

## Development of an on-line ultra violet radiation pyrolysis-GC/MS (UV/Py-GC/MS) system for rapid and sensitive weathering test of materials

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### Abstract

A new analytical instrument using an on-line micro-ultra violet (UV) radiator combined with the multi-functional micro-furnace pyrolyzer attached to a capillary GC/MS was developed for rapid and sensitive evaluation of the material deterioration and its fundamental performance was evaluated using polystyrene.

Most of the physical and chemical performances of polymeric materials gradually degrade due to external effects such as heating, photoradiation, oxidation, and mechanical stress [1]-[5]. During the degradation process, not only the decomposed components formed from the sample materials but also the structural alternations of the substrate polymers are important targets to analyze. Detail information obtained by the analysis is often beneficial to prepare the advanced materials by modifying its molecular structures and/or selecting appropriate additives. However, the conventional weathering test followed by various analytical methods is laborious and time consuming [5].

In this work, a novel analytical instrument using an on-line micro-ultra violet (UV) radiator combined with the multi-functional micro-furnace pyrolyzer (PY-2020iD, Frontier Lab, Japan) attached to a capillary GC/MS was developed for rapid and sensitive evaluation of the material deterioration [6]-[8].

Figure 1 shows the schematic diagram of the developed analytical system. UV wavelength was ranging from 210 to 400 nm, and its intensities at 254 and 340 nm were about 15 and 300  $\mu\text{W}/\text{cm}^2$ , respectively. A small diameter (*ca.* 3 mm) of UV beam was irradiated on a minute amount (several hundred  $\mu\text{g}$ ) of polymer sample taken in a sample cup of the pyrolyzer through a fiber optical cable (core o.d. 0.8 mm) under oxidative and temperature regulated atmosphere at 50 - 100°C. The air carrier gas flow rate was normally set to about 5 ml/min. The trace amounts of evolved gases from the irradiated polymer sample were trapped at the head of the separation column during irradiation and the following thermal desorption by soaking in liquid nitrogen before GC/MS analysis. After the irradiation of the sample, carrier gas was changed to helium with almost the same carrier gas flow rate. Then the furnace heater temperature was increased rapidly to an appropriate temperature and holding several minutes in order to fully desorb the degraded and oxidized compounds in the polymer sample. After complete thermal desorption, the column was taken from the liquid nitrogen Dewar and was stored in the GC oven to start the GC/MS analysis.

Furthermore the deteriorated polymer sample remaining in the sample cup was flash pyrolyzed using the pyrolyzer at high temperature typically around 600°C to get a

specific pyrogram, or subjected to conventional evolved gas analysis (EGA) typically by temperature programming up to 700°C to get a thermogram which provides the structural information of the deteriorated polymer. Based on the information obtained both for volatile components and deteriorated residue, the deterioration mechanism of the polymeric material during photo, thermal and oxidative decomposition and the effect of additives such as photo-stabilizer and UV-absorber can be evaluated using sub-milligram order of polymer sample within a relatively short test period. Here the basic performance of this system was examined using polystyrene (PS) as a representative polymeric sample materials.

Figure 2 shows the chromatographic data of the desorbed products from the PS samples without (A) and with (B) UV radiation for 3 hrs at 100°C under oxidative atmospheres and then heated to 150°C for 5 min under helium atmosphere. On the chromatogram for PS with UV radiation (B), oxygen containing products such as benzaldehyde (B-al), acetophenone (Ap) and benzoic acid (B-ac) are clearly observed. The observed reproducibilities of the absolute peak area for 25µg of PS expressed in relative standard deviation for 5 runs were 2.89, 2.79 and 6.79 % for B-al, Ap and B-ac, respectively.

Figure 3 shows the comparative thermograms taken by EGA technique for the PS samples, without and with UV radiation for 3 hrs under air atmosphere at 100°C. It is interesting to note that the peak top temperature and the whole profile for the PS sample with UV radiation shifted lower by ca. 25°C. These results strongly suggest that the molecular weight (MW) of the substrate polymer might be reduced during the photo, thermal and oxidative degradation.

