

Highly sensitive determination of a polymeric hindered amine light stabilizer in polypropylene by reactive thermal desorption–gas chromatography using nitrogen-specific detection

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Abstract

Highly sensitive and specific determination of trace amounts of a polymeric hindered amine light stabilizer (HALS) in polypropylene (PP) materials could be established by improving reactive thermal desorption–gas chromatography (RTD–GC) in the presence of an organic alkali, tetramethylammonium hydroxide. By using nitrogen–phosphorus detection, highly selective detection of the HALS-related components was attained. In addition, the use of a polar poly(ethylene glycol) separation column alleviated the adsorption of minor specific pyrolysis products. This modified RTD–GC method allowed the determination of the polymeric HALS (M_r 1900) in PP even for trace concentrations between 100 and 500 ppm, through observing selectively the characteristic products containing a tetramethylpiperidine moiety, which had been impossible to detect under the previous RTD–GC conditions using a non-polar separation column and conventional flame ionization detection.

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1. Introduction

Hindered amine light stabilizers (HALSs) are commonly added to various polymeric materials in outdoor uses as excellent radical scavengers in order of 1000 ppm or less for the prevention of their

photodegradation [1]. In practical use, oligomeric or polymeric HALSs are often employed to suppress their bleeding-out from the substrate polymers. Generally, HALSs in polymer materials have been determined by means of gas chromatography (GC) or liquid chromatography (LC) after their extraction from the substrate materials [2–7]. However, the extraction process is often tedious and time-consuming especially for the polymeric HALSs. In addition, the quantitative recovery of the higher-molecular-

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mass HALSs is not always attained because of their low solubility.

Recently, to determine a polymeric HALS in polypropylene (PP), the authors have developed a novel reactive thermal desorption–gas chromatography (RTD–GC) method [8], which is based on thermally assisted hydrolysis and methylation GC in the presence of an organic alkali, tetramethylammonium hydroxide $[(\text{CH}_3)_4\text{NOH}, \text{TMAH}]$ [9]. This technique allowed the precise determination of the HALS at concentrations between 1000 and 50 000 ppm in PP as its methylated fragments on the resulting chromatogram without the need for any extraction procedure. For the samples containing less than 1000 ppm of the HALS, however, accurate determination was difficult even by the RTD method because the adsorption of the target trace components in the separation column and the interference with the pyrolysis products of PP on the chromatograms became substantial.

In this work, a separation column more polar than the former dimethylsiloxane one [8] was adopted for

RTD–GC both to prevent the undesirable adsorption of the components derived from the HALS and to eliminate the compositional interference with those from the PP substrate. Furthermore, nitrogen–phosphorus detection (NPD) was employed to detect selectively and sensitively in nitrogen-containing compounds from the HALS, rather than the universal flame ionization detection (FID) [8]. By using the thus modified RTD–GC method, trace determination of the polymeric HALS contained in PP composites down to less than 1000 ppm was tried.

2. Experimental

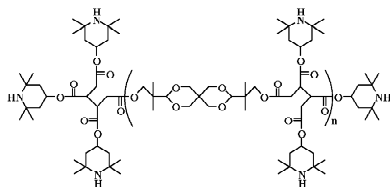
2.1. Samples

Similarly to our previous work, Adekastab LA-68LD (Asahi Denka Kogyo, Tokyo, Japan; M_r 1900) was used as the polymeric HALS. PP substrate in powdered form was a commercial product with melt flow index of 1.0 without containing any additives.

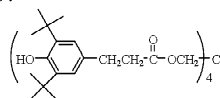
Table 1
Amount of the HALS and antioxidants in prepared PP compositions

Composition code	Content of stabilizers ^a		
	Adekastab LA-68LD (ppm)	Irganox 1010 (ppm)	Irgafos 168 (ppm)
S-1	100	3000	3000
S-2	250	3000	3000
S-3	500	3000	3000
S-4	1000	3000	3000
S-5	2500	3000	3000
S-6	5000	3000	3000
S-7	10000	3000	3000
S-8	25000	3000	3000
S-9	50000	3000	3000

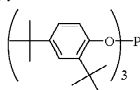
^a Adekastab LA-68LD



Irganox 1010:



Irgafos 168:



Before preparing PP composites, antioxidants, Irganox 1010 (Ciba Geigy, Basle, Switzerland) and Irgafos 168 (Ciba Geigy), were added to the powdered PP material at 3000 ppm each to prevent thermal degradation of PP during kneading. A series of model PP composites containing the polymeric HALS were prepared by the following procedure. First, weighed amounts of PP (ca. 30 g) blended with the antioxidants (Irganox 1010 and Irgafos 168) were kneaded at 180–190 °C for 5 min. Then, the polymeric HALS was promptly added to the melted PP and kneaded again for 3 min. Table 1 shows the formulation of PP samples thus prepared along with the structure of the stabilizers. Prior to RTD–GC measurements, the thus formulated PP samples were powdered in a freezer mill (Spex, Metuchen, NJ, USA; Model 6750) both to homogenize the composite materials and to improve the following reactive thermal desorption of the additives in the presence of reagent.

2.2. RTD–GC measurement

Fig. 1 shows the schematic diagram of the pyrolysis–GC system for the RTD–GC method used in this work. Except for the separation column and the detection system, the main apparatus employed is basically the same as that in our previous work [8] which consists of a double-shot pyrolyzer (Frontier Lab, Koriyama, Japan; Model PY-2020D), and a gas chromatograph (Hewlett-Packard, Avondale, PA, USA; Model 6890 plus). Here, two kinds of metal capillary separation columns [Frontier Lab Ultra

ALLOY-PY1, 30 m×0.25 mm I.D., coated with non-polar polydimethylsiloxane in 0.25 μm film thickness, and Frontier Lab Ultra ALLOY-CW, 30 m×0.25 mm I.D., coated with polar poly(ethylene glycol) (PEG) in 0.25 μm film thickness] were comparatively examined. About 150 μg of the powdered PP sample and 2 μl of a methanol solution (25%, w/w) of TMAH (Aldrich, Steinheim, Germany) taken in a platinum cup were introduced into the heated center of the pyrolyzer at 300 °C under the flow of helium carrier gas (50 ml min⁻¹). The RTD conditions such as RTD temperature and the amount of reagent were determined empirically from our previous work [8]. The main flow of He carrier gas containing the trace components thermochemically formed from the HALS in the pyrolyzer was reduced to 1 ml min⁻¹ at the entrance of the capillary separation column by means of a splitter. The column temperature was programmed from 50 °C to a final set temperature (300 °C for the nonpolar column and 230 °C for the polar one) at 5 °C min⁻¹ and then maintained for 20 min at the final temperature. The components thus separated were finally

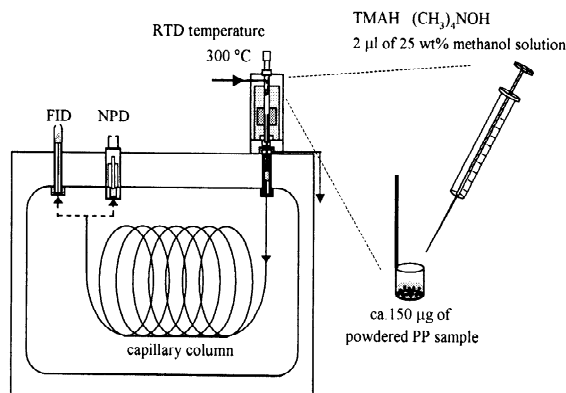


Fig. 1. Schematic diagram of RTD–GC system using NPD.

