

Catalytic Synthesis of Diphenolic Acid from Levulinic Acid over Bronsted Acidic Ionic Liquids

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SO₃H-based acidic ionic liquids were used as Brønsted acid catalysts for synthesis of diphenolic acid (DPA) from the condensation of phenol and levulinic acid, a platform chemical from renewable materials. Evidence is presented that the product with *p,p'*- and *o,p'*-isomers was obtained. Under the optimal conditions, the 93.2 mol% yield of DPA and close to 100% selectivity to *p,p'*-DPA were achieved in a process promoted by [BSMim]HSO₄. The favorable results can be attributed to the special structures of ionic liquids and thiol compound involvement. Furthermore, a mechanism of condensation promoted by acidic ionic liquid with ethanethiol is proposed.

Keywords: Diphenolic acid; Levulinic acid; Ionic liquids; Condensation; Platform chemical

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INTRODUCTION

Nowadays, with increasing awareness that depletion of non-renewable resources can adversely affect our environment and human development, efficient exploitation and more effective utilization of biomass-derived levulinic acid (LA) have attracted much attention all around the world (Corma *et al.* 2007). Moreover, the development of ecologically friendly polymer monomers based on biomass platform chemicals has received significant attention. The national renewable energy laboratory (Denver, USA) identified LA as one of a number of key sugar-derived platform chemicals that can be produced from lignocellulosic biomass through hydrolysis/dehydration of hexose sugar (Bozell and Petersen 2010; Rackemann and Doherty 2011; Vyver *et al.* 2011). Levulinic acid that is obtained from bio-refinery operations can be expected to open up new opportunities for the cost-effective production of chemicals from the bio-renewable feedstocks. LA has frequently been suggested as the starting material for a wide number of compounds (Bozell *et al.* 2000; Cha and Hanna 2002; Chen *et al.* 2011; Yan *et al.* 2013; Yan and Chen 2013). Condensation of LA with two moles of phenol to the polymer monomer diphenolic acid (DPA) is a potentially important application in light of growing interest in biomass-derived platform molecules (Zúñiga *et al.* 2012).

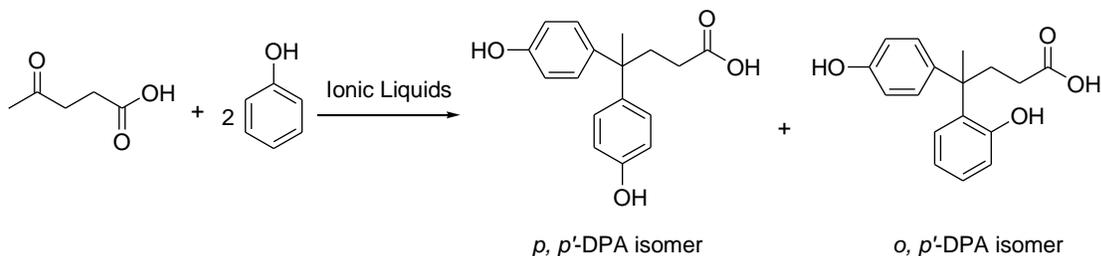
DPA is expected to be a potential substitute for bisphenol A, the primary raw material of epoxy resin and polycarbonates (Kricheldorf *et al.* 2003; Zúñiga *et al.* 2011), which are widely used as a chemical intermediate in paint formulations, protective and decorative coatings and finishes, lubricating oil additives, cosmetics, surfactants, plasticizers, and textile chemicals (Liu *et al.* 2012). Also, DPA is expected to be amenable to chemical modification of its multifunctional groups, potentially offering

much more functionalized materials (Zhang and Moore 2002). The development of DPA as a replacement for bisphenol A and the investigation of the properties of the resulting polymers will provide new sustainable opportunities for the chemical industry (Mehdi *et al.* 2008).

