Supplementary Information

Synthesis and characterization of amino-functionalized Poly(propylene carbonate)

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Contents

Experimental Section

Measurements

The products were characterized by Fourier Transform Infrared spectoscopy (FT-IR) using the United States Digilab Merlin FTS 3000 FT - IR infrared spectrometer.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-400 NMR spectrometer using tetramethylsilane as an internal standard and D-chloroform ($CDCl_3$) as solvent.

The molecular weights (M_w and M_n) of products were measured using a gel permeation chromatography (GPC) system (The United States Waters GPC2000). The GPC system was calibrated by a series of polystyrene standards with polydispersities of 1.02, which were supplied from THF (HPLC grade) was used as an eluent. The concentration of the sample is 1.0 g L^{-1}.

The concentration of the sample is 1.0 g L^{-1}. Differential scanning calorimetry (DSC, Mettler instruments) was used to determine the glass transition temperature of the polymer samples.

PPC-DBAG and PPC-NH_2 samples performed on the contact angle (CA) measurements. These were prepared by spin-coating on a silica wafer from THF solutions of the polymers (10% w/v). Static contact angles to water (distilled twice) were measured by placing a small droplet on the surface and recording the angle between the horizontal plane and the tangent to the drop at the point of contact to the substrate.

Materials

CO_2 with a purity of 99.99 % was commercially obtained without further purification. Propylene oxide (PO) and epichlorohydrin (ECH) of 99.5 % purity stored over 0.4 nm molecular sieves prior to use. Diphenylamine and ceric ammonium nitrate (CAN) were purchased from Alfa Aesar China (Tianjin) Co., Ltd., which of 99% purity and used without purification. Solvents such as ethanol and chloroform were of analytical reagent grade and used as received.

Preparation of Catalysts

Zinc glutarate (ZnGA) was prepared as described elsewhere. That is, GA (98 mmol) was dissolved in 150 mL toluene in a round bottom flask (250 mL) equipped with a Dean-Stark trap to separate and remove water byproduct and a reflux condenser with a drying tube. Then, fine powdery ZnO

(100 mmol) in fine powder was added to the GA solution in toluene. After the addition was completed, the slurried mixture was stirred vigorously at 55 ℃ for 7 h. After being cooled to room temperature, the reaction mixture was filtered and washed with acetone several times, giving powdery zinc glutarate. It was dried under vacuum at 100 ℃ for 24h, followed by grinding in a mortar.

Synthesis of N, N-Dibenzyl Amino Glycidol (DBAG)

N, N-Dibenzyl-3-chloro-2-hydroxypropylamine (**A**) Synthesis. Dibenzylamine (40.0 g, 202 mmol, 1 equiv) and 19.7 g of epichlorohydrin (212 mmol, 1.05 equiv) were dissolved in 300 mL of methanol and stirred for 16 h. Solvent and excess of epichlorohydrin were removed under reduced pressure to obtain a pale-yellow oil (yield >95%). The crude product is sufficiently pure to be directly converted.

