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DBU-intercalated γ -titanium phosphate as a latent thermal catalyst in the reaction of glycidyl phenyl ether (GPE) and hexahydro-4-methylphthalic anhydride (MHHPA)

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The capabilities and performance of γ -titanium phosphate (γ -TiP) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a latent thermal catalyst were investigated by the copolymerization of glycidyl phenyl ether (GPE) and hexahydro-4-methylphthalic anhydride (MHHPA) at different temperatures for a period of one hour. Polymerization was not observed until the reactants were heated to 100 °C. Upon increasing the temperature to 120 °C, the conversion in the presence of γ -TiP·DBU as a catalyst showed 98% conversion in 1 h. The thermal stability of GPE and MHHPA reacted in the presence of γ -TiP·DBU at 40 °C for 144 h resulted in less than 7% conversion of GPE. The conversion of GPE did not show a significant increase at 40 °C.

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1. Introduction

The nanolayered structures of α -M(HPO₄)₂·H₂O and γ -M(HPO₄)₂·2H₂O (M = Ti, Zr, Sn, Ge, Pb, *etc.*) have attracted increasing attention in recent decades due to their ion exchange capacity and application in drug delivery.^{1–5} α -Zirconium phosphate (α -ZrP) with a small metal cation or interlaced with an amine can provide a larger interlayer distance for the further uptake of species such as a metal cation with a large ionic radius, an alcohol/glycol, and a quaternary ammonium cation, which can be considered as a catalyst and reinforcement of polymers.^{6–10} Thermal latent catalysts and initiators are highly attractive for use in chemical industries such as adhesives, paints, and molding materials. Salt-type and non-salt-type thermal latent initiators such as sulfonium salt, phosphonium salt, pyridinium salt, *N*-heterocyclic carbene, aminimide, phosphoramidates, *O,O*-di-*t*-butyl phenyl phosphonate and phosphonic amide ester are used in polymerization.¹¹ We have already reported that primary alkylamines intercalated with α -ZrP can serve as latent thermal initiators in the reaction of glycidyl phenyl ether (GPE)¹² and that 1,4-diazabicyclo (2,2,2) octane (DABCO) and 1,8-diazabicyclo (5,4,0) undec-7-ene (DBU) are intercalation compounds with α -ZrP.¹³ Furthermore, we examined the performances of some imidazoles intercalated

with α -ZrP as thermal latent initiators.^{14,15} α -ZrP·DABCO and α -ZrP·DBU show good performance as latent thermal catalysts in the reaction of GPE and hexahydro-4-methylphthalic anhydride (MHHPA). However, α -ZrP-intercalated DBU needs a higher temperature for the reaction of GPE and MHHPA. Therefore, researchers mainly focused on developing a highly active latent catalyst to avoid the need for high-temperature curing. γ -Insoluble acid salts are tetravalent metals that can be obtained with a different layered structure, first obtained by Clearfield.¹ Furthermore, the layers of γ -titanium phosphate (γ -TiP) and α -ZrP are packed at different interlayer distances, and hence, they show different ion exchange properties.¹ The interlayer distance of α -Zr (HPO₄)₂·H₂O (7.6 Å) and γ -Ti (HPO₄)₂·2H₂O (11.6 Å) has been reported.¹⁶ The wide interlayer distance of γ -TiP might show high reactivity compared with α -ZrP. γ -TiP can be easily prepared by converting amorphous TiP with the treatment of concentrated H₃PO₄ at 225 °C for 48 h.¹⁷

In the present study, we report that γ -TiP intercalated with DBU was synthesized. This material could be a cheaper and alternative thermal latent catalyst than α -ZrP for the reaction of GPE and MHHPA. Therefore, the enhancement effects of γ -TiP as a potential thermal latent catalyst on the acceleration of the reaction between GPE and MHHPA were extensively studied.

