Phosphonamidates as Thermally Latent Anionic Initiators of Glycidyl Phenyl Ether: Substituent Effect on the Initiator Activity

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ABSTRACT: Novel phosphonamidates, *O*-*tert*-butyl *P*-phenyl 1-piperidinyl phosphonamidate (**1**), *O*-*tert*-butyl *P*-phenyl *N*,*N*-diethyl phosphonamidate (**2**), *O*-*tert*-butyl *P*-phenyl 1-morpholinyl phosphonamidate (**3**), *O*-*tert*-butyl *P*-phenyl *N*-methyl-*N*-phenyl phosphonamidate (**4**), *O*-2-phenylpropyl *P*-phenyl 1-piperidinyl phosphonamidate (**5**), and *O*-1-phenylethyl *P*-phenyl 1-piperidinyl phosphonamidate (**6**) were synthesized from phenylphosphonic dichloride with the corresponding amines, followed by reaction with 2-methyl-2-propyl alcohol, 2-phenylpropyl alcohol, or 1-phenylethyl alcohol in the presence of sodium hydride. Their initiator activities were examined in the polymerization of GPE. GPE did not react with **1**−**4** below 110 °C, but it smoothly polymerized above 110 °C to afford the polymer with M_n of (0.7−1.4) × 10^3. The polymerization of GPE did not proceed with **5** and **6** below 90 and 170 °C, respectively, but proceeded rapidly above those temperatures. The phosphonamidates **1**−**6** served as thermally latent anionic initiators in the polymerization of GPE. The activities of **1**−**6** were affected by the decomposition rates of the ester parts and the basicity of the corresponding amines. The initiating species were identified as the amines by a ^{15}N-labeled NMR experiment.

Introduction

"Latent initiators" show no activity under normal conditions but form active species to initiate polymerization by certain external stimulation like heating and photoirradiation. Crivello et al. and we have developed various onium salts such as diaryliodonium and triarylsulfonium salts,[1] arylmethylsulfonium,[2] pyridinium,[3] and phosphonium salts[4] as latent thermal and photoinitiators. Latent initiators can control the initiation and curing steps in polymerization and curing to achieve one component system possessing excellent processability and resin properties, which are very important in industrial fields. Therefore, onium-salt-type latent initiators are employed in a diversity of industrial applications such as paints, inks, adhesives, epoxy molding compounds, and photoresists using thermosetting materials like epoxy resin and multifunctional vinyl ethers.[5] Despite the possibility of considerable growth in the future, onium-salt-type latent initiators are accompanied by several problems including low solubility in monomers and solvents, residual inorganic compounds in polymers, and high cost for industrial use. It is desirable to design and develop a novel latent initiator without salt structure to overcome these problems. Some research groups[6] and we have developed non-salt-type latent cationic initiators such as *N*-substituted phthalimides,[7] carboxylates,[8] sulfonates,[9] and phosphonium ylides,[10] some of which are now available as commercial products.

Organophosphorus compounds have been extensively employed in the fields of medicine, agriculture, plasticizers, and polymer additives because of easy molecular design and synthesis, wide application, and low cost.[11] Therefore, we selected organophosphorus compounds as a new candidate of non-salt-type latent initiator. We have recently reported that phosphonates serve as latent initiators in the polymerization of glycidyl phenyl ether (GPE).[12]

Amines are widely used as anionic hardeners of epoxy resin, especially containing an acid anhydride as a curing promoter.[13] Amines react with epoxides even at room temperature; hence, several attempts have been made to develop one-paste epoxy resin utilizing a protected amine as the precursor of an amine as an initiator. Aminimides,[14] imidazoles,[15] ketimines,[16] piperazine−acid salts,[17] and oxazolidines[18] are the candidates for the anionic latent initiators, releasing amines as active species. We have recently communicated that phosphonamidate, *O*-*tert*-butyl *P*-phenyl 1-piperidinyl phosphonamidate, **1**, can serve as an excellent thermally latent anionic initiator for the polymerization of GPE, where the active species is piperidine formed via the reaction of GPE with **1** above 110 °C.[19] The aim of this article is to elucidate the substituent effect on the initiator activity of phosphonamidates **1**−**6** (Chart 1).

Experimental Section

Materials. Commercially available extra pure phenylphosphonic dichloride (TCI, 97%), piperidine (TCI, 99%), *N*,*N*-diethylamine (TCI, 99%), ^{15}*N*,^{15}*N*-diethylamine (EURISO-TOP, 99% atom ^{15}N), morpholine (TCI, 99%), *N*-methylaniline (TCI, 98%), 2-methyl 2-propyl alcohol (TCI, 99%), 2-phenylpropyl alcohol (TCI, 98%), and 1-phenylethyl alcohol (TCI, 98%) were used as received without further purification. Tetrahydrofuran (THF) was dried over Na−benzophenone and distilled under nitrogen before use. GPE was dried and distilled over calcium hydride before use. Piperidine and *N*-methylaniline as an initiator were dried and distilled over KOH.

