Butanol Alcoholysis Reaction of Polyethylene Terephthalate Using Acidic Ionic Liquid as Catalyst

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ABSTRACT: The alcoholysis reaction of polyethylene terephthalate (PET) and *n*-butanol to produce dibutyl terephthalate (DBTP) and ethylene glycol (EG) was investigated in the presence of a Brönsted–Lewis acidic ionic liquid (IL). It was found that a synergetic effect of Brönsted and Lewis acid sites enhanced the IL catalytic performance, and (3-sulfonic acid) propyltriethylammonium chlorozincinate $[HO_3S\text{-}(CH_2)_3\text{-}NEt_3]Cl\text{-}ZnCl_2$ (molar fraction of $ZnCl_2$ (x) was 0.67) was a good catalyst for the reaction. The conversion of PET was 100%, and the yields of DBTP and EG were 95.3% and 95.7% at 205°C for 8 h, respectively. The reusability of IL was good and after it was used seven times, PET conversion and the yields of DBTP and EG did not significantly decrease. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 1840–1844, 2013

INTRODUCTION

Polyethylene terephthalate (PET) is a semi-crystalline thermoplastic polyester and widely used in the manufacture of apparel fibers, disposable soft-drink bottles, photographic films, etc.[1] The 2009 global aggregate PET output summed up 49.2 m tons, of which PET fiber accounted for about two thirds, whereas PET for packages and films accounted for 34%, and its consumption is still in growth every year. Therefore, large numbers of post-consumer PET products must be concerned because of their substantial volume fraction in the solid waste streams, their high resistance to the atmosphere, their poor biodegradability and photo degradability, though they do not create a direct hazard to the environment.[2] Recently, recycling of PET waste has received a great deal of attention, which leads to various advantages: consuming waste to get new useful material or changing of a non-biodegradable polymer to a biodegradable one.[3,4] Chemical recycling of PET includes chemolysis of the polyester with an excess of reactants such as water (hydrolysis),[5,6] alcohol (alcoholysis),[7] and amine (aminolysis) to get monomers,[8] such as terephthalic acid and its methyl ester, terephthalamide, and ethylene glycol (EG). However, the quality of the obtained monomer is poor and not used directly in the polymerization. Recently, the alcoholysis of PET with long carbon chain alcohol, such as butanol and 2-ethylhexanol, to perform the plasticizer is getting more and more attention from reacher.[9–12] The obtained plasticizer primarily imparts flexibility to the polymer, such as PVC, and improves its workability, which is wildly used in the polymer working. Usually, acidic or basic catalysts were used in the alcoholysis,[10–12] and the shortcomings of such process include too large amount of catalyst, serious corrosion of equipment, complicated technique, non-recyclability of catalyst, and serious environmental pollution. In this context, mesoporous molecular sieves were reported as catalysts in the alcoholysis of PET,[13] but they also have shortcomings of restricted accessibility of the matrix-bound acidic sites, high molecular weight/active-site ratios, and rapid deactivation from coking. Therefore, it is necessary to design and synthesize a catalytic system that is of excellent catalytic performance and may be stable, easily separable, and reusable.

As a kind of environmental-friendly catalysts, Brönsted or Lewis acidic ionic liquids (ILs) have attracted the attentions of researchers, and many organic reactions, such as esterification,[14] dehydration,[15] alkylation,[16] and carbonylation,[17] were reported with excellent selectivity and outstanding recyclability. In our laboratory, some Brönsted–Lewis acidic ILs were synthesized, characterized, and used in the polymerization.[18,19] The results indicated that the Brönsted–Lewis acidic ILs were both Brönsted and Lewis acidic and had better catalytic performance for the polymerization than the traditional catalysts, Brönsted or Lewis acidic ILs. Due to the presence of Brönsted and Lewis acid sites, these ILs can selectively catalyze different reaction mechanisms to enhance the conversion and selectivity of the reaction. As an
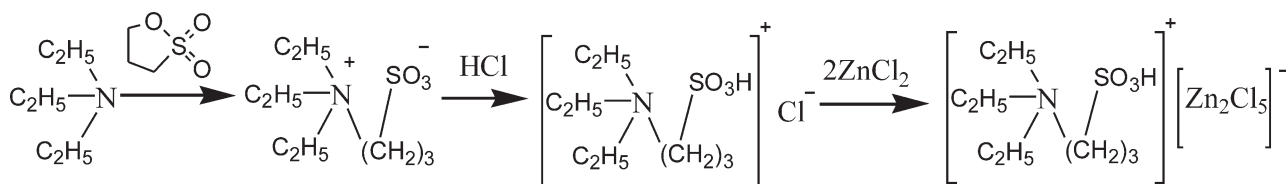
Figure 1. Synthesis of IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$).

