

# Phase Behavior and Reaction of Nylon 6/6 in Water at High Temperatures and Pressures

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**ABSTRACT:** The phase behavior and reaction of nylon 6/6 in water were studied with a diamond anvil cell (DAC) technique and visual microscopy. Nylon 6/6 concentrations in water and cell temperatures were varied from 11 to 46% and from 264 to 425°C, respectively. The pressures studied ranged from 30 to 900 MPa. When an aqueous solution of 27% nylon 6/6 was rapidly heated (2.6°C/s) to 372°C at 30 MPa, the solution became homogeneous at 331°C. Upon cooling, the final pressure was 30 MPa and both particles and gas were observed. Analysis of the particles by Raman indicated decomposed nylon 6/6 solid. When an aqueous solution of 31% nylon 6/6 was rapidly heated (2.9°C/s) to 425°C at 58 MPa, the solution became homogeneous at 323°C. Upon cooling, the final pressure was 143 MPa, and, remarkably, only a second liquid precipitated and no gas or solids were observed. From the experiments, we concluded that the reaction pathways are completely different between the subcritical and supercritical water conditions. For the case of subcritical conditions, the final products were solid particles having a nylon character along with a considerable amount of gas. At supercritical water conditions, the final products were liquids having little nylon character and no gas. Experiments were performed at a constant temperature of 272°C at initial pressures ranging from 87 to 400 MPa. As the reaction proceeded, the pressure was measured at 30-s intervals. At average pressures less than 300 MPa, the nylon 6/6 samples melted and appeared to become homogeneous. At average pressures higher than 520 MPa, the nylon 6/6 samples remained heterogeneous. From these results, the rate of hydrolysis was concluded to increase with pressure. The reaction volume was found to be  $-21.1 \text{ cm}^3/\text{mol}$ , which can be explained by the overall formation of water-soluble products. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1062–1073, 2000

**Key words:** nylon 6/6; supercritical water; DAC; hydrolysis; phase behavior; polymer

## INTRODUCTION

Recovery of fuels and chemicals from plastic wastes is an important research area in plastics recycling.<sup>1</sup> The proposed methods include chemical recycling with oxidation in caustic solutions,<sup>2</sup>

catalytic pyrolysis,<sup>3</sup> hydrous pyrolysis,<sup>4</sup> homogeneous catalytic hydrolysis,<sup>5</sup> and noncatalytic methods based on supercritical fluids.<sup>6,7</sup> In this work, we were concerned with supercritical fluids, which has been a very active area in polymer science research.<sup>8</sup>

Adschiri et al.<sup>6</sup> found that many polymers could be decomposed to liquid products or to their monomers in the presence of high-temperature, high-pressure water. The conversion appears to be most effective in the supercritical region ( $T > 374^\circ\text{C}$ ,  $P > 22.1 \text{ MPa}$ ). In the supercritical

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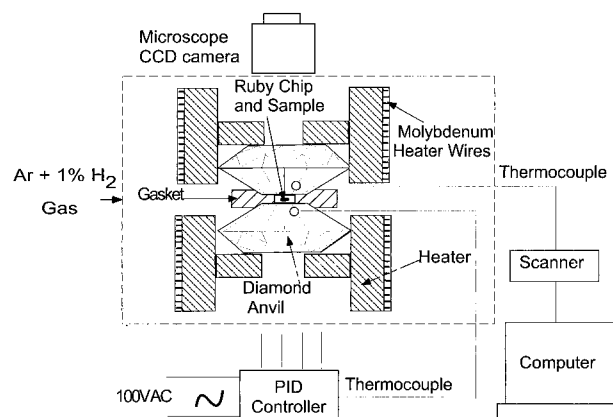
region, water achieves a highly compressible condition and, further, the change in the physical properties of water allow it to dissolve many higher molecular weight hydrocarbons.<sup>9</sup> For cellulose, poly(ethylene terephthalate) (PET), nylon 6/6, polystyrene, and other polymers, 100% liquid yield or 100% conversion with very low gas yield are obtained without catalysts under conditions of 400°C at approximately 30 MPa for a 10-min reaction time.<sup>7,9</sup> For the case of PET, reaction in supercritical water produced terephthalic acid and its monomer, ethylene glycol. All these factors make recycling or conversion of polymers in supercritical water a very attractive area for industrial development. Further examples can be found in the literature for phenol resins<sup>10a,b</sup> cellulose,<sup>11</sup> and nylon fibers.<sup>12</sup>

Because conditions are relatively extreme, little is known of the phase behavior under reactive conditions, especially regarding visual observations. Fang et al.<sup>13</sup> found that a number of phenomena occur when PET is heated with water to supercritical water conditions ( $T > 374^{\circ}\text{C}$ ,  $P > 22.1$  MPa). During the heating of PET with water, simultaneous crystallization and crystal dissolution occurs when samples are well dispersed and heated rapidly. Complete dissolution of PET in supercritical water was possible.<sup>4</sup> For polyethylene (PE), Fang et al.<sup>14</sup> found that the system remained as a heterogeneous system during heating and reaction. Brilliant red and yellow color changes were noted during the reaction. Only after PE decomposed to lower molecular weight hydrocarbons above about 565°C could homogeneous conditions be obtained.

The above studies show that the phase behavior of polymer + water systems under reactive conditions is very different for the two studies that have been reported. Further, the phase behavior is very important for the practical recycling and handling of polymers with a supercritical water solvent. For the case of nylon 6/6, little is known on the phase changes during the reaction at high-temperature and high-pressure conditions in the presence of water. The purpose of this work was to study and quantify the phase changes of nylon 6/6 in sub- and supercritical water during the reaction process.

