

Article

Imidazoles-Intercalated α -Zirconium Phosphate as Latent Thermal Initiators in the Reaction of Glycidyl Phenyl Ether (GPE) and Hexahydro-4-Methylphthalic Anhydride (MHHPA)

Osamu Shimomura ^{1,*}, Kensuke Tokizane ¹, Takatoshi Nishisako ¹, Shunro Yamaguchi ^{2,*}, Junko Ichihara ², Manabu Kirino ³, Atsushi Ohtaka ¹ and Ryôki Nomura ¹

¹ Department of Applied Chemistry, Osaka Institute of Technology, 5-16-1 Omiya, Ashahi-ku, Osaka 535-8585, Japan; konnkonnkitune127@yahoo.co.jp (K.T.); nt2435@icloud.com (T.N.); atsushi.otaka@oit.ac.jp (A.O.); ryoki.nomura@oit.ac.jp (R.N.)

² Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan; ichihara@sanken.osaka-u.ac.jp

³ R & D Group, ThreeBond Co., Ltd., 1-1 Oyama-cho, Midori-ku, Sagamihara, Kanagawa 252-0416, Japan; m-kirino@threebond.co.jp

* Correspondence: osamu.shimomura@oit.ac.jp (O.S.); shunro@sanken.osaka-u.ac.jp (S.Y.); Tel.: +81-6-6954-4269 (O.S.); +81-6-6879-8473 (S.Y.)

Academic Editor: Monica Pica

Received: 16 February 2017; Accepted: 19 May 2017; Published: 1 June 2017

Abstract: The capabilities of imidazoles-intercalated α -zirconium phosphate (α -ZrP-imidazole): imidazol (α -ZrP·Im), 2-methylimidazole (α -ZrP·2MIm), and 2-ethyl-4-methylimidazole (α -ZrP·2E4MIm) as latent thermal initiators were examined by the copolymerization of glycidyl phenyl ether (GPE) and hexahydro-4-methylphthalic anhydride (MHHPA) with the imidazoles-intercalated α -zirconium phosphate at varying temperatures for one-hour periods. Polymerization was not observed until the reactants were heated to 100 °C or above. Increasing the temperature, polymerization in the presence of α -ZrP·Im, α -ZrP·2MIm, or α -ZrP·2E4MIm proceeded at 140 °C for 1 h with over 90% conversion. The thermal stabilities of α -ZrP·Im, α -ZrP·2MIm, and α -ZrP·2E4MIm in the reaction at 40 °C for 264 h were tested. With α -ZrP·2MIm, the conversion was less than 15% up to 96 h. In the cases of α -ZrP·Im and α -ZrP·2E4MIm, the conversion reached less than 15% at 264 h. The thermal stabilities of α -ZrP·Im, α -ZrP·2MIm, and α -ZrP·2E4MIm at 40 °C were superior to those of the commercially available thermal latent initiators: HX-3088 and HX-3722.

Keywords: latent thermal initiator; intercalation; α -zirconium phosphate; imidazole; glycidyl phenyl ether

1. Introduction

There has been considerable interest in the development of latent polymerization catalysts that are inert in the monomer or prepolymer under storage conditions. These catalysts can initiate polymerization under external impetus such as thermal or photo irradiation. Various kinds of latent catalysts are used in the polymerization reaction such as sulfonium salt [1–4], phosphonium salt [5], pyrazinium salt [6], *N*-heterocyclic carbene [7], aminimide [8], and sulfonate [9]. We have previously reported that primary alkylamines intercalated with α -zirconium phosphate (α -ZrP) can serve as latent thermal initiators in the reaction of glycidyl phenyl ether (GPE) [10] and that intercalation compounds of 1,4-diazabicyclo(2,2,2)octane (DABCO) and 1,8-diazabicyclo(5,4,0)undec-7-ene (DBU) with α -ZrP:

α -ZrP·DABCO and α -ZrP·DBU show good performance as latent thermal catalysts in the reaction of GPE with hexahydro-4-methylphthalic anhydride (MHHPA) [11].

Aside from DBU and DABCO, imidazoles have been widely used for curing epoxy resins as cured epoxy resins give good thermal resistance and physical properties because of the reactivity in chain polymerization with epoxide [12,13]. Latent thermal initiators of imidazoles have been developed. Romanchick prepared 1,3-dialkylimidazolium salts in the curing of epoxy resin [14]. In this case, the activation of catalyst needs a high temperature around 200 °C. Shin reported using microencapsulated imidazoles with polycaprolactone [15]. Arimitsu et al. proposed using the Michel addition products of imidazoles and fumarate ester to improve the low miscibility in epoxy resin [16]. However, these catalysts remain the blocking residues following the reaction to epoxy groups. These residues might be attributed to the deterioration of the resin. Amine-intercalated α -ZrP can act as latent thermal initiators [17,18] and the blocking residues of α -ZrP can act as additives for reinforcement of resins [19–21].

A series of imidazoles are expected to have different pK_a due to their substituents and to have different reactivity as the intercalation compounds of α -ZrP. We prepared intercalation compounds of imidazole (Im), 2-methylimidazole (2MIm), and 2-ethyl-4-methylimidazole (2E4MIm) with α -ZrP (hereafter abbreviated as α -ZrP·Im, α -ZrP·2MIm, and α -ZrP·2E4MIm) and examined the capabilities of α -ZrP·Im, α -ZrP·2MIm, and α -ZrP·2E4MIm as latent thermal initiators in the curing of GPE with hexahydro-4-methylphthalic anhydride (MHHPA). The pK_a value of Im, 2MIm, and 2E4MIm were 6.99 [22], 7.75 [22], and 8.3 [23], respectively. Latent thermal initiators containing imidazoles have been developed and the polymer-encapsulated imidazoles HX-3088 and HX-3722 are now commercially available. For comparison, the commercially available latent thermal initiators HX-3088 and HX-3722 were tested in the polymerization of GPE with MHHPA.

