

# Phase Behavior and Kinetics of Polystyrene Degradation in Supercritical Toluene

H. Jie, H. Ke, T. Lihua, W. Jiachun, Z. Zibin, Y. Weiyong

*Institute of Chemical Technology, East China University of Science and Technology, Shanghai 200237, China*

Received 2 November 2006; accepted 12 February 2008

DOI 10.1002/app.28405

Published online 3 June 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The phase behavior of polystyrene (PS) degradation in toluene was investigated in a visual high-pressure reactor. The system of PS and toluene was heated from room temperature and atmospheric pressure to 350°C and 5.0 MPa. It was observed that during this process, PS dissolved quickly, and then, the system appeared to be a homogeneous phase, and PS degradation occurred in this system. With another high-pressure batch reactor, PS degradation was studied in the temperature range 275–360°C and the pressure ranges 4.5–10.5 MPa. The drop-in molec-

ular weights in the temperature ranges and the amount of PS converted into volatile products were observed. Moreover, the effects of the temperature, pressure, and ratio of toluene to PS on the rate of PS degradation are discussed. The kinetic studies showed that the rate of PS degradation in supercritical toluene increased substantially because the degradation occurred in a homogeneous phase. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3596–3602, 2008

**Key words:** degradation; polystyrene

## INTRODUCTION

The exploration of supercritical fluids as solvents and reaction media for polymer degradation has attracted particular interest during the past decade.<sup>1–4</sup> Because of their unique physical and chemical properties, supercritical fluids have many advantages when used in polymer degradation, such as reaction in the homogeneous phase and high decomposition rates.<sup>5,6</sup> Several articles have been concerned with the thermal degradation of polystyrene (PS) in supercritical water, which have implied that supercritical water affects the course of PS degradation significantly and leads to much higher yields in the monomer than those observed without water.<sup>3,4,7</sup> Fang and Kozinski<sup>4</sup> studied the phase behavior of PS decomposition in supercritical water using a diamond anvil cell. However, their results show that little of the PS sample was dissolved in water until it was depolymerized into volatile products; that is, two heterogeneous liquid phases of water and molten PS were present throughout the entire degradation process. Compared with water, the application of organic solvents as supercritical media to decompose PS has additional advantages. In general, organic solvents have mild critical conditions and dissolve PS easily. Karaduman et al.<sup>8</sup> used various organic solvents as supercritical media to decompose PS and obtained high conversions of PS degradation. Hwang et al.<sup>9</sup> studied PS

degradation in supercritical *n*-hexane and investigated the effects of the temperature, pressure, and ratio of solvent to PS on the conversion of PS.

PS degradation is a typical radical chain process and includes random scission, depolymerization, recombination, hydrogen abstraction, and other reactions. It is well known that when the temperatures are lower than about 300°C, PS degradation takes place with negligible volatile products and the result of degradation is a decrease in the molecular weight. However, when PS degradation is carried out at higher temperatures, a drop in the molecular weight followed by a drop in the amounts of volatile products have been observed.<sup>10–12</sup>

On the basis of the mechanism of PS degradation, the kinetics has been studied extensively. It is widely accepted that the kinetics of PS degradation in the range 300–400°C follow the first order.<sup>13–16</sup>

The conversion (*c*) can be calculated from the following equation:

$$c = (1 - m/m_0) \times 100\% \quad (1)$$

where  $m_0$  is the weight of PS at the initial time (*g*) and  $m$  is the weight of the dried residual solid at time *t*. The first-order rate equation is defined as

$$\frac{dc}{dt} = k(1 - c) \quad (2)$$

where  $k$  is the apparent rate constant of PS degradation. The rate constant may be evaluated from the integrated form of eq. (2):

Correspondence to: H. Ke (ecusthk@163.com).

$$-\ln(1 - c) = kt \quad (3)$$

Moreover, a decrease in the molecular weight of PS has been observed during the process of degradation. On the basis of the mechanism of PS degradation, Sterling et al.<sup>17</sup> developed a general model for PS degradation at low temperatures by concurrent random scission and depolymerization reaction with continuous distribution kinetics. The rate constant of the random scission reaction ( $k_r$ ) can be calculated by the following equation:

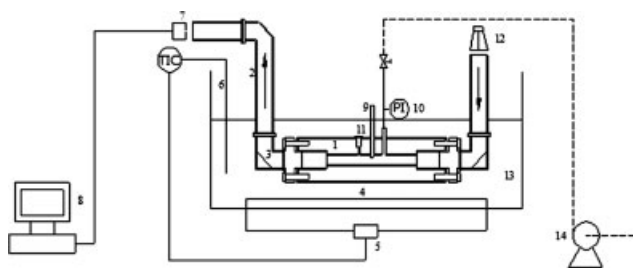
$$1/M_n = 1/M_{n0} + k_r t \quad (4)$$

where  $M_{n0}$  and  $M_n$  are the number-average molecular weights of PS at zero and at time  $t$ , respectively. We proposed a quick-depolymerization assumption and used continuous distribution kinetics to determine the reaction rate coefficients for PS degradation at high temperatures.<sup>18</sup> Our result indicate that  $M_n$  of PS followed the same trends when the degradation was carried out at high temperatures.

