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Short Communication

Preparation of novel magnetic dicationic ionic liquid polymeric phase transfer catalyst and their application in nucleophilic substitution reactions of benzyl halides in water

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ABSTRACT

PEG-based magnetic dicationic ionic liquid was successfully prepared and evaluated as phase-transfer catalyst for nucleophilic substitution reactions of benzyl halides for the synthesis of benzyl azides and cyanides from good to excellent yields at 90 °C in water. The reactions occur in water and furnish the corresponding benzyl derivatives in high yields. No evidence for the formation of by-product for example benzyl alcohol of the reaction was observed and the products were obtained in pure form without further purification.

1. Introduction

Green chemistry is a major issue of modern chemistry currently. The use of environmentally benign solvent instead of traditional organic solvents is the important and efficient strategy in green chemistry. Water is a promising green solvent to use in chemistry because it is cheap, readily available, and nontoxic. There is increasing recognition that organic reactions carried out in water may offer advantages over those in organic solvents [1,2]. However, the poor solubility of reactants in water is the main obstacle of the use of water as reaction solvent. One of the most important strategies to overcome this limitation is the utilization of phase transfer catalyst such as ionic liquid (IL).

Phase transfer catalysis is a widely accepted method in industry and organic synthesis as an effective synthetic tool by which liquid–liquid or liquid–solid phase-separated reactions are accelerated [3]. Extensive reviews both on chemistry and engineering viewpoints of phase transfer catalysts (PTCs) have been published in the last few decades [4]. PTCs are also widely used in manufacturing specialty chemicals [5–7].

Phase-transfer catalysis (PTC) is a well-known method of promoting reactions between reagents with opposite solubility preferences. In such systems each reactant is dissolved in the appropriate solvent. Commonly, the two solvents are immiscible to one another, and then a phase-transfer catalyst is added to facilitate the transport of one reactant into the other phase. By means of the catalytic step, the enhanced reactivity between the ionic species leads to the increase of the rate of the desired reaction [8–11].

The design of efficient and recoverable phase-transfer catalysts has become an important issue for reasons of economic and environmental impact, in recent years. In particular, PEG based dicationic ionic liquid has considerable advantages, including easy catalyst recovery and product isolation, and employment of a continuous flow method owing to the two-phase nature of the system, which make the technique attractive for industrial applications [12,13].

In the field of ionic liquids, our interests center on the development of some new magnetic ionic liquids based on imidazolium and cations, and studying their applications in catalytic organic synthesis as energetic materials. Recently, as part of our efforts to introduce novel PTC systems for the synthesis of organic compounds [14].

Even though some anticancer natural product, drug candidates, synthetic intermediates, and insecticides possess cyanide, azide or thiocyanate functional groups, there are few reported practical synthetic routes in the literature for these classes of compounds [15,16]. Owing to the widespread applications of the described compounds, and our interest in developing a true water tolerant catalyst using inexpensive and nonpolluting reagents, herein we report the synthetic applicability of PEG-MDIL as novel phase-transfer catalyst for the rapid and efficient preparation of benzyl azides and cyanides in water by nucleophilic substitution reactions.

2. Results and discussion

Polyethylene glycol functionalized magnetic dicationic ionic liquid (PEG-MDIL) was synthesized as shown in Scheme 1. Polyethylene glycol dichloride was prepared in high yield following a literature method [17]. They were further treated with two equivalents of 1-

