Continuous Monitoring of Thermooxidative Degradation Products of Polystyrene by Membrane Extraction with Sorbent Interface and Gas Chromatography

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Abstract

A novel method for the continuous monitoring of thermooxidative degradation products of polystyrene by membrane extraction with sorbent interface (MESI) and gas chromatography (GC) is developed. The results are compared with solid-phase microextraction–GC, which can extract gases, vapors, and aerosols. The volatile and semivolatile degradation products are identified by mass spectrometry. The membrane used in the MESI–GC analysis shows a high permeation for volatile aromatic hydrocarbons; a low permeation for corresponding volatile aldehydes; and no permeation for less volatile alcohols, acids, and degradation products with a high molecular weight, thus reducing significantly the number of compounds detected from MESI–GC. Sensitivity of the method depends on the time of trapping, which is limited by the breakthrough of the trap. By heating the trap at fixed intervals of time, consecutive gas chromatograms are obtained.

Introduction

The widespread use of polymer materials requires the evaluation of possible health hazards, which may arise during their production, processing, use, and recycling. The processing of plastics into final products by extrusion, thermoformation, and injection molding is performed at an elevated temperature in the presence of ambient oxygen. In these conditions an oxidative thermal degradation occurs, leading to a complicated mixture of products, which are volatile enough to be released into the surrounding atmosphere. Aromatic hydrocarbons and their oxidation products (such as styrene, α-methyl styrene, benzaldehyde, and acetophenone) generated by the oxidative thermal degradation of polystyrene (PS) are an important group of suspect cocarcinogenics, tumor-promoting agents, and irritant compounds. Styrene has already been detected by purge-and-trap gas chromatography (GC) in many foods (1–3) packed in PS containers and in the urine and blood of exposed workers (4,5).

A detailed characterization of the main products of the thermal degradation of PS has been carried out by GC–mass spectrometry (MS) (6–12) and infrared (IR) (8,13) and nuclear magnetic resonance spectroscopy (NMR) (3). The thermal degradation of PS has been performed by pyrolysis (5–8), thermal volatilization (1,2,6), and thermogravimetry (9). Before injection in GC, the volatile products are concentrated by purge and trap (1–5), cooling (7–11), or they are dissolved into a solvent (6,11). The major degradation components are aromatic hydrocarbons.

Continuous detection and quantitative measurements of these thermodegradation emissions presented in environmental ambient air is of considerable importance for keeping an emission inventory and immediate corrective actions of the industrial processing. Spectroscopic methods such as IR and NMR could be ideal for continuous monitoring because of their high analysis speed, but they are not used because it is difficult to identify individual organic compounds in a complex mixture using these approaches. MS alone can also be used, but the big challenge with MS is the presence of air and water from atmosphere. Also, all of these techniques are quite expensive.

GC is an excellent technique for the continuous monitoring of volatile organic compounds in a complex mixture, because they are first separated and the time of separation is significantly reduced by fast GC (14). A continuous GC monitoring involves a continuous extraction of analytes from matrix (their concentration followed by injection into a capillary column). The approach for achieving this goal is a focusing inlet system consisting of trapping by cooling (14), adsorption (15), or both in combination with a multiport gas sample valve. However, the cryogenic traps are not suitable in the presence of humidity, the valve is not fast enough, and no information is available in the period between injections. All of these disadvantages can be avoided by trapping at room temperature using a membrane extraction with a sorbent interface (MESI)

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as the inlet system (16). The membrane in an MESI system acts as a selective barrier between the sample matrix and chromatographic column. The analytes selectively extracted are concentrated by adsorption on a sorbent material and by heating the sorbent at regular intervals; a very narrow plug of analytes are injected into the column. MESI is a focusing inlet system that performs automatic, reproducible, and very fast injections without moving parts.

The objective of this study was to present data describing continuous monitoring by MESI–GC of the thermooxidative degradation products released into a surrounding atmosphere in PS processing at an elevated temperature. The degradation products passing through the membrane were identified by GC–MS and compared with those obtained by solid-phase microextraction (SPME)–GC analysis.