2. Results and Discussion

The intercalation compounds were prepared by mixing imidazole (Im), 2-methylimidazole (2MIm), or 2-ethyl-4-methylimidazole (2E4MIm) with α -ZrP by a similar procedure of another reported method [24]. The compositions determined by elemental analyses were $Zr(HPO_4)_2(C_3H_4N_2)_{0.78} \cdot 1.1H_2O$ (α -ZrP·Im), $Zr(HPO_4)_2(C_4H_6N_2)_{0.96} \cdot 1.2H_2O$ (α -ZrP·2MIm), and $Zr(HPO_4)_2(C_6H_{10}N_2)_{0.65} \cdot 0.6H_2O$ (α -ZrP·2E4MIm), respectively. Assuming that the weight loss after the weight loss of water was attributed to that of imidazoles, each of the compositional formula was calculated; α -ZrP·Im: $Zr(HPO_4)_2(C_3H_4N_2)_{0.87} \cdot 0.92H_2O$, α -ZrP·2MIm: $Zr(HPO_4)_2(C_4H_6N_2)_{0.94} \cdot 1.5H_2O$, and α -ZrP·2E4MIm, $Zr(HPO_4)_2(C_6H_{10}N_2)_{0.72} \cdot 0.13H_2O$. The basal distances of 10.7 Å ($2\theta = 8.2^\circ$) for α -ZrP·Im, 12.1 Å ($2\theta = 7.3^\circ$) for α -ZrP·2MIm and 12.9 Å ($2\theta = 6.9^\circ$) for α -ZrP·2E4MIm expanded compared with that of pristine α -ZrP (7.6 Å, $2\theta = 11.7^\circ$). The thermal properties of these α -ZrP-imidazoles intercalation compounds were examined by thermogravimetric analysis (TGA) shown in Figure 1. The thermal weight loss around 100 °C showed a decrease of water. After the weight loss of water, α -ZrP·Im was stable up to 250 °C and weight decreased until 600 °C. In α -ZrP·2MIm and α -ZrP·2E4MIm, the weights gradually decreased from 175 °C until 600 °C. Up to 140 °C of the curing temperature (discussed later), these α -ZrP-imidazoles intercalation compounds thermally lost H_2O rather than the imidazoles. Polymerization of GPE with MHHPA in the presence of α -ZrP·Im, α -ZrP·2MIm, and α -ZrP·2E4MIm containing 3 mol % of each intercalation compound for GPE at 140 °C was performed to produce poly(GPE-co-MHHPA) as shown in Scheme 1. The molecular weights and the molecular weight distribution of the resulting poly(GPE-co-MHHPA) were determined by GPC: $M_n = 2000$, $M_w/M_n = 1.4$ for α -ZrP·Im at 140 °C for 2 h, $M_n = 2100$, $M_w/M_n = 1.4$ for α -ZrP·2MIm at 140 °C for 1 h, and $M_n = 3100$, $M_w/M_n = 1.3$ for α -ZrP·2E4MIm at 140 °C for 1 h, respectively. The conversion of GPE for α -ZrP·Im was 72% at 140 °C for 1h, the reaction time was extended to 2 h to obtain the quantitative conversion. The molecular weight and molecular weight distribution of poly(GPE-co-MHHPA) were previously reported as $M_n = 2600$, $M_w/M_n = 1.4$ for α -ZrP·DABCO, and $M_n = 720$ and $M_w/M_n = 1.2$ for α -ZrP·DBU [11].

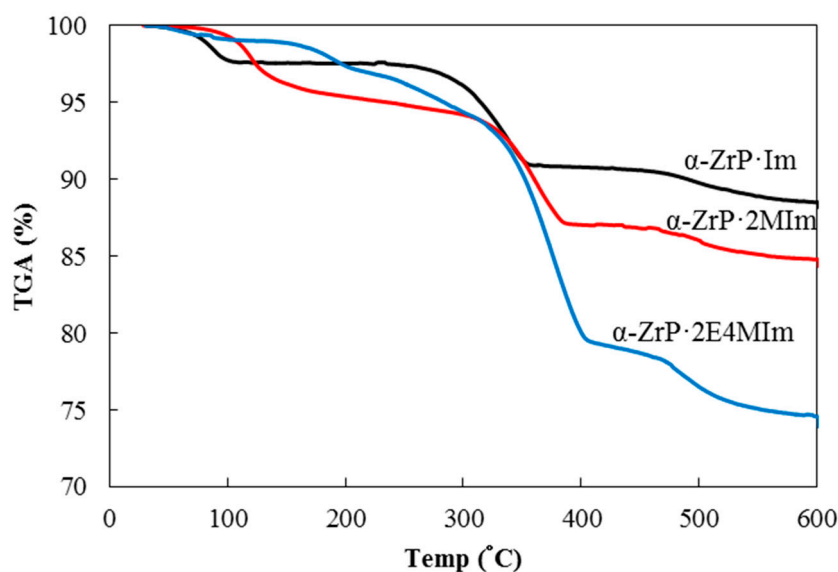
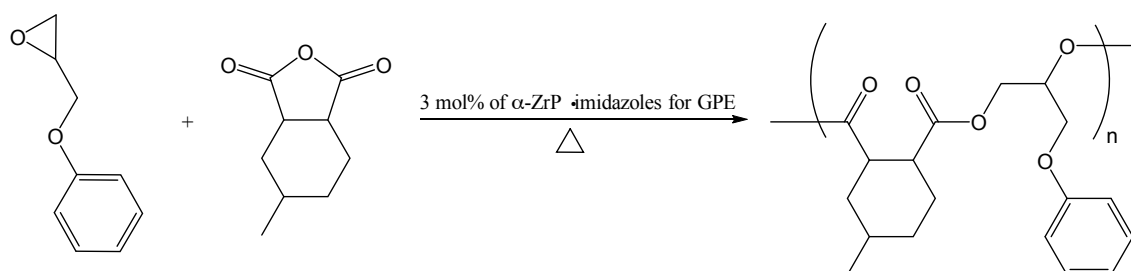


Figure 1. TGA curves of α -ZrP·Im (—), α -ZrP·2MIm (—), and α -ZrP·2E4MIm (—).



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

The capabilities of the α -ZrP·Im, α -ZrP·2MIm, and α -ZrP·2E4MIm as latent initiators were examined in the reactions of GPE with MHHPA containing 3 mol % of each intercalation compound for GPE at varying temperatures for 1 h periods by $^1\text{H-NMR}$ technique as shown in Figure 2. The conversions of GPEs were measured from the area ratio of the aromatic protons at δ 6.9 and the methylene protons of δ 2.92 (indicated by arrows), which relatively decreased with an increase in the reaction temperature from 80 to 140 °C (Figure 2).

Figure 3 shows the conversions of GPE in the reaction with α -ZrP·Im, α -ZrP·2MIm, or α -ZrP·2E4MIm at these temperatures over a 1 h period. In each case, GPE did not substantially change below 80 °C. Particularly in the case of α -ZrP·Im, the reaction did not proceed at 100 °C. With an increase in temperature, the reactions with any α -ZrP intercalation compound gradually proceeded and reached over 94% of conversions at 140 °C. These α -ZrP intercalation compounds were thermally stable and required 140 °C of curing temperature as initiators. Commercially available latent thermal curing agents such as the microencapsulated imidazoles of HX-3088 and HX-3722 also did not effectively initiate the reaction up to 80 °C. When the temperature was increased, the reaction fairly proceeded at 100 °C with 66% conversion for HX-3088 and 75% conversion for HX-3722. However, these initiators required 140 °C of curing temperature as well as the imidazoles-intercalated α -ZrP. Arimitsu et al. reported that the imidazole derivatives prepared from fumarate ester as latent thermal initiators of butyl glycidyl ether. The reaction completely proceeded at 150 °C for 30 min [16].

