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Functional Polymers. XXVII**: 2[2-Hydroxy-4-acryloxy(methacryloxy)phenyl]2*H*-benzotriazole: Monomers, Polymers, and Copolymers***

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2(2,4-Dihydroxyphenyl)2*H*-benzotriazole has been prepared in about 50% yield by condensation of *o*-nitrobenzenediazonium chloride with resorcinol followed by reductive cyclization of the initially obtained azo compound with zinc and sodium hydroxide. The condensation of the diazonium salt had to be carried out under carefully controlled conditions and in acidic medium, otherwise "bis"-condensation occurred which, after reductive cyclization, yielded 2(2,4-dihydroxyphenyl)1,3-2*H*-dibenzotriazole. 2(2,4-Dihydroxyphenyl)2*H*-benzotriazole was allowed to react with acryloyl or methacryloyl chloride. Monoacylation in the 4-position occurred by interfacial acylation technique and 2[2-hydroxy-4-acryloxy (or 4-methacryloxy)]2*H*-benzotriazole was obtained in over 60% yield. The two monomers were homopolymerized and copolymerized with styrene, methyl methacrylate, and *n*-butyl acrylate to polymers of high molecular weight. Incorporation of 2[2-hydroxy-4-acryloxy (or 4-methacryloxy)]2*H*-benzotriazole into the copolymer was from 1 to 10 mol% of the comonomer mixture. The ultraviolet spectra of monomers, homo- and copolymers were also determined.

[Keywords: 2(2-Hydroxyphenyl)2H-benzotriazole; Polymerizable stabilizers; Ultraviolet spectra]

** Part XXVI: *W. Dickstein* and *O. Vogl*, J. Macromol. Sci., Chem., in press.

*** This paper is dedicated to Professor Dr. *Karl Schlögl* on the occasion of his 60th birthday with our warmest wishes.

Funktionelle Polymere, 27. Mitt.: 2[2-Hydroxy-4-acryloxy (bzw. 4-methacryloxy)phenyl]2H-benzotriazol: Monomere, Polymere und Copolymere

2(2,4-Dihydroxyphenyl)2*H*-benzotriazol wurde mit 50% Ausbeute über die Kondensation von *o*-Nitrobenzoldiazoniumchlorid mit Resorcin, gefolgt von reduktiver Cyclisierung der ursprünglich erhaltenen Azoverbindung mit Zn/NaOH, erhalten. Die Kondensation des Diazonium-Salzes hatte unter sorgfältig kontrollierten Bedingungen und im sauren Medium zu erfolgen, da ansonsten „Bis"-Kondensation auftrat, die nach der reduktiven Cyclisierung 2(2,4-Dihydroxyphenyl)1,3-2*H*-dibenzotriazol ergab. 2(2,4-Dihydroxyphenyl)2*H*-benzotriazol wurde mit Acryoyl- bzw. Methacryloylchlorid zur Reaktion gebracht, wobei die Monoacetylierungsprodukte in über 60% Ausbeute gewonnen wurden. Die beiden Monomeren wurden homopolymerisiert und mit Styrol, Methylmethacrylat und *n*-Butylacrylat zu Polymeren hohen Molekulargewichts copolymerisiert. Die Inkorporierung von 2[2-Hydroxy-4-acryloxy (bzw. 4-methacryloxy)]2*H*-benzotriazol in das Copolymer erfolgte zwischen 1 und 10 mol% der Comonomer-Mischung. Die UV-Spektren der Monomeren, Homo- und Copolymeren sind angegeben.

Introduction

2(2-Hydroxyphenyl)2*H*-benzotriazoles with various substituents on the hydroxy substituted phenyl ring or the aromatic ring of the benzotriazole group have been shown to have outstanding properties as ultraviolet absorbers and stabilizers, especially for plastics materials[1—2]. Recently, 2(2-hydroxyphenyl)2*H*-benzotriazoles with polymerizable vinyl and isopropenyl groups have been reported as a novel class of permanent and effective ultraviolet stabilizers[3—8].

All well-known 2(2-hydroxyphenyl)2*H*-benzotriazole ultraviolet absorbers (stabilizers) are benzotriazolized derivatives of 4-substituted or 2,4-disubstituted phenols[9—11], substituted with alkyl, usually with methyl or tertiary butyl groups.

Early papers on the condensation of *o*-nitrobenzenediazonium chloride followed by reductive cyclization mentioned the preparation of benzotriazolized resorcinol[12, 13]. It was reported that a mono- and a dibenzotriazolized product had been identified. We have repeated this sequence of reactions and also obtained a mixture of two compounds which could be separated by laborious recrystallization into two products, the monobenzotriazolized compound 2(2,4-dihydroxyphenyl)2*H*-benzotriazole (*BDH*), m.p. 200 °C, and the dibenzotriazolized compound 2(2,4-dihydroxyphenyl)1,3-2*H*-dibenzotriazole (*DBDH*), m.p. 212 °C[14]. *BDH* was again prepared later[15], and the reaction of *BDH* with methacryloyl chloride for the synthesis of *BDHM* was studied. (There is no mention that *BDHA* had been prepared.)