Experimental

Material and apparatus

PS without additives and styrene were obtained from Polysciences, Inc. (Warrington, PA). Benzaldehyde, acetophenone, phenylacetaldehyde, styrene oxide, and cinnamaldehyde were obtained from Aldrich-Sigma (Oakville, ON, Canada) and were used as the standard for identification and calibration. The sorbent in the microtrap was Tenax-TA from Supelco (Bellefonte, PA). SPME was performed manually with 100-µm polydimethylsiloxane (PDMS) and 65-µm PDMS–divinylbenzene fibers (Supelco). Helium and hydrogen (Praxis, Waterloo, ON, Canada) were used as carrier gases.

GC–MS analyses with SPME and MESI were performed with a Varian (Mississauga, ON, Canada) GC Model STAR 3400 equipped with an RTX-1 capillary column (30-m × 0.32-mm i.d. and 0.25-µm film thickness) (Restek, Bellefonte, PA) and coupled with a Varian Ion Trap MS–MS Model Saturn 4D. The carrier gas was helium at 10 psig. The MS spectra were recorded by the electron ionization (EI) mode with a scan range from 40 to 250 amu. The filament emission current was 16 µA and was turned off for the first 40 s. The transfer line temperature was 280°C and the ion-trap manifold temperature was set at 220°C. The electron multiplier voltage and automatic gain control target were set automatically.

MESI–GC continuous monitoring was performed with a portable SRI (Torrence, CA) GC Model 8610C equipped with a flame ionization detector, a hydrogen generator, and an MTX-1 silicosteel capillary column (3-m × 0.28-mm i.d. and 3-µm stationary phase thickness) (Restek). The membrane module had a flat membrane with a thickness of 0.025 mm and an outlet surface of 163 mm^2. The membrane was made from 40% bisphenol A polycarbonate and 60% PDMS by Specialty Silicone Products Inc. (Ballston Spa, NY). The trap was made by packing deactivated stainless steel tubing (0.53-mm i.d. and 0.65-mm o.d.) of 1.8 cm length with 1.2 mg Tenax TA (40–60 mesh) between two plugs of glasswool. Hydrogen was used as the carrier gas at 10 mL/min, and the temperature of the capillary column was constant at 110°C.

The temperature of the heated degradation element was controlled and kept constant with the Digital Temperature Microcontroller CN 132, and the temperature in the degradation chamber was measured with the Microprocessor Thermometer HH22 (both were obtained from Omega Inc. (Stamford, CT)).

Thermooxidative degradation, collection, and analysis of samples

A general scheme of the system used for polymer degradation, collection, concentration, and introduction of the volatile products into a GC for analysis is presented in Figure 1. The degradation of PS was carried out on the surface of an electrical heated element in a degradation chamber made by a 3000-mL glass jar with a screw cap and three lateral orifices plugged with silicone rubber for SPME collection and thermocouple wires. The heating element was covered with an aluminum foil. A solution of 30% PS in ethyl acetate was used to create a very thin film of polymer on the surface of the aluminum foil. Most of the solvent was removed under vacuum at room temperature overnight. The heating element was hung in the degradation chamber with electrical wires, which were inserted through a cap screw hole and connected to a temperature controller. The temperature of the heating element was measured with a thermocouple fixed under the aluminum foil and was set up with a digital temperature microcontroller. The temperature in the degradation chamber was held constant at 23°C and 40°C with an external thermostat and was measured with another thermocouple and a digital thermometer. The membrane module was hung in the upper part of the degradation chamber, and the connecting tubes were inserted through a sealed hole in the cap screw. The design of the membrane module, heated connection tubes, and microtrap have already been presented (16).

