the fraction of acid–oxazoline AB species rises to a maximum at a blend composition of 50 mol % EMAA[44] and then decreases in the manner of a bell-shaped curve. The fraction of ABA species has the form of a skewed curve with a maximum value at about 66 mol % EMAA[44]—i.e., in EMAA-rich blends.

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Registry No. EMAA, 25053-53-6; PEOX, 25805-17-8.

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Notes

New Route to the Synthesis of 2-(2-Hydroxy-3-vinyl-5-methylphenyl)-2*H*-benzotriazole

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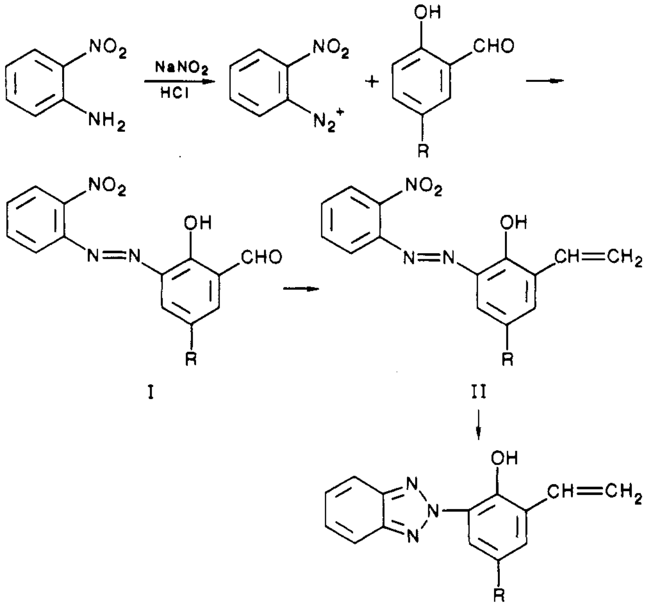
Introduction

Many polymers tend to degrade on prolonged exposure to ultraviolet light, and many classes of compounds, collectively referred to as "UV stabilizers", have been examined as additives to such polymers in attempts to improve the resistance of the polymers to degradation by ultraviolet light.

It is known[1] that compounds that comprise the 2-(2-hydroxyphenyl)benzotriazole group are particularly useful as UV stabilizers. However, there is a tendency for such 2-(2-hydroxyphenyl)benzotriazoles to be poorly compatible with polymer chains, with the result that they separate from the polymer and their effectiveness is reduced. It has been proposed[2] that the poor compatibility may be overcome by incorporating a vinyl substituent in the 2-(2-hydroxyphenyl)benzotriazole such that at least in the case of addition polymers, the UV stabilizers might be copolymerized into the polymer backbone. Methods have been reported in the literature[3,4] for the synthesis of 2-(2-hydroxyphenyl)benzotriazoles bearing such groups as methacryloylamino, acryloylamino, allyloxy, vinylsulfonyl, and vinyloxy groups, which allow such benzotriazoles to be copolymerized with conventional vinyl monomers. For example, the preparation of 2-(5-vinyl-2-hydroxyphenyl)benzotriazole by a six-step sequence and the copolymerization thereof with styrene and methyl methacrylate, as well as the synthesis of 2-(hydroxyphenyl)benzotriazole compounds having polymerizable unsaturated groups on the phenyl ring of the benzotriazole group, have been reported.[5]

Scheme I



We have now devised a simple three-step process for the preparation of 2-(vinylhydroxyphenyl)benzotriazoles.

Results and Discussion

The process for the preparation of 2-(vinylhydroxyphenyl)benzotriazoles is reported in Scheme I.

