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Alcoholysis of Polyethylene Terephthalate for Dioctyl Terephthalate Using Choline Chloride-Based Deep Eutectic Solvents as Efficient Catalysts

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Abstract

Dioctyl terephthalate (DOTP) is a new kind of green and non-toxic plasticizer. The traditional process to prepare DOTP is costly and complicated, thus, it is very necessary to find an efficient and environmentally-friendly way to obtain DOTP. In this study, we prepared DOTP from the alcoholysis of polyethylene terephthalate (PET) by 2-ethyl-1-hexanol (2-EH) as solvent, and used choline chloride-based deep eutectic solvents (ChCl-based DESs) as the catalysts due to their cheapness, low toxicity and easy preparation. Under the optimized conditions (ChCl/Zn(Ac)$_2$ 1:1, 5 wt%, 180 °C, 60 min, PET:2-EH 1:5 molar ratio), the conversion of PET and yield of DOTP were 100% and

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84.7%, respectively. Furthermore, the possible mechanism was proposed through density functional theory (DFT) calculations and experimental results. It revealed that the hydrogen bonds (H-bonds) formed between 2-EH and DESs played a key role to accelerate the degradation process. Furthermore, the kinetics of the reaction was also investigated, and the results indicated that the alcoholysis of PET is a first-order reaction with an activation energy of 95.05 kJ/mol. This work confirmed that ChCl-based DESs are favorable for the degradation of PET to prepare DOTP under mild conditions, which can also be used for other polymer degradation strategies.

Introduction

Dioctyl terephthalate (DOTP), a new kind of green plasticizer[1] to replace dioctyl phthalate, has received more and more attention due to its good insulation, cold resistance, heat resistance, pullout resistance, softness and low volatility.[2] DOTP can be used in a lot of fields, not only as a non-toxic main plasticizer for medical polyvinyl chloride products or plastic toys,[3] but also as the lubricant or additive in the manufacture of nitrile rubber, artificial leather products, polyethylene, etc. However, DOTP is usually prepared from p-phthalic acid (PTA) or dimethyl terephthalate[4] in industry, both of which have some shortcomings such as long reaction process, high energy consumption and low economic efficiency. While using polyethylene terephthalate (PET) as raw material promises to overcome these problems, it can reduce production costs greatly. Meanwhile PET is a widely used polyester,[5, 6] and many studies showed it can be degraded by hydrolysis,[7, 8] aminolysis[9, 10] and alcoholysis[11, 12] to obtain high value products like PTA,[13, 14] p-phenylenediamine[15] or bis (2-hydroxyethyl)

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terephthalate.[16] Moreover, the global PET market is expected to grow rapidly from 6.5 million tons in 2000 to 23.4 million tons by 2020, with a compound annual growth rate of approximately 7.0%.[8, 17] Environmental problems are getting increasingly serious, therefore, preparing DOTP from PET is a good choice for both economic effect and green issues.

In recent years, researchers have developed a variety of catalysts such as acids, bases and metal salts[16, 18, 19] or some intensification methods, including microwave-assisted technology[20, 21] and supercritical method[22-24] for PET degradation. Although these methods have already been widely studied and applied in PET recycling, there are still some drawbacks to resolve. For example, acid or base catalysts can cause corrosion of equipment or environmental pollution, and the catalytic efficiency isn't very high. Although microwave-assisted technology can increase the reaction rate, it usually requires high temperature and tremendous power. High yield of DOTP can be obtained by the supercritical method, but the reaction conditions are very severe (300–450 °C, 14–50 MPa). Thus, it is important to find an efficient way for the alcoholysis of PET to prepare DOTP under mild reaction conditions.

Deep eutectic solvents (DESs) are fleetly emerging as a new kind of sustainable and green solvent, since being introduced by Abbott et al. in 2003,[25] and they have been research hotspots for a long time.[26-28] Furthermore, DESs are also considered to be a new generation of ionic liquids (ILs), with similar excellent properties,[29, 30] and a lot of ILs have already been widely used for the degradation of PET,[16, 31] DESs were usually synthesized by simply mixing the hydrogen bond acceptors (HBAs) and hydrogen bond

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donors (HBDs) together.[27] It is noteworthy that DESs have many advantages compared with the conventional ILs, which rest with the simpler preparation, cheaper materials and no need for further purification,[32, 33] so DESs are deemed to have great application prospects.[34, 35] Wang et al.[36] showed that urea/metal salt DESs have high catalytic activity on PET alcoholysis with ethylene glycol (EG) by the action of both H-bond and coordination bond. Cho et al.[37] used the DESs for the modification of PET polyester surfaces. These examples fully demonstrate that DESs have great potential in the field of PET degradation. In addition, Multiple studies have shown that choline chloride (ChCl) has a potential green profile owing to its low toxicity and high level of biodegradability,[38] and the ChCl-based DESs are generally considered to be non-toxic salts, some of which have been approved as nutritional additives.[39] Compared with other transition metals, Zn^{2+} tend to have higher catalytic activity for PET degradation[40] and $COOH^-$ is also friendly to the environment, so zinc acetate ($Zn(Ac)_2$) can be a good choice as the HBA.[36]

In this work, in order to get an efficient and green catalyst for the PET degradation, ChCl and $Zn(Ac)_2$ were selected as HBD and HBA. Then a series of DESs ($ChCl/Zn(Ac)_2$ from molar ratio 2:1 to 1:6) were synthesized to be investigated, and the reaction conditions such as reaction temperature, reaction time, ratio of solvent and content of catalyst were optimized. The prepared DESs were characterized by Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance spectroscopy (^1H NMR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Through high performance liquid chromatograph

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(HPLC), the yield of DOTP was obtained and the main product was identified by FT-IR and ^{1}H NMR. In addition, the DES-catalyzed mechanism of PET degradation was proposed by density functional theory (DFT) calculations and scanning electron microscopy (SEM). Finally, the kinetics of the reaction was studied to get the reaction rate constants of different temperatures and the activation energy.

