Supporting Information

Chemical Recycling of Polycarbonate and Polyester without Solvent and Catalyst: Mechanochemical Methanolysis

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Materials and Methods

<u>Materials</u>

All reagents were purchased from Alfa Aesar and used without further purification. The PC pellet had the shape of an elliptical column, with an average width of 3.9 mm, length of 2.8 mm, and height of 3.0 mm from Lotte Chemical in South Korea (SC-1190P, M_n = 16.4 Kg/mol, Đ = 2.15). The PLA cup was made of 100% PLA and was purchased from e·SOL company in South Korea (M_n = 80.6 Kg/mol, Đ = 2.51). The ball-milling experiments were conducted using a Retsch Planetary Mill PM 100 instrument with either a 25 mL or 125 mL stainless-steel vessel and stainless-steel balls with diameters of 5 mm. To obtain PET powder, PET cup pieces were placed in a SUS 25 mL mixer mill container, frozen in liquid nitrogen, and milled twice for 3 min using a Retsch Mixer Mill MM 400. The general ball-milling experiments were performed using a Retsch Planetary Mill PM 100 instrument with either a 25 mL or 125 mL stainless-steel vessel and stainless-steel balls with diameters of 5 mm.

<u>Measurement</u> <u>Methods</u>

The ^{1}H NMR spectra were measured by a Bruker AVANCE III HD-400 MHz Fourier transform NMR spectrometer at the Future Energy Convergence Core Center (FECC). The number-average molecular weights (M_n) and dispersity (Đ) were estimated using a size exclusion chromatography (SEC) equipped with a refractive index (RI) detector. The equipment consisted of a Waters 1515 isocratic pump, a Waters 2414 differential refractive index detector, and a column-heating module with Shodex HK-0403 and HK-404L columns placed in series. The samples were eluted with HPLC-grade tetrahydrofuran (THF) at 40 degrees and 1.0 mL/min. A calibration curve was obtained with 16 monodispersed polystyrene standards (purchased from Alfa Aesar).

<u>Procedure and Optimization results: DPC model study (Fig.2 & Table S1)</u>

- ***Solution methanolysis of DPC (Entry 4)***

Diphenyl carbonate (DPC) (0.21 g, 1.0 mmol of carbonate functionality) and methanol (2.8 mL, 0.070 mol) were added in 4 mL glass vial. The vial was placed in a reaction block of 100 °C. During stirring for 9 h, an aliquot of the reaction mixture at 1, 3, 6, and 9 h was taken for ^{1}H NMR analysis in CDCl$_3$.

- ***Mechanochemical methanolysis of DPC (Entry 7)***

Diphenyl carbonate (DPC) (0.21 g, 1.0 mmol of carbonate functionality) and methanol (2.8 mL, 70 mmol) were added in a stainless steel container (12 mL) having 50 stainless steel balls with a diameter of 5 mm. The vessel was placed in a planetary ball-milling machine and milled at 600 rpm for 5 h. After milling, the container was opened and an aliquot of the reaction mixture was taken and filtered through a syringe filter (45 μM) for ^{1}H NMR analysis in CDCl$_3$.

Table S1.
Catalyst-free DPC methanolysis to DMC

| | | | DPC | 70 mmol | |
| DPC 1.0 mmol | | | | | |
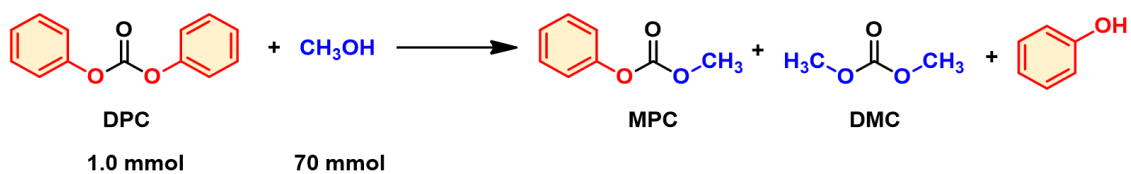
entry	time	DPC Conversion (%)	MPC (%)	DMC (%)
Solution Reaction, 100 ºC				
1	1 h	57	51	6
2	3 h	80	65	15
3	6 h	93	62	31
4	9 h	95	55	40
Planetary ball-milling, SUS 12 mL, 5 mm x 50 ea, 600 rpm				
5	1 h	75	60	15
6	3 h	>99	27	73
7	5 h	>99	0	>99

