

# A Comparative Study of Polystyrene Decomposition in Supercritical Water and Air Environments Using Diamond Anvil Cell

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**ABSTRACT:** Polystyrene (PS) decomposition in supercritical water (SCW) and in air was studied with the diamond anvil cell (DAC) technique coupled with microscopy and FTIR. Apparent concentrations were calculated by using digital imaging analysis. When PS + water systems (11.8–22.6 wt % PS) were rapidly heated at a rate of 2.3°C/s, the PS particle melted at 279.8–320.2°C. After formation of a globule at 409.3–452.5°C, the globule started to dissolve in color to yellow at 496.1°C. At 570.3°C and 742.5 MPa, solubility reached the maximum of 91.5 wt % (11.8 wt % PS). The soluble material was a styrenelike liquid, which was identified by IR after cooling. In isothermal runs at 400 and 450°C, two heterogeneous liquid phases consisting of water and decomposed PS were found. Styrenelike liquid products were identified after the reactions. PS decomposition stages in air consisted of melting, gas generation, liquid ring configuration, and finally yellow volatile products formation at 583.2°C. The results show conclusively that PS can be dissolved in SCW above 496.1°C and homogenous reaction is likely to occur above 570.3°C. Reactions in SCW at 400 and 450°C take place in heterogeneous liquid phases, while in the PS + air system, a formed liquid ring undergoes depolymerization. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3565–3577, 2001

**Key words:** polystyrene; supercritical water; diamond anvil cell; thermal decomposition; depolymerization

## INTRODUCTION

Recovery of styrene monomer from polystyrene (PS) via pyrolysis was studied extensively. The techniques included pyrolysis in a fluidized-bed reactor,<sup>1,2</sup> in a batch reactor,<sup>3–5</sup> in steam,<sup>6</sup> in vacuum,<sup>7</sup> and in the presence of a catalyst.<sup>8</sup> A method based on supercritical water (SCW) is a relatively new and effective technique used to recycle or decompose polymers.<sup>9–16</sup> Water near its

supercritical point (374°C, 22.1 MPa) behaves like a perfect organic solvent with acidlike properties. Thus, it has potential as an extractive agent and a medium for chemical reaction processes. Bertini et al.<sup>17</sup> found that the presence of water increases the yield of volatile products with a higher monomer selectivity from PS in subcritical water (300–320°C, 1–24 h). It has also been reported that 97 wt % liquid without residue was obtained from PS in SCW at 400°C, 0.5 g/cm<sup>3</sup> water density, and 10-min residence time.<sup>10</sup> However, only 92 wt % liquid with 7 wt % solid was converted under pyrolytic conditions in a nitrogen atmosphere at 401°C and 21 min.<sup>3</sup>

Even though an effective conversion of solid PS to liquid was achieved, little is known about the phase changes during the PS depolymerization

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process in SCW. In fact, it is not known whether the reactions occur in a homogeneous or a heterogeneous environment. Recently, Fang et al.,<sup>18,19</sup> Smith et al.,<sup>20</sup> Fang and Kozinski,<sup>21</sup> and Arai and Adschiri<sup>22</sup> applied a diamond anvil cell (DAC) technique to the study of phase behavior and reaction phenomenon of polymer + water systems. In their work, a homogenous phase was found for condensation polymers (such as polyethylene terephthalate and nylon) and cellulose in subcritical water, whereas polyethylene (paraffin-like polymer) could dissolve in SCW only after it decomposed above 565°C.

In this work, a hydrothermal DAC technique coupled with digital image analysis and FTIR spectroscopy was applied to study the phase changes and reaction of PS in supercritical water and in air at temperatures up to 583.2°C and pressures up to 742.5 MPa.

## EXPERIMENTAL

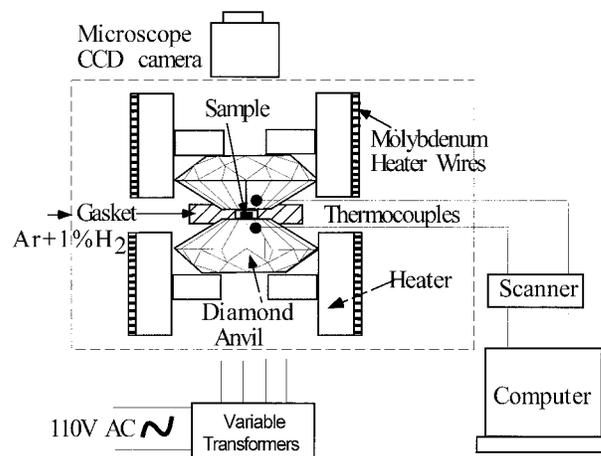
### Materials

The PS powder used was from Aldrich (Milwaukee, WI). The PS had a density of 1047 kg/m<sup>3</sup>; melting point ( $T_m$ ) of 237.5°C; glass point ( $T_g$ ) of 100°C; and average molecular weight ( $M_w$ ,  $C_w$ , GPC) of 280,000.

### Hydrothermal DAC

A hydrothermal DAC developed by Bassett et al.<sup>23,24</sup> was used for phase-change observations of a PS + H<sub>2</sub>O system up to supercritical regions or visual observations of a PS + air system. The experimental setup, in which tests can be conducted in fluids at pressures up to 2.5 GPa and temperatures up to 1200°C, is shown in Figure 1. Pressure is produced by two opposing diamond anvils inside a 50-nL chamber hole (ID = 508 μm, thickness = 250 μm) made of an inconel gasket. After being pressed by the two diamond anvils, the actual chamber volume decreases to 30–40 nL, corresponding to the chamber height of 150–200 μm. If a 50 vol % sample is loaded, the quantities of the sample and water are 15 and 20 nL, respectively. The pressure can be adjusted by turning screw nuts of the DAC. A PS sample was loaded by placing a droplet of water onto the gasket hole with a microsyringe.

The DAC chamber was heated by two individual microheaters that transfer heat to the dia-



**Figure 1** Bassett-type DAC and experimental setup.

mond anvils. Argon gas with 1% H<sub>2</sub> was introduced into the cell to protect the diamond anvils from oxidization and to increase the cooling rates at the end of the experiment (see Fig. 1).

### Temperature

Temperature was measured by two K-type thermocouples attached to each of the diamond anvils by a ceramic cement (Fig. 1) and was recorded every 0.1 s by a data shuttle (Strawberry Tree, Model DS-12-8-TC, Sunnyvale, CA). The thermocouples were previously calibrated<sup>18</sup> by loading powder form samples contained in a gasket of reference metals tin ( $T_m = 232.00^\circ\text{C}$ ) and zinc ( $T_m = 419.58^\circ\text{C}$ ) and observing their melting points with a slow (<5°C/min) heating rate. The accuracy of the temperature measurement is estimated to be  $\pm 0.5^\circ\text{C}$  for temperatures up to 400°C, and  $\pm 1.0^\circ\text{C}$  for temperatures above 400°C. The temperature difference between the anvils was generally below 10°C. Temperatures reported are the average of the both anvils.

