

POLYMERIC PHOTOSTABILIZERS CONTAINING TWO KINDS OF PHOTOSTABILIZING GROUPS II. SYNTHESIS AND PHOTOSTABILITY OF COPOLYMERS OF 2,2,6,6-TETRAMETHYL-4-PIPERIDINYL METHACRYLATE AND β -HYDROXY- γ -(ORTHO-HYDROXY BENZOXY) PROPYL METHACRYLATE

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ABSTRACT

A new kind of photostabilizers, copolymer of 2, 2, 6, 6-tetramethyl-4-piperidinyl methacrylate and β -hydroxy- γ -(ortho-hydroxy benzoxy) propyl methacrylate, has been synthesized. The spectral behaviors of these copolymers were studied in detail. In the presence of salicyl group a strong absorption in the region of 280—330 nm could be observed, and an unusual Stoke's shift appeared in the fluorescence spectrum excited by 310nm. The photostabilization ability of these copolymers in the process of photodegradation of *cis*-poly (butadiene) was studied. Results indicated that these compounds possess excellent photostabilization ability.

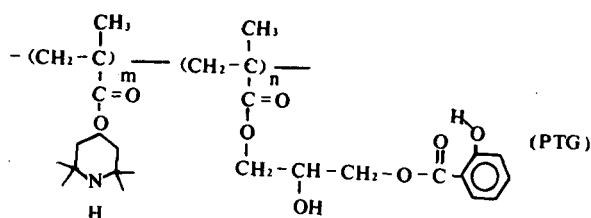
In the past ten years, hindered amine light stabilizers (HALS)^[1,2] have been developed rapidly due to their very efficient photostability on the photodegradation of polymers. However, the very low absorption of this stabilizer^[3] in the region of 280—350nm is a main deficiency for the photostabilization. So, a new stabilizer—2, 2, 6, 6-tetramethyl-4-piperidinyl salicylate has been synthesized in our lab.^[4] This compound not only possesses the photostabilizing function of HALS, but also has very strong absorption at 280—330 nm. It can rapidly lose its energy absorbed by emission of fluorescence with long wavelength. In the comparative experiments of poly(butadiene) photostabilization by different photostabilizers, it can be found that the new compound has better effect than that of Tinuvin 770. In order to improve the compatibility between photostabilizer and polymer materials a new polymeric photostabilizer containing two kinds of photostabilizing group—copolymer of 2, 2, 6, 6-tetramethyl-4-piperidinyl methacrylate and β -hydroxy- γ -(ortho-hydroxy benzoxy) propyl methacrylate has been prepared in this work. Their physical properties were characterized in detail and the effect of photostabilization of this compound has been evaluated as well.

EXPERIMENTAL

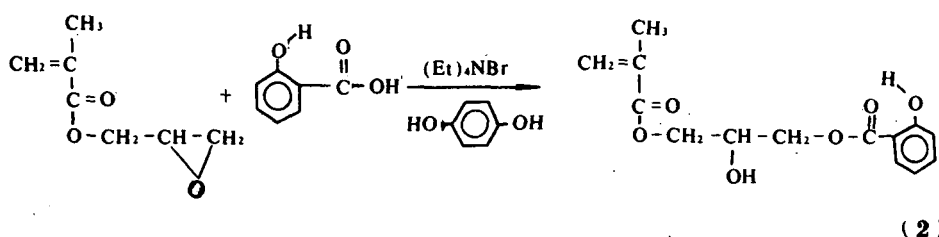
New photostabilizer (referred to as PTC) synthesized in this work has the following structure:

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Monomer 1—2,2,6,6-tetramethyl-4-piperidinyl methacrylate was obtained from the Beijing Chemical Works No.3, and used without further purification. Monomer 2— β -hydroxy- γ -(*o*-hydroxy benzoxy) propyl methacrylate was synthesized in our lab by following method:



According to the reference^[5], the solution of salicylic acid(0.1 Mol) in toluene-methanol (4:1, *V/V*) and small amount of hydroquinone and $(\text{Et})_4\text{NBr}$ were placed in a flask equipped with a stirrer, dropping funnel and reflux condenser. The orange solution was stirred and heated at 110°C on an oil bath, while 0.13 mole of glycidyl methacrylate was added dropwise through the funnel to the flask for two hours. The resulting solution was yellowish. The product was purified by distillation and the yield was above 50%. Its ^1H NMR data in CDCl_3 are as follows: $\delta = 1.90$ (S; $-\text{CH}_3$; 3H), $\delta = 3.80\text{--}4.56$ (M; $-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{O}-$; 5H), $\delta = 5.44, 6.10$ (S, S; $\text{H}_2\text{C}=\text{C}$; each 1H), $\delta = 6.85\text{--}7.87$ (M; $-\text{C}_6\text{H}_4-$; 4H), $\delta = 10.46$ (S; $-\text{OH}$; 1H). The results conform with monomer 2.

The polymerization was carried out in nitrogen atmosphere at 60°C for 15 hours using benzene as solvent and AIBN as initiator. The resulting polymer was purified by precipitation in large amount of methanol several times, and then dried under vacuum at room temperature. According to the nitrogen content in resulting polymers by elemental analysis, the composition of PTG polymers is listed in Table 1.

Table 1 The composition of PTG polymers

Number of copolymer	Molar % of Monomer 1	Molar % of Monomer 2
0	0	100
1	50	50
2	60	40
3	70	30
4	80	20
5	90	10

The absorption spectra and fluorescence emission spectra of the studied polymers were recorded on the Hitachi 340 UV-Vis spectrophotometer and Hitachi MPF-4 fluorescence spectrophotometer, respectively. The mixtures of tetrahydrofuran and 1,2-dichloroethane (1:9, *V/V*) was used as solvent in the spectrum measurements. The THF was purified by distillation several times, till the foreign peak in spectrum disappeared.

In experiments for evaluating the effect of photostabilization of the title polymers, *cis*-1,4-poly(butadiene) was selected as an evaluating reference. The change of viscosity of poly(butadiene) solution with or without photostabilizer studied in this work was measured after irradiation at different time intervals, and used as an evaluating standard^[4].

RESULTS AND DISCUSSION

The absorption spectra of PTG and PDS^[6] (copolymer of styrene and 2,2,6,6-tetramethyl-4-piperidiny methacrylate) solution are shown in Fig. 1. It can be seen that in the spectrum of PDS there is no absorption at the region of 300—310 nm, and the absorption at 250—260 nm should be assigned to the phenyl group existing in PDS molecule. In contrary, a stronger absorption in the same region could be observed in the spectrum of PTG, their molar absorption coefficients are about 10^3 order. It also can be shown that the optical density of these polymers at

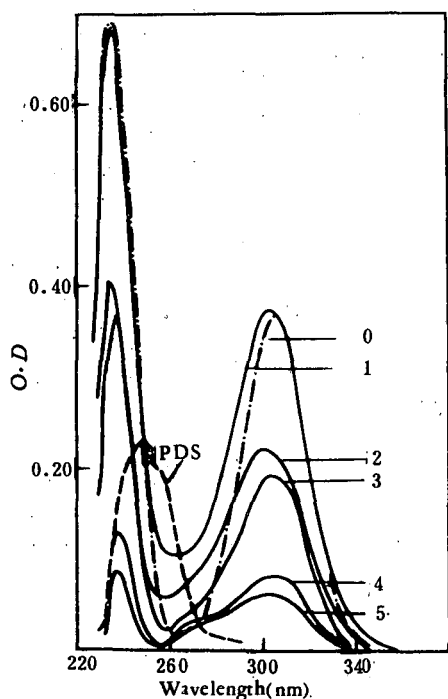


Fig. 1 Absorption spectra of PTG and PDS photostabilizers in tetrahydrofuran /1,2-dichloroethane(1:9) solution
Concentration: 1×10^{-4} mol./L

