

NEW!

Powerful tool for designing and developing materials

Rapid photo / thermal - oxidative degradation analysis
of polymeric materials

“Micro-UV Irradiator” UV-1047Xe

US Patent: US7655185B2



Features of Micro-UV Irradiator (UV-1047Xe) - GC/MS System

Weather-induced degradation tests of polymeric material usually requires weeks or months to complete. Frontier Laboratory's new Micro-UV irradiator uses a xenon lamp to provide UV light intensity about 2000 times stronger than that of a deuterium lamp. This reduces the time necessary to acquire meaningful data reflecting the degradation of the sample.

UV/Py-GC/MS technique --- The effects of "weather" upon exposure to the photo / thermal - oxidative degradation process can quickly be evaluated. This information invaluablely facilitate designing and developing new materials. The same system can also be applied to other analytical areas such as elucidation of the effects of additives on a polymer's physical and chemical behavior (e.g. antioxidants). Photochemical reactions and UV curing can also be examined.

1) Analysis of volatiles generated from the photo / thermal - oxidative degradation process

Small amounts of photo / thermal - oxidative degradation products are generated when a polymeric material is irradiated by UV irradiation in air while being heated. The qualitative or quantitative analysis of the degradation products can be accomplished by cryo-trapping the degradation products at the head of a separation column prior to chromatographic separation.

2) Analysis of polymeric materials degraded by exposure to a photo/thermal-oxidative environment

The irradiated polymer can be evaluated by evolved gas analysis (EGA-MS) or flash pyrolysis (Py-GC/MS). This resulting data often provide information on the structural changes in the polymeric material.

UV/Py-GC/MS System Configuration and Basic Performance

The configuration of UV/Py-GC/MS system is shown in Fig. 1.

UV light from a xenon (Xe) arc lamp is delivered via an optical fiber cable to the center of the pyrolyzer furnace. The sample mounted in the sample cup is directly irradiated. The sample can be heated to any desired temperature in an atmosphere (e.g. air) during UV irradiation. Photo/thermal-oxidation induced volatile degradation products are cryo-trapped by immersing a short length of the column head into liquid N₂ (The Micro-Jet Cryo-Trap is also available; option). The condensed volatile components are then analyzed by TD-GC/MS. In addition, the residual deteriorated polymeric material in the sample cup can be analyzed by either EGA-MS or Py-GC/MS.

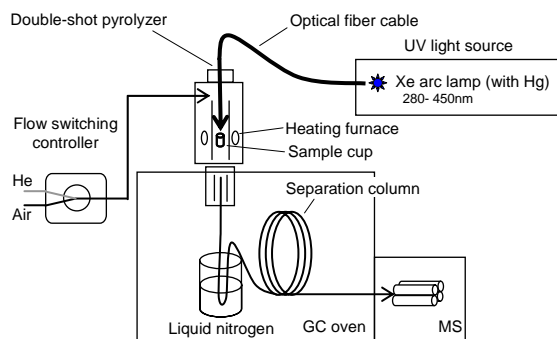


Fig. 1 UV/Py-GC/MS system configuration

Analysis of the volatiles and the degraded PS after UV irradiation

1. Analysis of volatile compounds generated during UV irradiation

Fig. 2 shows chromatograms of the volatiles observed before and after 1 hr UV irradiation. The PS sample was held at 60°C under air atmosphere. UV irradiation of the PS produced various photo / thermal - oxidative degradation products such as benzaldehyde (BA) and acetophenone (AP) with reproducibility of RSD 7% or below.

2. Analysis of degraded PS --- EGA and PY analyses of the degraded PS provide information on the deterioration of PS.

In the EGA thermogram shown in Fig. 3, UV irradiation shifted the peak top temperature for PS down by 6°C, while the thermal decomposition onset temperature decreased from 360°C down to 300°C. This result indicates that the average molecular weight (Mn) of the base polymer is lowered after being irradiated. The pyrograms in Fig. 4 show that the peak area value for the styrene trimer diminished after UV irradiation, reflecting the decreased average Mn of PS.