Although PS degradation has been investigated with different organic solvents as supercritical media, less information about the phase behavior and kinetics of PS degradation in supercritical organic solvents has been reported. In our previous study,<sup>19</sup> we examined PS degradation in different supercritical solvents and found that toluene was the most effective supercritical solvent for the recovery from PS among the solvents used in our experiments. In this study, we aimed first to investigate experimentally the phase behavior of PS degradation in supercritical toluene; second to investigate the degradation dependence on the temperature, pressure, and ratio of toluene to PS; and third to investigate the kinetics of PS degradation.

## EXPERIMENTAL

Figure 1 shows the schematic diagram of the apparatus used to observe the phase behavior of PS degradation in supercritical toluene. It consists mainly of a high-pressure visual reactor, a constant-temperature salt bath ( $\text{KNO}_3$  and  $\text{NaNO}_2$ ), a vacuum pump, a pickup camera, and a computer. The reactor, with a volume of  $4 \text{ cm}^3$ , was composed of a stainless body and two quartz windows and was heated by salt bath. The design temperature and pressure of this reactor were  $400^\circ\text{C}$  and  $12 \text{ MPa}$ , respectively. The temperature was maintained by a temperature controller in conjunction with a thermocouple immersed in the salt bath. To avoid the effect of atmosphere on PS degradation, the atmosphere in the reactor was extracted by a vacuum pump after  $0.2 \text{ g}$  of PS (number-average molecular weight =  $88,700$  and weight-average molecular weight =  $265,000$ ) was fed, and then, toluene was



**Figure 1** Schematic diagram of the apparatus used to observe the phase behavior of the PS degradation in supercritical toluene: (1) reactor, (2) tube for light, (3) refractor, (4) heater, (5) temperature controller, (6) thermocouple, (7) pickup camera, (8) computer, (9) thermowell, (10) pressure pickup, (11) feed inlet, (12) light, (13) salt bath, and (14) vacuum pump.

input by the negative pressure. The amount of toluene was determined by the ratio of toluene to PS (10/1). The reactor was immersed in the salt bath, and the thermocouple and pressure indicator were used to detect the temperature and pressure of the reaction system. The pickup camera and computer were used to observe and store the phenomenon inside the reactor. When the reaction ended, the reactor was taken out and immersed quickly in water.

The apparatus used to investigate the effects of the temperature, pressure, and ratio of toluene to PS on PS degradation was shown in detail elsewhere.<sup>19</sup> The pressure of system, measured with pressure transducers within an error of  $\pm 0.1 \text{ MPa}$ , was controlled by the amount of injected solvent at the given temperature. It took less than  $5 \text{ min}$  to reach the predicted temperature and pressure, and the typical temperature and pressure curves for PS degradation were shown elsewhere.<sup>19</sup> PS degradation in supercritical toluene gave mainly liquid products with a negligible amount of gas. The liquid products were vacuum-distilled, and the residue was weighted to calculate the PS conversion with an absolute error of  $4.0 \text{ wt } \%$ . A certain amount of residue, including oligomers and PS not degraded completely, was diluted in tetrahydrofuran (Fisher high performance liquid chromatography grade) and analyzed with HPLC–gel permeation chromatography (GPC). The HPLC system consisted of gradient pump that pumped tetrahydrofuran at a flow rate of  $1 \text{ mL/min}$  and an online UV detector. The GPC system (Waters Co., Shanghai, China) consisted of three gel columns with different sizes and an online refractive-index detector. The chromatograph of the sample injected in the HPLC–GPC provided the molecular weight versus retention time.

## PHASE BEHAVIOR OF PS DEGRADATION IN SUPERCRITICAL TOLUENE

Figure 2 shows the visual observation of PS degradation in toluene. The reaction system consisted of gas,

