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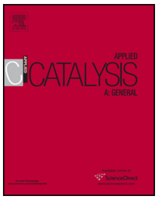

Reusable and efficient polymer nanoparticles grafted with hydroxyl-functionalized phosphonium-based ionic liquid catalyst for cycloaddition of CO_2 with epoxides

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ABSTRACT

A promising new strategy for fabricating polymer nanoparticles that are grafted with hydroxyl-functionalized phosphonium-based ionic liquid (PNPs-HPIL) through copolymerization of EGDMA and HPIL was established. The PNPs-HPIL catalyst exhibits good catalytic activity for the synthesis of cyclic carbonates through cycloaddition of CO_2 to epoxides. At a catalyst loading as low as 0.47 mmol%, the PC yield is above 96.0% and PC selectivity almost 100%. It is noted that the hydroxyl groups of PNPs-HPIL play an important role for facilitating the cycloaddition reaction through the hydrogen bonding between hydroxyl groups and epoxides. Furthermore, the PNPs-HPIL catalyst shows good stability and reusability, which are beneficial to practical application in industry.

1. Introduction

Carbon dioxide (CO_2) is regarded both as greenhouse gas and C1 building block. Nowadays, with the concept of green chemistry and sustainable development, chemical fixation of CO_2 to useful chemicals has attracted much attention. Although there are over 20 reaction processes that use CO_2 as a raw material, successful industrial processes are limited [1,2]. One of the few industrial processes is the synthesis of cyclic carbonates *via* cycloaddition of CO_2 to epoxides. In terms of "green chemistry" and "atom economy", this process is promising and attractive, because there is no by-products [3–5]. Moreover, cyclic carbonates as valuable chemicals are extensively used as aprotic solvents, electrolytes in secondary batteries, precursors for synthesizing polymeric materials, and intermediates for the production of pharmaceuticals, fine chemicals, and agricultural chemicals [6–9].

In order to be more efficient in the synthesis of cyclic carbonates through the cycloaddition reaction, a considerable number of homogeneous and heterogeneous catalyst systems, such as alkali metal salts [10], metal oxide [11,12], modified molecular sieve [13,14], organometallic complexes [15–17], and ionic liquids (ILs) [18,19] were explored. Among them, those of ILs are especially highlighted. Since 2000s, the use of ILs (such as, imidazolium salts [20–23], quaternary ammonium salts [24,25], quaternary phosphonium salts [26–28], pyridinium salts [29], guanidinium salts [30–32], and other ILs [33,34]) as catalysts for the cycloaddition of CO_2 with epoxides has attracted much interest, because of their negligible vapor pressure and good thermal stability as well as their unique tunable structure and polarity. Compared with imidazolium-based ILs, the quaternary phosphonium-based ILs are not as extensively studied due to the less tailored structures and limited heterogenizing method. Recently, polyfluoroalkyl phosphonium iodides [35], $ZnCl_2$-quaternary phosphonium halides [36], and $ZnBr_2$-Ph_4PI [26] systems were evaluated for the cycloaddition reaction. Despite exhibiting good catalytic activity, the systems require harsh reaction conditions and the use of metal halide as co-catalyst. Moreover, the quaternary phosphonium-based ILs, such as PPh_3BuBr, PPh_3BuCl, PPh_3BuI, PPh_3EtBr, PPh_3PrBr, PPh_3HeBr and PPh_4I, are themselves low in catalytic activity [26,37]. Recently, however, the "tailor-made" task-specific ILs that were prepared by introducing certain functional groups into the cation and/or anion of traditional ILs,

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exhibit higher catalytic performance than traditional ILs toward the cycloaddition reaction [20,38–40]. Hereby, we report for the first time the synthesis and evaluation of novel phosphonium-based ILs that are functionalized with hydroxyl, carboxyl and amino groups, as catalysts for the synthesis of cyclic carbonates through the cycloaddition reaction in the absence of co-catalyst and solvent [28]. The results indicate that those functionalized phosphonium-based ILs show good catalytic activity, especially the hydroxyl- and carboxyl-functionalized ones. However, the inherent homogeneous property of ILs makes them difficult to separate from the products. With good stability and recyclability, it is envisaged that the functionalized phosphonium-based ILs are promising candidates for the fabrication of efficient heterogeneous catalysts by means of heterogenization.

Nevertheless, studies on the heterogenization of phosphonium-based ILs are few. Xiong et al. [41] reported a polymer-immobilized tetraphenylphosphonium chloride catalyst that exhibits good activity for the cycloaddition reaction at 160 °C and 3 MPa in 3 h. Two years later the authors reported a polystyrene bead-supported tributylphenylphosphonium chloride catalyst that performed better but under more demanding reaction conditions (150 °C, 5 MPa, 6 h) [42]. Furthermore, Song et al. [43] synthesized fluorous polymer immobilized tributylbenzylphosphonium chloride that showed good catalytic performance. But the high cost of fluorous cross linker, supercritical condition (150 °C, 8 MPa), and long reaction time (8 h) seriously limit its application. It is noted that the active species of the above mentioned catalysts are all traditional phosphonium-based ILs. It is hard to introduce the task-specific ILs onto the support surface, which hinders the improvement of the catalytic performance. Therefore, the development of new and environment-benign heterogeneous phosphonium-based ILs catalysts for efficient synthesis of cyclic carbonates from CO_2 and epoxides is still a challenge.

