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Condensation of 9-fluorenone and phenol using the ionic liquid and mercapto compound synergistic catalyst

Lei Yan^{ab}, Limei Yu^{*ab}, Maochang Shen, Shikang Luo and Zhanxian Gao^b

A series of ionic liquids (ILs) were synthesized and their Hammett acidities (H_0) were determined using 4-nitroaniline as the indicator. The relationship among IL's structure, the acid strength, and the catalytic performance in the condensation reaction of 9-fluorenone with phenol was discussed. The effective H_0 range of ionic liquids that can catalyse the condensation reaction was obtained. Moreover, the catalysis of the mercapto compound co-catalyst was also systematically studied. According to the analysis of how the structure of the sulfydryl co-catalyst affects the percent conversion of 9-fluorenone and the selectivity of BHPF, a mechanism for the reaction in the IL-thiol cooperative catalytic system was proposed. The present work gave a clear clue to design novel IL catalysts for the synthesis of BHPF.

Introduction

The bisphenol compounds, a series of fine chemical raw materials, can be applied in many fields and prepared by condensation of aldehyde, ketone or keto acid with phenol. For example, 9,9-Bis (4-hydroxyphenyl) fluorene (BHPF) has been studied due to its unique cardo-ring structure, which acts as the monomer or modifying agent to manufacture polymers, such as epoxy resin^{1, 2}, polycarbonate³ and polyethersulfone^{4, 5} etc.. The polymers exhibit good rigidity and thermal stability, good optical properties and excellent formability⁶, so they have been widely used in aerospace, electronics and automotive industries⁷⁻¹⁰.

Synthesis of BHPF from condensation of 9-fluorenone with phenol is a complex process, which uses acid-thiol cooperative catalytic system, the acid as catalyst and mercapto compound as co-catalyst. The classical acid catalyst includes strong mineral acid^{11, 12}, heteropoly acid¹³, and acidic cation exchange resin¹⁴ etc. However, these catalysts have several disadvantages, such as severe corrosion of the equipment, serious environmental pollution, long reaction time and low yield, massive usage of catalyst while difficulty of recycle. At present, the commonly used co-catalyst is thioglycolic acid or mercaptopropionic acid. The co-catalyst can accelerate the reaction rate, but the mechanism is not clear yet. Thus, the development of an efficient catalyst system and the exploration of the mechanism in the synthetic reaction of BHPF are still deemed worthy of pursuit.

lonic liquids (ILs) have excellent physicochemical natures and are considered to be a new type of green solvent and catalyst^{15, 16}. Recently, the applications of functionalized acidic ILs instead of traditional liquid or solid acid catalysts in diverse organic reactions have been reported. The acidic IL catalysts are used widely in alkylation¹⁷, esterification^{18, 19, 20}, nitration²¹, hydrogenation^{22, 23}, hydration²⁴, oxidation^{25, 26, 27}, cyclization²⁸ and Diels-Alder reaction^{29, 30}, and so on. However, it has seldom reported on ILs catalysing the synthesis of bisphenol fluorenone.

In this work, we synthesized nine SO_3H -functionalized IL catalysts, and characterized the structures of the ILs by Fourier transform infrared spectrum (FT-IR), nuclear magnetic resonance spectrum (NMR), and electrospray ionization mass spectrometry (EI-MS). The thermal stability of ILs was detected by thermogravimetry - differential thermogravimetry (TG-DTG). The acidity of the ILs was determined through UV-vis spectroscopy. In the condensation of 9-fluorenone with phenol, the relationship between the structures of the acidic ILs and thiol co-catalysts and their catalytic effect has been scrutinized. The minimum acidity H_0 initiating reaction was investigated. Meanwhile the mechanism of the IL catalyst was also examined.



Experimental

Reagents and solvents

Pyridine, triethylamine, imidazole, benzyl mercaptan, 1, 3propane sultone, *p*-mercaptobenzoic acid, 1-butanethiol, thioglycolic acid and 3-mercaptopropionic acid were obtained from Aladdin. *p*-Toluenesulfonic acid was obtained from Shanghai Macklin Biochemical Co.. Sulphuric acid, phosphoric acid, tetrafluoroborate acid, diethyl ether and phenol were obtained from Sino pharm Chemical Keagent Co.. Methanol was obtained from Tianjin KeMiou Chemical Co.. The 9-

^a State Key Lab of Fine Chemicals, Dalian University of Technology, Dalian, Liaoning 116024, China. *Email: ochem@dlut.edu.cn; Tel: +86 13942698335.