## EXPERIMENTAL

The nylon 6/6 pellets used in all the experiments was from Aldrich (Tokyo, Japan). The nylon 6/6



**Figure 1** Diamond anvil cell experimental arrangement.

had a density of 1090 kg/m<sup>3</sup>. Its onset melting point ( $T_m$ ) of 255.4°C was measured by DSC (TA Instruments 2910, New Castle, USA). The monomers of nylon 6/6 hexamethylenediamine ( $T_m = 41$ –42°C) and adipic acid ( $T_m = 153^{\circ}\text{C}$ ) were of 95 and 99.5% purity, respectively, and were obtained from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan). The water used was high-purity HPLC grade (Aldrich).

A diamond anvil cell consists of two opposing diamonds that apply pressure to a thin metal gasket that contains a small hole for the sample. In our measurements, a Bassett-type diamond anvil cell (DAC) was used.<sup>15,16</sup> The Bassett-type cell can be applied to hydrothermal systems at pressures up to 30 GPa and temperatures up to 1200°C.

The experimental setup is shown in Figure 1. The diamond anvils (1-mm faces) used in this work could produce pressures up to approximately 2.5 GPa. The gaskets used were made of inconel and were 0.25 mm thick with microdrilled holes of 0.5-mm i.d. The sample was heated by two individual microheaters that transferred heat to the diamond anvils. Temperature from both anvils was recorded by a scanner (Hewlett-Packard Model, 34970A, Palo Alto, CA) at approximately every 0.1 s. Pressure was measured by ruby fluorescence, as described below, at either initial and final conditions, or at 30-s intervals for the isothermal runs at 272°C. The DAC had an outside cover that allowed the entire heater and diamond anvil assembly to be surrounded by inert gas. In our experiments, argon gas with 1% hydrogen was introduced into the cell jacket as shown in Figure 1 to prevent the diamonds from

becoming oxidized at the higher temperatures (>300°C) and to increase the cooling rate in some cases.

The experimental setup was improved over that used in ref. 13. It is apparent from the above description that the entire sample size and heating area are very small. For example, the sample volume is nominally 50 nL and the each diamond had a weight of roughly 1/8 carat. In this work, a high-speed PID controller (RKC Instrument Inc., REX-G9 Series/A, Tokyo) with a 0.1-s sampling rate was used. The controller could maintain temperature to within  $\pm 0.1^\circ\text{C}$  at temperatures up to 500°C. The improved control allowed constant temperature runs while simultaneously monitoring pressure and making visual observations. Control parameters were  $P = 8.9\%$ ,  $I = 12\text{ s}$ , and  $D = 3\text{ s}$  with an allowed maximum full output voltage of 2 V ac.

The reported temperatures are the average of the top and bottom anvil temperatures. At the highest heating rates, the maximum temperature difference between the anvils was  $10^\circ\text{C}$  with typical values being  $2\text{--}3^\circ\text{C}$ . For the constant temperature runs, the temperature differences between top and bottom anvils was generally no greater than  $0.5^\circ\text{C}$ .

The phase transitions and phase behavior of the samples in the DAC were recorded by a CCD camera (Olympus KY-F55MD, Tokyo) after  $100\times$  magnification by a microscope (Olympus SZH10, Tokyo). Product residues were analyzed by laser Raman spectroscopy (JASCO NRS-2000C). Recorded photos were analyzed with digital imaging to calculate the apparent concentration (area %) and to obtain phase transition rates.

The pressure was measured by ruby fluorescence  $R_1$  and  $R_2$  lines with the equations of Forman et al.<sup>17</sup>:

$$P_1 = -(\omega_1 - \omega_{01})/0.77 \quad (1)$$

$$P_2 = -(\omega_2 - \omega_{02})/0.84 \quad (2)$$

where  $P_1/P_2$  and  $\omega_1/\omega_2$  are the pressures and frequencies of the ruby  $R_1$  or  $R_2$  lines having units of kbar and  $\text{cm}^{-1}$ , respectively. The  $\omega_1 - \omega_{01}$  and  $\omega_2 - \omega_{02}$  refer to the wavenumber shift that occurs when the ruby is taken from room temperature and ambient pressure to the temperature and pressure of interest. In principle, either of the  $R$  lines can be used for pressure measurement.

At higher temperatures, eqs. (1) and (2) can be still used, provided that the temperature-depen-

dent coefficients,  $d\omega_i/dT$ , are known. The temperature coefficients for the ruby shift were shown to be independent of pressure by Shchanov and Subbotin<sup>18</sup> for the  $R_1$  line and by Grzanna<sup>19</sup> for the  $R_2$  line. Researchers commonly produce calibration curves for a range of temperatures.<sup>18,19</sup> In this work, however, pressure was only measured under conditions of either room temperature or at a constant elevated temperature. The following coefficients were determined with our experimental setup for the temperature dependence of the ruby  $R$  lines at  $272^\circ\text{C}$ :

$$d\lambda/dT = 0.153\text{ cm}^{-1}/^\circ\text{C} \quad R_1\text{ line} \quad (3)$$

$$d\lambda/dT = 0.150\text{ cm}^{-1}/^\circ\text{C} \quad R_2\text{ line} \quad (4)$$

where  $\lambda$  is the wavelength.

Pressures can be determined from either eq. (1) or (2). In this work, we used both  $R_1$  and  $R_2$  lines [eqs. (1) and (2)] and averaged the values. This is because as the temperature becomes higher the two peaks merge. For short time runs, pressures were always measured at initial and final conditions at room temperature. For the isothermal runs at  $272^\circ\text{C}$ , pressures were determined with eqs. (1)–(4) as the average of the  $R_1$  and  $R_2$  lines.

The general procedure is that the DAC is disassembled and the diamond anvils are cleaned with acetone until no lint, foreign particles, or oils can be seen under the microscope. Then, a gasket is mounted to the lower anvil with a thin piece of electrical tape that has a slotted cutout. The cutout ensures that the sample area never comes in contact with the tape. Then, the ruby and the polymer are loaded. Finally, a drop of water is placed over the gasket hole with a  $10\text{-}\mu\text{L}$  syringe and the top anvil is mounted. If the loading is successful, only the water, ruby, and polymer can be seen under the microscope.