As not uncommon in the patent literature, the work is not well documented, and the m.p. of *BDH* is given as 260 °C instead of 200 °C as we have determined;

we had also found the melting point of dibenzotriazolized resorcinol, *DBDH*, to be 212 °C. The melting point of *BDHM* is claimed in the patent to be 184 °C. In our hands, the melting point of fully characterized *BDHM* is 117–119 °C.

It was the object of this work to clarify the identity of *BDH*, to develop a high-yield synthesis of *BDH* free of other products, especially *DBDH*, so that even the crude compound could be used for further reactions. Reaction with acryloyl chloride or methacryloyl chloride was expected to give monomers for polymerization and copolymerization.

Experimental Part

A. Materials

o-Nitroaniline (Aldrich Chemical Co.) and resorcinol (Matheson, Coleman and Bell) were used as received.

Chloroform (Fisher Scientific Co.) was washed 3 times with 5% aqueous sulfuric acid, 3% aqueous sodium hydroxide solution, and water, dried over molecular sieves (Davidson Chemicals), distilled into a solvent storage bottle, and kept under nitrogen.

Methacryloyl chloride (Aldrich Chemical Co.), acryloyl chloride (Polysciences, Inc.), methyl methacrylate (*MMA*) (Eastman Kodak Co.), and *n*-butyl acrylate (*BA*) (Polysciences, Inc.) were distilled twice under reduced pressure (20 mm Hg) immediately before use. Styrene (*St*) (Aldrich Chemical Co.) was washed twice with 5% aqueous sodium hydroxide and twice with water to remove the inhibitor, and, after drying over calcium sulfate, it was distilled in a nitrogen atmosphere.

Azobisisobutyronitrile (*AIBN*) (Aldrich Chemical Co.) was recrystallized three times from absolute methanol and dried for one day at 0.01 mm Hg at room temperature.

Solvents such as benzene, ethanol, and methanol were used without distillation.

Deuterochloroform (min. 99.8% D) (Norell, Inc.) and dimethyl sulfoxide-d_6 (*DMSO*) (99.9% D) (Aldrich Chemical Co.) were used as received.

N,N'-Dimethyl acetamide (*DMAc*), when used as solvent for polymerization and for the measurements of inherent viscosities of the polymers, was reagent grade (Fisher Scientific Co.) and was used directly from freshly opened bottles.

B. Measurements

Infrared spectra were recorded on a Perkin-Elmer Spectrophotometer, Model 283. Solid samples were measured in the form of potassium bromide pellets.

^{1}H NMR spectra were recorded on a Varian A-60 spectrometer and ^{13}C NMR spectra on a Varian CTF-20 spectrometer with complete proton decoupling; *TMS* was used as the internal standard. The compounds were measured in deuterated *DMSO* in 15% or saturated solutions. Conditions for acquiring the spectra were as follows: spectral width: 4 000 Hz, number of transients: > 6 000, acquisition time: 1.023 s, pulse width: 19 s, pulse delay: 1.0 s, and data points: 8 184.

Ultraviolet absorptions were measured in chloroform solution (Spectrograde, Fisher Scientific Co.) or *DMAc* (Spectrograde, Eastman Kodak Co.) with a

Beckman MVI spectrometer in a double-beam servo mode (1.0 cm optical path length). The maximum absorbances and corresponding wavelengths were determined by dialing in the wavelength and recording the absorbance value presented on the digital display.

Melting points were determined on a MELT-TEMP Capillary melting point apparatus at a heating rate of 2 °C/min and are uncorrected.

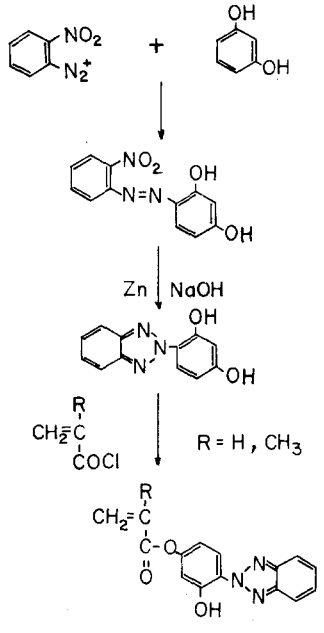
Microanalyses were carried out at the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

C. Procedures

1. Preparation of 4(2H-Benzotriazole-2-yl)1,3-Dihydrobenzene (BDH) [2-(2,4-Dihydroxyphenyl)2H-Benzotriazole] (Improved method for the preparation of monobenzotriazole-substituted resorcinol)

In a one liter beaker equipped with a mechanical stirrer, a fine solid dispersion of *o*-nitroaniline hydrochloride was prepared by rapidly quenching, with vigorous stirring, a warm solution of *o*-nitroaniline (55 g, 0.4 mol) in 150 ml of concentrated hydrochloric acid to 0 °C. Diazotization was carried out by dropwise addition of a solution of sodium nitrite (28 g, 0.4 mol) in water (100 ml) over a period of one hour at 0–5 °C. In the final stage of addition, the mixture became homogenous. Care was taken to avoid an excess of sodium nitrite. After the addition was completed, a small amount of insoluble material was removed by filtration, while the solution was maintained near 0 °C. The solution of the diazonium salt was added through a dropping funnel to a stirred solution (cooled

Scheme 1



to 5–10 °C) of resorcinol (44 g, 0.4 mol) in ethanol (400 ml) and water (400 ml) over a period of one hour. The azo compound separated immediately as red crystals; the reaction mixture was stirred at room temperature for 2 h, filtered, and the red solid was washed with water. The solid was dissolved in 600 ml of aqueous 2 *N* sodium hydroxide, the solution was placed in a cooled two-liter beaker, and zinc powder (120 g, 1.84 mol) was added in small portions over a period of 4 h to the mechanically stirred solution; a 40% aqueous solution of sodium hydroxide (150 ml) was also added over a period of 4 h at the same time.

