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Functional Polymers LII**
Synthesis and Polycondensation of 2(2,4-Dihydroxyphenyl)2*H*-1,3-bis[4-carboxy (or 4-carbomethoxy)2*H*-benzotriazole]

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Carboxy- and carbomethoxy derivatives of resorcinols with two benzotriazole substituents have been synthesized. 2(2,4-Dihydroxyphenyl)2*H*-1,3-bis-(4-carboxybenzotriazole) [2,4-bis(2*H*-4′-carboxybenzotriazole-2-yl)-1,3-dihydroxybenzene] (*DCBDH*) was prepared by azo coupling of 4-carboxy-2-nitrobenzene diazonium chloride with resorcinol followed by reductive cyclization. 2(2,4-Dihydroxyphenyl)2*H*-1,3-bis(4-carbomethoxy-benzotriazole) [2,4-bis-(2*H*-4′-carbomethoxy-benzotriazole-2-yl)-1,3-dihydroxybenzene] (*DCMBDH*) was obtained by esterification of the free dicarboxylic acid with methanol. The compounds were characterized by their elemental analyses and melting points, and by their IR, UV, ^{1}H NMR, and ^{13}C NMR spectra.

Copolycondensations were carried out to incorporate *DCBDH* or *DCMBDH* into polyamides or polyesters. The condensation copolymers were briefly characterized.

(Keywords: 2(2-Hydroxyphenyl)2H-benzotriazoles; Ultraviolet absorbers; Condensation copolymers; Polyamides; Polyesters; Polycarbonates)

Funktionelle Polymere, 52. Mitt.: Synthese und Polykondensation von 2(2,4-Dihydroxyphenyl)2H-1,3-[bis-4-carboxy (oder 4-carbomethoxy)2H-benzotriazol]

Es wurden Carboxy- und Carbomethoxy-Derivate von Resorcin mit zwei Benzotriazol-Substituenten dargestellt. 2(2,4-Dihydroxyphenyl)2*H*-1,3-bis-(4-carboxybenzotriazol) [2,4-Bis(2*H*-4′-carboxybenzotriazol-2-yl)-1,3-dihydroxybenzol] (*DCBDH*) wurde über Azokupplung von 4-Carboxy-2-nitrobenzoldiazoniumchlorid mit Resorcin, gefolgt von reduktiver Cyclisierung, synthetisiert.

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2(2,4-Dihydroxyphenyl)2*H*-1,3-bis-(4-carbomethoxybenzotriazol) [2,4-Bis-(2*H*-4′-carbomethoxybenzotriazol-2-yl)-1,3-dihydroxybenzol] (*DCMBDH*) erhielt man mittels Veresterung der freien Dicarbonsäure mit Methanol. Die Verbindungen wurden mittels Elementaranalysen und spektroskopisch charakterisiert (IR, UV, ^{1}H und ^{13}C NMR). Es wurden Copolymerisationen zur Inkorporierung von *DCBDH* und *DCMBDH* in Polyamide und Polyester durchgeführt. Die Kondensationskopolymeren werden kurz charakterisiert.

Introduction

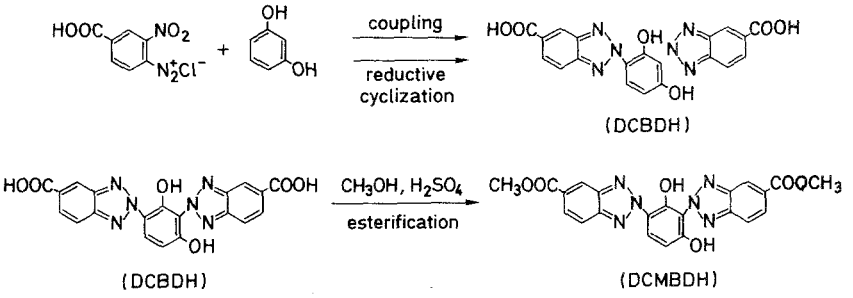
2(2-Hydroxyphenyl)2*H*-benzotriazole compounds are excellent ultraviolet absorbers and have become important ultraviolet stabilizers for the protection of plastic materials.