Measurements. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a JEOL EX-400 spectrometer using tetramethyl-

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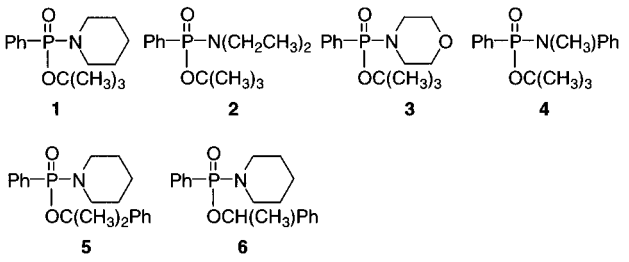
Chart 1



silane or 85% H_3PO_4 as an internal or external standard in $CDCl_3$ (or NO_2Ph-d_5 in the case of thermal reaction). ^{15}N and ^{14}N NMR spectra were recorded with a JEOL Lambda-500 spectrometer using NO_2CH_3 as an external standard in $CDCl_3$ (or NO_2Ph-d_5 in the case of thermal reaction). IR spectra were measured with a JASCO 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, equipped with two consecutive polystyrene gel columns [TSK gels G2500HXL (2×10^4: molecular weight of exclusion limit) and G4000HXL (4×10^5: molecular weight of exclusion limit] at 40 °C, using THF as an eluent with a flow rate of 1.0 mL/min by polystyrene calibration, and with a differential refractometer detector and Tosoh UV-8020 ultraviolet detectors (254 nm). Elemental analyses were carried out with a Yanaco Type MT-5 CHN, and a SX-Elements micro analyzer YS-10. GC-mass spectra were measured with a Shimadzu GCMS-QP5000.

Synthesis of *O-tert*-Butyl *P*-Phenyl 1-Piperidinyl Phosphonamidate, 1. Compound **1** was prepared according to the previously reported method.[19]

Synthesis of *O-tert*-Butyl *P*-Phenyl *N,N*-Diethyl Phosphonamidate, 2. To a solution of phenyl phosphonic dichloride (2.88 g, 14.7 mmol) in THF (30 mL) was added a solution of *N,N*-diethylamine (1.12 g, 15.3 mmol) and triethylamine (2.04 g, 20.2 mmol) in THF (20 mL) at 0 °C under nitrogen. The mixture was stirred at room-temperature overnight. A mass precipitated (triethylamine hydrochloride) was filtered off and the filtrate was concentrated by evaporation of the solvent to obtain *P*-phenyl *N,N*-diethyl phosphonamidic chloride as a transparent liquid.

To a suspension of sodium hydride (0.61 g (60% in oil), 15 mmol) in THF (20 mL) was added a solution of 2-methyl-2-propyl alcohol (1.09 g, 14.5 mmol) in THF (20 mL) at 0 °C under nitrogen. After the evolution of hydrogen gas stopped, a solution of crude *P*-phenyl *N,N*-diethyl phosphonamidic chloride in THF (40 mL) was added to the solution at 0 °C. The resulting solution was stirred at room temperature for 1 h and refluxed for 5 h. After removal of THF by evaporation, the residue was dissolved in chloroform and the resulted 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 ethyl acetate as an eluent to afford 2.10 g (7.8 mmol, 53%) of slightly yellow color oil. IR (NaCl, cm^{-1}): 3059, 2974, 2934, 2872, 1466, 1439, 1369, 1236, 1209, 1172, 1120, 1033, 983, 725, 700, 569. ^1H NMR: δ 7.62−7.27 (m, 5H, $-C_6H_5$), 2.97 (s, 4H, $-2(-CH_2-)$), 1.45 (s, 9H, $-3(CH_3)$), 0.94 (s, 6H, $-2(CH_3)$). ^{13}C NMR: δ 134.7, 132.9, 130.4, 127.4, 80.9, 38.4, 29.9, 13.4. ^{31}P NMR: δ 18.04. ^{14}N NMR: δ −318.1. Anal. Calcd for $C_{14}H_{24}NO_2P$: C, 62.44; H, 8.98; N, 5.20. Found: C, 62.66; H, 8.67; N, 5.12.

Synthesis of *O-tert*-Butyl *P*-Phenyl $^{15}N,^{15}N$-Diethyl Phosphonamidate, 2′. Compound **2′** was synthesized from phenylphosphonic dichloride (0.46 g, 2.4 mmol), $^{15}N,^{15}N$-diethylamine (0.24 g, 2.3 mmol), and 2-methyl-2-propyl alcohol (0.19 g, 2.5 mmol) in a manner similar to that used for **1**.