^{b.} School of Chemical Engineering, Dalian University of Technology, Dalian, Liaoning

^{116024,} China.

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fluorenone was self-made, and its purity was greater than 99%. All reagents were used directly without further purification.

Synthesis of ionic liquids

The SO₃H-functionalized ILs (IL1-IL8 as shown in Scheme 1) were synthesized using two-step process³²⁻³⁴. Firstly, (0.2 mol) pyridine or triethylamine was added to a 100 mL round bottom flask containing absolute ethanol (20 mL), and then equimolar 1, 3-propane sultone was slowly added to the round bottom flask under stirring at 298 K. After reacting 4-12 h, a large amount of solid precipitate emerged. Then the precipitate was washed with ether for 3 times and dried at 353 K under vacuum to get the white solid precursor zwitterions. The yield of precursor is about 85-95%.

Secondly, a stoichiometric amount of sulfuric acid, phosphoric acid, tetrafluoroboric acid or *p*-toluenesulfonic acid (0.05 mol) was added to the aqueous solution of the precursor (0.05 mol). The mixture was stirred at 353 K for 8 h to form the ionic liquid. The product mixed liquor was distilled under reduced pressure to remove water and then afforded a viscous liquid. The liquid was washed thoroughly with diethyl ether to remove residual acid, and finally dried at 373 K under vacuum to obtain the corresponding acidic ionic liquid. The yield of ionic liquid is nearly 90-98%.

The IL9 (Scheme 1) was synthesized according to the literature³⁵. Sodium ethoxide (0.21 mol) was added to a solution of imidazole (0.2 mol) in ethanol (50 mL), and the mixture was stirred at room temperature for 4 h. Then 1, 3-propanesultone (0.42 mol) was added and the mixture was stirred at the same temperature for 6 h. After the solvent was removed by vacuum distillation, the obtained mixture was repeatedly washed with ethanol, and subjected to evaporation under vacuum to give the white solid precursor.

Sulfuric acid (0.1 mol) was added to the solution of the precursor (0.05 mol) in water (15 mL) at 298 K. The mixture was stirred at 363 K for 10 h and concentrated under vacuum. The obtained precipitate was washed with a mixture solution of methanol and Et_2O , then filtrated and dried under vacuum at 373 K to gain IL9.

Characterization of ionic liquids

The structures of precursors and the SO₃H-functionalized ILs were fully characterized by Fourier transform infrared (FT-IR), ¹H, ¹³C NMR spectroscopy analysis and electrospray ionization mass spectrometry (ESI-MS; Q-TOF Micro Mecromous, VK). Among them, FT-IR spectra in the frequency range of 4000-400 cm⁻¹ were recorded on a Nicolet 460 spectrometer (Nicolet, USA) using KBr pellets and liquid membrane method. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance II 400 MHz with TMS as an internal standard. The parameters about the thermal stability of ILs were obtained by TGA (Shimadzu TGA-50) at a heating rate of 10 K/min under nitrogen. The structural information of ILs is in good agreement with those reported in literatures³³⁻³⁵. The spectral data were given in the Supporting Information. UV-vis spectra were recorded on an UV (HP-8453) spectrophotometer at room temperature.

