Polymerization of Glycidyl Phenyl Ether with Phosphonic Acid Esters as Novel Thermally Latent Initiators

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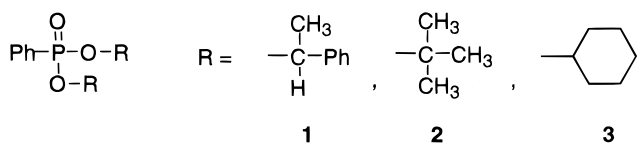
ABSTRACT: Novel phosphonic acid esters, *O*,*O*-di-1-phenylethyl phenylphosphonate (**1**), *O*,*O*-di-*tert*-butyl phenylphosphonate (**2**), and *O*,*O*-dicyclohexyl phenylphosphonate (**3**), were synthesized from phenylphosphonic dichloride and the corresponding alcohols. The phenylphosphonic esters **1**−**3** decomposed into phenylphosphonic acid and the corresponding olefins by heating at 150−170 °C. Their initiator activities were examined in the cationic polymerization of glycidyl phenyl ether (GPE). They converted GPE only 4% even at 190 °C in the absence of $ZnCl_2$. In the presence of $ZnCl_2$ along with **1**−**3**, GPE did not convert below 90 °C in the case of **1** and **2**, and below 140 °C in the case of **3**, but it rapidly converted to afford polyGPE with M_n of 2000−7000 above those temperatures. It was found that **1**−**3** served as thermally latent initiators in the polymerization of GPE in the presence of $ZnCl_2$.

Introduction

"Latent initiators", which show no activity under normal conditions but initiate the polymerization by certain external stimulation like heating and photoirradiation, are important in the field of thermosetting materials such as epoxy resin and multifunctional vinyl ethers.[1] Crivello et al. have reported that diaryliodonium and triarylsulfonium salts can generate active species by photoirradiation, which are useful as efficient initiators for epoxy resin.[2] We have reported that several onium salts such as benzylsulfonium,[3] pyridinium,[4] and phosphonium[5] salts serve as thermally latent and photolatent initiators releasing a benzyl cation or proton as an active species. Further, we have developed non-salt-type latent initiators such as N-substituted phthalimides,[6] aminimides,[7] carboxylic acid esters,[8] and sulfonic acid esters[9] to enhance the solubility of the initiators in monomers. Phosphonic acid esters are well-known as insecticides, plasticizers, and polymer additives.[10] Phosphonic acid esters can be easily synthesized and are expected to generate phosphonic acid as an initiation species. Higashimura et al. have succeeded in living polymerization of a vinyl ether with the adduct of the vinyl ether and phosphoric acid in the presence of zinc iodide.[11] To develop a new non-salt-type latent initiator, we have employed phosphonic acid esters having a labile C−O bond. This article deals with the possibility of phosphonic acid esters (**1**, **2**, and **3**) as thermally latent initiators in the polymerization of GPE.



1 **2** **3**

Experimental Section

Materials. Commercially available extra pure phenylphosphonic dichloride, 1-phenylethanol, *tert*-butyl alcohol, and cyclohexanol were used as received without further purification. Solvents (tetrahydrofuran, diethyl ether, and pyridine) were distilled after removal of contaminated water by usual methods. Zinc chloride (Aldrich; 1.0 M solution in diethyl ether) was used as received. GPE was distilled over calcium hydride.

Measurements. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded with JEOL JNM-EX-90 and JNM-EX-400 spectrometers using tetramethylsilane or 85% H_3PO_4 as an internal or external standard in $CDCl_3$. IR spectra were measured with a JEOL JIR-5300 spectrophotometer. Melting points (mp) were measured on a Yanaco Micro Melting Point apparatus. Number- and weight-average molecular weights (M_n and M_w) and polydispersity ratios (M_w/M_n) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC HLC-8120 system, equipped with two consecutive polystyrene gel columns (TSKgels G4000HXL and G2500HXL), using THF as an eluent with a flow rate of 1.0 mL/min by polystyrene calibration, and refractive index and ultraviolet detectors. Elemental analyses were carried out with a Yanaco type MT-5 CHN and a SX-Elements microanalyzer YS-10. GC-mass spectra were measured with a Shimadzu GCMS-QP5000.

