Recyclable polymeric ionic liquids applied as metal-free transfer hydrogenation catalysts

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ABSTRACT

A new methodology for immobilizing a triazolium salt onto polyethylene glycols (PEG) was developed. The immobilization is a two-step reaction, involving the tosylation of PEGs followed by a neat reaction between the PEG tosylates and the triazole. It is a high-yielding reaction conducted under mild conditions with a simple workup procedure. Hence, the salt 1-benzyl-4-phenyl-1H-1,2,3-triazolium iodide was immobilised onto PEGs of varying chain lengths ($PEG_{300–8000}$) to yield various polymeric ionic liquids (PILs). All the PIL compounds were characterised by spectroscopic analysis and utilised as homogeneous metal-free organocatalysts for the transfer hydrogenation of ketones to alcohols in isopropanol as solvent and hydrogen source. The metal-free PIL catalysts showed activity for transforming acetophenone to 1-phenyl alcohol at up to 87% conversion. The representative PEG_{600} system was recycled three times with minimal loss in activity. The mechanism of a possible catalyst leaching was investigated using computational calculations. The results reveal that the promoter, isopropanol, also promotes the leaching of the triazole from the PEG backbone.

KEYWORDS

computational chemistry, metal-free catalysis, polymeric ionic liquids, transfer hydrogenation

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INTRODUCTION

Recent interest in catalysis devoted to the development of metal-free organocatalysts that exceed the efficiencies of metal-mediated or enzyme-catalysed transformations has been growing with the emergence of organocatalysis as a bourgeoning, powerful and promising catalytic alternative to the more established traditional methods. Generally, organocatalysts are cheap, air-stable, easy to handle and may be used in water.[1] However, most organocatalyzed transformations reported to date involve high concentrations of the 'catalyst',[2–4] leading to the undesirable generation of unwanted waste products that may require extra measures for isolation from the reaction medium. In addition, in comparison to metal-mediated reactions, organocatalysis results in agglomeration and aggregation of the active sites, which often lead to a higher required molar concentration of the catalyst [3]. Hence, the use of stoichiometric amounts of organocatalysts is a drawback,[3] and this is probably why they have seldom been applied in industry,[5] a fact that can also be attributed to their low efficiency. In addition, the workup procedure for separating the organocatalyst from the product is often tedious and laborious hence the need for their immobilisation/functionalisation. Isolation of these catalysts from the reaction is often cumbersome, and interest in the design of recoverable versions of organocatalysts has increased profoundly in catalysis research.[5–7] Heterogenization of active organic entities promises to be a viable method to alleviate these shortcomings,[8–10] and although it invariably increases the stages of synthetic pathways, the design of effective heterogenized organocatalysts will improve activity, selectivity and recoverability;[11] the benefits of which will by far offset any additional synthetic challenges. Despite the above merits, very few reports of heterogenized organocatalysts can replicate the levels of activity and selectivity observed in homogeneous systems.[12–14] As a result, there is an urgent need to develop a design rationale that could serve as a basis for robustly anchoring homogeneous organocatalysts.[9] Two of the more widely used support systems for the immobilisation of organocatalysts are the use of high molecular weight organic polymers like polyethylene glycols (PEG)[15–18] and anchoring on inorganic oxides like silica.[19–21] When compared to inorganic supports, polymers offer several advantages. They can easily be functionalized, and most of the hydrocarbon polymers are chemically inert; hence the supports will not interfere with the catalyst.[22] The low molecular weight polyethylene glycol (PEG Mn_{400}) was used as the solvent and medium for catalyst recycling in the synthesis of isatin chalcones.[23] The PEG_{400} anchored catalyst was recovered by simple distillation and recycled five times; each cycle was quenched with water. In related studies, the PEG Mn_{400} was used as an immobilization phase for proline-catalyzed aldol reactions.[24] The system allowed the catalyst and solvent to be recycled 10 times without activity loss. Wang et al. have reported a PEG_{1000}-bridged dicationic amine functionalized ionic liquid [PA-PEG1000-DIL][BF4] that demonstrated temperature-dependent phase behaviour with water.[25] The catalyst system was effectively applied in one-pot synthesis of tetrahydrobenzopyrans where separation of products was achieved through filtration and the catalyst was used five times without further treatment. In light of the advantages and disadvantages of both homogeneous and heterogeneous catalyzed reactions, we were inspired to develop a new methodology to immobilize triazolium salts on PEGs for use as recyclable catalyst for the transfer hydrogenation (TH) of ketones. TH involving hydrogen donors such as isopropanol or formates is a much safer, greener and more desirable alternative to conventional hydrogenation with potentially hazardous molecular hydrogen.[26,27] Compared to traditional hydrogenation methods, TH offers operational advantages due to safer operational conditions, low toxicity of reagents and generated byproducts (acetone for isopropanol and carbon dioxide for formates).[28,29] Although alternative approaches based on inexpensive and non-toxic iron group metals have been developed,[30,31] the complexes used as catalysts are prepared via multi-step, low atom economical and low-yielding reactions. Even when isolated, many of the complexes suffer from stability concerns under the basic conditions of the TH process. Hence, to develop much cheaper, sustainable and environmentally benign catalyst systems, we reported a set of imidazolium-based organocatalysts for the TH of ketones.[32] However, the use of imidazolium salts is inherently limited by the fact that the acidic C(2) proton of imidazoles is very susceptible to deprotonation in the presence of strong bases, resulting in the generation of reactive carbenes.[33] The so-called *N*-heterocyclic carbenes have been reported to react directly with carbonyl groups during the course of the TH process to produce unwanted adducts.[34]

