Characteristics and Kinetics of Degradation of Polystyrene in Supercritical Water

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ABSTRACT: The degradation of polystyrene (PS) in sub- or supercritical water was carried out at reaction temperatures ranging from 370°C to 420°C and pressures of 240 to 320 bar. At 370°C, where water is in a subcritical state, the degradation was in equilibrium in about 5 min, whereas at 380°C and 390°C, where water is in a supercritical state, it was completed in 15 and 3 min, respectively. The equilibrium conversion in the supercritical state (100 wt %) was higher than that in the subcritical water (ca. 80 wt %). The dependence on time of selectivity for the degradation products—styrene monomer, styrene dimer, styrene trimer, toluene, ethyl benzene, isopropyl benzene, and triphenyl benzene—were investigated at 400°C and 280 bar. As the reaction proceeded, selectivity for styrene monomers, dimers, and trimers decreased, whereas that for toluene, ethyl benzene, and isopropyl benzene increased because of the diffi-

culty of decomposing the benzene rings and phenyl radicals. Triphenyl benzene increased with reaction time for the same reason. With increasing temperature, selectivity for the styrene monomers and dimers decreased slightly, whereas selectivity for toluene and ethyl benzene increased a little. The kinetic behavior of PS in supercritical water along with supercritical acetone and *n*-hexane were investigated. The degradation processes of PS in such supercritical fluids could be formulated by the first-order kinetic law at the initial stage of the reaction. The activation energy for the degradation in supercritical water was evaluated to be 157 kJ/mol compared to an activation energy of 132 kJ/mol in the supercritical *n*-hexane. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 695–700, 2006

Key words: degradation; kinetics; polystyrene

INTRODUCTION

In recent years chemical recycling of waste plastics has been gaining interest as a means of obtaining valuable products. Waste plastics are treated chemically to recover low-molecular-weight monomers or other useful compounds. Many studies on the degradation of various plastics in supercritical water, methanol, and other organic solvents have been published, and supercritical fluids have been proven to be promising reaction media. Supercritical fluids have properties of both the liquid and gas phases. A supercritical fluid possesses a density close to that of liquid and has the ability to dissolve many components, whereas its high diffusivity and low viscosity enable it to behave in a manner similar to gas. Koll and Metzger used supercritical acetone to study the degradation of cellulose and chitin.[1] Dhawan et al. decomposed polyisoprene and waste rubber using supercritical toluene.[2] Watanabe et al. compared the results of general thermolysis with those of supercritical fluid degradation.[3] They used both technologies to disintegrate polyeth-

ylene, which accounts for most waste plastics. The experimental temperature in that study ranged from 400°C to 450°C. They found that the supercritical fluid method produced hydrocarbon products composed of shorter carbon chains and exhibited a higher ratio of 1-alkene to *n*-alkane than that yielded through general thermolysis.

Supercritical water techniques have been employed to degrade or reform high-molecular-weight hydrocarbons. Tagaya et al. carried out a decomposition reaction of polycarbonate in sub- and supercritical water to make clear reactivity of polycarbonate in water.[4] Their results indicated that subcritical water also is a superior medium for the decomposition reaction of polymeric compounds. Moriya and Enomoto conducted thermal cracking and supercritical cracking of polyethylene to compare the cracked products and their structures and yields.[5] The degradation mechanism of polyethylene and the contribution of supercritical water to degradation also were considered by analyzing the products in the aqueous phase after the reaction. Dai et al. carried out the decomposition reaction of polyol in supercritical water at a temperature of 380°C–430°C and a reaction time of 10–90 min to obtain the hydrolysis products hydroxyacetone and diols.[6] Smith et al. studied the phase behavior and reaction of nylon-66 in water using a diamond anvil

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cell technique and visual microscopy.[7] They concluded that the reaction pathways of subcritical and supercritical water were completely different. Furthermore, they discussed the relationship between reaction volume and activation energy, concluding that the rate of hydrolysis increased with increasing pressure. Takeshita et al. decomposed poly(vinyl chloride) plastics completely to form nonhalogenated plastics with water in saturated pressure and sub- and supercritical water.[8] They observed chlorine in poly(vinyl chloride)–dissolved organic compounds in the liquid and gas fractions after treatment at 300°C. Further decomposition at a temperature above 350°C in supercritical water produced acetone, phenol, benzene, benzene derivatives, and aliphatic alkane and alkene in the liquid and gas fractions. Supercritical water has been used as an inexpensive, nontoxic, and nonpolar solvent for the chemical recycling of polymer wastes.

