

Short communication

Synthesis of plasticizer ester using acid-functionalized ionic liquid as catalyst

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Abstract

Several plasticizer esters were synthesized by using acid-functionalized ionic liquids as catalyst. The results indicated that HSO₃-functionalized Brønsted acidic ionic liquids show better catalytic and reusable performance than non-functionalized ionic liquids. For each plasticizer ester examined, one or two ionic liquids with high catalytic activity were chosen. Especially, the ionic liquids could be separated easily from the products and be reused at least six times with the conversion of the acid not less than 95%. Therefore, an environmental friendly approach for the synthesis of plasticizer ester is provided.

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1. Introduction

Plasticizer esters are a kind of critical accessory ingredient for the macromolecule materials, which can promote the plasticization efficiency and integration processing performance of these materials. The catalysts used in traditional plasticizer esters synthesis process were mainly sulfuric acid, titanate and solid acid. The sulfuric acid cannot be reused and have many disadvantages such as equipment corrosion, more byproduct, tedious workup procedure. Also, the titanate [1] catalysts have some disadvantages such as high cost, difficult recovery and more consumption of energy. Although solid acid [2] catalyst can overcome some of the above-mentioned shortcomings, it has its own disadvantages such as easy deactivation, operation loss and high mass transfer resistance, which limit its application. The room temperature ionic liquid, a kind of environment-friendly solvent and catalyst, got broad attention of scholars from various fields such as synthesis, catalysis, separation and electrochemistry [3], due to its adjustable physical and chemical properties. In recent years, research of ionic liquids is focused on functionalized ionic liq-

uids (FIL), which can provide better specialized functions with functional group linked with its cation or anion. Since 2002, Cole et al. [4] first published an article about sulfonic FIL with strong Brønsted acidity; the research and application of various FILs have received more and more attention [5,6]. Among them there were many articles on the subject of FIL used in different esterifications [7,8], but to the best of our knowledge, no articles about synthesis of those plasticizer ester using FIL has been published.

In this work, we wish to report that several HSO₃-functionalized Brønsted acidic ionic liquids (Fig. 1.) were prepared and they were used in the synthesis of plasticizer ester. The stability and reuse performance of these FIL were examined in comparison with the non-functionalized ionic liquids. A group of ionic liquids that showed the best catalytic activity and reused performance is found in the synthesis of plasticizer ester.

2. Experimental

2.1. Chemicals and instruments

1-Methylimidazole (MIM, 99%), purchased from Zhejiang Kaile Chemicals Co. Ltd.; 1,3-propane sulfone (1,3-PS, 99%),

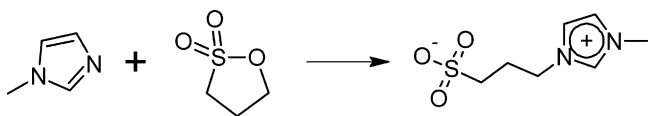
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provided by WuhanFengfan Chemicals Co. Ltd.; All other chemicals (AR) were commercially available and used without further purification unless otherwise stated. NMR spectra were recorded on a BRUKER AV500 spectrometer in D₂O and calibrated with tetramethylsilane (TMS) as the internal reference. IR measurements were performed on a Nicolet 510P FT-IR absorption spectrometer using KBr optics and liquid film.

2.2. Preparation of functionalized ionic liquids

2.2.1. 3-(1-Methylimidazolium-3-yl)propane-1-sulfonate (MIM-PS)

Under vigorous stirring, 1,3-propane sulfone was dissolved in toluene; equal-mole 1-methyl imidazole was dropped slowly in an ice bath. After the dropping was finished, the mixture was slowly heated up to room temperature and stirred for 2 h, and then the reaction mixture was filtered to get the white precipitate. The precipitate was washed with ethyl acetate three times and dried at 100 °C for 5 h, giving MIM-PS as a white powder (yield 95.6%). ¹H NMR (500 MHz, D₂O): δ 2.26(m, 2H), 2.86(t, 2H), 3.83(s, 3 H), 4.30(t, 2H), 7.38(s, 1H), 7.46(s, 1H), 8.70(s, 1H). ¹³C NMR (125 MHz, D₂O): δ 24.79, 35.46, 46.97, 47.41, 121.85, 123.50, 135.82. IR(KBr): ν 3450, 3154, 3110, 1640, 1575, 1195, 1043, 746, 622, 532.



