Experimental Section

Carbon dioxide with a purity of 99.99% was provided from commercial source. Azobisisobutyronitrile (AIBN) was purchased from Shanghai Chemical Reagent Company. Propylene oxide, styrene oxide, allyl glycidyl ether, ethylene dimethacrylate (98%) and 4-vinylbenzyl chloride were brought from Aladdin Reagent Co.. Other reagents, such as epichlorohydrin (ECH), acetone, THF, methanol, diethyl ether and triphenylphosphorus were A.R. grade. All the reagents above were used as received.

Phosphorous ionic liquid, 4-vinylbenzyltriphenyl phosphorous chloride was prepared as follows: 4-vinyl benzyl chloride (8.4 g, 55 mmol), triphenylphosphorus (14.9 g, 57 mmol) and acetone (50 mL) were introduced into a dried flask with a magnetic stirrer. The mixture was stirred at 45 °C under N₂ for 50 h. Then, PIL monomer was obtained by filtration and washed with acetone. The solid was dried overnight under vacuum at room temperature to give a white power (Yield: 85.0%). The structure of PIL was characterized by ¹H and ¹³C NMR (Bruker 400 MHz NMR spectrometer) using D₂O as solvent (see Figure S1 and S2 in Supporting Information).

Cross-linked polymeric nanoparticles (CLPN) were prepared by conventional radical copolymerization of PIL and ethylene dimethacrylate (EDMA). A typical synthetic procedure was as follows: EDMA (1 g, 5 mmol), PIL (1.037 g, 2.5 mmol) and AIBN (0.02 g, 0.12 mmol) were
dissolved in methanol (100 mL), and the mixture was stirred at 70 °C for 48 h. Then, the solution was poured into acetone; the products were precipitated and washed with THF and distilled water, respectively. The products were dried under vacuum at 70 °C for 12 h. (Yield: 76.0%) The products were characterized by solid state $^{13}$C NMR (Varian Infinity Plus 300WB, USA) as shown in Figure S3 and thermogravimetric analysis (TG-DTA 2000S, Mac Sciences Co. Ltd., Yokohama, Japan) at a heating rate of 10 °C min$^{-1}$. The X-ray diffraction analysis was recorded on a Philips X’Pert using Cu Kα radiation at 40 kV. The morphology of the product was observed by scanning electron microscope (JSM 6700F, Japan), transmission electron microscope (Philips CM120) and atom force microscope (Nanoscope III microscope). All the samples were prepared according to the standard methods. The dynamic light scattering (DLS) measurements were performed at 25 °C and at a scattering angle of 90° on a commercial laser light scattering (ALV/SP-125) equipped with an ALV-5000 multi-τ digital time correlator and ADLAS DPY425 solid-state laser (output power=22 mW at $\lambda$=632.8 nm). The content of P element was determined by atom absorbance spectrograph using a PerkinElmer optima 4300 DV as emission spectrometer (USA). Zeta potential of cross-linked polymeric nanoparticles were measured by Malvern Zetasizer Nano ZS90 (Malvern instruments Ltd., UK). Each sample was analyzed in triplicate, and the zeta potential values were calculated according to Smolochowski equation. The surface charge density was calculated according to the equation: $\zeta = \sigma \varepsilon / r$, in which $\sigma$ and $\varepsilon$ were the surface charge density and dielectric constant, $r$ was the radius of NPs measured by DLS. X-ray photoelectron spectra (XPS) were taken with a ESCALAB 210 instrument. The reported values of the binding energies are relative to C 1s taken as 285.0 eV. The excitation source was the nonmonochromatic Kα radiation of a magnesium anode (1253.6 eV) and the X-ray gun was operated at 300 W power. FTIR were measured on a DigiLab FTS 3000 IR-spectrometer.
The cycloaddition reactions were carried out in a 100 mL stainless steel reactor with magnetic stirrer and automatic temperature control system. After appropriate amounts of ECH and catalyst were charged into, the reactor was heated to desired temperature. Then CO₂ was introduced into and the pressure was kept constantly during the reaction. After the proper reaction time, the reactor was cooled to 0 °C by using iced water. Then CO₂ was released through a cold trap with N,N-dimethylformamide to capture the reactants and products entrained by CO₂. The mixture was filtrated after the catalyst was precipitated and the resulting filtrate together with the absorbant was analyzed by GC (GC2010AF). The retention time of the products were compared with available authentic standards. To reduce the loss of catalyst, the mixture after the cycloaddition reaction was centrifugated (4000 rmin⁻¹) before filtration. In the recyclability of the CLPN catalyst, several parallel experiments in the first run were conducted to provide enough catalysts for the next run. The cyclic carbonates were analyzed at room temperature on a Bruker 400 MHz NMR spectrometer using CDCl₃ as solvent (Figure S11-S14 in the Supporting Information).

Figure S1. ¹H NMR(400MHz, D₂O) spectra of the phosphonium ionic liquids
Figure S2. $^{13}$C NMR(400MHz, D$_2$O) spectra of the phosphonium ionic liquids

Figure S3 Solid state $^{13}$C NMR of the cross-linked polymeric nanoparticles (entry 2 in Table 1)

Figure S4. Digital photo of cross-linked polymer solution with different molar ratio of EGMA to PIL
Figure S5 XPS spectra of cross-linked polymeric particles with the molar ratio of EDMA and PIL of 1:1 and 2:1 and homopolymers of cross-linker and PIL

Figure S6 TGA curve of the cross-linked polymeric nanoparticles (entry 2 in Table 2)

Figure S7 XRD curve of the cross-linked polymeric nanoparticles (entry 2 in Table 2)
Figure S8 AFM image of the cross-linked polymeric nanoparticles (entry 2 in Table 2)

Figure S9 FTIR spectra of the catalysts (before and after use) and cyclic carbonate

Figure S10 TGA curves of the nanocatalyst before use and after use
Figure S14