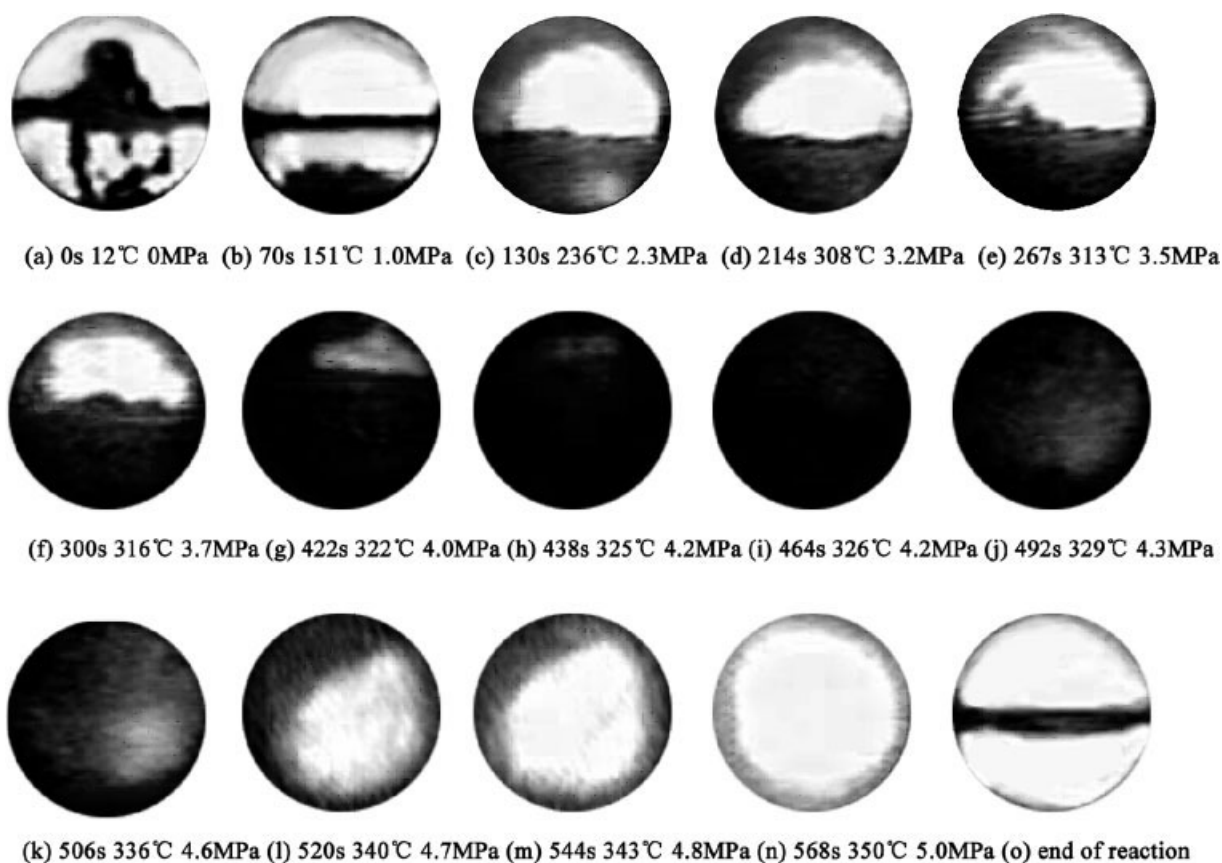


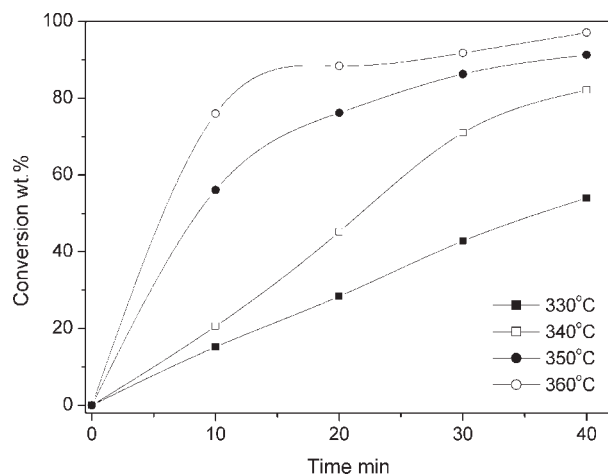
Figure 2 Phase behavior of the PS degradation in supercritical toluene.

liquid, and PS particles at room temperature and atmospheric pressure [Fig. 2(a)]. The reactor was heated by a salt bath, and PS melted and dissolved quickly into toluene [Fig. 2(b)]. After PS dissolved completely, the opalescence phenomenon was observed in the liquid phase; that is, the liquid phase looked like a dense fog [Fig. 2(c)]. With increasing temperature, the meniscus level gradually ascended [Fig. 2(c–h)] and then disappeared at the top of the optical cell [Fig. 2(i)] when the temperature and pressure reached 326°C and 4.2 MPa, respectively, which were above the critical temperature and pressure of toluene ( $T_c = 318.7^\circ\text{C}$ ,  $P_c = 4.11$  MPa). At this time, the reactor was full of solution, which indicated that the system appeared to be a homogeneous phase. During the process, critical opalescence was observed only in the liquid phase, which meant the temperature and pressure were near the critical parameters. When the temperature was higher than 326°C, the cross section of the reactor became more and more light [Fig. 2(j–n)]. As the reactor was heated to 350°C and held for 20 min, the system appeared to be transparent [Fig. 2(n)], and PS degradation occurred in this homogeneous phase. After cooling, two gas–liquid phases reappeared [Fig. 2(o)].