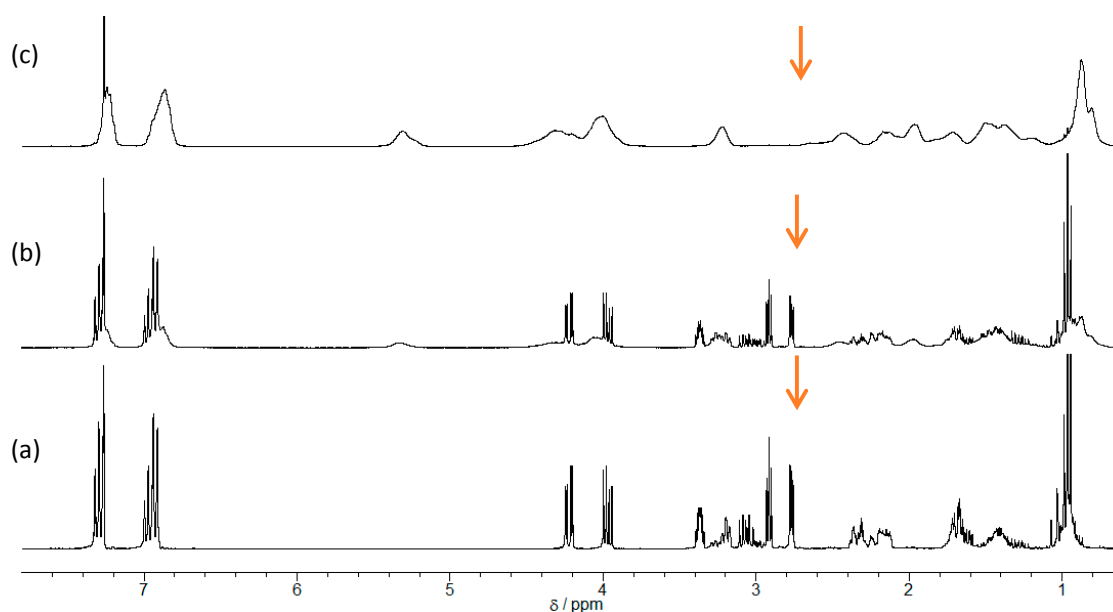


Figure 2. The $^1\text{H-NMR}$ spectra of GPE-MHHPA (glycidyl phenyl ether- hexahydro-4-methylphthalic anhydride) with $\alpha\text{-ZrP}\cdot\text{Im}$ at (a) 80 °C, (b) 120 °C, and (c) 140 °C for 1 h.

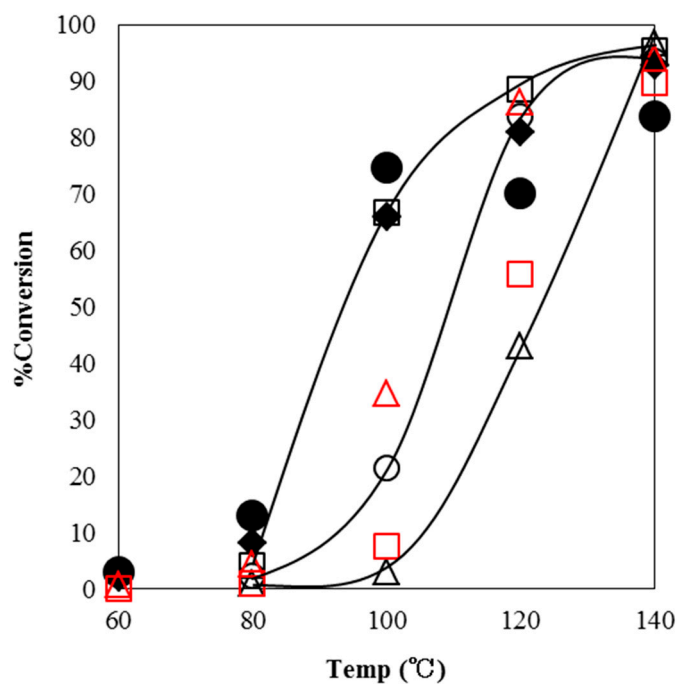


Figure 3. The conversion of GPE after 1 h as a function of temperature during polymerization with $\alpha\text{-ZrP}\cdot\text{Im}$ (- Δ -), $\alpha\text{-ZrP}\cdot\text{2MIm}$ (- \square -), $\alpha\text{-ZrP}\cdot\text{2E4MIm}$ (- \circ -), $\alpha\text{-ZrP}\cdot\text{DABCO}$ (\square) [11], $\alpha\text{-ZrP}\cdot\text{DBU}$ (Δ) [11], HX-3088 (\blacklozenge), and HX-3722 (\bullet).

The thermal stabilities of $\alpha\text{-ZrP}\cdot\text{Im}$, $\alpha\text{-ZrP}\cdot\text{2MIm}$, $\alpha\text{-ZrP}\cdot\text{2E4MIm}$, HX-3088, and HX-3722 were tested with the following conversion of GPE at 40 °C as shown in Figure 4. With $\alpha\text{-ZrP}\cdot\text{2MIm}$, the conversion was less than 15% up to 96 h. In the cases of $\alpha\text{-ZrP}\cdot\text{Im}$ and $\alpha\text{-ZrP}\cdot\text{2E4MIm}$, the conversion reached less than 15% at 264 h. The thermal stabilities of $\alpha\text{-ZrP}\cdot\text{Im}$, $\alpha\text{-ZrP}\cdot\text{2MIm}$, and $\alpha\text{-ZrP}\cdot\text{2E4MIm}$ were superior to those of HX-3088 and HX-3722.