N, N-Dibenzyl Amino Glycidol Synthesis. **A** (36.0 g, 125 mmol) was dissolved in 200 mL of tert-butanol. KOH (11 g, 167 mmol) dissolved in a minimal volume of water was added, and the reaction mixture was stirred for 16 h. KCl was filtered off, and the solvent removed under reduced pressure. The product was purified by column chromatography with solvent (ligroin / diethyl ether (8/1 by volume)) on silica, resulting in monomer **A** of a light yellow liquid at room temperature. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.42 -7.32 (m, 10H, arom.), 3.84 (d, 2H, CH$_2$Ph), 3.60 (d, 2H, CH$_2$Ph), 3.13-3.04 (m, 1H, CH), 2.85-2.67 (m, $_2$H, CH$_2$ ring), 2.51 -2.42 (m, CHCH$_2$N). ^{13}C NMR (75.5 MHz, CDCl$_3$, δ): 139.28, 128.73, 128.18, 126.19 (aromatic), 58.82 (CH$_2$Ph); 55.78 (CH); 51.01 (CH$_2$ ring); 44.90 (CHCH$_2$N).
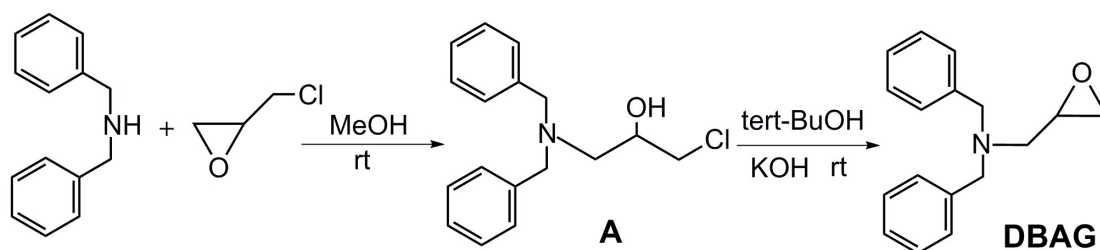
Scheme S1. Synthesis of N, N-Dibenzyl Amino Glycidol (DBAG)
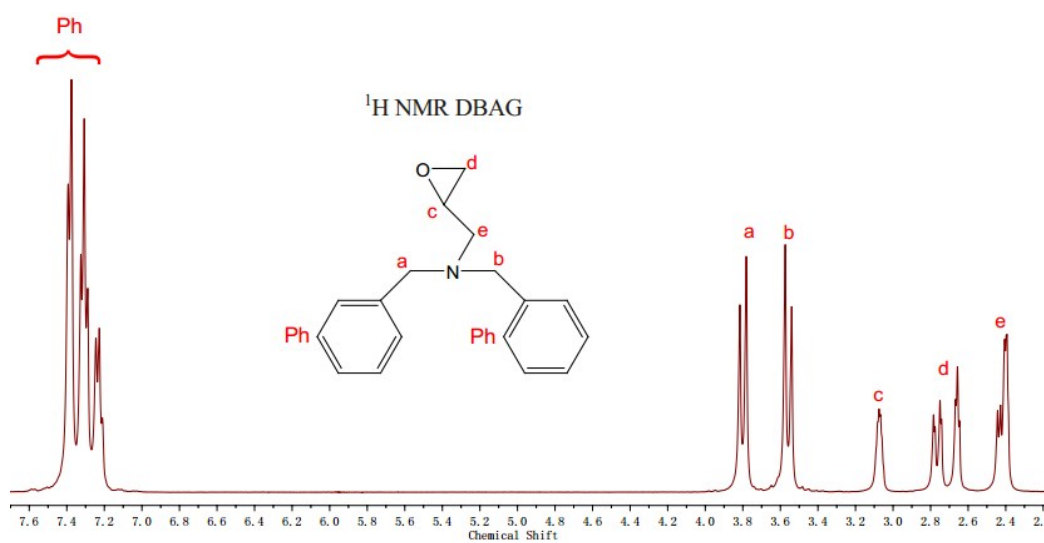
Figure S1. ^{1}H NMR spectra of N, N-Dibenzyl Amino Glycidol (**DBAG**).(in CDCl$_3$)