Sample: 20 µg (thin film), temp.: 60°C, irradiation time: 1 hour, atmosphere gas: air, flow rate: 1 ml/min, split ratio: 1/10, Ultra ALLOY metal capillary column: UA1_30m (0.25e) 0.5 µm, GC: 50 - 240°C (20°C/min)

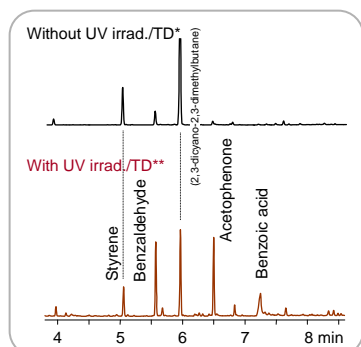


Fig. 2. Chromatograms of volatile degradation products

Table1 Reproducibility (RSD%) of the peak area ratio

	Peak area ratio		
	BA m/z=106	AP m/z=120	BAC m/z=122
1	0.483	0.235	0.282
2	0.471	0.237	0.292
3	0.512	0.244	0.245
4	0.485	0.249	0.267
5	0.424	0.228	0.348
Avg	0.475	0.239	0.286
RSD	6.78	3.30	13.5

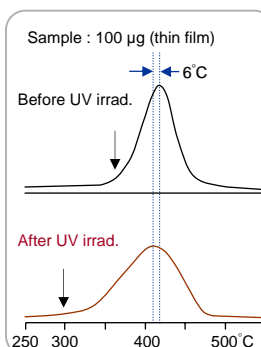


Fig. 3 EAG thermogram

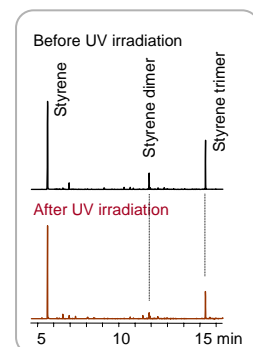
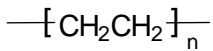


Fig. 4 Pyrograms (600°C)

*: Analysis of volatiles produced during UV irradiation, **: Analysis of volatiles without UV irradiation

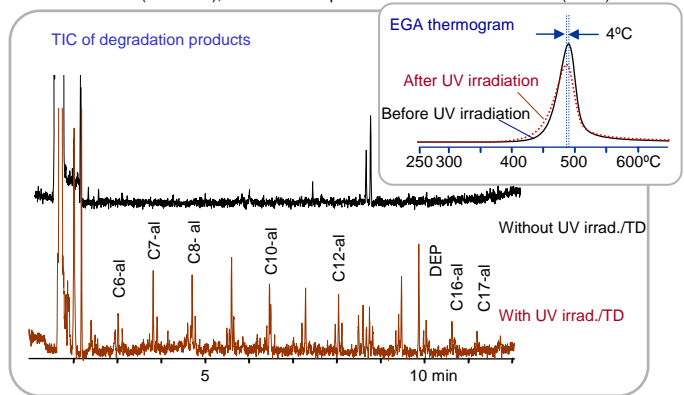
Applications Using UV/Py-GC/MS System

1. High density polyethylene (HDPE)

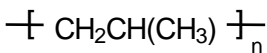


Upon UV irradiation, various aldehydes were observed as degradation products. These compounds are considered to have been generated from the main chain scission of the polymer and successive oxidation caused by photo / thermal - oxidation. The subsequent EGA analysis of the degraded polymer showed that the main peak ascribed to the polymer backbone scission had shifted down by 4°C, indicating that the MW of the base polymer had decreased.

Irradiation temp.: 60°C, UV irradiation time: 3 hrs, sample size: 100 µg (powder), atmosphere gas: air, split ratio: 1/10, separation column, UA1, 30m (0.25ø) 0.5 µm, GC oven: 40 – 320°C(20°C/min), Thermal desorption after UV irradiation: 200°C (5 min)

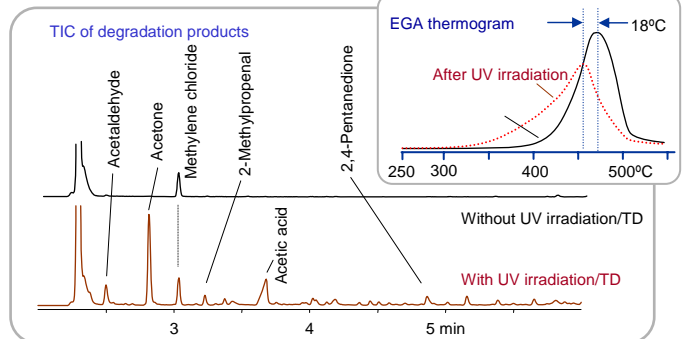


2. Polypropylene (isotactic)(PP)

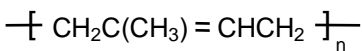


Acetic acid, aldehydes, and ketones were observed as volatile degradation products after UV irradiation. The subsequent analysis of the degraded polymer by EGA revealed that the main peak attributed to the scission of the polymer backbone chain had shifted to lower temperatures, and that the decomposition onset temperature had been lowered from 400°C to 300°C, suggesting that the irradiation resulted in a decrease in the MW of the base polymer.

