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Synthesis of 2-(2-Hydroxyphenyl)-2*H*-benzotriazole Monomers and Studies of the Surface Photostabilization of the Related Copolymers

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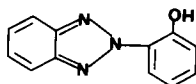
ABSTRACT: An improved three-step process for the synthesis of 2-(vinylhydroxyphenyl)-2*H*-benzotriazole derivatives is discussed. In addition, some studies of the surface photooxidation of styrene/vinylbenzotriazole copolymers were carried out. The results indicate that the 2-(vinylhydroxyphenyl)-2*H*-benzotriazole derivatives, whether used as an additive or introduced into the polymer chain, are unsuitable as a photostabilizer for the surface of polystyrene while the bulk of polystyrene is protected when very low concentrations of the derivatives are used.

Introduction

For most commercial polymers (acrylics, cellulose, polyesters, polystyrene, poly(vinyl chloride), etc.), some type of photostabilization is required in order to protect such materials against the effect of UV irradiation. For example, after a few weeks of exposure to sunlight, polypropylene deteriorates severely and unsaturated polyesters yellow.

Several types of heat and light stabilizers can be employed:¹⁻¹⁶ (a) UV screeners; (b) UV absorbers; (c) excited-state quenchers; (d) free radical scavengers and/or hydroperoxide decomposers. The choice of satisfactory photostabilizers for light exposure depends upon the end use to which the polymer is put. Generally, a combination of different additives is necessary to obtain a synergistic effect.

2-(2-Hydroxyphenyl)-2*H*-benzotriazoles have been indicated as powerful ultraviolet-absorbing molecules, and a number of compounds with this basic structure have been synthesized and used as UV absorbers.^{2-4,17-19}



When the surface to volume ratio is high, as in films, coatings, and fibers, such additives, because of their low molecular weights, may exhibit low compatibility and can also be lost by exudation, volatilization, or leaching during fabrication or end use. In recent years, a significant

effort has been made to prepare stabilizers with better compatibility and higher molecular weight by introducing long alkyl chains into the additive molecule² or by synthesizing the appropriate monomer and copolymerizing it into the polymer backbone.²⁰⁻³⁰

Methods have been reported in the literature for the synthesis of such monomers; the most important structures are shown in Table I. These monomers have been then introduced by random copolymerization or by grafting. Styrene, acrylates, and butadiene derivatives of (vinylhydroxyphenyl)-2*H*-benzotriazoles have been obtained in this way.

It has not yet been demonstrated whether the presence of a photostabilizing moiety in the surface (outermost 50 Å) is capable of inhibiting surface photooxidation. In fact, ESCA studies on the surface photooxidation of commercial polymers such as polystyrene indicate that the extent and nature of the degradation are not typical of the bulk material and thus conventional photostabilizing substances may not be effective. In addition, the photostability of the appropriate stabilizer in the surface regions, where the partial pressures of oxygen and the photon flux are higher than those in the bulk material, may differ from that of the bulk material.

Polyesters containing low percentages of (hydroxyphenyl)-2*H*-benzotriazole in the chain have been studied by ESCA in earlier work.³¹ Initially, the ESCA analysis showed that the amount of nitrogen (arising from the UV stabilizer) on the surface layer was similar to that found by elemental nitrogen analysis of the bulk poly-

Table I

HVB monomer	copolymer applicatn	ref
	polyesters, polyamides, etc.	27
	polyesters, polyamides, etc.	27
	MMA, BA, St	22-24
	MMA, BA, St	23, 29
	MMA, BA, St	25

mer. After accelerated aging by vigorous photooxidation, where the polymer was excessively degraded at the surface, it was found that the nitrogen content of the surface layer had not decreased, indicating that the UV stabilizer had remained in place throughout the entire degradation process.