### Pressure

Pressure was determined from the equation of state (EOS) of water<sup>25</sup> on the basis of the negligible changes of chamber volume. The isochore chamber was confirmed through the observation of the interference fringes (chamber thickness) between anvil faces radiated by a green light ( $\lambda = 532 \text{ nm}$ ).<sup>24</sup> When the sample and water were loaded into the DAC chamber, air bubbles would appear. Heating the chamber caused the liquid to expand and the air bubbles to shrink until it disappeared, at which point the chamber was

filled with the expanded liquid at the homogenization temperature ( $T_h$ ). The pressure at this point ( $P_h$ ) was the vapor pressure along the two-phase (liquid-vapor) curve of water at  $T_h$ , and the bulk specific volume ( $v_h$ ) or density ( $\rho_h = 1/v_h$ ) of the water was that of the liquid water along the liquid-vapor curve at  $T_h$ . If heated further, pressure would increase according to the pressure-temperature path of the isochore ( $v = v_h$ ). Assuming that only water contributed to the pressure, it could be calculated knowing the temperature and  $v_h$ . In the runs in air atmosphere, pressure was calculated by the ideal gas EOS at an isochore.

For all runs, pressures only at  $T_h$  and maximum reaction temperatures were calculated. The DAC screw nuts were adjusted prior to experiments obtaining the initial pressure desired.

### Procedure

The experimental sequence was as follows. First, the hole of the gasket was centered and fixed by tape on the low anvil diamond. A PS particle and water were loaded into the gasket hole. After that, the DAC was closed. The DAC screw nuts were tightened and adjusted to obtain the proper size of the air bubbles, allowing for the achievement of the desired homogenous temperature ( $T_h$ ) or pressure ( $P_h$ ). Finally, the heaters and thermocouples were connected in preparation for heating while the samples were observed at 110 $\times$  magnification by a microscope (Olympus SZ11) and the images recorded by a Panasonic 3CCD camera (AW-E300). For pyrolytic runs, only PS without water was loaded.

The PS + H<sub>2</sub>O or PS + air system was heated for a predetermined time. The sample was subsequently rapidly cooled by cutting the power to the heaters while maintaining Ar gas flow. After the experiment was completed, the DAC was disassembled and the residues remaining on the diamond anvil faces or inside the chamber were analyzed by FTIR spectroscopy coupled with infrared microscope (Bio-Rad Excalibur FTS3000 and UMA 500 Shadow, MA). The IR analysis was conducted under reflection mode due to IR absorption by diamonds. Details of the experimental setup and procedure can be seen elsewhere.<sup>18,21</sup>

### Digital Image Analysis

Recorded images were changed to 24-bit RGB bitmap files via a video capture board and analyzed with digital imaging software (scion image, Scion

Corp., MD) to calculate the apparent concentration of the sample and to obtain phase transition rates. The areas of the sample and the chamber were determined by counting the number of pixels of the corresponding defined zone. The apparent area concentration was obtained from the sample : chamber area ratio by normalizing to water area in the chamber at room temperature ( $T_r$ ) with the densities of water at  $T_h$  ( $\rho_h$ ) and  $T_r$ . The mass concentration can be calculated by knowing the area concentration along with the PS and water densities. The solubility was defined as the difference between the initial and the instant concentration divided by the initial concentration. Because the image analysis is two-dimensional, the calculated results are semiquantitative.

## RESULTS

Experiments of PS decomposition in air atmosphere and reaction in supercritical water were conducted. Experimental conditions, visual observations, image analyses, and reaction products are summarized in Table I. Decomposition of PS in air was studied in runs 1–3. Reaction of PS in supercritical water was studied in runs 4–9. Visual observations are given in Figures 2–10. Reaction temperature profiles are illustrated in Figure 11. FTIR spectra of the residues are given in Figure 12. Digital imaging analyses are presented in Figure 13.

### Decomposition in Air (Run 1–3)

Figure 2 shows a sequence of images of the PS + air system in the closed chamber of DAC at 0.1 MPa (run 1). As the temperature was increased at a rate of 2.9°C/s [temperature profile, Fig. 11(a)], the PS particle started to melt at its melting point of 237.5°C [Fig. 2(b)]. The liquid PS started flowing to the wall of the chamber along with the appearance of a gas bubble at 397.2°C [Fig. 2(c)]. A circular liquid ring with several gas bubbles was formed at the maximum temperature and pressure of 479.8°C and 0.25 MPa, respectively [Fig. 2(d)]. The sample was rapidly cooled to room temperature at a maximum rate of –24.5°C/s. The liquid ring expanded and most of the bubbles disappeared [Fig. 2(e)]. After the DAC was opened, the waxlike liquid ring was still present on the diamond [Fig. 2(f)]. Figure 12(a) (run 1) indicates that the liquid residue [Fig. 2(f), A] was a mixture of styrene and its oligomers (mainly

Table I Experimental Summary of Conditions and Results

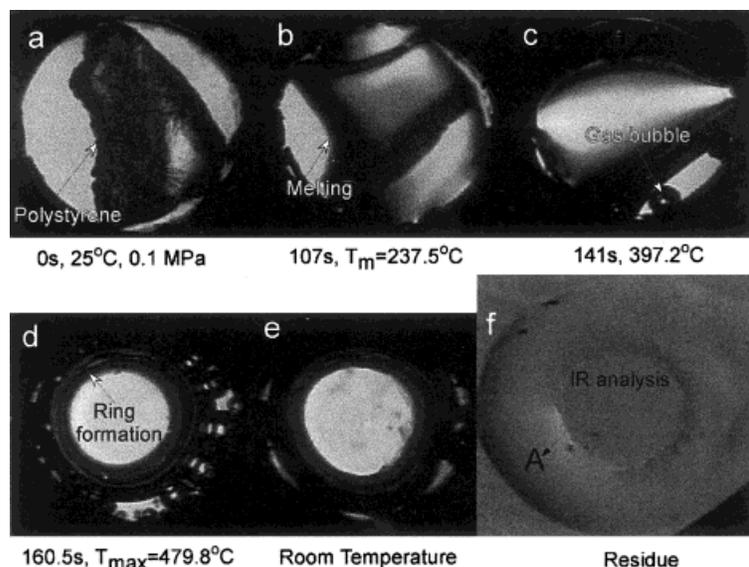
Experiments: Systems:	Decomposition in Air			Reaction in Supercritical Water					
	Run 1 PS + air	Run 2 PS + air	Run 3 PS + air	Run 4 PS + H <sub>2</sub> O	Run 5 PS + H <sub>2</sub> O	Run 6 PS + H <sub>2</sub> O	Run 7 PS + H <sub>2</sub> O	Run 8 PS + H <sub>2</sub> O	Run 9 PS + H <sub>2</sub> O
Conditions									
Max. $T$ ( $T_{\max}$ , °C)	479.8	583.2	400	464.4	570.3	400	400	450	450
Pressure at $T_h$ (MPa)	0.1 (25°C)	0.1 (25°C)	0.1 (25°C)	0.15	0.56	0.57	1.01	0.10	0.88
Density of water at $T_h$ (kg/m <sup>3</sup> )	—	—	—	950.4	912.6	910.4	886.6	958.3	892.8
Max. pressure at $T_{\max}$ (MPa)	0.25	0.29	0.23	681	742.5	435.3	374.6	681.2	476
Average heating rate (°C/s)	2.9	3	2.9	2.3	2.3	1.5	1.5	2.2	1.9
Max. heating rate (°C/s)	9.7	18.6	8.8	10.5	9.5	4.9	12.6	7.2	7.7
Max. cooling rate (°C/s)	-24.5	-30.8	-16.2	-22.9	-27.2	-16.8	-16.5	-19.7	-17.5
Run time <sup>a</sup> (s)	160.5	186.5	20 min	188	241	10 min	20 min	10 min	20 min
Visual observation									
Homogenization $T$ ( $T_h$ , °C)	—	—	—	110.9	154.8	157.1	180.5	100.2	174.7
Melting $T$ (°C)	237.5	237.5	237.5	320.2	279.8	290.7	289.3	313.7	271.7
Gas bubble $T$ (°C)	397.2	413.9	400 (0 s)	—	—	400 (2m)	400 (2m)	—	450 (1m)
Color change $T$ (°C)	—	583.2	400 (2.73 m)	—	496.1	400 (5m)	400 (5m)	450 (0s)	450 (0s)
Residue <sup>b</sup>	WL	YL	WYL	solid	WYL	WL	WYL	WL	WYL
Image analyses									
Apparent concentration									
Initial (wt, %)	—	—	—	22.6	11.8	35.3	29.4	23.3	24.0
Initial (area, %) <sup>c</sup>	60.0	64.3	50.3	27.8	12.8	51.9	39.7	29.0	30.0
Reaction products by FTIR <sup>d</sup>	D-PS	Styrene-like	Styrene-like	PS	Styrene-like	Styrene-like	Styrene-like	Styrene-like	Styrene-like

