Depolymerization of polycarbonate with catalyst in hot compressed water in fused silica capillary and autoclave reactors

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Experimental section

The phase changes of polycarbonate (PC) in water with or without catalyst during heating, reaction and cooling were observed under a microscope and recorded continuously on a computer through a digital camera in FSCR. Fig. S1 shows the photograph of FSCR containing PC and water with or without catalyst.

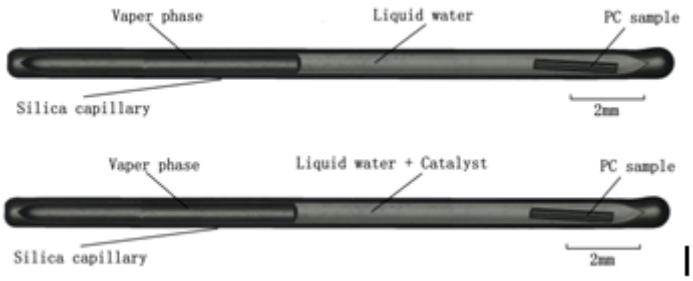

Fig. S1 Photograph of fused silica capillary reactor containing PC and water with or without catalyst.

Figure S2 is a photograph of the INSTEC (INS0908051) heating–cooling stage. An INSTEC heating–cooling stage including an STC200 temperature controller and a SN2-SYS liquid nitrogen cooling system was used to control the FSCR sample temperatures. The sample holder of this stage has a sample slot (40 mm × 1 mm × 2.5 mm) located at the middle of a silver plate (43 mm × 16 mm × 2.5 mm). A thin silica-glass plate was mounted at the bottom part of the slot and an FSCR was placed in the slot on

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top of the glass plate. The sample holder, together with the FSCR sample, was then inserted into the sample chamber of the stage, which has a 60 mm × 40 mm window.

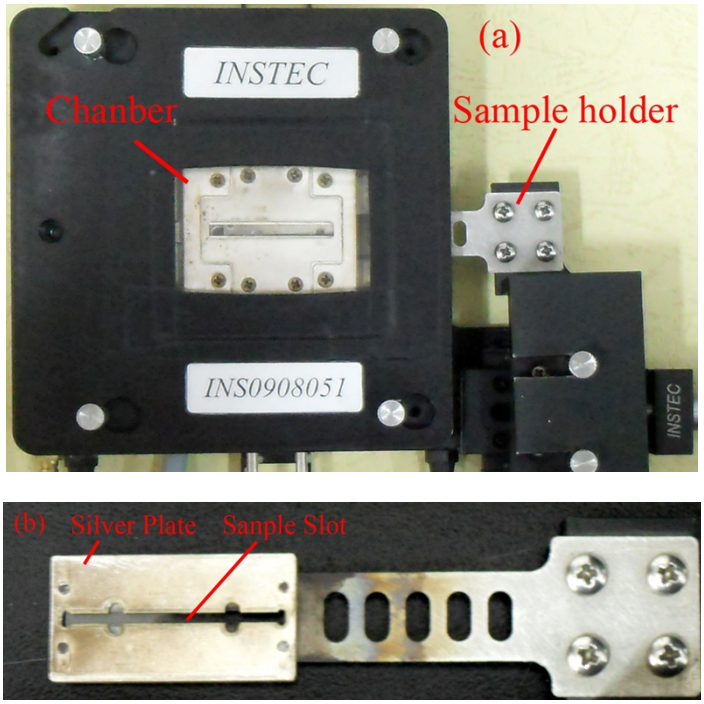
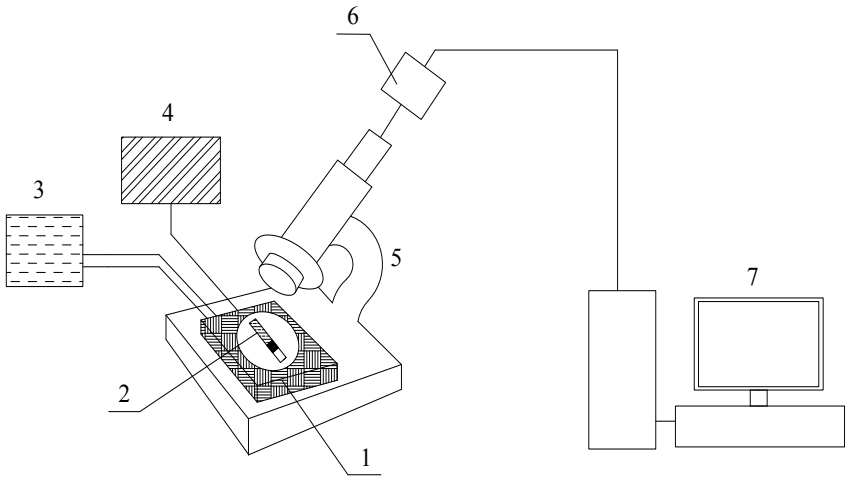


