

Functional Polymers

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46. Incorporation of Dihydroxy 2(2-Hydroxyphenyl) 2H-Benzotriazole Derivatives into Polycarbonates

Peter M. Gomez¹, Liping Hu¹, and Otto Vogl^{2}**

¹ Polytechnic University of New York,
Brooklyn, NY 11201, USA

² Herman F. Mark Professor of Polymer Science, Polytechnic University of New York,
Brooklyn, NY 11201, USA

This paper is dedicated to Professor Richard S. Stein on the occasion of his 65th birthday with warmest personal wishes

SUMMARY

Polycarbonates of Bisphenol A were prepared with 2(2,4-dihydroxyphenyl)2H-4-hydroxybenzotriazole or 2(2,4-dihydroxyphenyl)2H-1,3-di(4-hydroxybenzotriazole) ultraviolet stabilizers permanently incorporated into the polycarbonate main chain. Direct polycarbonate formation from Bisphenol A and diphenyl carbonate or transesterification using previously prepared polycarbonate in the melt with ultraviolet stabilizers 2(2,4-dihydroxyphenyl)2H-4-hydroxybenzotriazole or 2(2,4-dihydroxyphenyl)2H-1,3-di(4-hydroxybenzotriazole) or the corresponding acetyl compounds gave the final polycarbonates which were characterized.

INTRODUCTION

2(2-Hydroxyphenyl)2H-benzotriazoles have been used as ultraviolet stabilizers in plastic materials for some time (1). Vinyl, isopropenyl, acrylate and methacrylate derivatives as polymerizable 2(2-hydroxyphenyl)2H-benzotriazoles have been incorporated into addition polymers, either by copolymerization or by grafting (2-6). One of the derivatives, 2[2-hydroxy-4-vinyl(or 4-isopropenyl)phenyl]2H-benzotriazole has been incorporated into polymerizing mixtures that produced UV stabilized unsaturated polyesters (7).

Two bisphenol type 2(2-hydroxyphenyl)2H-benzotriazoles have also been prepared: 2(2,4-dihydroxyphenyl)2H-4-hydroxybenzotriazole (HBDH) was prepared from 2(2,4-dihydroxyphenyl)-2H-4-methoxybenzotriazole, and 2(2,4-dihydroxyphenyl)2H-1,3-di(4-hydroxybenzotriazole) (HDBDH) was synthesized from 2(2,4-dihydroxyphenyl)2H-1,3-di(4-methoxybenzotriazole), both by demethylation with dry hydrogen bromide in dimethylformamide (8,9). HBDH and HDBDH were incorporated into polyesters by direct ester formation from the diesters of

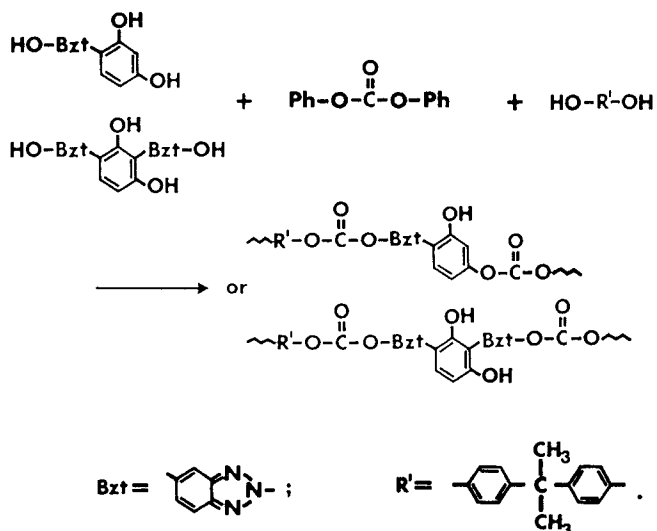
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** To whom all correspondence should be addressed

dicarboxylic acids with glycols (1-10 mole % of HBDH or HDBDH were incorporated) or by transesterification of HBDH or HDBDH, or better, of 2(2,4-dihydroxyphenyl)2H-1,3-di(4-acetoxybenzotriazole) (AcDBDH) with the polyesters.

