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The role of quinoid derivatives in the UV-initiated synergistic interaction mechanism of HALS and phenolic antioxidants

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ABSTRACT

Within this work, UV-initiated interaction mechanisms between the phenolic antioxidant Irganox 1330 and nine commercially used hindered amine light stabilizers (HALS) were successfully studied using high-performance liquid chromatography (HPLC) coupled to UV and high-resolution mass spectrometric detection (MS). An analytical evaluation of the stabilizer performances in the polypropylene-mimicking solvent squalane revealed that all investigated HALS exhibited a strong synergism when combined with the phenolic antioxidant. Up to now, the synergistic interaction was described as a result of the hydrogen transfer from a hydroxylamine derived from HALS to the oxidized form of a primary antioxidant, whereby the phenol is regenerated. Investigations on degradation products, however, indicated that the proposed interaction mechanism cannot be applied to a sterically hindered phenol such as Irganox 1330. Instead, a completely new stabilization mechanism of phenolic antioxidants in the presence of HALS, involving the formation of quinoid derivatives, was discovered and confirmed by using a model compound.

1. Introduction

Hindered amine light stabilizers (HALS) represent an important class of stabilizers protecting polymeric materials against UV as well as thermal radiation-induced degradation. Due to their high molecular weight they almost show no migration from the polymer matrix which makes them especially suitable for long-term stabilization. Nevertheless, HALS fail as processing stabilizers, wherefore they have to be combined with primary or secondary antioxidants such as sterically hindered phenols or phosphites [1]. Various studies have shown that combinations with phenolic antioxidants may cause both synergism [2–5] as well as antagonism [6–11] mainly depending on the kind of aging (thermal, photochemical). Allen et al. [12,13] were one of the first to report about the differences in the thermal and photochemical oxidation behavior of these two stabilizer classes in polyolefinic films. Within their investigations most HALS-phenol combinations revealed quite opposite stabilizing efficacies under thermal and photochemical aging.

Under thermal-oxidative conditions stabilizer efficacy ratings done in the polypropylene-mimicking model compound squalane proved a strong antagonistic effect between phenolic antioxidants and HALS [7], leading to useless consumption of both stabilizer groups. Although it is well known that phenols accelerate the formation of nitroxide radicals which constitute the active HALS species [14], H-atom transfer from the phenol (R-OH) to the nitroxide radical (R-N—O•) leads to inactive hydroxylamine (R-N—OH) species. Besides, Lucki et al. [8] describe the antagonistic effect observed as a result of the recombination reaction between a nitroxide radical and a phenoxy radical, also leading to inactive coupling products. Unlike thermal aging, UV radiation results in a synergism pronounced for most HALS-phenol combinations. Not much work has been published yet explaining where this difference in the stabilization efficacies results from. A possible explanation

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was offered by Ohkatsu et al. [2–5], who ascribe the observed synergism to a regeneration of the phenolic antioxidant after oxidation to a quinone. The suggested mechanism is based on the observation that dibutylhydroxytoluene (BHT) shows a better oxidation inhibition when a small amount of HALS is added. In an effort to explain those findings the reaction of 2,5-di-*tert*-butyl-*p*-benzoquinone (2,5-DBBQ) with a HALS and the corresponding nitroxide and hydroxylamine derivatives was monitored in a UV spectrometer [3]. After irradiation with UV light, the original peak at 268 nm coming from 2,5-DBBQ was decreased while a new peak at 294 nm slightly increased. This new peak was ascribed to 2,5-di-*tert*-butyl-hydroquinone (2,5-DBHQ), which was apparently formed by a reduction reaction of 2,5-DBBQ with a hydroxylamine. Another evidence for the formation of a phenol by reaction of a quinone with a HALS was brought by the same authors using FT-IR and prussian blue test [5].

To simplify tests on effects of stabilizers, squalane was used as a liquid polypropylene-mimicking model compound [6,15,16]. This model provides the major advantage that only stabilizers of interest can be individually studied in sufficient concentrations whereas polymeric materials always contain processing stabilizers which may cause unwanted interactions with other added additives. Besides, stabilizers can be easily dissolved in the liquid squalane without requiring extensive compounding of the polymeric material and the antioxidants to be investigated. Results obtained by such a model cannot necessarily be applied to polymeric materials in general but may still be interesting to get more comprehensive insight into potentially occurring reactions between stabilizer classes. In the current work we investigated the influence of UV light on the interaction of nine different HALS-phenol formulations using high-performance liquid chromatography (HPLC) with UV and mass spectrometric (MS) detection. Stabilizer-containing squalane samples were subjected to an accelerated aging in a xenon test chamber and extracted with methanol. The obtained extracts were then analyzed with HPLC coupled to UV and high-resolution MS detection. Based on the findings in the MS, we revealed that reaction mechanisms suggested so far [2–5] cannot be applied to a sterically hindered phenol such as Irganox 1330. Instead, a completely new interaction mechanism between HALS and phenolic antioxidants involving the formation of quinoid derivatives was discovered and confirmed using a model compound.