## RESULTS

Six runs were made in which the nylon 6/6 + water solutions were rapidly heated for less than 1 min above the  $T_m$ . Five runs were made in which the nylon 6/6 + water solutions were held isothermally at  $272^\circ\text{C}$  for approximately 11.7 min at various pressures. Tables I and II summarize the experimental conditions, visual observations, image analyses, and reaction products for the rapid heating and isothermal runs, respectively. Reac-

**Table I** Conditions and Results for Rapid Heating Runs (264–425°C)

Analyses	Subcritical				Supercritical	
	Run 1 Nylon 6/6 + H <sub>2</sub> O	Run 2 Nylon 6/6 + H <sub>2</sub> O	Run 3 Nylon 6/6 + H <sub>2</sub> O	Run 4 Nylon 6/6 + H <sub>2</sub> O	Run 5 Nylon 6/6 + H <sub>2</sub> O	Run 6 Nylon 6/6 + H <sub>2</sub> O
<b>Conditions</b>						
Max temperature ( $T_{\max}$ ) (°C)	264.4	340.5	347.1	371.7	391.1	424.7
Initial pressure (MPa)	30	115	173	30	86	58
Final pressure (MPa)	87	142	316	30	231	143
Heating rate to $T_{\max}$ (°C/s)	2.2	1.9	2.6	2.6	3.7	2.9
Max heating rate (°C/s)	4.5	6.4	8.9	8.3	7.4	6.75
Max cooling rate (°C/s)	-11.4	-12.6	-17	-17.3	-18.5	-17.9
Run time above $T_m$ (s)	4	31	23	35	36	57
Run time until $T_{\max}$ (s)	112	165	127	137	101	141
<b>Visual observations</b>						
Near $T_m$	Melted	Melted	Melted	Melted	Melted	Melted
> $T_m$	Expanded	Expanded	Expanded	Expanded	Expanded	Expanded
Homogenization at $T$ (°C)	—	337	330	331	353	323
Precipitation $T$ (cooled) (°C)	—	274	290	90	—	400
Final Image analyses	Globule	Particle	Particle	Particle and gas	Liquid	Liquid
<b>Apparent concentration</b>						
Initial (area %)	11.6	19.4	12.9	26.6	14.7	30.9
<b>Reaction products</b>						
By Raman	DN solid AP(C—H)	DN solid AP(C—H)	DN solid AP(C—H)	DN solid AP(C—H)	DN liquid NP(N—H)	DN liquid NP(N—H)

DN, decomposed nylon 6/6; AP(C—H), additional peak of  $\nu$ (C—H) at 2904  $\text{cm}^{-1}$ ; NP(N—H), no peak for  $\nu$ (N—H) at 3303  $\text{cm}^{-1}$ .

tion of nylon 6/6 in subcritical water was studied in runs 1–4 and in runs 7–11. Reaction of nylon 6/6 in supercritical water was studied in runs 5 and 6. Visual observations, reaction temperature profiles, and Raman analyses are given in Figures 2–5, Figure 6, and Figures 7 and 8, respectively. Digital imaging analyses and pressures for the isothermal runs are given in Figures 9 and 10, respectively. Each of these are discussed in more detail below.

## Rapid Heating Runs

### Subcritical Water

In run 1 (Fig. 2), nylon 6/6, water, and a ruby fragment were loaded into the sample chamber as shown in the photo at 0 s. The concentration was estimated by 2-D digital imaging to be 11.6% nylon and the initial pressure was 30 MPa (Table I). The average heating rate was

2.2°C/s, with the maximum heating rate being 4.5°C/s (Table I). At 237°C, the nylon particle melted (Fig. 2) and then expanded by 82.6% as it was heated from 237 to 264.4°C. The nylon particle turned transparent and then the sample was rapidly quenched by turning off the current to the heaters and increasing the gas flow to the DAC jacket. The cell was opened and the residue was analyzed with Raman as shown in Figure 8. Characteristic peaks of nylon 6/6 are the amine N—H stretching at 3303  $\text{cm}^{-1}$  and the C—H stretching at 2922  $\text{cm}^{-1}$ . For reference, hexamethylenediamine and adipic acid spectra are also shown. As shown in Figure 8, an additional C—H stretching band appeared at 2904  $\text{cm}^{-1}$ , indicating that nylon reacted with water although a strong nylon character remained as evident by the N—H peak. It is clear from Figure 2 that the system was heterogeneous throughout the reaction.

**Table II** Conditions and Results for Isothermal (272°C) Runs

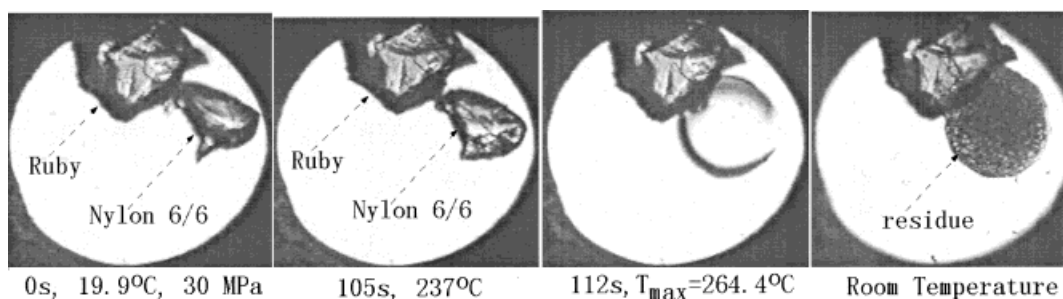
Analyses	Heated to 272°C with Rate of 6.2°C/s (40s) and Holding 11.7 min				
	Run 7 Nylon 6/6 + H <sub>2</sub> O	Run 8 Nylon 6/6 + H <sub>2</sub> O	Run 9 Nylon 6/6 + H <sub>2</sub> O	Run 10 Nylon 6/6 + H <sub>2</sub> O	Run 11 Nylon 6/6 + H <sub>2</sub> O
<b>Pressure conditions</b>					
25°C					
Initial pressure (MPa)	150	260	115	87	400
Final pressure (MPa)	150	260	230	230	400
272°C					
Average pressure (MPa)	110	220	300	520	900
Slope (MPa/s)	-0.01	0.046	0.015	-0.063	-0.047
<b>Visual observations</b>					
At 272°C, 11.7 min	Homogeneous	Homogeneous	Homogeneous	Heterogeneous (L + S)	Heterogeneous (L + S)
<b>Image analyses</b>					
Apparent concentration initial (area %)					
	36.6	25.9	46.3	34.3	36.7
<b>Reaction products</b>					
By Raman	DN solid + gas AP(C—H)	DN solid + gas AP(C—H)	DN solid + gas AP(C—H)	DN solid AP(C—H)	DN solid AP(C—H)

