Monatshefte für Chemie 113, 603—622 (1982)

Monatshefte für Chemie
Chemical Monthly

Functional Polymers. XII[a, b]: Synthesis and Polymerization of 2(2-Vinyl-4-hydroxyphenyl)2*H*-benzotriazole and 2(3-Vinyl-4-hydroxyphenyl)2*H*-benzotriazole

Shohei Yoshida, **C. Peter Lillya**[c], and **Otto Vogl***

Polymer Science and Engineering Department, University of Massachusetts,
Amherst, MA 01003, U.S.A.

(Received 9 November 1981. Accepted 3 December 1981)

Condensation of diazotized *o*-nitroaniline with 3-ethylphenol or with 2-ethylphenol followed by reduction of the resulting azo compound with zinc dust in sodium hydroxide solution gave 2-(2-ethyl-4-hydroxyphenyl)2*H*-benzotriazole and 2(3-ethyl-4-hydroxyphenyl)2*H*-benzotriazole, respectively. The individual compounds were acetylated, brominated with *N*-bromosuccinimide to the corresponding 1-bromoethyl compounds which were then dehydrobrominated with triethyl amine in acetonitrile and hydrolyzed to 2(2-vinyl-4-hydroxyphenyl)2*H*-benzotriazole or 2(3-vinyl-4-hydroxyphenyl)2*H*-benzotriazole. The two monomers could be polymerized and copolymerized with styrene and methyl methacrylate. The ethyl as well as the vinyl compounds and the corresponding polymers, when tested, are ineffective as ultraviolet absorbers as they have structures of 4-hydroxyphenyl rather than 2-hydroxyphenyl compounds with respect to the benzotriazole ring. A careful NMR analysis for the correct structural assignment is also described.

(Keywords: Benzotriazole formation; NMR-structure analysis; Polymerization and copolymerization; Ultraviolet absorbers; 2[2-Vinyl-4-hydroxyphenyl]2H-benzotriazole; 2[3-Vinyl-4-hydroxyphenyl]2H-benzotriazole)

Funktionelle Polymere, XII: Synthese und Polymerisation von 2(2-Vinyl-hydroxyphenyl)2H-benzotriazol und 2(3-Vinyl-4-hydroxyphenyl)2H-benzotriazol

Diazotiertes *o*-Nitroanilin wurde mit 3-Ethylphenol bzw. mit 2-Ethylphenol kondensiert. Reduktion der Diazoverbindung mit Zinkstaub in Na-

---

[a] This paper is dedicated to Professor *George Butler* on the occasion of his 65th birthday, with best personal wishes.

[b] Part XI: *S. Yoshida* and *O. Vogl*, Makromol. Chem., in press.

[c] Department of Chemistry, University of Massachusetts, Amherst, MA 01003, U.S.A.

0026-9247/82/0113/0603/$ 04.00

triumhydroxid ergab 2-(2-Ethyl-4-hydroylphenyl)2*H*-benzotriazol, bzw. 2-(3-Ethyl-4-hydroxyphenyl)2*H*-benzotriazol. Nach Acetylierung der freien Phenolgruppe wurden diese Verbindungen mit *N*-Bromsuccinimid zu den entsprechenden 1-Bromethylverbindungen umgewandelt und daraufhin in Acetonitril mit Triethylamin dehydrobromiert. Darauf folgende Hydrolyse führte zu 2(2-Vinyl-4-hydroxyphenyl)2*H*-benzotriazol bzw. zu 2(3-Vinyl-4-hydroxyphenyl)2*H*-benzotriazol. Beide monomeren Verbindungen wurden sowohl homopolymerisiert als auch mit Styrol oder mit Methylmethacrylat copolymerisiert. Weder die Ethyl- noch die Vinylverbindungen oder deren Polymere erwiesen sich als UV-Stabilisatoren, eine Eigenschaft die den 2(2-Hydroxyphenyl)2*H*-Benzotriazolen eigen ist. Eine Methode der Strukturbestimmung mit Hilfe einer detaillierten NMR-Analyse wird ebenfalls beschrieben.

Introduction

Over the years extensive work has been carried out in our research effort to prepare polymerizable ultraviolet absorbers and to study polymeric UV absorbers and their effectiveness for protecting common plastic materials against photooxidation[1–5]. Vinyl derivatives of salicylic acids specifically their methyl esters[6,7], methyl 3-vinylsalicylate[8], methyl 4-vinylsalicylate[9] and methyl 5-vinylsalicylate[10] were synthesized. Derivatives of other important ultraviolet absorbing classes have been reported as, for example, 4′-vinyl-2,4-benzophenone[11] and 4-vinyl-α-cyano-β-phenylcinnamate[12,13]. Most recently the synthesis of 2(2-hydroxy-5-vinylphenyl)2*H*-benzotriazole has been accomplished[14,15].

The synthesis was accomplished with *o*-nitroaniline as the starting material. It was diazotized, condensed with 4-ethylphenol, the azo compound dissolved in sodium hydroxide solution and reduced with zinc powder to 2(2-hydroxy-5-ethylphenyl)2*H*-benzotriazole (2H5E). In preparation for the bromination of the methylene group of the ethyl substituent, the phenolic hydroxy group was acetylated and the acetyl compound successfully brominated with *N*-bromosuccinimide. Dehydrobromination yielded 2(2-acetoxy-5-vinylphenyl)2*H*-benzotriazole (2A5V) which was hydrolyzed to 2(2-hydroxy-5-vinylphenyl)2*H*-benzotriazole (2H5V).

It was the purpose of this work to investigate whether the condensation of 2-ethylphenol or 3-ethylphenol with the diazonium salt of *o*-nitroaniline could be used to synthesize 2(2-hydroxy-4-vinylphenyl)-2*H*-benzotriazole (2H4V) or 2(2-hydroxy-3-vinylphenyl)2*H*-benzotriazole (2H3V). It was uncertain whether the condensation of the diazonium salt of *o*-nitroaniline would occur in *ortho* or *para* position of 2-ethyl- or 3-ethylphenol. The condensation with 4-ethylphenol, where the *para* position is blocked by the ethyl group can occur only in the desired *ortho* position. In the case of a condensation with 2-ethylphenol or 3-ethylphenol, both *ortho* and *para* positions were open for condensation. As it will become apparent from the description in this paper, the condensation reaction actually led to the synthesis of the isomers 2(4-hydroxy-2 or 3-ethylphenyl)2*H*-benzotriazole (2E4H or 3E4H) obtained from *para*-condensation rather than the corresponding 2(2-hydroxy-3 or 5-ethylphenyl)2*H*-benzotriazoles (2H3E or 2H5E) from the *ortho* condensation of the diazonium salt to the phenolic hydroxyl group of the ethylphenols.

Experimental

Materials

2-Ethylphenol and 3-ethylphenol (Aldrich Chemical Co.), *o*-nitroaniline (Aldrich Chemical Co.), acetic anhydride (J. T. Baker Chemical Co.), dimethylformamide (*DMF*) (Aldrich Chemical Co.), zinc dust (Fisher Scientific Co.), alumina (neutral, Brockman Activity 1, 80 ~ 200 mesh) (Fisher Scientific Co.), and *N*-bromosuccinimide (*NBS*) (Eastman Kodak Co.) were used without purification.

Triethylamine (99%, Aldrich Chemical Co.) and tri-*n*-butylamine (97%, Aldrich Chemical Co.) were dried by heating to reflux for 5 h over potassium hydroxide pellets and distilled under reduced pressure.

Acetonitrile (J. T. Baker Chemical Co.) and dimethylacetamide (*DMAc*) (Aldrich Chemical Co.) were dried by heating to reflux for 3 h over phosphorus pentoxide and distilled.

