

Isolation and Identification of Oxidation Product of 2,6-Di-(Tert-Butyl)-4-Methylphenol from Polyethylene Film¹

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ABSTRACT

2,6-Di-(tert-butyl)-4-methylphenol is a widely used antioxidant in the production of polyethylene. An oxidation product of this antioxidant was isolated from aged polyethylene film and purified by preparative thin layer chromatography. This compound was identified as 3,3', 5,5'-tetra-bis(tert-butyl)-stilbenequinone with the aid of IR- and mass spectroscopy. The generation of this oxidation product can lead to the discoloration of polyethylene film, and its formation can be catalyzed by contact with carbon black.

INTRODUCTION

Polyethylene is the highest production synthetic packaging material in the world. The total polyethylene film production in the U.S. is estimated to be in excess of 1.1 billion lb annually, of which more than 50% is used in food packaging.

Like most other polymeric materials, polyethylene will degrade under the influence of the environment, with oxidation being the major cause of degradation during processing and aging. The stability of polymeric materials toward oxidation can be enhanced by the incorporation of antioxidants into the film during processing. However, antioxidants present in the film also are subject to chemical reaction, and the resulting product(s) can contribute to the overall changes observed in the film.

Rothstein (1) has evaluated a series of antioxidants in high density polyethylene for color and physical property stabilization during processing and thermal aging. The higher degree of discoloration observed in the sample containing 2,6-Di(tert-butyl)-4-methylphenol (BHT), as compared to the control (5 weeks' storage at 120 C), seems to indicate that, in this case, the BHT contributed to the overall discoloration of the film.

BHT is the most widely used antioxidant in the production of polyethylene film; and, while nearly 20 oxidation products have been isolated and characterized from the oxidation of BHT with a variety of oxidizing agents (2), no reports are available on the oxidation products derived from the oxidation of BHT added to film.

The present study separated and identified an oxidation product resulting from the oxidation of BHT in polyethylene film.

EXPERIMENTAL PROCEDURES

Isolation of BHT Oxidation Product

A yellow substance (A) was isolated from 100 g commercial type polyethylene film (aged at room temperature for 2 years) by Soxhlet extraction with chloroform. The chloroform extract was concentrated, and the residual semisolid was purified by column chromatography. A silica gel column (ht, 15 cm; diameter, 2.5 cm) was employed. The column was eluted with 750 ml hexane, followed by elution with 750 ml toluene. The toluene eluate was concentrated, and further purification of the yellow extract

was achieved by preparative thin layer chromatography (TLC).

TLC was carried out on Silica Gel F 254 plates using hexane-toluene (80:20 v/v) as the developing media. The materials on the plates were visualized by their visible absorption and viewing under UV light. The separated material was recovered by extraction of the desired band with acetone.

Analytical Methods

A Beckman model DB-G recording spectrophotometer was used for the determination of visible spectra. Samples were scanned from 700-300 m μ using 10 mm path quartz cells. Absorption at 442 m μ was used for quantitation of A (3).

Samples were analyzed on a Perkin-Elmer model 421 IR spectrophotometer. A beam condenser employed in conjunction with an ultramicro liquid cell was used to analyze small samples.

Mass spectral analyses were performed using a Hitachi-Perkin-Elmer RMU 7 double focusing mass spectrometer.

Synthesis of Authentic Compound

3,3', 5,5'-Tetra-bis(tert-butyl)-stilbenequinone, was prepared by the oxidation of BHT following the method of Zykova and Stolyarov (4). The crude reaction product was purified by preparative TLC using conditions identical to those employed in the purification of the unknown substance A.

Aging of Polyethylene Film in Presence of Carbon Black

Carbon black, polyethylene film laminates were prepared by placing a slurry of carbon black in acetone between 5 in. squares of film. After the acetone was evaporated, the film was pressed between two glass plates and the resulting laminates stored in a constant temperature oven. The film was extracted with 3 x 50 ml chloroform and filtered to remove the carbon black. The visible spectrum of the yellow filtrate was recorded to determine the concentration of A.

RESULTS AND DISCUSSION

Isolation and Identification of Substance A

The main yellow fraction isolated from column chromatography of the polyethylene film extract, when examined by TLC, showed one major yellow spot (R_f 0.58). To obtain sample of A sufficiently purified for mass and IR spectrometries, at least three TLC purifications were required. In addition to this major spot, 4 minor yellow spots were observed (R_f 0.45, 0.27, 0.19, and 0.04). When visualized under UV light, 5 additional UV absorbing components were observed (R_f 0.67, 0.52, 0.35, 0.23, and 0.06). These materials were present in low concentrations, and no attempt was made to isolate and characterize each component.

The yellow substance A isolated from polyethylene film (aged at room temperature for 2 years) exhibited an IR spectrum with a major absorption at 1600 cm⁻¹ (6.25 μ). An absorption at this frequency is characteristic of a carbonyl group in a highly conjugated system and is

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TABLE I

Relative Abundance of Major Ions in Mass Spectra of the Synthetic 3,3', 5,5'-Tetra-Bis-(Tert-Butyl)-Stilbenequinone and Substance A^a

m/e	Relative abundance	
	Synthetic	Substance A
57	29.4	Not measurable above scale
203	6.1	4.4
217	4.8	3.5
219	7.2	3.8
419	3.9	2.9
434	100.0	100.0
435	34.8	37.0
436	24.3	32.8
437	10.5	11.4

^aSee text for a description of Substance A.

indicative of a quinonoid structure (5).

