

STUDY ON THE PHOTOLYSIS MECHANISM OF POLYESTER FROM SUCCINIC ACID AND N- β -HYDROXYETHYL 2,2,6,6-TETRAMETHYL- 4-HYDROXY PIPERIDINE (TINUVIN-622)

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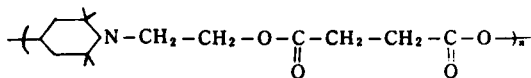
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ABSTRACT

The photolysis mechanism of polyester of succinic acid with N- β -hydroxyethyl 2,2,6,6-tetramethyl-4-hydroxy piperidine (Tinuvin-622) has been studied by instrumental analysis. The results show that Tinuvin-622 can be easily photolysed. Based on the results of IR, NMR, ESR, GPC, GC, MS, the photolysis mechanism of Tinuvin-622 has been proposed.

INTRODUCTION

It is well known that the hindered amine light stabilizer (HALS) is the most effective light stabilizer now. However, small molecular weight hindered amine is easy to evaporate. Therefore, the effectiveness of HALS is affected. A new trend in synthesis of HALS is to prepare polymeric HALS. Tinuvin-622 is a commercial polymeric HALS.



It (622) possesses a good heat stability and good extracting resistance. However, it contains the structure of ester carbonyl and piperidinyl in the backbone. The former can be photolysed by Norrish reaction⁽¹⁾ and the latter can be degraded by forming stable nitroxy free radical. Both can destroy the main chain. Therefore, the effectiveness of Tinuvin-622 is decreased. In this paper, the photolytic mechanism of Tinuvin-622 was studied by IR, NMR, GPC, GC, MS, by using high pressure mercury lamp as light source. The results are as follows:

EXPERIMENTAL

1. Photolysis of sample

Tinuvin-622 was supplied by Ciba-Geigy Company. The photolysis reaction of Tinuvin-622 was carried out in a quartz reactor shown in Fig. 1, the reactor was fed into air or argon, and a high pressure mercury arc lamp (GGU-500) used as light source, power is 500 W. The distance between

sample and lamp is 24 cm, and reaction temperature is 50°C. The energy distribution of this lamp is shown in Fig. 2. After irradiation, the sample was determined by IR, NMR, ESR, GPC, GC, MS.

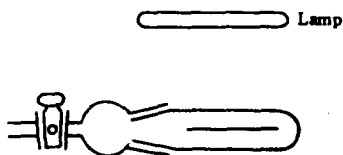


Fig.1 The reactor for photolysis

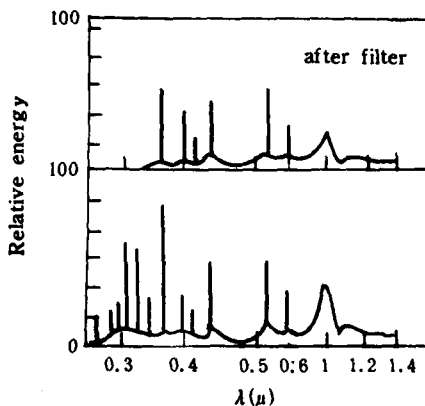


Fig.2 Energy distribution of GGU-500

2. Instruments

IR — Perkin Elmer-180 Infrared spectrometer

NMR — FX-100 Nuclear magnetic resonance (Japan)

ESR — ESR was made by China Mineral Mechanic Factory, determined at 22°C.

MS — MS-50 mass spectrometer was used (UK).

GPC — was carried out on the LC-10 liquid chromatography; THF as solvent and mobile phase; column is model-80, 500MM × 8MM (packing with polystyrene gel) the rate of THF is 1.5ml/min.. (Japan)

GC — SP 2307 Gas chromatography was used. (It was made in China) (silicone oil 9% — 6201 carrier), 100 × 5mm using hydrogen flame ionization detector.

RESULTS AND DISCUSSIONS

The IR spectrum of Tinuvin-622 is shown in Fig. 3. It can be seen that after 35 h irradiation the ester carbonyl (1735cm^{-1}) and ester group (1170cm^{-1}) as well as methyl (2970cm^{-1}) are decreased, and hydroxyl (3450cm^{-1}), carboxyl group ($2400\text{--}2600\text{cm}^{-1}$), carboxylate (1570cm^{-1}) and double bond (1640cm^{-1}) are formed. These results show that the photolysis of Tinuvin-622 has occurred.

The NMR spectrum of Tinuvin-622 was shown in Fig. 4. It can be seen that after irradiation the methyl (1.14–1.18 ppm) in piperidine and methylene group (2.6 ppm) in backbone are decreased. The new peaks at 3.38 ppm ($-\text{OCH}_3$) and at 1.42 ppm (one proton at the alkene) have been formed.