In recent years, substantial efforts have been made to synthesize polymerizable 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives in attempts to prepare more effective ultraviolet stabilizers with broad ultraviolet absorption, high extinction coefficient, good compatibility and low mobility in the polymer matrix. A number of such polymer-bound ultraviolet stabilizers which are not leachable, or volatile in vacuum and at elevated temperatures have now been synthesized. They include polymerizable 2(2-hydroxyphenyl)2*H*-benzotriazoles with vinyl, isopropenyl, and (meth)acrylate as polymerizable groups [1–11, 14], compounds with more than one benzotriazole group in the molecule [12–15], and compounds with one 2(2-hydroxyphenyl)2*H*-benzotriazole and one 2-hydroxybenzophenone (or acetophenone) chromophore in the same molecule [16, 18]. The polymerization and copolymerization of such polymerizable acrylates, methacrylates, and vinyl or isopropenyl derivatives of 2(2-hydroxyphenyl)2*H*-benzotriazole [3–9, 14], as well as their grafting [17] has been accomplished. 2(2-Hydroxyphenyl)2*H*-benzotriazoles with hydroxy- and acetoxy-groups have been synthesized and incorporated into polyesters and polycarbonates [19–21].

The 2(2-hydroxyphenyl)2*H*-benzotriazoles are powerful ultraviolet absorbers; their spectra cover a broad absorption range from 250 to 370 nm with high extinction coefficients and a sharp cut-off at about 380 nm.

As part of our continued effort to prepare new classes of polymerizable 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives, we attempted the synthesis of 2(2-hydroxyphenyl)2*H*-benzotriazoles with carboxy- or carbomethoxy-groups as substituents on the benzotriazole ring. It was our specific objective to prepare 2(2,4-dihydroxyphenyl)2*H*-1,3-bis(4-carboxybenzotriazole) [2,4-bis(2*H*-4′-carboxybenzotriazole-2-yl)-1,3-dihydroxybenzene] (*DCBDH*) and 2(2,4-dihydroxyphenyl)2*H*-1,3-bis(4-carbomethoxybenzotriazole) [2,4-bis(2*H*-4′-carbomethoxybenzotriazole-

2-yl)-1,3-dihydroxybenzene] (*DCMBDH*) with the additional goal of incorporating *DCBDH* or *DCMBDH* into condensation copolymers, such as polyamides or polyesters. (Equation.)



Experimental

4-Aminobenzoic acid (Aldrich Chemical Co.), resorcinol (A.R., Bai-he Chemical Plant), sodium nitrite (99.0%, The First Shanghai Reagent Plant), urea (A.R., The First Shanghai Reagent Plant), zinc powder (90%, Shanghai Sulfuric Acid Plant), and sodium hydrosulfite (88%, Shanghai Sulfuric Acid Plant) were used as received. 3-Nitro-4-aminobenzoic acid was prepared according to established procedures. Acetic acid, fuming nitric acid, sulfuric acid, hydrochloric acid, and sodium hydroxide, as well as the solvents acetone, methanol, chloroform, pyridine, and *m*-cresol were of pure chemical grade. Lithium carbonate and zinc acetate were A.R. grade reagents. Diphenyl carbonate, Bisphenol A, the salt of sebacic acid and decanediamine, and tetramethylene sulfone were purified before use. Dimethylsulfoxide-d_6 (*DMSO*) (99.9% d) was obtained from the Aldrich Chemical Co.

Infrared spectra were measured on a Perkin-Elmer spectrometer, Model 983G, the solid samples in the form of potassium bromide pellets. Ultraviolet absorption spectra were measured on a Graphic Printer PR-1 spectrometer in a double-beam servo mode (1.0 cm optical path length). ^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer using *TMS* as the internal standard and *DMSO*-d_6 as the solvent. Melting points were determined on a melting point apparatus, Model X-6, produced at The Third Optical Instrument Plant of Beijing. ^{13}C NMR spectra were measured and microanalyses were carried out at the Analysis Laboratory, Shanghai Medicine Institute of the Academia Sinica, Shanghai.

