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Temperature-Dependent Enhancement Effects for TBD (1,5,7-Triazabicyclo[4.4.0]dec-5-ene) with 2-Methylimidazole-Intercalated α -Zirconium Phosphate as a Latent Thermal Initiator in the Reaction of Glycidyl Phenyl Ether

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Abstract: The catalytic effects of 1,1,3,3-Tetramethylguanidine (TMG), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in the reaction with glycidyl phenyl ether (GPE) at 40 °C were investigated. For the reaction, the %conversion of GPE was only 11%, carried out at 40 °C over 14 days in the presence of TBD. Additionally, there was little catalytic activity for the same reaction performed under typical storage conditions at 25 °C. The effect of TBD with 2-methylimidazole-intercalated α -zirconium phosphate (α -ZrP·2MIm), as a latent thermal initiating system in the reaction with GPE, was then examined. The reaction did not proceed within 1 h at 80 °C. On increasing the temperature to 120 °C, the %conversion reached 75% for reaction at 1 h. Under typical storage conditions (7 days at 25 °C), the %conversion of GPE was only 7%. With addition of TBD to α -ZrP·2MIm, reagent stability was maintained, and the polymerization reaction proceeded rapidly with the application of heat.

Keywords: α -zirconium phosphate; intercalation; 2-methylimidazole; TBD; latent thermal initiator

1. Introduction

There has been considerable interest in the development of latent polymerization catalysts and initiators that are inert in monomer or prepolymer systems under typical storage conditions. Latent thermal initiators must remain inactive under storage conditions, but show high activity at specific temperatures [1–10]. Latent thermal initiators are used in adhesives, sealing agents, electrical devices, paints, and composite materials. One-pot resin composites using a latent thermal initiator offer some attractive features for synthesis: (1) weighing errors are eliminated and there is no requirement for mixing at time of use, (2) the reactions may be automated, and (3) it is possible to reduce resin waste because the resin may be stored for long periods. Thus, the development of latent thermal initiators with high storage stability and high reactivity at designated temperatures is very important for synthetic applications in the chemicals industry.

We have previously reported that primary alkylamines intercalated with α -zirconium phosphate (α -ZrP) may serve as latent thermal initiators in the reaction of glycidyl phenyl ether (GPE) [11,12], and that the compounds 1,4-diazabicyclo[2,2,2]octane (DABCO), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), imidazole (Im), 2-methylimidazole (2MIm), 2-ethyl-4-methylimidazole (2E4MIm), and benzimidazole (Bim) intercalated with α -ZrP show good performance as latent thermal initiators in the reaction of GPE

with hexahydro-4-methylphthalic anhydride (MHHPA) [13–16]. However, it is important to develop a highly active latent initiating system to avoid the need for high-temperature curing. Therefore, using GPE as a model epoxy compound, we have studied the enhancement effects of bases with α -ZrP-2MIm as a potential thermal latent initiator in the acceleration of the reaction with GPE.

2. Results and Discussion

The use of latent thermal initiators enables stable storage conditions to be maintained for relatively long periods of time without the occurrence of undesirable curing reactions. To evaluate the effect on the storage stability of GPE, curing experiments in the presence of the following bases, 1,1,3,3-Tetramethylguanidine (TMG), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were carried out at a temperature of 40 °C (Figure 1a and Scheme 1). The %conversion values for GPE with TMG, DBN, DBU, and MTBD using a 20% conversion level as a typical benchmark were 22% (1 day), 20% (1 day), 26% (2 days), and 32% (4 days), respectively. Thus, the aforementioned bases in GPE did not show good storage stability at 40 °C. Further, for the addition of TBD, the %conversion value for GPE at 40 °C was only 11% after 14 days, that is, the addition of TBD hardly accelerated the reaction of GPE. The %conversion values for GPE with TBD for a 1 h reaction over the temperature range 60 to 120 °C are shown in Figure 1b, and it is clear that the polymerization reaction did not proceed under the specified conditions.