Fig. S2. Photograph of the INSTEC heating–cooling stage.
(a) INSTEC heating–cooling stage with a chamber area of 60 mm × 40 mm, showing the whole silver plate of the sample holder. (b) Sample holder in the INSTEC heating–cooling stage with a slot (40 mm × 1 mm × 2.5 mm) at the center of a silver plate (43 mm × 16 mm × 2.5 mm). A fused-silica capillary reactor up to 3 cm long can be placed in this slot.

Fig. S3 shows diagram of the experimental flow in FSCR experiment.



1-heating-cooling stage 2-FSCR 3-pump 4-temperature monitor 5- polarizing microscope 6- digital Camera 7-computer
Fig. S3 Schematic diagram of the experimental flow

The gaseous product of depolymerization of PC is CO_2, and we can estimated the depolymerization process of PC by monitoring the CO_2 peak area in vapor phase in the FSCR by Raman spectra. And Raman spectra were obtained using a JY/Horiba LabRam HR 800 system (Horiba Jobin Yvon,

Villeneuve d'Ascq, France) equipped with a 531.95 nm (frequency doubled Nd: YAG, 50 mW) laser excitation, a ×10 Olympus (Tokyo, Japan) objective with 0.25 numerical aperture, and an 1800-grooves/mm grating with a spectral resolution of 1 cm^{-1}. The CO_2 spectra were collected in the range 1200–1500^{-1} for qualitative and quantitative analysis.

The reaction of PC in an FSCR was carried out in hot-air oven. The self-made hot-air oven setup is shown in Figure S4. The apparatus includes an FSCR, oven, digital temperature indicators, and temperature controller for the oven.

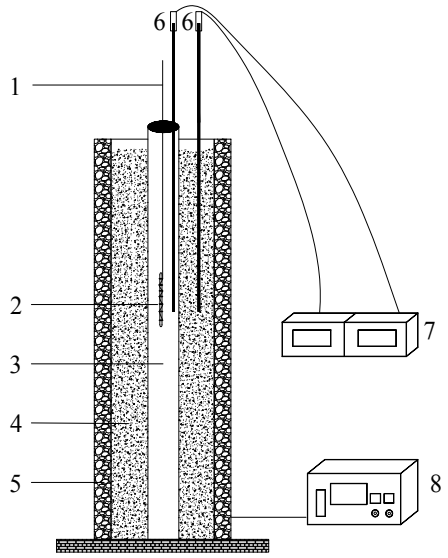
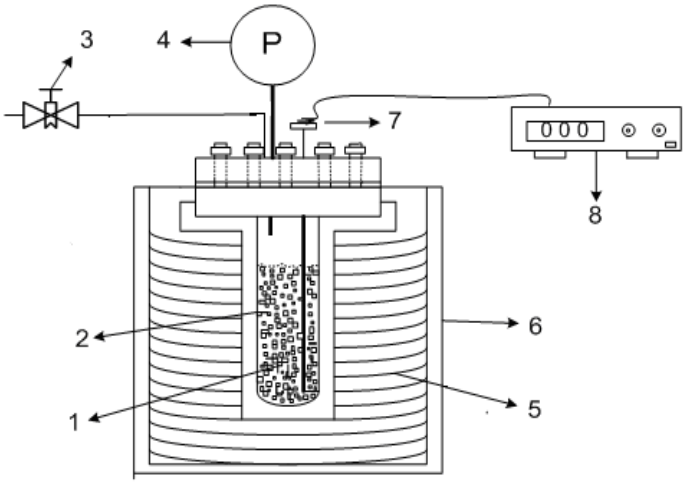


