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Polymer Bulletin

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

1. Ultraviolet spectra and efficiency of photostabilization of 2(2-hydroxy-4-acryloxyphenyl)2H-benzotriazole, its polymers and copolymers*

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SUMMARY

The absorption spectra of 2[2-hydroxy-5-(meth)acryloxyphenyl]2H-benzotriazoles, their homo- and copolymers were studied. The immediate environment (next monomer units in copolymers) determine the details of the spectral characteristics. Copolymers are more efficient in photostabilizing poly-cis-1,4-butadiene-1,3 in solution than the monomer or the homopolymer.

INTRODUCTION

Sunlight with wavelengths shorter than 280 nm is absorbed or scattered by the atmosphere. Solar radiation with wavelengths longer than 280 nm, particularly the region of 300 to 350 nm, is still harmful to human skin and to polymeric materials; such radiation can cause photodegradation and photochemical initiation of reactions that lead to autooxidation and to general deterioration, known as weathering [1,2].

In order to prevent, inhibit or at least delay the effect of solar radiation on polymers, photostabilizers (and antioxidants) are commonly added to polymeric materials to protect them against the adverse effects of the environment. The interest in research to understand the effect of photostablizers, the optimization of their effectiveness, and the utilization of ultraviolet stabilizers has therefore been increasing. A series of different types of ultraviolet absorbers have been studied in the past, initially salicylic acid derivatives, o-hydroxybenzophenones, and most recently 2(2-hydroxyphenyl)-2H-benzotriazole derivatives.

For an ultraviolet stabilizer to be effective for the protection of polymers against photodegradation it has to have the proper photophysical properties. It should also be compatible with the polymer, distributed properly in the polymer matrix, should not be lost during the (melt) fabrication process and the period of use of the material. One logical approach for photostabilizers that might fit these requirements are polymerizable ultraviolet absorbers (stabilizers). Examples of

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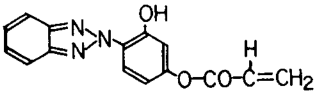
** To whom offprint requests should be sent polymerizable ultraviolet absorbers of the above categories have been described [3-10]. The evaluation of these types of stablizers and their full utilization is only in its beginning stages [11-18].

It was the objective of this work to study the spectral behavior of 2(2-hydroxyphenyl)2H-benzotriazole ultraviolet absorbers with polymerizable acrylate groups in the polymer.

EXPERIMENTAL PART

The structures of the ultraviolet absorbers: monomers, polymers and copolymers are shown below.

(1)



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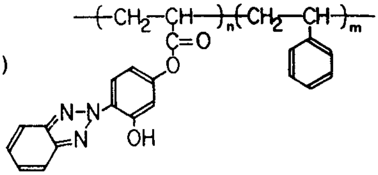

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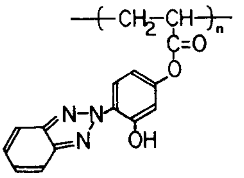

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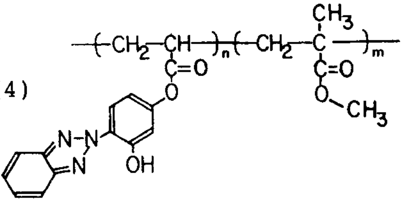


(m:n=9:1)

The syntheses and polymerizations of the 2(2-hydroxyphenyl) 2H-benzotriazole derivatives discussed in this paper have been published elsewhere [9,10].

The absorption spectra of the 2(2-hydroxyphenyl)2H-benzotriazole derivatives were measured on a Hitachi 340 UV-VIS spectrophotometer and the fluorescence emission spectra on a Hitachi MPF-4 fluorescence spectrophotometer. The measurements were carried out in chloroform solutions at concentrations of 1×10^{-4} molar and at room temperature.

The 2(2-hydroxyphenyl)2H-benzotriazole ultraviolet absorbers were studied for their effectiveness as photostabilizers. The photooxidation of poly-cis-1,4-butadiene-1,3 (PB) (Goodrich, Ameripol CB 200, reprecipitated several times before use) was studied in solution with and without ultraviolet stabilizers. The progress of the photooxidation was measured by determining the decrease of the viscosity of the PB solution (and presumably the decrease of the molecular weight of PB) at different time intervals. Viscosity measurements were carried out in a quartz viscometer [19].

Irradiation was carried out with an USHIO UI-501 Xenon lamp as the light source.