Experimental

Materials

PET pellets (2.0×2.5×2.7 mm) were purchased from Jingdong Commercial Co., Jiangsu Province, China. The pellets were ground into 40-60 mesh by small grinding miller (ZN-02). Choline chloride (ChCl), anhydrous zinc acetate ($Zn(Ac)_2$), cobalt acetate ($Co(Ac)_2$), ferric chloride ($FeCl_3$), tetrabutyl titanate ($Ti(OC_4H_9)_4$), 2-ethyl-1-hexanol (2-EH), dioctyl terephthalate (DOTP) standard sample and the other reagents were purchased from Sinopharm Chemical Reagent Beijing Co., China. All reagents were used as purchased without further purification.

Preparation of Choline Chloride-Based DESs

A series of ChCl-based DESs were synthesized by mixing ChCl and $Zn(Ac)_2$ from 2:1 to 1:6 (molar ratio) at a moderate temperature for 2h-8h with strong agitation in a round flask. Until a clear and homogeneous liquid formed, the reaction was stopped and the product was collected.

Characterizations of catalysts and main products

Fourier transform-infrared (FT-IR) spectra of the synthesized DESs and the main product were obtained with a Nicolet 380 (Thermo Fisher Scientific, U.S.A.)

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spectrometer, using KBr as blank in the range 4000-400 cm^{-1}. ^1H Nuclear magnetic resonance (^1H NMR) spectra were recorded on an AVANCE-III 600 NMR spectrometer operating at 600 MHz in DMSO-d6 solution. Thermogravimetric analysis (TGA) of the synthesized DESs was done using DTG-60H in nitrogen atmosphere by heating sample from 25 ºC to 600 ºC at the rate of 10 ºC/min. Differential scanning calorimeter (DSC) scans of the synthesized DESs were obtained using DSC-1 STAR^e system by heating from 0 ºC to 500 ºC at a heating rate of 10 ºC/min in an atmosphere of nitrogen with a flow rate of 20 mL/min. The morphologies of fresh PET and residual PET were observed with scanning electron microscope (SEM, Hitachi, SUB020, Japan). The content of product was analyzed with a ACQUITY HPLC (Waters, 2695, U.S.A.) equipped with a refractive index detector (Waters, 2414, U.S.A.), and BET C 18 column (Waters, U.S.A.) under the condition of an oven temperature 30 °C, detector temperature 50 °C, solvent chromatographic is grade ethanol and flow rate 0.2 mL/min. Gel permeation chromatography (GPC) analysis were performed on a PL-GPC 50 system (Agilent, U.S.A.) under the condition of oven temperature of 30 °C, solvent trichloromethane and flow rate 1.0 mL/min. Three columns (PLgel 5um Guard, length 50mm, 7.5mm i.d. PLgel 5um MIXED-C, length 300mm, 7.5mm i.d. PLgel 5um MIXED-D, length 300mm, 7.5mm i.d.) were used. The detector used on the GPC is a refractive index (RI) detector.

General procedure for the catalytic degradation of PET

In each experiment, 5 g of PET pellets were degraded, using 2-EH in the presence of ChCl or one kind of previously synthesized DES catalysts. A 100 mL double-necked

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round-bottom glass flask equipped with a thermometer, a magnetic stirrer and a reflux condenser was needed for all the degradation experiments. The degradation reactions were carried out under atmospheric pressure at reaction temperatures ranging from 155 °C to 185 °C for reaction times of 20-180 min. The flask was immersed in an oil bath at aspecific temperature for the required time. When the reaction terminated, the reaction mixture was cooled to room temperature. Then the reaction mixture was filtered by a decompress filter, the flask washed with ethanol, to separate the liquid product from the undegraded PET (because of the high viscosity, the catalyst adhered to the flask wall). The filter residue was dried at 80 °C for 24 h, weighted to calculate the conversion of PET, which is defined by the following Eq.(1):

$$Conversion\ of\ PET = \frac{W_0 - W_1}{W_0} \times 100\% \qquad (1)$$

Where W_0 represents the initial weight of PET, W_1 represents the weight of undegraded PET. In addition, the filtrate was distilled at atmospheric pressure to remove ethanol and then vacuum distillation was used to remove EG and 2-EH. A light yellow transparent liquid was collected and all characterization techniques showed that this light yellow transparent liquid was DOTP. Moreover, the product can be further purified by silica gel column. The selectivity and yield of DOTP are defined by Eqs. (2) and (3):

$$Selectivity\ of\ DOTP = \frac{n_{DOTP}}{n_{units}} \times 100\% \qquad (2)$$

$$Yield\ of\ DOTP = S_{DOTP} \times C_{PET} \qquad (3)$$

where n_{DOTP} represents the number of moles of DOTP, n_{units} represents the number of moles of the degraded PET units, S_{DOTP} represents the selectivity of DOTP and C_{PET}

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represents the conversion of DOTP.

DFT calculations

All calculations were operated using the Gaussian 09 program. The M06-2X-D3/6-311+G**, lanl2DZ method was used for structure optimizations, and subsequent frequency calculations at the same level verify the optimized structures to be ground states without imaginary frequencies (NImag = 0).

