Polymer Degradation and Stability 121 (2015) 378–384

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Structure elucidation of photoluminescent degradation products from polyolefins and evaluation of stabilizer formulations

L. Maringer [a, *], M. Himmelsbach [a], M. Nadlinger [b], G. Wallner [c], W. Buchberger [a]

[a] Johannes Kepler University Linz, Institute of Analytical Chemistry, Altenberger Straße 69, 4040 Linz, Austria
[b] Johannes Kepler University Linz, Institute of Organic Chemistry, Altenberger Straße 69, 4040 Linz, Austria
[c] Johannes Kepler University Linz, Institute of Polymeric Materials and Testing, Altenberger Straße 69, 4040 Linz, Austria

ARTICLE INFO

Article history:
Received 23 July 2015
Accepted 7 October 2015
Available online 22 October 2015

Keywords:
Photoluminescence
Degradation
Polyolefins
Liquid chromatography
Mass spectrometry

ABSTRACT

In the present work, we focused on the aging behavior of stabilized and unstabilized polyolefins using the solvent squalane as a polypropylene-mimicking model. It was found that squalane as well as polypropylene show aging-induced photoluminescence emissions at elevated temperatures. To separate and identify the photoluminescent species from other aging-induced degradation products, a high performance liquid chromatography method using photoluminescence detection ($\lambda_{Ex} = 375$ nm, $\lambda_{Em} = 410$ nm) was developed. Comparison of the integrated photoluminescence intensities allowed performing a stabilizer efficacy rating of different squalane-antioxidant formulations. For characterization and structure elucidation of the photoluminescent degradation products, the liquid chromatogaphic method was adapted for coupling to a high resolution Orbitrap mass spectrometer. It was possible to assign the observed masses to (multiple) unsaturated carbonyl compounds, which is in accordance to previous investigations.

1. Introduction

Since polyolefins are prone to oxidative degradation leading to undesirable changes in mechanical and optical properties, combinations of polymer stabilizers with different stabilization mechanisms are added. However, these stabilizers do not always show synergistic effects [1–3], so that it is necessary to test the different polymer stabilizers with regard to their stabilization efficacies. It has been shown that the polyolefin-mimicking solvent squalane (SQ) can be used as screening model [4,5], whereby a rating of the stabilizer efficacies is possible by comparing the amount of degradation products derived from a stabilized squalane sample with an unstabilized one [2,3]. Although this method proved to be successful, it requires an expensive time-of-flight mass spectrometer for detection. In the present work, we studied the aging behavior of stabilized and unstabilized polyolefins using the polypropylene-mimicking solvent squalane as well as real polypropylene (PP) samples. To this end, a simple reversed phase high performance liquid chromatography (RP-HPLC) method with photoluminescence detection was developed. In contrast to other polymer aging characterization methods such as infrared (IR) spectroscopy, differential scanning calorimetry (DSC) [6] or tensile testing [7], photoluminescence spectroscopy is the only method showing aging induced changes within the induction period of the polymer degradation process. Thus, photoluminescence spectroscopy has turned out to be the method of choice when studying polyolefin degradation at the initial stage of the aging process [8–11].

Although one would not expect highly pure hydrocarbons like polypropylene and polyethylene (PE) to absorb light in the ultraviolet or visible spectrum, photoluminescence emissions are nevertheless observed [8–10,12–19]. Allen et al. [14–17] found that PP shows aging induced fluorescence ($\lambda_{Ex,max} = 295$ nm, $\lambda_{Em,max} = 345$ nm) and phosphorescence emissions ($\lambda_{Ex,max} = 260$, 280, 330 nm, $\lambda_{Em,max} = 415$, 455, 485 nm), which increase within the first 45 min of the aging process at 130 °C and then decrease. At the same time a new phosphorescence band with a different wavelength ($\lambda_{Ex,max} = 310$ nm, $\lambda_{Em,max} = 450$ nm) was observed. Comparison of the PP fluorescence/phosphorescence excitation spectra with the absorption spectra of pent-3-ene-2-one and *trans*,*trans*-2,4-hexadienal led them to the conclusion that the fluorescence emissions were caused by the presence of enone-

* Corresponding author.
E-mail address: Leila.Maringer@jku.at (L. Maringer).

http://dx.doi.org/10.1016/j.polymdegradstab.2015.10.005
0141-3910/

type chromophoric products, while the phosphorescence emissions were attributed to dienal oxidation products. They further postulated a conversion of α,β-unsaturated carbonyls to their saturated equivalents after irradiation, thereby explaining the decrease of the initial fluorescence. Jacques and Poller [18,19] also supported the idea of enones being responsible for the initial fluorescence. They proved their assumption by incorporating different α,β-unsaturated carbonyls into the polymer. Depending on the amount of added model compound more or less intense fluorescence bands could be observed, even though none of the model compounds showed a fluorescence emission outside the polymer. Further, a post-oxidation fluorescence emission ($\lambda_{Ex,max}$ = 390 nm, $\lambda_{Em,max}$ = 460 nm) was obtained for all model compounds after 58 min of heat treatment at 130 °C, which was assumed to be due to the formation of short polyene units and conjugated carbonyl compounds. For this reason carbonyl model compounds with short polyene units were synthesized and incorporated into the polymers. Surprisingly, none of these compounds, which were believed to cause this post-oxidation fluorescence, showed any emissions neither in solution nor when present in the polymer matrix. No satisfactory explanation has been found for these findings until now. In an effort to clarify this ongoing debate we developed a new concept to detect the photoluminescent species directly in the polymer. In contrast to the above mentioned approaches the evidence is not provided by comparison of the photoluminescence spectra with standards or by addition of different model compounds to the polymers but by separation of the photoluminescent species from the polymer matrix and subsequent detection by a high-resolution Orbitrap mass spectrometer. Comparing the information provided by the mass spectra with literature data, directly helps to match the masses to certain structural elements.