extension of our ongoing studies of these acidic ILs, we studied herein the *n*-butanol alcoholysis of PET to produce dibutyl phthalate (DBTP) in the presence of Brönsted–Lewis acidic ILs.

To our surprise, IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$) was of well catalytic activity for the PET alcoholysis. The conversion of PET was 100%, and the yields of DBTP and EG were 95.3% and 95.7% at 205°C for 8 h, respectively. The reusability of IL was good and after it was used seven times, PET conversion and the yields of DBTP and EG did not significantly decrease. Otherwise, it was found that a synergetic effect of Brönsted and Lewis acid sites of IL enhanced its catalytic performance in the alcoholysis.

EXPERIMENTAL

Materials and Instructions
Materials. Waste no-colored PET fiber ($M_w = 23,500$) was obtained from Qingdao Weifeng Co., Ltd. (Qingdao, China), and other chemicals (analytic purity) were commercially available and used without further purification.

Instructions. IR spectra were recorded by a Nicolet 510P FTIR spectrometer in the range of 4500–400 cm^{-1}. NMR spectra were taken by a Bruker AV500 Fourier-Transform spectrometer with reference to SiMe$_4$, using solvent DMSO containing 5 wt % of the sample. ESI-MS spectra were recorded by a Shimadzu LC-MS 2010A equipped with a Shimpeck VP-ODS 15 cm × 2.0 mm and a Shimpack GVP-ODS guard column 5 cm × 2.0 mm, using a mixed solvent of DMSO and methanol containing 1 wt % of the sample, and ions were formed for mass spectrometric detection using positive ion electron impact ionization (EI) at

the electron energy of 70 eV. GC was taken in a HP6890 GC equipped with an HP-5column, 30 m × 0.32 mm × 0.25 μm.

Methods
Preparation of Catalysts. 1,3-Propane sultone was reacted with triethylamine to give 3-(triethylamine-*N*-yl)-propane-1-sulfonate (TEA-PS) as a white powder. Then TEA-PS was reacted with an equal mole of hydrochloric acid to give (3-sulfonic acid)-propyltriethylammonium chloride [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl as a white viscous liquid at room temperature. The Brönsted–Lewis acidic ILs were prepared by the reaction of [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl with metal chlorides, including FeCl$_3$, ZnCl$_2$, FeCl$_2$, and CuCl$_2$. The Lewis acidity of IL depends on the metal chloride mass. When the molar fraction of metal chloride was less than 0.5, IL only had Brönsted acidity and no Lewis acidity, and above this value, the obtained IL was Brönsted–Lewis acidic.[19] The reaction formula for the synthesis of IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$) is shown in Figure 1. [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.64$): IR (KBr disc, cm^{-1}): v 3351, 2989, 1621, 1484, 1455, 1396, 1255, 1228, 1151, 1039, 948, 813, 791, 735, 694, 598, 521.^{1}H-NMR (500MHz, D$_2$O, δ): 1.24 (t, $J = 7$ Hz, 3H; CH$_3$), 1.83 (m, 2H; CH$_2$), 2.83 (t, $J = 7$ Hz, 3H; CH$_3$), 3.08 (q, $J = 7$ Hz, 2H; CH$_2$), 4.65 (t, $J = 7$ Hz, 2H; CH$_2$).^{13}C-NMR (500 MHz, D$_2$O, δ): 8.24, 16.85, 47.89, 53.82, 55.93. HRMS (ESI, m/z): 170.7 [ZnCl$_3^-$], 224.1 [HO$_3$S-(CH$_2$)$_3$-N$^+$Et$_3$], 306.6 [Zn$_2$Cl$_5^-$]. The results of IL characterizations indicated that the synthesized IL was the objective compound. Especially, it was concluded that IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.64$) processed Brönsted and Lewis double acidities

