

Thermal degradation products of homopolymer polystyrene in air

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PFÄFFLI, P., ZITTING, A. and VAINIO, H. Thermal degradation products of homopolymer polystyrene in air. *Scand. j. work environ. & health* 4 (1978): suppl. 2, 22—27. Polystyrene without additional compounds was treated in a laboratory oven at elevated temperatures (200°, 350°, 500°C) under slight air flow (0.7 l/min). The thermal degradation products appearing in different phases (gases, vapors, aerosols) were collected and analyzed by methods of chromatography. Thermogravimetric analysis showed the thermal degradation of the polymer to begin at 270°C in air and stop at 425°C. The main groups of vaporized compounds generated were mono-alkyl-substituted aromatic hydrocarbons and their oxidized products, of which styrene monomer and benzaldehyde were the most abundant. Only trace amounts of carbon monoxide and aliphatic compounds (hydrocarbons, aldehydes, and acids) were produced. The aerosol produced, the amount of which increased as the temperature rose, contained mainly fragments of the polymer chain (e.g., dimers and trimers of styrene). The traces of styrene, cumene, and ethylbenzene that appeared at 200° could represent residual compounds in the initial polymer and indicate the beginning of the thermal degradation. If proportional concentrations are kept as a criterion, the important products, from the point of view of industrial hygiene, were styrene, benzaldehyde, styrene oxide, acetophenone, and 1-phenyl-ethanol. The large amount of aerosol that appeared may also be of practical importance.

Key words: polystyrene, styrene, thermal degradation, working air.

Polystyrene is one of the most widely produced thermoplastics, and it is used for many different purposes (9). The working temperatures for polystyrene vary from 150° to 300°C, and in some operations, like wire-cutting, they may rise considerably higher. At these elevated temperatures the polymer is degraded to some extent, and the degradation products are emitted to the work environment. So far interest in the thermal degradation of plastics has been limited to polymer

science and technology, which have primarily concentrated on the identification of plastics and their additives and also on the toxicity of combustion products. In these studies the degradation conditions (high temperature, inert atmosphere) have been different from those existing in industrial processes, and under these conditions the pyrolysis of polystyrene has been studied by several investigators (2, 3, 6, 7). However, in our study we were interested in studying the thermal degradation products of polystyrene at temperatures close to those used in industry, and in the presence of air, for the evaluation of possible occupational health hazards.

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MATERIALS AND METHODS

Thermal degradation and collection of samples

The polymer used was homopolymer polystyrene (PS-RH, obtained from Stymer Ltd., Finland). According to the manufacturer the plastic contained no additives, and its residual monomer content was less than 0.02 %.

A sample (100 mg) of polystyrene was thermally degraded in a J-shaped glass tube (inner diameter 4 mm, wall thickness 1 mm, the total length 30 cm) inserted through a hole into the laboratory oven (fig. 1). The short arm of the tube was placed completely inside the oven so that the temperature would definitely be the same in both the tube and the oven. The temperatures used were 200°, 350°, and 500°C, as well as 700°C for the analysis of polynuclear aromatic hydrocarbons. Air was conducted by an air pump through the degradation tube for 15 min at a rate of 0.7 l/min. The degradation products were collected in glass spirals (inside diameter 4 mm, wall thickness 1 mm, total length of the spiral 80 cm) immersed in liquid nitrogen. The gases which were not trapped in this manner were collected in plastic laminated bags (polyethylene terephthalate — aluminum foil — polyethylene, obtained from Euran Paperi Ltd., Finland). The liquidized gases in the cold traps were allowed to reach room temperature and were also collected in these bags. Aerosols were collected on glass fiber filters (Sartorius Type 13400, diameter 37 mm), which were extracted before use with cyclohexane. Samples were also taken by liquid absorption for the analysis of aldehydes. Sodium bisulphite (25 ml of 0.1 M NaHSO_3) was used as the absorption liquid for both the total aldehydes and formaldehyde

collections, and ethanol (20 ml, 99.5 %) for the absorption of acrolein. Bubblers equipped with capillaries were used for absorption.