The volatile and semivolatile degradation products of PS were collected discontinuously by SPME and continuously by MESI. In the SPME procedure, the syringe needle was inserted through the septum hole on the lateral side of the degradation chamber. The PDMS fiber was lowered in the headspace by depressing the plunger and was exposed to the sample for 30 min at different temperatures (23°C and 40°C); then, the

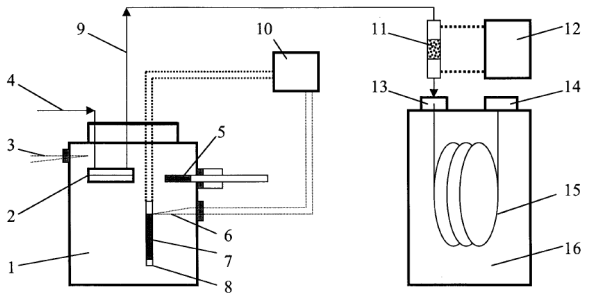

Figure 1. Schematic diagram of the experimental thermooxidative degradation and MESI–GC system: degradation chamber, 1; membrane module, 2; thermocouple, 3; carrier gas inlet, 4; PDMS fiber, 5; heating element thermocouple, 6; PS film, 7; heating element, 8; connection tube heated at 120°C, 9; temperature controller, 10; Tenax TA trap, 11; capacitive discharge power supply, 12; GC injector, 13; detector, 14; capillary column, 15; and GC oven, 16.

needle within the fiber was withdrawn and introduced into the GC injector at 280°C for 30 min. The MESI procedure consisted of a continuous permeation of volatile analytes through a membrane, concentration onto a sorbent trap, and their injection into the GC capillary column by heating the trap. The membrane module was held at the temperature of the degradation chamber. The volatile degradation products were retained by sorbent at room temperature and desorbed applying from time to time direct voltage on the metal tube of the trap using a capacitive discharge power supply. The cycle of trapping and heating was repeated automatically with the use of an electronic timer. The trapping time could be selected with the timer to be between 6 s and several hours. The trap was electronically heated at approximately 250°C, which produced a minimal decomposition of the sorbent material and 98% desorption of the analytes. The connecting tubes between the membrane module and GC injector were from deactivated metal tubes and were held at 120°C with a heating tape.

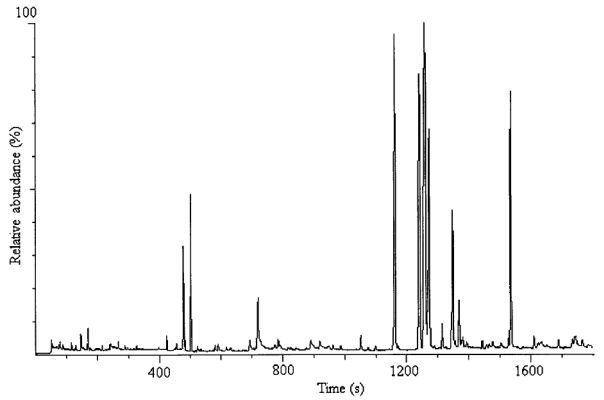

Figure 2. GC–MS total ion chromatogram of the thermooxidative degradation products of PS at 150°C. The extraction was with a PDMS fiber. The GC oven temperature program was from 90°C to 150°C at 15°C/min and then to 280°C at 15°C/min. The other GC–MS conditions can be found in the Experimental section.

Results and Discussion

The degradation products that formed during the thermal-oxidative treatment of PS were first extracted by an SPME fiber. Figure 2 shows the GC–MS total ion chromatogram obtained after extraction at 40°C with a PDMS fiber of the degradation products of PS generated at 150°C. The melting point of PS is 250°C (17), but the degradation process was started at a lower temperature because of the presence of weak links (18). Figure 3 shows that by increasing the degradation temperature to 250°C, the amount of volatile and less volatile degradation products increased. This phenomenon can be explained by a higher degradation rate of the polymer at a high temperature and a higher vapor pressure of the volatile compounds. The degradation process was started on the surface between the heater and polymer by generating oligomers. The degradation products must permeate from this surface through the polymer film into the analysis chamber. By increasing the temperature, complex pyrolytic and thermooxidative processes took place in the whole film and the polymer