a. Conversions and yields were determined by ^{1}H NMR spectroscopy.
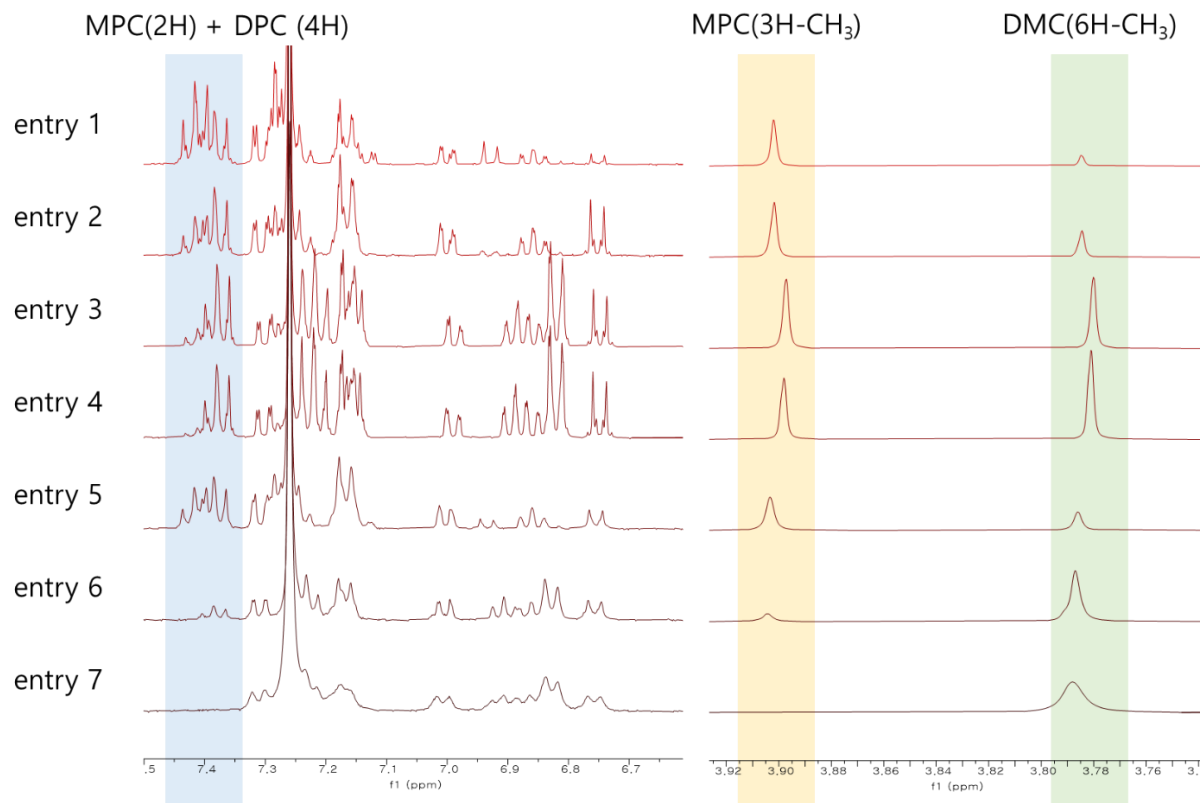
Fig. S1.
^{1}H NMR Spectra used for Table S1

Table S2.