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Facile, cheap and stable metal-free TH protocols are desirable. Hence, as a follow-on effort, we envisioned that using triazolium based salts immobilized on PEG could overcome some of these shortcomings. We chose PEG as a support because it is easy to functionalize (serve as an anchor for the salt), is robust (the hydrocarbon backbone is chemically inert) and could improve catalyst recovery and recyclability via thermoregulated pathways.[35] In addition, the immobilization of uncoordinated homogeneous catalysts sometimes improves their activity and selectivity by preventing the formation of inactive dimers, agglomerates and aggregates. Hence, presented in this report is a demonstration of the potential for recycling a polymer-bound azolium ionic liquid, and in order to guide future development of polymer immobilized catalysis, we also propose a mechanism using density functional theory (DFT) calculations that explains some of the key observations from the study.

Experimental

All chemicals and reagents were of reagent grade and were used as purchased. All NMR spectra were recorded in deuterated solvents using a Bruker Ultra-Shield™ spectrometer AVANCE^{III} operating at a frequency of 400 MHz and ambient temperature. Chemical shifts were recorded as δ values in reference to $SiMe_3$ at 0.00 parts per million (ppm) at 25 °C. ^{1}H NMR was reported as chemical shifts (δ, ppm) and referenced to the solvent peak $CDCl_3$ (7.26 ppm); multiplicity and number of protons are presented in parentheses. The proton decoupled ^{13}C NMR was conducted to obtain the carbon skeleton of the triazoles and was presented as chemical shifts (δ, ppm) and referenced to the solvent peak $CDCl_3$ (77.16 ppm) with the specific carbon indicated in parentheses. The IR spectra were recorded on a Perkin Elmer Attenuated Total Reflectance (ATR) spectrophotometer in the 4000-400 cm^{-1} region. Melting point measurements were performed using a Stuart Scientific melting point apparatus. The mass-to-charge ratio (m/z) of the compounds was determined using Bruker Micro TOF-Q11 mass spectrometry with electron spray ionisation (ESI) and a sample concentration of approximately 1 ppm. Synthetic details on compounds **14**-**17** (Scheme 1) were reported elsewhere.[3]

General procedure for the synthesis of the recyclable polymeric ionic liquid (PIL) compounds (18–23)

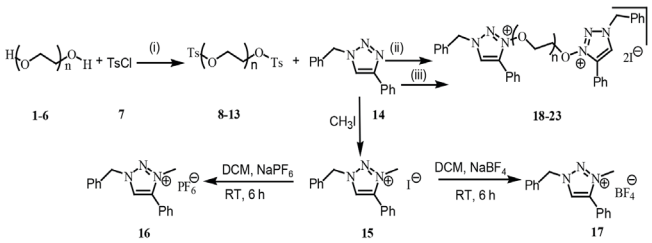
The procedure for the synthesis of the PILs is presented in Scheme 1; the multi-stage process is described in detail below, beginning with the functionalisation of commercially obtained polyethylene glycols (PEG).

Synthesis of PEG ditosylates (8–13)

The procedure is generic for the synthesis of all the PEG ditosylates: **8** (Mn = 300), **9** (Mn = 600), **10** (Mn = 1000), **11** (Mn = 2000), **12** (Mn = 4000) and **13** (Mn = 8000). The procedure for PEG Mn_{300} is thus described: To a stirred mixture of PEG Mn_{300} **1**, (3.000 g, 10 mmol) and p-toluenesulfonyl chloride **7** (3.813 g, 20 mmol) in 20 ml dichloromethane at 0 °C was added triethylamine 2, 2 equiv. dropwise over 10 min. The reaction mixture was then stirred under reflux (40 °C) for 12 hours, followed by cooling to ambient temperature. The reaction mixture was poured into 100 ml of water in a separation funnel. Extraction was done three times using 40 ml dichloromethane; the combined organic layers were washed with 100 ml of brine and dried over anhydrous $MgSO_4$. Evaporation of dichloromethane produced the PEG ditosylate as colourless oil in high yield.

PEG Mn_{300} ditosylate (8)

The starting materials used: p-toluenesulphonyl chloride **7** (2.542 g, 13.3 mmol), triethylamine (1.348 g, 13.3 mmol) and PEG Mn_{300} **1** (3.000 g, 0.01 mol). Colourless oil, 2.731g 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.80 (d, 4H, J = 8.16 Hz, Ar), 7.44 (d, 4H, J = 8.20, Ar), 3.67-3.55 (m, 33H, $(OCH_2CH_2)_n$), 2.45 (s, 6H, 2×CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.5, 134.4, 133.6, 131.2, 129.1, 55.1, 49.8, 49.6, 49.4, 49.2, 49.0, 48.8, 48.6, 21.8 IR; (ATR cm^{-1}): 3412, 2873, 2113, 1650, 1598, 1452, 1350, 1293, 1245.



