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Living Cationic Polymerization of Isobutyl Vinyl Ether by Me_3SiI/Lewis Acid Systems in the Presence of Acetone: Initiation via a Silyloxycarbocation[1]

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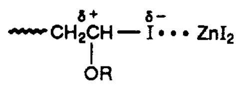
ABSTRACT: In the presence of acetone, the trimethylsilyl iodide/zinc iodide (Me_3SiI/ZnI_2) initiating system induced living cationic polymerization of isobutyl vinyl ether in toluene below 0 °C. The number-average molecular weight ($\bar{M}_n$) of the polymers was directly proportional to monomer conversion and in excellent agreement with the calculated value, assuming that one polymer chain forms per Me_3SiI molecule. Accordingly, the $\bar{M}_n$ values (at 100% conversion) were inversely proportional to the initial concentration of Me_3SiI but were independent of the initial ZnI_2 concentration; the molecular weight distribution of the polymers stayed very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) throughout the reaction. The rate of the living polymerization was in first order with respect to monomer, Me_3SiI, and ZnI_2, respectively. When iodine (I_2) was used instead of ZnI_2, living cationic polymerization also occurred in toluene at −40 °C. Thus, in the presence of acetone, the Me_3SiI/Lewis acid (ZnI_2 or I_2) system mediated a new type of living cationic polymerization where the initiation is via a silyloxycarbocation ($Me_3SiOC^+Me_2 \cdot I^-$) that is generated by a reaction of Me_3SiI with acetone. The product polymers were shown to carry one silyloxyl terminal group per chain, the acidolysis of which gave a hydroxyl terminal group.

Introduction

Trimethylsilyl iodide (Me_3SiI) and related trialkylsilyl compounds have been used widely as electrophilic reagents in organic synthesis;[2] the trialkylsilyl group is often equivalent in function to a proton (thus called a "bulky proton"). Although this similarity suggests that the organosilicon compounds may initiate cationic polymerization, it is indeed recently that trimethylsilyl trifluoromethanesulfonate[3] and methanesulfonate[4] have been employed to polymerize isobutyl vinyl ether (IBVE), styrene, and other cationically polymerizable vinyl and oxacyclic monomers.[3,4]

In a recent preliminary paper,[5] we have reported that trimethylsilyl iodide (Me_3SiI), in conjunction with zinc iodide (ZnI_2), leads to living cationic polymerization of IBVE in toluene below 0 °C. An initiating system closely related to the Me_3SiI/ZnI_2 combination is a binary mixture of hydrogen iodide and zinc iodide (HI/ZnI_2), and the Me_3SiI/ZnI_2 system has been designed to replace the hydrogen iodide in HI/ZnI_2 with Me_3SiI.[6,7] In fact, the living polymerizations by the two initiating systems exhibit very similar characteristics; i.e., the number-average molecular weights ($\bar{M}_n$) of the produced polymers increase in direct proportion to monomer conversion, with the molecular weight distribution (MWD) very narrow, and they are in excellent agreement with the calculated values, assuming that one polymer chain forms per Me_3SiI or hydrogen iodide molecule.

It has thus been demonstrated that living cationic polymerization can be achieved by combining an electrophile, not only hydrogen iodide but Me_3SiI as well, with an appropriate Lewis acid like ZnI_2. The living propagating species therein is most likely represented as 1, which bears a carbon–iodine terminal bond that is originated from hydrogen iodide or Me_3SiI and is electrophilically activated by ZnI_2.[6,7] The generation of 1 in the polymerization by Me_3SiI/ZnI_2, however, has not been confirmed yet.



$$\sim\!\sim\!\sim CH_2\underset{OR}{\overset{\delta+}{C}}H-\overset{\delta-}{I}\cdots ZnI_2$$

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Though apparently similar to the hydrogen iodide based counterpart, however, the Me_3SiI/ZnI_2 system was unique in one aspect:[5] Unlike hydrogen iodide, Me_3SiI needs acetone for quantitative initiation, a fact that implies that acetone plays an important yet unknown role in the initiation step of this process. In this study, we investigated in detail the kinetics and initiation mechanism of the Me_3SiI/ZnI_2-mediated living polymerization of IBVE, along with the role of acetone therein.

Results and Discussion

1. Kinetics. The kinetics of the IBVE polymerization by Me_3SiI/ZnI_2 was studied and compared with that by HI/ZnI_2 to clarify the mechanism of this living process; unless otherwise specified; the polymerization mixture contained acetone (5.0 vol %, 680 mM; in large molar excess over Me_3SiI and ZnI_2) that was used to dissolve ZnI_2 (see the Experimental Section).

Effects of Concentrations of Me_3SiI and ZnI_2. Two series (A and B) of kinetic study were performed in toluene at −40 °C to see how polymerization rate depends on the concentrations of Me_3SiI and ZnI_2 in the presence of excess acetone. In series A, the initial concentrations of the monomer ($[M]_0$) and zinc iodide ($[ZnI_2]_0$) were kept constant, whereas that of trimethylsilyl iodide ($[Me_3SiI]_0$) was varied. In series B, constant $[M]_0$ and $[Me_3SiI]_0$ were employed with varying $[ZnI_2]_0$.