Results and Discussion

Screening of catalysts for PET degradation

Under the same reaction conditions, the catalytic performance of DESs (ChCl/$Zn(Ac)_2$ from molar ratio 2:1 to 1:6) in PET alcoholysis was investigated, and the results were shown in **Figure 1**. It showed that with the change of the ratio, the C_{PET} and Y_{DOTP} increased first and then decreased, and the best catalytic performance appeared when the ratio of the two components was 1:1, the C_{PET} and Y_{DOTP} were almost 100% and 84%, respectively. In addition, the catalytic performance of the DESs synthesized from the other metal salts and some kinds of other catalysts together were shown in **Table 1**. According to the experimental results, some metal salts ($Zn(Ac)_2$, $Mn(Ac)_2$, $FeCl_3$, etc.) can catalyze the degradation of PET, and $Zn(Ac)_2$ showed the best catalytic performance. Moreover, it was found that when ChCl was used alone as catalyst, the PET degradation rate was very low. But when $Zn(Ac)_2$ was added, 5 g PET can be completely degraded in 1 h, which indicated that metal ions may played the main catalytic role and ChCl played the role of cocatalyst. Compared with references,[1, 2, 41] the yield of DOTP in this work (84.2 %) was lower than that reported in the references

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(93.1 %, 97 % and 97.6 % respectively). However, the time required for complete degradation of PET using ChCl/Zn(Ac)$_2$ as catalyst was 1 hour, which was much shorter than that reported in the references (5h, 2h and 8h respectively). In addition, the experimental conditions adopted in this work were milder, and the methods of the references usually need higher temperature and pressure, or needs substantial cosolvent such as [Bmim]Cl.

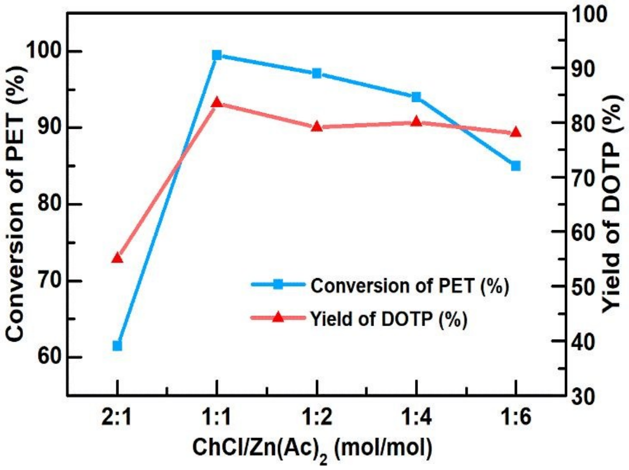

Figure 1. Performance of DESs with different proportion of ChCl and Zn(Ac)$_2$. Reaction conditions: PET (5.0 g), 2-EH (17.0 g), DES (0.25 g), atmospheric pressure, 185 ºC, 60 min.

Table 1. The catalytic activities of PET degradation with different catalysts [a]

Entry	Catalysts	Temperature (ºC)	time (h)	Conv.$_{PET}$ (%)	Yield$_{DOTP}$ (%)	Ref.
1	–	185	1	1.5	–	This work
2	ChCl	185	1	3.4	–	
3	ChCl/Zn(Ac)$_2$ (1:1)	185	1	≈100.0	84.2	
4	ChCl/Mn(Ac)$_2$ (1:1)	185	1	96.5	80.6	
5	ChCl/Co(Ac)$_2$ (1:1)	185	1	90.4	74.1	
6	ChCl/Cu(Ac)$_2$ (1:1)	185	1	91.7	76.2	
7	ChCl/FeCl$_3$ (1:1)	185	1	94.5	78.3	
8	Zn(Ac)$_2$	185	1	46.4	40.6	

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9	$Mn(Ac)_2$	185	1	44.2	36.6	
10	$Co(Ac)_2$	185	1	32.9	27.1	
11	$Cu(Ac)_2$	185	1	33.8	27.6	
12	$FeCl_3$	185	1	43.8	35.7	
13	$CoCl_2$	185	1	31.6	26.5	
14	H_2SO_4	185	1	41.4	34.5	
15	$Ti(OC_4H_9)_4$	185	1	78.5	63.8	
16	$Zn(Ac)_2$[b]	200	5	100	93.1	1
17	–[c]	300	2	100	97.0	2
18	$[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}FeCl_3$[d]	210	8	100	97.6	41

[a] Experiment conditions: Conditions: PET (5.0 g), 2-EH (17.0 g), catalysts (0.25 g), atmospheric pressure.

[b] 2-EH (10.0 g), [Bmim]Cl as cosolvent (10.0 g), catalyst (0.06 g).

[c] 2-EH (20.4 g) and at high pressure.

[d] [Bmim]Cl as cosolvent (10.0 g), catalyst (1.00 g).

Characterizations of DESs

FT-IR, NMR, DSC and TGA were carried out to identify the structure of the prepared DES (ChCl/$Zn(Ac)_2$ (1:1)). FT-IR spectra were shown in **Figure 2.** It showed that the spectrum of DES basically contains all functional groups of two kinds of raw materials, such as peaks at 950.5, 950. 2 and 950.3 cm^{-1}, but there are some obvious differences between them. Compared with the peaks at 1481.5 and 1562.3 cm^{-1} on the FT-IR spectra of ChCl and $Zn(Ac)_2$, it can be seen that a new peak at 1587.1 cm^{-1} appeared, which indicated that a new amido bond (in-plane bending vibration) was formed by the coordination between ChCl and $Zn(Ac)_2$. At the same time, methyl group and carbon-

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chlorine bond in ChCl showed obvious red shifts from 1409.5 to 1391.4 cm^{-1} and from 621.2 to 618.3 cm^{-1}, which suggested that the new bonds formed also have an effect on the bond energies of other functional groups.

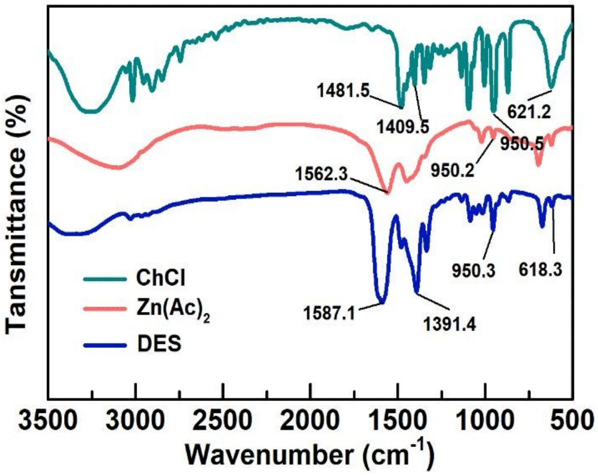

Figure 2. FT-IR spectra of DES, Zn(Ac)2 and ChCl

^{1}H NMR spectra were shown in **Figure 3**. By comparing the ^{1}H NMR peaks of two raw materials and DES, it was found that DES basically contains all the peaks of the two raw materials. However, it is worth noting that an obvious signal at δ 5.660 ppm on the spectrum of ChCl disappeared on the spectrum of DES, which indicated that the hydroxyl on ChCl participated in the synthesis of DES and formed H-bonds with the oxygen on carbonyl group of $Zn(Ac)_2$.

