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

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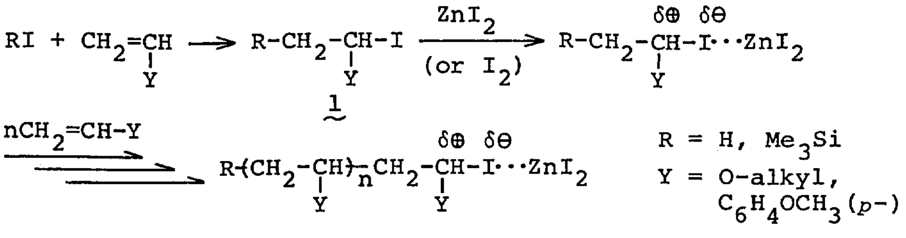
SUMMARY

Trimethylsilyl iodide in conjunction with zinc iodide (Me_3SiI/ZnI_2) 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 (ZnI_2 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 ($\bar{M}_w/\bar{M}_n <$ 1.1).

INTRODUCTION

Recently, we found that hydrogen iodide-based initiating systems such as HI/I_2 (1) and HI/ZnI_2 (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 ($\underset{\sim}{1}$; 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.



$$RI + \underset{\substack{|\\Y}}{CH_2{=}CH} \longrightarrow \underset{\substack{1\\\sim}}{R{-}CH_2{-}\underset{\substack{|\\Y}}{CH}{-}I} \xrightarrow[\text{(or } I_2)]{ZnI_2} R{-}CH_2{-}\underset{\substack{|\\Y}}{\overset{\delta\oplus}{CH}}{-}\overset{\delta\ominus}{I}\cdots ZnI_2$$

$$\xrightarrow{nCH_2{=}CH{-}Y} R{+}CH_2{-}\underset{\substack{|\\Y}}{CH}{+}_n CH_2{-}\underset{\substack{|\\Y}}{\overset{\delta\oplus}{CH}}{-}\overset{\delta\ominus}{I}\cdots ZnI_2$$

$R = H,\ Me_3Si$

$Y = O\text{-alkyl},\ C_6H_4OCH_3\,(p\text{-})$

Scheme 1

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* 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; Me_3SiI) as an equivalent of hydrogen iodide in the HI/I_2 and HI/ZnI_2 initiating systems. Since the trimethylsilyl group is generally regarded as "bulky proton" (5), Me_3SiI may form with a vinyl monomer an initiating adduct (1; R = Me_3Si) that carries a potentially reactive carbon-iodine linkage. Me_3SiI 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 Me_3SiI/ZnI_2 system.

RESULTS AND DISCUSSION

Living Polymerization of IBVE by Me_3SiI/ZnI_2

IBVE was polymerized by the Me_3SiI/ZnI_2 initiating system (5:1 molar ratio) in toluene at +25, 0, and -40°C. Me_3SiI and ZnI_2 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

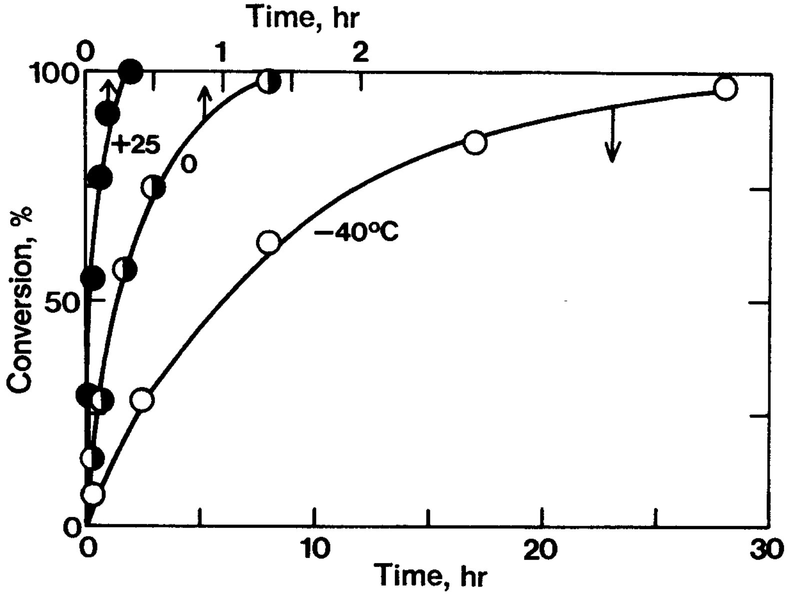

Figure 1. Time-conversion curves for the polymerization of IBVE with Me_3SiI/ZnI_2 in toluene at -40 (o), 0 (◑), and +25°C (●): $[IBVE]_0$ = 0.38 M; $[Me_3SiI]_0$ = 5.0 mM; $[ZnI_2]_0$ = 1.0 mM.

completely colorless and homogeneous throughout; Me_3SiI or ZnI_2 alone did not polymerize IBVE at all under these conditions.