HBDH, although a tri-, and HDBDH, although a tetraphenol act as bisphenols; one of the hydroxy groups in HBDH is hydrogen bonded to the benzotriazole rings, two of the hydroxyl groups in HDBDH are also hydrogen bonded and less reactive. Since only two hydroxyl groups in HBDH or HDBDH are fully reactive, linear polyesters could be prepared by polyesterification. The hydrogen bonded hydroxyl groups were, however, reactive for polyester synthesis with diacid chlorides as the acid derivatives. In these cases, branched and cross-linked polyesters were obtained (10).

It was the objective of this investigation to prepare linear polycarbonates with 2(2-hydroxyphenyl)2H-benzotriazole UV absorbing groups (HBDH or HDBDH) incorporated into the polycarbonate main chain by direct synthesis of the polycarbonate from the UV absorbers, Bisphenol A, and diphenyl carbonate or by transesterification. (Equation)



EXPERIMENTAL PART

A. Materials

Chloroform was washed with water and dried. Dimethylacetamide (DMAc) was distilled from calcium hydride at 20 mm Hg.

Recrystallized and dried for at least one day at 1.5 mm Hg over phosphorous pentoxide were: diphenyl carbonate (from 95% ethanol) and 2,2'-bis(4-hydroxyphenyl)propane (Bisphenol A) (from toluene). All other solvents and reagents were used as received. (All materials were obtained from the Aldrich Chemical Co.)

Silicon oil baths were used for heating reaction tubes to temperatures up to 250°C. The following vapor baths were used for higher temperatures: phenylacetic acid for 265°C, dimethyl phthalate for 282°C, diethylene phthalate 298°C.

B. Measurements

UV absorption spectra were measured in chloroform (spectral grade) solutions using a Varian Cary 15 or a Varian Cary 2300 Spectrophotometer in a double beam servo mode (1.0 cm optical path length).

C. Procedures

Polycarbonate from Bisphenol A and Diphenyl Carbonate:

A 100 mL round-bottom flask equipped with side-arm and nitrogen inlet capillary was charged with freshly recrystallized diphenyl carbonate (10.7 g, 50 mmol), Bisphenol A (11.4 g, 50 mmol), and zinc oxide (about 1 mg). The flask was heated to about 200°C with a steady stream of nitrogen flushing through the molten liquid. The distilled phenol was collected in a 100 mL flask attached to the side-arm (heating tape was used to prevent phenol condensation in the side-arm). After 2 hours, the nitrogen line was disconnected and a vacuum line attached to the collecting flask via an adaptor. The pressure was lowered to 0.5 mm Hg over 15 minutes and heating was continued for 3 hours at around 230°C. After one more hour at 250°C, the flask was cooled and the contents dissolved in DMAc (150 mL). The DMAc solution was then poured into rapidly stirred methanol (400 mL); the polycarbonate precipitated as a fine white powder, which was collected and washed with methanol, then dried in a vacuum desiccator. A yield of 11.2 g (88%) was obtained; inherent viscosity $[\eta] = 0.35$ dL/g (0.5% in 1,2-dichloromethane solution at 30°C).

Polycarbonate from Bisphenol A and Diphenyl Carbonate with HBDH or HDBDH incorporated: Using a similar procedure to that described for the preparation of polycarbonate, modified polycarbonate samples were prepared with UV absorbers HBDH and HDBDH in 0.1, 0.5, 1.0 and 3 mol % in the monomer feed. The apparatus was modified such that three reactions could be run simultaneously. Three 50 mL test tubes with ground-glass joints were charged with the reactants [25 mmol of diphenyl carbonate and 25 mmol of the diols (Bisphenol A plus HBDH or HDBDH)] and attached via still-heads to three necks of a four-neck flask (250 mL). Nitrogen gas was passed to the bottom of each tube, the exit port being the fourth neck of the receiving flask. Each run was conducted with one blank sample and two reaction mixtures involving HBDH or HDBDH.

The UV spectrum of each sample was run in chloroform (2×10^{-5} mol/L of HBDH and HDBDH) with the concentration of HBDH and HDBDH based on the feed composition; no further analysis was carried out; a λ_{\max} of 337 nm was observed for samples which had HDBDH incorporated and a λ_{\max} of 342 nm for those with HBDH incorporated into the polycarbonate.