## CONVERSION OF PS DEGRADATION

### Effect of the parameters on the conversion of PS degradation

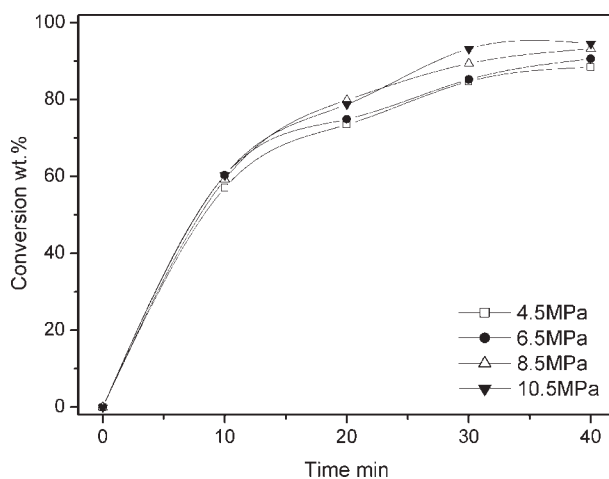
The conversion of PS decomposed in supercritical fluids depends on many factors, including as temperature, residence time, pressure, and solvents. To investigate how the reaction temperature and residence time impacted the PS degradation, experiments were carried out in the temperature range 330–360°C. The amounts of toluene used were about 12, 11.5, 11, and 10.5 g at 330, 340, 350, and 360°C, respectively, to keep the pressure fixed at 4.5 MPa. The amount of PS used was determined by the ratio of toluene to PS (10/1). As shown in Figure 3, the conversion of PS increased quickly with increasing temperature. The conversion of PS increased from 42.8% at 330°C to 91.8% at 360°C with a residence time of 30 min. The conversion of PS reached very high values in the first stage of the reaction, that is, within 20 min, at 350 and 360°C; then, the conversion increased slowly with longer residence time. Although the degradation was carried out at 340°C, the conversion increased from 20.6% at 10 min to 82.1% at 40 min.



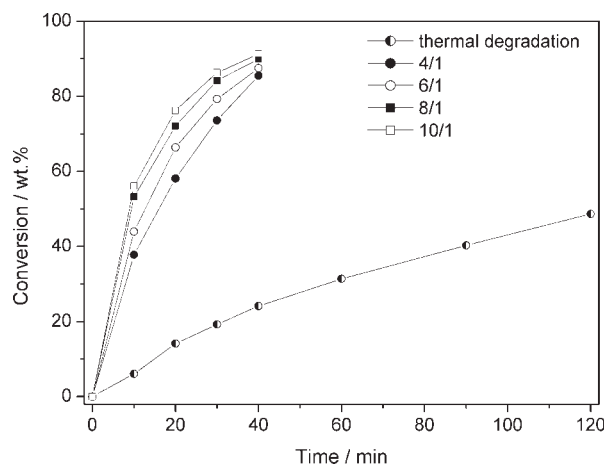
**Figure 3** Conversion of PS versus the residence time at different temperatures (reaction pressure = 4.5 MPa, toluene/PS ratio = 10/1).

The effect of pressure on the PS conversion was studied in the pressure range 4.5–10.5 MPa at 350°C. The amounts of toluene used were about 11, 11.5, 12, and 12.5 g, and the amounts of PS used were determined by the ratio of toluene to PS (10/1). As shown in Figure 4, the conversion increased slightly as the pressure increased. This result implies that the pressure had a smaller influence on the PS conversion than the temperature. We also studied the variation of the conversion with the ratio of toluene to PS. The amounts of PS were about 1.10, 1.38, 1.83, and 2.75 g with ratios of 10/1, 8/1, 6/1, and 4/1, respectively, when the amount of toluene was 11 g.

As depicted in Figure 5, the conversion fell drastically with the decrease in solvent-to-PS ratio. The conversion dropped from 76.2% at a ratio of 10/1 to 58.1% at a ratio of 4/1 for 20 min. The thermal deg-



**Figure 4** Conversion of PS versus the residue time at different pressures (reaction temperature = 350°C, toluene/PS ratio = 10/1).



