On-line GC/MS Identification of volatile organics formed during the UV irradiation of polymeric materials

R. R. Freeman, Quantum Analytics, Foster City, USA
T. Yuzawa, Frontier Laboratories, Koriyama, Japan

Introduction

The physical and chemical characteristics of most polymeric materials gradually degrade due to environmental factors such as heat, photo irradiation, oxidation and mechanical stress. During the degradation process, both the degradation products and the structural changes in the sample itself are of interest. Historically, the performance of polymeric materials is determined using data from conventional atmospheric exposure tests or weather meters. Both techniques require weeks, if not months, before performance variations in the polymer can be detected; consequently, it is a costly process and only a limited number of very promising formulations undergo such tests. Despite the well documented testing protocols used in these tests, the results are often disappointing. There is no information on the volatiles formed as the material undergoes "stress". Without this information, postulated reaction sequences are based more on theory and experience and not analytical data.

Interest in identifying and quantifying the volatile organic compounds formed as a polymeric material is irradiated and recent advances in analytical instrumentation have lead to the development of a new analytical technique: UV/Py-GC/MS[1]. Using a pyrolyzer as an inlet to a GC/MS satisfies a number of operational needs. It is a closed system; evolving volatiles are focused on the column and not lost. Virtually all environmental factors (temperature, surrounding atmosphere, humidity, light intensity, wavelength, exposure time, etc.) can be controlled and measured. GC/MS is well established as the best tool for separating and identifying volatile organic compounds. Being able to control the operational variables reduces the time it takes to detect change in the test sample from days and weeks to hours. The implications of this are astounding. Subtle changes in formulation can be evaluated quickly, which will facilitate the development of new materials and improve the performance of many polymers in use today.

The basic performance of the newly developed UV irradiation system was studied using polystyrene as a representative polymeric material.

Experimental

High purity polystyrene was dissolved in dichloromethane. The concentration of polystyrene was 5μg/μL. 5μl of the solution was put in an 80μL sample cup. The dichloromethane was allowed to evaporate prior to analysis. This technique ensures that the polystyrene is a thin film on the bottom surface of the cup. The sample cup was then fitted onto the tip of the quartz light pipe and positioned above the furnace.

The analytical platform is shown in Figure 1. A Frontier Laboratories 2020iD pyrolyzer fitted with a 1047Xe UV irradiator was mounted on an Agilent 5975C GC/MS. The separation column was 30M X 0.25mm id (film thickness 0.25µm) coated with 5% diphenyl 95% dimethylpolysiloxane. A loop of the column was immersed in a Dewar of liquid nitrogen. This served to focus the volatiles as they were formed during irradiation. The focusing step is an essential element of the process. Often the irradiation continues for several hours and it is critical that the initial band width of the volatile organics be as narrow as possible.
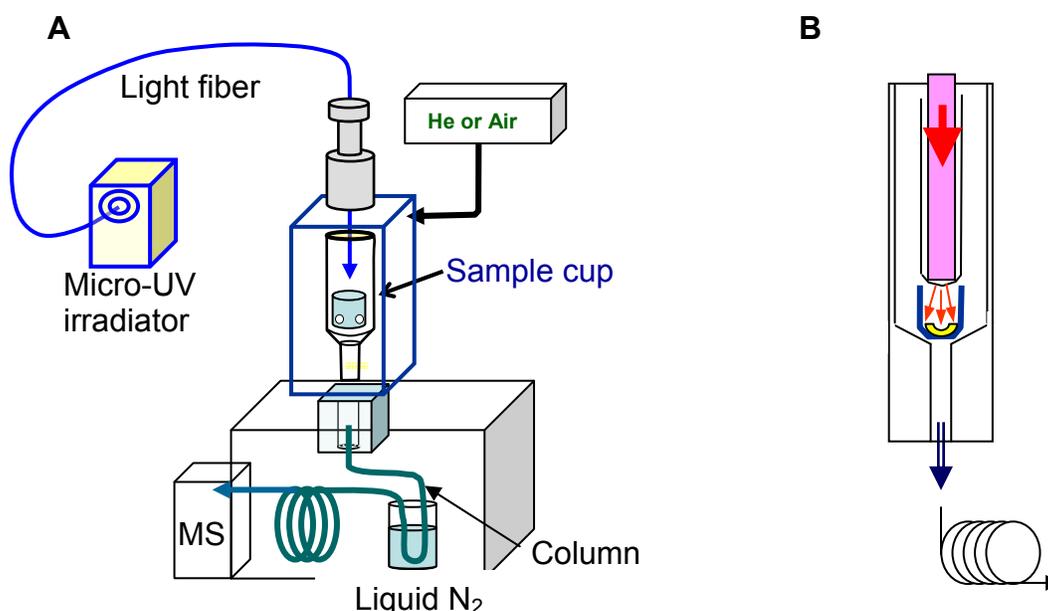