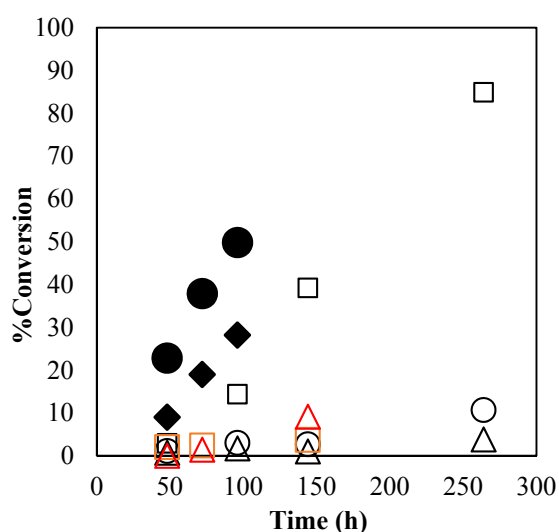


Figure 4. The conversion of GPE after 1 h as a function of time during polymerization with α -ZrP·Im (Δ), α -ZrP·2MIm (\square), α -ZrP·2E4MIm (\circ), α -ZrP·DABCO (\square) [11], α -ZrP·DBU (Δ) [11], HX-3088 (\blacklozenge), and HX-3722 (\bullet) at 40 °C.

This reaction system of GPE-MHHPA has an advantage for characterization of the resulting imidazoles-intercalated α -ZrPs after the reaction. Thus, the resulting ones can be easily isolated by simply washing the products with an organic solvent. After the reaction of GPE with MHHPA in the presence of imidazoles-intercalated α -ZrPs at 140 °C for 2 h or 1 h, the resulting imidazoles-intercalated α -ZrPs (hereafter abbreviated as α -ZrP·Im-RXN, α -ZrP·2MIm-RXN, and α -ZrP·2E4MIm-RXN) were isolated and characterized by XRD, NMR, and elemental analyses. Basal distances, chemical shifts of the main signals, and elemental analyses are listed in Table 1.

Table 1. Elemental analysis, basal distance, and MAS NMR chemical shift of imidazoles-intercalated α -ZrP (α -ZrP·Im) and those of imidazoles-intercalated α -ZrP (α -ZrP·Im-RXN) after the reaction at 140 °C.

α -ZrP·Im	C (%)	H (%)	N (%)	d (Å)	^{31}P (δ)	^{13}C (δ)
α -ZrP·Im	7.87	2.09	5.61	10.7	−15.9, −16.8, −23.7	134.2, 120.2
α -ZrP·Im-RXN	15.02	2.53	3.84	24.4	−16.1, −22.2	158.8, 134.1, 132.4, 129.8, 119.8, 116.7, 67.9
α -ZrP·2MIm	12.08	2.66	7.00	12.1	−21.0, −22.2, −23.4	143.8, 142.4, 122.0, 120.2, 117.3, 13.4, 10.3
α -ZrP·2MIm-RXN	17.85	2.87	3.60	24.4	−21.5	158.9, 145.3, 141.0, 129.2, 120.3, 117.6, 114.9, 68.9, 12.6, 11.4, 10.2
α -ZrP·2E4MIm	12.85	2.68	4.78	12.9	−16.1, −22.2	147.3, 129.4, 116.5, 18.9, 11.4, 8.8
α -ZrP·2E4MIm-RXN	22.75	2.94	2.75	24.1	−14.8, −20.6	159.1, 147.7, 128.5, 118.1, 69.2, 19.1, 10.1

The XRD patterns of pristine α -ZrP is shown in Figure 5a. The peak corresponding to the basal distance of 7.6 Å was expanded with the intercalation of imidazoles. The XRD patterns of α -ZrP·Im and α -ZrP·Im-RXN are shown in Figure 5b,c. In addition to the peak corresponding to 10.7 Å of α -ZrP·Im, a small broad peak was observed at 24.4 Å ($2\theta = 3.6$) in that of α -ZrP·Im-RXN. In the ^{31}P MAS NMR spectra of α -ZrP·Im and α -ZrP·Im-RXN, the main signals at −15.9, −16.8, and

−23.7 ppm shifted to −16.1 and −22.0 ppm as shown in Figure 6a,b. In the ^{31}P MAS NMR spectra of intercalation compounds of $\alpha\text{-ZrP}\cdot\text{Im}$ and $\alpha\text{-ZrP}\cdot 2\text{E4MIm}$, the peak of deprotonated phosphate groups were observed at δ value of −15.9 and −16.8 for $\alpha\text{-ZrP}\cdot\text{Im}$ and −16.1 for $\alpha\text{-ZrP}\cdot 2\text{E4MIm}$. The single peak of pristine $\alpha\text{-ZrP}$ is shown at a δ value of −20.1 [10]. The peak δ value of higher than that of −20.1 for $\alpha\text{-ZrP}\cdot 2\text{MIm}$ doesn't observed. That might show the separation of 2MIm from phosphate group. In the ^{13}C CPMAS NMR spectra presented in Figure 6d,e, the aromatic carbons associated with the GPE at $\delta = 158.8, 132.4, 129.8,$ and 116.7 ppm and the structural main chain methylene groups at $\delta = 67.9$ were observed. However, the carbonyl carbon of the resulting poly(GPE-co-MHHPA) at $\delta = 172.9$ in Figure 6e was not observed in that of $\alpha\text{-ZrP}\cdot\text{Im}\cdot\text{RXN}$. The resulting products were derived from GPE. A possible phosphate ester formed by PO_4 of $\alpha\text{-ZrP}$ with GPE may be denied by the chemical shifts in the ^{13}C CP MAS NMR spectra. Phosphate esters produced by the reaction of $\alpha\text{-ZrP}$ and 1,2-epoxydodecane, the carbons generated from epoxide were observed at $\delta = 61.6$ and 71.2 for β -cleavage and $\delta = 79.6$ and 71.2 for α -cleavage in ^{13}C CP MAS NMR spectra [25]. Epoxy-ring opening products, such as the homo-oligomer of GPE, exist in the interlayer. In the following cases, the epoxy-ring opening products are formed in the interlayer.

In the XRD patterns of $\alpha\text{-ZrP}\cdot 2\text{MIm}$ and $\alpha\text{-ZrP}\cdot 2\text{MIm}\cdot\text{RXN}$ (shown in Figure 5d,e), the basal distances were shortened from 12.1 to 11.3 Å and a broad peak was observed at 24.4 Å ($2\theta = 3.6$). In the ^{31}P MAS NMR spectra, the main signals at −21.0, −22.2, and −23.4 ppm shifted to −21.5 ppm. Similarly, the aromatic carbons and methylene groups derived from GPE were observed in the ^{13}C CPMAS NMR spectra.

