

A STUDY ON THE SPECTRUM CHARACTER AND PHOTOSTABILIZATION ABILITY OF A NOVEL UV-ABSORBER—DIBENZOYL METHANE

WU Shikang(吴世康), DAI Guangsong(戴光松) and LIU Lusheng(刘鲁生)
(Institute of Photographic Chemistry, Academia Sinica Beijing)

ABSTRACT

The absorption and fluorescence spectra of dibenzoyl methane have been studied. From the absorption spectra it was found that there are two peaks locating at 252 nm and 340 nm, respectively, similar to that of *o*-hydroxy benzophenone which can form intra-molecular hydrogen bond. Besides, an uncommonly large Stoke's shift of fluorescence can be observed in fluorescence spectra. The photostabilizing effects of dibenzoyl methane and UV-531 on the photodegradation of poly (*cis*-1, 4-butadiene) in solution have been investigated and compared. A possible mechanism was discussed.

INTRODUCTION

Recently, a very important kind of photostabilizers—UV-absorbers have received extensive attention. Different types of UV-absorbers such as salicylic esters^[1,2], *o*-hydroxy benzophenone^[3,4] and *o*-hydroxy phenyl benzotriazole^[5] etc. have been widely applied for protecting the human skin and stabilizing polymer materials in a large scale. Some results have been obtained in the research on its stabilizing mechanism. It is clear that in the molecule of these compounds used as a UV-absorber there is an intra-molecular hydrogen bond which can form a six-member ring. In this case the energy absorbed could be lost by the mechanism of tautomerism. The knowledge of the photostabilizing mechanism could help us to develop new type of UV-absorber. In this work a new UV-absorber—dibenzoyl methane was investigated.

EXPERIMENTAL

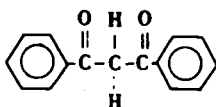
Materials

Dibenzoyl methane was obtained from Beijing Chemical Works and purified by recrystallization before use. A well known UV-absorber 2-hydroxy-4-octoxy benzophenone (UV-531) was used as a reference for comparison. All solvents used in this work, chloroform, tetrahydrofuran and pyridine were analytical grade.

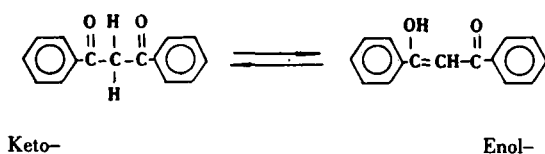
For evaluating the stability effect of dibenzoyl methane on the polymer materials, poly (*cis*-1, 4-butadiene) (Goodrich, AMERPOL CB200) was selected. The viscosities of polybutadiene solution with and without dibenzoyl methane and reference compound were measured at different time intervals of irradiation by USHIO UI-501 Xenon lamp. The absorption and fluorescence emission spectra of these compounds were recorded on the HITACHI 340 UV-Vis spectrophotometer and HITACHI MPF-4 fluorescence spectrophotometer, respectively.

RESULTS AND DISCUSSION

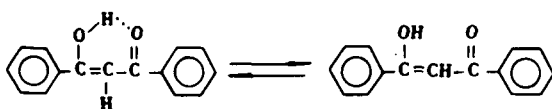
The molecular structure of dibenzoyl methane is as follows:



Since the hydrogen atoms in the methylene group between two carbonyl groups are very active, dibenzoyl methane has enol-and keto-tautomers in ground state.



The result obtained from the H-nmr spectrum of this compound is as follows: in CDCl_3 , 6.8 ppm ($=\text{CH}$, 1H, S), 7.4—8.3 ppm (phenyl, 10H, M), 17.1 ppm ($-\text{OH}$, 1H, S). It can be seen that the equilibrium of tautomerism described above shifted to the side of enol-tautomer. Meanwhile, the chemical shift of the proton of hydroxy group moved to a low field. It means that there is a hydrogen bond structure in the molecule.



From the absorption spectra (Fig.1) of dibenzoyl methane and UV-531, it can be seen that there are two peaks in the spectrum of dibenzoyl methane at 250nm and 340 nm, respectively, and the

Table 1 The molar absorption coefficients of several compounds with similar structure

Compounds	Molar absorption coefficients		
	254 nm	313 nm	360 nm
Methyl phenyl ketone	1000	40	5
Bibenzoyl	15000	500	70
Benzophenone	17000	50	70
Dibenzoyl methane	9600	12000	26000(340 nm)
UV-531	13200	12400	12800(330 nm)

intensity of the latter is higher than that of the former. In Table 1, molar absorption coefficients of a series of compounds which have similar structure are listed. It is evident that compounds which can form intra-molecular hydrogen bond possess stronger absorption in the region near 340 nm (Fig.2). It indicated further that intra-molecular hydrogen bond existed in the molecule of dibenzoyl methane.

