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Phosphonates as non-salt-type latent initiators for vinyl ether polymerization

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Abstract

Phosphonates, *O*,*O*-di-1-phenylethyl phenylphosphonate (**1**), *O*,*O*-di-*tert*-butyl phenylphosphonate (**2**), and *O*,*O*-dicyclohexyl phenylphosphonate (**3**), were examined as non-salt-type latent initiators in the polymerization of isobutyl vinyl ether (IBVE), phenyl vinyl ether (PVE), and tri(ethylene glycol) divinyl ether (DVE-3). The polymerization of IBVE and PVE did not proceed below 90 and 120°C, but rapidly proceeded above these temperatures with **1**, respectively. DVE-3 cured with **1** quantitatively at 150°C for 12 h to afford brown gel insoluble in common organic solvents. The phosphonates served as novel non-salt-type latent initiators in the polymerization of the vinyl ether monomers. © 2001 Published by Elsevier Science Ltd.

Keywords: Latent initiator; Phosphonate; Vinyl ether

1. Introduction

'Latent initiators' show no activity under ambient condition, but generate active species by external stimulation such as heating and photoirradiation. Much attention has been given to the development of latent initiators since they can cure epoxy resin and multifunctional vinyl ethers [1], some of which are already industrialized in the fields of coatings, adhesives, packings, and inks. Crivello et al., Yagci et al., and we have developed various onium salts such as diaryl iodonium and triaryl sulfonium salts [2,3], sulfonium [4–14], pyridinium [15–22], and phosphonium salts [23–28] as latent thermal and photo initiators. Several problems have been found while extending the use of the onium salts for practical purposes, i.e. lower solubility in monomers and solvents, remaining of inorganic compounds in polymers, and higher cost. Much effort has been made to overcome the disadvantage and to design non-salt-type initiators with desired properties [29–33]. We have recently developed non-salt-type latent initiators, *N*-substituted phthalimides [34], aminimides [35], carboxylates [36], sulfonates [37,38], and phosphonium ylides [39]. Organophosphorous compounds possess various benefits; easy molecular design and synthesis, wide application, lower cost, and they are utilized as medicines, agricultural chemicals, plasticizers, and polymer additives [40,41]. Considering the advantages of organophosphorous compounds, we have examined the possibility of phosphonates as thermally latent initiators in the polymerization of glycidyl phenyl ether (GPE) [42–45]. In the absence of $ZnCl_2$, the phosphonates can scarcely polymerize GPE (conversion $< 5\%$) even at 190°C to afford a trace amount of GPE oligomer. On the contrary, they can efficiently polymerize GPE in the presence of $ZnCl_2$ as a coinitiator. $ZnCl_2$ coordinates the phosphonate to lower the thermal dissociation temperature and nucleophilicity of the phosphonate anion formed. Consequently, phosphonates can serve as thermally latent initiators for GPE in the presence of $ZnCl_2$. However, the use of $ZnCl_2$ is the subject of controversy for the development of non-salt-type latent initiators. Vinyl ethers are utilized as pharmaceutical, motor oil additives, ion-exchange resins, and reactive monomers in the various industrial fields [46]. Vinyl ethers cationically polymerize more rapidly than epoxides. Therefore, phosphonates may polymerize vinyl ethers without the assistance of $ZnCl_2$. This article deals with the possibility of phosphonates as non-salt-type latent initiators in the polymerization of vinyl ether monomers.

2. Experimental section

2.1. Materials

Phosphonates **1**, **2**, and **3** as initiators were prepared

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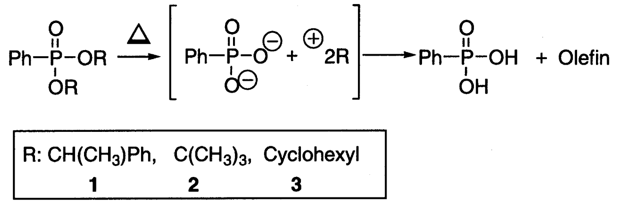


Scheme 1.

according to the previously reported method [42–45]. GPE, glycidyl *tert*-butyl ether (G-*t*-BuE), 3-ethyl-3-[(2-ethylhexyloxy)methyl]oxetane (OX) (Toagosei Co.), and tri(ethylene glycol) divinyl ether (DVE-3) (ISP Technology INC) were dried and distilled over CaH_2 under reduced pressure. Isobutyl vinyl ether (IBVE) was distilled over sodium metal. Phenyl vinyl ether (PVE) was synthesized from 2-bromo-1-phenoxyethane prepared by the reaction of ethylene dibromide with phenol according to the method reported [47], and purified by distillation over calcium hydride.

2.2. Measurements

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a JEOL EX-400 spectrometer using tetramethylsilane (TMS) or 85% H_3PO_4 as an internal or external standard in $CDCl_3$. 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, equipped with two consecutive polystyrene gel columns (TSK gels G2500HXL (exclusion limit of molecular weight: 2×10^4) and G4000HXL (exclusion limit of molecular weight: 4×10^5)) at 40°C, using THF as an eluent with a flow rate of 1.0 ml/min by polystyrene calibration, and with a differential refractometer detector and Tosoh UV-8020 ultraviolet detectors (254 nm). TGA was done with a Seiko Instruments EXSTAR TG/DTA 6200 from 30 to 500°C at a heating rate of 10°C/min under a nitrogen atmosphere.

