

Curing of Epoxides with *O,O*-Di-*t*-butyl Phenylphosphonate as Thermally Latent Initiator

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ABSTRACT: The polymerization of glycidyl phenyl ether (GPE) was examined with *O,O*-di-*t*-butyl phenylphosphonate (BP) as an initiator in the presence of several Lewis acids, ammonium salts, and methyl cyanoacetate. BP served as an excellent thermally latent initiator in the polymerization of GPE in the presence of ZnCl_2 and $\text{Zn}(\text{acac})_2$. Epikote 828 was cured with BP (5 mol %) in the presence of ZnCl_2 at 150°C to afford the solvent-insoluble gelled epoxy resin quantitatively, which was thermally more stable than was the one cured without ZnCl_2 . No curing took place at room temperature for 7 months. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2347–2351, 2001

Key words: latent initiator; phosphonic acid ester; epoxy; hardner

INTRODUCTION

Latent initiators show no activity under normal conditions but generate active species by external stimulation such as heating and photoirradiation. During the past decades, increasing attention has been paid to a number of latent initiators, since they can cure epoxy resin and multifunctional vinyl ethers,¹ some of which are already industrialized as hardeners of coatings, adhesives, packings, and inks. Crivello et al. and the present authors have developed various onium salts such as diaryl iodonium and triaryl sulfonium salts,² sulfonium,³ pyridinium,⁴ and phosphonium salts⁵ as latent thermal and photoinitiators. However, onium salts involve several problems: lower solubility in monomers and solvents, residual inorganic compounds in polymers, and high cost for

practical use. Much effort has been made to overcome these disadvantages and to design nonsalt-type initiators with the desired properties.⁶ We recently developed nonsalt-type latent initiators, *N*-substituted phthalimides,⁷ aminimides,⁸ carboxylic acid esters,⁹ sulfonic acid esters,¹⁰ and phosphonium ylides.¹¹ More recently, we reported that phosphonic acid esters serve as nonsalt-type latent initiators in the polymerization of glycidyl phenyl ether (GPE) as shown in Scheme 1.¹² This article deals with the polymerization of GPE and curing of epoxy resin with *O,O*-di-*t*-butyl phenylphosphonate (BP) as a thermally latent initiator in the presence of several additives.

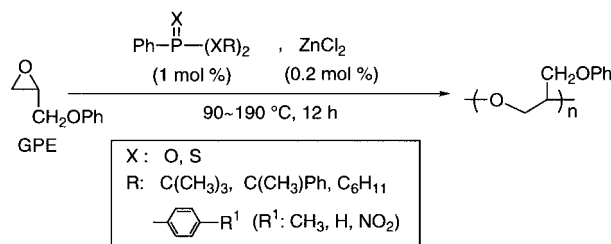
EXPERIMENTAL

Materials

ZnCl_2 (Aldrich, Tokyo; 1.0M solution in diethyl ether) was used as received. Zinc acetylacetonate

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Scheme 1

(Tokyo Kasei Kogyo Co.), zinc trifluoromethanesulfonate (Tokyo Kasei Kogyo Co.), $\text{Mg}(\text{ClO}_4)_2$ (Koso Chemical Co.), tetrabutyl ammonium bromide (Tokyo Kasei Kogyo Co.), tetraethyl ammonium perchlorate (Tokyo Kasei Kogyo Co.), and tetraethyl ammonium *p*-toluenesulfonate (Tokyo Kasei Kogyo Co.) were dried *in vacuo* more than 6 h before use. Methyl cyanoacetate (Tokyo Kasei Kogyo Co.) was distilled over calcium hydride under reduced pressure before use. Tri-*n*-butyl borate (Tokyo Kasei Kogyo Co.) was distilled under reduced pressure before use. GPE was dried and distilled over calcium hydride before use. Bisphenol-A-type epoxide oligomers (Epikote 828) was obtained from the Yuka Shell Epoxy Co. (Tokyo) and used as received. BP was synthesized according to the reported procedure.^{12a}

Measurements

^1H -, ^{13}C -, and ^{31}P -NMR spectra were recorded with JEOL EX-400 and Lambda-300 spectrometers using tetramethylsilane or 85% H_3PO_4 as an internal or external standard in CDCl_3 . IR spectra were measured with a JEOL JIR-5300 spectrophotometer. 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 system, equipped with two consecutive polystyrene gel columns (TSK gels G4000HXL and G2500HXL), using THF as an eluent with a flow rate of 1.0 mL/min by polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors. Differential scanning calorimetry (DSC) was done with a Seiko Instruments DSC 220C from room temperature to 300°C at a heating rate of 10°C/min under a nitrogen atmosphere. TGA was done with a Seiko Instruments TG/DTA 220 at a heating rate of 10°C/min under a nitrogen atmosphere.