Figure 1. (A) The light from the Xe source is directed onto the sample. Volatiles formed during the irradiation are carried by the carrier gas through a splitter and onto a cold spot at the head of the column. The chromatographic separation occurs when the light source is turned OFF and the Dewar removed. The temperature of the separation column is programmed up. (B) The sample is located 5mm from the tip of the fiber optics cable and the entire surface of the sample is irradiated.

Before the start of the irradiation, three conditions must be satisfied: (1) the pyrolyzer furnace must be at the set point, (2) the helium in the system must be purged and replaced by the atmospheric gas of choice (e.g., air, oxygen, etc) and (3) the head of the column must be immersed in liquid nitrogen. Once these three criteria have been satisfied, the sample is lowered into the furnace and the UV irradiation (Xe lamp, 280-450nm) commences. The experiment terminates when the UV light is turned off, the reactant gas is replaced by helium and the Dewar is removed from the column. These activities signal the GC START RUN. The trapped volatiles are separated and fragmented using electron impact mass spectrometry.

Detailed Characterization of polystyrene

Over the years there has been considerable discussion about the effect of UV radiation on the degradation of polystyrene. One school of thought supports a Norrish type I reaction, the other a Norrish type II.[2] These discussions suffered from a lack of empirical data. There was no analytical method that could be used to identify the volatiles formed as the polystyrene was irradiated. Thus, one of the first applications of the UV-PY-GC/MS system was the determination of the volatiles formed when

polystyrene is irradiated. The two photochemical reaction sequences are summarized in Figure 2. One path favors the formation of benzaldehyde and benzoic acid, the other acetophenone.
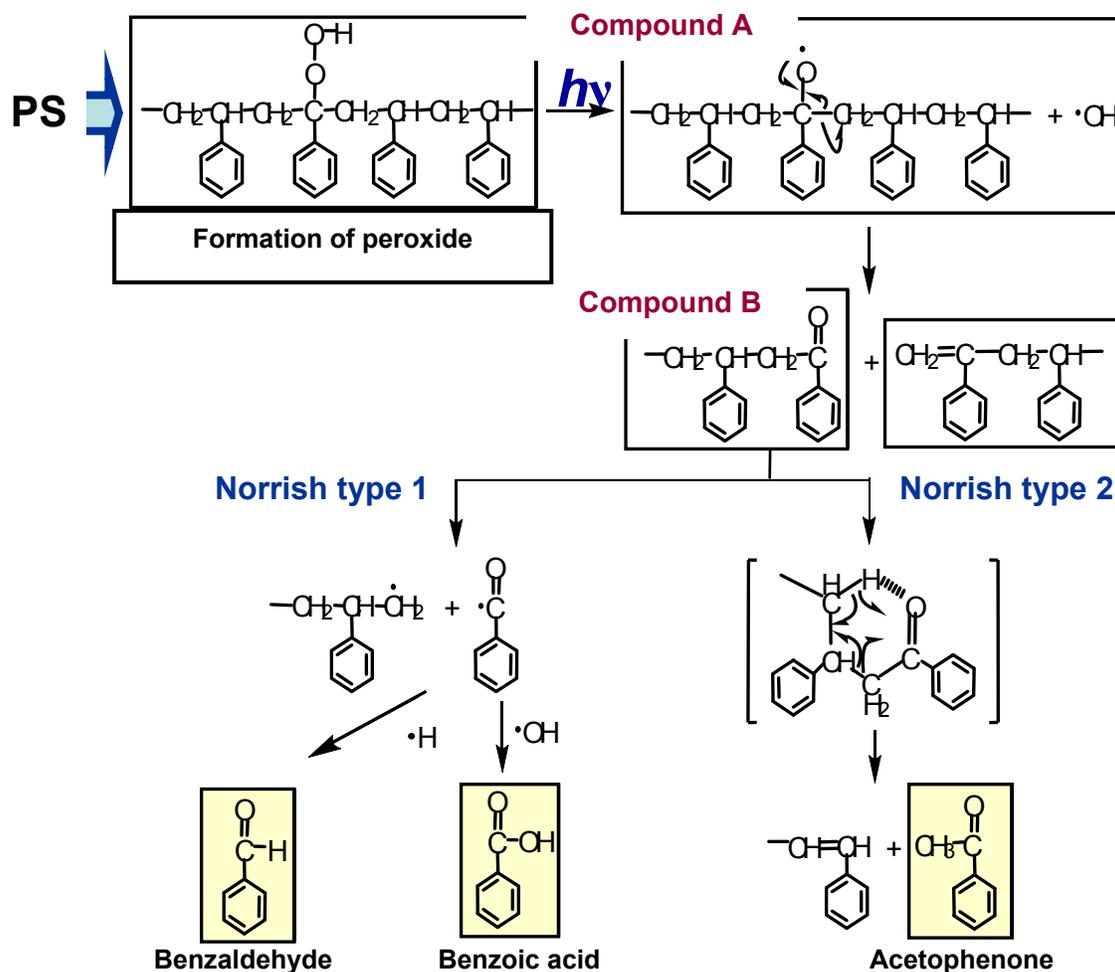