Quantitative polymerizations occurred without an induction phase at all concentrations, and the rate increased with increasing $[Me_3SiI]_0$ or $[ZnI_2]_0$. Figure 1 shows the logarithmic conversion data, $\log([M]_0/[M])$ ($[M]$ is the monomer concentration at time t), plotted against t. In both series A and B, the polymerization proved to be of first order with respect to monomer:

$$-d[M]/dt = k[M] \qquad (1)$$

The first-order rate constant, k, was directly proportional to either $[Me_3SiI]_0$ or $[ZnI_2]_0$ (Figure 2); i.e.

$$-d[M]/dt \propto [M][Me_3SiI]_0[ZnI_2]_0 \qquad (2)$$

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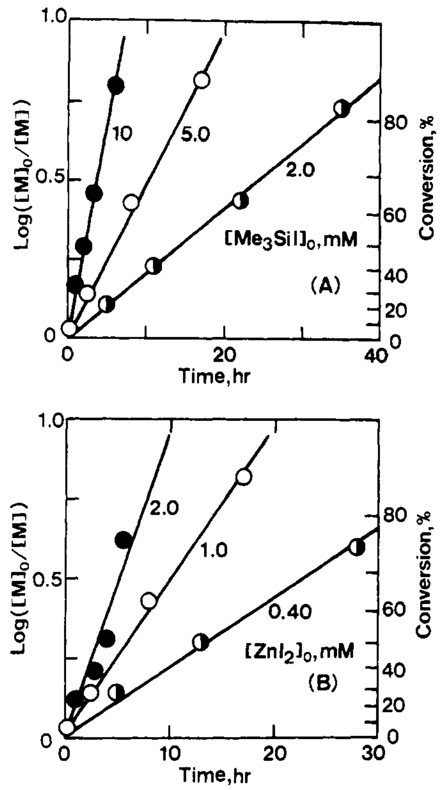


Figure 1. First-order plots for the IBVE polymerization by Me_3SiI/ZnI_2 in toluene at −40 °C at variable Me_3SiI (A) or ZnI_2 (B) concentrations: (A) $[M]_0$ = 0.38 M; $[ZnI_2]_0$ = 1.0 mM; $[Me_3SiI]_0$ = 10 (●), 5.0 (○), 2.0 (◑) mM; (B) $[M]_0$ = 0.38 M; $[Me_3SiI]_0$ = 5.0 mM; $[ZnI_2]_0$ = 2.0 (●), 1.0 (○), 0.40 (◑) mM. ZnI_2 was dissolved in acetone (0.25 mL).

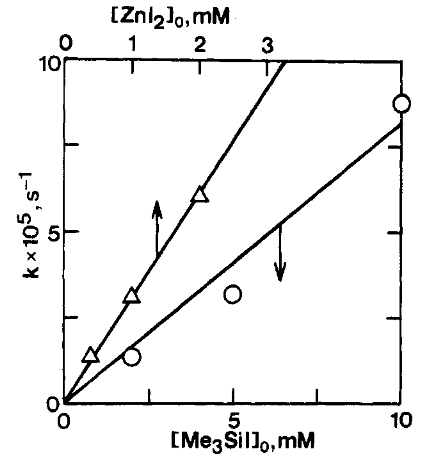


Figure 2. First-order rate constant, k (eq 1), for the IBVE polymerization by Me_3SiI/ZnI_2 in toluene at −40 °C, as a function of $[Me_3SiI]_0$ (○) or $[ZnI_2]_0$ (△): $[M]_0$ = 0.38 M; $[Me_3SiI]_0$ = 2.0–10 mM; $[ZnI_2]_0$ = 0.40–2.0 mM; data from Figure 1.

A similar relation ($-d[M]/dt \propto [M][HI]_0[ZnI_2]_0$) holds in the polymerization by the HI/ZnI_2 initiating system.[7]

The Me_3SiI/ZnI_2-initiated polymerizations were living irrespective of the variations in $[Me_3SiI]_0$ (series A) and $[ZnI_2]_0$ (series B). In both series, the MWDs were very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) (Figure 3), and the $\bar{M}_n$'s of the produced polymers were directly proportional to monomer conversion (see Figure 3B, for example). The $\bar{M}_n$ values are inversely proportional to $[Me_3SiI]_0$ (Figure 3A; conversion = 100%; constant $[ZnI_2]_0$) but are independent of $[ZnI_2]_0$ (Figure 3B; constant $[Me_3SiI]_0$). Though based on a polystyrene calibration, they are invariably in excellent agreement with the calculated values, assuming that one living polymer forms per Me_3SiI molecules (diagonal solid lines, Figure 3A,B).

