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Eu^{3+} and lysine co-intercalated α-zirconium phosphate and its catalytic activity for copolymerization of propylene oxide and CO_2

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A novel composite material, α-$Zr(HPO_4)_2 \cdot 1.5$Lysine:$0.06Eu^{3+}$ (designated ZLE), has been prepared through intercalation of L-lysine (Lys) molecules and Eu^{3+} ions into between the layers of α-$Zr(HPO_4)_2$ (α-ZrP). It is proposed that the ZLE material contains Eu complexes lying between adjacent layers of Lys molecules which are attached on the inner surface of α-ZrP, and the Eu^{3+} ions are coordinated by carboxyl groups of Lys molecules. The ZLE composite in combination with Al(*i*-Bu)$_3$ and glycerin has been used as a catalyst for the copolymerization of propylene oxide (PO) and CO_2, and the catalytic system exhibits performance superior to the previously reported $Y(P_{204})_3$-Al(*i*-Bu)$_3$-glycerin system.

KEY WORDS: layered composite compound; zirconium phosphate; rare earth complex; propylene oxide; CO_2; copolymerization.

1. Introduction

Layered inorganic materials such as clays, dichalcogenides and metal phosphates have been extensively studied due to growing interest in their catalytic activity, ion-exchange capacity and physical-chemical stability [1]. The important feature of these materials is their ability to incorporate guest molecules which form highly ordered arrays between adjacent layers. On the basis of this feature, many novel assembly structures can be tailored at the molecular level through the design of the host and the guest species [2]. These assembly structures have been utilized widely in the preparation of functional materials such as catalysts [3], conducting polymers [4], energy storage devices [5], and receptors [6].

It is known that α-zirconium phosphate with a layered structure is very similar to that of smectite clays [7]. Crystallographic studies [8] reveal that each layer of α-ZrP consists of zirconium atoms lying nearly in a plane and bridged through tetrahedral PO_3–OH groups located alternately above and below the plane of zirconium atoms. The interlayer spacing of α-ZrP is about 7.58 Å. Each phosphate group in α-ZrP carries one ionizable hydroxyl group that can be readily deprotonated and the resulting ionic sites serve to bind cations. Studies on α-ZrP have been mainly focused on synthesis, ion exchange, thermal stability, adsorption and catalysis [9], whereas intercalation into α-ZrP was mainly concentrated on transition metal compounds and porphyrins [10]. There are very few reports on rare earth (RE) metal complexes intercalated into layered α-ZrP [11].

Some RE elements and their ions have been widely used in the preparation of materials with useful optical, magnetic properties and catalytic activities [12]. Recent progress has shown that the molecular environment influences the photophysical and photochemical process of the RE ion to a great extent [13]. For many RE complexes, light is absorbed by the ligands as an antenna and energy is transferred to the emitting metal ion. Especially if these complexes are modified by interaction with a host compound, their chemical and photophysical properties will have unexpected changes [12].

Carbon dioxide (CO_2) is an ideal synthetic feedstock since it is abundant, inexpensive, nontoxic, and nonflammable. It is estimated that nature uses CO_2 to make over 200 billion tons of glucose by photosynthesis each year, but human being have had little success in exploiting this attractive raw material [14–16]. Recent research suggests that copolymerization of carbon dioxide with epoxides to produce polycarbonates may become a very useful and practical route to take advantage of CO_2 effectively [17,18]. The search of new, efficient catalysts for this polymerization process is a significant scientific goal because of the low cost, accessibility of the monomers, and the attractive properties of polycarbonates [19–22]. But due to the inert characteristic of CO_2, it is difficult to develop a highly effective catalyst for this type of polymerization to proceed. As yet catalytic systems concerning this reaction include: (a) zinc-based catalysts, such as $Zn(C_2H_5)_2$–H_2O, $Zn(C_2H_5)_2$-di- or tri-hydric phenol, and multiprotic compounds [19,23–25]; (b) (ttp)AlCl (H_2ttp = tetraphenylporphyrin) and its derivatives [26–28]; (c) zinc salts [29]. However, the catalytic activity of most known systems is still not high enough so that copolymerization is yield-low and long reaction time is needed. Many attempts to improve the catalytic activity have been made. For example, for the zinc-based catalysts, the use of diethyl zinc/polyhydric phenol

