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Thermal stability and thermal decomposition study of hindered amine light stabilizers

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Abstract

The thermal decomposition of hindered amine light stabilizers for polyolefins based on bis(2,2,6,6-tetramethyl-4-piperidinyl) terephthalate (**I**), bis(2,2,6,6-tetramethyl-4-piperidinyl) *o*-phthalate (**II**) and 2,2,6,6-tetramethyl-4-piperidinyl stearate (**III**) has been studied using TG, DSC as well as FTIR of solid and GC/MS of high boiling decomposition products. The onset of weight loss in TG increases in the series: **III** < **II** < **I**. Ester cleavage by the β-elimination mechanism, scission of C–N bonds of the piperidine ring and aminolysis of the ester group have been shown to account for the formation of the decomposition products in the temperature range of 200–350 °C. The aminolysis reaction depresses the thermal stability of the studied compounds, in addition to the scission of the ester and C–N bonds. The yield of the products of aminolysis is higher from (**I**) and (**II**) compared to that from (**III**). The mass spectra of decomposition products and the decomposition scheme of the compounds under study are discussed.

Keywords: HALS; Thermal stability; Pyrolysis; Thermal analysis; FTIR

1. Introduction

Hindered amine light stabilizers (HALS) are commonly added to various polymeric materials in outdoor applications to prevent their photodegradation. They are composed of a secondary or tertiary cyclic amine unit and of a carboxylic acid component, and their function is ascribed [1] to radical scavenging by the nitroxide that can be formed by the oxidation of the HALS. In addition, HALS can be used as synergists to enhance flame retardancy of polymeric materials [2–4].

In order to be useful, any polymer additive must survive high temperatures used in the processing of polymeric materials (for instance, 250–270 °C for polyamides), therefore thermal stability studies of HALS are of importance. For example, a synthesis of more than 100 hindered piperidine compounds was reported [5], however only few were effective as light stabilizers, mainly because of poor thermal stability. This factor was likely to be a consequence for possible candidates for HALS to exhibit either high volatility or ability to decomposition resulting in the loss of their structure.

The development of HALS at the Research Institute for Physical Chemical Problems of the Belarusian State University has been a subject for many years [6,7], as there is a growing demand in stabilized polyolefin, polyester and polyamide polymers produced by the Belarusian industry. An important part of this work is studying thermal stability and thermal decomposition of the developed products, aimed at elucidation of the influence of the functional groups, the amine group or the ester group, on the loss of their structure. In this respect the work of Blazsó [8] is of importance, in which the effect of the ester group was shown in high temperature pyrolysis (400–900 °C) of HALS containing a tertiary amine group.

In addition, knowledge of decomposition products of HALS has to be taken into consideration, when plastic materials containing HALS are subjected to thermal recycling. It can be also used in sensitive and specific determination of HALS in

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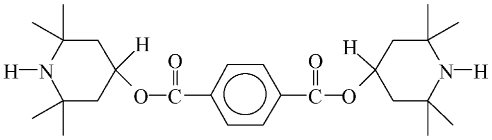
polymeric materials [9]. Our study contributes to these topics of pyrolysis chemistry.

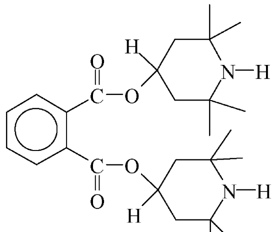
2. Experimental

2.1. Materials

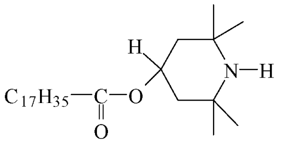
The objects of this study were a composition (HALS-1) of bis(2,2,6,6-tetramethyl-4-piperidinyl) terephthalate (**I**) (88% as determined by NMR spectroscopy), methyl 2,2,6,6-tetramethyl-4-piperidinyl terephthalate (10% by NMR) and dimethyl terephthalate (2% by NMR), which is an effective light stabilizer in polyolefins [5], bis(2,2,6,6-tetramethyl-4-piperidinyl) *o*-phthalate (**II**, HALS-2) and 2,2,6,6-tetramethyl-4-piperidinyl stearate (**III**, HALS-3), both with purity of about 97% (by NMR). They were prepared by transesterification reaction of either dimethyl terephthalate or dibutyl *o*-phthalate or ethyl stearate by 2,2,6,6-tetramethyl-4-piperidinol in *o*-xylene or dimethylformamide using a Lewis acid-type catalyst. HALS-1, -2, -3 were purified by precipitation with water from acetone solution. The yield of the synthesized products was of 85–95%. ^{1}H NMR of **I** (CD_3OD): $\delta H = 8.07$ (s, 4H, p-C_6H_4), 5.65–5.25 (m of nine lines, 2H, CH_2–CH–CH_2), 2.15–1.90 (dd, 4H, $(CH_3)_2C$–CH–CH), 1.60–1.35 (d, 4H, $(CH_3)_2C$–CH–CH), 1.35–1.10 (d, 26H, $(CH_3)_2C$ + NH) ppm. ^{1}H NMR of **II** ($CDCl_3$): $\delta H = 7.80$–7.40 (m, 4H, o-C_6H_4), 5.65–5.25 (m of nine lines, 2H, CH_2–CH–CH_2), 2.20–1.90 (dd, 4H, $(CH_3)_2C$–CH–CH), 1.40 (s, 2H, $(CH_3)_2C$–CH–CH), 1.35–1.05 (d, 30H, $(CH_3)_2C$ + $(CH_3)_2C$–CH–CH + NH) ppm. ^{1}H NMR of **III** ($CDCl_3$): $\delta H = 5.40$–5.00 (m of 9 lines, 1H, CH_2–CH–CH_2), 2.45–2.15 (t, 2H, CH_2–CH_2–CO), 2.05–1.65 (dd, 2H, $(CH_3)_2C$–CH–CH), 1.70–0.88 (m, 48H, CH_3 + CH_2 + NH) ppm. The NMR measurements were carried out using a TESLA BS-587A spectrometer operating at 80 MHz.