Synthesis of O,O-Di-1-phenylethyl Phenylphosphonate ***1.*** To a solution of 1-phenylethanol (4.09 g, 33.5 mmol) and pyridine (3.83 g, 48.4 mmol) in THF (40 mL) was added a solution of phenylphosphonic dichloride (3.76 g, 19.3 mmol) in THF (10 mL) at 0 °C under an atmosphere of nitrogen. The mixture was stirred at room temperature for 2 h and refluxed overnight. The precipitate formed in the reaction mixture was filtered off and washed with ether. After the removal of ether, the residue was dissolved in chloroform, and the resulting solution was washed with water several times and a dilute sodium bicarbonate aqueous solution. The organic phase was dried over anhydrous magnesium sulfate and concentrated by evaporation to give light yellow oil, which was purified by silica gel column chromatography using a solution of *n*-hexane and ether (v/v = 10/90) as an eluent to afford 3.88 g (10.6 mmol, 63.3%) of colorless oil. IR (NaCl, cm^{-1}): 3063, 3034, 2982, 2832, 1637, 1452, 1440, 1377, 1248, 1132, 970, 823. ^1H NMR ($CDCl_3$): δ 7.85−7.09 (m, 15H, −3 (C_6H_5)), 5.70−5.35 (m, 2H, 2 (−CH−)), 1.65−1.43 (m, 6H, $2CH_3$). ^{13}C NMR ($CDCl_3$): δ 142.1, 141.5, 131.9, 131.4, 128.2, 127.6, 125.8, 125.6, 75.2, 75.0, 24.3, 24.1. ^{31}P NMR ($CDCl_3$): δ 17.70 (t, J = 2.5 Hz). Anal. Calcd for $C_{22}H_{23}PO_3$: C, 72.12; H, 6.33. Found: C, 71.82; H, 6.33.

Synthesis of O,O-Di-tert-butyl Phenylphosphonate ***2***. To a solution of sodium hydride (2.00 g (60% in oil), 50 mmol) in

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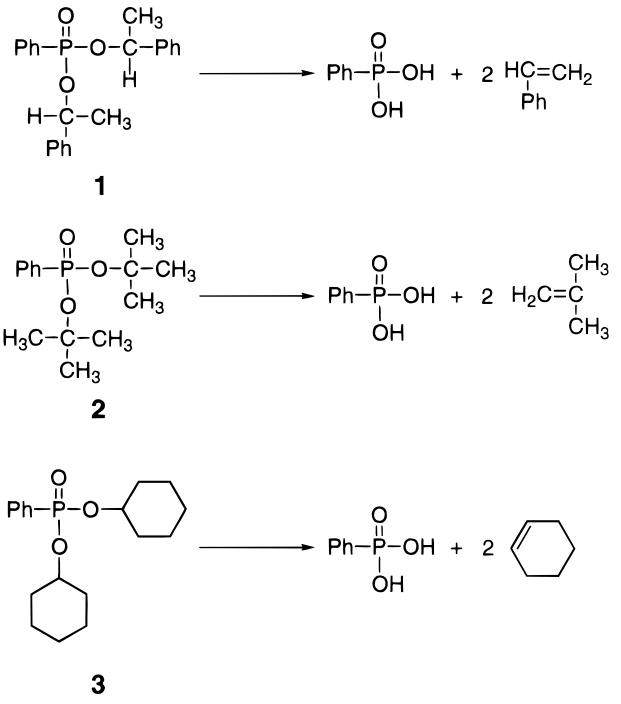
Scheme 1



THF (20 mL) was added a solution of *tert*-butyl alcohol (3.91 g, 52 mmol) in THF (30 mL) at 0 °C under an atmosphere of nitrogen. After the evolution of hydrogen gas stopped, a solution of phenylphosphonic dichloride (4.38 g, 22.5 mmol) in THF (40 mL) was added to the solution at 0 °C. The resulting solution was refluxed for 5 h and stirred at room temperature overnight. The workup and purification were identical with those for **1** to yield 5.11 g (18.9 mmol, 84.1%) of white solid, which was recrystallized from *n*-hexane to give white crystals (mp 52−54 °C). IR (KBr, cm^{-1}): 3059, 2980, 2930, 1651, 1475, 1439, 1394, 1369, 1259, 1172, 1128, 979, 918. ^1H NMR ($CDCl_3$): δ 7.82−7.40 (m, 5H, $-C_6H_5$), 1.43 (s, 18H, −6 (CH_3)). ^{13}C NMR ($CDCl_3$): δ 134.5, 132.5, 130.9, 130.8, 130.7, 127.6, 127.4, 81.6, 30.0. ^{31}P NMR ($CDCl_3$): δ 10.15. Anal. Calcd for $C_{14}H_{23}PO_3$: C, 62.21; H, 8.58. Found: C, 62.08; H, 8.73.