DN, decomposed nylon 6/6; AP(C—H) additional peak of  $\nu$ (C—H) at 2904 cm<sup>-1</sup>.

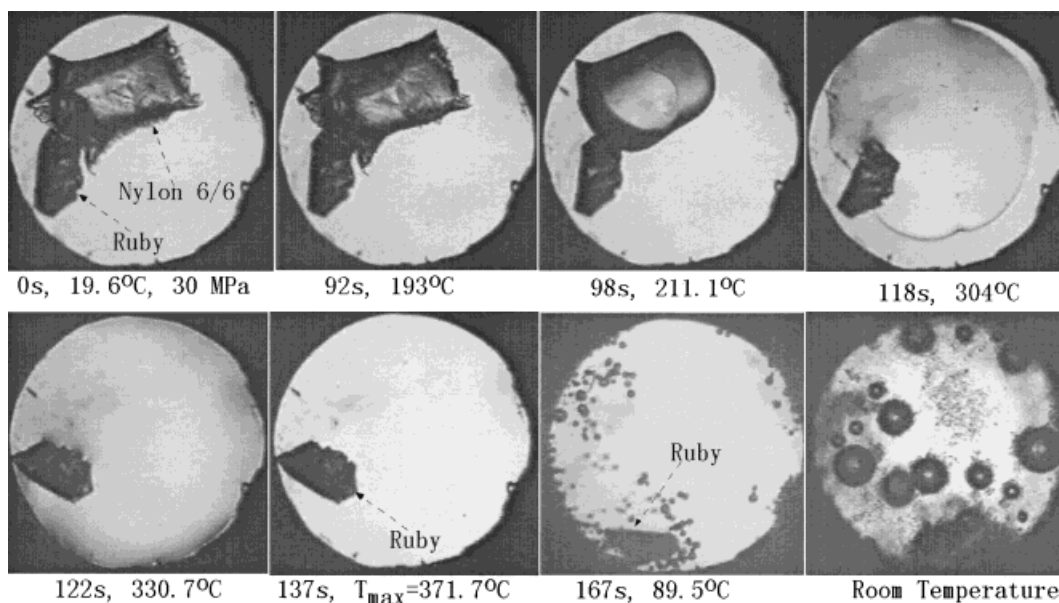
For successive runs, new samples were loaded and the experiments were run as in Table I. As the temperature was elevated, the phase behavior and final products were noted. In runs 2 and 3, nylon became homogeneous (sample chamber became clear) at 337 and 330°C, respectively, and each run produced a solid and liquid product with no gas. Run 4

became homogeneous at 331°C and produced a solid and liquid product with gas. Run 4 is discussed next in detail.

Figure 3 shows photos of the nylon 6/6 + water solution being heated to the near critical region of water. The particle melted somewhat below the  $T_m$  and then dispersed on the lower anvil throughout the cell. At 331°C, the sample



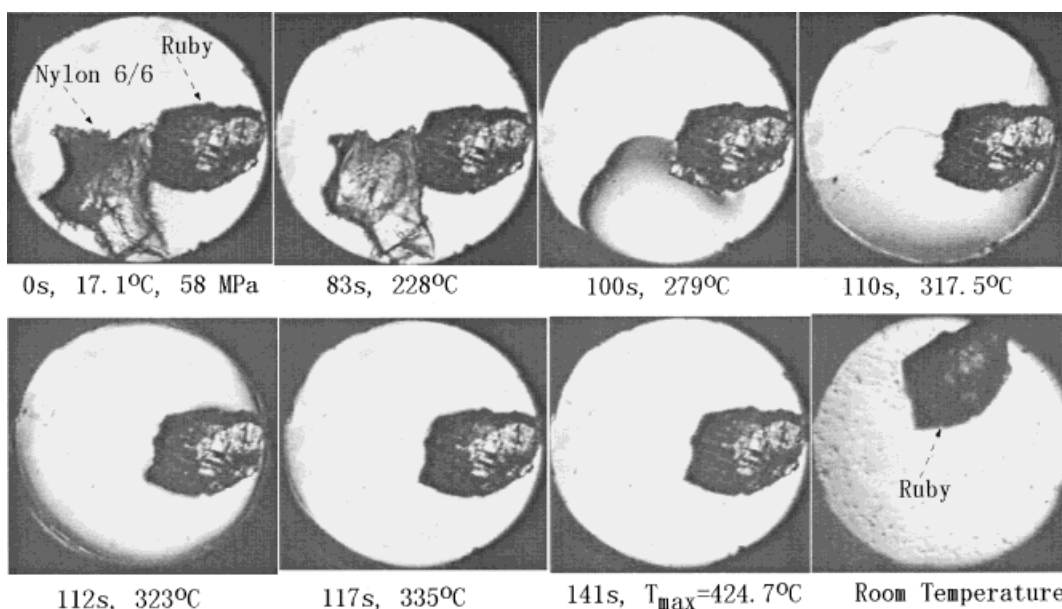
**Figure 2** Visual observation (run 1) for heating nylon 6/6 + water to 264.4°C at an initial pressure of 30 MPa.



