



An efficient and facile synthesis of the coumarin and ester derivatives using sulfonated polyionic liquid as a highly active heterogeneous catalyst

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ABSTRACT

In this research, a novel solid acid catalyst, sulfonic acid immobilized on poly ionic liquid (SPIL), was described. The final catalyst, SPIL, which was simply synthesized and characterized by fourier transform infrared spectroscopy and thermo-gravimetric analysis, was found to be an efficient and environmentally benign solid acid for the Pechmann and esterification reactions under the solvent free conditions. The studies showed that the catalyst could be easily recovered and reused at least three reaction cycles without any significant loss in catalytic activity and efficiency.

1. Introduction

Ionic liquids, a class of low-melting chemical compounds that include an organic cation and an organic/inorganic anion, are known as molten salts. Generally, the cation is an organic species containing heteroatoms such as phosphorous, sulfur, and nitrogen and the anion may be varied as chloride, bromide, iodide, tetrafluoroborate, hexafluorophosphate, nitrate, and acetate [1]. Because of their unique properties such as non-volatility, non-flammability, safety, recyclability and ability to dissolve a wide range of compounds, a variety of ionic liquids have been used in organic synthesis [2-6]. In recent years, synthesis of Poly (ionic liquids) from polymerizable ionic liquids, because of their unique properties and broad applicability such as gas separation materials [7], catalytic membranes [8], polymer electrolytes [9], and ionic conductive materials [10], have received more attention in which the functionality of ILs is combined with the spatial control of IL moieties provided by polymer architectures. PILs can alter their physical and chemical properties easily by counter ions exchange, an effect well-known to the IL community. Free radical polymerization of IL monomers led to the preparation of PILs with various forms in cations and anions. Particularly, PILs having imidazolium moieties

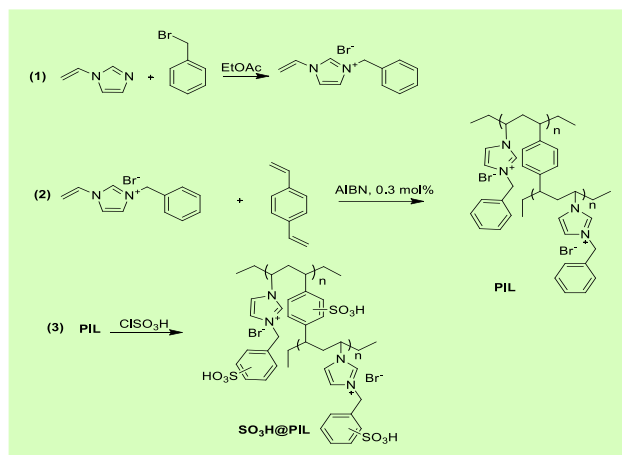
in each repeating unit are the most studied ones.

A restriction on the use of homogeneous catalysts in industry is the difficulty of catalyst separating from the reaction mixture or the product continuously. The development of heterogeneous catalyst to replace the homogeneous one for the production of fine chemicals in industrial processes remains with many challenges [11], because heterogeneous catalysts have some beneficial features such as simple separation, low toxicity, moisture resistance, air tolerance, greater selectivity, easier handling, and low cost [12]. In order to achieve this issue, homogeneous catalysts could be immobilized on the surface of solid materials such as mesoporous silicas, polymers and magnetic nanoparticles [13-15]. In addition, supported ionic liquid phases have recently attracted noticeable attention as important scaffold for the immobilization and stabilization of various catalysts [16].

Acid catalysis is by far the most important area of processes employed by industries in all sectors of chemical manufacturing. Some of the major reaction in organic chemistry generally catalyze by conventional mineral or Lewis acid. Although such homogeneous acid catalysts are highly active, they have serious drawbacks, such as the production of waste, separation

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from the product, and corrosion of equipment. The use of heterogeneous solid acids as an alternative to conventional homogenous acid catalysts in organic synthesis are beginning to play a significant role in the greening of fine and speciality chemicals manufacturing processes [17]. To the best of our knowledge, no systematic empirical research exists addressing the use of PILs as a support to immobilize the sulfonic acid moiety. Hence, we wish to disclose that supported sulfonic acid moieties on the poly ionic liquids (Scheme 1) can be considered as an efficient catalyst for the Pechmann and esterification reactions.