Traditionally, the synthesis of DPA has been investigated using strong Brønsted mineral acids such as H_2SO_4 and HCl . These acids usually suffer from disadvantages such as corrosivity, difficulties in separation, and expensive waste treatment (Bader and Kontowicz 1954). In recent years, the environmental and economic considerations have encouraged the replacement of the toxic and corrosive reagents so that heterogeneous solid acid catalysts have played a key role in the production of DPA. The synthesis of DPA has been investigated using mesoporous $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{SBA-15}$ composite as a heterogeneous catalyst, and excellent TOF over 50 h^{-1} was obtained at $100 \text{ }^\circ\text{C}$ (Guo *et al.* 2007, 2008; Li *et al.* 2009). In addition, 85% of DPA yield was obtained over Cs-substituted Wells-Dawson type heteropolyacid as catalyst at $150 \text{ }^\circ\text{C}$ (Yu *et al.* 2008). Furthermore, sulfonated hyperbranched poly(arylene oxindole)s was synthesized to catalyze the condensation of phenol and LA with 1:1 molar ratio of thiols as additive (Vyver *et al.* 2012). Although these more robust and greener catalysts were examined, the intrinsic drawbacks of solid heterogeneous catalysts including low catalytic active sites and their high susceptibility to leaching have given rise to moderate yields of DPA, and there is still a need for further improvement.

Ionic liquids are the focus of interest of various research and development groups based on their interesting chemical and physical properties (Werner *et al.* 2010). Some acidic ionic liquids have been shown to be excellent catalytic media and have been applied to many kinds of organic reactions (Wang *et al.* 2011), especially for reactions involved in bio-based chemicals (Tan *et al.* 2009; Pinkert *et al.* 2009; Ya'aini and Amin 2013), due to their inherent strong acidity and thermal stability. Thiol-containing acid ionic liquids were prepared for the condensation of phenol and LA, which offered both a high yield of DPA (over 90 mol%) and the ratio exceeding 100 of *p,p'*-DPA to *o,p'*-DPA (Liu *et al.* 2013). However, there is still a considerable incentive for the development of effective, accessible, and low-cost acidic ionic liquids because of the difficulty and high price of the synthesis of CF_3SO_3 -based ionic liquids.

In this paper, we synthesized a series of acidic ionic liquids from low-cost mineral acid (H_2SO_4) as catalysts for the DPA synthesis as shown in Scheme 1.



Scheme 1. Condensation of LA and phenol to DPA catalyzed by ionic liquid

In terms of the application of these acidic ionic liquids for DPA synthesis, they possess at least two advantages: (1) designable structure which enables the preparation of task-specific catalysts containing both acid sites and thiols, and (2) low solubility in some organic extracts allowing easy recycling. We first report the favorable results on the

condensation of phenol and renewable feedstock LA, which is catalyzed with [BSMim]HSO₄ ionic liquid by adding a catalytic amount of ethanethiol to improve the yield of DPA. Furthermore, a plausible mechanism of condensation promoted by acidic ionic liquid with ethanethiol will be proposed.

EXPERIMENTAL

Materials

Pyridine, phenol, H₂SO₄, acetone, ethanol, magnesium sulfate, diethyl ether, and ethyl acetate were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. *N*-Methylimidazole, butyl chloride, 1,4-butane sultone, trifluoromethanesulfonic acid, allyl chloride, sulfamic acid, and levulinic acid were supplied by J&K chemical Ltd. and used as received. Nanopure water was used for all reactions. All chemicals were analytical grade reagents and used as received without further purification.

