



Short communication

# Highly cross-linked cationic polymer microspheres as an efficient catalyst for facile CO<sub>2</sub> fixation

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## ABSTRACT

In this study, a new type of highly cross-linked cationic polymer microspheres was synthesized by a simple procedure of combining 1,2,4,5-tetrakis(bromomethyl)benzene and 4,4'-bipyridine. The influence of solvent used on the material structure and morphology was investigated and the obtained cationic polymers were fully characterized by FT-IR, BET, SEM, EDS, and TGA. Catalytic tests in the synthesis of cyclic carbonate from carbon dioxide (CO<sub>2</sub>) and epoxides under mild conditions, along with comparisons to various counterparts, well demonstrate that the newly designed cross-linked cationic polymer with regular spherical structure exhibits high activity and selectivity, coupled with easy recovery and steadily reuse.

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## 1. Introduction

Catalyst-mediated reactions of carbon dioxide (CO<sub>2</sub>) represent one potential positive contributor to climate-relevant carbon capture and storage/sequestration, albeit a far from sufficient one to satisfy this enormous challenge [1–3]. Well-designed reactions that utilize CO<sub>2</sub> in the production of commercially relevant chemicals are receiving increased attention, including the chemical fixation of CO<sub>2</sub> [4–9]. The conversion of CO<sub>2</sub> to cyclic carbonates *via* epoxide substrates is an atom-economical reaction, and the products can serve as excellent aprotic polar solvents and as intermediates in the production of pharmaceuticals and fine chemicals [10–12].

In the past few decades, numerous homogeneous and heterogeneous catalysts have been developed for the synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>, such as salen-metal compounds [13], transition metal complexes [14], alkali metal salts [15], ionic liquids (ILs) [16], metal oxides [17], metal–organic frameworks [18], and so on. Among them, ILs with halogen anions are especially highlighted because of that the ILs can be tailored by designing their cations or anions with various functionalities for different applications [19,20]. However, ILs always cause homogeneous reactions because of their good solubility in polar media, resulting in the difficulty of ILs isolation. To recover the ILs, ILs usually be heterogenized by chemical immobilization onto solid supports, such as silica, activated carbon, and polymeric microsphere [21–24]. Nevertheless, this method depends on the modified solid supports and specific functionalized ILs. Thus, developing a

new strategy for synthesis of heterogeneous ILs catalysts with high catalytic activity is still highly desirable.

Recent years have witnessed considerable interest in narrow or monodisperse highly cross-linked spherical polymer particles in the micrometer-size range due to their great potential in a wide range of materials science applications [25,26]. Meanwhile, IL is an ideal building block for constructing multi-functional cationic polymer materials owing to the features of negligible vapor pressure, ionicity and versatile functional groups [27–29]. Herein, 1,2,4,5-tetrakis(bromomethyl)benzene (TBB) was selected as an ideal four-connected building unit to construct highly cross-linked cationic polymer microspheres by reacting with the 4,4'-bipyridine in various solvents (Fig. 1), and the resulting samples can be sufficiently applied for the production of cyclic carbonates from CO<sub>2</sub> and epoxides, and then can be easily separated from the reaction mixture to reuse.

## 2. Experimental section

## 2.1. Materials and characterization

All chemicals were commercially available and used as received. FT-IR spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4000–400 cm<sup>-1</sup> region. Liquid-state <sup>1</sup>H NMR spectra were measured with a Bruker DPX400 spectrometer at ambient temperature using TMS as internal reference. Field emission scanning electron microscope (FESEM; Hitachi S-4800, accelerated voltage: 5 kV) accompanied by Energy dispersive X-ray spectrometry (EDS; accelerated voltage: 20 kV) was used to study the morphology and the elements distribution. TG analysis was performed with a STA409 instrument in dry air at a heating

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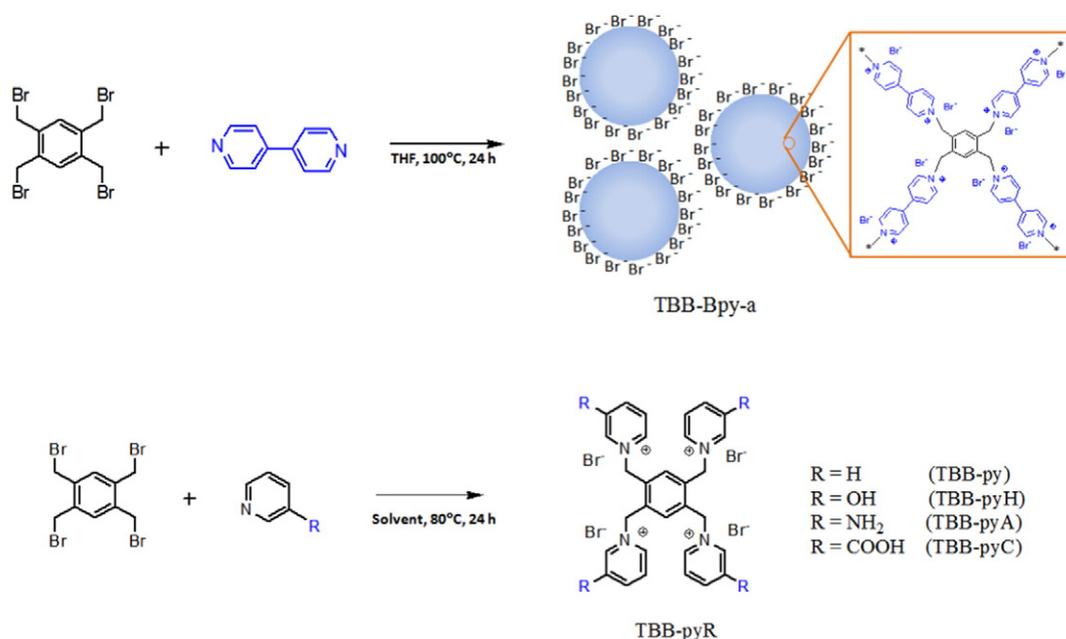


Fig. 1. Synthesis of cross-linked cationic polymer microspheres TBB-Bpy-a and ionic compounds TBB-pyR.

rate of 10 °C/min. CHN elemental analysis was carried out on an elemental analyzer Vario EL cube.

