PYROLYSIS OF POLYSTYRENE IN A BATCH-TYPE STIRRED VESSEL

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Abstract–Isothermal pyrolysis of PS was investigated in the relatively low temperature range of 370 to 400°C, using a stirred tank of batch-type with respect to the liquid phase; the gas phase was operated in an open system. To maintain an isothermal condition, the stirring speed was 80 rpm. At the initial stage of pyrolysis at each temperature, the first-order kinetic law was found to be operative. The activation energy was evaluated to be 224 kJ/mol, a value close to the previously reported one. The main liquid products were single and double aromatic ring species: styrene, α-methylstyrene, toluene and 1,3-diphenylpropane, 1,3-diphenylbutene. The yield of styrene was much larger than any other product and amounted to ca. 70 % by weight. The present reactor, operated in an open system with respect to the gas phase, tends to suppress the scission of volatile diphenyl radicals because of short residence times of these radicals.

Key words : Pyrolysis, Polystyrene, Waste Plastics

INTRODUCTION

The increase in the human population and rapid expansion of industry have been inducing massive production and consumption of energy and materials. The environmental impact due to the rapid increase in waste materials has led to serious social problems. Among various kinds of waste materials, synthetic polymer wastes like synthetic resin, rubber, fiber, tire, etc. tend to own strong resistances to natural degradation by sunlight and microorganisms, and besides, are too bulky to handle. As for technologies to deal with the massive exhaust of such polymeric wastes, presently such countermeasures as landfill, reuse, incineration, thermal degradation, decomposition in supercritical fluids etc. are available. To reduce pollution and at the same time to reutilize the potential energy of the polymer wastes, various kinds of thermal and catalytic degradation processes have been proposed [Sinn et al., 1976; Poller 1980; Kaminsky et al., 1984]. And operational conditions and catalysts yielding high activity and selectivity to intermediate chemicals and fuels have intensively been searched for and prepared, respectively. Specifically, the thermal degradation process has an inherent feature that it is successful for treatment of mixed plastic materials. In fact, optimum designs, conditions and/or catalysts tend to vary with the plastic material to be treated. Kinetics of thermal degradation of polymers have been evaluated from thermogravimetric analysis (TGA) at linear rates of temperature rise in a number of studies [Ghim, 1992; Shin and Seul, 1994; Kim and Chun, 1995].

Scott et al. [1990] investigated the pyrolysis of PS using a fluidized bed reactor in the temperature range of 532 to 708 °C. Later, Kaminsky et al. [1991] independently studied the

pyrolysis of PS using a similar fluidized bed at a temperature of 580 °C. They obtained liquid products by 83 to 88 % and 85 %, respectively, but gaseous products amounted to more than 10 %. Due to the temperature profile inside the fluidized bed reactor, various kinds of liquid species were produced.

John et al. [1994] conducted an isothermal degradation of PS using a batch-type reactor set up in a heavy oil bath. The temperature range to be considered was 370 to 415 °C. Five principal liquid species like styrene, methylstyrene, toluene, etc. were produced, and gaseous species were only slightly detected. But the percentage of styrene monomer was not so high (about 52 %). If a batch-type reactor, which means batch-type with respect to the liquid phase and open system in the gas phase, is adopted as a pyrolysis reactor, the yield of styrene is expected to increase. This is because the scission reactions of volatile dimeric radicals tend to be suppressed [Camiti et al., 1991].

In the present work, using a stirred tank of batch-type with respect to the liquid phase, we investigated the isothermal pyrolysis of PS in a rather low temperature range of 370 to 400 °C. The gas phase was operated in an open system. The stirring speed required for maintaining an isothermal and homogeneous distribution condition was 80 rpm. Operational conditions giving high yields of liquid products as well as limited numbers of liquid components were searched for. Furthermore, the overall (lumped) kinetic law of pyrolysis and the mechanism of decomposition accompanying the pyrolysis were discussed.