Scheme 1: schematic representation of catalyst preparation

2. Results and Discussion

As outlined in Scheme 1, in the first step the polymerizable ionic liquid was synthesized through a simple nucleophilic substitution reaction between benzyl bromide and 1-vinylimidazole. To confirm the monomer structure, ^1H NMR analysis of the monomer was performed in DMSO- d_6 (Figure S1). As it is clearly shown, the spectra confirm the accuracy of the produced monomer. In the next step, polymerization of 1-vinyl-3-benzyl imidazolium bromide and divinyl benzene (DVB) in the presence of catalytic amount of azobisisobutyronitrile (AIBN) was accomplished.

DVB must potentially be useful as a cross-linker and also to enhance the hydrophobicity of final PIL. Finally, desired catalyst ($\text{SO}_3\text{H@PIL}$) was achieved via sulfonation of prepared PIL using chlorosulfonic acid under mild reaction condition. The resulting $\text{SO}_3\text{H@PIL}$ was characterized by means of infrared Fourier transform (FT-IR) spectroscopy and thermogravimetric analysis (TGA). The presence of organic groups such as ionic liquid moieties, phenyl and aliphatic chains are also well confirmed by FT-IR technique (Figure 1). Specially, 3052 cm^{-1} peak could be related to the asymmetric stretching vibration of C-H in the phenyl ring or imidazole moieties [18]. Alkyl chain functional groups in the PIL have also several peaks at the $2930\text{-}3000\text{ cm}^{-1}$ (aliphatic C-H stretching) [18]. Moreover, the presence of ionic liquid is generally emphasized by peaks at 1620 cm^{-1} that related to the stretching vibration of C=N bonds [19]. Additionally, phenyl groups can be confirmed by peak at the 1512 cm^{-1} which corresponds to the stretching vibration of C=C bonds [18]. Furthermore, the band at 3331 cm^{-1} corresponds to the OH in SO_3H . To better conclude about the thermal properties of the final $\text{SO}_3\text{H@PIL}$, we decided to examine the thermal gravimetric of the final catalyst (Figure 2). Absence of any remarkable weight loss before $250\text{ }^\circ\text{C}$ indicates high thermal stability and hydrophobic character of the catalyst. Moreover, the first weight loss around $300\text{ }^\circ\text{C}$ could be related to the liberating of the HBr molecules. The main weight loss between $300\text{-}500\text{ }^\circ\text{C}$ corresponds to the decomposition of the two different functional groups: ionic liquids which thermally bonded to the polymer network and also some fraction of the phenylene groups. Main fractions of phenylene functional groups might be decomposed after evaluating the temperature up to $800\text{ }^\circ\text{C}$. Finally, amount of the loaded ionic liquids and sulfonic acids were estimated to be 1.2 and 0.46 mmol g^{-1} respectively using elemental analysis (CHNS) which are in good agreement with TG pattern. Additionally, amount of immobilized sulfonic acids were also confirmed using the titration method [20].