Tetrahydrofuran (*THF*) (Aldrich Chemical Co.) was dried by heating to reflux for 5 h over calcium hydride and distilled.

Methyl methacrylate (*MMA*) (Eastman Kodak Co.), styrene (*St*) (AldrichChemical Co.), and *n*-butyl acrylate (*BA*) (Polysciences, Inc.) were distilled twice at 10 mm immediately before use to remove the inhibitors.

Picric acid (Eastman Kodak Co.) was dried at 0.05 mm for a day.

Azobisisobutyronitrile (*AIBN*) (Aldrich Chemical Co.) was recrystallized three times from dry methanol and dried for 1 day at 0.05 mm and room temperature.

Deuterated solvents: deuterated chloroform (min. 99.8% D, Norell Chemical Co.), acetone-d_6 (99.5% D, Aldrich Chemical Co.) and dimethylsulfoxide-d_6 (99.5% D, Aldrich Chemical Co.) were used as received.

Measurements

Infrared spectra were recorded on a Perkin-Elmer Model 727 Spectrophotometer.

Solid samples of low molecular weight compounds were measured as KBr pellets; low melting compounds were spread between hot sodium chloride plates; polymers were measured as films on sodium chloride plates, cast from chloroform solutions.

^{1}H NMR spectra of low molecular weight compounds were measured on a 60 MHz R-24 Hitachi Perkin-Elmer spectrometer. Polymers were measured on the same instrument at low scan speed (20 mm/min) and low concentration (3 wt/vol%).

The ^{13}C NMR spectra were measured on a Varian CFT-20 Spectrometer under complete proton decoupling. The measurements were carried out in 25%

or saturated deuterated chloroform solutions at room temperature with *TMS* as the internal standard.

Acquisition conditions were as follows: spectral width: 4000 Hz; number of transients: over 3600, acquisition time: 1.023 s; pulse width: 8 μs, pulse delay: 0.017 s, and data points: 8184.

Ultraviolet absorptions were measured on a Beckman MVI spectrometer in a double-beam servo mode. The sample solutions were held in 1.0 cm quartz cells. The maximum absorbances and corresponding wavelengths were determined by dialing in the wavelength and recording the absorbance value presented on the digital display.

Regular melting points were measured on a MEL-TEMP capillary melting point apparatus at 2 °C/min rate and are uncorrected.

Microanalyses were done by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

Preparations

Diazotation of o-Nitroaniline, Coupling with 2-Ethylphenol and Reductive Ring Closure: *o*-Nitroaniline (55.2 g, 0.4 mol) was diazotized, and the filtered diazonium solution coupled with 2-ethylphenol (49 g, 0.4 mol). The red azo compound in 400 ml of aqueous 2 *N*-sodium hydroxide (0.8 mol) was reductively ring closed with zinc dust (120 g, 1.84 mol) and gave crude 2(3-ethyl-4-hydroxyphenyl)2*H*-benzotriazole (3E4H) in 80% yield based on *o*-nitroaniline.

2(3-Ethyl-4-acetoxyphenyl)2H-benzotriazole (3E4A): 3E4H (90 g) was acetylated with acetic anhydride (400 ml, 4 mol) and 0.2 ml of sulfuric acid catalyst by allowing it to stand at room temperature for a few days. Ammonium acetate (1.0 g) was added, acetic acid and excess acetic anhydride were removed under reduced pressure and the product was distilled at 0.05 mm., b.p. 210 °C (33 g, 29%), which solidified readily. Vacuum fractionation followed by chromatography on a neutral alumina column (3 cm diameter, 3 cm length) and recrystallization at —78 °C gave needles of 3E4A (52%), m.p. 124 to 125.5 °C.

The ^{1}H NMR spectrum is listed in Table 2 and the ^{13}C NMR spectrum in Table 1.

Anal.: Calcd. for $C_{16}H_{15}N_3O_2$: C 68.31%, H 5.37%, N 14.94%. Found: C 68.14%, H 5.31%, N 14.89%.

2(3-Ethyl-4-hydroxyphenyl)2H-benzotriazole (3E4H): 3E4H was obtained by hydrolysis of the pure 3E4A. A solution of 3E4A (2.0 g, 7.1 mmol) in 25 ml of methanol was poured into a 5% aqueous solution of sodium hydroxide (24 g, 30 mmol); the fine suspension was heated to reflux for 5 h, and methanol was removed under reduced pressure. Acidification with 6*N*-HCl resulted in the precipitation of a solid which was collected by filtration, dried, decolorized, recrystallized from carbon tetrachloride and *n*-hexane to give white cylindrical crystals of pure 3E4H (60%), m.p. 148 to 149 °C.

The ^{1}H NMR chemical shift data are listed in Table 2 and the ^{13}C NMR chemical shift data in Table 1. The UV spectrum showed one strong absorption band at 310 μm.

Anal.: Calcd. for $C_{14}H_{13}N_3O$: C 70.28%, H 5.48%, N 17.56%. Found: C 70.13%, H 5.77%, N 17.34%.

Diazotization of o-Nitroaniline and Coupling with 3-Ethylphenol: A similar procedure was used for the preparation of 2(2-ethyl-4-hydroxyphenyl)2*H*-benzotriazole (2E4H), as has been used for the synthesis of 3E4H. The oily viscous crude material of 2E4H was obtained in about the same yield.

2(2-Ethyl-4-acetoxyphenyl)2H-benzotriazole (2E4A): A similar procedure was used for the synthesis of 2E4A; a yield of 37 g (32%) was obtained.

The crude solid was fractionally distilled under reduced pressure; the product was chromatographed and recrystallized from carbon tetrachloride and *n*-hexane to give white hexagonal crystals (60%), m.p. 68 to 69 °C.

The ^{1}H NMR data are listed in Table 2 and the ^{13}C NMR spectrum in Table 1.

Anal.: Calcd. for $C_{16}H_{15}N_3O_2$: C 68.31%, H 5.34%, N 14.94%. Found: C 69.02%, H 5.73%, N 15.28%.

2(2-Ethyl-4-hydroxyphenyl)2H-benzotriazole (2E4H): 2E4H was obtained by hydrolysis of pure 2E4A (2.0 g, 7.1 mmol), followed by recrystallization from chloroform/*n*-hexane to give 2E4H as white needles (60%), m.p. 103.0 to 104.0 °C.

The ^{1}H NMR chemical shift data are listed in Table 2 and the ^{13}C NMR spectrum in Table 1. The UV spectrum showed one strong absorption at 310 μm.

Anal.: Calcd. for $C_{14}H_{13}N_3O$: C 70.28%, H 5.48%, N 17.56%. Found: C 70.06%, H 5.66%, N 17.57%.

2[3(1-Bromoethyl)-4-acetoxyphenyl]2H-benzotriazole (3B4A): Crude distilled 3E4A (38 g, 0.13 mol), *NBS* (72 g, 0.21 mol) and 200 ml of carbon tetrachloride were heated in an oil bath to reflux temperature. *AIBN* (0.44 g, 2.7 mmol) was added every hour for 3 h as a catalyst to promote the radical bromination. The reaction progress was followed by ^{1}H NMR measurements of aliquots. After a reaction time of 3 h, the methyl proton resonance of the starting material had disappeared and a methine proton absorption of the bromoethyl group of the product appeared and increased simultaneously until an integration equivalent to 86% yield was reached.