2. Results and discussion

The intercalation of DBU into the layers of γ -TiP was carried out by a similar procedure of intercalation into α -ZrP. The mixture of DBU and γ -TiP in methanol was stirred at ambient temperature for 24 h. After the reaction, the intercalation compound

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was recovered by centrifugation and dried under vacuum. The ratio of C, H, and N of the product was 14.81%, 2.60%, and 3.84%, and the composition was $\text{Ti}(\text{HPO}_4)_2 \cdot 0.40\text{DBU}$, as determined by elemental analysis. The interlayer distance of the intercalation compound of $\gamma\text{-TiP} \cdot \text{DBU}$ was 19.6 \AA ($2\theta = 4.5^\circ$) expanded from 11.5 \AA ($2\theta = 7.7^\circ$) of pristine $\gamma\text{-TiP}$ estimated by XRD patterns, as shown in Fig. 1(a) and (b). The thermal properties of $\gamma\text{-TiP} \cdot \text{DBU}$ were examined by TG and DSC, as shown in Fig. 2 and 3. Pristine $\gamma\text{-TiP}$ loses two molecules of crystal water from 50 to $100 \text{ }^\circ\text{C}$.¹⁶ As shown in Fig. 2, $\gamma\text{-TiP} \cdot \text{DBU}$ gradually lost the weight in the first step until $220 \text{ }^\circ\text{C}$ (6.5% of weight loss). The DSC curve up to $220 \text{ }^\circ\text{C}$ shows two endothermic peaks, and the peak temperatures are $104.4 \text{ }^\circ\text{C}$ and $193.3 \text{ }^\circ\text{C}$, as shown in Fig. 2. The third endothermic peak was observed at $423.4 \text{ }^\circ\text{C}$ from $300 \text{ }^\circ\text{C}$ to $550 \text{ }^\circ\text{C}$. Assuming that the weight loss of 20.8% from $25 \text{ }^\circ\text{C}$ to $590 \text{ }^\circ\text{C}$ was attributed to that of DBU, the compositional formula was calculated as $\text{Ti}(\text{HPO}_4)_2 \cdot (\text{C}_9\text{H}_{16}\text{N}_2)_{0.41}$. From the compositional formula calculated from the elemental analysis, the composition was $\text{Ti}(\text{HPO}_4)_2 \cdot (\text{C}_9\text{H}_{16}\text{N}_2)_{0.40}$. The decreasing weight was in good accordance with the deintercalation of DBU. It could be explained that $\gamma\text{-TiP}$ shows a two-step titration curve with a NaOH-NaCl solution.¹ At least two peaks would be indicated in the DSC curve. The reaction of GPE-MHHPA with $\gamma\text{-TiP} \cdot \text{DBU}$, as shown in Scheme 1, was carried out at $120 \text{ }^\circ\text{C}$ for 4 h, the polymer products obtained were washed out with THF and the residue of $\gamma\text{-TiP} \cdot \text{DBU}$ ($\gamma\text{-TiP} \cdot \text{DBU} \cdot \text{RXN}$) was recovered. The interlayer distance of $\gamma\text{-TiP} \cdot \text{DBU} \cdot \text{RXN}$ was 25.7 \AA ($2\theta = 3.4^\circ$) expanded from $\gamma\text{-TiP} \cdot \text{DBU}$, as shown in Fig. 1(c).

The expansion of the basal distance and an increase in the C content were recognized. The ^{13}C CPMAS NMR spectrum of $\gamma\text{-TiP} \cdot \text{DBU}$ and $\gamma\text{-TiP} \cdot \text{DBU} \cdot \text{RXN}$ are shown in Fig. 4. In the ^{13}C CPMAS NMR spectrum, the aromatic carbons, methine, and methylene groups derived from GPE are shown in Fig. 4(b). The copolymer of GPE-MHHPA, carbonyl carbon, must be observed at $\delta 175$. In the ^{13}C CPMAS NMR of $\gamma\text{-TiP} \cdot \text{DBU} \cdot \text{RXN}$, carbonyl carbon was not observed at $\delta 175$. A similar result was observed with $\alpha\text{-ZrP}$ imidazoles.¹⁴ The C, H, and N ratio of the product by elemental analysis was 33.03 : 3.46 : 1.28. Based on the result, the reaction products exist in the interlayer of $\gamma\text{-TiP} \cdot \text{DBU}$, and the composition was estimated as $\text{Ti}(\text{HPO}_4)_2 \cdot \text{DBU}_{0.20} \cdot (\text{GPE})_{1.15}$. At 50%, the interlayer of DBU remained after the reaction of GPE-MHHPA. We have already reported using $\alpha\text{-ZrP} \cdot \text{DBU}$ that the remaining DBU was 20%.¹³ The deintercalated DBU initiated the copolymerization of GPE and MHHPA. The deintercalation ratio would be affected by the reactivity of GPE-MHHPA. The FT-IR spectra of $\alpha\text{-ZrP} \cdot \text{DBU}$ and $\alpha\text{-ZrP} \cdot \text{DBU} \cdot \text{RXN}$ are shown in Fig. 5(b) and (c). The peak due to DBU ($\nu \text{C}=\text{N}$) and $\alpha\text{-ZrP}$ ($\nu \text{P}-\text{O}$) was detected at 1650 and 983 cm^{-1} in Fig. 5(b). The aromatics ($\nu \text{C}-\text{C}$ at 1600 and 1548 cm^{-1}) and ether groups ($\nu \text{C}-\text{O}-\text{C}$ at 1230 cm^{-1}) in the products of GPE are observed in Fig. 5(c).

