Determination of the Hindered Amine Additive CGL-144 in Polypropylene by High-Performance Liquid Chromatography

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Synopsis

A method was developed to determine CGL-144 (Tinuvin 144) in polypropylene. Polypropylene pellets were dissolved in hot decalin. The solution was cooled to precipitate the polymer. A portion of the filtered extract solution was injected onto a normal-phase high-performance liquid chromatography (HPLC) system consisting of a μ-Porasil stationary phase and a chloroform:ethanol:ammonia (95:5:0.05) mobile phase. The amount of CGL-144 was determined by peak height measurement from an ultraviolet absorption detector set at 280 nm. Injections could be made every 10 min. The limit of detection for the method as described is 0.06% CGL-144 in polypropylene. There are no known interferences with this method.

INTRODUCTION

Analyses of polyolefin additives are usually carried out *in situ*[1,2] or after lengthy extraction procedures requiring several hours.[2-5] Recently, a new rapid extraction technique using heated decalin for the determination of BHT, Irganox 1076, and Irganox 1010 in polyethylene and polypropylene was described by Schabron and Fenska.[6] The present paper describes the successful extension of this technique for extraction of CGL-144 in polypropylene followed by determination by high-performance liquid chromatography (HPLC). The additive CGL-144 is a hindered phenol/hindered amine antioxidant and light absorber used in polyolefin formulations. Its structure is shown in Figure 1. The HPLC mobile phase used was a halogenated solvent/alcohol/ammonia mixture, similar to combinations traditionally used for silica thin-layer chromatography of amines.[7]

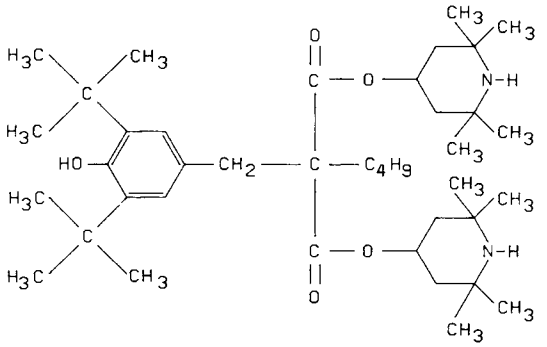

Fig. 1. Chemical structure of CGL-144.

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EXPERIMENTAL

Instrumentation

The liquid chromatograph used in this study was a Waters Model 204 liquid chromatograph equipped with two Model 6000-A pumps, a Model 660 solvent programmer, and a Valco 7000 psi HPLC injector with a 25-μL sample loop. Elution was monitored with a Waters Model 450 variable wavelength detector set at 280 nm and a 10-mV strip chart recorder. Two Waters μ-Porasil 3.9-mm i.d. × 30-cm columns in tandem packed with 10-μm porous silica connected to a 3.9 mm × 3 cm Waters precolumn dry packed with 37–50-μm C_{18}-Corasil were employed.

Two Thermolyne-type 1000 stir plates were obtained from Sargent Welch. Stir bars were $\frac{3}{8}$-in. O.D. × 1 $\frac{1}{2}$-in. Teflon coated magnetic stir bars.

The sample filtering apparatus used is shown in reference 6. A Waters 20–30-μm stainless-steel solvent reservoir filter was connected to ~5 in. length of 3-mm i.d. Teflon tubing. The other end of the Teflon tubing was connected to a 1 $\frac{1}{2}$-in. long blunt 16-gauge luer lok needle with a $\frac{1}{16}$-in. stainless-steel nut and ferrule at the end of the needle. The needle was connected to a Hamilton No. 1010W gastight 10-mL syringe with Teflon plunger.

Reagents

Chloroform was Mallinkrodt AR grade from Scientific Products and ethanol was absolute ethanol. The above mobile phase solvents were filtered through Millipore type F-H 0.5 micron filters prior to use. Ammonia was Mallinkrodt 27% and was not filtered. CGL-144 was from Ciba-Geigy, Ardsley, N.Y. and was used as received.

Procedure

A 50-mL portion of a standard solution containing about 0.3 mg/mL of CGL-144 was pipetted into a 100-mL beaker. A stirring bar was added and the solution was heated to 110°C with gentle stirring for 45 min. The solution was transferred to a cool stirrer and cooled to room temperature. This heated and cooled standard solution was used to obtain quantitative data on the sample extract solutions.

About 2-g polypropylene pellets were weighed into a 100-mL beaker. A stirring bar was added and 50-mL decalin were pipetted into the beaker. The mixture was heated to 110°C on a hot plate with gentle stirring for about 45 min or until dissolution was complete. The beaker was then transferred to a cool stirrer and cooled to room temperature with stirring to precipate the polypropylene.

The precipitated polypropylene from the above extraction was pushed aside with a microspatula. The porous metal filter portion of the filter aparatus was inserted into the solution and ~5–10 mL of solution was drawn into the syringe. The Teflon tube was removed from the ferrule on the needle and the filtered solution was dispensed into a 20-mL vial. The filter apparatus was rinsed with acetone and dried between samples. After extensive use the metal filter became partially clogged and was regenerated by placing it in hot decalin and stirring.

