



Monitoring the degradation of stabilization systems in polypropylene during accelerated aging tests by liquid chromatography combined with atmospheric pressure chemical ionization mass spectrometry



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ABSTRACT

Degradation pathways of three commonly used antioxidants were successfully studied by using accelerated aging tests for polymers. Additionally, thermal stability and resistance to discoloration of seven stabilizers were investigated by aging pure stabilizers dissolved in the polymer-mimicking solvent squalane. Methods based on high-performance liquid chromatography hyphenated with highly sensitive tandem mass spectrometric detection (HPLC-MS) were developed for structural elucidation of degradation products. Subsequent quantification was done using UV-detection. While Irganox 1330, Irganox 3114 and Cyanox 1790 showed a similar degradation mechanism with highly colored decomposition products, no corresponding oxidized species could be found for other stabilizers and less discoloration was observed. For Irganox 1010, hydrolysis was the preferred degradation mechanism, leading to products with an increased solubility in water. Therefore this stabilizer is less suitable for materials intended for water applications. In the aged materials previously unknown degradation mechanisms were observed for Irganox 1010 and Irgafos 168 which also contribute to the inhibition of autoxidation of the polymer.

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1. Introduction

The implementation of novel polymeric materials in solar-thermal systems has great potential as they provide substantial advantages in comparison to traditional materials [1–5]. A key challenge is to maintain required durability for extended lifetimes, since these materials are prone to degradation caused by reactions with oxygen or UV-light [6,7]. Such reactions lead to undesirable changes in the properties of the polymer. To minimize decomposition during processing, storage and use, different kinds of stabilizers are added to the polymer prior to the compounding procedure. The protection of the polymer depends on the presence of these additives in sufficient concentrations. Therefore the identification and quantification of stabilizers and their possible decomposition products are of major importance for quality control, troubleshooting and life test studies. In addition, resistance to discoloration is a specific requirement for polymer additives, as it is

known that degradation products are one cause of yellowing in polymeric materials [8]. However, both identification and quantification can be very challenging for several reasons. Firstly, the complexity of additives and additive formulations has increased over the last decade. Additionally, the amount added is often small and can be further decreased due to degradation. Furthermore, assignment of decomposition products to the corresponding stabilizers is difficult.

Nowadays there are various different analytical tools available for analyzing polymer additives, which generally require the extraction from the particular matrix as a first step. Of the different procedures to analyze polymer additives, chromatographic methods play a dominant role. Besides the application of gas chromatography (GC) and pyrolysis coupled to gas chromatography (Py-GC) [9–11], high performance liquid chromatography (HPLC) in combination with ultraviolet (UV) detection or mass spectrometric (MS) detection is commonly applied [12–16]. Much work has been put into the development of methods for the analysis of different kinds of stabilizers, but less attention has been paid to the extension of these methods for identification of degradation products [14,16–19].

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The present work is a detailed study on the formation of degradation products of commonly used antioxidants in order to provide a better insight into the stabilization mechanism of some commonly used polymer additives. It is known that primary and secondary antioxidants can transform when stabilizing the polymer against oxidation or radical attack. Characterization of degradation pathways is of great importance since it is not yet fully clear which additive package provides the best performance for a given application. Additionally, structure elucidation of degradation products provides information about their contribution to polymer discoloration. HPLC combined with MS and sophisticated tandem mass spectrometry (MS/MS) was selected as an appropriate analytical method to gain insight into the structure of the various degradation products.

2. Material and methods

2.1. Chemicals

The following polymer stabilizers were included in this work: Irganox 1010, Irganox 1330, Irganox 1135, Irganox 3114, Irganox 1076, Cyanox 1790 and Irgafos 168. Their chemical structures are given in Fig. 1. Irganox-types were obtained from Ciba (Basel, Switzerland), Irgafos 168 from Ciba (Lampertheim, Germany) and Cyanox 1790 from Cytec Industries (Woodland Park, USA). Squalane was obtained from Chrompack (Middelburg, Netherlands). Toluene was purchased from VWR (Fontenay-sous-Bois, France), acetonitrile from VWR (Leuven, Belgium). 18 M Ω water obtained from a

Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout the work. All chemicals had a purity of >99%.

2.2. Instrumentation

All MS-measurements were performed on an Agilent MSD SL ion trap mass spectrometer (Agilent Technologies, Waldbronn, Germany) equipped with an atmospheric pressure chemical ionization (APCI) source. Chromatography was performed on an Agilent Series 1100 HPLC system (Agilent, Palo Alto, CA, USA), equipped with vacuum degasser, quaternary pump, autosampler, and UV–vis diode array detector. The separation column was a Kinetex C18 (50 \times 3.0 mm, 2.6 μ m particle size) from Phenomenex (Phenomenex, Aschaffenburg, Germany). HPLC-MS using positive and negative ion mode was used for the separation and identification of stabilizers and degradation products.

