Degradation of Polystyrene in Supercritical n-Hexane

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Abstract−Degradation of polystyrene was carried out in supercritical n-hexane under reaction temperature ranging from 330 °C to 390 °C, pressure ranging from 30 bar to 70 bar and reaction duration of 90 min. The conversion of polystyrene increased with rising temperature and pressure. The degradation performance was influenced by the temperature rather than applied pressure. Polystyrene rapidly degraded in 30 min after reaching a prescribed temperature ranging from 350 °C to 390 °C. At a prescribed temperature of 390 °C, the degree of degradation was higher than 90%. The degradation reaction was examined experimentally at a relatively low temperature of 330 °C. The degradation of polystyrene by using supercritical n-hexane has been found to be more effective compared to general pyrolysis (thermal degradation). Among the selectivity of liquid products. that of a single aromatic ring group like styrene at 390 °C increased up to 65% in 90 min. It was found from the analysis by a gel permeation chromatograph (GPC), that high molecular-weight compounds decreased but oligomers increased with rising temperature.

Key words: Degradation. Polystyrene, Supercritical n-Hexane, Pyrolysis

INTRODUCTION

Recycling of waste plastics has always received much attention as an interesting research topic, although it often requires the most sophisticated technology available today. The chemical recycling of waste plastic (polymers) has an advantage of converting into reusable materials like monomer or raw material of the petrochemical industry or fuel [Song and Hyun, 1999; Kim et al., 1999]. The production of oil through the pyrolysis of synthetic polymer waste has been receiving more and more attention, as a technology not only for treating environmentally unfriendly plastic but also for developing renewable energy. However, this method still has problems such as high-temperature conditions (at least 600°C), excessively long degradation time, generation of toxic gases, secondary pollution due to incomplete combustion and byproduct like char.

Supercritical fluids (SCF) have recently been used in the treatment of waste plastic to solve the problems induced in pyrolysis of waste plastics. Koll and Metzger [1978] used supercritical acetone to study the degradation of cellulose and chitin. Model [1985] developed a process in which supercritical water was used to degrade organic materials. Dhawan et al. [1993] decomposed polyisoprene and waste rubber using super critical toluene. Kocher et al. [1993] decomposed poly (vinyl chloride) using supercritical water. Adschiri et al. [1997] decomposed waste polyethylene terephthalate (PET) into terephthalic acid up to 91% under the conditions of 400°C, 40 MPa and a reaction time of 12.5 min. Using supercritical methanol, Kim et al. [2001] decomposed waste PET into dimetylterephthalate (DMT) up to 97%. Watanabe et al. [1998] compared the result of general thermolysis and SCF thermolysis. He used both technologies to disintegrate polyethylene. This accounts for most waste plastics. The experimental temperature ranged from 400°C to 450 °C. He found that the supercritical fluid method produced hydro-

carbon products of shorter carbon chain and a higher ratio of 1-alkene/n-alkane than those yielded through general thermolysis. Chen et al. [1995] decomposed natural rubber using supercritical water and carbon dioxide at 380 °C and 276 bar.

Joung et al. [1999, 2001] reported seven types of solvents like toluene and cyclohexane; and selected solvents that are most appropriate to waste tire processing. At the conditions of 300°C, 10 MPa and a reaction time of 1 hr, cyclohexane decomposed waste tires into lower molecular weight substances. Supercritical toluene also gave a similar result. Hwang et al. [2001] used supercritical acetone in the degradation of PE, PP and their mixture.

Lee et al. [1998] used supercritical tetrahydrofuran in decomposing cis-polyisoprene rubber, and got products of narrow distribution. Also they determined an appropriate pressure for the decomposition. In case of thermolysis of PS, monomers of PS are gained because the main chain tends to be cut. Carniti et al. [1995] reported that the yield rate of oil through the thermolysis of PS was about 80%, whereas the yield of gaseous products was less than 10%. Yang and Shibasaki [1998] reported the degradation mechanism of PS thermolysis. Hwang et al. [1999] used supercritical acetone in decomposing waste PS. The total conversion of waste PS, composition of the decomposed products and the yield of monomer for various solvent densities were determined.

In this study, the degradation of waste polystyrene was performed in super critical n-hexane that has relatively lower critical pressure and temperature. The conversion of polystyrene, molecular-weight distribution of products and residual elements were measured to understand the degradation mechanism.

EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental apparatus designed for the degradation of PS in supercritical fluid, shown in Fig. 1, includes a high-pressure reactor where the super critical reaction takes place, the temperature controller and the separator to recover the reaction products.

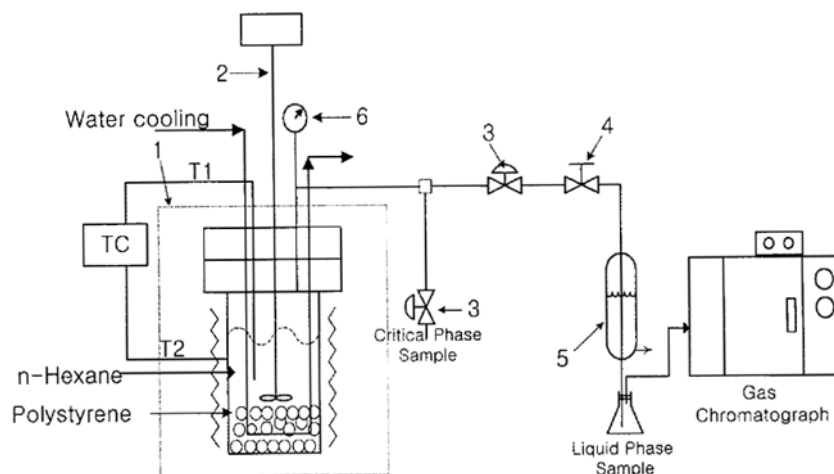†To whom correspondence should be addressed.
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Fig. 1. Schematic diagram of experimental apparatus.

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

The 1 *l* stainless steel (SUS316) reactor of 1 liter capacity manufactured by Autoclave Engineers Co., Seoul, also has thermocouples (T1, T2) and a stirrer. The permissible reactor conditions are 427 °C and 503 bar. A water-cooling system is also installed inside the reactor in order to prevent any drastic temperature change there during the recovery of the products. The temperature of the reactor and the electric furnace is controlled within a permissible range of ±1 °C by using the temperature controller with a PID controller (PC 600 Series, Jung Kyung Instrument CO, Ltd.). The check valve was used to prevent a reflux of the fluid during the reaction. Given that the test is done under high pressure, a safety valve, outside of the reactor, with a rupture disc was used that can work at up to 400 bar.

The sample tested was GPPS (general purpose polystyrene, HF-2660) manufactured by Jeil Industries, Inc. The Average molecular weight was about 220,000. The sample was a transparent column shape with diameter of 2.3-2.6 mm, height of 2.8-3.3 mm and weight of 14-18 mg. The polystyrene employed in the test is often used in manufacturing medical containers, toys, food containers and furniture. n-Hexane is a first-grade chemical (with at least 99.5% of purity) manufactured by Duksan Pure Chemical CO., LTD., and was used without any further purification. The critical temperature and pressure of n-hexane was 507.6 K and 30.25 bar.

Preliminarily, the PS sample was put in a 70 °C oven for at least 24 hr to make the sample dense and dry for the purpose of reducing heat transfer resistance and to enhance heat and mass transfer efficiency. At room temperature, both n-hexane (whose was determined beforehand) and dried 10 g PS were fed into the reactor. Argon (Ar) gas purging was done at a speed of 200 ml/min for 30 min to remove oxygen completely inside the reactor and to make the test environment inert. The heating rate was 7 °C/min until the temperature reached a prescribed level. The stirring speed was adjusted at 300 rpm. The reaction pressure was controlled through the change of the n-hexane volume fed into the reactor. When reaching the reaction conditions, the reaction was continued for a certain period of time that had been set in advance. Then, by the cooling system using water, the temperature of the reactor after the reaction was lowered

to room temperature. The discharging products from the reactor were recovered in the condenser by using liquid nitrogen. The products of a liquid-type and sludge type whereat the sludge type product was oligomer or PS and did not react further during the test, were separated and recovered. The solid residual substances inside the reactor were dissolved in acetone, recovered, and then oven-dried to remove the solvent to weigh.

Qualitative and quantitative analyses of the liquid type product after the reaction were made by using gas chromatography (GC 14A, Shimadzu, Japan) and GC-MS (Fisons 8000 series HRGC, MD800 MS).