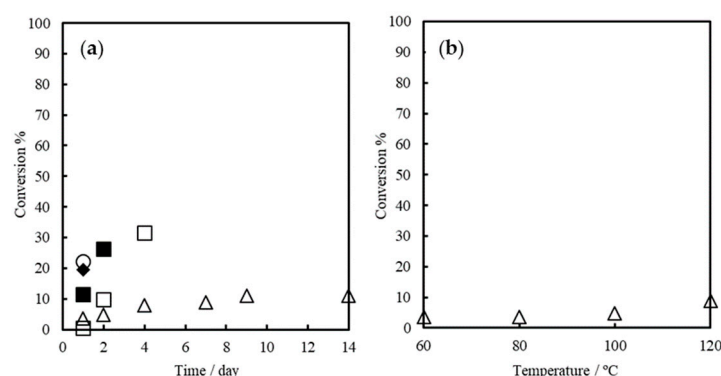
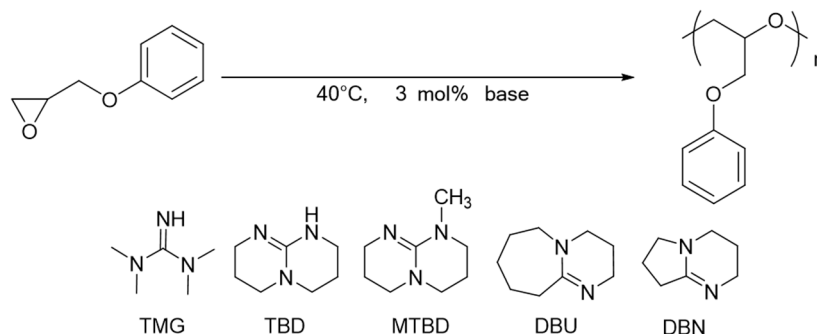


Figure 1. (a) The %conversion values for glycidyl phenyl ether (GPE) as a function of time during reaction with 1,1,3,3-Tetramethylguanidine (TMG) (○), 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) (Δ), MTBD (□), 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (DBU) (■), and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (◆) at 40 °C; (b) The %conversion values for GPE as a function of temperature during reaction with TBD (Δ).



Scheme 1. Reaction of GPE with bases.

The %conversions values for the reactions of GPE with TBD and α -ZrP-2MIm (abbreviated as α -ZrP-2MIm-T) over 1 h for the temperature range 60 to 120 °C are presented in Figure 2a. The intercalated compound α -ZrP-2MIm was prepared by a reported method [14]. At 100 °C,

the %conversion value was 28% for α -ZrP·2MIm-T, whereas a reaction did not occur for the addition of α -ZrP·2MIm alone. At 120 °C, the %conversion value increased to 75%, thus confirming the remarkable differences in reactivity as a result of TBD addition. To further examine the enhancement effects of TBD, the reactions were performed for 9 h at 100 °C (Figure 2b). For reactions of 2 h duration, the %conversion values were 54% (α -ZrP·2MIm-T) and 6% (α -ZrP·2MIm). When the reaction time was extended to 9 h, the %conversion value reached 89% for α -ZrP·2MIm-T.

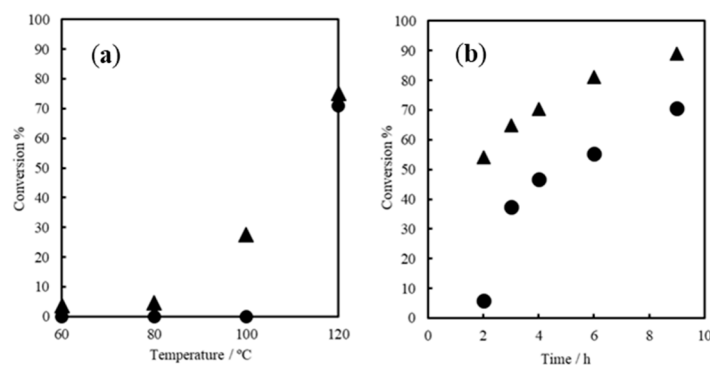


Figure 2. (a) The %conversion values for GPE after 1 h as a function of temperature during reaction with 2MIm intercalated α -zirconium phosphate (α -ZrP·2MIm) (●) and α -ZrP·2MIm with TBD (α -ZrP·2MIm-T) (▲); (b) the %conversion values for GPE as a function of time during reaction with α -ZrP·2MIm (●) and α -ZrP·2MIm-T at 100 °C (▲).

