Hydrolysis of polycarbonate in sub-critical water in fused silica capillary reactor with *in situ* Raman spectroscopy†

Zhiyan Pan,*[a] I-Ming Chou[b] and Robert C. Burruss[b]

The advantages of using fused silica capillary reactor (FSCR) instead of conventional autoclave for studying chemical reactions at elevated pressure and temperature conditions were demonstrated in this study, including the allowance for visual observation under a microscope and *in situ* Raman spectroscopic characterization of polycarbonate and coexisting phases during hydrolysis in subcritical water.

The increasing consciousness of environmental protection in recent years has greatly enhanced our attention to recycling of polymer wastes.[1] Material recycling, thermal recycling, and chemical recycling are the three main methods for recycling of polymer wastes. Chemical recycling is the most desirable process by which some polymers are converted to their monomers.[2] Polymers with ether, ester, or acid amide linkages are easily depolymerized to their monomers by solvolysis or hydrolysis with or without catalyst in sub- or supercritical fluids (SCFs).

Near or over their critical points, fluids have a strong dissolving power, similar to that of liquid, but, in contrast to liquid, SCFs are far more compressible and have better transmission performance.[3] Therefore, SCFs have been applied to a variety of reactions including homogeneous and heterogeneous.[4]

Bis-phenol A poly(carbonate) (PC) is applied widely in the electronics industry, automobile industry, and other fields. The depolymerization of PC in sub-critical or SCFs has been studied by many researchers in order to obtain monomer (bisphenol A, BPA) by using various solvents, including water,[5] ethanol,[6] benzene,[7] toluene,[8] methanol,[9] methanol with co-solvent.[10] In addition to BPA, phenol, *p*-isopropenylphenol and *p*-isopropylphenol were also produced in the depolymerization.

All previous studies were performed in autoclaves with large volume, and samples were analyzed after quench. In most cases, the products of hydrolysis in water were extracted with organic solvents for GC and GC/MS analyses. The drawbacks in the autoclave studies include: (1) it was not possible to observe phase changes during reactions, and (2) the progress of reactions could not be monitored. To solve these problems, we developed a new method for studying hydrolysis of PC in sub-critical water. A fused silica capillary reactor, instead of an optical fiber capillary flow cell,[11] was used together with *in situ* Raman spectroscopy for the analysis of liquid, solid, and vapor phases at various pressure–temperature conditions. This paper describes our new method, gives results based on visual observations of phase changes and *in situ* Raman analyses of reactants and products during hydrolysis of PC in water in FSCR, and shows the advantages of this method over the conventional autoclave method.

The FSCR containing PC and water (Fig. 1) was inserted into the sample chamber of a USGS-type heating–cooling stage,[12] and hydrolysis of PC in sub-critical water was investigated under different temperature, reactant ratio, and reaction time conditions. Under the microscope, phase changes during the reaction were observed and images were recorded continuously in a digital video disc (DVD) recorder (Fig. 2). Raman spectroscopy was used to analyze the reactants or products, including the gas, liquid, and solid phases. At 553 K and about 6.4 MPa, *in situ* Raman analysis of the vapor phase showed the presence of CO_2 (Fig. 3), which was produced by the hydrolysis of PC. Also, temperature was found to be the key factor for the hydrolysis of PC, as indicated by the fast reaction we observed at 573 K in different runs.
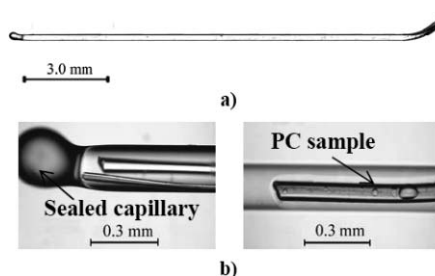

Fig. 1 Photomicrographs of fused silica capillary reactor (300 µm ID, 660 µm OD, and ~25 mm long) containing PC and water (a), and magnification of the left end of the reactor showing the seal and solid PC sample (b).