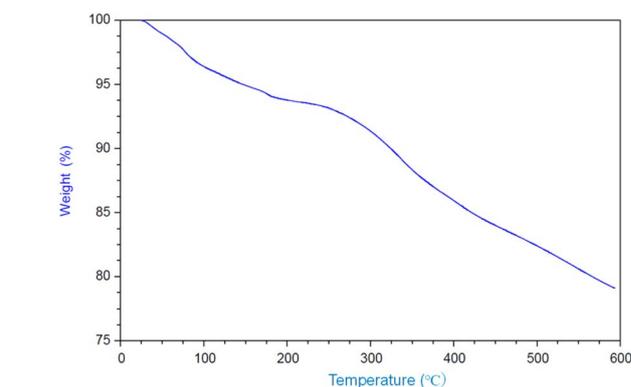


Fig. 2 TGA curve of $\gamma\text{-TiP} \cdot \text{DBU}$.

The estimation of the catalytic activity of $\gamma\text{-TiP} \cdot \text{DBU}$ and the copolymerization of GPE and MHHPA was carried out as shown in Fig. 6. The reaction of GPE-MHHPA with $\alpha\text{-ZrP} \cdot \text{DBU}$ has already been reported.¹³ In comparison to GPE conversions at $100 \text{ }^\circ\text{C}$, the greatest difference between the conversions was 68% and 35% with $\gamma\text{-TiP} \cdot \text{DBU}$ and $\alpha\text{-ZrP} \cdot \text{DBU}$, as determined by the $^1\text{H-NMR}$ spectra. Conversions at $120 \text{ }^\circ\text{C}$ were 98% and

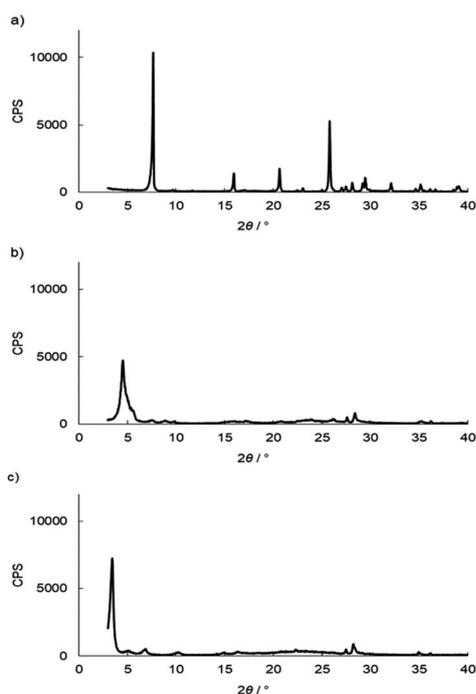


Fig. 1 XRD patterns of (a) pristine $\gamma\text{-TiP}$, (b) $\gamma\text{-TiP} \cdot \text{DBU}$, and (c) $\gamma\text{-TiP} \cdot \text{DBU} \cdot \text{RXN}$.