Figure 4 shows the comparative pyrograms for the PS samples treated without (A) and with (B) UV radiation taken by flash pyrolysis-GC/MS technique at 600°C. Although the peak intensities for major components such as styrene monomer and dimer were almost comparable, trimer ratio against monomer for the PS sample without UV radiation, 15.2% decreased to 10.3% for the sample with UV radiation, which might be attributed to the reduction of the average MW during the deterioration. By using the developed on-line UV/PY-GC/MS system, the deterioration of polymeric material such as PS during UV irradiation under thermal and oxidative atmosphere was evaluated within relatively short test period.

#### References

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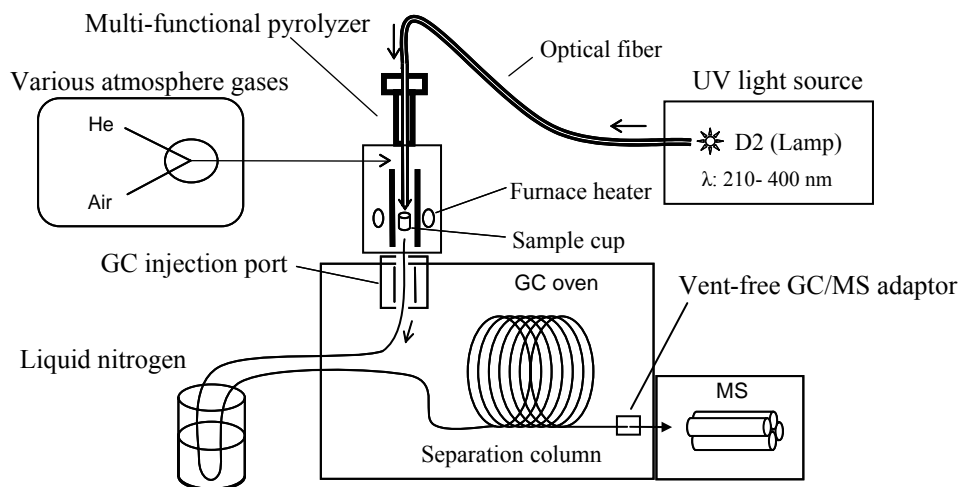


Figure 1 Configuration of on-line UV/PY – GC/MS system for analyzing photo, thermal, and oxidative degradation products generated by UV irradiation

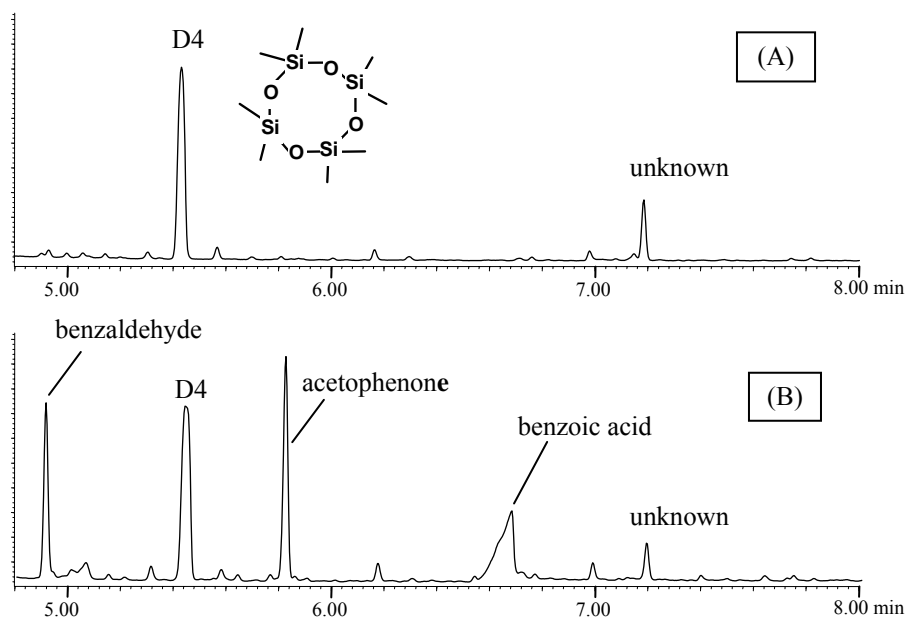


Figure 2 Gas chromatograms of desorbed products from PS treated under thermal and oxidative atmosphere for 3 hrs at 100°C, (A): without UV radiation, (B): with UV radiation