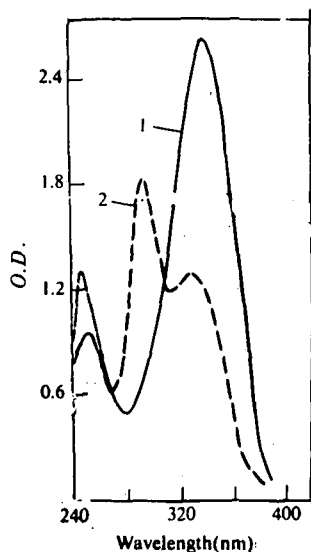


Fig. 1 Absorption spectra of dibenzoyl methane and UV-531
1, Dibenzoylmethane; 2, UV-531

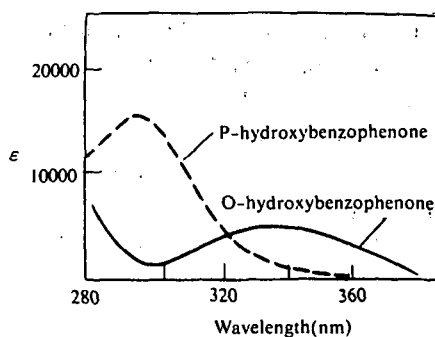


Fig. 2 Absorption spectra of different hydroxybenzophenone

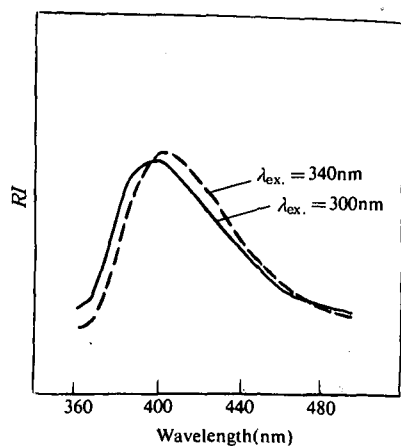


Fig. 3 The fluorescence emission spectra of dibenzoyl methane in chloroform ($1 \times 10^{-4} M$).

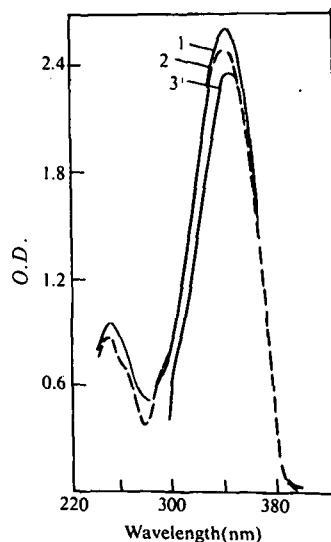
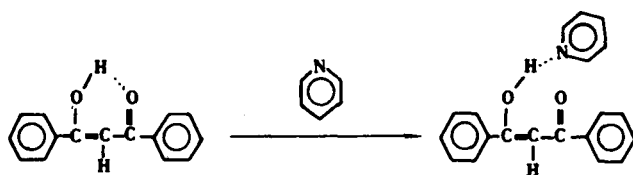


Fig. 4 The absorption spectra of dibenzoyl methane in different solvents ($1 = 10^{-4} M$)
1. in $CHCl_3$; 2. in THF; 3. in Pyridine

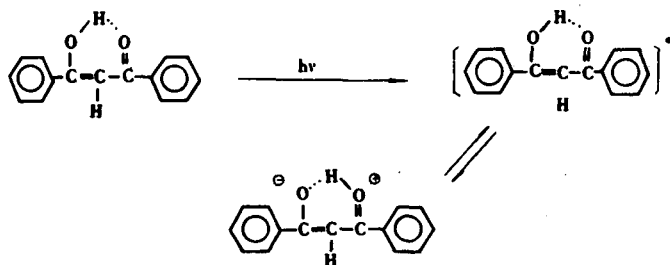
From the fluorescence emission spectra (Fig.3) it was shown that an uncommonly large stoke's shift (about 100 nm) could be observed in the fluorescence emission spectra of dibenzoyl methane excited by different wavelengths. This is a very important phenomenon for the efficient UV-absorber. Besides that, the fluorescence emission intensity of this compound is very weak. All of these indicated that the compound studied here could efficiently dissipate the energy absorbed from light irradiation.