Polymerization of GPE

Typical procedure: BP (13.5 mg, 0.05 mmol) and an additive (0.01 mmol) were fed into a glass tube.

The tube was closed with a three-way stopcock and a cycle of vacuum–nitrogen was repeated three times. Into the glass tube was fed GPE (751 mg, 5 mmol) with a syringe under nitrogen. The tube was sealed under a vacuum using the freeze–thaw technique and heated at a set temperature in an oil bath. After a set time, the tube was cooled in a dry ice–acetone bath and the reaction mixture was diluted with chloroform (1 mL). The mixture was then poured into methanol (50 mL) to precipitate the polymer. The polymer was separated from the supernatant by decantation and dried *in vacuo*. The monomer conversion was determined by ^1H -NMR spectroscopy before precipitation with methanol, and the molecular weight of the polymer was determined by GPC. The obtained polymer was identified to be polyGPE by ^1H -NMR, ^{13}C -NMR, and IR spectroscopy.

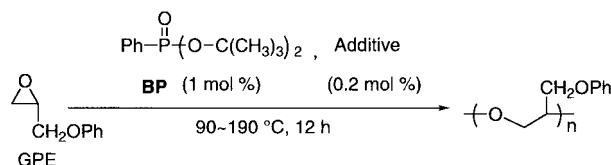
Curing of Epikote 828

Typical procedure: BP (13.5 mg, 0.05 mmol) and Epikote 828 (341 mg, 1 mmol) were fed into a glass tube. The tube was closed with a three-way stopcock and dried *in vacuo* to remove oxygen. If necessary, into the glass tube was fed a 1.0M solution of ZnCl_2 in diethyl ether (10 μL , 0.01 mmol) with a syringe under nitrogen. A small portion of the resulting mixture was introduced into a sample cell and the curing process was monitored by DSC. The tube was heated at 150°C for 12 h in an oil bath. The mixture was then poured into methanol (100 mL), to obtain the cured polymer, and it was washed with CHCl_3 and methanol. The polymer was dried *in vacuo*. The obtained polymer was identified to be cured epoxy resin by IR spectroscopy.

RESULTS AND DISCUSSION

Polymerization of GPE with BP

The conversion of GPE was below 4% in the polymerization with the phosphonate BP (1 mol %) as an initiator at 190°C for 12 h, which resulted in a trace amount of the GPE oligomer ($M_n = 400$).^{12a} Therefore, several Lewis acids, ammonium salts, and methyl cyanoacetate were added to the polymerization mixture to activate BP and stabilize the propagating cationic species (Scheme 2).¹³ The activation status of BP with the Lewis acids was examined by ^{31}P -NMR spectroscopy at 50°C. Two peaks assignable to phenylphosphonic mono- and



Scheme 2

diacids appeared at 14 and 18 ppm besides the peak of BP at 10 ppm in the ^{31}P -NMR spectra of BP by the addition of ZnCl_2 and $\text{Mg}(\text{ClO}_4)_2$, but did not appear in the cases of $\text{B}(\text{O-}n\text{-Bu})_3$, tetrabutyl ammonium bromide, tetraethyl ammonium perchlorate, tetraethyl ammonium *p*-toluenesulfonate, and methyl cyanoacetate, providing evidence of the coordination of BP with ZnCl_2 and $\text{Mg}(\text{ClO}_4)_2$. In the presence of ZnCl_2 , $\text{Zn}(\text{acac})_2$, and $\text{B}(\text{O-}n\text{-Bu})_3$, GPE was not converted below 90–110°C, but converted rapidly above those temperatures to afford the polymer with an M_n of 2500–7000 as shown in Figure 1. The GPE conversion increased with the temperature, while the M_n of the obtained polymer decreased, probably due to some side reactions such as chain transfer and formation of cyclic oligomers. The activity order of the additives was $\text{ZnCl}_2 > \text{Zn}(\text{acac})_2 > \text{B}(\text{O-}n\text{-Bu})_3$, reflecting the Lewis acidities. The polymerization, with ZnCl_2 alone as the initiator, afforded a low molecular weight ($M_n = 600\text{--}900$) oligomer with only 5–10% GPE conversion at 150–190°C, while that with $\text{Zn}(\text{OSO}_2\text{CF}_3)_2$

