Thermal Decomposition of Polystyrene in Supercritical Methanol

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ABSTRACT: The degradation of polystyrene (PS) in supercritical methanol was carried out under reaction temperatures ranging from 340 to 420°C and pressures of 10–30 MPa. The selectivity of liquid products was investigated at various reaction conditions. As the reaction proceeded, the selectivity of styrene monomer, dimer, 1,3-diphenyl propane, and 1,3-diphenyl butane had a declining tendency, whereas that of the rest (i.e., toluene, ethyl benzene, isopropyl benzene, and 3-phenyl propanol, etc.) had an inclining tendency. The sequences of decomposition reaction could be reasoned by analyzing the variation of selectivity of liquid products. The kinetic behavior of PS in supercritical methanol had been investigated. The degradation processes of PS in such supercritical fluids could be formulated by the first-order kinetic law at the initial stage of reaction. The activation energy for the degradation in supercritical methanol was evaluated to be 117.2 kJ/mol and it was also compared with the activation energies for depolymerization in other supercritical fluids and that for thermal pyrolysis. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3467–3472, 2008

Key words: recycling; polystyrene; degradation; kinetics

INTRODUCTION

A serious environmental pollution is caused by the treatment of waste plastics, especially incineration generates toxic and hazardous materials. In recent years chemical recycling of waste polymers has been gaining greater attention as a means of obtaining valuable products from waste plastics.[1] Polystyrene (PS) is one of the commodity plastics that is used in various products, such as the molded parts on the inside of cars, drinking cups, toys, and the household articles like hairdryers, computers, and kitchen appliances. It is also used as packaging and insulation materials. Waste PS is becoming a major environmental concerns, because of its large production quantities and nonbiodegradable nature. Since PS could be thermally depolymerized into styrene monomer with a high selectivity at high temperature, many technologies have been suggested to increase the yield of styrene.[2–4] Commonly, pyrolysis or thermal degradation has been employed for the chemical recycling of waste PS. This, however, has some disadvantages such as nonuniform heat transfer, low yields of desired products, and excessive char and gas formation.[5] The degradation of various plastics in supercritical fluid has been proposed and studied to complement some of these problems. Koll et al.[6] conducted the degradation of chitin and cellulose using supercritical acetone. Yang et al.[7] used supercritical methanol to depolymerize polyethylene terephthalate for chemical recycling. Tagaya et al.[1] used sub- and supercritical water to study the decomposition of polycarbonate. Moriya and Enomoto[3] compared the results of hydrothermal cracking of polyethylene using supercritical water with those of water-free thermal pyrolysis. However, there are few studies on the degradation of waste PS in supercritical fluids. Lilac and Lee[8] applied the supercritical water partial oxidation (SCWPO) technology to depolymerize PS. Huang et al.[9,10] performed the styrene monomer recovery from waste PS by several supercritical solvents and studied kinetics for degradation of PS in sub- and supercritical toluene.

In our work, we performed decomposition of PS in supercritical methanol to confirm reactivity of PS in methanol and investigate the degradation characteristics. The weight selectivity of liquid products of varying reaction conditions was measured and the degradation sequences were reasoned. A kinetic analysis of the degradation of PS in supercritical methanol was determined at the initial stage of the reaction and compared with that of similar degradation processes in some other supercritical fluids.

EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental apparatus designed for the degradation of PS in supercritical methanol is shown in
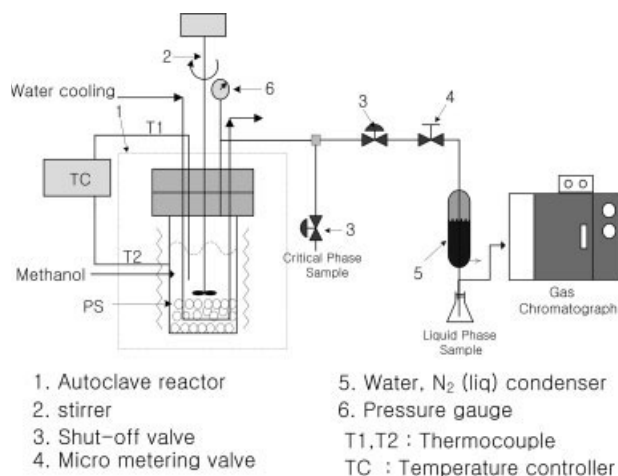
Figure 1 Experimental apparatus for the degradation of PS in supercritical methanol.

