Communications to the Editor

Polymerization of Glycidyl Phenyl Ether with Phosphonic Amide Ester as a Novel Thermally Latent Anionic Initiator

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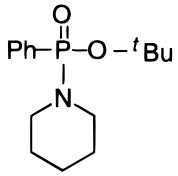
Latent initiators show no activity under normal conditions but release active species by external stimulation such as heating and photoirradiation. They have been widely used in several industrial fields such as paints, inks, epoxy molding compounds, and photoresists. Several onium salts such as sulfonium, pyridinium, and phosphonium salts[1] as well as diaryliodonium and triarylsulfonium salts[2] have been developed as thermally latent initiators or photoinitiators. However, onium salts have a limitation on industrial application because they have several problems such as low solubility in monomers and solvents, remaining of inorganic compounds in polymers, and high cost. In recent years considerable efforts have been made to overcome these problems by developing non-salt-type initiators.[3] Recently, we have reported N-substituted phthalimides,[4] aminimides,[5] carboxylic acid esters,[6] and sulfonic acid esters[7] as non-salt-type latent initiators. Organophosphorus compounds have been utilized for medicines, agricultural chemicals, plasticizers, and polymer additives.[8] Organophosphorus compounds possess various merits such as easy molecular design, easy synthesis, wide application, and low cost. We have recently reported that phosphonic acid esters can serve as non-salt-type *cationic* latent initiators in the polymerization of glycidyl phenyl ether (GPE).[9] This communication deals with a phosphonic amide ester, *O-tert*-butylpiperidinyl phenylphosphonate (**1**), as a novel thermally latent *anionic* initiator in the polymerization of GPE.



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The phosphonic amide ester **1** was synthesized in 73% yield by the reaction of phenylphosphonic dichloride with piperidine, followed by the reaction with *tert*-butyl alcohol in the presence of sodium hydride.[10] Prior to the

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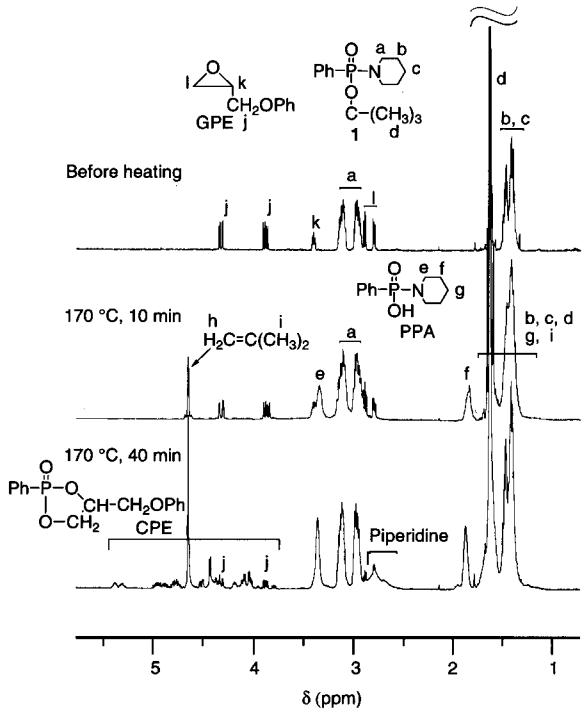

Figure 1. ^{1}H NMR spectra of the solution of phosphonic amide ester **1** (1.7 M) and GPE (0.56 M) in nitrobenzene-d_5 before and after heating at 170 °C for 10 and 40 min in a sealed NMR sample tube. ^{1}H NMR measurement was carried out after the tube had been cooled to room temperature.

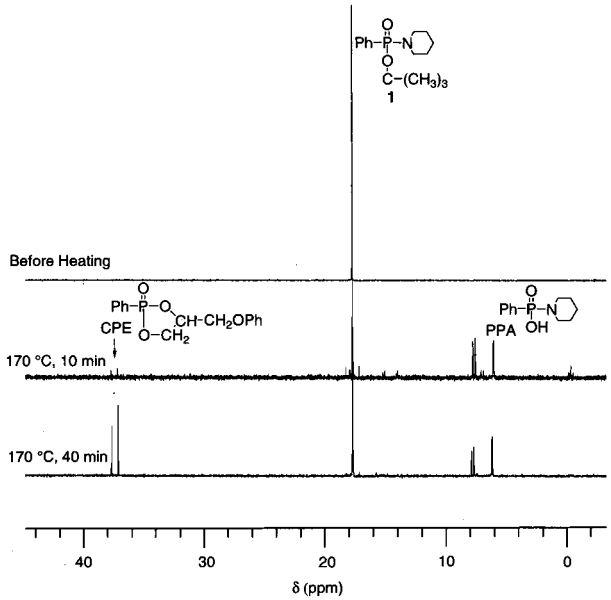

Figure 2. ^{31}P NMR spectra of the solution of phosphonic amide ester **1** (1.7 M) and GPE (0.56 M) in nitrobenzene-d_5 before and after heating at 170 °C for 10 and 40 min in a sealed NMR sample tube. ^{31}P NMR measurement was carried out after the tube had been cooled to room temperature.

