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A Novel Thermally Latent Anionic Initiator. Polymerization of Epoxide with Hydroxylamide Based on Thermal Dissociation

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Latent initiators show no activity under normal conditions but release active species by external stimulation such as heating and photoirradiation to initiate polymerization. They have been widely applied to paints, inks, epoxy molding compounds, and photoresists. Several onium salts like sulfonium, pyridinium, phosphonium salts,[1] and diaryliodonium and triarylsulfonium salts[2] have been developed as thermally latent initiators and/or photoinitiators. However, onium salts suffer low solubility in monomers and solvents, high cost, and residue of inorganic compounds in polymers, which causes toxicity and lowering of product properties such as insulation. Considerable efforts have been made to overcome these problems by developing non-salt-type initiators.[3] We have demonstrated that N-substituted phthalimides,[4] aminimides,[5] carboxylic acid esters,[6] and sulfonic acid esters[7] serve as non-salt-type latent initiators for epoxide polymerization. Recently, we have reported that phosphonic amide esters also serve as thermally latent anionic initiators in the polymerization of glycidy phenyl ether (GPE), wherein the active species is an amine released from the phosphonic amide esters by elimination of isobutene followed by successive reaction with GPE and formation of a cyclic amide ester releasing the amine (Scheme 1).[8] The key point of this initiator system is amide−ester exchange reaction releasing the amine by formation of a stable cyclic compound, although the nucleophilicity of the hydroxyl group is smaller than that of the amine. It may be expected that utilization of intramolecular reaction between amide and hydroxyl groups enables us to develop a new latent initiator. This paper communicates a novel simple thermally latent initiator system based on the thermal dissociation accompanying amide−ester exchange reaction.

Hydroxylamides **1a** and **1b** were synthesized by the reaction of piperidine with γ-butyrolactone and phthalide at room temperature overnight according to a manner similar to the literature, respectively (Scheme 2).[9] They were obtained as a colorless oil (**1a**) and solid (**1b**; mp 90−92 °C, lit.[9] 80−90 °C) after purification by silica gel column chromatography eluted with n-hexane/ethyl acetate = 1:2 (volume ratio) in 67 and 63% yields, respectively.

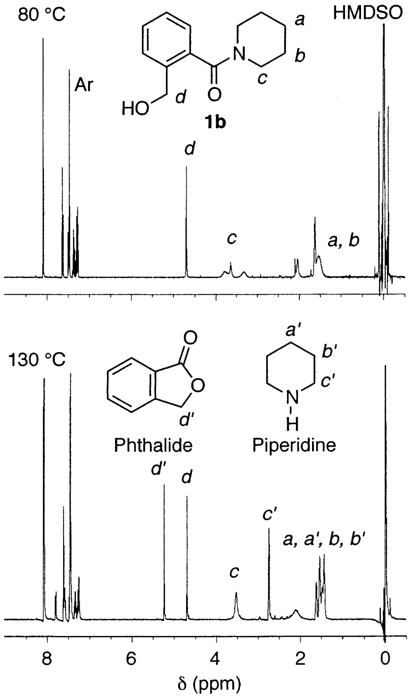
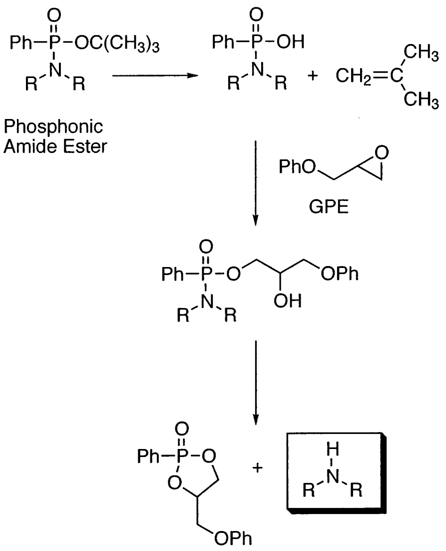


Figure 1. ^{1}H NMR (500 MHz) spectra of **1b** measured in nitrobenzene-d_5 at 80 and 130 °C. HMDSO = hexamethyldisiloxane. The measurement was carried out at the temperatures after heating the samples in an NMR probe for 1 h.

Scheme 1



Prior to polymerization, we checked the thermal dissociation behavior of the hydroxylamides **1a** and **1b** by NMR spectroscopy. Figure 1 depicts the ^{1}H NMR spectra of **1b** measured in nitrobenzene-d_5 at 80 and 130 °C. It was confirmed that **1b** was inert at 80 °C but dissociated into piperidine and phthalide at 130 °C, where the ratio of **1b**:piperidine:phthalide was 1:1:1. The driving force for transformation of amide into ester should be the regeneration of a stable five-membered

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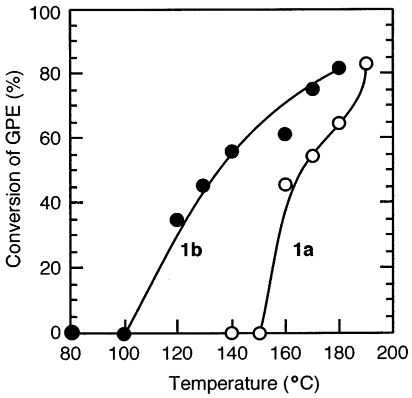
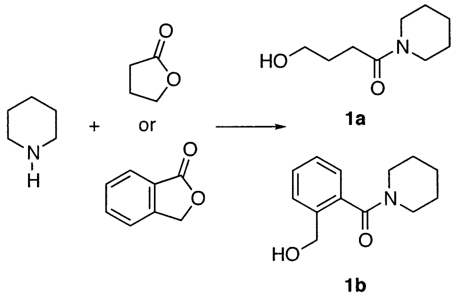


Figure 2. Relationships between GPE conversion and temperature in the polymerization of GPE with 10 mol % **1a** and **1b** for 12 h.

Scheme 2



lactone ring. This enables the hydroxyl group, which is less nucleophilic than amino group, to attack the amide carbonyl carbon in a manner similar to the phosphonic amide esters previously reported.[8] On the other hand, the thermal dissociation of **1a** could not be confirmed at 130 °C by NMR spectroscopy. It is likely that **1a** also dissociates in a manner similar to **1b** at higher temperature. In fact, it has been reported that **1a** cannot be distilled without thermal dissociation.[10] However, we could not check it by NMR spectroscopy because of limitation of the measuring temperature of the NMR apparatus.

The polymerization of GPE with hydroxylamides **1a** and **1b** was carried out in sealed glass ampules. Since **1a** and **1b** were easily soluble in GPE, the polymerizaion proceeded homogeneously to afford the polymers with weight-average molecular weights of ca. 1000. The active species of the polymerization should be piperidine as confirmed by the NMR spectroscopic study described above. Figure 2 depicts the relationships between GPE conversion and temperature in the polymerization of GPE with 10 mol % **1a** and **1b** for 12 h. GPE did not polymerize below 150 and 100 °C but polymerized rapidly above the temperatures. It was confirmed that **1b** was more active than **1a**. The rigid structure of **1b** due to the benzene ring may be preferable to formation of a lactone ring compared to **1a**. Both of the hydroxylamides could cure bisphenol A digylycidyl ether (Epikote 828) quantitatively at 180 °C for 12 h.

In summary, we have demonstrated that the hydroxylamides **1a** and **1b** serve as excellent thermally latent non-salt-type initiators for polymerization of epoxide. We believe that our simple and low-cost initiator system is a promising candidate for practical hardeners of epoxy resin.

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