Living cationic polymerization of isobutyl vinyl ether initiated by the trimethylsilyl iodide/zinc iodide system*

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SUMMARY
Trimethylsilyl iodide in conjunction with zinc iodide (Me3SiI/ZnI2) as an initiating system led to living cationic polymerization of isobutyl vinyl ether in toluene at 0 or -40°C or in methylene chloride at -40°C (ZnI2 was dissolved in acetone). The number-average molecular weight of the polymers was directly proportional to monomer conversion and in excellent agreement with the calculated value assuming that one polymer chain forms per unit trimethylsilyl iodide. At room temperature (+25°C), however, the polymerization failed to give perfectly living polymers; the polymer molecular weight was smaller than the calculated value. On addition of a fresh feed of monomer at the end of the polymerization at -40°C, the added feed was smoothly polymerized at nearly the same rate as in the first stage, and the polymer molecular weight continued to increase in direct proportion to monomer conversion. Throughout the reaction, the molecular weight distribution of the polymers stayed very narrow (Mw/Mn < 1.1).

INTRODUCTION
Recently, we found that hydrogen iodide-based initiating systems such as HI/I2 (1) and HI/ZnI2 (2) effectively polymerize vinyl ethers and p-methoxystyrene (3) to yield living polymers with a controlled molecular weight and a narrow molecular weight distribution (MWD). In these living polymerizations (Scheme I), hydrogen iodide quantitatively adds to the vinyl monomers to form adducts (1; R = H) which, as the initiating species, start living propagation via electrophilic activation of their carbon-iodine bonds by iodine (4) or zinc iodide (2) as the activators.

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\begin{align*}
RI + CH_2-CH-Y & \rightarrow R-CH_2-CH-I \quad \text{(or } I_2) \quad \rightarrow R-CH_2-CH-I \cdots ZnI_2 \\
nCH_2=CH-Y & \rightarrow R\{CH_2-CH\}_nCH_2-CH-I \cdots ZnI_2 \\
\end{align*}
\]

Scheme 1

* Living cationic polymerization of vinyl ethers by electrophile/Lewis acid initiating systems, part 2. For part 1 see ref. 2
In this study, we employed trimethylsilyl iodide (iodotrimethylsilane; Me₃SiI) as an equivalent of hydrogen iodide in the HI/I₂ and HI/ZnI₂ initiating systems. Since the trimethylsilyl group is generally regarded as "bulky proton" (5), Me₃SiI may form with a vinyl monomer an initiating adduct (I; R = Me₃Si) that carries a potentially reactive carbon-iodine linkage. Me₃SiI and related trialkylsilyl compounds have been used widely as electrophiles in organic synthesis (5-7) but very little as initiators for cationic polymerization. An example of the latter category was reported by Gong and Hall who used trialkylsilyl trifluoromethanesulfonates to polymerize cationically N-vinylcarbazole, p-methoxystyrene, and related vinyl or oxacyclic monomers (8); none of these polymerizations are living, however.

We investigated in this study the possibility of living cationic polymerization of isobutyl vinyl ether (IBVE) initiated by the Me₃SiI/ZnI₂ system.

RESULTS AND DISCUSSION

Living Polymerization of IBVE by Me₃SiI/ZnI₂

IBVE was polymerized by the Me₃SiI/ZnI₂ initiating system (5:1 molar ratio) in toluene at +25, 0, and -40°C. Me₃SiI and ZnI₂ were added into a monomer solution as an n-hexane and acetone solutions, respectively (see below). As shown in Figure 1, a quantitative polymerization occurred smoothly without an induction phase at all temperatures. Under the conditions shown in Figure 1, the reaction was completed in 20 min at +25°C, in 80 min at 0°C, and in 28 hr at -40°C. The polymerization mixtures remained

![Figure 1](image-url)

Figure 1. Time-conversion curves for the polymerization of IBVE with Me₃SiI/ZnI₂ in toluene at -40 (○), 0 (●), and +25°C (●): [IBVE]₀ = 0.38 M; [Me₃SiI]₀ = 5.0 mM; [ZnI₂]₀ = 1.0 mM.