Synthesis of Ionic Liquids

Ionic liquids used were prepared according to the methods in the literature (Yoshizawa *et al.* 2001). A typical procedure for preparation of [BSMim]HSO₄ was as follows: To 150 mL toluene in a 500 mL three-necked round-bottom flask equipped with mechanical stirrer, 1,4-butanedisulfone (51.1 mL, 0.5 mol) was added followed by an equal-molar amount of *N*-methylimidazole (39.6 mL, 0.5 mol) transferring at room temperature. The mixture was kept stirring for overnight to form white precipitate. Then the white solid was filtered out, washed with diethyl ether thrice (30 mL × 3 mL) to remove non-ionic residues, and dried at 80 °C under vacuum for overnight to get the zwitterion, 4-(1-methylimidazolium-3-yl)butane-1-sulfonate (yield 97.1 %). ¹H NMR data confirming this composition were as follows: (400 MHz, D₂O): δ 1.670 (m, 2H), 1.977 (m, 2H), 2.878 (m, 2H), 3.851 (s, 3H, *J* = 3.0 Hz), 4.203 (m, 2H), 7.414 (m, 1H), 7.475 (m, 1H), 8.710 (s, 1H). Next, the white zwitterion was charged into 100 mL H₂O in a 500 mL round-bottom flask, and a stoichiometric amount of concentrated sulphuric acid was added dropwise at room temperature under vigorously magnetic stirring. Then, the reaction mixture was gradually heated up to 90 °C and kept stirring for 8 h followed by removing water under vacuum at 90 °C, giving 1-(4-sulphonic acid)butyl-3-methylimidazolium hydrogen sulphate ([BSMim]HSO₄) ionic liquid (yield 98.0 %). ¹H NMR data confirming this composition were: (400 MHz, DMSO): δ 1.586 (m, *J* = 7.32 Hz, 2H), 1.905 (m, *J* = 7.44 Hz, 2H), 2.624 (t, *J* = 7.56 Hz, 2H), 3.873 (s, 3H), 4.204 (t, *J* = 7.04 Hz, 2H), 7.724 (m, *J* = 1.64 Hz, 1H), 7.786 (m, *J* = 1.64 Hz, 1H), 9.177 (s, 1H), 9.294 (bs, 2H).

Synthesis of DPA

The condensation of LA with phenol was carried out in a sealed stainless vessel with magnetic stirrer, and given as an example of the procedure. A typical experiment included a mixture of LA (5.0 g, 43.4 mmol), phenol (16.3 g, 173.7 mmol), and [BSMim]HSO₄ ionic liquid (6.9 g, 21.7 mmol). The reaction mixture was heated to 60 °C with stirring for 24 h. After cooling to room temperature, a measured amount of methanol was added, and the resulting mixture was sampled and analyzed by high-performance liquid chromatography (HPLC; Agilent 1200; USA) with a DAD detector at 280 nm. Chromatographic separation was performed on a ZORBAX Eclipse XDB-C18 column

(300 × 7.8 mm) (1200 series, Agilent Technologies, 250 × 4.6 mm, USA) at 30 °C. The eluent of MeOH-H₂O (70: 30) was used with a volumetric flow rate of 0.5 mL min⁻¹. The temperature of DAD detector was 40 °C, and the injection volume was 20 μL. The concentrations of LA, DPA (*p,p'*) and DPA (*o,p'*) were determined simultaneously with the retention time of 5, 9, and 11 min, respectively, using calibration curves obtained by external standard method based on the equation. The system was set up as follows: DPA: Area = 5048.03192 × Amt-2.6597099, LA: Area = 3396.888 × Amt-1.4218025. The products were also confirmed with GC-MS (Agilent 6890-5973). The column used was ZB-5ms from Phenomenex (30 m × 0.25 mm × 0.50 μm). Furthermore, the liquid mixture was extracted with ethyl acetate for three times. After the extract was dried over magnesium sulfate, evaporation of the ether gave the product which was recrystallized from ethanol (51% yield; mp 168 °C).

RESULTS AND DISCUSSION

Screening of Ionic Liquids and Acidic Catalysts

In a continuation of our earlier studies on ionic liquid-catalyzed organic reaction (Liu *et al.* 2013), some acidic ionic liquids and conventional acidic catalysts were screened for the condensation of LA with phenol under the same reaction conditions, and the results are presented in Table 1. The weight of the ionic liquids was varied to maintain the mole amount of acidic catalyst in every reaction.