Solution reaction with a fine stainless powder of SUS 304 (100 mesh)
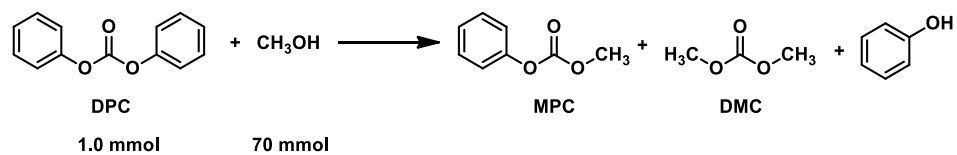
entry	Condition	time	DPC Conversion (%)	MPC (%)	DMC (%)
Solution Reaction, 100 ºC					
1	None	1 h	69	60	9
2	SUS 304 (50 wt%, 0.1 g)	1 h	67	58	9
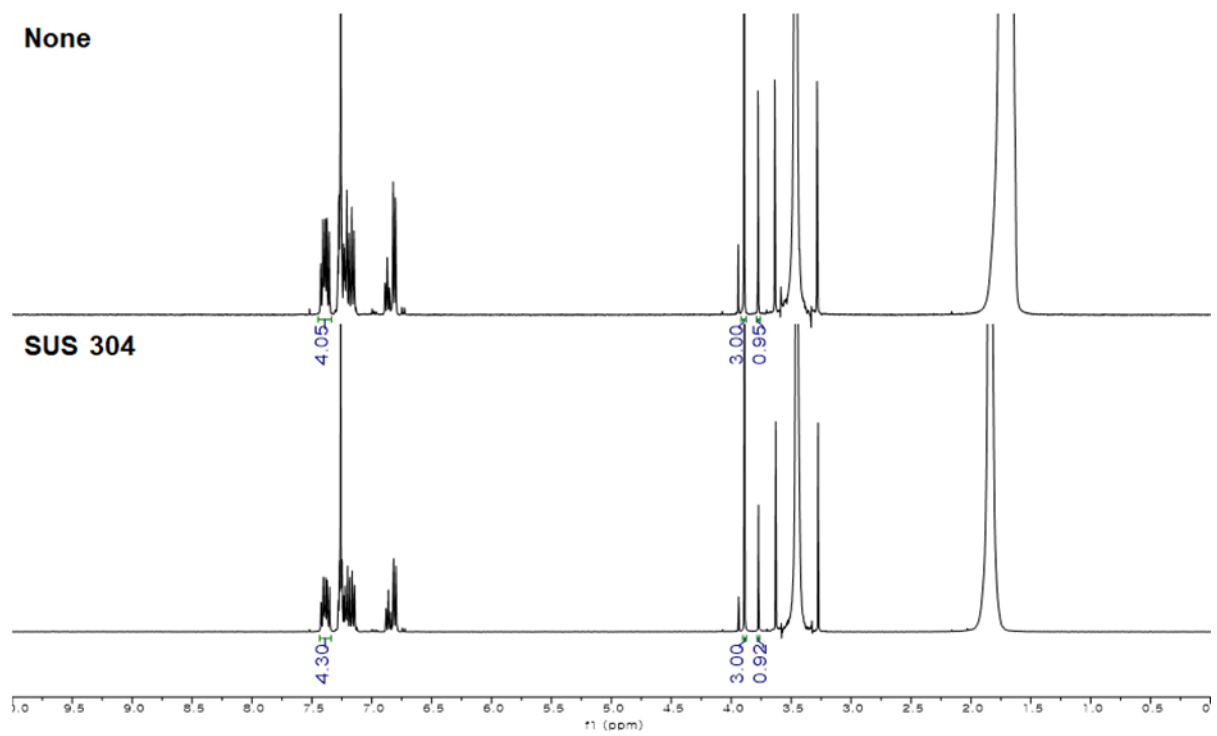
Fig. S2.

   ^{1}H NMR comparison of DPC methanolysis: (top) no-additive and (bottom) SUS 304 mesh additive

Mechanochemical Depolymerization of BPA-PC (Table 1)

- ***Solution procedure for BPA-PC methanolysis (Entry 1)***

PC powder (0.25 g, 1.0 mmol of carbonate functionality) and methanol (2.8 mL, 70 mmol) were added in 4 mL glass vial. The vial was placed in a reaction block of 100 °C. After stirring for 6 h, the solvent was removed under reduced pressure, and the analysis was performed by ^{1}H NMR in CDCl3.