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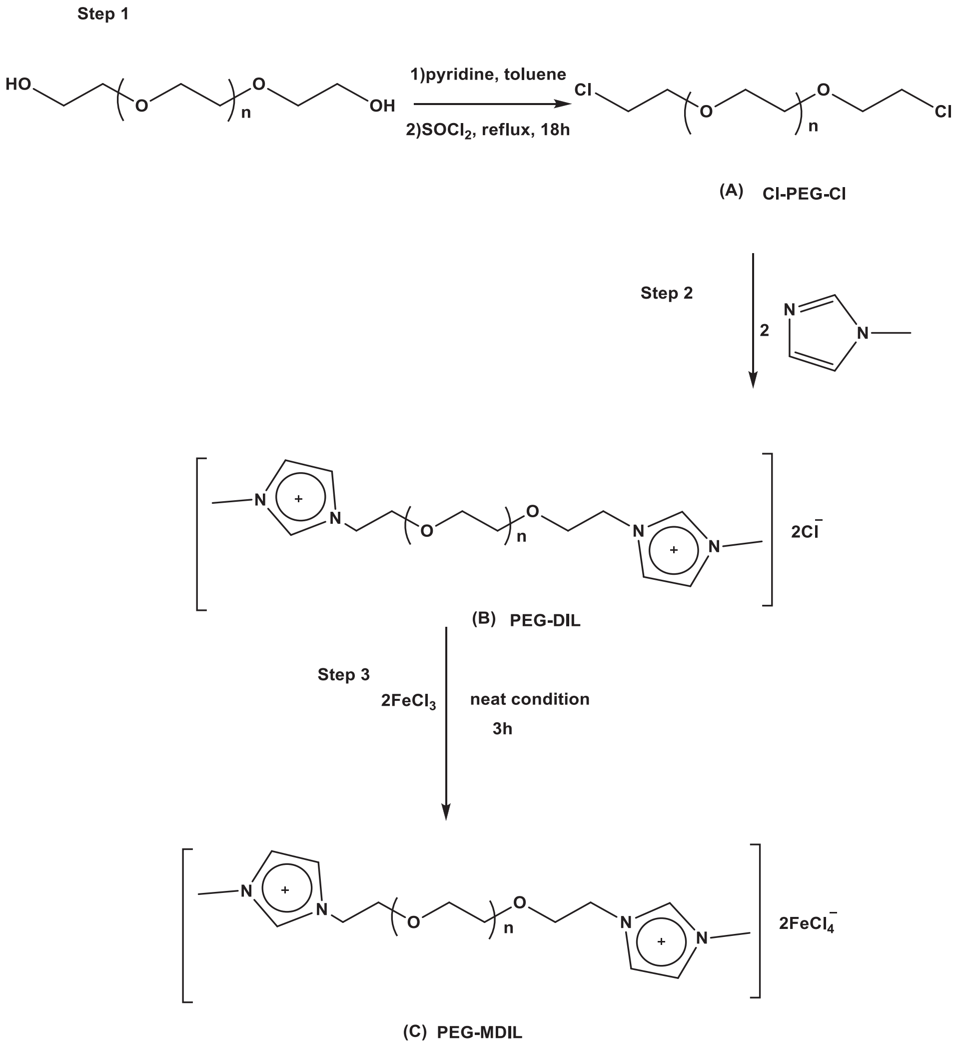


Scheme 1. Synthesis of PEG-MDIL.

methylimidazole, respectively, under neat reaction conditions, to form dicationic chloride bridged by polyether linkage chains in high yields. With the exception of one compound containing one ether linkage chain (solid), the diimidazolium chloride derivatives are sticky colorless liquid.

In the latest step, the anions of imidazolium based dicationic room temperature ionic liquid, Cl^-, were easily changed with $FeCl_4^-$ anions by the simple mixing of $FeCl_3$ under neat conditions.

Due to the paramagnetic nature of the polyethylene glycol functionalized magnetic dicationic ionic liquid, nuclear magnetic resonance