The mixture was kept at room temperature for 3 days. After one day, the suspension changed color from red to green, which indicated that most of the azo compound had been reduced and cyclized. The suspension was decanted, the residue extracted twice (200 ml, 5% aqueous NaOH), the combined solution was cooled and then acidified to *pH* 2 with concentrated hydrochloric acid; the suspension containing a creamy precipitate was filtered, air dried, and extracted with ethanol in a *Soxhlet* extractor for two days. *BDH* was isolated from the ethanol extract in 50% yield (45 g). The compound was almost pure and had an m.p. of 198–200 °C. The ^{1}H NMR spectrum showed that it did not contain any *DBDH*. *BDH* was recrystallized from ethanol : water (1 : 1) and gave white needles, m.p. 199–200 °C.

2. *Monomer Preparations*

2(2-Hydroxy-4-Acryloxyphenyl)2H-Benzotriazole (BDHA)

Into a 500-ml three-neck flask, equipped with a mechanical stirrer and a funnel, was placed pure *BDH* (6.81 g, 0.03 mol) and sodium hydroxide (2.40 g, 0.06 mol) in water (250 ml); the mixture was stirred at room temperature until all the *BDH* was in solution.

Acryloyl chloride (2.75 ml, 0.033) in chloroform (50 ml) was placed in the dropping funnel and then added dropwise with vigorous stirring over a period of 1.5 h at room temperature into the aqueous sodium hydroxide solution of *BDH*. After the addition was completed, the reaction mixture was stirred at room temperature for 1 h. The chloroform layer was separated, washed twice with water, dried, and the chloroform was removed on a rotating evaporator. A yield of 6.25 g (74%) of *BDHA* was obtained.

Crude *BDHA* was dissolved in absolute ethanol; a small amount of insoluble material was removed by filtration, and the solution was chilled overnight in the refrigerator. Pale yellow crystals, m.p. 156–157 °C, were recovered in 75% yield.

The ultraviolet absorption data are presented in Table 2, and the spectrum in Figure 3 B; IR (KBr): 1 720 cm^{-1} ($\nu_{C=O}$ stretching).

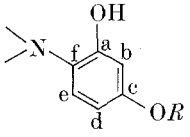
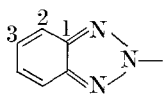
The ^{1}H NMR spectrum showed: δ 5.8 to 6.8 ppm (protons of phenoxy group, 3 H), 6.8 (—CH=, 1 H), 7.3 and 7.8 (protons of benzotriazole group, 4 H), 8.1 (=CH_2, 2 H), 11.2 (—OH, 1 H). ^{13}C NMR chemical shift data are presented in Table 1 and the spectrum in Figure 1.

Anal. Calcd. for $C_{15}H_{11}N_3O_3$: C 64.05, H 3.94, N 14.93. Found: C 63.62, H 3.88, N 14.89.

2(2-Hydroxy-4-Methacryloxyphenyl)2H-Benzotriazole (BDHM)

The synthesis of *BDHM* followed essentially the same procedure as described for the synthesis of *BDHA*. To the solution of *BDH* (2.27 g, 0.01 mol), sodium hydroxide (0.52 g, 0.0125 mol) and water (60 ml) were added dropwise to a solution of methacryloyl chloride (1.1 ml, 0.011 mol) in chloroform (30 ml) over a period of 1.5 h at room temperature under vigorous stirring.

Table 1. ^{13}C *NMR chemical shift data for 2[2-hydroxy-4-acryloxy(methacryloxy)phenyl]2H-benzotriazole*

Group Assignment	Chemical Shift	*BDHA* Obs. Cs	*BDHA* Calcd. Cs	*BDHM* Obs. Cs	*BDHM* Calcd. Cs	*Poly (BDHM)* Obs. Cs	*Poly (BDHM)* Calcd.[a] Cs
	a	151.2	151.3	150.7	151.0	150.9	150.7
	b	111.9	110.0	112.1	109.5	110.6	112.1
	c	150.6	155.6	152.2	155.3	151.2	152.2
	d	113.5	113.7	113.7	113.2	112.1	113.7
	e	122.0	124.9	123.1	124.6	124.6	123.1
	f	123.2	125.7	121.9	123.9	[b]	121.9
	1	142.7	143.2[c]	142.7	143.2[b]	142.8	142.7
	2	117.6	117.7	117.6	117.7[b]	117.4	117.6
	3	127.8	127.0[c]	127.8	127.0[b]	127.1	127.8
—**C**O—		163.9	165.5	165.3	167.7	174.9	
—**C**H=CH_2		127.5	128.7				
—CH=**C**H_2		133.2	130.5				
—**C**=CH_2				18.4	18.4		
—**C**=CH_2				135.7	136.8		
—C=C**H**$_2$				127.7	125.2		
—**C**H—CH_2—							
—CH—**C**H_2—							
—**C**—CH_2—						18.0[d]	
—**C**—CH_2—						45.5	
—C—**C**H_2—						53.0[d]	

[a] From *BDHM*. [b] Obscured by broadened peaks. [c] From *BDH*. [d] Broad.