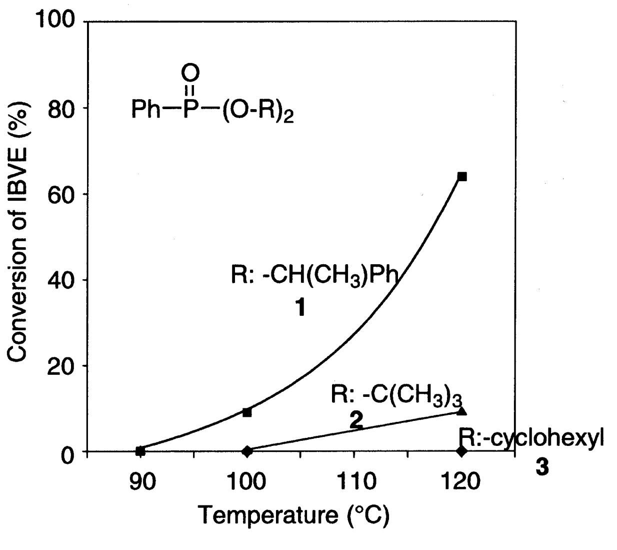
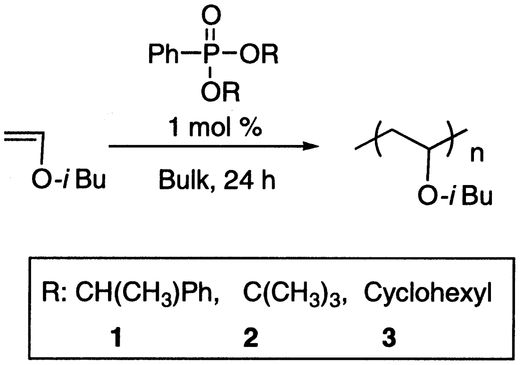


Fig. 1. Temperature-conversion curves in the polymerization of IBVE with phosphonates **1**, **2**, and **3** (1 mol%) for 24 h.



Scheme 2.

2.3. Polymerization

In a typical procedure, initiator **1** (18.3 mg, 0.05 mmol) was fed into a glass tube. The tube was closed with a three-way stopcock, and a cycle of vacuum nitrogen was repeated thrice to remove oxygen. IBVE (500 mg, 5 mmol) was fed into the glass tube with a syringe under nitrogen. The tube was sealed under vacuum using the freeze–thaw technique, and heated at a set temperature in an oil bath. After 24 h, the tube was cooled in a dry ice–acetone bath. The monomer conversion and the molecular weight of the polymer were determined by ^{1}H NMR spectroscopy, and GPC, respectively.

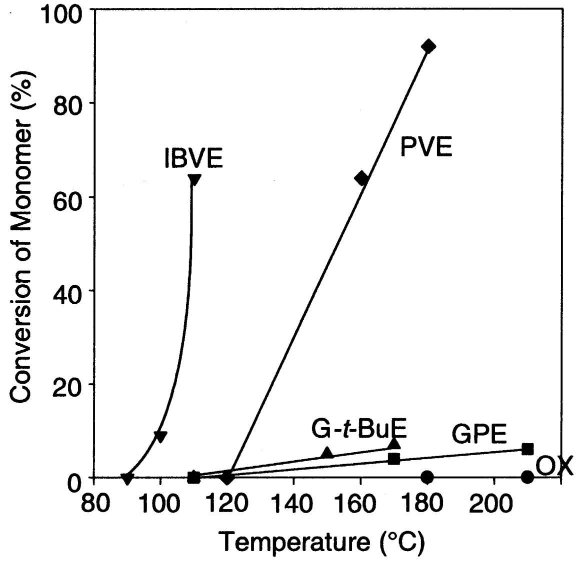


Fig. 2. Temperature-conversion curves in the polymerization of PVE, G-*t*-BuE, GPE, and OX with **1** (1 mol%) for 24 h.

3. Results and discussion

As reported previously, phenylphosphonates with 1-phenylethyl (**1**), *tert*-butyl (**2**), and cyclohexyl (**3**) groups thermally dissociate into phenylphosphonic acid and the corresponding olefins, via phenylphosphonate anion and alkyl cations as shown in Scheme 1.

IBVE was submitted to polymerization to examine the possibility of phosphonates as non-salt-type latent initiators. The polymerization of IBVE with **1**, **2**, and **3** (1 mol%) was carried out at 90–120°C for 24 h (Scheme 2). The phosphonates were completely soluble in IBVE at ambient temperature, and the polymerization proceeded homogeneously. IBVE did not convert with **1** below 90°C, but did above the temperature to afford the polymer with the M_n of 800, as shown in Fig. 1. Phosphonate **1** served as a non-salt-type latent initiator in the polymerization of IBVE. Meanwhile, **2** achieved only 9% IBVE conversion and no polymerization with **3** even at 120°C. The activity order was $\mathbf{1} > \mathbf{2} > \mathbf{3}$, which well agreed with our previous result in the polymerization of GPE in the presence of $ZnCl_2$ [42–45].