The reaction mixture was filtered to remove unreacted *NBS* and succinimide. The combined organic solutions were washed with 5% aqueous solution of sodium bicarbonate and water, dried and concentrated to a volume of 100 ml, and poured into 500 ml of methanol. The yellow precipitate was filtered, washed with fresh methanol and dried at 0.05 mm; 47 g (96% yield) of brominated product was obtained (80% purity).

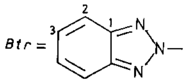
After recrystallization from hot ethanol and chromatography of the chloroform solution, a 60% yield of pure 3B4A was obtained; m.p. 168 to 169 °C.

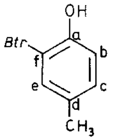
The ^{1}H NMR spectrum is shown in Table 2.

Anal.: Calcd. for $C_{16}H_{14}BrN_3O$: C 53.35%, H 3.92%, N 11.67%, Br 22.18%. Found: C 54.47%, H 4.00%, N 12.00%, Br 23.72%.

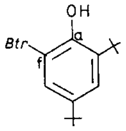
2[2(1-Bromoethyl)4-acetoxyphenyl]2H-benzotriazole (2B4A): 2E4A (87 g, 0.3 mol) was brominated using *NBS* (164 g, 0.92 mol) in 500 ml of carbon tetrachloride with *AIBN* (1 g, 6.1 mmol) as the catalyst. After 2 h the methyl proton chemical shift of the starting material had disappeared, and the methine proton absorption of the bromoethyl group of the reaction product had

Table 1. *Chemical shift data of ^{13}C NMR spectra*

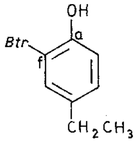




2H5M

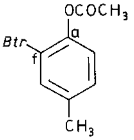


2H35B

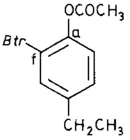


2H5E

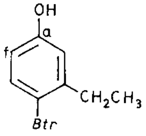
Assign-ment	Chemical Shift	Obs.		Calcd.	Obs.		Calcd.	Obs.		Calcd.
		Int.	CS	CS	Int.	CS	CS	Int.	CS	CS
Phenoxy Group	a	21	142.9	142.6	18	142.6	142.7	11	143.0	142.9
	b	65	118.8	116.4	15	138.6	138.5	55	118.9	116.5
	c	70	131.2	131.0	46	125.1	123.7	61	130.1	129.8
	d	21	129.4	131.2	18	141.6	144.0	10	136.1	137.6
	e	58	121.2	120.8	b		124.3	48	120.2	119.6
	f	8	125.0	122.3	43	116.2	114.9	6	125.1	122.4
Benzo-triazole Group	1	19	147.8		14	146.8		15	148.0	
	2	112	117.6		85	117.5		94	117.7	
	3	139	127.5		89	127.3		120	127.6	
Sub-stituent Group	$-CH_2-$					Int.	ppm	39	28.1	
	$-CH_2-\mathbf{C}H_3$				C	18	35.7	40	15.6	
	$-Ar-CH_3$	26	20.5		C	11	34.6			
	$-CO-\mathbf{C}H_3$				CH_3	107	31.6			
	$-CO$				CH_3	125	29.7			



2A5M



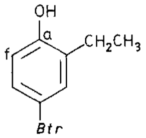
2A5E



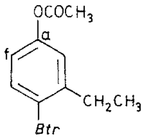
2E4H

Assign-ment	Chemical Shift	Obs.		Calcd.	Obs.		Calcd.	Obs.		Calcd.
		Int.	CS	CS	Int.	CS	CS	Int.	CS	CS
Phenoxy-Group	a	12	140.8	138.1	12	141.2	138.4	37	157.9	155.8
	b	74	125.9	122.1	74	124.7	122.2	64	116.6	116.0
	c	79	130.6	130.0	59	129.4	129.2	23	141.6	135.7
	d	19	136.9	135.3	17	143.2	141.7	13	132.8	127.4
	e	78	124.6	119.8	65	124.9	118.6	64	127.9	120.1
	f	7	132.5	128.0	6	132.8	128.1	61	113.8	113.8
Benzo-triazole Group	1	18	144.8		15	145.0		12	144.6	
	2	121	118.3		98	118.4		116	118.2	
	3	150	124.2		120	124.2		120	127.1	
Sub-stituent Group	$-CH_2-$				42	28.3		52	24.7	
	$-CH_2-\mathbf{C}H_3$				41	15.2		37	14.5	
	$-Ar-CH_3$	58	20.9							
	$-CO-\mathbf{C}H_3$				29	20.9				
	$-CO$	13	169.3		7	169.2				

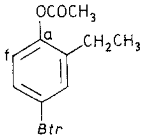
of various 2(hydroxyphenyl) benzotriazole derivatives[a]



3E4H

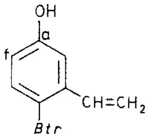


2E4A

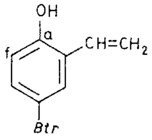


3E4A

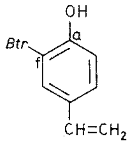
		3E4H			2E4A			3E4A		
Assignment	Chemical Shift	Obs. Int.	Obs. CS	Calcd. CS	Obs. Int.	Obs. CS	Calcd. CS	Obs. Int.	Obs. CS	Calcd. CS
	a	18	154.7	155.3	12	151.6	151.3	9	149.3	150.8
	b	15	131.7	132.1	55	122.9	121.7	17	137.3	137.8
Phenoxy-Group	c	48	122.0	119.6	16	141.1	134.7	54	121.6	118.6
	d	7	134.0	127.9	6	137.4	131.5	10	138.3	132.0
	e	48	119.7	117.4	57	127.5	119.1	57	119.2	116.4
	f	51	115.8	116.5	56	119.8	119.5	57	123.3	122.2
Benzo-triazole Group	1	20	144.8		15	144.9		17	145.2	
	2	91	118.1		101	118.4		104	118.4	
	3	110	127.0		120	126.9		120	127.1	
	$-CH_2-$	44	23.2		50	25.0		48	23.5	
Sub-stituent Group	$-CH_2-\mathbf{C}H_3$	32	13.8		37	14.4		38	13.9	
	$-Ar-CH_3$									
	$-CO-\mathbf{C}H_3$				29	21.0		31	20.7	
	$-CO$				12	108.6		12	168.8	



2V4H



3V4H



2H5V

		2V4H			3V4H			2H5V		
Assignment	Chemical Shift	Obs. Int.	Obs. CS	Calcd. CS	Obs. Int.	Obs. CS	Calcd. CS	Obs. Int.	Obs. CS	Calcd. CS
	a	20	159.4	155.7	18	153.9	153.5	17	142.8	144.8
	b	36	116.4	114.2	20	126.0	125.4	59[d]	119.1	116.4
Phenoxy-Group	c	12	135.5	129.0	47	119.8	117.8	69	128.0	128.0
	d	10	128.1	125.6	6	134.2	127.8	16	130.2	130.9
	e	41	128.8	120.0	44[c]	121.3	119.3	60[d]	119.0	117.8
	f	48	117.2	115.7	54	116.6	116.4	6	125.2	123.2
Benzo-triazole Group	1	8	145.7		18	144.9		17	149.4	
	2	56	119.0		102	118.2		92	117.6	
	3	78	127.6		107	127.0		120	127.2	
	$-CH_2-$									
Sub-stituent Group	$-CH_2-\mathbf{C}H_3-$									
	$-Ar-CH_3$									
	$-CO-CH_3$									
	$-CO$									
	$-CH=$	36	133.1		49	130.7		51	135.4	
	$-CH=\mathbf{C}H_2$	36	113.3		36[c]	117.3		56	113.0	

Calcd.: Calculated values. Obs.: Observed values. Int.: Relative intensity.
CS: Chemical Shift (ppm) from Si $(CH_3)_4$.

