Analysis of degraded polystyrene by UV irradiation using high-resolution MALDI-TOFMS and pyrolysis-GC-QMS

Product: Mass Spectrometer (MS)

Polymers can be degraded by the effects of light, oxygen, heat, etc. so it is important to understand how the polymer structures change during degradation. Pyrolysis gas chromatograph quadrupole mass spectrometer (Py-GC-QMS) and matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOFMS) are powerful tools for analyzing polymeric materials. Py-GC-QMS is a method that instantaneously heats a sample with a pyrolyzer and then analyzes the pyrolysis products by GC-MS. Since most of the pyrolysis products are related to monomers and dimers, this technique allows for easy identification of the polymer substructures which is useful for identifying changes to the polymer when degradation occurs. MALDI-TOFMS involves a soft ionization technique that can directly ionize and analyze the intact polymer molecules and often produces singly-charged ions even for high molecular weight compounds. As a result, the *m/z* axis of the mass spectrum is equal to the mass of the ions, thus making it easy to interpret polymer distributions. Additionally, when MALDI is used with a high-resolution TOFMS, the accurate mass of each ion in the polymer series can be used to calculate their elemental compositions. Moreover, the molecular weight distribution of polymers can be calculated from the ion intensity distribution. In this work, we used Py-GC-QMS and high-resolution MALDI-TOFMS to evaluate the effects of UV irradiation on polystyrene (PS).

JMS-Q1500GC

JMS-S3000 "SpiralTOF™-plus"

Experiment

Polystyrene (A-5000, molecular weight 5000, end groups H/C_4H_9) manufactured by Tosoh Corporation was used for the sample. For the degraded sample, the PS was UV-irradiated for 3 hours using a Portable Cure 100 (SEN LIGHTS Co., Ltd.). A JMS-Q1500GC equipped with a pyrolyzer (Frontier Labs) was used for the Py-GC-MS measurements. For these measurements, the samples before and after UV irradiation were weighed to ~0.2 mg and measured using the conditions shown in Table 1. Analyzer Pro (SpectralWorks Ltd.) was used to directly compare their differences, and NIST library searches were used to identify the compounds that showed significant differences between the before and after UV irradiation.

A JMS-S3000 was used for the MALDI-TOFMS measurements. The samples before and after UV irradiation was dissolved in tetrahydrofuran (THF) at 1 mg/mL. DCTB (20 mg/mL THF solution) and silver trifluoroacetate (AgTFA, 1 mg/mL THF solution) were used as matrix and the cationization agent, respectively. The mixture of the sample solution, matrix solution and cationizing agent solution at a ratio of 1:10: 1 (v/v/v) was pipetted on the target plate and air-dried. Mass spectra were acquired in high resolution SpiralTOF positive ion mode. Afterwards, Kendrick mass defect (KMD) analysis was performed by using the JEOL msRepeatFinder software.

Table 1 Measurement condition of Py-GC-QMS

Pyrolysis condition	
Pyrolyzer	PY-3030D (Frontier Laboratories Ltd.)
Pyrolysis temperature	600℃

GC condition	
GC	7890A (Agilent Technologies, Inc.)
Column	ZB-5 (Phenomenex Inc.) 30 m×0.25 mm I.D., df=0.25 μm
Injection port temperature	320℃
Oven temperature	40℃(2 min)→20℃/min→320℃ (20min)
Injection mode	Split 100:1
Carrier gas	He, 1.0 mL/min (Constant Flow)

MS condition	
Spectrometer	JMS-Q1500GC (JEOL Ltd.)
Ion source temp.	250℃
Interface temp.	320℃
Ionization mode	EI
Ionization energy	70 eV
Ionization current	50 μA
Mesurement mode	Scan (*m/z* 29~600)
Relative EM Voltage	100 V

Results of Py-GC-MS

The total ion current chromatogram (TICC) before and after UV irradiation is shown in Figure 1. The major components observed in these measurements were styrene monomer, dimer, and trimer with no significant differences observed before and after UV irradiation. Analyzer Pro was then used to quickly analyze the data for differences and found that the peaks at R.T. 6.17 and 7.05 min (Figure 3A [1], [2]) were found only in the after UV irradiation sample. Next, an NIST library search for these peaks showed high scoring match factors (M.F.) for acetophenone and benzoic acid, respectively (Figure 3B [1], [2]). Interestingly, the extracted ion chromatogram (EIC) for *m/z* 106 (C_7H_6O), which is a common fragment ion for these two compounds, also showed a peak at R.T. 5.26 min that was only present in the irradiated sample (Figure 3A [3]). The NIST library search helped to confirm that this compound is likely benzaldehyde, which is structurally similar to the other 2 compounds. According to Reference 1, there are no oxygen-containing compounds in the major pyrolysis products for PS. Moreover, since the end groups for this PS are H and C_4H_9, the original sample material does not contain oxygen. Therefore, these three pyrolysis products detected after UV irradiation are most likely the result of photo-oxidation by UV irradiation.