Recently, we have devised a simple three-step process for the preparation of 2-(vinylhydroxyphenyl)benzotriazoles.³² In this work this route has been improved and used to prepare different systems. In addition, we report the main results of work carried out in the last few years on the surface photooxidation of copolymers with styrene, methyl methacrylate, and butyl acrylate containing such moieties in the chain.³³⁻³⁵ Comments are also made on the fast photodegradation of such materials in the surface.

Results and Discussion

A simple three-step process for the preparation of 2-(2-hydroxyphenyl)benzotriazoles³² is reported in Scheme I. 2-Nitroaniline is used in the first step; the diazotization may be carried out under the usual conditions.

The Wittig reagent used in the past³² was a phosphonium salt, preferably derived from triphenylphosphine by reaction with a lower alkyl halide. In this work sodium amide has been used to neutralize the hydroxyl functionality and to produce the ylide. In particular, a commercial "instant ylide" (an equimolar amount of methyltriphenylphosphonium bromide/sodium amide) was used. Reaction times could be reduced (10 h as compared to 48 h), and many handling difficulties avoided. In addition, this increased the yield of this step and thus the overall yield (see Experimental Section). For example in the case of compound **1b** the yield was 60% as compared to 32% by past methods.³² Zinc dust in the presence of strong alkali such as sodium hydroxide solution, as a reducing agent, is suitable. This reaction is preferably carried out at about 0 °C. In order to synthesize monomer **2** we have carried out a Friedel-Crafts acylation on the azo compound followed by the Wittig reaction and ring closure reduction (Scheme I).

The monomers have been homopolymerized and copolymerized with styrene, methyl methacrylate, and butyl acrylate. It has been possible to carry out surface photooxidation studies by ESCA only on the styrene copol-

ymers since the presence of acrylate carbonyl functionalities did not allow us to follow the oxidation process by measurement of the increase in CO content.

Figure 1 shows the C_{1s} and N_{1s} core level spectra for the unexposed and irradiated films of the product obtained by the homopolymerization process of monomer **1**. The C_{1s} envelope for the unexposed film exhibits a principal photoionization peak centered at 285.0 eV due to carbon not bonded to oxygen or nitrogen. The shoulder on the higher binding energy side of this peak arises from carbon-oxygen and carbon-nitrogen environments. A $\pi \rightarrow \pi^*$ shake-up satellite diagnostic of unsaturation in the polymer is also present at a binding energy of 291.6 eV. The N_{1s} core level consists of two peaks centered at 400.0 and 402.6 eV with an intensity ratio of 2:1, respectively. The N_{1s}/C_{1s} area ratio for the unexposed film is 0.24:1, which is in close agreement with the theoretical value of 0.27 obtained from the N/C atomic ratio of the monomer and the relevant experimentally determined sensitivity factors.

On exposing such a homopolymer to UV in air, distinct changes in both the C_{1s} and N_{1s} core level spectra are observed. For the C_{1s} envelope the region on the higher binding energy side of the main photoionization peak at 285.0 eV becomes more complex due to the appearance of carbonyl (C=O) and carboxylate (O-C=O) functionalities. The contributions to the C_{1s} envelope arising from the various functionalities as a function of exposure times and the corresponding O_{1s}/C_{1s} and N_{1s}/C_{1s} area ratios are shown in Figures 2 and 3. From these data we conclude that there is an induction period of about 1 day before the onset of extensive oxygen uptake at the surface. After 3 days of exposure, oxidation begins to plateau, indicating a balance between further photooxidation and the desorption of low molecular weight species.

The N_{1s} envelope loses the 2/1 intensity ratio character of the unexposed polymer due to the appearance of a third component at a binding energy of 401.6 eV. Because of the relatively small range of chemical shifts exhibited by the more common nitrogen functionalities, a specific assignment of this new peak is not possible at this stage.³⁶ From the data in Figure 4, where the changes in the N_{1s} envelope during exposure are displayed, it is evident that the appearance of the new component is concomitant with the onset of extensive oxygen uptake at the surface (Figures 2 and 3). Although the nature of the nitrogen changes during photooxidation, the amount of nitrogen on the surface relative to carbon is, after extensive oxygen uptake, essentially the same as that for the starting material. This should not be taken to indicate that there is no loss of nitrogen during exposure, as previously reported,³¹ but rather to indicate the proportionality of carbon and nitrogen in the species desorbed from the surface.

