Polymer Bulletin 20, 161–168 (1988)

Polymer Bulletin

Functional polymers. LV. Photochemical behavior of 2(2-hydroxyphenyl)2H-benzotriazole derivatives

3. Effects of the position of the substituents*

Yongcai Jiang[1], Shikang Wu[1], Andres Sustic[2], Fu Xi[2], and Otto Vogl[2]

[1] Institute of Photochemistry, Academia Sinica, Beijing, Peoples Republic of China
[2] Polytechnic University, Brooklyn, NY 11201, USA

SUMMARY

Polymerizable 2(2-hydroxyphenyl)2H-benzotriazole ultraviolet absorbers have the normal hydrogen bonded λ maximum at 340 nm. When more than one ortho-hydroxy group capable of hygen bonding is present in the molecule the extinction coefficient increases dramatically; the fluorescence spectra are also affected. It is expected that these compounds are very effective ultraviolet stabilizers.

INTRODUCTION

2(2-Hydroxyphenyl)2H-benzotriazole derivatives have been extensively studied because they are excellent ultraviolet absorbers and effective photostabilizers for polymer materials. The stabilizing mechanism of these types of compounds is based on the formation of intramolecular hydrogen-bonds between the ortho-hydroxyl group of the phenyl ring and the nitrogen atom of the benzotriazole moiety. The intramolecular hydrogen bond has been found to be the most important structural element that provides photostability [2]. In photoexcited 2(2-hydroxyphenyl)2H-benzotriazole molecules, a mechanism exists which dissipates the energy of the photoexcited state into vibrational energy, based on the rapid tautomerism of the excited species [1-3].

When ultraviolet absorbers are irradiated with light (according to Foerster's theory [4]), the relative increase of the acidity/basicity relationship of intramolecular proton-donor/acceptor structures in the excited state causes proton transfer and consumes absorbed energy from the photoexcited state, preventing excitation of the substrate which ultimately results in the photostabilization of the material.

In order to improve the efficiency of photostabilizing compounds which can lead to their practical application, two typical approaches have been used.

---

* Functional Polymers. LIV., G.S. Dai, S.K. Wu, A. Sustic, F. Xi, and O. Vogl, Polymer Bulletin 20, 67 (1988)

The most efficient class of modern photostabilizers have the 2(2-hydroxyphenyl)2H-benzotriazole as the chromophore. One approach to further the understanding of how these type of ultraviolet absorbers function is to synthesize selected multihydroxy and/or multibenzotriazole substituted 2(2-hydroxyphenyl)2H-benzotriazoles in an effort to enhance the intramolecular hydrogen bonding of the molecule with the expectation to increase the photostabilizing capability of the ultraviolet absorber [5-7].

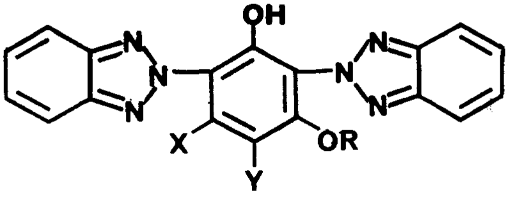
The other approach is to synthesize 2(2-hydroxyphenyl) 2H-benzotriazole derivatives which might have better compatibility of the ultraviolet stabilizer with the polymeric materials [8]. One very efficient way to accomplish this is to prepare polymerizable and polymer-bound ultraviolet absorbers of the 2(2-hydroxyphenyl)2H-benzotriazole type [8-10].

It was the objective of this work to study in detail the ultraviolet spectra of a series of "multi" hydroxyl-substituted mono-, di- or tri-benzotriazole ultraviolet absorbers [11-14] and to evaluate the behavior of 2(2-hydroxyphenyl)2H-benzotriazole derivatives which have polymerizable groups as one of the substituents.

EXPERIMENTAL PART

2(2-Hydroxyphenyl)2H-benzotriazole derivatives with one, two or three benzotriazole groups on the same benzene ring and compounds with acryloxy-, methacryloxy- or undecenoxy-substituents as polymerizable groups attached to the phenyl rings were synthesized according to the literature [5,11-14]. Their structures are shown in Table 1.