Initially, the condensation reaction between phenol and LA gave rise to only 2.7% conversion of LA in the absence of catalyst, which indicated that the reaction could not be auto-catalyzed by the carboxylic group of LA. The ionic liquid [BSMim]CF₃SO₃ gave the best result with 80.7% conversion of LA and 79.3% yield of DPA (entry 3) among these acidic catalysts for condensation of LA with phenol. A plausible explanation is based on the known ability of fluorine-containing ILs to eliminate HF in the presence of a trace amount of water under elevated temperatures that should catalyze the condensation process (Putilova *et al.* 2005; Wasserscheid and Welton 2008). The [BSMim]OAc was also active for the reaction, and only 33.6% of product was formed (entry 2), which probably was due to the relative low acidity of [BSMim]OAc compared with [BSMim]CF₃SO₃. As for [BSMim]HSO₄, 75.1% conversion of LA and 73.8% yield of DPA were obtained (entry 4), which was better than the data derived from the ionic liquid [Bpy]HSO₄ (entry 5). This demonstrated that the anions of ionic liquids used herein played a dominant role in this condensation, which is a typical Brønsted acid-catalyzed reaction. At this rate, it could be illustrated that the SO₃H group attached to the cations of ionic liquids provided less function than anions of ionic liquids to this reaction, as can be seen from the comparison results of [BSMim]OAc, [BSMim]CF₃SO₃, and [BSMim]HSO₄. In addition, it is worth noting that the yield of DPA was not decreased dramatically when no additive of ethanethiol was introduced, but the selectivity to *p,p'*-DPA was affected significantly. It has been stated that the condensation of phenol with acetone can be catalyzed by strong acids alone, but the activity and selectivity can both be increased dramatically by adding a thiol (Margelefsky *et al.* 2008; Zeidan *et al.* 2006). Thus, these results underscore the indispensability of sulfur-containing compounds in the diphenolic acid production.

Generally, the two structural isomers of DPA were formed in the condensation of LA with phenol, and striving for the high selectivity to *p,p'*-isomer always is of important

meaning to researchers. It can be seen that the selectivity to *p,p'*-DPA isomer over the *o,p'*-DPA isomer obtained from the condensation catalyzed by ionic liquids were obviously higher than other acidic catalysts, especially in the cases of [BSMim]OAc, [BSMim]CF₃SO₃ and [BSMim]HSO₄. From the results of entry 4 generated without ethanethiol, it was demonstrated that the selectivity to *p,p'*-isomer was controlled by not only ionic liquid but also the thiol additive.

In addition, it can also be seen that [AMim]Br and [BMim]Cl gave rise to parallel yields (Table 1, entry 6-7), which were worse than those from the organic acid catalysts such as *p*-toluenesulphonic acid (entry 9) and the sulfamic acid (entry 8) under the same reaction conditions. Based on the findings mentioned above, [BSMim]HSO₄ was selected as the representative catalyst for the investigation reported in the following sections. There appeared to be considerable scope to improve its activity and in view of its low cost compared with CF₃SO₃⁻ based ionic liquid.

Table 1. Condensation of LA with Phenol Catalyzed by Different Catalysts. ^a

Entry	Catalysts	Conversion of LA (mol%)	Yield of DPA (mol%)	Selectivity to <i>p,p'</i> -DPA (%)	Selectivity to <i>o,p'</i> -DPA (%)
1	No catalyst	2.7	----	----	----
2	[BSMim]OAc	35.4	33.6	~100 ^d	----
3	[BSMim]CF ₃ SO ₃	80.7(73.3) ^b	79.3 (73.1) ^b	~100 ^d (95.7) ^b	----
4	[BSMim]HSO ₄	75.1	73.8	~100 ^d	----
5	[Bpy]HSO ₄	68.2	67.7	98.9	1.1
6	[AMim]Br	17.6	13.5	75.8	24.2
7	[BMim]Cl	13.7	13.4	82.1	17.9
8	NH ₃ SO ₃ H	57.8	57.6	88.1	11.9
9	<i>p</i> -TSA ^c	24.7	22.4	79.7	20.3
10	HCl	64.5	62	66.7	33.3

^a: Reaction conditions: 60 °C, 24 h, molar ratio of LA to phenol is 1: 4, 50 mol% of catalyst and 1 mol% of ethanethiol based on LA; ^b: no ethanethiol; ^c: *p*-toluenesulfonic acid; ^d: no *o,p'*-DPA was detected.