Previous studies carried out on model compounds in solution have shown the formation of peroxycyclohexadienones and other products during the thermal and photochemical oxidations of such benzotriazoles derivatives.³⁷ If the reactions observed in such model systems occur also in the homopolymer undergoing photooxidation in the solid state, analogous or similar oxidation products might be formed, and such products could act as photosensitizers and enhance the rate of photooxidation of the polymer.

This hypothesis is supported by the fact that, whereas the homopolymer reaches a steady state with respect to oxygen uptake in 3-5 days of exposure, the copolymers containing different percentages of UV stabilizer moi-

Scheme I

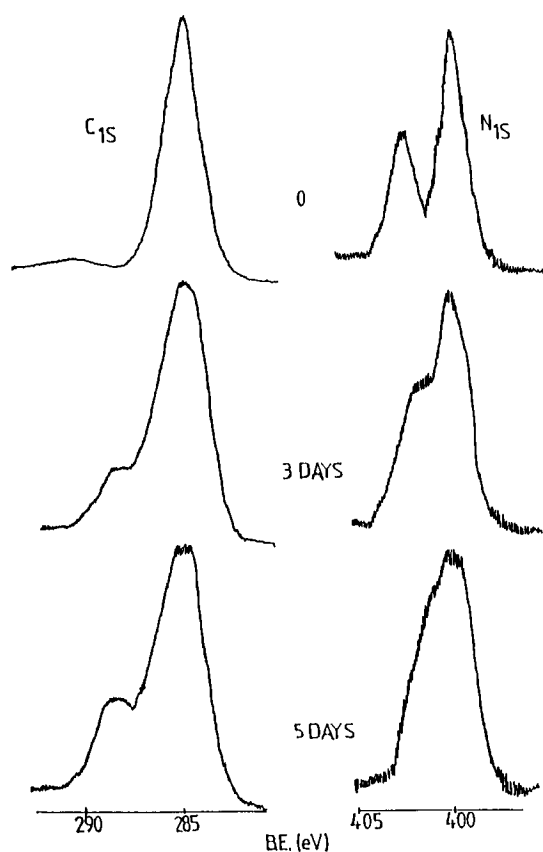
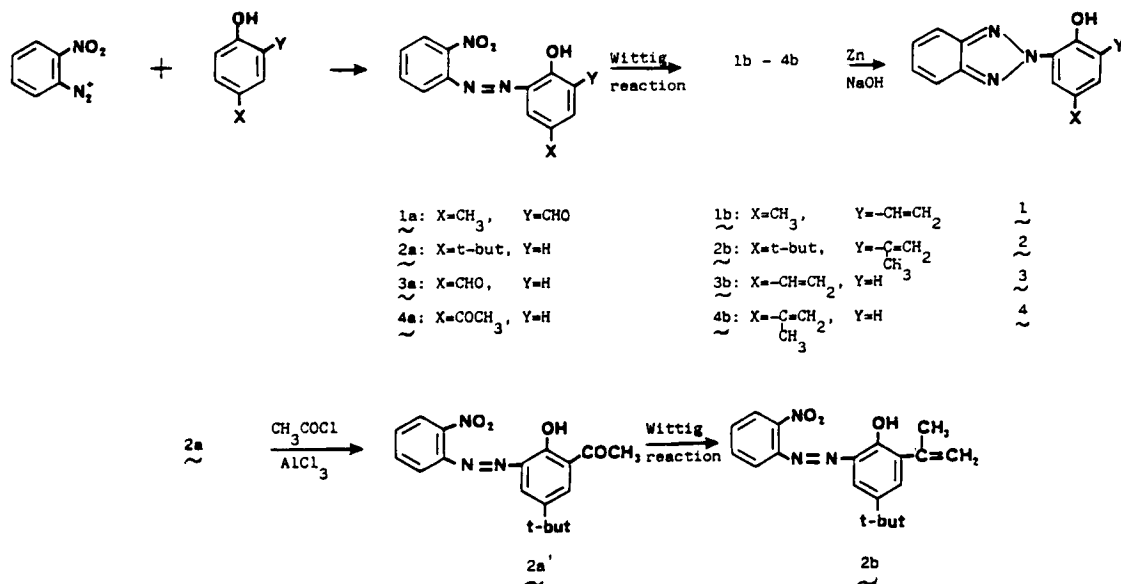