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[30], zinc glutarate and its derivatives [31,32], and cadmium(II) carboxylates [33] as the catalysts were found to enhance the reactivity of CO_2 with propylene oxide (PO) to some extent. At present, zinc glutarate is regarded as the most promising catalyst used in the industrial production of the polycarbonate. In recent publications, RE metal coordination catalysts exhibiting reasonable activity in the copolymerization of PO and CO_2 have also been reported [20,34–37]. The typical catalytic system among these is $RE(P_{204})_3$–Al(*i*-Bu)$_3$–glycerin [20] (RE = La, Nd, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Sc, and Y with the $Y(P_{204})_3$–Al(*i*-Bu)$_3$–glycerine system showing the highest catalytic activity, where P_{204} stands for $CH_3(CH_2)_3CH(C_2H_5)CH_2O)_2P(O)O$–). The RE metal is the catalytic center for these systems. In this paper, we describe a novel composite that has been obtained through cointercalation of amino acid and Eu^{3+} complex into layered α-ZrP. In this composite compound, the Eu complex is sandwiched between layers of amino acid molecules attached on the inner surface of the layered α-ZrP, the Eu^{3+} ions coordinating with the carboxyl groups of the amino acid molecules. The catalytic activity of Eu^{3+} ions incorporated in ZLE was also investigated for the copolymerization of CO_2 and PO. We found that the RE metal Eu in the composite compound could incorporate more CO_2 into polymer, in comparison with the Y in the $Y(P_{204})_3$–Al(*i*-Bu)$_3$–glycerin system reported in the literature [20] and the total amount of copolymer produced by the composite catalyst was considerably large than that produced by the zinc glutarate in terms of per mole metal.

2. Experimental

2.1. Materials

L-lysine, $ZrOCl_2$, H_3PO_4, $EuCl_3 \cdot 6H_2O$, Al(*i*-Bu)$_3$ and carbon dioxide (purity more than 99.9%) were used as received without further purification. PO was distilled under reduced pressure over CaH_2. 1,4-dioxane and other solvents were purified by the conventional methods before use [38].

2.2. Preparation of α-ZrP-Lys-Eu (ZLE) composite

The preparation procedure for the precursor materials, $Zr(HPO_4)_2$ and $Zr(HPO_4)_2 \cdot 1.85$ Lys (ZL), was the same as that referred to in the literature [39,40]. While the α-ZrP-Lys-Eu (ZLE) composite was prepared through mechanical grinding of a mixture of 1 g ZL solid powder and 0.05 g $EuCl_3 \cdot 6H_2O$. The mixture was ground in a mortar for about 3 h. The final mixture obtained was washed with distilled water until the filtrate contained no Eu^{3+} ions and then dried at room temperature.

2.3. Copolymerization

The ZLE sample was dried in vacuum at 60 °C for 24 h before copolymerization. It was then mixed with Al(*i*-Bu)$_3$ for 10 h in a 1,4-dioxane solution under the protection of N_2 and finally a white slurry was obtained. The slurry, PO and glycerin were mixed in an 80 ml stainless steel autoclave, again under the protection of N_2. CO_2 gas was loaded from a gas cylinder into the autoclave followed by venting from the autoclave. This process was repeated for three times in order to get rid of the previously loaded N_2. Copolymerization of carbon dioxide with PO was conducted at 60 °C and at a pressure of CO_2 ranging from 3 to 4 MPa. After proceeding for 12 h, the CO_2 in the autoclave was driven out until the pressure of CO_2 in the autoclave decreased to 1 atm. The autoclave was opened and a methanol solution containing 5% hydrochloric acid was added into the autoclave to terminate the reaction. A white solid product was obtained by addition of water, washed with distiller water, and then dried in vacuum at room temperature. The relevant molar ratios and concentrations for the reaction are as follows: $[Eu] = 1.0 \times 10^{-2}$mol/L; Al/Eu = 8.0; glycerin/Al = 0.5; [PO] = 2.5 mol/L. 1,4-dioxane was used as the solvent. The weight of the copolymer was that of the white solid product minus the weight of the catalyst. For comparison, the catalytic performance of $EuCl_3 \cdot 6H_2O$ was also tested under similar conditions.

2.4. Characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5005 diffractometer with CuK_α ($\lambda = 1.5418$ Å) radiation. The X-ray photoelectron spectroscopy (XPS) of the powders was performed on a VG Escalab MK II spectrometer with MgK_α radiation. The UV–vis absorption spectra were measured using a Perkin-Elmer Lambda 20 spectrometer, whereas the infrared (IR) spectra were recorded on a Nicolet Impact-410 FTIR spectrophotometer using KBr pellets. Thermogravimetric and differential thermal analyses (TG-DTA) of the samples were conducted on a Netzsch STA-449C thermal analyzer. The photoluminescent spectra were obtained on a Spex Fluorolog-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source (the slits of the excitation state and the emission state were 5.0 and 1.5 nm, respectively). All the samples were measured under the same conditions. The luminescence lifetime measurements were performed on a Spex 1934D phosphorimeter. The distance between the sample and the center of the lamp was 14 cm. The contents of metal ions in the compounds were analyzed on a Perkin-Elmer Optima 3300 DV inductively coupled plasma (ICP) spectrometer, whereas the C, H and N elemental analysis was performed on a Perkin-Elmer 2400 elemental analyzer. The ^{1}H NMR spectrum of the copolymer was measured at room temperature on a Bruker Avance-500 NMR spectrometer using tetramethylsilane (TMS) as the internal reference. Gel permeation chromatography (GPC) was performed on a HP 1100 Plgel MIXED-B Column X3 chromatograph by using polystyrene as the standard. Before the ^1H NMR and GPC measurements, the sample was fully dissolved in $CDCl_3$ (or $CHCl_3$) and the solid residue was removed.