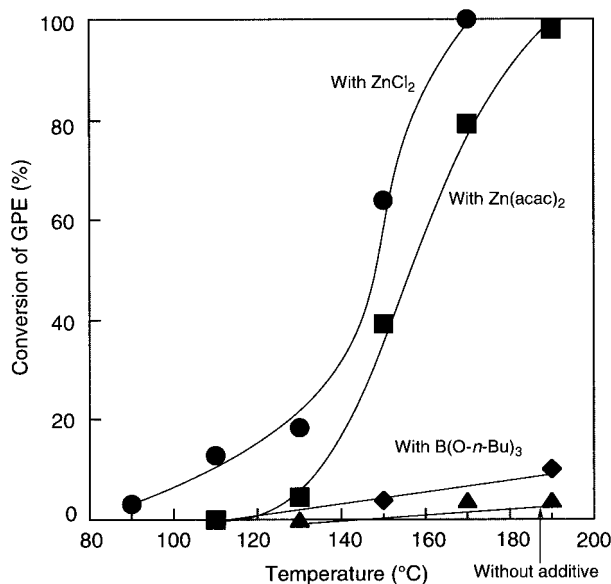


Figure 1 Temperature-conversion curves in the polymerization of GPE with BP (1 mol %) in the absence and the presence of additives (0.2 mol %) for 12 h.

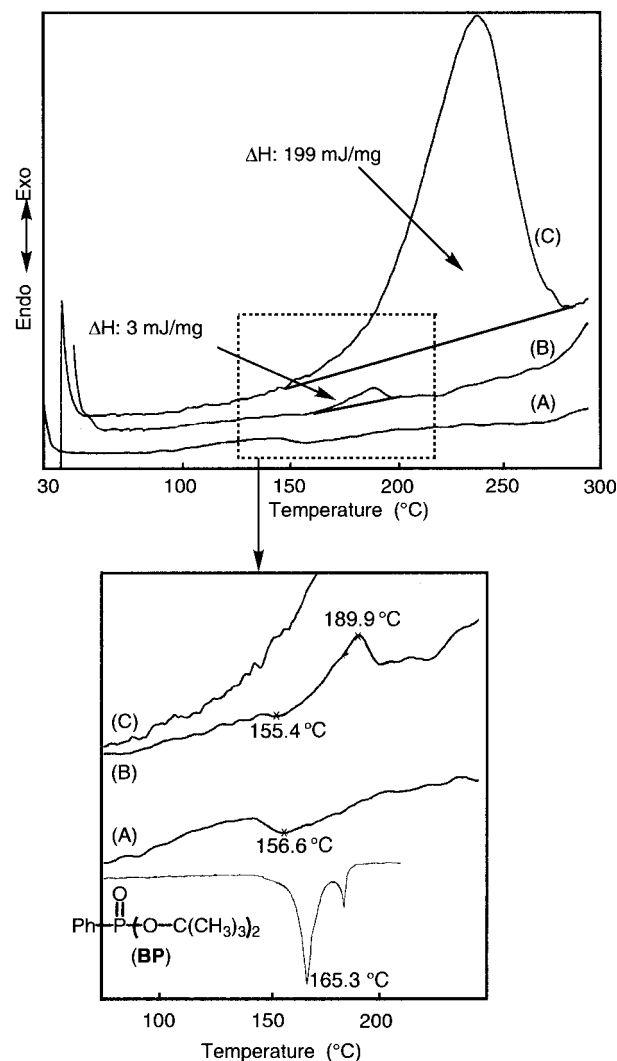


Figure 2 DSC thermograms of epoxy resin with BP: (A) BP (1 mol %) in the absence of ZnCl_2 ; (B) BP (5 mol %) in the absence of ZnCl_2 ; (C) BP (5 mol %) in the presence of ZnCl_2 (1 mol %).

and $\text{Mg}(\text{ClO}_4)_2$ alone as the initiator achieved 90% GPE conversion.¹⁴ The polymerization of GPE with BP in the presence of other additives, tetrabutyl ammonium bromide, tetraethyl ammonium perchlorate, tetraethyl ammonium *p*-toluenesulfonate, and methyl cyano acetate, afforded oligomers with only about 10% conversion at 170–190°C.