Figure 1. C_{1s} and N_{1s} core level spectra for unexposed and exposed homopolymer of monomer 1.

eties reach this condition in 5–8 weeks.^{33–34} In addition, the photooxidation behavior of such styrene/(vinyl-hydroxyphenyl)benzotriazoles copolymers was dependent on the concentration of the (hydroxyphenyl)benzotriazole molecules on the surface; i.e., oxygen uptake was more rapid as the content was increased. These observations suggest that there is the same interaction between such moieties on the surface of the homopolymer and copolymers which can result in an enhanced susceptibility to photooxidation. Such interactions could be due to a product similar to that observed for the model compounds.³⁷ When the concentration of the (hydroxyph-

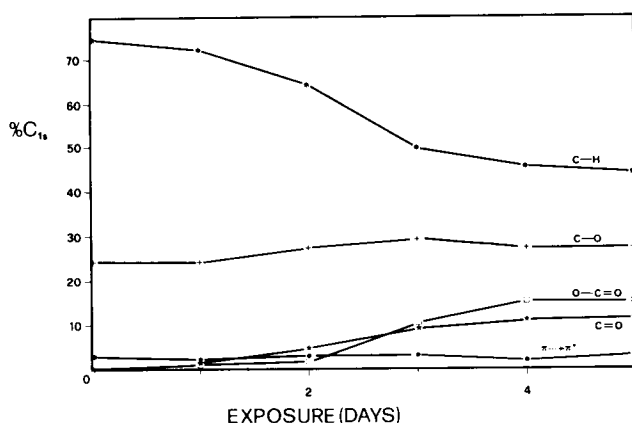


Figure 2. C_{1s} component contributions for homopolymer of monomer 1 as a function of UV exposure time.

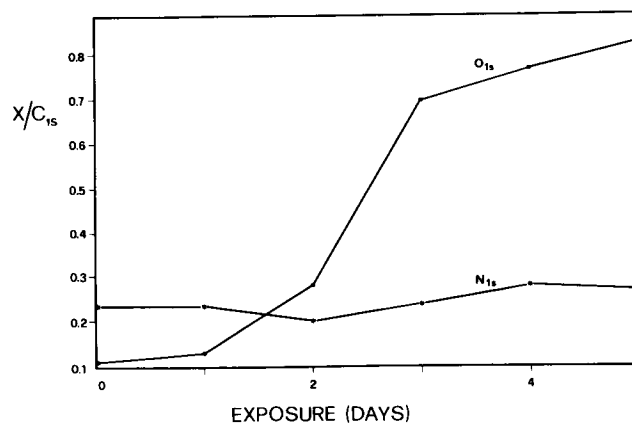


Figure 3. O_{1s}/C_{1s} and N_{1s}/C_{1s} area ratios for homopolymer of monomer 1 as a function of UV exposure.

nyl)benzotriazole molecules is low (i.e. 0.5% copolymer³⁴) and hence interactions negligible, the polymer surface photooxidizes at rates similar to that of polystyrene with 0.5% of (hydroxyphenyl)benzotriazole as an additive and to that of pristine polystyrene.³⁴

In conclusion, it is evident that such molecules, whether used as an additive or introduced into the polymer chain, are unsuitable as a photostabilizer for the surface of polystyrene while the bulk of polystyrene is protected when