RESULTS AND DISCUSSION

The absorption spectra of compounds 1-4 are shown in Figure 1; they exhibit two absorption bands in the region of 300 to 350 nm, with the band between 335 and 350 nm more intense. The absorption spectra of some typical 2(2-hydroxyphenyl)2H-benzotriazole derivatives are shown in Figure 2. When comparing the ultraviolet absorption spectra of the compounds shown in Figure 1 with those shown in Figure 2, it is evident that the 2(2-hydroxyphenyl)2H-benzotriazole chromophores exhibit two absorption peaks. 2-Phenyl-2H-benzotriazoles display only one absorption peak at 300-310 nm, but hydrogen-bonded 2(2-hydroxyphenyl)2H-benzotriazole derivatives are capable of undergoing photoexcitation that gives absorption bands between 335 to 350 nm depending on the individual substituents on the phenyl or benzotriazole ring of the 2(2-hydroxyphenyl)2H-benzotriazole chromophores.

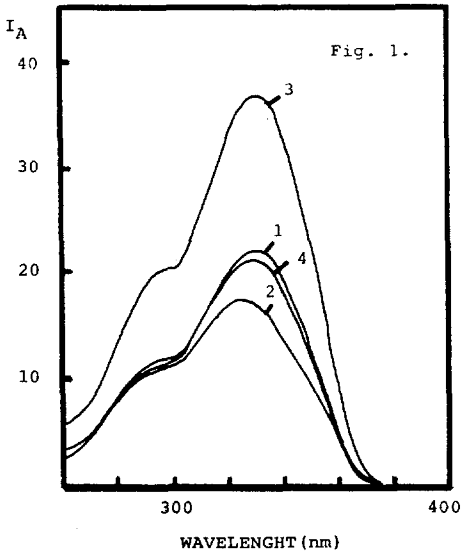


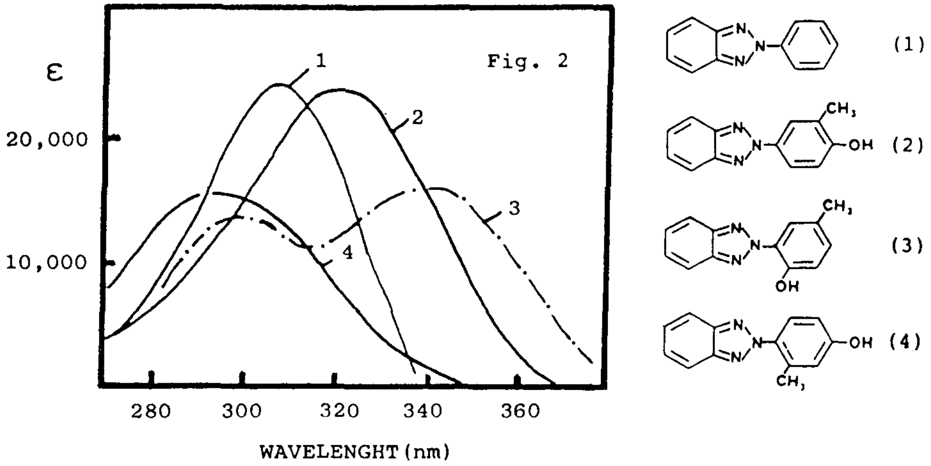
Fig. 1.

Absorption Spectra of Compounds 1-4 in Chloroform Solution: 1x10^{-4} Molar.

It is now well established that the intramolecular hydrogen bonded structure of the 2(2-hydroxyphenyl)2H-benzotriazole forms a six membered excited state ring commonly written as a zwitterionic species of the protonated benzotriazole cation and the phenolate anion. Figure 1 shows that the absorption spectra of compounds 1-4 are different from each other; the polymer concentration was calculated on a molar basis equivalent to the monomer unit. The intensity of the absorption maximum was somewhat different; the order of the absorption intensities of the compounds was found to be as follows:

(3)>(1)>(4)>(2).

The difference in the absorption intensity between compound 1 (the monomer) and the other chromophore units might be that 1 is in solution, only in the proximity of solvent molecules and consequently homogeneously distributed, while 2, poly[2(2-hydroxy-4-acryloxyphenyl)2H-benzotriazole], the homopolymer of 2, has the monomer unit incorporated as part of the macromolecular chain. In both cases, monomer 1 and polymer 2 are dissolved in chloroform but they act differently toward the solvent, with the monomer as part of the polymer chain being more responsive toward the neighboring unit than to the type of solvent. In other words, the mutual proximity of the monomer units of the homopolymer of 1 generate interactions with one another which must be taken into consideration.



Absorption Spectra of Various 2(2-Hydroxyphenyl)-2H-benzotriazole Derivatives in Chloroform Solution.