(**I**)



(**II**)



(**III**)

2.2. Thermal analysis

Thermal analysis was carried out using a Mettler TA 3000 thermal analyzer provided with a thermogravimetry (TG) module and a differential scanning calorimetry (DSC) cell. Standard measurements were performed at a heating rate of 10 °C min^{-1} under an argon flow of 60 cm^3 min^{-1}. The non-volatile fraction reproducibility was ±0.5%. The sample size was of about 10 mg.

2.3. Products of thermal degradation

For details of the thermal degradation procedure, the reader is referred to Ref. [10]. In short, high boiling decomposition products (HBPs) were collected under argon or helium in a degradation tube, the bottom part of which was hold at isothermal temperature 350 °C for 15 min, using samples of approximately 100 mg; whereas gaseous decomposition products were trapped at liquid nitrogen temperature and successively analyzed by GC/MS. The HBPs condensed in the upper part of the test tube were washed out by acetone, and the acetone solution was subsequently subjected to a GC/MS analysis (GC/MS model HP 6890/5972A) using a HP-1 60 m column which was temperature programmed from 50 °C (3 min) to 290 °C (20 min) at a heating rate of 10 °C min^{-1}. For analysis of gaseous products, the 60 m HP-1 capillary column was also found to be an appropriate column. The column was heated to 250 °C at a heating rate of 10 °C min^{-1} after an initial 3 min period at −40 °C. The mass spectra were obtained by electron ionization at 70 eV keeping the source at 180 °C. A mass spectrometric identification was carried out using Wiley and NBS libraries. In the few cases, when compounds were not included in the libraries, they were identified on the basis of both the molecular ion *m*/*z* value and of the ion decomposition pattern constructed for the best fit with the mass spectrum.

Solid residues collected at different steps of thermal decomposition in TG were investigated by IR spectroscopy on a Perkin Elmer "Spectrum 1000" FTIR spectrometer using KBr pellets.

3. Results and discussion

3.1. Thermal analysis

When heated at 10 °C min^{-1}, the studied HALS melt and exhibit an endothermal one stage weight loss process between 170 and 320 °C (Figs. 1 and 2). The onset temperature of weight loss (thermal stability) increases in the series HALS-3 < HALS-2 < HALS-1. The melting point temperature also increases in a similar way, i.e. 41 °C at HALS-3, 97 °C at HALS-2, and 204 °C at HALS-1. There was some black solid residue left after thermal decomposition (Fig. 1).

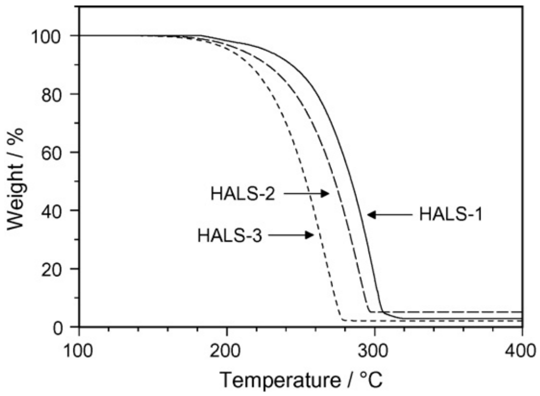


Fig. 1. Thermogravimetry of HALS-1, HALS-2, and HALS-3. Heating rate of 10 °C min^{-1} under nitrogen flow of 60 cm^3 min^{-1}.