3-Nitro-4-aminobenzoic Acid [22, 23]

3-Nitro-4-aminobenzoic acid was obtained in 85% yield, m.p. 290–292 °C from 4-acetylaminobenzoic acid; it was sufficiently pure for the next step of the synthesis; it could also be recrystallized from ethanol.

2(2,4-Dihydroxyphenyl)2H-1,3-Bis(4-carboxybenzotriazole) [2,4-bis(2H-4'-carboxybenzotriazole-2-yl)-1,3-dihydroxybenzene] (DCBDH)

(a) The preparation of the diazonium salt solution (diazotization) was carried out as follows: In a 500 ml three-neck, round-bottom flask, a mixture of conc.

hydrochloric acid (60 ml, 0.72 mol) and water (60 ml) was cooled to 0 °C with stirring and a sodium nitrite solution [1.4 g, 0.02 mol in water (20 ml)] was added. In a beaker, 3-nitro-4-aminobenzoic acid (18.2 g, 0.10 mol) was dissolved in a solution of sodium hydroxide (4 g, 0.10 mol) in water (150 ml), 7.0 g sodium nitrite (0.10 mol), dissolved in 50 ml of water, was added and the resultant solution was added dropwise to the acid solution kept at 5–10 °C, with stirring. After completing the addition, the mixture was allowed to stir for 30 min; urea [1.2–1.8 g, 0.02–0.03 mol] dissolved in water (30 ml) was added to destroy the excess nitrous acid. The mixture was tested with starch-potassium iodide paper until the iodine reaction was negative. A small amount of insoluble material was removed from the yellowish diazonium salt solution.

(b) The azo-compound (coupling reaction) was prepared as follows: In a 2 000 ml three-neck flask, resorcinol (5.5 g, 0.05 mol) was dissolved in a mixture of pyridine (200 ml) and water (200 ml). The solution was cooled, and the freshly prepared diazonium salt solution was added dropwise with stirring for one hour while the temperature was maintained at 0 °C. The reaction mixture was then kept at 10 °C for one hour, at room temperature for another one-hour period, and the suspension was filtered. The orange-red-colored filter cake was washed several times with water.

(c) The reductive cyclization was carried out in a 2 000 ml three-neck flask. The azo compound was suspended in a 5% aqueous solution of sodium hydroxide (1 200 ml) and sodium hydrosulfite ($Na_2S_2O_4$) (80 g) was added in small portions. The reaction was continued with stirring under a nitrogen atmosphere for 24 h at room temperature. The orange-red solution was neutralized to *pH* 4–5 with 35% aqueous acetic acid, whereby the reaction product precipitated. After filtration, the yellowish filter cake was dissolved in a 2*N* aqueous solution of sodium hydroxide (800 ml) and zinc powder (80 g) was added in small portions. The reaction proceeded rapidly and formed a greenish-yellow suspension; the stirring was allowed to continue for an additional 24 h at room temperature. After addition of more sodium hydrosulfite, the reaction was stopped and the suspension filtered to remove the zinc sludge. The filtrate was acidified with dilute hydrochloric acid (conc. HCl : water = 1 : 2) to *pH* 2 to precipitate the crude, yellow product. After filtration, the filter cake was washed three times with water and extracted with hot acetone (800 ml). Crude *DCBDH* (10.8 g, 25% yield) was obtained by evaporating the extract to dryness. Pale yellow crystals of pure *DCBDH* could be obtained by recrystallizing crude *DCBDH* twice from 90% aqueous acetic acid, m.p. 356–358 °C (with decomp.). The ultraviolet absorption values are presented in Table 1 and the spectra in Fig. 1. IR (KBr): 3 400 cm^{-1} (—OH absorption), 1 694 cm^{-1} (COOH absorption). ^1H NMR, in ppm: 13.28 (—COOH, 2 H); 10.18 (—OH, 2 H); 6.86–8.68 (protons of the substituted benzene ring, 8 H). The ^{13}C NMR chemical shift data are presented in Table 2. Elemental analysis: Calculated for $C_{20}H_{12}N_6O_6$: C 55.56%, H 2.78%, N 19.44%. Calcd. for $C_{20}H_{12}N_6O_6 \cdot H_2O$: C 53.33%, H 3.11%, N 18.67%. Found: C 53.37%, H 2.81%, N 18.80%.

