Supplementary Information:

Experimental

Materials. CO_2 of a purity of 99.99 % was commercially obtained without further purification. PO of 99.5 % purity was pretreated by potassium hydroxide and refluxed over calcium hydride for 24 h. It was then distilled under dried nitrogen gas and stored over 0.4 nm molecular sieves prior to use. Pyromellitic dianhydride (PMDA) was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. It was chemical pure and used without purification. Solvents such as ethanol and chloroform were of analytical reagent grade and used as received.

Preparation of PIPPCNs. The diagram of synthesis of PIPPCNs is shown in Fig. S1. It was carried out in a 100 mL autoclave reactor equipped with a magnetic stirrer. The pre-dried 0.1 g zinc glutarate (ZnGA) used as the catalyst and a proportion of PMDA were putted into the autoclave as quickly as possible. The autoclave reactor was capped with its head and the catalyst and PMDA were further dried for 24 h under vacuum at 100 ^{o}C and then were cooled to 20 ^{o}C. Subsequently, the autoclave was purged carefully with N_2 and evacuated alternatively for three times, followed by injecting 30 mL PO with a syringe. The autoclave reactor was then pressurized to 5.4 MPa via a CO_2 cylinder. Terpolymerization was performed at 70 ^{o}C under stirring for 36 h and afterwards the autoclave was cooled to room temperature and the pressure was released. The hard-lump product (as seen in Fig. S2) was unloaded and some sample was immediately detected by ^{1}H NMR spectra test in acetone-d6 solvent using Bruker AV 400 nuclear magnetic resonance spectrometer. The residue was dissolved in a sufficient volume of chloroform containing 5 % solution of hydrochloric acid to

decompose the catalyst. There is a portion of white insoluble substances which is the highly cross-linked terpolymers gel. The organic layer was washed to the neutral reaction and 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 PIPPCNs were dried at 80 ^{o}C under vacuum to a constant weight and calculated the yields.

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

Measurements. The molecular weights (M_w and M_n) of products were measured using a gel permeation chromatography (GPC) system (Waters 515 HPLC Pump, Waters 2414 detector) with a set of three columns (Waters Styragel 500 A, 10,000 A, and 100,000 A). The GPC system was calibrated by a series of polystyrene standards with polydispersities of 1.02, which were supplied from Shodex Inc. THF (HPLC grade) was used as an eluent. The concentration of the sample is 1.0 g L^{-1}.

The products were characterized by Attenuated Total Reflectance (ATR) infrared spectrophotometry using Nicolet 6700 Fourier transform infrared spectrometer.

The gel content of PIPPCNs 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 ℃ 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.

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

Thermogravimetric analysis measurements were performed on a PerkinElmer simultaneous thermal analyer (Model STA 6000). The samples were tested under nitrogen flow of 40 mL min^{-1} from 25 ^{o}C to 400 ^{o}C at a heating rate of 20 ^{o}C min^{-1}.

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 -25 –200 ^{o}C at a heating rate of 10 ^{o}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.

The mechanical properties were tested at 23 ^{o}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.

