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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 non-polluting 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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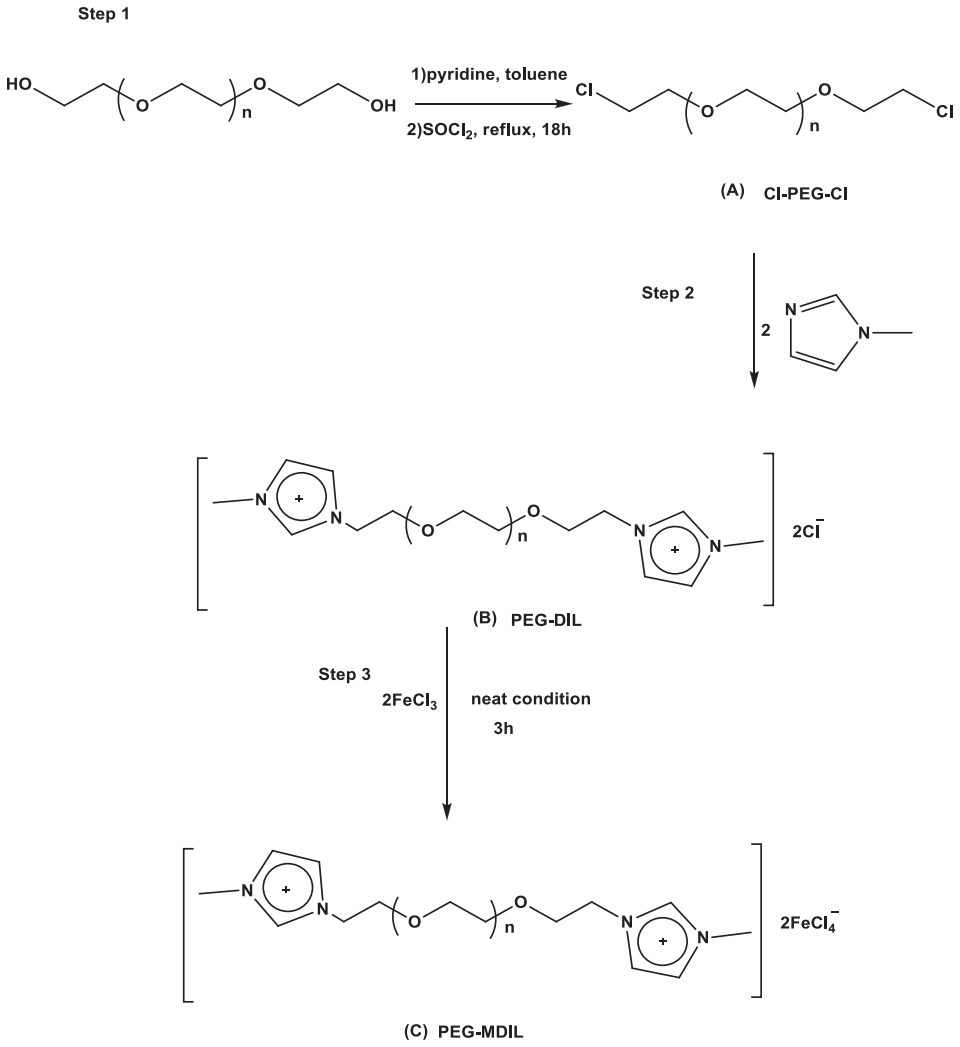

Scheme 1. Synthesis of PEG-MDIL.

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

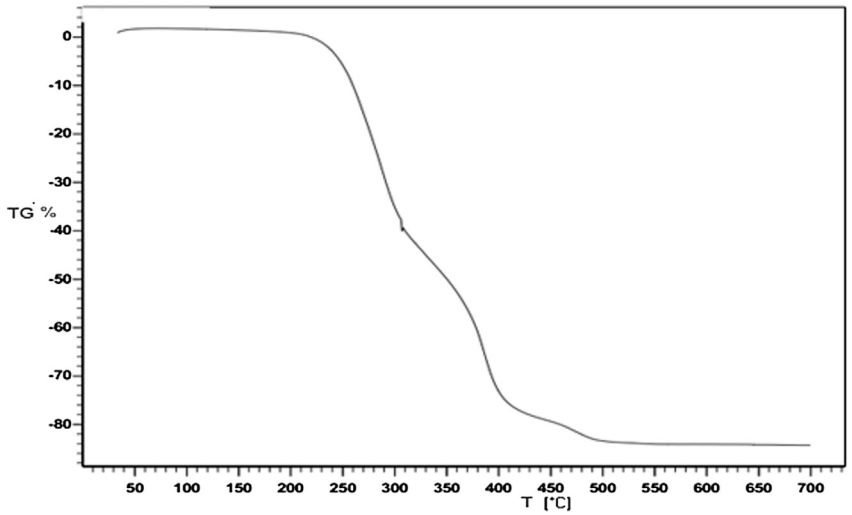

Fig. 1. TGA of PEG-MDIL.