In copolymer 3 (the styrene-copolymer) and copolymer 4 (the methyl methacrylate copolymer), the situation is somewhat different, because the concentration of the monomer units in the macromolecular chain is lower, about 15 mole %, consequently the comonomer units are clearly separated from each other by the monomer units of styrene or methyl methacrylate. In a separate work it has been established that the copolymerization parameters do not indicate any tendency of block copolymer formation. Since the concentrations of the monomer units in the copolymers are low, we assume that the ultraviolet absorbing monomer units are clearly separated from each other and act independently from each other. As a consequence, the absorption intensity of the monomer units in 3 or 4 are higher than in homopolymer 2. Furthermore, the absorbance of the monomer unit in copolymer 3 is higher than that of monomer 1 and of homopolymer 1. The comonomer units in copolymer 3, the phenyl groups of the styrene units of the copolymer, are part of the macromolecular chain of 3 and change the local environment of the 2(2-hydroxyphenyl)2H-benzotriazole monomer unit, acting as a "solvent" would act on the chromophore. The 2(2-hydroxy-4-acryloxyphenyl)2H-benzotriazole units are isolated, their spectral characteristics are influenced by the next neighbor of the copolymer and the absorption spectrum of the excited state (at 340 nm to 350 nm) appears as if the spectrum was taken in toluene and not in the actual solvent: chloroform.

The fluorescence emission spectra of compounds 1-4 are shown in Figure 3 (A-D). The fluorescence intensity of the spectra of these compounds, when excited with a λ of 335 nm are lower than when excited with a λ of 300 nm. It has been known from previous experiments that the absorption intensity of low molecular 2(2-hydroxyphenyl)2H-benzotriazoles or of the monomer units in polymer bound 2(2-hydroxyphenyl)2H-benzotriazoles at the λ of about 340 nm are higher than at the λ of about 300 nm. The characteristic absorbances at around 300 nm and about 340 nm have been assigned previously to the absorption of 2(2-hydroxyphenyl)2H-benzotriazole in a non-planar configuration and to the six membered intramolecular hydrogen-bonded ring intermediate, respectively.

The cause for the weak fluorescence emission obtained by exciting the 2(2-hydroxyphenyl)2H-benzotriazole molecules with light of 335 nm is due to the six membered hydrogen bonded ring intermediate which is highly efficient in dissipating the absorbed energy through rapid tautomerism of the excited state. The relatively strong emission obtained by exciting the molecule with light of 300 nm may be caused by the involvement of a state of the 2(2-hydroxyphenyl)2H-benzotriazole group where hydrogen bonding is not involved. Based on the results described above, it appears that an equilibrium exists between a state which can form a hydrogen-bonded configuration (H) and a ground state which cannot directly form a hydrogen-bonded configuration (N).

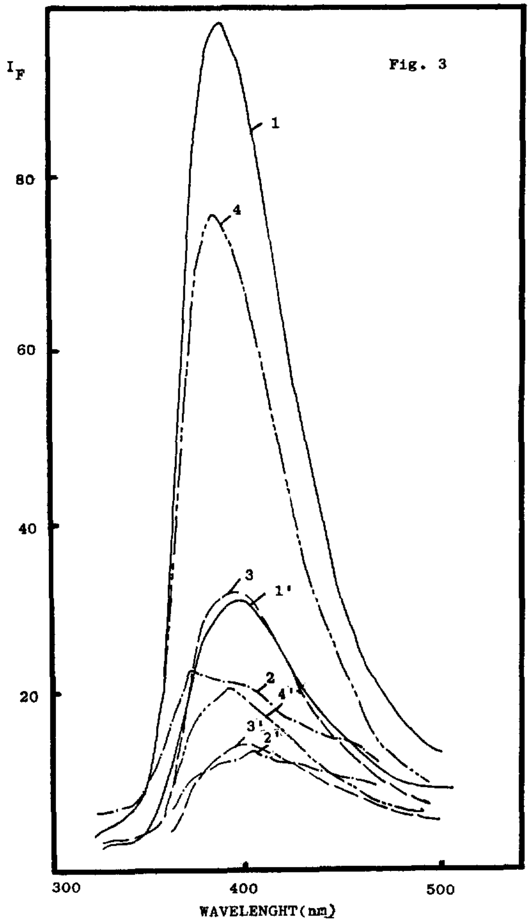
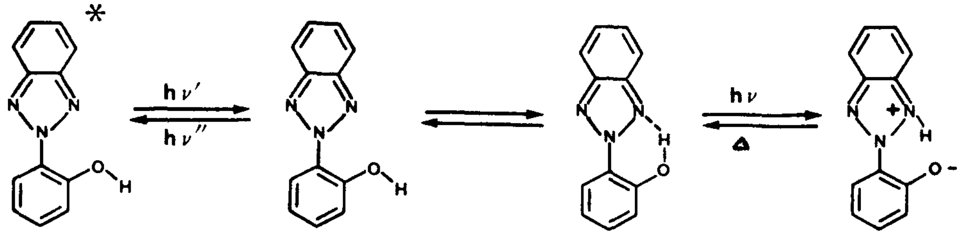