- ***Representative procedure for BPA-PC methanolysis (Entry 7)***

PC pellet (0.25 g, 1.0 mmol of carbonate functionality) and dimethyl carbonate (0.17 mL, 2.0 mmol) were added to a stainless steel container (25 mL) having 50 stainless steel balls with a diameter of 5 mm. The vessel was placed in a planetary ball-milling machine and milled at 600 rpm for 30 min. After milling, methanol (1.2 mL, 30 mmol) was added, and the mixture was further milled at 600 rpm for 6 h. The container was opened and an aliquot of the reaction mixture was taken, and filtered through a syringe filter (45 µM) for ^{1}H NMR (CDCl$_3$) and SEC analysis.
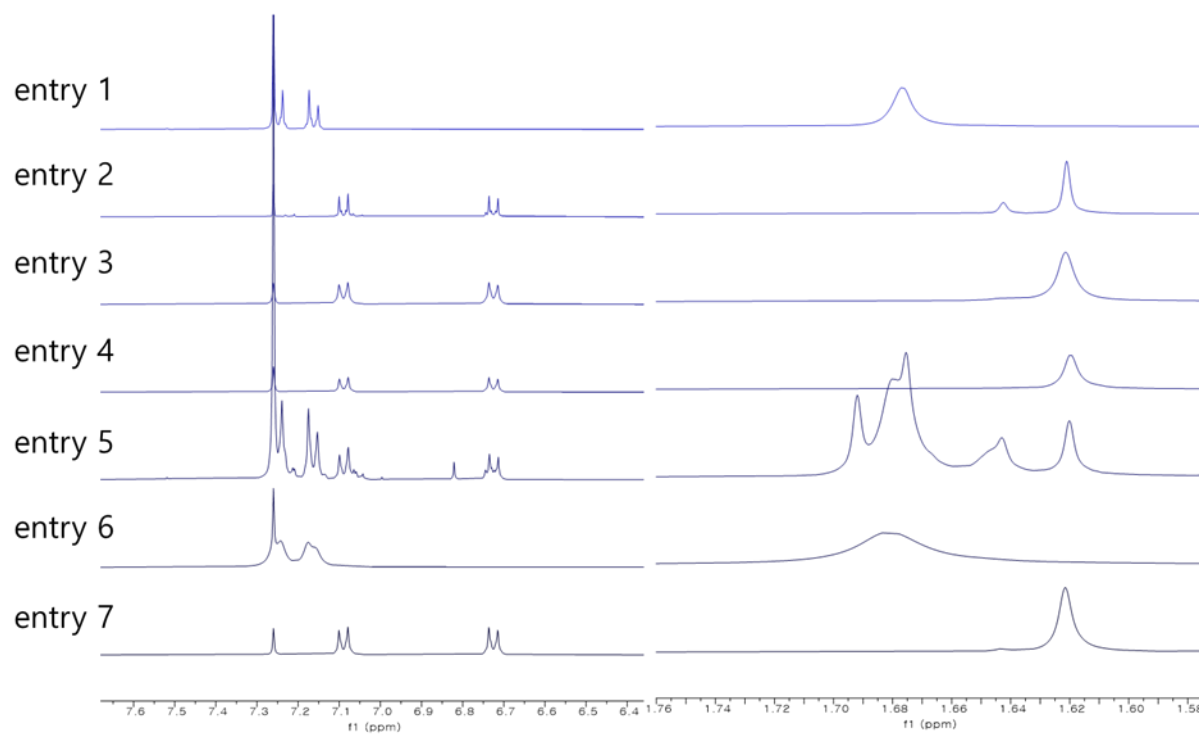
Fig. S3.
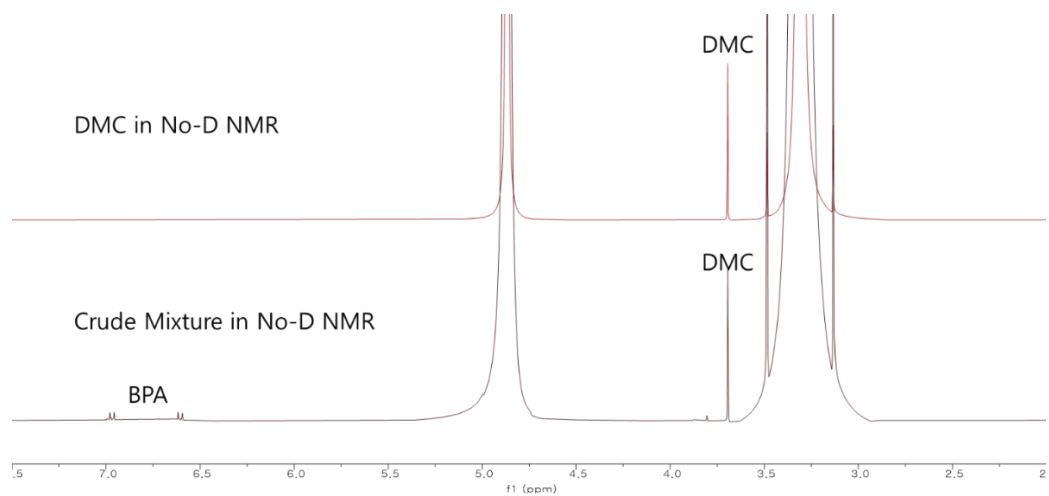^{1}H NMR Spectra used for Table 1