2(2,4-Dihydroxyphenyl)2H-1,3-bis(4-carbomethoxybenzotriazole)

[2,4-bis(2H-4'-carbomethoxybenzotriazole-2-yl)-1,3-dihydroxybenzene] (DCMBDH)

Crude *DCBDH* (1 g) was placed in the thimble of a *Soxhlet* extractor; 300 ml anhydrous methanol and 5 ml conc. sulfuric acid were added to the round-bottom

Table 1. *Ultraviolet absorption of DCBDH, DCMBDH, and their copolyesters and copolyamides**

Sample	Solvent	λ_{max} (nm)	$\varepsilon \cdot 10^{-4}$ ($l\,mol^{-1}\,cm^{-1}$)	λ_{max} (nm)	$\varepsilon \cdot 10^{-4}$ ($l\,mol^{-1}\,cm^{-1}$)
DCBDH	CH_3OH	298	1.39	345	2.05
	DMAc	293	2.06	344	1.56
DCMBDH	$CHCl_3$			341	3.85
	DMAc	293	2.08	344	1.56
Polycarbonate-co-*DCMBDH*	$CHCl_3$			341	1.45
Nylon 10,10-co-*DCBDH*	*m*-cresol			340	2.19

* Absorption spectra were determined in concentration of $2 \cdot 10^{-5}\,mol\,l^{-1}$

flask, heated to reflux and the extraction was allowed to proceed for 24 h. The solution was concentrated on a rotary evaporator at room temperature to about 100 ml, and the mixture was poured into a mixture of ice and water (500 ml). A yellowish precipitate was obtained which was isolated by filtration. Pure *DCMBDH* (0.8 g, 75% yield) was obtained by recrystallization from chloroform/methanol 1 : 1, m.p. 236 – 238 °C.

The ultraviolet absorption values of *DCMBDH* are shown in Table 1 and the spectra in Fig. 2. IR (KBr): 3400 cm^{-1} (—OH absorption), 1726 cm^{-1} (ester group absorption). ^1H NMR chemical shift, in ppm: 11.18, 10.79 (—OH, 2 H); 6.84–8.72 (protons of the substituted benzene ring, 8 H); 3.94 (—CH, 6 H). The ^{13}C NMR chemical shift data are presented in Table 2. Elemental analysis: Calcd. for $C_{22}H_{16}N_6O_6$: C 57.39%, H 3.48%, N 18.26%. Found: C 57.12%, H 3.53%, N 18.02%.

Regeneration of DCBDH by Hydrolysis of DCMBDH

In a 250 ml round-bottom flask, a mixture of an aqueous solution of sodium hydroxide (100 ml, 1 *N*), methanol (50 ml), and recrystallized *DCMBDH* (0.30 g) was heated to reflux under nitrogen at 60 °C for 6 h; the solution was cooled to 10 °C and acidified with dilute hydrochloric acid to *pH* 1–2, which caused a precipitate to form. Most of the methanol was evaporated on a rotary evaporator, the residue was cooled to 10 °C, the suspension filtered, washed with water (*pH* 4–7) and gave 0.28 g of pure *DCBDH*. The hydrolysis was almost quantitative and the product purity of a sample of *DCBDH* prepared by hydrolysis of purified *DCMBDH* was much better than the *DCBDH* synthesized directly by procedure (c).