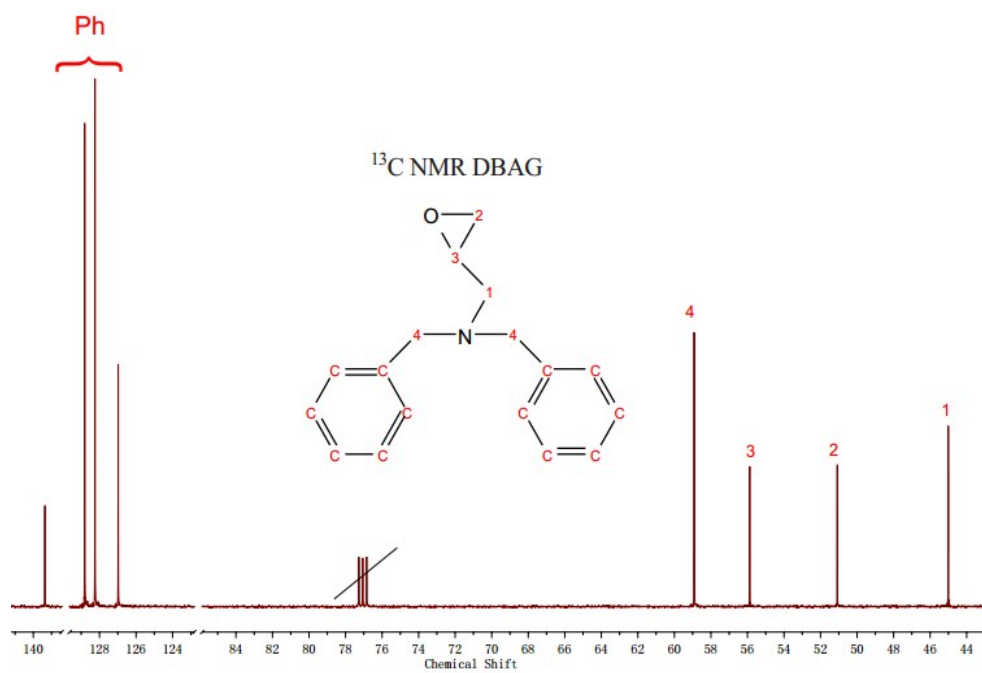**Figure S2**. ^{13}C NMR spectra of N, N-Dibenzyl Amino Glycidol (**DBAG**) (in CDCl$_3$)

Preparation and characterization of PPC-DBAG

Terpolymerization of DBAG, PO, and CO_2 was achieved using a zinc glutarate (ZnGA) catalyst. The copolymerization was carried out in an autoclave of 50 mL volume. The reactor was charged with 50 mg of ZnGA and various amounts of DBAG. Subsequently, the autoclave was purged with carbon dioxide and evacuated alternatively for three times, followed by adding purified PO using a large syringe. Then the autoclave was pressurized to 5.0 MPa via a CO_2 cylinder. The copolymerization was performed at 80 ℃ under stirring for 20 h, after which the reactor was cooled in an ice bath. The pressure was released and the reaction mixture subjected to a dynamic vacuum for 1 h at room temperature to remove the volatiles. The polymer was precipitated from acetone into methanol three times, collected, and then PPC-DBAGs were dried at 40℃ under vacuum to a constant weight and calculated the yields.

Table S1 Terpolymerization of CO_2, PO and DBAG[a]

Sample	CO_2 (MPa)	Temperature(℃)	Time(h)	Catalyst(g)	Yield (g/mol of Zn)
PPC-DBAG	3	60	40	0.1	923
PPC-DBAG	4	60	40	0.1	1298
PPC-DBAG	5	60	40	0.1	2153
PPC-DBAG	5	40	40	0.1	793
PPC-DBAG	5	80	40	0.1	2829
PPC-DBAG	5	80	10	0.1	836
PPC-DBAG	5	80	20	0.1	2871
PPC-DBAG	5	80	20	0.03	2955
PPC-DBAG	5	80	20	0.05	5365

[a]All the terpolymerization was performed in autoclave and DBAG/PO =1/15 (mol/mol).