Gel permeation chromatography (GPC, manufactured by Waters) was employed for identifying solid residual substances that had a high boiling point in order to find out the molecular weight distribution and the degree of PS reaction completion. The standard sample was polystyrene, the mobile phase was tetrahydrofuran (THF), the fluid flow was fixed at 1.0 ml/min, the column temperature was 35 °C and the RI (refraction index) detector was used.

RESULTS AND DISCUSSION

1. Reaction Temperature and Reaction Time

To find out how the reaction temperature and time impact on the PS disintegration pattern, tests were made at the following conditions: the temperature at the starting point was 330 °C, a relatively lower temperature. Then, it went up to a preset temperature of 350 °C to 390 °C at 20 °C intervals. The reaction time ranged up to 90 min. See Fig. 2 for details. The reaction pressure was fixed at 50 bar, which is above the critical point for n-hexane. The amount of supercritical fluid (n-hexane) used was about 140 g, 130 g, 110 g and 100 g. Time 0 min means the beginning point after the temperature and pressure reached the preset values. It took about 33-49 min to reach the preset conditions. The PS conversion was calculated from

$$\text{Conversion [wt\%]} = [1 - (WR/WI)] \cdot 100$$

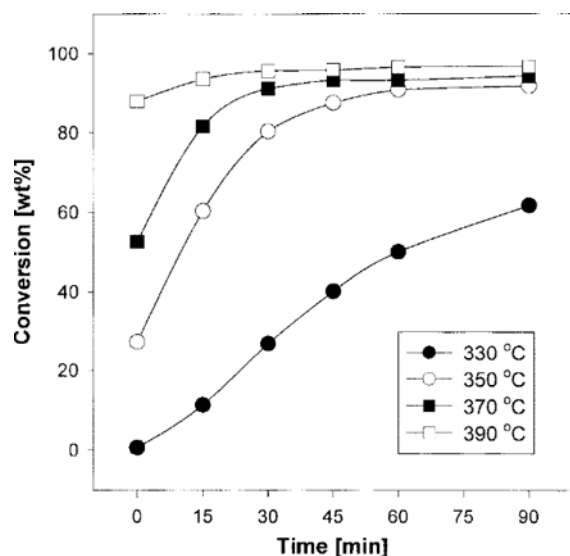where WR refers to the weight of the dried residual solid in grams

Fig. 2. Effect of reaction temperature on time dependence of conversion of PS [wt%] in supercritical n-hexane at 50 bar.

after the reaction and WI refers to the weight of the PS sample in grams used initially.

As can be seen in Fig. 2, the PS conversion was higher at higher temperatures and longer reaction times. The PS conversion was very high at the early stage of the reaction, i.e., within 30 min. At temperatures of 370 °C and 390 °C, there appeared almost no changes in the conversion after 30 minutes elapsed, which means the reaction reached a kind of equilibrium. In the case of 390 °C, at least 87% of the PS was converted when reaching the preset conditions. This means that the PS kept being disintegrated while the temperature increased to the preset temperature.

2. Reaction Pressure

The pressure was changed from about 30.25 bar, a critical pressure for n-hexane up to 70 bar at an interval of 10 bar. The test pressure was controlled within ±1 bar by controlling the volume of the
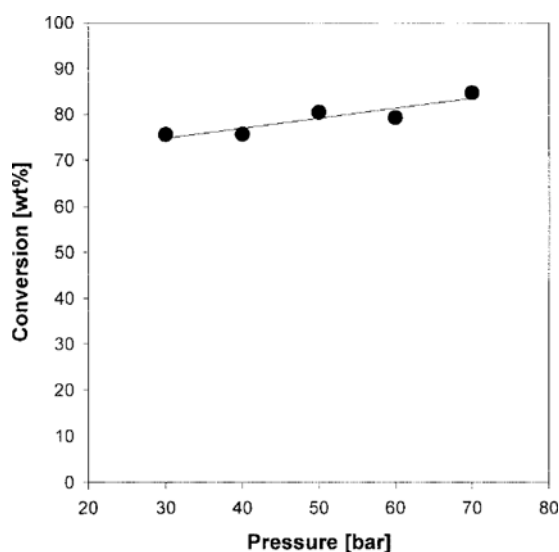
n-hexane fluid. The temperature was fixed at 350 °C and the reaction time was set at 30 min in order to investigate the PS conversion pattern according to the pressure change. The relationships between the PS conversion and the volume of the solvent used are shown in Fig. 3. In the case of using the supercritical fluid in the degradation of PS, the pressure variant is dependent on the volume of the solvent, i.e., the increases in pressure mean more solvents.