2.2.2. 1-Methyl-3-(3-sulfopropyl)-imidazolium hydrogensulfate ([HSO₃-pmim][HSO₄])

Under vigorous stirring, MIM-PS was dissolved in water and equal-mole sulfuric acid was dropped slowly at room tempera-

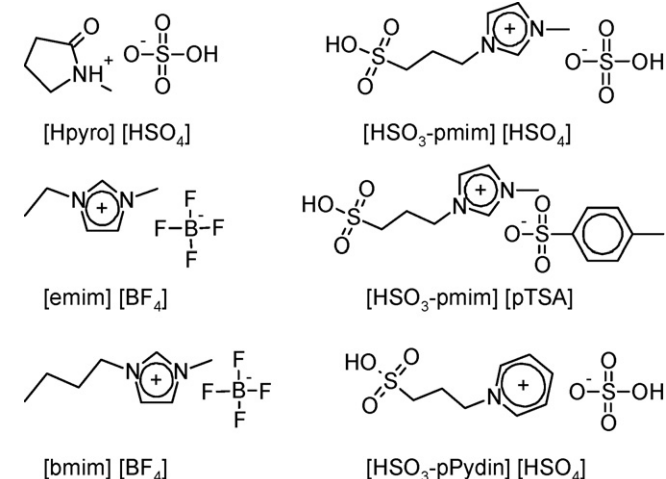
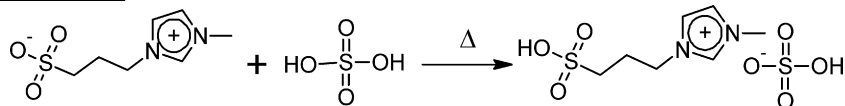


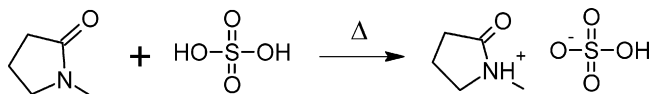
Fig. 1. Structures of ionic liquids prepared and used in this paper.

ture. After the dropping was finished, the system was slowly heated up to 90 °C and stirred for 2 h, then the water was removed under vacuum (5–10 mmHg) at 90 °C, giving [HSO₃-pmim][HSO₄] as a light yellow viscous liquid (yield 99%). ¹H NMR (500 MHz, D₂O) δ 2.11(m, 2H), 2.71(t, 2H), 3.71(s, 3H), 4.16(t, 2H), 7.25(s, 1H), 7.32(s, 1H), 8.53(s, 1H). IR(LF):ν 3437, 3157, 2970, 1722, 1653, 1574, 1230, 1172, 1029, 853, 582.



2.2.3. 1-Methyl-2-oxopyrrolidinium hydrogen sulfate ([Hpyro][HSO₄])

Under vigorous stirring, weighed 1-methylpyrrolidin-2-one placed in flask and equal-mole sulfuric acid was dropped in slowly at room temperature. After the dropping was finished, the system was slowly heated up to 90 °C and stirred for 2 h, then the water was removed under vacuum (5–10 mmHg) at 90 °C, giving [Hpyro][HSO₄] as a light yellow viscous liquid (yield 98%). ¹H NMR (500 MHz, D₂O) δ 1.49 (m, 2H), 1.93 (t, 2H), 2.28 (s, 3H), 2.95 (t, 2H). IR (LF): ν 3384, 2973, 2888, 2482, 1684, 1485, 1303, 1164, 1042, 975, 873, 578. Other ionic liquids (Fig. 1) used in this paper were synthesized according to literatures [4,6–9].