[a] Measured in acetone-d_6.

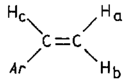
[b] Overlapped on c.

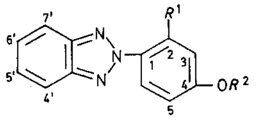
appeared and increased to indicate a 75% yield. 2B4A (85 g, 77%) was isolated and was purified as described for 3B4A with a final recrystallization from methanol to give a 28% yield. Yellow cylindrical crystals of 2B4A, m.p. 84 to 85 °C, were obtained.

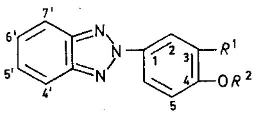
The ^1H NMR chemical shift data is shown in Table 2.

Anal.: Calcd. for $C_{16}H_{14}BrN_3O_2$: C 53.35%, H 3.92%, N 11.67%, Br 22.18%. Found: C 55.30%, H 4.22%, N 12.11%, Br 23.15%.

Table 2. *Chemical shift data of ^1H NMR spectra of 2- and 3-sub*

	R^2						
Compound	$—CH_2—\mathbf{CH_3}$	$—\mathbf{CH_2}—CH_3$	$CHBr—\mathbf{CH_3}$	$—\mathbf{CH}Br—CH_3$	a	b	c
2E4H	1.02 (t)	2.56 (d)	—	—	—	—	—
2E4A	1.10 (t)	2.76 (d)	—	—	—	—	—
2B4A	—	—	2.13 (d)	6.01 (d)	—	—	—
2V4A	—	—	—	—	5.35 (d)	5.78 (d)	6.90 (dd)
2V4H	—	—	—	—	5.28 (d)	5.75 (d)	6.75 (dd)
3E4H	1.32 (t)	2.75 (d)	—	—	—	—	—
3E4A	1.27 (t)	2.66 (d)	—	—	—	—	—
3B4A	—	—	2.14 (d)	5.35 (d)	—	—	—
3V4A	—	—	—	—	5.40 (d)	5.86 (d)	6.75 (dd)
3V4H	—	—	—	—	5.32 (d)	5.90 (d)	7.05 (dd)





2(3-Vinyl-4-acetoxyphenyl)2H-benzotriazole (3V4A): 3B4A (40 g, 0.10 mol) acetonitrile (200 g), triethylamine (67 g, 0.66 mol) and picric acid (2 g, 8.7 mmol) were heated rapidly to reflux temperature by immersing the flask in an oil bath. The reaction was monitored using ^1H NMR. After 4 h the mixture was cooled in an ice-water bath, acidified by the slow addition of 2*N*-aqueous hydrochloric acid and the product quickly extracted with carbon tetrachloride (to avoid hydrolysis). The dried organic phase after filtration and concentration under reduced pressure was recrystallized from carbon tetrachloride to give a yellow crystalline product: 13.7 g (35% yield).

To obtain polymerization grade product the compound was further purified by distillation: 3V4A (5.8 g, 21 mmol), cuprous chloride (0.1 g), copper powder (0.1 g) and picric acid (0.5 g) were charged in a 10 ml flask equipped with a magnetic stirrer and a *Claisen* head. To avoid the polymerization of 3V4A, the distillation was carried out quickly by immersing the flask into a hot oil bath (200 °C) and it was completed within 10 min at 0.005 mm. The distillate solidified and gave 3.2 g (54% yield) of a crystalline product in 97% purity, which was recrystallized from aqueous methanol.

The ^1H NMR chemical shift data are listed in Table 2.

2(2-Vinyl-4-acetoxyphenyl)2H-benzotriazole (2V4A): 2B4A (45 g, 0.12 mol) was dehydrobrominated in acetonitrile (200 g), with triethylamine (75 g, 0.74 mol) and picric acid (2 g, 8.7 mmol) as described above for the dehydrobromination of 3B4A. After 3 h a 84% yield was indicated. Normal work-up and recrystallization from carbon tetrachloride/acetone gave yellow crystals in 35% yield.

The ^{1}H NMR data is shown in Table 2.

stituted derivatives of 2(4-hydroxyphenyl)2H-benzotriazoles[a]

R^1		4-Hydroxyphenyl groups				Benzotriazole group	
OH	$\overset{O}{\overset{\|}{C}}CH_3$	2	3	5	6	5′, 6′	4′-7′
(7.6)	—	—	6.25 (d)	6.18 (d)	6.40 (d)	7.2 ~ 7.55	7.7 ~ 8.1
—	2.28 (s)	—	7.10 (d)	7.00 (dd)	7.60 (d)	7.2 ~ 7.55	7.8 ~ 8.1
—	2.30 (s)	—	7.64 (d)	7.22 (dd)	7.84 (d)	7.2 ~ 7.60	7.7 ~ 8.1
—	2.30 (s)	—	7.50 (d)	7.70 (dd)	7.61 (d)	7.3 ~ 7.7	7.8 ~ 8.2
9.7	—	—	7.28 (d)	6.98 (dd)	7.57 (d)	7.31-7.50	7.85-8.05
(5.9)	—	8.10 (d)	—	6.89 (d)	8.00 (dd)	7.20-7.60	7.75-8.10
—	2.30 (s)	8.25 (d)	—	7.16 (d)	8.18 (d)	7.2-7.5	7.7-8.0
—	2.37 (s)	8.52 (d)	—	7.22 (d)	8.25 (dd)	7.2 ~ 7.6	7.7-8.10
—	2.39 (s)	8.48 (d)	—	7.15 (dd)	8.29 (d)	7.20-7.50	7.65-7.90
10.3	—	8.03 (d)	—	7.04 (dd)	8.38 (d)	7.20-7.4	7.7-7.9

[a] Signal multiplicity in parenthesis following the chemical shift value (ppm), s = singlet, d = doublet, dd = doublet of doublets.

2(3-Vinyl-4-hydroxyphenyl)2H-benzotriazole (3V4H): 3V4A (6.0 g, 21 mmol) and picric acid (0.5 g, 2.2 mmol) were dissolved in acetone (20 ml). The solution was added to a 5% aqueous solution of sodium hydroxide, the resulting fine dispersion heated to 55 °C, and after 2 h the acetone was removed under reduced pressure. The solution was cooled to 0 °C, acidified with 2 *N*-hydrochloric acid; the reaction product was immediately extracted with chloroform from the aqueous phase.

Removal of the solvent and recrystallization from aqueous methanol gave 2.4 g (47% yield) of pure 3V4H, m.p. 154 to 156 °C.

The ^{1}H NMR chemical shift data are listed in Table 2 and the ^{13}C NMR data in Table 1.

Anal.: Calcd. for $C_{14}H_{11}N_3O$: C 70.87%, H 4.67%, N 17.71%. Found: C 69.63%, H 4.79%, N 17.28%.

2(2-Vinyl-4-hydroxyphenyl)2H-benzotriazole (2V4H): 2V4A (4.1 g, 14.5 mmol, 80% purity) was dissolved in acetic acid (20 ml) and 50 ml of 2 *N*-hydrochloric acid and picric acid (0.5 g, 2.2 mmol) were added. The suspension was heated to reflux temperature, and some methanol was added to obtain a homogeneous solution. After 2 h the mixture was cooled to give needle-like crystals which were washed with 50% aqueous methanol and dried; a total yield of 3.2 g (91%) was obtained.

Purification to produce polymer grade 2V4H was done by chromatography of the acetone solution of 2V4H over alumina and followed by recrystallization from acetone to give a white powder: 1.6 g (50% yield), m.p. 172 to 173.5 °C.