Fig. 2(a) shows phase behavior changes of PC in water during the heating process. PC swelled at 373 K, intenerated at 423 K, and remained in solid form below this temperature. There are three phases (i.e., PC in solid form, aqueous fluid, and vapour phase) in FSCR below 423 K. PC melted at 473 K and formed liquid spherules of PC, which coexist with aqueous fluid and vapour phase. Note that the liquid PC does not dissolve totally in sub-critical water, and there are still three phases after the melting of the solid PC. Fig. S2 (ESI †) shows *in situ* Raman spectra of solid or liquid PC at various temperatures. The results

[a]*Department of Environmental Engineering, Zhejiang University of Technology, Hangzhou, 310032, P.R. China. E-mail: panzhiyan@zjut.edu.cn; Fax: +86 571-88320061; Tel: +86 571-88320061*
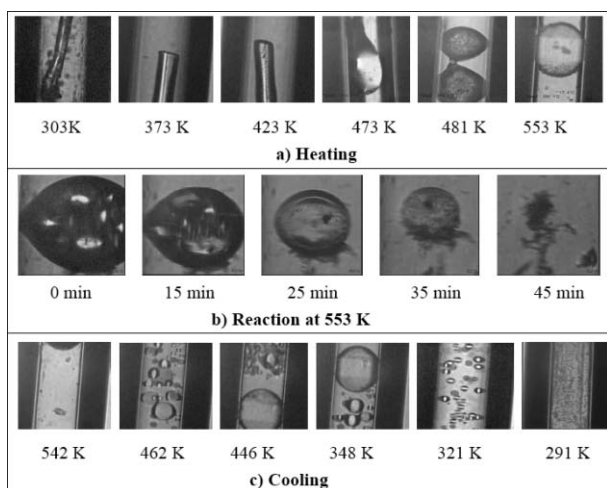[b]*U.S. Geological Survey, Reston, VA 20192, USA*

Fig. 2 Photomicrographs of PC in water in FSCR during heating process (a), reaction at 553 K at different time (b), and cooling process (c). Note that above 473 K shown in (a), PC was in liquid form, which shrank during reaction at 553 K, as shown in (b).
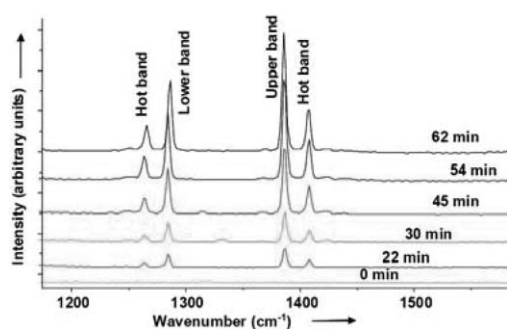

Fig. 3 Raman spectra of CO_2 produced by the hydrolysis of PC in sub-critical water at 553 K and at different reaction times. The spectra were collected under similar conditions, and the increase of CO_2 signals (lower and upper bands and hot bands) indicates the progress of hydrolysis.

show that PC is stable up to at least 539 K, where no CO_2 was detected in the coexisting vapour phase.

As shown in Fig. 2(b), the liquid PC spherule shrank and hydrolyzed gradually at 553 K. A heterogeneous liquid–liquid phase reaction was found and BPA and CO_2 were generated continually. *in situ* Raman analysis of the vapour phase showed that the increase of CO_2 signals (Fig. 3) indicates the progress of hydrolysis. At the end of reaction, the liquid PC phase disappeared and only two phases (i.e., liquid phase and vapour phase) were left.

During the cooling process, phase separation occurred at 462 K and suspending oily spheres were observed as shown in Fig. 2(c). The amount of spheres increased substantially at 442 K, and these spheres became smaller below 300 K.

The hydrolysis yield can be estimated by the amount of CO_2 being produced. To show the effects of reaction time on PC hydrolysis, *in situ* Raman spectra of the vapor phase were collected at different reaction times (up to 62 min) at 553 K in the FSCR, and the results were shown in Fig. 3. Note that the amount of CO_2 dissolved in the aqueous phase at the experimental conditions is less than 0.6 mole kg^{-1},[13] and can

be neglected. Informative spectra of the aqueous phase were not available because of high florescence of the sample.

Analyses of quenched products by both GC and GC-MS indicated that the only product in the liquid phase was BPA (see ESI†). Also, Raman spectra of the gas phase (Fig. 3) indicated that CO_2 was the only gas product in the vapor phase. Thus, in water at 553 K, PC was hydrolyzed to bisphenol A and CO_2 according to Scheme 1.
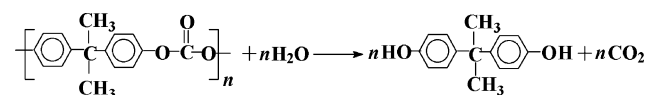
Scheme 1 Reaction equation of PC hydrolysis in sub-critical water.

