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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.

1. Introduction

The nanolayered structures of α-$M(HPO_4)_2 \cdot H_2O$ and γ-$M(HPO_4)_2 \cdot 2H_2O$ (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 alkanol/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, phosphonamidates, *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 $(HPO_4)_2 \cdot H_2O$ (7.6 Å) and γ-Ti $(HPO_4)_2 \cdot 2H_2O$ (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 H_3PO_4 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 $Ti(HPO_4)_2 \cdot 0.40DBU$, as determined by elemental analysis. The interlayer distance of the intercalation compound of γ-TiP·DBU was 19.6 Å ($2\theta = 4.5°$) expanded from 11.5 Å ($2\theta = 7.7°$) of pristine γ-TiP estimated by XRD patterns, as shown in Fig. 1(a) and (b). The thermal properties of γ-TiP·DBU were examined by TG and DSC, as shown in Fig. 2 and 3. Pristine γ-TiP loses two molecules of crystal water from 50 to 100 °C.[16] As shown in Fig. 2, γ-TiP·DBU gradually lost the weight in the first step until 220 °C (6.5% of weight loss). The DSC curve up to 220 °C shows two endothermic peaks, and the peak temperatures are 104.4 °C and 193.3 °C, as shown in Fig. 2. The third endothermic peak was observed at 423.4 °C from 300 °C to 550 °C. Assuming that the weight loss of 20.8% from 25 °C to 590 °C was attributed to that of DBU, the compositional formula was calculated as $Ti(HPO_4)_2 \cdot (C_9H_{16}N_2)_{0.41}$. From the compositional formula calculated from the elemental analysis, the composition was $Ti(HPO_4)_2 \cdot (C_9H_{16}N_2)_{0.40}$. The decreasing weight was in good accordance with the deintercalation of DBU. It could be explained that γ-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 γ-TiP·DBU, as shown in Scheme 1, was carried out at 120 °C for 4 h, the polymer products obtained were washed out with THF and the residue of γ-TiP·DBU (γ-TiP·DBU·RXN) was recovered. The interlayer distance of γ-TiP·DBU·RXN was 25.7 Å ($2\theta = 3.4°$) expanded from γ-TiP·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 γ-TiP·DBU and γ-TiP·DBU·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 δ 175. In the ^{13}C CPMAS NMR of γ-TiP·DBU-RXN, carbonyl carbon was not observed at δ 175. A similar result was observed with α-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 γ-TiP·DBU, and the composition was estimated as $Ti(HPO_4)_2 \cdot DBU_{0.20} \cdot (GPE)_{1.15}$. At 50%, the interlayer of DBU remained after the reaction of GPE-MHHPA. We have already reported using α-ZrP·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 α-ZrP·DBU and α-ZrP·DBU-RXN are shown in Fig. 5(b) and (c). The peak due to DBU (ν C=N) and α-ZrP (ν P–O) was detected at 1650 and 983 cm^{-1} in Fig. 5(b). The aromatics (ν C–C at 1600 and 1548 cm^{-1}) and ether groups (ν C–O–C at 1230 cm^{-1}) in the products of GPE are observed in Fig. 5(c).

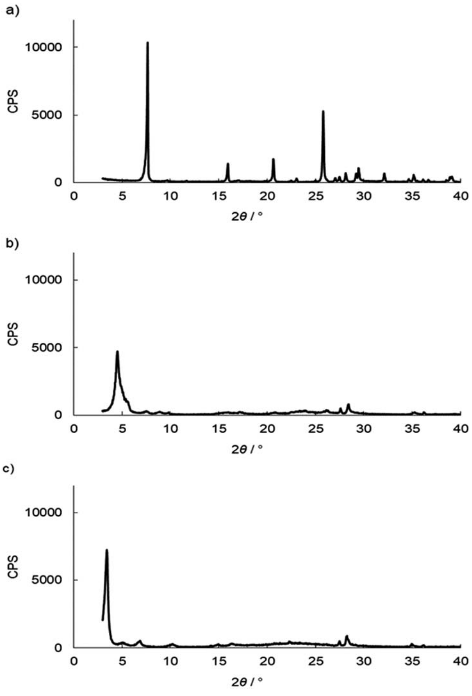


Fig. 1 XRD patterns of (a) pristine γ-TiP, (b) γ-TiP·DBU, and (c) γ-TiP·DBU-RXN.