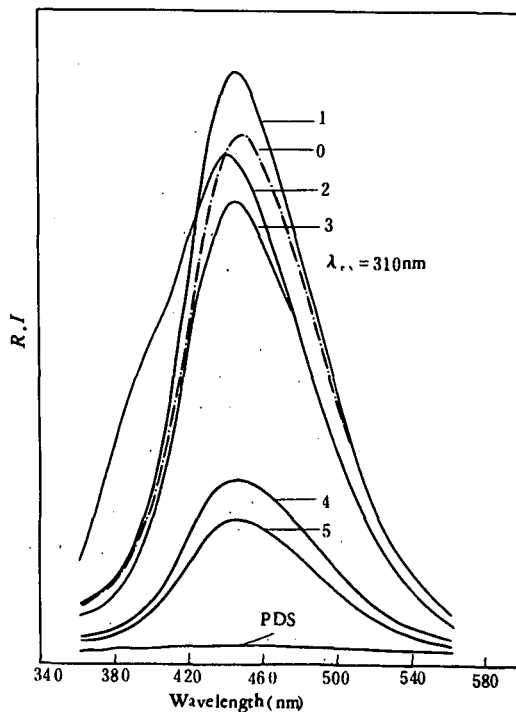


Fig. 2 Fluorescence emission spectra of PTG and PDS photostabilizers in tetrahydrofuran /1,2-dichloroethane(1:9) solution
Concentration: 1×10^{-4} mol /L

300—310 nm increases with increasing content of salicylate group in PTG molecule, and another peak at 240 nm is probably associated with the absorption of piperidinyl group. As regard to the absorption at 310 nm, in general, it should be assigned to the intramolecular hydrogen bond which was formed in the salicylate group^[7]. In Fig. 2 the fluorescence spectra ($\lambda_{ex} = 310$ nm) of PTG were recorded. It can be shown from this figure that the fluorescence spectra of PTG showed a maximum emission peak at 440—450 nm. The uncommonly large Stoke's shift is about 130—140 nm which was similar to methyl salicylate in nonpolar solvent^[7]. It is interesting to note that when this kind of polymer was excited by different wavelength of light, they showed only one fluorescence emission band at the region of 440—450 nm, (Fig. 3). This result is different from that of methyl salicylate. As well known^[8,9] that for the methyl salicylate different emission spectra could be recorded when it was excited by different wavelengths of light. For example, the emission spectrum with only one maximum at 440—450 nm was obtained by excitation of 310 nm, but the spectrum with two peaks at 350 nm and 450 nm was obtained by excitation of 280 nm. These results may be used to explain the existence of different tautomer structures which are in equilibrium with each other in the ground state. So, it shows different emission spectrum by excitation with different wavelength of light. For the salicylate compounds, it could be considered that there are two kinds of intramolecular hydrogen bond structure existing in the system as follows: Tautomer A emits blue light (440—450 nm) and tautomer B emits UV emission^[10].

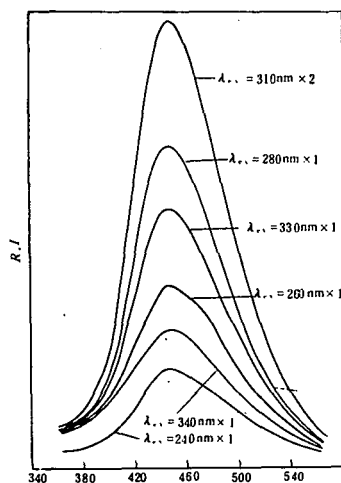


Fig. 3 Fluorescence emission spectra of PTG-1 in tetrahydrofuran/1,2-dichloroethan (1:9) solution when excited with light of different wavelength.
Concentration: 1×10^{-4} mol/L

The spectrum behaviors of PTG stabilizer in which there is no dual fluorescence could be considered as the equilibrium described above shifts to the formation of tautomer A in PTG system. It seems to be in contradiction with the presence of piperidinyl group in PTG molecule, because the piperidinyl group has very strong effect to destroy the hydrogen bond structure (tautomer A). But, it should be noted that the destruction of intramolecular H-bond and the equilibrium between two tautomers are different processes. While the intramolecular H-bond of tautomer A is destroyed by the addition of piperidinyl group, the equilibrium shifts to the tautomer A simultaneously.

