UV Degradation Studies of Polyisoprene Rubbers Using the Photoprobe

Application Note
UV-Irradiation of Polymers

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Abstract
This application note presents data on a rapid, automated polymer degradation study of rubber under ultraviolet (UV) light in air.

Introduction
Ultraviolet (UV) radiation is a form of electromagnetic radiation with wavelengths shorter (<400 nm) than that of visible light. UV radiation accounts for 10% of the total radiation output from the Sun, but it can be enough energy to damage polymers due to its higher photon energy. For example, elastomeric materials derived from dienes are especially prone to oxidative degradation.[1] This degradation occurs when free radicals formed from the radiation causes bonds to cleave in the presence of oxygen from air. ASTM G154 and G155 methods, which utilize accelerated weathering devices, are widely adopted to measure such impact. More intense UV radiation than sunlight weathering can take a few months by simulating UV between wavelengths the of 295 to 365 nm. The CDS Analytical Photoprobe can further accelerate weathering with its Xenon arc lamp, covering a wider range of the sunlight spectrum (260 nm to 400 nm) and producing 40,000 times more light intensity.

In this application note, two naturally aged polyisoprenes were exposed to the Photoprobe's UV light in air under a temperature controlled environment. Volatiles generated from the UV light were sent to the sorbent trap on the 6200, which was desorbed to the GC-MS for analysis.

Experiment Setup
A CDS 6200 Pyroprobe Autosampler installed with a Photoprobe was used for analysis. In May of 2023, Polyisoprene (pi) samples which were manufactured in 1976, were irradiated in the Drop-in-Sample-Chamber (DISC) in air at an elevated temperature. The volatiles generated from the photo-degradation were trapped on the analytical trap, and then desorbed to the GC-MS. A DISC tube was used as the sample vessel.

Pyroprobe 6200 w/ Photoprobe

Method 1 - UVirradiation

DISC:	60°C
Photoprobe:	
UV irradiation:	8 min 100% intensity
Purge Gas:	Air 25mL/min
Trap Rest:	45°C
Trap Final:	300°C 3 min
Trap Sorbent:	Tenax
Interface:	300°C

Method 2 - Pyrolysis

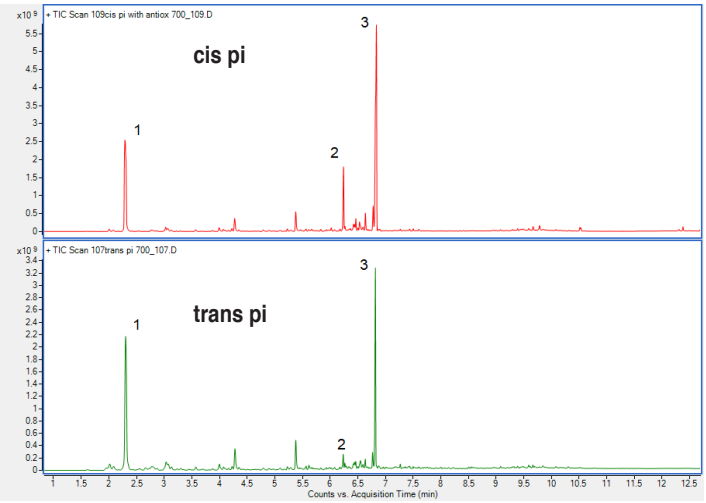
DISC:	700°C 30s
Interface:	300°C
Valve Oven:	300°C
Transfer Line:	325°C

GC-MS

Column:	5% phenyl (30m x 0.25mm)
Carrier:	Helium, 50:1 split
Column Flow:	1.25mL/min
Injector:	320°C
Oven:	40°C for 2 minutes
	15°C/min to 320°C
Mass Range:	35-600 amu

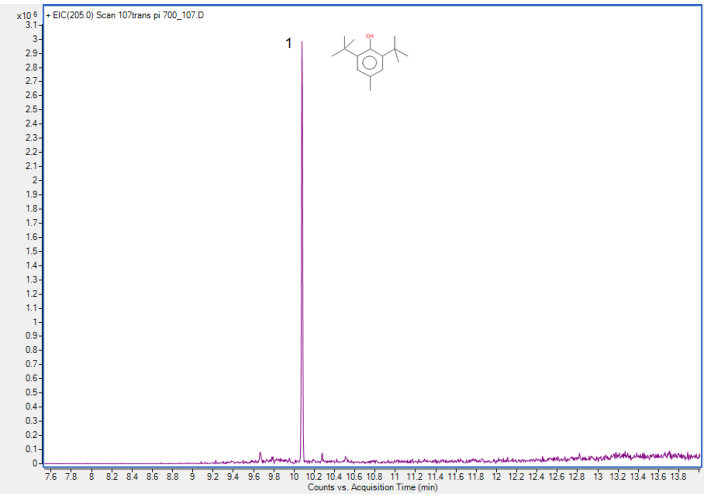
Results and Discussion

First, pyrolysis at 700°C was performed on the two polyisoprenes. This is shown in Figure 1. As bond cleavage occurs along the polymer backbone, pyrolysis creates a series of isoprene oligomers[2]. The most recognizable peaks in polyisoprene are the monomer, and dimer, isoprene and limonene, respectively. Each polyisoprene was also found to have an anti-oxidant, butylated hydroxytoluene (BHT), to protect the rubbers from oxidative degradation. Figure 2 depicts an extracted ion chromatogram of 205 to show the presence of BHT.