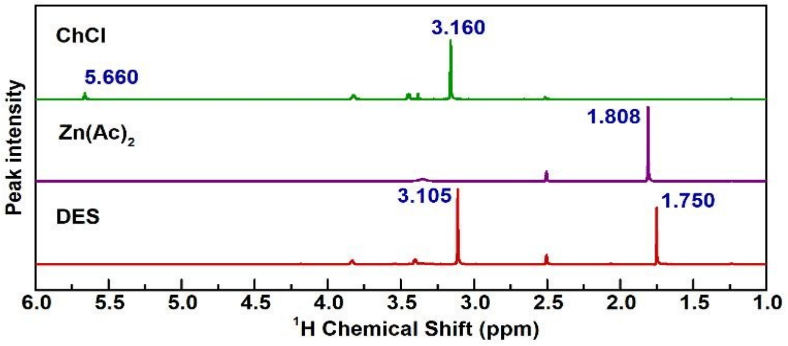

Figure 3. ^{1}H NMR patterns of DES, $Zn(Ac)_2$ and ChCl

The DSC curves of DES was depicted in **Figure. 4**. There was a sharp endothermic

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peak, and the melting onset temperature of DES was 182.4 °C, which was lower than that of ChCl (302 °C) and $Zn(Ac)_2$ (237 °C). This accorded with the physical and chemical properties of DESs, and proved that a homogeneous DES has been prepared. The TGA curve of the DES was shown in **Figure 5**. It showed an obvious weight loss at approximately 214 °C, and the weight loss was nearly 72% in the range 214–478 °C. The decomposition temperature of the DES (214 °C) was higher than the reaction temperature (180 °C), so DES can exist stably in the reaction system and can hardly be decomposed by heat.[40]

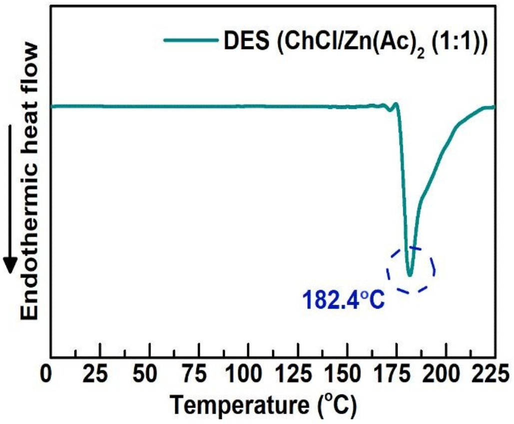

Figure 4. DSC curves of DES (ChCl-$Zn(Ac)_2$ (1:1))

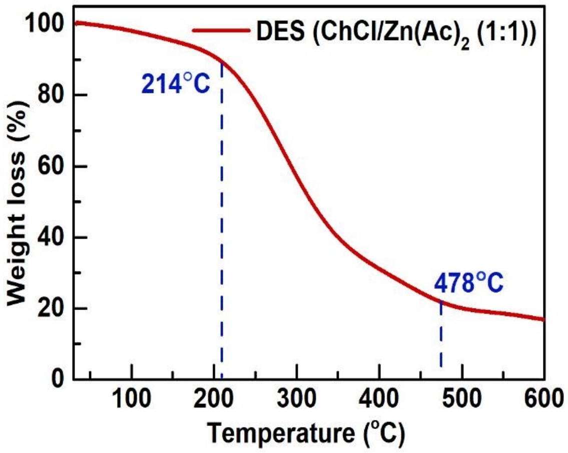

Figure 5. TGA curves of DES (ChCl-$Zn(Ac)_2$ (1:1))

Effect of experiment conditions on the PET degradation

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The effect of reaction temperature on PET degradation in a particular set of condition (viz. 5 g PET, 60 min, 5 wt% catalyst/PET ratio, PET:2-EH 1:5 molar ratio, atmospheric pressure) using ChCl/Zn(Ac)$_2$ (1:1) as catalyst and the results were shown in **Figure 6**. When the temperature as low as 155 ºC, The degradation rate of PET was very low, only about 35%, and the yield of DOTP was 32%, but the selectivity was higher at low temperature, which exceeded 90%. With the increasing of reaction temperature from 155 °C to 185 °C, the degradation rate of PET and yield of DOTP increased, but the selectivity of DOTP decreased. The highest C_{PET} and Y_{DOTP} were obtained at 180 °C, which were 100% and 84.5%, respectively. When the temperature continued to rise, the C_{PET} remained unchanged, but the side reactions increased so that the Y_{DOTP} and S_{DOTP} decreased.

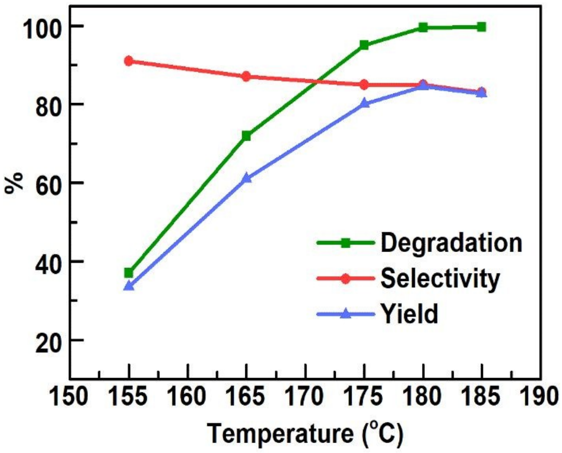

Figure 6. Effect of temperature on PET degradation. Reaction conditions: PET (5.0 g), 2-EH (17.0 g), DES (0.25 g), atmospheric pressure, 60 min.