It is well known that a kinetic investigation is very important for obtaining information necessary to rationally design a reactor for the degradation of plastics in supercritical fluids. Unfortunately, such factors as characteristic physicochemical properties, reaction conditions, complicated compositions of degradation products, and difficulty in continuous operation tend to limit the kinetic study of degradation in supercritical fluids.

Thus, in the present work, degradation of polystyrene (PS) was performed in supercritical states using a semibatch-type autoclave reactor. Supercritical water was shown to be a successful degradation medium for PS, in particular because of its relatively high selectivity for styrene monomer. The distribution of the products varied with the operational conditions. The degradation sequences were speculated about. A kinetic analysis of the process of degradation of PS in supercritical water, and the kinetic law was determined at the initial stage of the degradation and compared with that of similar degradation processes in supercritical *n*-hexane and acetone.

EXPERIMENTAL

The experimental apparatus designed for the degradation of PS in supercritical fluid is shown in Figure 1. The reactor, manufactured by Autoclave Engineers Co. (Erie, PA), was made of stainless steel 316 and had a volume of 1 liter. Its maximum attainable temperature and pressure were 427°C and 503 bar, respectively. A water-controlled condenser system was installed as an annex to the reactor to prevent the inevitable rapid rise in temperature during the reaction. The temperature of the reactor and electric furnace was controlled within a permissible range of ±1°C by using the temperature controller with a PID control (PC600 Series, Jung Kyung Instrument Co. Ltd., Korea). The check valve was used to prevent reflux of the
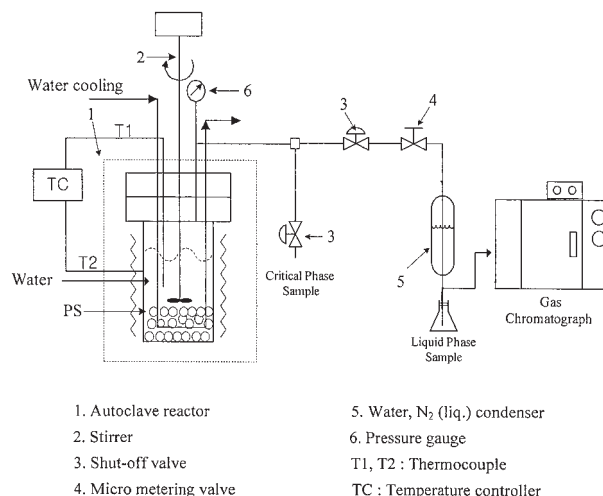

1. Autoclave reactor
2. Stirrer
3. Shut-off valve
4. Micro metering valve
5. Water, N₂ (liq.) condenser
6. Pressure gauge
T1, T2 : Thermocouple
TC : Temperature controller

Figure 1 Experimental setup for the degradation of PS in supercritical water.

fluid during the reaction. Given that the test was done under high pressure, a safety valve with a rupture disc outside was installed that could work at a pressure of up to 400 bar.

The sample tested was GPPS (general purpose polystyrene, HF-2660) manufactured by Jeil Industries, Inc. (Korea). The average molecular weight was about 220,000. The sample was transparent and column shaped, with diameter of 2.3–2.6 mm, height of 2.8–3.3 mm, and weight of 14–18 mg. The PS employed in the test is often used in manufacturing medical containers, toys, food containers, and furniture. Supercritical water was used as the supercritical fluid. The critical temperature and pressure of the water were 374°C and 217.7 bar, respectively.