Scheme 1: Synthesis of PEG immobilised salts of varying molecular sizes. *(i)* Triethylamine, DCM, 40 °C, 12 h; (ii) heated neat at 80 °C, 6 h; (iii) NaI, DCM, RT, 6 h.

PEG Mn_{600} ditosylate (9)

The starting materials used: p-toluenesulphonyl chloride **7** (1.907 g, 0.01 mol), triethylamine (1.012 g, 0.01 moles) and PEG Mn_{600} **2** (3.000 g, 5 mmol). Colourles oil 4.096 g, 90% yield^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.91 (d, 4H, J = 8.04 Hz, Ar), 7.79 (d, 4H, J = 7.92 Hz, Ar), 3.72-3.58 (m, 58H, $(OCH_2CH_2)_n$), 2.45 (s, 6H, 2×CH_3); ^{13}C NMR, (100 MHz, $CDCl_3$, ppm): δ 146.8, 144.7,141.6, 132.9, 130.2, 129.8, 129.5, 127.0, 72.5, 71.3, 70.6, 70.5, 70.4, 70.2, 69.2, 68.6, 21.7, 21.6; IR (ATR cm^{-1}) 3469, 2870, 1797, 1452, 1352, 1293, 1174, 1095.

PEG Mn_{1000} ditosylate (10)

The starting materials used: p-toluenesulphonyl chloride **7** (1.907 g, 10.0 mmol) and triethylamine (1.012 g , 10.0 mmol) and PEG Mn_{1000} **3** (5.000 g, 5 mmol). Colourless oil 5.568 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.92 (d, 2H, J = 7.92 Hz, Ar), 7.79 (d, 2H, J = 7.80 Hz Ar), 7.42 (2H, d, J = 7.88, Ar) 7.34 (2H, d, J = 12.48, Ar) 3.73–3.58 (m, 110H, $(OCH_2CH_2)_n$), 2.50 (s, 3H, CH_3) 2.45 (s, 3H, CH_3); ^{13}C NMR, (100 MHz, $CDCl_3$, ppm): δ 146.8, 144.7,141.6, 132.9, 130.2, 129.7, 127.9, 126.9, 72.5, 70.6, 70.5, 70.2, 69.2, 68.6, 61.6, 53.5, 52.1, 21.7, 21.5; IR (ATR, cm^{-1}) 3392, 2928, 1615, 1498, 1451, 1301, 1151,1041, 729, 505.

PEG Mn_{2000} ditosylate (11)

The starting materials used: p-toluenesulphonyl chloride **7** (0.953 g , 5 mmol), PEG Mn_{2000} **4** (5.000 g, 2.5 mmol) triethylamine (0.506 g, 5 mmol). White solid, 5.313 g, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.93 (d, J = 8.44 Hz, 2H, Ar), 7.41(d, J = 8.24 Hz, 2H, Ar), 7.43-7.40 (2H, d, Ar) 7.36-7.33 (2H, d, Ar) 4.17-3.58 (m, 130H, $(OCH_2CH_2)_n$), 2.49 (s, 3H, CH_3) 2.45 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 146.8, 144.7,141.7, 133.0, 130.2, 129.8, 127.0, 71.3, 70.7, 70.5, 69.2, 68.6, 21.8, 21.6; IR (ATR, cm^{-1}) 3700, 3085, 2965, 2876, 2364, 1954, 1621, 1239, 1161, 1155, 1004, 679.

PEG Mn_{4000} ditosylate (12)

The starting materials used: p-toluenesulphonyl chloride **7** (0.456 g, 2 mmol), PEG Mn_{4000} **5** (4.000 g, 1 mmole) triethylamine (0.243 g, 2 mmol). White solid, 3.405 g, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.93(d, J = 8.44 Hz, 4H, Ar), 7.41 (d, J = 8.24 Hz, 4H, Ar), 3.75-3.67 (m, 83H, $(OCH_2CH_2)_n$), 2.49 (s, 6H, CH_3); ^{13}C NMR, (100 MHz, $CDCl_3$, ppm): δ 146.8, 144.7,141.6, 132.9, 130.2, 129.8, 128.6, 127.9, 127.0, 126.1, 71.3, 70.7, 70.5, 69.2, 68.6, 21.8, 21.6; IR (ATR, cm^{-1}) 3060, 3085, 2965, 2876, 2364, 1954, 1621, 1594, 1493, 1239, 1155, 679, 562.