Table I. Effects of Different Catalysts on Alcoholysis Reaction of PET[a]

Entry	Catalysts	C_P (%)	Y_D (%)	P_D (%)	Y_E (%)
1	Blank	0	0	0	0
2	ZnCl$_2$	91.6	87.5	96.2	88.1
3	Zn(CH$_3$COO)$_2$	92.7	88.4	96.5	88.6
4	Ti (CH$_3$CH$_2$CH$_2$CH$_2$O)$_4$	93.4	89.7	97.6	89.9
5	H$_2$SO$_4$	70.3	67.3	94.3	67.2
6	[HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl	29.2	25.8	93.6	26.1
7	[HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$)	100	95.3	98.5	95.7
8	[HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-FeCl$_3$ ($x = 0.67$)	89.4	85.8	97.6	85.7
9	[HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-FeCl$_2$ ($x = 0.67$)	89.2	85.5	97.8	85.6
10	[HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-CuCl$_2$ ($x = 0.67$)	81.3	77.8	97.2	77.9
11	[C$_4$mim]Cl-ZnCl$_2$ ($x = 0.67$)	40.3	36.4	95.6	36.6

[a]PET 10.0 g, catalyst 2.0 g, *n*-butanol 11.6 g, $t = 8$ h, $T = 205$°C.

Table II. Effects of Different Mole Ratios of IL Components on Alcoholysis Reaction of PET[a]

Entry	Catalysts	C_P (%)	Y_D (%)	P_D (%)	Y_E (%)
1	[HO$_3$S-(CH$_2$)$_3$-NEt$_3$] Cl-ZnCl$_2$ ($x = 0.50$)	34.5	30.0	94.7	29.4
2	[HO$_3$S-(CH$_2$)$_3$-NEt$_3$] Cl-ZnCl$_2$ ($x = 0.64$)	94.1	90.2	97.6	89.9
3	[HO$_3$S-(CH$_2$)$_3$-NEt$_3$] Cl-ZnCl$_2$ ($x = 0.67$)	100	95.3	98.5	95.7
4	[HO$_3$S-(CH$_2$)$_3$-NEt$_3$] Cl-ZnCl$_2$ ($x = 0.75$)	100	95.9	98.8	95.8

[a]PET 10.0 g, IL 2.0 g, n-butanol 11.6 g, $t = 8$ h, $T = 205°C$.

from the result of HRMS. IL 1-butyl-3-methylimidazolium chlorine [C$_4$mim]Cl was synthesized according to the Ref. 20.

Alcoholysis Reaction of PET. In a typical experiment, 10.0 g PET, 11.6 g n-butanol, and 2.0 g IL were reacted at 205°C for 8 h in a stainless steel autoclave with a 400 r/min stirring agitation (The air in the reactor was excluded with N$_2$ before heating in order to avoid the oxidation reaction, and the pressure of the reaction came from the butanol gasification.). After the reaction, the reaction mixture was cooled to room temperature, and then the unreacted PET was separated by filtration. The filtrate, containing the product DBTP, n-butanol, EG, and IL, was of demixing, and then the product DBTP, EG, and n-butanol were separated from the IL layer at the bottom simply by decantation. The IL layer was reused directly in the cycle experiments. The product DBTP (w_1) was obtained after removing n-butanol and EG by distillation, and its purity (P_D%) was determined by the method of GB 11405-8. The content of EG in the fraction was determined with HP6890 GC, and its yield (w_2) was obtained by the system of GC chemstation according to the area of each chromatograph peak. The conversion of PET was defined as C_B which was the wt % of PET consumed in the reaction. The yield of products DBTP (Y_D) and EG (Y_G) were calculated by: $Y_D\% = (w_1 \times P_D\%)/w_D \times 100$ and $Y_G\% = w_2/w_G \times 100$, where w_D and w_G were the theoretical yield of DBTP and EG, respectively.