To serve as a latent thermal initiator, the initiator in the epoxy monomer and prepolymer needs to have a high curing capability at the desired temperature and also display high stability under the recommended storage regime. To evaluate the long-term storage stability, the %conversion values for GPE at 25 and 40 °C were studied for periods up to 14 days, and the results are presented in Figure 3. With respect to storage stability and using a 20% conversion level as a typical benchmark, the %conversion values were 19% at 25 °C for 14 days and 16% at 40 °C for 4 days storage. The latent thermal initiating system of α -ZrP·2MIm-T in GPE gave high reactivity at 100 °C and was shown to be stable for periods up to 14 days at a temperature of 25 °C.

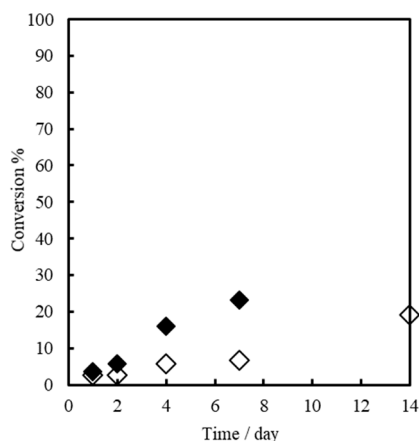


Figure 3. The %conversion values for GPE as a function of time for reaction with α -ZrP·2MIm-T at 40 °C (◆) and 25 °C (◇).

To study the reaction behavior of GPE with α -ZrP·2MIm-T, the changes in composition after reaction of α -ZrP·2MIm (abbreviated as α -ZrP·2MIm-RXN) and α -ZrP·2MIm-T (abbreviated as α -ZrP·2MIm-T-RXN) were investigated. For this, an elemental analysis was performed after washing the reaction mixtures with THF to remove the reaction product of GPE. The elemental ratios for C, H, and N in α -ZrP·2MIm-RXN were C: 13.93, H: 1.86, and N: 6.89 at 100 °C and C: 43.00, H: 3.72, and N: 0.97

at 120 °C. In the case of α -ZrP·2MIm-T-RXN, the respective ratios were C: 17.46, H: 2.02, and N: 6.19 at 100 °C and C: 40.28, H: 3.41, and N: 1.76 at 120 °C. The respective deintercalation ratios for 2MIm from the interlayer of α -ZrP·2MIm were estimated as 4% and 74% and 9% and 57% from α -ZrP·2MIm-T at 100 °C and 120 °C, respectively (Table 1). Estimations of the respective elemental compositions after reaction at 120 °C for α -ZrP·2MIm-RXN and α -ZrP·2MIm-T-RXN were $\text{Zr}(\text{HPO}_4)_2 \cdot 0.25\text{C}_4\text{H}_6\text{N}_2 \cdot 2.73\text{C}_9\text{H}_{10}\text{O}_2$ and $\text{Zr}(\text{HPO}_4)_2 \cdot 0.41\text{C}_4\text{H}_6\text{N}_2 \cdot 2.27\text{C}_9\text{H}_{10}\text{O}_2$, thus signifying intercalation of the reaction product of GPE. The value for the deintercalation ratio for α -ZrP·2MIm-T (57%) was clearly lower than that for α -ZrP·2MIm (74%), suggesting enhanced reactivity for α -ZrP·2MIm-T for GPE.

Table 1. Deintercalation ratios after 1 h of reaction with α -ZrP·2MIm and α -ZrP·2MIm-T at 100 °C and 120 °C, and the respective elemental compositions.

After Reaction of Initiator	Temperature/°C	Deintercalation Ratio%	Composition
α -ZrP·2MIm-RXN	100	4	$\text{Zr}(\text{HPO}_4)_2 \cdot 0.91\text{C}_4\text{H}_6\text{N}_2 \cdot 0.07\text{C}_9\text{H}_{10}\text{O}_2$
	120	74	$\text{Zr}(\text{HPO}_4)_2 \cdot 0.25\text{C}_4\text{H}_6\text{N}_2 \cdot 2.73\text{C}_9\text{H}_{10}\text{O}_2$
α -ZrP·2MIm-T-RXN	100	9	$\text{Zr}(\text{HPO}_4)_2 \cdot 0.86\text{C}_4\text{H}_6\text{N}_2 \cdot 0.25\text{C}_9\text{H}_{10}\text{O}_2$
	120	57	$\text{Zr}(\text{HPO}_4)_2 \cdot 0.41\text{C}_4\text{H}_6\text{N}_2 \cdot 2.27\text{C}_9\text{H}_{10}\text{O}_2$