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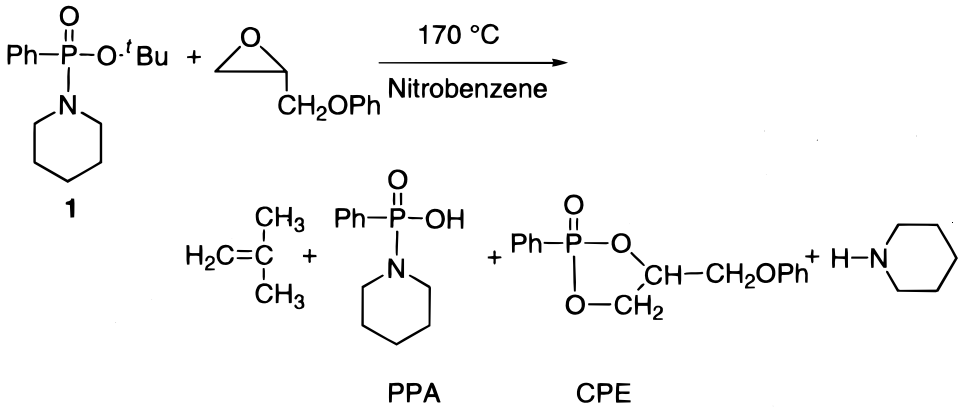
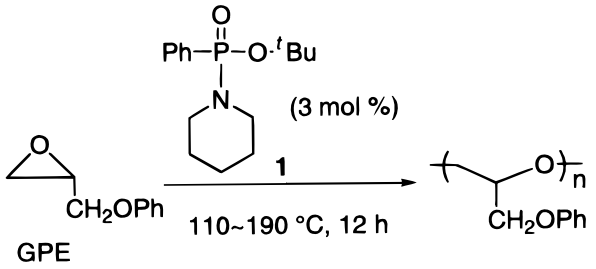
Scheme 1



Scheme 2



polymerization of GPE with **1** as an initiator, the thermal reaction of **1** was carried out in the presence of $^1/_3$ equiv of GPE at 170 °C for 40 min in nitrobenzene-d_5 in a sealed NMR sample tube as shown in Scheme 1. Figures 1 and 2 show time dependence of the ^{1}H and ^{31}P NMR spectra of the reaction mixture of **1** and GPE. The ^{1}H NMR spectrum showed a signal *h* corresponding to isobutene at 4.66 ppm after heating for 10 min. The amount of isobutene increased as the reaction time. Simultaneously, signals *e* and *f* assignable to piperidinylphenylphosphonamidic acid (PPA)[11] appeared at 3.4 and 1.9 ppm. The signals at 3.7−5.2 ppm could be assignable to a cyclic phosphonic acid ester (CPE),[12] which should be formed by the addition of PPA with GPE, followed by the elimination of piperidine accompanying cyclization.[13] The signals at 2.8 ppm indicated the formation of piperidine and an adduct of piperidine with GPE, acting as initiation species. The relative intensity of the ^{31}P NMR signal of CPE at 37 ppm increased as the reaction time. All the products detected by NMR spectroscopy were also confirmed by GC−mass spectrometry.[14]

The bulk polymerization of GPE with the phosphonic amide ester **1** (3 mol %) was carried out at 110−190 °C for 12 h (Scheme 2), where **1** was completely soluble in GPE in all cases. The polymerization did not proceed below 110 °C but proceeded rapidly above the temperature as shown in Figure 3. The number-average molecular weights of the obtained polymers were ranging from 900 to 1000. The yield of *n*-hexane-insoluble polymer increased with the conversion. Signals based on piperidine were observed at 1.1−3.3 ppm in the ^{1}H NMR spectrum of the obtained polymer, supporting that the piperidine had initiated the polymerization.[15] Incorporation of piperidine in the polymer was also confirmed by elemental analysis. The ^{31}P NMR of the polymerization mixture did not show change before and after polymerization at 110 °C but showed the formation of CPE above the temperature, indicating the formation of piperidine.

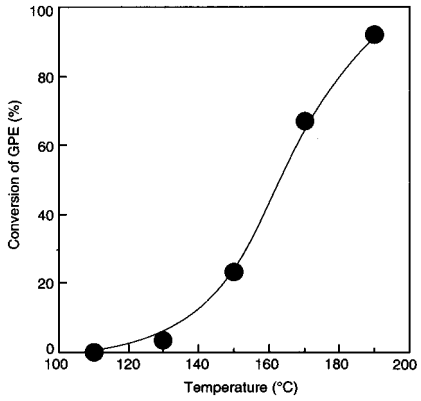


Figure 3. Temperature−conversion curve in the polymerization of GPE with **1** (3 mol %) for 12 h.

In the control experiments, piperidine polymerized GPE with 78% conversion at 190 °C and 20% even at 110 °C,[16] while the phosphonic amide ester **1** did not at 110 °C, indicating thermal latency. Additionally, the polymers obtained by the polymerization with **1** and piperidine at 190 °C showed a similar N content (0.31 and 0.39%, respectively), indicating that piperidine was the initiation species in both cases.

