Polymer Degradation and Stability **40** (1993) 375–378

A study of the photolysis of a commercial hindered amine light stabilizer

Pan Jiang-Qing & Cui Song

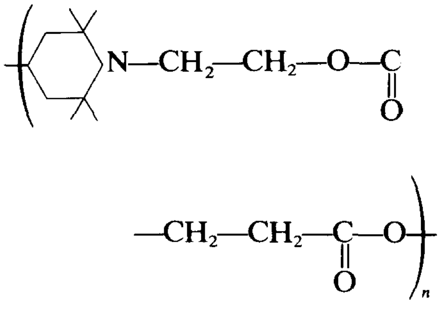
Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing, 100080 China

(Received 27 March 1992; revised version received 17 July 1992; accepted 5 August 1992)

The photolysis of a commercial hindered amine light stabilizer (HALS) has been studied with a range of experimental methods. The results show that the stabilizer is easily photolyzed and photolysis mechanisms are proposed.

INTRODUCTION

It is well known that hindered amine light stabilizers (HALS) are the most effective class of light stabilizers for polymers. However, low-molecular-weight HALS evaporate rather easily, reducing their long-term effectiveness. A new trend in HALS synthesis is to prepare polymeric HALS, and a good example is the polyester of succinic acid with *N*-*β*-hydroxyethyl-2,2,6,6-tetraethyl-4-hydroxypiperidine (H1, Ciba-Geigy Tinuvin 622).



(Tinuvin-622)

H1 has good thermal stability and good extraction resistance. However, it has ester carbonyl and piperidinyl groups in the backbone. The former can be photolyzed by the Norrish reaction[1,2] and the latter can be oxidized to the nitroxyl radical; both reactions can break the polymer chain and decrease the effectiveness of the HALS. In this paper we report a study of the photolysis of H1, using a wide range of experimental methods.

EXPERIMENTAL

Tinuvin 622 was supplied by Ciba-Geigy AG. Its photolysis was carried out in a tubular quartz cell, exposed to a 500 W high-pressure mercury lamp through a filter which removed all radiation below 300 nm. The sample was kept 24 cm from the lamp and the temperature at the sample was 50°C.

IR spectroscopy was performed with a Perkin–Elmer 180 spectrometer, NMR with a JEOL FX-100 and mass spectroscopy with an AEI MS 50 spectrometer. ESR spectra were recorded at 22°C using a spectrometer produced by the China Mineral Manufacturing Co. GPC was carried out on an LC10 liquid chromatograph (Japan Analytical Industry Co. Ltd) using THF as a solvent (flow rate 1·5 ml min^{-1}) and a model 80 polystyrene gel column 500 mm long and 8 mm diameter. GC was performed in a Chinese manufactured SP2307 chromatograph (Beijng Analytic Instrument Works) using a flame-ionization detector. The column was 1 m long, 5 mm in diameter and packed with 9% silicone oil on a silica support.

Results and discussion

Figure 1 shows the IR spectrum of H1 before and after 35 h of irradiation. After irradiation, bands associated with ester (1735 cm^{-1}, 1170 cm^{-1}) and methyl (2970 cm^{-1}) groups have decreased and hydroxyl (3450 cm^{-1}), carboxyl (2400–2600 cm^{-1}), carboxylate (1570 cm^{-1}) and double bonds