The analyses

The gases collected in the plastic laminated bags were analyzed directly by gas chromatography. The compounds condensed in the cold traps were washed out for gas chromatography with 1 ml of either carbon disulfide or acetone. The aerosol filters were dried in a desiccator, weighed, and extracted in Soxhlet extraction with 25 ml of benzene, methanol and cyclohexane. The solvents were evaporated nearly to dryness, and the residue was dissolved in 1 ml of cyclohexane or methanol for chromatographic analysis. The identification and quantification of the compounds were performed by the comparison of their retention values and peak areas in chromatography to those of commercial reference substances or, in the case of aerosols, by gas chromatography/mass spectrometry. (Details of the chromatographic analyses are presented in table 1.) The total aldehyde amount was determined by the sodium bisulphite/titration method (5). Formaldehyde was analyzed with chromotropic acid (1) and acrolein by the 4-hexylresorcinol method (4). The organic acids (e.g., benzoic acid) were analyzed by gas chromatography after conversion with diazomethane to corresponding methyl esters. Formic acid was measured by gas chromatography after esterification with diazomethane and conversion with dimethylamine to dimethylformamide (8). Carbon monoxide was measured by gas indicator tubes ("Dräger"-tubes, Drägerwerk AG, West Germany).

A thermogravimetric analysis (Mettler, TA 1, Switzerland) of the polymer was also made. A 10-mg sample of poly-

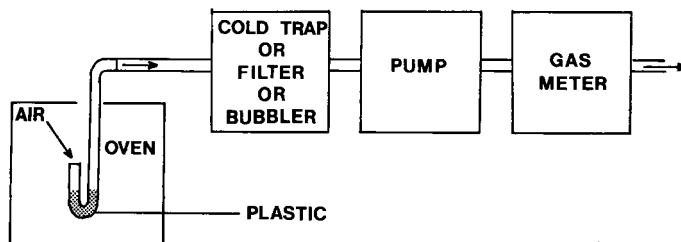


Fig. 1. Diagram of the thermal degradation arrangement.

Table 1. Analytical methods used for identifying the thermal degradation products of polystyrene.

Method	Gases	Vapors	Aerosols	Polystyrene
Gas-liquid chromatography (packed columns)		X ^a		
Gas-liquid chromatography (capillary columns)	X ^d	X ^{b, c, d}	X ^{b, c}	X ^d (monomer content)
Gas-liquid chromatography/mass spectrometry (capillary columns)			X ^e	
High-pressure liquid chromatography			X ^f	
Thin layer chromatography		X ^g	X ^g	
Thermogravimetric analysis				X
Gas indicator tubes	X			

^a Hewlett-Packard 5720 A, Carbowax 20 M on Chromosorb W, packed, glass, 2 m, 2 mm ID, 80–250°C, FID.

^b Hewlett-Packard 5720 A, FFAP, glass capillary, 50 m, 0.7 mm ID, 70–230°C, FID.

^c Varian 1400, SE 30, glass capillary, 25 m, 0.3 mm ID, 80–280°C, FID.

^d Perkin-Elmer F 6, PPG, metal capillary, 50 m, 120°C, FID.

^e Varian 1400/Varian MAT 112 S with electron impact detection, SE 54, glass capillary, 25 m, 80–280°C.

^f Varian 8500/Vari-Chrom, Mikro-Pak, MC 1–10, 25 cm × 2 mm, acetonitrile/water 54:46.

^g Polygram gel, 300 AC-30, 0.1 mm, acetylated cellulose, ethanol/chloroform/water 20:10:1.

Table 2. Aromatic hydrocarbons and their oxidized products released from 100 mg of polystyrene. (mg, mean of 5 samples ± SD)

Product	200°C	350°C	500°C
Aromatic hydrocarbons			
Benzene		0.03 ± 0.02	0.01 ± 0.01
Toluene		0.03 ± 0.02	0.10 ± 0.03
Ethylbenzene	trace	0.04 ± 0.01	0.01 ± 0.01
Cumene	trace	0.02 ± 0.01	0.01 ± 0.01
Styrene	trace	5.22 ± 0.83	5.84 ± 1.94
Allylbenzene		0.09 ± 0.02	0.03 ± 0.01
Alpha-styrene		0.12 ± 0.02	0.07 ± 0.01
n-Propylbenzene		< 0.01	< 0.01
Oxidized aromatic compounds			
Benzaldehyde		3.44 ± 0.97	0.87 ± 0.21
Cinnamaldehyde		< 0.01	< 0.01
Acetophenone		0.15 ± 0.03	0.02 ± 0.01
Benzyl alcohol		< 0.01	< 0.01
Styrene oxide		0.14 ± 0.03	0.07 ± 0.01
1-Phenylethanol		0.98 ± 0.40	0.08 ± 0.05
Benzoic acid		—	0.03 ± —
Phenol		0.12 ± 0.04	0.02 ± 0.01

styrene was heated in air, and the thermogram was recorded as weight loss versus temperature when the heating rate was 10°C/min.