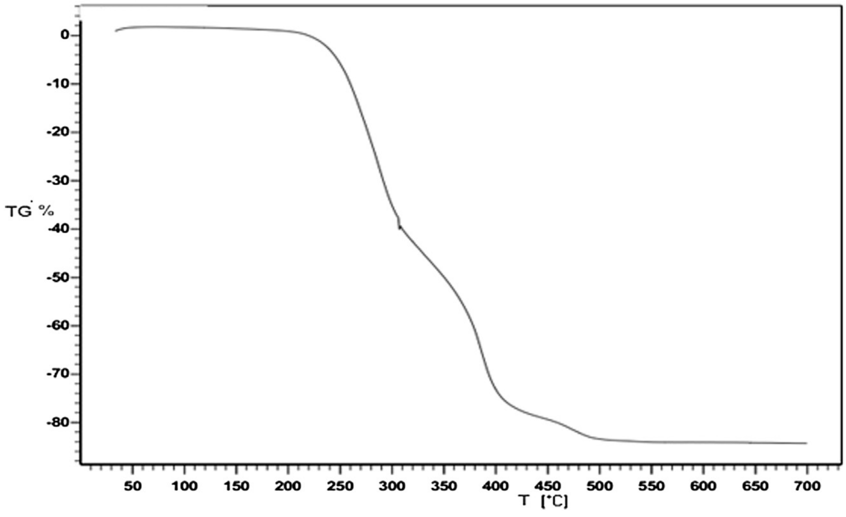


Fig. 1. TGA of PEG-MDIL.

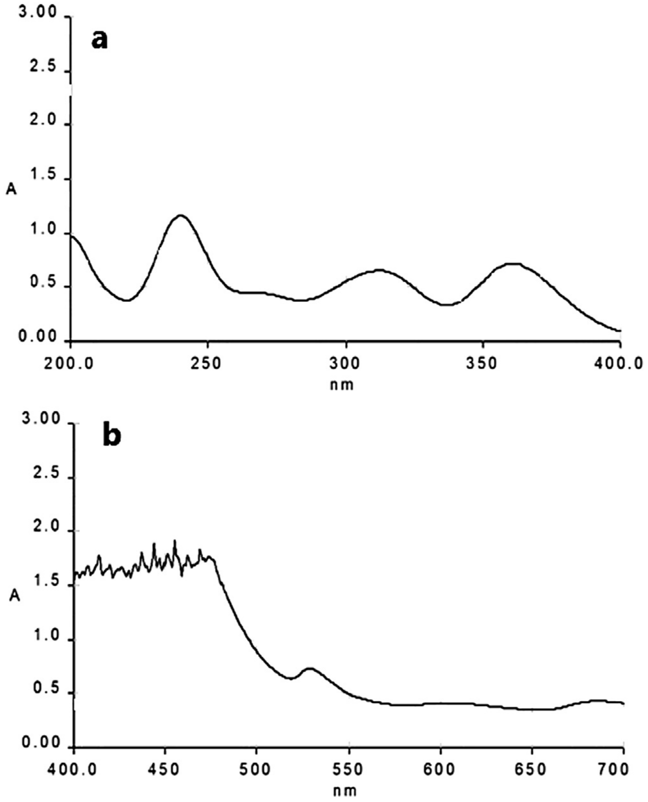


Fig. 2. Visible spectrum of PEG-MDIL (200–400 nm) (a), UV spectra of PEG-MDIL (400–700 nm) (b).

technique could not be used to confirm its structure. Instead, UV and IR spectra were used to characterize the PEG-MDIL structure.

The thermal gravity analysis curve of catalyst under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} is shown in Fig. 1. There were three main steps of weight loss, and the decomposition events took place at 220 °C, 310 °C and 400 °C. On the basis of weight changes, the first process PEG-MDIL spectra exhibited absorption bands that were attributed to the loss of ether linkage (found 38%, calc. 39%). The second event corresponded to the loss of FeCl$_4^-$ (found 38%, calc. 42%). The weight loss (about 17%) from 400 °C to 500 °C was attributed to the decomposition of 1-methylimidazole.