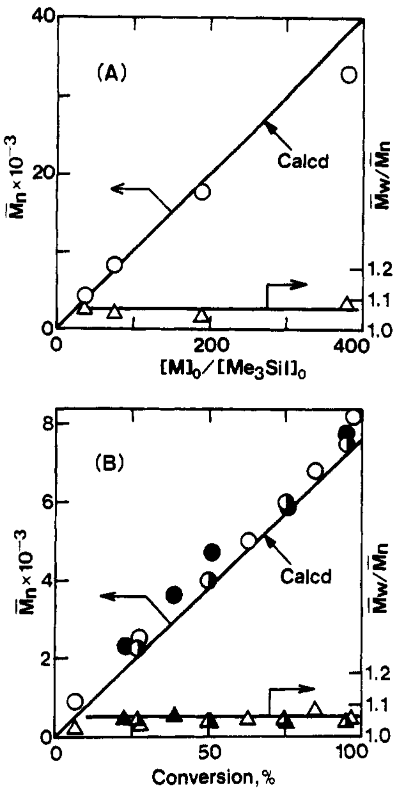


Figure 3. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of poly(IBVE) obtained with Me_3SiI/ZnI_2 in toluene at −40 °C at variable Me_3SiI (A) or ZnI_2 (B) concentrations: (A) plotted against the $[M]_0/[Me_3SiI]_0$ ratio, $[M]_0$ = 0.38 M, $[Me_3SiI]_0$ = 1.0–10 mM, $[ZnI_2]_0$ = 1.0 mM, conversion = 100%; (B) plotted against conversion, $[M]_0$ = 0.38 M, $[Me_3SiI]_0$ = 5.0 mM, $[ZnI_2]_0$ = 2.0 (●), 1.0 (○), 0.40 (◑) mM. The diagonal solid lines indicate the calculated $\bar{M}_n$, assuming the formation of one living polymer per Me_3SiI molecule. ZnI_2 was dissolved in acetone (0.25 mL).

These kinetic data indicate that Me_3SiI acts as an initiator, which generates the initiating species, while ZnI_2 serves as an activator, which triggers its propagation (cf. formula 1). A similar conclusion has been reached for the HI/ZnI_2 system, where hydrogen iodide is an initiator like Me_3SiI.[7]

Comparison with HI/ZnI_2. Because of the observed similarity in kinetics, the living IBVE polymerizations by Me_3SiI/ZnI_2 and by HI/ZnI_2 were then compared under the same reaction conditions, i.e., at the same reagent concentrations ($[Me_3SiI]_0 = [HI]_0$ = 5.0 mM) in toluene at −40 °C in the presence of 5.0 vol % acetone (680 mM; solvent for ZnI_2; see the Experimental Section).

As summarized in Figure 4, both initiating systems induced polymerizations that are living and almost identical in terms of overall rate (Figure 4A), polymer molecular weight, and MWD (Figure 4B). The $\bar{M}_n$ values increased in direct proportion to monomer conversion and were in excellent agreement with the calculated values (the diagonal solid line), assuming that one polymer chain forms per Me_3SiI or hydrogen iodide molecule; and the MWDs were very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) throughout the reactions. These agreements show the polymerizations by Me_3SiI/ZnI_2 and HI/ZnI_2 to proceed via a common propagating species (1; see below).

Polymerization by Me_3SiI/I_2: Effect of the Lewis Acid Component. It has already been demonstrated that when coupled with hydrogen iodide, not only ZnI_2 but iodine as well induce living cationic polymerizations of vinyl ethers.[8] With use of iodine as a Lewis acid, therefore, the Me_3SiI-mediated polymerization of IBVE was carried out in toluene at −40 °C; as with ZnI_2, iodine was employed as an acetone solution.

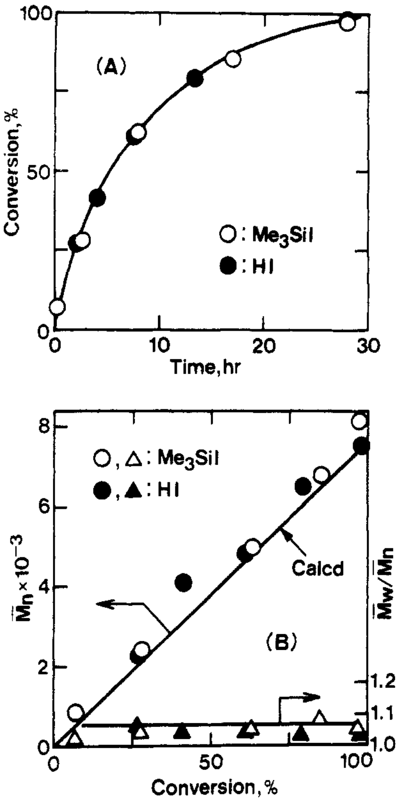


Figure 4. Time–conversion curves for the polymerizations of IBVE by Me_3SiI/ZnI_2 (○) and HI/ZnI_2 (●) in toluene at -40 °C (A); $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of poly(IBVE) obtained with Me_3SiI/ZnI_2 (○,△) and HI/ZnI_2 (●,▲) (B): $[M]_0 = 0.38$ M; $[Me_3SiI]_0 = [HI]_0 = 5.0$ mM; $[ZnI_2]_0 = 1.0$ mM. ZnI_2 was dissolved in acetone (0.25 mL). The diagonal solid line in (B) indicates the calculated $\bar{M}_n$, assuming the formation of one living polymer per Me_3SiI or HI molecule.

