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Polymerization of Glycidyl Phenyl Ether with Benzyl Phenylphosphonates as Novel Thermally Latent Initiators

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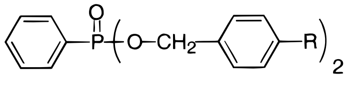
ABSTRACT: The cationic polymerization of glycidyl phenyl ether (GPE) was examined with novel phosphonic acid esters, *O*,*O*-di-*p*-methylbenzyl phenylphosphonate (**1a**), *O*,*O*-dibenzyl phenylphosphonate (**1b**), and *O*,*O*-di-*p*-nitrobenzyl phenylphosphonate (**1c**), as initiators. GPE did not convert with **1a**−**c** even at 210 °C in the absence of $ZnCl_2$. In the presence of $ZnCl_2$ along with phosphonic acid esters **1a**, **1b**, and **1c**, the polymerization of GPE did not proceed below 90, 130, and 170 °C, respectively, but it rapidly proceeded to afford polyGPE with M_n of 2500−5000 above those temperatures. It was found that **1a**, **1b**, and **1c** served as thermally latent initiators in the polymerization of GPE in the presence of $ZnCl_2$. Electron-donating substituents on the benzyl group of the phosphonic acid esters increased the initiator activity. The initiation species was identified as a benzyl cation by ^{13}C-labeled experiments.

Introduction

Latent initiators show no activity under normal conditions but generate active species by external stimulation such as heating and photoirradiation. Crivello et al. and we have developed various onium salts such as diaryliodonium and triarylsulfonium salts,[1] sulfonium,[2] pyridinium,[3] and phosphonium salts[4] as latent thermal and photoinitiators. They have been widely used in industrial fields such as coatings, adhesives, packings, and inks for polymerization or curing of epoxy resin and multifunctional vinyl ethers.[5] However, onium salts accompany several problems: low solubility in monomers and solvents, remaining of inorganic compounds in polymers, and high cost for practical use. We have also developed non-salt-type latent initiators, *N*-substituted phthalimides,[6] aminimides,[7] carboxylic acid esters,[8] and sulfonic acid esters[9] to overcome the problems. Organophosphorus compounds are widely utilized for medicines, agricultural chemicals, plasticizers, and polymer additives.[10] Recently, we have reported that phosphonic acid esters[11] and phosphonic amide esters[12] can serve as non-salt-type latent initiators in the polymerization of glycidyl phenyl ether (GPE). This article deals with thermal latency of *O*,*O*-dibenzyl phenylphosphonate derivatives (**1a**−**c**) with electron-donating and -withdrawing groups at the para position of the benzyl group in the polymerization of GPE in the presence of $ZnCl_2$.



R : CH_3 (**1a**) H (**1b**) NO_2 (**1c**)

Experimental Section

Materials. Commercially available extra pure phenylphosphonic dichloride, benzyl alcohol, benzyl-7-^{13}C alcohol, *p*-nitrobenzyl alcohol, and *p*-methylbenzyl alcohol were used as received without further purification. Tetrahydrofuran (THF) was dried over Na−benzophenone and was distilled under an atmosphere of nitrogen before use. $ZnCl_2$ (Aldrich; 1.0 M solution in diethyl ether) was used as received. GPE and 1,2-epoxydodecane (EPD) were dried and distilled over calcium hydride before use.

Measurements. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with JEOL EX-400, Lambda 300, and Lambda 500 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 (TSK gels G4000HXL and G2500HXL), using THF as an eluent with a flow rate of 1.0 mL/min by polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. Elemental analyses were carried out with a Yanaco type MT-5 CHN and a SX-Elements microanalyzer YS-10. Temperatures with 5% weight loss (T_{d5}) were determined by a Seiko Instruments TG/DTA 220 at a heating rate of 10 °C/min under a nitrogen atmosphere.