Fig. S4. Schematic diagram of the experimental setup: 1. fused-silica capillary reactor holder; 2. fused-silica capillary reactor; 3. fluidized bed (with isothermal region of length about 6 cm); 4. quartz sand; 5. oven; 6. K-type thermocouples; 7. digital temperature indicators; 8. temperature controller for the oven.

The depolymerization of PC in hot compressed water was carried out in a stainless-steel batch-type autoclave reactor (50 mL). PC, water and catalyst were loaded into the autoclave in a typical run. The autoclave was heated by an electric heater and the reaction temperature was controlled by controller with a K-type thermocouple. Fig.S5 shows diagram of the experimental flow in autoclave.



1. autoclave 2. reactant 3. valve 4. pressure gauge 5. resistance wire 6. electic heater 7. K-type thermocouple 8. temperature controller

Fig. S5 Schematic diagram of the experimental flow in autoclave

Analysis of products in liquid phase

The liquid product of PC depolymerization were analyzed by GC and GC-MS. The comparison of mass spectrum of standards taken from MS library and that of liquid products is shown in Fig. S6-S9. The liquid products were identified as phenol, p-Tert-butylphenol, p-Isopropenylphenol, and Bisphenol A, respectively.

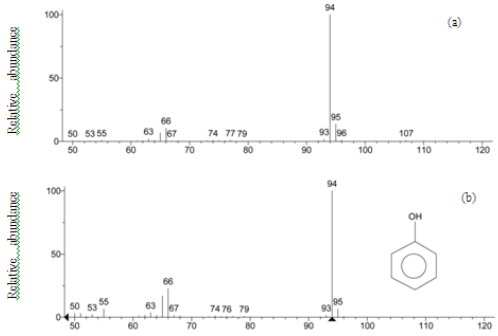


Fig. S6 Mass spectra plot of phenol in liquid products (a) and phenol (b) from MS library.

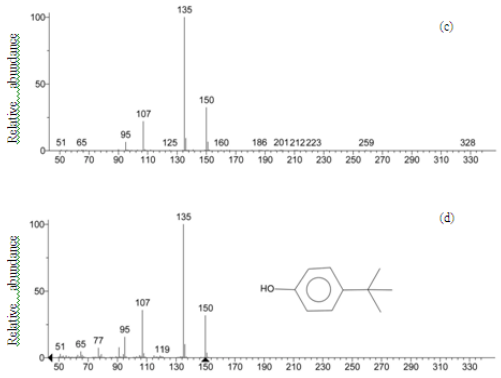


Fig. S7 Mass spectra plot of phenol in liquid products (c) and p-tert-butylphenol (d) from MS library.

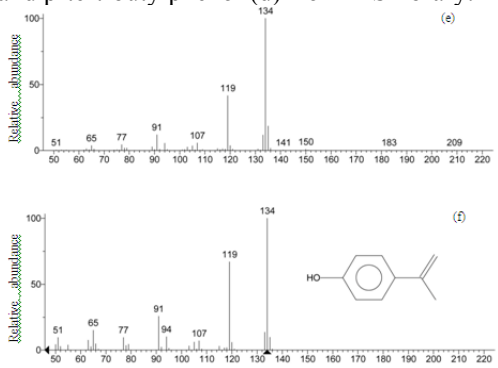


Fig. S8 Mass spectra plot of p-isopropenylphenol in liquid products (e) and p-isopropenylphenol (f) from MS library

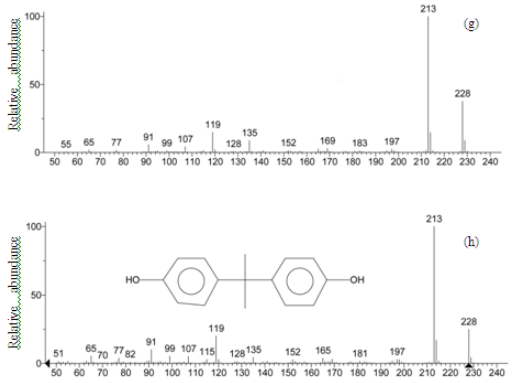


Fig. S9 Mass spectra plot of bisphenol A in liquid products (g) and bisphenol A (h) from MS library.