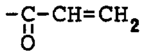
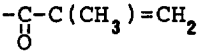
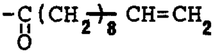
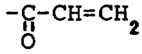
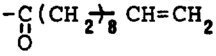
The general structure of the 2(2-hydroxyphenyl)2H-benzotriazole derivatives studied in this work is as follows:



Dichloroethane (analytical grade) was used as solvent for the measurements of the ultraviolet spectra. The concentrations were 1x10^{-5} Molar.

The absorption spectra and fluorescence spectra were measured at room temperature on a Hitachi 340 UV-VIS Spectrometer and a Hitachi MPF-4 fluorescence spectrometer respectively.

Table 1

Sample No.	Name of Compounds	X	Y	R
1	2,4-(1,3-dihydroxyphenyl)-di(2H-benzotriazole	-H	-H	-H
2	1,3-(2-Hydroxy-4-acryloxy-phenyl)-di(2H-benzotriazole)	-H	-H	 $-\underset{\underset{O}{\|}}{C}-CH=CH_2$
3	1,3-(2-Hydroxy-4-methacryloxy-phenyl)-di(2H-benzotriazole)	-H	-H	 $-\underset{\underset{O}{\|}}{C}-C(CH_3)=CH_2$
4	1,3-(2-Hydroxy-4-undecenoxy-phenyl)-di-(2H-benzotriazole)	-H	-H	 $-\underset{\underset{O}{\|}}{C}(CH_2)_8CH=CH_2$
5	2,4-(1,3,5-Trihydroxyphenyl)-di(2H-benzotriazole)	-OH	-H	-H
6	2,4-(1,3-dihydroxy-5-acryl-oxyphenyl)-di(2H-benzotriazole)	-OH	-H	 $-\underset{\underset{O}{\|}}{C}-CH=CH_2$
7	2,4-(1,3-dihydroxy-5-undecen-oxyphenyl)-di(2H-benzotriazole)	-OH	-H	 $-\underset{\underset{O}{\|}}{C}(CH_2)_8CH=CH_2$
8	2,4,6-(1,3,5-trihydroxyphenyl)-tri(2H-benzotriazole)	-OH	-Bzt	-H

RESULTS AND DISCUSSION

The absorption spectra of eight 2(2-hydroxyphenyl)2H-benzotriazole derivatives are shown in Figure 1; typical absorption spectra of 2(2-hydroxyphenyl)2H-benzotriazoles are also shown in [15,16]. In all cases, the spectra have similar absorptions at 280-300 nm and at 335-350 nm. Previous work had demonstrated that the absorption at 280 to 300 nm is caused by the 2-phenyl-2H-benzotriazole structure. As soon as a hydroxyl group is introduced into the ortho-position of the linkage of the phenyl ring to the benzotriazole ring, the entire 2-phenyl-2H-benzotriazole structure changes its character and becomes capable of hydrogen-bonding between the hydroxyl group of the phenyl ring and the nitrogen atom of the benzotriazole ring. This new absorption maximum at longer wavelength (335-350 nm) is caused by the hydrogen bonded structure.

Compounds 1, 5 and 8, have two or three benzotriazole moieties and in the phenyl ring, at least two hydroxyl- groups in ortho-position to the benzotriazoles; consequently only the absorption at around 340 nm was observed: the absorption of the regular nonhydrogen-bonded 2(2-hydroxyphenyl)2H-benzotriazole at 280-300 nm had almost dissappeared, or only a shoulder was left.

This shoulder may still have a significant extinction coefficient. Compounds 2, 3 and 4 show absorption maxima at around 290 nm caused by the presence of the normal 2-phenyl-2H-benzotriazole ring absorption which does not form or cannot form intramolecular hydrogen bonds. Compounds 6 and 7, similarly to compounds 1, 5, and 8, have a 2(2-hydroxyphenyl)2H-benzotriazole functionality which is capable of forming hydrogen bonds. The polymerizable acryloxy- group seems to affect the formation of hydrogen bonds and seems to modify the absorption at 280-300 nm as seen in the absorption spectra of compounds 1, 5 & 8.