Optimization of Reaction Conditions

To obtain the optimum conditions for the condensation of LA with phenol, the effect of reaction time, temperature, catalyst amount, the molar ratio of phenol to LA on DPA yield, and the selectivity to *p,p'*-DPA isomer in the presence of [BSMim]HSO₄ ionic liquid were investigated, as described in the following subsections.

Effect of reaction time

Initially, the experiments were studied at different time periods up to 48 h, and the results of condensation of LA with phenol were estimated by withdrawing samples at specific time intervals at 60 °C with 4 phenol/LA molar ratio catalyzed by 50 mol% of [BSMim]HSO₄ and 2 mol% of ethanethiol based on LA.

As shown by the data presented in Fig. 1, the yield of DPA reached 38.1% within 12 h, 71.3% within 22 h, and 79.1% within 30 h. When the reaction time was extended to 36 h, 83.5% of yield of DPA could be achieved. With a further prolongation of 12 h, 6.8% of DPA yield was added. It seemed that much longer reaction time had little effect on practically improving DAP yield, but had an undesirable effect on the selectivity to *p,p'*-DPA isomer. From Fig. 1, it can be seen that the selectivity to *p,p'*-DPA always

approached 100% for reaction times up to 30 h, but afterwards, the selectivity further decreased gradually with further reaction time. Undoubtedly, too long reaction is not always good for the production of *p,p'*-DPA due to the formation of *o,p'*-DPA isomer. This situation probably can be attributed to the damage of *p,p'*-isomer or the loss of thiol compound. On the basis of the above viewpoints, 30 h was selected as reasonable for the optimal reaction time in the [BSMim]HSO₄ catalytic system.

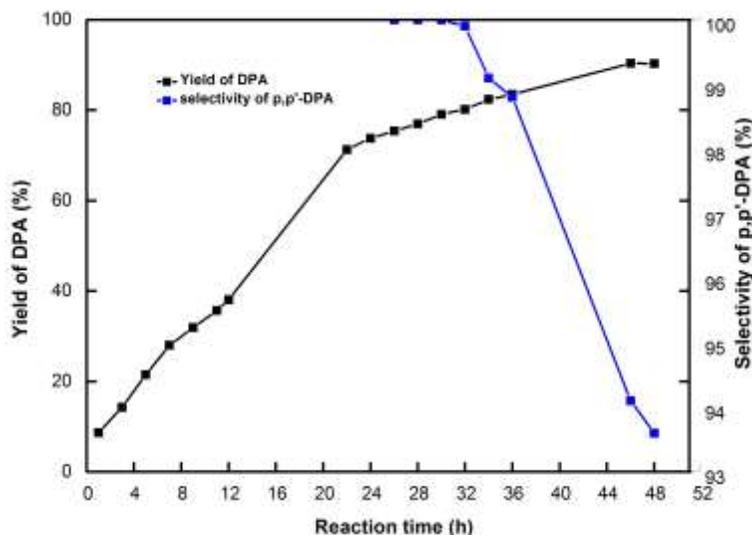


Fig. 1. Effect of reaction time on the condensation of phenol and LA catalyzed by [BSMim]HSO₄

Effect of reaction temperature

In order to evaluate the influence of reaction temperature on the production of DPA, the catalytic condensation of phenol and LA catalyzed by [BSMim]HSO₄ was monitored over 30 h at different temperatures.