In view of the superiority of the functionalized phosphonium-based ILs reported by us earlier [28], we synthesized a novel cross-linked polymer nanoparticles that are grafted with hydroxyl-functionalized phosphonium-based IL (denoted herein as PNPs-HPIL). The PNPs-HPIL catalysts were evaluated as reusable and efficient heterogeneous catalyst for the synthesis of cyclic carbonates from CO_2 and epoxides in the absence of co-catalyst and solvent. The influence of hydroxyl groups, the ratio of IL monomer to crosslinker, as well as the reaction parameters (the amount of catalyst, temperature, initial CO_2 pressure and time) on catalytic performance were systematically investigated.

2. Experimental

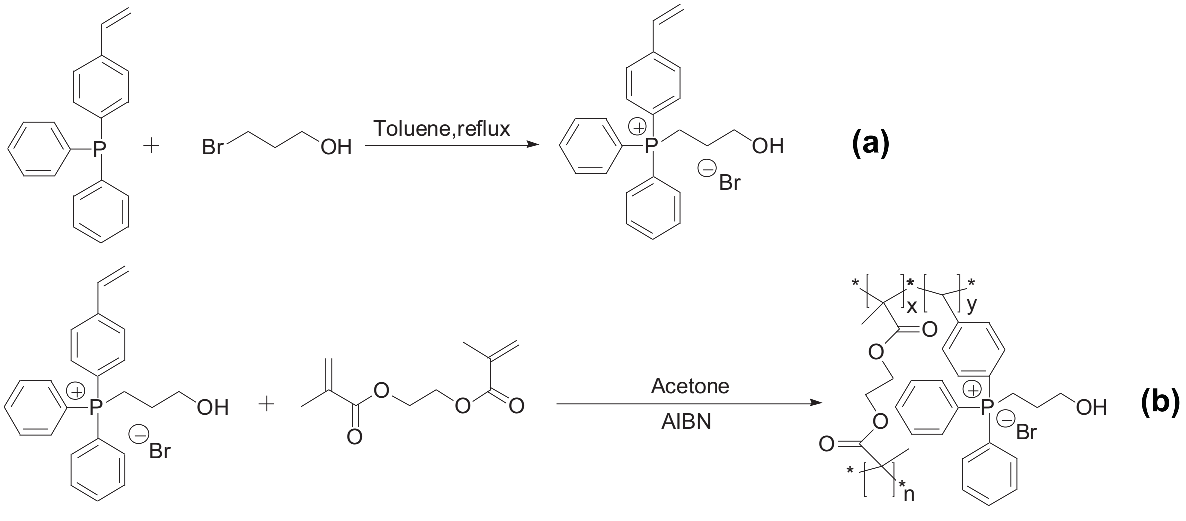
2.1. Reagents

The ethylene glycol dimethylacrylate (EGDMA), 3-bromopropanol, 1-bromopropane, diphenyl(*p*-vinylphenyl)phosphine, and 2,2′-azobis(isobutyronitrile) (AIBN) were purchased from Aldrich Chemical Co. Propylene oxide was from Sinopharm Chemical Reagent Co., Ltd. The other epoxides were from Alfa Aesar China Co., Ltd. All chemicals were used as received. The CO_2 (99.9% purity) purchased from Nanchang Guoteng Gas Co. was used without any further treatment.

2.2. Preparation of PNPs-HPIL

The steps to prepare the cross-linked polymer nanoparticles that was grafted with hydroxyl-functionalized phosphonium IL (PNPs-HPIL) are shown in Scheme 1. First, diphenyl(*p*-vinylphenyl)(3-hydroxylpropyl)-phosphonium bromide (denoted as HPIL) was synthesized according to the procedure described in Scheme 1a. In a typical reaction, a solution of diphenyl(*p*-vinylphenyl)phosphine (4 mmol) and 3-bromopropanol (4.4 mmol) in 5 mL toluene was added into a 50 mL flask, and heated at 85 °C for 24 h under a N_2 atmosphere. After reaction, the mixture was cooled to room temperature. The top phase was poured out, and the residue was washed twice with toluene and diethyl ether respectively, and then dried at 60 °C for 6 h under vacuum to give the product HPIL in the form of pale yellow viscous liquid. ^{1}H NMR (400 MHz, DMSO-d6, δ/ppm): 7.90-7.37 (m, 14H), 6.91–6.84 (m, 1H), 6.12 (d, J = 17.6, 1H), 5.55, (d, J = 10.8, 1H), 4.82 (s, 1H), 3.56–3.49 (m, 4H), 1.66–1.64, (m, 2H). HR-MS (QTOF): m/z = 428.0734, calcd. for $C_{23}H_{24}OPBr$ (M+H): 428.0728.

Then, the PNPs-HPIL catalyst was prepared by radical copolymerization of the as-synthesized HPIL with EGDMA (Scheme 1b). In a typical experiment, HPIL (4 mmol), EGDMA (12 mmol) and AIBN (1 mmol, as initiator) were dissolved in 45 mL of acetone. The mixture was heated and subject to reflux for 12 h under a N_2 atmosphere. After reaction, the as-obtained solid product was filtered out and washed three times with acetone and diethyl ether. Then the solid was dried at 60 °C for 6 h under vacuum to give the product, denoted herein as PNPs-HPIL-3. Following a similar procedure, the other PNPs-HPIL catalysts, *i.e.*, PNPs-HPIL-1, PNPs-HPIL-2 and PNPs-HPIL-4, were also synthesized by regulating the EGDMA/HPIL molar ratio to 1, 2 and 4, respectively.



Scheme 1. Synthesis procedure of PNPs-HPIL.