Synthesis of *O*,*O*-Di-*p*-methylbenzyl Phenylphosphonate (1a). To a solution of *p*-methylbenzyl alcohol (3.75 g, 30.7 mmol) and triethylamine (4.54 g, 44.3 mmol) in THF (40 mL) was added a solution of phenylphosphonic dichloride (3.16 g, 16.2 mmol) in THF (30 mL) at 0 °C under a nitrogen atmosphere. The mixture was stirred at room temperature overnight. The precipitate formed in the reaction mixture was filtered off and washed with THF. After the removal of THF, 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 a rotary evaporator to give light yellow oil, which was purified by silica gel column chromatography using ether as an eluent to afford 4.81 g (13.1 mmol, 81%) of white solid. It was further purified by recrystallization from *n*-hexane and ether to give white crystals (mp: 65.5−66.5 °C). IR (KBr, cm^{-1}): 3034, 2918, 2860, 1518, 1439, 1238, 1132, 1020, 974, 794, 694, 576. ^{1}H NMR ($CDCl_3$): δ 7.83−7.12 (m, 13H, $-C_6H_5$, $-2(C_6H_4)$), 5.01 (m, 4H, $2(-CH_2-)$), 2.34 (s, 6H, $-2(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 138.2, 133.2, 132.4, 131.8, 129.2, 128.4, 128.3, 128.1, 67.5, 21.2. ^{31}P NMR ($CDCl_3$): δ 19.9. Anal. Calcd for $C_{22}H_{23}PO_3$; C 72.12; H, 6.33. Found: C, 71.83; H, 6.59.

Synthesis of *O*,*O*-Dibenzyl Phenylphosphonate (1b). The compound **1b** was synthesized from phenylphosphonic dichloride and benzyl alcohol in a similar manner as **1a**. Yield 92%; mp 48−50 °C. IR (KBr, cm^{-1}): 3065, 3036, 2946, 2888,

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1441, 1379, 1253, 1132, 993, 873. ^{1}H NMR ($CDCl_3$): δ 7.97−7.14 (m, 15H, $-3(C_6H_5)$), 5.12−5.01 (m, 4H, 2 ($-CH_2-$)). ^{13}C NMR ($CDCl_3$): δ 136.0, 132.4, 131.9, 131.5, 128.7, 128.4, 128.2, 128.0, 127.8, 67.4. ^{31}P NMR ($CDCl_3$): δ 20.2. Anal. Calcd for $C_{20}H_{19}PO_3$: C, 71.00; H, 5.66. Found: C, 70.98; H, 6.01.

Synthesis of *O,O*-Dibenzyl-*7-^{13}C* Phenylphosphonate (1b′). The compound **1b′** was synthesized from phenylphosphonic dichloride and benzyl-*7-^{13}C* alcohol in a similar manner as **1a**. Yield 74%; mp 48−49 °C. IR (KBr, cm^{-1}): 3063, 3032, 2930, 2879, 1454, 1440, 1371, 1238, 1132, 991, 740, 696. ^{1}H NMR ($CDCl_3$): δ 7.84−7.30 (m, 15H, $-3(C_6H_5)$), 5.31−4.83 (m, 4H, 2 ($-CH_2-$)). ^{13}C NMR ($CDCl_3$): δ 136.4, 135.9, 132.5, 131.8, 128.7, 128.4, 128.3, 128.0, 67.9. ^{31}P NMR ($CDCl_3$): δ 20.1 (t, $J = 5$ Hz). Anal. Calcd for $^{12}C_{18}{}^{13}C_2H_{19}PO_3$: C, 71.15; H, 5.59. Found: C, 70.89; H, 5.71.

Synthesis of *O,O*-Di-*p*-nitrobenzyl Phenylphosphonate (1c). The compound **1c** was synthesized from phenylphosphonic dichloride and *p*-nitrobenzyl alcohol in a similar manner as **1a**. Yield 84%; mp 78−79 °C. IR (KBr, cm^{-1}): 3113, 3082, 2949, 2856, 1606, 1522, 1348, 1251, 1132, 1028, 860. ^{1}H NMR ($CDCl_3$): δ 8.20−7.29 (m, 13H, $-C_6H_5$, $-2(C_6H_4)$), 5.28−5.16 (m, 4H, 2($-CH_2-$)). ^{13}C NMR ($CDCl_3$): δ 147.6, 142.9, 133.0, 131.6, 128.6, 127.8, 123.5, 66.1. ^{31}P NMR ($CDCl_3$): δ 21.3. Anal. Calcd for $C_{20}H_{17}N_2PO_7$: C, 56.08; H, 4.00; N, 6.54. Found: C, 56.04; H, 4.17; N, 6.51.