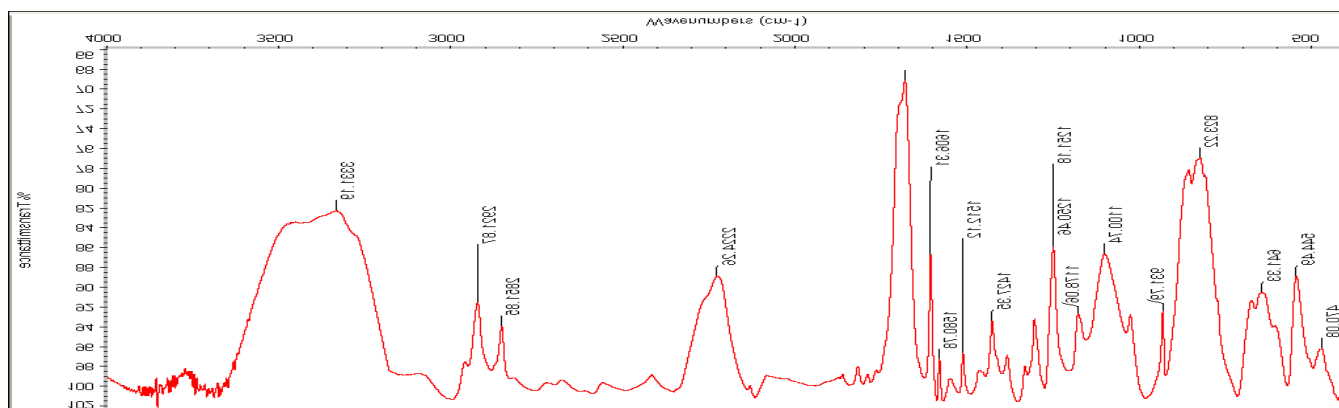


Figure 1: FT-IR spectra of the resulting $\text{SO}_3\text{H@PIL}$.

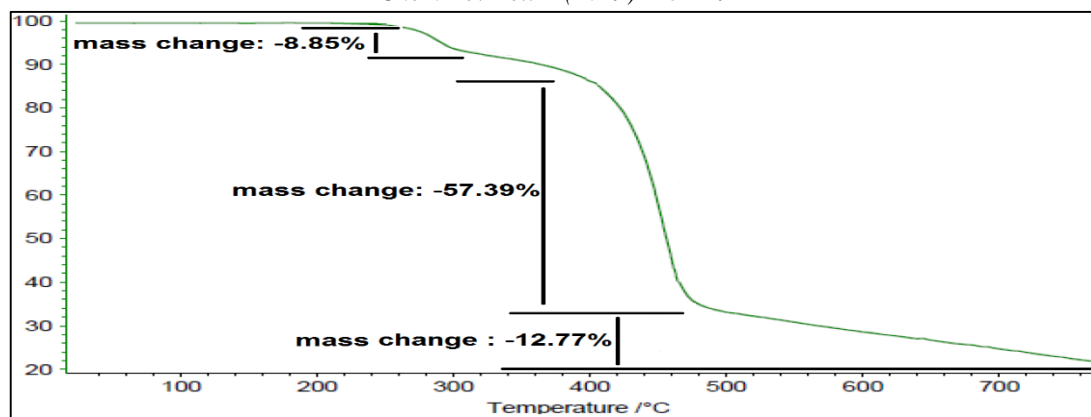
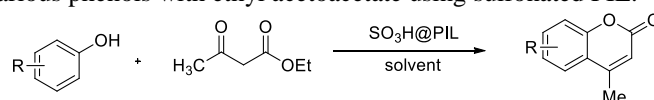


Figure 2: Thermal gravimetric analysis of SO₃H@PIL.

In continuation, in order to explore the catalytic properties of the synthesized PIL-SO₃H system, two important acid catalyzed processes which generate water as byproduct such as Pechmann and esterification reactions have been investigated under solvent-free reaction conditions using the prepared solid acid catalyst. In the first study, the Pechmann condensation was examined. In order to optimize the best reaction conditions, we primarily tested various conditions in the reaction of 3-OH-phenol and ethyl acetoacetate as model reaction. The experiment results show that the catalyst (4 mol%) is less efficient in the presence of solvents such as toluene, acetonitrile and *n*-hexane, while the higher level of reaction

conversion achieved under the solvent free condition at 60 °C (Table 1, entry 4 vs entries 1-3). To obtain the better results, we then tested the mentioned reaction at higher temperature and various amount of catalyst (Table 1, entries 5-9) and it was found that the best results were gained in the presence of 7 mol% of catalyst at 130 °C (Table 1, entry 9). After optimization of the reaction conditions, the possibility of other phenol derivatives with ethyl acetoacetate was investigated and the results were presented in Table 1, entries 10-13. It can easily be seen that the Pechmann condensation proceeded smoothly under mentioned conditions and afforded good to excellent yields ranging from 87% to 96%.