RESULTS AND DISCUSSION

Effects of Different Catalysts on the Alcoholysis Reaction

The catalytic performances of different catalysts are given in Table I. It is seen that, when the traditional catalysts were used (Entries 2–5), the PET conversions and the yields of products were less than 90 %. It was indicated that the alcoholysis reaction of PET was not complete. Particularly, the separation of the acidic sludge or emulsion during work-up in those processes was very troublesome. When Lewis acidic IL [C$_4$mim]Cl-ZnCl$_2$ ($x = 0.67$) or Brönsted acidic IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl was used as a catalyst (Entries 11 and 6), the alcoholysis reaction could slightly occur, and PET conversion and yields of both products were poor. Comparing with the above catalysts, Brönsted–Lewis acidic IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$) exhibited better catalytic performance with the 100% conversion of PET and more than 95% yields of products (Entry 7).

The good catalytic performance may be due to the Brönsted and Lewis acidities of IL and their synergetic effect, which is similar to that of a zeolite.[21] The result from IL 1-butyl-3-methylimidazolium chlorozincinate [C$_4$mim]Cl-ZnCl$_2$ ($x = 0.67$) was also determined to show this effect on the catalytic performance of Brönsted–Lewis acidic IL (Entry 11). The metal chlorides had a decisive influence on ILs catalytic performances (Entries 7–10). IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$) showed the best catalytic performance (Entry 7), and IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-CuCl$_2$ ($x = 0.67$) was poor (Entry 10). These results are due to the difference in the Lewis acidic strength of IL. With increasing of the acidity of metal chloride, the Lewis acidity of IL becomes stronger, and IL has a higher catalytic activity.[22] As a result, the catalytic activity of [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$) is higher.

The effects of different mole ratios of ILs components on alcoholysis reaction of PET were also investigated, and the results are summarized in Table II. It was found that the conversion of PET and the yields of products increased with increasing of the molar fraction of ZnCl$_2$ (x). When x value was 0.50, the PET conversion and the DBTP yield were only 34.5% and 30.0%, respectively (Entry 1). The result was similar to that of IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl (Table I, Entry 6). This is due to the fact that IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.5$) only has Brönsted acidity and no Lewis acidity. When x value was more than 0.50 (Entries 2–4), the PET conversion and the DOTP yield rapidly increased, and the alcoholysis reaction was effectively catalyzed. This is explained by that, when the molar fraction of metal chloride (x) is more than 0.5, IL is Brönsted and Lewis acidic, and by increasing x value, the Lewis acidity increases,[22] which increases the catalytic activity of IL. So the alcoholysis reaction is smoothly carried out.

Effects of Reaction Conditions on the Alcoholysis Reaction

The effects of reaction conditions are shown in Table III. The reaction temperature was very important for the alcoholysis reaction. When the temperature was 195°C (Entry 1), PET conversion and the yields of products were only 87.5% and 83.2%, respectively, which was not satisfied. When the temperature was higher than 195°C (Entries 2–3), the PET conversion reached 100% and the yields of products were more than 95%. It was indicated that the alcoholysis reaction easily occurred when the

Table III. Effects of Reaction Conditions on Alcoholysis Reaction of PET[a]

Entry	T (°C)	IL (g)	n-Butanol (g)	C_P (%)	Y_D (%)	P_D (%)	Y_E (%)
1	195	2.0	11.6	87.5	83.2	96.7	83.1
2	205	2.0	11.6	100	95.3	98.5	95.7
3	215	2.0	11.6	100	95.5	98.7	95.8
4	205	1.5	11.6	89.5	85.4	96.6	85.7
5	205	2.5	11.6	100	95.8	98.4	96.1
6	205	2.0	13.5	100	94.9	98.2	95.2
7	205	2.0	9.7	91.4	87.1	95.9	87.2

[a]PET 10.0 g, $t = 8$ h. IL: [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$).
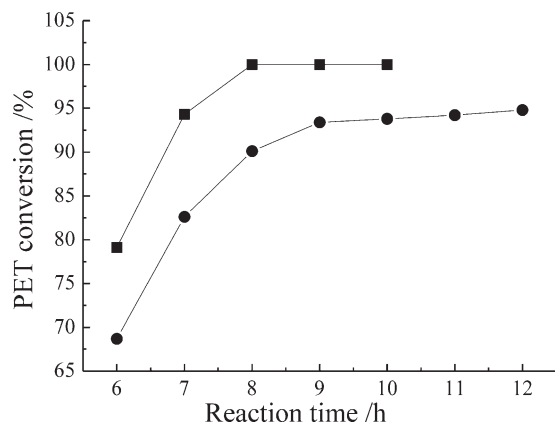
Figure 2. Changes of PET conversion with reaction time at 205°C ($\blacksquare$) and 195°C ($\bullet$).