3. Results and discussion

The synthesis of the composite compound ZLE involves two steps. The first step is the intercalation of the Lys molecules into between the layers of α-ZrP by ion-exchange reaction at high levels of Lys [40]. This step results in the formation of a $Zr(HPO_4)_2 \cdot 1.85Lys$ phase with an interlayer spacing of 23.1 Å [40]. Taking into account the length of the Lys molecule and the thickness of an individual α-ZrP sheet, it is inferred that there are two layers of Lys molecules between the inorganic sheets of α-ZrP and the skeletal chain of Lys molecule makes a tilt angle of ca. 45° with the phosphate sheet [40]. The second step is the incorporation of Eu^{3+} ions into between the two layers of the Lys molecules located on the inner surface of α-ZrP by solid grinding of $EuCl_3 \cdot 6H_2O$ and ZL. The solid grinding causes two adjacent inorganic layers of ZL to slide and the Lys molecules in ZL are exposed to guest species so that $EuCl_3 \cdot 6H_2O$ molecules are easy to be associated with the Lys molecules in ZL. Repeating experiments proved that the solid grinding method is highly reproducible for the incorporation of Eu^{3+} ions in the ZL material. Although we mixed ZL and $EuCl_3 \cdot 6H_2O$ in distilled water and stirred at 60 °C for 15 days in order to intercalate the Eu^{3+} ions into the inner space of the ZL, the intercalation failed. It is believed that the interaction between adjacent inorganic layers in ZL is strong that $EuCl_3 \cdot 6H_2O$ molecules have few chances to touch the Lys molecules when the ZL material is treated under too mild conditions.

The empirical compositions of the ZL and ZLE compounds are calculated on the basis of the results of ICP, elemental and thermogravimetric analyses (table 1). From table 1 it is seen that the loss of the amino acid molecules is not distinct after solid grinding. On the other hand, Eu does exist in the ZLE material but the molar ratio of Eu/Lys in the ZLE material is 0.04, suggesting that only a small fraction of the Lys molecules in ZLE are directly associated with the Eu species incorporated between the layers. However, this does not mean that the rest of the Lys molecules are not affected by the presence of the Eu complexes. Actually, the Lys molecules may re-arrange after the Eu complexes are incorporated in between the layers as discussed below.

Table 1
The elemental contents of Zr, Eu, C and N found in the α-ZrP-Lys (ZL) and the α-ZrP-Lys-Eu (ZLE) samples and the corresponding empirical compositions for these two compounds

Sample	Found (wt%)				Empirical composition
	Zr	Eu	C	N	
ZL	16.2		23.2	9.4	$Zr(HPO_4)_2 \cdot 1.85Lys$
ZLE	16.0	1.6	18.7	7.2	$Zr(HPO_4)_2 \cdot 1.5Lys : 0.06Eu$

Figure 1 shows the XRD patterns of the ZL and ZLE powder samples. One sees that the first peak reflecting the interlayer distance moves towards lower diffraction angle after ZL is ground with $EuCl_3 \cdot 6H_2O$ to form ZLE, confirming the incorporation of Eu complex into ZL. The value of the interlayer distance for ZLE is 20 Å larger than that for ZL. This interlayer distance increase is considerable, and it should be due to the collective effect of the Eu complex incorporation and the re-arrangement of the Lys molecules pre-intercalated in the α-ZrP material. The crystal structure of $EuCl_3 \cdot 6H_2O$ contains $[Cl_2Eu(H_2O)_6]^+$ complex species which are held together by O–H···Cl bonds and one third of the chlorine atoms are not bonded to the central Eu atoms [41]. The diameter of the $[Cl_2Eu(H_2O)_6]^+$ complex is about 7 Å [41], and this diameter value is far shorter than the enlarged interlayer distance (20 Å) for ZLE in comparison with ZL. The presence of the complex alone between the layers cannot account for the interlayer distance enlargement. Therefore, it is speculated that the complex incorporation through solid grinding leads to a tilt angle change of the Lys molecules. From an arrangement with a tilt angle of about 45°, the Lys molecules may re-order with their chains nearly perpendicular to the phosphate layers upon the incorporation of the Eu complexes which are sandwiched by the Lys molecular layers.