Table 1: Pechmann reaction of various phenols with ethyl acetoacetate using sulfonated PIL.^a



Entry	R	Cat. (mol%)	Solvent	Temp. (°C)	Time (h)	Yield (%) ^b
1	3-OH	4	toluene	60	24	22
2	3-OH	4	acetonitrile	60	24	9
3	3-OH	4	<i>n</i> -hexane	60	24	16
4	3-OH	4	-	60	24	58
5	3-OH	4	-	80	18	73
6	3-OH	7	-	80	10	79
7	3-OH	4	-	100	10	82
8	3-OH	7	-	100	5	88
9	3-OH	7	-	130	1	94
10	H	7	-	130	2	92
11	2-Me-3-OH	7	-	130	0.35	96
12	3-MeO	7	-	130	0.3	87
13	3,5-(OH)	7	-	130	0.25	96

^areaction conditions: phenol derivative (1 equiv.), acetoacetate (1.2 equiv.) and solvent (2ml). ^bIsolated yields of pure products.

In the next stage of our study, we then examine activity enhancement of presented solid acid ($\text{SO}_3\text{H@PIL}$) in the esterification reaction of various acids and alcohols (Table 2). The influence of different reaction parameters such as temperature and amount of catalyst were examined in the reaction of palmitic acid and methanol as model reaction (Table 2, entries 1-4) and revealed that the best results were obtained in the presence of 3 mol% of catalyst, at 70 °C under solvent free condition (Table 2, entry 4). Pechmann (the reaction of 3-OH-phenol with acetoacetate) and esterification reactions (the reaction Under these optimum reaction conditions, different alcohols and carboxylic acids as the reactants were also tested and the results were summarized in Table 2 entries 5-8. It could be seen that excellent yields ranging up to 99% for corresponding esters were obtained in all reactions under investigation. of palmitic acid with methanol) after reusing in 3 and 5 consecutive runs, respectively (Figure 3). These this research, we tested the reusability of the supported acid catalyst in the mentioned reactions. To do this, the catalyst easily separated from the reaction mixture after each run and reused in the next cycle. The results indicated that the catalyst showed no considerable losing in yield in both results reveal that the present supported system not only has superior activity in two mentioned reactions, but also provides a recoverable heterogeneous acid catalyst for these reactions.

but also provides a recoverable heterogeneous acid catalyst for these reactions.

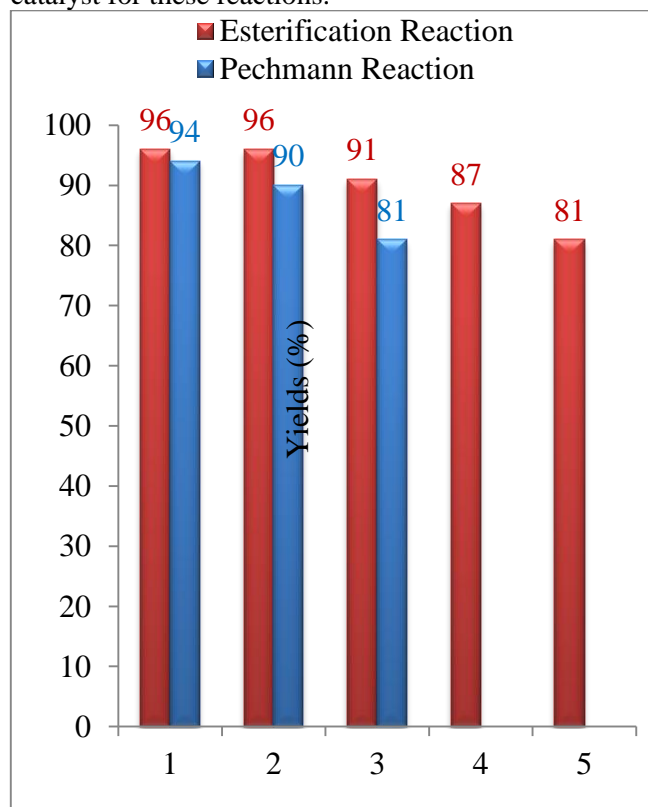


Figure 3: Recovery of the $\text{SO}_3\text{H@PIL}$ in the esterification and pechmann reactions