Curing of Epoxy Resin

As described above, we confirmed that the combination of phosphonate BP with ZnCl_2 could achieve thermally latent polymerization of GPE. We further examined curing of the epoxy resin with this initiator system by differential scanning

calorimetry (DSC). BP (1–5 mol %) and ZnCl_2 (1 mol %) were completely soluble in epoxy resin (Epikote 828) at ambient temperature. Figure 2 shows the DSC traces of Epikote 828 with BP (1–5 mol %) in the absence and presence of ZnCl_2 (1 mol %). The thermograms with 1 and 5 mol % of BP in the absence of ZnCl_2 [Fig 2(A,B)] showed endothermic peaks corresponding to the decomposition temperature of BP at 155–157°C. One mol percent of BP resulted in no exothermic peak, and 5 mol % of BP was slightly exothermic with a ΔH of 3 mJ/mg. The $^1\text{H-NMR}$ -determined epoxide conversion was below 8% in curing with 5 mol % of BP, similar to the polymerization of GPE.¹² Meanwhile, the thermogram [Fig. 2(C)] with 5 mol % of BP and 1 mol % of ZnCl_2 showed a large exothermic peak with a ΔH of 199 mJ/mg, indicating the progress of epoxide curing on heating. The epoxy resin was cured with BP (5 mol %) at 150°C for 12 h in the presence of ZnCl_2 (1 mol %), resulting in a solvent-insoluble gelled epoxy resin quantitatively. Figure 3 shows the IR spectra of the resin before and after curing. The absorption assignable to C—O stretching of the epoxide at 916 cm^{-1} almost disappeared after curing, indicating that BP served as an efficient hardener of the epoxy resin in the presence of ZnCl_2 .

Figure 4 shows TGA thermograms of the epoxy resin (A) before and after curing with phosphonate BP (5 mol %) in (B) the absence or (C) the presence of ZnCl_2 (1 mol %). The resin cured in the presence of ZnCl_2 was thermally more stable than was the one cured without ZnCl_2 .

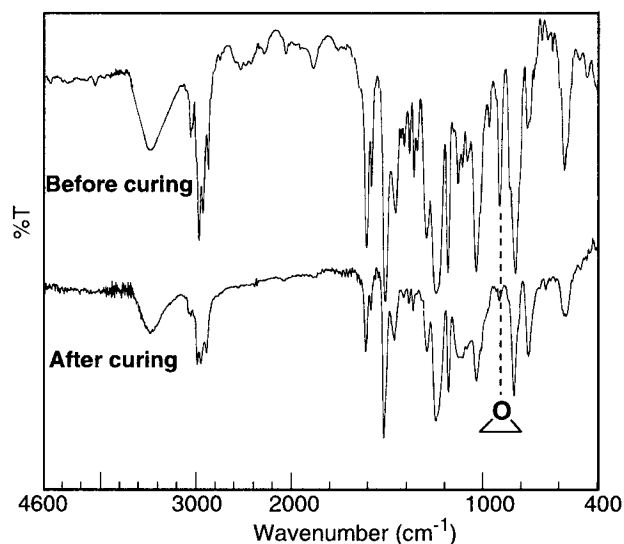


Figure 3 IR spectra of Epikote 828 before and after curing with BP (5 mol %) in the presence of ZnCl_2 (1 mol %) at 150°C for 12 h.

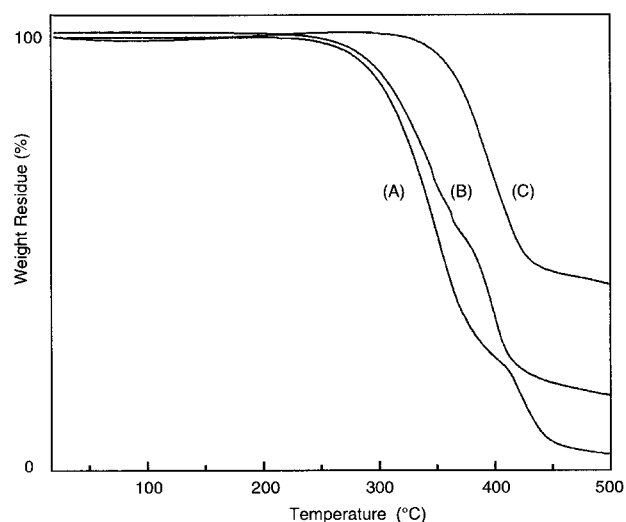


Figure 4 TGA curves of Epikote 828 before and after curing with BP: (A) Epikote 828; (B) cured with BP (5 mol %) in the absence of ZnCl_2 at 150°C for 12 h; (C) cured with BP (5 mol %) in the presence of ZnCl_2 (1 mol %) at 150°C for 12 h.

Storage Stability

Storage stability is important for latent initiators in polymerization and curing systems. A mixture of GPE, phosphonate BP (1 mol %), and ZnCl_2 (0.2 mol %) was allowed to stand for 7 months at room temperature and for 10 days at 55°C to examine the storage stability. No curing took place at room temperature during this period. The formation of a phosphonic acid was less than 1% at 55°C after 10 days. In summary, although the phosphonate BP alone showed little activity as an initiator of GPE polymerization and a hardener of Epikote 828, it showed excellent thermally latent activity in the presence of ZnCl_2 , along with long storage stability.

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