The PS conversion gradually increased as the pressure increased (see Fig. 3). At 30 bar, the conversion was 75.53 wt% and at 70 bar, 84.64 wt%. A gap of 40 bar (between 30 bar and 70 bar) led to about 10 wt% difference. This implies that the pressure has a smaller influence on the PS conversion than do the reaction time/temperature. In other words, the temperature increase is more effective than the pressure increase for the PS disintegration.

3. PS/n-Hexane Ratio

It is necessary to know the optimized amount of plastic for a certain volume of solvent if we want to commercialize this type of technology in plastic recycling. Therefore, we have studied the variation of the conversion pattern with the PS/n-hexane ratio. The test conditions were fixed at 350 °C (a relatively low temperature) and 50 bar. The reaction time was 60 min. See Fig. 4 for details.

The amount of PS sample ranged from 10 g to 50 g with an interval of 10 g, whereas the amount of the n-hexane used was 130 g. The PS conversion depicted in Fig. 4 shows that the conversion was depressed as the sample amount increased. In particular, the PS conversion fell down drastically at sample amounts of 30 g to 40 g. The conversion was 90.86% when the PS sample was 10 g, while it was only 64.22% when the PS sample was 50 g. This reflects well the nature of the plastics. Plastic has a big heat transmission resistance, so heat energy provided to the sample is not required during the sample decomposition immediately. Instead, heat energy is accumulated until the temperature reaches a starting point for disintegration. Such heat energy accumulation once continued till a certain point, often leads to a drastic increase in the disintegration reaction. Here, it takes longer to disintegrate the samples when the amount of sample increases, i.e., the sample increase means a larger
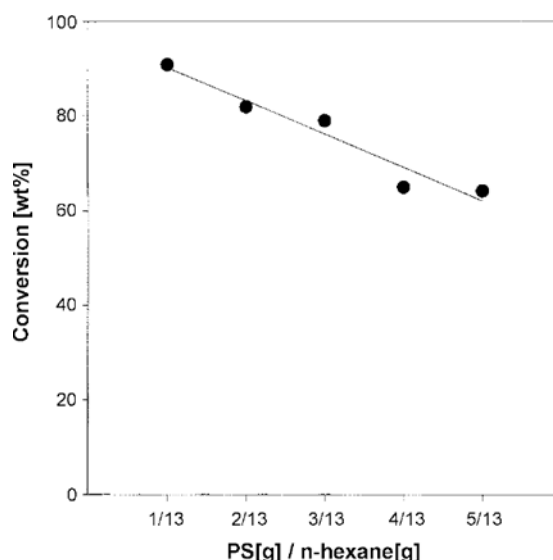

Fig. 3. Effect of reaction pressure on conversion of PS [wt%] in supercritical n-hexane at 350 °C for 30 min.

Fig. 4. Effect of weight ratio of PS to n-hexane on conversion of PS [wt%] in supercritical n-hexane at 350 °C for 60 min.
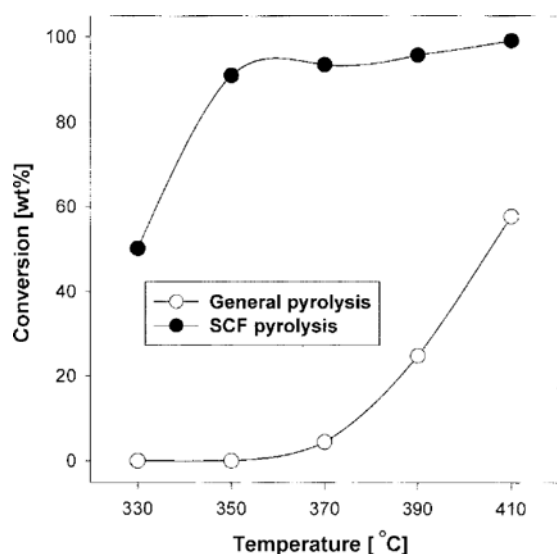
Fig. 5. Comparison of general pyrolysis and degradation of PS in supercritical n-hexane at various temperatures for 60 min.

heat transmission resistance. So this explains a big gap of the conversions between the 10 g sample and the 50 g sample tests.

4. Comparison with the General Thermolysis

The conversions of the general thermal decomposition and the supercritical n-hexane degradation are shown in Fig. 5.