3. Experimental

3.1. General procedure for the preparation of 1-vinyl 3-benzyl imidazolium bromide:

1-Vinyl-3-benzyl imidazolium bromide was prepared according to standard methods and their purities were established before utilization by NMR spectroscopy. Briefly, a solution of distilled ethylacetate (50 mL), freshly distilled 1-vinylimidazole (73.1 mmol) and benzyl bromide (80.3 mmol) was refluxed for 24 h under an argon atmosphere. The resulting two phase reaction mixture was then allowed to cool at room temperature. The separated ionic liquid (IL) layer was washed with ethyl acetate and diethylether and was dried under vacuum over night.

3.2. General procedure for the preparation of poly ionic liquid (PIL) based on 1-vinyl-3-benzyl imidazolium bromide and divinyl benzene:

A solution containing 1-vinyl-3-benzyl imidazolium bromide and divinyl benzene (DVB) in chloroform was added to a flame-dried two neck flask. Then 0.3 mol% AIBN in chloroform was added and polymerized at 60-70 °C for 24h. The desired poly ionic liquid was quantitatively precipitated after addition of ethyl acetate as anti-solvent. The final PIL was severally washed with ethyl acetate for resulting high pure material.

3.3. General procedure for the Pechmann reaction of Phenolic derivatives with ethyl acetoacetate:

In a typical reaction, to the mixture of phenolic compound (10 mmol) and ethyl acetoacetate (12 mmol), 7 mol% of $\text{SO}_3\text{H@PIL}$ was added in a glass flask equipped with a magnetic stirrer and condenser. The mixture was heated at 130 °C with constant stirring for the desired period as indicated in Table 1. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with ethanol and the crude products was purified by column chromatography on silica gel using a mixture of *n*-hexane and ethylacetate (10:1). After recrystallization of products from hot ethanol, the yields of pure products were stated in Table 1.

3.4. General procedure for the esterification reaction of acid and alcohol derivatives:

In a typical reaction the mixture of acid, alcohol (Alcohol:Acid molar ratio= 10:1, Table 2, entries 1-6 or 1:10 in entries 7 and 8) and 3 mol% of $\text{SO}_3\text{H@PIL}$ were placed in a glass flask equipped with a magnetic stirrer and condenser. The mixture was heated at 70 °C with constant stirring for the desired period as indicated in Table 2. After completion of the reaction

(monitored by TLC-I₂), evaporation the filtrated gave the pure products which showed in Table 2.

3.4.1.-(1-Vinyl-3-benzyl imidazolium bromide): ¹H NMR (400 MHz; CDCl₃): δ 11.18 (s, 1H, NCHN), 7.74 (dd, 1H, J 8.4, 15.6, -CH=CH₂), 7.55-7.57 (m, 2H, -CH=CH-), 7.29-7.46 (m, 5H, -C₆H₅), 5.98 (dd, 1H, J 2.8, 15.6, *trans*-N-CH=CHH), 5.69 (s, 2H, -CH₂), 5.4 (dd, 1H, J 2.8, 8.4, *cis*-N-CH=CHH); ¹³C NMR (100 MHz, CDCl₃): δ 136.0, 132.5, 129.7, 129.5, 129.2, 128.1, 122.3, 119.1, 110.2, 53.6.

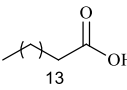
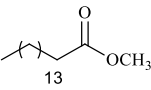
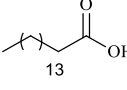
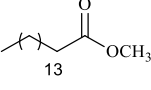
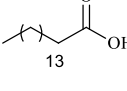
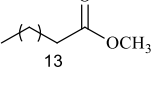
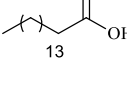
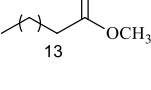
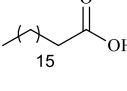
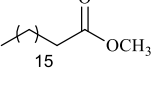
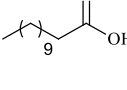
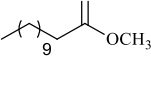