The UV spectrum is shown in Fig. 2. The UV–vis absorption spectra of PEG-MDIL in acetonitrile consist of two main bands at 310–425 nm and 240–300 nm (see Fig. 2a). The shorter wavelength band is attributed to the π → π* transition in the imidazole ring, and the longer wavelength band was found to be due to the n → π* transition. PEG-MDIL spectra exhibited absorption bands in the visible region at 534,473 nm which are characteristic for the FeCl$_4^-$ anion (Fig. 2b)

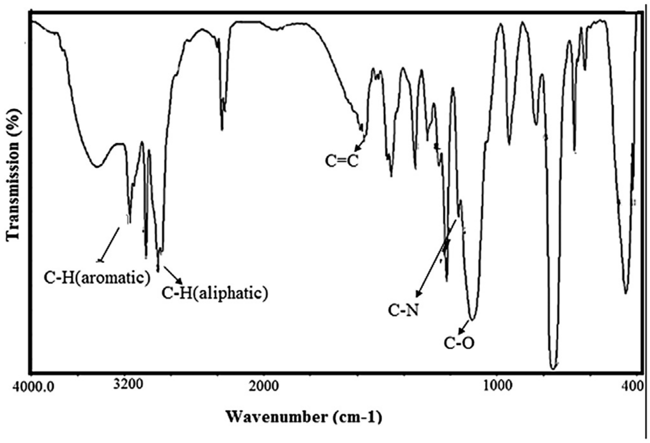


Fig. 3. FT-IR spectra of PEG-MDIL.

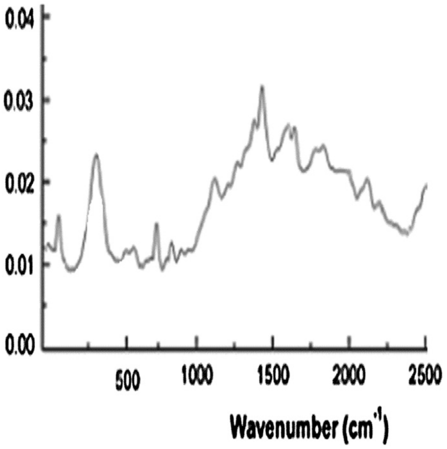
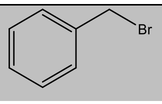
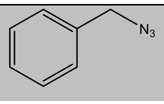
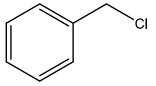
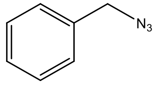
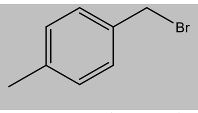
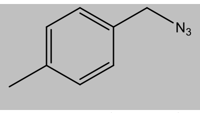
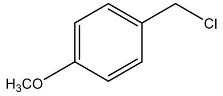
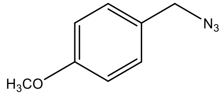
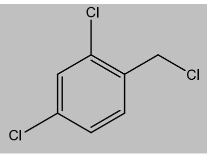
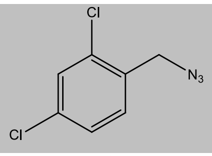
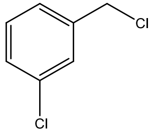
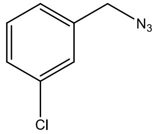
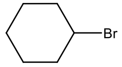


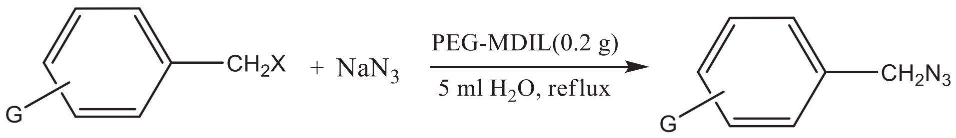
Fig. 4. Raman spectrum of PEG-MDIL.

To characterize the PEG-MDIL, we used the FT-IR spectrum. The FT-IR spectrum of native PEG-MDIL sample is shown in Fig. 3. The results show that the band at about 3200–3500 cm^{-1} was attributed to the OH stretching vibrations. But, after functionalization, the bending vibration absorption peak of O–H at about 3200–3500 cm^{-1} disappeared. There

Table 1
Reaction of various benzyl halides with sodium azide in the presence of PEG-MDI in water.

