Study of UV Stabilizer in Polypropylene Using the Photoprobe

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Application Note
UV-Irradiation of Polymers

Abstract
This application note presents data on a rapid, automated polymer degradation study of polymers containing UV stabilizers under ultraviolet (UV) light in a temperature controlled environment.

Introduction
UV radiation consists of photons with higher energy relative to visible light that can cause bond cleavage in susceptible polymers. Some polymers withstand UV exposure better than others. Any polymer that does not contain chromophoric groups are less susceptible to photodegradation. For example, polyolefins, like polypropylene, are inherently resistant to UV degradation due to their lack of chromophoric groups[1]. UV stabilizers are added to absorb the UV irradiation, and dissipate the energy harmlessly, acting as a screen[2] to further protect polymers from UV degradation.

The traditional method to study UV degradation of a polymer material is to follow ASTM G154 and G155 methods by an accelerated weathering device. These methods typically last a few months by simulating the ultraviolet (UV) part of the sunlight from 295 nm to 365 nm. The Photoprobe covers a wider range of sunlight spectrum from 260 nm to 400 nm compared to the ASTM method as well as about 40,000 times more powerful in terms of light intensity to complete the study in minutes. In this application note, polypropylene samples, each formulated with different UV stabilizers, were exposed to the Photoprobe's UV light under an inert atmosphere. 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. Polypropylene samples were irradiated in the Drop-in-Sample-Chamber (DISC) in an inert gas at a slighly 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:	80°C 30 min
Photoprobe:	
UV irradiation:	30 min 100% intensity
Purge Gas:	He 25mL/min
Trap Rest:	45°C
Trap Final:	300°C 3 min
Trap Sorbent:	Tenax

Method 2 - Multi-Step Pyrolysis

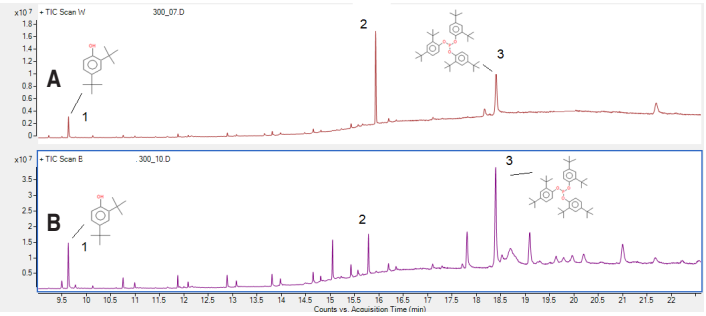
DISC:	300°C, 700°C 30s
Interface:	300°C
Valve Oven:	300°C
Transfer Line:	325°C

GC-MS

Column:	5% phenyl (30m x 0.25mm)
Carrier:	Helium, 50:1 split
Column Flow:	25mL/min
Injector:	320°C
Oven:	40°C for 2 minutes
	15°C/min to 320°C
Mass Range:	35-600amu

Results and Discussion

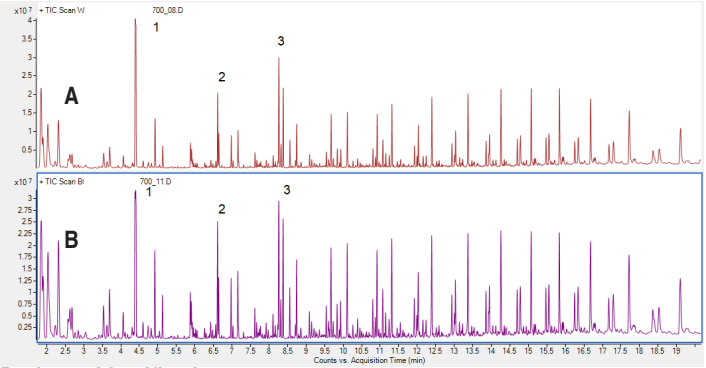
First, multi-step pyrolysis at 300°C and 700°C was performed on each polypropylene formulation. Figure 1 shows the two formulations at 300°C. At this temperature, compounds such as residual monomer and oligomer, contamination, and additives, including a UV stabilizer Alkanox 240, were swept to the GC. From these chromatograms, it can be seen that some of the peaks differ between the formulations, indicating that different additive combinations were used in each polypropylene formulation. A UV stabilizer additive, which is Alkanox 240, was identified in both samples.