In order to confirm the existence of intra-molecular hydrogen bond in the molecule of dibenzoyl methane, the absorption and fluorescence spectra of dibenzoyl methane in different protonaccepting solvents such as tetrahydrofuran and pyridine were measured^[6] (Fig.4 and 5). Through the comparison of absorption and fluorescence emission intensities of dibenzoyl methane in different solvents indicated above, we can see that the optical density (absorption) is the smallest in the solvent pyridine which has the strongest proton accepting ability among the solvents used, and the absorption is the largest in chloroform. But in pyridine the fluorescence intensity is the strongest, while in chloroform is the weakest. These results were due to the pyridine and tetrahydrofuran have strong proton accepting abilities, in the solution of dibenzoyl methane they would influence the intra-molecular hydrogen bond formation, therefore reduce the absorption at 340 nm, and promote the fluorescence intensity through the reduction of energy dissipation. The solvents effects could be demonstrated in the following equation:



These results verify that the intra-molecular hydrogen bond is present in the system studied.

In regard to the mechanism of energy dissipation of this compound, it could be still explained by the following equation^[7].



It means that dibenzoyl methane dissipates the energy of photoexcitation through the process of tautomerism.

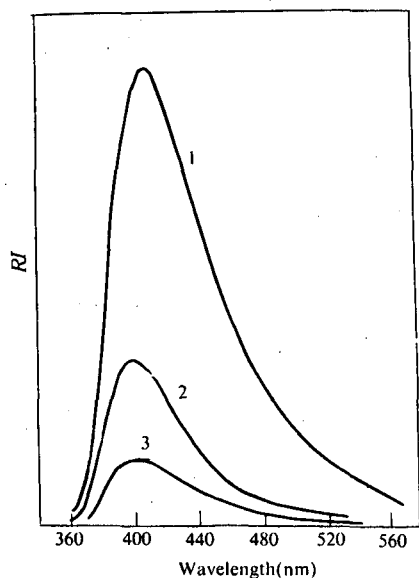


Fig. 5 The fluorescence spectra of dibenzoyl methane in different solvents ($1 \times 10^{-4} M$)
1. in Pyridine; 2. in THF; 3. in $CHCl_3$

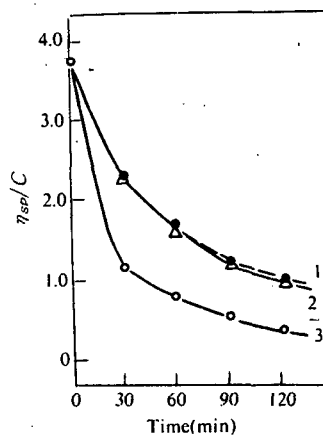


Fig. 6 The viscosity change of poly-butadiene solution with different UV-absorbers in different time of irradiation.

Solvent: Benzene: $CHCl_3$ = 10:1; Polymer: 1.36g/100ml;
UV-absorbers: $9.09 \times 10^{-3} M$.

1, With UV-531; 2, With dibenzoyl methane;
3, Without stabilizers

For examining the ability of photostabilization of dibenzoyl methane, the viscosity changes of polybutadiene solutions with and without UV-absorber under irradiation have been measured (Fig.6). In the case of the polybutadiene solution without UV-absorber, the viscosity decreased rapidly after irradiation, but if the UV-absorbers studied here had been introduced into the polybutadiene solution, the rate of viscosity change after irradiation was reduced. These results indicate that dibenzoyl methane and UV-531 possess similar photostabilizing ability for inhibiting the photodegradation of polymers. It demonstrates that dibenzoyl methane is a promising photostabilizer.

Keywords:

β -diketones; UV-absorber; Photostabilizer; Intra-molecular hydrogen bond

REFERENCES

- [1] Tirrell, D. and Vogl, O., *Makromol. Chem.* **1980** 181, 2097.
- [2] Iwasaki, M.; Tirrell, D. and Vogl, O., *J. Polym. Sci.(Chem.)*, **1980**, 18, 2755.
- [3] Osawa, Z.; Suzuki, K. and Ogiwara, Y., *J. Macromol. Sci.(Chem.)*, **1971**, A5, 275.
- [4] Osawa, Z.; Matsui, K. and Ogiwara, Y., *J. Macromol. Sci.(Chem.)*, **1967**, A1, 581.
- [5] Li, S.; Bassett, W.Jr.; Gupta, A. and Vogl, O., *J. Macromol. Sci. (Chem.)*, **1983**, A20, 309.
- [6] Ganguly, T.; Mal, S. and Mukherjee, S., *Spectrochimica Acta* **1983**, 39A, 657.
- [7] Klopffer, W., *J. Polym. Sci., Symposium*, **1976**(57), 205.