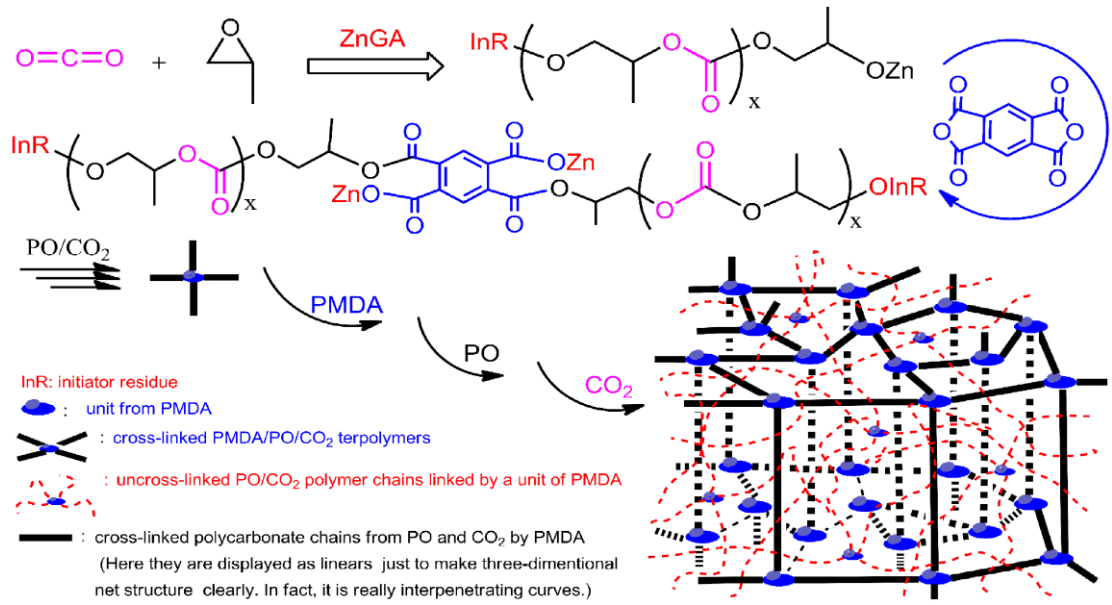

Fig. S1 Diagram of formed PIPPCNs based on randomly cross-linked terpolymers and uncross-linked PPC.

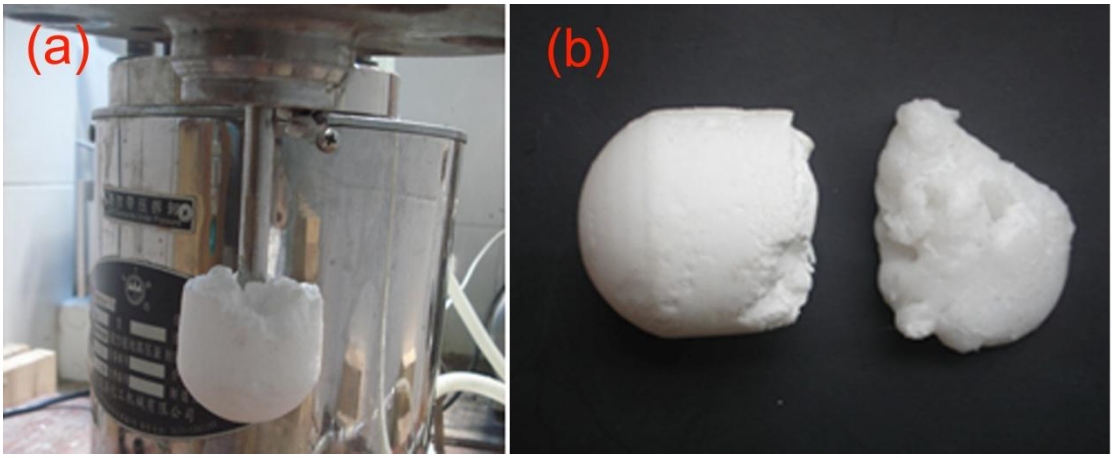

Fig. S2 (a) Hard mass morphology of untreated PIPPCNs and (b) comparison with untreated PPC after polymerization.

Table S1 Thermal and mechanical properties of neat PPC, PIPPCNs and the composite of PPC with PMDA.

Sample	$T_{d,\ -5\%}$ /°C	$T_{d,\ max}$ /°C	T_g / °C	Tensile strength /MPa	Young's modulus /MPa	Elongation at break (%)
PPC	231	247	38.3	19.5 ± 1.4	411 ± 16	832 ± 15
PIPPCNs1[a]	270	288	40.0	25.9 ± 2.0	549 ± 18	700 ± 10
PIPPCNs2[a]	277	298	41.9	31.7 ± 1.9	732 ± 13	481 ± 13
PIPPCNs3[a]	281	306	43.9	41.0 ± 1.5	662 ± 15	406 ± 9
PIPPCNs4[a]	278	309	43.2[c]	45.7 ± 1.2	1016 ± 18	120 ± 7
PPC+PMDA[b]	253	275	33.8	8.8 ± 0.6	123 ± 10	1180 ± 16

[a] They correspond to a PMDA content of 1, 2, 3, and 4 mol% relative to PPO in the CO_2/PO/PMDA terpolymerization, respectively.

[b] The physical composite of PPC with 4 mol% PMDA compared to PO units in PPC, which is prepared by uniform mixing of PPC with PMDA in acetone followed by evaporation of solvent under stirred and dried at 80 °C *in vacuo* to a constant weight.