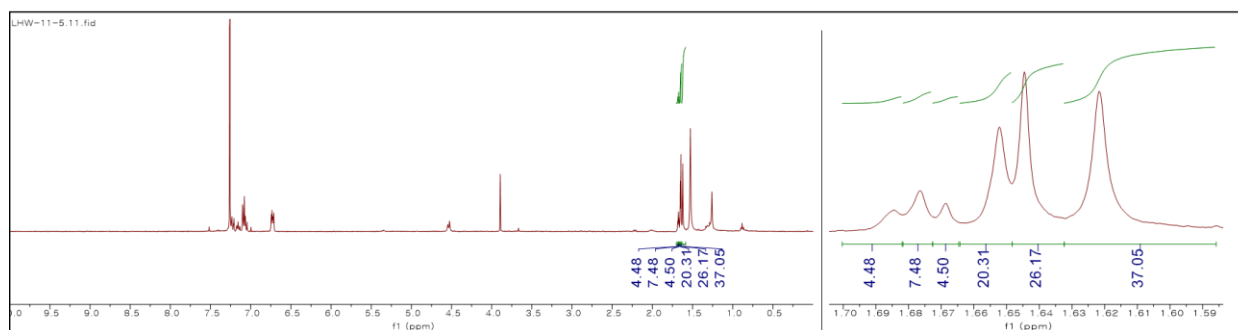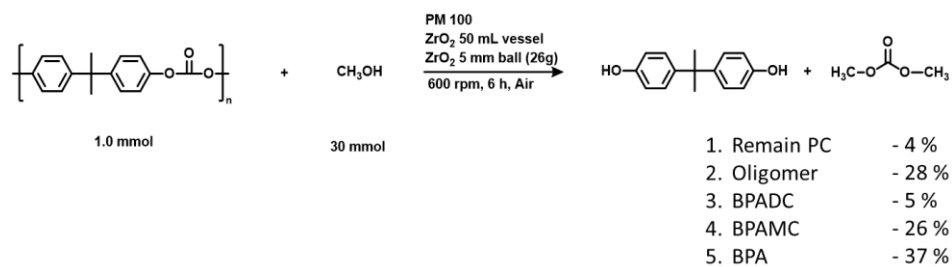**Fig. S4.**
Detection of DMC in No-D NMR

Fig. S5.

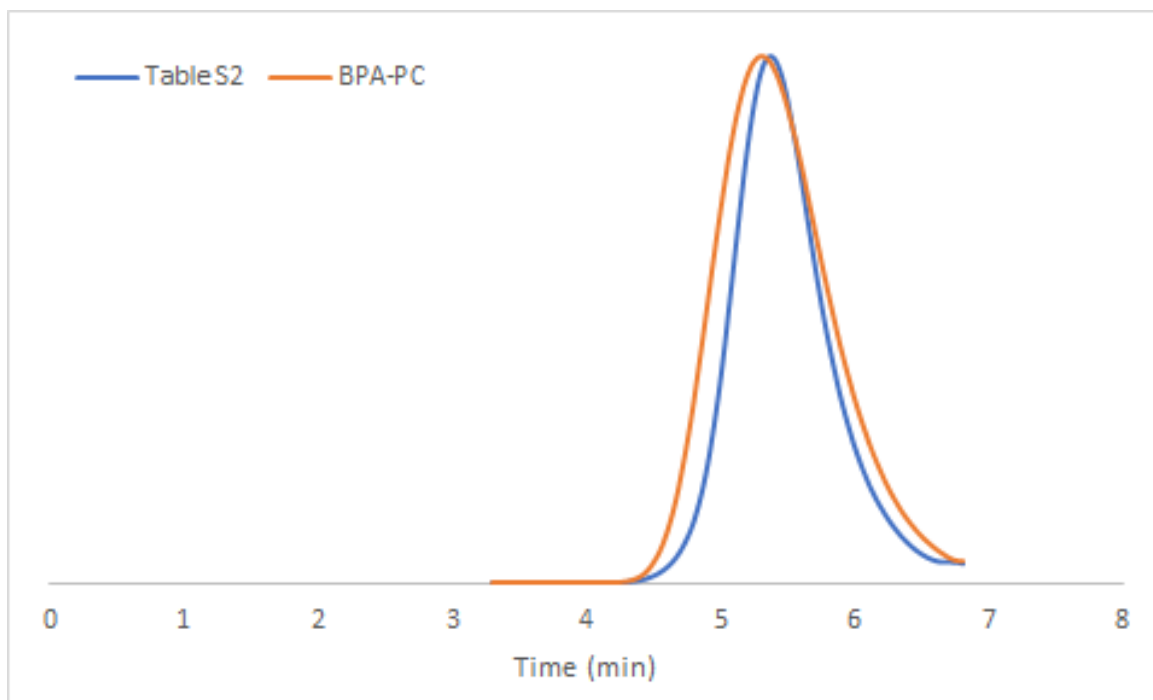PC depolymerization using a zirconia jar and balls

Fig. S6.