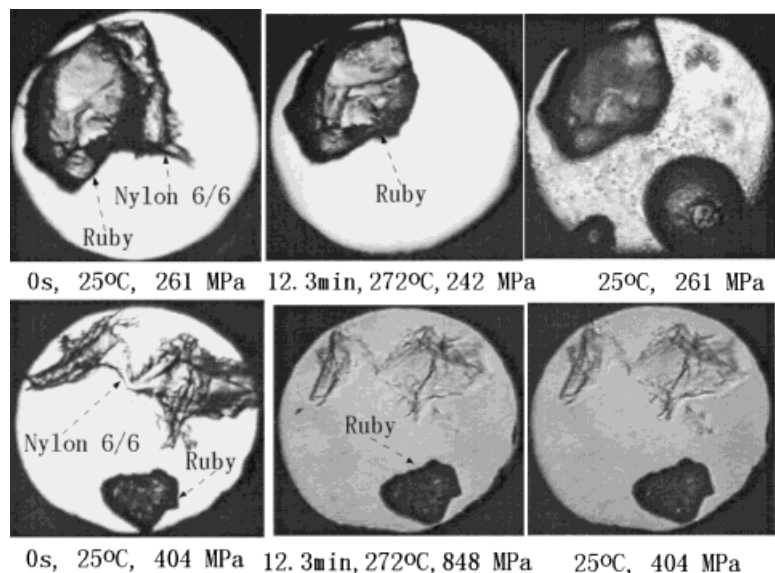
**Figure 3** Visual observation (run 4) for heating nylon 6/6 + water to 371.7°C at an initial pressure of 30 MPa.

appeared to be nearly homogeneous, and as the temperature was elevated to 371.7°C, the sample chamber definitely became completely transparent (137 s). Upon cooling, gas bubbles formed at 167 s and these bubbles increased in size as the cell was cooled to room temperature, which confirmed the true presence of gas. As

shown in the slide, solid particles also precipitated. Raman analysis of the particles showed a similar character as that of the solid in run 1. However, as shown in Figure 7, the ratio of the additional C—H stretching ( $2904\text{ cm}^{-1}$ ) to the nylon C—H stretching ( $2922\text{ cm}^{-1}$ ) gradually increased as the temperature was increased

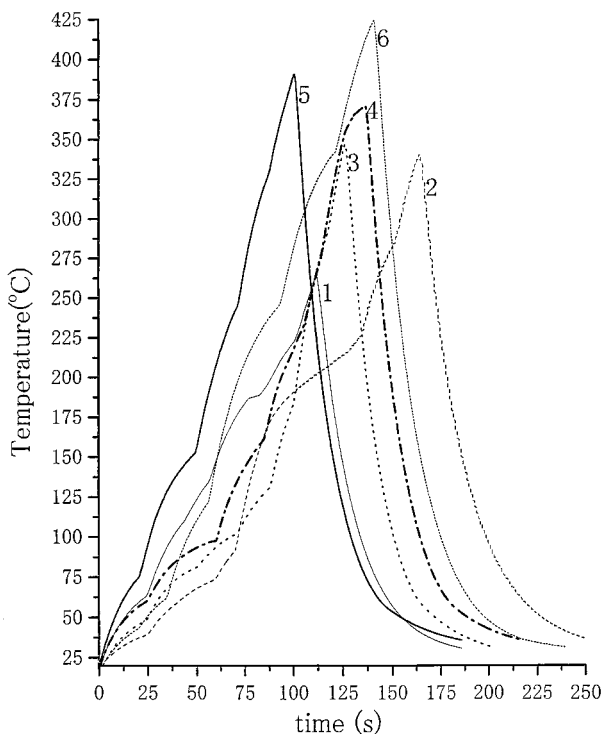


**Figure 4** Visual observation (run 6) for heating nylon 6/6 + water to 424.7°C at an initial pressure of 58 MPa.



**Figure 5** Visual observations and (runs 8 and 11) for isothermal heating nylon 6/6 + water for 12.3 min total heating time at 272°C. Upper set of photos: run 8 at 220 MPa; lower set of photos: run 11 at 900 MPa.

from 264.4 to 371.7°C (runs 1–4). The runs at supercritical conditions showed strikingly different behavior.



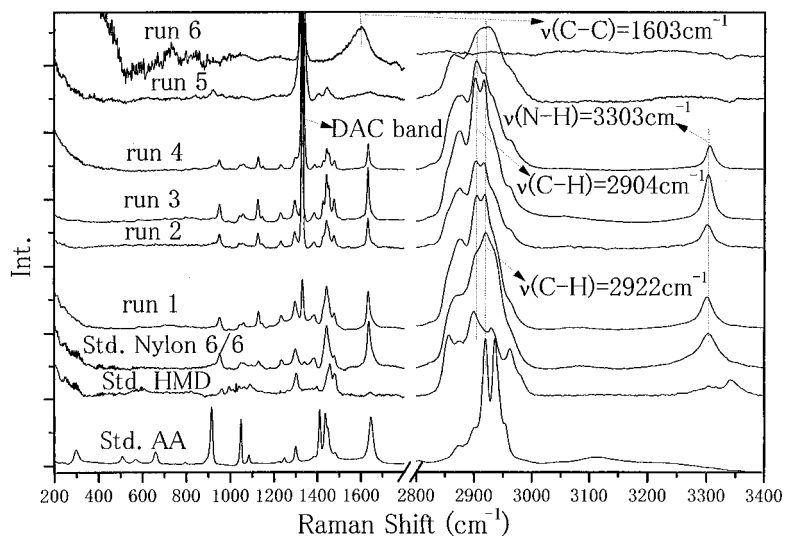
**Figure 6** Temperature profiles for rapid heating of nylon 6/6 + water solutions (runs 1–6) under subcritical and supercritical conditions.

