

Novel Method for Polystyrene Reactions at Low Temperature

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Abstract: Thermal decomposition reactions of polystyrene using a new heating medium were carried out by a batch system at 190~280 °C to clarify the manner in which decomposition is initiated. Polystyrene obtained from a commercial source and low molecular weight compounds obtained from the thermal decomposition were analyzed by GC, GPC, IR, ¹³C-NMR and GC-MS. The main chain underwent virtually no change by heat application. Polystyrene underwent decomposition below its molding temperature and the major decomposition products were 2,4,6-triphenyl-1-hexene (trimer), 2,4-diphenyl-1-butene (dimer) and styrene (monomer). Ethylbenzene, propylbenzene, naphthalene, benzaldehyde, biphenyl and 1,3-diphenylpropane were detected as minor products. This paper presents a new method for examining the decomposition of polystyrene at low temperature into volatile low molecular weight compounds.

Keywords: polystyrene, 2,4-diphenyl-1-butene (styrene dimer), 2,4,6-triphenyl-1-hexene (styrene trimer), endocrine disruptor, low temperature decomposition.

Introduction

Polystyrene (PS) is quite frequently used as material for food and medical product containers.¹ Styrene (monomer) in food containers has been examined as a potential source of toxic contamination.²⁻⁴ Internal metabolism and carcinogenicity and the mutagenicity of metabolites of monomer have been studied in detail.⁵

Studies on the toxicity of 2,4-diphenyl-1-butene (dimer) and 2,4,6-triphenyl-1-hexene (trimer) as well as styrene monomer on the environment and contamination in food appeared in the literature.^{6,7} Low molecular weight compounds such as PS components have been examined for toxicity in the human body, as also have components from urea resin,⁸ epoxy resin⁹ and polycarbonate.¹⁰ These low molecular weight compounds under 250 °C may be present in very

small quantities, 1% or less of the weight of original PS.¹¹ Organism toxicity, mutagenicity and carcinogenicity will occur when the decomposition products are present at very low concentrations (under ppm).¹²⁻¹⁴ Initial chemical changes due to the heating and photo-degradation of plastics should be taken into account for accurate assessment of toxicity. However, little progress has been made in such research due to the absence of adequate methods for analyzing initial chemical reactions. Initial chemical reactions¹⁵ of PS were examined in this study at low temperature and analysis of ultratraces of low molecular weight compounds was made. PS was found to decompose below its molding temperature and benzaldehyde with high toxicity was detected along with the monomer, dimer and trimer as low molecular weight compounds. These low molecular weight compounds have been proven to be significant sources of toxicity in the body.¹⁶

Possible origins of endocrine disruptors from PS are discussed.

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Experimental

Materials. The PS used in this study was an unmolded pellet obtained commercially. A 20 g PS was dissolved in 500 mL benzene, reprecipitated two times in 1,500 mL methanol and allowed to dry for 10 days *in vacuo* (3 Torr) at 25°C.

The heating medium (polyethylene glycol, PEG; reagent grade) was used without purification (WAKO, Tokyo Japan).

The solvent for extraction and GPC were of reagent grade (Wako, Tokyo Japan).

The PS from which low molecular weight compounds had been removed as much as possible by reprecipitation (2.1) was cut into small pieces with scissors. 0.100 g of this material was accurately weighed out for use.

Thermal Decomposition. This process was conducted in 4.90 g heating medium (PEG) in a 20 mL round-bottomed flask submerged in a silicone oil bath. A stirrer chip was provided at the bottom of the flask and at the top of which a Y-tube was attached. Via the Y-tube a thermocouple, N₂ gas tube and reflux condenser were connected. N₂ gas was introduced at a rate of 50 mL/min by a regulator from an N₂ container at room temperature for 10 min. Oil bath temperature was maintained 2 or 4°C above the fixed reaction temperature. When the internal temperature became stable, 0.100 g PS was added to the PEG with stirring at 500 rpm. The reaction was considered to begin at the fixed temperature. Reaction temperature was maintained within $\pm 1^\circ\text{C}$ of the fixed temperature by the thermocouple digital thermometer (CUSTOM CT-1310, Tokyo, Japan) placed in the reaction solution.

Sample Preparation and Analysis of Commercial PS. The PS was allowed to react at a fixed temperature for a specified time and was recovered completely with 10 mL

benzene. The reaction mixture was transferred to a separatory funnel, washed three times with 10 mL purified water to remove the heating medium (PEG). The mixture was transferred to 10 mL methanol and the portion of the polymer was precipitated. The sample was thawed after 3 hrs freezing at -80°C to facilitate the precipitation and then centrifuged at 5000 rpm for 10 min. The supernatant was decanted and dried on anhydrous sodium sulfate overnight. The solution was filtered and internal standard (phenanthrene) was added while maintain the volume constant (25 mL), as shown in Figure 1(a). Preparation and analysis scheme of the commercial PS are shown in Figure 1(b).