No variation of **1** was detected at 90°C, but did above at 100°C by the ^{31}P NMR spectra of the reaction mixture measured after the polymerization of IBVE with **1** at 90–120°C for 24 h. Although the IBVE conversion was 64% at 120°C, further polymerization was not examined above the temperature due to the boiling point (83°C). We performed the polymerization of PVE instead (boiling point 52°C/18 mmHg) with phosphonate **1** at 120–180°C as shown in Fig. 2, along with the polymerization of G-*t*-BuE, GPE, and OX for comparison. Phosphonate **1** did not polymerize PVE below 120°C, but did above the temperature to afford the oligomer [48,49], showing the behavior as a latent initiator. The ^{31}P NMR spectra of **1** exhibited no variation at 120°C after the polymerization, but complete decomposition above 160°C. The conversion of G-*t*-BuE and GPE was below 9%. OX did not convert in spite of complete decomposition of **1** even at 210°C. The reactivity order of the monomers was IBVE > PVE > G-*t*-BuE > GPE > OX.

As described above, we confirmed that the phosphonates could act as non-salt-type latent initiators in the polymerization of vinyl ether monomers.[1] We next examined curing of a bifunctional vinyl ether, DVE-3. The reaction of DVE-3 was carried out with **1** (1 mol%) at 150°C for 12 h to quantitatively afford brown gel insoluble in common organic solvents. The reaction without **1** afforded colorless solvent-soluble viscous liquid. This result implies that thermal oligomerization of DVE-3 spontaneously proceeded under the condition, but the crosslinking efficiency was quiet low without phosphonate **1**. Fig. 3 shows the TGA thermograms of the products obtained by curing reaction of DVE-3 with (A) and without (B) **1** at 150°C for 12 h. The product obtained with **1** was thermally more stable than the one obtained without **1**, supporting the higher crosslinking density of the former.

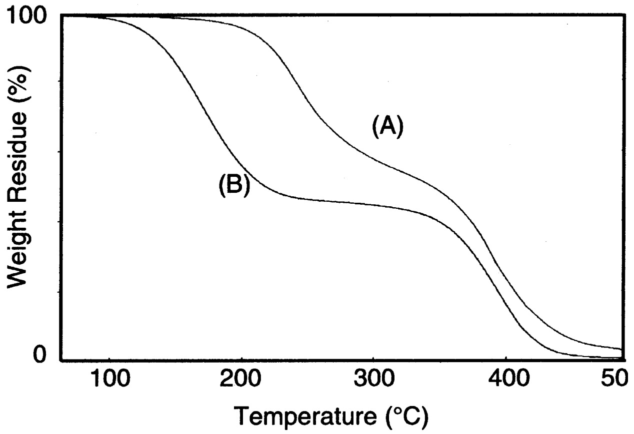


Fig. 3. TGA curves of product obtained after curing of DVE-3 (A) with and (B) without phosphonate **1** at 150°C for 12 h.

In summary, we could demonstrate that the phosphonates served as non-salt-type latent initiators for vinyl ether monomers.[2] Further research on the molecular design of phosphonates and the polymerization of indene, *N*-vinylcarbozole, and styrene derivatives is now in progress.

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[1] We have to admit that the activities of the phosphonates are lower compared to those of several salt-type initiators previously reported. This is evident because the phosphonates can hardly polymerize GPE even at 190°C as described Section 1 [42], while a salt-type phosponium initiator, benzyl triphenylphosphonium hexafluoroantimonate can polymerize GPE quantitatively at 160°C [23]. In the presence of $ZnCl_2$ as an activator, the phosphonates can polymerize GPE efficiently at the temperature. In the present paper, the phosponates can polymerize vinyl ether monomers without the assistance of $ZnCl_2$ because vinyl ether monomers are more reactive to cationic initiators than GPE.

[2] We could not find concrete evidence of the initiating species, proton and/or alkyl cation because of overlap of signals around 1–3 ppm in the ^1H NMR spectra of the polymers obtained by the polymerization with phosphonates **1**, **2**, and **3**. A trace amount of aromatic proton signals was detected, presumably attributable not to the initiating end but to phenylphosphonate terminating end because they were detected even in the cases with phosphonates **2** and **3**. Chain transfer reaction should occur to a considerable extent at this high polymerization temperature (90–120°C), which would also make structure elucidation difficult. Further, we examined the polymerization of IBVE with phenylphosphonic acid at room temperature to obtain the polymer quantitatively. Therefore, we can say that a proton of phenylphosphonic acid eliminated from the phosphonates can initiate the polymerization of IBVE. However, we cannot exclude the possibility of initiation by alkyl cation. In fact, we previously confirmed that alkyl cation served as an initiating species in the polymerization of GPE [45].

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