Fig. 3

Fluorescence Spectra of Compounds 1-4 in Chloroform
Solution: $1x10^{-4}$ Molar.
Excitation Wavelenght:
300 nm: 1,2,3,4. 335 nm: 1',2',3',4'.
1, 1' = Monomer 1 ; 2, 2' = Homopolymer 2;
3, 3' = Styrene Copolymer 3;
4, 4' = Methyl Methacrylate-Copolymer 4.



300 nm (N) (H) 335 nm

Figure 3 shows that the fluorescence emission maxima of structures 1-4 are around 400 nm regardless of the wavelength of excitation (300 nm or 335 nm). Unlike the case of the fluorescence behavior of salicylate derivatives for which a Stoke's shift of about 150 nm was noted [20], the fluorescence emission of the 2(2-hydroxyphenyl)2H-benzotriazoles was very weak.

The fluorescence emission intensity of the monomer unit in polymer 2 is of lower intensity than that of monomer 1. This seems to suggest that when the monomer unit 1 is incorporated into the macromolecular chain, a high local concentration of chromophoric units seem to act cooperatively causing self-absorbance of the emitted radiation. The emission process of the excited monomer units in polymer 2, which causes a lower fluorescence emission also seems to operate in copolymer 3; it gives a weak fluorescence emission, which might be in part caused by self-absorbance.

The efficiency of 2(2-hydroxyphenyl)2H-benzotriazole derivatives in the photostabilization of PB in solution is shown in Figure 4. Compounds 1-4 are good ultraviolet stabilizers; they inhibit the photo-degradation of PB as shown by only a small change of the solution viscosity. The photostabilizing efficiency of the respective 2(2-hydroxyphenyl)2H-benzotriazoles follow in this sequence:(3)>(4)>(2)=(1).

The styrene-copolymer of 2(2-hydroxy-4-acryloxyphenyl)-2H-benzotriazole 3, is the best photostabilizer of this series. This finding is in good agreement with the highest absorbance registered for this compound and the weakest fluorescence emission observed. The efficiency of the photostabilization of PB by monomer 1 and homopolymer 2 are almost the same. Monomer 1 could have been polymerized during the process of irradiation and could have been transformed into homopolymer 2. Monomer 1 could also have been grafted onto PB and produced a new polymer-bound stabilizer with the same efficiency of photostabilization as homopolymer 2.

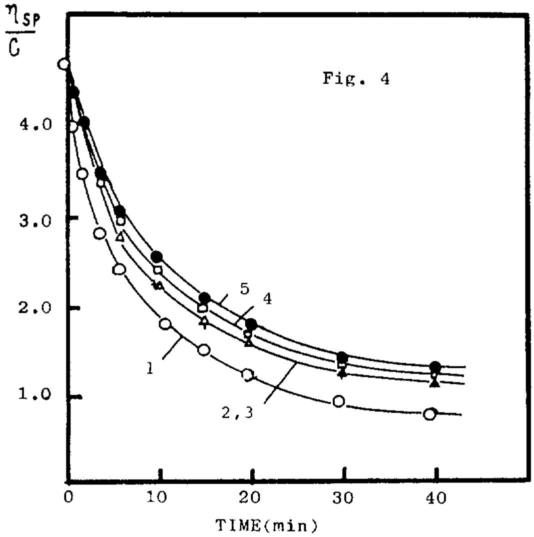


Fig. 4

Viscosity Decrease of the PB Solution as a Function of Irradiation Time in the Presence and Absence of Ultraviolet Stabilizer. Concentration of Rubber (PB) Solution: 0.01 gram Poly-cis-1,4-butadiene-1,3; 1 Molar in Chloroform.

1 - without Ultraviolet Absorber.
2-5 - with: 2.) Monomer 1
3.) Homopolymer 2
4.) Styrene-Copolymer 3
5.) Methyl Methacrylate-Copolymer 4
Concentration: $1x10^{-4}$ Molar.

Conclusions: Measurements of the ultraviolet absorption spectra and the fluorescence emission spectra are useful for understanding and evaluating the efficiency of photostabilization of polymerizable and polymer-bound ultraviolet stabilizers. The spectral behavior of the 2(2-hydroxyphenyl)2H-benzotriazoles studied in this work agree well with the results obtained from testing directly these ultraviolet stabilizers for their photostabilizing efficiency on a selected type of polymer (PB).

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