<sup>a</sup> Heating time to  $T_{\max}$  for short time runs 1–2, 4–5, or Holding time at 400 or 450°C for long time runs 3, 6–9. In long time runs, heating time (s) to 400°C is 130.5 for run 3, 255 for run 6, 251.5 for run 7. Heating time (s) to 450°C is 192 for run 8 and 229 for run 9.

<sup>b</sup> WL, white liquid; YL, yellow liquid; WYL, white and yellow liquid.

<sup>c</sup> Area ratio of PS to chamber for runs 1–3.

<sup>d</sup> D-PS, decomposed polystyrene.

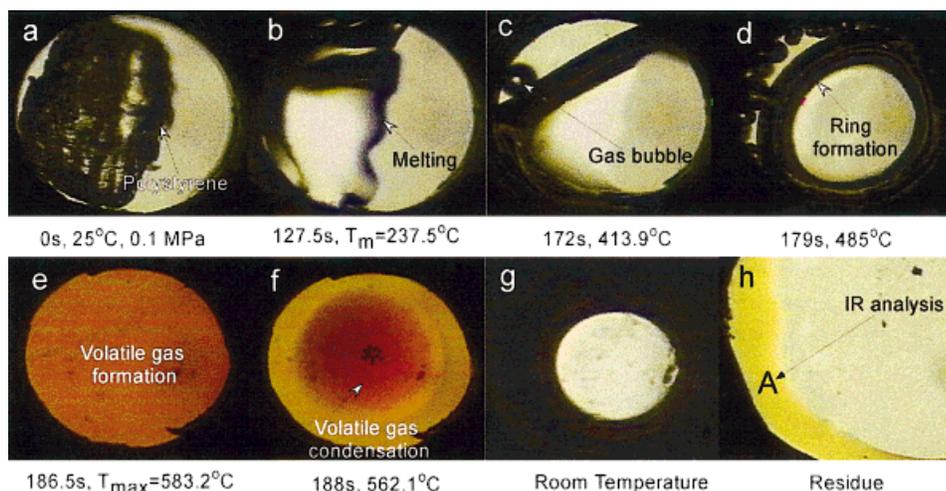


**Figure 2** Evolution of PS during heating to  $479.8^\circ\text{C}$  and 0.25 MPa in an air atmosphere at an initial pressure of 0.1 MPa. (run 1).

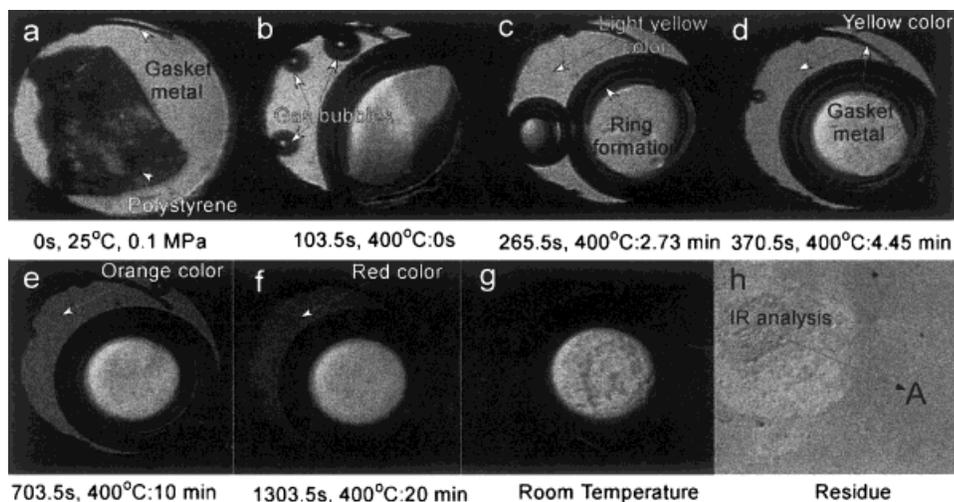
dimer and trimer); styrene C—H bands at 2858, 2933, 3028, 3061, and  $3082\text{ cm}^{-1}$ ; and several PS peaks from 200 to  $2000\text{ cm}^{-1}$  (such as at 1208 and  $1948\text{ cm}^{-1}$ ) are present as compared to the standard styrene and PS spectra. However, the liquid had stronger absorption at  $3028\text{ cm}^{-1}$  than that of styrene.

In run 2 (Fig. 3), the PS + air system was heated to the maximum temperature and pressure of  $583.2^\circ\text{C}$  and 0.29 MPa, respectively. After melting of the PS at  $237.5^\circ\text{C}$  [Fig. 3(b)] and the appearance of a gas bubble at  $413.9^\circ\text{C}$  [Fig. 3(c)],

a circular liquid ring with several gas bubbles was formed at  $485^\circ\text{C}$  [Fig. 3(d)]. The liquid ring disappeared and the chamber was filled with yellow volatile compounds at the maximum temperature of  $583.2^\circ\text{C}$  [Fig. 3(e)]. Upon cooling, the volatile products were condensed and a yellow globule formed at  $562.1^\circ\text{C}$  in the center of the chamber [Fig. 3(f)]. The liquid ring, however, was visible again at room temperature [Fig. 3(g)]. After the DAC was opened, a yellow liquidlike product had flown to the border of the diamond [Fig. 3(h)]. The IR spectrum [Fig. 12(a), run 2] of liquid A reveals



**Figure 3** Evolution of PS during heating to  $583.2^\circ\text{C}$  and 0.29 MPa in an air atmosphere at an initial pressure of 0.1 MPa. (run 2).



**Figure 4** Evolution of PS during heating to 400°C and 0.23 MPa for 20 min in an air atmosphere at an initial pressure of 0.1 MPa. (run 3).