Yield: 0.27 g (1.0 mmol, 44%, slightly yellow color oil). IR (NaCl, cm^{-1}): 2976, 2932, 2872, 1465, 1438, 1369, 1235, 1166, 1122, 1024, 982, 790, 726, 699, 564. ^1H NMR: δ 7.66−7.29 (m, 5H, $-C_6H_5$), 3.08−2.92 (m, 4H, $-2(-CH_2-)$), 1.46 (s, 9H, $-3(CH_3)$), 0.98−0.94 (m, 6H, $-2(CH_3)$). ^{13}C NMR: δ 135.1 (d, J = 5.5 Hz), 133.3 (d, J = 5.5 Hz), 130.8, 127.8, 81.4 (d, J = 7.4 Hz), 38.8 (dd, J_1 = 5.5, J_2 = 5.5 Hz), 30.3, 13.8. ^{31}P NMR: δ 18.25 (d, J = 17.6 Hz). ^{15}N NMR: δ −313.35 (d, J = 18 Hz). Anal. Calcd for $C_{14}H_{24}{}^{15}NO_2P$: C, 62.21; H, 8.95; N, 5.55. Found: C, 62.20; H, 8.87; N, 5.30.

Synthesis of *O-tert*-Butyl *P*-Phenyl 1-Morpholinyl Phosphonamidate, 3. Compound **3** was synthesized from phenylphosphonic dichloride (3.02 g, 15.5 mmol), morpholine (1.32 g, 15.1 mmol), and 2-methyl-2-propyl alcohol (1.16 g, 15.4 mmol) in a manner similar to that used for **1**.

Yield: 3.02 g (10.7 mmol, 69%, white powder). Mp: 58−59 °C. IR (KBr, cm^{-1}): 2982, 2961, 2912, 2851, 1442, 1371, 1255, 1230, 1114, 966, 733, 702, 565, 515. ^1H NMR: δ 7.75−7.42 (m, 5H, $-C_6H_5$), 3.61 (s, 4H, $-O(CH_2)_2$), 3.05 (m, 4H, $-N(CH_2)_2$), 1.57 (s, 9H, $-3(CH_3)_3$). ^{13}C NMR: δ 133.2, 131.4, 131.1, 128.2, 82.3, 66.9, 44.0, 30.6. ^{31}P NMR: δ 16.5. ^{14}N NMR: δ −313.6. Anal. Calcd for $C_{14}H_{22}NO_3P$: C, 59.35; H, 7.83; N, 4.94. Found: C, 59.14; H, 7.89; N, 4.82.

Synthesis of *O-tert*-Butyl *P*-Phenyl *N*-Methyl-*N*-Phenyl Phosphonamidate, 4. Compound **4** was synthesized from phenylphosphonic dichloride (2.78 g, 14.2 mmol), *N*-methyl aniline (1.44 g, 13.4 mmol) and 2-methyl-2-propyl alcohol (1.08 g, 14.4 mmol) in a manner similar to that used for **1**.

Yield: 1.29 g (4.3 mmol, 32%, white powder). mp: 64−65.5 °C. IR (KBr, cm^{-1}): 3059, 2978, 2932, 1599, 1494, 1439, 1369, 1273, 1242, 1122, 983, 889, 754, 727, 696, 567, 542. ^1H NMR: δ 7.70−6.98 (m, 10H, $2(-C_6H_5)$), 3.18 (d, J = 8.3 Hz, 3H, $-CH_3$), 1.54 (s, 9H, $-3(CH_3)$). ^{13}C NMR: δ 145.0, 133.9, 131.2, 130.9, 128.5, 128.2, 122.6, 121.5, 83.3, 35.8, 30.3. ^{31}P NMR: δ 15.6. Anal. Calcd for $C_{17}H_{22}NO_2P$: C, 67.31; H, 7.31; N, 4.62. Found: C, 67.25; H, 7.32; N, 4.48.

Synthesis of *O*-2-Phenylpropyl *P*-Phenyl 1-Piperidinyl Phosphonamidate, 5. Compound **5** was synthesized from phenylphosphonic dichloride (2.95 g, 15.1 mmol) and piperidine (1.34 g, 15.7 mmol), followed by reaction with 2-phenylpropyl alcohol (2.04 g, 15.0 mmol) in a manner similar to that used for **1**.