### Supercritical Water

In runs 5 and 6, nylon 6/6 and water were heated to the supercritical region of water. Figure 6 shows visual observations for the case of heating a nylon 6/6 + water solution to 424.7°C (run 6). Upon heating, the sample became homogeneous at approximately 330°C. At 424.7°C, the sample chamber was totally transparent and free of particles. Upon cooling, no gas was observed; however, a white liquid formed that redissolved into the solution. This can be seen in the last slide of Figure 4 by the apparent particlelike features in the liquid solution. Raman analyses for both samples (runs 5 and 6) showed no N—H stretching ( $3303\text{ cm}^{-1}$ ), indicating no unreacted nylon 6/6. An additional peak appeared for run 6, indicating a C=C stretching mode ( $1603\text{ cm}^{-1}$ ).

### Digital Analysis

All runs that were studied under rapid heating conditions were analyzed with digital imaging to study phase-behavior changes under the given conditions as shown in Figure 9. As shown in Figure 9, the curves could be broken into melting and expansion curves. All samples tended to decrease in area just before melting and subsequently dispersed throughout the chamber to fill it completely. This is a desirable quality considering polymer processing with aqueous solutions.



**Figure 7** Raman spectra of the reaction products formed from rapid heating of nylon 6/6 + water solutions (runs 1–6) under subcritical and supercritical conditions. Reaction time above  $T_m$  is less than 1 min.

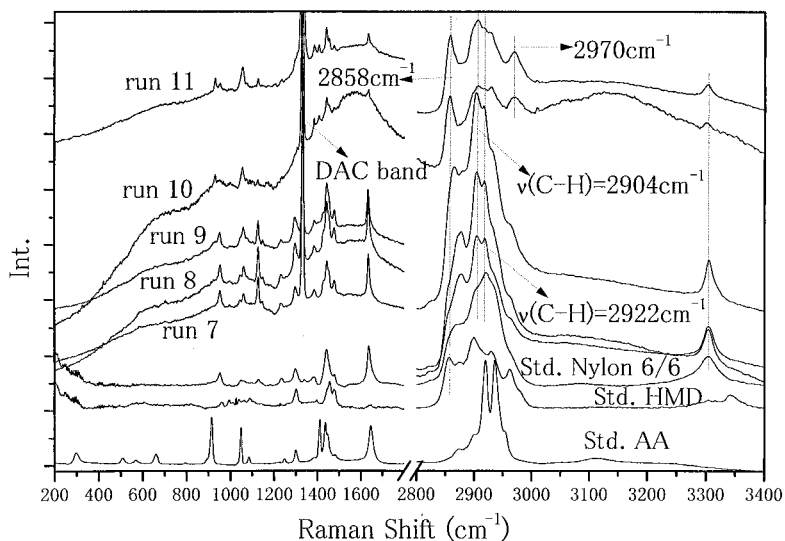
For polymers such as polyethylene, this dispersion does not occur, which is likely to require additional processing steps or components to promote mixing.<sup>5</sup>

#### Isothermal Runs

In the next series of experiments, nylon 6/6 + water samples were heated to 272°C and maintained at this temperature for a longer period of time

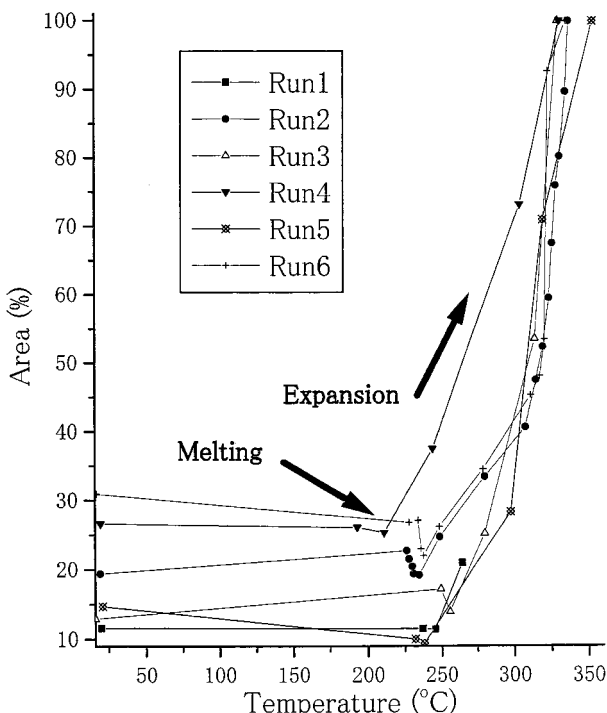
than in the runs above. The temperature was chosen so as to be above the melting point of nylon 6/6 and to be as high as possible such that the ruby peaks could be clearly separated and pressure could be measured.

Conditions and results for isothermal runs are summarized in Table II. As shown in Table II, runs 7–9 became homogeneous as the solutions were heated for 12 min or so at average pressures of 113, 217, and 299 MPa, respectively. As an



**Figure 8** Raman spectra of the reaction products formed during isothermal (272°C) heating of nylon 6/6 + water solutions (runs 7–11). Reaction time is approximately 11.7 min.





**Figure 9** Digital image analysis of visual observation for rapid heating of nylon 6/6 + water solutions (runs 1–6) under subcritical and supercritical conditions. Reaction time above  $T_m$  is less than 1 min.

example, Figure 5 (top) shows that the sample was homogeneous after heating for 12.3 min at 272°C and 242 MPa. Upon cooling, particles and gas formed similar to those of the subcritical runs above. From the Raman analyses, nylon 6/6 had decomposed as judged by the appearance of the additional C—H stretching at  $2904\text{ cm}^{-1}$ .

