Polymerization of Glycidyl Phenyl Ether with a Thiophosphonic Acid Ester as a Novel Thermally Latent Initiator

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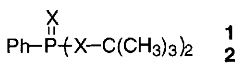
(Received November 9, 1999; CL-990959)

S,*S*-Di-*t*-butyl phenylthiophosphonate (**1**) served as a novel thermally latent initiator in the polymerization of glycidyl phenyl ether (GPE) in the presence of $ZnCl_2$.

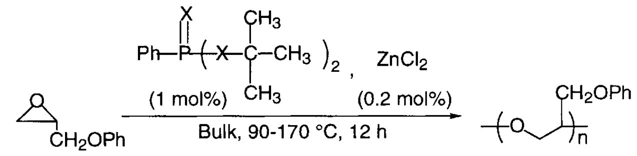
Latent initiators can generate active species for polymerization by external stimulation such as heating or photoirradiation, which have been widely used in industrial fields such as coatings, adhesives, and inks. Crivello et al.[1] and we[2] have developed several onium salts such as sulfonium, pyridinium, phosphonium, diaryl iodonium, and triaryl sulfonium salts, which are useful as efficient latent thermal and photo initiators. Meanwhile, *N*-substituted phthalimides,[3] aminimides,[4] carboxylic acid esters,[5] and sulfonic acid esters[6] have succeeded as non-salt-type latent initiators, overcoming the problems of onium salts such as low solubility in monomers and solvents, remaining of inorganic compounds in polymers, and high cost. Recently, we have reported that phosphonic acid esters can serve as non-salt-type latent initiators in the polymerization of glycidyl phenyl ether (GPE).[7] We report herein a novel latent initiator, thiophosphonic acid ester (**1**) in comparison with the corresponding phosphonic acid ester (**2**).



$Ph-\overset{X}{\overset{\|}{P}}(X-C(CH_3)_3)_2$

1 : X = S
2 : X = O

S,*S*-Di-*t*-butyl phenylthiophosphonate (**1**) was synthesized by the reaction of phenylthiophosphonic dichloride with *t*-butyl mercaptan in the presence of sodium hydride, and the structure was confirmed by ^1H, ^{13}C, ^{31}P NMR, and IR spectroscopy besides element analysis.[8] Polymerization of GPE with **1** (1 mol%) was carried out at 170-190 °C for 12 h. The phenylthiophosphonate (**1**) was completely soluble in GPE at ambient temperature and the polymerization proceeded homogeneously, but the conversion of GPE was below 4% under these conditions to obtain only a trace amount of GPE oligomer (M_n 400). The nucleophilic thiophosphonate anion formed by the thermal decomposition of **1** might terminate the cationic polymerization of GPE. We have recently found that $ZnCl_2$ is effective to decrease the nucleophilicity of a phosphonate anion generated from a phosphonic acid ester, resulting in a high initiator activity.[7] Therefore, the polymerization of GPE with **1** (1 mol%) was carried out in the presence of $ZnCl_2$ (0.2 mol%) at 90-170 °C for 12 h (Scheme 1). The polymerization of GPE did not proceed below 90 °C, but proceeded rapidly above 90 °C to afford the polymers with M_n of 2500-3500, as shown in Figure 1 and Table 1. GPE was converted quantitatively at 170 °C. The activity of thiophosphonate **1** was higher than that of the corresponding phosphonate **2**.[9,10]



Scheme 1.