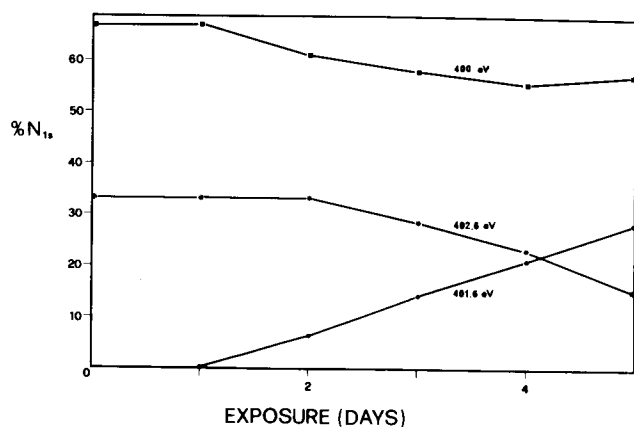


Figure 4. Changes in the component contributions to the N_{1s} spectra of homopolymer of monomer 1 during UV exposure.

very low concentrations of such molecules are used. It is known that useful commercial stabilization systems for polystyrene have been based on UV absorbers such as (hydroxyphenyl)benzotriazole compounds in the presence of antioxidants such as 2,6-di-*tert*-butyl-4-methylphenol to obtain a synergistic combination. We are therefore investigating by ESCA the surface photooxidation of the copolymers in the presence of such antioxidants in order to shed some light on the effective possibility of protecting properly the surface of such materials.

Experimental Section

Synthesis of Monomers 1–4 (Scheme I). 5-Methylsalicylaldehyde was prepared by refluxing a solution of *p*-cresol and chloroform for 30 min and a 50% (w/w) solution of sodium hydroxide and benzene in the presence of a catalytic amount of tri-*n*-butylamine (62% yield).³⁸

p-*tert*-Butylphenol, *p*-hydroxybenzaldehyde, and 4-hydroxyacetophenone were commercially available.

Preparation of the Azobenzenes 1a–4a. 2-Nitroaniline (0.10 mol) was added to concentrated HCl (40 mL), and the resulting mixture was warmed to 70 °C and then allowed to cool to room temperature. To this suspension was added a solution of sodium nitrite (0.10 mol) in distilled water (20 mL) dropwise at 0 °C with vigorous stirring. These conditions were maintained for 30 min, and then a small quantity (approximately 1 g) of urea was added to eliminate the unreacted nitrous acid.

The reaction mixture was filtered, and the solid was added slowly to a solution of the phenol (5-methylsalicylaldehyde or *p*-*tert*-butylphenol or 4-hydroxybenzaldehyde or 4-hydroxyacetophenone) (0.10 mol), sodium hydroxide (0.10 mol), and sodium carbonate (0.3 mol) in 300 mL of distilled water at 15 °C. The azo-coupling reaction was complete after 2 h. The reaction mixture was then filtered, and the red-brown solid was purified. The methods of purification, the melting points, and the yields are reported in Table II.

Acylation of Azobenzene 2a. 2-Nitro-2'-hydroxy-5'-*tert*-butylazobenzene (2a) (3 g, 0.01 mol) was added to a mixture of 4.4 mL (0.06 mol) of freshly distilled acetyl chloride and 8 g (0.06 mol) of anhydrous aluminum chloride in 100 mL of dichloromethane. The mixture was then allowed to react at the refluxing temperature for 24 h and then poured into a mixture of ice, HCl, and dichloromethane. The organic layer was then washed three times with water and dried with sodium sulfate. The method of purification, the melting point, and the yield of the azobenzene 2a' are reported in Table II as well as the $^1\text{H-NMR}$ data in Table III.