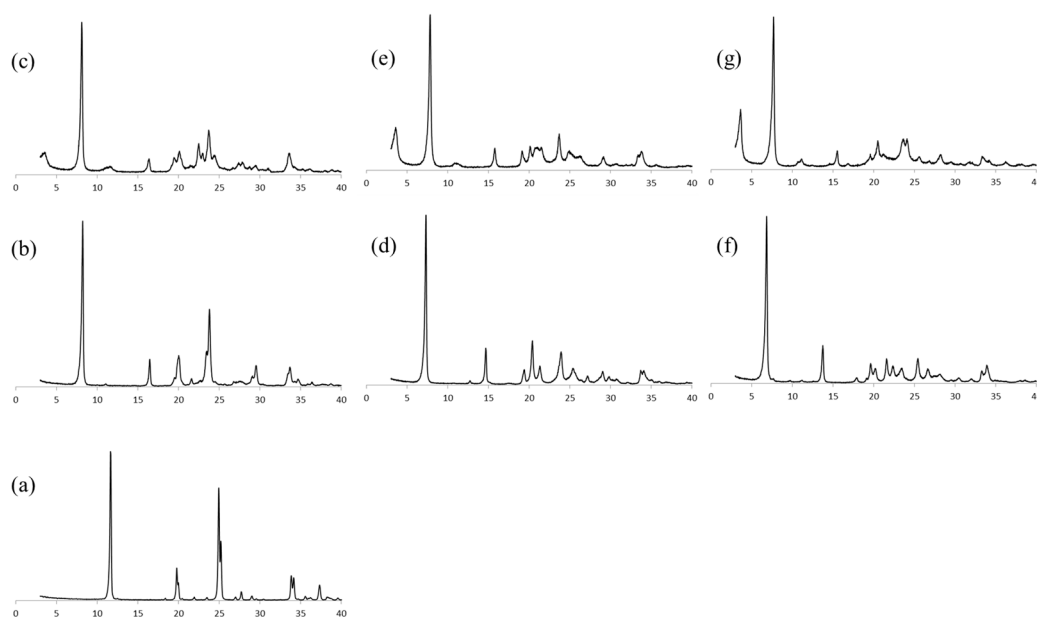


Figure 5. XRD patterns of (a) pristine $\alpha\text{-ZrP}$, (b) $\alpha\text{-ZrP}\cdot\text{Im}$, (c) $\alpha\text{-ZrP}\cdot\text{Im}\cdot\text{RXN}$, (d) $\alpha\text{-ZrP}\cdot 2\text{MIm}$, (e) $\alpha\text{-ZrP}\cdot 2\text{MIm}\cdot\text{RXN}$, (f) $\alpha\text{-ZrP}\cdot 2\text{E4MIm}$, and (g) $\alpha\text{-ZrP}\cdot 2\text{E4MIm}\cdot\text{RXN}$.

In the case of $\alpha\text{-ZrP}\cdot 2\text{E4MIm}$, similar to $\alpha\text{-ZrP}\cdot 2\text{MIm}$, the basal distances were shortened from 12.9 to 11.5 Å and a broad peak was observed at 24.1 Å ($2\theta = 3.7$). In the ^{31}P MAS NMR spectrum, the main signals at −16.1, and −22.2 ppm shifted to −14.8 and −20.6 ppm. In the ^{13}C CPMAS NMR spectrum, the aromatic carbons and methylene groups derived from GPE were similarly observed.

In any case, with the expansion of the basal distances, an increase in C content was recognized. Moreover, the ^{13}C CPMAS NMR suggested the presence of substances derived from GPE in the interlayer. Based on the elemental analyses, the compositions were calculated to give $\text{GPE}/\text{Im} = 0.7$, $\text{Zr}(\text{HPO}_4)_2(\text{C}_3\text{H}_4\text{N}_2)_{0.51}\cdot(\text{GPE})_{0.34}$ for $\alpha\text{-ZrP}\cdot\text{Im}\cdot\text{RXN}$, $\text{GPE}/2\text{MIm} = 0.8$, $\text{Zr}(\text{HPO}_4)_2(\text{C}_4\text{H}_6\text{N}_2)_{0.50}\cdot(\text{GPE})_{0.42}$

for α -ZrP·2MIm-RXN, and GPE/2E4MIm = 1.5, $\text{Zr}(\text{HPO}_4)_2(\text{C}_6\text{H}_{10}\text{N}_2)_{0.41} \cdot (\text{GPE})_{0.61}$ for α -ZrP·2E4MIm-RXN. Thus, 35% of imidazole, 48% of 2-methylimidazole, or 37% of 2-ethyl-4-methylimidazole was deintercalated in each case. These deintercalated imidazoles initiated the copolymerization of GPE and MHHPA. Since there was not a substantial difference among the catalytic activities of imidazole, 2-methylimidazole, and 2-ethyl-4-methylimidazole in this reaction, the amount of deintercalated imidazoles must affect reactivity (as shown in Figure 3) and thermal stability (as shown in Figure 4). In fact, the order of thermal instability and that of reactivity were α -ZrP·2MIm > α -ZrP·2E4MIm > α -ZrP·Im, which corresponded to the amount of the deintercalated imidazoles.