Synthesis of O,O-Dicyclohexyl Phenylphosphonate ***3.*** The colorless oil compound **3** was synthesized from phenylphosphonic dichloride and cyclohexanol in a similar manner with **1**.

Yield: 75.5%. IR (NaCl, cm^{-1}): 2938, 2858, 1450, 1248, 1132, 1045, 990, 893. ^1H NMR ($CDCl_3$): δ 7.75−7.31 (m, 5H, $-C_6H_5-$), 4.33 (m, 2H, 2(−CH−)), 1.13−1.89 (m, 20H, 2 ($-C_6H_{10}$)). ^{13}C NMR ($CDCl_3$): δ 131.7, 131.6, 131.5, 131.4, 131.3, 128.8, 128.1, 127.8, 75.2, 33.3, 33.2, 24.9, 23.4, 23.3. ^{31}P NMR ($CDCl_3$): δ 17.25. Anal. Calcd for $C_{18}H_{27}PO_3$: C, 67.06; H, 8.44. Found: C, 66.98; H, 8.60.

Polymerization. In a typical procedure, initiator **1** (18.3 mg, 0.05 mmol) was fed into a glass tube. The tube was closed with a three-way stopcock, and a cycle of vacuum−nitrogen was repeated three times to remove oxygen. GPE (751 mg, 5 mmol) was fed into the glass tube with a syringe under nitrogen. The tube was sealed under vacuum using the freeze−thaw technique and heated at a set temperature in an oil bath. After a set time, the tube was cooled in a dry ice−acetone bath, and the reaction mixture was diluted with chloroform (1 mL). The mixture was then poured into methanol (50 mL) to precipitate a polymer. The polymer was separated from the supernatant by decantation and dried in vacuo at 50 °C. The monomer conversion was determined by ^1H NMR spectroscopy before precipitation with methanol, and the molecular weight of the polymer was determined by GPC.

Molecular Orbital Calculation. Calculation was carried out with MacSpartan plus. All geometries were fully optimized by the 3-21G* basis set.

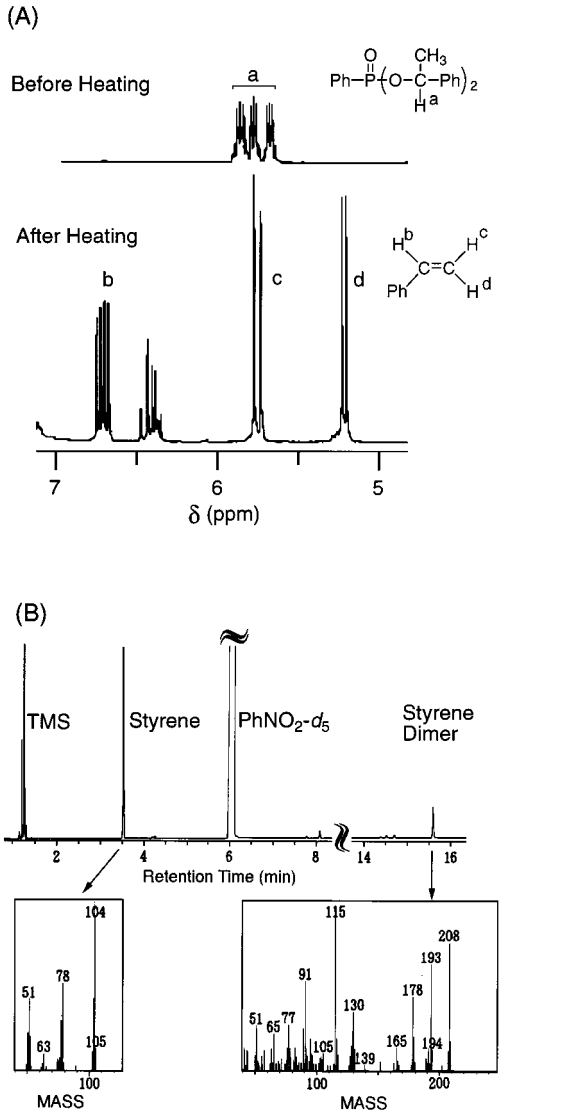


Figure 1. Thermal decomposition of phosphonic acid ester **1**: (A) extended ^1H NMR spectra of **1** before and after heating in nitrobenzene-d_5 at 150 °C for 4 h; (B) GC-mass spectra of **1** after heating in nitrobenzene-d_5 at 150 °C for 4 h.