PEG Mn_{8000} ditosylate (13)

The starting materials used: p-toluenesulphonyl chloride **7** (0.191 g, 1 mmol), PEG Mn_{8000} **6** (4.000 g, 0.5 mmole) triethylamine (0.101 g, 0.5 mmol). White solid, 3.698 g, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.36 (d, J = 8.36 Hz, 4H, Ar), 7.35 (d, J = 8.24 Hz, 4H, Ar), 3.57 (s, 99H, $(OCH_2CH_2)_n$), 2.42 (s, 6H, 2×CH_3); ^{13}C NMR, (100 MHz, $CDCl_3$, ppm): δ 146.7, 144.7,141.6, 133.0, 130.2, 129.8, 127.9, 70.7, 70.5, 69.2, 68.6, 21.8, 21.6; IR (ATR, cm^{-1}) 3434, 2882, 2740, 2226, 1958, 1650, 1466, 1454, 1413, 1359, 1341, 1279, 1146, 1060, 946, 841.

Click reaction for the synthesis of 1-benzyl-4-phenyl-1H-1,2,3-triazole (14)

The triazole compound **14** was synthesised via the Cu catalysed [2+3] cycloaddition reaction of an organic azide and an alkyne, a so-called 'click' reaction.[37] Successful isolation was confirmed by spectroscopic analysis:

Starting materials were benzyl bromide (2.880 g, 16.8 mmol), NaN_3 (1.314 g, 20.2 mmol) and phenylacetylene (1.720 g, 16.8 mmol). White solid 3.33 g, 84% yield, mp 125 -126 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.79 (d, J = 7.20 Hz, 2H, Ar) 7.66 (s, 1H, triazole, C=CH) 7.38 (d, J = 17.81 Hz, 5H, Ar) 7.31 (d, J = 2.20 Hz, 3H, Ar) 5.57 (s, 2H, CH_2); ^{13}C NMR (100 MHz $CDCl_3$, ppm): δ 148.2, 134.6, 130.5, 129.1, 128.8, 128.7, 128.1, 128.0, 125.7, 119.5, 54.2; IR (ATR, cm^{-1}) 3143, 3083, 3029, 2977, 1694, 1606, 1469, 1450, 1362, 1223, 1046, 767, 728, 694.

Immobilization of compound 14 unto PEG compounds 8-13 to yield PIL compounds 18–23

An immobilization protocol that involved a simple solvent-free reaction between the synthesized PEG ditosylates and the triazole compound at a moderate temperature was followed (Scheme 1). Hence, in a typical reaction, a mixture of compound **8**, PEG Mn_{300} ditosylate (1.074 g, 1.75 mmol) and compound **14** (0.825 g, 3.51 mmol) were heated neat in a 100 ml round-bottomed flask at 80 °C for 6 h. After cooling to ambient temperature, 20 ml of dichloromethane and 1.052 g (7.02 mmol) of NaI were added and stirred at room temperature for a further 6 h followed by filtration over a pad of Celite. Excess solvent was removed in vacuo to afford 1.581 g of a brick red ionic liquid **18** at 88% yield. Following a similar protocol, PEG immobilised compounds **19** (Mn = 600), **20** (Mn = 1000), **21** (Mn = 2000), **22** (Mn = 4000) and **23** (Mn = 8000) were isolated and characterised.

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Brick red ionic liquid 1.581 g, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.89 (s, 1H, triazole)7.96–7.95 (d, 2H, Ar), 7.79–7.36 (m, 6H, Ar), 5.82 (s, 2H, CH_2) 3.77–3.49 (m, 25H, $(OCH_2CH_2)_n$); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 146.5, 135.9, 131.4, 130.5, 129.2, 129.1, 190.0, 128.8, 127.8, 125.1, 69.7; (ATR, cm^{-1}) 2869, 1918, 1597, 1495, 1351, 1291, 1246, 1174, 1095, 916; HRMS cald for $[C_{15}H_{13}N_3 + H]^+$ 236.2838 found 236.1192, 331.1229 (M^+, n = 7), 385.1170 (M^+, n = 8), 430.1877 (M^+, n = 9), 474.2156 (M^+, n = 10), 518.2422 (M^+, n = 11), 566.2264 (M^+, n = 12) 610.2563 (M^+, n = 13), 654,2843 (M^+, n = 14), 698.311 (M^+, n = 15), 742.3390 (M^+, n = 16), 786.3654 (M^+, n = 17), 870.3342 (M^+, n = 19), 914.3605 (M^+, n = 20).

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The starting materials used were: compound **14** (0.789 g, 3.36 mmol), PEG ditosylate Mn_{600} 1.530 g, 1.68 mmol to yield a brick red ionic liquid 1.977 g, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.42 (s, 1H, triazole) 7.88-7.88 (d, 2H, Ar), 7.88–7.31 (m, 8H, Ar), 5.70 (s, 2H, CH_2) 3.68–3.63 (m, 83H, $(OCH_2CH_2)_n$); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 147.6, 137.4, 134.5, 131.8, 130.1, 130.1, 130.0, 129.9, 129.7, 129.6, 129.6, 129.4, 129.0, 128.8, 128.5, 128.3, 128.1, 125.8, 121.8, 120.3, 71.8, 71.6, 71.1,70.369.0, 54.3; (ATR, cm^{-1}) 3439, 3015, 2871, 2503, 1902, 1615, 1349, 1209, 1094, 946, 768, 717; HRMS cald for $[C_{15}H_{13}N_3N_a]^+$ 258.1007 found 258.1059, 745.1083 (M^+, n = 17), 789.1354 (M^+, n = 18), 833.1626 (M^+, n = 19), 1053.3004 (M^+, n = 24).