EXPERIMENTAL APPARATUS AND PROCEDURE

A schematic diagram of the pyrolysis apparatus, which is heated by means of an indirect heating system, is shown in Fig. 1. The cylindrical pyrolysis reactor, which is made of

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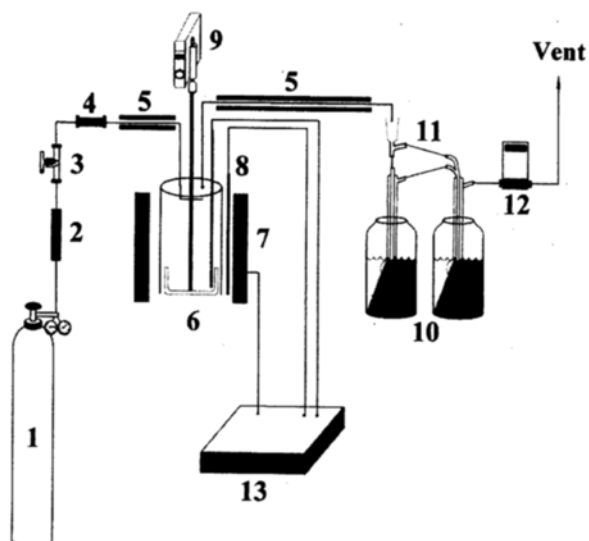E-mail : bae5272@email.hanyang.ac.kr

Fig. 1. Schematic diagram of PS pyrolysis apparatus.

1. N$_2$ bomb	8. Chromel-Alumel thermo couple
2. Silica gel trap	9. Agitator
3. Control valve	10. Liquid N$_2$ trap
4. Check valve	11. Condenser
5. Heating band	12. Gas flow monitor
6. Batch reactor	13. Temperature controller
7. Electric furane	

stainless steel, has a 124 mm inside diameter, 134 mm outer diameter and 205 mm height. The reactor is equipped with a mechanical agitator to minimize the temperature profile in it. The decomposed gas was condensed with liquified nitrogen. To this end, two condensers made of pyrex glass were connected to the reactor. The temperature of the pyrolysis reactor was adjusted by means of a PID temperature controller equipped with a programming device. The heating band was wound around the tubes connected to the reactor.

GPPS (general purpose polystyrene) labelled HF-2660 which is produced by Cheil Industry, was used as a polystyrene sample. It is a pellet type polymer of 0.26 mm in diameter and 0.33 mm in length, and the weight of a pellet is 16 mg. The average molecular weight is about 222,000.

The sample polystyrene was dried in an oven at 115 °C for 24 hours. A 100 gram dried sample was put into the pyrolysis reactor. To eliminate oxygen in it, the reactor was heated under nitrogen condition with an agitation speed of 80 rpm. The volumetric flow rate of nitrogen was fixed at 400 ml/min. The heating rate was controlled at 11.3 to 12.3 °C/min in order to heat up to the pyrolysis temperature, 370, 380, 390 and 400 °C from the initial temperature, 30 °C, in 30 min. The deviation of temperature in the reactor was ±1 °C for the pyrolysis temperature of 370 and 380 °C, and ±3 °C for the pyrolysis temperature of 390 and 400 °C. After 25 min from an onset of heating, a small amount of oil species was detected in the condenser. Then the oil products were collected for every 5 min of time interval. After being weighed, the components in the collected products were identified and compositions were determined with the aid of a GC/MS (QP-5000, Shimadzu, Japan) and a gas chromatograph (DS-6000, Donam, Korea).

In order to maintain a constant temperature profile in the stirred batch reactor, variable mixing speeds ranging from 80 rpm to 500 rpm were attempted to see the effect of mixing rate in relation to the temperature in the stirred batch reactor. The rate of mixing did not have an effect on the temperature in the reactor; thus, the mixing rate was set at 80 rpm throughout the experiment.