The molar extinction coefficients of the 2(2-hydroxyphenyl)2H-benzotriazole derivatives are listed in Table 2. In Figure 2, the extinction coefficients at λ max. of three compounds (1 and 8 in Table 2 and compound 3 in Fig. 2 [15]) are plotted as a function of the number of hydrogen bonds in the molecules.

The values clearly indicate that the intensity of the absorption at a maximum of 340 nm is determined by the number of the ortho-hydroxyl groups which can form intramolecular hydrogen bonds. The absorption at the wavelength of 335-350 nm is attributed to the formation of hydrogen bonds between the triazole nitrogen atoms of the benzotriazole substituent with the orthohydroxy groups of the phenyl ring. The increase in the number of the benzotriazole units and ortho-hydroxyl groups in one molecule is one way to enhance the potential of dramatically increasing the photostabilizing capability of the basic 2(2-hydroxyphenyl)2H-benzotriazole chromophore. The fluorescence spectra of a series of 2(2-Hydroxyphenyl)2H-

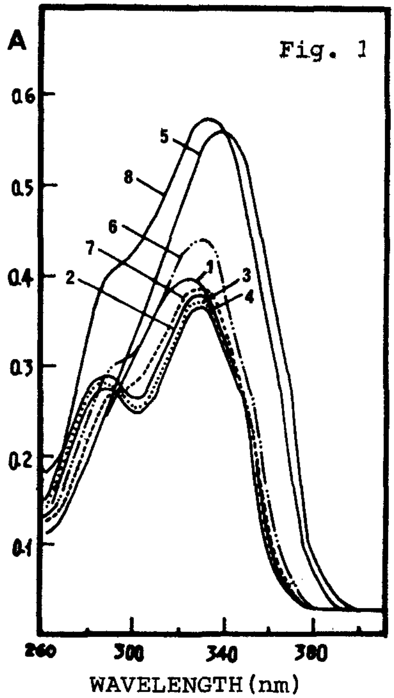


Fig. 1

Absorption Spectra of Compounds 1 to 8 in Dichloroethane Solution. Conc.: 1×10^{-5} Molar.

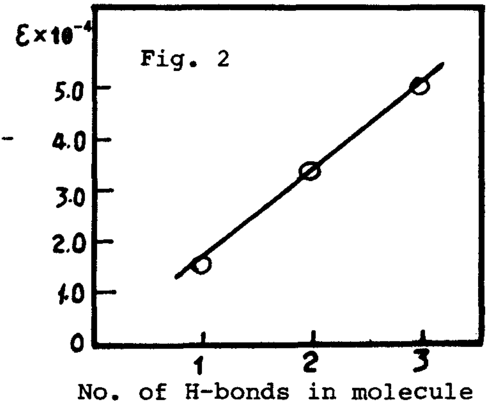


Fig. 2

Relationship Between the Number of Intramolecular Hydrogen bonds with the Extinction Coefficient at ~340 nm.

Table 2. Extinction Coefficient Values of 2(2-Hydroxyphenyl)2H-benzotriazole Compounds

Compound No	Extinction coefficients x 10^{-4} λ = 290 nm	λ = 340 nm
1	---	3.4
2	2.3	3.0
3	2.4	3.3
4	2.3	3.0
5	---	4.6
6	2.6	3.8
7	2.4	3.5
8	---	4.8

