

Living cationic polymerization of isobutyl vinyl ether by the diphenyl phosphate/zinc iodide initiating system*

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SUMMARY

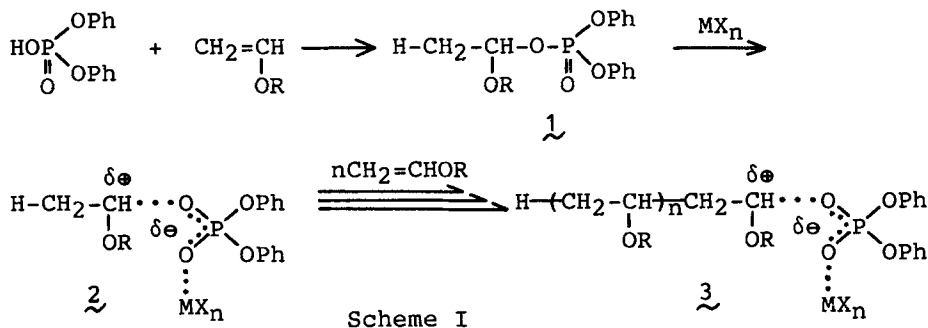
The first example of the living cationic polymerization of isobutyl vinyl ether via the phosphate counteranion has been achieved in toluene below 0°C with a new initiating system that consists of diphenyl phosphate and zinc iodide, $(C_6H_5O)_2P(O)OH/ZnI_2$. The number-average molecular weight of the polymers increased in direct proportion to monomer conversion, and was in excellent agreement with the calculated value assuming that one polymer chain forms per unit diphenyl phosphate. On addition of a fresh feed of monomer at the end of the polymerization, the added feed was smoothly polymerized at nearly the same rate as in the first stage, and the polymer molecular weight further increased in direct proportion to monomer conversion. Throughout the reaction, the molecular weight distribution of the polymers stayed very narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$). At room temperature (+25°C), however, the molecular weight distribution of the polymers slightly broadened ($\bar{M}_w/\bar{M}_n \sim 1.2$) at high conversions where the polymer molecular weight became smaller than the calculated value. Evidently, the $(C_6H_5O)_2P(O)OH/ZnI_2$ system indeed generates a propagating species of a long lifetime at room temperature, but the perfectly living polymerization by this system operates below 0°C.

INTRODUCTION

We have recently found that adequate combinations of an electrophile and a Lewis acid lead to initiating systems for living cationic polymerizations of vinyl ethers (1,2) and *p*-methoxystyrene (3). These initiating systems include HI/I₂ (1), HI/ZnX₂ or SnX₂ (X = I, Br, Cl) (2,3,4) and Me₃SiI/ZnI₂ (5), where HI or Me₃SiI, as the electrophile, generates the propagating species with a terminal C-I bond that is in turn activated by the Lewis acid (I₂, ZnX₂, or SnX₂) to commence the living polymerization.

In this study, we employed diphenyl phosphate [(PhO)₂P(O)OH] as an electrophile instead of HI or Me₃SiI. (PhO)₂P(O)OH and related phosphoric diesters were reported to add to vinyl ethers, giving adducts (e.g., 1, Scheme I) (6), and they are also used for the oligomerization of styrene derivatives (7). As yet, however, these diesters of phosphoric acid have not been employed for cationic polymerization in general and for living cationic polymerization in particular. On the analogy of the polymerization initiated by the HI/I₂ initiating system, it is expected that (PhO)₂P(O)OH quantitatively adds to vinyl monomers to form adducts 1 which, as the initiating species, may start living propagation via electrophilic activation of their C-OP(O)(OPh)₂ bonds (see 2) by adequate Lewis acids MX_n (Scheme I).

* Living cationic polymerization of vinyl ethers by electrophile/Lewis acid initiating systems, part 4. For part 3, see ref. 4



If this initiating system induces living cationic polymerization, it will then provide the first example of living processes via a propagating species (3) bearing the phosphate counteranion. Furthermore, $(\text{PhO})_2\text{P}(\text{O})\text{OH}$, commercially available and easy to handle, offers advantages over hydrogen iodide, which is a highly volatile and corrosive gas at room temperature.

In this study, we thus investigated the possibility of living cationic polymerization of isobutyl vinyl ether (IBVE) initiated by the $(\text{PhO})_2\text{P}(\text{O})\text{OH}/\text{ZnI}_2$ system.