Entry	Benzyl halide	Product[a]	Time (min)	Yield[b] (%)
1			50	86
2			55	84
3			50	86
4			55	87
5			60	83
6			50	84
7			45	82
8		-	300	-

[a] Products were identified by comparison of their physical and spectral data with those of authentic samples.
[b] Isolated yields.



Scheme 2. Synthesis of benzyl azide from benzyl halide in the presence of magnetic phase transfer catalyst.

are peaks at about 1165 cm^{-1}, which were assigned to the characteristic absorption of N–CH_2 in functionalized PEG-MDIL. The absorption bands at 3152 and 3013 cm^{-1} (imidazolium CH stretching modes) presented in the inset of Fig. 3 demonstrate modification of the PEG. The absorption at 2911 cm^{-1} is usually assigned to CH_2 stretching of the polyether linkage chains. The absorption observed at 1571 cm^{-1} is also characteristic of the imidazolium ring and is assigned to imidazolium ring stretching.

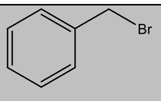
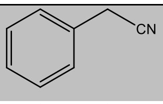
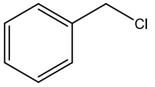
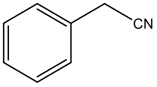
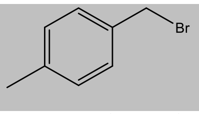
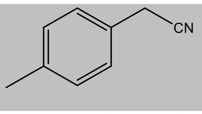
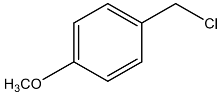
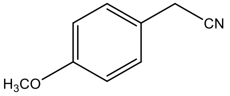
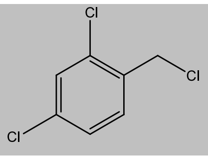
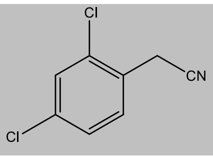
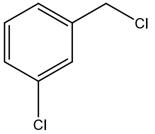
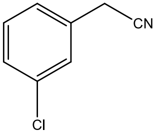
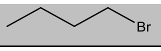
Moreover, this PEG-MDIL was characterized via Raman spectroscopy and proved to be identical with an authentic material reported in literature [18]. The peak at 333 cm^{-1} is due to $FeCl_4^-$, indicating that the anion of this PEG-MDIL is $FeCl_4^-$ (Fig. 4).

To evaluate the catalytic activity of PEG-MDIL, the reaction of benzyl halides with NaN_3 was examined as a model reaction. The results are summarized in Table 1.

We first examined the catalytic ability of PEG-MDIL for conversion of benzyl halides to benzyl azide with NaN_3 in water at room temperature and under reflux conditions (Scheme 2). This catalyst acted very efficiently and it converts different benzyl halides to their corresponding benzyl azide in high isolated yields. The obtained results of the reaction are given in Table 1.

^1H NMR spectra of the crude products clearly showed the formation of benzyl azide and no evidence for the hydrolysis of benzyl halides to the alcohols was observed, which proved that the reactions proceeded cleanly. On the other hand, in the absence PEG-MDIL, the reaction was sluggish and, even after prolonged reaction time, a considerable amount of starting material remained. Moreover, the reaction mixture was contaminated with alcohol. This observation was confirmed with the presence of alcohol on the TLC plate.

Table 2
Reaction of various benzyl halides with NaCN in the presence of PEG-MDIL in water.

Entry	Benzyl halide	Product	Time (min)	Yield (%)
1			60	88
2			55	87
3			55	83
4			60	88
5			75	84
6			60	86
7			50	82

[a] Products were identified by comparison of their physical and spectral data with those of authentic samples.
[b] Isolated yields.

To evaluate the catalytic activity of PTC, the reaction of benzyl halides with NaCN was examined as a model reaction. The results are summarized in Table 2.

The effect of the reaction temperature on the reaction time of benzyl bromide was investigated at reaction temperatures ranging from 25 to 90 °C. The results show that the suitable reaction temperature is 90 °C.