As can be seen in Fig. 2, along with the reaction temperature increasing from 25 to 60 °C, the reaction accelerated correspondingly, and the yield of DPA increased about 41.8 % for a 35 °C rise in temperature during the same reaction time. Consequently, when the reaction was performed at 80 °C, the yield of DPA could reach the highest value (89.4%). However, the selectivity to *p,p'*-DPA decreased slightly compared with that at 60 °C. It has been proposed that a low temperature is essential for the *p,p'*-isomer synthesis (Liu *et al.* 2013). Furthermore, the yield of DPA decreased gradually above 80 °C, and 82.8% of DPA yield was obtained at 120 °C, which is probably due to the alteration of DPA at higher temperature. Considering the selectivity to *p,p'*-DPA, 60 °C was judged to be reasonable for optimal reaction temperature.

Effect of the ratio of phenol to LA

Generally, a cost-efficient substrate molar ratio is critical for the industrial production. Hence the influence of molar ratio of phenol to LA on the condensation was also studied at 60 °C for 30 h with 50 mol% [BSMim]HSO₄ ionic liquid catalyst, and the results are listed in Fig. 3. As expected, the DPA yield increased gradually in pace with the increase in amount of phenol, and 64.3% of DPA yield was promoted when the phenol/LA ratio was increased from 2 to 6. At the same time, a higher phenol/LA ratio

could not always benefit the selectivity to *p,p'*-DPA. Below 4.5 phenol/LA ratio, the selectivity to *p,p'*-DPA remained at almost 100%, whereas afterward a little *o,p*-DPA was gradually produced. In order to obtain the yield as high as possible in the condensation, 4.5 phenol/LA ratio was desirable.

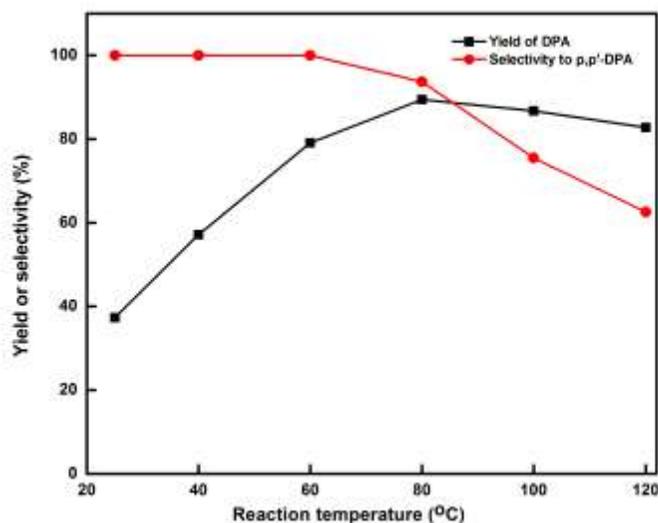


Fig. 2. Effect of reaction temperature on the condensation of phenol and LA catalyzed by [BSMim]HSO₄