Polymerization. In a typical procedure, initiator **1** (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. Into the glass tube were fed GPE (751 mg, 5 mmol) and subsequently a 1.0 M solution of $ZnCl_2$ in diethyl ether (10 μL, 0.01 mmol) 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 into 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. The monomer conversion was determined by ^{1}H NMR spectroscopy before precipitation with methanol, and the molecular weight of the polymer was determined by GPC. The obtained polymer was identified to be polyGPE by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy.

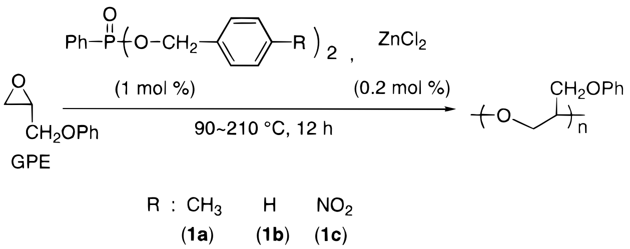
Ab Initio Calculation. All calculations were carried out with the Gaussian 94 program on a Silicon Graphics Indigo 2 IMPACT 10000. Geometries were fully optimized by the HF/STO-3G basis set, followed by a single point calculation by the HF/6-311G** basis set.

Results and Discussion

Initiator Synthesis. The phosphonic acid esters **1a**, **1b**, and **1c** were synthesized by the reaction of the corresponding alcohols with phenylphosphonic dichloride in the presence of triethylamine. The structures of **1a**, **1b**, and **1c** were confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and IR spectroscopy besides element analysis.

Polymerization of GPE with Phosphonic Acid Esters. Polymerization of GPE with the phosphonic acid esters **1a**, **1b**, and **1c** (1 mol %) was carried out at 190 and 210 °C for 12 h. The phosphonic acid esters were completely soluble in GPE at ambient temperature, but GPE did not convert at all under this condition. Therefore, $ZnCl_2$ was added to the polymerization system, because it was reported as an effective additive for activation of phosphonic acid esters[13b] and stabilization of propagating cationic species.[13] The polymerization of GPE with **1a**, **1b**, and **1c** (1 mol %) was carried out in the presence of $ZnCl_2$ (0.2 mol %) at 90−210 °C for 12 h (Scheme 1). The polymerization of GPE did not proceed with **1a**, **1b**, and **1c** below 90, 130, and 170 °C, respectively, but proceeded rapidly above those temperatures to afford the polymers with M_n of 2500−5000, as shown in Figure 1 and Table 1. The conversion increased as the temperature, but the M_n of the obtained polymer decreased probably due to some side reactions such as chain transfer and formation of cyclic oligomers. The polymerization with $ZnCl_2$ alone as initiator afforded a low molecular weight (M_n 600−900) oligomer only with 5−10% GPE conversion at 150−210 °C.[11] The activity order was **1a** > **1b** > **1c**, similar to that of benzyl sulfonium salts initiating the polymerization of GPE with the benzyl cation.[2] The benzyl cation formed from the phosphonic acid esters may be stabilized by the electron-donating group at the para position. No siginificant difference was observed in the microstructures of the polymers obtained by the polymerization with **1a**−**c**, i.e., regioregularity (head-to-tail content) 70−80%, tacticity (isotactic/syndiotactic = 55/45), which were determined by ^{13}C NMR spectroscopy.[14,15]

Scheme 1



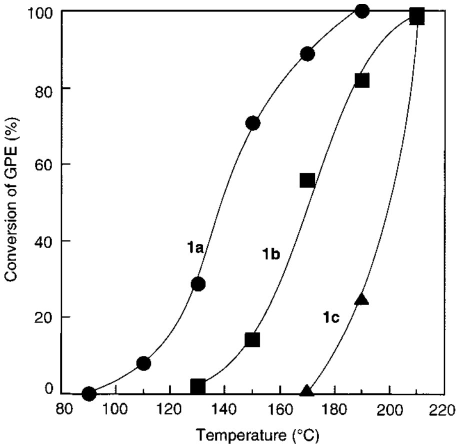


Figure 1. Temperature−conversion curves in the polymerization of GPE with phosphonic acid esters **1a**, **1b**, and **1c** (1 mol %) in the presence of $ZnCl_2$ (0.2 mol %) for 12 h.