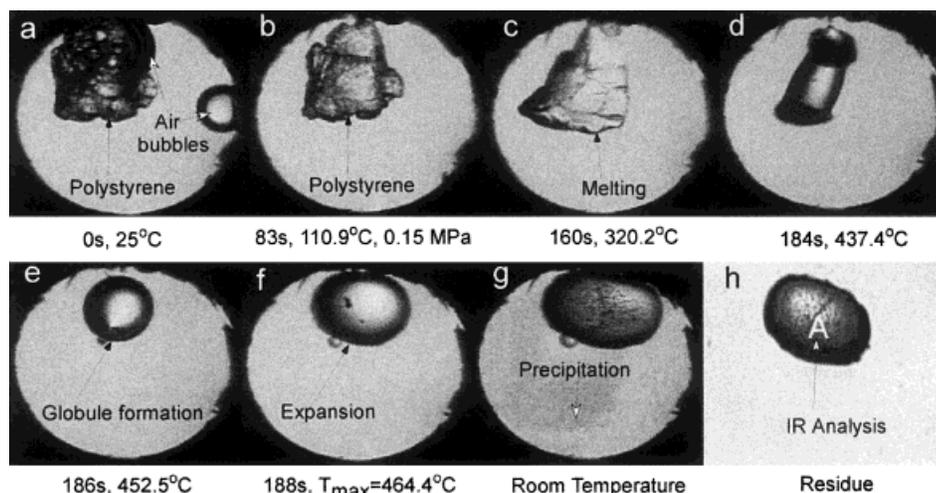
that it was decomposed and had more styrenelike characters than that in run 1 because of two styrene C—H bands exhibited at 3028 and 3061  $\text{cm}^{-1}$ , but no PS peaks at 1948  $\text{cm}^{-1}$ . The styrene peaks at 2858 and 2933  $\text{cm}^{-1}$  were not detected because of a too small IR analytical area.

In run 3 (Fig. 4), the PS + air was heated to 400°C and held for 20 min. After PS melting, gas bubbles appeared at 400°C and 0.23 MPa [Fig. 4(b)]. During the isothermal reaction at 400°C for 20 min, a liquid ring together with a large gas bubble and light yellow volatile compound outside the ring was seen at 2.73 min [Fig. 4(c)]. The volatile materials changed to yellow at 4.45 min,

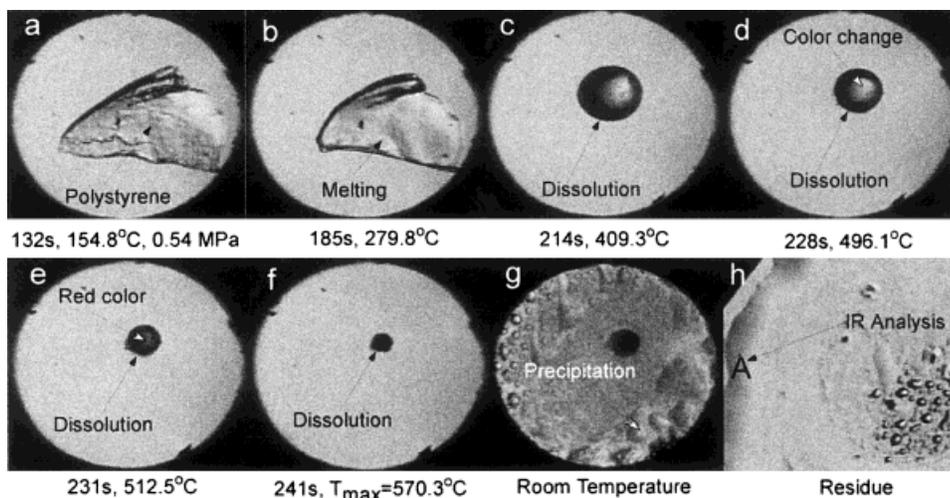
to orange at 10 min, and finally to red at 20 min, whereas the liquid ring underwent little change [Fig. 4(d–f)]. After cooling, the liquid ring expanded while the color of the volatile still stayed red at room temperature [Fig. 4(g)]. The liquid residue A with yellow and white colors on the diamond [Fig. 4(h)] was analyzed with FTIR. Figure 12(a) (run 3) shows that the oil has a similar spectrum to that in run 1, with an absence of a PS peak at 1948  $\text{cm}^{-1}$ .

#### Reactions in Supercritical Water (Runs 4–9)

In run 4 (Fig. 5), 22.6 wt % PS + water with air bubbles [Fig. 5(a)] were heated at a heating rate



**Figure 5** Images of PS evolution during heating of 22.6 wt % PS + water to 464.4°C and 681 MPa. Homogeneous conditions are 0.15 MPa and 110.9°C (run 4).

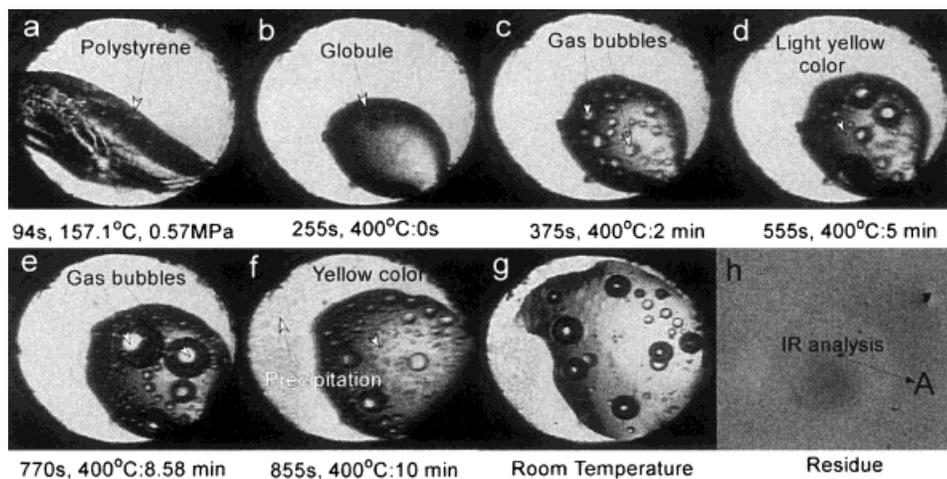


**Figure 6** Images of PS evolution during heating of 11.8 wt % PS + water to 570.3°C and 742.5 MPa. Homogeneous conditions are 0.56 MPa and 154.8°C (run 5).

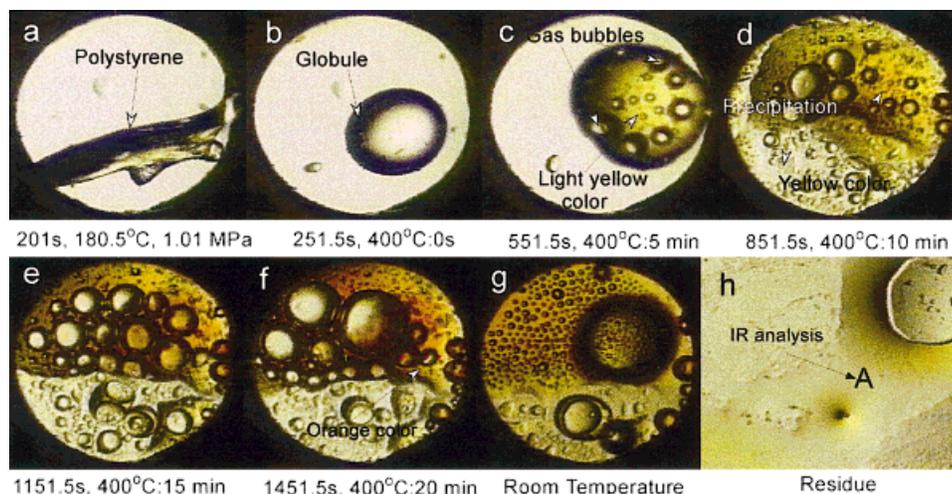
of 2.3°C/s to a maximum temperature and pressure of 464.4°C and 681 MPa, respectively. At 110.9°C ( $T_h$ ), the air bubble disappeared [Fig. 5(b)]. The pressure at  $T_h$  was calculated as 0.15 MPa. As the sample was isochorically heated, the PS particle started to melt at 320.2°C [Fig. 5(c)] above its normal melting point of 237.5°C. At 452.5°C, a globule formed [Fig. 5(e)] and expanded until the maximum temperature of 464.4°C was reached [Fig. 5(f)]. After cooling, the globule expanded and resolidified with numerous liquidlike particles precipitating at room temperature [Fig. 5(g)]. When DAC was opened, most of the liquid precipitates evaporated while the solid-