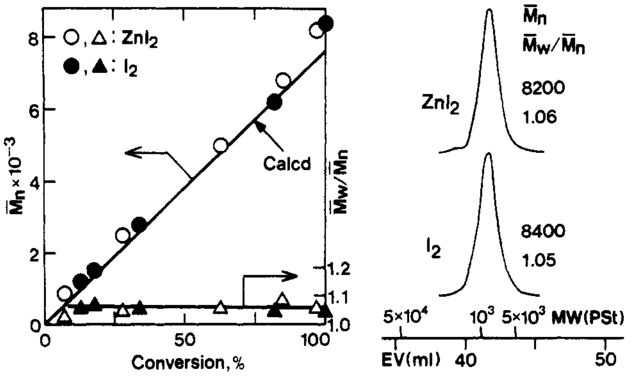


Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(IBVE) obtained with Me_3SiI/ZnI_2 (○,△) and Me_3SiI/I_2 (●,▲) in toluene at -40 °C: $[M]_0 = 0.38$ M; $[Me_3SiI]_0 = 5.0$ mM; $[ZnI_2]_0 = [I_2]_0 = 1.0$ mM. ZnI_2 and I_2 were dissolved in acetone (0.25 mL). Conversions for MWD ≃ 100%. The diagonal solid line indicates the calculated $\bar{M}_n$, assuming the formation of one living polymer per Me_3SiI molecule.

The polymerization by the Me_3SiI/I_2 system occurred without an induction phase and was completed in 30 h. As in the case with Me_3SiI/ZnI_2, the $\bar{M}_n$ values of the polymers were directly proportional to monomer conversion and in excellent agreement with the calculated values, assuming that one polymer chain forms per Me_3SiI molecule (Figure 5). The MWDs stayed very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) throughout the polymerization. Thus, living IBVE polymerization is feasible with use of Me_3SiI in conjunction with iodine. This fact also indicates that Me_3SiI acts as an initiator in a similar manner to hydrogen iodide.

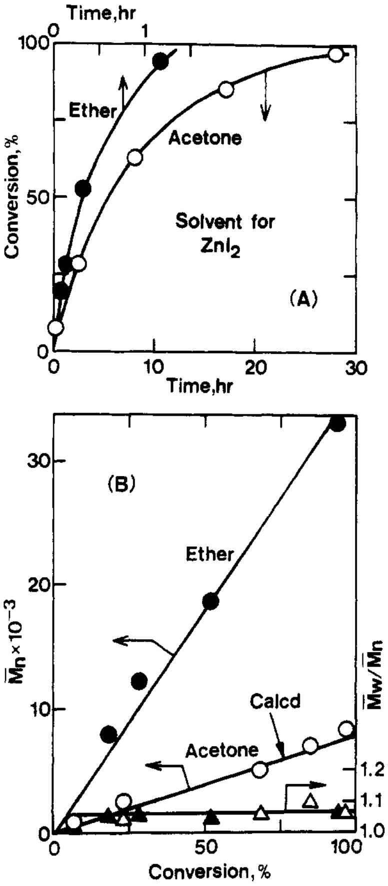


Figure 6. Effects of the solvent for ZnI_2 on the polymerizations of IBVE by Me_3SiI/ZnI_2 in toluene at -40 °C: $[M]_0 = 0.38$ M; $[Me_3SiI]_0 = 5.0$ mM; $[ZnI_2]_0 = 1.0$ mM. ZnI_2 was dissolved in acetone (0.25 mL) (○,△) or diethyl ether (0.50 mL) (●,▲). The "Calcd" solid line in (B) indicates the calculated $\bar{M}_n$, assuming the formation of one living polymer per Me_3SiI molecule.

2. Role of Acetone. Polymerization in the Absence of Acetone. ZnI_2 dissolves only in such polar solvents as acetone and diethyl ether, and in the kinetic study discussed in the preceding section, the zinc salt was used as an acetone solution. Because acetone, thus present in the reaction mixture, may affect the pathway of the Me_3SiI/ZnI_2-mediated living polymerization,[5] another series of experiments was carried out in toluene at -40 °C, where ZnI_2 was now dissolved in diethyl ether (10 vol % in the reaction mixture).

The polymerization with the ether solution was quantitative and ca. 20 times faster than that with the acetone solution (5.0 vol %) (Figure 6A). The MWDs of the product polymers were very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) throughout the reaction, and the $\bar{M}_n$ values increased in direct proportion to monomer conversion (Figure 6B). However, the $\bar{M}_n$'s were about 4 times as large as the calculated values, assuming that one polymer chain forms per Me_3SiI molecule; note that the use of the acetone solution of ZnI_2 led to $\bar{M}_n$ being in excellent agreement with the calculated molecular weights. In the absence of acetone, therefore, the initiation by Me_3SiI is not quantitative, although the overall polymerization rate is larger than that in the presence of acetone.

The effect of the solvents for the Lewis acid component was also studied in the IBVE polymerization by the Me_3SiI/I_2 system, where iodine (Lewis acid) was dissolved in acetone and diethyl ether as well as in toluene (unlike ZnI_2, iodine is soluble in this nonpolar solvent). The results are summarized in Table I, in terms of the livingness and initiation efficiency (based on a polymer's $\bar{M}_n$) of the

Table I
Living Polymerization of IBVE by Electrophile/Lewis Acid Initiating Systems: Effects of the Solvents for Lewis Acid on Livingness and Initiation Efficiency (f)[a]

initiating system		nature of growing species: solvent for Lewis acid		
electrophile	Lewis acid	acetone	ether	toluene
Me_3SiI	ZnI_2	living ($f = 1$)	living ($f < 1$)	b
Me_3SiI	I_2	living ($f = 1$)	long-lived[c] ($f < 1$)	long-lived[c] ($f < 1$)
HI	ZnI_2	living ($f = 1$)	living ($f = 1$)	b
HI	I_2	living ($f = 1$)	living ($f = 1$)	living ($f = 1$)