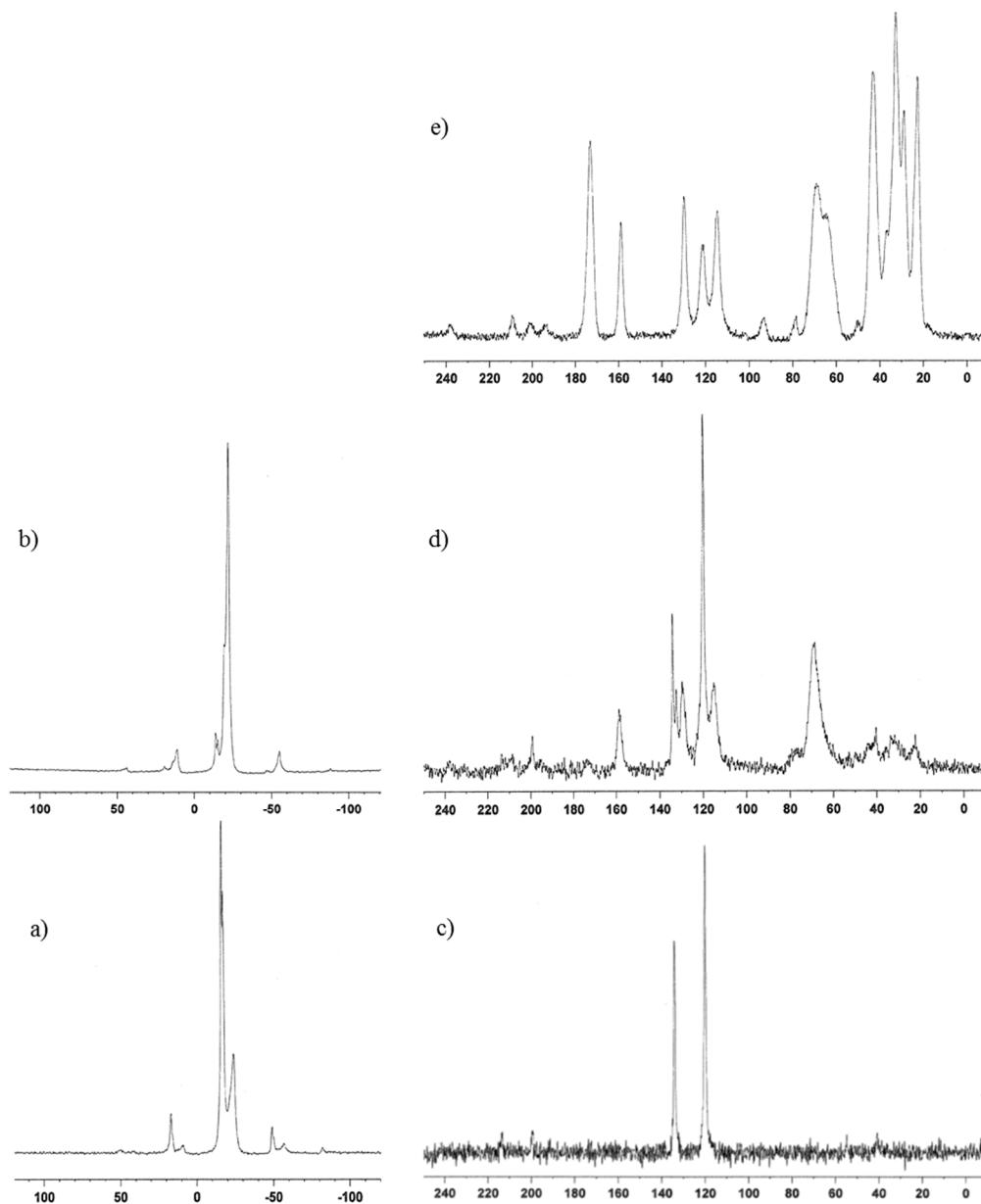


Figure 6. ^{31}P NMR spectra of (a) α -ZrP·Im and (b) α -ZrP·Im-RXN, and ^{13}C NMR spectra of (c) α -ZrP·Im, (d) α -ZrP·Im-RXN, and (e) poly(GPE-co-MHHPA).

In these cases, while the imidazoles were deintercalated, the intercalation of GPE and successive reactions occurred. In the preceding paper, the interlayer polymerization of GPE- MHHPA with α -ZrP·DBU; in contrast, the lack of interlayer polymerization with α -ZrP·DABCO were observed [11].

The compositions after the polymerization of α -ZrP·DBU and α -ZrP·DABCO were calculated based on the contents of N% and H% of the elemental analyses. The results are as follows: α -ZrP·DBU (basal distance: 20.0Å): $\text{Zr}(\text{HPO}_4)_2(\text{C}_9\text{H}_{16}\text{N}_2)_{0.83} \cdot 2.8\text{H}_2\text{O}$, α -ZrP·DBU-RXN: GPE-MHHPA/DBU = 3.7, $\text{Zr}(\text{HPO}_4)_2(\text{C}_9\text{H}_{16}\text{N}_2)_{0.24} \cdot (\text{GPE-MHHPA})_{0.89}$, α -ZrP·DABCO (basal distance: 16.1Å): $\text{Zr}(\text{HPO}_4)_2(\text{C}_6\text{H}_{12}\text{N}_2)_{0.69} \cdot 1.5\text{H}_2\text{O}$, α -ZrP·DABCO-RXN: $\text{Zr}(\text{HPO}_4)_2(\text{C}_6\text{H}_{12}\text{N}_2)_{0.63} \cdot (\text{GPE-MHHPA})_{0.03}$. Thus, 72% of DBU and 9% of DABCO were deintercalated in these cases; at the same time, in TG-DTA data of imidazoles-, DBU-, and DABCO-intercalated ZrPs, these amines appeared not to be deintercalated up to 140 °C, and sufficient deintercalation of the amines in the reactants took place at 140 °C. Accordingly, when the intercalated amine was sufficiently deintercalated to afford enough space for GPE, the interlayer reaction occurred to expand the basal distance.

In our system, control of the deintercalation of amines was an important factor in the design of the latent thermal initiator. In addition to the pK_a of the amines, the basal distances related to the molecular shape and size of the amines, the shape and size of α -zirconium phosphate, the structural design of the intercalation compounds, and the equilibrium of the reactants should be thermodynamically considered.

3. Experimental Section

3.1. Materials

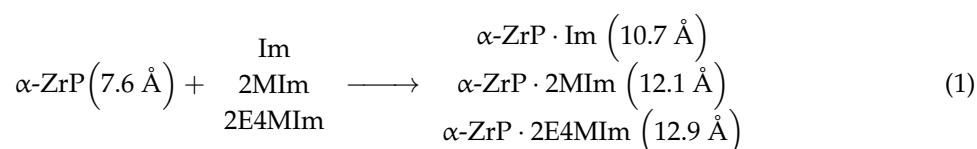
$\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (CZP-100) was purchased from Daiichi Kigenso Kagaku Kogyo Co., Ltd. (Osaka, Japan); GPE from Aldrich Chemical Co., Inc. (Tokyo, Japan); imidazole, 2-methylimidazole, 2-ethyl-4-methylimidazole, and MHHPA from Tokyo Chemical Industries, Co., Ltd. (Tokyo, Japan); HX-3088 and HX-3722 from Asahi Kasei Co. Ltd. (Tokyo, Japan). Solvents were used as received without further purification.

3.2. Measurements

X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT2200 (Rigaku CO., Ltd., Tokyo, Japan) with Cu K α radiation over a scan range of 3–40° at a rate of 2° min⁻¹. NMR spectra in solution were recorded on a Varian Unity-300 spectrometer (Varian Co., Inc., Palo Alto, CA, USA) using tetramethylsilane (TMS) as an internal standard. The contents of imidazoles and water in the intercalation compounds of α -ZrP were measured using a Yanaco CHN Corder MT-5 (Yanako Co., Ltd., Kyoto, Japan). ³¹P MAS and ¹³C CPMAS NMR spectra were recorded on a Bruker AVANCEIII600WB NMR spectrometer (Bruker Co. Inc., Billerica, MA, USA). Thermogravimetric analyses (TGA) were carried out with a Shimadzu DTG-60 (Shimadzu Co., Ltd., Kyoto, Japan) at a heating rate of 10 °C/min under nitrogen. Gel permeation chromatographic analyses (GPC) were carried out on a Shodex GPC-101 (LF804*3 and KF-800RF*3, THF as eluent) (Showa Denko Co. Ltd., Tokyo, Japan) using polystyrene standards.