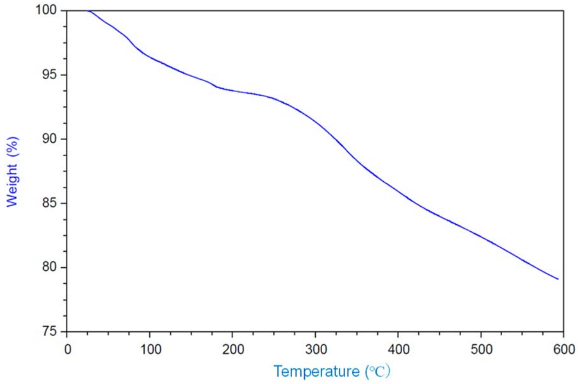


Fig. 2 TGA curve of γ-TiP·DBU.

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

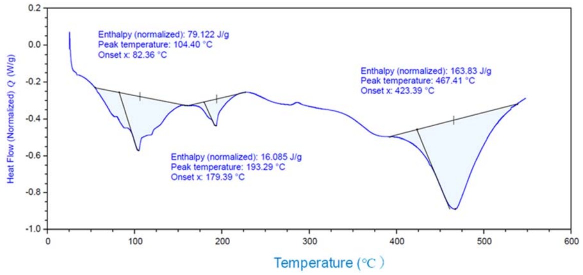
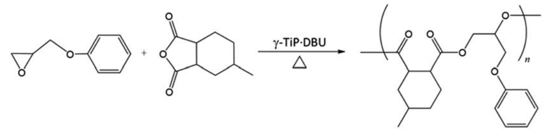


Fig. 3 DSC curve of γ-TiP·DBU.



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

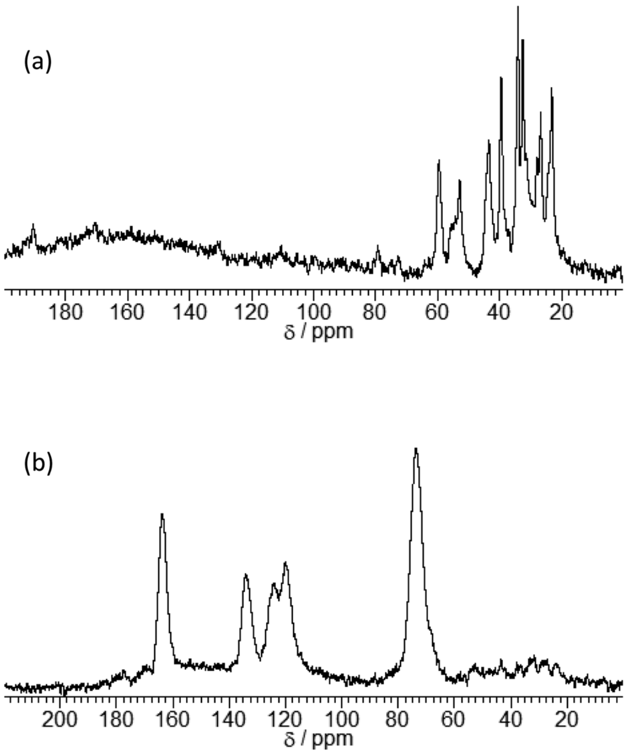


Fig. 4 ^{13}C-NMR spectra of (a) γ-TiP·DBU and (b) γ-TiP·DBU-RXN.

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 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.