Preliminarily, the PS sample was put in a 70°C oven for at least 24 h to make the sample dense and dry in order to reduce heat transfer resistance and to enhance heat and mass transfer efficiency. At room temperature, a 30-g portion of dried PS along with water was fed into the reactor. Argon gas purging was done at a volumetric flow rate of 200 cm³/min for 30 min in order to completely remove oxygen from the reactor and to make the test environment inert. The heating rate was maintained at 7°C/min until the prescribed temperature was reached. The agitation speed was adjusted to 300 rpm. The reaction pressure was controlled by changing the volume of water fed into the reactor. After reaching the prescribed reaction conditions, the reaction was continued for a predetermined time. After the reaction finished, the temperature of the reactor was rapidly lowered to room temperature by the cooling system using water. The reaction is believed to have proceeded very little during the cooling period. The products discharged from the reactor were recovered in the condenser using liquid nitrogen. The liquidlike product was separated from water
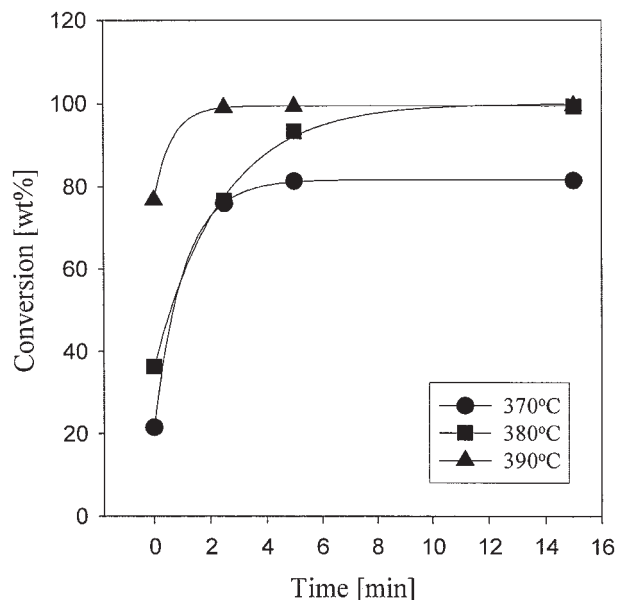
Figure 2 Dependence of conversion on time for the degradation of PS in sub- or supercritical water at 240 bar and temperatures of 370°C, 380°C, and 390°C.

Figure 3 TIC of liquid products for the degradation of PS in supercritical water at 420°C and 320 bar, with a reaction time of zero: (1) toluene, (2) ethyl benzene, (3) styrene monomer, (4) α-methyl styrene, (5) 1,3-diphenyl propane, (6) 1,3-diphenyl butane, (7) styrene dimer, (8) styrene trimer, (9) triphenyl benzene.

by a separate funnel. The solid residual substances inside the reactor were dissolved in acetone, recovered, and then dried in an oven to remove the solvent.

Qualitative and quantitative analyses of the liquidlike products were done by gas chromatography (GC-14A, Shimadzu, Japan) and GC-MS (Fisons 8000 series HRGC, MD800 MS, Italy).

RESULTS AND DISCUSSION

Degradation characteristics

First, the dependence on time of total conversion for the degradation of PS in sub- or supercritical water at a pressure of 240 bar and temperatures of 370°C, 380°C, and 390°C is shown in Figure 2. The reaction time was specified as zero when a prescribed temperature was reached. Accordingly, degradation occurred to some extent while the temperature was increasing to a prescribed one. At 370°C, where water is in a subcritical state, degradation was in equilibrium in about 5 min, and the equilibrium conversion reached about 80 wt %. At 380°C and 390°C, where water is in a supercritical state, degradation was completed in 15 and 3 min, respectively, and equilibrium conversion reached 100 wt % at both temperatures. Thus, equilibrium conversion was higher in supercritical water than in subcritical water. For a prescribed temperature above 400°C, conversion reached 100% before that temperature was reached by heating at a rate of 7°C/min.

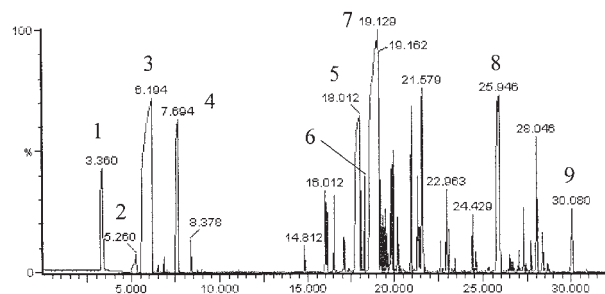After completion of the reaction, the liquidlike product was recovered by condensing. The liquid

products were analyzed by GC and GC-MS. The total ion chromatogram (TIC) of the liquid products is shown in Figure 3. Styrene monomers, styrene dimers, styrene trimers, α-methyl styrene, toluene, ethyl benzene, triphenyl benzene, and others were detected by GC-MS.