Irradiation temp.: 60°C, UV irradiation time: 1 hr, other conditions: see those of HDPE above

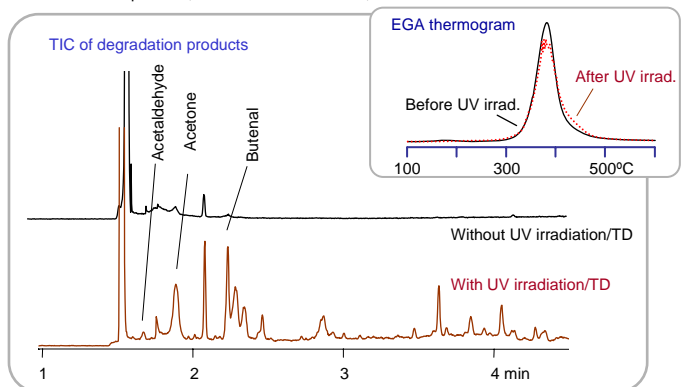


3. Natural rubber (polyisoprene) (NR)

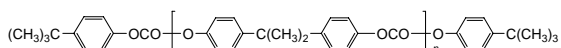


UV irradiation of natural rubber yielded various aldehydes, ketones, and organic acids as volatile degradation products. The subsequent EGA analysis of the UV-degraded polymer resulted in a shift to a higher evolved temperature which suggests that the MW of the base polymer had increased due to a crosslinking reaction.

Irradiation temp.: 60°C, UV irradiation time: 1 hr, other conditions: see those of HDPE

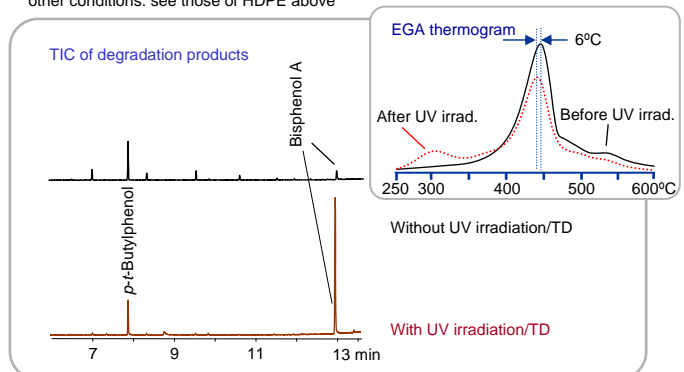


4. Polycarbonate (PC) (solution process)



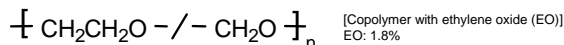
t-Butylphenol (an endcapping agent for PC) and bisphenol A (monomer) were observed upon UV irradiation. This is probably caused by the repeated scissions of carbonate bonds of the polymer. The subsequent analysis of the degraded polymer by EGA revealed that after UV irradiation, the main peak had shifted to lower temperatures. This indicates that the average MWt has decreased due to the scission of the polymer backbone chain.

Irradiation temperature: 60°C, UV irradiation time: 1 hr, sample size: 10 µg (thin film), thermal desorption after UV irradiation: 330°C (5 min), for other conditions: see those of HDPE above



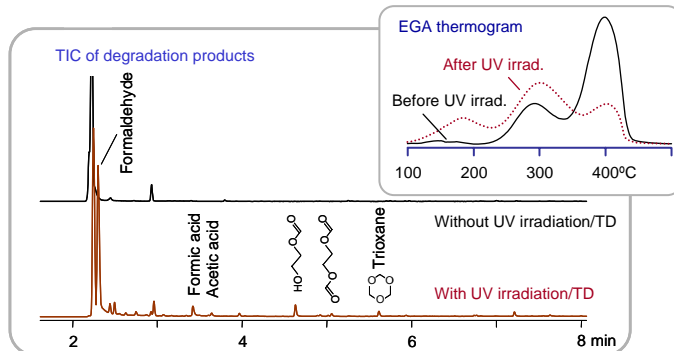
Applications Using UV/Py-GC/MS System

5. Polyacetal



After irradiation, the monomer (form-aldehyde), trimer (trioxane) and formic acid ester of ethylene glycol originated from ethylene oxide units were observed. The subsequent EGA analysis of the degraded polymer, clearly showed a significant increase in the amount of evolved gas at temperatures below 230°C. Thus, the thermal stability of the degraded polymer proved to be lowered.