ified globule stayed on the diamond, as shown in Figure 5(h). IR analysis of solid A was conducted; the spectrum is given in Figure 12(a) (run 4). Little reaction occurred because of the spectrum similarities between 2800 and 3200  $\text{cm}^{-1}$  and 400 and 2000  $\text{cm}^{-1}$ , as compared to that of the standard styrene.

In run 5 (Fig. 6), 11.8 wt % PS + water system was heated to a higher maximum temperature and pressure of 570.3°C and 742.5 MPa, respectively. After melting and formation of the globule [Fig. 6(b–c)], the liquid PS started dissolving at 496.1°C, yielding a yellow-colored substance [Fig. 6(d)]. At 512.5°C, the globule became smaller and changed to



**Figure 7** Images of PS evolution during heating of 35.5 wt % PS + water to 400°C and 435.3 MPa for 10 min. Homogeneous conditions are 0.37 MPa and 157.1°C (run 6).

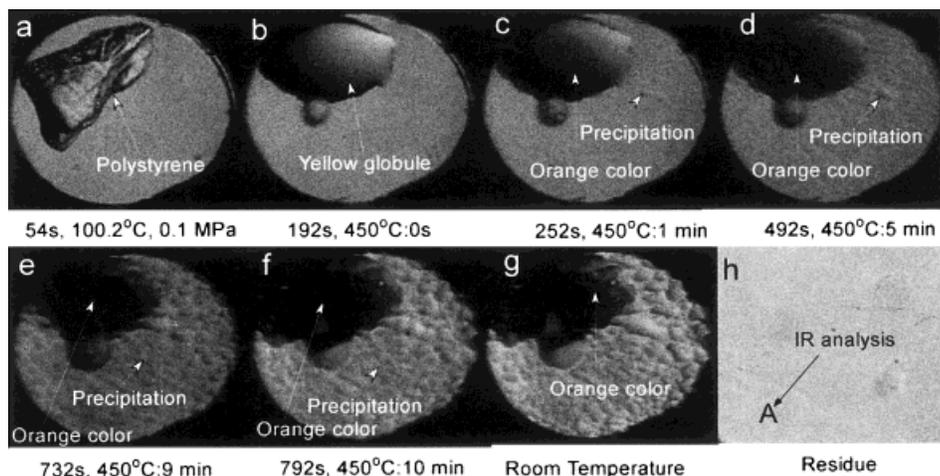


**Figure 8** Images of PS evolution during heating of 29.4 wt % PS + water to 400°C and 374.6 MPa for 20 min. Homogeneous conditions are 1.01 MPa and 180.5°C (run 7).

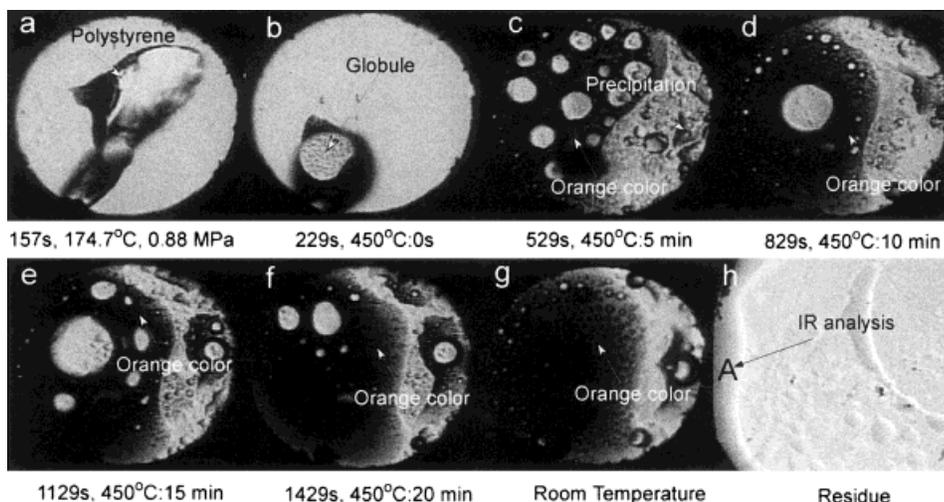
red [Fig. 6(e)]. The solubility reached the maximum of 91.5 wt % at 570.3°C [Fig. 6(f)]. Figure 13 shows the change in PS particle area and its derivative with the temperature. The curve for run 5 encompasses the PS particle shape-change (25–279.8°C), melting (279.8–496.1°C), and dissolution (496.1–570.3°C) process. After cooling, numerous liquid particles precipitated [Fig. 6(g)]. The IR spectrum [Fig. 12(b), run 5] shows that liquid A [Fig. 6(h)] has similar chemical structure with lower styrenelike character, as compared with that in run 2.

In run 6 (Fig. 7), 35.3 wt % PS was used, heated to 400°C, and held for 10 min. After melting, a globule formed at 400°C and 435.3 MPa, respectively [Fig. 7(b)]. During the isothermal reaction

at 400°C for 10 min, gas bubbles appeared on the surface of the globule at 2 min [Fig. 7(c)]. The bubbles grew larger and the globule expanded along with the color change from light yellow at 5 min to yellow at 8.58 min [Fig. 7(d–e)]. At 10 min, the yellow globule reached the maximum area while numerous liquid particles precipitated [Fig. 7(f)]. The two phases of liquid globule and water were always present during 10-min reaction runs. These phases are not clearly visible because they constitute a transparent part of the chamber. The development of the bubbles [Fig. 7(c–f)] indicated the release of the volatiles during the PS decomposition. The globule expanded and the bubbles reappeared because pressure had dropped [ $< 0.6$



**Figure 9** Images of PS evolution during heating of 23.3 wt % PS + water to 450°C and 681.2 MPa for 10 min. Homogeneous conditions are 0.10 MPa and 100.2°C (run 8).



**Figure 10** Images of PS evolution during heating of 24.0 wt % PS + water to 450°C and 476.0 MPa for 20 min. Homogeneous conditions are 0.88 MPa and 174.7°C (run 9).

MPa in Fig. 7(a)] after cooling to room temperature [Fig. 7(g)]. After the DAC was opened, liquid products were covered on the lower diamond [Fig. 7(h)]. IR spectrum of liquid A in Figure 12(b) (run 6) indicates styrenelike chemical structure similar to that in run 3 (decomposition in air, 20 min at 400°C).