Table 1. Polymerization of GPE with 1a, 1b, and 1c (1 mol %) in the Presence of $ZnCl_2$ (0.2 mol %)

initiator	temp (°C)	conv[a] (%)	yield[b] (%)	M_n[c]	M_w/M_n[c]
1a	130	29	4	2800	3.15[d]
	150	71	66	2800	1.24
	170	89	76	2600	1.29
	190	100	73	2200	1.23
1b	150	14	<2	5000	4.82[d]
	170	58	16	3600	1.32
	190	82	62	2500	1.26
	210	99	44	1900	1.29
1c	190	25	3	4600	1.49[d]
	210	99	32	2400	1.84[d]

[a] Determined by ^{1}H NMR. [b] Methanol-insoluble part. [c] Estimated by GPC based on polystyrene standard samples. [d] Contained a shoulder at a high molecular weight region.

Ab initio calculations were carried out to examine the relationship between the activity of the phosphonic acid esters and substituents on the phenyl group. Figure 2 illustrates the relationship of Hammett's constant δp

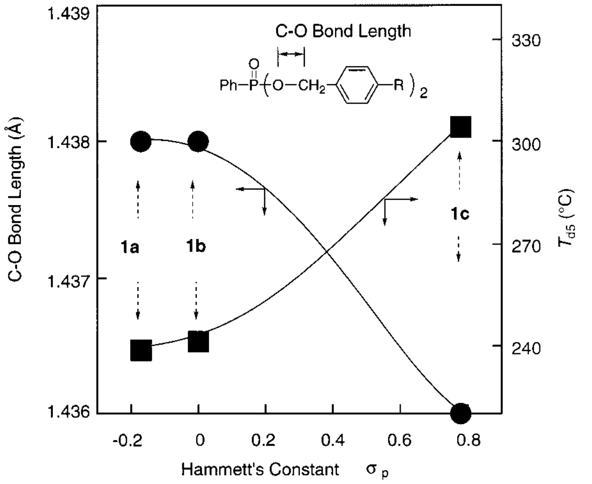


Figure 2. Hammett's plot of C−O bond length calculated by Gaussian 94 and decomposition temperature of phosphonic acid esters **1a**, **1b**, and **1c**.

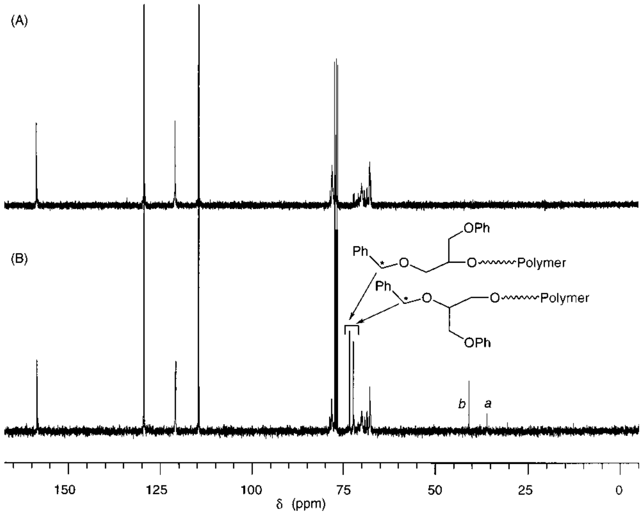


Figure 3. ^{13}C NMR spectra (100 MHz, CDCl$_3$) of polyGPE obtained by the polymerization of GPE with phosphonic acid esters (1 mol %) (A) **1b** and (B) ^{13}C-labeled **1b′** in the presence of ZnCl$_2$ (0.2 mol %) at 170 °C for 12 h.