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The starting materials used were: compound **14** (0.652 g, 2.77 mmol), PEG Mn_{1000} ditosylate **10** (1.817 g, 1.30 mmol). Brick red viscous liquid, 1.864 g, 78% yield. ^{1}H NMR (400 MHz, $(CD_3)_2SO$, ppm): δ 8.64 (s, 1H, triazole) 7.85–7.85 (d, 2H Ar), 7.85–7.84 (d, 2H, Ar) 7.83–7.74 (m, 4H, Ar) 7.48–7.32 (m, 3H, Ar), 5.64 (s, 2H, CH_2) 3.53–3.43 (m, 51H, $(OCH_2CH_2)_n$); ^{13}C NMR (100 MHz, $(CD_3)_2SO$, ppm): 130.6, 129.7, 129.0, 128.8, 128.7, 128.1, 127.8, 125.1, 121.5, 69.7; (IR, ATR, cm^{-1}) 3469, 3061, 2868, 1963, 1635, 1456, 1348, 1297, 1249, 1091, 946, 697; HRMS cald for $[C_{15}H_{13}N_3N_a]^+$ 258.1007 found 258.1215, 557.3431 (M^+, n = 12), 623.3912 (M^+, n = 14), 711.6539 (M^+, n = 16), 799.5116 (M^+, n = 18).

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The starting materials used were: compound **14** (0.782 g, 3.33 mmol), PEG Mn_{2000} ditosylate **11** (3.84 g, 1.66 mmol). Brick red viscous liquid, 3.262 g, 72% yield. ^{1}H NMR (400 MHz, $(CD_3)_2SO$, ppm): δ 8.65 (s, 1H, triazole) 7.87–7.85 (d, 2H, Ar), 7.83–7.32 (m, 8H, Ar), 5.764 (s, 2H, CH_2) 3.56-3.46(m, 71H, $(OCH_2CH_2)_n$); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 140.8, 133.0, 129.9, 129.3, 128.9, 128.7, 126.2, 126.1, 70.5; (IR, KBr, cm^{-1}) 3462, 3142, 2977, 1966, 1469, 1449, 1361, 1223, 1075, 1046, 728, 767, 694; HRMS cald for $[C_{15}H_{13}N_3N_a]^+$ 258.1007 found 258.1104, 748.0179 (M^+, n = 17).

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The starting materials used were: compound **14** (0.498 g, 2.12 mmol), PEG Mn_{4000} ditosylate **12** (2.449 g, 1.05 mmol). Brick red viscous liquid, 4.102 g, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.03 (s, 1H, triazole) 7.93–7.91 (m, 2H, Ar), 7.84–7.78 (m, 6H, Ar), 5.61 (s, 2H, CH_2) 3.69–3.58 (m, 161H, $(OCH_2CH_2)_n$); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 130.2, 129.8, 129.2, 129.0, 128.8, 128.3, 127.9, 127.0, 126.2, 126.1, 70.5; (IR, KBr, cm^{-1}) 3440, 3143, 2977, 2872, 1607, 1469, 1450, 1362, 1224, 1076, 747, 728, 694; HRMS cald for $[C_{15}H_{13}N_3N_a]^+$ 258.1007 found 258.1366, 459.1501 (M^+, n = 10), 679.3110 (M^+, n = 15).

23

The starting materials used were: compound **14** (0.461 g, 1.96 mmol), PEG Mn_{8000} ditosylate **13** (8.149 g, 0.98 mmol). Brick red viscous liquid, 7.270 g, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.79 (s, 1H, triazole) 7.83–7.77 (q, 4H, Ar), 7.42–7.28 (t, 4H, Ar), 7.20–7.18 (d, 2H, Ar) 5.62 (s, 2H, CH_2), 3.77–3.58 (m, 290H, $(OCH_2CH_2)_n$); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 140.8, 129.2, 129.0, 128.9, 128.3, 126.2, 126.0, 71.3, 70.5, 54.9; (IR, KBr, cm^{-1}) 3439, 3142, 3029, 2977, 1986, 1966, 1607, 1582, 1469, 1450, 1362, 1223, 1046, 767; HRMS cald for $[C_{15}H_{13}N_3N_a]^+$ 258.1007 found 258.1389, 679.3200 (M^+, n = 15).

General procedure for the transfer hydrogenation reactions

A catalytic amount of salts **15–23** (2.5 mol%) and KOH (0.112 g, 0.2 M) in isopropanol (10 ml) as solvent and hydrogen donor were placed in a Schlenk tube, followed by the addition of the respective ketones (2.2 mmol). The mixture was refluxed at 82 °C for 12 hr. The reaction progress was monitored by taking aliquots at time intervals, passed through a pad of silica and injected into a GC. The identities of the products were assessed by comparison of their retention times with commercially available (Aldrich Chemical Co.) samples. The percentage conversions were obtained from integration values of the GC peaks, which were related to residual unreacted ketones.