Apparatus. IR spectra were recorded on a JASCO IR- 810 spectra and NMR spectra in CDCl₃, on a JNM GSX-400 FT NMR with tetramethylsilane (TMS) as internal standard. GC-MS spectra were obtained using a Jeol Auto MS-II. GC was performed with a Shimadzu GC-14A with a hydrogen flame ionization detector. The column for separation of thermal decomposition products by a.GC, b.GC-MS and c.GPC was a. DB-5 (30 m Length \times 0.32 mm I.D. film 0.25 μm thick), b. DB-17 (30 m Length \times 0.32 mm I.D. film 0.25 μm thick) and c. Asahipak GF-7M HQ (Asahi Chemical Industry, Co. Ltd. Tokyo Japan). Conditions for GC-MS: Column temperature; 40°C (hold for 5 min) to 280°C (15°C/min); Carrier gas, He (1.5 mL/min); Sample injection volume, 1 μL , splitless; MS Interface temperature, 180°C; Ion source temperature, 200°C and Ionization voltage, 70 eV.

Results and Discussion

Recovery and Analysis of Low Molecular Weight Compounds from Thermal Decomposition. Sato *et al.*¹⁵ examined the effects of various solvents on the thermal decomposition of the PS at 300~450°C in an autoclave.

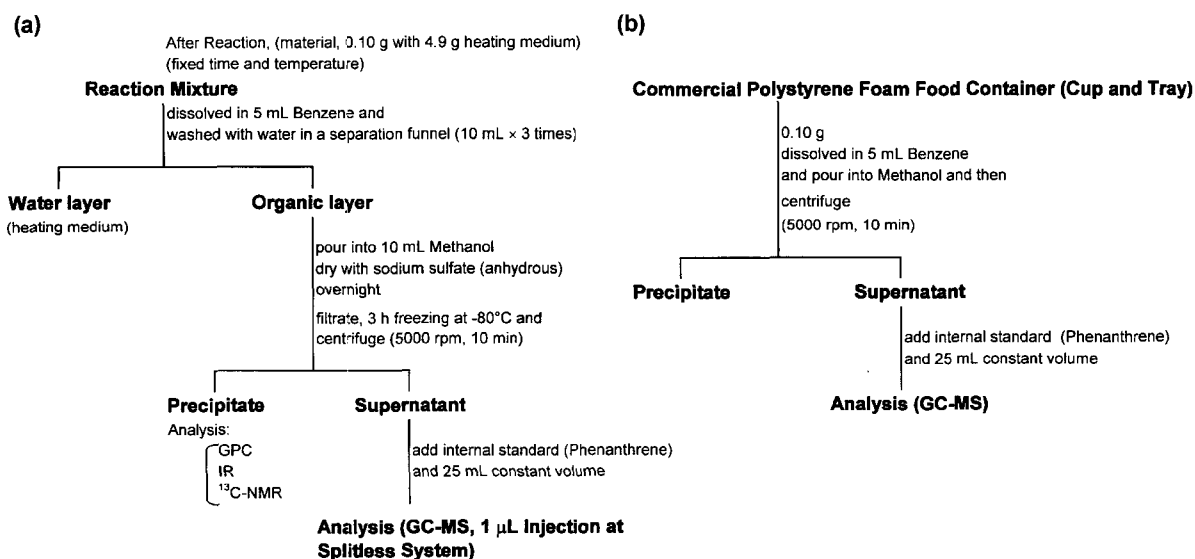


Figure 1. Sample preparation for thermal decomposition product analysis.

Madras *et al.* carried out this thermal decomposition of PS using mineral oil at 240–300 °C and clarified the kinetics involved.¹⁶ GPC and GC-MS were employed for product analysis. The mineral oil used in the study of Madras *et al.*¹⁶ made the analysis by GC and HPLC difficult. Consequently, these methods may not be considered adequate for analysis. The heating medium (PEG) in this study melted with the monomer, dimer and trimer produced from PS. PS in the reaction flask was thus immediately brought into sufficient contact with the heating medium and dispersed. PS was considered to be uniformly heated. Side reactions were made minimal by conducting the reactions in a flow of N₂ gas. Following the completion of the reactions, the reaction mixture was separated by solvent extraction with a benzene/water system. The benzene layer was transferred to methanol and PS was precipitated and removed. The separation and analysis of all low molecular weight compounds from the thermal decomposition of PS were thus achieved, with results expressible at the 10⁻⁹ level (ppb).

After 0.100 g PS had decomposed thermally at 280 °C for 120 min, GC-MS analysis was carried out according to the splitless method. The chromatogram obtained is shown in Figure 2(a).