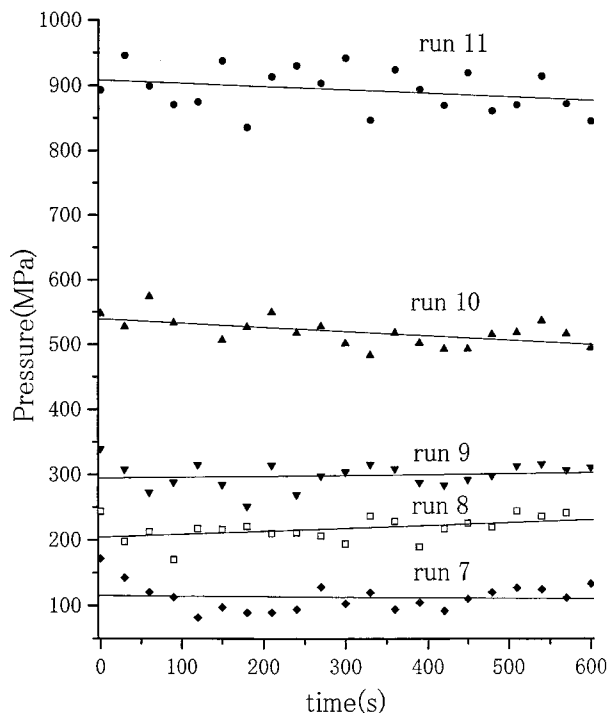
In runs 10 and 11, solutions were heated for 12 min or so at 272°C, but the average pressures were increased to 520 and 894 MPa, respectively. As shown in Figure 5 (bottom) for run 11, the nylon 6/6 sample remained solid even at this temperature. Upon cooling, no particles or gas formed. Raman spectra of the residues showed an additional peak at  $2970\text{ cm}^{-1}$  (Fig. 8), which indicates that the higher pressure promotes decomposition of nylon 6/6, most probably to liquid products. Pressure effects are discussed next.

#### Pressure Effect

From the spectra for the isothermal runs (Fig. 8), it can be seen that the relative peak height of the C—H stretching at  $2904\text{ cm}^{-1}$  to that at  $2922\text{ cm}^{-1}$  became higher as the average pressure increased. This means that the rate of hydrolysis

increased with the pressure. However, judging from the visual observations in Figure 5, the reaction environment was totally different for low pressures (runs 7–9) and high pressures (runs 10 and 11).

At a 272°C (run 8) constant temperature (Fig. 5, run 8), the nylon 6/6 + water became the homogeneous phase at 12.3 min at a pressure of 242 MPa. When the sample was quenched, solid particles and gas formed. On the other hand, at 272°C constant temperature (Fig. 5, run 11) at higher pressures, the nylon 6/6 seemed to become highly crystalline in appearance and the nylon particle did not melt. When the sample was quenched as before, no additional solid particles or gas was produced. Examination of the Raman analyses for the two runs (Fig. 8, runs 8 and 11) showed that more of the nylon 6/6 had reacted, as can be seen by the ratio of the C—H ( $2904\text{ cm}^{-1}$ ) stretching to that of the C—H ( $2922\text{ cm}^{-1}$ ) stretching and also by the smaller amine N—H ( $3303\text{ cm}^{-1}$ ) peak for each run. This led us to the conclusion that at higher pressures primarily a liquid product must be formed since no solid particle precipitates were produced upon quenching and, further, since the Raman measurements indicated a smaller amine N—H ( $3303\text{ cm}^{-1}$ ) peak.



**Figure 10** Pressures during reaction for isothermal (272°C) heating of nylon 6/6 + water solutions (runs 7–11). Reaction time is approximately 11.7 min.

At the higher pressures (500–848 MPa), any gas produced might be soluble in the liquid phase. However, no solid precipitates were produced at those conditions, which confirms that degradation solids were not produced. Kabyemela et al.<sup>20</sup> and Adschiri et al.<sup>21</sup> reported for the case of biopolymers, such as cellulose and cellulose oligomers, that homogeneous reaction conditions may be the reason for high conversions obtained in supercritical water. In the examples reported here, however, reactions at higher pressures (>500 MPa) under heterogeneous conditions gave higher liquid product yields than those under homogeneous conditions at lower pressures.

For each of the isothermal reactions (runs 7–11), pressure was measured at 30-s intervals as shown in Figure 10. At the lower average pressures of 113–299 MPa (Table II), pressure tended to increase with time. This is also true for run 7 if the first few points are disregarded, since this was probably an artifact of the DAC pressure-adjustment process. At higher pressures ranging from 520 to 894 MPa (Table II), the pressure tended to decrease with time. The Raman spectra of the residues formed at the higher pressures had an additional peak at 2970  $\text{cm}^{-1}$  (Fig. 8). These data, along with the Raman spectra, clearly show that there is a moderate pressure effect on the nylon 6/6 + water reaction. The higher pressures seem to promote the decomposition of nylon to liquid or solid products.