Computational details

Input structures **24** and **26** were energy optimized to their respective output structures **25** and **27** without symmetry constraints using the Gaussian 16 Rev. C01 program.[38] The hybrid B3LYP functional[39,40] and the standard 6-31+G(d,p) basis set[41] were used for the optimizations. This level of theory has shown comparable results to those obtained from experiments.[42] The effect of isopropanol solvent on the PEG tethered IL was probed using the implicit default (PCM) model.[43] Possible π/π interactions were accounted for by including Grimme's empirical correction for dispersion.[44] Optimized global minimum energy structures were verified by frequency calculation, and no imaginary frequency was obtained, and coordinates of the energy-minimized structures are provided in the ESI.

RESULTS AND DISCUSSION

The main azolium backbone was synthesised following standard copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) "click" reaction of an *in situ* generated organic azide with a terminal alkyne.[37] Covalent immobilization of **14** onto PEGs of varying molecular sizes (Mn = 300–8000) yielded PEG ionic liquid compounds **18–23** that were confirmed by ^{1}H NMR analysis. This protocol involves the tosylation of PEG diols followed by a neat reaction between the synthesized tosylate and the triazole at a moderate temperature (Scheme 1). It is a high-yielding reaction with a simple workup.

The traditional method of preparing tosylated alcohol derivatives follows a well-accepted procedure based on pyridine as both the base and solvent, but the technique requires over 10 equiv. of the pyridine base to prevent the formation of undesired intermediates. Tanabe et al. developed a pyridine-free amine-catalyzed tosylation of alcohols in water; however, the method suffered from hydrolysis of the sulfonyl chlorides by moisture and requires pH adjustments.[45] Herein a facile method for the tosylation of alcohols in refluxing dichloromethane was adopted.[46] Well-resolved ^{1}H NMR and ^{13}C NMR spectra were obtained for all the synthesized PEG tosylates. For example, Figure 1 shows the ^{1}H NMR spectrum of PEG_{300} ditosylate **8**. The appearance of a singlet signal at 2.45 ppm, which integrated into six protons, confirms the presence of two methyl groups attached to the benzene ring as constituted. In comparison, the presence of the polymer backbone was established by the appearance of a multiplet between 3.68–3.51 ppm (d,e Figure 1).

The ^{1}H-NMR spectrum of **18** (see ESI, Figure S23) showed the appearance of protons from the triazolium moiety as constituted. The downfield shift of the typical triazole fingerprint proton from 7.6 ppm to 8.7 ppm affirmed that a formal positive charge was formed on the triazolium heterocyclic ring upon PEG immobilization. Integration of the ^{1}H-NMR band at 3.6 ppm corresponded to the PEG backbone $(OCH_2CH_2)_n$ of compound **18**. The MS results of the immobilized compounds correlated well with observed values. The fragmentation patterns of the polymeric backbones showed molecular weights of different oligomeric units separated by the mass of the repeating unit (see ESI). IR spectroscopy also confirmed the immobilization of **14** onto the various PEGs with all characteristic functional group bands observed. It is essential to highlight that the as-prepared PEG triazolium salts were supported by tosylate conterions, which were subsequently substituted with iodide ions via salt metathesis, the success of which was evidenced by the disappearance of proton and carbon signals of the tosyl group from the ^{1}H- and ^{13}C-NMR spectra respectively.

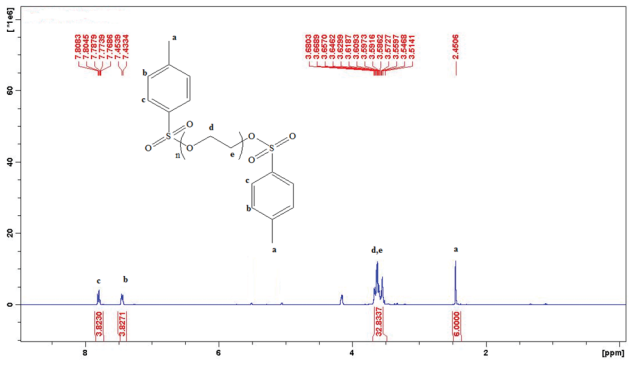


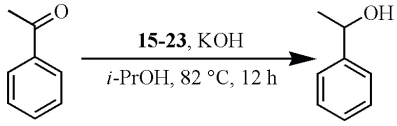
Figure 1: ^{1}H NMR spectrum of PEG_{300} ditosylate **8**.

Catalytic transfer hydrogenation (CTH) reaction

Because of growing global concerns for the health of the environment and the need to develop sustainable processes, we envisioned that triazolium-based organocatalysts would share similarities in catalytic performance to related imidazolium analogues reported to be active in CTH reactions.[32] Also, the stability and resistance of triazolium C(4,5) protons to deprotonation by bases is well-documented, which is in stark contrast to the susceptibility of the acidic imidazolium C(2) proton to attack under such conditions.[33] As a follow-up to our previous report [32] on using imidazolium salts as organocatalysts for CTH, we hypothesized that a triazolium salt would thus possess added advantages for CTH reactions that are promoted by inorganic bases such as KOH.