SEC spectra of BPA-PC before (orange) and after (blue) ball-mill grinding for 6 h
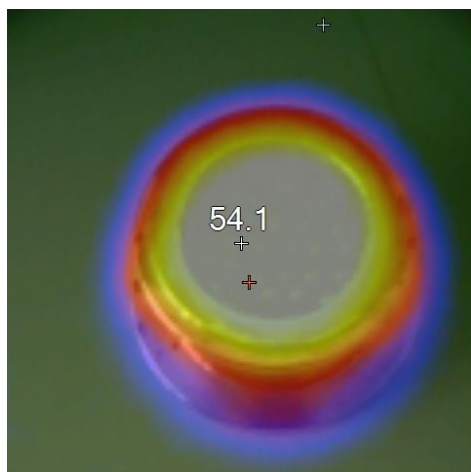
Fig. S7.
Temperature measurement at the end of reaction by IR thermometer

Gram-scale Methanolysis of BPA-PC, PLA, and PET

- ***Chemical Recycling of Compact Disc (Fig. 4)***

CD (5.0 g, 20 mmol of repeat unit) and dimethyl carbonate (3.4 mL, 40 mmol) were added to a stainless steel container (125 mL) containing 500 stainless steel balls with a diameter of 5 mm. The vessel was placed in a planetary ball-milling machine and milled at 600 rpm for 30 min. After milling, methanol (24 mL, 600 mmol) was added, and the mixture was further milled at 600 rpm for 6 h. The resulting mixture was transferred with methanol to a round-bottom flask, and the solvent was removed. The flask was subjected to acid work-up using 1 M HCl and then separated with dichloromethane. The product was purified by silica filter to afford BPA (4.1 g, 90%).

- ***Chemical Recycling of PLA cup (Fig. 5)***

PLA cup (2.2 g, 30 mmol of repeat unit) was added to a stainless steel container (125 mL) containing 250 stainless steel balls with a diameter of 5 mm, along with methanol (24 mL, 600 mmol). The vessel was placed in a planetary ball-milling machine and milled at 600 rpm for 6 h. The resulting mixture was transferred to a round-bottom flask with methanol, and the solvent was removed. The flask was subjected to acid work-up using 1 M HCl and then separated with dichloromethane. A solvent removal afforded methyl lactate (3.1 g, 98%).