Figure 2. **Assumed reaction paths for photo, thermal, and oxidative degradation of PS**

Figure 3 is the total ion chromatogram of the volatile organic compound formed when polystyrene is irradiated in air, at 100°C for three hours. Identifications are based upon the mass spectrum of each peak.
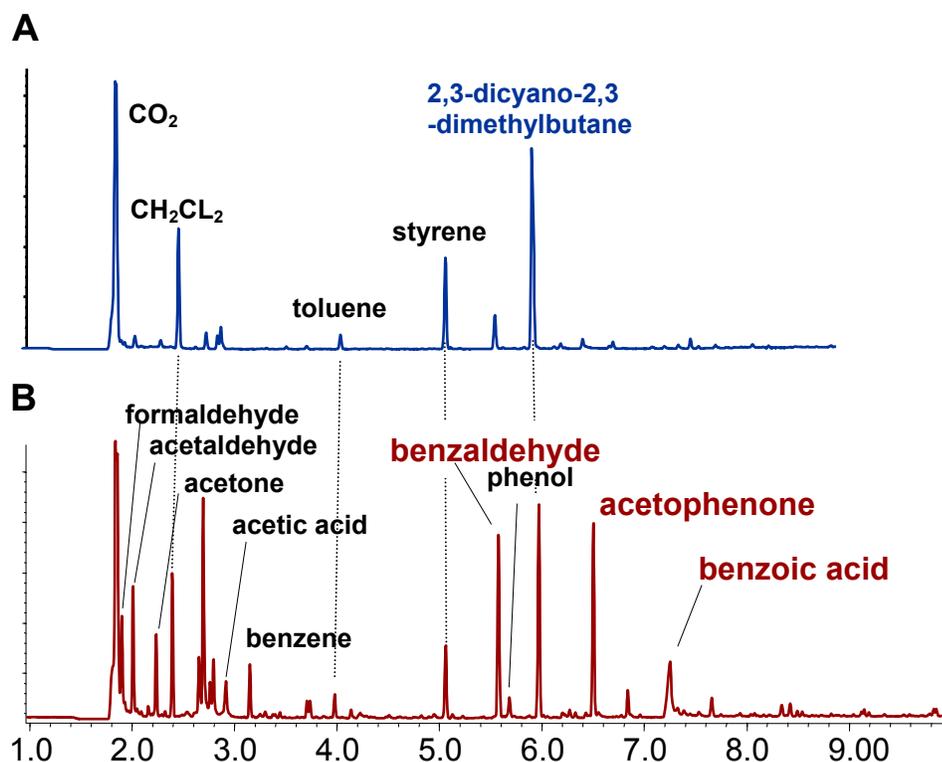
Figure 3. Total ion chromatogram of the volatile degradation products formed when polystyrene is irradiated at 60°C for one hour in air. (A) UV irradiation OFF, (B) UV irradiation ON. (PS sample: 20 μg, air flow rate: 10 mL/min, GC injection port temp.: 200ºC, Sample heated after UV irradiation: 100 to 250ºC (20ºC/min, 5min hold), GC oven temp.:40 to 300ºC (20ºC/min, 5 min hold), He: 1 mL/min, MS scan range: 29-300 amu.