Figure 4 shows the dependence on time of the selectivity for the degradation products—styrene monomers, styrene dimers, styrene trimers, toluene, ethyl benzene, isopropyl benzene, and triphenyl benzene—at 400°C and 280 bar. As the reaction proceeded, the selectivity for styrene monomers, dimers, and trimers decreased, whereas the selectivity for toluene, ethyl benzene, and isopropyl benzene increased, suggesting that the latter should be produced by de-
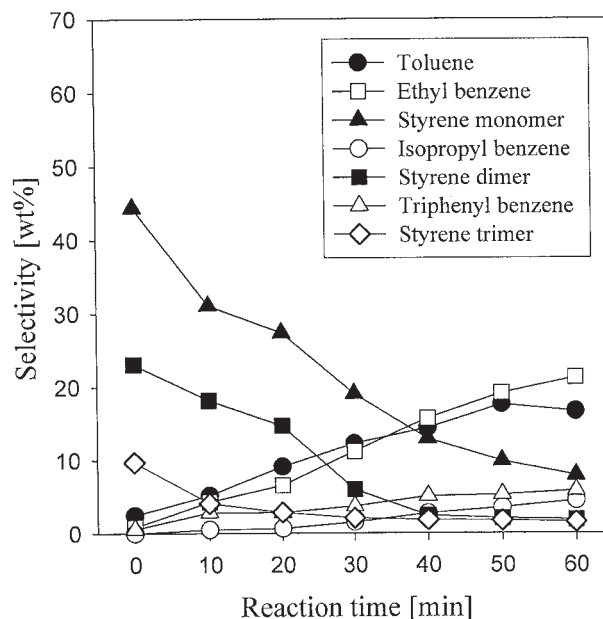

Figure 4 Dependence on time of the weight selectivity of the liquid products for the degradation of PS in supercritical water at 400°C and 280 bar.

composition of the former. It is hard to decompose triphenyl benzene, and it increases with reaction time. Taking the degradation products shown in Figures 3 and 4 into consideration, the degradation sequences can be speculated as follows:

Styrene trimers

- styrene trimer → styrene dimers + ethyl benzene
- styrene trimers → 1,3-diphenyl propane + α-methyl styrene
- α-methyl styrene → isopropyl benzene
- styrene trimers → 1,3-diphenyl butane + ethyl benzene

Styrene dimers

- styrene dimers → styrene monomers + ethyl benzene
- styrene dimers → α-methyl styrene + toluene
- α-methyl styrene → isopropyl benzene
- styrene dimers → 1,3-diphenyl butane

Styrene monomers

- styrene monomers → ethyl benzene, α-methyl styrene, toluene
- α-methyl styrene → isopropyl benzene

Phenyl radicals

- ph · → phenyl benzene → diphenyl benzene → triphenyl benzene

Though styrene dimers are not always produced from styrene trimers, the main route to styrene dimers may be from styrene trimers. To degrade styrene monomers, dimers, and trimers like these, a lot of hydrogen radicals are required. H radicals may be generated from supercritical water.