Soxhlet Extraction of Polycarbonates: Samples of polycarbonates with 3 mol % of HBDH and HDBDH (2 g each) were placed in a Soxhlet extractor and extracted for 1 day with

n-hexane (75 mL). In both cases, no trace of HBDH or HDBDH could be detected when the solutions were evaporated and the residue was subjected to TLC analysis.

Polycarbonate Transesterified with AcDBDH: In a polymerization tube equipped with a side-arm and an inlet for nitrogen, a sample was placed from previously prepared polycarbonate₅ (2g, $[\eta] = 0.35$ dL/g) together with (AcDBDH) (25mg, 5.4×10^{-5} mol) and zinc oxide (2 mg). The mixture was heated to 298°C for 2 hours with nitrogen passing through the molten reactants. The pressure was then lowered to 1.5 mm Hg within 10 minutes and maintained for 5 hours. After cooling the tube the yellow glassy solid was dissolved in chloroform (25 mL) and this solution added to stirred methanol (15 mL). The polymer, which precipitated as a light yellow powder, was washed with more methanol (2 x 75 mL) and extracted with n-hexane (100 mL) for 1.5 days in a Soxhlet extractor before being dried overnight at reduced pressure in the dessiccator. The UV spectrum of this sample in chloroform solution (2×10^{-5} mol/L based on a feed ratio, assuming complete incorporation) showed λ_{\max} at 330 nm ($\epsilon = 3.6 \times 10^4$ L/mol.cm).

RESULTS AND DISCUSSION

Polycarbonates with Bisphenol A permanently attached to the polycarbonate main chain with 1-3 mol % of HBDH or HDBDH have been synthesized; the amount of UV absorbing compounds incorporated was 0.1, 0.5, 1.0 and 3 mol %. The polycarbonate samples were prepared by direct synthesis from diphenyl carbonate and Bisphenol A at 25 mmol quantities of Bisphenol A and diphenyl carbonate. The relative amounts of Bisphenol A, HBDH or HDBDH were adjusted so that the total amount of the two components was 25 mmols. The polymers obtained had molecular weights whose inherent viscosity ranged $[\eta]$ from 0.2 to 0.5 dL/g and had all the UV absorbing compounds incorporated in approximately the amount that was placed in the feed. Extraction of the polycarbonate powders showed that no UV absorbing compound was extractable; (judged by TLC analysis of the residue of the n-hexane extract) this extraction technique is extremely sensitive to even small amounts of the compounds.

We must conclude that the composition of HBDH and HDBDH was the same as the amount in the feed. UV absorption spectra of the polycarbonates with the UV absorbers in the polymer main chain are shown in Figure 1; the λ_{\max} were at 337 nm for the HDBDH containing samples and at 342 nm for the HBDH samples. This small difference in λ_{\max} does not seem significant and is within the experimental error range. The same can be said about the value of the extinction coefficient of the various curves. (Figure 2)

It was found that HBDH and HDBDH could be incorporated into polycarbonates by transesterification. The incorporation of HDBDH was also carried out by transesterification of AcDBDH as can be seen in Figure 3, which shows the approximate molar extinction coefficient of samples of polycarbonate with various amounts of HBDH and HDBDH incorporated in the polymer. It can be clearly seen that the λ_{\max} of these samples are around 340 nm, typical for the