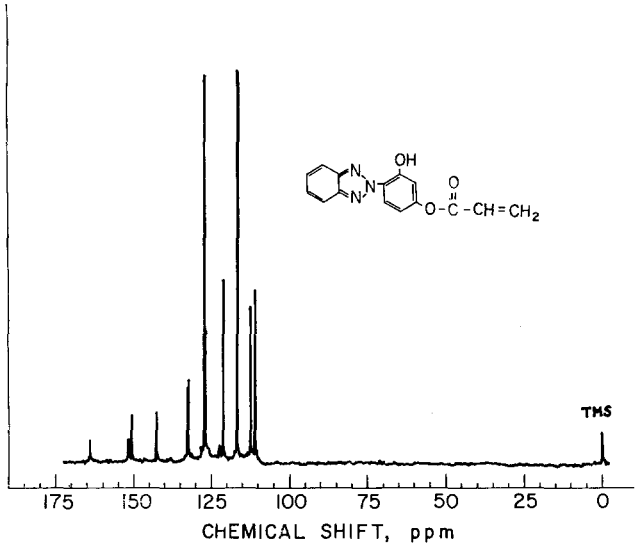


Fig. 1. ^{13}C NMR spectrum of 2(2-hydroxy-4-acryloxyphenyl)2*H*-benzotriazole (*BDHA*)

The work-up procedure and the isolation of crude *BDHM* were essentially the same as that described for the synthesis of *BDHA*. Crude *BDHM* (2.36 g, 80% yield) was purified by recrystallization from absolute ethanol; it gave white crystals, m.p. 117–119 °C (75% recovery).

The numeric values of the ultraviolet absorption spectrum are presented in Table 2 and the spectrum in Figure 3 C; IR (KBr): 1 740 cm^{-1} ($\nu_{C=O}$ stretching).

The ^1H NMR spectrum showed: δ 2.1 ppm (—CH_3, 3 H), 5.8 and 6.4 (=CH_2, 2 H), 6.7–6.8, 6.8–7.1, and 8.3–8.4 (protons of phenoxy group, 3 H), 7.2–7.5 and 7.7–8.0 (protons of benzotriazole group, 4 H), 11.6 (—OH, 1 H). ^{13}C NMR chemical shift data are presented in Table 1 and the spectrum in Figure 2.

Anal. Calcd. for $C_{16}H_{13}N_3O_3$: C 65.08, H 4.44, N 14.23. Found: C 64.99, H 4.67, N 14.14.

Table 2. *Ultraviolet spectral data for 2[2-hydroxy-4-acryloxy(methacryloxy)phenyl]2H-benzotriazole (absorption determined in DMAc solutions; concentration: 2×10^{-5} mol/l)*

	λ_{max} [nm]	ε [l mol^{-1} cm^{-1}] $\times 10^{-3}$	λ_{max} [nm]	ε [l mol^{-1} cm^{-1}] $\times 10^{-3}$
BDHA	290	18.6	270	13.0
Poly-BDHA	290	14.6	270	11.1
BDHM	290	18.5	270	13.5
Poly-BDHM	290	14.4	270	11.3

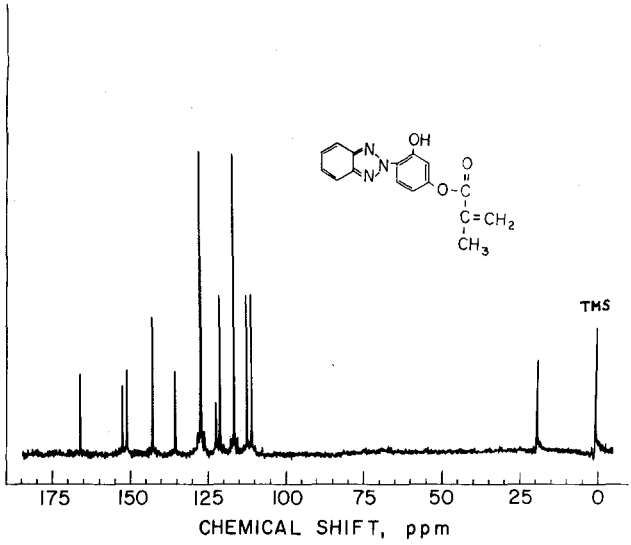


Fig. 2. ^{13}C NMR spectrum of 2(2-hydroxy-4-methacryloxyphenyl)2*H*-benzotriazole (*BDHM*)

3. Polymerizations

a) Homopolymerizations of 2[2-Hydroxy-4-Acryloxy(Methacryloxy)phenyl]2H-Benzotriazole

