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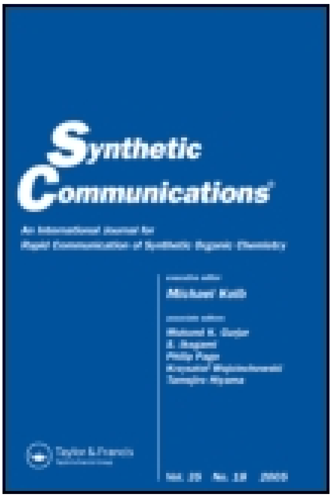

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Synthesis of Novel Poly(ethyleneglycol)-400 Ionic Liquid and Its Application in Morita-Baylis-Hillman Reaction

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SYNTHESIS OF NOVEL POLY(ETHYLENEGLYCOL)-400 IONIC LIQUID AND ITS APPLICATION IN MORITA–BAYLIS–HILLMAN REACTION

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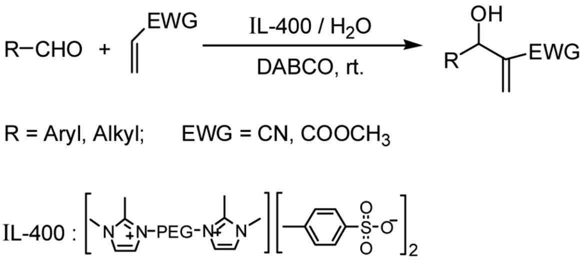
[2]*School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan, China*

GRAPHICAL ABSTRACT



Abstract *Novel Poly(ethyleneglycol)-400 ionic liquid containing imidazolium cations have been synthesized by the atom-efficient reaction of 1,2-dimethylimidazole with* p-*toluenesulfonate; the* p-*toluenesulfonate provides the anionic component of the resultant ionic liquid. It have been used for the first time as a new solvent for the Morita–Baylis–Hillman reaction under ambient conditions. A wide variety of aldehydes and active olefins participate very efficiently, resulting in good to excellent yields of products.*

Keywords 1,2-Dimethylimidazole; ionic liquid; Morita–Baylis–Hillman reaction; *p*-toluenesulfonate; synthesis

INTRODUCTION

Ionic liquids (ILs) are emerging as effective promoters and solvents for green chemical reactions, and during the past few years, a variety of organic reactions have been successfully conducted using ILs as solvents.[1] Many interesting results have been obtained that demonstrate advantages of using ILs as alternative for traditional organic solvents. One of the most important advantages of ILs is the good solvating property for both inorganic and organic compounds, which provides a homogeneous

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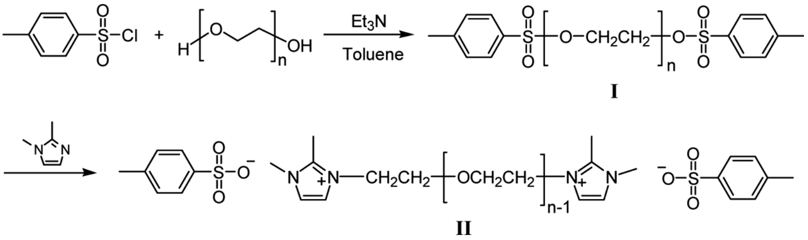


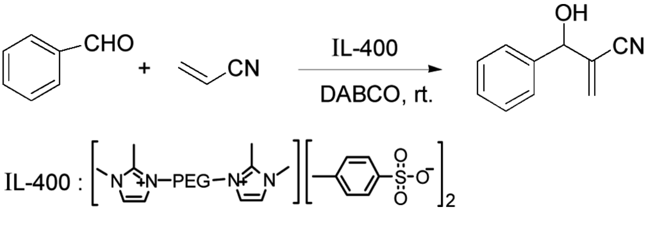
Scheme 1. Synthesis of IL-400 ionic liquid.

system and accelerates multicomponent reactions (MCRs) in comparison with conventional solvents.