[a] $[M]_0 = 0.38$ M; $[\text{electrophile}]_0 = 5.0$ mM; $[\text{Lewis acid}]_0 = 1.0$ mM; in toluene at −40 °C. Initiation efficiency $f = [\text{polymer chain}]/[\text{electrophile}]_0$; the [polymer chain] was determined from $\bar{M}_n$ by SEC. [b] Not studied because of the insolubility of ZnI_2 in toluene. [c] "Long-lived" indicates a polymerization where the $\bar{M}_n$ of the polymer initially increases with monomer conversion but then levels off during the later stages.

polymerization. Living polymerization through quantitative initiation from Me_3SiI was feasible specifically when an acetone solution of iodine was employed (100% conversion after ca. 2 days). In contrast, the use of diethyl ether and toluene resulted in much slower polymerizations, completed after ca. 25 days, where the $\bar{M}_n$ of the polymers indeed increased with conversion but was consistently higher than the calculated value and leveled off during the later stages (thus indicated as "long-lived" in Table I). Thus, acetone was also required for quantitative initiation by Me_3SiI/I_2.

Such a specific effect of acetone, however, was absent in the corresponding polymerizations by HI/ZnI_2 and HI/I_2 (Table I). As long as hydrogen iodide was employed in place of Me_3SiI, living polymerization *and* quantitative initiation (from hydrogen iodide) were attained irrespective of the solvents for the Lewis acid components (ZnI_2 and iodine). Inspection of Table I shows, therefore, that acetone is primarily needed not for living propagation but for quantitative initiation from Me_3SiI.

Effects of Acetone Concentration. The critical role of acetone for the Me_3SiI/ZnI_2 (or Me_3SiI/I_2) system was further demonstrated in the polymerizations carried out in toluene at −40 °C at its varying concentrations [0–680 mM (0–5.0 vol %)]. In these experiments, ZnI_2 was added as a diethyl ether solution, whereas a predetermined amount of acetone was mixed in a monomer solution prior to initiation.

As shown in Figure 7, quantitative polymerizations occurred without an induction phase at all acetone concentrations, but they became progressively slower with increasing acetone dose. When acetone was in large excess over Me_3SiI (680 and 100 mM vs 5.0 mM), the $\bar{M}_n$ of the polymers increased in direct proportion to monomer conversion and agreed with the calculated values, assuming that one living chain forms per Me_3SiI molecule (Figure 8). The MWDs were very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) throughout the reactions. Living polymerizations via a quantitative initiation by Me_3SiI were thus feasible in the range of these concentrations of acetone.

At lower concentrations of acetone or in its absence (10–0 mM), on the other hand, the polymerizations were still apparently living (progressive and near linear increase in $\bar{M}_n$), but the polymer molecular weights clearly exceeded the calculated values (one polymer chain per Me_3SiI molecule); the lower the acetone concentration, the higher the molecular weight. The polymers maintained narrow

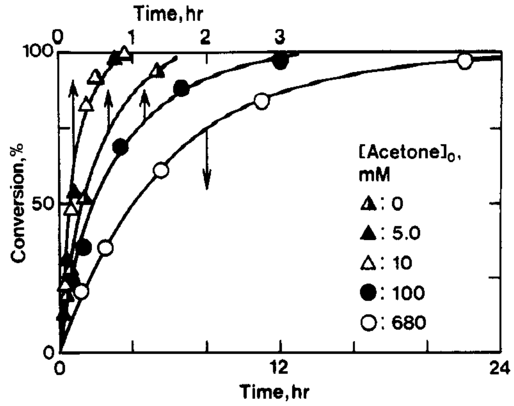


Figure 7. Time–conversion curves for the IBVE polymerization by Me_3SiI/ZnI_2 in toluene at −40 °C at variable acetone concentrations: $[M]_0 = 0.38$ M; $[Me_3SiI]_0 = 5.0$ mM; $[ZnI_2]_0 = 1.0$ mM; $[\text{acetone}]_0 = 0$ (▲), 5.0 (▲), 10 (△), 100 (●), 680 (○) mM. ZnI_2 was dissolved in Et_2O (0.50 mL).

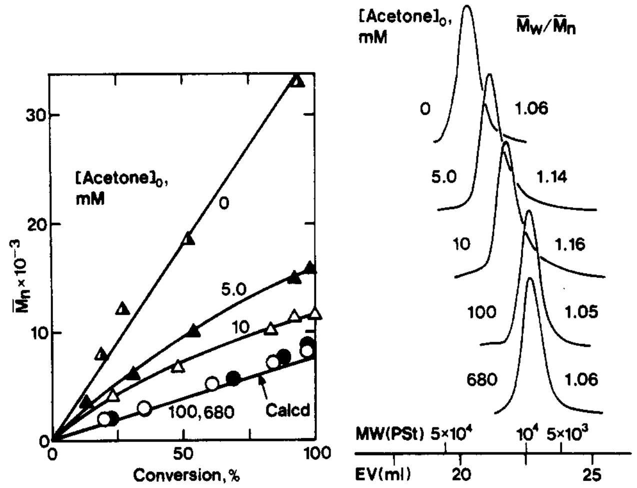


Figure 8. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(IBVE) obtained with Me_3SiI/ZnI_2 at variable acetone concentrations: $[\text{acetone}]_0 = 0$ (▲), 5.0 (▲), 10 (△), 100 (●), 680 (○) mM. See Figure 7 for reaction conditions. Conversions for MWD ≃ 100%. The "Calcd" solid line indicates the calculated $\bar{M}_n$, assuming the formation of one living polymer per Me_3SiI molecule.