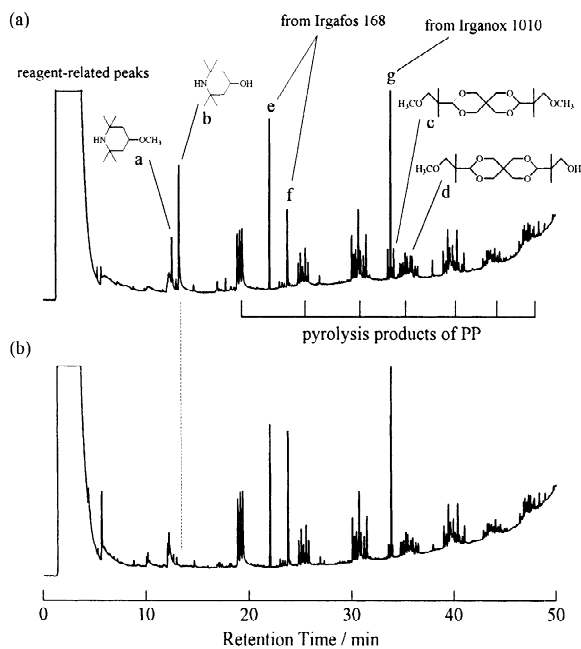


Fig. 2. RTD–GC chromatograms at 300 °C, detected by FID using a non-polar separation column. (a) PP composite (S-6), (b) PP composite (S-3).

detected either by conventional FID or by nitrogen-specific NPD equipped for GC in parallel.

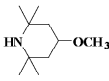


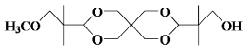
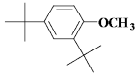
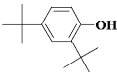
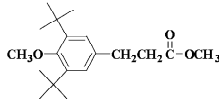
3. Results and discussion

Fig. 2 shows the chromatograms for (a) S-6 and (b) S-3 obtained by RTD–GC at 300 °C in the presence of TMAH under conditions similar to our previous report [8] using a non-polar separation column and FID. The structures of the characteristic products in the chromatograms assigned by GC–MS are given in Table 2. On the chromatogram for S-6 containing 5000 ppm of the polymeric HALS (Fig. 2a), four products formed as a result of the selective hydrolysis of ester bondings in the HALS, LA-68LD; two containing a tetramethylpiperidine moiety (peaks a and b) and two reflecting the spiro chain structure (peaks c and d), are clearly observed along

with those derived from the antioxidants (peaks e–g) [8,9]. These characteristic peaks are scarcely interfered by those of the pyrolysis products from PP. However, on the chromatogram for S-3 containing only 500 ppm of the HALS (Fig. 2b), those characteristic peaks of the HALS were hardly detected at all even for peak b. This fact should be attributed mainly to the considerable adsorption of the characteristic products on the inner surface of the non-polar separation column. Therefore, the polar separation column with poly(ethylene glycol) stationary phase was then utilized to suppress the adsorption of the specific trace components in the column. Moreover, NPD was used instead of FID to detect selectively the components containing the tetramethylpiperidine moiety from the HALS.

Fig. 3 shows the RTD–GC chromatograms using the polar separation column for S-3 detected by FID (a), S-3 detected by NPD (b) and S-1 detected by

Table 2
Assignments of peaks on the chromatograms of PP composite

Peak number	Retention time (min)	Chemical structure	Origin ^a
a	12.5		P
b	13		P
c	34.2		S
d	36		S
e	22		I-168
f	24		I-168
g	33.8		I-1010

^a P, piperidine moiety; S, spiro-chain moiety; I-168, Irgafos 168; I-1010, Irganox 1010.

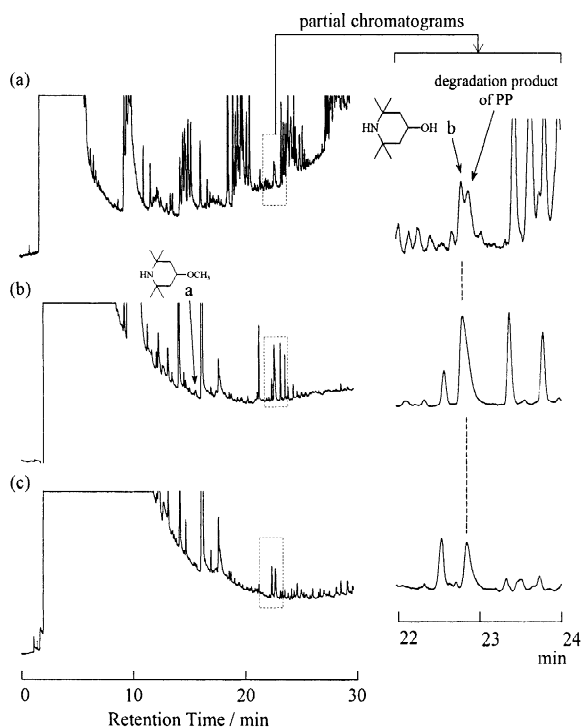


Fig. 3. RTD–GC chromatograms at 300 °C using a polar separation column. (a) PP composite (S-3) detected by FID, (b) PP composite (S-3) detected by NPD, and (c) PP composite (S-1) detected by NPD.