[c] There exists a melting point of 86.7 ℃ besides the T_g of 43.2 ℃ for PIPPCNs4.

Table S2 The thermal stabilities of the soluble and insoluble portion of PIPPCNs.[a]

Sample	SPP1[b]	SPP2[b]	SPP3[b]	SPP4[b]	IPP1[c]	IPP2[c]	IPP3[c]	IPP4[c]
$T_{d,\ -5\%}$/°C	264	273	277	281	260	261	264	272
$T_{d,\ max}$/°C	285	285	296	297	305	308	310	314

[a] The soluble and insoluble portion of PIPPCNs were prepared as follow. PIPPCNs were extracted in boiling chloroform for 24 h using a Soxhlet extractor. The soluble portion was precipitated from ethanol. They are then dried at 80 °C in *vacuo* to a constant weight.

[b] SPP1, SPP2, SPP3 and SPP4 corresponds to the soluble portion of PIPPCNs1, PIPPCNs2, PIPPCNs3 and PIPPCNs4, respectively. [c] IPP1, IPP2, IPP3 and IPP4 corresponds to the insoluble portion of PIPPCNs1, PIPPCNs2, PIPPCNs3 and PIPPCNs4, respectively.

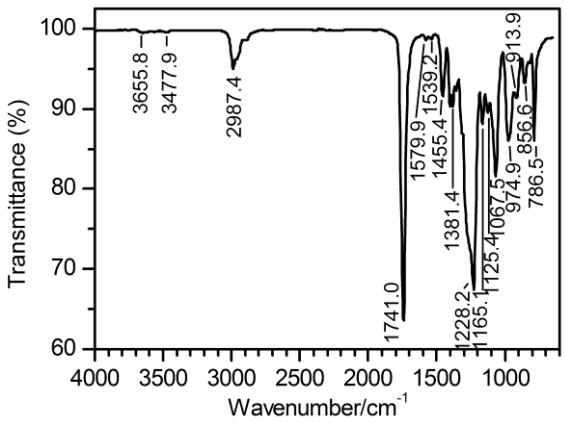

Fig.S3 FT-IR spectrum of PPC

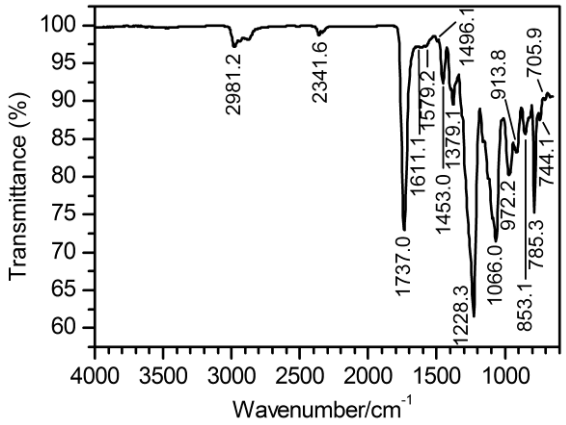

Fig.S4 FT-IR spectrum of PIPPCNs2

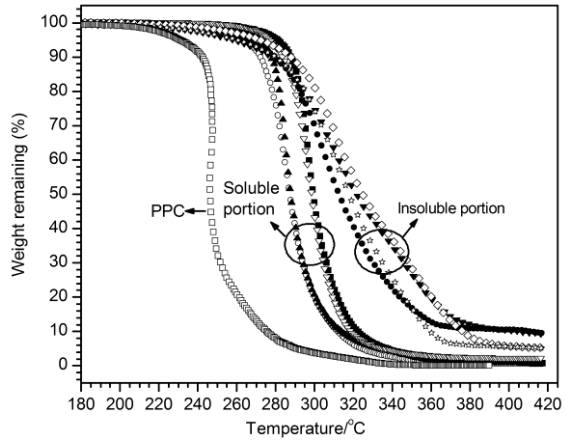

Fig.S5 TGA curves for neat PPC (open square), the soluble portion of PIPPCNs1 (open circle), PIPPCNs2 (solid uptriangle), PIPPCNs3 (open downtriangle) and PIPPCNs4 (solid square) respectively and the insoluble portion of PIPPCNs1 (solid circle), PIPPCNs2 (open star), PIPPCNs3 (solid downtriangle) and PIPPCNs4 (open diamond) respectively.