Figure S3. The presence of DBAG groups can be deduced from the resonances in the aromatic region (δ = 7.66 – 7.97 ppm). The polymer constitutions were derived from the integral values of the resonances at 1.20–1.50 ppm. The molar quantities of benzyl units increased with the concentration of DBAG in the feed.
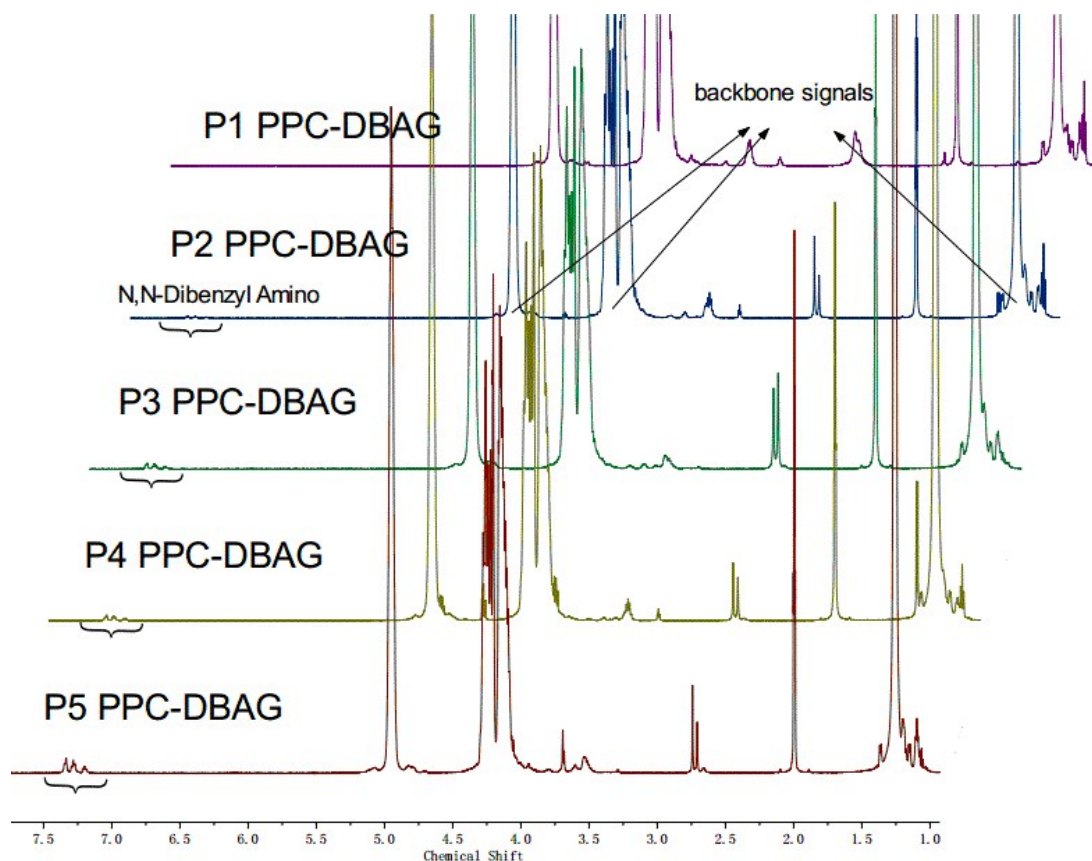

Figure S3. ^{1}H NMR spectra of PPC-DBAG

Preparation and characterization of Amino-Functionalized PPC

At room temperature to a solution of PPC-DBAG (0.5 g) in Solvent (30ml, CH_3CN/H_2O = 5/1) was added $Ce(NH_4)_2(NO_3)_6$ (5.0 g, 3 eq.). The resulting mixture was stirred at room temperature for 16 hours and TLC analysis indicated that the starting material was completely consumed. The reaction was quenched with water (10 ml) the phases separated and the aqueous layer extracted with AcOEt (3 x 10 ml). The combined organic phases and evaporated under reduced pressure.

