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Phosphonamidodithioate as a novel thermally latent initiator in the polymerization of glycidyl phenyl ether

Moonsuk Kim,[a] Fumio Sanda[a] and Takeshi Endo[b,*]

[a]*Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan*

[b]*Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan*

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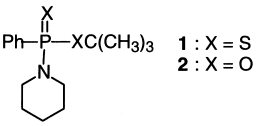
Abstract

S-tert-Butyl-*P*-phenyl-1-piperidinyl phosphonamidodithioate (**1**) served as a novel thermally latent anionic initiator in the polymerization of glycidyl phenyl ether. © 2000 Published by Elsevier Science Ltd.

Latent initiators can generate active species for polymerization by external stimulation such as heating or photoirradiation, which have been industrially used in coatings, adhesives, and inks. Crivello and Lam[1] and Endo and Sanda[2] have developed several onium salts such as sulfonium, pyridinium, phosphonium, diaryl iodonium, and triaryl sulfonium salts, which are useful as efficient latent thermal and photo initiators. Since onium salts are accompanied by several problems such as low solubility in monomers and solvents, remaining of inorganic compounds in polymers, and high cost for practical use, we have developed *N*-substituted phthalimides,[3] aminimides,[4] carboxylates,[5] sulfonates,[6] and phosphonates[7] as non-salt-type latent initiators to overcome the problems. Recently, we have reported that a phosphonamidate (**2**) can serve as a non-salt-type latent initiator in the polymerization of glycidyl phenyl ether (GPE).[8] We report herein a novel latent initiator, phosphonamidodithioate (**1**) in comparison with the corresponding phosphonamidate (**2**).



* Corresponding author. Tel: +81-238-26-3090; fax: +81-238-26-3092; e-mail: tendo@poly.yz.yamagata-u.ac.jp

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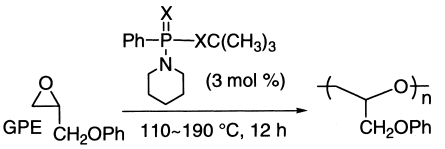
S-*tert*-Butyl-*P*-phenyl-1-piperidinyl phosphonamidodithioate (**1**) was synthesized by the reaction of phenylthiophosphonic dichloride with piperidine in the presence of triethylamine, followed by the reaction with *tert*-butyl mercaptan in the presence of sodium hydride, and the structure was confirmed by ^{1}H, ^{13}C, ^{31}P NMR, and IR spectroscopy besides element analysis.[9] Polymerization of GPE was carried out with **1** (3 mol%) at 110–190°C for 12 h (Scheme 1). The phosphonamidodithioate (**1**) was completely soluble in GPE at ambient temperature and the polymerization proceeded homogeneously. No polymerization of GPE proceeded below 110°C, but proceeded rapidly above 110°C to afford the polymers with the M_n of 600–1000, as shown in Fig. 1 and Table 1, containing the data of **2** for comparison. GPE was converted quantitatively at 170°C with **1**, while 67% of GPE was converted with **2**. Phosphonamidodithioate **1** showed activity higher than the corresponding phosphonamidate **2**.



Scheme 1.

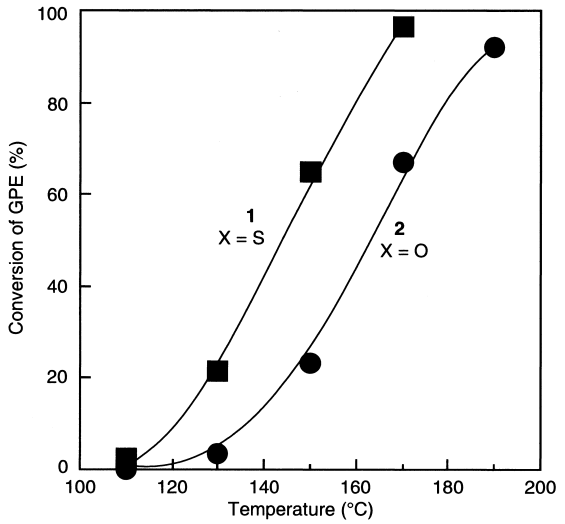


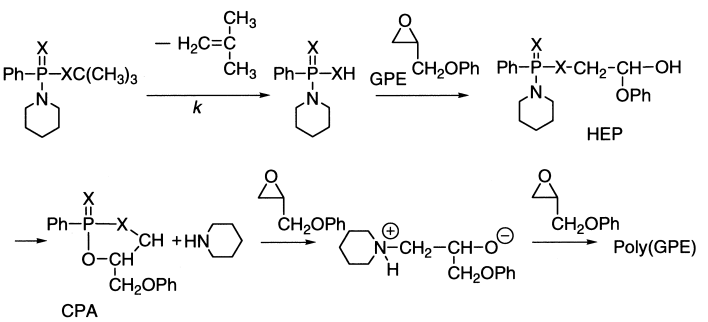
Figure 1. Temperature–conversion relationships in the polymerization of GPE with **1** and **2** (3 mol%) for 12 h