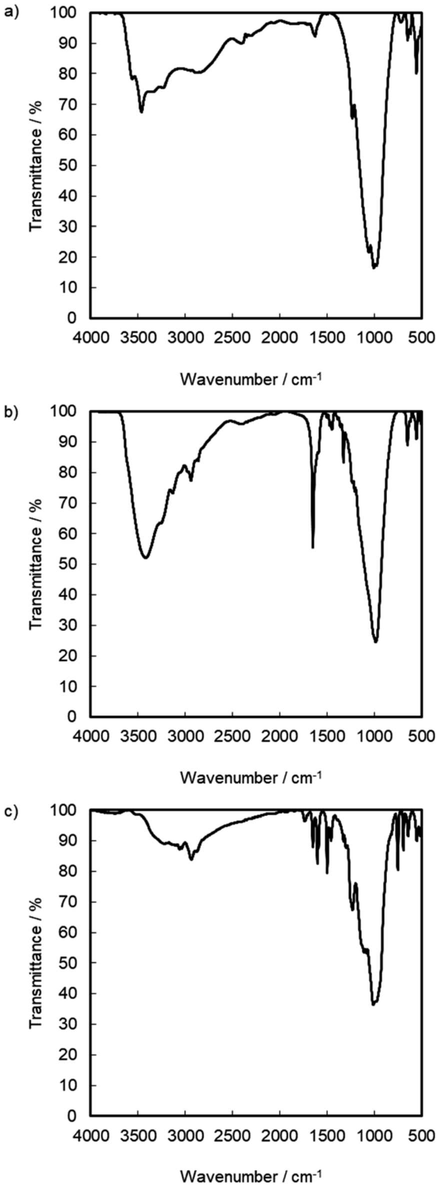


Fig. 5 FT-IR spectrum of (a) pristine γ-TiP, (b) γ-TiP·DBU, and (c) γ-TiP·DBU-RXN.

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

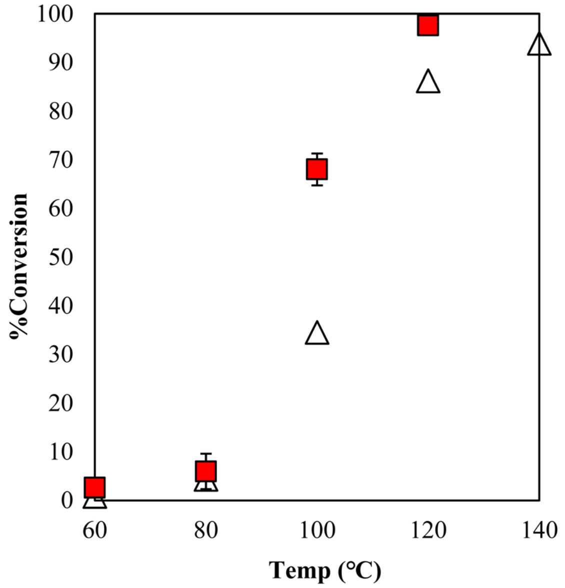


Fig. 6 Conversion of GPE after 1 h as a function of temperature during polymerization with γ-TiP·DBU (🟥) and α-ZrP·DBU (Δ).[13]

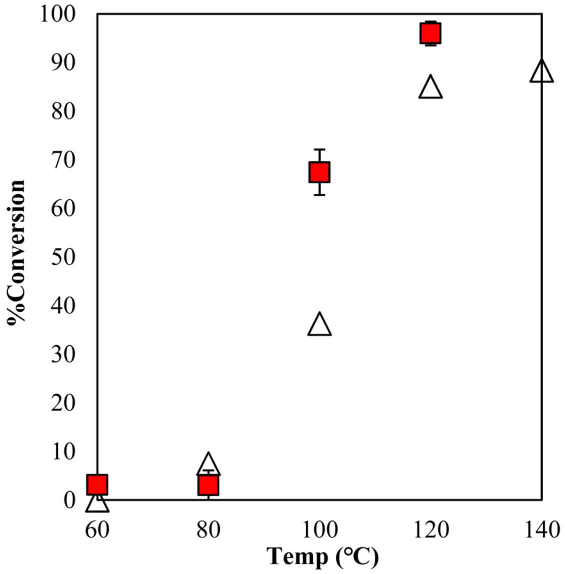


Fig. 7 Conversion of MHHPA after 1 h as a function of temperature during polymerization with γ-TiP·DBU (🟥) and α-ZrP·DBU (Δ).[13]