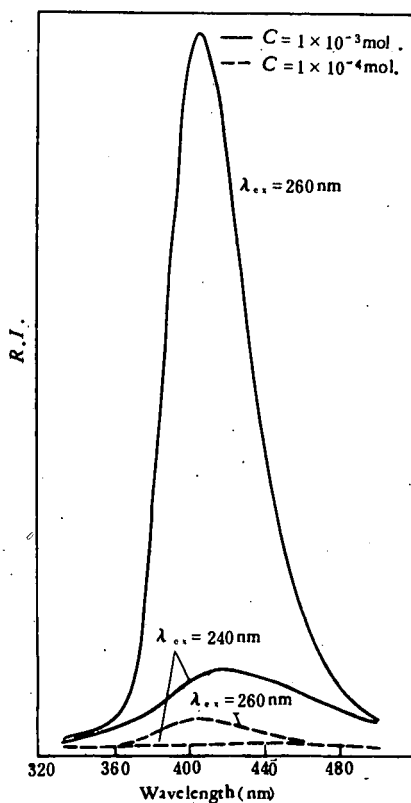
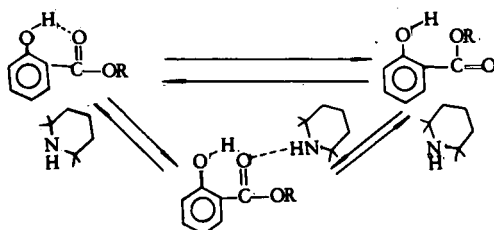


Fig. 4 Fluorescence emission spectra of mixture of methyl salicylate and 2,2,6,6-tetramethyl-4-piperidinol (M/M = 1/1) in tetrahydrofuran/1,2-dichloroethane (1:9) during different concentration

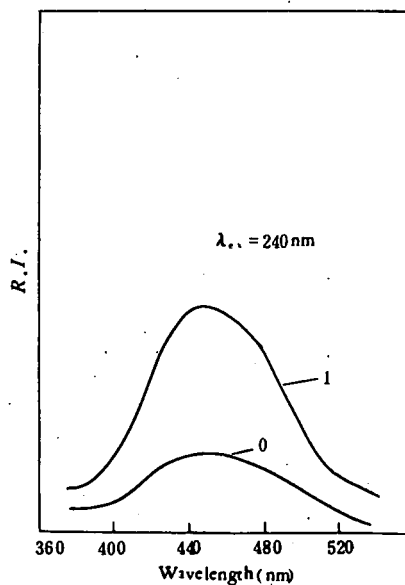


Fig. 5 Fluorescence emission spectra of PTG-0 and PTG-1 in tetrahydrofuran/1,2-dichloroethane (1:9) solution excited by wavelength of 240 nm
Concentration: 1×10^{-4} mol/L

The results of experiments indicated that the introduction of piperidinyl group and the existence of large R group in PTG molecule favour the equilibrium to shift to the tautomer A formation. Owing to the decrease of tautomer B, the phenomenon of dual fluorescence was disappeared. But it did not indicate that the effect of photostabilization of the title compounds was promoted.

In the previous work we found that when methyl salicylate was excited by 220–240 nm, the fluorescence with wavelength above 400 nm could not be observed in the spectrum. However, 2,2,6,6-tetramethyl-4-piperidinyl salicylate excited by the same wavelength can emit fluorescence with wavelength over 400 nm. It means that an intramolecular energy transfer process could occur in the excited molecule of tetramethyl-4-piperidinyl salicylate. Fig. 4 is the fluorescence spectra of the mixture of methyl salicylate and 2,2,6,6-tetramethyl-4-piperidinol. It shows that the fluorescence with wavelength above 400 nm could be observed by excitation of 240 nm when the concentration of the two ingredients is $10^{-3}M$, whereas the long-wavelength emission disappeared when the concentration is $10^{-4}M$. This means that $10^{-4}M$ is below the critical concentration of energy transfer between the two ingredients. But, for the PTG copolymer system (Fig. 5), when the concentration of salicylate fraction is $10^{-4}M$, the emission intensity of copolymer No. 1 in the region above 400 nm is higher than that of copolymer No. 0 (i. e. homopolymer of salicylic monomer). This result indicated that due to the coexistence of two monomers in a polymeric chain, the critical concentration of energy transfer lowered.