^{1}H NMR spectra of P1-P5 PPC-NH$_2$ are shown in Figure S4 and reaction with cerium ammonium nitrate (CAN) lead to a complete cleavage of the DBA groups. The poly(propylene carbonate) (PPC) backbone was not affected was concluded from a comparison of the ^{1}H-NMR spectra and gel permeation chromatography(GPC) results of PPC-DBAG and PPC-NH$_2$ samples (Figure S5). Signals of the methylene and methyl entities attributed by PPC are conserved, whereas signals related to the DBA groups disappear. GPC results in Figure S4 showed that deprotection was harmless to backbone of PPC samples.
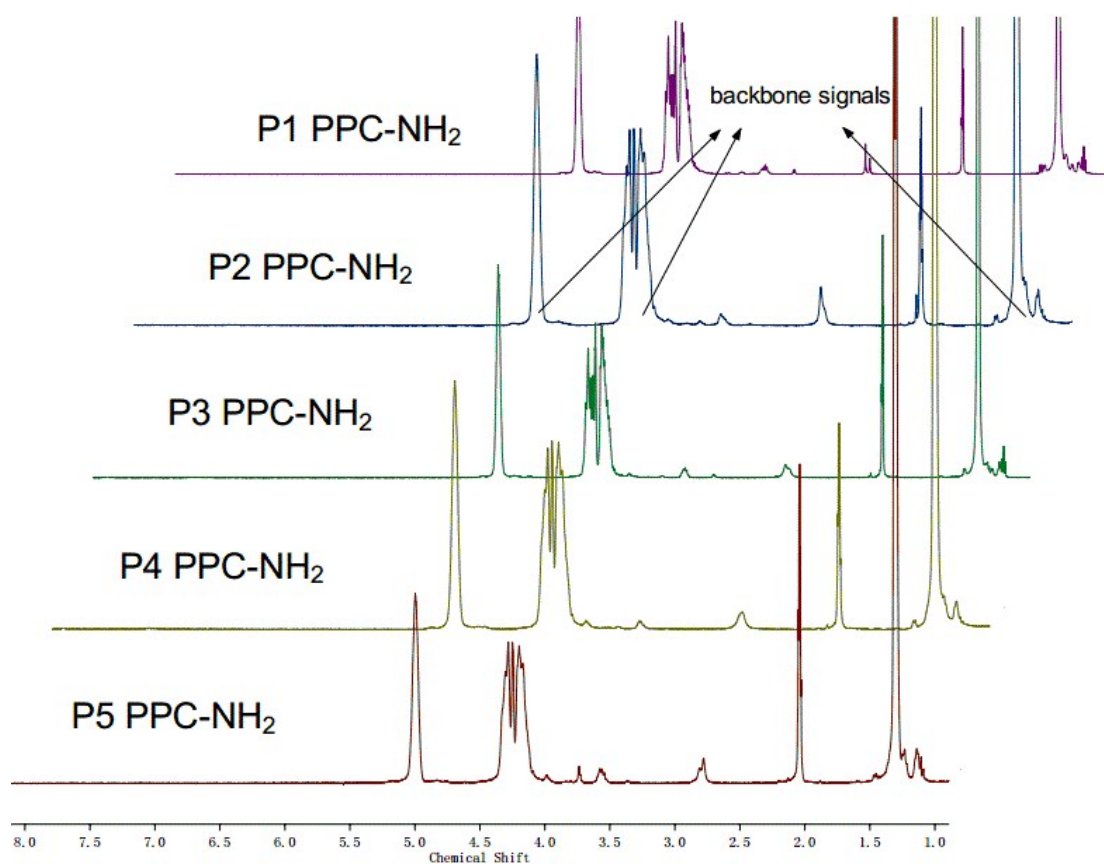

Figure S4. ^{1}H NMR spectra of PPC-NH$_2$
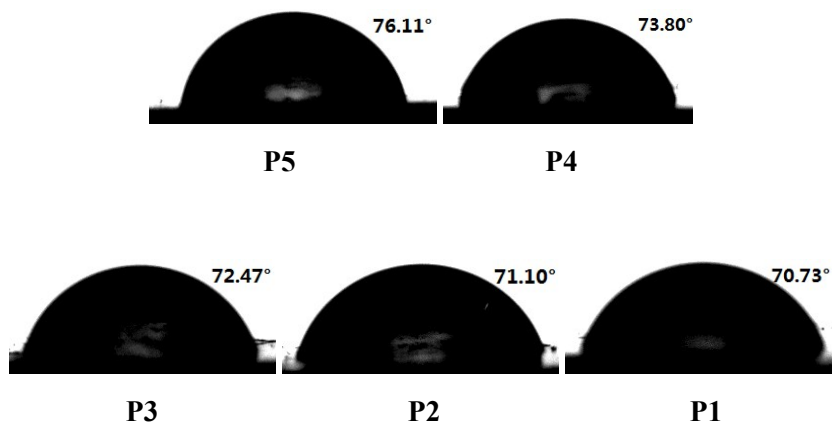
7