Yield: 3.73 g (10.9 mmol, 72%, colorless oil). IR (NaCl, cm^{-1}): 3060, 2981, 2934, 2851, 1438, 1383, 1236, 1165, 1122, 1069, 981, 923, 729, 698, 562. ^1H NMR: δ 7.80−7.24 (m, 10H, $2(-C_6H_5)$), 3.08−2.92 (m, 4H, $-N(CH_2-)_2$), 1.95 (d, J = 18.6 Hz, 6H, $-2CH_3$), 1.55−1.42 (m, 6H, $-(CH_2)_3$). ^{13}C NMR: δ 146.9 (d, J = 7.4 Hz), 133.8, 132.0, 130.9 (d, J = 9.1 Hz), 128.1, 127.9 (d, J = 11.0 Hz), 126.9, 124.3 (d, J = 7.4 Hz), 83.2 (d, J = 9.2 Hz), 44.5, 31.0, 30.1, 25.5 (d, J = 5.5 Hz), 24.4. ^{31}P NMR: δ 17.7. Anal. Calcd for $C_{20}H_{26}NO_2P$: C, 69.95; H, 7.63; N, 4.08. Found: C, 70.03; H, 7.87; N, 3.97.

Synthesis of *O*-1′-Phenylethyl *P*-Phenyl 1-Piperidinyl Phosphonamidate, 6. Compound **6** was synthesized from phenylphosphonic dichloride (2.94 g, 15.1 mmol) and piperidine (1.31 g, 15.4 mmol), followed by reaction with 1-phenylethyl alcohol (1.82 g, 14.9 mmol) in a manner similar to that used for **1**.

Yield: 3.81 g (11.6 mmol, 77%, white powder). mp 80−81 °C. IR (KBr, cm^{-1}): 2932, 2851, 1439, 1379, 1234, 1163, 1124, 1070, 1010, 993, 958, 731, 698, 559. ^1H NMR: δ 7.81−7.26 (m, 10H, $2(-C_6H_5)$), 5.64 (m, 1H, $-CH-$), 2.80 (m, 4H, $-N(CH_2-)_2$), 1.68 (d, J = 6.3 Hz, 3H, $-CH_3$), 1.39−1.19 (m, 6H, $-(CH_2)_3$). ^{13}C NMR: δ 142.8, 131.1, 130.5, 128.5, 128.3, 128.2, 127.9, 72.9, 44.8, 25.5, 24.3. ^{31}P NMR: δ 21.3. Anal. Calcd for $C_{19}H_{24}NO_2P$: C, 69.28; H, 7.34; N, 4.25. Found: C, 69.23; H, 7.35; N, 4.24.

Polymerization. Typical procedure: initiator **1** (42.2 mg, 0.15 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 12 h, 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 *n*-hexane (70 mL) to precipitate

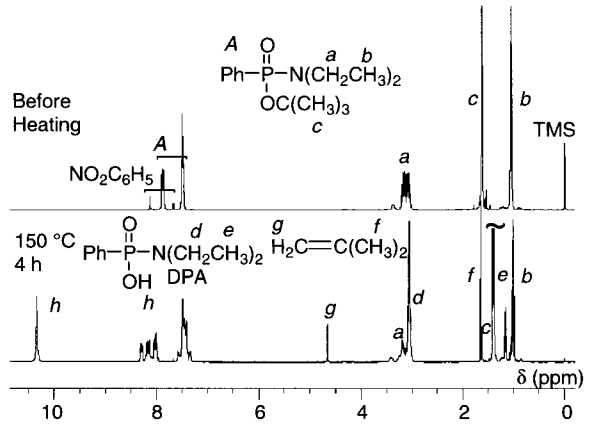


Figure 1. Thermal reaction of *O-tert*-butyl *P*-phenyl *N*,*N*-diethyl phosphonamidate (**2**) (0.3 M). ^{1}H NMR (400 MHz) spectra of **2** before and after heating in nitrobenzene-d_5 at 150 °C for 4 h.

the polymer. The polymer was separated from the supernatant decantation and dried in vacuo. The monomer conversion was determined by ^{1}H NMR spectroscopy before precipitation with *n*-hexane, and the molecular weight of the polymer was determined by GPC. The obtained polymer was identified to be polyGPE by ^{1}H NMR [δ 7.99−7.65 (m, 5H, $-C_6H_5$), 4.80−3.25 (m, 5H, $-OCH_2CH(CH_2Ph)-$) in $CDCl_3$] and IR spectra [3036, 2930, 2876, 1599, 1495, 1244, 1132, 1044, 754 (NaCl, cm^{-1})].

Results and Discussion

Initiator Synthesis. The phosphonamidates (**1**−**6**) were synthesized by the reaction of phenyl phosphonic dichloride with various amines, followed by reaction with 2-methyl-2-propyl alcohol, 2-phenylpropyl alcohol, or 1-phenylethyl alcohol in the presence of sodium hydride. The structures of **1**−**6** were confirmed by ^{1}H, ^{13}C, ^{31}P, and ^{14}N NMR, IR, and elemental analysis.

