

## Supporting Information

### Hydrolysis of Polycarbonate in Sub-critical Water in Fused Silica Capillary Reactor with in Situ Raman Spectroscopy

Zhiyan Pan\*, I-Ming Chou, Robert C. Burruss

*Department of Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, P.R. China*

*National Center, U.S. Geological Survey, Reston, VA 20192, USA*

#### Experimental section

The fused silica capillary reactor used in this study was constructed from capillary tubing OD660 $\mu\text{m}$  /ID300 $\mu\text{m}$ , purchased from Polymicro Technology, LLC ([www.polymicro.com](http://www.polymicro.com)). For optical observation and spectroscopic analysis, the protective polyimide layer coated on the capillary tubing was removed by burning in a hydrogen flame before the samples were loaded.

The amount of Si dissolved in the aqueous phase at the experimental conditions is less than 2000 ppm (see Fig. 1 of R. O. Fournier and J. J. Rowe, *Amer. Mineral.*, 1977, 62, 1052), and has negligible effect on our experimental system.

Polycarbonate samples, purchased from Sinopharm Chemical Reagent Co., Ltd., having glass transition temperature about 423 K (with molecular weight of Mn 8439/Mw 16667), were first loaded in the tube in solid forms, about 6-cm long having one end sealed, and then distilled de-ionized water was loaded in the tube and centrifuged to the closed end. After centrifugation, the open end of the tube was connected to a vacuum line and sealed by fusion in a hydrogen flame. For micro-thermometric measurements in a USGS-type heating-cooling stage, capillary reactors less than 25 mm in length were prepared.

Raman spectra were acquired with a JY/Horiba Lab Ram HR Raman system, using 532.06 nm (frequency doubled Nd : YAG) laser excitation, a 40x Olympus objective with 0.25 numerical aperture, a 600-groove/mm grating with a spectral resolution of about 2  $\text{cm}^{-1}$ . Laser power at the back of the

objective was ~18 mW laser light was focused on the vapor, aqueous solution or solid sample during measurement. Spectra were collected in one to three spectrographic windows (50~4200  $\text{cm}^{-1}$ ) for various lengths of time (1~120 sec) with two to five accumulations per spectrum.

A schematic diagram for the sample loading system and the formation of FSCR is shown in Figure S1.

### **In situ Raman spectra of solid or liquid PC in water**

In situ Raman spectra of solid or liquid PC at various temperatures were shown in Fig. S2, indicating that PC was stable up to at least 539 K, where no  $\text{CO}_2$  was detected in the coexisting vapor phase. However, at 553 K and about 6.4 MPa, in situ Raman analysis of the vapor phase showed the presence of  $\text{CO}_2$  (Fig. 3), which was produced by the hydrolysis of PC. Note that in Fig. S2, Raman signals for PC in water at 553 K were very weak due to short acquisition time necessary for a high-fluorescence sample.

### **Analysis of products in liquid phase**

Quenched products extracted from the FSCR in acetone solution were analyzed by GC and GC-MS (HP6890 GC/MS). The chromatographic conditions are as follows: column: HP-5MS, 30m $\times$ 250 $\mu\text{m}$ , 0.25 $\mu\text{m}$  film, carrier gas: helium with a flow rate of 1.0  $\text{ml min}^{-1}$ , oven temperature was increased from 413 to 553 K at 20  $\text{K min}^{-1}$ . EI: 70eV. Scan: 35-350amu. Figure S3 shows the comparison of mass spectrum of BPA taken from MS library and that of liquid products. Figure S4 shows GC chromatogram of product in the liquid phase, which was identical to that taken from reagent BPA.

## Figures

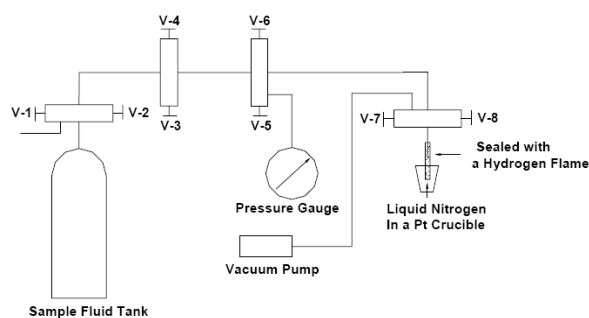


Figure S1. A schematic diagram of the vacuum and sample loading system [11] (V-1 to V-8: high-pressure valves).

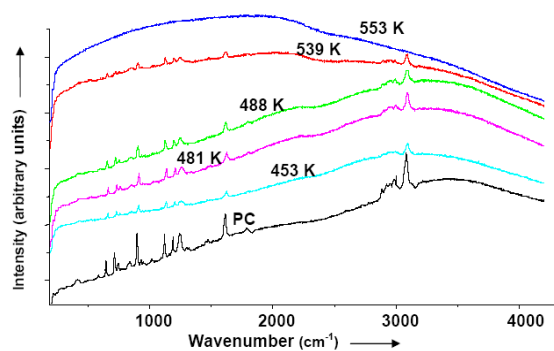


Figure S2. Raman spectra of PC in water at different temperatures

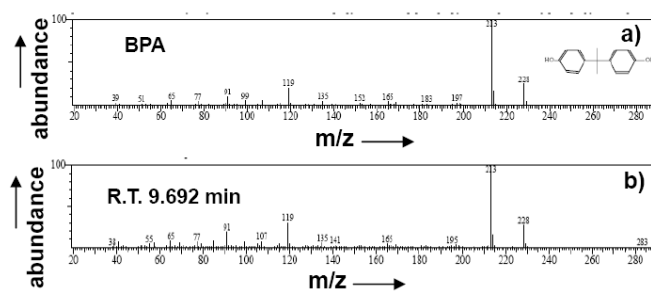


Figure S3. Comparison of mass spectra of BPA from a) MS library and b) liquid products

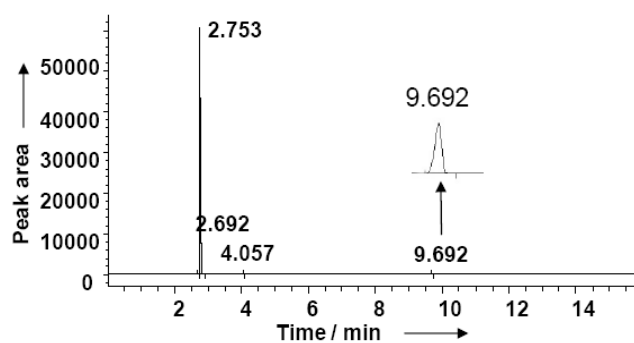


Figure S4. Gas chromatogram of liquid products, Signal at the retention time of 9.692 was from BPA, and all other signals were from acetone and its contaminants.