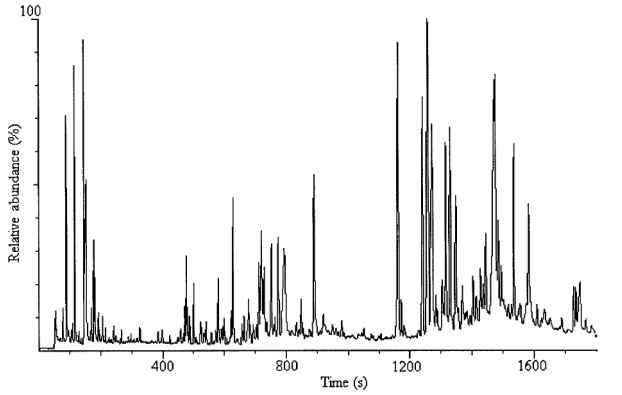

Figure 3. GC–MS total ion chromatogram of the thermooxidative degradation products of PS at 250°C. For experimental conditions see Figure 2.

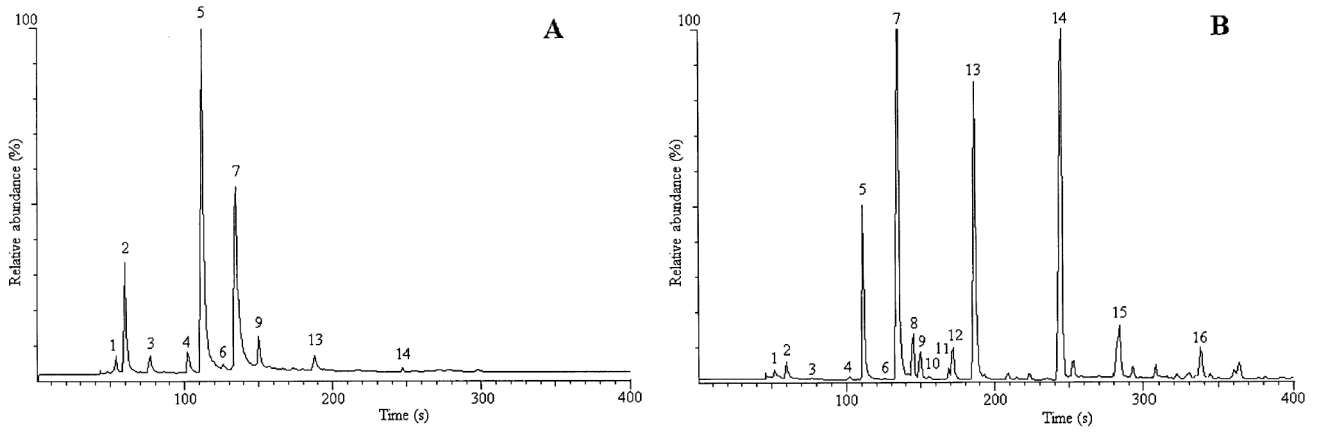

Figure 4. GC–MS total ion chromatograms of the thermooxidative degradation products of PS at 250°C using (A) MESI and (B) SPME in the same GC conditions. The GC oven temperature program was from 60°C to 100°C at 15°C/min and then to 120°C at 5°C/min. The time of trapping was 400 s and the breakthrough was 1200 s. The other GC–MS conditions can be found in the Experimental section. The numbered peaks are identified in Table I.

became yellow. From Figure 3 it can be seen that there were three groups of degradation products. The first group was between 50 and 400 s, the second between 400 and 1100 s, and the third between 1100 and 1800 s. In each group the aromatic hydrocarbons and their oxidized derivatives were identified. The first group had only one aromatic cycle, the second had two, and the last group had three. The thermal degradation of PS has been extensively investigated by pyrolysis (12), but the mechanism and kinetics of degradation remains subjects of discussion (7). Three phases of degradation products were obtained: gases, vapors, and aerosols. The vapors and aerosols were condensed at room temperature on the wall of the degradation chamber, and soon afterwards the glass wall became opaque. The amount of compounds extracted by SPME at room temperature was higher because the less volatile compounds condensed on the surface of PDMS and the partition coefficient of the volatile compounds in the PDMS fiber was increased at low temperature.