In conclusion, we have developed phosphonic amide ester **1** as a novel thermally latent anionic initiator, releasing piperidine as an initiating species by heating. We believe that this novel catalytic system can be applicable to a hardner of epoxy resin. Further research such as the substituent effect of the phosphonic amide ester on the initiator activity is now in progress.

Supporting Information Available: Experimental section; GC−mass spectra of the solution of phosphonic amide ester **1** (1.7 M) and GPE (0.56 M) in nitrobenzene-d_5 after heating at 170 °C for 40 min (Figure S1); ^{1}H NMR spectrum of the polymer obtained by the polymerization of GPE with phosphonic amide ester **1** at 190 °C for 12 h (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Endo, T.; Sanda, F. *Macromol. Symp.* **1996**, *107*, 237.
(2) (a) Crivello, J. V.; Lam, H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977. (b) Crivello, J. V. In *Developments in Polymer Photochemistry*; Allen, N. S., Ed.; Applied Science Publishers: Essex, England, 1981; Chapter 1.
(3) (a) Reetz, M. T.; Ostarek, R. T. *J. Chem. Soc., Chem. Commun.* **1988**, 213. (b) Reetz, M. T. *Angew. Chem.* **1988**, *100*, 1026. (c) Reetz, M. T.; Hutte, S.; Goddard, R.; Miner, U. *J. Chem. Soc., Chem. Commun.* **1995**, 275. (d) Zagala, A. P.; Hogen-Esch, T. E. *Macromolecules* **1997**, *30*, 6695.

(e) Baskaran, D.; Chakrapani, S.; Sivearam, S.; Hogen-Esch, T. E.; Muller, A. H. *Macromolecules* **1999**, *32*, 2865.
(4) Takata, T.; Menceloglu, Y. Z.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 501.
(5) Lee, S. D.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 689.
(6) Moriguchi, T.; Nakane, Y.; Takata, T.; Endo, T. *Macromolecules* **1995**, *28*, 4334.
(7) (a) Lee, S. D.; Takata, T.; Endo, T. *Macromolecules* **1996**, *29*, 3317. (b) Lee, S. D.; Takata, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 293.
(8) Pudovik, A. N. In *Chemistry of Organophosphorus Compound*; Mir Publishers: Moscow, 1989.
(9) Kim, M. S.; Sanda, F.; Endo, T. *Macromolecules* **1999**, *32*, 8291.
(10) The detail of the synthesis of *O-tert*-butyl piperidinyl phenylphosphonate (**1**) is described in the Supporting Information.
(11) The ^{1}H NMR and ^{31}P NMR signals were assigned according to the spectroscopic data of the authentic sample as follows. (The synthetic procedure of the sample is described in the Supporting Information.) ^{1}H NMR (nitrobenzene-d_5): δ 7.68−7.40 (m, 5H, $-C_6H_5$), 3.27 (s, 4H, $-N(CH_2-)_2$), 1.79 (s, 4H, $-(CH_2)_2CH2$), 1.55 (s, 2H, $-(CH_2)_2CH2$). ^{31}P NMR (nitrobenzene-d_5): δ 5.9.
(12) The ^{1}H NMR and ^{31}P NMR signals were assigned according to the spectroscopic data of the authentic sample synthesized by the reaction of phenylphosphonic dichloride with 3-phenoxy-1,2-propanediol. (The synthetic procedure of the sample is described in the Supporting Information.) ^{1}H NMR ($CDCl_3$): δ 8.02−6.89 (m, 10H, 2($-C_6H_5$)), 5.19−4.14 (m, 5H, $-CHCH_2CH_2-$). ^{31}P NMR ($CDCl_3$): δ 37.13 (J = 31.3 Hz).
(13) (a) Nuretdinova, O. N.; Arbuaov, B. A. *Izv. Akad. Nauk SSSR., Ser. Khim.* **1981**, 1130. (b) Nuretdinova, O. N.; Arbuaov, B. A. *Izv. Akad. Nauk SSSR., Ser. Khim.* **1983**, 675. (c) Nuretdinova, O. N.; Guseva, F. F. *Izv. Akad. Nauk SSSR., Ser. Khim.* **1984**, 2136. (d) Nuretdinova, O. N.; Novikova, V. G. *Izv. Akad. Nauk SSSR., Ser. Khim.* **1986**, 2787. (e) Biela, T.; Kubisa, P. *Makromol. Chem.* **1991**, *192*, 473.
(14) GC−mass spectra of the solution of phosphonic amide ester **1** (1.7 M) and GPE (0.56 M) in nitrobenzene-d_5 after heating at 170 °C for 40 min are shown in the Supporting Information (Figure S1).
(15) The ^{1}H NMR spectrum of the polyGPE obtained by the polymerization of GPE with phosphonic amide ester **1** at 190 °C for 12 h is shown in the Supporting Information (Figure S2). Incorporation ratios of piperidine in the polymer calculated by ^{1}H NMR and elemental analysis were 3.2 and 3.4%, respectively.
(16) The polymerization of glycidyl phenyl ether with piperidine gradually proceeded even at room temperature.

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