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ORIGINAL ARTICLE

Thermoregulated biphasic ionic liquids: Effective catalysts in aldehydic–amide condensation reaction

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Abstract Novel acid polymeric ionic liquids with thermoregulated biphasic performance were synthesized and applied in the aldehydic–amide condensation reaction. The yields were satisfactory and the catalysts showed a unique thermoregulated self-separating nature in the reaction system. Such catalytic system was proved to be applicable to several substrates. Recycling experiment showed the catalyst could be easily recovered and reused for six times without appreciable loss of activity.

1. Introduction

In recent years, the study of the effective and recyclable catalytic system has been the research focus in green chemistry. A recyclable catalyst with high activity and selectivity is highly appreciated in the environmental friendly subject and has been developing rapidly. Acidic ionic liquids (ILs) are deemed as one of the most promising alternatives of conventional acid catalysts for its benign solubility in organic and inorganic matters and high catalytic performance [1–3]. However, they are plagued by a number of serious disadvantages, such as separation and purification from the reaction system, which have limited their application. Thermoregulated biphasic system can address the challenges for its miscibility and detachability with solvents by temperature change. The catalyst can be miscible with organic solvents at high temperatures to form a homogeneous catalysis system and separated by reducing the reaction temperature [4–6]. This procedure combines the advantages of high catalytic activity, easy separation of components, homogeneous catalysis and has attracted much attention during the past few decades [7–13]. In 2002, Van den [14] synthesized a series of fluorinated ionic liquids, and utilized toluene as reaction media to construct a biphasic system for the hydrosilylation of olefins with an average loss of catalyst activity of 6%. Later, Behr and co-workers [15] reported a thermoregulated ionic liquid system consisting of ionic liquid, acetonitrile and fatty acid ester for Diels–Alder reaction of conjugated ethyl linoleate and methyl vinyl ketone, but the separation and recyclability of the catalyst were still to be examined based on the presented results. Hu[16] reported chloromethylation reaction of aromatic hydrocarbons with the catalyst of PEG-1000DIL/toluene thermoregulated biphasic system, and the yields were 75–88%, without reducing the catalytic properties after recycling 6 times. Thus, the thermoregulated biphasic system has the advantages of high catalytic activity, easy

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separation and recyclability [17,18]. However, the drawbacks of high attrition rate still existed.

Inspired by the satisfactory recyclability of macromolecular polymer [19], our research focused on combining both advantages of ionic liquids and macromolecular polymer to form homogeneous and recyclable catalysts, which meets the requirement of "one-phase catalysis and two-phase separation". Acid polymeric ionic liquid (PIL) with thermoregulated biphasic performance was synthesized using polyethylene glycol as the main chain and double bonds imidazole-based ionic liquid as the crosslinking agent through the free radical polymerization. Its catalytic effects were also investigated in amine-aldehyde condensation reaction.

2. Experimental

2.1. Materials and equipments

All chemicals were of reagent grade and used as purchased. The solvents were freshly distilled and dried by known procedures [20]. The IR spectra were recorded on a Nicolet IS-10 spectrometer and expressed in cm^{-1} (KBr). ^1H NMR spectra were recorded on a Bruker DRX300 (500 MHz) spectrometer. The Molar mass moments were recorded on a Waters GPC spectrometer. The product N-benzalaniline was analyzed by HPLC (high performance liquid chromatography) using a C18 column and methyl alcohol as eluent. The flow rate equaled 1 mL/min. The analysis was carried out at 40 °C, using a UV detector at 215 nm wavelengths.

2.2. Synthesis of PILs

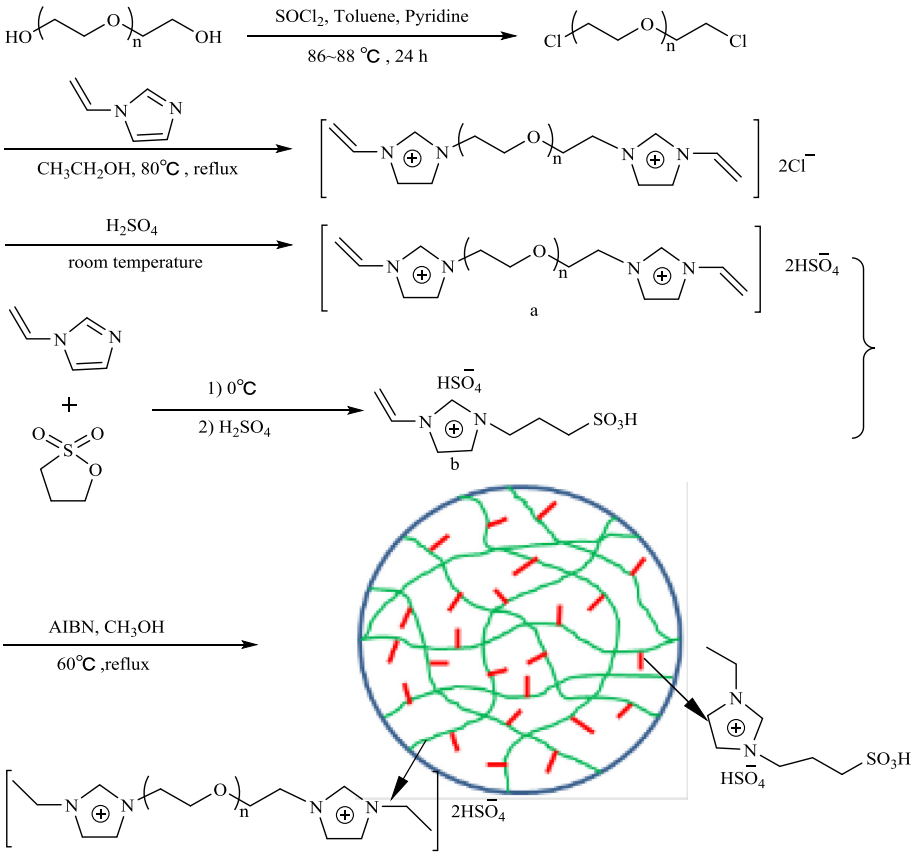
The total synthesis route is illustrated in Scheme 1.

2.2.1. Synthesis of polyethylene glycol dichloride (PEG1000-Cl_2)

PEG1000-Cl_2 were prepared following the procedures reported previously [21,22]. PEG-1000 (0.05 mol) and anhydrous toluene (100 mL) were charged in a 250-mL three-neck flask equipped with a reflux condenser and a magnetic stirrer, followed by addition of thionyl chloride (0.1 mol) in a dropwise manner within a period of 3 h. The resultant mixture was heated to 90 °C for 24 h under nitrogen. The obtained mixture was cooled to room temperature and evaporated under reduced pressure. The residue was dissolved in dichloromethane and excess of cold diethyl ether was added. The precipitate was filtered and dried in vacuum. Yield: 92%.

2.2.2. Synthesis of [PEG-1000VIL][HSO_4]

1-vinylimidazole (0.02 mol), PEG1000-Cl_2 (0.01 mol) obtained above and anhydrous ethanol (25.0 mL) were charged in a 100-mL three-neck flask, the mixture was stirred at 80 °C for 96 h under nitrogen. After removal of ethanol in vacuum, the solid residue was dissolved in dichloromethane and excess of cold



Scheme 1 The procedures for the synthesis of PILs.