Catalytic experiment of functional ILs

The experimental procedure (Scheme 2) was carried out as following: 9-fluorenone(0.02 mol), phenol(0.12.1976));91(0.0025 mol), and co-catalyst(1.0 mmol) were added to a 50 mL threenecked flask equipped with a thermometer, a spherical condenser and a magnetic stirrer. Under stirring, the reactants were heated at 110 $^\circ \mathrm{C}$ for 6 hours. The qualitative analysis of crude product was conducted on a LC/MS (Agilent 1100 / 6130) with a Hypersil ODS-2 column. To further distinguish the target molecule and by-products, the crude products were purified by column chromatography on silica gel (eluent: V (petroleum ether) / V (dichloromethane) = 5:1) to obtain the relative pure compounds, and their structures were characterized by ¹H and ¹³C NMR spectra (see the Supporting Information). The quantitative analysis of the reaction was carried out on an HPLC (Agilent HP1100) with a XB-C₁₈ column (5 μ m × 250 mm × 4.6 mm), and the chromatographic conditions: 30 °C constant temperatures; mobile phase: methanol / water (volume ratio: 60:40 to 100:0 within 30 min); flow rate: 1.0 mL / min; injection volume: 5µL; detector: UV (257 nm and 275 nm).



Results and discussion

Determination of ionic liquid acidity

The acidities of ILs were determined on the basis of the Hammett acidity function method^{36, 37}. The Hammett function (H_0) was calculated by the following equation:

 $H_0 = pK(B)_{aq} + log([B] / [BH^+])$ [1]

Where pK $(B)_{aq}$ is the pKa value (0.99) of the aqueous solution of 4-nitroaniline, $[BH^{\dagger}]$ and [B] are respectively the molar concentrations of the protonated and unprotonated indicator, which can be determined by UV-visible spectroscopy.

lonic liquids, H_2SO_4 and $HSCH_2COOH$ were prepared under the same concentration of aqueous solution (c = 0.02 mol/L), and the absorbance was measured with 4-nitroaniline as the indicator. The Hammett function values (H_0) were calculated according to the equation [1] and the results were shown in Table 1.

In Table 1, IL1 - IL4 have different anions but the same cation $(PyN^{+} (CH_2)_3SO_3H)$, in which the H₀ values are 1.46, 1.70, 1.94 and 1.60, respectively. The IL3 with H₂PO₄⁻ anion has the largest H₀ value indicating that the IL3 is a weaker acid. The H₀ values of IL5 - IL8 show the same pattern. So the anionic structure of the IL has crucial influence on its acidity. In addition, the H₀ values of IL1 and IL5 with different cations and same anion (HSO₄⁻) are similar to that of sulfuric acid. Thus the acidity of IL is determined by the anion of IL and H₀ value is almost equivalent to that of the corresponding inorganic acid.

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59 60 The other series of ILs sharing same anion but different cations exhibit similar trend. So the cation of IL affects less on the acid strength of IL.

ILs	A _{max}	[B] / %	[BH ⁺] / %	H₀
Bank	2.09	100	0	-
H_2SO_4	1.54	73.68	26.32	1.44
HSCH₂COOH	2.00	95.69	4.31	2.34
IL1	1.59	74.64	25.36	1.46
IL2	1.75	83.73	16.27	1.70
IL3	1.88	90.43	9.57	1.94
IL4	1.68	80.38	19.62	1.60
IL5	1.59	74.64	25.36	1.46
IL6	1.74	83.25	16.75	1.69
IL7	1.87	89.47	10.53	1.92
IL8	1.68	80.38	19.62	1.60
IL9	1.50	70.60	29.40	1.37

The IL9 bearing two alkyl sulfonic acid groups has much stronger acidity than the IL1 and IL5 with only one alkyl sulfonic acid group, which suggests the number of alkyl sulfonic acid group of the IL will influence the acidity. However the H_0 value of thioglycolic acid is 2.34 resulting in a very weak acidity.

Catalytic effect of ILs

To investigate how the H₀ of acid catalyst influences the condensation reaction of 9-fluorenone with phenol, a series of experiments with absence of co-catalyst were carried. The reaction conditions are as follows: 9-fluorenone 0.02 mol, molar ratio of phenol / 9-fluorenone / catalysts = 6: 1: 0.125, 6 h, 110°C. From Table 2 it can be seen that, for different acid catalysts (H₂SO₄ and IL1 - IL9), the percent conversion of 9-fluorenone (Con(9-fluorenone)/%^[a]) is 59.4%, 53.7%, 29.9%, 6.9%, 46.1%, 54.8%, 31.4%, 9.1%, 42.5% and 64.2%, respectively.

We do simply linear association between the H_0 of ILs and the conversion of 9-fluorenone in Fig.1.