Peak	Identification
1	2,4-Di-tert-butylphenol
3	Succinic acid, di(2-tert-butylphenyl) ester
2	Trisdibutylphenyl phosphite (Alkanox 240)

Figure 1. Two Polypropylene Samples at 300°C.

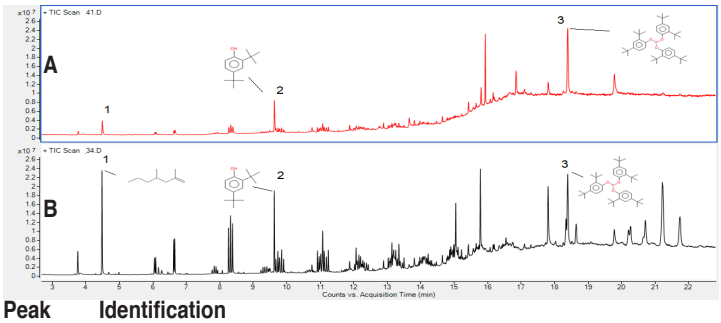
At 700°C, the polymeric portion of the samples pyrolyze. This is shown in Figure 2. As all the carbon-carbon bonds in polypropylene are about the same strength, all the bonds break at about the same time, producing a series of hydrocarbons with methyl branches indicative of polypropylene's original structure[3]. The most recognizable peaks in polypropylene are the trimer, tetramer, and pentamer peaks, marked in Figure 2.



Peak	Identification
1	Polypropylene Trimer
2	Polypropylene Tetramer
3	Polypropylene Pentamer

Figure 2. Two Polypropylene Samples at 700°C.

After the original polymers were studied with multi-step pyrolysis, fresh samples were subjected to the UV light of the Photoprobe in a purge flow of Helium for 30 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. Chromatograms are shown in Figure 3. Each polypropylene outgassed peaks for additives and polypropylene degradation compounds, including the trimer, tetramer, and pentamer peaks.



Peak	Identification
1	Polypropylene Trimer
2	2,4-Di-tert-butylphenol
3	Trisdibutylphenyl phosphite (Alkanox 240)

Figure 3. Polypropylene Samples UV degradation products.

Multi-step pyrolysis at 300°C and 700°C of the samples were included in the programmed sequence, and and so automatically performed on the remaining UV exposed polymer. The thermal extraction runs at 300°C were clean, indicating no semi-volatiles remained on the polymers (Figure 4).

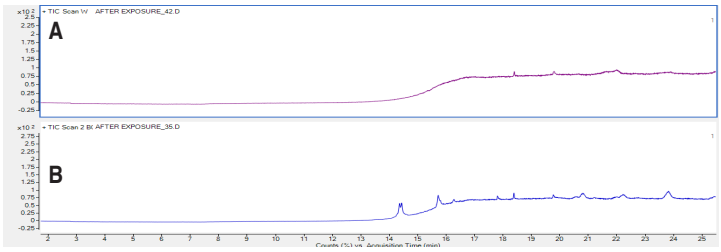


Figure 4. UV exposed Polypropylene Samples 300°C.

The 700°C run shows the familiar repeating pattern of the pyrolysis of polypropylene (Figure 5). Figures 6 and 7 show 700°C expanded runs of the samples before and after UV exposure. Peak area ratios between the trimer and the pentamer peaks shows a decrease in pentamer, and increase in trimer after UV exposure, indicating that the nature of the polymer had changed with UV exposure. This is finding consistent with a previous application note[4], and other studies showing the decrease of larger pyrolysis products with environmental exposure[5]. This may be the result of chain scission by photolysis of the polymer backbone decreasing