3.3. Preparation of Imidazole-Intercalated α -ZrP (α -ZrP·Im)

The intercalation of imidazole into the layers of $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ (α -ZrP) was carried out using a previously reported method [16]. α -ZrP (10 g) was added to 142 mL of a 0.7 mol dm⁻³ imidazole aqueous solution. The reaction mixture was then allowed to stand at 40 °C for 24 h, before the product was collected by centrifugation and washed with water several times. The resulting residue was dried under vacuum. The intercalation of 2-methylimidazole (2MIm) and 2-ethyl-4-methylimidazole (2E4MIm) were carried out by the same procedure for the preparation of α -ZrP·Im.



3.4. Typical Polymerization Procedure

A mixture of GPE (151 mg, 1.0 mmol), MHHPA (172 mg, 1.0 mmol), and intercalation compound of imidazole with α -ZrP (α -ZrP·Im) (11.0 mg, 0.031 mmol, content of imidazole: 0.024 mmol) was heated at 140 °C for 1 h. A small aliquot of the reaction mixture was dissolved in CDCl_3 , and its $^1\text{H-NMR}$ spectra was acquired to determine the extent of the conversion of GPE and MHHPA. In the case of 40 °C, the small aliquot of sample was collected every determined time. The polymerization with intercalation compound of 2-methylimidazole with α -ZrP (α -ZrP·2MIm) (11.7 mg, 0.031 mmol, content of 2-methylimidazole: 0.029 mmol) and intercalation compound of 2-ethyl-4-methylimidazole with α -ZrP (α -ZrP·2E4MIm) (11.2 mg, 0.031 mmol, content of 2-ethyl-4-methylimidazole: 0.020 mmol) were carried out by the same procedure for the preparation of poly(GPE-co-MHHPA) with α -ZrP·Im. Commercial agents of the encapsulation of imidazoles, ca. 10 mg of HX-3088 and HX-3722 were used by the same procedure.

3.5. Polymerization Procedure for Preparation of Poly(GPE-co-MHHPA) with α -ZrP·Im

A mixture of GPE (7.51 g, 50.0 mmol), MHHPA (8.41 g, 50.0 mmol), and α -ZrP·Im (535 mg, 1.50 mmol, content of imidazole: 1.17 mmol) was heated at 140 °C for 2 h. After the reaction, tetrahydrofuran (THF) was added to the mixture and filtered off, and the residue, α -ZrP·Im-RXN, was rinsed to wash the polymer. The obtained α -ZrP·Im-RXN was dried under vacuum and served to measure the XRD analysis. The obtained polymer was isolated by the precipitation with methanol and dried under vacuum with 50% yield. The copolymer was identified as poly(GPE-co-MHHPA) by $^1\text{H-NMR}$ spectra. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) were found to be 1990 and 1.4, respectively (GPC, calibrated by polystyrene standards). The polymerization with α -ZrP·2MIm and α -ZrP·2E4MIm was carried out at 140 °C for 1 h to obtain the corresponding poly(GPE-co-MHHPA). α -ZrP·2MIm: $M_n = 2080$, $M_w/M_n = 1.4$, α -ZrP·2E4MIm: $M_n = 3120$, $M_w/M_n = 1.3$.

4. Conclusions

The activities of α -ZrP·Im, α -ZrP·2MIm, and α -ZrP·2E4MIm in the copolymerization of GPE and MHHPA as latent thermal initiators were examined in this study. Compared with the commercially available thermal latent initiators HX-3088 and HX-3722, α -ZrP·Im, α -ZrP·2MIm, and α -ZrP·2E4MIm were more thermally stable at 40 °C and effectively initiated the reaction at 140 °C. Imidazoles intercalated α -ZrP were stable under 40 °C because of the fixation of acid–base interaction and physical protection by the interlayer of α -ZrP. The intercalation compounds of the order of thermal instability and that of reactivity were α -ZrP·2MIm > α -ZrP·2E4MIm > α -ZrP·Im, which corresponded to the amount of the deintercalated imidazoles. Thus, control of the amount of the deintercalated imidazoles from α -ZrP·Im, α -ZrP·2MIm, and α -ZrP·2E4MIm is an important factor in thermal latent initiators. We are studying further to control the amount of deintercalation and the relation of molecular shape, size, and properties.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/7/6/172/s1, Figure S1, ^{31}P NMR spectra of (a) α -ZrP·2MIm; (b) α -ZrP·2MIm-RXN and ^{13}C NMR spectra of (c) α -ZrP·2MIm; (d) α -ZrP·2MIm-RXN; and (e) poly[GPE-co-MHHPA]. Figure S2, ^{31}P NMR spectra of (a) α -ZrP·2E4MIm; (b) α -ZrP·2E4MIm-RXN and ^{13}C NMR spectra of (c) α -ZrP·2E4MIm; (d) α -ZrP·2E4MIm-RXN; and (e) poly[GPE-co-MHHPA].

Acknowledgments: This work was performed under the Cooperative Research Program of Network Joint Research Center for Materials and Devices. We also thank M. Shizuma and S. Kawano of Osaka Research Institute of Industrial Science and Technology for GPC analyses.

Author Contributions: Osamu Shimomura and Shunro Yamaguchi conceived, designed and wrote the article; Kensuke Tokizane and Takatoshi Nishisako performed the experiments; Junko Ichihara, Manabu Kirino, Atsushi Ohtaka and Ryōki Nomura contributed to a helpful discussion.

