

SYNTHESIS AND EVALUATION OF A NEW PHOTOSTABILIZER—2,2,6,6-TETRAMETHYL-4- PIPERIDINYL SALICYLATE FOR POLYMERS

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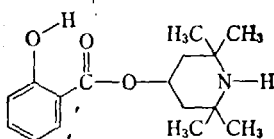
ABSTRACT

A new photostabilizer — 2,2,6,6-tetramethyl-4-piperidylsalicylate (TMPS) has been synthesized by ester-exchange reaction between 2,2,6,6-tetramethyl-4-piperidinol and methylsalicylate. The photostabilizing effect of TMPS and Tinuvin 770, PDS on the photodegradation of *cis*-1,4-polybutadiene has been investigated for comparison. The results observed show that the most effective stabilizer of the three is TMPS. The reason of the good photostabilizing effect of TMPS was discussed by fluorescence spectra.

Since the discovery of the photostabilizing effect of 2,2,6,6-tetramethyl-4-piperidine derivatives by Japanese chemists of the Sankyo Company Ltd. in 1967, there have been a great surge of activity in this field^[1,2,3]. Many commercial stabilizers of this kind often referred to as HALS (Hindered amine light stabilizer) were introduced on the market and various reviews have been published which discuss the photostabilization mechanisms and effects. HALS are multi-functional photostabilizers and their performance surpasses the effectiveness of classical UV screeners, as well as that of carbon black. But, they have only a very low absorption in the region of 280–350 nm, so these compounds could not be used as a UV absorbent for losing the energy absorbed.

In this work, a new kind of photostabilizer which can absorb the UV light—2,2,6,6-tetramethyl-4-piperidyl salicylate (TMPS) has been synthesized and its effect of photostabilization on polymers has been evaluated preliminarily.

The chemical structure of 2,2,6,6-tetramethyl-4-piperidyl salicylate is as follows:



TMPS was synthesized by the ester-exchange reaction between 2,2,6,6-tetramethyl-4-

piperidinol and methyl salicylate according to the method published previously^[4]. Magnesium methoxide is used as catalyst for the reaction.

The physico-chemical characterization of this compound was carried out by several methods including the data of nitrogen content, infrared spectrum (Perkin-Elmer 577), and NMR spectrum (Varian EM-360L). The pure product is colorless crystal with m.p. 208°C.

Nitrogen content (%): 4.94 (calculated); 5.05 (found).

Infrared spectrum (KBr) cm^{-1} : 3400 ($\nu_{\text{N-H}}$); 1670 ($\nu_{\text{C=O}\cdots\text{H}}$); 1480 ($\nu_{\text{C=C-C-C}}$); 1180 ($\nu_{\text{C-O}}$, ester).

Proton magnetic resonance (D_2O) ppm: 1.3 (singlet, 12H, four $-\text{CH}_3$); 1.9–2.1 (multiplet, 4H, two $-\text{CH}_2$), 6.8–7.8 (multiplet, 4H, $-\text{C}_6\text{H}_4-$).

These results obtained are in agreement with the structure of this compound.

The absorption spectra of solution of compounds studied here were recorded on the Hitachi 340 UV-Vis spectrophotometer. The fluorescence emission spectra were taken on the Hitachi MPF-4 fluorescence spectrophotometer. The purified tetrahydrofuran (THF) was used as solvent in the measurement. All of the measurements were carried out at room temperature.

The photostabilizing effect of TMPS, Tinuvin 770 and PDS (copolymer of styrene and 2,2,6,6-tetramethyl-4-piperidiny methacrylate) have been measured by the following way. The *cis*-1,4-poly(butadiene) was selected as a model polymer. The viscosity of poly(butadiene) solution with or without photostabilizers were measured after irradiation at different time intervals. The *cis*-poly(butadiene) sample is a commercial product from Goodrich Corp. (Ameripol CB200). It was purified by reprecipitation several times before use. For irradiation, the Philips HPK-125W mercury lamp was employed as a light source.

The absorption spectra of TMPS, 2,2,6,6-tetramethylpiperidine and 2,2,6,6-tetramethylpiperidine-1-oxyl in THF solution are shown in Fig. 1. It is evidently seen that the latter two compounds have very weak absorption at the region of 280–330 nm, whereas the TMPS has strong absorbance in this region due to the presence of the salicylate group which can form an intramolecular hydrogen bond between the proton of phenolic OH group and the carbonyl oxygen. The value of molar absorption coefficient of TMPS is about 4–5 orders of magnitude higher than that of the others. It shows probably that the TMPS could screen the detrimental light for protecting the polymer materials.

In Fig. 2 the fluorescence spectra of TMPS were recorded. From this we can see that the fluorescence spectrum of TMPS has an uncommonly large Stoke's shift which was similar to that of methyl salicylate. The shift value is more than about 110 nm. It indicates clearly that this compound may be used as a UV absorber.

As well known that the methyl salicylate shows two different strong fluorescence emission band in the region of 350 nm and 450 nm, when it is excited by different wavelength of light. This result can be attributed to the presence of two different species which are in equilibrium with each other already in the ground state^[5]. However, in the spectra of TMPS only one fluorescence emission peak at 410 nm can be observed when it is excited by different wave length of light. Because the light in region of 350 nm is still detrimental to photostabilization of polymers, from this point of view, it can be concluded that the photostability of TMPS is better than that of methyl salicylate.