RESULTS AND DISCUSSION

According to the thermal analysis (fig. 2) the degradation of polystyrene began at

about 270°C. The degradation was faster when the temperature was rising, and it stopped at about 425°C. The thermal degradation products could be collected in three phases: gases, vapors, and aerosols. The main volatile products in the vapor phase were monoalkyl-substituted aromatic hydrocarbons and their oxidized products (fig. 3). The main compounds in this group were styrene monomer, benzaldehyde, and 1-phenylethanol (table

2). The amount of styrene generated was nearly the same (i.e., 5–6 %) at 350°C as at 500°C. On the contrary, the amounts of oxidized products and other hydrocarbons were less at 500°C than at 350°C, possibly because of a more rapid degradation at higher temperatures and a shorter exposure time to oxygen.

The aromatic compounds generated at 350° and 500°C are listed in table 2. The trace amounts of styrene, cumene, and ethylbenzene that appeared at 200°C, probably represent both residual compounds in the initial polymer and the slow beginning of the thermal degradation.

Only small amounts (trace to 0.17 %) of aliphatic compounds were produced by the thermal degradation of polystyrene, the concentrations being slightly more abundant at 350° than at 500°C (table 3). The larger amount of carbon monoxide at 500° (2.1 %) than at 350° (0.4 %) also indicates less effective oxidation at higher temperatures. The measurement of total

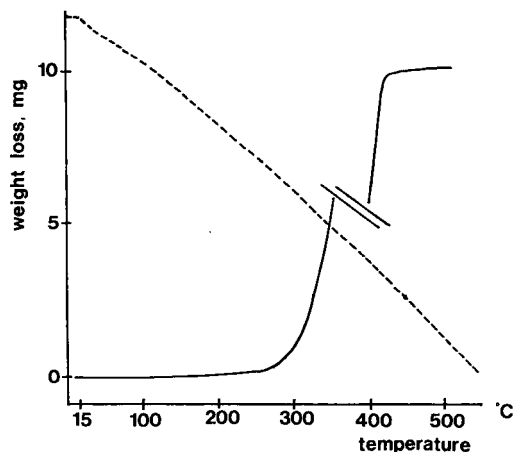


Fig. 2. Thermogravimetric record of a 10-mg sample of polystyrene (Stymer PS-RH). The heating rate was 10°C/min from the ambient temperature to 600°C. (— thermogram; ---- temperature rise)

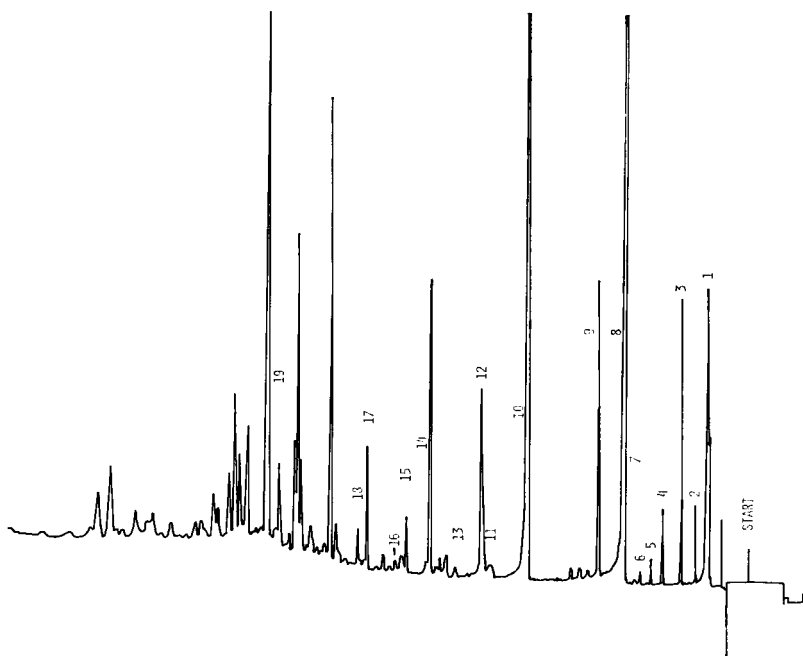


Fig. 3. Thermal degradation products of homopolymer polystyrene at 350°C — aromatic compounds of the vapor phase. (1 = solvent, 2 = benzene, 3 = toluene, 4 = ethylbenzene, 5 = cumene (iso-propylbenzene), 6 = n-propylbenzene, 7 = styrene, 8 = allylbenzene, 9 = alpha-methylstyrene, 10 = benzaldehyde, 11 = styrene oxide, 12 = acetophenone, 13 = naphthalene (?), 14 = 1-phenylethanol, 15 = benzylalcohol, 16 = 2-phenylethanol, 17 = phenol, 18 = cinnamaldehyde, 19 = dimer) (Gas chromatograph: Hewlett-Packard 5720 A; column: FFAP, 50 m Ø 0.7 mm; column temperature 50°C to 200°C, rate 4°C/min; detector: FID)

Table 3. Aliphatic compounds and oxides released from 100 mg of polystyrene (mg, mean of 3 samples).