MWDs similar to those for the higher acetone levels, although the MWDs for 5.0 and 10 mM acetone were slightly broader.

These results led to the following conclusions for the role of acetone in the Me_3SiI-mediated polymerization of IBVE: (1) The primary effect of acetone is on the initiation step, and it should be in large excess over Me_3SiI for the quantitative initiation from the silyl iodide. (2) The livingness of the polymerization is virtually unaffected by acetone. (3) Acetone decelerates the polymerization. Conclusion (2) implies, in turn, that acetone herein is *not* such an external Lewis base as esters and ethers, which are employed for the living cationic polymerization by cationogen/ethylaluminum dichloride initiating systems.[9] In those living processes, esters and ethers are directly responsible for the formation of living growing species that are nucleophilically stabilized by the Lewis bases. Conclusion (3) is attributed to the decrease in the effective concentration of ZnI_2, which results from complexation of ZnI_2 by acetone.

3. Polymerization Mechanism. End-Group Analysis. To clarify the initiation mechanism further, a sample of oligo(IBVE) ($\overline{DP}_n = 5$) was synthesized by the Me_3SiI/ZnI_2 initiating system in toluene at −40 °C in the presence of acetone ($[Me_3SiI]_0/[ZnI_2]_0/[\text{acetone}]_0 = 40/$

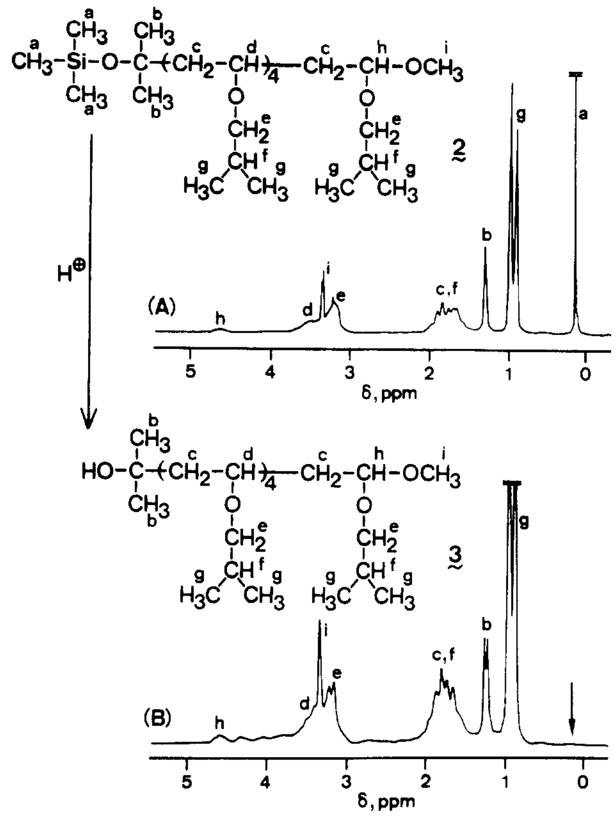


Figure 9. ^{1}H NMR spectra in $CDCl_3$: (A) 2 ($\overline{DP}_n$ = 5) obtained with Me_3SiI/ZnI_2 in toluene at −40 °C: $[M]_0$ = 0.20 M; $[Me_3SiI]_0$ = 40 mM; $[ZnI_2]_0$ = 2.0 mM. ZnI_2 was dissolved in acetone (0.25 mL). (B) 3 with an alcoholic end, obtained from sample (A).

Table II
$\overline{DP}_n$ and the Number of Terminal Groups per Chain for Oligo(IBVE) Obtained with Me_3SiI/ZnI_2[a]

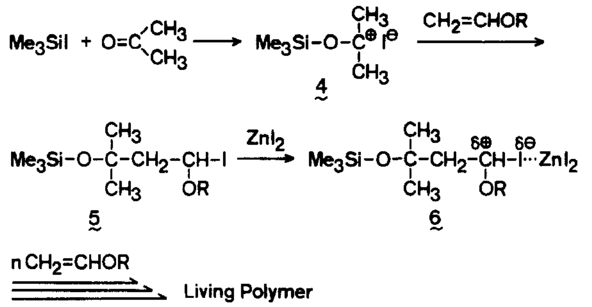
sample	$\overline{DP}_n$ calcd[b]	$\overline{DP}_n$ obsd[c]	terminal group Me_3Si-[d]	terminal group $-OCMe_2-$[e]
(A) before acidolysis	4.85	5.06	0.87	1.09
(B) after acidolysis	4.80	5.08	0	1.12

[a] See Figure 9 for synthetic conditions; analysis by ^{1}H NMR spectroscopy. [b] $\overline{DP}_n$(calcd) = $([M]_0/[Me_3SiI]_0)$(% convn/100). [c] Determined from the NMR peak intensity ratio of the pendant methyl (peak g) to the terminal methine (peak h) protons (Figure 9): $\overline{DP}_n$(obsd) = $g/6h$. [d] $a/9h$. [e] $b/6h$.