The test conditions were temperature of 330-410 °C at 20 °C interval, a pressure of 50 bar and a reaction time of 60 min. The general thermolysis test was done under the same conditions without any supercritical fluid added. In case of the general thermolysis, there was almost no reaction below 370 °C, while at least 90% of the sample conversion was recorded in a supercritical n-hexane at

the same temperature (370 °C). This means that the degradation reaction takes place rapidly even at relatively low temperature and pressure, if supercritical fluid is used.

The general thermolysis decomposition test showed that more than 50% conversion was attained only at 400 °C and higher. It should be noted that under supercritical fluid conditions, more than 50% conversion has been attained even at 330 °C. A drastic increase in the degree of decomposition was observed when the temperature went up from 390 °C to 410 °C in case of general thermolysis, while a drastic increase in the degree of degradation in supercritical fluid was observed at 330 °C to 350 °C.

5. Analysis of Products

High molecular weight substances that possess ester bonds like PET, nylon and urethane, were more highly converted into monomers through thermolysis, while substances like PE and PP, which account for most plastics, exhibited lower conversions into monomers. What we wanted to get was recycled oil (oil with less than C_{30} molecules). In case of PS, its repeating unit has a benzene ring, which makes the destruction of the monomer (repeating unit) very difficult. Therefore, the yield of monomer from PS through the low-temperature (500 °C or lower) thermolysis was relatively high. Also, even at a higher temperature, PS was partially broken down while most of PS remained in the form of oil, which means less likelihood of its disintegration into a gas form [Kim et al., 2000].

The product selectivity depending on variants was checked through the qualitative and quantitative analysis of gas chromatography and GC-MS of yielded liquid type products. GPC analysis was done for solid type substances in order to see the molecular weight distribution and the degree of reaction. The analysis showed that more than 30 products were formed through the reaction. Among them, 18 substances with a high equal quality were selected for qualitative analysis. PS was converted into monomers mostly, then dimers

Table 1. Weight selectivities of liquid products |wt%| at 330 °C

Component	Time [min]					
	0	15	30	45	60	90
Toluene	3.47	3.72	3.83	4.16	5.09	5.01
Ethylbenzene	-	-	-	0.11	0.16	0.36
Styrene	37.72	35.31	34.39	33.73	31.50	30.47
iso-propylbenzene	-	-	-	-	-	-
n-propylbenzene	-	-	-	-	-	-
α-methylstyrene	-	1.88	2.14	2.46	2.31	3.18
n-butylbenzene	-	-	0.16	0.17	0.17	0.20
n-pentylbenzene	-	-	-	0.08	0.08	0.10
Octylbenzene	2.18	1.79	1.77	1.83	1.95	2.30
3-methyl-1-methylenebutylbenzene	1.16	1.21	1.25	1.34	1.37	1.49
3-methyl-1-methylenepentylbenzene	2.46	2.48	2.47	2.61	2.69	2.90
1,2-diphenyletane, 1,2-diphenylethylene	1.00	0.59	0.44	0.45	0.55	0.59
1,2-diphenylpropane, 1,2-diphenylpropene	0.00	0.43	0.47	0.50	0.51	0.56
1,3-diphenylpropane	5.25	6.57	7.03	7.17	6.91	7.82
1,3-diphenylbutane, 1,3-diphenylbutene	22.55	25.08	25.53	26.07	24.91	23.32
1,5-diphenyl-1-pentene	0.89	0.64	0.81	0.45	0.64	0.56
1,5-diphenyl-1,3-pentadiene	0.75	1.02	0.99	0.75	0.93	0.91
triphenyl-hexene or Trimer	14.03	14.51	14.16	13.52	13.04	10.07
Others	8.54	4.77	4.56	4.60	7.19	10.16