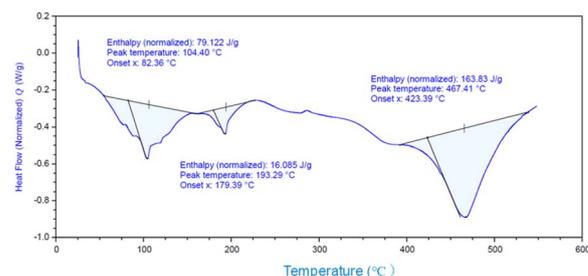
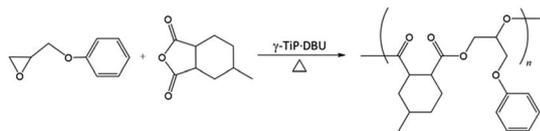
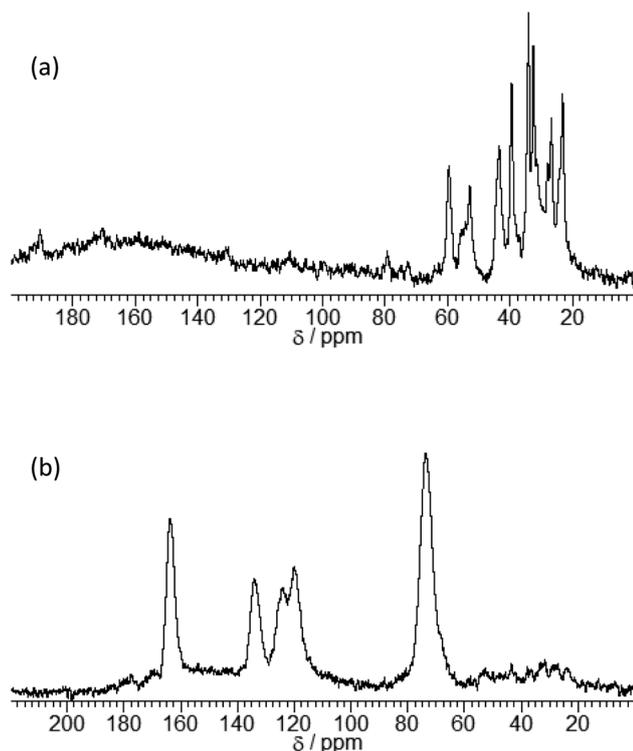


Fig. 3 DSC curve of $\gamma\text{-TiP} \cdot \text{DBU}$.





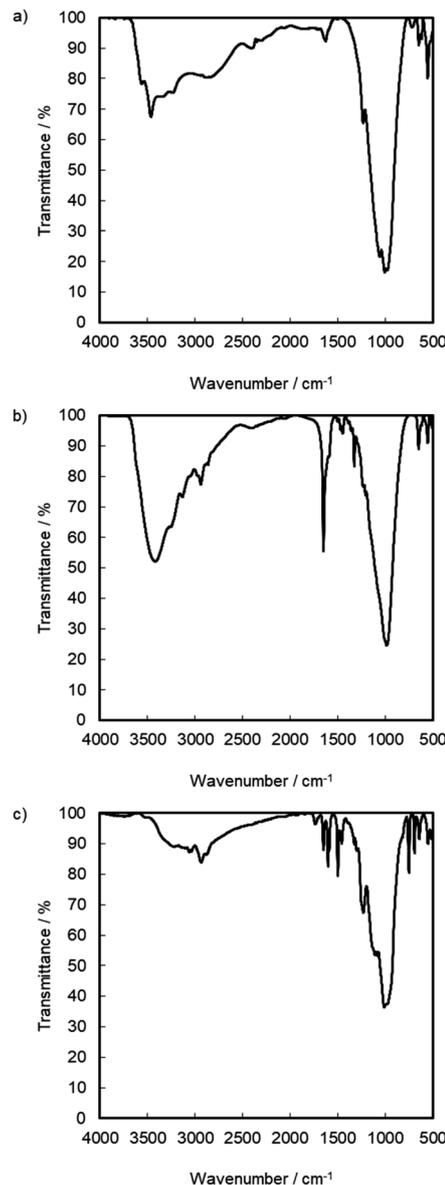
Scheme 1 Synthesis of poly(GPE-co-MHHPA).

Fig. 4 ¹³C-NMR spectra of (a) γ -TiP-DBU and (b) γ -TiP-DBU-RXN.

86% with γ -TiP-DBU and α -ZrP-DBU. The reaction with γ -TiP-DBU quantitatively proceeded at 120 °C and γ -TiP-DBU was higher reactivity at the same reaction temperature.