The reaction was carried out in diethyl ether, n-hexane, acetonitrile, dichloromethane, ethyl acetate and water. From the results, it follows that the best solvent for this reaction is water. Thus, water is an excellent solvent in terms of cost, availability, and environmental impact and shorter reaction times. Benzyl halide bearing activated and deactivated groups was quickly and efficiently converted to the virtually pure corresponding products in high isolated yields. No evidence for the formation of alcohol by products of the reactions was observed and the products were obtained in pure form without further purification. As expected the typical steric effect on the rate of S_N2 reactions was observed. The primary alkyl halides could be efficiently converted to the corresponding alkyl azide, whereas secondary alkyl halides such as bromo cyclohexane did not convert after 5 h (Table 1, entry 8). All the products were characterized and identified by comparison of their spectral data (IR, ^1H NMR and ^{13}C NMR) with those of authentic samples.

The success of the above reactions prompted us to investigate the recyclability of catalyst. We carried out our study by using the reaction benzyl bromide with NaN_3 and under optimal conditions as a model study. The aqueous phase was then subjected to distillation at 80 °C under reduced pressure (10 mm Hg) for 4 h to recover the PEG-MDIL almost completely. The hydrophobic IL was purified by repeated washing with deionized water and evaporation. The catalyst could be reused for the fourth time without significant decrease in catalytic activity (Table 3). The IR, UV, and TGA analyses of reused catalyst indicated that no detectable changes of the catalyst occurred during the reaction and the recycling stages (Figs. 5, 6).

PEG-MDIL showed remarkable reactivity as a Lewis acid reagent and considerably accelerated the reactions. It seems that polyethylene glycol units in PEG-MDIL encapsulate alkali metal cations, much like crown ethers, and these complexes cause the anion to be activated. The 1-methylimidazol-3-ium units introduced ionic liquid property to the catalyst. In addition, $FeCl_4^-$ groups of the IL, probably, facilitate the substitution reaction (Scheme 4).

3. Experimental

3.1. Material and methods

Melting points were measured on an Electro thermal 9100 apparatus and are uncorrected. ^1H NMR & ^{13}C NMR spectra were recorded on a Bruker Advanced DPX 400 MHz instrument spectrometer using TMS

Table 3
The reusability of the catalyst in the reaction benzyl bromide with NaN_3.

Cycle	Fresh	First	Second	Third	Fourth
Yield (%)	86	84	81	76	72

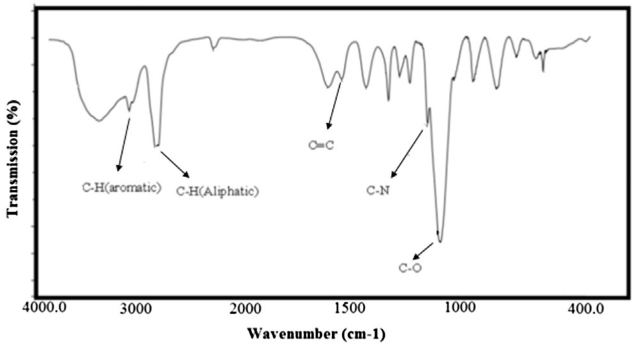


Fig. 5. FT-IR of reused catalyst.

as the internal standard in $CDCl_3$. IR spectra were recorded on a BOMEM MB-Series 1988 FT-IR spectrometer. Raman spectroscopy was recorded on a Bruker RFS 100/s Raman spectrometer. Benzyl halide and PEG-600 were purchased from Merck Company in high purity. Products were characterized by comparison of their physical and spectroscopic data with those of known samples. The purity of products and reaction monitoring was accomplished by TLC on silica gel Polygram SILG/UV 254 plates.