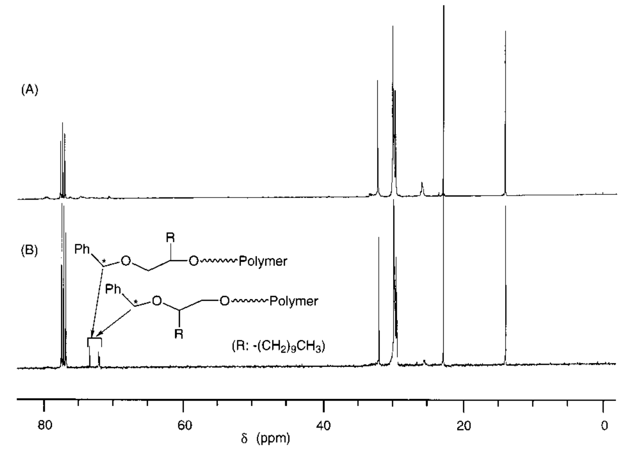
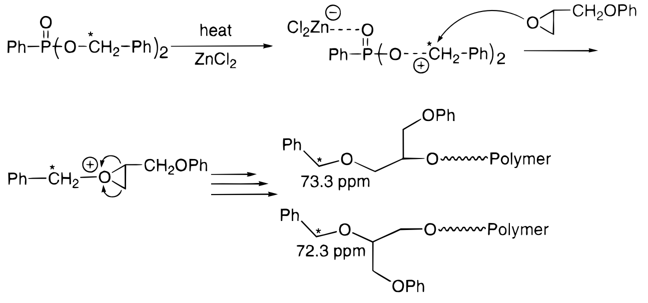
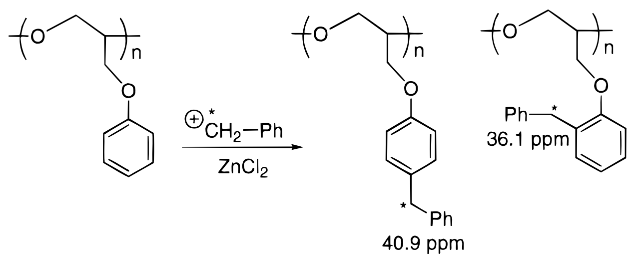


Figure 4. ^{13}C NMR spectra (100 MHz, CDCl$_3$) of polyEPD obtained by the polymerization of EPD with phosphonic acid esters (1 mol %) (A) **1b** and (B) ^{13}C-labeled **1b′** in the presence of ZnCl$_2$ (0.2 mol %) at 190 °C for 12 h.

Scheme 2



Scheme 3



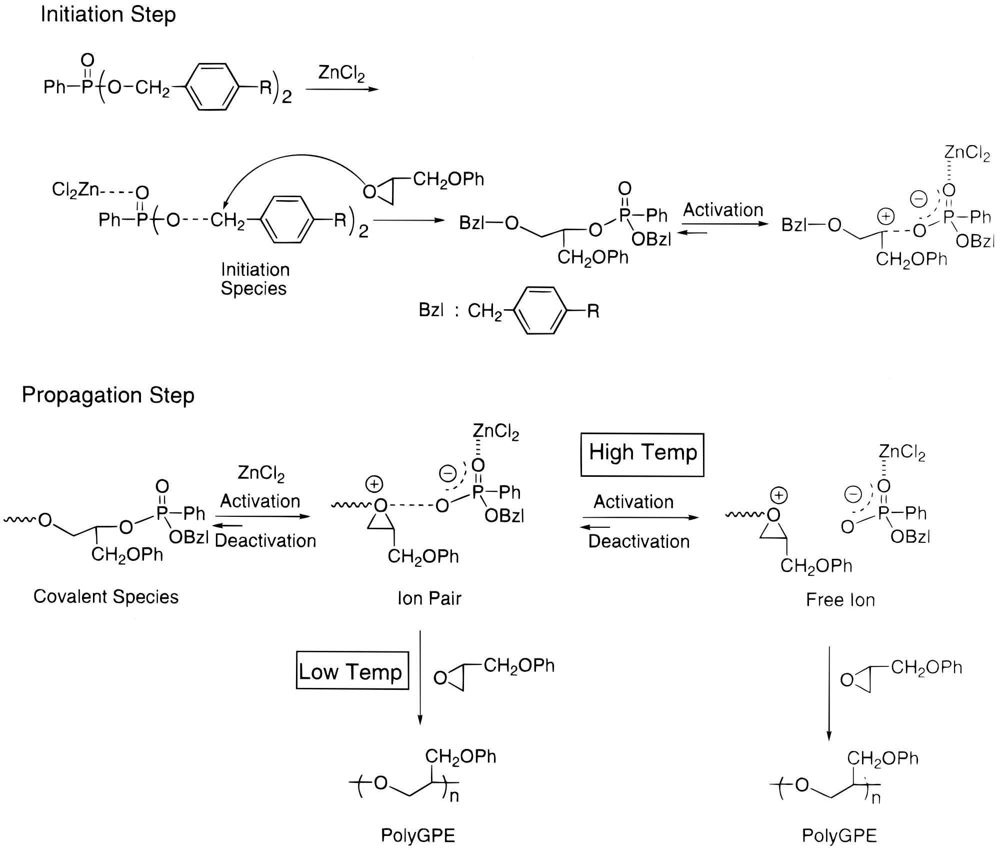
for the substituent on the phenyl group and the calculated C−O bond length of the phosphonic acid esters **1a**, **1b**, and **1c**, along with T_{d5} measured by TGA. The smaller the δp value was, the longer the C−O bond length and the lower the T_{d5} were, which could well explain the activity order.