Peak	Identification
1	Isoprene
2	Cyclohexene, 4-ethenyl-1,4-dimethyl
3	Limonene

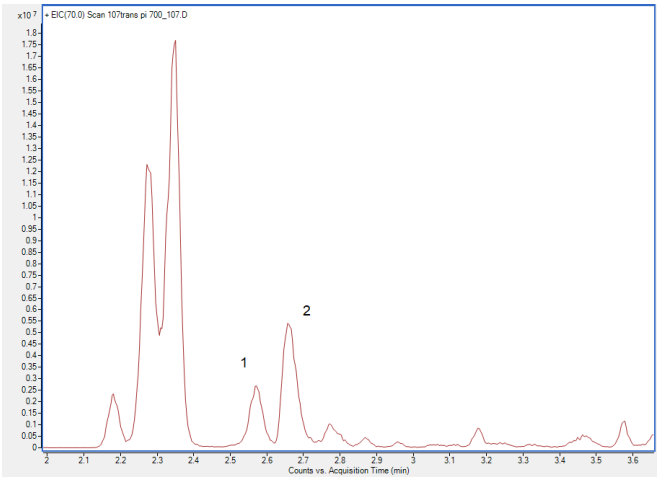
Figure 1. Polyisoprene (pi) Samples at 700°C.



Peak	Identification
1	butylated hydroxytoluene

Figure 2. pi at 700°C, m/z 205 extracted to show BHT.

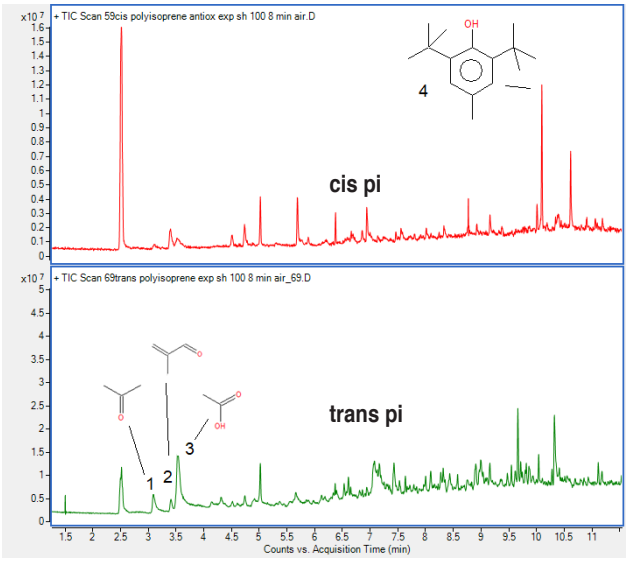
When m/z 70, which represents isoprene with a carbonyl group replacing the alkene, is extracted in trans polyisoprene, peaks become visible for methalcrolein and methyl vinyl ketone.This is due to the formation of allyl radicals, which are converted to peroxy radicals in the presence of oxygen which then decompose into alkoxy radicals that can be transformed to ketonic groups. It is an indication that photo-oxidation of the polymer since the manufacturing date of 1976.[1]



Peak	Identification
1	methalcrolein
2	methyl vinyl ketone

Figure 3. m/z 70 to show degradation peaks in pi

The aged polyisoprenes were then subjected to the UV light of the Photoprobe in a purge flow of air for 8 minutes. Under these conditions, all off gases from the UV exposure were collected onto the sorbent trap of the Pyroprobe, and then sent to the gas chromatograph for analysis. Outgassed components included the antioxidant, as well as oxygenated compounds like acetone, methalcrolein, and acetic acid, most abundant in trans pi.