In run 7 (Fig. 8), a longer reaction time of 20 min was applied at 400°C to depolymerize PS (29.4 wt % concentration). After the formation of the globule, gas bubbles appeared and grew, while the globule expanded and changed to a yellow color between 0 and 10 min [Fig. 8(b–d)]. The globule changed to orange liquidlike compounds along with larger gas bubbles present for the rest of the 10-min time [Fig. 8(e–f)]. The spectrum [Fig. 12(b), run 7] reveals that liquid A [Fig. 8(h)] is a styrenelike material. However, it has weaker absorption at 2858 and 2933  $\text{cm}^{-1}$ , as compared to the spectra of the standard styrene and the liquid residue in run 6.

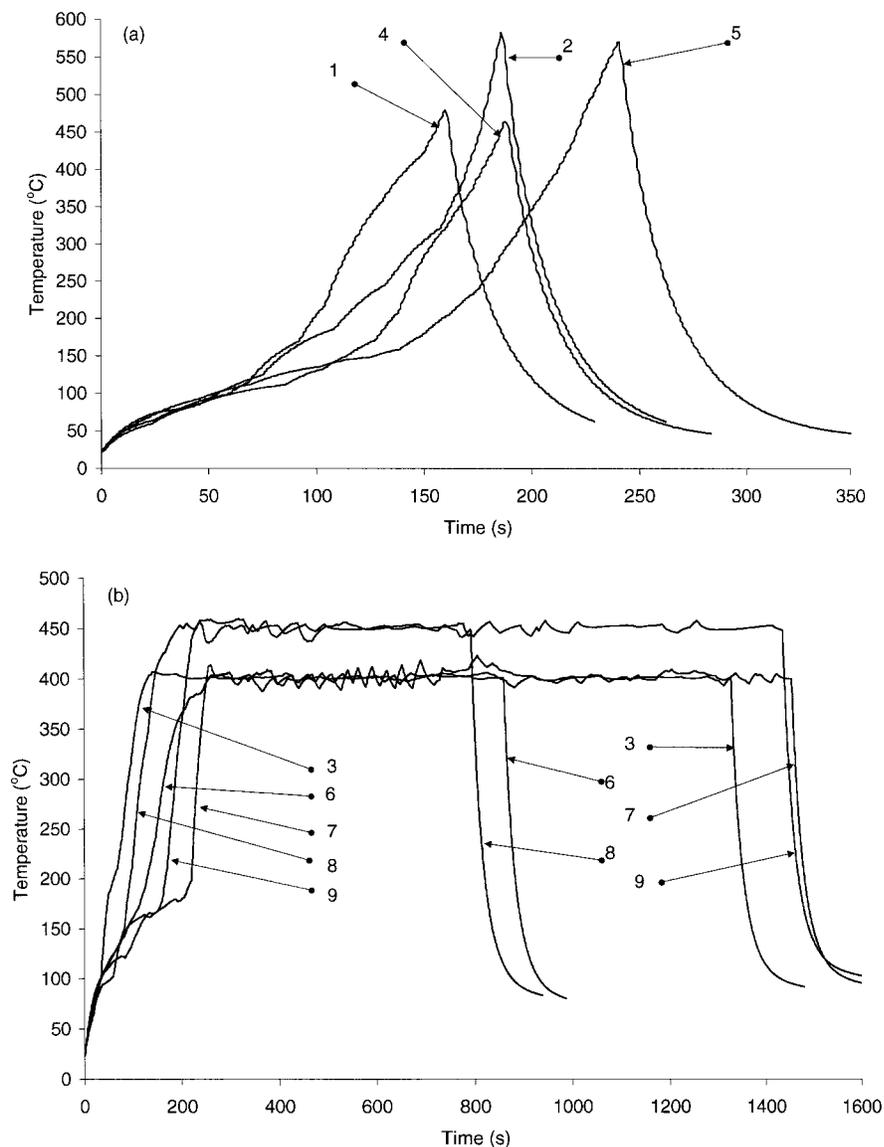
In run 8 (Fig. 9), 23.3 wt % PS was heated to 450°C and held for 10 min. When a temperature of 450°C and pressure of 681.2 MPa were reached, a yellow globule was formed [Fig. 9(b)]. As the reaction time at 450°C was increased to 10 min, the globule changed gradually to red while colorless liquid compounds started precipitating from the solution [Fig. 9(c–f)]. After cooling and opening the DAC, the colorless liquid remained on the diamond while the red globule had evaporated [Fig. 9(h)]. The colorless liquid shows some styrenelike character with its spectrum similar to that in run 2.

In run 9 (Fig. 10), 24 wt % PS was heated to 450°C and held for 20 min. After a temperature of 450°C and pressure of 476 MPa were achieved, an orange-colored liquid was formed along with an appearance of gas bubbles and particles precipitating from solution at 5 min [Fig. 10(c)]. There was little change as the sample was depolymerized after 20 min of reaction [Fig. 10(d–f)]. After cooling to room temperature, the orange-colored liquid still remained [Fig. 10(g)]. When the DAC was opened, only yellow liquid was present at the edge of the diamond [Fig. 10(h)]. The liquid had similar chemical character as that in run 8 [Fig. 12(b), runs 8 and 9].

## DISCUSSION

It was reported<sup>7</sup> that rapid decomposition of PS mainly to styrene monomer and partly to dimer takes place at a temperature of 400–500°C at atmospheric pyrolysis. At 310 to 350°C, slow decomposition occurs with the formation mostly of the monomer, a good deal of the dimer, and some trimer. In our fast pyrolysis runs (2.9–3°C/s), formation of gas bubbles began at 397–413.9°C (Table I, runs 1–3), which indicated the beginning of decomposition process.

Liu et al.<sup>1</sup> recovered styrene and other monoaromatics (boiling point < 200°C) by using a fluidized bed reactor (heating rate of 6.6°C/s to 600°C), with the yield increased from 70 to 86.6 wt % as the temperature rose from 450 to 600°C, respectively. The styrene yield reached a maxi-