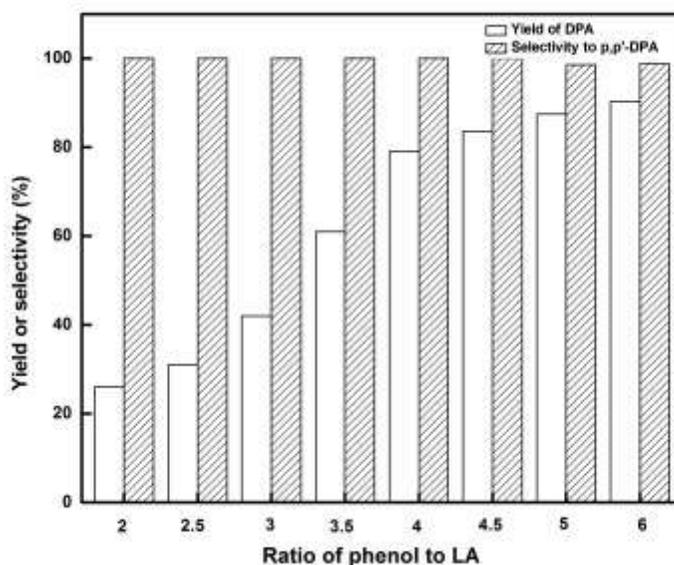


Fig. 3. Effect of the ratio of phenol to LA on the condensation of phenol and LA

Effect of ionic liquid content

The influence of ionic liquid amount on the condensation of phenol with LA was investigated, and results are shown in Fig. 4. It can be observed that as the proportion of

[BSMim]HSO₄ ionic liquid was increased, there was a significant rise in the DPA yield when the ionic liquid amount was less than 50 mol% (based on LA). When further increasing the proportion of ionic liquid to 150 mol%, the increased rate of product yield started to decrease slightly. For a rise in the amount of ionic liquid from 50 mol% to 150 mol%, the yield of DPA increased only by about 10% under the same reaction conditions. As for the selectivity to *p,p'*-DPA, in the wake of ionic liquid amount increasing to 120 mol%, the only DPA isomer product is *p,p'*-DPA. However, it appeared that too much ionic liquid had a detrimental effect on the dispersion of ionic liquid in the reaction mixture, so that the selectivity to *p,p'*-DPA was decreased slightly when 150 mol% ionic liquid was used. Taking the reusability of ionic liquid into account, 120 mol% proportion of ionic liquid with 93.2% DPA yield was chosen as the best option.

With the increasing worldwide interest in green chemistry, the eco-efficiency should be an important parameter to an industrial process. In order to investigate the feasibility of recycling the [BSMim]HSO₄ ionic liquid, a recycling experiment was carried out under the optimal conditions as outlined above. It is worth noting that the products could be simply separated by the common procedure. After the reaction, the mixture was extracted with ethyl acetate three times. The extract was combined and analyzed by HPLC. The ionic liquids were regenerated simply by removal of residual extract under vacuum. As a result, the yield of DPA just decreased slightly to 85.3% after [BSMim]HSO₄ had been used four times. The decrease of the yield was mainly because of ionic liquid loss during the separation process including phase separation and decantation. However, the color of ionic liquid become gradually deeper and deeper as run times were lengthened, which maybe was owing to the increasing levels of oxidized impurities.