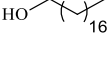
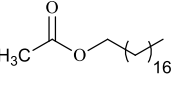

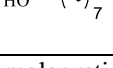
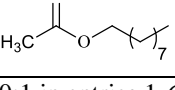
3.4.2.-(7-hydroxy-4-methyl-2H-chromen-2-one) (Table 3, entry 9): ¹H NMR (400 MHz; CDCl₃): δ 7.53 (d, 1H, J 8.8, -C₆H₅-), 7.01 (d, 1H, J 2.4, -C₆H₅-), 6.87-6.90 (dd, 1H, J 2.4, J 8.4, -C₆H₅-), 6.18 (s, 1H, -CH=CH-), 2.44 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ

162.5, 160.1, 155.5, 153.8, 126.5, 114.1, 113.6, 112.1, 103.8, 19.2.

3.4.3.-(4-methyl-2H-chromen-2-one) (Table 3, entry 10): ¹H NMR (400 MHz; CDCl₃): δ 8.59-8.62 (dd, 1H, J 3.6, J 6.0, -C₆H₅-), 7.89-7.93 (dd, 1H, J 3.6, J 6.8, -C₆H₅-), 7.74 (d, 1H, J 8.8, -C₆H₅-), 7.68 (d, 1H, J 7.2, -C₆H₅-), 6.42 (s, 1H, -CH=CH-), 2.57 (s, 3H, -CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 161.4, 153.9, 151.0, 135.2, 129.1, 127.6, 123.6, 123.1, 115.6, 114.8, 112.5, 19.6.

3.4.5.-(7-hydroxy-4,8-dimethyl-2H-chromen-2-one) (Table 3, entry 11): ¹H NMR (400 MHz; CDCl₃): δ 7.38 (d, 1H, J 8.4, -C₆H₅-), 6.82 (d, 1H, J 8.8, -C₆H₅-), 6.17 (s, 1H, -CH=CH-), 2.42 (s, 3H, CH₃), 2.36 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ 168.3, 161.8, 155.8, 153.6, 132.9, 131.4, 129.3, 123.0, 112.1, 68.6, 14.5, 11.4.

Table 2: Esterification reaction of various acids and alcohols using sulfonated PIL.^a

Entry	Acid	Alcohol	Product	Cat. (mol%)	Temp. (°C)	Yield ^b (%)
1		CH ₃ OH		3	50	46
2		CH ₃ OH		3	60	58
3		CH ₃ OH		3	70	77
4		CH ₃ OH		5	70	96
5		CH ₃ OH		5	70	98
6		CH ₃ OH		5	70	98
7				5	70	99
8				5	70	92

^aReaction conditions: Alcohol:Acid molar ratio= 10:1 in entries 1-6 and 1:10 in entries 7 and 8, 30 h. ^bIsolated yield

3.4.6.-(7-methoxy-4-methyl-2H-chromen-2-one)

(Table 3, entry 12): ^1H NMR (400 MHz; CDCl_3): δ 7.53 (d, 1H, J 8.8, $-\text{C}_6\text{H}_5$), 6.88-6.91 (dd, 1H, J 2.4, J 8.4, $-\text{C}_6\text{H}_5$), 6.85 (d, 1H, J 2.8, $-\text{C}_6\text{H}_5$), 6.17 (s, 1H, $-\text{CH}=\text{CH}-$), 3.90 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 163.1, 161.8, 155.8, 153.0, 126.0, 114.0, 112.8, 112.4, 101.3, 56.2, 19.2.

3.4.7.-(5,7-dihydroxy-4-methyl-2H-chromen-2-one)

(Table 3, entry 13): ^1H NMR (400 MHz; CDCl_3): δ 9.51 (br, 1H, $-\text{OH}$), 9.25 (br, 1H, $-\text{OH}$), 6.37 (d, 1H, J 7.6, $-\text{C}_6\text{H}_5$), 6.92 (d, 1H, J 8.8, $-\text{C}_6\text{H}_5$), 5.85 (s, 1H, $-\text{CH}=\text{CH}-$), 2.58 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 161.4, 160.5, 158.1, 157.6, 155.0, 110.2, 103.2, 99.6, 95.6, 23.5.

