

Weather-Induced Degradation Study of Polystyrene Using the Photoprobe

Application Note

UV-Irradiation of Polymers

Author:

Karen Sam

Abstract

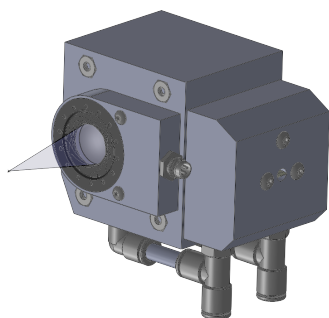
This application note presents reproducibility study on a rapid, automated polymer degradation setup that introduces user-settable ultraviolet (UV) light, reactant gas and controlled temperature in a closed system.

Introductions

Environmental conditions play a critical role on polymer lifetime, and traditional degradation study takes time ranging from hours to days due to limited light intensity. CDS's Photoprobe is using free-space focusing technology and improves the light intensity to 800 mW/mm² from 260 nm to 400 nm wavelength, which reduces the time on weather-induced degradation study down to minutes.

Experimental Parameters

A CDS 6200 Pyroprobe equipped with Drop-In-Sample Chamber (DISC) and Photoprobe was used, and an autosampler module was installed to automate the weathering-pyrolysis sequence. 11 µg of polystyrene was irradiated in the DISC with the presence of air as reactant gas at a flow rate of 10 ml/min. The volatiles generated from the photo-reaction were trapped on the analytical trap, and then desorbed to the GC/MS after the photo reaction is completed. The remaining polymer was pyrolyzed at 600°C as the last step. A DISC quartz tube was used as the sample vessel.



Photoprobe Module

CDS Pyroprobe Setting:

Method 1 - Weathering

DISC: 60°C
 Photoprobe: 60% Intensity
 UV irradiation: 5 min
 Reactant Gas: Air 10mL/min
 Trap Rest: 40°C
 Trap Final: 300°C 3 min
 Trap Sorbent: Tenax
 Interface: 300°C
 Valve Oven: 300°C
 Transfer Line: 300°C

GC/MS Setting:

Column: 5% phenyl
 (30m x 0.25mm)
 Carrier: Helium, 20:1 split
 Column Flow: 1.25mL/min
 Injector: 320°C
 Oven: 40°C for 2 minutes
 12°C/min to 320°C
 Mass Range: 35-600amu

Method 2- Pyrolysis

DISC: 600°C 30seconds
 Trap: (no trapping)
 Interface: 300°C
 Valve Oven: 300°C
 Transfer Line: 300°C

Results

Weathering studies of polymers with the Photoprobe took minimal time on the scale of minutes compared to hours from traditional techniques. The Photoprobe supplies free-space focused UV light to the sample under a user selected temperature and reactant gas, sending resulting products to a sorbent trap. Once the irradiation has completed, the trap is automatically placed online with the GC/MS and heated, sending volatiles to the GC using the GC's inert carrier gas.

Polystyrene under UV irradiation and an air atmosphere at a 60°C set-point produces many UV thermal oxidative degradation products, ranging from volatile to non-volatile components. The resulting chromatogram is shown in Figure 1.

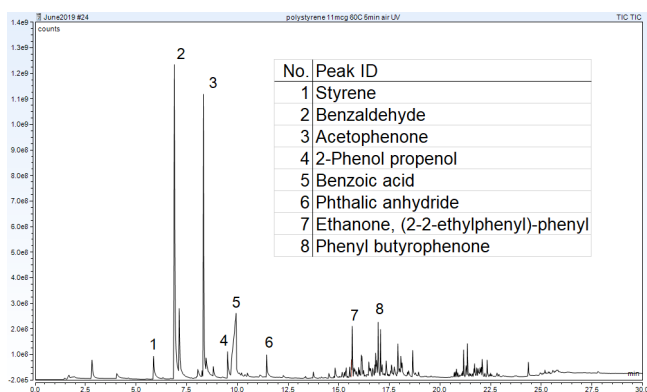


Figure 1. Photo-thermal oxidative degradation products of polystyrene

Six replicates of the volatiles from weathering polystyrene provided area ratio RSDs $\leq 5.25\%$ for Benzaldehyde, Acetophenone and Styrene (Table 1). After this degradation analysis, the remaining degraded polymer was automatically pyrolyzed and studied with a second GC/MS run (Figure 2). Six replicates of the pyrolysis of weathered polystyrene produced an area ratio RSD of 3.00% (Table 2).

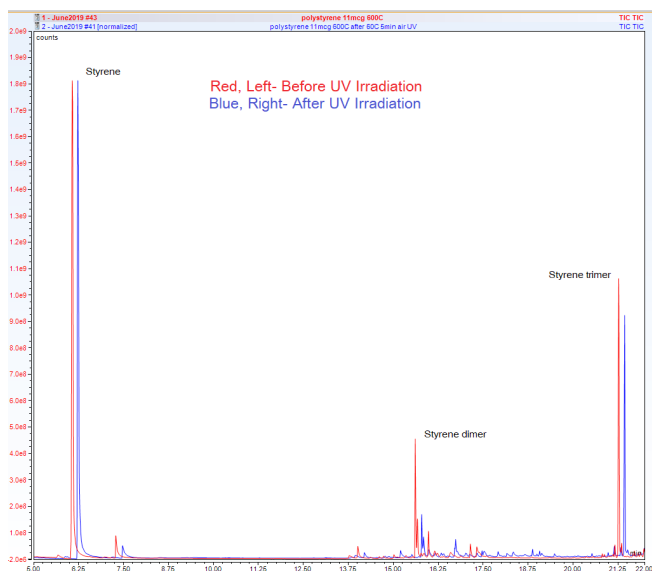


Figure 2. Overlay (retention time shifted) of polystyrene pyrograms (600°C) before and after UV irradiation.

	BA:S	AP:S	BA:AP
Rep 1	8.23	5.24	1.57
Rep 2	8.88	5.98	1.49
Rep 3	7.90	5.75	1.37
Rep 4	8.52	5.91	1.44
Rep 5	8.14	5.48	1.49
Rep 6	8.21	5.96	1.38
Avg.	8.31	5.72	1.46
RSD%	4.09	5.26	5.16

Table 1. Peak Area Ratio Reproducibility of degradation products: BA-Benzaldehyde (Peak 2), S-Styrene (Peak 1), AP-Acetophenone (Peak 3)

S:ST	Rep1	Rep2	Rep3	Rep4	Rep5	Rep6
m/z 104:91	2.93	3.02	2.93	2.93	3.15	3.07
Avg.	3.00					
RSD%	3.00					

Table 2. Peak Area Ratio Reproducibility of weathered polystyrene: S-Styrene, ST-Styrene Trimer

Conclusion

In addition to analytical pyrolysis, the Photoprobe, the newest member of the CDS Pyroprobe family, can perform quantitative online weathering studies within minutes with highly reproducible data.