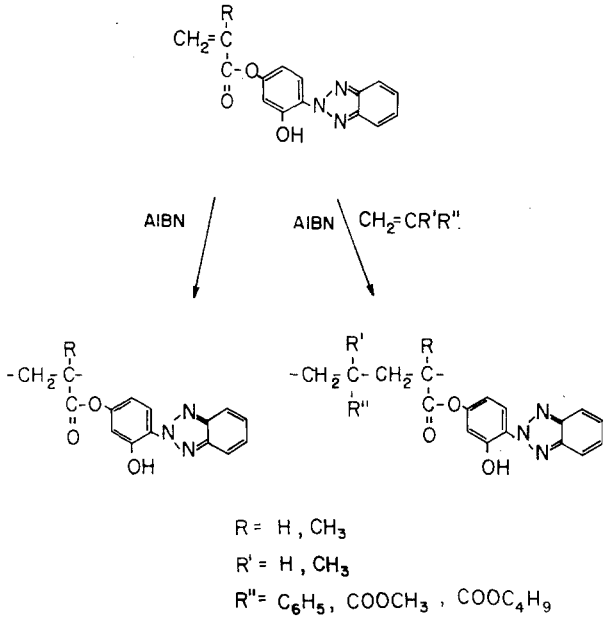
A 10-ml polymerization tube was charged with *AIBN* (6.6 mg, 0.2 mol%), *BDHA* (0.56 g, 2 mmol) (or 0.59 g of *BDHM*), and *DMAc* (4 ml, or 2 ml for *BDHM*). After three freeze-thaw cycles at 0.05 mm Hg pressure to degas the homogeneous solution, the tube was sealed and allowed to react for 2.5 days at 50 °C; the tube was opened and the solution was poured slowly into methanol (300 ml). Polymer, which precipitated, was allowed to settle for 3 h; it was filtered and dried at 0.1 mm Hg, dissolved in *DMAc* (5 ml) and precipitated again into methanol (200 ml). After drying for two days at 66 °C and 0.1 mm Hg, poly-*BDHA* (or poly-*BDHM*) was obtained in 80% yield (0.45 g) [or 98% yield (0.58 g)], respectively. The results of all polymerizations carried out during this work are presented in Tables 1 and 2.

b) Copolymerization of 2[2-Hydroxy-4-Acryloxy(Methacryloxy)phenyl]2H-Benzotriazole with Styrene, Methyl Methacrylate, and n-Butyl Acrylate

2[Hydroxy-4-acryloxy(methacryloxy)phenyl]2*H*-benzotriazole (*BDHA* or *BDHM*) were copolymerized with styrene (*St*), methyl methacrylate (*MMA*), and *n*-butyl acrylate (*BA*), respectively, with *AIBN* as the initiator (Tables 3 and 4). Typical copolymerization experiments were carried out as follows:

Poly (BDHA-co-St): BDHA (0.56 g, 2 mmol) and *AIBN* (6.6 mg, 0.04 mmol) were dissolved in 4 ml of *DMAc* and the solution was charged into a 10-ml Pyrex polymerization tube. *St* (1.87 g, 18 mmol) was then added and the tube was degassed by three freeze-thaw cycles (liquid nitrogen) before it was sealed at 0.05 mm Hg and placed in a constant temperature bath at 50 °C. After 2.5 days, the tube was opened and the solution was poured into 300 ml of

Scheme 2



methanol. *Poly (BDHA-co-St)* precipitated and was collected by filtration. After drying overnight at 0.1 mm Hg, the polymer was dissolved in *DMAc* (5 ml) and precipitated again into methanol (200 ml); the polymer was dried for 2 days at 66 °C (0.1 mm Hg); yield was 1.29 g (53%); the inherent viscosity was 0.90 dl/g (0.5 g/dl in *DMAc*, 30 °C).

Poly (BDHM-co-MMA): BDHM (0.59 g, 2 mmol) and *AIBN* (6.6 mg, 0.04 mmol) were dissolved in 2 ml of *DMAc* and the solution was charged into a 10-ml Pyrex polymerization tube. *MMA* (1.8 g, 18 mmol) was then added and the tube was degassed by three freeze-thaw cycles and then sealed at 0.05 mm Hg. After keeping the sealed tube at 50 °C for 2.5 days, the tube was opened and the contents were poured into 300 ml of methanol. The polymer precipitated immediately and the suspension was allowed to settle for 2 h; after filtration, the solid polymer was dried at 0.1 mm Hg: It was dissolved in *DMAc* (5 ml) and precipitated again into methanol (200 ml). After drying for 2 days at 66 °C and 0.1 mm Hg, *poly (BDHM-co-MMA)* was obtained in 97% yield (2.31 g) and had an inherent viscosity of 2.23 dl/g (0.5 g/dl in *DMAc*, 30 °C).

Poly (BDHA-co-BA): A 10-ml Pyrex polymerization tube was charged with *AIBN* (6.6 mg, 0.04 mmol), *BDHA* (0.56 g, 2 mmol), *n*-butyl acrylate (2.56 g, 18 mmol), *DMAc* (4 ml), and dichloromethane (6 ml). The homogeneous mixture was degassed, sealed at 0.05 mm Hg, and placed in a constant temperature bath of 50 °C for 2 days. The tube was opened and the solution was poured into methanol (300 ml); polymer precipitated immediately as a rubbery mass. After 2 h, the methanol was decanted, the copolymer dissolved in *DMAc* (5 ml), and precipitated by pouring the solution into methanol (200 ml). After filtration and drying at 0.1 mm Hg and 66 °C for two days, *poly (BDHA-co-BA)* was obtained in 77% yield (2.4 g); inherent viscosity: 0.96 dl/g (0.5 g/dl in *DMAc*, 30 °C).