Table 2. Weight selectivities of liquid products [wt%] at 350 °C

Component	Time [min]					
	0	15	30	45	60	90
Toluene	4.02	6.27	6.59	8.29	9.37	9.71
Ethylbenzene	0.27	0.36	0.57	1.00	1.18	2.88
Styrene	34.69	33.11	31.38	28.28	24.14	23.08
iso-propylbenzene	-	0.14	0.16	0.19	0.20	0.46
n-propylbenzene	-	0.06	0.07	0.08	0.10	0.14
α-methylstyrene	2.72	3.68	4.07	4.83	4.70	6.40
n-butylbenzene	0.29	0.20	0.27	0.33	0.37	0.59
n-pentylbenzene	-	0.16	0.15	0.19	0.23	0.36
Octylbenzene	2.37	1.56	1.94	2.74	3.30	5.10
3-methyl-1-methylenebutylbenzene	2.11	1.41	1.63	2.26	1.56	1.92
3-methyl-1-methylenepentylbenzene	3.65	2.80	3.48	4.41	3.14	4.25
1,2-diphenyletane, 1,2-diphenylethylene	1.42	1.02	0.70	0.90	0.85	0.91
1,2-diphenylpropane, 1,2-diphenylpropene	1.07	0.21	0.48	1.04	1.08	0.76
1,3-diphenylpropane	7.94	7.18	8.60	10.67	9.61	11.45
1,3-diphenylbutane, 1,3-diphenylbutene	22.09	19.61	18.52	17.79	17.60	14.24
1,5-diphenyl-1-pentene	0.83	0.59	0.68	0.74	0.63	1.04
1,5-diphenyl-1,3-pentadiene	1.07	0.92	0.98	0.78	0.70	0.92
triphenyl-hexene or Trimer	9.43	7.45	6.39	5.99	4.86	3.13
Others	6.03	13.27	13.34	9.49	16.38	12.66

and then trimers. What was outstanding was the production of octylbenzene. Octylbenzene seemed to have been produced when supercritical n-hexane was directly involved in the decomposition reaction.

The results from quantitative analysis are shown in Table 1 through Table 4. Regarding selectivity in the PS disintegration reaction, high selectivity into monomers, dimers and trimers was observed, within 30 min of reaction time. However, the selectivity into secondary products increased, as the reaction time was continued longer. The selectivity of styrene decreased with a gentle slope at temperatures of 330 °C and 350 °C, whereas it decreased with a steep slope at temperatures of 370 °C and higher, and instead secondary products like toluene and ethylbenzene increased. Unlike general thermolysis, this supercritical fluid degradation was done under closed sys-

Table 3. Weight selectivities of liquid products [wt%] at 370 °C

Component	Time [min]					
	0	15	30	45	60	90
Toluene	2.72	6.57	6.68	6.92	7.05	7.93
Ethylbenzene	0.42	2.36	3.56	4.05	7.25	9.11
Styrene	30.66	25.36	20.39	19.27	15.43	11.25
iso-propylbenzene	0.05	0.12	0.66	0.59	1.28	1.56
n-propylbenzene	0.05	0.12	0.13	0.21	1.16	1.58
α-methylstyrene	2.90	5.31	5.63	5.38	7.10	6.33
n-butylbenzene	0.23	0.39	0.67	1.03	1.16	1.57
n-pentylbenzene	0.15	0.29	0.51	0.77	0.88	1.37
Octylbenzene	1.16	2.41	4.36	5.47	6.00	6.94
3-methyl-1-methylenebutylbenzene	0.49	1.08	1.53	1.85	1.48	2.15
3-methyl-1-methylenepentylbenzene	1.56	2.32	3.57	4.40	6.07	5.84
1,2-diphenyletane, 1,2-diphenylethylene	0.39	0.96	1.26	1.40	1.52	2.07
1,2-diphenylpropane, 1,2-diphenylpropene	0.34	0.60	0.87	1.01	1.48	1.59
1,3-diphenylpropane	7.36	10.47	10.99	10.40	11.40	10.41
1,3-diphenylbutane, 1,3-diphenylbutene	20.98	16.94	12.60	11.73	7.89	6.08
1,5-diphenyl-1-pentene	0.49	1.19	1.27	1.46	1.10	1.19
1,5-diphenyl-1,3-pentadiene	1.08	2.51	2.79	2.32	2.61	3.63
triphenyl-hexene or Trimer	9.29	4.42	3.41	3.16	2.13	1.52
Others	19.68	16.58	19.12	18.58	17.01	17.88