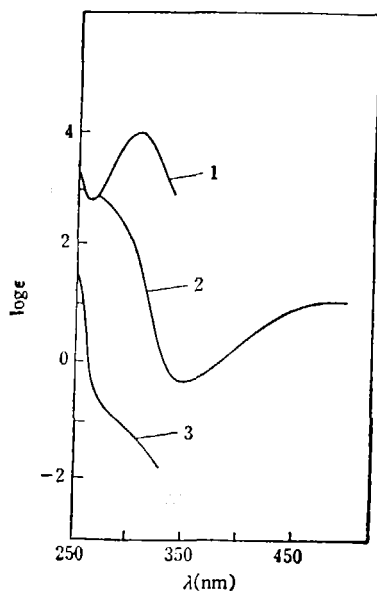


Fig. 1 Absorption spectra of TMPS, (1) 2,2,6,6-tetramethylpiperidine-1-oxyl (2) and 2,2,6,6-tetramethylpiperidine (3) in THF solution

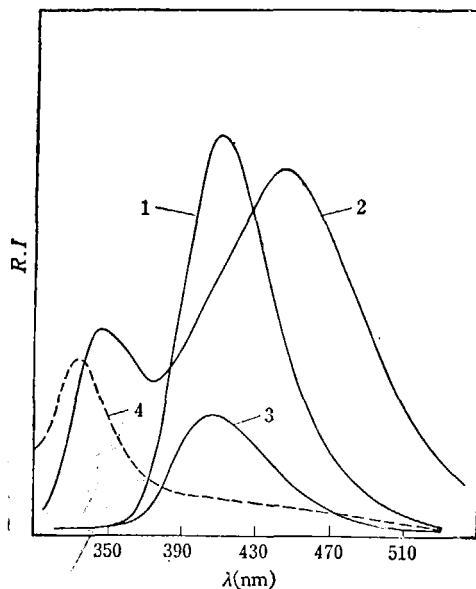


Fig. 2 The fluorescence spectra of TMPS and methyl salicylate in THF solution
Concentration: $1 \times 10^{-4} M$

1. TMPS ($\lambda_{ex} = 305 \text{ nm}$, $\times 0.1$);
2. Methyl salicylate ($\lambda_{ex} = 305 \text{ nm}$, $\times 3$);
3. TMPS ($\lambda_{ex} = 280 \text{ nm}$, $\times 0.3$);
4. Methyl salicylate ($\lambda_{ex} = 280 \text{ nm}$, $\times 3$).

In Fig. 3, the fluorescence spectrum of TMPS excited by wave length of 220 nm was recorded. It is known that the absorption peak at 220 nm is assigned to the piperidinyl group, so, this result shows an intramolecular energy transfer existed in the TMPS molecule.

The photostabilizing effect of TMPS, Tinuvin 770 and PDS on the photodegradation of *cis*-poly(butadiene) solution has been compared by the change of viscosity of solutions (Fig. 4).

Result in Fig. 4 indicates that for the poly(butadiene) solution without stabilizers, the viscosity of polymer solution decreases rapidly after irradiation. But, when the photostabilizers studied in this work introduced to the poly(butadiene) solution the rate of viscosity change was reduced. Results showed evidently that the most effective photostabilizer of these compounds studied here is the TMPS.

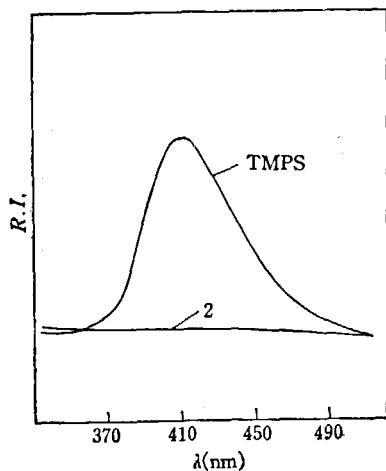


Fig. 3 The fluorescence spectra of TMPS and methyl salicylate (2) in THF solution
 $\lambda_{ex} = 220$ nm

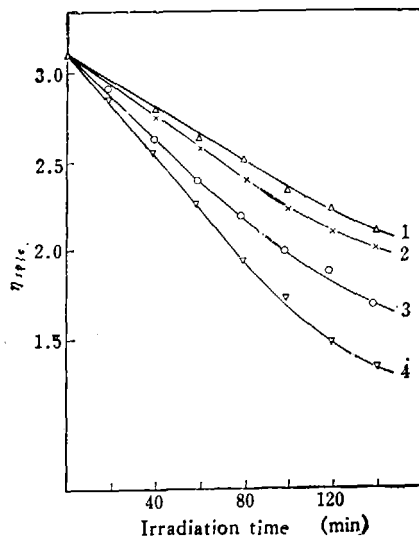


Fig. 4 The change of viscosity of poly(butadiene) solution during photoirradiation in the presence of air

1. TMPS; 2. Tinuvin 770;
 3. PDS; 4. Without stabilizer.

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