Results and Discussion

2(2,4-Dihydroxyphenyl)2*H*-benzotriazole (*BDH*) has been prepared in good yield and free of "dibenzotriazolized" resorcinol (*DBDH*); the reaction for the monoacylation on the 4-hydroxy group has been worked out.

In our previous paper [14] we described an improved method for the reaction of *o*-nitrobenzenediazonium chloride (*ONBD*) with resorcinol which led, after reductive cyclization, to the benzotriazole derivative. This reaction had been described first by *Elbs*[13], but also in a more recent patent[15]. Under these reaction conditions (and we[14] confirmed those findings), a high yield of the crude reaction products (80 to 90%) could be obtained, which were mixtures of *BDH* and *DBDH* of various compositions depending upon the exact reaction conditions. The composition of the mixtures contained anywhere from 20 to 60% *BDH*. Pure *DBDH* was also obtained by adding the resorcinol solution to an excess of the *ONBD* solution (followed by reductive cyclization of the initial azo compound). The type and degree of benzotriazole substitution depended on the ratio of *ONBD* to resorcinol, the type and rate of the addition of the two solutions (*ONBD* to resorcinol, resorcinol to *ONBD*), the solution concentration of the two solutions, but even more importantly, on the *pH* of the solutions in the beginning and, at the end of the reaction.

We now found that, when *ONBD* was added to a resorcinol solution in ethanol : water (1 : 1) without any base added at a ratio of *ONBD* to resorcinol of 1 : 1 while maintaining the reaction temperature at 0–5 °C, red crystals of the azo compound were formed in high yields. After reductive cyclization, *BDH* was isolated in 50% yield which already had a melting point of 198–200 °C. Recrystallization from aqueous ethanol gave white needles, m.p. 199–200 °C. This modification of the reaction conditions gave pure *BDH* directly in good yield and free of *DBDH* and thus makes *BDH* readily available.

BDH is formally quite similar to 2,4-dihydroxybenzophenone, a compound that had been used extensively as an ultraviolet stabilizer. *BDH* is benzotriazolized in the same position of the resorcinol ring as 2,4-dihydroxybenzophenone is benzoylated. 2,4-Dihydroxybenzophenone is probably the first ultraviolet absorber that had been transformed by acylation with acryloyl or methacryloyl chloride into polymerizable ultraviolet absorbers: 2-hydroxy-4-acryloxybenzophenone and 2-hydroxy-4-methacryloxybenzophenone[16–22].

We have succeeded in the acylation of *BDH* with acryloyl chloride to 2(2-hydroxy-4-acryloxyphenyl)2*H*-benzotriazole (*BDHA*) and with methacryloyl chloride to 2(2-hydroxy-4-methacryloxyphenyl)2*H*-benzotriazole (*BDHM*). The reaction is most effectively carried out in a

two-phase system, similar to the *Schotten-Baumann* reaction, the acid chlorides being dissolved in chloroform, and *BDH* in sodium hydroxide solution. The acylation gave *BDHA* or *BDHM* in above 75% yield. Attempts to carry out the acylations in solution gave also some diacylation and, generally speaking, mixtures which included also starting material.

The ^{1}H spectrum of *BDHA* showed the normal chemical shift values expected for *BDH*, but in addition the methine proton at 6.8 ppm, and the methylene proton of the vinyl protons of the acrylate group at 8.1 ppm. The ^{1}H NMR spectrum of *BDHM* showed the peak for *BDH* and additional chemical shift values at 2.1 ppm for the protons of the methyl group and 5.8 to 6.4 ppm for the methylene of the methacrylate group.

The ^{13}C NMR chemical shift values of *BDHA* and *BDHM* are compiled in Table 1; the actual spectra in Figure 1 and Figure 2, respectively.

The numerical values of the ultraviolet absorption spectra of *BDHA* and *BDHM* are presented in Table 2; the actual spectra are shown in Figure 3. The ultraviolet spectrum of *BDH* is also shown for comparison. In chloroform, the spectra of *BDHA* have a λ_{max} of 334 nm (and an extinction coefficient ε of 24.6×10^3 l mol^{-1} cm^{-1}), 295 (13.4×10^3), 244 (11.7×10^3). The same values for *BDHM* are a λ_{max} of 334 nm (ε 24.2×10^3), 295 (13.4×10^3), 246 (11.2×10^3).

In *DMAc* solution, the shape of the spectrum is drastically changed, and for *BDHA* at a λ_{max} of 290 nm (18.6×10^3), 270 (13.0×10^3) were observed. For *BDHM*, there is a λ_{max} of 290 nm (18.5×10^3), 270 (13.5×10^3).

The monomers *BDHA* and *BDHM* were homopolymerized and copolymerized with *St*, *MMA*, *BA*, with *AIBN* as the initiator. The polymers were obtained in good yields. The reaction conditions for the homo- and copolymerization of *BDHA* are described in Table 3 and those for the homo- and copolymerization of *BDHM* in Table 4.