The ESR of Tinuvin-622 shows that the stable nitroxyl free radical $>\text{NO}\cdot$ can be formed during irradiation^[2,3]. Obviously, this $>\text{NO}\cdot$ free radical is a result of scission of $>\text{N}-\text{CH}_2-$ and then oxidation. (Fig. 5).

The determination of GPC shows that the molecular weight of Tinuvin-622 was decreased about 50% after 35 hrs irradiation without filter. At this time a precipitation in CHCl_3 was observed; the determination of IR shows that this precipitation contains carboxylate (1570cm^{-1}).

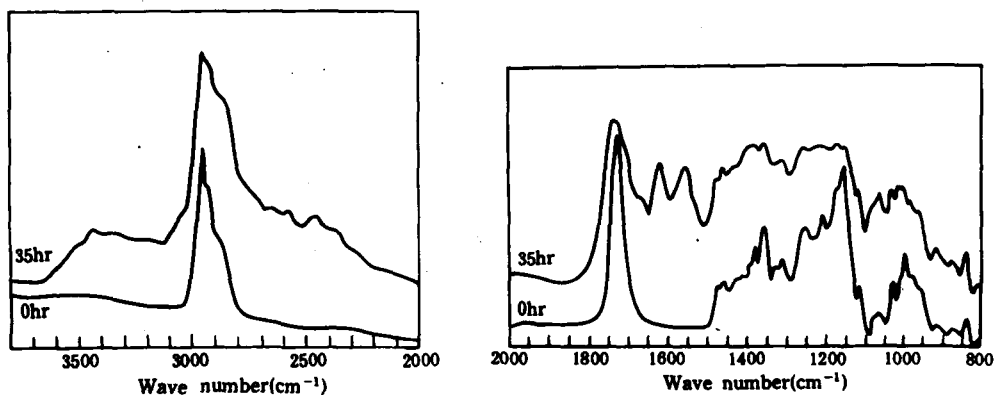


Fig.3 The IR spectrum of 622

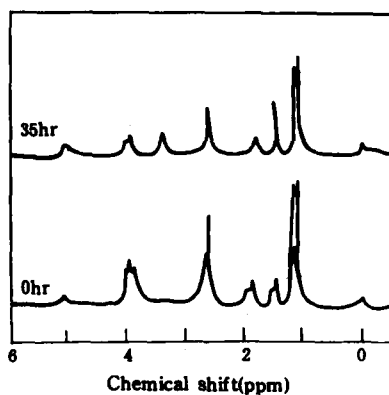


Fig.4 The NMR spectrum of 622

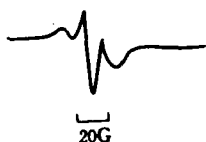


Fig.5 The ESR signal of 622 after irradiation.

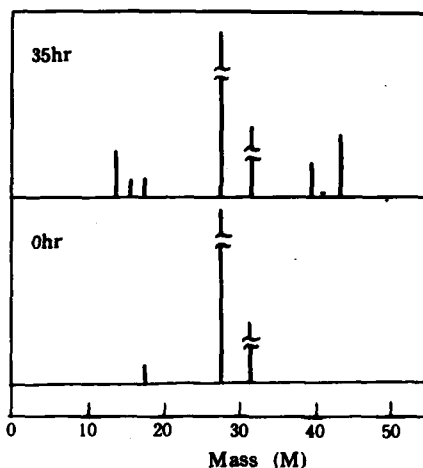


Fig.6 The MS of gas products from photolysis of 622.

The gaseous products of photolysis from Tinuvin-622 have been identified by GC and MS. Acetaldehyde and methane have been detected (Figs. 6, 7).