The following equation could be obtained through fitting the experimental data, as:

Using thioglycolic acid as a co-catalyst, the catalytic activities of ILs in the condensation reaction were further investigated, and the results are shown in Table 2.

Table 2 Catalytic activities of ILs in the condensation of 9-fluorenone and phenol								
	Con(9-	Con(9-	Selectivity / % [b]					
Catalyst	fluorenone)	fluorenone)	A(BHPF)	В	С			
	/% [8]	/% [0]						
H_2SO_4	59.4	100	87.9	8.5	3.6			
IL1	53.7	100	87.4	8.8	3.8			
IL2	29.9	100	86.5	9.4	4.1			
IL3	6.9	10.4	84.0	16.0	0			
IL4	46.1	100	86.6	9.4	4.0			
IL5	54.8	100	87.7	8.5	3.8			
IL6	31.4	100	86.8	9.1	4.1			
IL7	9.1	37.1	84.5	15.5	0			
IL8	42.5	100	86.9	9.1	4.0			
IL9	64.2	100	86.9	9.1	4.0			

Reaction conditions: 9-fluorenone 0.02 mol, molar ratio of phenol / 9-fluorenone / SO₃H-functionalized IL = 6: 1: 0.125, 6 h, 383 K. a: without co-catalyst ^[38]; b: with co-catalyst (thioglycolic acid 1 mmol, IL / thioglycolic acid = 5:2).

Table 2 shows that SO₃H-functionalized ILs and H₂SO₄ do work well in the condensation of 9-fluorenone, the conversion of 9-fluorenone is nearly 100% and the selectivity of BHPF is about 87%, except IL3 and IL7 with same anion H₂PO₄⁻. The conversion of 9-fluorenone for IL3 and IL7 is separately 10.4% and 37%. It reinforces further that the lower acidity of acid catalyst may strongly affect the condensation reaction.

The H₀ values of IL1, IL2, IL4, IL5, IL6, IL8, IL9 and H₂SO₄ are in the range of 1.45 $\sim\,$ 1.70, which shows that all of them can fully convert 9-fluorenone. Thus the acid catalyst that H₀ value is less than 1.70 may have practical significance in the condensation reaction.

Moreover, the co-catalyst plays an important role in the condensation of 9-fluorenone. Because IL1 catalyzes the condensation reaction, without or with thioglycolic acid, the conversion of 9-fluorenone changes from 53.7% to 100%.

Catalytic effect of the mercapto compounds

Using IL1, IL5 as acid catalyst, and p-HSC₆H₄COOH, HSCH₂COOH, HSCH₂CH₂COOH, CH₃CH₂CH₂CH₂SH and C₆H₅CH₂SH as co-catalyst, several experiments were carried to find the catalytic effect of co-catalyst. The results are shown in Table 3.

As shown in Table 3, the co-catalysts will obviously affect the conversion of 9-fluorenone and the selectivity of BHPF when the reaction time changes from 1 h to 6 h.

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	Table 3 Catalytic effect of co-catalysts at different reaction time in the condensation of 9-fluorenone with phenol			DOI: 10.1039/C9NJ0	
Catalyst	Co-catalyst	[Con(9-flurenone)/%] ^a	[S(BHPF)/%] ^a	[Con(9flureone)/%] ^b	[S(BHPF)/%] ^b
Blank	RSH*	0	0	0	0
	Blank	20.5	89.3	46.5	87.6
	<i>p</i> -HOOCC ₆ H₄SH	28.6	84.2	80.2	88.9
11.1	HOOCCH ₂ SH	81.5	82.4	100	87.4
ILI	HOOCCH ₂ CH ₂ SH	98.4	89.2	100	90.8
	CH ₃ CH ₂ CH ₂ CH ₂ SH	100	92.6	100	91.6
	$C_6H_5CH_2SH$	100	91.5	100	91.5
	Blank	25.0	89.9	53.7	87.7
IL5	<i>p</i> -HOOCC ₆ H₄SH	32.9	84.0	84.7	88.7
	HOOCCH ₂ SH	89.7	81.9	100	87.7
	HOOCCH ₂ CH ₂ SH	97.9	89.5	100	90.8
	$CH_3CH_2CH_2CH_2SH$	100	92.4	100	91.6
	$C_6H_5CH_2SH$	100	91.4	100	91.6