It has been known that CO_2 pressure (or density) is related to its Raman peak area by a linear relation in a calibrated Raman spectrometer.[14] As shown in Fig. 4, the peak area increases with the reaction time at 553 K, and it levels off (with peak area = S^*) at about 46 min, indicating the completion of PC hydrolysis. Therefore, the hydrolysis yield at time t, having a peak area of S, can be calculated from:

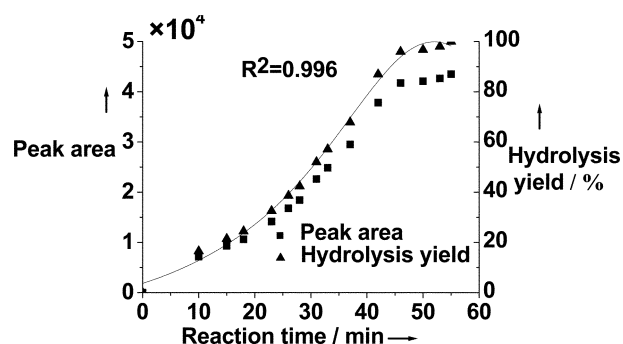$$\text{Hydrolysis yield (\%)} = \frac{S}{S^*} \times 100$$

Fig. 4 Relationships of Raman peak area of CO_2 (squares) and hydrolysis yield (triangles) *vs* reaction time at 553 K.

Raman spectroscopic analyses did not show the presence of methane, ethane, or propane in the vapour phase, indicating that no random chain scission occurred in hydrolysis at 553 K. On the other hand, the presence of CO_2 in the vapour phase indicates the chain scission at the ester bond. As shown in Fig. 4, during hydrolysis at 553 K, the slopes of the hydrolysis yield curve increase with the reaction time, indicating the reaction rates increase. In the hydrolysis, the polymer chain starts to break up into shorter chains, which were more soluble and reacted faster in the near-critical water than the long chains, thus the reaction rate increased as the reaction proceeds. On the other hand, it is also possible that the hydrolysis of PC in water is a self-catalytic hydrolysis by carbonic acid (H_2CO_3) formed from CO_2 dissolved in water at the initial period. As the reaction progresses, the concentration of carbonic acid increases and, therefore, the concentration of hydrogen ions ([H^+]) increases. The more hydrogen ions being produced, the faster the hydrolysis rate of the ester becomes due to acid catalysis. The proposed mechanism can be shown in Scheme 2.
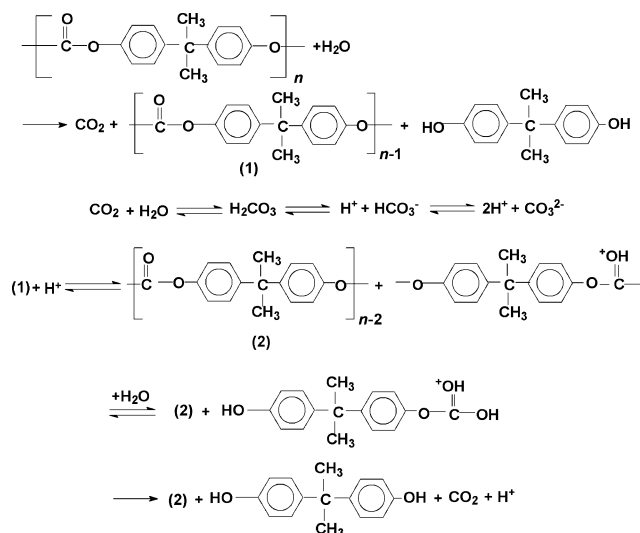
Scheme 2 Mechanism of PC hydrolysis in sub-critical water.

In summary, a new method for studying hydrolysis of PC in sub-critical water in FSCR was developed. *in situ* Raman spectroscopy was used to analyze the products qualitatively and quantitatively. During hydrolysis of PC, the phase behavior was observed under a microscope and the images were recorded in a DVD recorder continuously. Quenched products extracted from the FSCR were also analyzed by GC and GC-MS.

Our results showed that (1) during the hydrolysis of PC in sub-critical water at 553 K, BPA was the only product detected in the liquid phase, (2) CO_2 was the only gas product, (3) the hydrolysis was a heterogeneous (liquid–liquid phase) reaction, and appeared to be a self-catalytic hydrolysis or promoted by the breakup of long-chain polymer in the near-critical water, and (4) the hydrolysis was influenced by temperature intensively. The new method has great advantages for studying chemical reactions in fluids at sub- or super-critical conditions, because (1) by using optically transparent capillary, the phase behavior can be observed and recorded, and reaction progress can be measured by Raman spectroscopy *in situ*; (2) due to the small size of reactor, it minimizes the resistances in mass transfer and heat transfer, such that the observed kinetics approaches to the intrinsic one, and (3) the volume of FSCR is much smaller than that of the autoclave (millilitre *vs* microlitre), so that it is safer and more environmentally friendly due to the smaller amount of material needed in the FSCR.

Acknowledgements

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