Figure 2 plots the number-average molecular weights ($\bar{M}_n$) and polydispersity ratios ($\bar{M}_w/\bar{M}_n$) of the polymers thus obtained. The $\bar{M}_n$'s for -40°C increased in direct proportion to monomer conversion and, though based on a polystyrene calibration, they were in excellent agreement with the calculated values assuming that one polymer chain forms per unit Me_3SiI (the solid line in Figure 2). All of the polymers exhibited very narrow molecular weight distributions (MWD), maintaining the $\bar{M}_w/\bar{M}_n$ ratio well below 1.1 over the whole conversion range.

The polymerization at 0°C gave similar results to those for -40°C, although the $\bar{M}_n$'s were slightly smaller than the calculated values at high conversions. In contrast, the $\bar{M}_n$'s of the polymers obtained at +25°C apparently leveled off at the later stage of the polymerization where they were smaller than the calculated values for living polymers. The polymers also exhibited MWDs broader than those for the lower temperatures.

These facts show that the Me_3SiI/ZnI_2 initiating system induces living polymerization of IBVE in toluene at low temperatures below 0°C where one living chain is generated per unit Me_3SiI. Similar living processes proved possible in methylene chloride at -40°C.

Under the same conditions, the overall polymerization rate with the Me_3SiI/ZnI_2 system is almost the same as that with the HI/ZnI_2 counterpart (2). When the initial concentration of HI or Me_3SiI is kept constant, the overall rate increases with increasing initial ZnI_2 concentration, but the $\bar{M}_n$ of the polymers remains independent of the latter variable. At the same ZnI_2 concentration and monomer conversion, the $\bar{M}_n$ is inversely proportional

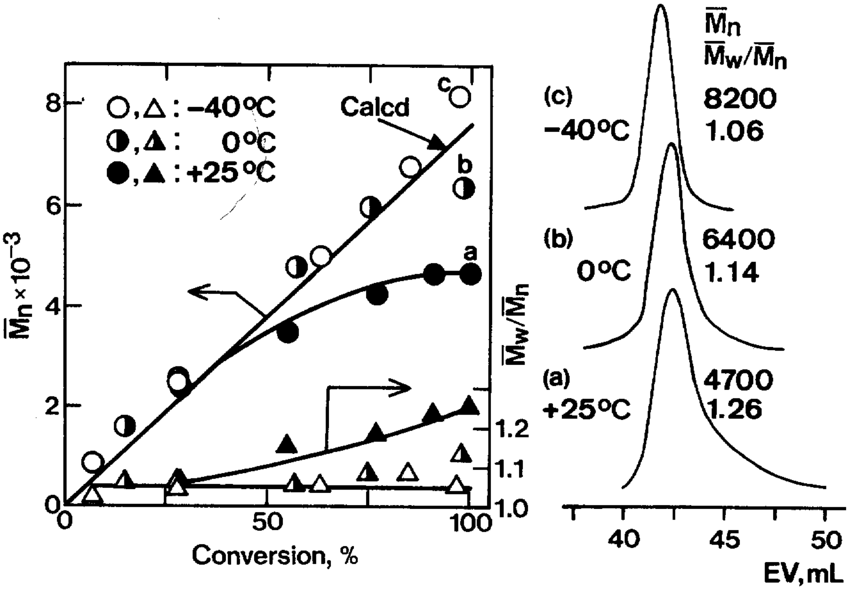

Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of poly(IBVE) obtained with Me_3SiI/ZnI_2 in toluene at -40 (o,Δ), 0 (◑,▲), and +25°C (●,▲): $[IBVE]_0$ = 0.38 M; $[Me_3SiI]_0$ = 5.0 mM; $[ZnI_2]_0$ = 1.0 mM. The same experiments as for Figure 1. MWD curves a, b, and c are for the samples corresponding to points a, b, and c in the $\bar{M}_n$-conversion profiles, respectively.

to the initial HI or Me_3SiI concentration. Therefore, ZnI_2 acts as an activator and both living processes apparently involve similar propagating species.