Preparation of Compounds 1b–4b. Sodium amide (0.023 mol) was added to a solution of 0.022 mol of azobenzene compounds (1a, 2a', 3a, and 4a) in 50 mL of dry tetrahydrofuran and the mixture stirred for 1 h in inert and dry atmosphere. The resulting solution was added to a slurry of 10 g (0.024 mol) of methyltriphenylphosphonium bromide/sodium amide (instant ylide)³⁹ in 50 mL of tetrahydrofuran freshly prepared. The mixture was stirred at room temperature for 10 h under nitrogen

Table II

compd	method of purification	mp, °C	yield, %
1	extraction with petroleum ether for 12 h	190–191	55
2a	none	57–58	70
2a'	elution with CH_2Cl_2 on silica gel	148–150	28
3a	elution with CH_2Cl_2 on silica gel	161–163	52
4a	elution with CH_2Cl_2 on silica gel	173–174	61
1b	elution with CHCl_3 /petroleum ether (50:50) on silica gel	111–112	60
2b	elution with CH_2Cl_2 /petroleum ether (60:40) on silica gel	89–90	52
3b	elution with CHCl_3 /petroleum ether (50:50) on silica gel	79–80	62
4b	elution with CHCl_3 /petroleum ether (50:50) on silica gel	95–96	45
1	elution with CHCl_3 /petroleum ether (70:30) on silica gel	109–110	49
2	elution with CHCl_3 /petroleum ether (70:30) on silica gel	92–93	45
3	elution with CHCl_3 /petroleum ether (70:30) on silica gel	112–113	48
4	elution with CHCl_3 /petroleum ether (70:30) on silica gel	124–125	43

Table III

$^1\text{H NMR}$ Chemical Shift Data^a for the New Compounds

compd	OH	ArH	COCH ₃	<i>t</i> -Bu	$\text{Ph}-\text{C}=\text{CH}_2$ CH_3	
2a'	13.11(s)	8.05–7.65(m)	2.75(s)	1.38(s)		
2b	12.89(s)	8.09–7.42(m)		1.36(s)	2.33(s)	5.47(m)
2	11.30(s)	8.36–7.31(m)		1.40(s)	2.26(s)	5.23(m)

^a Abbreviations: s, singlet; m, multiplet.

atmosphere and then poured onto crushed ice, neutralized carefully with dilute hydrochloric acid, and extracted with ethyl ether. The organic layer was separated, washed with water, and dried. The methods of purification, the melting points, and the yields are reported in Table II, and the $^1\text{H NMR}$ data are reported in Table III for the new compound 2b.

Preparation of Compounds 1b–4b. The monomers were obtained by reduction of 1b–4b with zinc and sodium hydroxide as described elsewhere.³² The methods of purification, the melting points, and the yields for compounds 1–4 are reported in Table II, and the $^1\text{H NMR}$ data for the new compound 2 are reported in Table III.

Synthesis of the Copolymers. The copolymers were synthesized following the procedures already described in literature.^{33–35}

UV Exposures. Polymer films were cast as thin films (0.5 μm) on stainless-steel probe tips used for the ESCA studies. They were exposed in air to the output from a black lamp ($\lambda > 300 \text{ nm}$; photon flux $\sim 0.25 \text{ W/m}^2$) for various periods of time.^{40,41}

ESCA spectra were recorded on a Kratos ES 300 electron spectrometer employing $\text{Mg K}\alpha$ X-rays. Binding energies were referenced to the C–H component in the C_{1s} spectra at 285.0 eV. Area ratios were computed with the aid of the Kratos DS 300 data system.

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Registry No. 1, 104585-00-4; 1 (homopolymer), 116803-05-5; **1a**, 114505-27-0; **1b**, 114505-28-1; **2**, 125846-37-9; **2a**, 27959-42-8; **2a'**, 125846-38-0; **2b**, 125846-34-6; **3**, 77865-92-0; **3a**, 125846-33-5; **3b**, 125846-35-7; **4**, 83739-91-7; **4a**, 93525-19-0; **4b**, 125846-36-8; methyltriphenylphosphonium bromide, 1779-49-3; sodium amide, 7782-92-5.