To study the changes in the interlayer distances, the reactions for α -ZrP·2MIm and α -ZrP·2MIm-T were next investigated. The interlayer distance for α -ZrP·2MIm did not change for a 1 h reaction performed at 100 °C. In the case of α -ZrP·2MIm-T, a small XRD peak at $2\theta = 3.4^\circ$ (25.9 Å) was observed, as shown in Figure 4b. This peak might reflect the intercalation of the products of GPE. At 120 °C, the interlayer distances were extended, and peaks were not detected from 3° to 40° for the two GPE products, as shown in Figure 4c,d. To detect peak shifts of less than 3° , the tube voltage was reduced from 40 kV to 20 kV and the XRD responses were recorded from 2° to 15° as shown in Figure 4c',d'. The peaks associated with the interlayer distances were $2\theta = 2.8^\circ$ (31.2 Å) for α -ZrP·2MIm-RXN and $2\theta = 3.1^\circ$ (28.2 Å) for α -ZrP·2MIm-T-RXN, respectively.

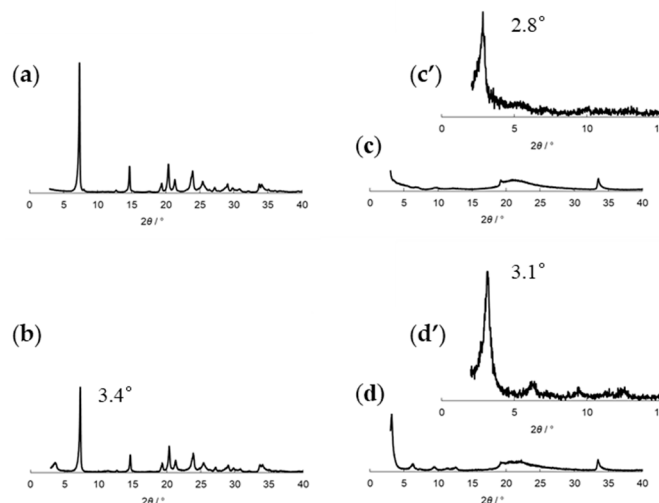


Figure 4. XRD patterns for (a) after reaction of α -ZrP·2MIm (α -ZrP·2MIm-RXN) at 100 °C, (b) after reaction of α -ZrP·2MIm-T (α -ZrP·2MIm-T-RXN) at 100 °C, (c) α -ZrP·2MIm-RXN at 120 °C, (c') α -ZrP·2MIm-RXN at 120 °C for $2\theta = 2^\circ$ – 15° , (d) α -ZrP·2MIm-T-RXN at 120 °C, and (d') α -ZrP·2MIm-T-RXN at 120 °C for $2\theta = 2^\circ$ – 15° .

To confirm the intercalation of the GPE products, FT-IR spectra were recorded and are presented in Figure 5. An absorption peak due to α -ZrP (ν P–O) was detected at 1006 cm^{-1} as shown in Figure 4a. Peaks associated with aromatic (ν C–C at 1600 , 1497 and 1458 cm^{-1}) and ether groups (ν C–O–C at

1248 cm^{-1}) in the respective products may be observed clearly in Figure 5b,c. No significant differences in the spectra in Figure 5b,c were noted.

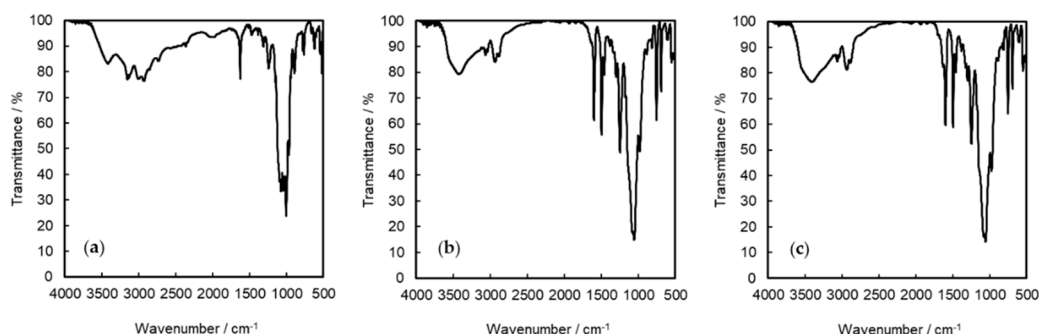


Figure 5. FT-IR spectra for (a) α -ZrP·2MIm, (b) α -ZrP·2MIm-RXN, and (c) α -ZrP·2MIm-T-RXN.