Results and Discussion

Initiator Synthesis. The phosphonic acid esters **1** and **3** were synthesized by the reaction of the corresponding alcohols with phenylphosphonic dichloride in the presence of pyridine. The ester **2** was synthesized by the reaction of phenylphosphonic dichloride with *tert*-butyl alcohol in the presence of sodium hydride, because the reaction in the presence of pyridine gave **2** in a low yield, probably due to the steric hindrance of the *tert*-butyl group. The structures of **1**, **2**, and **3** were confirmed by ^1H NMR, ^{13}C NMR, ^{31}P NMR, and IR spectroscopy besides element analysis.

Thermal Decomposition of Phosphonic Acid Esters. The thermal decomposition of phosphonic acid esters was monitored in nitrobenzene-d_5 to examine the thermal property. Figure 1 shows the ^1H NMR and GC-mass spectra of the solution before and after heating at 150 °C for 4 h. In the ^1H NMR spectrum after heating, the signals **a** of the benzyl protons of **1** completely disappeared, and the signal **b**−**d** assignable to the vinyl group of styrene appeared at 6.7, 5.7, and 5.2 ppm, respectively. GC-mass spectra confirmed the formation of styrene and styrene dimer.[12] The thermal

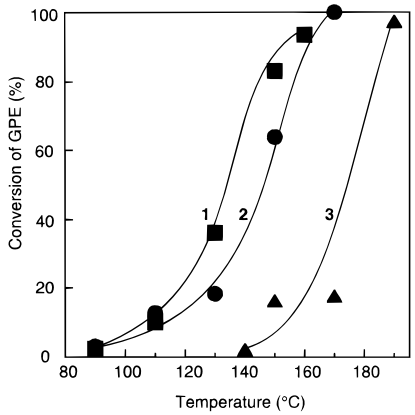


Figure 2. Temperature−conversion curves in the polymerization of GPE with **1**, **2**, and **3** (1 mol %) in the presence of $ZnCl_2$ (0.2 mol %) for 12 h.

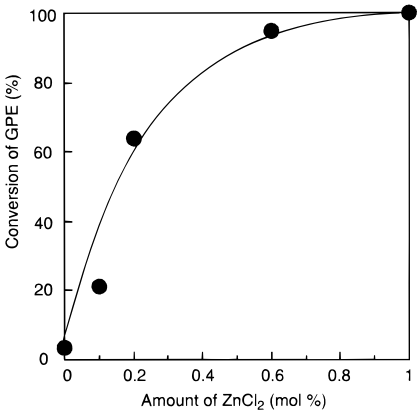
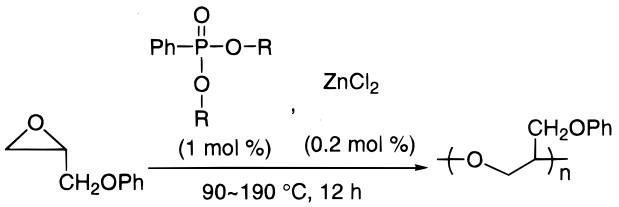


Figure 3. Effect of amount of $ZnCl_2$ on the polymerization of GPE with **2** (1 mol %) at 150 °C for 12 h.

Scheme 2



decomposition of **2** and **3** afforded isobutene and cyclohexene, respectively. These results imply that phosphonic acid esters **1**−**3** thermally decompose to form phosphonic acid and the corresponding olefins as shown in Scheme 1.