2. Materials and methods

2.1. Chemicals

The following polymer stabilizers were included in this work: Irganox 1330 (IX 1330), Tinuvin 622, Chimassorb 119 and Chimassorb 944 from Ciba (Basel, Switzerland), Tinuvin 770 and Uvinul 4050 from BASF (Ludwigshafen, Germany), Chimasorb 2020 from BASF (Kaisten, Switzerland), Hostavin N 30 from Clariant (Frankfurt am Main, Germany), Uvasorb HA 88 from 3V Sigma (Milano, Italy) and Cyassorb UV 3529 from Cytec (West Paterson, NJ, USA). Squalane and ammonium formate were obtained from Sigma-Aldrich (Steinheim, Germany), acetonitrile and methanol from VWR (Leuven, Belgium). 18 MΩ cm water was prepared by a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.2. Instrumentation

Accelerated aging experiments under UV light were performed in a xenon test chamber from HN Sunlight GmbH (Hanau, Germany) with a light filter to eliminate radiations below 300 nm. The chromatographic separations were performed on an Agilent (Waldbronn, Germany) Series 1260 HPLC system. The separation column was a Kinetex C18 (50 × 3.0 mm, 2.6 μm particle size) from Phenomenex (Aschaffenburg, Germany). Detection was performed on an Agilent 1260 Infinity Diode Array Detector. The mass spectrometric devices involved in this work included an Agilent 6510 Quadrupole Time-of-Flight MS (QTOF-MS) and an Agilent 6420 Triple Quadrupole MS system (QQQ-MS), both equipped with an electrospray ionization (ESI) source.

2.3. Sample preparation and aging conditions of squalane-stabilizer formulations

The apolar solvent squalane was used as a polypropylene-mimicking model compound [6,15,16]. For aging characterization 10 mg of the stabilizers were separately added to 4 g squalane each (0.25 wt%). Additionally, binary formulations of the phenolic antioxidant Irganox 1330 with nine HALS were prepared. The solutions were subjected to an accelerated aging under UV light in a xenon test chamber. At various times 100 μL of each sample were taken and the stabilizers along with their degradation products were extracted by shaking with 900 μL methanol. After separation of the layers, the sample was diluted (1:2) with methanol.

2.4. Synthesis of oxidized Irganox 1330

In analogy to a known procedure [17], 396.1 mg (0.12 mmol) $K_3[Fe(CN)_6]$ and 71 mg (0.13 mmol) KOH, both dissolved in 1.6 mL H_2O, were added to a solution of 78.0 mg (0.10 mmol) Irganox 1330 in 8 mL heptane. After stirring the mixture for 10 min, the aqueous phase was separated from the organic solvent and extracted with heptane twice. The combined organic phases were then washed with brine, dried over Na_2SO_4 and evaporated to dryness to yield the oxidized Irganox 1330 (77.3 mg, 0.10 mmol, >99%) as yellow solid. ^1H NMR (300 MHz, δ, $CDCl_3$, 298 K): 1.12–1.23 (m, 27H), 1.35 (s, 27H), 2.09 (bs, 9H), 6.66–6.74 (m, 3H), 7.07–7.19 (m, 6H) ppm.

2.5. Conditions for chromatography with UV and mass spectrometric detection

Quinoid derivatives from Irganox 1330 were analyzed with HPLC-UV and HPLC-QQQ-MS using an acetonitrile/water mobile phase gradient at a flow rate of 1.2 mL min^{-1} for the UV detection and 0.75 mL min^{-1} for the MS detection (Table 1). For improved ionization in the MS, a make-up flow of 0.2 mL min^{-1} consisting of 25 mM ammonium formate in water was added between the end of the HPLC column and the ion source. The following ESI parameters were employed: nebulizer gas pressure 55 psi, drying gas flow rate 10 L min^{-1}, drying gas temperature 325 °C and capillary voltage −4000 V.

Carbonylic squalane degradation products were quantified using HPLC with QQQ-MS detection employing the same MS parameters as listed above. The QQQ system was operated in the multiple reaction monitoring (MRM) mode. A ternary methanol/

Table 1
Binary mobile phase gradient for HPLC-UV and HPLC-QQQ-MS analysis of quinones derived from IX 1330.

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