Figure 1. The reactor, manufactured by Autoclave Engineers Co., was made of stainless steel 316, and had a volume of 1 L. Its maximum attainable temperature and pressure were 427°C and 50.3 MPa, respectively. The temperature of the reactor is controlled within a permissible range of ±1°C by using the temperature controller with a PID controller (PC600 Series, Jung Kyung Instrument Co., Korea).

The sample tested was general purpose polystyrene (GPPS, HF-2660) manufactured by Cheil Industries, Inc., Korea. The average molecular weight was about 220,000. The sample granules were transparent and of column shape with diameter of 2.3–2.6 mm, height of 2.8–3.3 mm, and weight of 14–18 mg. Methanol was used as supercritical fluid. The critical temperature and pressure of methanol are 240°C and 7.87 MPa.

Preliminarily, the PS sample was put in a 70°C oven for at least 24 h to make the sample dense and dry for the purpose of reducing heat transfer resistance and enhancing heat and mass transfer efficiency. At room temperature, both methanol and dried 30 g PS were fed into the reactor. Ar purging was to remove oxygen completely inside the reactor and to make the test environment inert. The heating rate was maintained at 7°C/min until the temperature reached a prescribed level. The agitation speed was adjusted at 300 rpm. The reaction pressure was controlled through the change of methanol volume fed into the reactor. After reaching the prescribed reaction conditions, the reaction was continued for a certain period of time that had been set in advance. After the reaction finished, the products were recovered in the condenser by using liquid nitrogen. The solid residual substances inside the reactor were dissolved in acetone, recovered, and then dried in an oven to remove the solvent. The conversion of the reactant was calculated by weighing remained substances.

Qualitative and quantitative analyses of liquid products were made by using gas chromatography (GC-14A, Shimadzu, Japan) and GC-MS (Fisons 8000 series HRGC, MD800 MS, Italy). All of the experiments were conducted twice and the mean average values of each experimental data were used.

RESULTS AND DISCUSSION

Degradation characteristics

First, the time dependence of total conversion for the degradation of PS in supercritical methanol at a pressure of 10 MPa and temperatures of 340, 360, 380, 400, and 420°C are shown in Figure 2. The reaction time was designated as zero, when the temperature reached a prescribed one. Accordingly, the degradation might proceed to some extent while the temperature rose to a prescribed one. At 380°C or more, the degradation was in equilibrium in about 15 min, and the equilibrium conversion reached about 92 wt %, whereas at 340 and 360°C, the degradation was completed in 60 min or over.

After the reaction completion, the liquid-like product was recovered by condensing. The liquid products were analyzed by GC and GC-MS. The total ion chromatogram (TIC) of liquid products is shown in Figure 3. Toluene, benzene, ethyl benzene, isopropyl benzene, α-methyl styrene, 3-phenyl propanol, 3-phenyl-1-butanol, 1,3-diphenyl propane, 1,3-diphenyl butane, styrene dimer, styrene trimer, and others were detected by GC-MS.
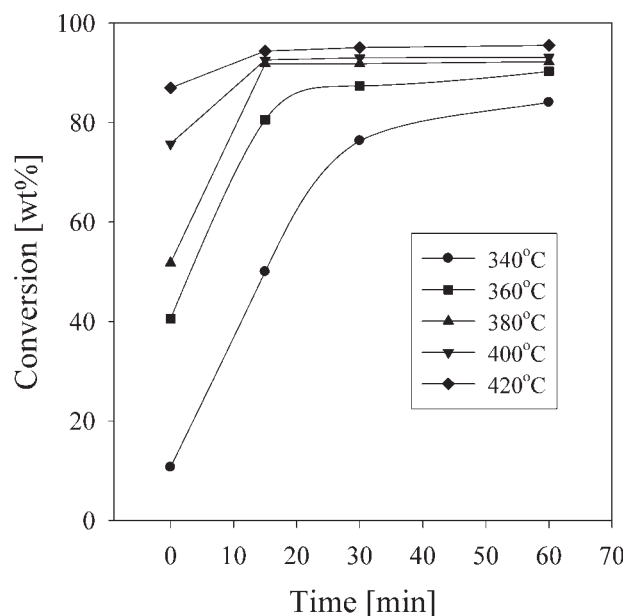