Thermal Decomposition of Phosphonamidates. First, the ^{1}H NMR spectroscopic change of **2** was monitored in nitrobenzene-d_5 to examine the thermal decomposition behavior. Figure 1 shows the ^{1}H NMR spectra of the solution before and after heating at 150 °C for 4 h. In the spectrum after heating, signals g and f assignable to isobutene appeared at 4.66 and 1.65 ppm, respectively. Signals h, d, and e assignable to hydroxyl, methylene, and methyl protons of *P*-phenyl *N*,*N*-diethyl phosphonamidic acid (DPA) also appeared at 10.3, 3.05, and 1.40 ppm, respectively.[20] It was also confirmed that isobutene and DPA were formed by GC−mass spcetrometry.

Thermal Reaction of Phosphonamidates with GPE. Our previous work has shown that *O-tert*-butyl *P*-phenyl 1-piperidinyl phosphonamidate (**1**) can serve as a thermally latent anionic initiator for the polymerization of GPE.[19] The special feature of the phosphonamidates is the formation of an initiating species (amine) accompanying cyclization after reaction with GPE (Scheme 1). The thermal reaction of **2** with GPE was monitored by NMR spectroscopy in the presence of GPE in nitrobenzene-d_5 at 150 °C for 4 h in a sealed NMR sample tube to confirm the formation of an amine. Figure 2 shows the time dependence of the ^{1}H NMR spectra of the reaction mixture of **2** and GPE. Signal g corresponding to isobutene and signals p, d, and e assignable to hydroxyl, methylene, and methyl protons of *P*-phenyl *N*,*N*-diethyl phosphonamidic acid (DPA) appeared at 10.5, 2.99, and 1.41 ppm, respectively, in a

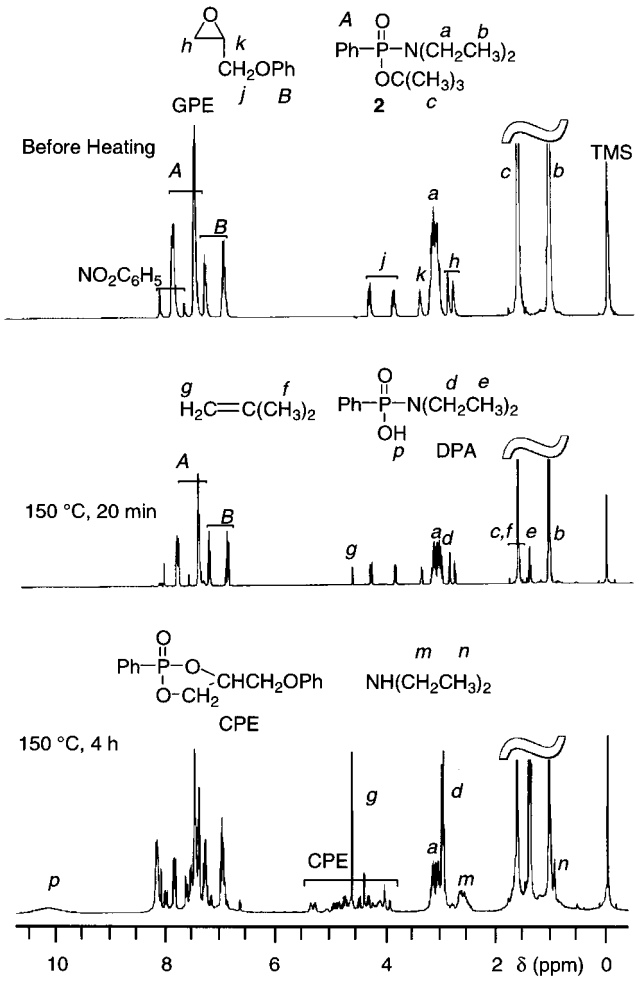
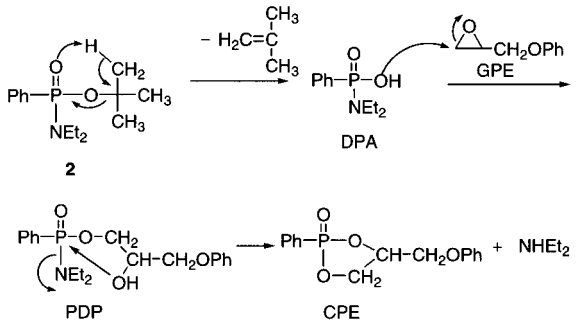


Figure 2. Thermal reaction of GPE (0.15 M) with *O-tert*-butyl *P*-phenyl *N*,*N*-diethyl phosphonamidate (**2**) (0.37 M). ^{1}H NMR (400 MHz) spectra of **2** before and after heating in nitrobenzene-d_5 at 150 °C for 20 min and 4 h.