RESULTS AND DISCUSSION

Living Polymerization of IBVE by $(\text{PhO})_2\text{P}(\text{O})\text{OH}/\text{ZnI}_2$

IBVE was polymerized by the $(\text{PhO})_2\text{P}(\text{O})\text{OH}/\text{ZnI}_2$ initiating system (1:1

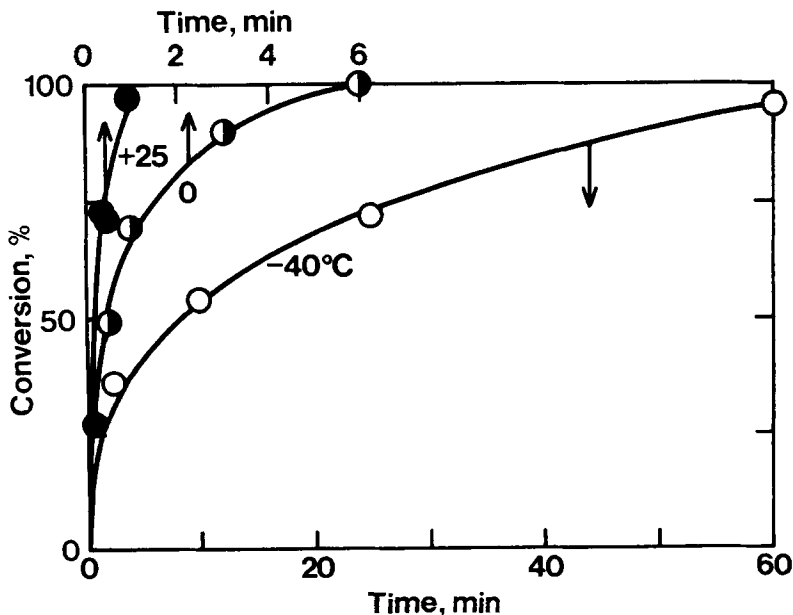


Figure 1. Time-conversion curves for the polymerization of IBVE with $(\text{PhO})_2\text{P}(\text{O})\text{OH}/\text{ZnI}_2$ in toluene at -40°C (○), 0°C (●), and $+25^\circ\text{C}$ (●): $[\text{IBVE}]_0 = 0.38 \text{ M}$; $[(\text{PhO})_2\text{P}(\text{O})\text{OH}]_0 = 5.0 \text{ mM}$; $[\text{ZnI}_2]_0 = 5.0 \text{ mM}$.

molar ratio) in toluene at +25, 0, and -40°C. Figure 1 shows the time-conversion curves. The polymerization was initiated by adding a solution of ZnI_2 (in diethyl ether) into a quiescent mixture of IBVE and $(\text{PhO})_2\text{P}(\text{O})\text{OH}$. At all temperatures, a rapid and quantitative polymerization occurred without an induction phase. The overall rate of polymerization was smaller than that with HI/ZnI_2 otherwise under the same conditions. At +25 and 0°C, the polymerization mixture remained completely colorless and homogeneous throughout, whereas at -40°C it became slightly cloudy as the polymerization proceeds; $(\text{PhO})_2\text{P}(\text{O})\text{OH}$ or ZnI_2 alone did not polymerize IBVE under the conditions shown in Figure 1.

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 values for -40 and 0°C were directly proportional 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 $(\text{PhO})_2\text{P}(\text{O})\text{OH}$ (the solid line in Figure 2). The MWDs of the polymers all stayed very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) over the whole conversion range.

The \bar{M}_n 's of the polymers obtained at +25°C also increased almost in direct proportion to monomer conversion below ca. 80%. At higher conversions, however, they became slightly smaller than the calculated values and, correspondingly, the MWDs broadened slightly ($\bar{M}_w/\bar{M}_n \sim 1.2$).

These facts show that the $(\text{PhO})_2\text{P}(\text{O})\text{OH}/\text{ZnI}_2$ initiating system induces the well-defined living polymerization of IBVE in toluene at temperatures below 0°C. The polymerization at +25°C evidently involves a long-lived growing species, but is not perfectly living; the optimization of reaction conditions for this higher temperature is now under way.