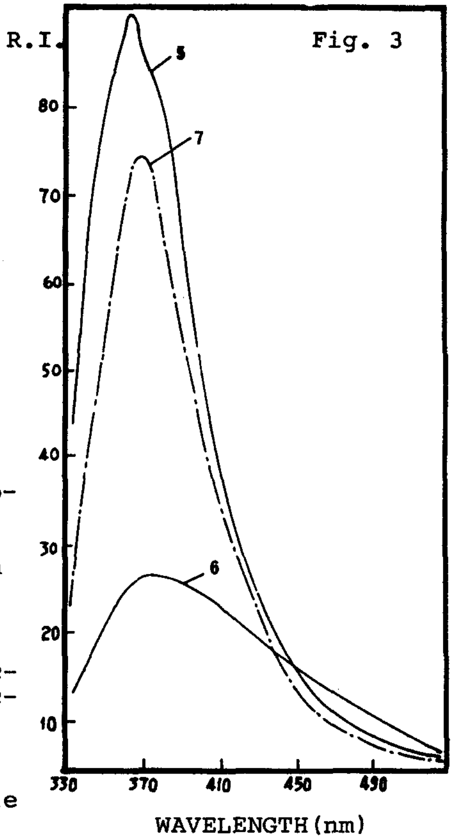
benzotriazole derivatives were also measured; the following results were obtained: (a) The fluorescence emission intensities of the various compounds were different when the compounds were excited with light of a wavelength of 290 nm or 330-340 nm. The fluorescence emission was strong when the compounds were irradiated with light of a wavelength of 290 nm while the fluorescence was weak when irradiated with light of 330-340 nm. This apparent discrepancy is related to the formation of structures with intramolecular hydrogen bonds. The consequence of this analysis is that the absorbed energy is rapidly consumed by intramolecular proton transfer resulting in only a weak fluorescence emission. When the compounds were irradiated with light with a wavelength of 290 nm, the excitation of the molecule does not involve 2-phenyl-2H-benzotriazole units to form hydrogen-bonds. This interaction shows stronger fluorescence since there is no simple mechanism for the excitation energy to be dissipated. (b) The fluorescence intensities (FI) of compounds 5, 6 and 7 (Figure 3), follow the following order:

$$FI(5)>FI(7)>FI(6).$$

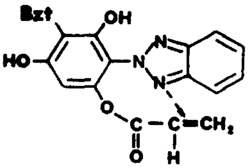
Compounds 6 and 7 are esters of 5 and have no ortho-hydroxy group capable of hydrogen-bond formation; in addition, 6 and 7 possess unsaturated double bonds. In compound 6, the double bond is directly attached to the ester group, an electron withdrawing group.

Compound 7, which is a 2(2,4-dihydroxyphenyl)2H-benzotriazole ester where the 4-hydroxy-group is esterified with 10-undecenoic acid, has 8 methylene carbon atoms between the double bonds of the vinyl group and the ester group, the double bond is far removed from the ester group and the substituent is essentially an aliphatic acyl group different from compound 6, which is an acrylic ester, where the vinyl group (which is electron defficient) of the acrylate unit is directly attached to the carboxylate group; this acrylate system influences strongly the electronic structure of the phenyl ring of the 2(2-hydroxyphenyl)2H-benzotriazole chromophore.

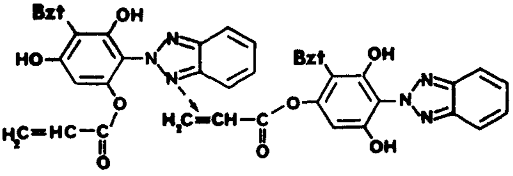
Based on our information, an electron-defficient double bond as the substituent is the cause for weaker fluorescence as exemplified in compound 6; this structural arrangement acts as an electron acceptor and quenches the fluorescence of the 2(2-hydroxyphenyl)2H-benzotriazole unit. A 2(2-hydroxyphenyl)2H-benzotriazole unit functions as an electron donor, leading to intramolecular or intermolecular exciplex formation upon irradiation [17].



Fluorescence Spectra of Compounds 5, 6 and 7 in Solution.



(intramolecular e - transfer)



(intermolecular e - transfer)

In order to prove this exciplex hypothesis, acrylic acid was used in an attempt to quench the fluorescence of 2(2-hydroxyphenyl)2H-benzotriazole derivatives in solution; the results are shown in Figure 4. It can be clearly seen that with increasing acrylic acid content the intensity of the fluorescence of the 2(2-hydroxyphenyl)2H-benzotriazole unit decreases. Since the absorption wavelength of acrylic acid is shorter than that of the 2(2-hydroxyphenyl) 2H-benzotriazole, the photo-quenching is not caused by energy transfer, but by electron transfer. Even though no obvious emission peak of the exciplex was observed at longer wavelengths, a "tail" absorption was found when the results were normalized. With increasing acrylic acid concentration, the emission of light of longer wavelength was enhanced indicating the existence of the new species of an exciplex.