Thus, the initiating system TBD with α -ZrP·2MIm showed good storage stability at 25 °C and high reactivity at 100 °C, and offers great potential as a latent thermal initiator in the curing of epoxy resin.

3. Experimental Section

3.1. Materials

$\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (CZP-100) was purchased from Daiichi Kigenso Kagaku Kogyo Co., Ltd. (Osaka, Japan). GPE was purchased from Aldrich Chemical Co., Inc. (Tokyo, Japan). TMG, TBD, MTBD, DBU, and DBN were purchased from Tokyo Chemical Industries, Co., Ltd. (Tokyo, Japan). The intercalated compound α -ZrP·2MIm was prepared by a reported method [14]. The chemical composition of α -ZrP·2MIm was $\text{Zr}(\text{HPO}_4)_2 \cdot 0.95\text{C}_4\text{H}_6\text{N}_2 \cdot 0.91\text{H}_2\text{O}$. Solvents were used as received without further purification.

3.2. Measurements

X-ray diffraction (XRD) patterns were obtained using a RINT2200 (Rigaku, Tokyo, Japan) under the following operating conditions: Cu K α radiation of 40 kV, 40 mA over a scan range of 3°–40° at a rate of 2° min^{-1} and for 20 kV, and 20 mA over a scan range of 2°–15° at a rate of 2° min^{-1} . NMR spectra of solutions were recorded on a Unity-300 spectrometer (Varian, Palo Alto, CA, USA) and a JNM-ECZS (400 MHz) spectrometer (JEOL, Tokyo, Japan) using tetramethylsilane (TMS) as an internal standard. Elemental analyses were carried out using a 2400II analyzer (PerkinElmer, Waltham, MA, USA). Fourier transform infrared spectroscopy (FT-IR) measurements were carried out with an ALPHA spectrometer (Bruker, Billerica, MA, USA).

3.3. Typical Polymerization Procedure

A mixture of GPE (150 mg, 1.0 mmol), TBD (4.2 mg, 0.030 mmol), and an intercalated compound of 2-methylimidazole with α -ZrP (α -ZrP·2MIm) (11.9 mg, 0.032 mmol, and content of 2-methylimidazole: 0.030 mmol) was heated at 120 °C for 1 h. A small aliquot of the reaction mixture was dissolved in CDCl_3 , and its ^1H -NMR spectrum was acquired to determine the extent of conversion of GPE.

3.4. Polymerization Procedure for Recovery of α -ZrP·2MIm (α -ZrP·2MIm-T-RXN) after the Reaction

A mixture of GPE (4.51 g, 30.0 mmol), TBD (126 mg, 0.91 mmol), and α -ZrP·2MIm (357 mg, 0.95 mmol, content of 2-methylimidazole: 0.90 mmol) was heated at 120 °C for 1 h. After the reaction, tetrahydrofuran (THF) was added to the mixture. The solution was filtered and the residue (α -ZrP·2MIm-T-RXN) was rinsed, dried under vacuum, and analyzed by XRD and FT-IR.

4. Conclusions

A temperature-dependent enhancement effect was found for TBD with α -ZrP·2MIm as a latent thermal initiator in the reaction of GPE. The reaction with GPE at 100 °C and for 1 h did not proceed, in contrast to that when TBD was added to α -ZrP·2MIm (α -ZrP·2MIm-T), and where a %conversion value of 28% was attained. By extending the reaction time to 9 h, the %conversion value reached 89% for α -ZrP·2MIm-T and 71% for α -ZrP·2MIm, respectively, confirming that the reactivity of GPE was increased by the addition of TBD. With respect to storage, α -ZrP·2MIm-T in GPE was found to be stable for 14 days, with the %conversion value being 19%. The latent thermal initiator α -ZrP·2MIm-T showed good stability under typical storage conditions (7 days at 25 °C) and was highly reactive with GPE. Thus, the mixed initiator α -ZrP·2MIm may be used as a latent thermal initiating system in the curing of epoxy resin.

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Conflicts of Interest: The authors declare no conflict of interest.

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