Polymer Degradation and Stability 0141-3910/93/$06.00

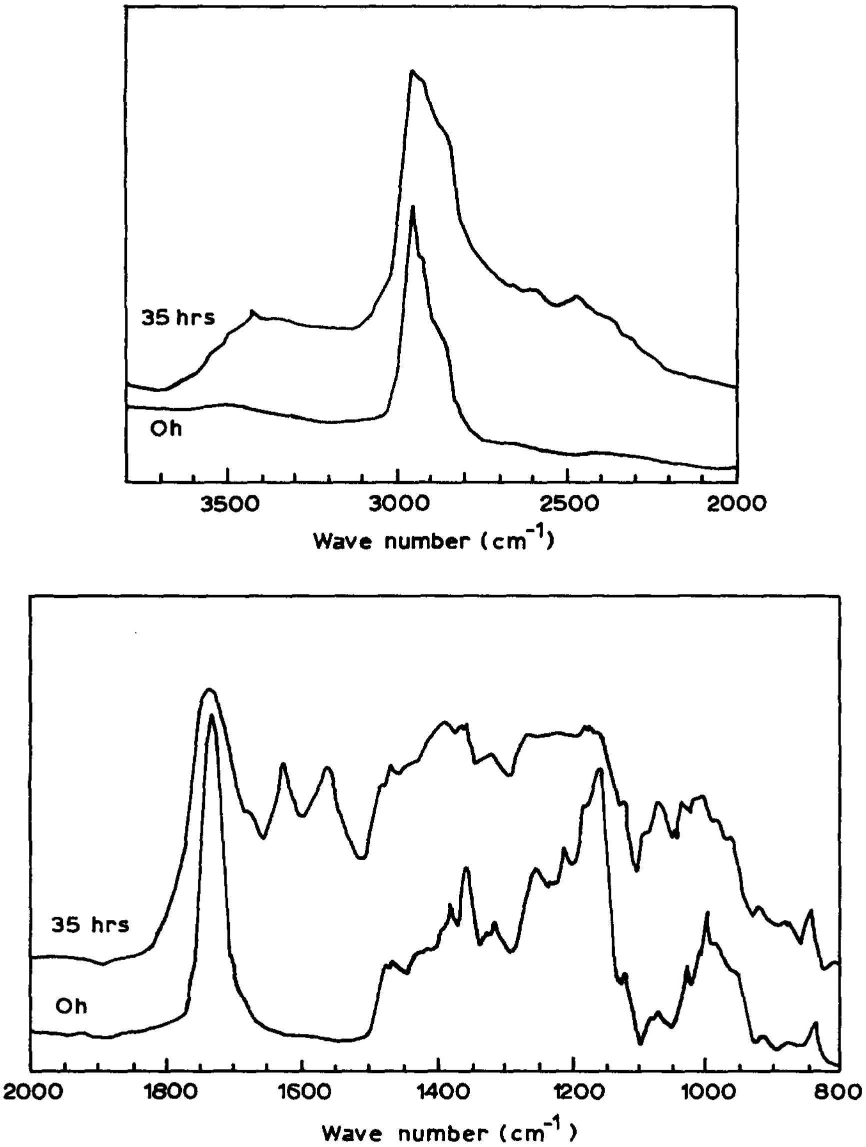


Fig. 1. The IR spectrum of H1 before and after irradiation.

($1640\,cm^{-1}$) are formed. These results demonstrate that photolysis has occurred.

Figure 2 shows the corresponding NMR spectra. After irradiation, the piperidine methyl (1·14–1·18 ppm) and backbone methylene (2·6 ppm) resonances have decreased and new peaks have appeared at 3·38, 1·42 and 5·10 ppm, assigned to OCH_3, CH_3 and an alkene proton respectively.

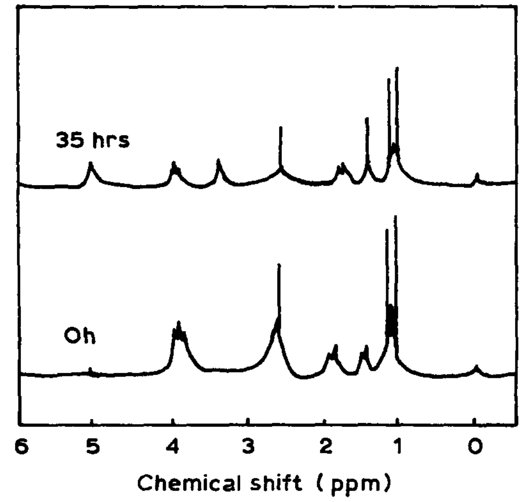


Fig. 2. The NMR spectra of Tinuvin-622 (in $CDCl_3$).

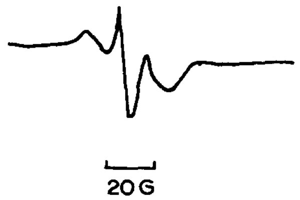


Fig. 3. The ESR signal of Tinuvin-622 after irradiation.

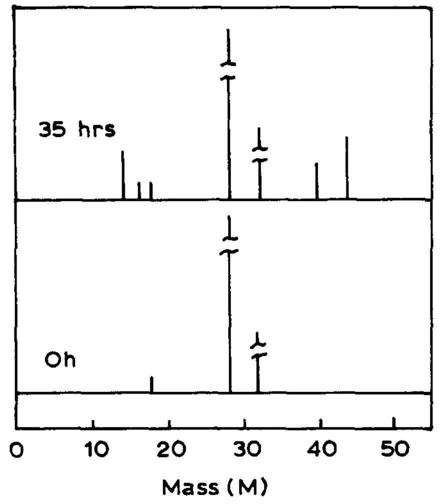


Fig. 4. The MS of gas products from photolysis of Tinuvin-622.