Scheme 1



decomposition similar to that of only **2** as shown in Figure 1. The formed DPA may favorably react with GPE to form 2-hydroxyl 3-phenoxypropyl *P*-phenyl *N*,*N*-diethyl phosphonamidate (PDP) as shown in Scheme 1.[21] The ^{1}H NMR signals at 3.7−5.2 ppm were assignable to a cyclic phosphonic acid ester (CPE), which would be formed by the cyclization of PDP accompanying amine liberation.[22] CPE formed in the thermal reaction had a specrtum identical with that of the authentic sample, which was synthesized either from phenylphosphonic dichloride and 3-phenoxy-2-propanediol or phenylphosphonic acid and GPE. Signal m at 2.65 ppm indicated the formation of diethylamine and an adduct of diethylamine with GPE. The phosphorus

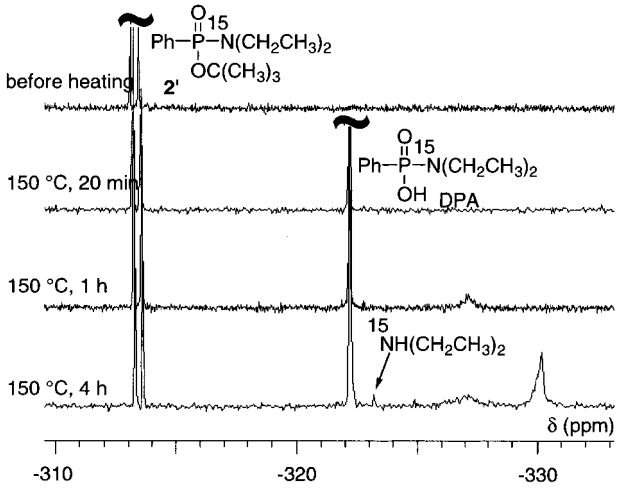


Figure 3. Thermal reaction of GPE (0.2 M) with *O*-*tert*-butyl *P*-phenyl ^{15}N,^{15}N-diethyl phosphonamidate (**2′**) (0.3 M). ^{15}N NMR (50.55 MHz) spectra of **2′** before and after heating in nitrobenzene-d_5 at 150 °C for 4 h.

signals of CPE and DPA were observed at 37 and 4.1 ppm in the ^{31}P NMR spectra, respectively, and the relative intensity increased with reaction time. All of the products detected by NMR spectroscopy were also confirmed by GC−mass spectrometry. These results agreed well with the thermal reaction behavior of *O*-*tert*-butyl *P*-phenyl 1-piperidinyl phosphonamidate (**1**) with GPE.[19]

Furthermore, the thermal reaction of ^{15}N-labeled phosphonamidates **2′** (0.3 M) and GPE (0.2 M) was carried out in nitrobenzene-d_5 at 150 °C for 4 h to elucidate the initiating species. Figure 3 shows the ^{15}N NMR spectra of the reaction mixture. A signal corresponding to DPA appeared at −322 ppm after heating for 20 min, and the relative intensity increased compared with the signal of **2′** at −313 ppm as the reaction time. Simultaneously, broad signals assignable to diethylamine−GPE adducts appeared around −327 and −330 ppm.[23] The signal of diethylamine was observed at −323 ppm after 4 h, probably due to the rapid reaction with GPE to form the adducts. Figure 4 exhibits the GC−mass spectra of the reaction mixture, confirming the formation of ^{15}N,^{15}N-diethylamine and *P*-phenyl ^{15}N,^{15}N-diethyl phosphonamidic acid, along with isobutene. Consequently, this suggests that diethylamine was formed as illustrated in Scheme 1, and reacted with GPE to afford the adducts.

Polymerization of GPE with Phosphonamidates. Polymerization of GPE was carried out with the phosphonamidates **1**−**4** (3 mol %) as an initiator at 110−190 °C for 12 h. The polymerization proceeded homogeneously throughout the reaction, because **1**−**4** were completely soluble in GPE at ambient temperature. Figure 5 shows the temperature−conversion relationships in the polymerization. No polymerization of GPE took place with **1**−**4** below 110 °C, whereas it proceeded at elevated temperatures. The activity order of the phosphonamidates was **1** > **2** > **3** > **4**. This agreed with the result that the reaction of epoxy compounds with amines is strongly depended on the nucleophilicity of the amine.[24−26] In fact, piperidine (3 mol %) as an initiator polymerized GPE with 78% conversion at 190 °C, while *N*-methylaniline (3−5 mol %) only below 8% conversion in the control experiments.[27] These results supported polymerization of GPE via an anionic mech-