The coupling of compound **14** to the PEG ditosylates (**8–13**) in high-yielding solvent-free reactions resulted in the isolation of corresponding PILs bearing the tosylate counterion. Initially, the CTH reactions were conducted using the tosylated PILs as catalysts, and in all cases, no conversion of acetophenone was observed. That was unusual because the base (KOH), in the reaction mixture could reduce acetophenone even when used alone (Table 1, entry 1). The lack of activity on the CTH of acetophenone using the PIL ditosylates is attributed to the preferential reduction of the tosylate group to hydro-sulfonyl benzene in direct competition with the substrate. Hence, to find the best counter ion for the PIL catalysts compounds **15-17** bearing three commonly encountered IL anions (I^-, PF_6^- and BF_4^-) were prepared from the precursor **14** (Scheme 1). The IL compounds **15-17** were screened as CTH organocatalysts, with the

Table 1: Transfer hydrogenation of acetophenone catalyzed by salts **15-23**.



Entry	Organocatalyst	Conversion (%)[a]
1[b]	–	42
2	**15**	87
3	**16**	53
4	**17**	65
5[c]	**15**	0
6[d]	**15**	0
7[e]	**15**	0
8[f]	**15**	38
9[g]	**15**	56
10	**18**	73
11	**19**	87
12	**20**	66
13	**21**	51
14	**22**	49
15	**23**	44

Except for d-g; reactions were conducted in air at 82 °C using acetophenone (2.2 mmol), KOH (0.112g) dissolved in 10 ml isopropanol. [a]Conversion was determined by GC analysis after 12 h (average of two runs within ±5%). [b]No catalyst. [c]No base. Reaction temperature = [[d]24 °C (RT), [e]50 °C, [f]60 °C and [g]70 °C].

results presented in Table 1 (entries 2–4). The results showed that the iodide-containing compound **15** (entry 2) is the more effective catalyst. Hence, we chose the iodide (in preference to bulkier PF_6^- and BF_4^-) as the counter ion for synthesising PILs **18-23** that were tested as catalysts, as presented in Table 1. The results (entries 5-9) confirm well-established facts about CTH, that the reaction requires a base (KOH, entry 5) and refluxing temperature, as confirmed by the results in entries 6-9 conducted at below reflux temperatures. In refluxing isopropanol at 82 °C, excellent conversions were observed due to increased reagent solubility and improved substrate/catalyst contacts.

PIL - CTH: the development of a recyclable catalyst

With PILs **18–23** as catalysts (Table 1, entries 10-15), it is clear from the data that their activity as catalysts decreased with an increase in polymer molecular weight, presumably due to poor substrate-catalyst interactions as viscosity increased with the higher molecular weight polymers (Mn = 2000–8000). It may also be attributed to a limitation in the accessibility to the reactive centres for the substrate associated with high molecular weights since the active organocatalytic sites are tethered at the terminal ends of the polymer chain. As a result, the ionic liquid compound **19** based on PEG_{600} was used as the model PIL catalyst for further study. In comparison, Wang et al. found PEG_{1000} to be the optimum for both the esterification and acetalization of aromatic acids and aldehydes.[47] In a related study, da Rosa et al. utilized a two-organic liquid biphasic system consisting of PEG, heptane and either CH_2Cl_2 or methanol in the catalytic hydrogenation of hex-1-ene using Wilkinson's catalyst or a cationic rhodium complex, respectively.[48] Generally, ionic liquids are immiscible with non-polar solvents like dialkyl ethers and saturated hydrocarbons.[49] Because the PIL catalyst **19** is substantially soluble in refluxing isopropanol (Figure 2a, left), a thermoregulated phase separation and recycling method for catalyst recovery was envisaged. Hence, we studied its recovery and recycle by using solvents that are immiscible with ionic liquids.

This involved cooling the reaction mixture at the end of a catalytic run, followed by the gradual addition of a counter-solvent that is immiscible with the ionic liquid catalyst to induce its precipitation and reuse. The addition of cold diethyl ether at the end of the reaction enabled distinct separation between the PEG-bound ionic liquid catalysts and isopropanol/ether (supernatant layer, Figure 2a, right). Hence, **19** was recycled by decantating the supernatant organic layer containing the product and unreacted substrate. When the lower IL layer was extracted with dichloromethane to remove excess KOH and analysed, no transfer hydrogenation product was observed, implying that it was all in the supernatant layer. Hence, the IL layer was recycled by adding fresh isopropanol, substrate and KOH. The results presented in Figure 1b show that PIL catalyst **19** could be recycled up to three times without any significant activity loss; however, after the third cycle, white sediments settled at the base of the reaction flask upon the addition of diethyl ether. This may have resulted from the detachment of the triazolium moiety from the polymer support, probably aided by the basic KOH, which could induce cleavage of the polymer-triazole N-O bond. Any residual moisture in the added reagents may also cause hydrolysis of the organocatalyst into an inactive state.[50]