NPD (c). The expanded chromatograms around 22–24 min are also shown to exhibit elution behavior of the component b reflecting the tetramethylpiperidine moiety. When using the polar separation column, compound b from sample S-3 containing only 500 ppm of the HALS is observed as a distinct peak in the chromatograms (Fig. 3a and b), although it was almost missing in the case using the nonpolar separation column (Fig. 2b). However, when FID was used (Fig. 3a), component b partly overlapped with a degradation product of PP. This fact makes it difficult to determine accurately the trace amount of HALS in PP by RTD–GC with FID even using a polar separation column. On the other hand, by using NPD, component b was separately observed for S-3 without any interference of the pyrolyzates of PP substrate (Fig. 3b). This specific peak is also clearly detected for S-1 containing only 100 ppm of the HALS (Fig. 3c). Here, the neighboring peaks at 22.5, 23.3 and 23.7 min for NPD might be attributed to the

nonspecific products for the HALS because there were no correlation between their observed intensities and the HALS contents. On the other hand, the ratio between peak a, which could be observed in Fig. 3a and b was almost constant through the HALS content from 500 to 50 000 ppm. These observations suggest that the trace amounts of the polymeric HALS (down to 100 ppm) in PP materials are to be determined from the observed intensity of peak b by the RTD–GC method using NPD.

Fig. 4 shows the relationship of the intensity of the peak b normalized by the sample mass obtained by use of NPD and the polar separation column as a function of the HALS contents in the PP samples. A quite good linear relationship was obtained for the whole range of the HALS contents down to 100 ppm, which was impossible to be determined by the previous RTD–GC method [8]. In addition, fairly

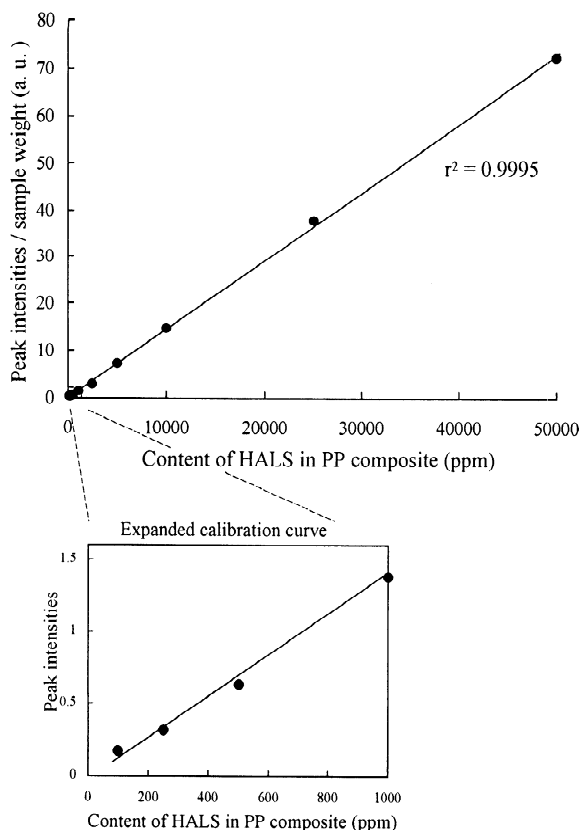


Fig. 4. Relationship between contents of HALS in PP compositions and peak intensity of product b.

good reproducibilities for the peak intensities were obtained; for example the relative standard deviation (RSD) for the PP sample containing 250 ppm of the HALS (S-2) was ca. 3% for three repeated runs. These results demonstrate that the highly sensitive determination of the polymeric HALS in PP materials is achieved by means of the modified RTD–GC method using the combination of a polar separation column and nitrogen-specific detection. The developed method could be commonly used for rapid, practical and highly sensitive analysis of various polymeric HALSs possessing ester bondings in polyolefin materials.

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