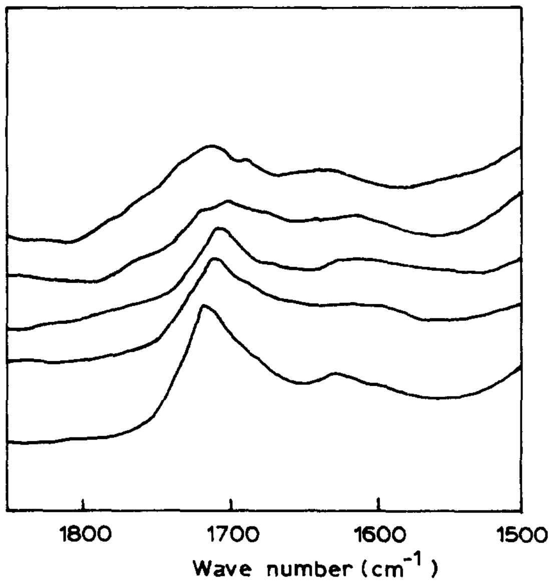


Fig. 6. The change of ester carbonyl in PP-film containing Tinuvin-622. From top to bottom: 58 h 30 min, 48 h 10min, 20 h 15 min, 9 h 30 min and 0 h.

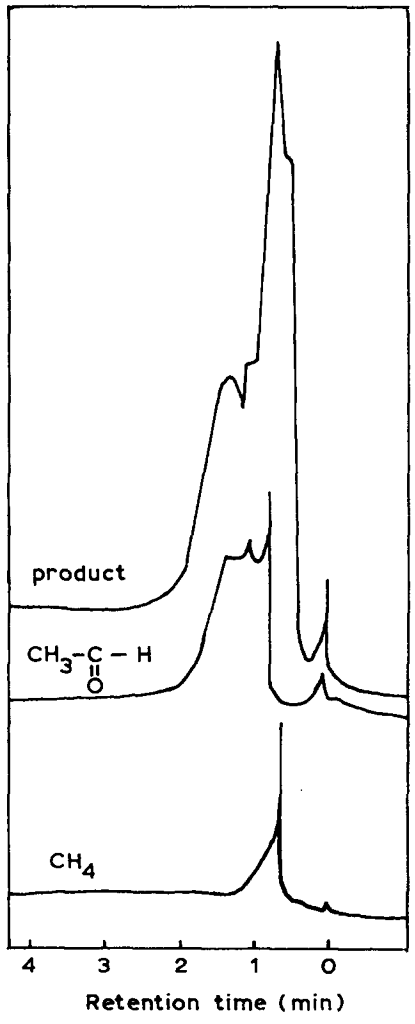


Fig. 5. The GC diagram of gas products from photolysis of Tinuvin-622.

During irradiation, an ESR signal appears (Fig. 3), showing that nitroxyl free radicals are formed.[2,3,4] These must result from scission of N—CH_2 bonds followed by oxidation.

GPC analysis showed that the molecular weight of H1 decreased by about 50% after irradiation. At this stage the polymer contained a chloroform-insoluble fraction which was shown by IR to contain carboxylate groups (1570 cm^{-1}).

The gaseous products of photolysis were analyzed by GC and MS, and acetaldehyde and methane were detected (Figs 4 and 5).