Table 4. Weight selectivities of liquid products [wt%] at 390°C

Component	Time [min]					
	0	15	30	45	60	90
Toluene	3.98	6.94	10.10	10.87	10.02	14.31
Ethylbenzene	1.48	5.50	8.69	7.84	10.14	14.81
Styrene	28.69	21.25	14.00	10.20	6.02	5.96
iso-propylbenzene	0.07	0.78	1.17	0.98	1.65	2.88
n-propylbenzene	0.07	0.43	0.57	0.60	0.63	0.78
α-methylstyrene	4.88	5.97	6.70	5.20	4.92	5.00
n-butylbenzene	0.55	1.55	2.24	2.66	3.15	3.07
n-pentylbenzene	0.44	1.30	1.85	2.17	2.57	2.81
Octylbenzene	2.04	5.18	6.95	7.34	9.05	8.18
3-methyl-1-methylenebutylbenzene	1.05	1.52	1.36	1.00	0.90	0.79
3-methyl-1-methylenepentylbenzene	2.43	4.43	4.73	6.14	6.36	4.28
1,2-diphenyletane, 1,2-diphenylethylene	0.82	1.01	1.00	2.61	2.59	2.22
1,2-diphenylpropane, 1,2-diphenylpropene	0.53	0.66	0.73	0.88	0.92	0.73
1,3-diphenylpropane	9.07	10.43	9.7	10.86	10.85	8.71
1,3-diphenylbutane, 1,3-diphenylbutene	17.65	9.89	7.20	5.12	4.60	2.85
1,5-diphenyl-1-pentene	1.23	1.60	1.46	1.90	1.65	0.93
1,5-diphenyl-1,3-pentadiene	1.04	3.46	2.47	3.84	3.89	3.11
triphenyl-hexene or Trimer	5.15	2.32	1.80	1.90	1.91	1.08
Others	18.83	15.78	17.28	17.89	18.18	17.50

tems, which kept monomers and dimers to remain inside the reactor. This resulted in an increase of secondary products like toluene and ethylbenzene, and the selectivity of styrene tends to decrease relatively.

The variations of product composition under the various temperatures and reaction times are shown in Fig. 6. In these figures, the monomer group is described as 1-ring, the dimer group as 2-ring and the trimer group as 3-ring. Regardless of the reaction temperature, the selectivity for 1-ring (monomer) was higher than that

for any other products. In particular, the highest selectivity of monomer (ca. 70 wt%) was achieved at 390°C and a reaction time of 90 min.

GPC analysis outcomes of solid residual substances after thermolysis are shown in Figs. 7 through 10. These show that PS disintegrated to produce molecules of lower molecular weights over time. As depicted in Fig. 2, the conversion of PS at 350°C reached a kind of equilibrium after 30 min elapsed. But GPC analysis exhibited that the decomposition reaction still continued slowly after

Fig. 6. Time dependence of weight selectivity of 1-ring, 2-ring and 3-ring groups at 330°C, 350°C, 370°C and 390°C.