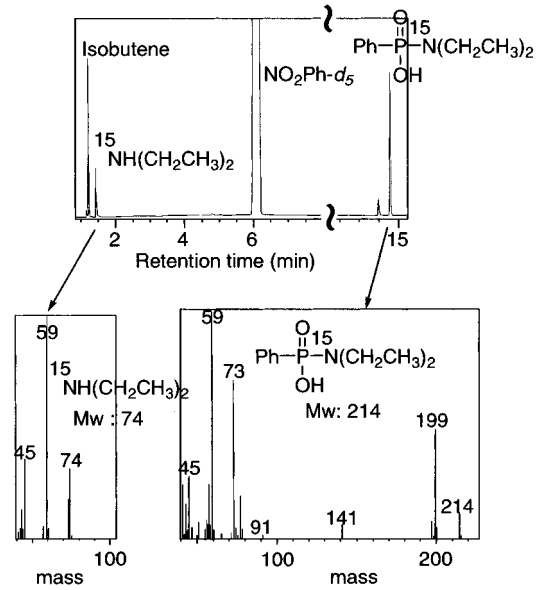


Figure 4. GC−mass spectra of the reaction mixture of GPE with *O*-*tert*-butyl *P*-phenyl ^{15}N,^{15}N-diethyl phosphonamidate (**2′**) after heating in nitrobenzene-d_5 at 150 °C for 4 h.

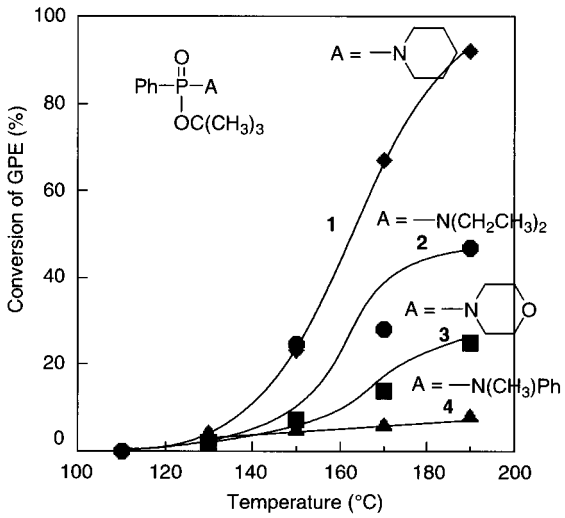


Figure 5. Temperature−conversion relationships in the polymerization of GPE with phosphonamidates **1**−**4** (3 mol %) for 12 h.

anism initiated by the amines formed from **1**−**4**.[28] No variation was observed in the ^{31}P NMR spectra of the reaction mixture before and after the polymerization at 110 °C, while the signal of CPE appeared after the polymerization above 110 °C, indicating the formation of amines. Therefore, the phosphonamidates **1**−**4** served as thermally latent anionic initiators for the polymerization of GPE. The obtained polymers had number-average molecular weights ranging from 700 to 1400.[29]

Further, polymerization of GPE was carried out using phosphonamidates **5** and **6** (3 mol %) with 2-phenyl-2-propyl and 1-phenylethyl ester parts at 90−190 °C for 12 h. No polymerization proceeded with **5** and **6** below 90 and 170 °C, respectively, but polymerization proceeded rapidly above those temperatures to afford the polymers (Figure 6). Hence, **5** and **6** also served as thermally latent initiators for the polymerization of GPE. The activity order was **5** > **1** > **6**.

Thermal decomposition of the phosphonamidates **1**, **5**, and **6** was monitored by ^{1}H and ^{31}P NMR spectroscopy

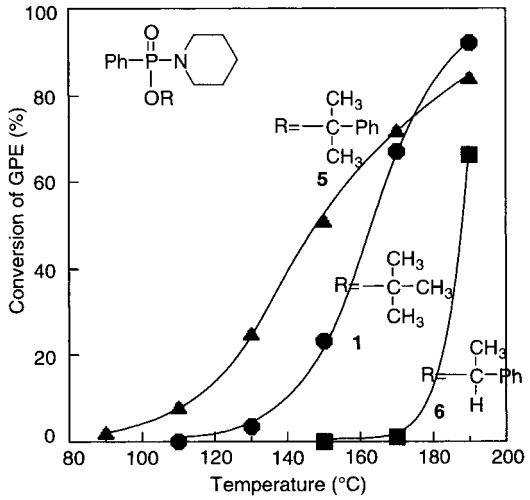


Figure 6. Temperature−conversion relationships in the polymerization of GPE with phosphonamidates **1**, **5**, and **6** (3 mol %) for 12 h.