Figure 3. FTIR spectra of the obtained DBTP.

reaction temperature was high. This is due to that high reaction temperature is in favor of the swelling of PET, and as a result to promote the alcoholysis reaction. With increasing IL dosage from 1.5 g to 2.5 g (Entries 2, 4, 5), PET conversion increased from 89.5% to 100%, and the yields of both products also increased obviously from 85% to 95%. When decreasing *n*-butanol dosage from 13.5 g to 9.7 g (Entries 2, 6, 7), PET conversion decreased from 100% to 91.4%, and DBTP yield also markedly decreased from 95.3% to 87.1%. This result is because, with decreasing amount of *n*-butanol, the solubility of PET in *n*-butanol decreases, which is not conducive to the reaction. So both too small IL and *n*-butanol dosage are unfavorable to PET alcoholysis reaction.

Effect of reaction time on the alcoholysis reaction was also investigated at different reaction temperature. The results are given in Figure 2. At 205°C, PET conversion was 100% when the alcoholysis reaction was carried out for 8 h. However, at 195°C, PET conversion was still less than 95% after 12 h. This is attributed to the difference in dissolubility or swelling of PET under different temperature. It is well known that PET is a soft polymer. It is extremely difficult for PET to react with *n*-butanol when PET dose not dissolve or swell in the reaction medium. However, it was observed that the swelling of PET was much better at 205°C than at 195°C during the experiment, so the reaction of *n*-butanol molecule with PET molecule was much more rapid at 205°C than at 195°C.

Reusability of ILs

The reusability of IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$) in the alcoholysis reaction was examined and the results are shown in Table IV. As shown in Table IV, IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$) was used for seven times without significantly decreasing PET conversion and the yields of DBTP and EG. Therefore, IL had an excellent reusable performance in PET alcoholysis reaction. It is well known that the main factor which affects the reusable performance of IL is its stability under the reaction temperature and reaction fluid surroundings. In the structure of IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$), the alkyl sulfonic acid group is covalently tethered in IL cation,[23] and the anion [Zn$_2$Cl$_5$]$^-$ of IL is inert and sTable in water and Brönsted acid. Therefore, it is reasonable that IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$) has a good reusable performance in the alcoholysis reaction of PET.

Characterization of the Obtained DBTP

The obtained upper phase during PET alcoholysis was distilled to remove *n*-butanol and EG. The residue mainly composed of DBTP was obtained and characterized by IR using a Nicolet 510P FTIR spectrometer. The IR spectrum is shown in Figure 3. The spectra data were as follows: IR (LF, cm^{-1}): ν 3012, 2983, 2924, 2911, 1772, 1630, 1462, 1322, 1296, 1162, 1153, 1066, 1031, 923, 815, 786. The IR spectra data indicated that the hydroxyl absorption peak (about 3400 cm^{-1}) of PET did not appear, and the characterized sample was only DBTP. It is demonstrated that PET is completely depolymerized into products of DBTP and EG and no intermediates of oligomers exist.

CONCLUSIONS

The *n*-butanol alcoholysis reaction of PET was investigated. IL [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$) was a good catalyst for the reaction with 100% conversion of PET and more than 95% yields of products. It was also found that a synergetic effect of Brönsted and Lewis acid sites enhanced the IL catalytic performance. The reusability of IL was good and after it was used

Table IV. Reusability of [HO$_3$S-(CH$_2$)$_3$-NEt$_3$]Cl-ZnCl$_2$ ($x = 0.67$)[a]

Item	Cycle						
	1	2	3	4	5	6	7
C_P (%)	100	100	100	100	100	100	100
Y_D (%)	95.3	94.8	95.2	95.0	94.6	94.3	94.9
P_D(%)	98.5	98.4	98.7	98.2	98.6	98.7	98.4
Y_E (%)	95.7	95.1	95.3	94.9	94.8	94.3	95.0

[a]PET 10.0 g, IL 2.0 g, *n*-butanol 11.6 g, $t = 8$ h, $T = 205$°C.

seven times, PET conversion and the yields of DBTP and EG did not significantly decrease.

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