**Figure 5** Conversion of PS versus the residence time at different ratios (reaction temperature = 350°C, reaction pressure = 4.5 MPa).

radation of PS without solvents was carried out to compare it with supercritical degradation. The conversion of PS in supercritical toluene was much higher than that of thermal degradation without solvents because PS degradation in supercritical toluene occurred in the homogeneous phase, which could have increased the reaction rate substantially.

### Kinetics of PS degradation

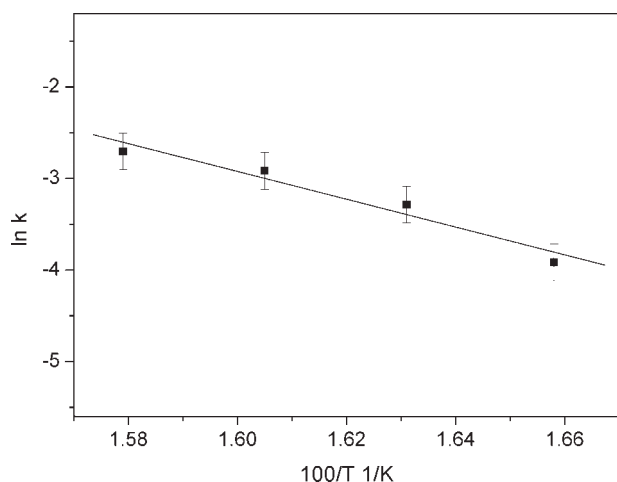
#### Temperature dependence of PS degradation

Many studies of PS degradation have demonstrated that temperature is the most key parameter affecting the degradation rate. According to eq. (3),  $k$  can be calculated from the linear plot of  $-\ln(1 - c)$  versus  $t$  at different temperatures. The dependence of  $k$  for PS degradation in supercritical toluene on the temperature ( $T$ ) is expressed by the following Arrhenius equation:

$$\ln k = \ln A - E/RT \quad (5)$$

where  $A$  is the frequency factor,  $E$  is the activating energy, and  $R$  is the gas constant.

The activation energy of PS degradation in supercritical toluene was obtained experimentally from the slope of a plot of  $\ln k$  versus  $1/T$ , as depicted in Figure 6, which was equal to  $126.9 \pm 0.9$  kJ/mol. In this study, the activation energy obtained from the supercritical region (330–360°C) was lower than the 175.9 kJ/mol obtained from the subcritical and supercritical regions (310–370°C) in our previous study.<sup>18</sup> Moreover, the activation energy in this study was lower than previously reported thermolysis values, which varied between 133 and 290 kJ/mol.<sup>15,16</sup> Compared with thermal degradation without solvents, PS degradation in supercritical toluene was in the homogeneous phase, which should have decreased the activation energy.

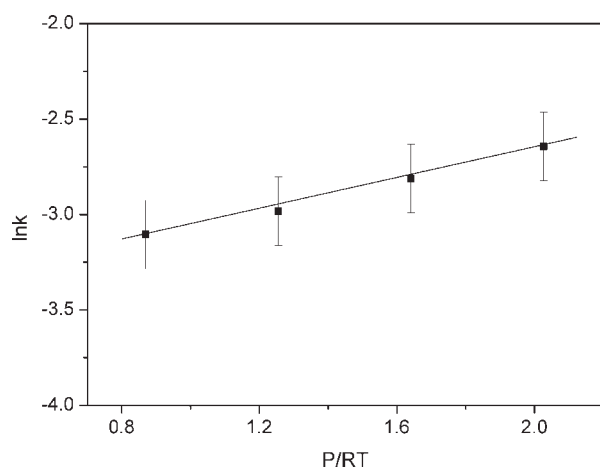


**Figure 6** Plot of  $\ln k$  versus  $1000/T$  at different temperatures.

#### Pressure dependence of PS degradation

The effect of the pressure on the rates of chemical reactions occurring in solution was studied earlier, and the fundamental theory and equations were transferred to chemical reactions conducted in supercritical fluids.<sup>20</sup> Increasing pressure leading to changes in the rates of chemical reaction may be summarized by a change in physical properties, such as viscosity, and a direct effect on the chemical reaction. The transition state theory used to explain the process of chemical reaction gives a relation between the chemical reaction rate constant and activation volume. The activation volume difference ( $\Delta V^\ddagger$ ) is given by the pressure derivative of the rate constant  $k$  and describes the kinetics pressure effect:

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^\ddagger}{RT} \quad (6)$$



**Figure 7** Plot of  $\ln k$  versus  $P/RT$  at  $350^\circ\text{C}$ .

Figure 7 shows  $\ln k$  as a function of  $P/RT$ , which falls on a straight line. Thus, PS degradation in supercritical toluene had a negative  $\Delta V^\ddagger$  equal to  $-273.2 \pm 63.1 \text{ cm}^3/\text{mol}$ . Moreover, this value was constant in the studied range of pressures. Equation (7) shows the dependence of  $k$  of PS degradation on the pressure:

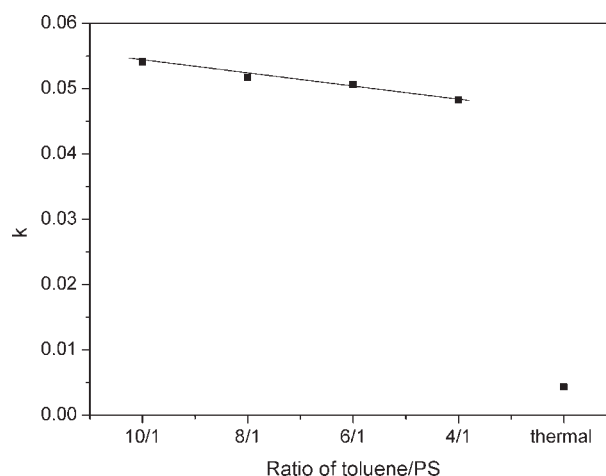
$$\ln k = -3.240 + 0.2732 \frac{P}{RT} \quad (7)$$

where  $P$  is the reaction pressure.

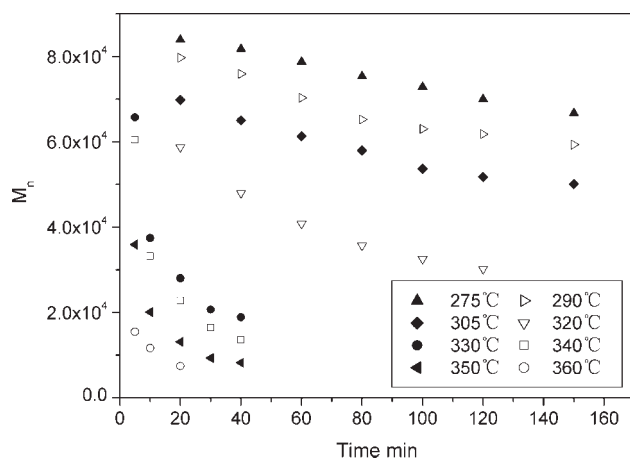
The process of PS degradation in supercritical toluene included nearly every type of radical reaction, and the solvent affected the reaction rate and activation volume. It was a rather difficult matter to extract the activation volume for any single step. Therefore, we can only give the values of  $\Delta V^\ddagger$  for the overall process of PS degradation, and more work should be done to investigate the influence of pressure on the PS degradation in supercritical fluids.

#### Dependence of PS degradation on the toluene/PS ratio

The ratio of toluene to PS also affected the rate of the chemical reaction, which is substantially important when polymer degradation is studied in solvents. The studies were carried out with an initial ratio of toluene to PS ranging from 10/1 to 4/1 at  $350^\circ\text{C}$ , and the rate constants at different ratios are depicted in Figure 8. It was clear that the rate constants of PS degradation dropped gradually with the decreasing ratio of toluene to PS. This result reflects that a decrease in the proportion of toluene increased the viscosity of the reaction system, which might have decreased the overall degradation rate.



**Figure 8** Plot of  $k$  versus the toluene/PS ratio at  $350^\circ\text{C}$ .



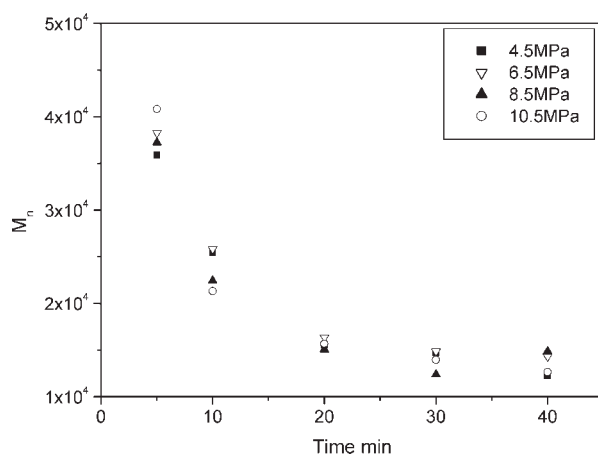
**Figure 9** Variation of  $M_n$  of PS versus the time at different temperatures.

Moreover, the rate constant of PS degradation without solvents was only about one-tenth of that of PS degradation in supercritical toluene. This meant that the use of supercritical solvents to decompose PS could substantially accelerate the reaction rate.