Comparison of depolymerization reaction with or without catalyst

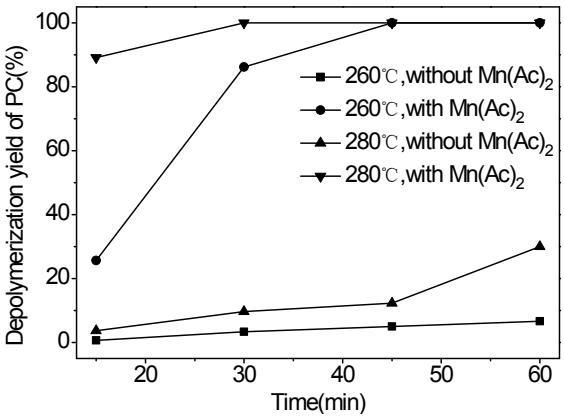


Fig. S10 Comparison of depolymerization yield of PC with or without catalyst

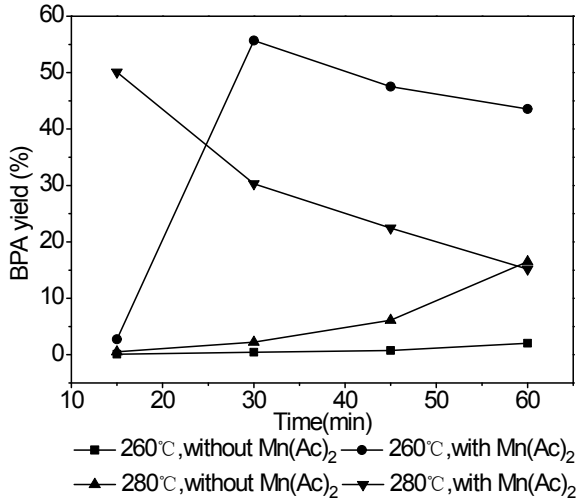


Fig. S11 Comparison of BPA yield with or without catalyst

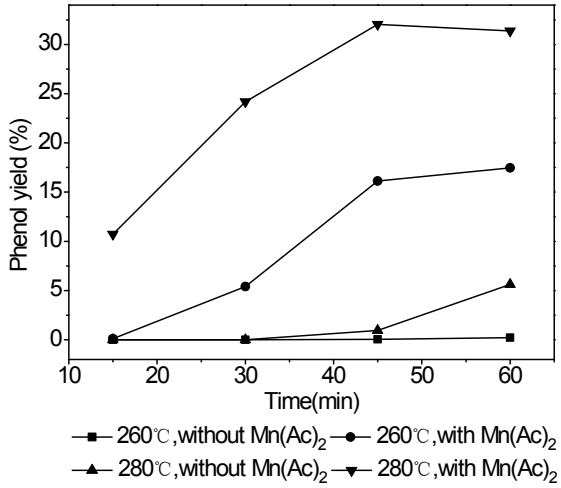


Fig. S12 Comparison of phenol yield with or without catalyst

From Fig.S10-12, we can know that the effect of $Mn(AC)_2$ catalyst for PC depolymerization was obvious. At 260℃and 280℃, the highest depolymerization yield of PC were 6.67% and 30% without catalyst, respectively. But the depolymerization yield of PC were both reached 100% at 260℃and 280℃ with the $Mn(AC)_2$ catalyst . And the yield of phenol and BPA were also increased when catalyst added. The use of Mn(AC)2 catalyst greatly reduced the reaction time and temperature for PC completely depolymerization.