3.4.8.-(Methylpalmitate)

(Table 2, entry 4):

^1H NMR (400 MHz; CDCl_3): δ 3.69 (s, 3H, OCH_3), 2.32 (t, 2H, J 7.6, $-\text{CH}_2\text{CO}-$), 1.60-1.66 (qui, 2H, J 7.2, $-\text{CH}_2-$), 1.30 (brs, 24H, $-\text{CH}_2-$), 0.90 (t, 3H, J 6.8 Hz, $-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3): δ 174.8, 51.9, 34.6, 32.4, 30.19, 30.18, 30.16, 30.10, 29.9, 29.8, 29.7, 29.6, 25.4, 23.2, 14.6.

3.4.9.-(Methyl stearate)

(Table 2, entry 5):

^1H NMR (400 MHz; CDCl_3): δ 3.69 (s, 3H, OCH_3), 2.33 (t, 2H, J 7.6, $-\text{CH}_2\text{CO}-$), 1.62-1.66 (qui, 2H, J 6.7, $-\text{CH}_2-$), 1.28 (brs, 27H, $-\text{CH}_2-$), 0.90 (t, 3H, J 6.4, $-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3): δ 174.8, 51.9, 34.6, 32.4, 30.2, 30.1, 29.9, 29.8, 29.7, 29.6, 25.4, 23.2, 14.6.

3.4.10.-(Methyl dodecanoate)

(Table 2, entry 6):

^1H NMR (400 MHz; CDCl_3): δ 3.69 (s, 3H, OCH_3), 2.33 (t, 2H, J 7.5, $-\text{CH}_2\text{CO}-$), 1.59-1.66 (qui, 2H, J 7.2, $-\text{CH}_2-$), 1.28 (brs, 14H, $-\text{CH}_2-$), 0.91 (t, 3H, J 6.4, $-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3): δ 174.8, 51.9, 34.6, 32.4, 30.1, 29.9, 29.8, 29.7, 29.6, 29.1, 25.4, 23.1, 14.6.

3.4.11.-(Octadecyl acetate)

(Table 2, entry 7):

^1H NMR (400 MHz; CDCl_3): δ 4.80 (t, 2H, J 6.8, OCH_2-), 2.07 (s, 3H, CH_3), 1.61-1.66 (qui, 2H, J 6.0, $-\text{CH}_2-$), 1.28 (brs, 30H, $-\text{CH}_2-$), 0.91 (t, 3H, J 6.8, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 171.7, 65.1, 32.4, 30.2, 30.08, 30.03, 29.8, 29.7, 29.2, 29.1, 26.4, 23.2, 21.5, 14.6.

3.4.12.-(Nonylacetate)

(Table 2, entry 8):

^1H NMR (400 MHz; CDCl_3): δ 4.08 (t, 2H, J 6.8 Hz, OCH_2-), 2.08 (s, 3H, CH_3), 1.58-1.64 (qui, 2H, J 6.8, $-\text{CH}_2-$), 1.34 (brs, 12H, $-\text{CH}_2-$), 0.91 (t, 3H, J 6.8 Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 171.9, 64.1, 30.2, 30.0, 29.9, 29.7, 29.0, 26.5, 22.8, 21.4, 14.6.

4. Conclusion

To summarize, a novel sulfonic acid based on poly ionic liquid with imidazolium and phenylene frameworks was synthesized and characterized by required techniques. The prepared solid sulfonic acid

was then carefully explored as a highly stable and efficient catalyst in the Pechmann and esterification reactions. For the both reactions, substrates were furnished to the corresponding products in good to excellent yield and selectivities. Additionally, the catalyst could be successfully recovered and reused for the at least three (Pechmann reaction) and five (esterification) reaction cycles without any remarkable decreasing in the catalyst activity and efficiency.

Supplementary Information

Supplementary Information (including ^1H NMR and ^{13}C NMR spectrums for all synthesized compounds)

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