The suitable diazotized nitroaniline that is used in the first step of the process is 2-nitroaniline, and the diazo-

Table I
Conditions of Polymerization Experiments with 2-(2-Hydroxy-3-vinyl-5-methylphenyl)-2*H*-benzotriazole (III)

III charged[a]	comonomer type	comonomer amt, mmol	total amount,[a] mmol	solvt	η_{inh},[b]
0.80	St	7.11	7.91		0.58
0.59	St	28.80	29.39		0.44
0.14	St	28.80	28.94		1.20
1.00	MMA	9.00	19.00	toluene, 2 mL	0.31
0.40	MMA	19.60	20.00	toluene, 2 mL	0.39
0.15	MMA	29.80	29.95	toluene, 3 mL	0.83

[a] In millimoles. [b] $C = 0.5$ g/dL in $CHCl_3$, $T = 30$ °C.

tization may be carried out under the usual conditions.

The Wittig reagent used in the second step is a phosphonium salt that is preferably derived from triphenylphosphine by reaction with a lower alkyl halide.

The suitable reducing agent used in the third step is zinc dust in the presence of strong alkali, such as aqueous sodium hydroxide solution. Such a reaction is preferably carried out at about 0 °C.

This route has been used for the synthesis of 2-(2-hydroxy-3-vinyl-5-methylphenyl)-2*H*-benzotriazole with yields of 54%, 34%, and 45% for the three steps, respectively (see the Experimental Section).

To test the effectiveness of monomer III, we have copolymerized it with styrene and methyl methacrylate. The relevant inherent viscosities of the copolymers are reported in Table I. The viscosities are significantly higher than those reported by using monomers containing the vinyl group on the phenyl ring of the benzotriazole group.[5]

In conclusion, the proposed route allows the introduction of the vinyl functionality in the benzotriazole ring in only three steps. In addition, the copolymers obtained by using monomer III as copolymerizing agent enable higher molecular weights to be obtained.

Investigations of the surface photooxidation of the styrene type copolymers have been recently reported,[6,8] and further studies on the bulk and surface photooxidation of all the materials described in this report are in progress.

Experimental Section

5-Methylsalicyl Aldehyde. The Duff reaction was carried out on *p*-cresol by following the procedure described in the literature:[7] ^1H NMR ($CDCl_3$, TMS) δ 2.32 (3 H, s, CH_3), 6.68–7.38 (3 H, m, ArH), 9.85 (1 H, s, CHO), 10.82 (1 H, s, OH).

Preparation of 2-Nitro-2′-hydroxy-3′-carbonyl-5′-methylazobenzene. 2-Nitroaniline (14.2 g, 0.10 mol) was added to concentrated hydrochloric acid (40 mL), and the resulting mixture was warmed to 70 °C and then allowed to cool to room temperature. To this suspension a solution of sodium nitrite (7.1 g) in distilled water (20 mL) was added 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 5-methylsalicylaldehyde (14.0 g, 0.10 mol), sodium hydroxide (2.05 g), and sodium carbonate (27 g) in distilled water (300 mL) at 15 °C. The azo-coupling reaction was complete after 5–6 h. The reaction mixture was then filtered, and the brown solid product was purified by recrystallization from $EtOH/CH_2Cl_2$, yielding 8.1 g of pure product (54% yield), mp 189–191 °C.

The IR spectrum (KBr) of the pure product showed absorptions at 3300–3600 (OH), 2825 (aldehydic CH), 1680 (aldehydic C=O), and 1520 and 1340 cm^{-1} (asymmetric and symmetric N=O). The proton magnetic resonance spectrum ($CDCl_3$, TMS) of the pure product had signals at δ 2.43 (3 H, s, CH_3), 7.61–8.08 (6 H, m, ArH), 10.47 (1 H, s, CHO), and 12.58 (1 H, s, OH). Microanalysis of the pure product gave the following results: C, 59.16; H, 4.27; N, 14.20 (calcd for $C_{14}H_{11}N_3O_4$: C, 58.94; H, 3.86; N, 14.73).