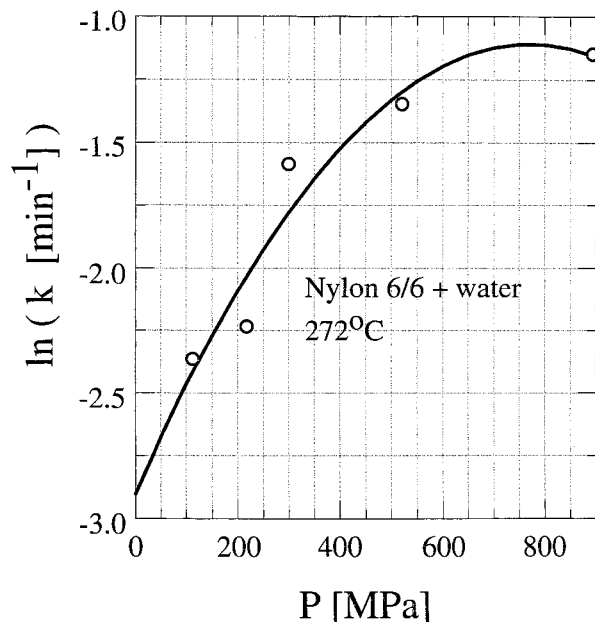
### Activation and Reaction Volumes

The data in the previous section can be interpreted in terms of activation and reaction volumes in solution.<sup>22</sup> The activation volume  $\Delta V^*$  is defined as the derivative of the reaction rate constant with pressure at constant temperature:

$$\Delta V^* = -RT(\partial \ln k / \partial P) \quad (5)$$

where  $\Delta V^*$  is the activation (partial molar) volume and  $k$  is the reaction rate. Based on this method of analysis, after the basic form of the rate law is established, the rate constant is measured over a range of pressures. Then, the data are plotted as  $\ln k$  versus  $P$  and the fitted equation is extrapolated to zero pressure. For this method of analysis, detailed kinetic data are required.

In this work, Raman analyses could only be made at the completion each experiment. However, by holding the reaction time and tempera-



**Figure 11** Apparent first-order rate constant plotted versus reaction pressure for nylon 6/6 + water reaction at 272°C.

ture constant, it is possible to estimate the reaction volume. In the Raman spectra for runs 7–11 (Fig. 8), a second C—H stretching appears at 2904  $\text{cm}^{-1}$  that is not present in the standard nylon 6/6 sample C—H stretching (2922  $\text{cm}^{-1}$ ). In this work, we used the (C—H at 2904  $\text{cm}^{-1}$ )/(C—H at 2922  $\text{cm}^{-1}$ ) ratio as an indication of the polymer conversion. Assuming that the change in the peak height ratio is directly proportional to conversion, each pressure provides a single apparent first-order reaction rate constant for the given time and initial concentration (25–40 wt %). Each rate constant can be plotted as a function of pressure as shown in Figure 11. To determine the activation volume, an equation is fitted to the data and the equation is extrapolated to zero pressure. The form of the equation that we chose was

$$\ln k = a + bP + cP^2 \quad (6)$$

where  $a$ ,  $b$ , and  $c$  are constants. The constants determined were  $a = -2.902$ ,  $b = 4.6466 \times 10^{-3} \text{ MPa}^{-2}$ , and  $c = -3.0209 \times 10^{-6} \text{ MPa}^{-2}$ , with  $k$  in  $\text{min}^{-1}$ . The reaction volume determined from eq. (6) after differentiation and extrapolation to zero pressure was  $-21.1 \text{ cm}^3/\text{mol}$ . This value is interpreted as follows: In general, bond forming gives a negative activation volume since there is a reduction in volume or packing and bond breaking

gives a positive activation volume since there is an increase in volume or the number of moles.<sup>23</sup> The degradation process, in general, should result in an increase in volume. However, during the degradation, there are a significant number of bond-forming processes. Many of the new components formed are miscible with the aqueous phase at the given conditions.

The data show typical behavior with a negative slope that tends to zero at high pressures.<sup>22</sup> At lower pressures (runs 7–9), slopes were slightly positive. At higher pressures (runs 10 and 11), the slopes were slightly negative. In terms of eq. (5), this means that competing pathways exist in the two different pressure regions, 100–300 MPa and 500–900 MPa. Whether these pathways are controlled by diffusion, viscosity, or other effects is not known at this point.

### Degradation Mechanisms

Degradation mechanisms for nylon 6/6 were summarized in detail by Thanki and Singh.<sup>24</sup> A model for the degradation of nylon 6/6 was proposed by Steppan et al.<sup>25</sup> In that work, it was noted that temperatures of 250–290°C are high enough to result in considerable nylon degradation. Further, if a significant amount of water is present during the degradation, then a large number of free amine groups will be present. These amine groups can combine and react with carboxylic acid groups to form a crosslink. In their work, reaction times were on the order of hours, whereas in this work, reactions were on the order of minutes. Considering the reaction time differences between their work and this work, the high-pressure conditions and, especially, the high-temperature conditions greatly accelerate the nylon 6/6 degradation. Steppan et al.<sup>25</sup> reported that during steam degradation the number of carboxylic acid groups decreased with time. In our measurements, carboxylic acid C=O stretching, if present, could not be observed with Raman, which may be due to the dilute nature of the components in solution.

In the above studies, thermal degradation studies yield carbon dioxide and ammonia. In our studies, we only noted gas in runs that were heated to subcritical temperatures (runs 4, 7–9). To some extent, however, if gases are formed, they may be soluble in the aqueous phase.

### CONCLUSIONS

Aqueous solutions of nylon 6/6 ranging from 11 to 31% polymer become homogeneous at temperatures from 330 to 340°C over pressures ranging from 30 to 230 MPa. Nylon 6/6 is very active in water and decomposes readily. At subcritical conditions, nylon reacts and usually forms solid particles and gas. In supercritical water, nylon reacts to form primarily liquid products without the formation of gas.

From isothermal experiments at 272°C at a 12.3-min reaction time, samples heated at lower pressures (<300 MPa) became homogeneous, whereas samples heated at higher pressures (>500 MPa) became more crystalline in appearance and remained heterogeneous. By Raman analysis, conversion of nylon increased with pressure, which suggests that heating nylon at higher pressures promotes the decomposition of nylon to liquid or water-soluble products. The isothermal reactions were analyzed to give estimates of the activation volume. From the analysis, the reaction volume was  $-21.1 \text{ cm}^3/\text{mol}$ , which can be explained by the overall formation of water-soluble products. Detailed kinetic studies are needed for many other polymer–water systems.

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