- ***Chemical Recycling of PET cup (Fig. 5)***

PET powder (2.8 g, 15 mmol of repeat unit) and methanol (43 mL, 1.05 mol) were added to stainless steel container (125 mL) having 300 stainless steel balls with a diameter of 5 mm. The vessel was placed in a planetary ball-milling machine and milled at 650 rpm for 6 h. The resulting mixture was transferred with methanol in a round bottom flask, and the solvent was removed. The flask was subjected to acid work-up using 1 M HCl and then separated with dichloromethane. The product was purified by silica filter to afford DMT (2.4 g, 82%).
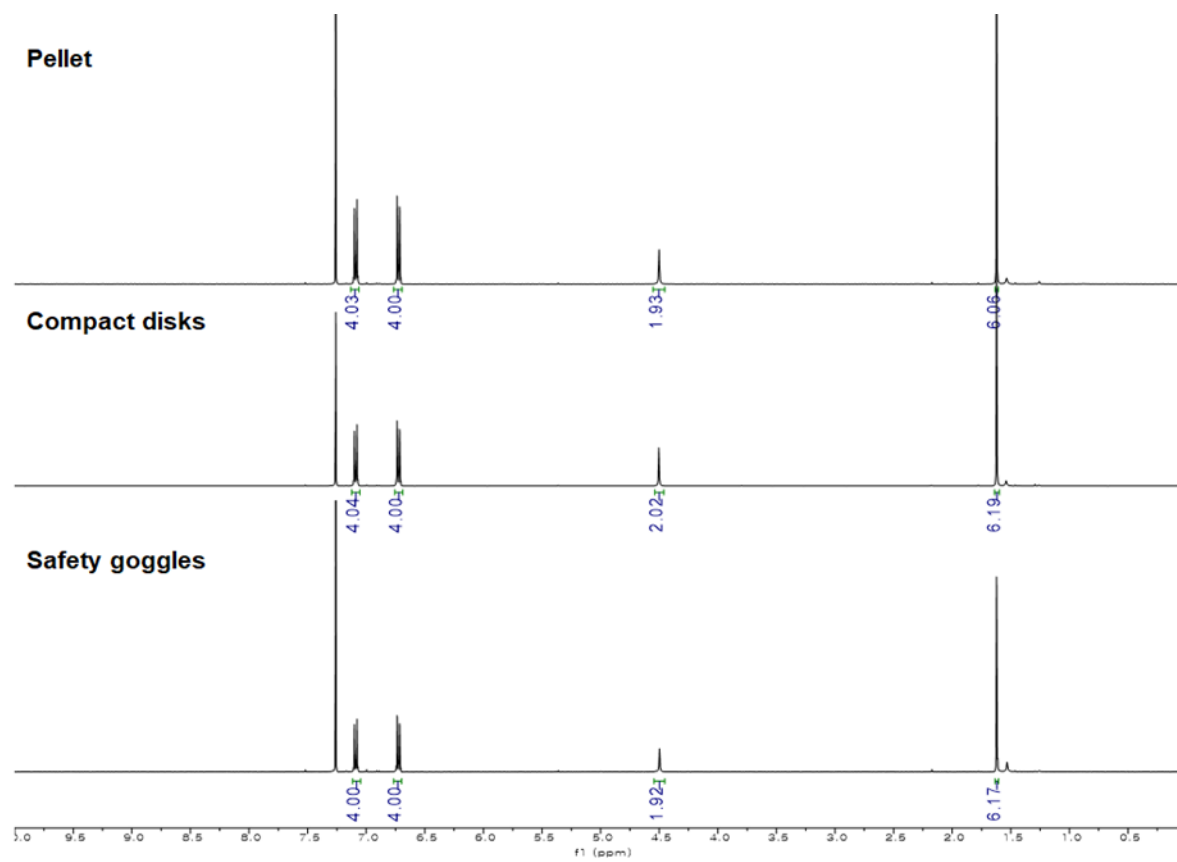
Fig. S8.
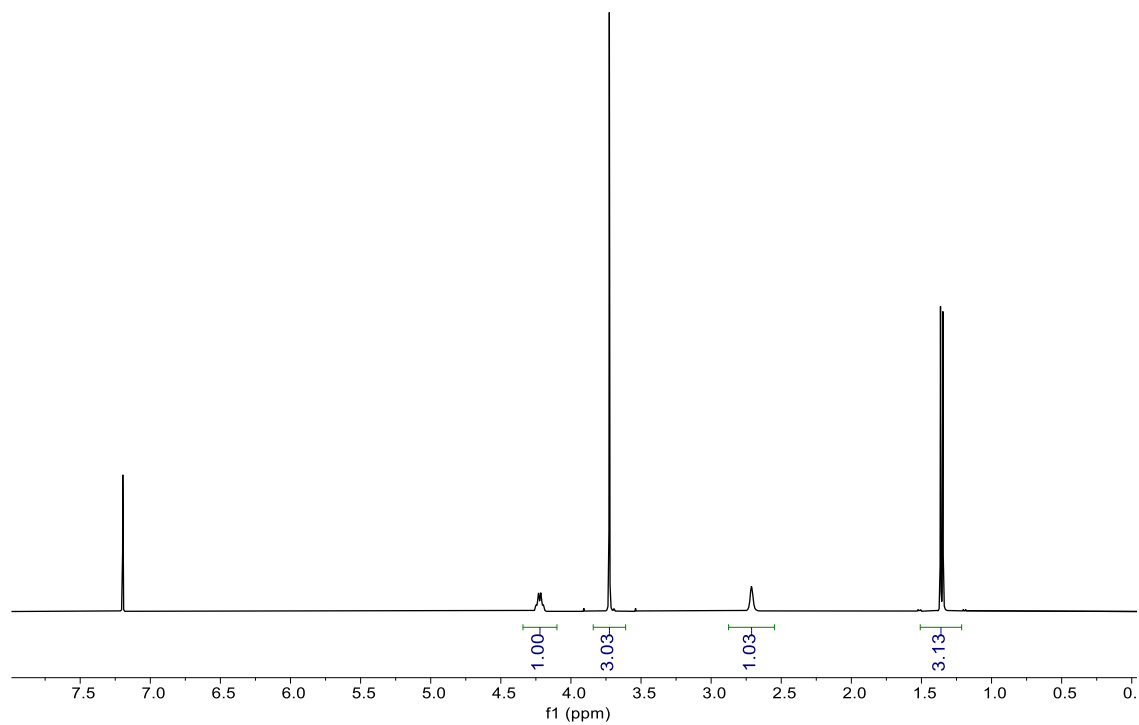Mechanochemical methanolysis of BPA-PC from various sources (5 g scale)

Fig. S9.