3.2. The synthesis of dichloro substituted PEG-600 (Cl-PEG-Cl)

PEG-600 (15 g, 0.025 mol) and pyridine (5 mL, 0.0625 mol) were dissolved in toluene (20 mL), stirred at 87 °C; thionyl chloride (5 mL, 0.0625 mol) was added slowly, and the resultant reaction mixture was stirred for 15 h at 87 °C. Then the resulting solid was removed by filtration. After removal of the solvent under reduced pressure a viscous liquid residual was collected as dichloro substituted PEG-600 (13.75 g, 91.6%).

3.3. Procedure for preparation of Poly(ethylene glycol) bis (methylimidazolium chloride) (PEG-DIL)

1-Methylimidazole (2 mmol) and polyethylene glycol dichloride (1 mmol) were placed in a Pyrex glass tube, sealed and heated at 80 °C for 16 h and 110 °C for 20 h, respectively. The organic solvent was removed and extracted with ethyl acetate (3 × 20 mL) which was then washed with water (2 × 20 mL) and ether (2 × 10 mL), and dried over anhydrous magnesium sulfate. The solvent was removed under vacuum at 65 °C overnight to give colorless product. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): $\delta H = 3.58$ (44 H, m, O–$\mathbf{CH_2}$–CH_2–O), 3.82 (4 H, t, O–$\mathbf{CH_2}$–CH_2–N), 4.01 (6 H, s, N–CH_3), 4.54 (4 H, t, N–$\mathbf{CH_2}$–CH_2–O), 7.74, 7.60 (4 H, C(4,5)–H), and 9.68 (2 H, C(2)–H).

3.4. Procedure for preparation of PEG-MDIL

PEG-MDIL was prepared by mixing PEG-DIL (1 mmol) with anhydrous $FeCl_3$ (2 mmol) at room temperature for 3 h, a dark brown liquid was obtained. The obtained PEG-MDIL was extracted with small amount of ethyl acetate. The solvent was evaporated and the resulting clear brown liquid was dried in vacuum oven at 60 °C for 24 h. The PEG-MDIL was obtained in high yield (87%). Elem. Anal. Calc. for $C_{34}H_{64}N_4O_{12}Cl_8Fe_2$: C, 51.58; H, 8.09; and N, 7.07. Found: C, 49.75; H, 7.81; and N, 6.62%.

3.5. Typical procedure for the nucleophilic substitution benzyl halides with sodium azide

To a mixture of the benzyl halide (1.0 mmol) and NaN_3 (3 mmol) in water (5 mL), PEG-MDIL (0.2 g) was added. The suspension was magnetically stirred under reflux conditions for the time shown in Table 1. After complete consumption of starting material as judged by TLC (using n-hexane–ethyl acetate as eluent), the mixture was extracted with ether (2 × 10 mL). The combined organic extracts (dried over $CaCl_2$) were evaporated under reduced pressure. The desired benzyl azide was obtained in good to excellent isolated yields.

3.6. Typical procedure for the nucleophilic substitution benzyl halides with NaCN

To a mixture of the benzyl halide (1.0 mmol) and NaCN (2 mmol) in water (5 mL), PEG-MDIL (0.2 g) was added. The suspension was magnetically stirred under reflux conditions for the time shown in Table 2. After completion of the reaction, the mixture was extracted with ether (2 × 10 mL). The combined organic extracts (dried over $CaCl_2$) were evaporated under reduced pressure. The desired benzyl cyanide was obtained in good to excellent isolated yields (Scheme 3).