The presence of formaldehyde, acetaldehyde, acetophenone and benzoic acid appears to support the Norrish type I reaction sequence. The mass spectrometer scanned down to 29 amu; hence, the presence or absence of carbon monoxide cannot be determined. The precision of the peak areas is outstanding: benzaldehyde - %RSD=3.55, Acetophenone - %RSD=2.67, benzoic acid - %RSD=7.53. Table 1 illustrates the precision of the peak area ratios for benzaldehyde and acetophenone.

N=6	Benzaldehyde Benzaldehyde + Acetophenone	Acetophenone Benzaldehyde + Acetophenone
Ave.	0.607	0.393
%RSD	2.25	3.31

Table I. Reproducibility of peak area ratio for benzaldehyde and acetophenone formed from PS sample during UV irradiation for 3 hours in an oxidative atmosphere at 100 ºC.
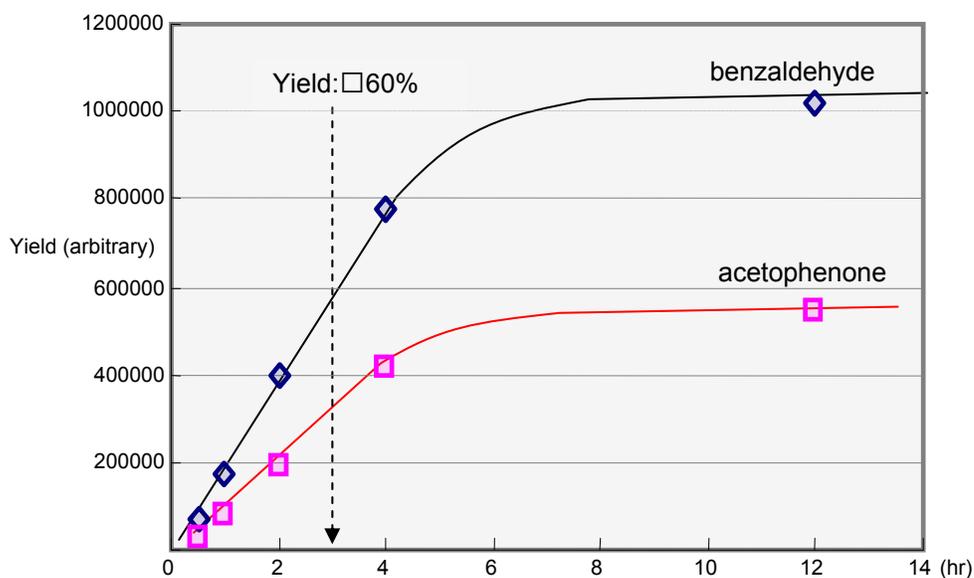
Figure 4. Relationship between peak area and UV irradiation time: 30 mL/min air at 100 ºC

The implication of the isotherms shown in Figure 4 is that the degradation of the polymer is a "surface effect." The plateau of the peak areas clearly indicates that further irradiation, at the same conditions (i.e., temperature, atmosphere, UV intensity, etc.), will not continue to degrade the polymer.