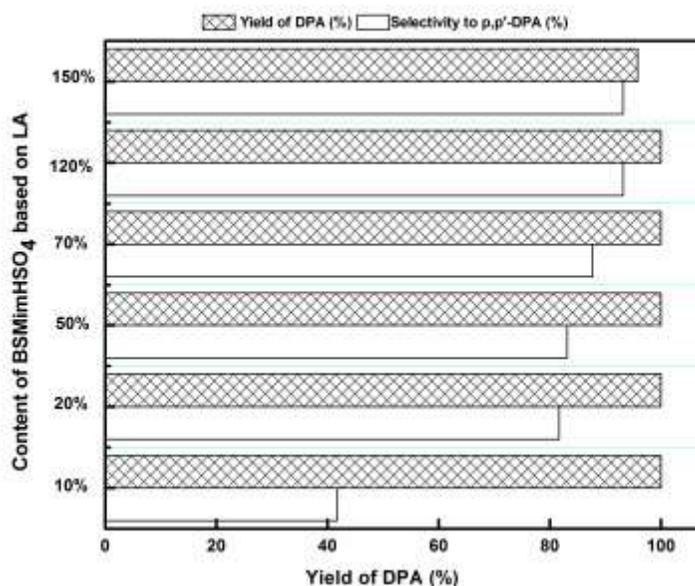
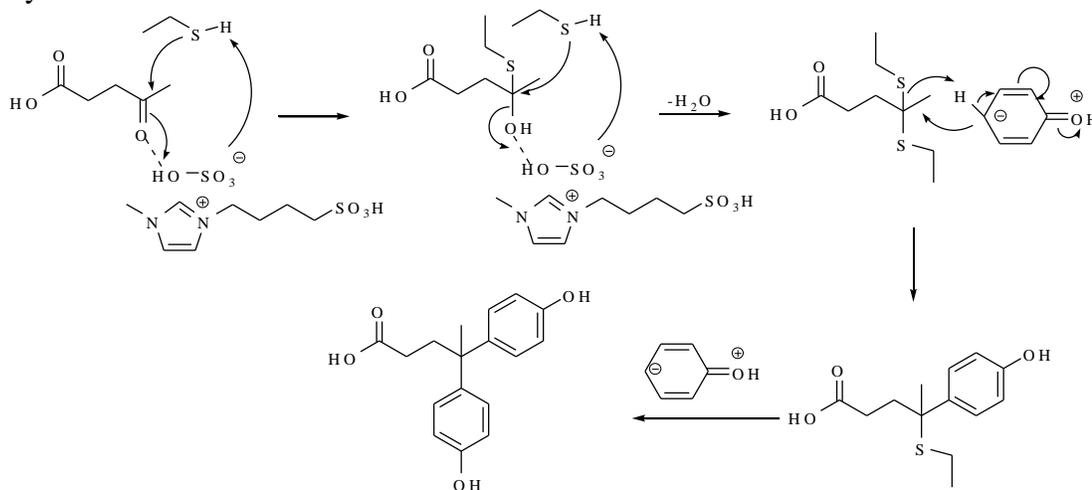


Fig. 4. Effect of the [BSMim]HSO₄ amount on the condensation of phenol with LA

Condensation Mechanism of Phenol and LA Catalyzed by Acidic Ionic Liquid

Based on the well-established mechanism of the synthesis of bisphenol A (Margelefsky *et al.* 2008; Zeidan *et al.* 2006), a reaction mechanism of the condensation of phenol and LA catalyzed by acidic ionic liquid, as well as the action of acid catalyst and thiol compound can be postulated, as shown in Scheme 2. It can be envisioned that the carbonyl group is activated by Brønsted acidic ionic liquid, and then is converted to hemi-ketal by nucleophilic attack of ethanethiol. Next, another ethanethiol nucleophilic attack once again causes the formation of thioketal. The formation of the intermediate could increase electrophilicity of the carbonyl and was considered as the active substrate for the coupling with phenol. Thus, given the nucleophilicity of sulfur, it is possible that the carbonyl carbon attached with two sulfurs is further activated to nucleophilic attack by phenol. Moreover, a higher regioselectivity toward *p,p'*-DPA is expected for reactions cocatalyzed by more hindered thiol groups. On the other hand, it is also possible that the Brønsted acid site activating carbonyl group is an $-\text{SO}_3\text{H}$ group bonded on an imidazolium cation, or anion and cation of ionic liquid, which both played a large role in the DPA production. This not only could cause increases in reaction rate, but also could block the formation of *o,p'*-DPA due to the steric hindrance increased by the bulky acidic ionic liquid, which would affect the approach of phenol and give rise to increased selectivity.



Scheme 2. Possible mechanism for thiol involvement in the condensation reaction of phenol and LA catalyzed by [BSMim]HSO₄ ionic liquid

CONCLUSIONS

1. Levulinic acid, a platform chemical from renewable materials, has been used as the starting material for the preparation of diphenolic acid catalyzed by acidic ionic liquids.
2. It was found that [BSMim]HSO₄ ionic liquids gave satisfactory yields (93.2%) in the condensation of phenol and LA. Such performance was derived from their special structures, and a selectivity to *p,p'*-DPA of nearly 100% was obtained under the optimized conditions.

3. Simple operation, insolubility in the organic phase, high yield, and the reusability are the key features of this methodology. Based on this combination of assets, it would appear that [BSMim]HSO₄ ionic liquid has great potential for green processing.

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