Based on these data, we propose the following

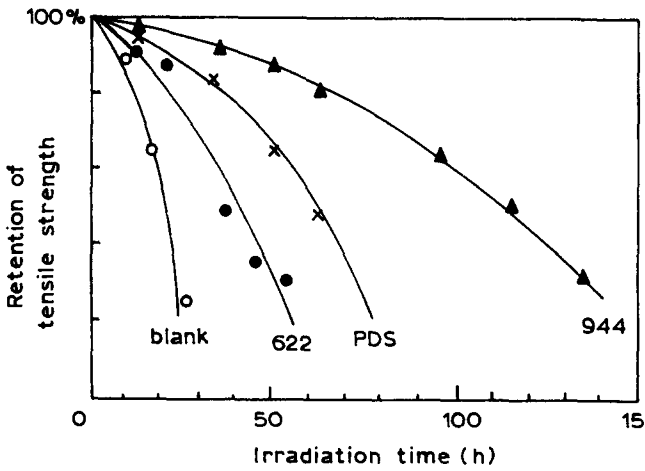
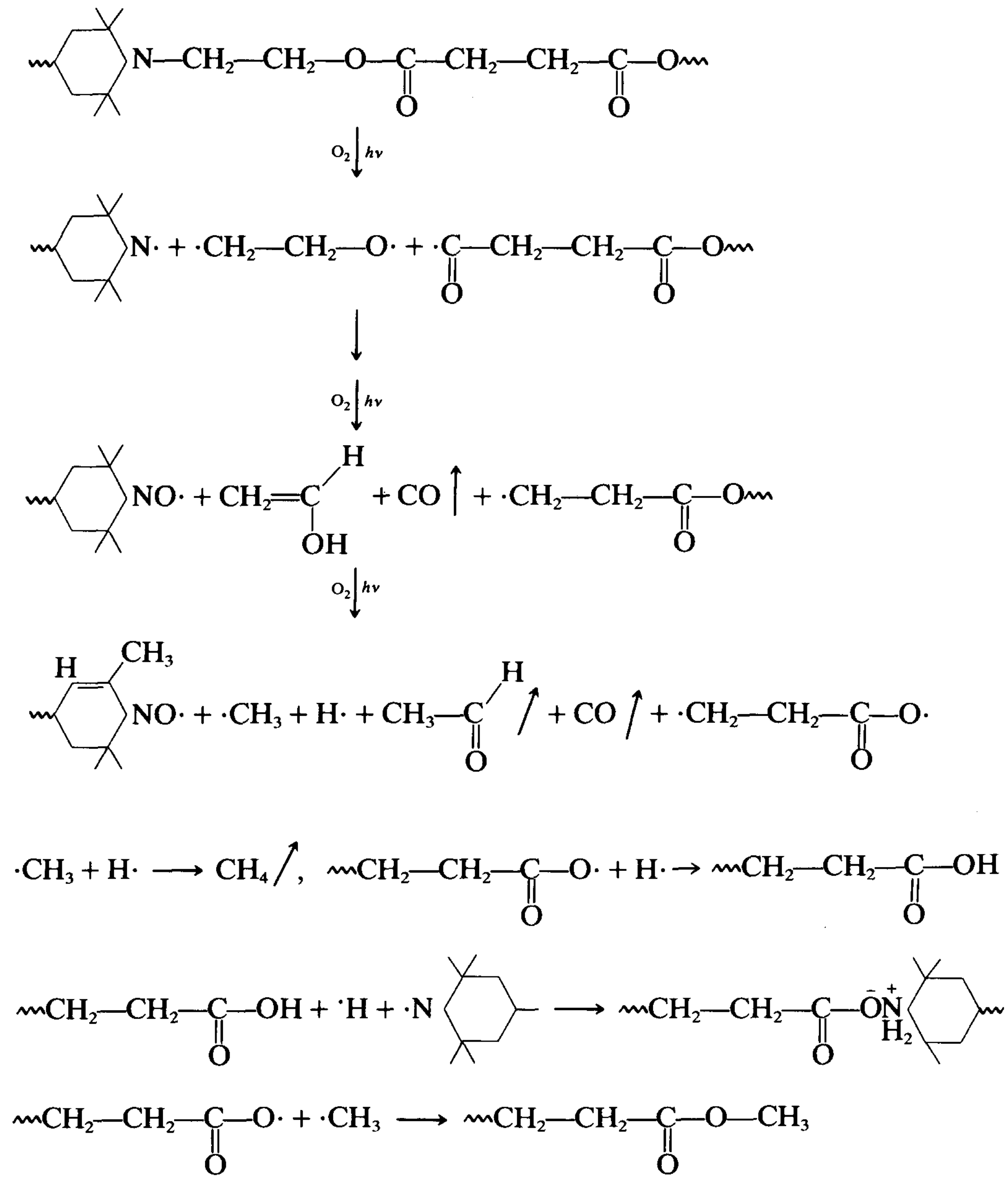


Fig. 7. The photoprotecting effectiveness of polymeric HALS for PP (irradiation in air). [HA] = 0·016 N/kg PP, the structures of HALS are in Ref. (4).

mechanism for photolysis of H1:



The photolysis of H1 can also be observed in polypropylene films, as seen in Fig 6 which shows the decrease in the ester carbonyl with photolysis.

The light-protecting effectiveness of H1 is compared in Fig. 7 with that of two other HALS which we have previously studied.[4] The relatively poor stabilizing effect of H1 may be because of its facile photolysis.

ACKNOWLEDGEMENTS

The authors would like to thank Ciba-Geigy and the National Natural Science Foundation of China (NSFC) for supplying Tinuvin-622 and for financial support of this work.

REFERENCES

1. Ranby, B. & Rabek, J. F., *Photodegradation, Photo-oxidation and Photostabilization of Polymers*. Wiley-Interscience, London, UK 1975.
2. Jiang-Qing, P., *Polym. Communications*, **3** (1985) 173.
3. Hodgeman, D. K. C., *J. Polym. Sci. Chem.*, **19**(3) (1981) 807.
4. Jiang-Qing, P. & Song, Y., *Polym. Deg. Stab.* **32**(1) (1991) 79.