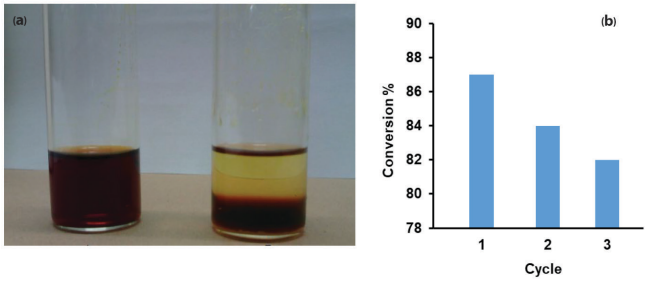


Figure 2: (a) (**left**) A homogeneous catalyst system and (**right**) post-reaction separation upon cooling and addition of ether, and (b) recycling studies (average of two runs within ±5%) for the PEG tethered IL catalyst **19**.

Geometry optimization

In computational modelling of organic molecules, the availability of computational resources and the time required to complete a given calculation are major limiting factors that should be carefully considered. In most cases, the computational time increases drastically with the size of the molecule being analysed. To this effect, we limited the chain length to as short as possible because the size of the PEG chain length used should not affect the insight derived from computational calculations. This follows that only one representative of the ILs (**18–23**) should provide enough picture of the reactivity/interaction of the IL with isopropanol. Therefore, a representative of ILs was constructed while minimizing the PEG chain length to n = 5. An equilibrium geometry was obtained using the Avogadro software[51] (**24**, Figure 3), followed by energy minimization in Gaussian 16. After full energy minimization, there was cleavage of the O4–N5 covalent bond that holds the IL bound on one end of the polymer support. Interestingly, the other triazole moiety remained bound to the polymer support. This clearly shows that leaching the polymer-bound triazolium salt is a stepwise process as supported by the recyclability of at least three cycles.

Mechanism of catalyst leaching

The product from optimization (**25**) represents a free radical that is usually very reactive and unstable. This geometry is preferred over **24** because of electrostatic stabilization caused by the dielectric continuum of isopropanol incorporated in the implicit solvent used.[52] To get a clearer picture of the leaching mechanism, two discrete solvent molecules of isopropanol were added to **25**, thereby generating a new input structure **26** (Figure 4). The discrete solvent molecules were deliberately positioned such that isopropanol interacted with the oxygen atoms of the parent PEG chain through classical hydrogen bonding. A full geometry optimization followed this. The geometry of the new output structure (**27**) shows that the hydrogen atoms H82 and H93 from isopropanol completely reduced the PIL back to the original PEG and the formation of acetone and neutral triazoles.

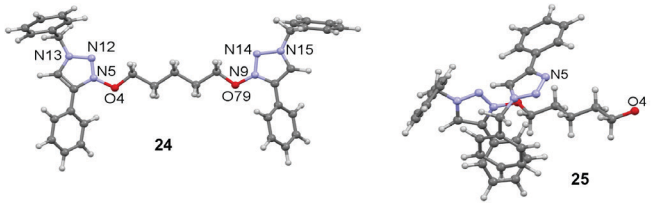


Figure 3: Ball and stick representation of PEG tethered IL before (**24**) and after (**25**) energy minimization in isopropanol, coordinates for 3D structures are available in the ESI.

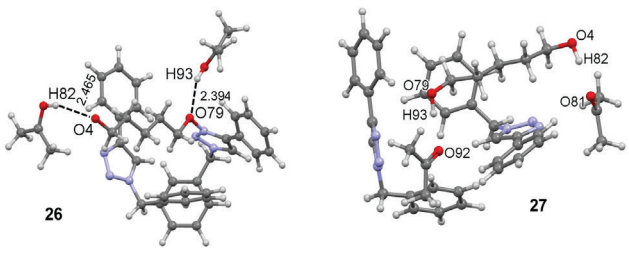


Figure 4: Ball and stick representation of (a) PEG bound IL **26** in the presence of two discrete solvent molecules of isopropanol before and after energy minimization, and (b) the leaching product **27**. Coordinates for 3D structures are available in the ESI.

CONCLUSION

In summary, a new series of triazolium ionic compounds were prepared and used to develop a set of metal-free organocatalysts for the transfer hydrogenation of acetophenone. Based on a triazolium active species tethered on PEG, a thermo-regulated counter-solvent technique was developed to recycle the catalysts up to three cycles without significant loss in the catalytic activity. However, the solvent isopropanol plays a dual role which eventually results in the complete leaching of the polymer-tethered IL. The key advantage of the present catalyst system for transfer hydrogenation is the potential for recyclability, which is absent for conventional homogenous TH catalyst systems.

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SUPPLEMENTARY MATERIAL

Supplementary information for this article is provided in the online supplement. This contains spectral characterization data for the title compounds, including copies of the IR, MS, ^{1}H NMR and ^{13}C NMR spectra (Figures S1-S40). Also included are the calculated Cartesian coordinates for compounds **24-27** (Table S1).

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