Separate experiments revealed that ZnI_2 should be dissolved in acetone to achieve the well-defined living polymerization by Me_3SiI/ZnI_2. Because ZnI_2 dissolves only in polar solvents (e.g., acetone, ether, and ethyl acetate), it turned out that selection of the solvent for this salt is one of the critical factors. For example, when the zinc salt was employed as a diethyl ether or ethyl acetate solution, living polymerization did occur in toluene at -40°C, but the polymer molecular weights were 3-4 times greater than the calculated values probably due to an imperfect initiation of Me_3SiI. This fact suggests the involvement of the polar solvent for ZnI_2 in the initiation and/or propagation processes.

Monomer-Addition Experiment

The living nature of the IBVE polymerization by Me_3SiI/ZnI_2 was further demonstrated by a so-called "monomer-addition" experiment in toluene at -40°C (Figure 3). Thus, a fresh feed of IBVE (0.38 M, equivalent to the first charge) was added to the reaction mixture when the initial supply of the monomer was polymerized completely. The added IBVE feed was smoothly polymerized at nearly the same rate as in the first stage. After the monomer addition, the polymer molecular weight increased in direct proportion to monomer conversion and was very close to the calculated value for living polymers (one polymer chain per unit Me_3SiI). The MWD of the polymers stayed very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) and free of tailing in the low molecular weight region.

In conclusion, this study has demonstrated that the Me_3SiI/ZnI_2 initiating system leads to living polymerization of IBVE.

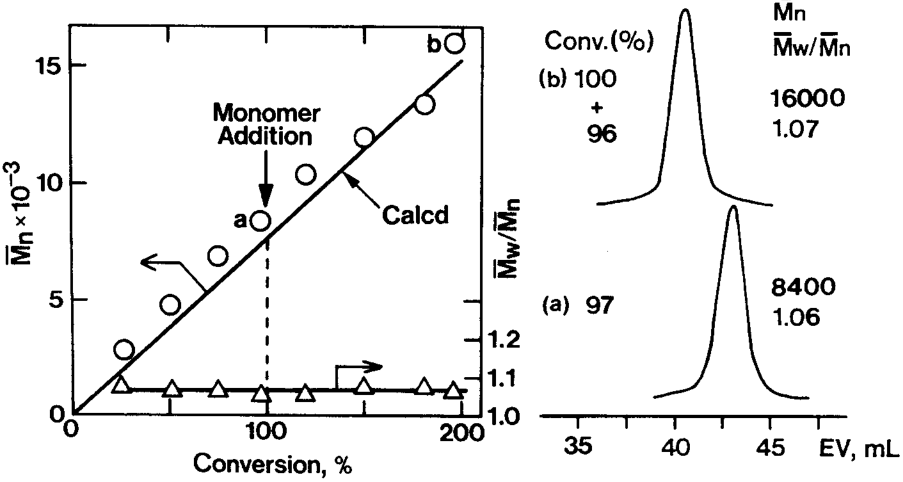

Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of poly(IBVE) obtained in a monomer-addition experiment in the polymerization by Me_3SiI/ZnI_2 in toluene at -40°C: $[IBVE]_0 = 0.38$ M; $[Me_3SiI]_0 = 5.0$ mM; $[ZnI_2]_0 = 1.0$ mM. The molar amount of the second IBVE feed was the same as in the first. MWD curves a and b are for the samples corresponding to points a and b in the $\bar{M}_n$-conversion profile, respectively.

EXPERIMENTAL

Materials

Me_3SiI (Tokyo Kasei) was used as received; the colorless liquid was dissolved in *n*-hexane (ca. 1 M), sealed in brown ampules under dry nitrogen, 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 dry box. The subsequent handling of both light-sensitive iodides was done in the dark under dry nitrogen. Acetone was dried overnight with anhydrous magnesium sulfate and doubly distilled before use. IBVE, toluene and *n*-hexane as solvents, and *n*-heptane as an internal standard for gas chromatography were purified by the usual methods (1) and distilled at least twice over calcium hydride before use.

Procedures

Polymerizations were carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. 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 a monomer solution [in toluene, 0.38 M (5.0 vol%); 4.25 ml] (2). The concentration of Me_3SiI in the stock solution was determined by the Volhard method. After a certain period, 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 (5.0 vol%). 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. The MWD of the polymers was measured by size-exclusion chromatography (SEC) in chloroform at room temperature on a JASCO Trirotar-II chromatograph equipped with three polystyrene gel columns (Shodex AC-802 and A-804 x 2). The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the polymers were calculated from SEC eluograms on the basis of a polystyrene calibration.

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