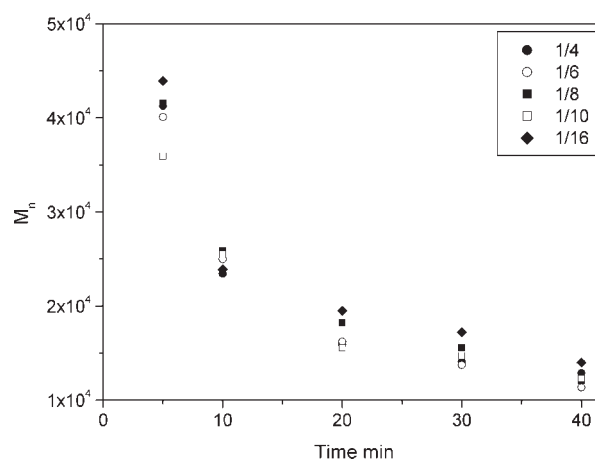
### CHANGES IN MOLECULAR WEIGHT

#### Effects of the reaction parameters on the decrease in $M_n$

During the process of PS degradation in supercritical toluene, as mentioned previously, random scission reactions took place in the main chain of PS, which led to a decrease in the molecular weight. Figure 9 shows the trends of  $M_n$ , depending on the reaction time, at temperatures varying from 275 to 360°C.  $M_n$  of PS dropped slowly in the subcritical region (275–320°C), whereas it decreased rapidly in the supercritical region (320–360°C). The explanation of this



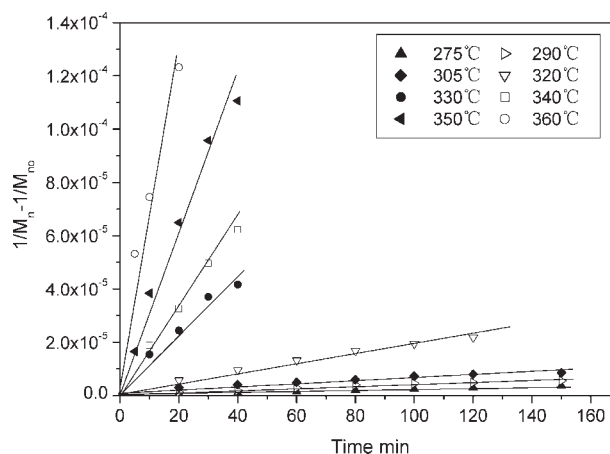
**Figure 10** Effect of pressure on the change in  $M_n$  of PS (350°C).



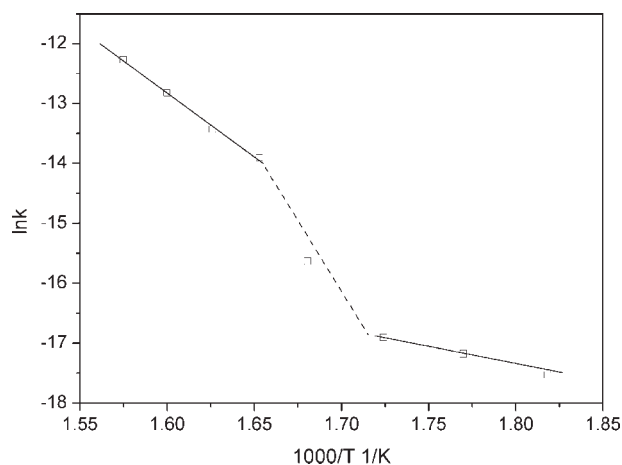
**Figure 11** Effect of the ratio on the change in  $M_n$  of PS (350°C).

result was that the rate of random scission reactions increased with increasing temperature. Moreover, PS converted into volatile products through unzipping reactions when the reaction temperature was above about 320°C, which also promoted the decrease in  $M_n$ .

It is known that the pressure and ratio of toluene to PS can lead to a significant increase in the conversion of PS degradation. However, as depicted in Figure 10, the pressure was changed from 4.5 to 10.5 MPa at an interval of 2 MPa, but  $M_n$  of PS showed no obvious variation as the pressure was increased. Furthermore, Figure 11 indicates that increasing the ratio of solvent to PS did not affect the change in  $M_n$ . These results imply that compared with temperature, the pressure and ratio of solvent to PS had a negligible influence on the rate of the random scission reaction. According to the complexity of PS degradation, the effects of the pressure and ratio of



**Figure 12** Plot of  $1/M_n - 1/M_{n0}$  versus  $t$  used to determine  $k$ , at various temperatures.



**Figure 13** Arrhenius plot of  $\ln k$  versus  $1000/T$ .

PS to solvent on the degradation process are not yet fully understood.