RESULTS AND DISCUSSION

Fig. 2 shows the results of PS pyrolysis after 25 min of heating. The yield of pyrolysis increased substantially with the temperature increase. The pyrolysis rate versus time is shown in Fig. 3. The maximum pyrolysis rate was observed approximately after 40 min of heating in the isothermal pyrolysis experiment that was performed at 370 °C whereas the maximum rate was achieved after 35 min of heating at 380, 390, 400 °C.
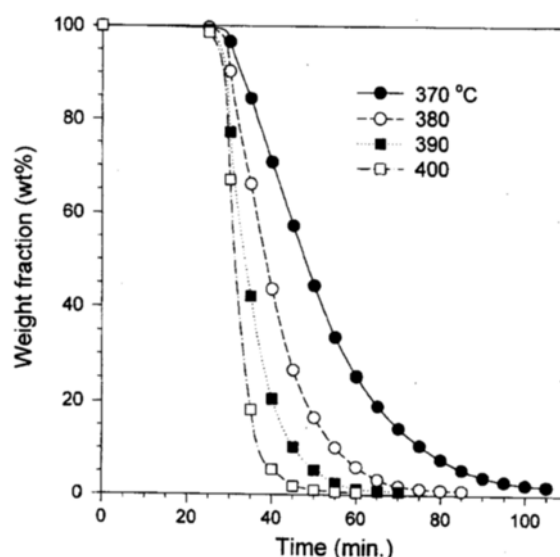

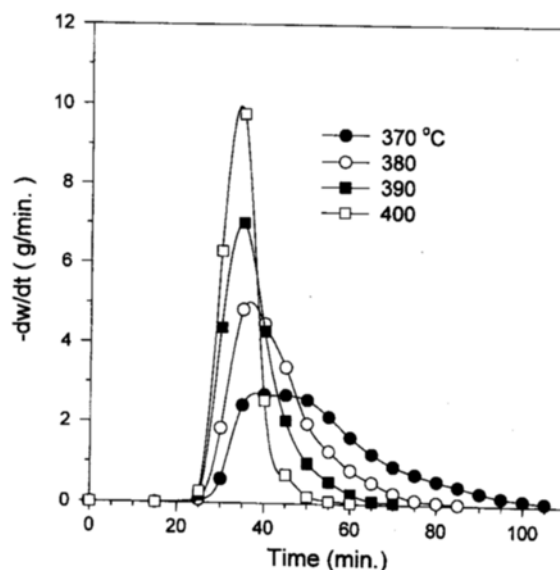**Fig. 2. Weight profiles from PS experiments at various temperatures.**

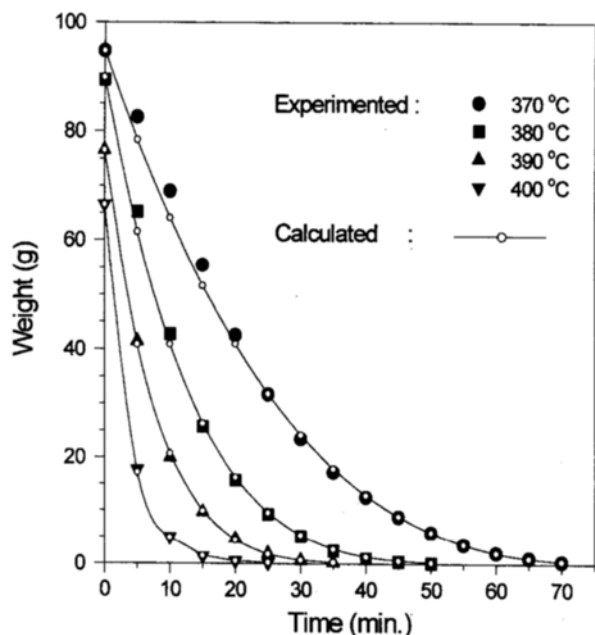**Fig. 3. Rates of degradation from PS isothermal pyrolysis.**

Fig. 4. Comparison of observed and calculated time dependences of PS weight during the isothermal pyrolysis at different temperatures.

First, the initiation of pyrolysis occurred after 25 min of heating where the temperature fluctuated until 30 min of heating. Subsequently, the temperature became constant after 30 min of heating where the analysis was carried out to obtain kinetics as a reference time. The time course of PS weight during the isothermal pyrolysis at different temperatures in the range of 370-400 °C is shown in Fig. 4. The time course here was simulated in terms of the integral reaction rate expression of n-order in PS :

$$w^{1-n}-w_o^{1-n}=(n-1)kt \qquad (1)$$

where "w" refers to the weight of pyrolyzed PS and w_o to the initial weight of PS, "t" denotes the reaction time.