Variation in selectivity for styrene monomers, styrene dimers, styrene trimers, toluene, and ethyl benzene with reaction temperature at reaction times of 0 and 30 min is indicated in Figure 5(a,b), respectively. It is apparent from Figure 5(a) that with increasing temperature, selectivity for styrene monomers and dimers decreased slightly, whereas selectivity for toluene and ethyl benzene increased slightly. A comparison of degradation at reaction time zero with that after 30 min of reaction [Fig. 5(a,b)] showed that the variation in selectivity for these four components with reaction temperature increased with reaction time. For a prescribed temperature above 400°C, conversion reached 100% before the prescribed temperature was reached. It should be noted that, as shown in Figure
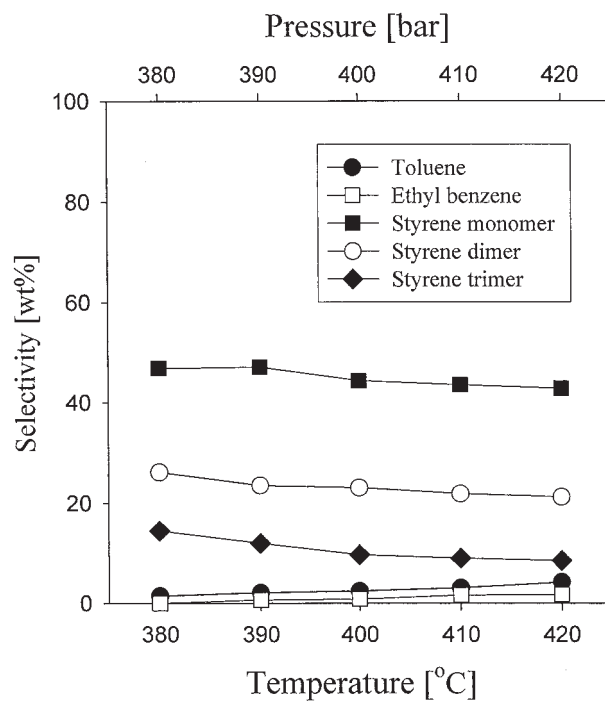
(a)
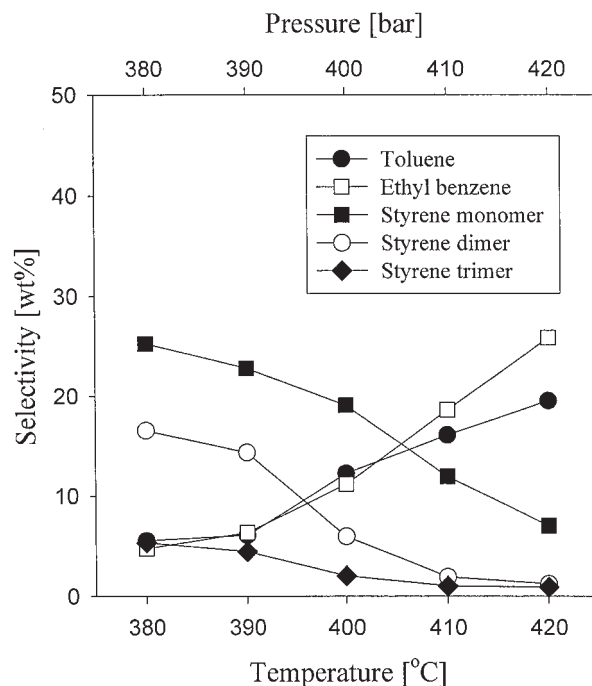
(b)

Figure 5 Effect of reaction temperature on the weight selectivity of liquid products for the degradation of PS in supercritical water at a reaction time of (a) zero and (b) 30 min.

5(a), the selectivity for these four components at reaction time zero was less affected by the prescribed reaction temperature than would be expected. Perhaps the selectivity for each degradation product at reaction time zero was influenced a little by the process of heating to the prescribed temperature.

The variation in selectivity for styrene monomers and dimers with reaction pressure at a constant temperature of 400°C and a reaction time of 10 min is shown in Figure 6. In turn, both styrene monomers and dimers somewhat increased with increasing pressure.

Degradation kinetics

The initial stage of the degradative and thermolytic processes was presumed to obey first-order kinetics[9]:

$$d[PS]/dt = -k_1[PS] \tag{1}$$

or

$$X = 1 - \exp(-k_1 t) \tag{2}$$

where k_1 is the first-order rate constant and X is the conversion of PS.