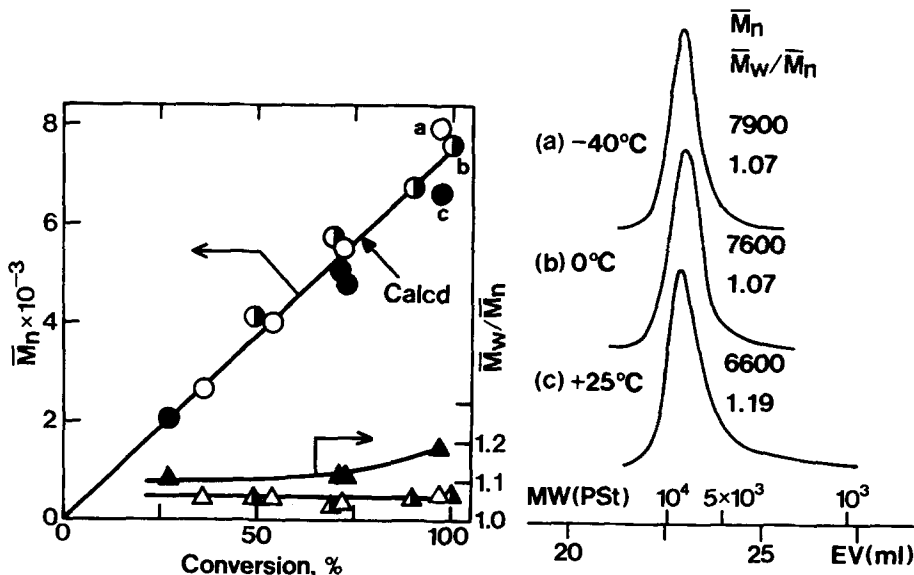


Figure 2. \bar{M}_n , \bar{M}_w/\bar{M}_n , and MWD of poly(IBVE) obtained with $(\text{PhO})_2\text{P}(\text{O})\text{OH}/\text{ZnI}_2$ in toluene at -40 (○,△), 0 (●,▲), and +25°C (●,▲): $[\text{IBVE}]_0 = 0.38 \text{ M}$; $[(\text{PhO})_2\text{P}(\text{O})\text{OH}]_0 = 5.0 \text{ mM}$; $[\text{ZnI}_2]_0 = 5.0 \text{ mM}$. 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.

Monomer-Addition Experiments

In order to demonstrate further the living nature of the IBVE polymerization by $(\text{PhO})_2\text{P}(\text{O})\text{OH}/\text{ZnI}_2$, a fresh feed of IBVE (0.38 M, equivalent to the first charge) was added to the reaction mixture where the initial supply of the monomer was polymerized completely in toluene at -40 , 0 , or $+25^\circ\text{C}$. Independent of the temperature, the added IBVE feed was smoothly polymerized at nearly the same rate as in the first stage. Even after the monomer addition, the polymer molecular weights for -40 and 0°C further increased in direct proportion to monomer conversion and were in good agreement with the calculated values for living polymers (Figure 3). The MWDs of the polymers stayed very narrow ($\bar{M}_w/\bar{M}_n \leq 1.1$), independent of monomer conversion, before and after the monomer addition (Fig. 3, a and a'; b and b').

The \bar{M}_n -conversion profile for $+25^\circ\text{C}$, however, increasingly deviated from the calculated line with increasing conversion after the monomer addition. The MWD curves (Fig. 3, c and c') suggest that at room temperature, some of the living propagating species were dead at or after the end of the first-stage polymerization, giving a bimodal distribution (curve c') after the second monomer addition.