The ^1H NMR data is shown in Table 2 and the ^{13}C NMR spectrum (20% in acetone-d_6) in Table 1.

Anal.: Calcd. for $C_{14}H_{11}N_3O$: C 70.87%, H 4.67%, N 17.71%. Found: C 70.39%, H 5.08%, N 17.16%.

Polymerization

Polymerization of 2(2-Vinyl-4-hydroxyphenyl)2H-benzotriazole (2V4H). A 5 ml polymerization tube was charged with *AIBN* (0.66 mg, 0.004 mmol), 2V4H (0.47 g, 2.0 mmol), tetrahydrofuran (1.0 ml) and acetone (2.0 ml) in this order. After the mixture became homogenous, the tube was degassed by three freeze-thaw cycles with nitrogen gas sweeps, sealed at 0.005 mm, and placed in a constant temperature bath at 50 °C. After 60 h, the contents of the tube had separated into two liquid phases. The tube was opened and the contents were dissolved in 50 ml of *DMF*, filtered, and the solution poured into 500 ml of methanol. The resulting suspension was filtered and washed with fresh methanol. The collected polymer was dried at 0.005 mm and gave 0.32 g (68% yield).

Copolymerization of 2(2-Vinyl-4-hydroxyphenyl)2H-benzotriazole (2V4H) with Methyl Methacrylate (MMA). A 5 ml polymerization tube was charged with *AIBN* (2.95 mg, 0.018 mmol), 2V4H (0.32 g, 1.35 mmol), *MMA* (0.77 g, 7.65 mmol), tetrahydrofuran (0.5 ml) and acetone (1.0 ml). The homogeneous mixture was degassed, sealed at 0.005 mm, and placed in a constant temperature bath of 50 °C. After 60 h the tube was opened, the viscous solution was diluted with 50 ml of acetone, filtered and poured into 500 ml of methanol. The precipitated polymer was collected by filtration, washed with methanol and dried at 0.005 mm; a yield of 0.94 g (85%) was obtained.

The ^1H NMR spectrum of the polymer in deuterated mixed solvent of *DMSO* and $CDCl_3$ (1/3) showed δ 6.40 to 17.95 (aromatic protons), 2.85 to 3.90 (methoxy protons) and 0.30 to 2.35 (methyl, methylene and methine protons). From the ratio of the intensity of the methoxy protons to the aromatic protons, a copolymer composition of 16 mol % 2V4H units was determined.

Copolymerization of 2(2-Vinyl-4-hydroxyphenyl)2H-benzotriazole (2V4H) with n-Butyl Acrylate (BA). A 5 ml tube was charged with *AIBN* (2.30 mg, 0.014 mol), 2V4H (0.25 g, 1.05 mmol), *BA* (0.76 g, 5.95 mmol), *THF* (0.5 ml) and acetone (1.0 ml). The homogeneous mixture was degassed, sealed at 0.005 mm and placed in a constant temperature bath at 50 °C. After 60 h the tube was opened, the viscous solution was diluted with 50 ml of *THF* and the solution was precipitated into 500 ml of methanol. The sticky polymer which had precipitated was collected by filtration, and was dried at 0.05 mm to give 0.82 g (81%) of polymer.

The ^1H NMR spectra in deuterated chloroform showed δ 6.32 to 8.08

(aromatic protons), 3.32 to 4.32 (methylene protons adjacent to oxygen), 0.52 to 2.82 (methyl, methylene and methine protons). From the intensity ratio of the methylene protons adjacent to oxygen to aromatic protons, a copolymer composition of 18 mol % 2V4H units was determined.

Polymerization of 2(3-Vinyl-hydroxyphenyl)2H-benzotriazole (3V4H). Polymerization of 3V4H was carried out as described for the polymerization of 2V4H with *AIBN* (0.66 mg, 0.004 mmol), 3V4H (0.47 g, 2.0 mmol) and acetone (10 ml), 0.033 g (7% yield) of the homopolymer of 3V4H was obtained.

Copolymerization of 2(3-Vinyl-4-hydroxyphenyl)2H-benzotriazole (3V4H) with Methyl Methacrylate (MMA). Copolymerization of 3V4H (0.32 g, 1.35 mmol), *MMA* (0.77 g, 7.65 mmol) with *AIBN* (2.95 mg, 0.018 mmol) in acetone (1.0 ml) was carried out in a vacuum sealed tube for 2.5 days at 50 °C. After precipitation of the acetone solution of the polymer into 500 ml of methanol, filtration and drying under vacuum (0.005 mm), 0.86 g, (79% yield) of 3V4H-co-*MMA* was obtained.

The ^{1}H NMR spectrum in 1/3 mixture of deqterated *DMSO* and $CDCl_3$ showed δ 6.60 to 8.13 (aromatic protons), 2.55 to 3.95 (methyoxy protons), 0.40 to 2.45 (methyl, methylene and methine protons). From the intensity ratio of aromatic protons to methoxy protons, a copolymer composition of 14 mol % of 3V4H units was determined.

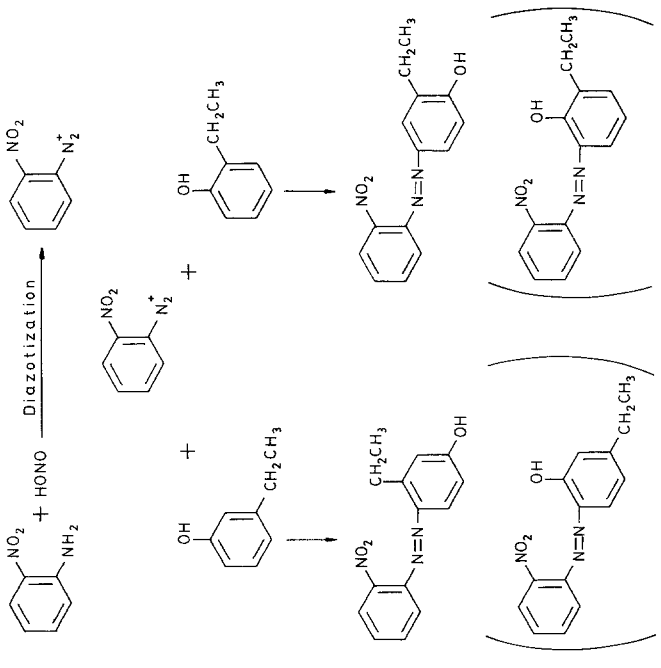
Copolymerization of 2(3-Vinyl-4-hydroxyphenyl)2H-benzotriazole (3V4H) with n-Butyl Acrylate (BA). Copolymerization of 3V4H (0.25 g, 1.05 mmol), *BA* (0.76 g, 5.95 mmol) with *AIBN* (2.30 mg, 0.014 mmol) in acetone (1.0 ml) was carried out in a vacuum sealed tube for 2.5 days at 50 °C. The mixture was dissolved in 10 ml of *THF*, filtered, and poured into 500 ml of methanol. The precipitated polymer was collected by filtration, washed with methanol and dried at 0.05 mm. The polymer was obtained in 65% yield (0.66 g) by freeze drying 10 ml of a benzene solution.

The ^{1}H NMR chemical shift data of the copolymer solution of this 1/3 mixture of *DMSO* and $CDCl_3$ showed δ 6.23 to 7.86 (aromatic protons), 3.15 to 4.35 (methylene protons adjacent to oxygen), 0.30 to 2.85 (methyl, methylene and methine protons). From the intensity ratio of the methylene protons adjacent to oxygen to aromatic protons, a copolymer composition of 12.5 mol % of 3V4H units in the poly(3V4H-co-*BA*) was determined.