Fig. 7. Molecular weight distribution of solid residue obtained from decomposition of PS in supercritical n-hexane at 330°C determined by GPC analysis.
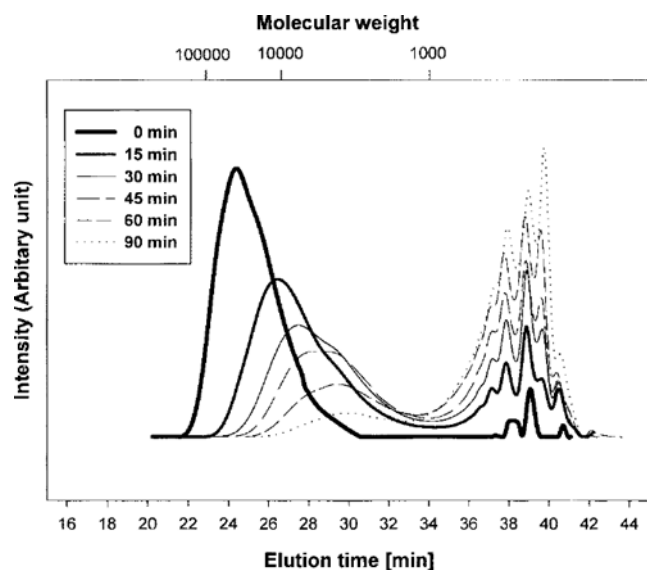
Fig. 8. Molecular weight distribution of solid residue obtained from decomposition of PS in supercritical n-hexane at 350 °C determined by GPC analysis.
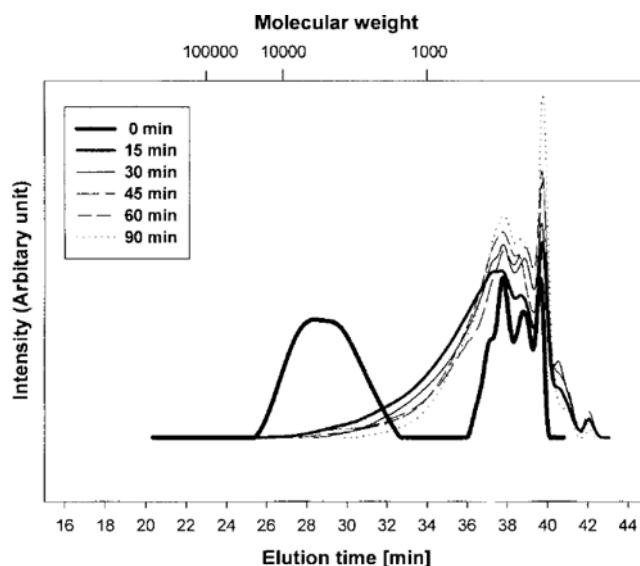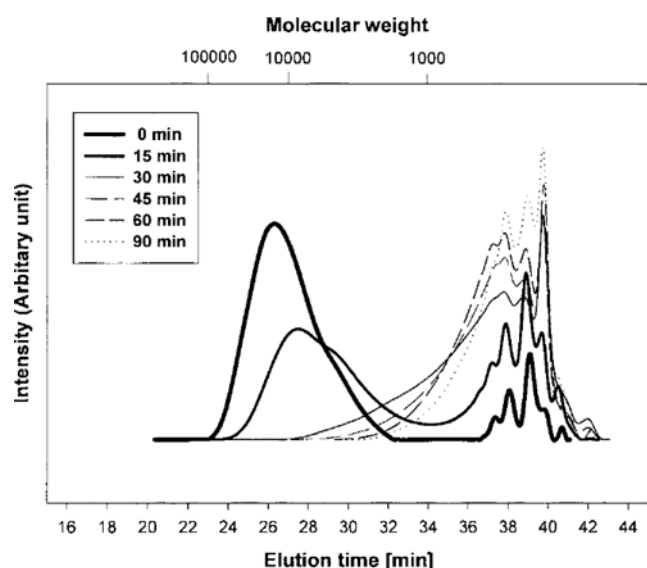

Fig. 9. Molecular weight distribution of solid residue obtained from decomposition of PS in supercritical n-hexane at 370 °C determined by GPC analysis.

that point passed. GPC analysis revealed that as a result of reaction, the length of the PS chain kept on shortening, then producing oligomers. In particular, at 390 °C, almost all of the PS were consumed and were converted into oligomers with molecular weights of less than 1,000.

CONCLUSIONS

The degradation of PS by using supercritical n-hexane was conducted at various combinations of conditions: temperature 330-390 °C; pressure 30-70 bar; and reaction time 0-90 min. The following information was obtained.

Fig. 10. Molecular weight distribution of solid residue obtained from decomposition of PS in supercritical n-hexane at 390 °C determined by GPC analysis.

1. The higher the temperature and the longer the reaction time, the higher PS conversion that was achieved. In particular, the decomposition peaked at an early stage within 30 min, i.e., the conversion increased drastically.

2. The pressure variation had a smaller impact on PS conversion than did the temperature variation. In other words, the temperature rise was more effective than the pressure increase for PS conversion.

3. As PS (sample amount) to n-hexane amount ratio increased, the conversion decreased. This is why an increase in the amount of PS results in a higher heat transfer resistance, which slows down the reaction, i.e., it takes longer to decompose the sample.

4. Regarding the comparison with general thermolysis: in general thermolysis, almost no reaction appears below a temperature of 370 °C, while more than 90% conversion can be achieved in the case of supercritical fluid degradation. Supercritical fluid degradation is faster than general thermolysis.

5. The selectivity of styrene decreased with a relatively gentle slope at 330 °C and 350 °C over time, while a drastic decrease occurred at temperatures of 370 °C or higher. Instead, secondary products such as toluene and ethylbenzene increased. Unlike the general thermolysis, this supercritical fluid degradation was done under closed systems, which kept monomers and dimers inside the reactor. This resulted in an increase of secondary products like toluene and ethylbenzene; and the selectivity of styrene relatively decreased.

6. GPC analysis exhibited a shortening of polymer chain length and an increase of oligomers. Especially, at 390 °C, almost all of PS sample was converted almost completely into oligomers with molecular weight of less than 1,000.

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