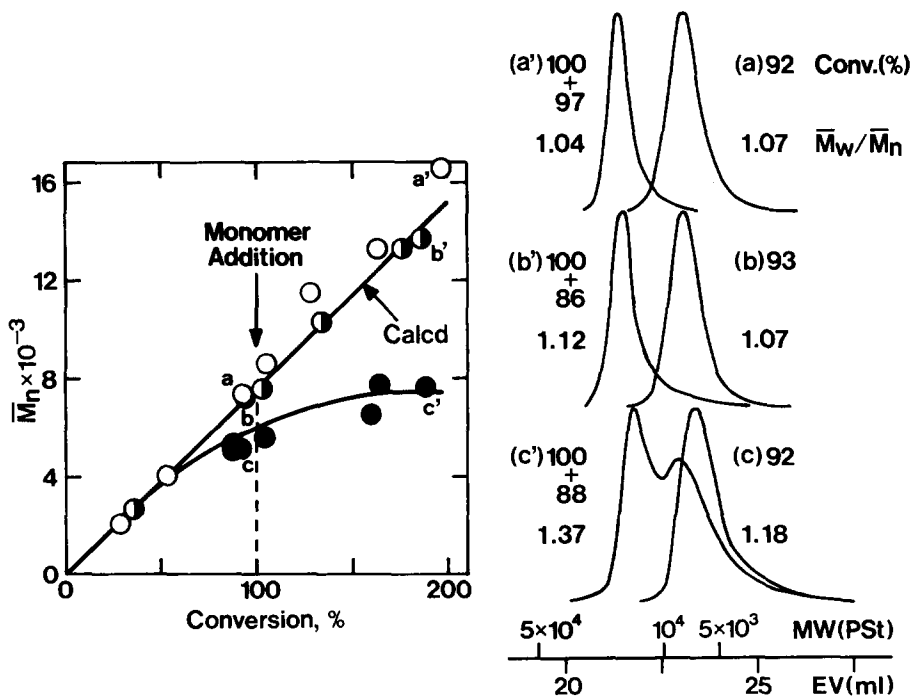


Figure 3. \bar{M}_n and MWD of poly(IBVE) obtained in a monomer-addition experiment in the polymerization by $(\text{PhO})_2\text{P}(\text{O})\text{OH}/\text{ZnI}_2$ in toluene at -40 (○), 0 (○) and $+25^\circ\text{C}$ (●): $[\text{IBVE}]_0 = 0.38 \text{ M}$; $[(\text{PhO})_2\text{P}(\text{O})\text{OH}]_0 = 5.0 \text{ mM}$; $[\text{ZnI}_2]_0 = 5.0 \text{ mM}$. The molar amount of the second IBVE feed was the same as in the first. MWD curves a, a', b, b', c, and c' are for the samples corresponding to points a, a', b, b', c, and c' in the \bar{M}_n -conversion profiles, respectively.

In conclusion, this study has demonstrated that the $(\text{PhO})_2\text{P}(\text{O})\text{OH}/\text{ZnI}_2$ initiating system leads to the well-defined living polymerization of IBVE in toluene at temperatures below 0°C . Separate preliminary experiments showed that the \bar{M}_n of the polymers is inversely proportional to the initial concentration of $(\text{PhO})_2\text{P}(\text{O})\text{OH}$ but independent of the ZnI_2 concentration; the rate of polymerization, however, increases with the latter valuable. These facts support the validity of Scheme I, where $(\text{PhO})_2\text{P}(\text{O})\text{OH}$ generates the living growing end \mathfrak{Z} , the phosphate moiety of which is activated by ZnI_2 so as to propagate.

The achievement of the living cationic polymerization by the $(\text{PhO})_2\text{P}(\text{O})\text{OH}/\text{ZnI}_2$ is important in that it demonstrates not only the iodide anion (I^-) but also the phosphate anion [$(\text{PhO})_2\text{P}(\text{O})\text{O}^\ominus$] to serve as a nucleophilic counteranion that stabilizes the growing carbocation and thereby gives living polymers in the presence of an appropriate Lewis acid activator.

EXPERIMENTAL

Materials

$(\text{PhO})_2\text{P}(\text{O})\text{OH}$ (Wako Chemicals, purity $> 97\%$) was used as received; the solid was dissolved in toluene (ca. 1 M), sealed in brown ampules under dry nitrogen, and stored in the dark in a refrigerator. ZnI_2 (Aldrich, purity $> 99.99\%$) was used as received. Commercial IBVE was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight with potassium hydroxide pellets, and doubly distilled over calcium hydride. Toluene and diethyl ether as solvents and carbon tetrachloride 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

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. The reactions were initiated by adding, via dry syringes, solutions of $(\text{PhO})_2\text{P}(\text{O})\text{OH}$ (in toluene; 0.50 ml) and ZnI_2 (in diethyl ether; 0.50 ml), sequentially in this order, into a monomer solution [in toluene, 0.38 M (5.0 vol%); 4.0 ml]. The concentration of $(\text{PhO})_2\text{P}(\text{O})\text{OH}$ in the stock solution was determined by titrating with a standard solution of 1/50 N NaOH. 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 carbon tetrachloride 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 in chloroform at room temperature on a JASCO Trirotar-II chromatograph equipped with three polystyrene gel columns (Shodex K-802, K-803, and 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.

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