## 2.2. Synthesis of cross-linked cationic polymers

The highly cross-linked cationic polymers were solvothermally synthesized from the reaction of TBB and 4,4'-bipyridine. As a typical example, TBB (2 mmol, 0.9 g) and 4,4'-bipyridine (4 mmol, 0.62 g) were dissolved in tetrahydrofuran (THF) (20 mL). After stirring at room temperature for 2 h, the mixture was solvothermally treated at 100 °C for 24 h. The yellow solid product was filtered and washed with THF for three times. After drying at 50 °C for 12 h, the product cross-linked cationic polymer was obtained, signed as TBB-Bpy-a, TBB-Bpy-b (obtained in toluene), TBB-Bpy-c (obtained in acetonitrile), and TBB-Bpy-d (obtained in ethyl acetate) were prepared in the same way with different solvents.

## 2.3. Synthesis of TBB-based ionic compounds

TBB-py: TBB (2 mmol, 0.9 g) and pyridine (8 mmol, 0.64 g) were dissolved in CH<sub>3</sub>CN (40 mL). After stirring for 24 h at 80 °C, the white precipitate formed was filtered and washed with CH<sub>3</sub>CN for three times, and dried in vacuum at 80 °C for 12 h. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, TMS) δ(ppm) = 6.09 (s, 8 H, CH<sub>2</sub>), 6.77 (s, 2 H, CH), 8.10 (t, 8 H, CH), 8.61 (t, 4 H, CH), 8.86 (d, 8 H, CH) (see Figure S1 in Supporting Information (SI)). CHN elemental analysis for TBB-py found (wt.%): C 47.05, H 3.86, N 7.28.

TBB-pyA: TBB (2 mmol, 0.9 g) and 3-aminopyridine (8 mmol, 0.76 g) were dissolved in CH<sub>3</sub>CN (20 mL). After stirring for 24 h at 80 °C, the yellow precipitate formed was filtered and washed with CH<sub>3</sub>CN for three times, and dried in vacuum at 80 °C for 12 h. TBB-pyA was unsuitable to be subjected to a <sup>1</sup>H NMR test because of that it is insoluble in commonly used deuterated solvents. Thus, CHN elemental analysis was carried out to determine its structure. CHN elemental analysis for TBB-pyA found (wt.%): C 43.65, H 4.10, N 13.63.

TBB-pyH: TBB (2 mmol, 0.9 g) and 3-hydroxypyridine (8 mmol, 0.72 g) were dissolved in acetone (20 mL). After stirring for 24 h at 60 °C, the white precipitate formed was filtered and washed with acetone for three times, and dried in vacuum at 50 °C for 12 h. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, TMS) δ(ppm) = 5.90 (s, 12 H, OH, CH<sub>2</sub>), 6.47 (s, 2 H, CH), 7.84 (t, 8 H,

CH), 7.95 (d, 4 H, CH), 8.25 (s, 4 H, CH) (Figure S2 in SI). CHN elemental analysis for TBB-pyH found (wt.%): C 43.44, H 3.58, N 6.70.

TBB-pyC: TBB (2 mmol, 0.9 g) and 3-carboxylicpyridine (8 mmol, 0.98 g) were dissolved in toluene (15 mL) and ethyl alcohol (30 mL), respectively. The mixture of the above two solutions was stirred at 80 °C for 24 h. After reaction, the white precipitate formed was filtered and washed with toluene and ethyl alcohol for many times, and dried in vacuum at 60 °C for 12 h. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, TMS) δ(ppm) = 6.07 (s, 8 H, CH<sub>2</sub>), 6.70 (s, 2 H, CH), 8.12 (t, 4 H, CH), 8.91 (d, 12 H, CH), 9.19 (s, 4 H, COOH) (Figure S3 in SI). CHN elemental analysis for TBB-pyC found (wt.%): C 43.27, H 3.22, N 5.93.

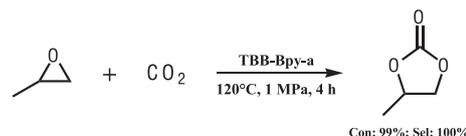
## 2.4. General procedures for the preparation of cyclic carbonates

Epoxide derivatives (20 mmol), such as propylene oxide (PO) and catalyst TBB-Bpy (0.08 g) were charged into the reactor vessel without using any co-solvent. The reaction vessel was placed under a constant pressure of CO<sub>2</sub> and then heated to 120 °C for 4 h (Scheme 1). After the reaction, the reactor was cooled to ambient temperature, and the resulting mixture was filtered. The liquid mixture was analyzed by gas chromatography (GC) using biphenyl as an internal standard (Figure S4 in SI). The solid catalyst was washed with ethyl alcohol, dried, and directly used for the next run.

## 3. Results and discussion

### 3.1. Preparation and characterization of TBB-Bpy

The cationic polymers are solvothermally synthesized by reacting of TBB with 4,4'-bipyridine in a stainless steel reaction still as shown in Fig. 1. The solvents used in the synthetic media are considered to be an important factor in the formation of microsphere structures. Thus, various



Scheme 1. Synthesis of propylene carbonate from propylene oxide and CO<sub>2</sub>.

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