In figure 2 the TG and DTA curves obtained in air for the ZL and ZLE samples are displayed. The curves show that the adsorbed water molecules are completely

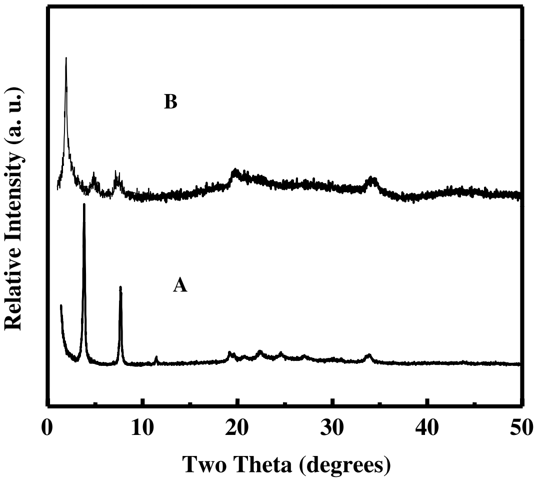


Figure 1. Powder XRD patterns of (a) ZL and (b) ZLE composite compounds.

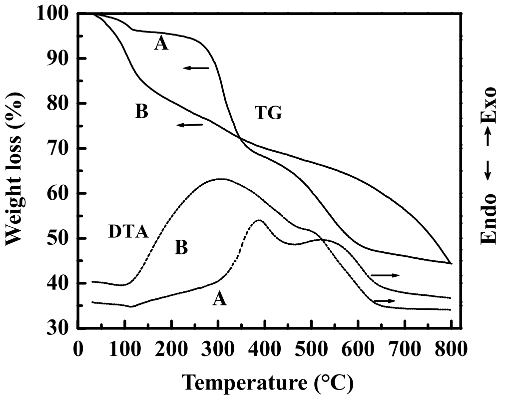


Figure 2. TG–DTA curves obtained in air for (a) ZL and (b) ZLE compounds.

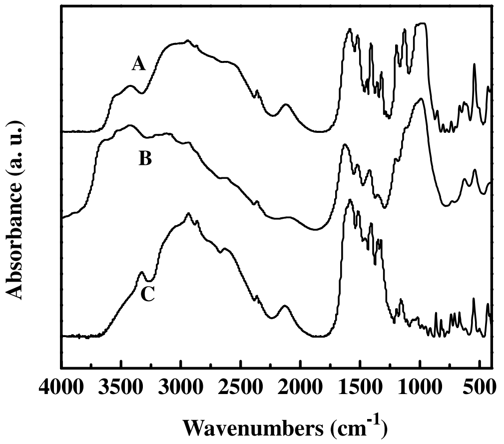


Figure 3. IR spectra of (a) ZL, (b) ZLE composite compounds and (c) lysine molecules.

removed at about 110 °C and the Lys molecules start to decompose at about 250 °C for both compounds. In the ZL material, the decomposition of Lys occurs with two main exothermic effects. The first exhibits a relatively sharp peak at 380–400 °C, and the second corresponds to a broad band at 470–570 °C. Whereas for the ZLE material, the DTA curve shows a broad exothermic band with a shoulder at about 500 °C. The maximum of the broad band occurs at a temperature lower than that for the ZL compound, indicating that some of the Lys molecules in ZLE decompose more easily than in ZL. It is believed that the shoulder of the DTA curve for ZLE arises from the Lys molecules that are not coordinated to the metal ions but directly associated with the host as in the ZL.

Figure 3 shows the IR spectra of ZL, ZLE and the lysine (Lys) molecules. For the pure Lys compound and the ZL sample the IR absorption of carboxyl groups is at 1587 cm^{-1} while for the ZLE sample the corresponding absorption shifts to 1630 cm^{-1}. This shift is a reflection of coordination and/or perturbation of the carboxyl groups by the Eu^{3+} ions. The absorptions of

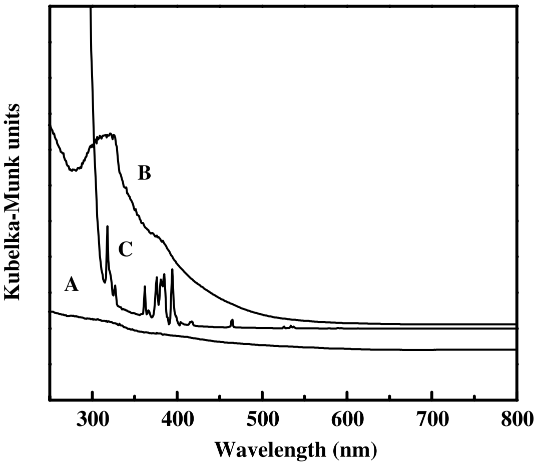


Figure 4. Diffuse reflectance UV–vis spectra for (a) ZL, (b) ZLE and (c) $EuCl_3 \cdot 6H_2O$.