Figure 2 Time dependence of conversions for the degradation of PS in supercritical methanol at 10 MPa and temperatures ranging from 340 to 420°C.
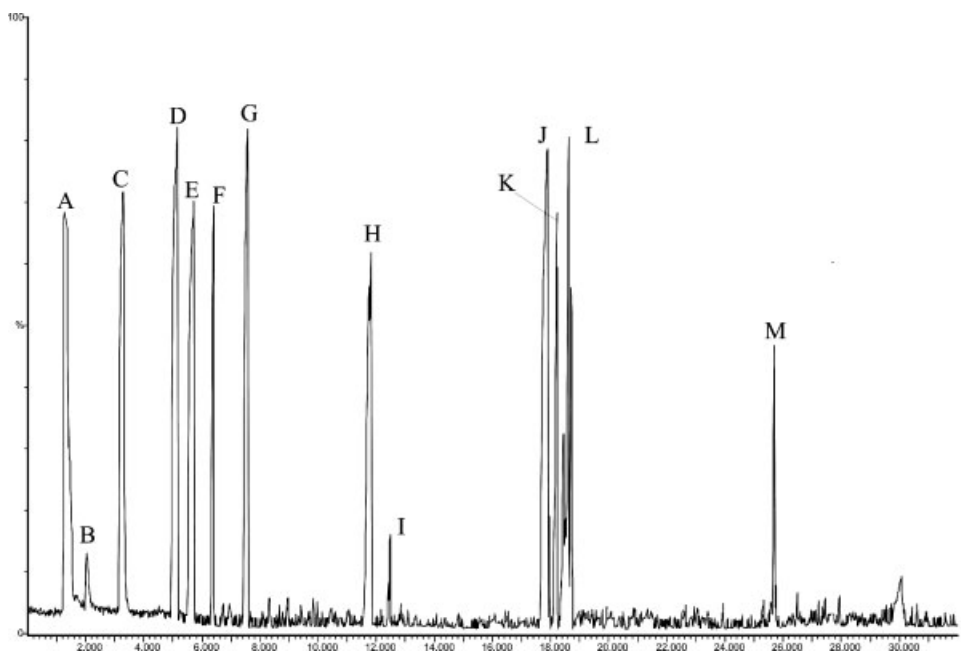
Figure 3 TIC of liquid products for the degradation of PS in supercritical methanol at 420°C, 10 MPa, and 5 min: (A) methanol, (B) benzene, (C) toluene, (D) ethyl benzene, (E) styrene monomer, (F) isopropyl benzene, (G) α-methyl styrene, (H) 3-phenyl propanol, (I) 3-phenyl-1-butanol, (J) 1,3-diphenyl propane, (K) 1,3-diphenyl butane, (L) styrene dimmer, and (M) styrene trimer.

Figure 4 shows effect of reaction time on weight selectivity of degradation products at 380°C and 10 MPa. As the reaction proceeded, the selectivity for styrene monomer, dimer, 1,3-diphenyl butane, and α-methyl styrene decreased, whereas the selectivity for toluene, ethyl benzene, and isopropyl benzene increased.

The variation of selectivity of degradation products with reaction temperature at reaction time zero and 30 min is indicated in Figure 5(a,b), respectively. It is apparent from Figures that the selectivity of styrene monomer, dimer, 1,3-diphenyl propane, and 1,3-diphenyl butane decreased with rising temperature, whereas that of toluene and ethyl benzene increased a little with rising temperature. Comparing Figure 5(a,b) it was found that 3-phenyl propanol appeared as a new product with rising temperature and time.

The variation of selectivity of liquid products with reaction pressure at a constant temperature of 420°C and a reaction time of 5 min is shown in Figure 6. The selectivity of styrene monomer and ethyl benzene decreased, whereas that of 3-phenyl propanol increased drastically.