Polymerization of Phosphonic Acid Esters with GPE. Polymerization of GPE with **1**, **2**, and **3** (1−3 mol %) was carried out at 150−190 °C for 12 h. The phosphonic acid esters were completely soluble in GPE at ambient temperature, and the polymerization proceeded homogeneously. The conversion of GPE was below 4% under these conditions, and only a trace amount of GPE oligomer (M_n 300−400) was obtained. This unsatisfactory result might be caused by the lower acidity of phenylphosphonic acid than phenylsulfonic acid.[13,14] The phosphonate anion formed by the thermal decomposition of the phosphonic acid esters might terminate the cationic polymerization of GPE. To enhance the initiator activity of **1**−**3**, it is necessary to decrease the nucleophilicty of the phosphonate anion generated from the phosphonic acid esters. For this purpose, $ZnCl_2$ was employed in this polymerization

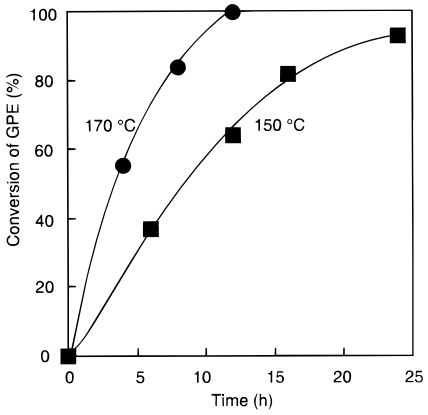


Figure 4. Effect of polymerization time on the polymerization of GPE with **2** (1 mol %) in the presence of $ZnCl_2$ (0.2 mol %) at 150 and 170 °C.

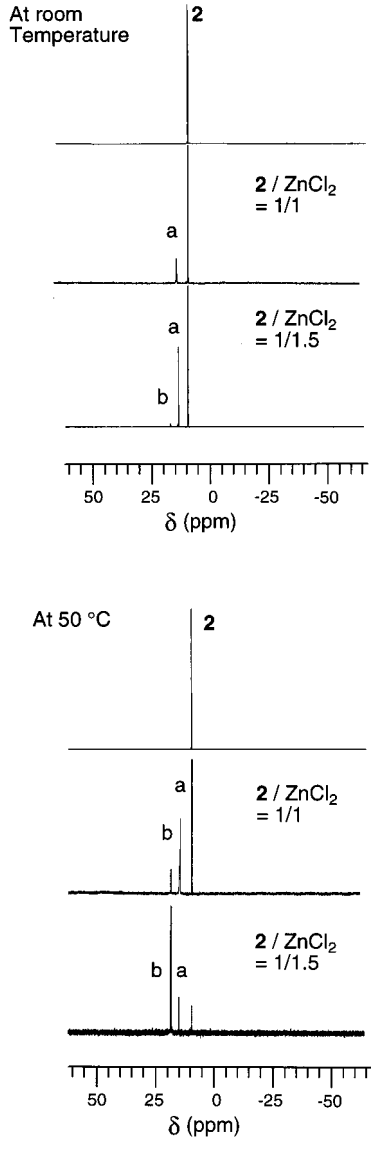
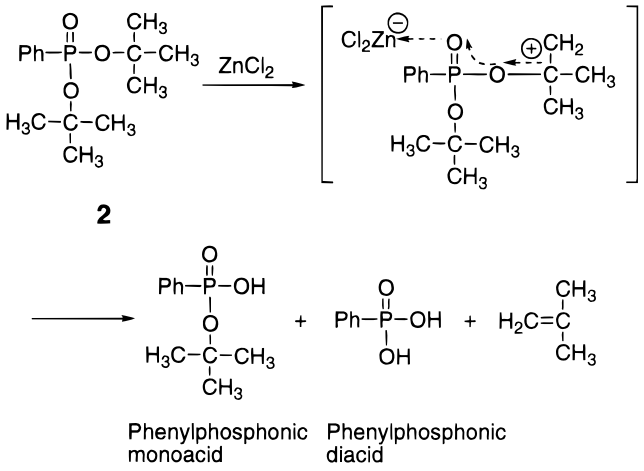


Figure 5. Changes of ^{31}P NMR spectra of **2** by the addition of $ZnCl_2$ at room temperature and at 50 °C measured in $CDCl_3$. [**2**] = 0.2 mol/L. Signals **a** and **b** are assignable to phenylphosphonic mono- and diacids, respectively.

process, because it has been reported as an effective additive in the living cationic polymerization of vinyl ethers.[15] Polymerization of GPE with **1**−**3** (1 mol %) was carried out in the presence of $ZnCl_2$ (0.2 mol %) at 90−