The effect of reaction time on PET degradation was investigated and presented in **Figure 7** by reacting 5 g of PET with 5 wt% catalyst/PET ratio and PET:2-EH 1:5 molar ratio at 180 °C under atmospheric pressure. It was observed that as time went on, the

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C_{PET} increased from 70% to 100%. Meanwhile, Y_{DOTP} and S_{DOTP} reached the maximums 84.4% and 84.6% when the reaction time was 60 min. After 60 min, there was a slight decrease in the Y_{DOTP} and S_{DOTP} as the extension of time, due to the existing equilibrium between DOTP, dimer and oligomer.

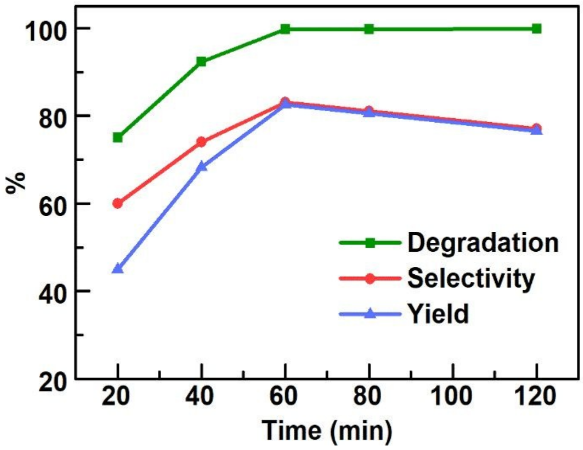

Figure 7. Effect of time on PET degradation. Reaction conditions: PET (5.0 g), 2-EH (17.0 g), DES (0.25 g), atmospheric pressure, 180 ºC.

To study the effect of the alcohol amount on the PET degradation, the experiments were performed at the following reaction conditions: 5 g PET, 5 wt% catalyst, 60 min, 180 °C, under atmospheric pressure and the results were shown in **Figure 8**. When the addition of 2-EH was small, although the C_{PET} could reach more than 90%, the Y_{DOTP} and S_{DOTP} were less than 60%. When 2-EH reached five times the molar amount of PET, the maximums of Y_{DOTP} and S_{DOTP} appeared, which were 84.5% and 84.7% respectively. The amount of 2-EH continued to increase and the Y_{DOTP} and S_{DOTP} decreased slightly, which may be owing to the lower concentration of reactants and the side reactions caused by excessive 2-EH.

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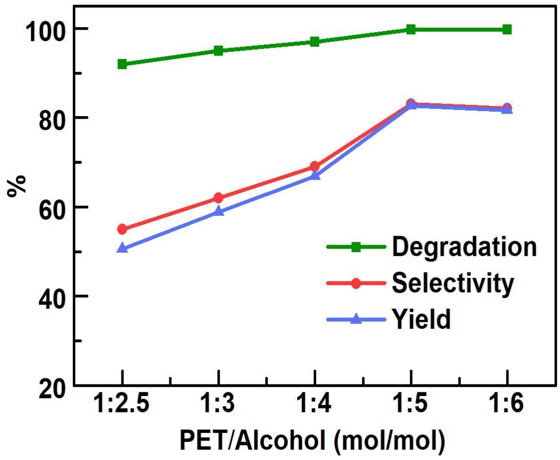

Figure 8. Effect of alcohol amount on PET degradation. Reaction conditions: PET (5.0 g), DES (0.25 g), atmospheric pressure, 180 ºC, 60 min.

The effect of catalyst amount on PET degradation was investigated at the following reaction conditions: 5 g PET, PET:2-EH 1:5 molar ratio, 60 min, 180 °C, atmospheric pressure, and the results were shown in **Figure 9**. It showed that when the catalyst amount reached 5 wt% of PET, the degradation rate reached almost 100%, and Y_{DOTP} and S_{DOTP} reached 83.6% and 83.2%, respectively. Continued to increase the amount of catalyst, the degradation rate remained unchanged. By comparing the above diagrams, it can be found that the reaction temperature and time have more influence on PET degradation, but the amount of alcohol and catalyst has less influence on the reaction.

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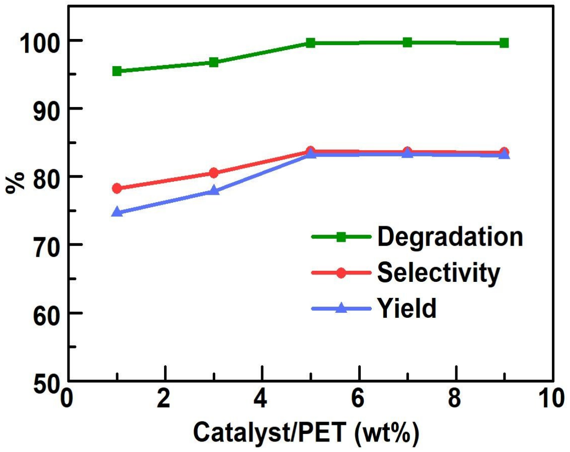

Figure 9. Effect of catalyst amount on PET degradation. Reaction conditions: PET (5.0 g), 2-EH (17.0 g), atmospheric pressure, 180 ºC, 60 min.