The main sequences of degradation can be reasoned by analyzing liquid products (Fig. 3) and Figures 4–6 are shown as follows:

2-Ring groups

- Styrene dimer → 1,3-diphenyl butane

- 1,3-diphenyl butane → styrene monomer + ethyl benzene
- 1,3-diphenyl butane → α-methyl styrene + toluene
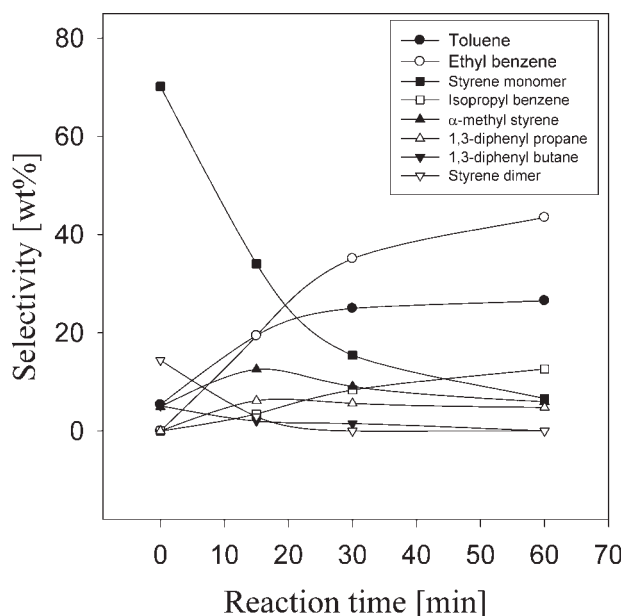- 1,3-diphenyl propane → styrene monomer + toluene

Figure 4 Effect of reaction time on weight selectivity of liquid products for the degradation of PS in supercritical methanol at 380°C and 10 MPa.

- α-methyl styrene + methanol → 3-phenyl-1-butanol

This decomposition sequences are similar to the generally accepted radical chain scission degradation process of PS and account for the formation of the main final stable products, i.e., toluene, ethyl benzene, and isopropyl benzene. Figures 4 and 5(a,b) shows that the selectivity of unsaturated compounds (styrene monomer, dimer, and α-methyl styrene) decreases with rising the reaction time or the reaction temperature. Therefore, the hydrogenation of the double bonds seems to be the predominant reaction. These data may be due to the closed reactor, or due to the presence of solvent (hydrogen donor effect).

The identification of the hydroxymethylated styrene and α-methyl styrene (H and I presented in Fig. 3) proves that an addition reaction takes place. It will be postulated that solvent is reacted with products as a reagent, that is, the electrophilic species is generated from supercritical methanol and acts as an electrophile during the hydroxymethylation of styrene[11] and α-methyl styrene.

Degradation kinetics

The degradation and thermolysis processes are presumed to obey the first-order kinetics at the initial stage of the reaction:[12]