The mass spectrum of A exhibited a base peak at m/e 434. Additional major ions were present at m/e 57, m/e 435, and m/e 436.

Heiss, et al., (6) reported the presence of (M + 2)⁺ peaks in the mass spectra of p-quinones and stilbenequinones. The (M + 2)⁺ peaks are produced mainly by residual moisture in the mass spectrometer, and their intensity is proportional to the redox potential of the p-quinonoid system.

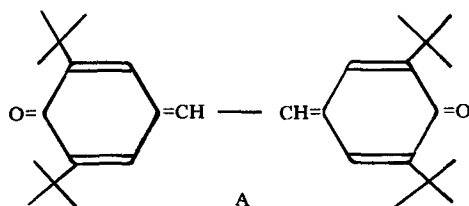
Substance A was assigned a quinonoid structure. Based upon this assignment, the m/e 434 peak was considered the molecular ion; the m/e 435 peak was considered due to the normal isotopic abundance of carbon-13; and the m/e 436 peak was assigned to the (M + 2)⁺ product of the redox reaction described by Heiss, et al., (6) as well as a peak due to the normal isotopic abundance of oxygen 18. The m/e 57 peak was assigned to a t-butyl ion (C₄H₉).

Based upon a mol wt of 434 and establishing the number of carbon atoms present from the mass spectrum (7), substance A was assigned a molecular formula of C₃₀H₄₂O₂.

The spectral properties of A are characteristic of an oxidation product of BHT (8). The major synthetic oxidation product of BHT showed IR and visible spectra identical to those of A.

The mass spectra of the synthetic product and A were compared and were similar. The mass spectrum of the synthetic product exhibited a base peak at m/e 434 and major peaks at m/e 57, m/e 435, and m/e 436. Table I shows the relative abundance of the major ions present in the mass spectra of the synthetic product and substance A. Extraneous peaks found in both spectra were due to minor impurities present in the samples.

The data indicate that the yellow substance A isolated from the film is an oxidation product of BHT. The structure of A is indicated as follows:



3,3', 5,5'-Tetra-bis-(tert-butyl)-stilbenequinone A has been isolated and characterized from the oxidation of BHT with a variety of oxidizing agents. However, the identification of compound A as an oxidation product of BHT in polyethylene film was not found in the literature.

Isolation and Identification of Precursor of A

During the TLC purification of A an UV absorbing substance B of R_f 0.67 was found to develop an intense

TABLE II

Relative Abundance of Major Ions in Mass Spectrum of Substance B^a

m/e	Relative abundance
57	9.6
203	2.8
204	4.8
219	100.0
220	20.3
423	2.4
424	1.4
438	30.0
439	10.1
440	1.8

^aSee text for a description of substance B.

TABLE III

Carbon Black Catalyzed Oxidation of 2,6-Di-(tert-butyl)-4-methylphenol in Polyethylene Film^a

Film ^b	Film wt (g)	Carbon black ^c wt (g)	Concentrate A (mg/gm film)
A	12.5	2.5	.025
B	20.0	4.0	.071
C	25.0	5.0	.072
D	25.0	5.0	.055
E	25.0	5.0	.014

^aSeven days at 75 C.^bCommercial-type packaging films.^cChannel type.

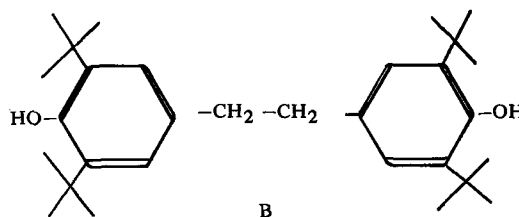
yellow color upon standing overnight. Simultaneously, the UV absorbing property of this material disappeared. This yellow substance was isolated and the IR and mass spectra recorded. They were found to be identical to the spectra of A.

Substance B, isolated directly after TLC, exhibited a mass spectrum with a molecular ion at m/e 438 and a base peak at m/e 219. The latter corresponds to a symmetric homolytic fragmentation of the molecular ion. Further support for the structure of B was evidenced by the presence of a peak at m/e 57, which corresponds to the tert-butyl ion (C₄H₉). Table II shows the relative abundance of the major ions present in the mass spectrum of substance B.

The elemental composition calculated from the mass spectrum (7) gave a molecular formula of C₃₀H₄₆O₂ for substance B.

The IR spectrum of B showed a major absorption at 3636 cm⁻¹ (2.75 μ), characteristic of a phenolic OH group (5).

These spectroscopic data indicated B was a dimerization product of BHT (8). The structure of B is indicated below:



3,3',5,5'-Tetra-bis-(tert-butyl)-4,4'-dihydroxy-1,2-diphenyl-ethane is a known precursor of A (2). However, no literature references were found describing B as an oxidation product of BHT present in polyethylene film.

Influence of Carbon Black on Oxidation of BHT in Polyethylene Film

The results of this study are tabulated in Table III. In all

cases where polyethylene film was contracted with carbon black, 3,3', 5,5'-tetra-bis-(tert-butyl)-stilbenequinone A was isolated as a major oxidation product, while little or no oxidation of BHT was evidenced under identical conditions in the absence of carbon black.

In this study, carbon black contacting the surface of the polyethylene film acted to catalyze the oxidation of BHT. A similar effect was reported by Hawkins and Worthington (9) and by Kapacuskene and Shlyapnikov (10) where carbon black was added directly to polyethylene.

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