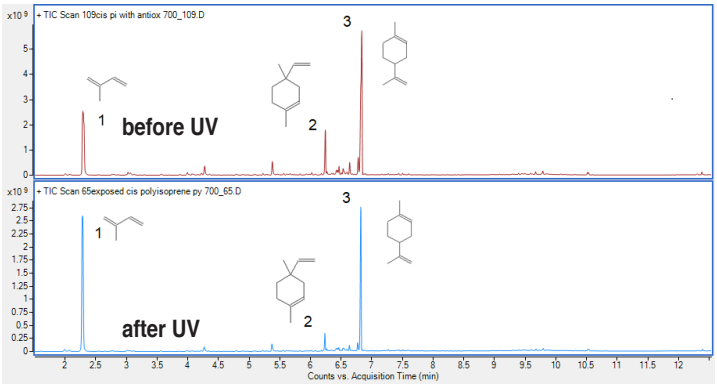


Peak	Identification
1	acetone
2	methyl vinyl ketone
3	acetic acid
4	butylated hydroxytoluene

Figure 4. Polyisoprene UV outgassing.

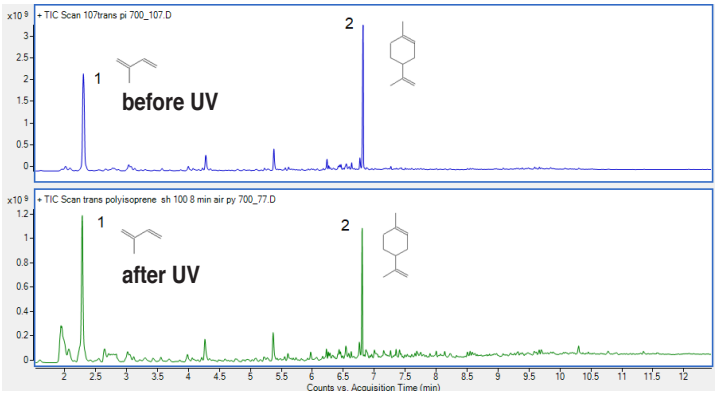
After the outgassing step, the remaining polymer was pyrolyzed at 700 °C (Figures 6 and 7). Pyrolysis of both the cis and trans polyisoprene exhibited a two-fold increase in isoprene, in relation

to limonene (Table 1).



Peak	Identification
1	isoprene
2	1-Methyl-4-(1-methylethenyl)-cyclohexene
3	limonene

Figure 6. Pyrolysis of aged cis pi before (top) and after (bottom) UV exposure.



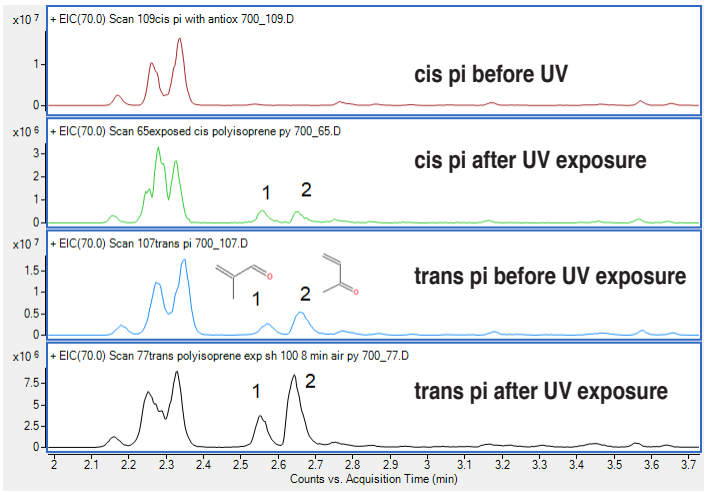
Peak	Identification
1	isoprene
2	limonene

Figure 7. Pyrolysis of aged trans pi before (top) and after (bottom) UV exposure.

Table 1. Monomer to Dimer increases in pi after UV exposure

PI type	Increase of Monomer to Dimer
cis	2.3
trans	1.9

When m/z 70 is extracted in the polyisoprenes photo-oxidized with the Photoprobe (Figure 8), methacrolein and methyl vinyl ketone, which are absent in cis pi before Photoprobe exposure, appear after exposure. When area ratios are performed with the isoprene peak in the trans pi, these compounds are increased by three-fold when compared to the pre-exposure sample. This showcases the Photoprobe's ability to accelerate polymer aging by photo-oxidation in just 8 minutes, versus decades of natural sunlight.



Peak	Identification
1	methalcrolein
2	methyl vinyl ketone

Figure 8. m/z 70 to show degradation peaks in non-exposed and UV exposed pi.

Conclusion

In addition to analytical pyrolysis, the Photoprobe, the newest addition to a Pyroprobe 6200 autosampler, can perform online Photo-oxidation studies in minutes as compared to months or years by sunlight. Photo-oxidized polymers can then be immediately and automatically studied by analytical pyrolysis.

References

1. Adam, C., Lacoste, J. and Lemaire, J. "Photo-Oxidation of Polyisoprene". Polymer Degradation and Stability, 1991, 32, 51-69.

2. Wampler, T., "Chapter 1: Analytical Pyrolysis: An Overview", Analytical Pyrolysis Handbook, edited by Wampler, T., and Sam, K., CRC Press, 2021 (1-22).