2.0/680 mM; conversion ≃ 100%), and the end group was analyzed by ^{1}H NMR spectroscopy (Figure 9A). In addition to signals c–g due to the IBVE repeat units, a singlet a appeared near 0 ppm, which is characteristic of a methyl group adjacent to silicon and assignable to the "head" $(CH_3)_3Si-$ group[10a] originated from Me_3SiI (structure 2 in the inset). The downfield signals h and i are assignable to the methine and the methoxide protons, respectively, of the terminal (tail) acetal[10b] that arises on quenching the living end with methanol. A distinctive absorption b at 1.2 ppm is attributed to the $-OC(CH_3)_2-$ group[10c] derived from acetone. These spectral data demonstrate that this oligomer has structure 2, which contains a Me_3Si- group and the acetone unit ($-OCMe_2-$) in the "head" terminal (or α-end).

As seen from Table IIA, the observed number-average degree of polymerization ($\overline{DP}_n$) of the oligomer, which was determined from the peak intensity ratio of the side-chain methyl group (peak g) to the terminal methine proton (peak h), is in good agreement with the calculated value, assuming one oligomer chain forms per Me_3SiI molecule. Integration of these NMR signals also showed that each oligomer chain possesses one acetone unit and nearly one Me_3Si- moiety. The slight loss of the silyl function (0.87 unit/chain) is apparently due to the elimination of the labile trimethylsilyloxyl group during workup (see below).

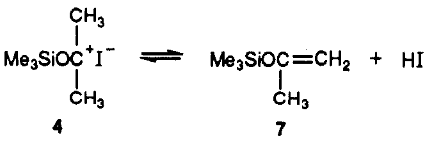
Scheme I



The terminal Me_3SiO- group was in fact easily converted into a hydroxyl group by treatment with a dilute acid; there was no change in the narrow and unimodal MWD of the sample. The ^{1}H NMR spectrum of the hydrolysis product is given in Figure 9B. After the acidolysis, the absorption a of the Me_3Si- group completely disappeared, but the acetone unit remained intact (one per chain; Table IIB). The splitting of the signal b into two peaks seems to be due to the fact that the methyl groups are now nonequivalent, as observed for related low molecular weight compounds.[10d]

Initiation Mechanism. On the basis of these kinetic studies and end-group analysis, we herein propose Scheme I for the initiation mechanism with the Me_3SiI/ZnI_2 initiating system. In the presence of excess acetone, Me_3SiI may react predominantly with the carbonyl oxygen of acetone rather than with the vinyl ether double bond. This selectivity is consistent with the much greater affinity of silicon for oxygen than for carbon.[2] The resulting silyloxy carbocation 4 in turn generates an initiating species 5 via addition to the vinyl ether. ZnI_2 then activates the carbon–iodine bond of 5 to trigger living polymerization that is mediated by species 6. It is worth noting that 6 has the same active site [~~~CH(OR)I···ZnI_2] as does the HI/ZnI_2-generated growing species 1.

The generation of the silyloxyl carbocation 4 and its analogues is well-known in the reaction of Me_3SiI with carbonyl compounds. Olah et al.[11] proposed, for example, that Me_3SiI adds to the carbonyl group of acetone to generate cation 4. The silyl iodide is also known to react with aldehydes to give iodohydrin trimethylsilyl ethers (Me_3SiI + O=CHR → $Me_3SiOCHRI$).[12] In some cases, however, cation 4 is not stable and decomposes into hydrogen iodide and the corresponding silyl enol ether 7 (eq 3), and in the



$$\underset{\mathbf{4}}{Me_3SiO\overset{CH_3}{\underset{CH_3}{C^+}}I^-} \rightleftharpoons \underset{\mathbf{7}}{Me_3SiO\underset{CH_3}{C}=CH_2} + HI \tag{3}$$

polymerization by Me_3SiI/ZnI_2, the resulting hydrogen iodide might initiate polymerization where enol ether 7 copolymerizes with IBVE to give Me_3SiO- groups in the polymers. This possibility, however, is excluded in our case, because the acetone units ($-OCMe_2-$) were found in the products (two methyl groups per chain; see Figure 9 and Table II).

Another experiment showed that in the presence of benzaldehyde the Me_3SiI/ZnI_2 initiating system mediates a living polymerization similar to that with acetone.[13] Because this aromatic aldehyde lacks α-protons and hence cannot form such an enol ether as **7**, this finding supports the mechanism where the polymerizations by Me_3SiI/ZnI_2 proceed via a silyloxycarbocation (like **4**) that is generated by the reaction of Me_3SiI with the carbonyl compound (acetone or benzaldehyde).