NH_3^+ groups at 3100 and at 2600 cm^{-1} remain unchanged for both ZL and ZLE samples, suggesting that the NH_3^+ groups are not disturbed by the incorporation of the Eu complexes. XPS indicates the presence of Eu and Cl in the ZLE material, indicating that the incorporated species is the Eu complex and not the Eu^{3+} ions alone. The binding energy of the Eu for $EuCl_3 \cdot 6H_2O$ is 137.6 eV, while that of the Eu in ZLE is 136.7 eV, and the binding energy of N for both ZL and ZLE is the same (401.2 eV). These binding energy values also suggest that it is the carboxyl groups of Lys that coordinate with Eu^{3+} ions whereas the N atoms of Lys in ZLE are not affected by the Eu^{3+} ions. The binding energy value of N atom being 401.2 eV indicates that the N atoms of Lys molecules in ZLE are protonated [42,43].

The diffuse reflectance UV-vis spectra of ZL, ZLE and $EuCl_3 \cdot 6H_2O$ are presented in figure 4. Hardly any absorption peaks for ZL are observable over the range from 300 to 600 nm whereas the absorption of the Eu chloride crystal consists of a group of sharp peaks in the same wavelength region. Unlike the $EuCl_3 \cdot 6H_2O$ that shows a sharp peak at 318 nm, the ZLE material has a broad absorption at 327 nm. The UV–vis spectra also confirm that the Eu complex has been incorporated into the zirconium phosphate, and the change of the micro-environment for the Eu^{3+} ions in the interlayer of ZLE results in a red shift and broadening of the Eu complex absorption. On the basis of the characterization results, a structure model for the ZLE is proposed as shown in figure 5. In this model, every incorporated Eu^{3+} ion is associated with the carboxyl group of the Lys molecules but there are still Cl^- anions coordinating to the Eu^{3+} ion. Some of the H_2O molecules surrounding the Eu^{3+} ion may have been replaced by the carboxyl groups after the Eu complex is incorporated. For charge balancing, additional free Cl^- anions are also included in the interlayer region (figure 5).

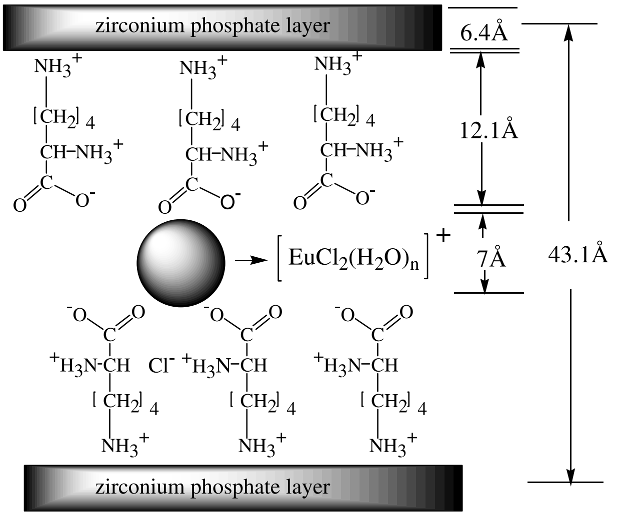


Figure 5. Schematic representation of the structure for α-ZrP-Lys-Eu (ZLE) in which the Eu complex is sandwiched between layers of amino acid molecules attached on the inner surface of the layered α-ZrP.

Figure 6 displays the excitation and emission spectra of $EuCl_3 \cdot 6H_2O$ and the composite compound ZLE. Considerable difference can be discerned between the spectra for these two compounds. For the ZLE material, the excitation spectrum consists of a broad band ranging from 250 to 450 nm and sharp narrow peaks with some of the latter being located in the same wavelength region as the former; while for the $EuCl_3 \cdot 6H_2O$, the excitation spectrum exhibits sharp narrow peaks only. The narrow peaks are related with the Eu^{3+} ions but the presence of the broad band strongly suggests that an efficient energy transfer from the ligands to Eu^{3+} ions has taken place after the Eu complex is incorporated into the ZL. From Figure 6 one also sees that the relative intensity for the excitation peaks is different between $EuCl_3 \cdot 6H_2O$ and ZLE. The emission intensity of the $^5D_0 \to {}^7F_2$ transition of Eu^{3+} ions ($\lambda = 612$ nm) is strongly dependent on the microenvironment due to its electric dipole character while the $^5D_0 \to {}^7F_1$ (ë = 589 nm) emission intensity is independent. The ratio of $^5D_0 \to {}^7F_2/{}^5D_0 \to {}^7F_1$ emission intensities gives valuable information about environment changes around the Eu^{3+} ion. The increase of $^5D_0 \to F_2/{}^5D_0 \to {}^7F_1$ from 1.73 in $EuCl_3 \cdot 6H_2O$ to 5.78 in the Eu complex intercalated into α-ZrP indicates that the symmetry around the Eu^{3+} ion in the ZLE composite is lower than in $EuCl_3 \cdot 6H_2O$. A low symmetry around the Eu^{3+} ion is also an indication of the replacement of H_2O molecules in the coordination sphere by the carboxylate groups of the Lys molecules in ZLE.