[Irradiation at 100°C in air carrier gas of 1 ml/min for 3 hrs and then thermal desorption from 100 to 150°C (5 min hold), split ratio: 1/5, GC/MS analysis: Oven 40 -300°C (at 20 °C/min), He: 1 ml/min, scan range: 29-200 amu, Column: UA5 (5% diphenyl95%dimethylpolysiloxane), 30 m, 0.25 mm i.d., 0.5 µm film thickness; D4 was formed by column bleeding]

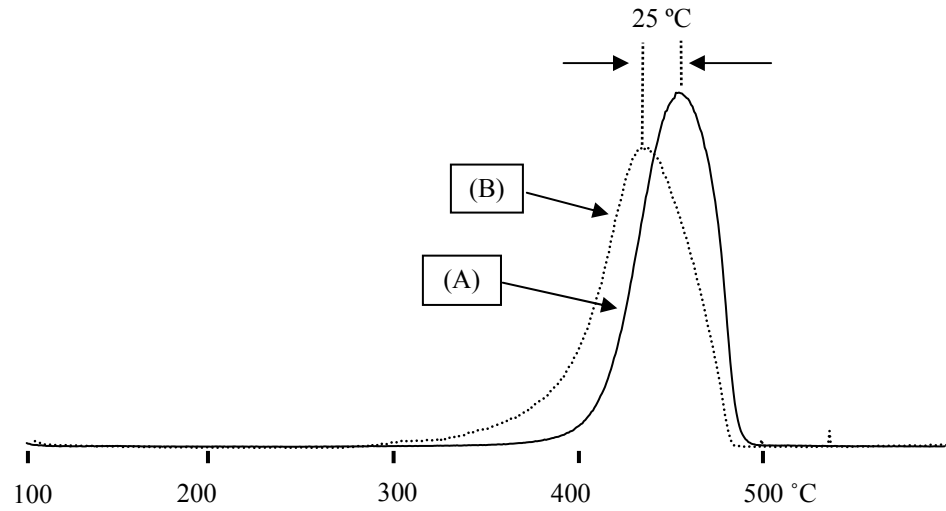


Figure 3 Thermal decomposition behaviors of deteriorated PS materials observed by EGA method (A): Treated without UV radiation, (B): Treated with UV radiation

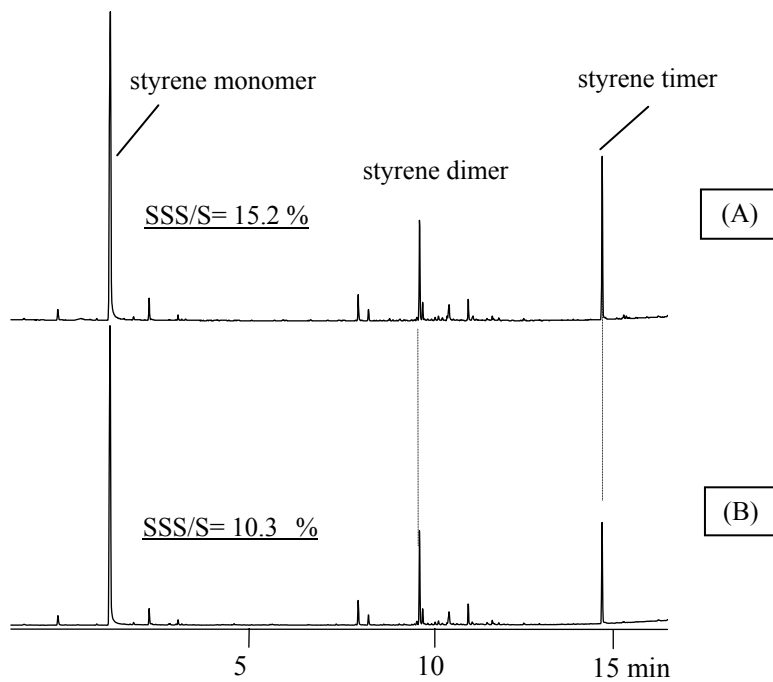


Figure 4 Pyrograms of deteriorated PS materials observed by Pyrolysis-GC/MS at 600 °C, (A): Treated without UV radiation, (B): Treated with UV radiation

[GC/MS analysis: Oven 40 -320 °C (at 20 °C/min), He: 1 ml/min, split ratio: 1/50, Column: UA5 (5% diphenyl 95%dimethylpolysiloxane), 30 m, 0.25 mm i.d., 0.5 µm film thickness]