Figure 4A shows the GC–MS total ion chromatogram of the degradation products of PS at 250°C obtained by MESI–GC analysis, and Figure 4B shows the GC–MS total ion chromatogram with SPME–GC analysis only for volatile products in the same GC separation conditions. The identification of the peaks in both chromatograms is presented in Table I and was performed using fragmentation rules from EI MS and by comparing them with library mass spectra. Peak No. 1 was the solvent used to apply a thin film of PS on the degradation element. A strong molecular ion ($M^{+\bullet}$) was typically observed in the EI mass spectra of compounds 1–11, 14, and 15. There were two exceptions for compounds 12 and 13 (which have smaller molecular ions). Compound 16 had no molecular ion because of the formation of a very stable fragment ion at *m/z* 131, $[Ph\text{-}CH{=}CH\text{-}C{=}O]^{+}$, from the molecular ion by loss of the OH^{-} free radical. The mass spectrum of peak 12 can be attributed to phenyl acetaldehyde or phenyl oxirane, because both gave similar mass spectra. However, the EI abundance of fragment ions *m/z* 91 (100%) and *m/z* 92 (31%) were more consistent with phenyl acetaldehyde.

The major volatile products in the SPME chromatogram were cinnamic aldehyde, acetophenone, benzaldehyde, and styrene. The number of products seen in the MESI chromatogram was considerably smaller than with the SPME fiber. The major products from MESI were benzene, styrene, benzaldehyde, and volatile and semivolatile compounds with a high coefficient of permeation through the membrane. The rate of permeation was the result of the diffusivity and solubility coefficients of the analytes. The selectivity of permeation through the membrane was achieved either by differences in solubility, diffusivity, or both. The PDMS–PC membrane had a high permeation rate for volatile and nonpolar compounds. Oxygenated compounds with a high polarity and boiling point

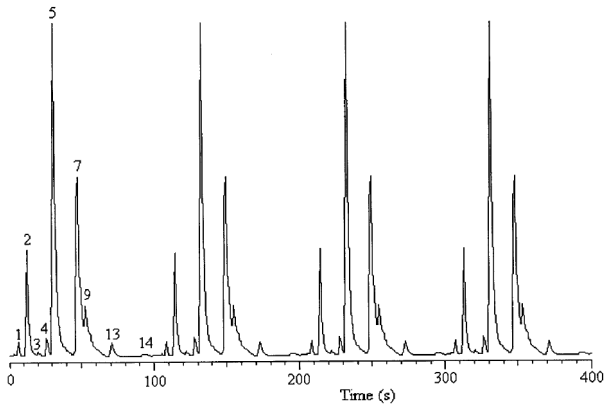

Figure 5. Successive gas chromatograms of continuous monitoring by MESI–GC of the thermooxidative degradation products of PS at 250°C. The experimental conditions can be found in the Experimental section. The numbered peaks are identified in Table I.