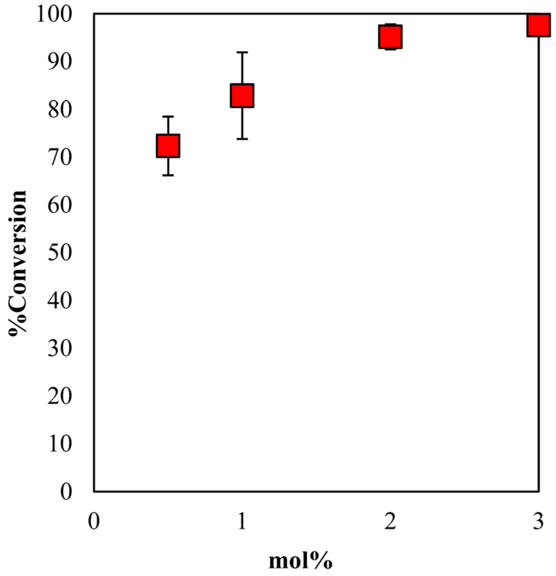


Fig. 8 Conversion of GPE after 1 h as a function of the content of DBU in γ-TiP·DBU during polymerization at 120 °C.

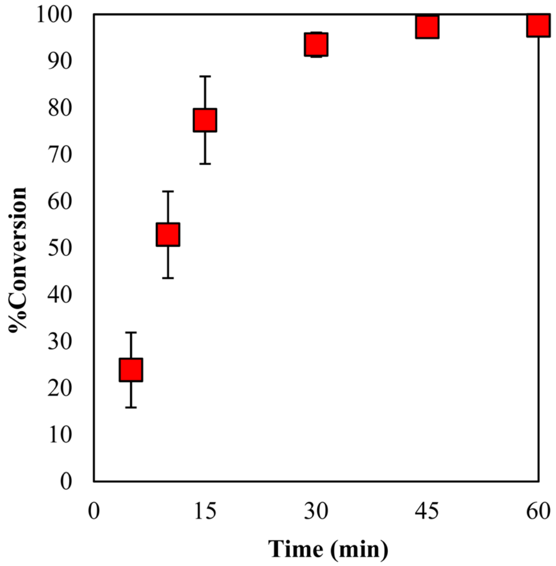


Fig. 9 Conversion of GPE as a function of time during polymerization with γ-TiP·DBU at 120 °C.

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$(HPO_4)_2 \cdot 2H_2O$ 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 Kα 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,

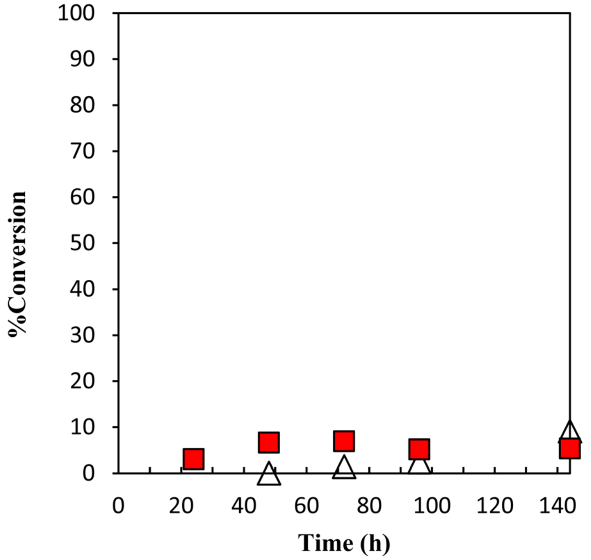


Fig. 10 Conversion of GPE as a function of time during polymerization with γ-TiP·DBU at 40 °C. γ-TiP·DBU (🟥) and α-ZrP·DBU (Δ).[13]

USA). The ^{13}C 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 $Ti(HPO_4)_2 \cdot 2H_2O$ (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 $TiP(HPO_4)_2 \cdot 0.40DBU$, 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 ^{1}H-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 ^{13}C 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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