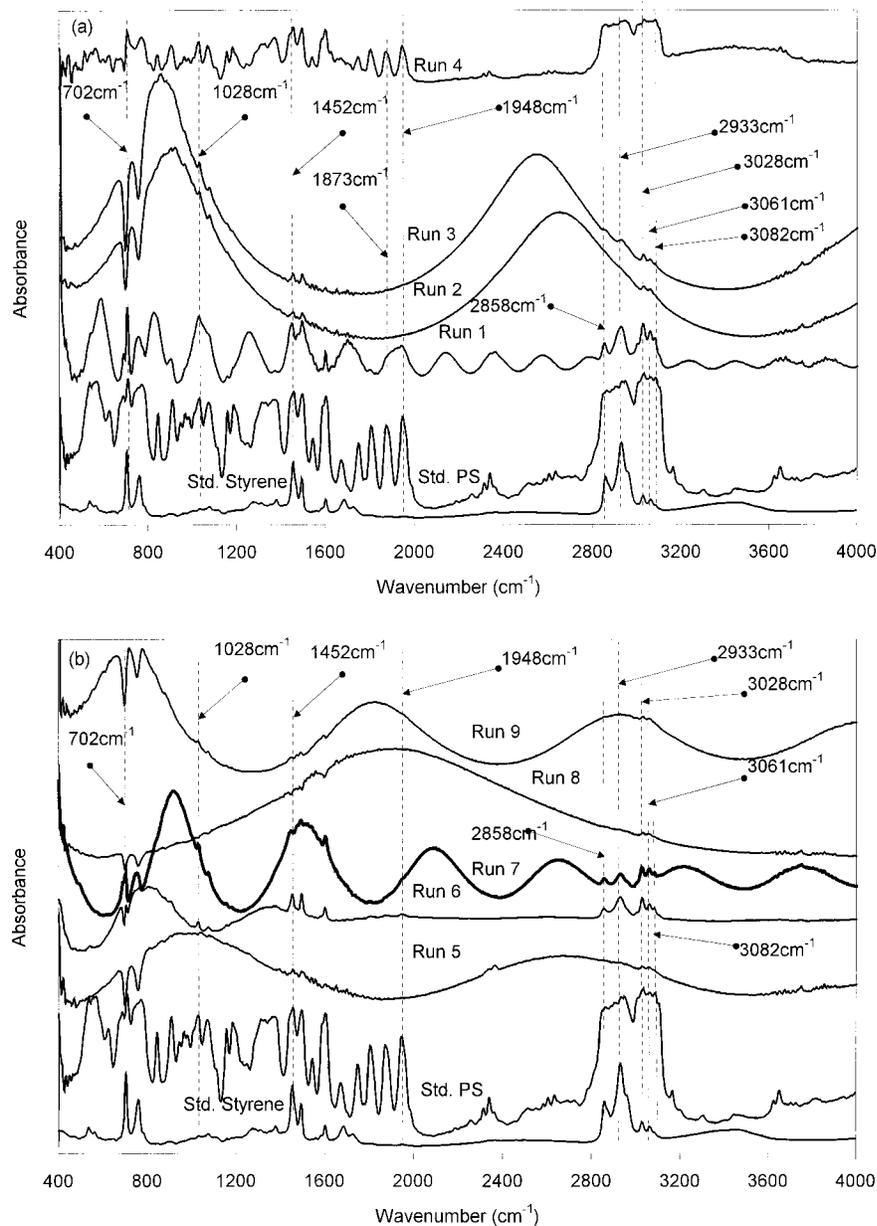


**Figure 11** Reaction temperature profiles for (a) short run time (runs 1, 2, 4, 5); (b) long reaction time (10 min: runs 6, 8; 20 min: runs 3, 7, 9).

imum of 78.7 wt % at 600°C. At 500°C, about 78% monomer, 7% dimer, and 6% trimer were obtained. In run 1 (480°C), the liquid residue [Fig. 2(f), A] was a mixture of styrene and its oligomers (mainly dimer and trimer), which was also confirmed by FTIR. The observed homogenous yellow volatile gas at the maximum temperature of 583.2°C (heating rate of 3.0°C/s) in run 2 [Fig. 3(e)] consists mainly of styrene and partly of other monoaromatic compounds. The IR spectrum showed that the liquid residue after cooling had styrenelike chemistry.

In the experiments of Simard et al.,<sup>3</sup> 81 wt % styrene was achieved at 401°C and 21 min

(these conditions are similar to those in run 3). Our IR spectra [Fig. 12(a)] showed that all pyrolytic liquid residues (runs 1–3) have the PS character because of the PS peak present at 1028  $\text{cm}^{-1}$ , the height and area of which are comparative or greater to those at 2933  $\text{cm}^{-1}$ , representing a characteristic band of styrene. The PS peak at 1028  $\text{cm}^{-1}$  is due to the vibration of the PS or the oligomers. Thus, most of the styrene (yield up to 81 wt %, boiling point of 145.4°C) produced in runs 1–3 evaporated or was lost, whereas most of the high-boiling fraction (dimer, trimer, and other oligomers) stayed on the diamonds.

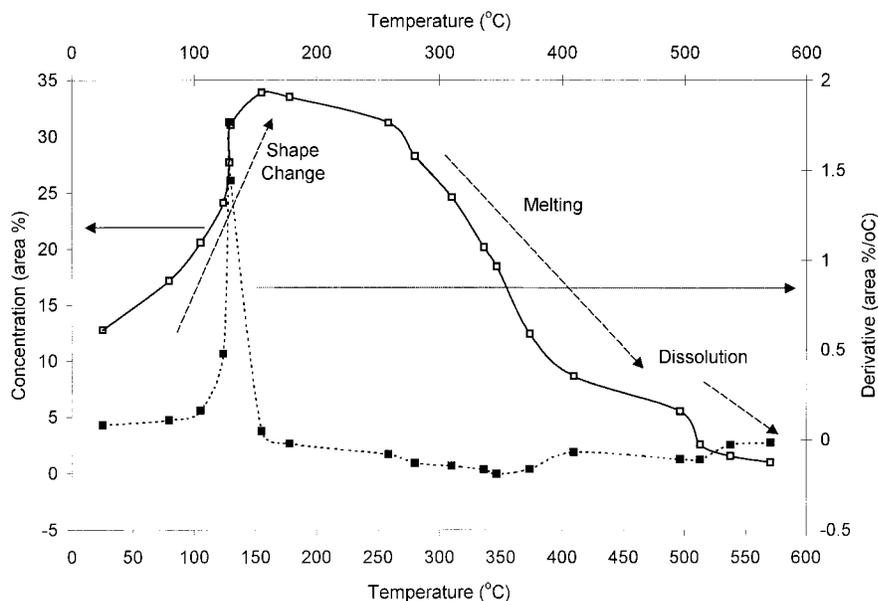


**Figure 12** IR spectra of the residues for (a) pyrolysis (runs 1–3), supercritical reaction (run 4); (b) supercritical reaction (runs 5–9).

Park et al.<sup>26</sup> studied oxidation of PS from 400 to 750°C at 2–5 residue time with 0.07–0.13 PS equivalence ratio (mole ratio of PS to oxygen divided by the stoichiometric ratio for the overall reaction:  $C_8H_8 + 10 O_2 \rightarrow 8 CO_2 + 4 H_2O$ ). The major product below 600°C was a monomer (up to 46 carbon mol %). In addition, 19 species (e.g., benzaldehyde  $\approx$  10 carbon mol % at 550–600°C, acrolein  $\approx$  1% at 600–680°C) were identified by GC and gas chromatography-mass spectroscopy. In our experiments, the presence of air in the

chamber could not be avoided during the loading of the PS. It was calculated, however, that the PS equivalence ratio in run 3 was about 11,800 at the highest air concentration (50 vol %, Table I, in the SCW runs; air volume was less than 33%). Therefore, oxidation caused by the air could be neglected.

In the SCW runs 4–9, the PS dissolution started at 496.1°C and reached the maximum at 570.3°C (run 5). The temperature for the maximum solubility is close to 600°C, at which a max-



**Figure 13** Digital image analysis of the area ratio profiles of sample to chamber and its derivative for supercritical water reaction (run 5: 570.3°C).

imum liquid yield of 98.7 wt % occurs (86.6% styrene, 10% dimer, and other medium boiling compounds; 200–350°C).<sup>1</sup> Thus, one may suggest that the dissolution phenomenon consists of the initial PS decomposition to styrenelike liquid, which subsequently dissolves in water above 496.1°C. The IR spectrum from the liquid precipitates in run 5 after cooling also confirmed this suggestion. However, the styrenelike liquid dissolves little in SCW at 400°C (runs 6–7, 10–20 min) and 450°C (runs 8–9, 10–20 min). PS could not dissolve in SCW below 464°C (run 4).