* HSR, R = $-CH_2COOH$, $-CH_2CH_2COOH$, $-CH_2CH_2CH_2CH_3$, $-CH_2C_6H_5$, $-C_6H_4COOH$; HSR 2.5 mmol; IL1: [PyN⁺(CH₂)₃SO₃H] [HSO₄⁻]; IL5: [(CH₃CH₂)₃N⁺(CH₂)₃SO₃H] [HSO₄⁻]; a: 1 h; b: 6 h. Reaction conditions: 9-fluorenone 0.02 mol, molar ratio of phenol / 9-fluorenone / SO₃H-functionalized ionic liquid = 6:1: 0.125, Co-catalysts 1.0 mmol, 110[°]C.

As previously mentioned when only mercapto compound was present without any ILs, the reaction would not occur. Yet if IL was only added without any co-catalysts, the reaction would be carried out in a low efficiency. In the IL catalyzing reaction system, even a small amount of thiol co-catalyst (except 4-mercaptobenzoic acid) was added, the conversion of 9-fluorenone could be remarkably increased. This illustrates that the IL catalyst and the thiol co-catalyst have a synergistic effect in the reaction process.

Comparing the experimental data of catalytic reactions at 1 h, it is shown that the type and structure of co-catalyst have vital influence on the conversion of 9-fluorenone. In the reactions using IL1 as catalyst and 4-mercaptobenzoic acid, thioglycolic acid, 3-mercaptopropionic acid, 1-butanethiol, benzyl mercaptan as co-catalyst, the conversion of 9fluorenone is 28.6%, 81.5%, 98.4%, 100% and 100%, respectively. The three mercaptan acid co-catalysts have lower conversion of 9-fluorenone, compared to that of the two mercaptan co-catalysts. As far as the three mercaptan acids are concerned, there is a consistent augment for the conversion of 9-fluorenone while the electron density (nucleophilicity) of -SH group in co-catalyst increases in turn. That means that -SH in co-catalyst directly participates in the reactive process.

When the reaction time extends from 1h to 6 h, 9fluorenone is fully converted except reactions with 4mercaptobenzoic acid as co-catalyst. This is due to the -SH group of 4-mercaptobenzoic acid having the lower nucleophilicity. Even so, in the reactions with IL1 as catalyst and 4-mercaptobenzoic acid as co-catalyst, along with the reaction time changing from 1h to 6h, the conversion of 9fluorenone also increases from 28.6% to 84.2%.

Using IL1 or IL5 as the catalyst and 4-mercaptobenzoic acid or thioglycolic acid as co-catalyst, the conversion of 9fluorenone is lower than 98% after reacting 1h. And the selectivity of BHPF changes nearly from 84% to 89% when reaction time expends to 6h. As to the reactions with 3mercaptopropionic acid, 1-butanethiol or benzyl mercaptan as co-catalyst, the conversion of 9-fluorenone closes to 100% and the selectivity of BHPF have no change over different reaction time. However the selectivity of BHPF slight drops with the prolongation of reaction time in IL-only system. In summary, the electron density of the -SH group and the size of mercapto compound affect the selectivity of BHPF. The fact reconfirms that -SH group in co-catalyst plays an important role in the reaction process.

The mechanism discussion

According to the above results and analysis as well as the existing references^{39, 40}, a possible mechanism is proposed for the condensation reaction of 9-fluorenone under the IL-thiol composite catalyst system (Scheme 3).



Scheme 3 The mechanism for the condensation of 9-fluorenone with phenol catalysing by the SO₃H-functionalized IL and thiol synergistic catalyst system.