Monomer, dimer and trimer formation was clearly confirmed. PS is shown to decompose at the initial stage of thermal decomposition since thermal decomposition began at lower temperature.

t_R , 7:53 peak in Figure 2(a), albeit unrecognizable due to the compound in trace (under ppb), represents a trace compound identified with benzaldehyde from M⁺ (106) and fragmentation m/z (77.51) in spite of reaction in the N₂ flow. The mechanism for the formation of this compound is not understood but organism toxicity was found to be high compared to that of general hydrocarbons. Figure 2(b) shows the results for commercial PS analysis. The trimer shown in Figure 2(a) and (b) are also shown present at the same 34 ppm. Numerous commercial PS were found in this study to contain the low molecular weight compounds. The polymer material itself was not toxic but low molecular weight compounds produced through thermal decomposition and photo-degradation or as unchanged monomer were found to be toxic.

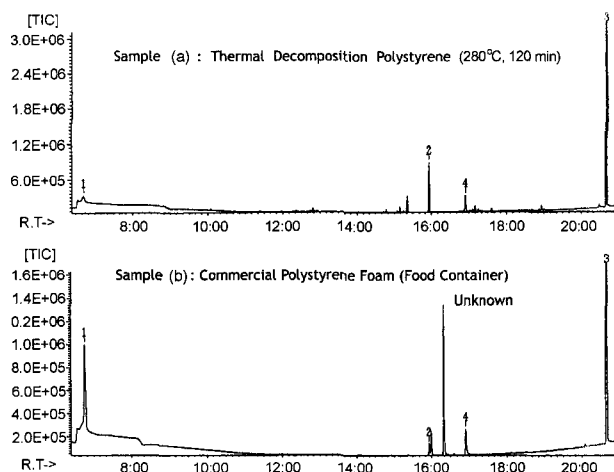


Figure 2. GC-MS chromatograms of low molecular weight compounds. Sample (1), (2) Peak 1: styrene monomer, Peak 2: dimer (2,4-diphenyl-1-butene), Peak 3: trimer (2,4,6-triphenyl-1-hexene), Peak 4: Phenanthrene (internal standard, 0.2 ppm).

Analysis of Products Derived from Thermal Decomposition of Commercial PS. Analysis was conducted by GC/MS, as shown in Figure 1(a) and the results are listed in Table I and Figure 2(b).

It is evident from Table I that different commercial products break down into the same compounds by thermal decomposition. Trimer was shown present at 2.93–26.95 ppm. Minimum and maximum values differ by almost an order of magnitude, possibly due to the particular methods of molding and processing. The manufacture and molding of PS polymer are clearly shown to be accompanied with the formation of low molecular weight compounds that are toxic toward the human body.

Effects of Reaction Temperature on the Conversion of Low Temperature Decomposition. Low molecular weight compounds were almost completely extracted from the starting material, PS, by reprecipitation with the benzene/methanol system, as shown in Figure 1(b). By GC/MS, monomer was determined present at 0.01, dimer at 0.02 and trimer at 0.08 ppm. Low molecular weight compounds are difficult to remove completely from PS and these values were used as

Table I. Analysis Results of Some Components in Commercial Polystyrene Foam for Foods Container in Japan (unit: ppm)

Components	Samples	1	2	3	4	5	6	7	8	9	10
Styrene Monomer		2.63	2.13	1.77	2.94	2.54	1.05	1.83	0.89	0.24	0.03
Styrene Dimer		1.13	1.37	1.38	1.57	2.16	0.59	0.86	0.92	0.87	0.56
Styrene Trimer		19.90	14.77	14.20	26.95	21.50	11.09	19.00	15.75	3.49	2.93
Diphenyl Propane		0.20	0.27	0.16	0.10	0.20	0.08	0.06	0.22	0.21	0.03

The commercial polystyrene was dissolved in 5 mL of benzene and the solution was transferred in 10 mL of methanol and the part of polymer was precipitated. 3 h freezing at -80 °C and centrifuged at 5000 rpm for 10 min. The supernatant was added an internal standard (Phenanthrene) and made up at constant volume (25 mL) by methanol. 1 μ L of the solution was analyzed by GC-MS.