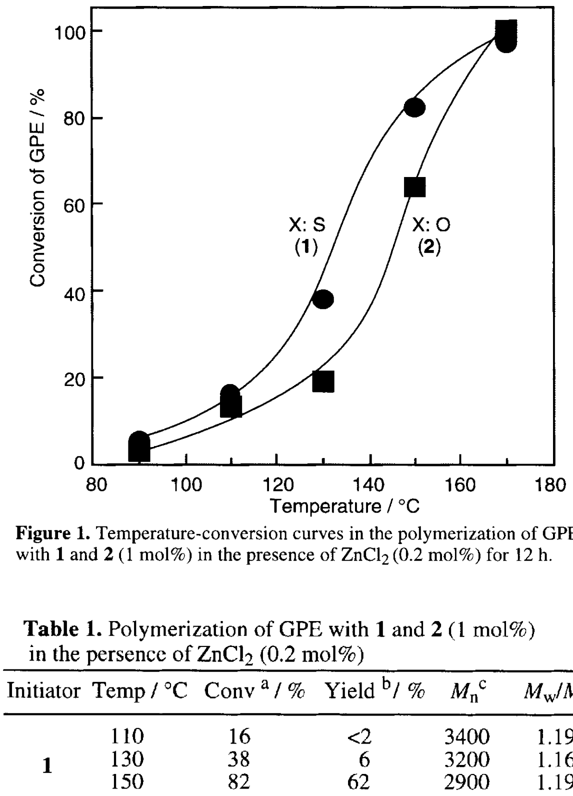


Figure 1. Temperature-conversion curves in the polymerization of GPE with **1** and **2** (1 mol%) in the presence of $ZnCl_2$ (0.2 mol%) for 12 h.

Table 1. Polymerization of GPE with **1** and **2** (1 mol%) in the persence of $ZnCl_2$ (0.2 mol%)

Initiator	Temp / °C	Conv [a] / %	Yield [b] / %	M_n [c]	M_w/M_n [c]
1	110	16	<2	3400	1.19
	130	38	6	3200	1.16
	150	82	62	2900	1.19
	170	97	84	2800	1.20
2	110	13	<1	6800	1.61
	130	19	<2	5900	1.44
	150	64	41	2700	1.13
	170	100	68	2700	1.24

[a] Determined by ^1H NMR. [b] Methanol-insoluble part.
[c] Estimated by GPC based on polystyrene standards.

Ab initio calculations were carried out to examine the difference of the initiator activity of the thiophosphonate **1** and the phosphonate **2**.[11] As shown in Table 2, the *t*-butyl proton of **1** showed a larger atomic charge and longer C-H bond length than those of **2**. It was confirmed that the *t*-butyl proton of **1** would be more easily eliminated to form phenyl thiophosphonic acid compared with **2**, resulting in the higher activity of **1** because the initiating species should be the eliminated proton

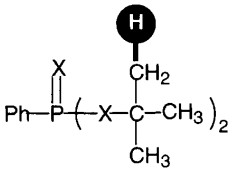


Table 2. Computed C-H bond length and atomic charge of the protons of the *t*-butyl groups in **1** and **2**

Initiator	Atomic charge / e	Bond length / Å
1	0.118	1.086
2	0.108	1.085

in this polymerization.[7] The polymer obtained in the cationic polymerization of GPE with **2** in the presence of $ZnCl_2$ at 110 °C exhibited a bimodal GPC peak, probably due to two kinds of active species; free ion and ion pair.[7] Meanwhile, the polymer obtained with **1** under the similar conditions showed a unimodal GPC curve, although it contained a small shoulder at a high molecular weight region.

In summary, although the thiophosphonate **1** alone showed little activity as the initiator of the polymerization of GPE, it served as a good thermally latent initiator in the presence of $ZnCl_2$. Ab initio calculation could explain the higher activity of **1** than the corresponding phosphonate **2**. As far as we know, this is the first attempt to enhance the activity of a latent initiator by replacing the oxygen atom into a sulfur atom.

References and Notes

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8 **1:** Yield: 76.2%. mp: 60.5-61.5 °C. IR (KBr, cm^{-1}): 3057, 2961, 2922, 2858, 1456, 1437, 1365, 1157, 1093, 1026, 802, 713, 688, 671; ^{1}H NMR ($CDCl_3$): δ 8.22-8.15, 7.52-7.26 (m, 5H, -C_6H_5), 1.45 (S, 18H, -6(CH_3)); ^{13}C NMR ($CDCl_3$): δ 139.1, 138.4, 131.4, 128.2, 54.7, 32.3; ^{31}P NMR ($CDCl_3$): δ 64.43. Anal. Found: C, 52.71; H, 6.89; S, 30.09%. Calcd for $C_{14}H_{23}PS_3$: C, 52.80; H, 7.28; S, 30.20%.

9 The regio regularities (head-to-tail contents) of polyGPEs obtained by the polymerization at 150 °C with **1** and **2** as the initiators were estimated to be 79 and 74%, respectively, by comparing the ^{13}C NMR integration ratio of the regio regular and irregular parts (NNE mode, 125.65 MHz, in $CDCl_3$). The assignment was based on Ref 10.

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11 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 by the HF/6-311G** basis set.