Copolycondensation of DCBDH with the Salt of Sebacic Acid and 1,10-Decanediamine

In a 50 ml three-neck flask equipped with a stirrer and a distillation apparatus, the salt of sebacic acid, 1,10-decanediamine (3.72 g, 10 mmol), and *DCBDH*

(22 mg, 0.05 mol) were dissolved in tetramethylenesulfone (15 ml); the reaction mixture was heated under nitrogen to 150–160 °C for 2 h; the temperature was raised to 180 °C and the pressure was reduced to 100 mm Hg. After one hour the reaction mixture was cooled, the polymer dissolved in *m*-cresol and precipitated by pouring the solution into a large amount of methanol. This procedure of dissolving and reprecipitating of the copolymer was repeated twice, the suspension was filtered, and a copolymer was obtained with an intrinsic viscosity (η) = 0.42 dl/g (30 °C in *m*-cresol). The ultraviolet absorption data of the polymer are shown in Table 1.

Copolycondensation of DCMBDH with Diphenyl Carbonate and Bisphenol A

A 50 ml 3-neck flask, equipped with a stirrer and a distillation apparatus, was preheated to 175 °C. The reactants, diphenyl carbonate (2.23 g, 10.4 mmol), bisphenol A (2.35 g, 10.3 mmol), *DCMBDH* (46 mg, 0.1 mmol), lithium carbonate (1 mg), and zinc acetate (1 mg) were placed into the reaction flask and heated. Initially, the reaction was allowed to proceed at 175–185 °C and 150 mm Hg; when the temperature of the still head decreased by 2–3 °C, the pressure was gradually lowered to 40 mm Hg and the pot temperature was increased to 230 °C. The pressure was lowered to 10 mm Hg and the reaction was maintained under these conditions for 10 min, and then the temperature of the reaction was raised to 295 °C (1 mm Hg) for one additional hour. After cooling under nitrogen, the polymer was dissolved in chloroform and precipitated into a large quantity of methanol. The condensation copolymer, after reprecipitating twice, had an intrinsic viscosity (η) = 0.35 dl/g (30 °C in chloroform). The ultraviolet absorption data of the polymer are tabulated in Table 1.

Results and Discussion

2(2-Hydroxyphenyl)2*H*-benzotriazole derivatives with carboxy- or carbomethoxy-groups on the benzotriazole part were prepared by allowing 2-nitro-4-carboxy-benzene diazonium chloride to react with resorcinol. The difunctional monomers *DCBDH* and *DCMBDH* were obtained (see Equation).

3-Nitro-4-aminobenzoic acid has strong electron withdrawing groups (a nitro and a carboxylic acid group) as substituents and is consequently a weak base. The compound was difficult to dissolve in hydrochloric acid and the diazotization could not be carried out by normal procedures. After careful investigations, the following procedure was found effective. A basic solution of 3-nitro-4-aminobenzoic acid and sodium nitrite was added to an aqueous hydrochloric acid solution. 120% of the theoretical amount of sodium nitrite was needed in order to complete the diazotization. 2-nitro-4-carboxybenzenediazonium chloride was stable even at room temperature and the diazotization temperature could be raised to complete the reaction.

Azo-coupling with resorcinol was readily carried out in aqueous sodium carbonate or sodium bicarbonate solutions and the disubstituted