Product	200°C	350°C	500°C
Formaldehyde	0.006	0.17	0.10
Acrylaldehyde	undetected	0.02	0.01
Formic acid	< 0.01	< 0.01	< 0.01
Hydrocarbons	undetected	< 0.01	< 0.01
Carbon monoxide	0.1 (7) ^a	0.4 (30) ^a	2.1 (120) ^a

^a Ppm (vol/vol) in outcoming air (12 l).

Table 4. Total amount of aerosol collected at different temperatures from 100 mg of polystyrene. The air flow was 0.7 l/min, and degradation time 15 min.

Temperature °C	Amount (mg) Mean ± SD	Range	Number of samples
200	0.1 ± 0.1	0.05— 0.3	7
350	18.9 ± 6.7	10.7 —26.7	11
500	26.5 ± 0.9	25.2 —27.4	10

aldehyde concentrations from the liquid absorption samples showed the same rate, i.e., 0.4 % at 200°, 3.5 % at 300°, and 1.1 % at 500°. These data also fit well the results of separate aldehyde measurements (benzaldehyde, cinnamaldehyde, acrolein, and formaldehyde).

In the thermal degradation of polystyrene also aerosol was produced. The aerosol amount increased as the temperature rose (table 4). According to Chang and Mead (2) and our preliminary gas chromatography/mass spectrometric studies, it seems to contain fragments of the polymer chain. The two highest tops in the capillary gas chromatogram gave mole-

cular ions, m/e 208 and 312, which correspond to the structure presented in fig. 4 (styrene dimer and trimer). In the aerosol phase no polynuclear aromatic hydrocarbons (conventional polyaromatic compounds) could be detected.

If proportional concentrations of compounds in air samples are kept as a criterion, the most important thermal degradation products of polystyrene are, from the industrial hygiene point of view, styrene monomer and oxidized aromatic compounds (e.g., benzaldehyde, styrene oxide, acetophenone and 1-phenylethanol). Also the considerable amounts of aerosols appearing may have practical importance.

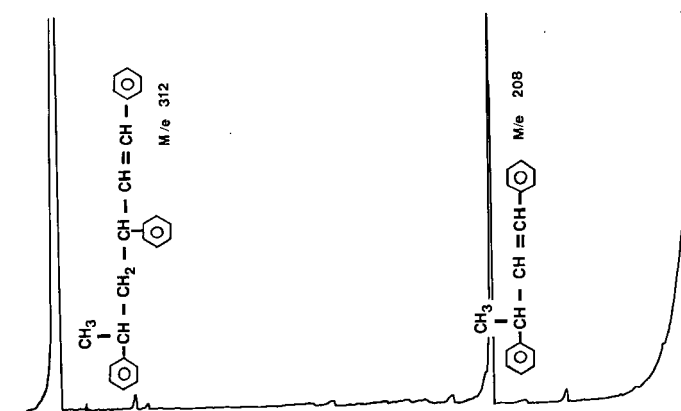


Fig. 4. Thermal degradation products of homopolymer polystyrene — the aerosol phase. (column: SE 54, glass capillary, 25 m; temperature: programed from 80°C to 280°C)

ACKNOWLEDGMENTS

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QUESTIONS AND ANSWERS

Question to Mr. ZITTING

Dr. RANTANEN:

Because the half-life of free radicals is surprisingly short, do you think the free radicals derived from styrene are not very reactive?

Mr. ZITTING:

According to our very preliminary results, the half-life of EST signals from the aerosol phase of the decomposition of both polystyrene and polyethylene is at least some hours. The free radicals themselves may be very reactive and have a short life-span, but the long existence of the radical nature of aerosol particles may be explained by the fact that in the particle the free radical reacts soon with other molecules and is finally eliminated only when reaching the surface of the particle and reacting with external molecules. Because of their long existence the radicals can easily reach the respiratory tract.