The copolymerizations were generally carried out in *DMAc* as the solvent, or in mixtures of *DMAc* and dichloromethane. The type of solvent and the monomer concentrations were selected to maintain the entire polymerization system in solution during the polymerization. The homopolymerization of *BDHA*, carried out in an about 15% monomer concentration in *DMAc*, produced a polymer with an inherent viscosity of only 0.12 dl/g.

The copolymerizations of *BDHA* were carried out with feed ratios of 3 and 10 mol% of *BDHA* in the mixtures. With *St* as the comonomer, the polymer yield was only about 50%, but the functional comonomer *BDHA* was incorporated in 6 mol% and 18 mol%, respectively, indicating that *BDHA* is favorably incorporated into the *St* copolymer and suggesting some alternating tendency of the comonomer pair. Copolymerization of *BDHA* with *MMA* gave polymers in nearly quantitative yields with incorporation of 7 mol% and 11 mol% of *BDHA*, respectively, but a high inherent viscosity of about 2 dl/g. Copolymerization of *BDHA* with *BA* gave a polymer yield of 75 to 85%

Table 3. *Reaction conditions for the homo- and copolymerization of 2(2-hydroxy-4-acryloxyphenyl)2H-benzotriazole (BDHA).* Polymerization conditions: initiator: *AIBN*, 0.2 mol-%, temperature: 50 °C, 2.5 days; sealed tube: pressure: 0.05 mm Hg

BDHA		Comonomer			Total amount of monomer		Solvent		Polymerization yield		Polymer composition in mol-%	η_{inh}[a] *DMAc*
g	mmol	type	g	mmol	g	mmol	type	amount ml	g	(%)	*BDHA* unit	(dl/g)
0.56	2.0		—		0.56	2.0	*DMAc*	4	0.45	80	100	0.12
0.17	0.6	*ST*	2.02	19.4	2.19	20.0	*DMAc*	2	1.12	51	5.7	0.58
0.56	2.0	*ST*	1.87	18.0	2.43	20.0	*DMAc*	4	1.29	53	18	0.90
0.17	0.6	*MMA*	1.94	19.4	2.11	20.0	*DMAc*	2	1.98	94	7	2.11
0.56	2.0	*MMA*	1.80	18.0	2.36	20.0	*DMAc*	4	2.27	96	11	1.74
0.17	0.6	*BA*	2.76	19.4	2.93	20.0	*DMAc*	4				
							CH_2Cl_2	6	2.52	86	3.3	1.04
0.56	2.0	*BA*	2.56	18.0	3.12	20.0	*DMAc*	4				
							CH_2Cl_2	6	2.40	77	12	0.96

[a] 0.5 g/dl in *DMAc*, 30 °C.

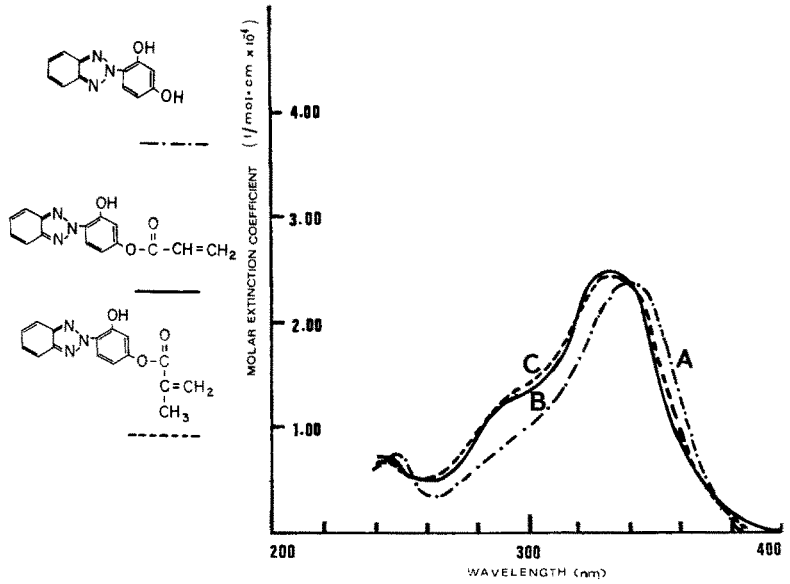


Fig. 3. Ultraviolet spectra of derivatives of 2(2,4-dihydroxyphenyl)2*H*-benzotriazole in chloroform: *A* 2(2,4-dihydroxyphenyl)2*H*-benzotriazole (*BDH*); *B* 2(2-hydroxy-4-acryloxyphenyl)2*H*-benzotriazole (*BDHA*); *C* 2(2-hydroxy-4-methacryloxyphenyl)2*H*-benzotriazole (*BDHM*)

with the same amount of comonomer incorporated into the polymer as was present in the initial monomer feed; an inherent viscosity of about 1 dl/g was measured for this copolymer.

Homo- and copolymerization of *BDHM* gave polymers of yields and compositions similar to those of the *BDHA* series. A homopolymer with an η_{inh} of 1.3 dl/g was obtained. The *St* copolymers with 3 mol% or 10 mol% of *BDHM* in the feed gave copolymers in 40 to 50% yield that had 5 and 12 mol% of *BDHM* comonomer units in the polymer and had an inherent viscosity of 0.4 and 1.0 dl/g, respectively.