Preparation of 2-Nitro-2′-hydroxy-3′-vinyl-5′-methylazobenzene. 2-Nitro-2′-hydroxy-3′-carbonyl-5′-methylazobenzene (6.6 g, 0.023 mol), potassium *tert*-butoxide (5.94 g, 0.0483 mol), and dried tetrahydrofuran (50 mL) were mixed in a four-neck round-bottom flask that had been flame-dried. To this mixture, cooled in an ice bath, a suspension of methyltriphenylphosphonium bromide (8.44 g, 0.023 mol) in dried THF (40 mL) was added slowly with vigorous stirring. The mixture was allowed to react under nitrogen atmosphere and vigorous stirring for 48 h. It was then added dropwise to water, neutralized with hydrochloric acid, and extracted with ethyl ether.

After drying over Na_2SO_4, the solvent was distilled under reduced pressure, and the product was purified by column chromatography. A pure product (2.2 g, 34% yield), mp 110–112 °C, was obtained. The IR spectrum (KBr) showed absorptions at 3300–3600 (OH) 1630, 1600, and 1570 (olefinic C=C stretch), 970 and 920 (olefinic C–H bend), 1520 and 1330 (N=O stretch), and 1420 cm^{-1} (olefinic C–H). The proton magnetic resonance spectrum ($CDCl_3$, TMS) had signals at δ 2.37 (3 H, s, CH_3), 5.36, 5.85, 7.10 (3 H, ABX system, $CH{=}CH_2$), 7.44–8.13 (6 H, m, ArH), 12.80 (1 H, s, OH). Microanalysis of the product gave the following results: C, 62.79; H, 4.84; N, 13.50 (calcd. for $C_{15}H_{13}N_3O_3$: C, 63.60; H, 3.86; N, 14.73).

Preparation of 2-(2-Hydroxy-3-vinyl-5-methylphenyl)-benzotriazole. Fine zinc dust (27 g) was added portionwise over 20 min to a mixture of 2-nitro-2′-hydroxy-3′-vinyl-5′-methylbenzene (1.5 g, 0.005 mol) and 2 N aqueous sodium hydroxidde solution (14 mL); 25% w/w aqueous sodium hydroxide solution (28 mL) was then added to the reaction mixture.

During both additions the reaction mixture was cooled with an ice bath and vigorously stirred. The reaction was allowed to proceed at room temperature with stirring for 2 h. After reaction was complete, the reaction mixture was neutralized with concentrated HCl to pH 7. The mixture was filtered to remove the unreacted zinc dust, and the solid was washed with dichloromethane. The filtrate was acidified to pH 1–2, and the organic phase was separated and dried over anhydrous $CaCl_2$. The solvent was then removed by rotary evaporation to leave a crude product, which was recrystallized from methanol yielding pure monomer (0.62 g, 45% yield), mp 108–110 °C. The IR spectrum (KBr) showed absorptions at 3300–3600 (OH) and 1630 and 1510 cm^{-1} (C=N stretch). The proton magnetic resonance spectrum ($CDCl_3$, TMS) had signals at δ 2.40 (3 H, s, CH_3), 5.37, 5.85, 7.20 (3 H, ABX system, $CH{=}CH_2$), 7.45–8.17 (6 H, m, ArH), and 11.53 (1 H, s, OH). Mass spectral data (70 eV) confirm the proposed structure with the parent ion at *m/z* 251. Microanalysis gave the following results: C, 71.2; N, 16.9; H, 5.4 (calcd for $C_{15}H_{13}N_3O$: C, 71.7; N, 16.7; H, 5.2).

Preparation of the Copolymers. The copolymers were synthesized following the procedures already described in literature.[5,6,8]

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Registry No. I (R = CH_3), 114505-27-0; II (R = CH_3), 114505-28-1; III (R = CH_3), 104585-00-4; (III (R = CH_3))(St) (copolymer), 104585-01-5; (III (R = CH_3))(MMA) (copolymer), 114505-57-6; 2-nitroaniline, 88-74-4; 5-methylsalicylaldehyde, 613-84-3; methyltriphenylphosphonium bromide, 1779-49-3.

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