Degradation mechanism for PET alcoholysis

In this work, the mechanism was studied by DFT calculations and the M06-2X-D3/6-311+G**, lanl2DZ method was used for structure optimizations. The interaction between DES and 2-EH was investigated in **Figure 10**, and it can be found that there are some possible stable interaction structures among the $Zn(Ac)_2$, ChCl and 2-EH, which is mainly formed by H-bonds and coordination bonds.[42] Among all these modes, structure B has the lowest energy, meaning it is more stable than the others. The H-bonds were formed by hydrogen of hydroxyl in ChCl and oxygen of carbonyl in $Zn(Ac)_2$, and by hydrogen of hydroxyl in 2-EH and oxygen of carboxylate in $Zn(Ac)_2$. The coordination bonds were formed between chloride ion in ChCl and zinc ion in $Zn(Ac)_2$. In addition, **Table 2** shows that the interaction between 2-EH and DES will bring changes to the bond lengths, and the O–H bond length of the hydroxyl group in 2-EH after interaction with DES in structures A, B, C and D, become longer than those before interaction (original 0.958 to 0.971, 1.006, 0.973 and 0.973), which leads to the hydrogen to be lost more quickly.[18]

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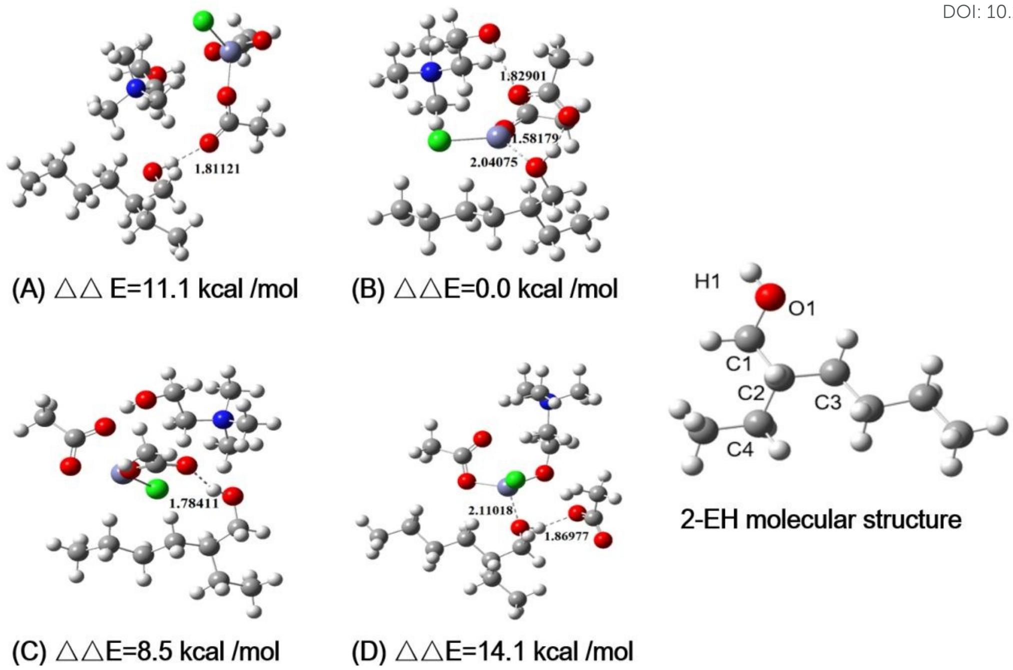

Figure 10. Optimized interaction structures among $Zn(Ac)_2$, ChCl and 2-EH by M06-2X-D3/6-311+G**, lanl2DZ with relative energies. Red: O; green: Cl; blue: N; white: H; dark grey: C; steel grey: Zn.

Table 2. Changes in bond length for 2-EH while it interacts with DES

Bond	2-EH	A	B	C	D
O1-H1	0.958	0.971	1.006	0.973	0.973
O1-C1	1.420	1.419	1.431	1.417	1.446
C1-C2	1.523	1.524	1.522	1.529	1.523
C2-C3	1.532	1.532	1.538	1.533	1.532
C3-C4	1.534	1.533	1.533	1.534	1.533

The interaction among DES, 2-EH and PET was studied in **Figure 11**, and it shows that different energy required for four different reaction paths. Zn^{2+} attacked the carbonyl group on PET to form carbon cation, which follows the acid-catalyzed mechanism,[36] $COOH^-$ simultaneously attacked the hydroxyl group on 2-EH, and then

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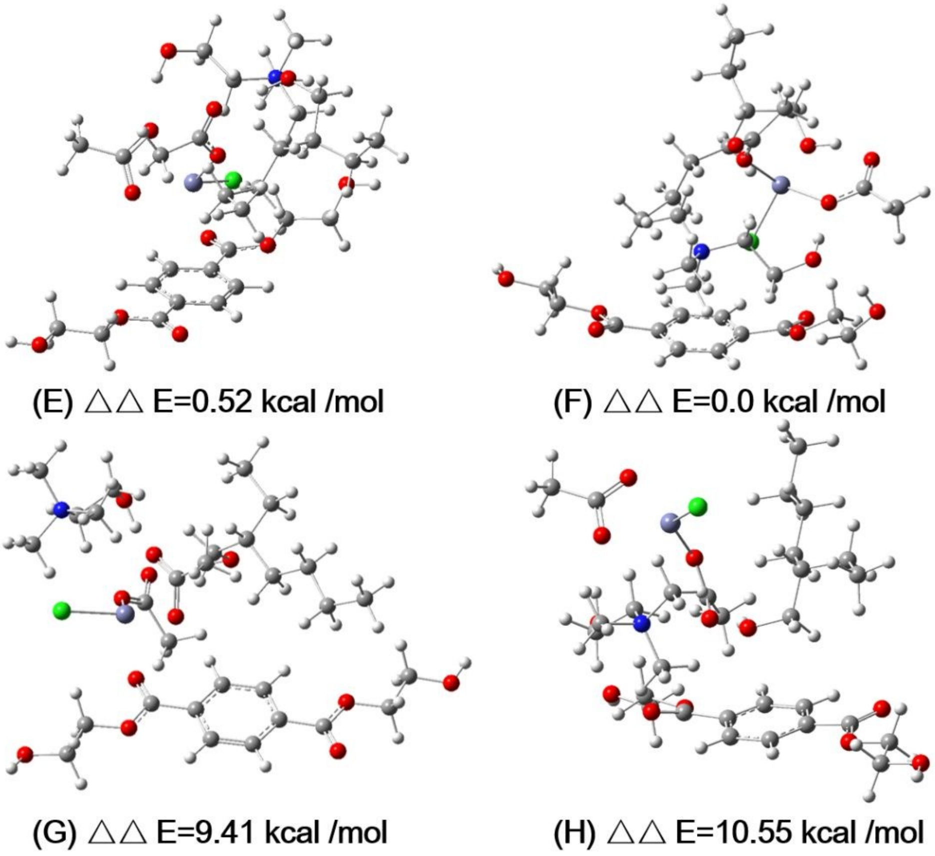
activated the carbonyl group, and this process in line with the base-catalyzed mechanism. Under this synergistic catalysis, the long chains of PET were rapidly broken, which has greatly accelerated the degradation rate of PET and then the transesterification reaction has completed. Furthermore, based on the DFT calculations and the experiments, the possible degradation mechanism of PET catalyzed by DES ($ChCl/Zn(Ac)_2$ 1:1) is illustrated in **Scheme 1**.