The Morita–Baylis–Hillman (MBH) reaction is an atom-economical and extremely useful C–C bond-forming reaction in organic synthesis.[2] This reaction involves three components: an activated alkene, an electrophile, and a tertiary amine. Lewis bases, such as 1,4-diazabicyclo[2.2.2]octane (DABCO),[3] dimethylaminopyridine (DMAP),[4] 1,8-diazabicyclo[5.4.]undec-7-ene (DBU)[5] and trimethylamine[6] are frequently used in these reactions as catalysts. In addition, Lewis acid-accelerated reactions using $TiCl_4$[7] and BF_3.[8] were also reported. However, they suffer from poor reaction rate and long reaction time. In view of this situation, numerous studies, including chemical as well as physical attempts, have been made to accelerate the reaction with some good results.[9] An earlier report described acceleration of the DABCO-catalyzed MBH reaction in an ionic liquid, 1-n-butyl-3-methyimidazolium hexafluoro-phosphate ([bmim][PF_6]).[10] However, it was later shown that the imidazolium salts, incorporating a hydrogen substituent at the C-2 position, are deprotonated under mild basic conditions and the corresponding carbenes are formed, which can cause undesired side reactions.[11] Because we were not satisfied with the results, we synthesized new imidazolium ionic liquid for the MBH reaction, in which its C-2 carbon is methylated (Scheme 1). In this article, we present an efficient and practical synthesis of a new room-temperature ionic liquid based on bis(1,2-dimethylimidazolium) cations involving ethylene glycol spacers and their application in the MBH reaction under mild conditions.

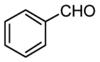
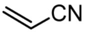
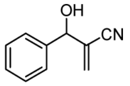
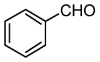
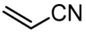
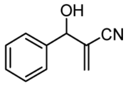
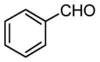
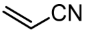
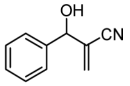
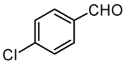
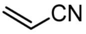
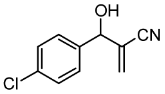
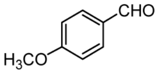
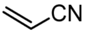
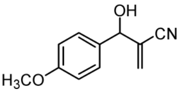
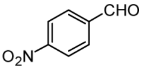
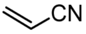
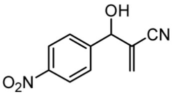
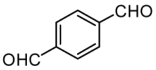
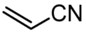
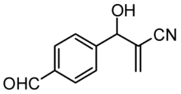
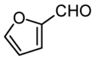
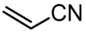
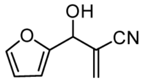
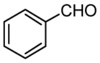
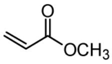
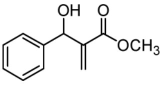
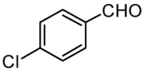
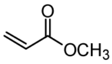
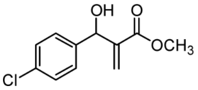
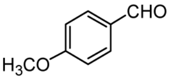
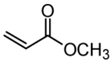
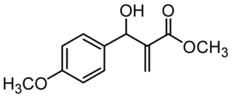
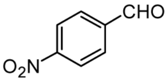
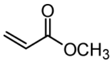
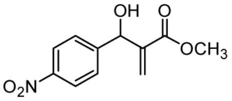
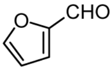
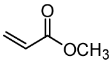
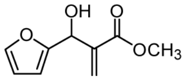
RESULTS AND DISCUSSION

Poly(ethyleneglycol)-400 and 1,2-dimethylimidazole are commercially available. The synthesis of poly(ethyleneglycol)-400 ionic liquid (IL-400) is straightforward



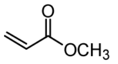
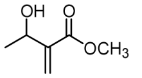
Scheme 2. Morita–Baylis–Hillman reaction in IL-400.

Table 1. Morita–Baylis–Hillman reactions in IL-400[a]

Entry	Aldehyde	Alkene	Products	Time (h)	Yield (%)[b]
1[c]				4	67
2[d]				4	78
3				3.5	89
4				4	90
5				8	68
6				3	93
7				4	84
8				4	82
9				5	79
10				8	88
11				10	63
12				4	89
13				5	87

(*Continued*)

Table 1. Continued

Entry	Aldehyde	Alkene	Products	Time (h)	Yield (%)[b]
14	CH_3-CHO			12	65

[a]All reactions were performed with aldehydes (5 mmol) and activated alkenes (10 mmol) in a mixture of IL-400 and water (v/v, 1:1, 10 ml) in the presence of appropriate catalyst DABCO (5 mmol) at ambient temperature.