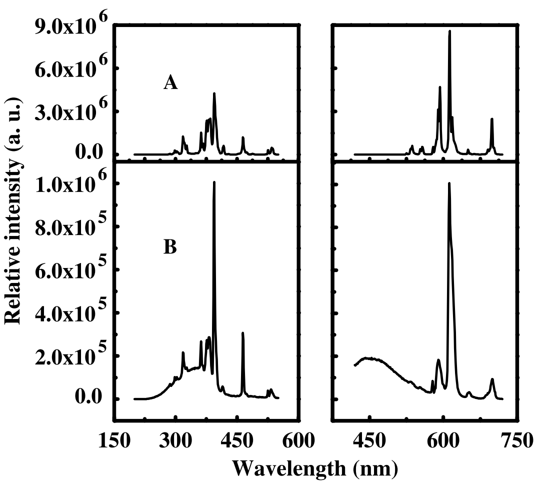
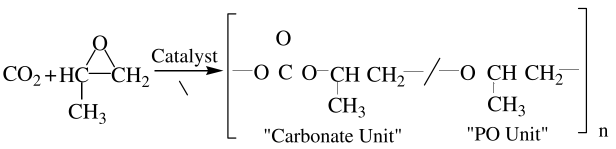


Figure 6. Excitation (left) and emission (right) spectra of (a) $EuCl_3 \cdot 6H_2O$ and (b) ZLE.

From the fluorescent decay data of Eu^{3+} ions related to the transition $^5D_0 \to {}^7F_2$ emission, the lifetime of the composite compound ZLE (0.2652 ms) is longer than that of $EuCl_3 \cdot 6H_2O$ (0.1791 ms). It is well known that the luminescent lifetime of Eu^{3+} ions is related to the vibration of the nearby ligands. The relatively rigid matrix structure limits the vibration of the ligands around Eu^{3+} ions, leading to longer luminescent lifetime of Eu^{3+} ions in the layered compounds than in $EuCl_3 \cdot 6H_2O$. The relative luminescent intensity of the ZLE in which the weight contents of the Eu^{3+} ion is 1.61% is 1.01×10^6, while that of $EuCl_3 \cdot 6H_2O$ in which the weight content of the Eu^{3+} ion is 41.5% is 8.57×10^6. This demonstrates that each unit Eu in ZLE gives stronger luminescence than in $EuCl_3 \cdot 6H_2O$. The reason is that the Eu^{3+} ions encapsulated in the layered compound are shielded and the organic molecules have replaced the H_2O molecules that provide routes for radiationless decay. Moreover, the ligands around Eu^{3+} ion in the ZLE have a larger absorption bands than in $EuCl_3 \cdot 6H_2O$, amplifying the range of excitation energies.

Scheme 1 shows that the product of CO_2 reacting with PO involves two types of unit: one is PO unit from homopolymerization of the PO and the other is carbonate unit from copolymerization of the CO_2 and PO. It has been demonstrated that $Al(i\text{-}Bu)_3$ is effective for homopolymerization of the PO, but it is not effective for the copolymerization of the CO_2 and PO [20,44]. Nevertheless, with the catalytic system consisting of $RE(P_{204})_3$ and $Al(i\text{-}Bu)_3$, polycarbonate can be obtained [20]. Our experiment has also confirmed that if the Al $(i\text{-}Bu)_3$ is used as the catalyst, only homopolymer of the PO can be obtained while no polycarbonate forms. At present, the catalytic mechanism of $RE(P_{204})_3$-Al



Scheme 1. Equation of polycarbonate synthesis using CO_2 and PO as reagents.

(i-Bu)$_3$–glycerin system for copolymerization of CO_2 and PO is still not very clear, but it is generally believed that a kind of active species is formed and there is a bond of RE-R in the structure of the active species which plays a key role in the copolymerization [44]. Recent reports have shown that organometallic compounds encapsulated in solid mesoporous materials are also effective for the copolymerization of ethane and propylene [45] and polymerization of ethylene [46].