(E) △△ E=0.52 kcal /mol

(F) △△ E=0.0 kcal /mol

(G) △△ E=9.41 kcal /mol

(H) △△ E=10.55 kcal /mol

Figure 11. Optimized interaction structures among DES, 2-EH and PET with relative energies.

Red: O; green: Cl; blue: N; white: H; dark grey: C; steel grey: Zn.

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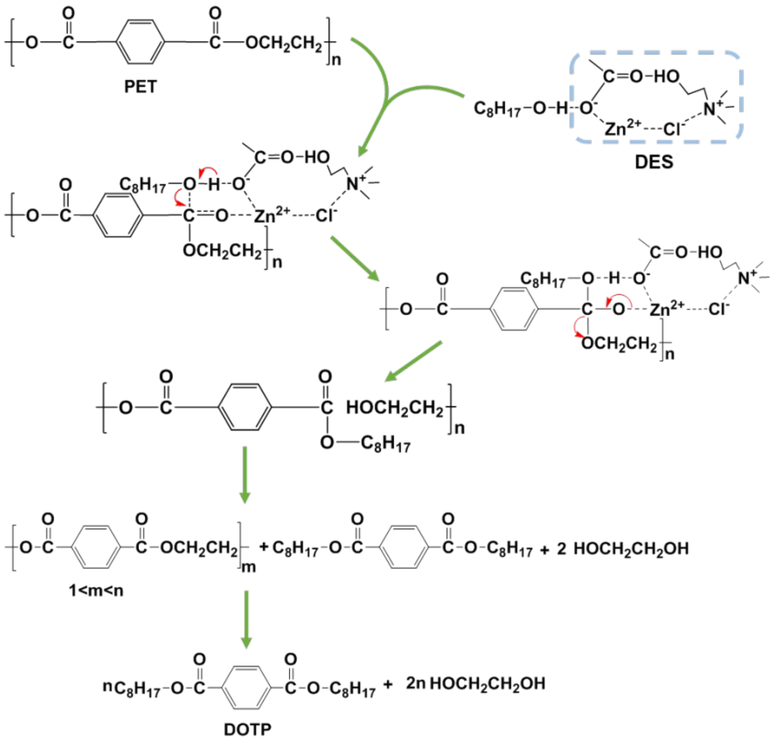

Scheme 1. Proposed mechanism for the PET degradation catalysed by DES

In studies of the PET degradation, the reaction is usually considered to occur on the surfaces of PET pellets, and then with the aggrandizement of cracks on the surfaces and increasing exposed areas, the reaction accelerated.[43, 44] The images of fresh PET and residual PET after different reaction time from 20 min to 60 min were observed by SEM, and the results were illustrated in **Figure 12**. The image presented in **Figure 12 (a)** shows that the surface of fresh PET is relatively smooth. After 20 minutes of reaction, the surface of PET was no longer smooth and there were a few cracks, as displayed in **Figure 12 (b)**. Then, after a longer reaction time, the surface cracks of PET increased and a lot of holes appeared, the images was shown in **Figure 12 (c)** and **Figure 12 (d)**. These images showed that the degradation process of PET began on the surface and slowly penetrated into the inner layer as the long chains were broken down. With DES as catalyst, PET particles were gradually eroded and many pores and fissures

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were formed on the surface, which reduced the degree of polymerization and this was more favorable for the further degradation.

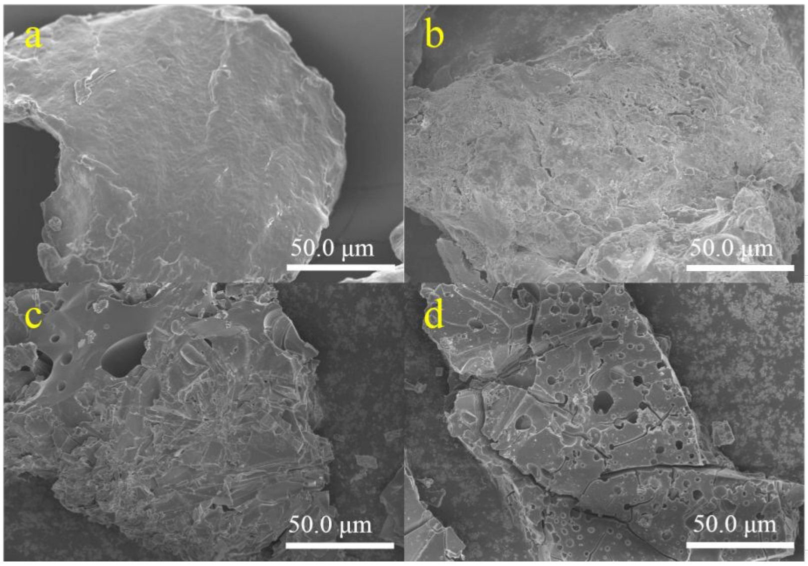

Figure 12. SEM of fresh PET (a) and residual PET (20min (b), 40 min (c), 60min (d))