Fang et al.,<sup>18</sup> Smith et al.,<sup>20</sup> and Fang and Kozinski<sup>21</sup> have found that some condensation polymers and cellulose could be completely dissolved even in subcritical water (polyethylene terephthalate at 297–318°C; nylon 6/6 at 323–353°C; cellulose at 330°C). One of the reasons for high solubility is their simultaneous hydrolysis and dissolution due to more acidlike character in subcritical water than in SCW.<sup>27</sup> In the case of PS, no hydrolysis took place because no ether, ester, and acid-amide bonds are present in its chemical structure. PS dissolution occurred at a high temperature above 496.1°C because of the isochorically increased temperature to the supercritical water region; the solubility of water increased due to the decrease in dielectric constant ( $\epsilon$ ) of water.<sup>27</sup>

From our visual observation, the PS reactions in SCW at 400 and 450°C took place in a hetero-

geneous environment consisting of water and liquid compounds. In the experiments in supercritical water (10 min at 400°C)<sup>10</sup> or in subcritical water (1–24 h at 300–320°C),<sup>17</sup> more liquid products or volatile products were obtained than at pyrolytic conditions. Bertini et al.<sup>17</sup> suggested that the presence of water, as a hydrogen donor, depressed the inter- and intramolecular hydrogen transfers between or along the macromolecules, thus decreasing the occurrence of the secondary reactions. Moriya and Enomoto<sup>16</sup> also found, by using  $^2\text{H}_2^{16}\text{O}$  and  $^1\text{H}_2^{18}\text{O}$  as tracers, that during liquefaction of polyethylene in SCW, hydrogen atoms from water are donated to produce cracked oils, and the oxygen atoms are donated to the gases and aqueous phase products. However, if the reaction temperature was increased to 570.3°C, a homogenous reaction condition could be achieved. The homogenous reaction might result in a different product distribution and reaction mechanism. However, we were unable to identify individual products with FTIR.

## CONCLUSION

A white waxlike residue was obtained by rapid heating (2.9°C/s) of PS at 0.1 MPa in an air atmosphere to 479.8°C and 0.25 MPa. The residue presents a styrenelike chemistry. Upon further

heating, all samples evolved into yellow volatile compounds at 583.2°C, which also revealed styrenelike character. For the isothermal pyrolysis at 400°C, after melting and forming a liquid ring, the volatile material changed from yellow to red in a 20-min reaction time. The liquid residue after cooling also exhibited the styrene character. In all the pyrolytic runs, gas bubbles appeared at 397.2–413.9°C.

PS can dissolve in supercritical water above 496.1°C after it is decomposed to liquid styrenelike products. Upon rapid heating of 11.8 wt % PS + water mixture, a 91.5 wt % PS dissolved in water at 570.3°C. Little reaction and dissolution occurred when the PS was rapidly heated (2.9°C/s) to supercritical water region of 464.4°C and 681 MPa. In all the supercritical runs, the PS melted at 271.7–320.2°C, above its melting point of 237.5°C.

In the long SCW reaction experiments (10–20 min) at 400 or 450°C, little sample was dissolved. The process revealed a globule formation with gas production, the globule color changes, and its expansion. Two heterogeneous liquid phases of water and molten PS/liquid compounds were always present throughout the entire decomposition process. The reacted liquid products on the diamond also showed styrene chemistry.

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## REFERENCES

- Liu, Y.; Qian, J.; Wang, J. *Fuel Process Technol* 2000, 63, 45.
- Williams, P. T.; Williams, E. A. *Environ Technol* 1999, 20, 1109.
- Simard, Y. D. M.; Kamal, M. R.; Cooper, D. G. *J Appl Polym Sci* 1995, 58, 843.
- Kim, Y. S.; Hwang, G. C.; Bae, S. Y.; Yi, S. C.; Moon, S. K.; Kumazawa, H. *Korean J Chem Eng* 1999, 16, 161.
- H. S. Song, and J. C. Hyun, *Korean J Chem Eng* 1999, 16, 316.
- Yamaguchi, T.; Watanabe, S.; Shimada, Y. *Chemosphere* 1973, 1, 7.
- Madorsky, S. L.; Straus, S. *J Res Natl Bur Stand* 1948, 40, 417.
- Ide, S.; Ogawa, T.; Kuroki, T.; Ikemura, T. *J Appl Polym Sci* 1984, 29, 2561.
- Funazukuri, T.; Takanashi, T.; Wakao, N. *J Chem Eng Jpn* 1987, 20, 23.
- Saito, S. *J Supercrit Fluids* 1995, 8, 177.
- Park, S.; Gloyna, E. F. *Fuel* 1997, 76, 999.
- Adschiri, T.; Sato, O.; Machida, K.; Saito, N.; Arai, K. *Kagaku Kogaku Ronbunshu* 1997, 23, 505.
- Minowa, T.; Fang, Z.; Ogi, T. *J Supercrit Fluids* 1998, 13, 253.
- Sato, Y.; Kato, K.; Takeshita, Y.; Takahashi, K.; Nishi, S. *Jpn J Appl Phys* 1998, 37, 6270.
- Watanabe, M.; Hirakoso, H.; Sawamoto, S.; Adschiri, T.; Arai, K. *J Supercrit Fluids* 1998, 13, 247.
- Moriya, T.; Enomoto, H. *Kagaku Kogaku Ronbunshu* 1999, 25, 940.
- Bertini, F.; Audisio, G.; Beltrame, P. L.; Bergamasco, L.; Castelli, A. *J Appl Polym Sci* 1998, 70, 2291.
- Fang, Z.; Smith, R. L., Jr.; Inomata, H.; Arai, K. *J Supercrit Fluids* 1999, 15, 229.
- Fang, Z.; Smith, R. L., Jr.; Inomata, H.; Arai, K. *J Supercrit Fluids* 2000, 16, 207.
- Smith, R. L., Jr.; Fang, Z.; Inomata, H.; Arai, K. *J Appl Polym Sci* 2000, 76, 1062.
- Fang, Z.; Kozinski, J. A. *Proc Combust Inst* 2000, 28, 2717.
- Arai, K.; Adschiri, T. *Fluid Phase Equilib* 1999, 158/160, 673.
- Bassett, W. A.; Wu, T. C.; Chou, I. M., Jr.; Haselton, H. T.; Frantz, J. B.; Mysen, O.; Huang, W. L.; Sharma, S. K.; Schiferl, D. *Miner Spectrosc* 1996, 5, 261.
- Bassett, W. A.; Shen, A. H.; Bucknum, M. *Rev Sci Instrum* 1993, 64, 2340.
- Saul, A.; Wagner, W. *J Phys Chem Ref Data* 1989, 18, 1537.
- Park, B. I.; Bozzelli, J. W.; Booty, M. R.; Bernhard, R. J.; Mesuere, K.; Pettigrew, C. A.; Shi, J. A.; Simonich, S. L. *Environ Sci Technol* 1999, 33, 2584.
- Marshall, W. L.; Franck, E. U. *J Phys Chem Ref Data* 1981, 10, 295.