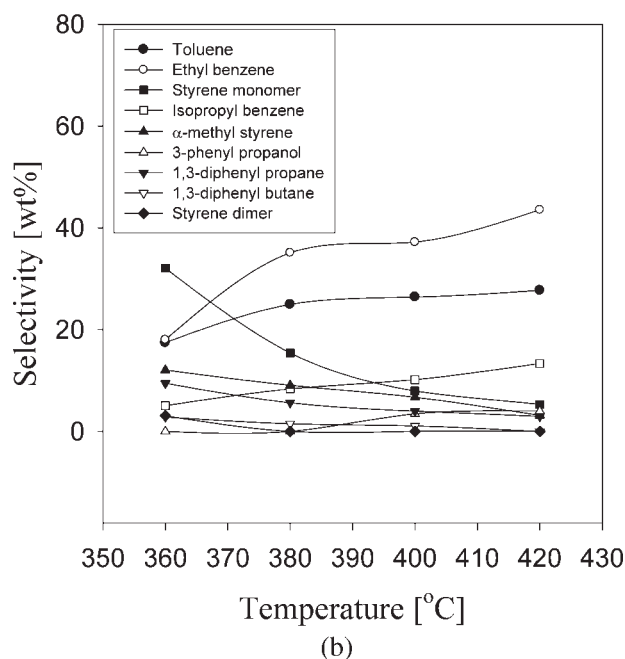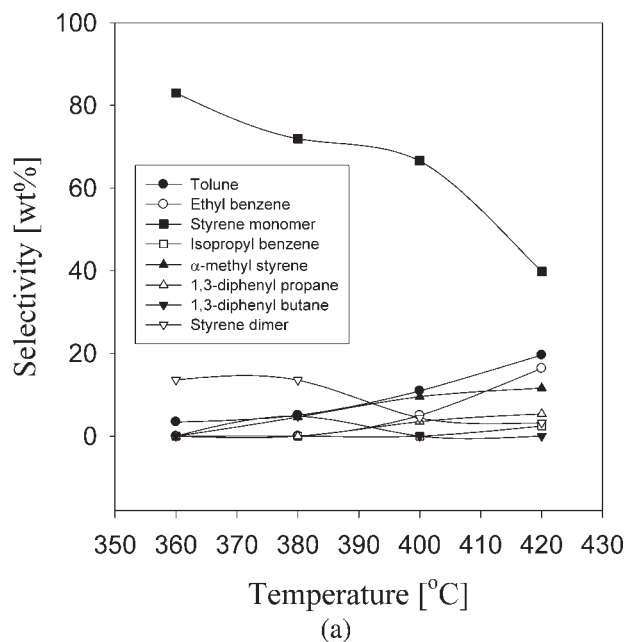$$d[\text{PS}]/dt = -k_1[\text{PS}]$$

Figure 5 (a) Effect of reaction temperature on weight selectivity of liquid products for the degradation of PS in supercritical methanol at reaction time zero and 10 MPa. (b) Effect of reaction temperature on weight selectivity of liquid products for the degradation of PS in supercritical methanol at reaction time 30 min and 10 MPa.

1-Ring groups

- Styrene monomer → ethyl benzene
- α-methyl styrene → isopropyl benzene

Reactions with methanol

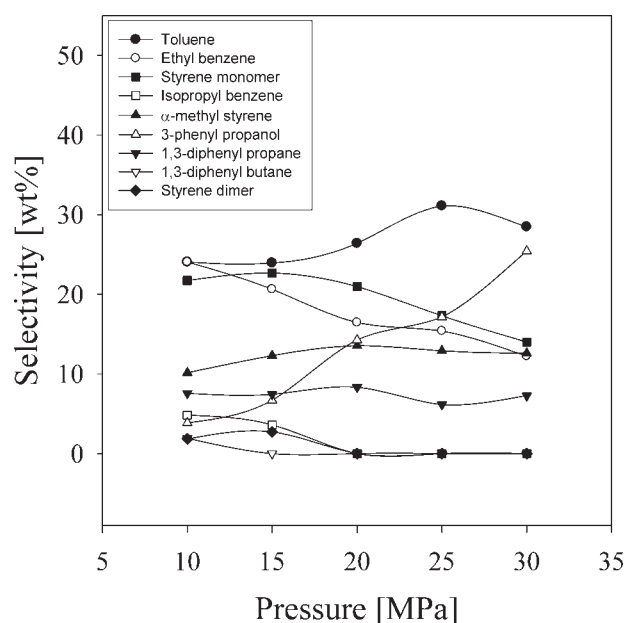- Styrene monomer + methanol → 3-phenyl propanol

Figure 6 Effect of reaction pressure on weight selectivity of liquid products for the degradation of PS in supercritical methanol at 420°C and reaction time 5 min.
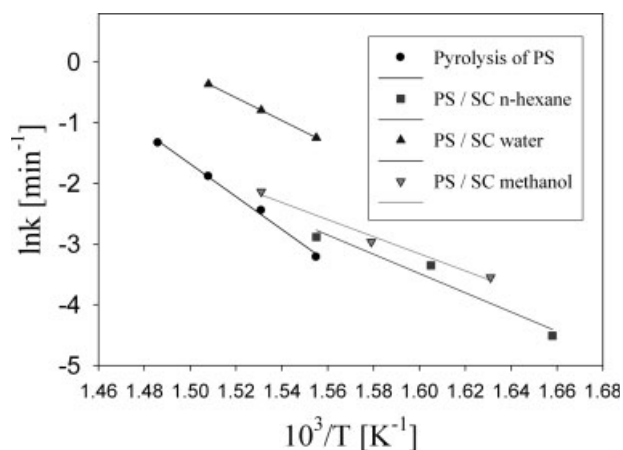
Figure 7 Arrhenius plot of the rate constants with temperature for the degradation of PS in supercritical fluids and for the thermal pyrolysis of PS.