Mechanistic Aspect. To clarify the initiation species of the phosphonic acid esters, the polymeriztion of GPE with ^{13}C-labeled benzyl phosphonic acid ester **1b′** (1 mol %) was carried out at 170 °C in the presence of ZnCl$_2$ (0.2 mol %). Figure 3 shows the ^{13}C NMR spectra of the GPE polymers obtained by the polymerization with **1b** and **1b′**. The latter one showed signals assignable to the ^{13}C-labeled benzyl carbon of the initiating polymer end at 73.3 and 72.3 ppm, as shown in Scheme 2. Unexpected signals *a* and *b* at 36.1 and 40.9 ppm may be assignable to ortho and para benzyl carbons of the benzylphenyl group, which would be formed by the Friedel−Crafts reaction of benzyl cation with the phenyl group of GPE as shown in Scheme 3.[16]

We further examined the polymerization of aliphatic epoxide, 1,2-epoxydodecane (EPD), with **1b** and **1b′** (1 mol %) in the presence of ZnCl$_2$ (0.2 mol %) at 190 °C to confirm the unexpected signals observed in Figure 3. Figure 4 shows the ^{13}C NMR spectra of the EPD polymers obtained by the polymerization of **1b** and **1b′**. The latter one showed signals assignable to ^{13}C-labeled benzyl carbon at 73.3 and 72.0 ppm, similar positions with the GPE polymer as shown in Figure 3. No signal assignable to Friedel−Crafts products was observed in this case. In addition, the EPD polymer showed UV absorption in GPC. These results indicate that the end group of the EPD polymer is a benzyl group; i.e., the initiation species is a benzyl cation.

The polymer obtained by the polymerization of GPE with **1b** in the presence of ZnCl$_2$ at 150 °C exhibited a bimodal GPC curve, and those with **1a** at 130 °C and **1c** at 190 and 210 °C exhibited a GPC curve with a shoulder at a high molecular weight region. This may indicate the presence of two kinds of propagating species, probably ion pair and free ion, both of which simultaneously afford polymers with low and high molecular weights, respectively. A similar result has been reported in the cationic polymerization of olefins in the presence of Lewis acids, where the obtained

Scheme 4



polymers exhibit bimodal GPC peaks due to two kinds of active species.[17] Meanwhile, the polymers obtained above those temperatures (130 °C for **1a** and 150 °C for **1b**) showed unimodal GPC curves, suggesting a free ionic mechanism. As mentioned above, the initiation species of the polymerization of GPE with the phosphonic acid esters **1a**, **1b**, and **1c** seems to be a benzyl cation which may be produced from the phosphonic acid esters activated by $ZnCl_2$. Scheme 4 represents a plausible mechanism of the polymerization. The phosphonic acid esters thermally decompose to generate a benzyl cation as an initiating species along with a phosphonate anion, which is coordinated by $ZnCl_2$. In the propagation step, the C−O bond of the covalent species is activated by $ZnCl_2$ to form ion pair and free ion, which afford the polymers with low and high molecular weights, respectively. At high temperature, the equilibrium lies to the free ion, which affords a polymer showing a unimodal GPC curve.

In summary, although the phosphonic acid esters **1a**, **1b**, and **1c** alone showed a little activity as the initiators of the polymerization of GPE, they served as good thermally latent initiators in the presence of $ZnCl_2$, which effectively decreased the decomposition temperature of the phosphonic acid esters as well as the nucleophilicity of the forming phosphonate anion. Both the initiation and propagation would be promoted by the coordination of $ZnCl_2$ to the phosphonate moiety. The initiation species was identified as a benzyl cation by the ^{13}C-labeled experiment.

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