[b]Refers to isolated, pure products after silica-gel chromatography.

[c]The reaction was performed with benzaldehyde (5 mmol) and acrylonitrile (10 mmol) in 5 ml of IL-400 in the presence of appropriate catalyst DABCO (2.5 mmol) at ambient temperature.

[d]The reaction was performed with benzaldehyde (5 mmol) and acrylonitrile (10 mmol) in 5 ml of IL-400 in the presence of appropriate catalyst DABCO (5 mmol) at ambient temperature.

(Scheme 1). In the first step, poly(ethyleneglycol)-400 was employed as a starting material to react with *p*-toluenesulfonyl chloride according to a literature procedure,[12] and the desired *p*-toluenesulfonate **I** could be obtained in 53% yield, which is low for practical use. Several improvement measures were used in this reaction, and when microwave irradiation was applied with triethylamine as catalyst instead of pyridine, we found that an excellent yield (83%) of *p*-toluenesulfonate **I** could be achieved and that it is pure enough to use in successive reactions. In the second step, 1,2-dimethylimidazole was used to react with *p*-toluenesulfonate **I**, and we found that the reaction could be carried out readily to give new IL-400 with 87% yield.

As a continuation of our work in MBH reactions,[13] IL-400 was tested as a solvent in the MBH reaction of acrylonitrile and benzaldehyde (Scheme 2), and the results are shown in Table 1. When 0.5 equiv of 1,4-diazabicyclo[2.2.2]octane (DABCO) was used as a catalyst at room temperature, benzaldehyde and acrylonitrile formed the desired product with 67% yield after 4 h. When increasing the amount of catalyst was increased to 1 equiv, better yield (78%) was obtained (Table 1, entry 2) in pure IL-400, and in the presence of 1 equiv catalyst, the optimal yield (89%) was achieved in the same volume of IL-400 and water mixture after 3.5 h (Table 1, entry 3). Under these optimum conditions, the MBH reactions of acrylonitrile or methyl acrylate with a variety of aldehydes were examined at room temperature (Table 1, entries 4–14). As demonstrated in Table 1, both aliphatic and aromatic aldehydes can undergo very efficient MBH reactions in the same volume of IL-400 and water mixture, and the corresponding M-B-H adducts in good to excellent yieldes (63–93%) were obtained. The electron-rich 4-methoxybenzaldehyde, which is usually quite an inert substrate, could provide a fairly good yield (68%, entry 5) under the present conditions, and the reaction of acrylonitrile with the electron-deficient 4-chlorbenzaldehyde provided an excellent yield of 90% after 3 h. To evaluate the possibility of recycling the ionic liquid used for the MBH reaction, the recycling performance of IL-400 was investigated in the reaction of benzladehyde with acrylonitrile. The results listed in Table 2 showed that the IL-400 could be reused five times with consistent activity.

Table 2. Reuse of IL-400[a]

Cycle	Yield (%)
1	89
2	90
3	91
4	89
5	87

[a]All reactions were performed with benzaldehyde (5 mmol) and acrylonitrile (10 mmol) in a mixture of IL-400 and water (v/v, 1:1, 10 ml) in the presence of appropriate catalyst DABCO (5 mmol) at ambient temperature.

CONCLUSIONS

In summary, we have present a novel ionic liquid based on poly(ethyleneglycol)-400 and 1,2-dimethylimidazole. New imidazolium IL-400 was prepared conveniently and in an environmentally friendly way in only two steps from poly(ethyleneglycol)-400 and 1,2-dimethylimidazole with good overall yields. Further study on its application as a green solvent in the MBH reaction showed that it is useful for the MBH reactions of a variety of aldehydes, including electron-deficient and electron-rich aromatic aldehydes and aliphatic aldehydes. In addition, IL-400 can be reused several times in the MBH reaction without much loss of its activity.