In our experiment, the ZLE–Al(i-Bu)$_3$–glycerin system has been repeatedly tested as a catalyst for the copolymerization of PO and CO_2 under the same condition and it is found that the catalytic performance of the ZLE–Al(i-Bu)$_3$–glycerin system is very stable from sample to sample. The temperature, the pressure and the procedure for the test are the same as reported previously [20]. First, a mixture is formed by the reaction of ZLE with Al(i-Bu)$_3$ and then the mixture is used to catalyze the reaction of CO_2 and PO. The IR spectra of the PO monomer, the product (P1) formed from propylene oxide and CO_2 using Al(i-Bu)$_3$ alone as the catalyst component and the product (P2) formed from PO and CO_2 using ZLE and Al(i-Bu)$_3$ together as the catalyst component are shown in figure 7. Strong absorption bands at 1740 and 1250 cm^{-1} due to C=O and C–O stretching vibrations of carbonate units are observed in the IR spectrum of P2 while these bands are not available in the spectra for PO and P1. The P1 is a homopolymer of the PO because the absorption band at 1090 cm^{-1} is characteristic of O–C–O linkages for a polyether compound. The IR spectra indicate that only through combination can Al(i-Bu)$_3$ and ZLE be catalytically active for the copolymerization of PO and CO_2.

In the literature [20], the Y(P_{204})$_3$–Al(i-Bu)$_3$–glycerin system among all the RE coordination catalysts composed of RE phosphonate, triisobutylaluminum and glycerin showed the highest activity and gave the highest yield within a short time for the copolymerization of PO and CO_2. Table 2 lists the catalytic performance of ZLE–Al(i-Bu)$_3$–glycerin system and that of the Y(P_{204})$_3$–Al(i-Bu)$_3$–glycerin system for the copolymerization of CO_2 and PO, respectively [20]. From the table, we see that 1 mol Eu can produce 349,50 g polymer in the reaction catalyzed by the ZLE–Al(i-Bu)$_3$–glycerin system while 1 mol Y can only produce 3274 g polymer in the reaction catalyzed by the Y(P_{204})$_3$–Al(i-Bu)$_3$–glycerin system. The turnover frequency of the former catalytic reaction is 2902 g polymer/(gEu h) while that of the latter is 193 g polymer/(gY h). These results indicate that the ZLE–Al(i-Bu)$_3$–glycerin system has much higher catalytic activity than the Y(P_{204})$_3$–Al (i-Bu)$_3$–glycerin system. We also tested the catalytic activity of $EuCl_3 \cdot 6H_2O$ compound in combination with Al(i-Bu)$_3$ and glycerin for the coploymerization of PO and CO_2, but the solid product obtained was proved to be the homopolymer of the PO by IR spectrum and the amount of the solid product was small. Therefore, it is concluded that $EuCl_3 \cdot 6H_2O$ compound is not effective for the coploymerization of PO and CO_2 and the catalytic mechanism of the system involving this compound is completely different from that involving ZLE.

The ^{1}H NMR spectrum (figure 8) of the copolymer product obtained from the ZLE–Al(i-Bu)$_3$–glycerin catalytic system shows chemical shifts from internal TMS at 1.3 ppm for CH_3, 3.5 ppm for ($CH + CH_2$) in the PO unit, 4.2 ppm for CH_2 in the carbonate unit, and 5.0 ppm for CH in the carbonate unit. Based on the ^{1}H NMR spectrum, the contents of carbonate unit (CU in mol%) and carbon dioxide (f(CO_2) in mol%) in the copolymer obtained in the reaction catalyzed by ZLE–Al(i-Bu)$_3$–glycerin system are 18 and 15 mol%, respectively, according to the following equations, $CU = A_{5.0} + A_{4.2}/A_{5.0} + A_{4.2} + A_{5.5}$ and $f(CO_2) = CU/CU + 1$; while the CU and f(CO_2) of the copolymer obtained in the reaction catalyzed by Y(P_{204})$_3$–Al (i-Bu)$_3$–glycerin system [20] were 30 and 23 mol%, respectively. Although the CU and CO_2 contents in the copolymer product from the ZLE catalyst system is somewhat lower than those from the Y(P_{204})$_3$ catalyst system, the total amount of CO_2 incorporated into the

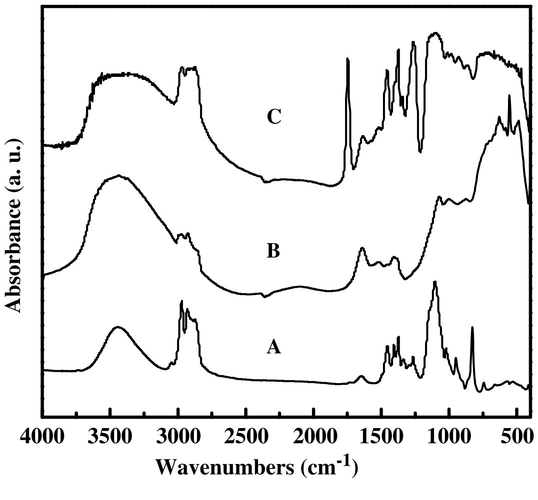


Figure 7. IR spectra of PO (a), the product (b) formed from PO and CO_2 using Al(i-Bu)$_3$ alone as the catalyst component and the product (c) formed from PO and CO_2 using ZLE and Al(i-Bu)$_3$ together as the catalyst component.