The copolymerization of GPE-MHHPA and homopolymerization of GPE might occur simultaneously. The conversion of MHHPA was confirmed by the integral ratio at different temperatures for 1 h (Fig. 7). However, γ -TiP-DBU has shown a conversion of 67% at 100 °C and increased the conversion rate by 96% at 120 °C. It can be explained that the conversion of GPEs was in good accordance with MHHPA and γ -TiP-DBU accelerates the reaction rate more than α -ZrP-DBU. The reaction with γ -TiP-DBU quantitatively proceeded at 120 °C and γ -TiP-DBU has higher reactivity at the same reaction temperature. It might be explained that γ -TiP shows a two-step titration curve with the NaOH-NaCl solution. Under a similar condition, α -ZrP shows a one-step titration curve, as reported in the literature.¹ It can affect the first step of deintercalation of DBU from the interlayer of γ -TiP.

The conversion of GPE after 1 h as a function of the content of DBU in γ -TiP-DBU during polymerization is shown in Fig. 8. When the mole concentration of DBU increased, and the

Fig. 5 FT-IR spectrum of (a) pristine γ -TiP, (b) γ -TiP-DBU, and (c) γ -TiP-DBU-RXN.

conversion rate also increased. The comparison of the conversions of GPE was 95% by using 2 mol% of γ -TiP-DBU. There is also a very important observation in the presence of γ -TiP-DBU; the use of more than 2 mol% γ -TiP-DBU resulted in copolymerization of GPE and MHHPA.

The conversion values for GPE with 3 mol% of γ -TiP-DBU at 120 °C for 0–60 min are displayed in Fig. 9. It can be seen that the conversion values increased with the increasing reaction time and reached 94% after 30 min. It is clear that the polymerization reaction proceeds within a short period after 30 min under specific conditions. In addition, by extending the time period, the conversion rate also increased and reached 97% conversion for 45 min.

The performance of the latent thermal initiator depends on the high curing capacity at the desired temperature and higher



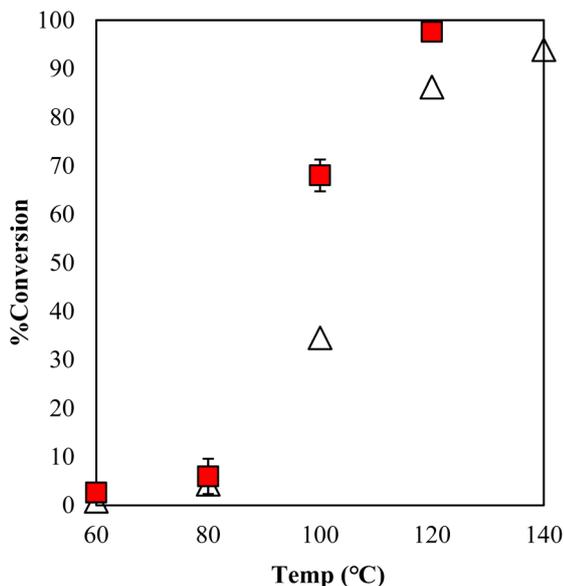


Fig. 6 Conversion of GPE after 1 h as a function of temperature during polymerization with γ -TiP·DBU (■) and α -ZrP·DBU (Δ).¹⁵

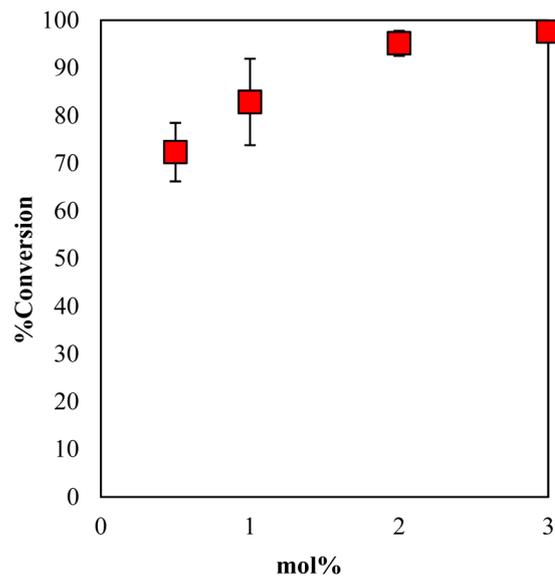


Fig. 8 Conversion of GPE after 1 h as a function of the content of DBU in γ -TiP·DBU during polymerization at 120 °C.