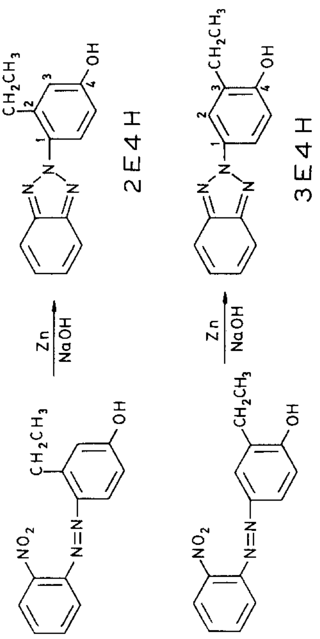
Results and Discussion

2V4H and 3V4H were prepared starting from diazotized *o*-nitroaniline and 2-ethylphenol or 3-ethylphenol, respectively. The condensation products were reduced and at the same time the benzotriazole ring was closed. The respective ethyl groups in the 2- and 3-positions of the benzotriazole ring were transformed into vinyl groups by bromination and dehydrobromination (Schemes 1-4).

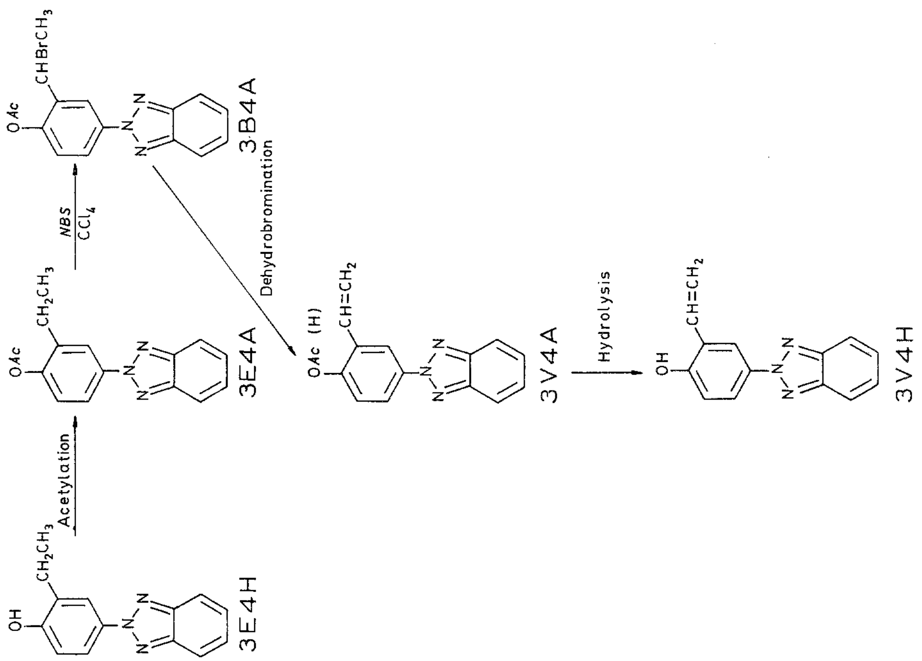
Scheme 1



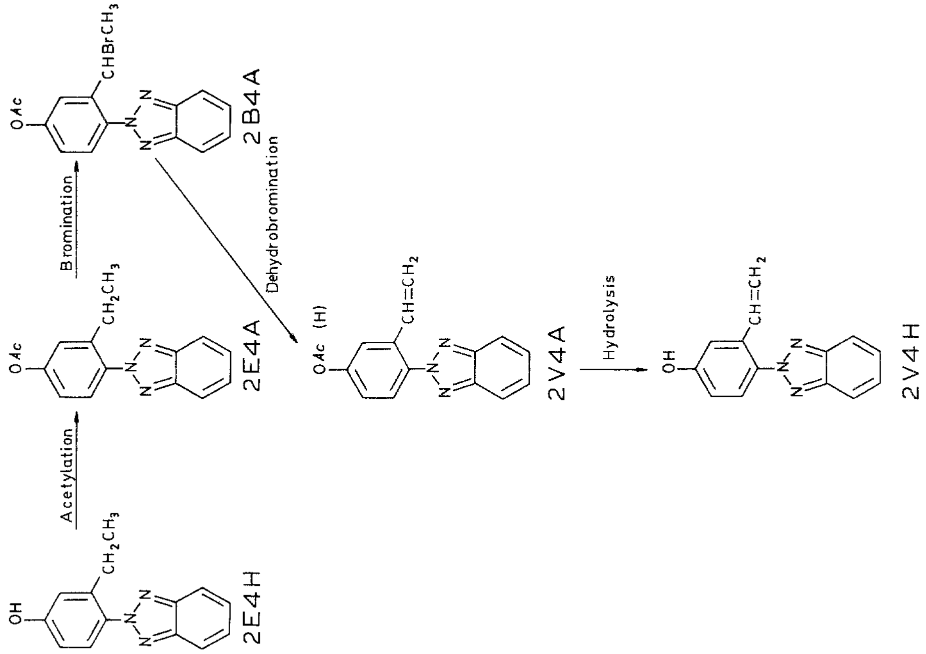
Scheme 2



Scheme 4



Scheme 3



Synthesis of 2(2-Vinyl-4-hydroxyphenyl)2H-benzotriazole and 2(3-Vinyl-4-hydroxyphenyl)2H-benzotriazole

When the diazotization of *o*-nitroaniline with sodium nitrite is complete and the ethyl phenol is added, the orange-red azo compounds precipitate; they were isolated and reduced with zinc and sodium hydroxide solution. The condensation of 2-ethylphenol and 3-ethylphenol was originally expected to give the *para*-condensation but also at least some of the *ortho*-condensation product. After reduction and cyclization, the *ortho*-condensation products were expected to give 2(2-hydroxy-3-ethylphenyl)2*H*-benzotriazole and 2(2-hydroxy-4-ethylphenyl)2*H*-benzotriazoles from which the corresponding vinyl compounds could have been prepared by bromination and dehydrobromination. These 2-hydroxyphenyl compounds were expected to give excellent polymerizable UV stabilizers with the hydroxy group in the appropriate 2-hydroxy position and the vinyl group in the 3- and 4-position of the phenol ring. Testing of our compounds revealed that none of them, neither monomers nor homo-or copolymers, were effective UV stabilizers. In our discussion of the NMR spectra we will show that condensation had occurred exclusively in *para*-position to give the 4-hydroxyphenyl compounds, with the ethyl group and ultimately the vinyl group in 2- or 3-position of the phenol ring. The 2(4-hydroxyphenyl)2*H*-benzotriazoles are not expected to be UV stabilizers, as the OH-group is not in *ortho* position to the triazole ring. Structural assignment and polymerization is the subject of this discussion. TLC analyses of the mother liquors of the reactions which led to the synthesis of 2E4H or 3E4H (obtained directly by reduction of the azo compounds) revealed that only one single compound, namely 2E4H and 3E4H had been obtained as the result of condensation *para* to the hydroxyl group. Within the accuracy of the TLC analysis no trace of the *ortho*-condensation product was found.

Details of the diazotization of *o*-nitroaniline and the condensation with 4-substituted phenols has been described in our earlier papers[15]. The condensation with the 2-ethylphenol and 3-ethylphenol as well as the reduction behaved in a qualitatively similar fashion. It was important to isolate, after the reduction, 2E4H or 3E4H by distillation in order to separate them from higher boiling condensation products.