As already shown in Figure 7, the initiation from Me_3SiI is not quantitative in the absence of a carbonyl compound, but a living polymerization indeed occurs. According to ^{1}H NMR analysis, the produced poly(IBVE) ($\bar{M}_n = 3000$) possesses a methyl group [$CH_3CH(OiBu)-$] in the "head" terminal (α-end) and no Me_3Si- group at all in the chain. Though not conclusive yet, this fact suggests that the initiation occurs not by Me_3SiI itself but by a proton, most probably arising from hydrogen iodide, which is generated by the reaction of Me_3SiI with a protonic impurity (for example, adventitious water; $Me_3SiI + H_2O \rightarrow HI + Me_3SiOH$). Even in the presence of a small amount of acetone, silyloxyl carbocation **4** is difficult to form quantitatively, and the initiation by hydrogen iodide may not be negligible. The higher the acetone concentration, the higher the yield of silyloxyl carbocation **4**; accordingly, the initiation efficiency of Me_3SiI is 100% above a threshold concentration of acetone.

In conclusion, living cationic polymerization of vinyl ethers has been achieved by the use of Me_3SiI (electrophile) in conjunction with ZnI_2 (Lewis acid) and acetone (carbonyl compound). As an electrophile, Me_3SiI is in fact similar to hydrogen iodide in that both generate the iodide counteranion, but the silyl compound uniquely needs a carbonyl compound for quantitative initiation (Scheme I). Thus, the Me_3SiI/ZnI_2-mediated polymerization is a new type of polymerization via silyloxycarbocation **4** and its adduct **5** as initiating species. It is significant that perfect living cationic polymerization has become possible by the quantitative initiation through an in situ reaction of the initiator (Me_3SiI) with a compound (acetone) other than monomer. Furthermore, the terminal Me_3SiO- group of the product polymers can readily be converted into a hydroxyl group (cf. Figure 9), giving end-functional polymers of vinyl ethers with alcoholic functions.

Experimental Section

Materials. Me_3SiI (Tokyo Kasei, purity >99%) was used as received; the colorless liquid was dissolved in *n*-hexane (ca. 1 M), sealed under dry nitrogen in brown ampules with aluminum (Mitsuwa, metal rods, purity >99.999%) as a stabilizer, and stored in the dark in a freezer. ZnI_2 (Aldrich, purity >99.99%) was used as received; it was vacuum dried at least overnight just before use and transferred to a flask in a nitrogen-filled drybox. The subsequent handling of both light-sensitive iodides was done in the dark under dry nitrogen. Iodine was sublimed at 100 °C in the presence of potassium iodide, sealed in ampules under dry nitrogen, and stored in a refrigerator. IBVE (Tokyo Kasei) was washed with 10% aqueous sodium hydroxide solution and then water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride before use. Acetone was dried overnight with anhydrous magnesium sulfate and doubly distilled before use. Toluene, *n*-hexane, and diethyl ether as solvents, and *n*-heptane as an internal standard for gas chromatography, were purified by the usual methods and distilled at least twice over calcium hydride before use.[8]

Polymerization Procedures. Polymerizations were carried out under dry nitrogen in baked glass tubes each equipped with a three-way stopcock; the polymerization solution was 5.0 mL in volume. A typical example is given below. The reactions were initiated by adding, via dry syringes, prechilled solutions of Me_3SiI (in *n*-hexane; 0.50 mL) and ZnI_2 (in acetone; 0.25 mL) sequentially in this order into monomer solution (in toluene; 4.25 mL) kept at the polymerization temperature. The polymerizations by Me_3SiI/I_2, HI/ZnI_2, and HI/I_2 were performed in the same way. When ZnI_2 and I_2 were dissolved in diethyl ether, the added volume of this solution was 0.50 mL.

The concentration of Me_3SiI in the stock solution was determined by treating an aliquot (0.50 mL) with an excess of standard aqueous silver nitrate solution (0.10 N; 20 mL) and then back-titrating the unreacted silver ion with a standard solution of ammonium thiocyanate (0.10 N) in the presence of iron(III) ammonium sulfate as an indicator.

The polymerization was terminated with prechilled ammoniacal methanol. Monomer conversion was determined from its residual concentration measured by gas chromatography with *n*-heptane as an internal standard (equivalent in volume to monomer). The polymer yield by gravimetry was in good agreement with the gas-chromatographic conversion of the monomer.

The quenched reaction mixtures were washed with 10% aqueous sodium thiosulfate solution and then with water to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.

Hydrolysis of Oligomer 2. Silyloxy-capped oligomer **2** (120 mg; $\overline{DP}_n = 5$) was dissolved in a mixture of toluene (10 mL) and methanol (2 mL) and then 2 N hydrochloric acid (1 mL: 10 equiv to the Me_3SiO- units in the polymer) was added. The mixture was magnetically stirred overnight, washed with water, evaporated to dryness under reduced pressure, and vacuum dried to give oligomer **3** (100 mg; isolated yield $\simeq$ 90%).

Measurements. The MWD of polymers was measured by size-exclusion chromatography in chloroform at room temperature on a Jasco Trirotar-II chromatograph equipped with three polystyrene gel columns (Shodex AC-802 + A-804 + A-804 or K-802 + K-803 + K-804). The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the polymers were calculated from size-exclusion eluograms on the basis of a polystyrene calibration. ^{1}H NMR spectra were recorded in $CDCl_3$ at 30 °C on a Jeol FX-90Q or GSX-270 spectrometer. Oligomer samples for ^{1}H NMR spectroscopy were purified by preparative size-exclusion chromatography (Jasco Megapak polystyrene gel 201).

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