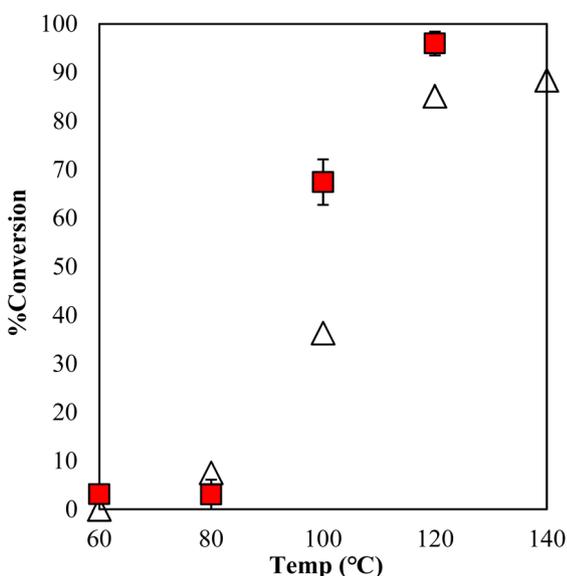


Fig. 7 Conversion of MHHPA after 1 h as a function of temperature during polymerization with γ -TiP·DBU (■) and α -ZrP·DBU (Δ).¹⁵

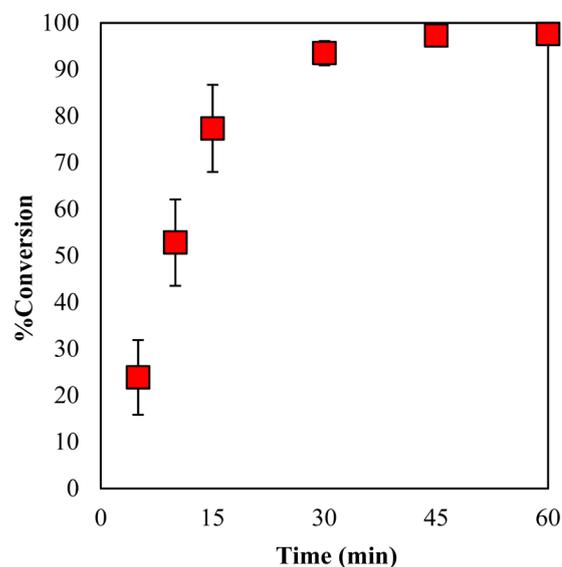


Fig. 9 Conversion of GPE as a function of time during polymerization with γ -TiP·DBU at 120 °C.

storage stability under the recommended storage conditions. The evaluation of the performance of storage stability is mainly based on the conversion of GPE as a function of time during polymerization with γ -TiP·DBU and α -ZrP·DBU at 40 °C, as presented in Fig. 10. The conversion did not show a significant increase, and the conversion was 5% for 144 h.

3. Experimental section

3.1. Materials

Ti(HPO₄)₂·2H₂O was purchased from Rasa Industries Ltd (Japan); GPE, DBU, and MHHPA from Tokyo Chemical

Industries, Co., Ltd (Japan). Solvents were used as received without further purification.

3.2. Measurements

X-ray diffraction (XRD) patterns were acquired using a Rigaku RINT2200 (Japan) with Cu K α radiation over a scan range of 3–40° at a rate of 2° min⁻¹. NMR spectra in solutions were recorded using a Varian Unity-300 spectrometer (Palo Alto, CA, USA) with tetramethylsilane (TMS) as an internal standard. The DBU contents in the intercalation compounds of γ -TiP were measured using a PerkinElmer 2400II analyzer (Waltham, MA,



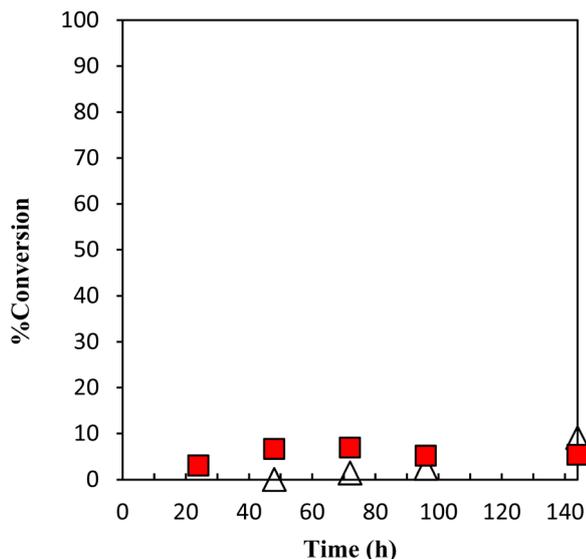


Fig. 10 Conversion of GPE as a function of time during polymerization with γ -TiP·DBU at 40 °C. γ -TiP·DBU (■) and α -ZrP·DBU (Δ).¹³

