Supplementary Information

A one-step strategy for cross-linkable aliphatic polycarbonates with high degradability derived from CO₂, propylene oxide and itaconic anhydride[†]

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Experimental Section

Materials

CO₂ with a purity of 99.99 % was commercially obtained without further purification. Propylene oxide (PO) of 99.5 % purity stored over 0.4 nm molecular sieves prior to use. Itaconic anhydride (IAn) was purchased from Alfa Aesar China (Tianjin) Co., Ltd., which of 97% 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 °C 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 °C for 24h, followed by grinding in a mortar.

Preparation of PPCIAn

All copolymerizations of CO_2 and PO were carried out in a 500 mL autoclave equipped with a sealed mechanical stirrer, a heating jacket, and a programmable temperature controller. The above catalysts were further dried at 100 °C for 24 h before being used for the polymerization process. Dry catalyst was then introduced into the autoclave as quickly as possible. The autoclave was finally capped with its head, and the autoclave with catalyst inside was further dried for 24 h under vacuum at 100 °C. 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 5.2 MPa via a CO_2 cylinder. The copolymerization was performed at 70 °C under stirring for 40 h. Thereafter, the autoclave was removed from the autoclave, then dissolved in a proper volume of chloroform, and there is a portion of yellow insoluble substances which is the highly cross-linked terpolymers gel. The organic layer was slowly added to excess

vigorously stirred ethanol precipitating the products which was washed by ethanol several times to remove a small amount of cyclic propylene carbonate. Then PPCIAn were dried at room temperature under vacuum to a constant weight and calculated the yields.

Preparation of PPC

For comparison between PPCIAns and PPC, PPC were also synthesized in the similar procedure to that of PPCIAns, except that no IAn was added into the autoclave.

Measurements

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

¹H NMR spectra were recorded on a Bruker DRX-400 NMR spectrometer using tetramethylsilane as an internal standard and D-chloroform (CDCl₃) 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 gel content of PPCIAns was determined according to ASTM D2765 method using a Soxhlet extractor. Weighed samples (W_0) in small pieces were refluxed in boiling chloroform for 24 h. The insoluble part was dried to a constant weight (W) at 80 °C in a vacuum. The gel content was calculated from weight percentage of the dried gel in the initial polymer according to the following equation. The data were recorded as the average value of three parallel determinations.

$$\text{Gel content}(\%) = \frac{W}{W_0} \times 100\%$$

Differential scanning calorimetry measurements were carried out using a Q100 TA Instrument under a high purity nitrogen flow of 40 mL min⁻¹ over the temperature range -50-150 °Cat a heating rate of 10 °C min⁻¹. The T_g of the sample was taken as the onset of the change in heat capacity as a function of temperature.

Thermogravimetric analysis (TGA) measurements were performed in a Perkin-Elmer TGS-2

under a protective nitrogen atmosphere. The temperature ranged from 50 °C to 500 °C at a heating rate of 10 °C/min.

The mechanical properties were tested at 23 °C and relative humidity of 50 ± 5 % using a CMT 6104 electronic tensile tester with a computer controlling system which was equipped with a 10 kN electronic load cell and mechanical grips according to the ASTM standard. The cross-head speed was 50 mm min⁻¹. The data were recorded as the average value of five parallel determinations. The samples for the tensile tests were prepared by hot-pressure molding in dumbbell shaped mold after extrusion using micro-twin-screw extruder.

Degradation experiments were carried out by means of the buffer solution processes. The initial weights (W_0) of the specimens were measured prior to tests. Thin-film specimens were prepared by casting 5 wt % PPC/chloroform solution. 15 mg of the PPCIAn film ($10 \times 5 \times 0.5$ mm) and 0.5mL of phosphate buffer (NaH₂PO₄/Na₂HPO₄, pH=7.4) were placed in a test tube. The container was then placed in a thermobath regulated at 37 °C. The films were removed from the buffer solution for various specified durations. Upon washing with distilled water, they were dried at room temperature under vacuum to constant weight. The film specimens, from buffer solution experiments, were dried with filter paper after washing with distilled water and weighed (W_1). The film specimens were dried in a vacuum oven to a constant weight (W_2). The amounts of water absorbed by the specimens were determined from the equation.

Water sorption (%) = $\frac{W_1 - W_2}{W_2} \times 100\%$

Weight loss(%) = $\frac{W_0 - W_2}{W_0} \times 100\%$



Fig. S1 FT-IR spectrum of PPCIAns and PPC.



Fig. S2 ¹H NMR spectra of PPC and PPCIAns (soluble part) in CDCl₃.



Fig. S3 Weight loss versus time for PPC and PPCIAn4 in buffer solution.



Fig. S4 Water sorption versus time for PPC and PPCIAn4 in buffer solution.

No.	Sample ^a	CO ₂ (MPa)	Temperature	Time (h)	Gel contents (%)
1	PPCIAn5	1	70	40	0
2	PPCIAn6	3	70	40	0
3	PPCIAn7	6.8	70	40	55.9
4	PPCIAn8	5.2	60	40	34.7
5	PPCIAn9	5.2	80	40	60.1
6	PPCIAn10	5.2	70	10	0
7	PPCIAn11	5.2	70	20	33.1
8	PPCIAn12	5.2	70	30	49.7

Table S1 The influence of polymerization conditions on the gel contents of PPCIAns

^aThe terpolymerization was performed in autoclave and IAn/PO =1/20 (mol/mol).

Table S2 Thermal properties of PPC and PPCIAns

No.	Sample	T _{d,-5%} (°C)	T _{d,max} (°C)	Т _g (°С)
1	PPC	194.7	241.5	34.9
2	PPCIAn1	247.7	276.2	38.1
3	PPCIAn2	259.2	282.1	39.3
4	PPCIAn3	257.8	286.1	39.4ª
5	PPCIAn4	251.3	284.7	39.7ª

^aThere exists a melting point of 97.6 °Cand 90.4 °C besides the T_g of 39.4 °Cand 39.7 °C for PPCIAn3 and PPCIAn4, respectively.