The apparent order of reaction was determined at each temperature by using a method of least squares. The values of apparent order of reaction and the rate constant at each temperature are listed in Table 1.

The order of reaction is calculated to be 0.88 and 1.05 at 390 and 400 °C, respectively, which is close to 1. At 370 and 380 °C, the order of reaction is determined to be 0.68 and 0.80, respectively, which shows some deviation from Eq. (1). Fig. 4 shows the difference of calculated and experimental values. The open circles in this figure represent the cal-

culated values. Results show good agreement in the entire temperature range. Differences in calculated and experimental values at 390 and 400 °C were smaller than those at 370 and 380 °C. But at the initial stage, only a slight difference was seen at each temperature. This fact may be due to the first-order kinetic law in the pyrolysis of plastics in the initial stage as reported by Carniti et al. [1991].

The time dependence of the fractional conversion of PS in the same temperature range is indicated as plots of $\ln(w_o/w)$ vs. time in Fig. 5. This figure reveals that at the initial stage of pyrolysis at each temperature, the first order kinetic law Eq. (2) seems to be operative, though at 400 °C the first-order kinetic law holds over the whole range of reaction time covered here.

$$\ln w_o/w=kt \qquad (2)$$

The initial slope of the relation of $\ln(w_o/w)$ vs. time yields the first-order reaction rate constant. The values of the calculated rate constant at different temperatures are listed in Table 2.

From the Arrhenius plot of first-order reaction rate constant, the activation energy can be evaluated to be 224 kJ/mol, a value close to the reported one by Carniti et al. [1991] (195 kJ/mol).

The yields of oil and gaseous products are listed in PS isothermal pyrolysis at different temperatures in Table 3.

The yield of gaseous products increases with increasing temperature. Carniti et al. [1991] have reported that the yield of
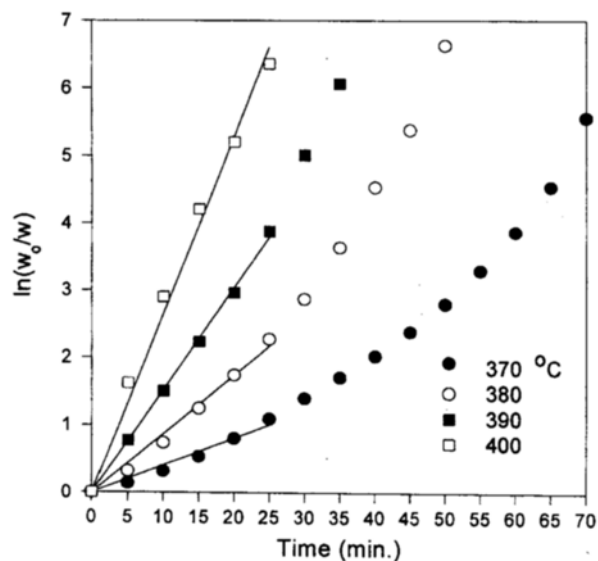
Fig. 5. Time dependence of $\ln(w_o/w)$ in PS isothermal pyrolysis at different temperatures.

Table 1. Apparent order of reaction and rate constant for an isothermal pyrolysis of PS at different temperatures

Reaction temperature (°C)	Order of reaction (n)	Rate constant (k)
370	0.68	0.16
380	0.80	0.18
390	0.88	0.20
400	1.05	0.23

Table 2. Rate constants of first-order reaction at the initial stage of PS isothermal pyrolysis at different temperatures

Reaction temperature (°C)	Rate constant k (min^{-1})
370	0.0402
380	0.0866
390	0.1520
400	0.2640

Table 3. Yields of oil and gaseous products in PS isothermal pyrolysis at different temperatures

Reaction temperature (°C)	Yield (wt%)	
	Oil	Gas
370	96.40	3.60
380	96.10	3.90
390	95.90	4.10
400	94.80	5.20

Table 4. Yields of volatile pyrolysis products (wt%) of PS at different temperatures