2.3. Sample preparation

A total of 10 mg of a modified polypropylene random copolymer model material was dissolved in 0.5 ml toluene in a closed vial. Tributyl phosphite was added to avoid oxidation of the stabilizers. Dissolution at 130 $^{\circ}$ C required 1 h. After precipitation of the polymer with 0.5 ml acetonitrile, the sample was centrifuged. A defined volume of the supernatant fluid was evaporated to dryness using a stream of nitrogen. The residue was redissolved with an equal volume of acetonitrile. The resulting solution was used without any further treatment for chromatographic analysis.

2.4. Chromatographic conditions

2.4.1. HPLC–UV–MS

A binary gradient with acetonitrile/water at a flow rate of 1.2 mL min $^{-1}$ was used (Table 1). The injection volume was 10 μ L. The column was maintained at 40 $^{\circ}$ C. The wavelength of the UV-detection was 210 nm for all analytes. APCI was selected as the ion source for MS detection as it provides very good performance for substances with low polarity. Both negative and positive ion modes were utilized. The following optimized parameters were employed: nebulizer gas pressure 60 psi, drying gas flow rate 11 L min $^{-1}$, drying gas temperature 350 $^{\circ}$ C, vaporizer temperature 400 $^{\circ}$ C, capillary voltage –3500 V/+3500 V (positive/negative), corona needle current +4000 nA/–20,000 nA (positive/negative).

2.5. Accelerating aging tests

All aging experiments were performed with a Binder FD 53 material test chamber. Different environments (air, deionized water) and different temperatures (95 $^{\circ}$ C–135 $^{\circ}$ C) were used in the tests. In order to be capable of carrying out aging tests in liquids at higher temperatures, an autoclave was constructed with a capacity of 0.42 L. Maximum pressure during aging in the autoclaves was

Table 1
Binary gradient for HPLC separation of stabilizers and their degradation products.

Time (min)	Acetonitrile (%)	Water (%)
0	60	40
4	60	40
7	75	25
10	87	13
14	92	8
17	92	8
23	100	0

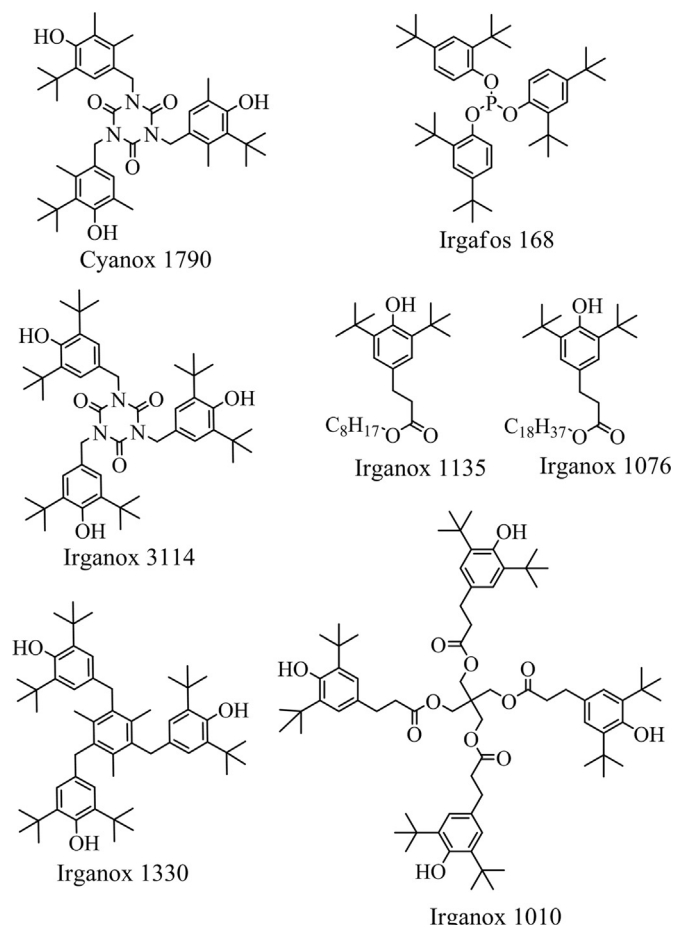


Fig. 1. Chemical structures of the antioxidants included in the present work.

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