Table 2. ^{13}C *NMR chemical shift data of DCBDH and DCMBDH*

Structure	Assignment	*DCBDH* (R = —H)		*DCMBDH* (R = —CH_3)	
		Observed[a]	Calculated[b]	Observed[a]	Calculated[b]
	a	148.0		148.0	
	b	120.3[c]		120.4[c]	
	c	155.8		155.8	
	d	107.6		107.7	
	e	126.9[c]		126.4[c]	
	f	120.9		121.1	
	g	166.5		166.5	
	h			52.1	
	1 (1′)	143.6 (142.5)	145.4 (144.0)	143.5 (142.5)	144.9 (143.5)
	2 (2′)	120.3[c] (119.5)	120.2 (119.4)	120.4[c] (119.2)	120.2 (119.4)
	3 (3′)	129.4 (129.8)	130.2 (130.8)	128.2 (128.5)	128.7 (129.3)
	4 (4′)	126.3 (126.9[c])	128.7 (129.3)	125.8 (126.4[c])	127.7 (128.3)
	5 (5′)	118.2 (117.7)	119.4 (118.6)	118.5 (118.6)	118.9 (118.1)
	6 (6′)	145.7 (144.7)	149.9 (148.4)	145.8 (144.8)	149.4 (148.0)

[a] Chemical shift in ppm relative to *TMS* in *DMSO-d_6*
[b] Calculated and assigned according to Ref. [24] by using 2(2,4-hydroxyphenyl)2*H*-1,3-bisbenzotriazole as model compound
[c] Tentative assignments

azo-compound was obtained in high yield. Even under weakly basic conditions, such as in aqueous pyridine, the azo-coupling was readily accomplished. The reductive cyclization of the ortho-nitro azo-compound to the benzotriazole was also not simple because the electron-withdrawing carboxy-group did not facilitate this reaction. An intermediate of the reductive cyclization reaction could be isolated whose elemental analysis agreed with a structure still having two oxygen atoms in the molecule, which could be the diazoxide.

Elemental analysis: Calcd. for $C_{22}H_{16}N_6O_8$: C 51.72%, H 2.59%, N 18.10%. Found: C 51.61%, H 2.59%, N 18.07%.

If the reductive cyclization of the *ortho*-nitro azo-compound to the benzotriazole derivative was carried out at higher temperatures (90 °C to 100 °C) other side reactions occurred. We found that a two-step procedure gave satisfactory results: initially, a homogeneous reductive cyclization with sodium hydrosulfite at room temperature was carried out, followed by a further reduction with zinc powder in strongly alkaline solution. It should be pointed out that resorcinol derivatives are easily auto-oxidized; consequently, the reactions had to be carried out under nitrogen and/or with excess reducing reagent.

The synthesis of *DCBDH* was not a high-yield process; only 25% of the theoretical yield was obtained. After the extraction of the reaction product with acetone, a substantial amount of undissolved residue was left which could contain additional product.

It was difficult to recrystallize crude *DCBDH*; 90% aqueous acetic acid was found to be the best solvent for recrystallization. Pure *DCBDH* still has one molecule of water of crystallization (as judged by elemental analysis) which could not be removed by drying the compound at 1 mm Hg and 110 °C.

Crude *DCBDH* could be esterified directly, using a *Soxhlet* extractor, to *DCMBDH*. This procedure avoided the contact of *DCBDH* with conc. sulfuric acid and resulted in relatively pure *DCMBDH* which was readily recrystallized to polymerization grade monomer (*DCMBDH*).

The IR spectra of *DCBDH* showed an absorption peak at 1 694 cm^{-1} (—COOH); after esterification, the ester absorption of *DCMBDH* at 1 726 cm^{-1} (—$COOCH_3$) was the dominant absorption peak. *DCBDH* was also prepared by hydrolyzing pure *DCMBDH* with sodium hydroxide and the *DCBDH* obtained by this procedure was very pure.

The ultraviolet absorption spectra of *DCBDH* were measured in methanol and in dimethylacetamide. Differences in the λ_{max} and the extinction coefficient of the absorption maximum (Table 1 and Figs. 1 and 2) are clearly noticeable. Detailed characteristics of the ultraviolet spectra of 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives depended to a great

extent on the types of solvent used for the measurements. The absorption at about 340 nm represents the absorption of the n-π^* transition of the co-planar conformation formed by the intramolecular hydrogen bonding of the 2(2-hydroxyphenyl)2*H*-benzotriazole molecule; this absorption peak is the main absorption in solvents of low polarity.