or

$$X = 1 - \exp(-k_1 t)$$

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

From the time dependence of the total conversion for the degradation of PS in supercritical methanol plotted in Figure 2, the logarithms of unconverted fractions $(1-X)$ were plotted against the reaction time. Substantially, linear relationships between these two factors at 340, 360, and 380°C, were obtained. From the slopes of the straight lines, the values of first-order rate constant at the three temperatures were evaluated to be 0.0287 min^{-1} at 340°C, 0.0516 min^{-1} at 360°C, and 0.118 min^{-1} at 380°C. Arrhenius plot of the first-order rate constants with temperature was shown in Figure 7. The activation energy was evaluated to be 117.2 kJ/mol.

In our preceding articles,[13] the time dependence of the conversion was drawn for the degradation of PS in supercritical water at 370, 380, and 390°C and at 23.5 MPa. Also the logarithms of unconverted fractions $(1-X)$ plotted against the reaction time, substantially gave a straight line. From the slopes of the straight lines, the values of first-order rate constant 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, which was plotted in Figure 7. The activation energy is evaluated to be 157 kJ/mol.

In our another article,[14] the time dependence of the conversion for the degradation of PS in supercritical n-hexane at 330, 350, and 370°C and at 5 MPa was drawn. At the three levels of reaction temperature, similarly linear relationships were obtained between the logarithm of unconverted fraction and the reaction time. From the slopes of each straight lines, the values of first-order rate constant were calculated as follows: 0.0111 min^{-1} at 330°C, 0.0354 min^{-1} at 350°C, and 0.0561 min^{-1} at 370°C. These values were plotted in Figure 7. The activation energy is evaluated to be 132 kJ/mol.

For the sake of comparison, the first-order rate constant data for the thermal pyrolysis of PS[15] was also plotted in the same figure. From this Arrhenius plot, the activation energy is evaluated to be 224 kJ/mol, a value close to the reported one (195 kJ/mol) by Carniti et al.[12] Thus, this shows that the activation energy for degradation in supercritical fluids, especially in methanol was lower than that for thermal pyrolysis.

CONCLUSIONS

The degradation of PS in supercritical methanol was carried out under reaction temperatures of 340–420°C and pressures of 10–30 MPa. The time dependence of selectivity of degradation products, styrene monomer, dimer, 1,3-diphenyl propane, 1,3-diphenyl butane, toluene, ethyl benzene, isopropyl benzene, 3-phenyl propanol and others was investigated. As the reaction proceeded, the selectivity of styrene monomer, dimer, 1,3-diphenyl propane, 1,3-diphenyl butane, and α-methyl styrene had a declining tendency, whereas the selectivity of toluene, ethyl benzene, and isopropyl benzene had an inclining tendency. This suggests that toluene is produced by decomposition of diphenyl compounds and ethyl benzene and isopropyl benzene are produced by hydrogenation of styrene monomer and hydrogenation of α-methyl styrene, respectively. Both styrene monomer and ethyl benzene decreased, whereas 3-phenyl propanol increased drastically with increasing pressure. It is speculated that methanol was reacted with unsaturated products as a reagent with increasing pressure. The degradation sequences could be reasoned by analyzing the variation of selectivity of liquid products.

The degradation process of PS in supercritical methanol could be formulated by the first-order kinetic law at the initial stage of reaction as encountered in the degradation of PS in supercritical water and n-hexane. The activation energies for the degradation in supercritical methanol, water, and n-hexane were evaluated to be 117.2, 157, and 132 kJ/mol, respectively. It is apparent that the activation energies for degradation in supercritical fluids, especially in methanol, were lower than that for thermal pyrolysis, so it is expected that the reaction rate of degradation in supercritical methanol can be faster than that of thermal pyrolysis at same or lower temperatures.

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