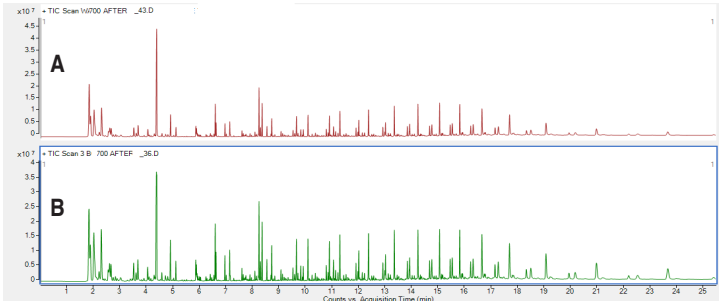
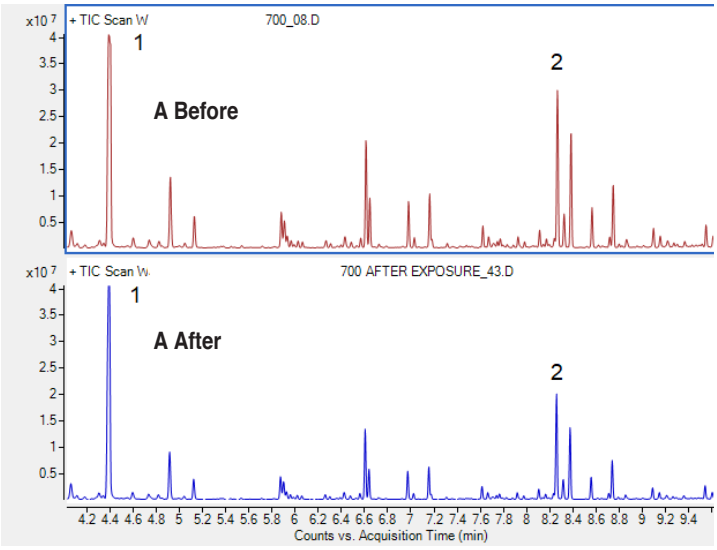


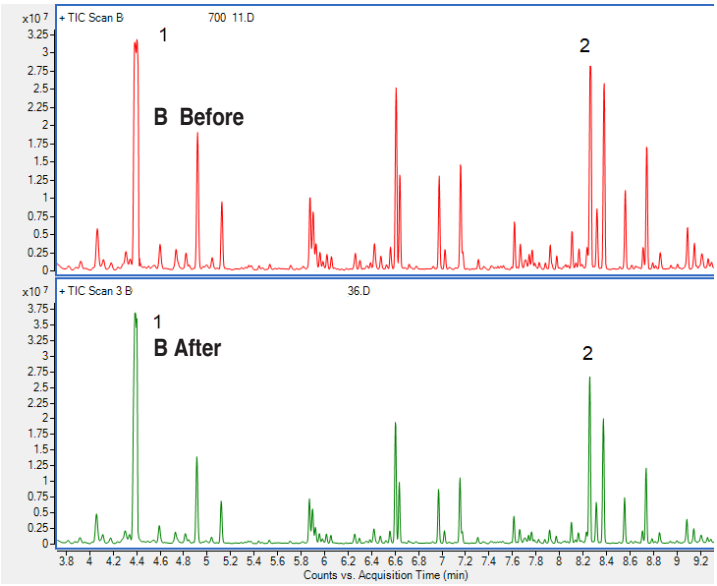
Figure 5. UV exposed Polypropylene Samples 700°C.

its molecular weight. Furthermore, Sample A exhibited more degradation than Sample B (Table 1), indicating that the amount and nature of the UV stabilizers have an impact on the photodegradation experienced by the polymer.



Peak	Identification
1	Polypropylene Trimer
2	Polypropylene Pentamer

Figure 6. Pyrolysis of Sample A before (top) and after (bottom) UV exposure.



Peak	Identification
1	Polypropylene Trimer
2	Polypropylene Pentamer

Figure 6. Pyrolysis of Sample B before (top) and after (bottom) UV exposure.

Conclusion

In addition to analytical pyrolysis, the Photoprobe, the newest addition to the Pyroprobe, can perform online UV exposure in minutes as compared to years or days by sunlight UV or UV chambers.

Table 1. Trimer to Pentamer Peak Area Ratio Differences for Samples A and B.

Sample	Peak Area Ratio Difference
A	1.0
B	0.6

References

1. Schnabel W., Polymer Degradation: Principle and Practical Applications. Chapter 14. München: Hanser Int; 1981.

2. Heskins, M., and Guillet, J.E.. “Mechanism of Ultraviolet Stabilization of Polymers.” Macromolecules, 1(1968):97-98.

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

4. Sam, K., Weather-Induced Degradation Study of Polystyrene Using the Photoprobe, CDS App Note #207.

5. Ter Halle, A. Jeanneau, L., Martingnac, M., Jardé, E., Pedrono, B., Brach, L., Gigault, J. (December 2013). “Nanoplastic in the North Atlantic Subtropical Gyre”. Environ. Sci. Tecnol, 2017, 51, 13689-13697.