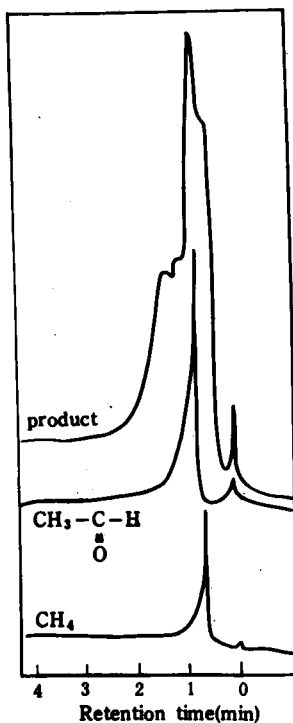
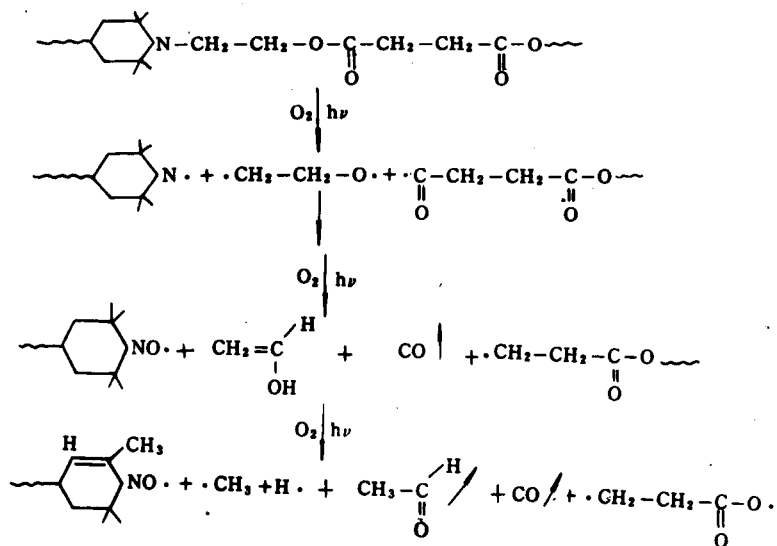
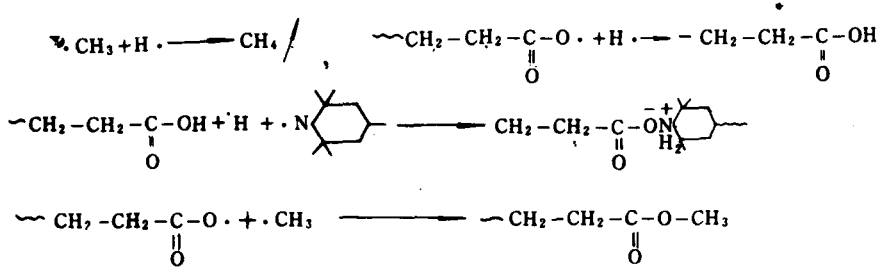


Fig.7 The GC diagram of gas products from photolysis of 622.

Based on the experimental results of IR, NMR, ESR, GPC, GC, and MS, the photolytic mechanism of Tinuvin-622 may be proposed as follows:



The photolysis of Tinuvin-622 can also be seen in polypropylene film containing Tinuvin-622, as shown in Fig. 8. It can be seen that with increasing irradiation time, the ester group decreased because of photolysis of Tinuvin-622.



The light protecting effectiveness of three polymeric hindered amine light stabilizers is shown in Fig. 9. It can be seen that the effectiveness of Tinuvin-622 is poor, and this may be related to the photolysis of Tinuvin-622 during light protecting.

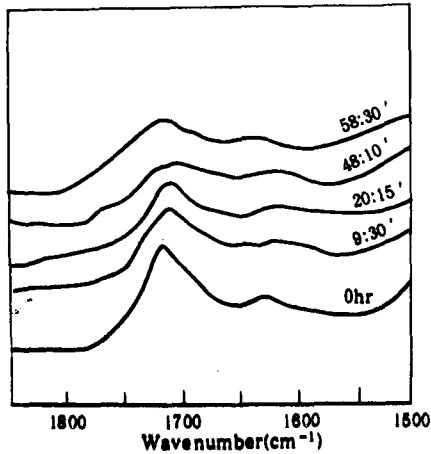


Fig.8 The change of ester carbonyl in PP-film containing 622

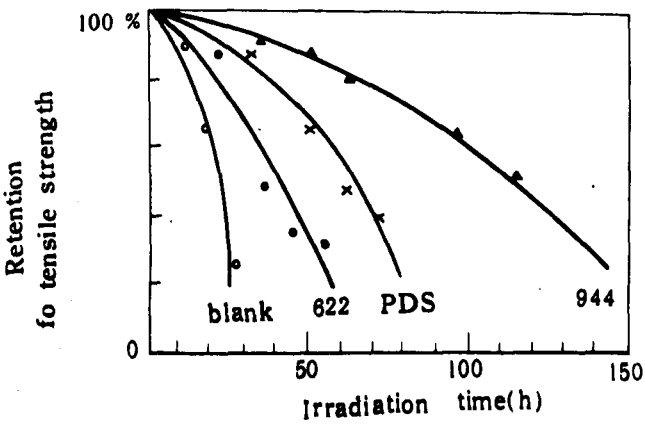


Fig.9 The photoprotecting effectiveness of polymeric HALS

Keywords:

Polyester of succinic acid; Hindered amine; Piperidine light stabilizer; Polymeric hindered amine light stabilizer; Photolysis of polymeric HALS.

REFERENCES

[1] Ranby, B., Rabek, J.F. "Photodegradation, Photo-oxidation and Photostabilization of Polymers", Wiley-Interscience London, 1975

[2] 潘江庚, 张 灿, 侯 贵, 马振民, 高分子通讯 (Polymer Communications), 1985 (3), 173.

[3] Hodgeman, D.K.C., J.Polym.Sci.,Chem., 1961 (3), 807.