2.3. General procedure for synthesis of plasticizer ester

Weighed amounts of acid, alcohol, ionic liquid, cyclohexane were added to a flask with a reflux condenser, a water segregator and magnetic stirring apparatus. The esterification reaction was typically carried out for 2–12 h at the desired temperature with vigorous stirring. Then reaction mixture became biphasic, the upper phase (volume V_R), which was mainly desired ester, could be isolated simply by decantation; the lower phase, viscous ionic liquid, could be reused without any disposal. Conversion data were based on acid through NaOH titration. Conversion of acid was calculated using the following formula:

$$\text{Conversion of acid} = \left(1 - \frac{C_{\text{NaOH}} \times V_{\text{NaOH}} \times V_{\text{R}}}{N_{\text{Acid}}} \right) \times 100\%$$

3. Results and discussion

Three kinds of plasticizer ester: dioctyl phthalate (DOP), dioctyl sebacate (DOS) and dibutyl phthalate (DBP) were synthesized using various kind ionic liquids and the results are shown in Table 1.

According to Table 1, using neutral ionic liquids as catalyst (Table 1 entries 3 and 4), the conversions of acid were only a little higher than that of blank experiment (Table 1 entry 1). Therefore, the neutral ionic liquids have weak catalytic activity due to their weak acidity. The catalytic activity of the [bmim][BF₄] (Table 1

Table 1
Results of plasticizer ester synthesis using different ionic liquids^a

Entry	Ionic liquid	Time (h)	DOP, PA conversions (%) ^b T = 120–130 °C	DOS, SA conversions (%) ^b T = 90–110 °C	DBP, PA conversions (%) ^b T = 120–135 °C
1	Blank	12	32	72	51
2	H ₂ SO ₄	1.5	98	99	98
3	[emim][BF ₄]	12	36	82	62
4	[bmim][BF ₄]	12	49	86	63
5	[Hpyro][HSO ₄]	1.5	Dissolved	99	Dissolved
6	[HSO ₃ -pmim][pTSA]	1.5	91	97	98
7	[HSO ₃ -pmim][HSO ₄]	1.5	98	99	99*
8	[HSO ₃ -pPydin][HSO ₄]	1.5	98*	98*	99*

PA: phthalic anhydride; SA: sebacic acid.

^a Reaction conditions: *n*(acid):*n*(alcohol) = 1:2.5; IL dosage: 5 wt%; 7 h.

^b Conversion data were based on acid through NaOH titration.

Table 2
The conversion of acid using reused ionic liquids^a

Ionic liquids	Ester	Conversion of acid (%)							
		Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7	Cycle 8
[HSO ₃ -pmim][pTSA]	DBP	99	99	98	97	96	95		
[HSO ₃ -pmim][HSO ₄]	DOP	99	99	98	99	98	97	96	95
[HSO ₃ -pmim][HSO ₄]	DOS	99	99	99	99	99	99	98	98
[Hpyro][HSO ₄]	DOS	99	99	99	99	99	99	99	99

^a Reaction conditions: IL dosage: 15 wt%; others were same as Table 1.

entry 4) was better than that of [emim][BF₄] (Table 1 entry 3), this is probably because the butyl on the ring of imidazole brings more lipophilicity [10] than the ethyl of the latter. This suggested that more dispersibility of ionic liquid in the reaction fluid could enhance its catalytic activity.

The ionic liquids, which have H⁺ on its anions [Hpyro][HSO₄] (Table 1 entry 5), could dissolve gradually in the reaction fluids (DOP and DBP) and could not be separated with the products. On the contrary, [Hpyro][HSO₄] showed good catalytic activity and separability when it was used in synthesis of DOS. This phenomenon can be explained in term of two aspects. First, the H⁺ on its anions bring it high acid catalytic activity than those of neutral ionic liquids. On the other hand, because of the linear molecular shape, DOS shows weaker polarity than DBP and DOP, which give it good separability with the polar ionic liquids [Hpyro][HSO₄]. It is suggested that both structure of

ionic liquid and product have significant effect on the uses of ionic liquids.