Contact angles of polymer samples

Figure S5. Contact angles of P1-P5 PPC-DBAG
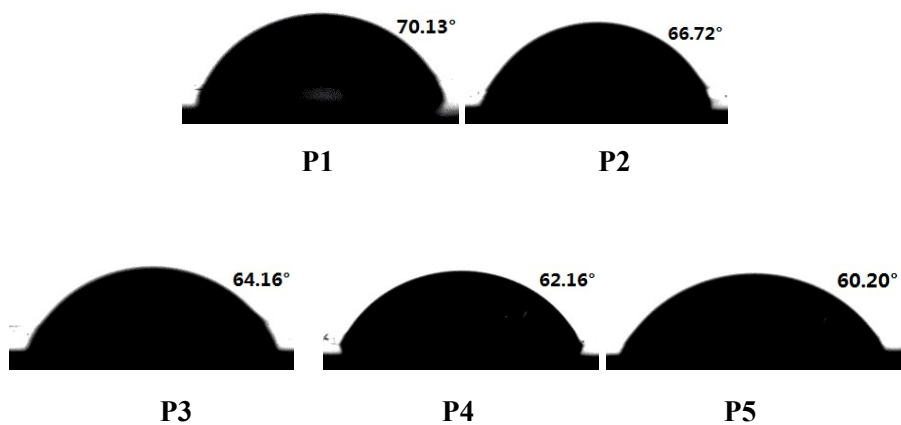

Figure S6. Contact angles of P1-P5 PPC-NH$_2$

8

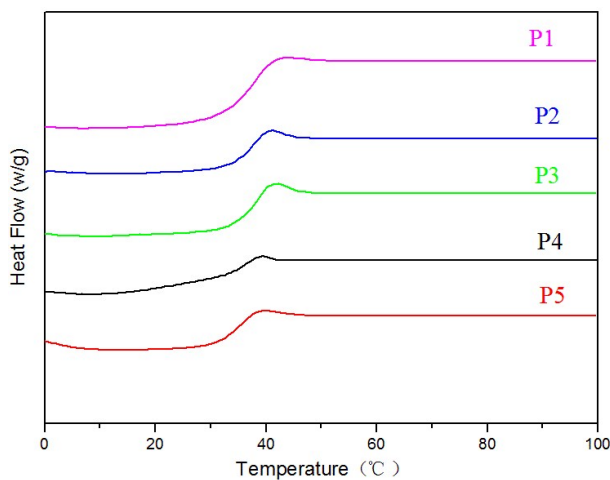## DSC curves of polymer samples
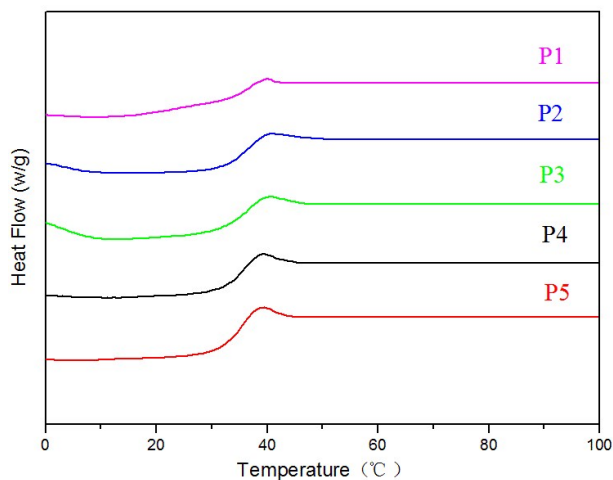

Figure S7. DSC curves of PPC-DBAG

Figure S8. DSC curves of PPC-NH$_2$

References

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3. Bull S D, Davies S G, Kelly P M. *J. Chem. Soc. Perkin Trans*, 2001, **(23):** 3106-3111.