The distilled compounds were immediately acetylated to the acetyl compounds, 2E4A and 3E4A, in yields of slightly higher than 50%. It was convenient to purify the acetyl compounds at this stage and to characterize them and the free phenols carefully, particularly by elemental analysis, and by ^1H NMR and ^{13}C NMR spectroscopy. The ^{13}C NMR chemical shift data of all compounds are described in Table 1. The detailed analysis of the NMR spectra is given below.

For subsequent bromination with *NBS*, the use of pure 2E4A and 3E4A is desirable although crude, but distilled 2E4A or 3E4A can also be used. Bromination was accomplished in refluxing carbon tetrachloride solution with a slight excess of *NBS* and with *AIBN* as the radical catalyst. The transformation of the ethyl group directly attached to an aromatic ring into a vinyl group can be readily achieved; mono-bromination of the *o*-acetyl phenol occurred exclusively in the methylene group even when a relatively large excess of *NBS* was used. The progress of the bromination can be measured by comparing the integrated ratio of the protons of the CHBr group to the aromatic protons. After about 3 h the starting material had disappeared as judged by the disappearance of the ethyl protons and reaction yields of approximately 85-90% bromination were estimated. Although a high yield of bromination products was obtained, it was difficult to isolate the bromo compound in high yield as the workup is relatively difficult and is accompanied by degradation.

Effective dehydrobromination of substituted 1-bromobenzyl derivatives is essential to introduce vinyl groups. Since the technique of dehydrobromination has been carefully studied previously for the preparation of the 2H5V and 2H5M5'V[15,19] the apparently best method was adapted for our dehydrobromination experiments. Dehydrobromination of 2B4A and 3B4A was achieved with acetonitrile and triethylamine in the presence of a small amount of picric acid. The dehydrobromination products have to be carefully purified in order to obtain polymerization grade 2V4H or 3V4H. First, crude 2V4A or 3V4A was dissolved in acetone and the vinyl compounds were hydrolyzed in 5% aqueous sodium hydroxide solutions. The yield in the last step was approximately 50%. After acidification of the basic solution, the 2V4H or 3V4H was immediately extracted with chloroform in order to avoid any polymerization or other side reactions. Hydrolysis of crude 2V4A could also be carried out in acetic acid solution with 1*N*-hydrochloric acid.

As in similar cases, it was important that distillations were carried out in a short path (Kugelrohr) distillation set-up rather than by regular fractional distillation through a small *Vigreux* column, in order to avoid, or at least to minimize the polymerization of the already formed vinyl compound. In most cases the 2V4A and 3V4A were not actually isolated but were immediately hydrolyzed to the corresponding 2V4H and 3V4H.

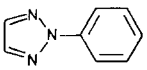
It is estimated that under the most favorable reaction conditions a 20-25% overall yield of 2V4H or 3V4H from *o*-nitroaniline was obtained.

Table 3. *Summary of the polymerization experiments of 2(2-Vinyl-4-Hydroxyphenyl)*

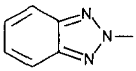
Monomer	Charged		Comomoner	Charged		Total of Monomer	
	g	(mmol)		g	(mmol)	g	(mmol)
2V4H	0.47	(2.0)	(Homopolymer)	0.47	(2.0)	0.47	(2.0)
2V4H	0.32	(1.35)	MMA	1.09	(9.0)	1.09	(9.0)
2V4H	0.25	(1.05)	BA	1.01	(7.0)	1.01	(7.0)
3V4H	0.47	(2.0)	(Homopolymer)	0.47	(2.0)	0.47	(2.0)
3V4H	0.32	(1.35)	MMA	1.09	(9.0)	1.09	(9.0)
3V4H	0.25	(1.05)	BA	1.01	(7.0)	1.01	(7.0)

To obtain polymerization grade monomer from 2V4H or 3V4H, further purification of the monomers has to be carried out, for example, by passing the monomer solution through a neutral alumina column to decolorize the product and to remove other impurities. Repeated recrystallization was also used to prepare polymerization grade monomers. In some cases the distillation of the crude vinyl compounds (2V4H or 3V4H) was more conveniently carried out with copper powder or copper salts as the inhibitors for polymerization rather than in the presence of picric acid. Picric acid is sometimes difficult to remove by recrystallization, therefore causing an inhibitory effect in subsequent polymerization.

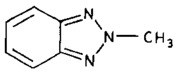
^{13}C chemical shift values for benzenoid carbons have been calculated. Shifts for 2-phenyl-1,2,3-triazole[16,17], **A**, have been used to estimate substituent chemical shifts for the benzotriazole substituent, **B**. The calculated chemical shifts along with relative intensity data allow assignment of the benzenoid carbon signals as reported in Table 1. The relative intensities and chemical shifts of the remaining aromatic signals conform closely to those expected for the benzotriazole moiety. Thus, the two sets of equivalent proton-bearing carbons, $C_2 + C_5$ and $C_3 + C_4$, exhibit the highest relative intensities in these spectra. Relative intensities for the non-proton-bearing set, $C_1 + C_6$, which experiences no nuclear *Overhauser* enhancement, are low. Observed chemical shifts, C_1 144.6–149.4, C_2 117.5–119.0, C_3 124.2–127.6 ppm are consistent with those of 2-methyl-1,2,3-benzotriazole, **C**, C_1 144.3, C_2 117.5, and C_3 125.9 ppm[18].



A



B



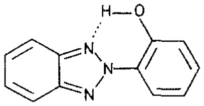
C

2H-benzotriazole (2V4H) and 2(3-vinyl-4-Hydroxyphenyl)2H-benzotriazole (3V4H)

Solvent for Polymerization in ml	Solvents for Polymer	Polymerization Yield g	(mmol)	Polymer Composition in mol% monomer unit
Acetone 2.0 *THF* 1.0	*THF/DMF*	0.32	(68)	
Acetone 1.0 *THF* 0.5	Acetone	0.94	(85)	16
Acetone 1.0 *THF* 0.5	*THF*	0.82	(81)	18
Acetone 1.0	Acetone	0.033	(7)	—
Acetone 1.0	Acetone	0.86	(79)	14
Acetone 1.0	$CHCl_3$/*THF*	0.66	(65)	13

Use of substituent chemical shift effects derived from monosubstituted benzenes to estimate shifts for polysubstituted benzenes is fraught with some risk. Effects of some substituent groups are a function of their conjugative interaction with the benzenoid pi electron system. Twisting such substituents out of the benzene ring plane diminishes conjugation and changes their chemical shift effects. Thus, *ortho* substituents which would cause twisting of the benzotriazole substituent out of the benzene ring plane should alter its chemical shift effects. The planar compound **A** will be a poorer model for such systems. *Begtrup* has demonstrated such conformational effects for several closely related systems including 1-phenylpyrrole, 1-phenylpyrazole, and 1-phenyl-1,2,3-triazole[16].

Agreement between our calculated and observed shifts is dependent on molecular structure in a way which is consistent with operation of such a conformational mechanism. All compounds which should have coplanar benzene and benzotriazole rings give excellent to good fits. The 2-hydroxyphenyl derivatives, 2H5M, 2H35B, and 2H5E, (Table 1) exhibit shifts which fall within 3 ppm of the calculated values. For most signals the difference is much less than 3 ppm. The *ortho*-hydroxy group has a small steric effect, and intramolecular hydrogen bonding would lock the two rings in a coplanar conformation, **D**.