Another phenomenon shown in Fig. 4 is that when the solution of the mixture of two small molecules stated above was excited by 260 nm, its intensity of fluorescence increased rapidly with increasing concentration of solution, meanwhile, the emission peak shifted from 410 nm to 400

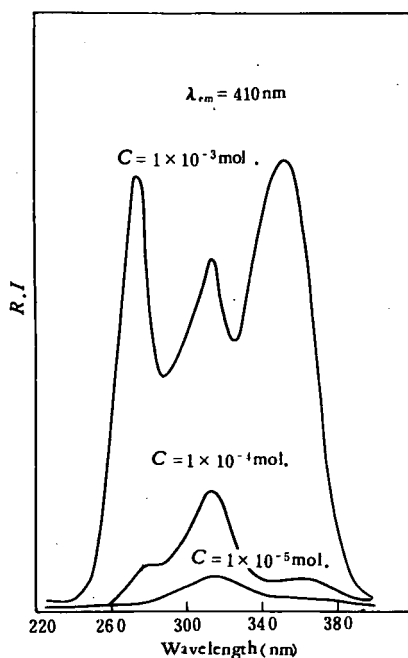


Fig. 6 Fluorescence excitation spectra of mixture of methyl salicylate and 2,2,6,6-tetramethyl-4-piperidinol ($M/M \approx 1/1$) in tetrahydrofuran/1,2-dichloroethane (1:9) solution, during different concentration:

nm. It seems that the addition of some proton-philic compound to the salicylic ester system might destroy the intramolecular hydrogen bond. This phenomenon can also be seen clearly in the fluorescence excitation spectra (Fig. 6). When the concentration of the solution increases from $10^{-5}M$ to $10^{-3}M$, the peak position in the excitation spectra changes evidently. At low concentration, the intramolecular hydrogen bond in salicylic ester cannot be destroyed by the molecule of piperidine. So, the absorption at 310 nm assigned to intramolecular H-bond keeps very strong. But, when the concentration of the solution of the mixture increases continuously, the interaction between piperidine and salicylic ester also increases indoubtedly, and it will destroy the intramolecular H-bond in salicylic ester. In this case, the absorption at 310 nm in excitation spectrum decreases and the absorption at 260 nm assigned to the benzoyl group increases evidently (the assignment of the absorption at 360 nm in spectrum is not clear yet). These results indicated that the presence of two different components in a system, though it will supply the photostabilization effect of the resultant stabilizer, the unsuitable ratio of the two components in the mixture or the copolymer, on the other hand, will produce negative effect.

The result in Fig. 7 indicated that for the poly (butadiene) solution without stabilizer, the viscosity of poly (butadiene) solution decreases rapidly after irradiation. It can be shown also in this figure that the title photostabilizers have the better effect of photo-stabilization than that of PDS stabilizer. Especially, the copolymer No. 1 is the best among these stabilizers (the molar ratio of the components in this copolymer is 1/1).

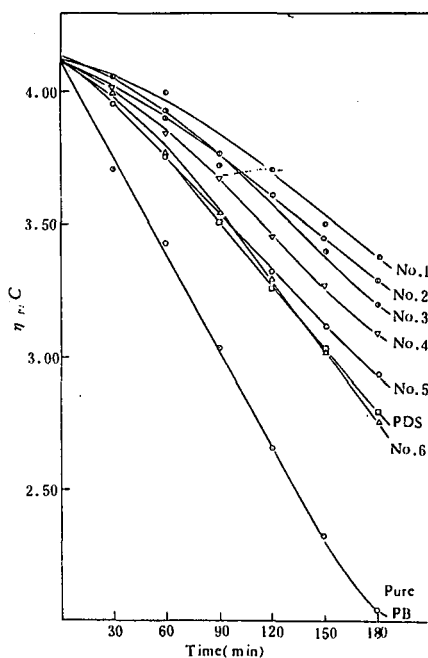


Fig. 7 The change of viscosity of *cis*-1,4-poly(butadiene) in THF/ $C_2H_4Cl_2$ (1:9) during photoirradiation in the presence of air

PB concentration: 1.09g/100ml. stabilizer concentration: 9.09×10^{-5} mol./l.

According to the results described above the addition effect of PTG series photo~~st~~abilizer has been demonstrated clearly, and the unsuitable ratio of two monomers in the copolymer will produce some undesirable effect.

Keywords:

Photostabilizer; Hindered amine; Salicylate ester

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