Table I. Selected Mass Spectra Data for the Numbered Peaks from Figures 3–5

Peak No.	Chemical abstract*	Boiling point (°C)	*m/z* (Relative intensity, %)
1	Acetic acid ethyl ester (ethyl acetate) (solvent)	77	88($M^{+\bullet}$)(9), 70(4), 61(13), 45(11), 43(100)
2	Benzene	80	78($M^{+\bullet}$)(100), 77(32), 63(5), 52(18), 51(22), 50(20)
3	Methyl-benzene (toluene)	110	92($M^{+\bullet}$)(45), 91(100), 77(3), 65(12), 63(9), 51(8)
4	Ethylbenzene (α-methylbenzene)	135	106($M^{+\bullet}$)(21), 105(12), 91(100), 78(8), 77(8), 65(10), 51(10)
5	Ethenyl-benzene (styrene)	145	104($M^{+\bullet}$)(100), 103(74), 78(29), 77(15), 63(7), 51(18)
6	1-Methylethyl-benzene (isopropylbenzene)	153	120($M^{+\bullet}$)(18), 105(100), 103(27), 91(7), 79(19), 78(15), 65(4), 51(11)
7	Benzaldehyde (phenylformadehyde)	178	106($M^{+\bullet}$)(32), 105(100), 78(11), 77(76), 51(32)
8	Phenol (hidroxybenzene)	182	94($M^{+\bullet}$)(100), 66(18), 65(23), 55(4)
9	1-Methylethenyl-benzene (α-methylstyrene)	169	118($M^{+\bullet}$)(18), 117(100), 106(53), 91(32), 78(41), 77(52), 63(12), 51(28)
10	Benzofuran (coumarone)	175	118($M^{+\bullet}$)(100), 90(44), 89(70), 63(26), 50(8)
11	Benzenemethanol (benzylalcohol)	205	108($M^{+\bullet}$)(69), 107(66), 79(100), 77(70), 51(25)
12	Benzeneacetaldehyde (phenylacetaldehyde)	194	120($M^{+\bullet}$)(3), 119(7), 92(31), 91(100), 77(3), 65(22), 51(5)
13	1-Phenyl ethanone (acetophenone)	202	120($M^{+\bullet}$)(3), 119(7), 105(100), 77(90), 51(26), 50(14), 43(13)
14	3-Phenyl-2-propenal (cinnamaldehyde)	248	132($M^{+\bullet}$)(18), 131(12), 104(39), 103(100), 77(53), 63(5), 51(17)
15	Benzoic acid (phenylcarboxylic acid)	249	122($M^{+\bullet}$)(63), 119(7), 105(100), 77(22), 51(14)
16	3-Phenyl-2-propenoic acid (cinnamic acid)	300	131(100), 103(50), 78(15), 77(20), 51(18)

* Another name for the chemical abstract is shown in parentheses.

such as benzoic acid and cinnamic acid did not permeate through the membrane. The Tenax TA trap retained oxygenated compounds when no membrane was in the system, but the presence of the membrane introduced the selectivity of permeation through the membrane. These characteristics of the membrane collection of the analytes has a great importance in the continuous monitoring of complex mixtures such as these degradation products of PS, giving a simpler chromatogram with the possibilities to reduce the analysis time.

Figure 5 shows successive gas chromatograms obtained by the MESI–GC continuous monitoring of the volatile and semivolatile products obtained by the thermal-oxidative degradation of PS. For a fast separation, a short capillary column was used and the carrier gas flow rate was higher than usual. The trapping time was 100 s and was selected to get a good separation of peak. Each heating of the trap generated a chromatogram. The maximum trapping time was a function of breakthrough of the trap, which in these experimental conditions was 340 s. By increasing the trapping time to 300 s, the extracted amount of analytes through the membrane and injected into the GC will be higher and the sensitivity of detection improved. The detection limit for styrene (as the major peak) was 0.12 ± 0.01 µg/L in air at a 100-s trapping. The detector was calibrated by direct injection.

Conclusion

The MESI–GC technique described in this article exhibits attractive characteristics for the continuous monitoring of the volatile and semivolatile products from thermooxidative degradation of PS. The collection of analytes by permeation through a membrane has a high selectivity for volatile and semivolatile aromatic compounds; a lower selectivity for their corresponding volatile aldehydes and ketones; and eliminates alcohol, acids, and heavy degradation products extracted by SPME, thereby simplifying the gas chromatogram. A fast GC analysis using a short capillary column and high carrier gas flow rate made possible a real-time monitoring of the level of degradation products into the surrounding atmosphere.

Acknowledgments

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