Kinetics of the PET alcoholysis

There has been some debates that the reaction order is usually considered to be first-order[40, 45] in the depolymerization kinetics of polymers. Consequently, the PET alcoholysis with the DES (ChCl/Zn(Ac)$_2$ 1:1) as catalyst was initially assumed to be controlled by the first-order kinetic equations:

$$\frac{d(C_{PET})}{dt} = -kC_{PET} \qquad (4)$$

where k is the rate constant of the reaction and C_{PET} is the concentration of the PET at time t

$$C_{PET} = C_{PET0}(1 - X) \qquad (5)$$

where X is the conversion of PET. And then Eq. (4) can be written as Eq. (6):

$$\frac{dX}{dt} = k(1 - X) \qquad (6)$$

Eq. (6) was integrated over time to provide Eq. (7):

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$$ln\frac{1}{1-X} = kt \qquad (7)$$

using the rate constant, the activation energy (E_a) can be obtained by Arrhenius equation:

$$lnk = \frac{-Ea}{RT} + lnA \qquad (8)$$

where A is the pre-exponential factor, R is the gas constant (8.31 J/k mol), and T is the temperature in Kelvin.

The effect of the reaction temperature on the alcoholysis rate of PET in the presence of DES (ChCl/Zn(Ac)$_2$ 1:1) is shown in **Figure 13**. The activation energy for this reaction, calculated from the slope of the Arrhenius plot shown in **Figure 14**, was 95.05 kJ/mol. All the linear correlation coefficients in **Table 3** are higher than 0.98, which suggests that ln[1/(1-X)] was proportional to the reaction time at different temperatures and that this process followed a first-order kinetic reaction. In addition, with the rise of temperature, the reaction constant increases rapidly, which indicates that the temperature has great influence on the PET degradation and this is consistent with the previous experiments.

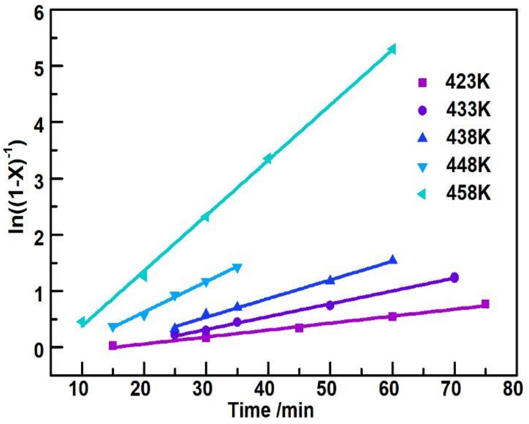

Figure 13. Effect of the temperature on the rate of alcoholysis of PET (Reaction condition: PET (5.0 g), 2-EH (17.0 g), DES (0.25 g), atmospheric pressure)

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Table 3. Linear regression results for the data in Figure 15 and Figure 16

Temp (K)	Rate constant	R^2	E_a (kJ/mol)	R^2
423	0.01236	0.9828	95.05	0.9852
433	0.02285	0.9905		
438	0.03318	0.9846		
448	0.05406	0.9941		
458	0.09825	0.9819		

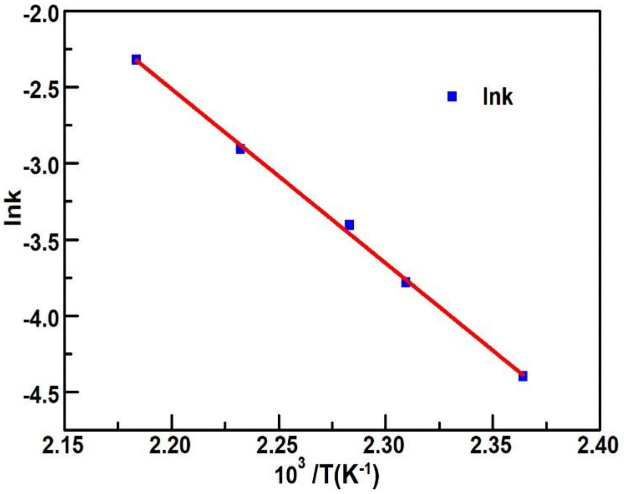

Figure 14. Arrhenius plots of the rate constant of alcoholysis of PET.

Conclusion

In summary, ChCl-based DES (ChCl/Zn(Ac)$_2$) were successfully synthesized and used as the catalysts in PET alcoholysis, and after a different proportion of screening, it was finally confirmed that the best molar ratio of ChCl and Zn(Ac)$_2$ is 1:1. The effects of reaction temperature, time, 2-EH amount and catalyst dosage on the results were investigated, and it is found that temperature and time are the main influencing factors. Under the optimized conditions (DES 5 wt%, PET:2-EH 1:5, 180 °C, 60 min), the C_{PET} and the Y_{BHET} were 100% and 84.7%. The possible mechanism proposed by DFT

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calculations revealed that the H-bonds formed between 2-EH and DESs played a key role, and the synergistic effect can enormously improve catalytic activity of the DESs. Moreover, the kinetics of the reaction was also investigated, and the results indicating that the alcoholysis of PET is a first-order reaction with an activation energy of 95.05 kJ/mol. Eventually, this work is supposed to provide some valuable references for polymer wastes degradation and other interesterification.

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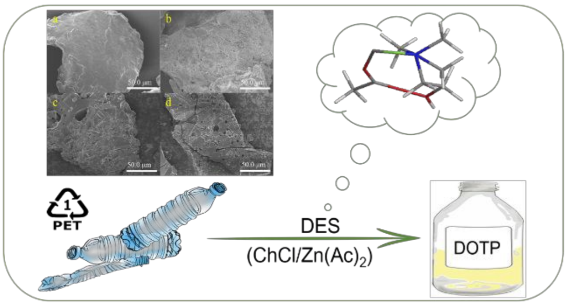

To prepare DOTP more cheaply and efficiently, PET was used as raw material and ChCl-based DES was synthesized as catalyst.