Compound	Reaction temperatures (°C)			
	370	380	390	400
Toluene	2.17	1.87	1.52	1.41
Ethylbenzene	0.69	0.43	0.23	0.09
Styrene	65.40	70.91	71.63	71.56
α-Methylstyrene	3.46	2.26	1.50	1.05
1,3-Diphenylpropane	4.16	2.39	1.82	1.33
1,3-Diphenylbutene	18.02	15.95	16.48	16.58
Trimer	4.12	4.59	5.36	6.45
Unknowns				
C_8-C_{11}	0.12	0.15	0.14	0.12
C_{13}-C_{17}	1.86	1.45	1.32	1.41

Note : C_{12} compounds were not found in Carniti et al.'s work [1991]

gaseous products is only less than 2 % of products in pyrolysis of PS using sealed tubes under vacuum in the range 360-420 °C. However, the yield of gaseous products obtained from the batch stirred reactor is 4.0 to 5.2 wt%.

The yields of volatile pyrolysis products at different temperatures are listed in Table 4.

The main products among those with a single aromatic ring are styrene, α-methylstyrene and toluene. The selectivity of styrene is much larger than that of the other two products, and is almost independent of reaction temperature. The selectivities of α-methylstyrene and toluene decrease with increasing temperature. In the present reactor, unsaturated products such as styrene and α-methylstyrene are detected, whereas ethylbenzene and cumene, being, respectively, the corresponding saturated compounds to styrene and α-methylstyrene, are detected little or not at all.

The main products among those with two aromatic rings were 1,3-diphenyl-propane and 1,3-diphenylbutene. Unsaturated compound, 1,3-diphenylbutene, was detected, while its saturated compound, 1,3-diphenylbutene, was not detected.

According to Carniti et al.'s work [1991] in the thermal degradation of PS using tubes sealed under vacuum, the main products with a single aromatic ring were toluene, ethylbenzene and cumene, and those with two aromatic rings 1,3-diphenylpropane and 1,3-diphenylbutane. Also Schroeder et al. [1984] observed in the same degradation in sealed ampule at 292-330 °C that styrene and α-methylstyrene(unsaturated compounds) are not stable final products, as toluene, ethylbenzene and cumene are.

In the present reactor in an open system with respect to the gas phase, the scission reactions of volatile diphenyl radicals predicted in Eqs. (16) and (17) in Carniti et al.'s paper [1991] tend to be suppressed because of the short residence times of these radicals. In sealed tubes and ampules [Carniti et al., 1991; Schroeder et al., 1984], hydrogen and other gaseous species at reaction temperature cannot escape from the reaction media. Therefore, here styrene and 1,3-diphenylbutene were mainly produced.

According to the above findings, the mechanism for the pyrolysis of PS can be described as follows :

PS → C_{13-24} fraction (mainly, 1,3-diphenylpropane and 1,3-diphenylbutene or hydrogenated compound 1,3-diphenylbutane)

→ C_{6-11} fraction (mainly, styrene, α-methylstyrene and toluene or hydrogenated compounds of the former two : ethylbenzene and cumene)

CONCLUSION

An isothermal pyrolysis of PS was investigated at a relatively low temperature range of 370 to 400 °C, using a stirred tank operated batch-type with respect to the liquid phase and in an open system with respect to the gas phase. To maintain an isothermal condition, the stirring speed was 80 rpm. At the initial stage of pyrolysis at each temperature, the first-order kinetic law was found to be operative. The activation energy was evaluated to be 224 kJ/mol, a value close to one previously reported.

The main liquid products were single and double aromatic ring species. The main products among those with a single ring were styrene, α-methylstyrene and toluene. The yield of styrene was much larger than that of the other two products and amounted to ca. 70 % by weight. The main products among those with two aromatic rings were 1,3-diphenylpropane and 1,3-diphenylbutene. In the present reactor operated in an open system with respect to the gas phase, the scission reactions of volatile diphenyl radicals tend to be suppressed because of short residence times of these radicals.

ACKNOWLEDGEMENTS

NOMENCLATURE

k	: rate constant [min⁻¹]
n	: reaction order [-]
t	: reaction time [min]
w_o	: initial weight of PS [g]
w	: pyrolyzed weight of PS [g]

where k is rate constant $[min^{-1}]$, n is reaction order [-], t is reaction time [min], w_o is initial weight of PS [g], w is pyrolyzed weight of PS [g].

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