Three kinds of HSO₃-functionalized ionic liquids (Table 1 entries 6, 7, and 8) were also examined and showed better catalytic activity than the above-mentioned ionic liquids and was nearly equivalent to that of H₂SO₄ (Table 1 entry 2). It was due to these HSO₃-FIL has two H⁺ at both anion and cation, which provide it more acidity.

[HSO₃-pmim][HSO₄] (Table 1 entry 7) has better conversions than that of [HSO₃-pmim][pTSA] (Table 1 entry 6). We could attribute this result to the following two reasons: first the acidity of HSO₄⁻ is stronger than the pTSA⁻ when the cation is same; secondly HSO₄⁻ presents better immiscibility with the produced ester which facilitates the shifting of the esterification reaction equilibrium to the product side. These were consistent with the results of literature 7.

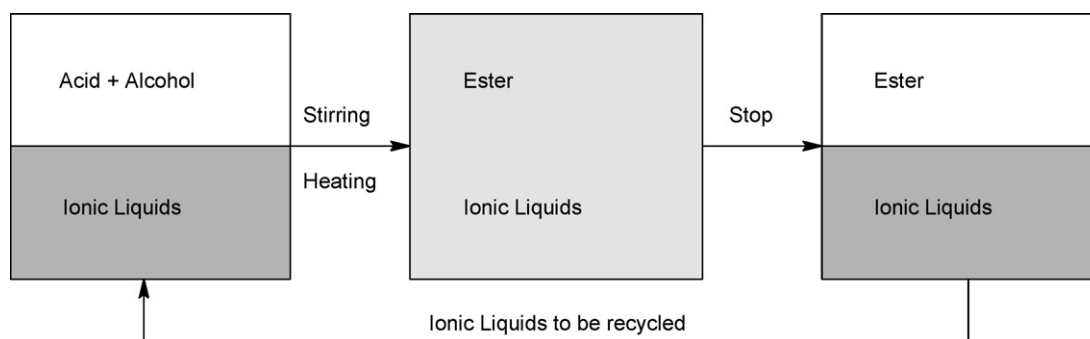


Fig. 2. Scheme of reaction procedure.

However, the reuse performance of three kinds of HSO₃-functionalized ionic liquids were greatly different. [HSO₃-pPydin][HSO₄] were decomposed quickly in all these three esters. It was probably because the cation structure of [HSO₃-pPydin] has less steric hindrance than [HSO₃-pmim] which has a more side chain, so that [HSO₃-pPydin] is liable to crystal and return to the form of intermediate salt among the reaction fluids. The same result was obtained when [HSO₃-pmim][HSO₄] was used in synthesis of DBP. It can be explained that DBP is the most polar ester compared with DOS and DOP, and the polarity facilitated the decomposing of [HSO₃-pmim][HSO₄].

The reuse results of chosen ionic liquids are shown in Table 2. Among the three plasticizers, DOS is of the weakest polarity. Two kinds of ionic liquid, fit for DOS, can be reused more than eight times and the conversion of acid is not less than 98%. On the contrary, only one ionic liquids [HSO₃-pmim] [pTSA] is suitable for DBP, which is of the strongest polar in these three esters. However, for this reaction, [HSO₃-pmim] [pTSA] can be reused for 6 times, and the final conversion of acid decrease to 95%.

In summary, the process of this reaction system could be expressed in the following schematic Fig. 2.

4. Conclusion

For the synthesis of plasticizer ester, HSO₃-functionalized Brønsted acidic ionic liquids show better catalytic and reuse performances than the non-functionalized ionic liquids. The polarity of ester has significant effect on the ionic liquids choosing. Therefore, an environment-friendly approach for the synthesis of plasticizer ester is provided.

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