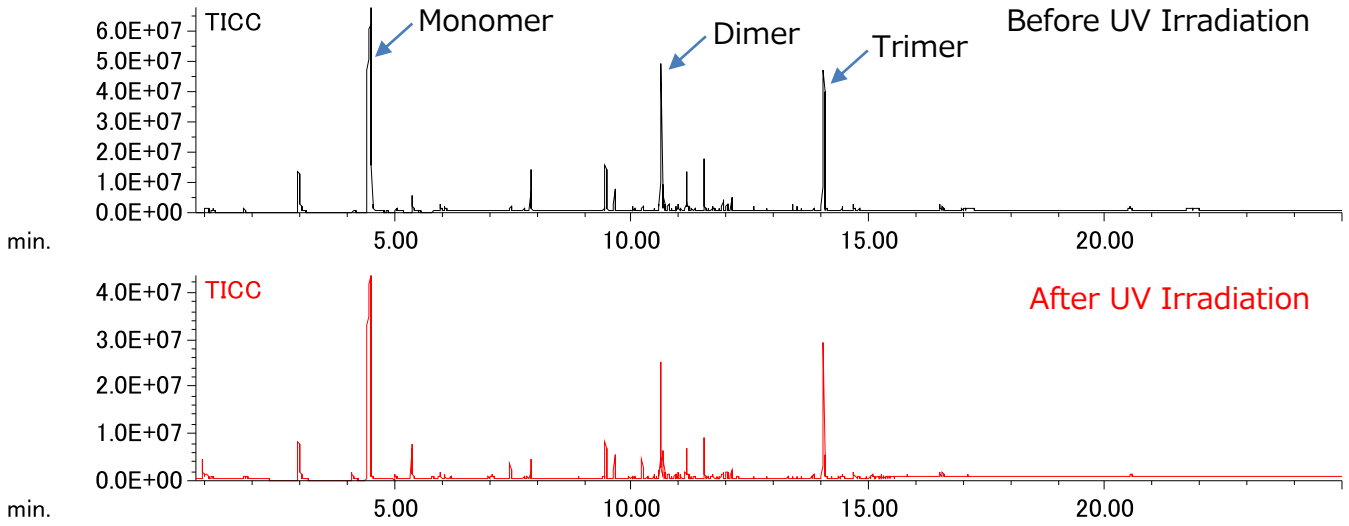


Figure 1 TICCs of PS before and after UV irradiation using Py-GC-QMS

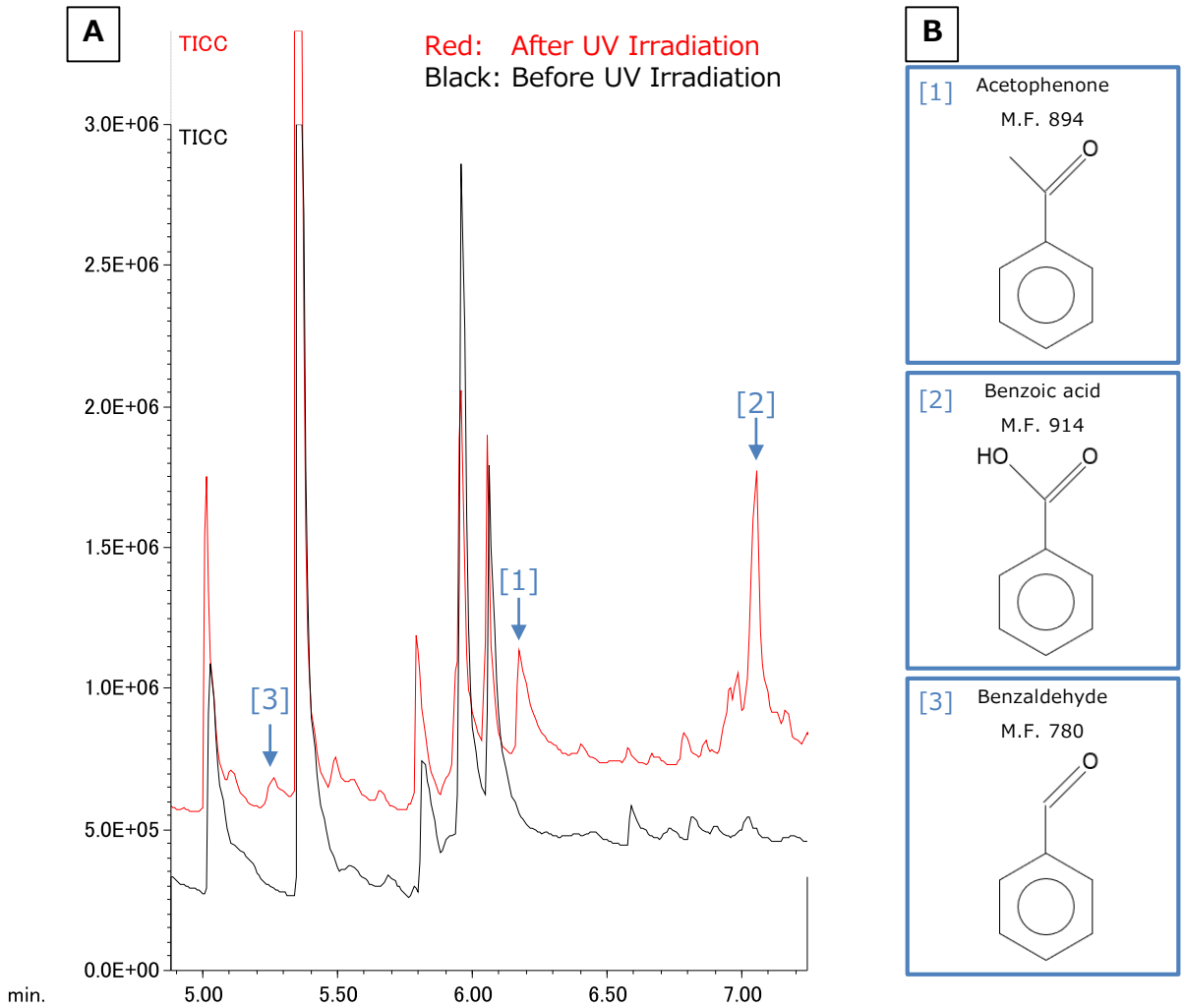


Figure 2 Differences in TICC before and after UV irradiation

Results of MALDI-TOFMS

The MALDI-TOFMS mass spectra before and after UV irradiation are shown in Figure 3a. Silver adduct PS ions ($[M+Ag]^+$) with the H/C_4H_9 end groups were observed in the mass spectra for both before and after UV irradiation. Figure 3b shows enlarged mass spectra around *m/z* 5000 that clearly shows the presence of 3 additional peak series in the irradiated sample that have a mass difference of an oxygen atom (15.995 Da), thus indicating the presence of one to three oxygens. The remainder Kendrick mass (RKM) plots for both mass spectra are shown in Figure 4. The RKM plot confirmed that one to four oxygens were present in the irradiated PS sample. Additionally, the overall molecular weight for the PS was reduced by UV irradiation. These results suggest that UV irradiation results in the addition of oxygen to the PS repeating structure as shown in Figure 5 (Reference 2).