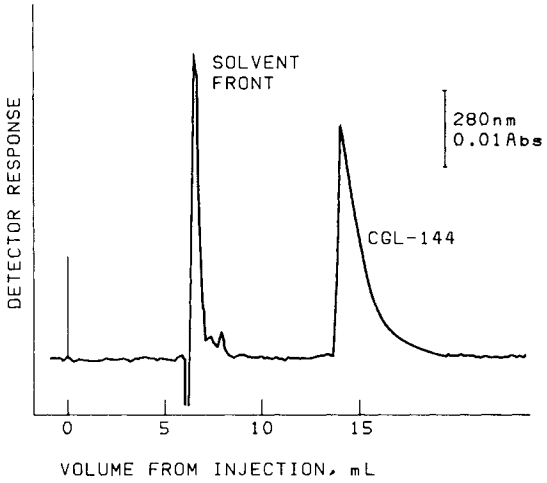

Fig. 2. Chromatogram of 12.6-μg CGL-144 standard in 25-μL decalin. HPLC conditions as in text.

The Model 450 UV detector was set at 0.1 absorbance units sensitivity at 280 nm and the recorder chart speed was 0.5 in./min. The HPLC mobile phase was chloroform:ethanol:ammonia (95:5:0.05) at 2 mL/min. Duplicate injections of 25 μL of each of the standard and sample solutions were made. The retention volume (V_R) of CGL-144 was about 14.0 mL. A typical chromatogram is shown in Figure 2. The amount of CGL-144 was determined from each sample injection by comparing peak heights for samples and standards. Peak heights of samples and standards were measured to the nearest 0.5 mm.

RESULTS AND DISCUSSION

Precision. Six replicate analyses were performed on a polypropylene sample. The results are listed in Table I. They show good precision for the method. The relative standard deviation was 2.3%.

Several polypropylene samples containing various amounts of CGL-144 were analyzed in duplicate. These results are listed in Table II. The pooled standard deviation was 0.0063.

Accuracy. Spiking experiments were performed with a polypropylene sample

TABLE I
Results of Six Replicate Determinations of CGL-144 in a Polypropylene Sample

Sample amount, g		Amount found, wt %
2.000		0.45
2.003		0.47
2.000		0.47
1.999		0.47
1.997		0.48
2.005		0.48
	$\bar{x}$ =	0.47
	s =	0.011
95% Confidence		±0.011

TABLE II
Results from Analyses of Six Polypropylene Samples

Sample	Sample amount, g	Amount CGL-144 found, wt %
A	2.000	0.36
A	2.000	0.36
B	2.008	0.50
B	2.002	0.50
C	2.001	0.52
C	2.006	0.53
D	2.002	0.68
D	2.002	0.68
E	2.003	0.86
E	2.008	0.86
F	2.010	0.54
F	2.005	0.56

initially containing no CGL-144. The experiments were performed by dissolving 2-g polypropylene in decalin containing known amounts of CGL-144. The results are listed in Table III. They show good recoveries at levels corresponding to 0.2, 0.4, and 0.8%, respectively, of CGL-144 in the polypropylene.

Sample size variation experiments were carried out also. The results are listed in Table IV. These results indicate the absence of significant constant error.

Limit of Detection. The limit of detection for the method as described was estimated to be 0.6-μg CGL-144 injected, at a S/N level of 2. This corresponds to 0.06% CGL-144 in a polypropylene sample.

Additional Considerations. The linearity of response with peak height for CGL-144 was checked. It was found to be linear from 0–12.5 μg injected in 25-μL decalin portions.

The V_R values for several other common UV absorbing additives were checked on the HPLC system used for CGL-144. The following additives eluted at the solvent front and thus would not interfere with CGL-144: Topanol CA, Goodrite

TABLE III
Recovery of CGL-144 From 2-g Portions of Polypropylene Pellets

Amount added, mg	Amount found, mg	Percent recovered
4.01	4.24	106
4.01	4.32	108
8.02	8.10	101
8.02	8.41	105
16.05	16.20	101
16.05	15.66	98

TABLE IV
Sample Size Variation Results with Polypropylene

Sample amount, g	Amount CGL-144 found, wt %
0.998	0.48
1.003	0.47
4.011	0.46
4.000	0.48

3114, Ethyl 330, Santonox R, BHT, Irganox 1076, Irganox 1010, Irganox 1024, and UV 531.

The V_R of CGL-144 was about 14.0 mL (7.0 min) as mentioned previously. This value varied slightly with different batches of mobile phase. A sample injection could be made approximately every 10 min.

After ~20–30 injections of polypropylene extract, the precolumn, which removes low-molecular-weight polymer from the system, had to be changed. If it was not changed in time, the system pressure would increase by several hundred psi per injection over the usual 1900–2000 psi level. When this occured, the system pressure could be restored easily by replacing the outlet filters of the analytical columns with either new filters or used filters cleaned in hot decalin. The filter replacement takes only a few minutes.

Polypropylene extraction with hot decalin takes a little longer than polyethylene. The time for polypropylene is about 45 min, while the time for polyethylene is about 30 min.[6]

The hot decalin extraction method described in reference 6 and in the present work may prove to be the cornerstone of a new series of specific analytical methods for various specialty polyolefin additives. This aspect is currently under investigation.

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