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## Supporting information for

# Capturing Ethylene Glycol with Dimethyl Carbonate Towards Depolymerisation of Polyethylene Terephthalate at Ambient Temperature

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#### 1. General

Post-consumer polyethylene terephthalate (PET) in beverage bottles was used for this study. The PET was washed with soap water for several times, and dried at ambient temperature. The dried PET films were cut to flake form (ca. 5 mm square), that was further pulverized at room temperature with crusher to make it powder form. The powder PET was sieved to three different sizes (53~106 μm,  $106 \sim 250 \ \mu m$ , and  $250 \sim 500 \ \mu m$ ). The powder with  $53 \sim 106 \ \mu m$  size was used for standard experiments. Other chemicals were purchased from chemical suppliers. Dimethyl carbonate, MeOH, and THF and dried over activated MS4A before to use. Solution NMR was measured with Bruker Avance III spectrometer (600 MHz for <sup>1</sup>H nuclei) using cryo-probe. All spectra were recorded at 25  $\pm$  1 °C. Chemical shifts ( $\delta$ ) are in parts per million relative to tetramethylsilane at 0 ppm for <sup>1</sup>H and <sup>13</sup>C. For <sup>7</sup>Li NMR measurements, a double tube was employed using 1 M LiCl in  $D_2O$  as an internal standard. The non-deuterated solution was charged in an outer tube, which is equipped with an inner tube charged with standard solution, and the Li<sup>+</sup> signal from inner tube was set as 0 ppm. Solid-state NMR was measured with Bruker Avance NEO spectrometer (400 MHz for <sup>1</sup>H nuclei) using HX double-channel 3.2 mm MAS probe. Standard ramped cross polarization (CP) was used to transfer polarization from the <sup>1</sup>H nuclei to the nucleus of interest (<sup>13</sup>C). SPINAL-64 <sup>1</sup>H heteronuclear decoupling was applied during acquisition. <sup>13</sup>C chemical shifts were referenced to tetramethylsilane at 0 ppm using adamantane as an external standard (38.52 ppm). Gas chromatographic (GC) analyses were performed on a Shimadzu GC-2014 using an DB-WAXETR column (0.25 mm x 30 m, Agilent Technologies). All samples were analyzed and quantified by using biphenyl as an internal standard. Inductively coupled plasma atomic emission spectroscopy (IPC-AES) was measured with Shimadzu ICPE-9800. The metal alkoxide reagents used in this study are strongly basic and must be handled without exposure to the skin.

#### 2. Procedure for the catalytic reaction

#### **General procedure**

In the vial (volume: 5 mL), PET (powder form, 100 mg (0.52 mmol based on an alternating unit)) and catalyst (5~10 mol%) were charged. The measured amount of DMC and MeOH were added to give colorless suspension. The vial was closed and placed in the aluminum block heater whose temperature setting was stabilized, and magnetically stirred for 5 hours under N<sub>2</sub>. Resulting reaction mixture was filtered using a syringe equipped with a PTFE filter (pore size:  $0.22 \mu m$ ). Extra DMC (1 mL) was used for a collection of residual chemicals in the vial and filtered. To a combined solution was then added measured amount of biphenyl (as an internal standard), and an aliquot was used for GC-FID measurement. Yields of DMT, EG, and EC were determined by standard calibration curve method.

#### **Isolation of products**

For 1 g scale experiment using PET flakes, the depolymerization reaction was performed in Schlenk tube. After stirring for 5 hours at 28 °C or 50 °C under N<sub>2</sub>, the colorless suspension was filtered through with a PTFE filter (pore size: 0.22  $\mu$ m). The insoluble solid was rinsed with DMC (2 mL) for four times and dried under reduced pressure. The filtrate was then concentrated under reduced pressure at an ambient temperature, giving wet colorless crystalline solid that was rinsed with deionized water (5 mL) for three times. The insoluble crystalline solid was further dried to give DMT as analytically pure form. The aqueous washings were concentrated under reduced pressure at 50 °C, affording crude EC as colorless liquid.

#### 3. Effect of particle size on reaction efficiency

We examined the catalytic PET methanolysis using three different sizes of PET powder that have been sieved after pulverisation (Table S1). The yields of DMT and EC slightly decreased when a larger size powder was employed. This result indicated that the depolymerisation reaction proceeds at an interface of PET and solution, and thereby faster for the substrate having higher relative surface area.

#### Table S1. Yields of DMT, EG, and EC from PET methanolysis using different sizes of PET powder



#### 4. NMR spectra of products



Figure S1. <sup>1</sup>H NMR spectrum (600 MHz, CDCl<sub>3</sub>, 298 K) of DMT obtained from PET depolymerisation.



Figure S2. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (150 MHz, CDCl<sub>3</sub>, 298 K) of DMT obtained from PET depolymerisation.



**Figure S3.** <sup>1</sup>H NMR spectrum (600 MHz,  $CDCl_3$ , 298 K) of crude EC obtained from PET depolymerisation. This NMR spectrum indicated the contamination of EG (~10%) and 1,2-dimethoxycarbonyloxyethane (~10%).<sup>1</sup>



Figure S4. <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (150 MHz, CDCl<sub>3</sub>, 298 K) of crude EC obtained from PET depolymerisation.

# 5. GC spectrum of isolated DMT



Figure S5. GC spectrum of isolated DMT obtained from PET depolymerisation.

## 6. <sup>7</sup>Li NMR spectroscopy of the catalytic solution



**Figure S6.** Solution-state <sup>7</sup>Li NMR of (a) 0.15 M LiOMe in MeOH/DMC (2:15 (v/v)), and (b) solution after the catalytic reaction using PET flakes at 50 °C for 5 h. 1 M LiCl in  $D_2O$  was used as an internal standard using a double tube and set the signal as 0 ppm.





**Figure S7**. Solid-state <sup>13</sup>C CPMAS NMR spectrum of an insoluble part after the reaction (Scheme 3) (a) and PET powder (b). Temperature: 298 K, MAS frequency: 16 kHz (3.2 mm rotor), CP contact time: 1 ms (a), 2 ms (b) Recycle deray: 3 s (a), 2 s (b), Number of scan: 8192 (a), 6144 (b). These spectra indicate that unreacted PET was not present in the insoluble part after the catalytic reaction. Two signals observed in (a) are attributed to chemically inequivalent carbons in Li(OCH<sub>2</sub>CH<sub>2</sub>OH).



**Figure S8**. Solution-state NMR analysis of an insoluble part after the reaction (Scheme 3) dissolved in D<sub>2</sub>O. <sup>1</sup>H NMR spectrum (a) and <sup>13</sup>C NMR spectrum (b) displayed signals assignable to free EG, which might be bound to Li<sup>+</sup> in solid form and released by the addition of D<sub>2</sub>O. <sup>7</sup>Li NMR spectrum (c) showed a signal close to 0 ppm, indicating the existence of Li<sup>+</sup> in the insoluble part.

# 8. References

1. Ube Industries, ltd. WO2009/102069 A1.