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

References

1. Kikkawa, A.; Takata, T.; Endo, T. Effect of alkyl substituents on initiator activity in cationic polymerization of styrene with p-methoxybenzylalkylsulfonium salts as initiators. *J. Polym. Sci. Part A Polym. Chem.* **1991**, *29*, 1089–1095. [[CrossRef](#)]
2. Shimomura, O.; Tomita, I.; Endo, T. Application of S-alkylsulfonium salts of aromatic sulfides as new thermal latent cationic initiators. *J. Polym. Sci. Part A Polym. Chem.* **2000**, *38*, 18–27. [[CrossRef](#)]
3. Crivello, J.V. Design of photoacid generating systems. *J. Photopolym. Sci. Technol.* **2009**, *22*, 575–582. [[CrossRef](#)]
4. Hacker, N.P.; Welsh, K.M. Photochemistry of triphenylsulfonium salts in poly[4-[(tert-butoxycarbonyl)oxy]styrene]: Evidence for a dual photoinitiation process. *Macromolecules* **1991**, *24*, 2137–2139. [[CrossRef](#)]
5. Toneri, T.; Sanda, F.; Endo, T. Polymerization of epoxide with a fluorenyltriphenylphosphonium salt as a photo-latent initiator. *J. Photopolym. Sci. Technol.* **1999**, *12*, 159–164. [[CrossRef](#)]
6. Kim, M.S.; Lee, K.W.; Endo, T.; Lee, S.B. Benzylpyrazinium Salts as Thermally Latent Initiators in the Polymerization of Glycidyl Phenyl Ether: Substituent Effect on the Initiator Activity and Mechanistic Aspects. *Macromolecules* **2004**, *37*, 5830–5834. [[CrossRef](#)]
7. Naumann, S.; Speiser, M.; Schowner, R.; Giebel, E.; Buchmeiser, M.R. Air Stable and Latent Single-Component Curing of Epoxy/Anhydride Resins Catalyzed by Thermally Liberated N-Heterocyclic Carbenes. *Macromolecules* **2014**, *47*, 4548–4556. [[CrossRef](#)]
8. Kirino, M.; Tomita, I. Aminimides Derived from Benzoylformic Acid Esters as Thermally Latent Base Catalysts. *Macromolecules* **2010**, *43*, 8821–8827. [[CrossRef](#)]
9. Sudo, A.; Yamashita, H.; Endo, T. Ring-opening polymerization of 1,3-benzoxazines by p-toluenesulfonates as thermally latent initiators. *J. Polym. Sci. Part A Polym. Chem.* **2011**, *49*, 3631–3636. [[CrossRef](#)]
10. Shimomura, O.; Maeno, K.; Ohtaka, A.; Yamaguchi, S.; Ichihara, J.; Sakamoto, K.; Nomura, R. Alkylamines-intercalated α -zirconium phosphate as latent thermal anionic initiators. *J. Polym. Sci. Part A Polym. Chem.* **2014**, *52*, 1854–1861. [[CrossRef](#)]
11. Shimomura, O.; Nishisako, T.; Yamaguchi, S.; Ichihara, J.; Kirino, M.; Ohtaka, A.; Nomura, R. DABCO- and DBU-intercalated α -zirconium phosphate as latent thermal catalysts in the copolymerization of glycidyl phenyl ether (GPE) and hexahydro-4-methylphthalic anhydride (MHHPA). *J. Mol. Catal. A Chem.* **2016**, *411*, 230–238. [[CrossRef](#)]
12. Ricciardi, F.; Romanchick, W.A.; Joullie, M.M. Mechanism of imidazole catalysis in the curing of epoxy resins. *J. Polym. Sci. Polym. Chem. Ed.* **1983**, *21*, 1475–1490. [[CrossRef](#)]
13. Farkas, A.; Strohm, P.F. Imidazole catalysis in the curing of epoxy resins. *J. Appl. Polym. Sci.* **1968**, *12*, 159–168. [[CrossRef](#)]
14. Ricciardi, F.; Romanchick, W.A.; Joullie, M.M. 1,3-Dialkylimidazolium salts as latent catalysts in the curing of epoxy resins. *J. Polym. Sci. Polym. Lett. Ed.* **1983**, *21*, 633–638. [[CrossRef](#)]
15. Shin, M.J.; Shin, Y.J.; Hwang, S.W.; Shin, J.S. Microencapsulation of imidazole curing agent by solvent evaporation method using W/O/W emulsion. *J. Appl. Polym. Sci.* **2013**, *129*, 1036–1044. [[CrossRef](#)]
16. Kudo, K.; Fuse, S.; Furutani, M.; Arimitsu, K. Imidazole-type thermal latent curing agents with high miscibility for one-component epoxy thermosetting resins. *J. Polym. Sci. Part A Polym. Chem.* **2016**, *54*, 2680–2688. [[CrossRef](#)]
17. Oono, Y.; Kato, H. Storage-Stable Thermosetting Epoxy Resin Compositions Containing Latent Curing Accelerators. 1993-195102, 07025989, 19930712, 1995.
18. Oono, Y.; Inuma, T.; Kato, H. Thermosetting Epoxy Resin Compositions Containing Latent Crosslinking Catalysts. 1993-26218, 06073162, 19930120, 1994.
19. Boo, W.J.; Sun, L.; Liu, J.; Clearfield, A.; Sue, H.-J. Effective Intercalation and Exfoliation of Nanoplatelets in Epoxy via Creation of Porous Pathways. *J. Phys. Chem. C* **2007**, *111*, 10377–10381. [[CrossRef](#)]
20. White, K.L.; Wong, M.; Li, P.; Miyamoto, M.; Higaki, Y.; Takahara, A.; Sue, H.J. Interlayer structure and self-healing in suspensions of brush-stabilized nanoplatelets with smectic order. *Soft Matter* **2015**, *11*, 954–971. [[CrossRef](#)] [[PubMed](#)]
21. Li, P.; White, K.L.; Lin, C.H.; Kim, D.; Muliana, A.; Krishnamoorti, R.; Nishimura, R.; Sue, H.J. Mechanical reinforcement of epoxy with self-assembled synthetic clay in smectic order. *ACS Appl. Mater. Interfaces* **2014**, *6*, 10188–10195. [[CrossRef](#)] [[PubMed](#)]

22. Armarego, W.; Chai, C. purification of organic chemicals In *Purification of Laboratory Chemicals*, 6th ed.; Elsevier: Oxford, UK, 2009; Chapter 4.
23. Kamon, T.; Saito, K.; Miwa, Y.; Saeki, K. The curing of epoxy resin (V): The curing of epoxy resins with imidazoles, and the structure and the properties of the cured resins. *Shikizai* **1976**, *49*, 82–89. [[CrossRef](#)]
24. MacLachlan, D.J.; Morgan, K.R. Phosphorus-31 solid-state NMR studies of the structure of amine-intercalated α -zirconium phosphate. 2. Titration of α -zirconium phosphate with n-propylamine and n-butylamine. *J. Phys. Chem.* **1992**, *96*, 3458–3464. [[CrossRef](#)]
25. Casciola, M.; Capitani, D.; Donnadio, A.; Munari, G.; Pica, M. Organically Modified Zirconium Phosphate by Reaction with 1,2-Epoxydodecane as Host Material for Polymer Intercalation: Synthesis and Physicochemical Characterization. *Inorg. Chem.* **2010**, *49*, 3329–3336. [[CrossRef](#)] [[PubMed](#)]



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).