USA). The ¹³C CPMAS NMR spectra were recorded using a JEOL ECA-600 NMR spectrometer (Tokyo, Japan). Thermogravimetric (TG) analysis was carried out using a TA instrument TGA-550 at a heating rate of 10 °C min⁻¹ under nitrogen. Differential scanning calorimetry (DSC) was carried out using a TA instrument DSC250 at a heating rate of 10 °C min⁻¹ under nitrogen.

3.3. Preparation of DBU-intercalated γ -TiP (γ -TiP·DBU)

The intercalation of DBU into the layers of $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ (γ -TiP) was carried out following a similar procedure for α -Zirconium phosphate. γ -TiP (4.98 g) and DBU (8.38 g) were added to methanol (75.2 mL). The reaction mixture was agitated at ambient temperature for 24 h before the product was collected by centrifugation and washed 3 times with methanol. The resulting residue was dried under vacuum. The ratio of C, H, and N in the product was 14.81 : 2.60 : 3.84, and the composition was $\text{TiP}(\text{HPO}_4)_2 \cdot 0.40\text{DBU}$, as determined by elemental analysis.

3.4. Typical polymerization procedure

A mixture of GPE (150 mg, 1.0 mmol), MHHPA (166 mg, 0.99 mmol), and γ -TiP·DBU (22.1 mg, 0.075 mmol, DBU content: 0.030 mmol) was heated at 100 °C for 1 h. A small aliquot of the reaction mixture was dissolved in CDCl_3 , and its ¹H-NMR spectrum was recorded to determine the extent of conversion of GPE.

3.5. Recovery of γ -TiP·DBU after the reaction with GPE and MHHPA (γ -TiP·DBU-RXN)

A mixture of GPE (7.51 g, 50.0 mmol), MHHPA (8.41 g, 50.0 mmol), and γ -TiP·DBU (535 mg, 1.82 mmol, DBU content: 0.73 mmol) was heated at 120 °C for 4 h. After the reaction, tetrahydrofuran (THF) was added to the mixture. The solution was

filtered and the residue, γ -TiP·DBU-RXN, was rinsed, dried under vacuum, and analyzed by XRD and ¹³C CPMAS NMR spectra. The C, H, and N ratio in γ -TiP·DBU-RXN was 33.03 : 3.46 : 1.28.

4. Conclusions

A temperature-dependent latent thermal catalyst γ -titanium phosphate (γ -TiP) intercalated with DBU has been introduced in the reaction of glycidyl phenyl ether (GPE) and hexahydro-4-methylphthalic anhydride (MHHPA) and compared with α -ZrP-intercalated DBU. The interlayer distance of the intercalation compound of γ -TiP·DBU has shown 19.6 Å expanded from 11.5 Å of pristine γ -TiP. In the reaction with GPE and MHHPA at 120 °C for 1 h, the conversion value of GPE has been reached at 99% by γ -TiP·DBU. In addition, the conversion of MHHPAs was in good accordance with the conversion of GPEs. The conversion values of GPE increased with the increasing reaction time and reached 96% after 30 min and 98% after 45 min, by the reaction as a function of time during polymerization with γ -TiP·DBU. The latent thermal catalyst γ -TiP·DBU showed good stability under typical storage conditions (144 h at 40 °C), and was highly reactive with GPE and MHHPA. Thus, it can be suggested that γ -TiP·DBU could be a good alternative as a latent thermal initiating system in curing epoxy resins.

Author contributions

Osamu Shimomura conceived, designed, and wrote the article; Ayumi Fujiwara, Hiroshi Furuya, and Motohiro Shizuma performed the experiments; Shekh Md. Mamun Kabir and Atsushi Ohtaka contributed to a helpful discussion.

Conflicts of interest

The authors declare no conflict of interest.

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