



Synthesis and characterization of a new hydroxyl functionalized diacidic ionic liquid as catalyst for the preparation of diester plasticizers



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ABSTRACT

Two new functionalized diacidic ionic liquids (FDAILs) including hydroxyl functionalized diacidic ionic liquid (HFDAIL) and sulfonated diacidic ionic liquid (SFDAIL) were synthesized and characterized by ¹HNMR, ¹³CNMR and FT-IR. The catalytic activities of these FDAILs were examined in esterification reaction of anhydrides with some alcohols to give corresponding dialkyl plasticizers under solvent-free conditions. The results indicate that HFDAIL, as hydroxyl-bearing catalyst, show better catalytic performance. Under the optimum conditions, using HFDAIL, the conversion of phthalic anhydride was high and diester plasticizers were obtained with good to excellent yields in the presence of only 10 mol% of ionic liquid. All the produced diesters could be easily recovered due to their immiscibility with the ionic liquid. Recycling experiments suggests that these ionic liquids can be reused several times without remarkable loss in their catalytic activity.

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1. Introduction

Plasticizers are almost a class of oligomers which are used in formulation of explosive fuels and leads to improvement in mechanical properties, softening polymeric tissue and flexibility [1–5]. One of the most popular plasticizers in double-based propellants are ester plasticizers such as diethyl, dibutyl and dioctyl phthalates, which are a class of the neutral plasticizers. Ester plasticizers are widely used in non-military industries, e.g. in formulation of PVC and cellulosic resins to manufacture of plastic products such as tube, blood bag and etc. [6–8]. The catalysts used in ester plasticizers synthesis process can be both homogeneous and heterogeneous. Most commonly used catalysts in traditional methods include sulfuric acid and solid acids [9–12]. The sulfuric acid cannot be reused and also has other disadvantages such as equipment corrosion, more byproducts production, tedious workup process and environmental problems. Furthermore, it is very difficult to separate and reuse the mineral acidic catalysts from the reaction mixture [13–16]. Solid acid catalysts [17–19] have capability to overcome many of the above mentioned defects. However, the use of solid acids in this reaction has many disadvantages including easy deactivation and high mass transfer resistance, which limit their efficiency [20]. Along this line, there is a need to expand an environmentally friendly and economic method for synthesis of ester plasticizers using esterification process.

On the other hand, the room temperature ionic liquids due to their tunable physical and chemical properties have attracted the attention of scientists in various fields such as synthesis, catalysis, separation and

electrochemistry [21]. In the recent years, researchers are focused on synthesis of functionalized ionic liquids (FILs), in order to obtain better characteristics. Cole et al. [22] reported a pioneering work on sulfonic FIL with strong Brønsted acidity. Many progress have been achieved in this field and divers FIL for special applications have been reported [23,24]. Among them there are many studies on the use of FIL in different esterification processes [25,26]. However, to the best of our knowledge, there is no report on the synthesis of plasticizers using ionic liquids of this study.

In continuation of our works on synthesis and application of ionic liquids in the organic synthesis [27–30], herein, we would like to introduce two novel functionalized diacidic ionic liquids to be used in synthesis of diester plasticizers (Scheme 1). We have chosen ILs with these functional groups as catalysts for esterification reactions because: (1) they are immiscible with a number of organic solvents, (2) they are soluble in a wide range of inorganic and organic materials, (3) high hydrophilicity and acidity of the hydroxyl functionalized catalyst and (4) They can be recycled for several times. The structures of ionic liquids used in this study are shown in Fig. 1.

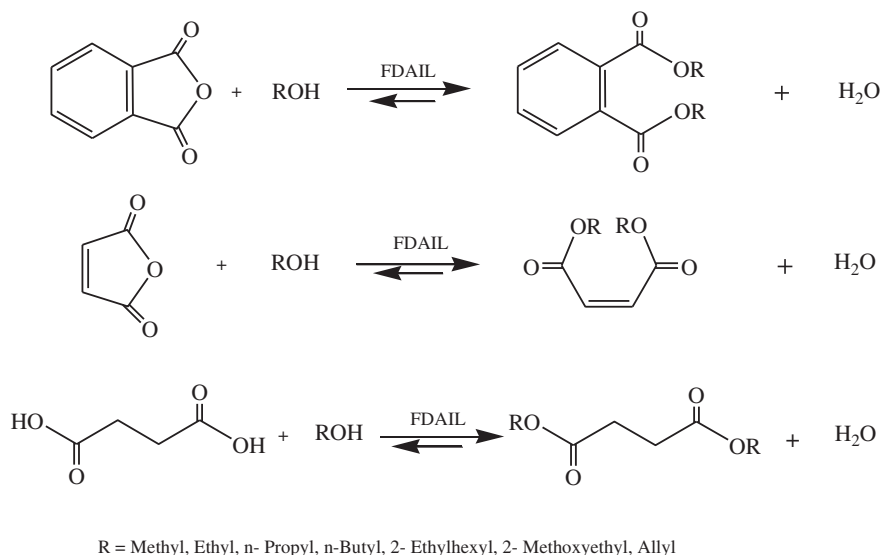
2. Experimental

2.1. Material and methods

All solvents and chemicals were commercially available and used without further purification and purchased from Merck and Fluka chemical companies. NMR spectra were recorded on a Bruker DRX - 500 spectrometer in DMSO or D₂O and calibrated with tetramethylsilane (TMS) as the internal reference. IR measurements were performed on a Nicolet 800

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Scheme 1. Esterification of phthalic and maleic anhydrides and succinic acid with alcohols using synthesized FDAILs.

instrument using KBr or liquid film. Quantitative product analysis was conducted by gas chromatography on Hewlett Packard HP-5890 instrument equipped with HP-1 column (30 m long, 0.5 mm diameter), and flame ionization detector (FDI), using N_2 as carrier gas at a flow rate of $2 \text{ mL} \cdot \text{min}^{-1}$.