After irradiation, the polymeric residue in the sample cup can be characterized using a variety of traditional methods, such as evolved gas analysis (EGA), thermal desorption (TD) and/or flash pyrolysis (PY). The total ion chromatograms of the residue analysis are presented in Figure 5.
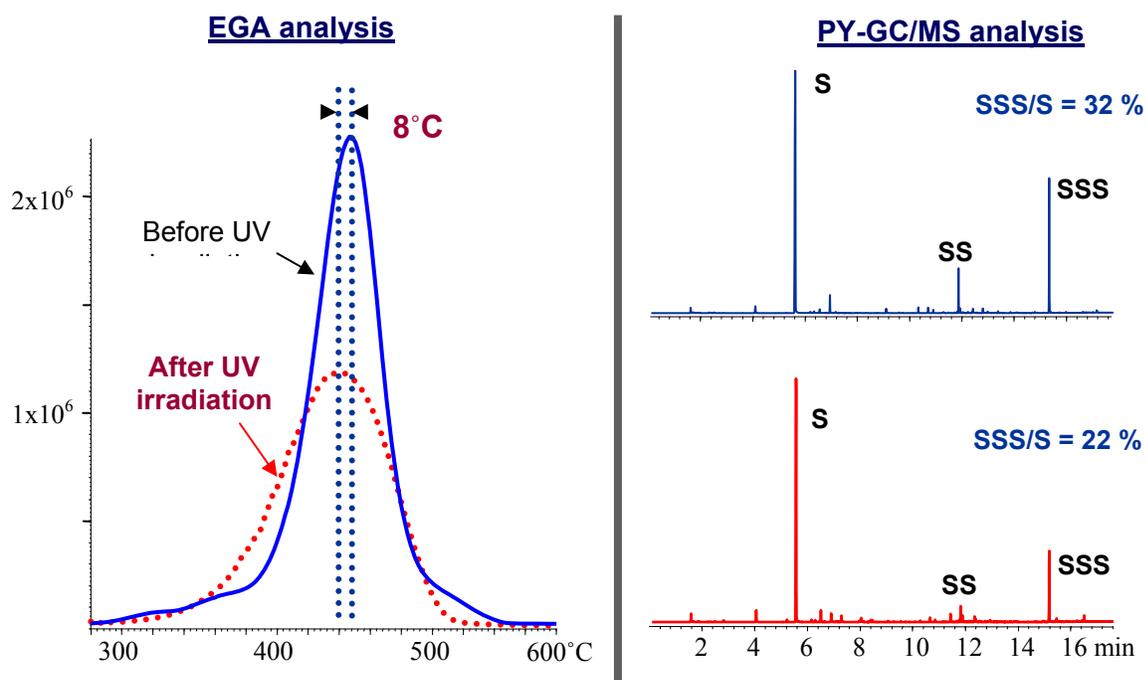

Figure 5. Total ion chromatograms obtained from an evolved gas analysis and flash pyrolysis of the irradiated polystyrene. PS sample: 100 µg, 60˚C for 1 hr in air. EGA at 20°c/min; Pyrolysis at 550°C, Column: UA-30M X 0.25mm id (film=0.5µm), GC temp.: 60 to 320ºC (20ºC/min)

The EGA results clearly indicate that the polystyrene has degraded. The distribution of the thermogram is broader and the apex has shifted 8°C. This is supported by the pyrolysis data. The pyrograms show that the SSS/S ratio has decreased over 30%. The decrease can be attributed to a decrease in the polymer stability; hence, the lower trimer response and the corresponding increase in the monomer response.

Summary

The ability to irradiate a polymeric material in a "closed" GC/MS system provides the chemists working with new additives and formulations with a unique, analytical tool. Virtually all environmental factors (wavelength, intensity, temperature, atmosphere and time) can be varied, thus extending the range of stresses that can be brought to bear when evaluating new materials. Information about a polymer, which has historically been collected using weather meters, can now be obtained much faster: 1 hour *vs*. 300 hours. This new analytical technique enables the analyst to quickly evaluate the effects that additives, such as photo stabilizers and UV-absorbers, have on the over all performance of a polymeric material.

References

1. C.Watanabe, H.Ohtani, S.Tsuge; *Polymer Degradation and Stability*, **94** (2009) 1467–1472.
2. *Named Organic Reactions*, 2nd Edition, Thomas Laue and Andreas Plagens, John Wiley & Sons: Chichester, England, New York, **2005**. 320 pp.