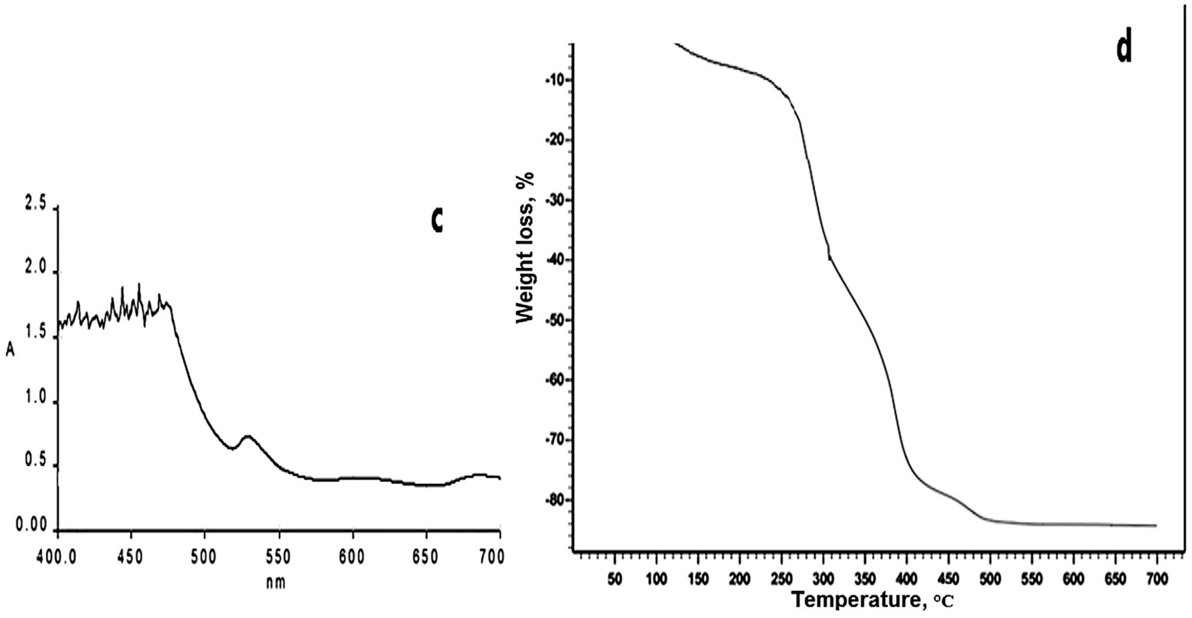
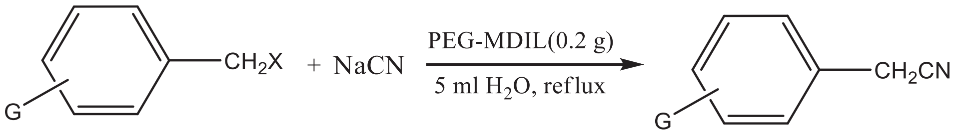
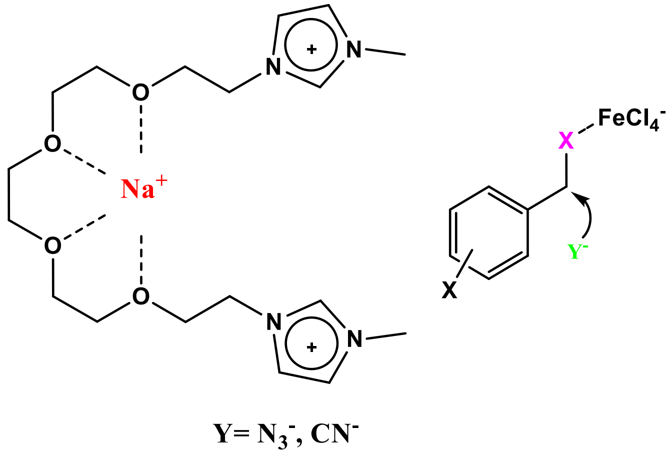


Fig. 6. UV spectra of reused catalyst (c) TGA of reused catalyst (d).



Scheme 3. Synthesis of benzyl cyanide from benzyl halide in the presence of magnetic phase transfer catalyst.



Scheme 4. Postulated roles of PEG-MDIL in the nucleophilic substitution.

4. Conclusion

In conclusion, we have successfully developed a simple and green catalytic procedure for the efficient synthesis of benzyl azides and benzyl cyanides using PEG-MDIL and under mild reaction conditions. PEG-MDIL can replace the ILs and other homogeneous catalysts with reasonable recovery and reusability and therefore suitable for industrial applications.

Acknowledgments

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