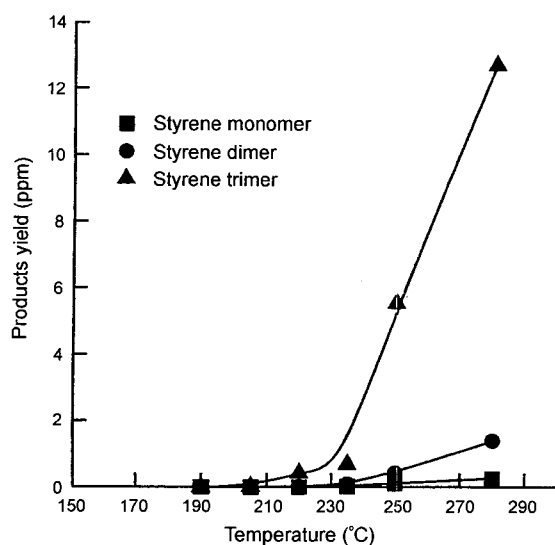


Figure 3. Effects of reaction temperature on thermal decomposition of polystyrene. Reaction time : 30 min. Material : reprecipitated PS, 0.100 g. Heating medium : 4.90 g.

background quantity. Figure 3 shows the effects of reaction temperature on the conversion of reaction products at low (190~280°C) temperature.

At 190~280°C, the thermal decomposition products of PS were the same as those of commercial products. Trimer was noted to be the first decomposition product by analysis of the commercial PS. The quantities of thermal decomposition products of commercial PS were considered to depend on temperature and time for molding and processing. The reaction mechanism for trimer, dimer and monomer production is described on another paper. These major products shown that the thermal decomposition of PS at low temperature was started by backbiting reaction.¹⁷

GPC and Molecular Weight. Subsequent to PS thermal decomposition at fixed temperature and specified time, 2 mg recovered PS by reprecipitation was dissolved in 200 μ L THF to examine molecular weight change by GPC. The results are shown in Table II. The molecular weight of PS before and after reaction differed little. The PS samples in

Table II were prepared as films for IR study. IR spectra were taken at 1596, 1492, 1448, 1070, 906, 756 and 699 cm^{-1} in consideration of the peculiar absorption band of PS. And there were no absorption at 825, 880, 965 and 1405 cm^{-1} which were produced by main chain scission.¹⁸ Virtually no change was detected in the heat-treated PS samples.

30 mg PS samples after thermal decomposition were dissolved in 400 μ L CDCl_3 with a small amount of TMS, followed by measurement of ^{13}C -NMR at 60°C and 16,000 scan. Spectral data were as follows: carbon (methine) of the main PS chain: 41.068~41.393 and methine; 42.458~47.148 and benzene ring carbon, C_4 : 126.083~126.392, $\text{C}_{2,3,5,6}$ (m); 127.761~129.119, C_1 (m); 145.571~146.589.

In ^{13}C -NMR, resonance signals of the original and heat-treated PS were basically the same. It is necessary that the PS molecular weight lowers to 3,000~5,000 in order to form the monomer, dimer and trimer. The separated component by GPC is only to shown the existence of the polymer, and the intense molecular lowering with the main chain scission in which volatile component is formed does not occur.¹⁹

Conclusions

The following results were obtained for the low thermal decomposition of PS using the new heating medium (PEG).

(1) Thermal decomposition started near 190°C at the molding temperature of PS.

(2) 2,4,6-Triphenyl-1-hexene (trimer) was shown to be the major product at the initial stage of decomposition.

(3) Product formation decreased in the order: trimer, dimer and monomer.

(4) Chemical compounds identified by GC-MS were benzaldehyde, ethylbenzene, xylene, 1-ethyl-4-methylbenzene, propylbenzene, 1-butylcyclohexene, tetrahydronaphthalene, naphthalene, 1,3-diphenylpropane, 1,4-diphenylbutane, 1-methyl-2-(2-phenylethyl)benzene, in addition to monomer, dimer and trimer. Endocrine disrupting substances as low molecular weight compounds with low boiling points were clearly shown produced through the thermal decomposition of PS at low temperature.

Table II. M_n , M_w and M_w/M_n Values of Polystyrenes after Thermal Decomposition

	Original Polystyrene (commercial)	Precipitated Polystyrene	220°C			250°C			280°C		
			30 min	60 min	120 min	30 min	60 min	120 min	30 min	60 min	120 min
M_n ($\times 10^5$)	1.60	1.38	1.66	1.11	1.33	0.85	1.18	1.36	0.99	1.15	1.33
M_w ($\times 10^5$)	5.20	5.66	4.96	4.96	4.58	4.39	3.91	3.53	2.69	3.66	3.21
M_w/M_n	3.26	4.11	3.00	4.49	3.45	5.14	3.32	2.59	2.71	3.18	2.42

Each Values were Calculated from Polystyrene Standard Calibration Curve by GPC Analysis.

GPC conditions, Column: Asahipak GF-7M HQ (Asahi Chemical Industry, Co., Ltd.), Detector : RI. Eluent: THF. Flow: 0.6 mL/min. Samples: 2 mg/200 mL dissolve in THF and 20 μ L injection. Temperature: 30°C.

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