Copolymerizations of *BDHM* with *MMA* gave, in quantitative yield, copolymers with 3 mol% and 14.5 mol% of *BDHM* in the copolymer and inherent viscosities of 1.7 and 2.2 dl/g, respectively.

Copolymerizations of *BDHM* and *BA* gave, in 80 to 90% yield, copolymers with 3.5 and 10.5 mol% of *BDHM* in the comonomer composition and inherent viscosities of 1.0 and 0.7 dl/g, respectively.

The composition of all copolymers was established by elemental analysis of nitrogen and was checked in selected cases by quantitative NMR analysis and the measurements of the ultraviolet spectra of the polymers.

Table 4. *Reaction conditions for the homo- and copolymerization of 2(2-hydroxy-4-methacryloxyphenyl)2H-benzotriazole (BDHM).* Polymerization conditions: initiator: *AIBN*, 0.2 mol-%, temperature: 50 °C, 2.5 days, sealed tube, pressure: 0.05 mm Hg

BDHA		Comonomer			Total amount of monomer		Solvent		Polymerization yield		Polymer composition in mol-%	η_{inh}[a] *DMAc*
g	mmol	type	g	mmol	g	mmol	type	amount ml	g	(%)	*BDHA* unit	(dl/g)
0.59	2.0		—		0.59	20.0	*DMAc*	2	0.58	98	100	1.34
0.18	0.6	*ST*	2.02	19.4	2.20	20.0	*DMAc*	2	0.90	41	4.8	0.42
0.59	2.0	*ST*	1.87	18.0	2.46	20.0	*DMAc*	2	1.28	52	12	1.00
0.18	0.6	*MMA*	1.94	19.4	2.12	20.0	*DMAc*	2	2.07	98	2.9	1.68
0.59	2.0	*MMA*	1.80	18.0	2.39	20.0	*DMAc*	2	2.31	97	14.5	2.23
0.18	0.6	*BA*	2.76	19.4	2.94	20.0	*DMAc*	4	2.27	77	3.4	1.02
							CH_2Cl_2	6				
0.59	2.0	*BA*	2.56	18.0	3.15	20.0	*DMAc*	4	2.89	92	11	0.72
							CH_2Cl_2	6				

[a] 0.5 g/dl in *DMAc*, 30 °C.

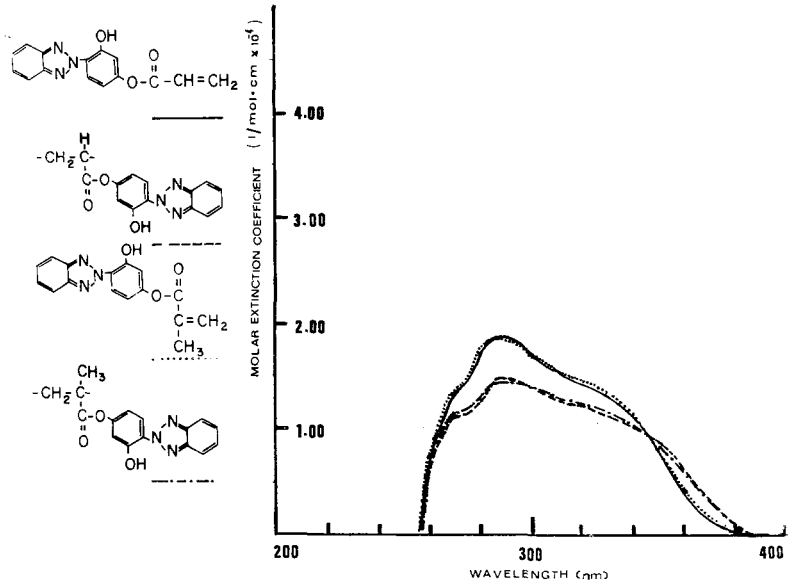


Fig. 4. Ultraviolet spectra of derivatives of 2(2,4-dihydroxyphenyl)2*H*-benzotriazole in *DMAc*: *A* 2(2-hydroxy-4-acryloxyphenyl)2*H*-benzotriazole (*BDHA*); *B* poly[2(2-hydroxy-4-acryloxyphenyl)2*H*-benzotriazole] (*poly-BDHA*); *C* 2(2-hydroxy-4-methacryloxyphenyl)2*H*-benzotriazole (*BDHM*); *D* poly[2(2-hydroxy-4-methacryloxyphenyl)2*H*-benzotriazole (*poly-BDHM*)

The ultraviolet spectra of *poly-BDHA* and *poly-BDHM* had to be measured in *DMAc*. They showed absorbances similar to those of *BDHA* and *BDHM* in *DMAc*, respectively. *Poly-BDHA* had λ_{max} at 290 nm (14.6×10^3) and 270 nm (11.1×10^3). *Poly-BDHM* had λ_{max} at 290 nm (18.5×10^3) and 270 nm (11.3×10^3).

In conclusion, we have demonstrated that *BDH* can be prepared in good yield and free of disubstitution. By two-phase acylation techniques, it could be transformed into *BDHA* or *BDHM* which could be readily homopolymerized and incorporated into copolymers of *St*, *MMA*, and *BA*.

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