### Kinetics of PS degradation

PS degradation was observed in the studied temperature range, as shown by the decreasing molecular weight. On the basis of the theoretical model, the rate coefficients of random scission reaction were calculated from the slope of  $1/M_n - 1/M_{n0}$  plotted versus time. Figure 12 clearly shows that the  $k_r$  values at the reaction temperatures 330–360°C were much higher than those at 275–305°C. Also known was the temperature dependence of the rate coefficients in an Arrhenius plot, as shown in Figure 13. Obviously, the plot was jumping around the temperature (305–320°C), which was near the critical temperature of toluene (318.7°C). The activation energy calculated from the slope of the temperature region between 275 and 305°C was only 55.6 kJ/mol, whereas the activation energy at 330–360°C was 176.4 kJ/mol. This could be explained because in the temperature range above 320°C, PS degradation in supercritical toluene occurred in the homogeneous phase, which substantially increased PS degradation. Another reason for this result was that depolymerization reactions took place above 320°C, which sped the decrease in  $M_n$ .

### CONCLUSIONS

The phase behavior of PS degradation in supercritical toluene was investigated, which showed that the system of toluene and PS formed a homogeneous reaction environment when the temperature was above the critical temperature of toluene.

In temperature range 330–360°C, the amounts of PS converted into volatile products and the conver-

sion of PS were dependent on the temperature, pressure, and ratio of toluene to PS. The kinetic studies indicated that the degradation rate increased with the increase in temperature and pressure, and the activation energy and the activation volume were determined to be  $126.9 \pm 0.9$  kJ/mol and  $-273.2 \pm 63.1$  cm<sup>3</sup>/mol, respectively. Furthermore, the rate constant of PS degradation without solvents was only about one-tenth that of PS degradation in supercritical toluene, and increasing the ratio of toluene/PS might have increased the degradation rate. This reflected that PS degradation in supercritical toluene occurred in the homogeneous phase, which substantially accelerated the reaction rate.

During the process of PS degradation, a decrease in  $M_n$  was observed in the studied temperature range. However, in the supercritical region,  $M_n$  dropped substantially, whereas  $M_n$  dropped slowly in the subcritical region. Consequently, the activation energy of random scission reactions at 275–305°C was 55.6 kJ/mol, and the activation energy at 330–360°C was 176.4 kJ/mol. This result also reveals that PS degradation in supercritical toluene can substantially increase the reaction rate.

### References

1. Watanabe, M.; Hirakoso, H.; Sawamoto, S.; Adschiri, T.; Arai, K. *J Supercrit Fluid* 1998, 13, 247.
2. Tagaya, H.; Katoh, K.; Kadokawa, J.; Chiba, K. *Polym Degrad Stab* 1999, 64, 289.
3. Lilac, W. D.; Lee, S. *Adv Environ Res* 2001, 6, 9.
4. Fang, Z.; Kozinski, J. A. *J Appl Polym Sci* 2001, 81, 3565.
5. Fang, Z.; Smith, R. L.; Inomata, J. H.; Arai, K. *J Supercrit Fluid* 1999, 15, 229.
6. Werner, H. H. *Chemosphere* 2001, 43, 123.
7. Bertini, F.; Audisio, G.; Beltrame, P. L.; Bergamasco, L.; Castelli, A. *J Appl Polym Sci* 1998, 70, 2291.
8. Karaduman, A.; Emir, H. S.; Burhanettin, C.; Ali, Y. B. *J Anal Appl Pyrol* 2002, 62, 273.
9. Hwang, G. C.; Choi, J. H.; Bae, S. Y.; Hidehiro, K. *Korean J Chem Eng* 2001, 18, 854.
10. Gupta, M. C.; Nath, J. D. *J Appl Polym Sci* 1980, 25, 1017.
11. Cameron, G. G.; McWalter, I. T. *Eur Polym J* 1982, 18, 1029.
12. Chiantore, O.; Guaita, M.; Grassie, N. *Polym Degrad Stab* 1985, 12, 141.
13. Nishizaki, H.; Yoshida, K.; Wang, J. H. *J Appl Polym Sci* 1980, 25, 2869.
14. Lehrle, R. S.; Peakman, R. E.; Robb, J. C. *Eur Polym J* 1982, 18, 517.
15. Simard, Y. D. M.; Kamal, M. R.; Cooper, D. G. *J Appl Polym Sci* 1995, 58, 843.
16. Carrasco, F.; Pages, P. *J Appl Polym Sci* 1996, 61, 187.
17. Sterling, W. J.; Walline, K. S.; McCoy, B. J. *Polym Degrad Stab* 2001, 73, 75.
18. Ke, H.; Lihua, T.; Zibin, Z.; Weiyong, Y. *J Anal Appl Pyrol* 2006, 76, 186.
19. Ke, H.; Lihua, T.; Zibin, Z.; Chengfang, Z. *Polym Degrad Stab* 2005, 89, 312.
20. Savage, P. E.; Gopalan, S.; Mizan, T. I.; Martino, C. J.; Brock, E. E. *AIChE J* 1995, 41, 1723.