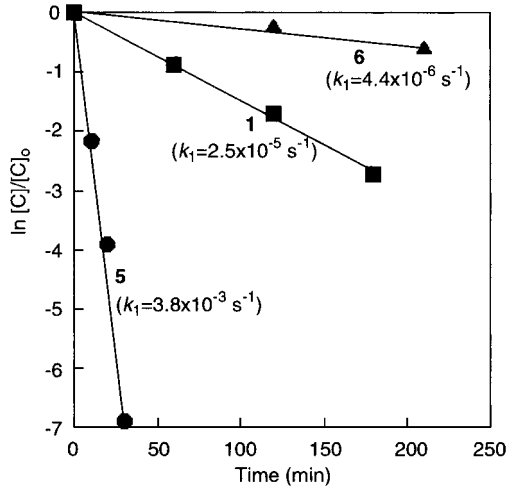


Figure 7. First-order plots of the thermal decomposition of phosphonamidates **1**, **5**, and **6** (0.2 M) in nitrobenzene-d_5 at 150 °C.

in nitrobenzene-d_5 at 150 °C to confirm the activity order. *P*-Phenyl 1-piperidinyl phosphonamidic acid and the corresponding olefins were formed. Olefins-elimination is considered as the rate-determining step, because the reaction rate constant for DPA (1 equiv) with GPE (15 equiv) was 7.7×10^{-3} s^{-1} as the pseudo-first order, while that for ester decomposition of phosphonamidate **1** was 2.5×10^{-5} s^{-1}. Figure 7 depicts the first-order plots of the decomposition of **1**, **5**, and **6**, whose decomposition rate constants (k_1) are determined from the slopes. The k_1 increased in the order of **5** > **1** > **6**, which agrees with the activity order for the polymerization of GPE.

The polymerization of GPE was carried out with ^{15}N-labeled phosphonamidate **2′** (3 mol %) at 190 °C. Signals derived from diethylamine were observed at 0.9−3.3 ppm in the ^{1}H NMR spectrum of the polymer obtained.[30] Figure 8 shows the ^{15}N NMR spectra of (A) **2′** and (B) the polymer. Signals assignable to the ^{15}N-labeled diethylamino moiety of the initiating polymer end were observed at around −315 to −317 ppm in the isolated polymer (B). These results indicate that the end group of the GPE polymer is an amino group; i.e., the initiating species is an amine.

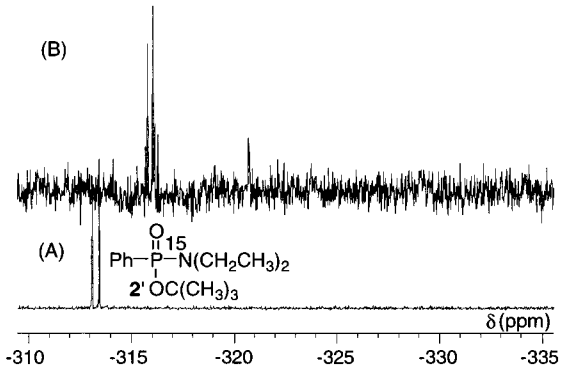


Figure 8. ^{15}N NMR spectra (50.55 MHz, $CDCl_3$) of (A) *O*-*tert*-butyl *P*-phenyl ^{15}N,^{15}N-diethyl phosphonamidate (**2′**) and (B) polyGPE obtained by the polymerization of GPE with (**2′**) (3 mol %) at 190 °C for 12 h. The sample was isolated by precipitation with *n*-hexane.

In summary, we demonstrated that the phosphonamidates successfully serve as thermally latent anionic initiators in the polymerization of GPE. Initiating may occur by amines released by successive reactions of olefin-elimination, GPE addition, and cyclization. The activities of the phosphonamidates were affected by the amide and ester substituents, i.e., the phosphonamidates with a larger decomposition rate of the ester part and the basicity of the corresponding amine showed higher activity. Determination of the pot-life of phosphonamidates is now underway and will be reported on in the future.

Supporting Information Available: Elemental analysis data of polymers obtained by **1** and piperidine as initiators (Table S1); detailed polymerization data corresponding to Figures 4 and 5 (Table S2); GC−mass spectra of CPE (Figure S1); ^{1}H NMR spectrum of the polymer obtained by the polymerization of GPE with phosphonamidate **2′** at 190 °C for 12 h (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Signals assignable to the vinylic end group, characteristic of anionic chain transfer, were observed at 5.5−6.5 ppm in the ^{1}H NMR spectrum of the polymer isolated by HPLC.
(29) The details of the polymerization including the polymer yield, M_n, and M_w/M_n are summarized in the Supporting Information (Table S2).
(30) Supporting Information (Figure S1): see the ^{1}H NMR spectrum of the polymer obtained by phosphonamidate **2′**.

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