In compound 7, because its double bond is isolated from the ester group by 8 methylene segments, the vinyl group has no influence on the spectral behavior; the substituent effect is similar to that of an ester of an aliphatic carboxylic acid, therefore its fluorescence intensity is similar to that of compound 5.

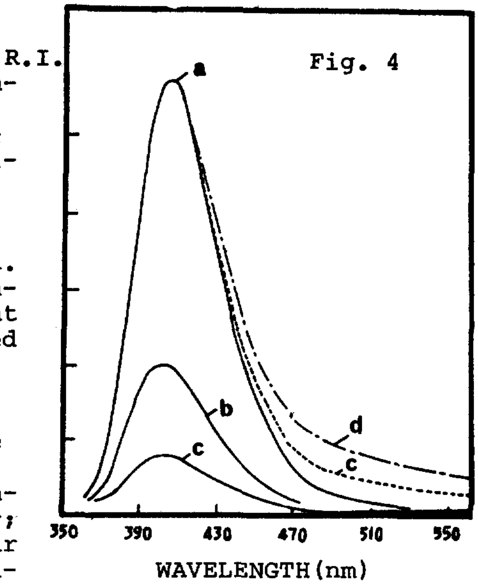


Fig. 4

Fluorescence quenching of benzotriazole by acrylic acid (dotted lines indicate normalization). Conc.: a = 0; b = 0.1 Molar; c = 0.2 Molar; d = 0.3 Molar.

Acknowledgements : This work was supported in part by the Mark Chair of the Polytechnic University and the Materials Research Group grant of the National Science Foundation. We like to thank Jingping Huang and Shanjun Li for their assistance during the preparation of this manuscript.

REFERENCES

1. B. Ranby and J. Rabek, "Photodegradation, Photooxidation and Photostabilization of Polymers, John Wiley & Sons, London, 1975.
2. J.-E. A. Otterstedt, J. Chem. Phys., 58, 5716 (1973)
3. D. Bailey and O. Vogl, J. Macromol. Sci., Macromol. Reviews, C14, 267 (1976).
4. Th. Foerster, Ann. Phys., 2, 55 (1948), Zeitschr. fuer Elektrochem. Angew. Phys. Chem., 54, 42 (1950).
5. S. J. Li, A. Gupta and O. Vogl, Monatsh. Chem., 114, 937 (1983).
6. S. J. Li, W. Bassett Jr., A. Gupta and O. Vogl, J. Macromol. Sci., Chem., A20, 309 (1983).

7. O. Vogl, Makromol. Chem., Suppl., 7, 1 (1984).
8. O. Vogl and S. Yoshida, Rev. Roum. de Chimie, 25, 1123 (1980).
9. S. Yoshida and O. Vogl, Makromol. Chem., 183, 259 (1982).
10. Z. Nir, A. Gupta and O. Vogl, J. Polym. Sci., Polym. Chem. Ed., 20, 2735 (1982).
11. S. J. Li, A. C. Albertsson, A. Gupta, W. Bassett Jr. and O. Vogl, Monatsh. Chem., 115, 853 (1984).
12. S. J. Li, A. Gupta, A. C. Albertsson, W. Bassett Jr. and O. Vogl, Polymer Bulletin, 12, 237 (1984).
13. F. Xi, W. Bassett Jr. and O. Vogl, Makromol. Chem., 185, 2497 (1984).
14. S.J. Li and O. Vogl, Polymer Bulletin, 12, 375(1984).
15. R. X. Liu, S. K. Wu, S. J. Li, F. Xi and O. Vogl, Polymer Bulletin, in press.
16. G. S. Dai, S. K. Wu, A. Sustic, F. Xi and O. Vogl, Polymer Bulletin, in press.
17. S.K. Wu, Y.C. Yang, F.M. Lu and S.D. Feng, Polymer Bulletin, 8, 275(1982).

Accepted June 9, 1988 K