EXPERIMENTAL

All melting points were measured on a WRS-1B digital melting-point meter and are uncorrected. The infrared (IR) spectra were determined on a Fourier transform (FT)–IR-8400 spectrometer by dispersing samples in neat or KBr disks. ^{1}H NMR spectra were measured on a DRX300 NMR spectrometer using tetramethylsilane (TMS) as an internal standard with $CDCl_3$ as solvent. All products (except IL-400) are known compounds, which were characterized by IR and ^{1}H NMR spectral data, and their melting points were compared with literature reports.[14]

Typical Procedure for the Microwave-Assisted Synthesis of IL-400

PEG 400 (23.4 mL, 60 mmol) was dissolved in toluene (180 mL), and then triethylamine (16.7 mL, 120 mmol) was added, followed by *p*-toluenesulfonyl chloride (24.78 g, 130 mmol) in small portions with constant stirring. Then the reaction mixture was irradiated with microwaves at 150 W at 20 °C for 600 s. when the reaction was completed (monitored by thin layer chromatography, TLC), the mixture was filtered. The filtrate was added to 1,2-dimethylimidazol (10.6 mL, 120 mmol), and the mixture was stirred at 85 °C for 22 h under nitrogen atmosphere. After the reaction, the ionic liquid layer was separated and washed with petroleum ether (3 × 10 mL). Evaporation of solvent under reduced pressure gave the desired pure product IL-400 in 86% yield. Pale yellow oil; IR (neat, cm^{-1}): 3408.0, 2873.7, 2702.1, 2497.6, 2360.7, 2248.8, 1608.5, 1535.2, 1454.2, 1396.3, 1352.0, 1190.0, 1120.2, 1010.6, 943.1, 817.8, 735.8, 582.8. ^1H NMR (300 MHz, $CDCl_3$): δ 7.60 d, $J = 2.0$ Hz, 2CH), 7.48 (d, $J = 2.2$ Hz, 2H, 2CH), 7.20(d, $J = 5.4$ Hz, 4H), 7.13 (d, $J = 5.2$ Hz, 4H), 3.75–3.73 (m, 40H), 3.71 (s, 6H, $2NCH_3$), 2.56 (s, 6H, CH_3), 2.36 (s, 6H), ^{13}C NMR (300 MHz, $CDCl_3$): δ 136.7, 123.3, 122.6, 69.4, 69.3, 68.5, 48.7, 37.5, 36.2.

General Procedure for the Morita–Baylis–Hillman Reaction

A solution of aldehyde (5 mmol) and activated alkene (10 mmol) in a mixture of IL-400 and water (v/v, 1:1, 10 ml) was stirred at room temperature (20–26 °C) in the presence of DABCO (5 mmol). The progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was extracted with ethyl ether (3 × 20 ml). Then the combined ethyl ether fractions were evaporated. The crude products thus obtained were purified by flash column chromatography (silica gel, 200–300 mesh; ethyl acetate/petroleum ether, 1:5–1:3). All desired products were characterized by IR and ^1H NMR. The ionic liquid was directly used in the next run.

Spectral Data of the Morita–Baylis–Hillman Adducts

3-Hydroxy-2-methylene-3-phenylpropanenitrile (Table 1, Entry 3). Yellow oil. IR (neat): 3442.8, 2224.7, 1604.9, 1340.8 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.18 (m, 5H), 6.10 (s, 1H), 6.08 (s, 1H), 5.91 (d, $J = 5.56$ Hz, 1H), 2.85 (br., s, 1H).

3-Hydroxy-2-methylene-3-(4-chlorophenyl)propanenitrile (Table 1, Entry 4). Yellow oil. IR (neat): 3435.1, 2227.1, 1495.9 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.24 (m, 4H), 6.07 (s, 1H), 6.01 (s, 1H), 5.24 (s, 1H), 3.25 (br., s, 1H).

3-Hydroxy-2-methylene-3-(4-methoxy-phenyl)propanenitrile (Table 1, Entry 5). Yellow oil. IR (neat): 3413.5, 2224.7, 1489.6 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, $J = 6.8$ Hz, 2H), 6.84 (d, $J = 7.3$ Hz, 2H), 6.24 (d, $J = 1.8$ Hz, 1H), 6.12 (d, $J = 1.3$ Hz, 1H), 5.24 (s, 1H), 3.82 (s, 3H), 2.25 (br., s, 1H).