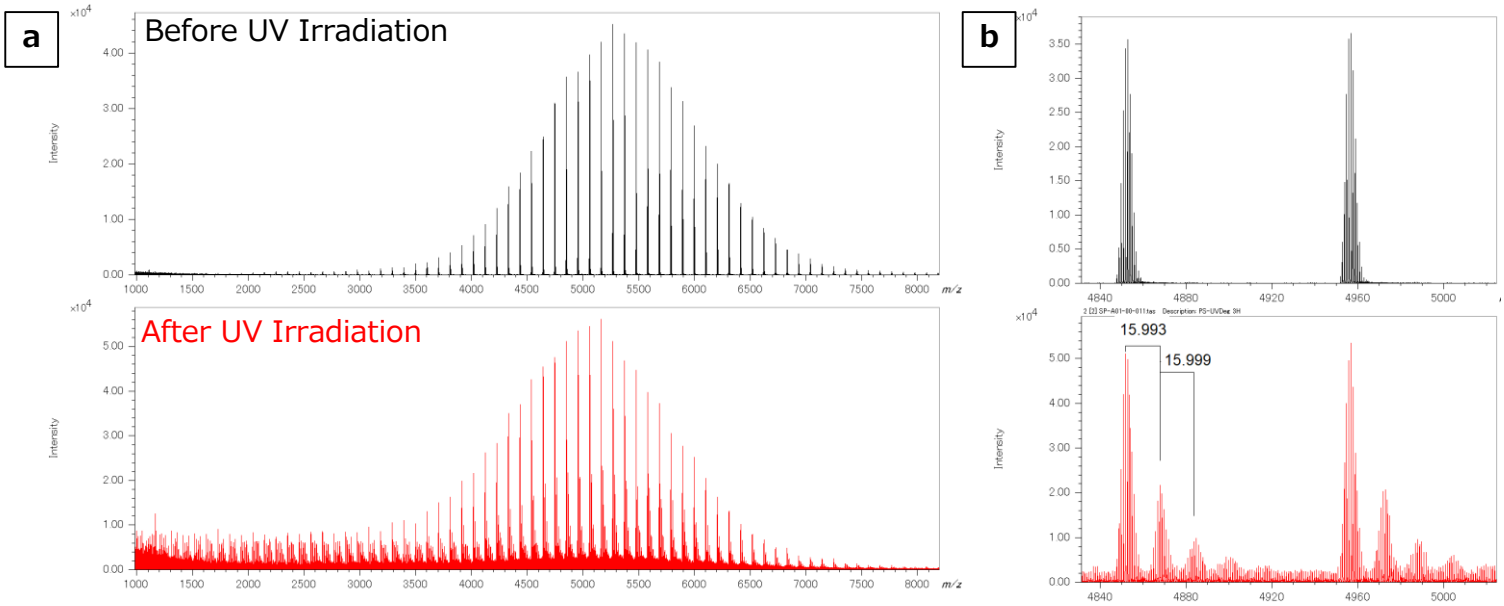
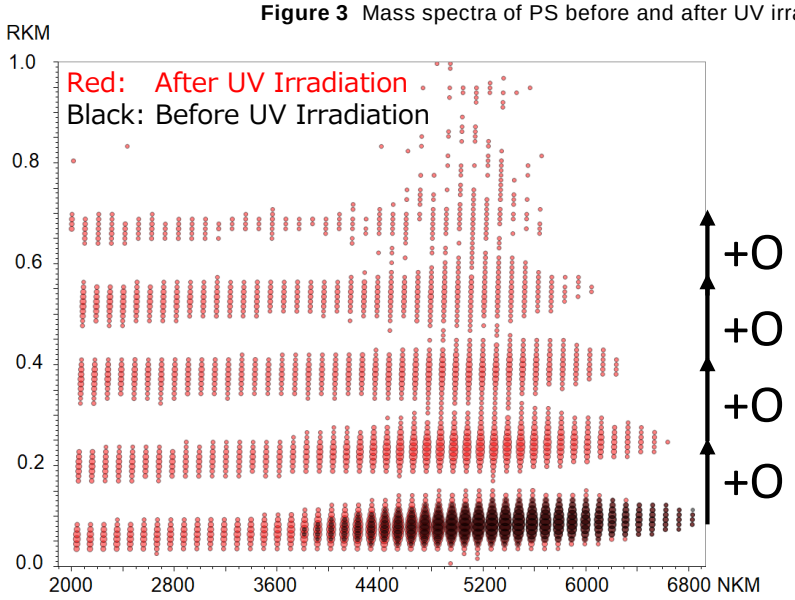


Figure 3 Mass spectra of PS before and after UV irradiation using MALDI-TOFMS



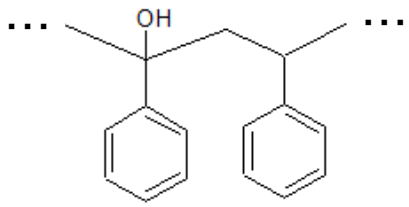


Figure 5 Estimated structure of PS after UV irradiation

Figure 4 RKM plot of PS before and after UV irradiation

Conclusion

The results for both Py-GC-QMS and MALDI-TOFMS showed that exposing PS to UV radiation caused photo-oxidation of the repeating structure. High resolution MALDI-TOFMS is a valuable technique for polymer analysis because it ionizes the intact polymer for accurate mass measurements that can be used for Kendrick mass analysis (KMD, RKM). On the other hand, Py-GC-QMS is useful for determining the partial structure information for polymers as well as identifying changes to their substructures during degradation. As a result, Py-GC-QMS and MALDI-TOFMS are complementary methods that can be useful for monitoring the degradation of polymer materials.

Reference

1. S. Tsuge, H. Ohtani, C. Watanabe: Pyrolysis - GC/MS Data Book of Synthetic Polymers: Pyrograms, Thermograms and MS of Pyrolyzates. First edition, Elsevier, 2011.

2. Mailhot and Gardette, Macromolecules, Vol. 25, No. 16, 1992.

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