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Firstly, sulfonic acid in Brønsted acidic ionic liquid activates carbonyl of 9-fluorenone to form intermediate (I). Because the hydroxyl group of the intermediate (I) is a poor leaving group, and the ortho (o-) or para (p-) carbon of phenol has a weak nucleophilicity, so it makes phenol difficult to directly react with the intermediate (I). Therefore, in the absence of cocatalyst, the overall reaction rate is slow and the conversion of 9-fluorenone is low. When the mercapto co-catalyst is added, the nucleophilicity of the -SH group is greater than that of o- or p- carbon of phenol, the intermediate (I) is converted to the sulfonium salt intermediate (II). The o- or p- carbon in phenol with partially negative charge acts as nucleophile to attack the intermediate (II) to form the tertiary carbocation intermediate (III, IV), meanwhile the thiol co-catalyst is released back to the reaction system.

Finally, the tertiary carbocation intermediate (III, IV) is combined with the other phenol molecule to obtain BHPF (A) or by-product 1 (B), and a proton is also released back and make the IL catalyst recruit. The tertiary carbocation (III) can also be combined with BHPF (A) to form by-product 2 (C).

The important step in the mechanism is that thiol cocatalyst takes part in the forming of the intermediate (II). Due to the strong nucleophilicity of -SH group in the thiol compound, the intermediate (II) is easily formed, and thus the subsequent reaction can proceed smoothly. This explains the significantly increasing of the conversion of 9-fluorenone after the addition of the thiol co-catalyst. According to the different electronic effect of thiol co-catalysts, if the nucleophilicity of -SH group in thiol compounds is larger, then the intermediate (I) is more easily converted to intermediate (II). At the same time the size of the mercapto compounds may determine the proportion of the intermediates (III) and the intermediates (IV), and thereby changes the selectivity of the BHPF.

Recycling of the acidic IL catalyst

In order to investigate the recyclable possibility and ability of the SO_3H -functionalized IL, the recycling experiment was conducted. After the reaction, deionized water is added to the reaction mixture, which is stirred at room temperature about 15 min, and then stands until the mixture separates to two layers. The IL catalyst is in the upper aqueous solution. The upper liquid is transferred to a 50 mL one-neck round bottom flask, and water is removed by rotary evaporator. The residue is washed three times with diethyl ether. Finally the residue is dried under vacuum drying oven at 100°C to obtain recycled IL catalyst. The recycled IL catalyst again is employed in the condensation of 9-fluorenone. The procedure is repeated five times at the same reaction conditions, the conversion of 9fluorenone firstly begins to reduce, and the result is shown in Fig. 2.

When the SO_3H -functionalized IL1 was recycled at the fifth time, the conversion of 9-fluorenone reduced from 100% to 98.5%. At the fifth cycle of IL1 catalyst, the selectivity of BHPF also decreased from 87.1% to 85.3%. It might result from the loss of IL1 during the workup. Thereof under this condition, our IL catalysts could be reused for 5 times.



Fig. 2 Recycling of $[PyN^*(CH_2)_3SO_3H][HSO_4^-]$ in the condensation reaction. Reaction conditions: 9-fluorenone 0.02 mol, molar ratio of phenol / 9-fluorenone / SO_3H-functionalized ionic liquid (the first dose) = 6: 1: 0.125, thioglycolic acid 1 mmol, 6 h, 383 K.

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Conclusions

In the present work, a reusable SO₃H-functionalized IL is used in the condensation of 9-fluorenone with phenol to replace normal acid catalysts. The H₀ of ILs is mainly controlled by its anion, and also affects its catalytic performance in the condensation reaction. If the H_0 of acid catalyst is greater than 2.01, the catalyst has no catalysis. When the H_0 of ILs is less than 1.70, 9-fluorenone can be fully converted and the best selectivity of BHPF is about 92% combinded with thiol cocatalyst. In addition, a series of mercapto compounds are used in the reaction system, and it is discussed in details how the electronic and spatial effect of co-catalysts works on the activity of the reaction and the selectivity of BHPF. Based on the experimental results, a mechanism is promoted and the significance of -SH group in the co-catalyst is clearly illustrated. Under the mechanism of the synergistic catalysis, the nucleophilicity of -SH group in the thiol co-catalyst and the H₀ of the IL catalyst have important influences on the conversion of 9-fluorenone and the selectivity of BHPF. The study on the synthesis of bisphenolfluorene under IL-thiol composite catalyst system provides valuable clues for the design of new IL catalysts that contain the bifunction of the composite catalysts in single IL structure.

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