Scheme 3

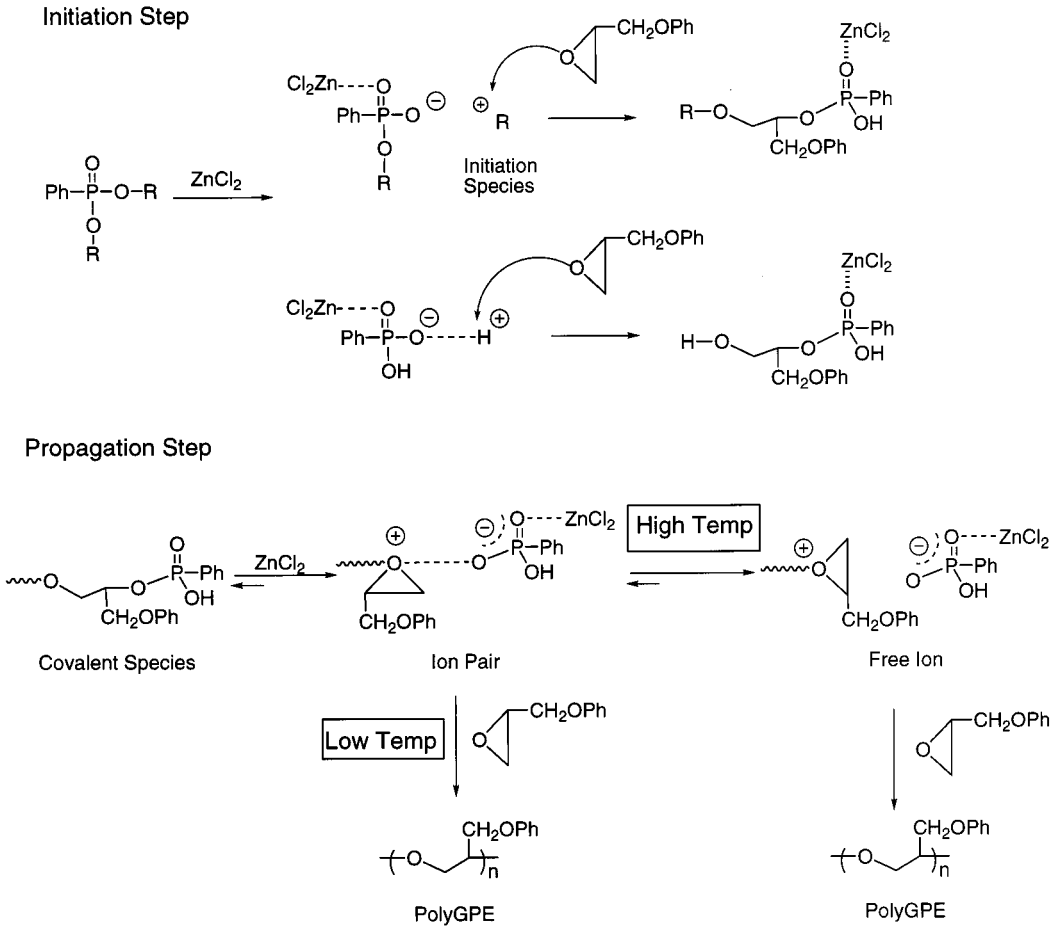


190 °C for 12 h (Scheme 2). The polymerization of GPE did not proceed with **1** and **2** below 90 °C and with **3** below 140 °C but proceeded rapidly above those temperatures to afford the polymers with M_n of 2000−7000, as shown in Figure 2.[16] GPE was converted quantitatively at 160−180 °C. Meanwhile, the polymerization with $ZnCl_2$ in the absence of **1**, **2**, and **3** afforded a trace amount of low molecular weight (M_n 800−900) oligomer only in 5−10% GPE conversion at 150−190 °C. This agreed with the result that the polymerization of epoxides with mild Lewis acids afforded only oligomers.[17] Hence, it was confirmed that the phosphonic acid esters **1**−**3** served as thermally latent initiators in the presence of $ZnCl_2$ for the cationic polymerization of GPE. The activity order was **1** > **2** > **3**. This order agreed with the solvolysis rates of the corresponding alkyl halides.[18]