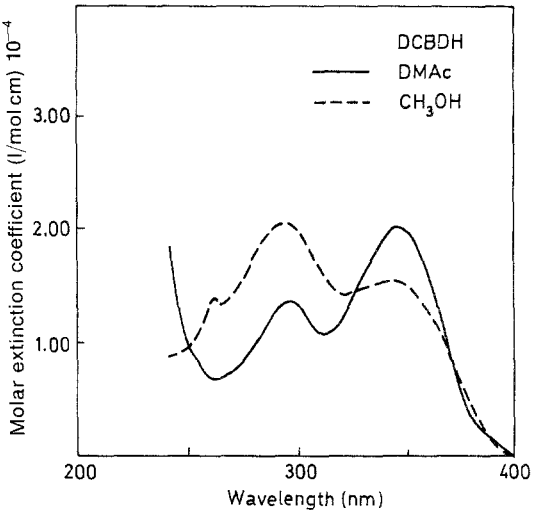


Fig. 1. Ultraviolet spectra of *DCBDH*

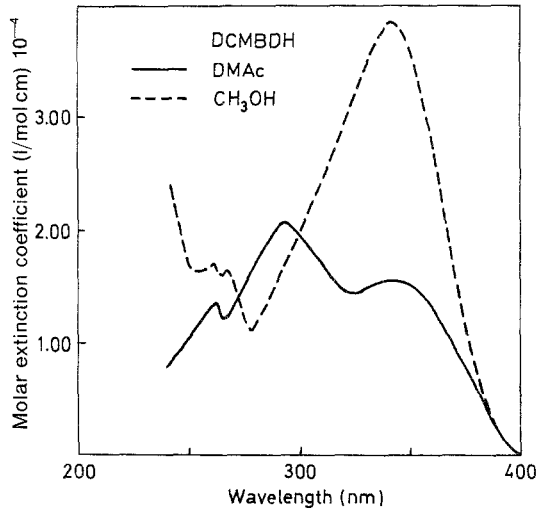


Fig. 2. Ultraviolet spectra of *DCMBDH*

The absorption at about 293 nm represents the n-π^* transition of the conformation of 2(2-hydroxyphenyl)2*H*-benzotriazole involving the free non-hydrogen bonded ortho-hydroxy group.

It had been found that in solvents of strong polarity or in hydrogen bonding solvents the intramolecular hydrogen bond is greatly diminished and the absorption at $\sim$ 340 nm becomes less intense; at the same time the absorption near $\sim$ 300 nm becomes more prominent and may even become the main absorption.

DCBDH or *DCMBDH* were incorporated into polyamides or polyesters by polycondensation (see also [25]).

Solution-polycondensation techniques with tetramethylenesulfone as the solvent gave soluble, apparently linear polyamides. The ultraviolet absorption spectra of the polymers of the copolycondensation of 2(2-hydroxyphenyl)2*H*-4-carboxybenzotriazole was measured after the polymer was purified by reprecipitation (Table 1).

Bulk polycondensation of *DCBDH* with the salt of sebacic acid and 1,10-decanediamine gave a cross-linked polymer. This means that not only the carboxy-groups, but also the hydrogen-bonded ortho-hydroxy groups took part in the polycondensation, forming a polyester bond as well.

DCMBDH could also be incorporated into polycarbonates by replacing part of the diphenyl carbonate needed for the polycondensation with bisphenol A.

The molar extinction coefficient of the *DCMBDH* unit, when it was incorporated into a polycarbonate, was almost the same as the extinction coefficient of the monomer, *DCMBDH*. The molar extinction coefficient of *DCBDH* in the polyester was only about half that of the value of the *DCBDH* monomer. It seems possible that the high melting point and the poor solubility of *DCBDH* in the polymerization mixture was the reason why *DCBDH* did not take fully part in the polycondensation reaction.

In conclusion, it was demonstrated that *DCBDH* and *DCMBDH* could be incorporated into polyamides, polyesters, and polycarbonates by reactions through the carboxy- or carbomethoxy-groups of the dibenzotriazole substituted 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives.

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