Scheme 2 illustrates a plausible mechanism of the polymerization, where the active species is piperidine formed by successive reactions of isobutene-elimination to form phosphonamidic acid or phosphonamidodithioic acid, addition with GPE, and cyclization.[8] The ^{1}H NMR spectrum of the polymer obtained by **1** showed signals derived from piperidine at 0.9–3.3 ppm. It was confirmed that the isolated polymer contained 0.6% of nitrogen by elemental analysis, and a vinylic end group that is characteristic of anionic chain transfer. Consequently, we can conclude that the polymerization proceeded via an anionic mechanism initiated with piperidine.[10,11] The decomposition rates k of **1** and **2** were determined by monitoring the disappearance of the signal of phosphonamidate or phosphonamidodithioate in ^{31}P NMR to compare the initiator activity. The rate of **1** was about six times larger than that of **2**.[12] Furthermore, ab initio calculations

Table 1
Polymerization of GPE with **1** and **2** (3 mol%) for 12 h

Initiator	Temp. (°C)	Conv.[a] (%)	Yield[b] (%)	M_n[c]	M_w/M_n[c]
1	110	2			
	130	22	7	600	1.4
	150	65	35	900	1.2
	170	97	51	900	1.3
2	130	3			
	150	23	15	900	1.2
	170	67	35	1000	1.3
	190	92	73	1000	1.4

[a] Determined by ^{1}H NMR.
[b] *n*-Hexane-insoluble part.
[c] Estimated by GPC based on polystyrene standard samples.

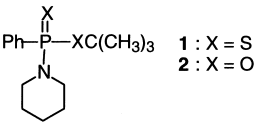


Scheme 2.

were carried out to examine the difference of the initiator activity (Table 2).[13] It was confirmed that **1** had longer C–H and P–N bond lengths, and a larger positive atomic charge of the *tert*-butyl proton than those of **2**. These data imply faster formation of piperidine by successive reactions as shown in Scheme 2, resulting in a higher activity of **1** in the polymerization. The reaction of isobutene-elimination is considered as the rate-determining step.

Table 2
Computed C–H and P–N bond length and atomic charge of the protons of the *tert*-butyl groups in **1** and **2**

Initiator (X)	Atomic charge (e)	Bond length (Å)	
		C–H	P–N
1 (S)	+0.116	1.086	1.832
2 (O)	+0.107	1.085	1.445



In summary, the phosphonamidodithioate **1** served as a good thermally latent initiator for the polymerization of GPE. The decomposition rate, as well as ab initio calculations, could explain the higher activity of **1** compared with the corresponding phosphonamidate **2**. We could demonstrate that replacement of oxygen to sulfur was a simple and effective method to enhance the initiator activity.

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9. *S-tert*-Butyl-*P*-phenyl-1-piperidinyl phosphonamidodithioate (**1**) was synthesized as follows: To a solution of phenyl thiophosphonic dichloride (2.99 g, 14.2 mmol) in THF (30 mL) was added a solution of piperidine (1.33 g, 15.6 mmol) and triethylamine (2.03 g, 20.0 mmol) in THF (20 mL) at 0°C under nitrogen. The mixture was stirred overnight at room temperature. The precipitated mass (triethylamine hydrochloride) was filtered off and the filtrate was concentrated by evaporation of the solvent to obtain *P*-phenyl-1-piperidinyl thiophosphonamidic chloride as a transparent liquid. To a suspension of sodium hydride (0.60 g (60% in oil), 15 mmol) in THF (20 mL) was added a solution of *tert*-butyl mercaptane (1.34 g, 14.9 mmol) in THF (30 mL) at 0°C under nitrogen. After the evolution of hydrogen gas stopped, a solution of crude *P*-phenyl-1-piperidinyl thiophosphonamidic chloride in THF (30 mL) was added to the solution at 0°C. The resulting solution was refluxed for 6 h and stirred overnight at room temperature. After removal of THF by evaporation, the residue was dissolved in chloroform and the resulting solution was washed several times with water 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 hexane and ether (v/v = 80/20) as an eluent to afford 3.11 g (9.9 mmol, 69.7%) of white solid. It was recrystallized from *n*-hexane and ether to give white crystals. Mp 54–55°C. IR (KBr, cm^{-1}): 3055, 2934, 2852, 1437, 1365, 1205, 1157, 1099, 1057, 945, 719, 650. ^{1}H NMR ($CDCl_3$): δ 8.08–7.44 (m, 5H, -C_6H_5), 3.17–3.01 (m, 4H, -$N(CH_2)_2$-), 1.56–1.43 (m, 15H, -$(CH_3)_3$, -$(CH_2)_3$). ^{13}C NMR ($CDCl_3$): δ 137.4, 131.4, 131.3, 131.2, 128.2, 128.1, 51.5, 46.2, 32.4, 32.3, 26.1, 24.5. ^{31}P NMR ($CDCl_3$): δ 77.9. Anal. calcd for $C_{15}H_{24}NPS_2$: C, 57.48; H, 7.72; N, 4.47; S, 20.46. Found: C, 57.27; H, 7.64; N, 4.36; S, 20.23.
10. One referee pointed out that the polymerization would be initiated from HEP without releasing piperidine because it was confirmed that the obtained polymer contained 1.83% sulfur by elemental analysis. However, we suppose that the presence of sulfur is responsible for the reaction of CPA with the polymer[11] because phenylphosphonic acid and *O,O*-di-*tert*-butyl phenylphosphonate did not convert the monomer under similar conditions.

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12. The decomposition rates were estimated by ^{31}P NMR (161.7 MHz) measurement of **1** and **2** in NO_2Ph-d_5 (0.2 M) at 150°C. k_1: 2.04×10^{-4} s^{-1}, k_2: 3.15×10^{-5} s^{-1}.
13. All calculations were carried out with the GAUSSIAN-94 programs 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 using the HF/6-311G** basis set.