Figure 3 shows the dependence of the GPE conversion on the amount of $ZnCl_2$ in the polymerization with **2** (1 mol %) at 150 °C for 12 h.[19] When no $ZnCl_2$ was added, the GPE conversion was only 4%. The conversion increased as the amount of $ZnCl_2$ increased and reached 100% with 1 mol % of $ZnCl_2$. $ZnCl_2$ might decrease the nucleophilicity of the phosphonate anion formed from the phosphonic acid ester **2**. It might also promote the decomposition of **2** by coordination. Figure 4 shows the time−conversion relationships for the polymerization of GPE with **2** in the presence of $ZnCl_2$ at 150 and 170 °C. The conversion increased as the time, but the M_n of the obtained polymer was almost constant (2100−2900) independent of the conversion.[20] Chain transfer would cause the low M_n of the polymer. The polymerization of **2** proceeded faster at 170 °C than that at 150 °C.

Mechanistic Aspects. Figure 5 depicts the change of the ^{31}P NMR spectra of **2** before and after the addition of 1 and 1.5 equiv of $ZnCl_2$ at room temperature and 50 °C in $CDCl_3$, which provides the evidence of coordination of **2** with $ZnCl_2$ resulting in the formation of phenylphosphonic acid as shown in Scheme 3. In Figure 5, two peaks assignable to phenylphosphonic mono- and diacids appeared by the addition of $ZnCl_2$ at 14 and 18 ppm, respectively. The relative intensity of the phenylphosphonic acid peaks increased as the temperature increased. The ^1H NMR spectra of the same samples confirmed the formation of isobutene from **2** by the addition of $ZnCl_2$. Ab initio calculation revealed that the

Scheme 4



coordination of phosphonic acid ester **2** with $ZnCl_2$ weakened the $O-C(CH_3)_3$ bond; i.e., the bond length increased from 1.48 to 1.50 Å by the coordination.

Kennedy et al. have reported the cationic polymerization with stable cationic species that are produced from oxo acids in the presence of Lewis acids,[21] where the obtained polymer generally exhibits bimodal GPC peaks due to two kinds of active species: free ion and ion pair. In this work, the cationic polymerization of GPE with **1** at 110−130 °C, **2** at 110 °C, and **3** at 170 °C in the presence of $ZnCl_2$ gives GPC curves containing shoulders at a high molecular weight region,[22] indicating the presence of two kinds of cationic species. Meanwhile, the polymer obtained with **1** and **2** above 150 °C and **3** at 190 °C showed GPC curves with the M_n of 2000−3000, without accompanying shoulders. Scheme 4 represents a plausible mechanism of the polymerization. The phosphonic acid esters thermally decompose to generate cationic initiating species (R^+ and/or H^+) along with a phosphonate anion, which is coordinated by $ZnCl_2$. In the propagation step, the covalent species is too stable to propagate alone. $ZnCl_2$ activates the C−O bond to form ion pair and free ion, which afford the polymers with low and high molecular weights, respectively. At high temperature, the equilibrium may be shifted to the free ion to afford a polymer showing a unimodal GPC curve. This system showed nonliving polymerization behavior, probably due to several side reactions such as chain transfer and formation of cyclic oligomers.

In summary, although the phosphonic acid esters **1**−**3** alone showed little activity as the initiators of the polymerization of GPE, they served as good thermally latent initiators in the presence of $ZnCl_2$, which might effectively decrease the nucleophilicity of the phosphonate anion as well as promote the decomposition of the phosphonic acid esters, resulting in the efficient catalytic system. We believe that this novel catalytic system can be applicable to cationic polymerization of other monomers as well as a hardner of epoxy resin. Further research on the molecular design of phosphonic acid esters and selection of additives to increase the molecular weight of the polymer is now in progress.

Supporting Information Available: Detailed polymerization data corresponding to Figures 2−4 and GPC charts of the polymers obtained by the polymerization of GPE with **1** (1 mol %) in the presence of $ZnCl_2$ (0.2 mol %) at 130 and 150 °C for 12 h. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The details of the polymerization including the polymer yield, M_n, and M_w/M_n are summarized in the Supporting Information (Table S2).

(20) The details of the polymerization including the polymer yield, M_n, and M_w/M_n are summarized in the Supporting Information (Table S3).

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(22) The GPC profiles of the polymers are illustrated in the Supporting Information (Figure S6).

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