Table 2
Catalytic performance for the copolymerization of carbon dioxide and PO[a]

Catalyst	f(CO_2)	TOP	TOC	Reference
ZLE–Al(i-Bu)$_3$	15	34950	4126	This work
Y(P204)$_3$–Al(i-Bu)$_3$	23	3274	604	18

[a] f(CO_2): content (mol%) of carbon dioxide in the copolymer of PO and CO_2; TOP: turnover number, g polymer/mol RE; TOC: turnover number, g CO_2/mol RE; RE = Eu for ZLE and Y for Y(P_{204})$_3$.

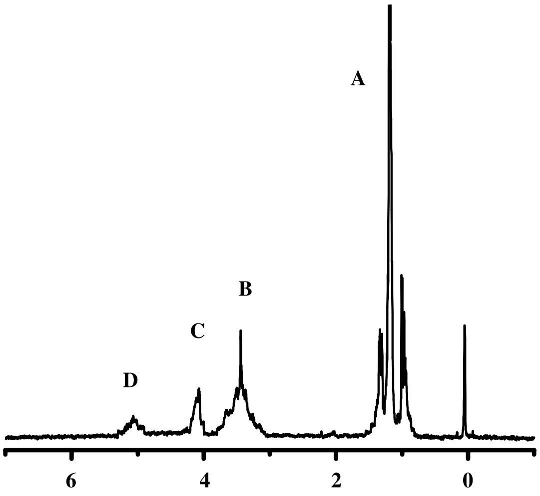


Figure 8. ^1H NMR spectrum of the copolymer formed from PO and CO_2 using α-ZrP-Lys-Eu (ZLE) as the catalyst component. (a) CH_3 in the PO unit and the carbonate unit; (b) $CH+CH_2$ in the PO unit; (c) CH_2 in the carbonate unit; (d) CH in the carbonate.

polymer for the former system is much larger than the latter system in terms of turnover number of each mole RE metal (see table 2). It is noted that 1 mol Eu of the ZLE–Al(*i*-Bu)$_3$–glycerin system is able to transfer 4126 g CO_2 into the copolymer whereas 1 mol Y of the Y(P_{204})–Al(*i*-Bu)$_3$–glycerin system just transfers 604 g CO_2. The GPC data show that the weight average molecular weight (M_w) of the copolymer produced from the ZLE catalyst system is about 12,000, with the ratio of weight- to number- average molecular weight (M_w/M_n) being 2.9. From the GPC data it is seen that the copolymer has a narrow molecular weight distribution. Although less amount of CO_2 can be incorporated into the copolymer using ZLE–Al(*i*-Bu)$_3$–glycerin as the catalyst in comparison with using zinc glutarate as the catalyst (4083 g CO_2 incorporated by 1 mol Eu versus 5972 g CO_2 by 1 mol Zn) [31], the amount of copolymer produced by the former catalytic system is significantly larger than that produced by the latter system in terms of per mole metal used (34,950 g copolymer produced by 1 mol Eu in comparison with 13,858 g copolymer produced by 1 mol Zn).

4. Conclusion

Solid grinding method has been employed to intercalate Eu complex into between the layers of $Zr(HPO_4)_2 \cdot 1.85$ Lys (ZL) at room temperature. The Eu^{3+} ions are coordinated with the carboxyl groups of Lys in the composite compound (ZLE) as indicated by IR, UV–vis, XPS and photoluminescence spectroscopies. There are Eu complexes sandwiched between the Lys layers that are attached on the inner surface of the α-ZrP. The molecular environment around the Eu^{3+} ion in ZLE is different from that of the Eu^{3+} ion in the raw compound $EuCl_3 \cdot 6H_2O$, leading to variation of the physical and chemical properties for the ZLE compound in comparison with $EuCl_3 \cdot 6H_2O$. Each unit Eu in ZLE gives stronger photoluminescence than in the $EuCl_3 \cdot 6H_2O$ because the Eu^{3+} ions encapsulated in the layered compound are shielded and the organic molecules have replaced the H_2O molecules around each Eu^{3+} ion. Moreover, the system, ZLE–Al(*i*-Bu)$_3$–glycerin, shows catalytic activity in the copolymerization of CO_2 and propylene (PO), while the $EuCl_3 \cdot 6H_2O$ compound in combination with Al(*i*-Bu)$_3$ and glycerin is not active at all for the copolymerization. Each unit Eu in the ZLE–Al(*i*-Bu)$_3$–glycerin system transfers much more CO_2 into polymer than each unit Y in the previously reported Y(P_{204})$_3$–Al(*i*-Bu)$_3$–glycerin system does, and the total amount of copolymer produced by our composite catalyst exceeds that produced by the well-known zinc glutarate to a great extent in terms of per mole metal. The preparation of the ZLE material and the demonstration of its catalytic performance open perspectives for the development of new types of copolymerization catalysts.

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