3-Hydroxy-2-methylene-3-(4-nitrophenyl)propanenitrile (Table 1, Entry 6). Pale yellow solid, mp 73.8–74.2 °C. IR (KBr): 3424.2, 2865.5, 2229.4 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.26 (d, $J = 5.8$ Hz, 2H), 7.60 (d, $J = 5.3$ Hz, 2H), 6.18 (1s, 1H), 6.10 (s, 1H), 5.44 (s, 1H), 2.85 (br., s, 1H).

3-Hydroxy-2-methylene-3-(4-formyl-phenyl)propanenitrile (Table 1, Entry 7). Pale white solid, mp 56.2–56.8 °C. IR (KBr): 3465.2, 2882.1, 2227.6, 1710.2 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.94 (s, 1H), 7.87 (d, $J = 5.97$ Hz, 2H), 7.55 (d, $J = 5.86$ Hz, 2H), 6.13 (d, $J = 1.72$ Hz, 1H), 6.02 (d, $J = 1.67$ Hz,1H), 5.36 (s, 1H), 3.85 (br., s, 1H).

3-Hydroxy-2-methylene-3-(2-furanyl)propanenitrile (Table 1, Entry 8). Pale yellow oil. IR (neat): 3431.2, 2874.8, 2227.6 cm^{-1}. ^1H NMR (300 MHz,

$CDCl_3$): δ = 7.34 (s, 1H), 6.35 (s, 1H), 6.30 (m, 1H), 6.24 (d, $J = 2.8$ Hz, 1H), 5.92 (s, 1H), 5.50 (s, 1H), 2.84 (br., s, 1H).

3-Hydroxy-2-methylene-3-phenylpropanoic acid, methyl ester (Table 1, Entry 9). Colorless oil. IR (neat): 3480.1, 2979.8, 1714.5 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.21 (m, 5H), 6.29 (s, 1H), 5.87 (s, 1H), 5.47 (s, 1H), 3.68 (s, 3H), 2.63 (br., s, 1H).

3-Hydroxy-2-methylene-3-(4-chlorophenyl)propanoic acid, methyl ester (Table 1, Entry 10). White solid, mp 43.2–44.0 °C. IR (KBr): 3485.7, 2984.8, 1726.4 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.29 (s, 4H), 6.32 (s, 1H), 5.80 (s, 1H), 5.51 (s, 1H), 3.71 (s, 3H), 2.59 (br., s, 1H).

3-Hydroxy-2-methylene-(4-methoxy-phenyl)propanoic acid, methyl ester (Table 1, Entry 11). Pale yellow oil. IR (neat): 3480.6, 2979.7, 1720.6 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.26–7.22 (m, 2H), 6.72–6.69 (m, 2H), 6.38 (s, 1H), 6.24 (s, 1H), 5.18 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.71 (br., s, 1H).

3-Hydroxy-2-methylene-3-(4-nitrophenyl)propanoic acid, methyl ester (Table 1, Entry 12). Yellow solid, mp 71.2–71.6 °C. IR (KBr): 3480.4, 2992.3, 1726.5, 1632.3, 1358.5 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.14 (d, $J = 6.4$ Hz, 2H), 7.53 (d, $J = 6.5$ Hz, 2H), 6.36 (1s, 1H), 5.71 (s, 1H), 5.62 (s, 1H), 3.74 (s, 3H), 2.95 (br., s, 1H).

3-Hydroxy-2-methylene-3-(2-furanyl)propanoic acid, methyl ester (Table 1, Entry 13). Pale yellow oil, IR (neat): 3447.3, 1721.4, 1635.1 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35 (s, 1H), 6.36 (s, 1H), 6.24–6.32 (m, 2H), 5.92 (s, 1H) 5.57 (s,1H), 3.74 (s, 3H), 2.87 (br., s, 1H).

3-Hydroxy-2-methylene-propanoic acid, methyl ester (Table 1, Entry 14). Yellow oil, IR (neat): 3470.3, 2937.1, 1723.6, 1637.8 cm^{-1}. ^1H NMR(300 MHz, $CDCl_3$): δ = 6.13 (s, 1H), 5.82 (d, $J = 0.9$ Hz, 1H), 4.74 (m, 1H), 3.72 (s, 3H), 2.88 (br., s, 1H), 1.27 (s, 3H).

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