</sup> An added base stabilizes carbocations, and/or would tune the Lewis acidity of a metal halide. Recently we found that SnCl<sub>4</sub> induced fast living cationic polymerization not only alkyl vinyl ethers but also functionalized counterparts in the presence of an added base such as an ester.<sup>6,7</sup>

Encouraged by these facts, we decided to explore a wide variety of Lewis acids for living cationic polymerization of vinyl ethers. Thus we examined cationic polymerization of an alkyl vinyl ether with FeCl<sub>3</sub>, less toxic among metal halides, in the presence of a cyclic ether. This system was shown to induce fast living cationic polymerization of isobutyl vinyl ether (IBVE).<sup>8</sup> Further extensive investigation revealed that living cationic polymerization can be achieved using various Lewis acids, some of which have rarely been even utilized for cationic polymerization.

### Experimental

**Materials.** Isobutyl vinyl ether (IBVE), ethyl acetate, 1,4-dioxane, 1,3-dioxolane, tetrahydrofuran (THF), and toluene were distilled twice over calcium hydride, lithium aluminum hydride, or metallic sodium before use. IBVE-HCl was prepared from the addition reaction of IBVE with dry HCl.<sup>9</sup> SnCl<sub>4</sub>, EtAlCl<sub>2</sub>, ZnCl<sub>2</sub>, TiCl<sub>4</sub>, and SiCl<sub>4</sub> solutions, commercially available, were used without further purification. Pure solid FeCl<sub>3</sub> and FeBr<sub>3</sub> were dissolved in diethyl ether, solid GaCl<sub>3</sub> in hexane, solid AlCl<sub>3</sub>, InCl<sub>3</sub>, ZrCl<sub>4</sub>, HfCl<sub>4</sub>, and BiCl<sub>3</sub> in ethyl acetate, and liquid GeCl<sub>4</sub> in dichloromethane just before use. All chemicals but toluene were stored in a brown ampule under dry nitrogen.

**Polymerization Procedure.** Polymerization was carried out at 0 °C under dry nitrogen in a glass tube equipped with three-way stopcock using a syringe technique. Recovery of the polymers was conducted as already reported.<sup>4,8</sup> The monomer conversion was determined by gravimetry.

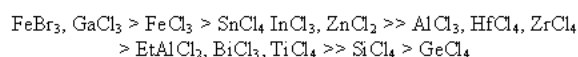
**Instrumentation.** The MWD of the polymers was measured by size exclusion chromatography (SEC) in chloroform at 40 °C on three polystyrene gel columns. The number-average molecular weight ( $M_n$ ) and  $M_w/M_n$  were calculated based on a polystyrene calibration.

### Results and Discussion

**Fast Living Cationic Polymerization of IBVE using FeCl<sub>3</sub> in the Presence of a Cyclic Ether.** The combination of FeCl<sub>3</sub> and 1,4-dioxane ( $pK_b = 5.85$ ) permitted living cationic polymerization of IBVE in toluene at 0 °C, being completed in 15 s ( $M_n = 18200$ ,  $M_w/M_n = 1.06$ ). In contrast, polymerization is less controlled in the presence of ethyl acetate (Table 1, entry 3). Thus, cyclic ethers are effective as an added base for achieving living polymerization with FeCl<sub>3</sub>.

Faster but living polymerization was achieved with a weaker base, such as 1,3-dioxolane ( $pK_b = 7.55$ ): the reaction reached quantitative monomer conversion in 3 s. The product polymers had very narrow molecular weight distributions (MWD), and the  $M_n$  increased in direct proportion to monomer conversion. The use of THF ( $pK_b = 4.22$ ), a stronger base, also induced living polymerization with very small reaction rate (Table 1, entry 13). Thus, the basicity of an added base greatly affected the polymerization rate and an appropriate combination of a weak Lewis base and FeCl<sub>3</sub> realized very fast living cationic polymerization.

**Scope of Metal Halides for Living Cationic Polymerization of Vinyl Ethers.** Cationic polymerizations of IBVE were examined using various Lewis acids in toluene in the presence of ethyl acetate, 1,4-dioxane, or THF at 0 °C. As shown in Table 1, the polymerization rates varied in the following order:



It should be noted that all Lewis acids listed in Table 1 realized living cationic polymerization if combined with an appropriate added base. For example, several acids with medium activity induced living cationic polymerization in the presence of ethyl acetate (entry 4-12). With FeBr<sub>3</sub> and GaCl<sub>3</sub>, however, less controlled polymerizations occurred, completed in a second under these reaction conditions. Combining these highly active acids with THF, in turn, led to well-controlled polymerization reactions (entry 13 and 14).

### Conclusions

This study demonstrated that living cationic polymerization of vinyl ethers can be achieved using a wide variety of Lewis acids in the presence of an added base. The new development of initiating systems using common metal halides would expand the versatility of living cationic polymerization of vinyl monomers.

**Table 1.** Cationic polymerization of IBVE with various Lewis acids in the presence of an added base

entry	Lewis Acid	Added Base	Time	Conv. (%)	$M_n$	$M_w/M_n$
1	FeBr <sub>3</sub>	EA	0.5 s	96	8000	1.71
2	GaCl <sub>3</sub>	EA	0.6 s	80	11000	1.38
3	FeCl <sub>3</sub>	EA	0.8 s	96	18200	1.34
4	SnCl <sub>4</sub>	EA	70 s	92	16200	1.03
5	InCl <sub>3</sub>	EA	7 m	92	19000	1.03
6	ZnCl <sub>2</sub>	EA	20 m	94	17000	1.05
7	AlCl <sub>3</sub>	EA	5 h	96	18000	1.10
8	HfCl <sub>4</sub>	EA	6 h	93	15500	1.09
9	ZrCl <sub>4</sub>	EA	6 h	92	12700	1.06
10	EtAlCl <sub>2</sub>	EA	22 h	93	18900	1.06
11	BiCl <sub>3</sub>	EA	30 h	90	14200	1.11
12	TiCl <sub>4</sub>	EA	120 h	97	12600	1.02
13	FeBr <sub>3</sub>	THF	30 m	95	18600	1.09
14	GaCl <sub>3</sub>	THF	35 m	93	19100	1.08
15	FeCl <sub>3</sub>	DO	15 s	96	18200	1.06
16	SiCl <sub>4</sub>	DO	336 h	66	8900	1.06*
17	GeCl <sub>4</sub>	DO	336 h	46	6500	1.04

In toluene at 0 °C. [IBVE]<sub>0</sub> = 0.76 M, [Lewis acid]<sub>0</sub> = 5.0 mM, [HCl-IBVE]<sub>0</sub> = 4.0 mM, [added base] = 1.0 M. EA: ethyl acetate, DO: 1,4-dioxane. \*For the main peak.

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