2.2. Preparation of hydroxyl and sulfonic acid functionalized diacidic ionic liquids

2.2.1. Preparation of 2,2-bis ((3-methylimidazolidin-1-yl) methyl) propane-1,3-diol bromide salt (IL-Br)

A mixture of 0.52 g 1-methylimidazole (6.25 mmol, 0.5 mL) and 0.65 g 2,2-bis (bromomethyl)-1,3-propanediol (2.5 mmol) was heated at 150°C for 8 h under magnetic stirring. After cooling to room temperature, the obtained solid was washed three times with acetonitrile and the residue was dried in an oven at 100°C for 2 h, giving IL-Br as a white powder (yield: 95.25%, melting point = 150°C). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ (ppm) = 3.24 (s, 4H; CH_2N), 3.84 (s, 6H; CH_3), 4.31 (s, 4H; CH_2OH), 4.72 (s, 2H; OH), 7.42 (dd, $J = 10 \text{ Hz}$, $J = 5 \text{ Hz}$, 4H; $\text{CH}=\text{CH}$), 8.72 (s, 2H; NCHN). $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO}-d_6$): δ (ppm) = 35.94, 45.21, 48.58, 58.48, 123.72, 123.86, 137.38. FT-IR (KBr, ν/cm^{-1}): 620.8, 770.7, 829.8, 1060.5, 1164.9, 1450.8, 1573.1, 1760.4, 1655.9, 2935.4, 3260.7.

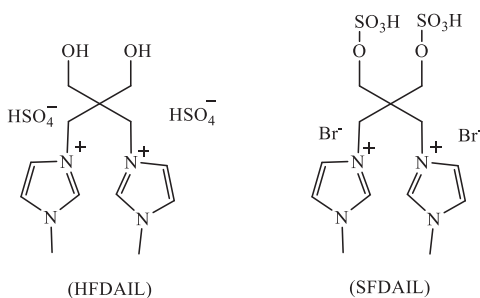
2.2.2. Preparation of 3,3'-(2,2-bis ((sulfoxy) methyl) propane-1,3-diyl) bis (1-methyl-1H-imidazole-3-ium) bromide (SFDAIL)

The sulfonic acid functionalized ionic liquid, was prepared by nucleophilic substitution reaction of IL-Br salt with chlorosulphonic acid. To

do this, 0.8 g IL-Br salt (2 mmol) was solved in acetonitrile. Then 0.5 mL chlorosulphonic acid (8 mmol) was dropped slowly at room temperature. After the dropping was finished, the mixture was stirred for 4 h at the same temperature. The reaction mixture was filtered to get the yellow precipitate. It was washed with toluene three times and dried under vacuum at 100°C for 1 h, giving SFDAIL as a yellow solid (yield: 97.5%). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ (ppm) = 3.33 (s, 4H; CH_2N), 3.47 (s, 6H; CH_3), 4.04 (s, 4H; CH_2OH), 5.33 (s, 2H; SO_3H), 7.06 (d, $J = 5 \text{ Hz}$, 4H; $\text{CH}=\text{CH}$), 8.30 (s, 2H; NCHN). $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO}-d_6$): δ (ppm) = 36.19, 43.83, 48.27, 63.89, 123.88, 124.26, 137.79. FT-IR (KBr, ν/cm^{-1}): 587.3, 782.5, 1019.1, 1251.7, 1458.7, 1584.9, 1709.1, 3160.1.

2.2.3. Preparation of 3,3'-(2,2-bis (hydroxymethyl) propane-1,3-diyl) bis (1-methyl-1H-imidazole-3-ium) hydrogen sulfate (HFDAIL)

The hydroxyl functionalized ionic liquid was prepared by anion exchange of IL-Br salt. 0.5 g (1.2 mmol) of IL-Br salt, obtained in the first stage, was dissolved in methanol (30 mL) under stirring. After that the system was slowly heated up to 60°C in an oil bath. Then 0.13 mL sulphuric acid (2.4 mmol) was dropped and stirred for 24 h. Upon completion of the reaction, the solvent was evaporated under vacuum. The resultant material was washed with dichloromethane ($3 \times 5 \text{ mL}$) and then dried under vacuum at 100°C for 2 h to afford HFDAIL as yellow viscous oil liquid at 95% yield. $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ (ppm) = 3.20 (s, 4H; CH_2N), 3.81 (s, 6H; CH_3), 4.27 (s, 4H; CH_2OH), 4.74 (s, 2H; OH), 7.39 (dd, $J = 10 \text{ Hz}$, $J = 5 \text{ Hz}$, 4H; $\text{CH}=\text{CH}$), 8.69 (s,



(SFDAIL): 3,3'-(2,2-Bis ((sulfoxy) methyl) propane-1,3-diyl) bis (1-methyl-1H-imidazole-3-ium) bromide
(HFDAIL): 3,3'-(2,2-Bis (hydroxymethyl) propane-1,3-diyl) bis (1-methyl-1H-imidazole-3-ium) hydrogen sulfate

Fig. 1. Structures of FDAILs used in this study.

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