Irradiation temp.: 60°C, UV irradiation time: 1 hr, for other conditions: see those of HDPE

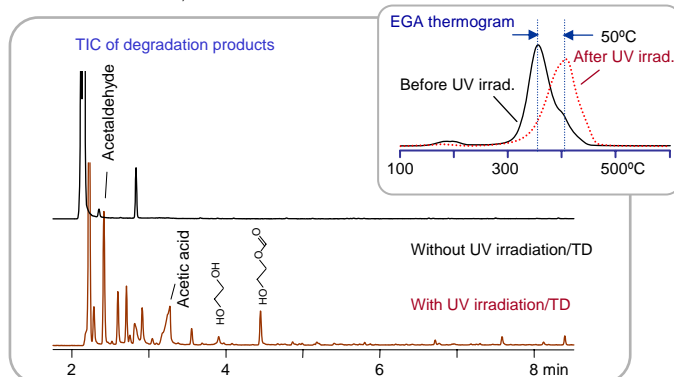


6. Polyhydroxyethylmethacrylate

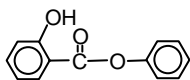


Acetic acid, ethylene glycol (generated from side-chain elimination) and its formic acid ester were observed as volatile degradation products. The subsequent EGA analysis of the degraded polymer revealed that the peak profile of the degraded polymer had shifted significantly to higher temperatures, suggesting a crosslinking reaction. This result also suggest an increase of the MW occurring during UV irradiation.

Irradiation temp.: 60°C, UV irradiation time: 1 hr, thermal desorption after UV irradiation: no, other conditions: see HDPE above



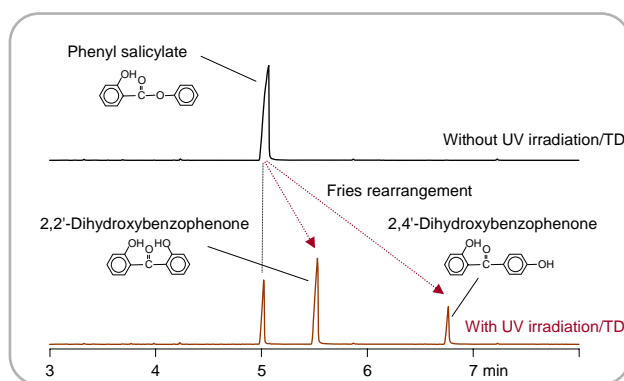
7. Application to photochemical reactions (Fries rearrangement of phenyl salicylate)



UV irradiation: 2 hours at 40°C,
thermal desorption after UV
irradiation: 40-250°C

Sample size: 5 µg (thin film), atmosphere gas: He, split ratio: 1/50
Ultra ALLOY metal capillary column: UA-Fries, 15 m (0.25φ) 0.05 µm
GC oven temp.: 60 - 220°C (20°C/min)

Under UV irradiation, phenyl salicylate, which is commonly added to cosmetics as a UV absorber, receives photo Fries rearrangement to give UV-absorbing 2,2'-dihydroxy-benzophenone and 2,4'-dihydroxybenzophenone. The figure on the right shows the on-line analysis of this reaction.



Specifications

- ◆ Wavelength range (at fiber end): 280 - 450nm [Xe arc lamp (contains Hg)]
- ◆ Light intensity: >60 mW/cm² at 365 nm, >700 mW/cm² in wavelength range of 280 - 450 nm
- ◆ Light intensity control: 0 - 100% (1% step), irradiation time: 1 min - 999 hours (1 min step), PC controlled via RS-232C
- ◆ Supported system: Double-shot pyrolyzer installed on a GC/MS system (no modifications of existing pyrolyzer required)

Standard accessories : UV light source, optical fiber cable/sampler, He/Air rapid pressure stabilizer, Ultra ALLOY metal capillary column, liquid nitrogen Dewar

Options: Xe arc lamp (contains no Hg), filters: 280 - 400 nm (band pass)/300 - 400nm (band pass), Ultra ALLOY metal capillary columns

Required utilities: Compressed air (300 - 500 kPa), liquid nitrogen, power: 100 - 240VAC (300W)



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