From the time dependence of the total conversion for degradation of PS in subcritical water at 370°C and in supercritical water at 380°C and 390°C, plotted in Figure 2, the logarithms of unconverted fractions (1 − X) were plotted against the reaction time. Substan-
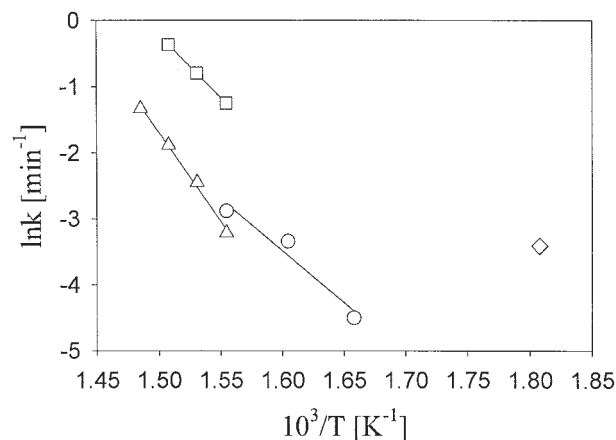
Figure 7 Dependence on temperature of first-order rate constants for: (□) the degradation of PS in supercritical water, (○) the degradation of PS in supercritical *n*-hexane, (♦) the degradation of PS in supercritical acetone, and (△) the thermal pyrolysis of PS.

tially linear relationships between these two factors were obtained at 370°C, 380°C, and 390°C. From the slopes of the straight lines, the first-order rate constants at the three temperatures were evaluated to be 0.287 min^{−1} at 370°C, 0.452 min^{−1} at 380°C, and 0.695 min^{−1} at 390°C. The temperature dependence of the logarithms of the first-order rate constant is shown in Figure 7 as a Arrhenius plot. The activation energy was evaluated to be 157 kJ/mol.

In our preceding article,[10] the time dependence of the conversion was determined for the degradation of PS in supercritical acetone at a weight ratio of acetone to PS at 280°C. Also, the logarithms of unconverted fractions (1 − X) plotted against the reaction time substantially showed a straight line. From the slope of the straight line, the value of the first-order rate constant was evaluated to be 0.033 min^{−1}, which was plotted in Figure 7.

In our another article,[11] the time dependence of conversion for the degradation of PS in supercritical *n*-hexane at 330°C, 350°C, and 370°C and at 50 bar was determined, which is shown in Figure 8. At the three reaction temperatures, similar linear relationships were obtained between the logarithm of the unconverted fraction and the reaction time. From the slope of each straight line, the first-order rate constant was calculated as 0.0111 min^{−1} at 330°C, 0.0354 min^{−1} at 350°C, and 0.0561 min^{−1} at 370°C, plotted in Figure 7. The activation energy was evaluated to be 132 kJ/mol.

For comparison, the first-order rate constant data for the thermal pyrolysis of PS also also plotted in the same figure.[12] From this Arrhenius plot, the activation energy was evaluated to be 224 kJ/mol, a value close to that reported (195 kJ/mol) by Carniti et al.[9] Thus, this shows that the activation energy for degradation in supercritical fluids was lower than that for thermal pyrolysis.
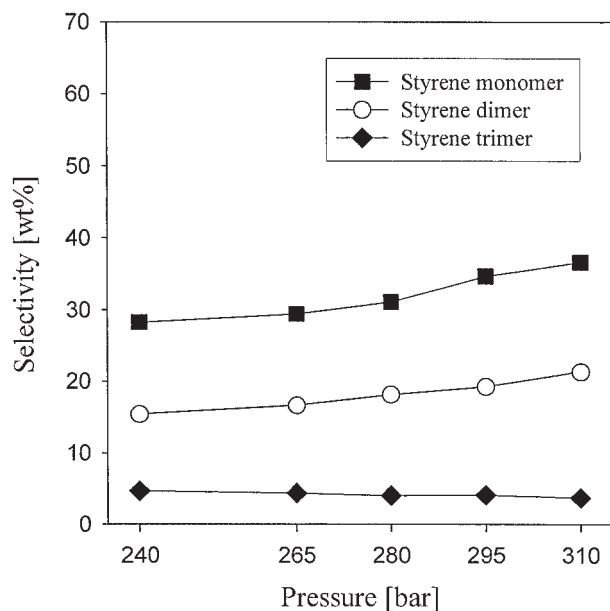