D

Acylation of the hydroxy group, 2A5M and 2A5E, reduces the quality of fit at carbons e and f. Compounds which lack substituents *ortho* to the benzotriazole group, 3E4H, 3E4A, and 3V4H, should have coplanar rings and do exhibit good fits. With the exception of the C_d signals which are deshielded by 6 ppm more than we calculate, differences between calculated and observed shifts are less than 3 ppm. In contrast, compounds 2E4H, 2E4A, and 2V4H, which should have non-coplanar rings owing to the steric effect of substituents *ortho* to the benzotriazole ring, exhibit much poorer fits. The largest effect is felt at carbons *ortho* to the benzotriazole group, c and e, which are deshielded 6–9 ppm more than we calculate. This is in accord with *Begtrup*'s observation that the major effect of rotating azole type substituents out of a benzene ring plane was to deshield the *ortho* carbons[16]. The magnitude of these shifts was 4–5 ppm, smaller than the 6–9 ppm we observe for the benzotriazole substituent. ^{13}C shift data for additional 2-(2-hydroxy) and 2-(2-acetoxyphenyl)benzotriazoles, reported in a following paper[19], are in full accord with the analysis above.

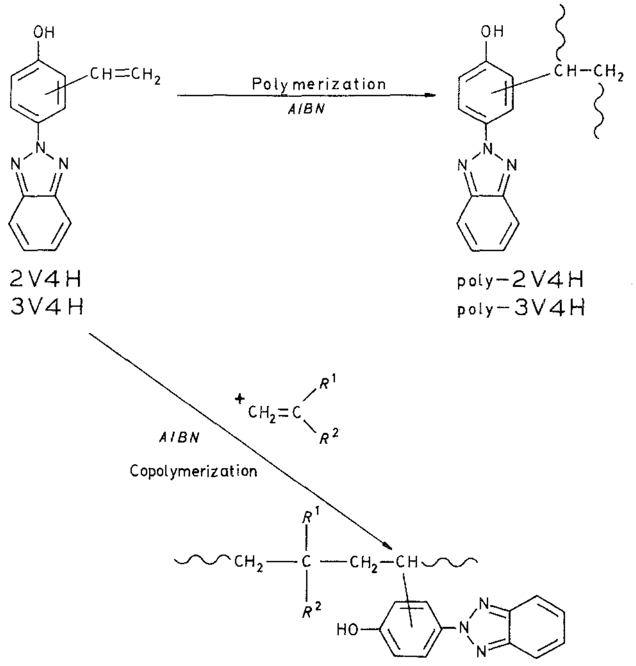
Taking specific conformational effects into account, we have derived a selfconsistent set of substituent chemical shifts which give calculated shifts which are in excellent agreement with experiments for all the compounds of this series. The parameters include special values for hydroxy and acetoxy, *ortho* to ethyl or vinyl, and for hydroxy and benzotriazole groups, *ortho* to each other. Owing to the probable narrow applicability of these parameters we do not reproduce them here.

Preparation and Characterization of Polymers and Copolymers of 2(2-Vinyl-4-hydroxyphenyl)2H-benzotriazole and 2(3-Vinyl-4-hydroxyphenyl)2H-benzotriazoles

As with other polymerizations where a free phenolic hydroxyl group is involved, the polymerization of 2V4H and 3V4H and the copolymerization of these compounds with styrene, *MMA* and *BA* had to be carried out in sealed glass tubes, completely excluding oxygen, otherwise the polymerization is inhibited. The results of the polymerization of these compounds are summarized in Table 3. The yields and inherent viscosities of these polymers should not be taken as the best results, obtainable under optimum conditions. In some cases, the polymerizations were carried out with relatively small amounts of not highly purified monomer (Scheme 5).

The polymerization of 3V4H and 2V4H were carried out in acetone in about 50% solution. For 2V4H, *THF* was used as cosolvent because the monomer is most readily soluble in acetone in the concentrations needed for copolymerizations. With the exception of the homopolymer of 3V4H all polymerizations gave good yields of polymer with adequately high inherent viscosity and molecular weight. The homopolymer of 2V4H was obtained in 68% yield while the copolymer of 2V4H with *MMA* was obtained in 85% and that with *BA* in 81% yield. The copolymer composition, analyzed from the ratio of aromatic and methoxy or methylene-oxy protons showed 16 and 18 mol % of 2V4H in the copolymer which compares to a 15 mol % feed ratio of 2V4H in the comonomers.

Scheme 5



R^1=H, R^2=C_6H_5: Styrene
R^1=CH_3, R^2=$COOCH_3$: Methyl methacrylate

Homopolymerization of 3V4H gave a low yield of poly 3V4H. Copolymers of 3V4H with *MMA* and *BA* were obtained in 79% and 65% yield respectively. The copolymer composition analyzed by comparing the aromatic protons to the methoxy or methylene-oxy protons showed a comonomer composition of 14 and 12.5 mol % respectively. This composition was obtained from a comonomer feed ratio of 15 mol % of 3V4H in each of the copolymerization reactions.

Acknowledgements

This work was supported by the Asahi Glass Company, Yokohama, Japan. *S. Y.* wishes to express his appreciation to the Asahi Glass Company for granting him a leave to work at the University of Massachusetts.

We would like to express our appreciation to *William Harris*, *Marie Hersman*, and *Paula Loeffler* for their assistance in the preparation of this manuscript.

References

[1] *Bailey D.*, *Vogl O.*, J. Macromol. Sci., Reviews, **C 14**, 267 (1976).

[2] *Tirrell D.*, *Bailey D.*, *Vogl O.*, Polymer Preprints, ACS Division of Polymer Chemistry **18**, 542 (1977).

[3] *Tirrell D.*, *Bailey D.*, *Vogl O.*, in: Polymeric Drugs (*Donaruma L. G.*, *Vogl O.*, eds.), p. 77. New York: Academic Press. 1978.

[4] *Vogl O.*, *Yoshida S.*, Preprints, Society of Polymer Science, Japan **29**, 648 (1980).

[5] *Vogl O.*, *Yoshida S.*, Rev. Roum. de Chimie **25**, 1128 (1980).

[6] *Heublein G.*, *Heublein B.*, *Heyroth B.*, *Bendel E.*, Z. Chem. **19**, 104 (1979).

[7] *Hartmann M.*, *Riedel B.*, *Wondraczek H.*, *Geschwend G.*, Z. Chem. **18**, 95 (1978).

[8] *Iwasaki M.*, *Tirrell D.*, *Vogl O.*, J. Polym. Sci., Polym. Chem. Ed. **18**, 2755 (1980).

[9] *Tirrell D.*, *Vogl O.*, Makromol. Chem. **181**, 2097 (1980).

[10] *Bailey D.*, *Tirrell D.*, *Vogl O.*, J. Polym. Sci., Polym. Chem. Ed. **14**, 2725 (1976).

[11] *Tirrell D.*, *Bailey D.*, *Pinazzi C.*, *Vogl O.*, Macromolecules **11**, 313 (1978).

[12] *Sumida Y.*, *Vogl O.*, Polymer J. (Japan), in press.

[13] *Sumida Y.*, *Yoshida S.*, *Vogl O.*, Polymer Preprints, ACS Division of Polymer Chemistry **21**, 201 (1980).

[14] *Yoshida S.*, *Vogl O.*, Polymer Preprints, ACS Division of Polymer Chemistry **21**, 203 (1980).

[15] *Yoshida S.*, *Vogl O.*, Makromolekulare Chemie, in press.

[16] *Begtrup M.*, Acta Chem. Scand. **27**, 3101 (1973).

[17] See also: *Ewing D. F.*, Org. Mag. Resonance **12**, 499 (1979).

[18] *Begtrup M.*, *Claramunt R. M.*, *Elgeno J.*, J. Chem. Soc., Perkin II **1978**, 99.

[19] *Yoshida S.*, *Lillya C. P.*, *Vogl O.*, J. Polym. Sci., Polym. Chem., in press.