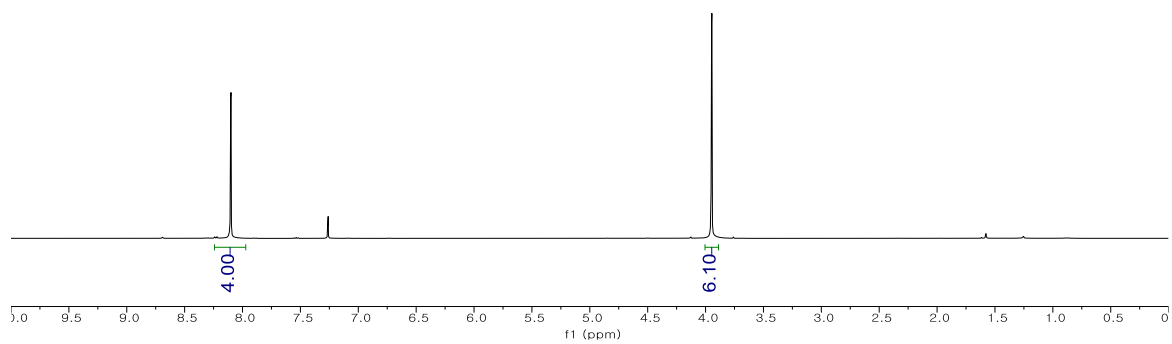Mechanochemical depolymerization of after-use PLA-cup

Fig. S10.
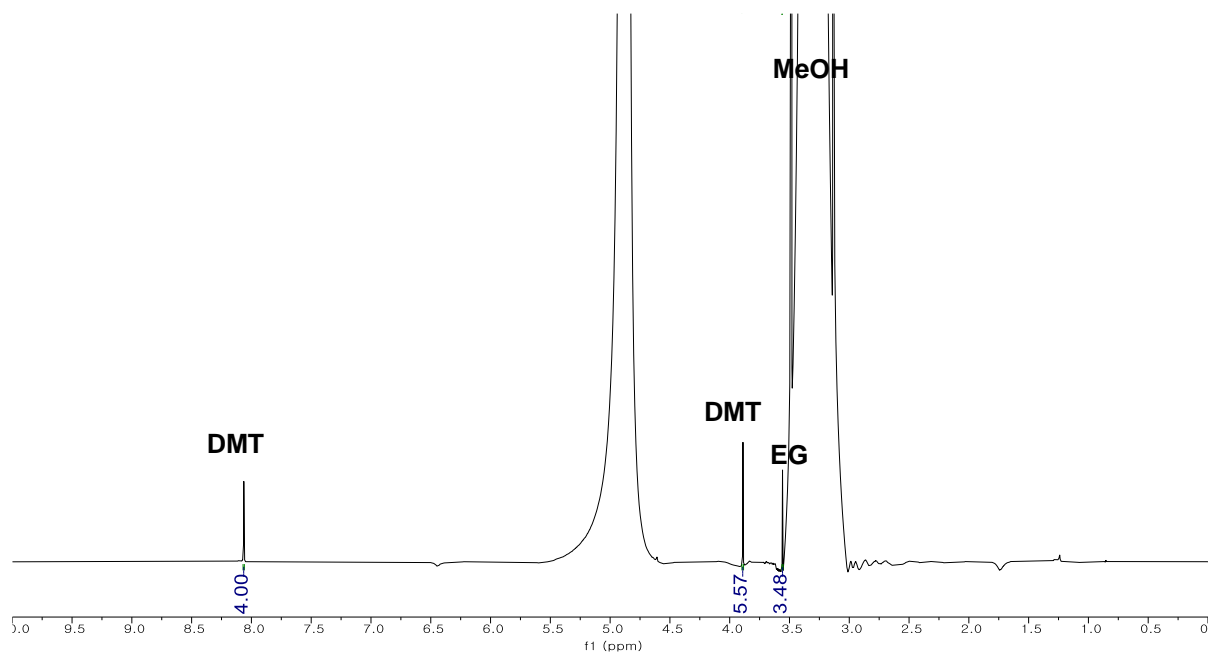
Mechanochemical depolymerization of PET bottle

Fig. S11.

No-D NMR of the crude mixture of PET depolymerization. A peak of 3.6 ppm is from ethylene glycol