2. Materials and methods

2.1. Chemicals

The following polymer stabilizers were included in this work: Irganox 1330 and Irganox PS 800 purchased from Ciba (Basel, Switzerland), Tinuvin 770 from BASF (Ludwigshafen, Germany), Irgafos P-EPQ from BASF (Basel, Switzerland) and Naugard 445 from Chemtura (Philadelphia, USA). The structures of these stabilizers are given in Fig. 1. Squalane and ammonium formate were obtained from Sigma–Aldrich (Steinheim, Germany), ethyl acetate from VWR (Fontenay-sous-Bois, France), methanol from VWR (Leuven, Belgium) and acetone from Fisher (Loughborough, UK). 18 MΩ water was prepared by a Milli-Q-water purification system (Millipore, Bedford, MA, USA). Ethylene/propylene random copolymer model materials (PP-R) with β-crystalline morphology were provided by the Institute of Polymeric Materials and Testing of the University Linz. The materials were base stabilized with 0.16 wt% Irganox 1010, 0.38 wt% Irganox 1330 and 0.08 wt% Irgafos 168.

2.2. Instrumentation

The chromatographic separations were performed on an Agilent 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 a Jasco 821-FP Intelligent Spectrofluorometer. The mass spectrometric (MS) devices involved in this work included an LTQ Orbitrap XL from Thermo Scientific and an Agilent 6420 Triple Quadrupole MS system (QqQ-MS), both equipped with an electrospray (ESI) source.

2.3. Sample preparation and aging conditions of squalane and PP-R

For aging characterization 5 g squalane with and without added stabilizers (0.1 wt%) were heated in a drying chamber from ambient conditions up to 130 °C. To accelerate the aging process the squalane vials were kept open during the whole experiment. At various times samples were taken, extracted with methanol (squalane:methanol = 1:4) and centrifuged to support phase separation. For analysis via HPLC with photoluminescence/Orbitrap-MS detection the methanolic extract was directly injected without further dilution. For analysis via HPLC/QqQ-MS Cyanox 1790 was added as internal standard before the extraction step with methanol (squalane:methanol = 1:11.5). After phase separation the methanolic extract was 1:11.5 diluted with water/methanol (1:1.5). The final concentration of the internal standard in the sample solution was 16 mg L^{-1}.

Accelerated aging tests of the PP-R model materials were performed at 135 °C in hot air in a Binder FED 53 (Tuttlingen, Germany) heating chamber with forced circulation on the Institute of Polymeric Materials and Testing of the University Linz [20]. For sample preparation of the 29.3 weeks aged PP-R 150 mg of the polymer were extracted with 800 μL acetone in a closed glass vial for 3 h at 130 °C. The acetone extract was then analyzed via HPLC with photoluminescence detection.

2.4. Conditions for chromatography with photoluminescence and mass spectrometric detection

For HPLC with photoluminescence and Orbitrap-MS detection an acetone/water/ethyl acetate mobile phase gradient at a flow rate of 0.6 mL min^{-1} was used (Table 1). The HPLC column was kept at a constant temperature of 37.5 °C. The injection volume was 25 μL. All samples were analyzed with an excitation wavelength (λ_{Ex}) of 375 nm and an emission wavelength (λ_{Em}) of 410 nm.

The following ESI-Orbitrap-MS parameters were employed: nebulizer gas flow 45 (arbitrary units), nebulizer gas temperature 350 °C, and capillary voltage −3500 V. For improved ionization in the MS a make-up flow consisting of 12 mM ammonium formate in 1:1 methanol/water was added between the end of the HPLC column and the ion source.

The mobile phase gradient for HPLC with ESI-QqQ-MS detection is given in Table 2. The HPLC column was kept at a constant temperature of 37.5 °C. The injection volume was 15 μL. The following ESI-QqQ-MS 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. The QqQ system was operated in the multiple reaction monitoring (MRM) mode.

3. Results and discussion

3.1. Influence of aging time on formation of photoluminescent degradation products

From previous oxidation studies with squalane, it is known that air aging at 130 °C leads to the formation of saturated carbonyl compounds [2,3]. At the same time discoloration (yellowing) accompanied by the appearance of photoluminescence emissions at 410 nm (λ_{Ex} = 375 nm, λ_{Em} = 410 nm) were observed. No elution of the photoluminescent species from a RP column could be achieved with commonly used solvents such as methanol or acetonitrile. Some experiments done on a reversed-phase thin-layer chromatography plate revealed that under all tested organic solvents only ethyl acetate, methyl tertiary butyl ether, tetrahydrofuran and acetone were able to elute the photoluminescent spot from the stationary phase. For this reason an acetone/water/ethyl