Figure 6 Effect of reaction pressure on the weight selectivity of styrene monomers and dimers for the degradation of PS in supercritical water at 400°C and a reaction time of 10 min.
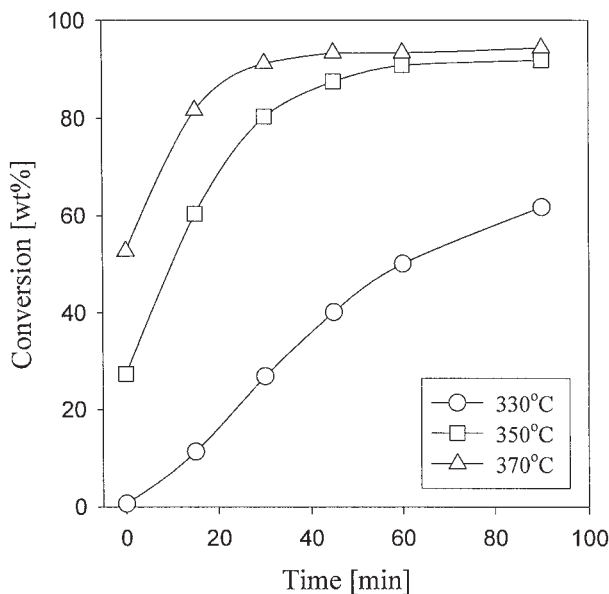
Figure 8 Dependence of conversion on time for the degradation of PS in supercritical *n*-hexane at 50 bar and temperatures of 330°C, 350°C, and 370°C.

CONCLUSIONS

The degradation of polystyrene (PS) in sub- or supercritical water was carried out at reaction temperatures of 370°C–420°C and pressures of 240–320 bar. The time dependence of selectivity for the degradation products—styrene monomers, styrene dimers, styrene trimers, toluene, ethyl benzene, isopropyl benzene, and triphenyl benzene—was investigated, especially at 400°C and 280 bar. As the reaction proceeded, the selectivity for styrene monomers, dimers, and trimers decreased, whereas selectivity for toluene, ethyl ben-

zene, and isopropyl benzene increased because of the difficulty of decomposing benzene rings and phenyl radicals. Triphenyl benzene increased with the reaction time for the same reason. With increasing temperature, selectivity for styrene monomers and dimers decreased slightly, whereas selectivity for toluene and ethyl benzene increased a little. The degradation process of PS in supercritical water could be formulated by the first-order kinetic law at the initial stage of reaction as found in the degradation of PS in supercritical acetone and *n*-hexane. The activation energy for degradation in supercritical water was evaluated to be 157 kJ/mol as compared to 132 kJ/mol in supercritical *n*-hexane.

References

1. Koll, P.; Metzger, T. Angew Chem Int Ed Engl 1978, 17, 754.
2. Dhawan, J.C.; Bencsath, A.F.; Legendre, R.C. J Am Chem Soc 1993, 380.
3. Watanabe, M.; Hirakoso, H.; Sawamoto, S.; Adschiri, K.; Arai, K. J Supercritical Fluids 1998, 13, 247.
4. Tagaya, H.; Katoh, K.; Kadokawa, J.; Chiba, K. Polym Degrad Stab 1999, 64, 289.
5. Moriya, T.; Enomoto, H. Polym Degrad Stab 1999, 65, 373.
6. Dai, Z.; Hatano, B.; Tagaya, H. Polym Degrad Stab 2003, 80, 353.
7. Smith, R.L., Jr.; Fang, Z.; Inomata, H.; Arai, K. J Appl Polym Sci 2000, 76, 1062.
8. Takeshita, Y.; Kato, K.; Takahashi, K.; Sato, Y.; Nishi, S. J Supercritical Fluids 2004, 31, 185.
9. Carniti, P.; Beltrame, P. L.; Armada, M.; Gervasini, A.; Audisio, G. Ind Eng Chem Res 1991, 30, 1624.
10. Hwang, G.-C.; Kim, B.-K.; Bae, S.-Y.; Yi, S.-C.; Kumazawa, H. J Ind Eng Chem 1999, 5, 150.
11. Hwang, G.-C.; Choi, J.-H.; Bae, S.-Y.; Kumazawa, H. Korean J Chem Eng 2001, 18, 854.
12. Kim, Y.-S.; Hwang, G.-C.; Bae, S.-Y.; Yi, S.-C.; Moon, S.-K.; Kumazawa, H. Korean J Chem Eng 1999, 16, 161.