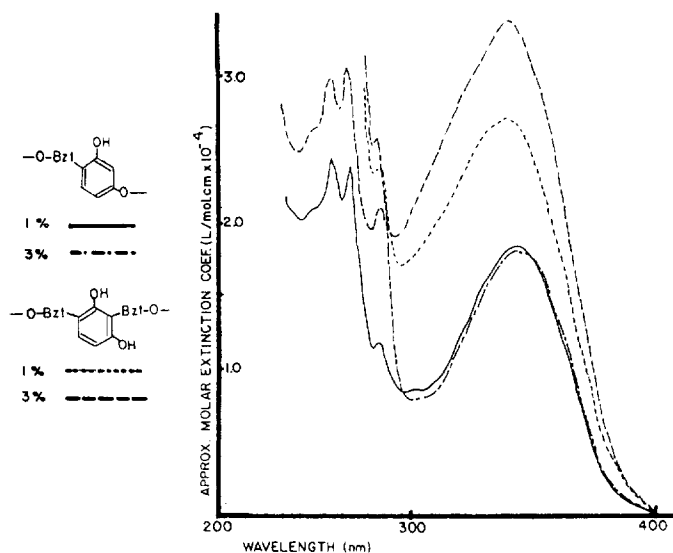


Figure 1: UV Spectra of Polycarbonates with HBDH and HBDH

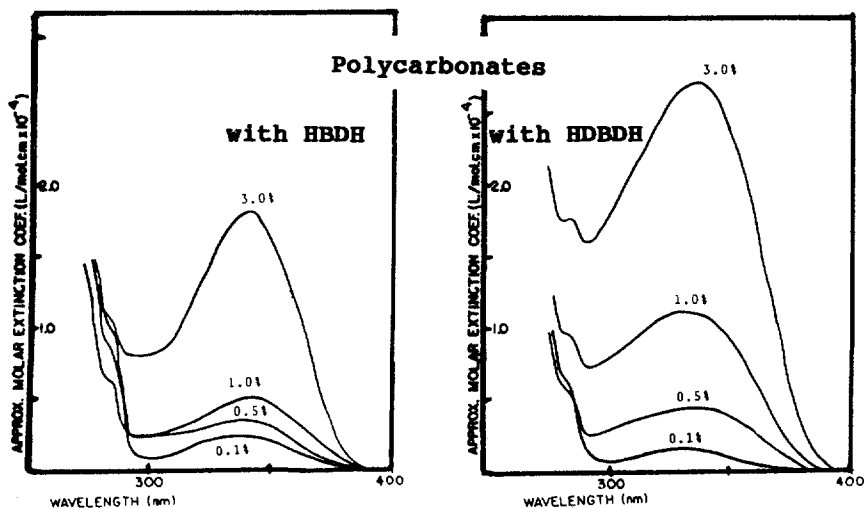


Figure 2: UV Spectra of various amounts of HBDH and HBDH

spectrum of hydrogen bonded 2(2-hydroxyphenyl)2H-benzotriazole units.

It is well known, that the λ_{\max} at 340 nm is caused by the structure involving the ortho-hydroxyl group, hydrogen bonded to the benzotriazole ring. When the ortho-hydroxy-position is blocked, (for example by acetylation) as can be seen by the λ_{\max} of 2(2-acetoxy-4-ethylphenyl)2H-benzotriazole), the λ_{\max} is shifted to 307 nm. The position of this λ_{\max} around 305 to 310 nm has also been observed in branched

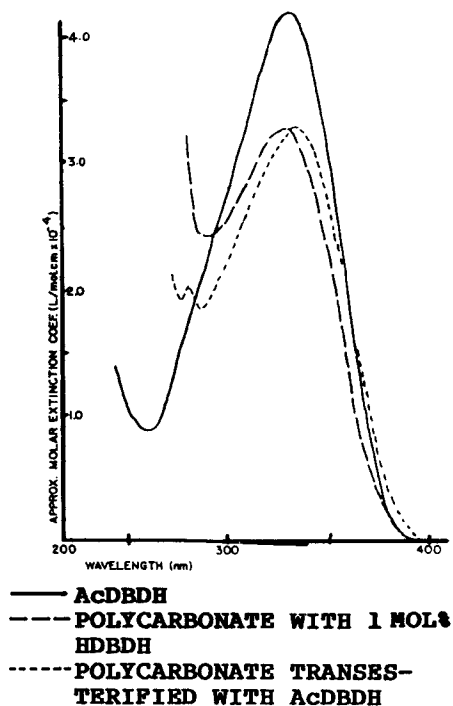


Figure 3: UV Spectra of Polycarbonate with AcDBDH by Transesterification

samples of polyesters which were prepared in the presence of HBDH or HDBDH by the acid chloride method (10) (branching occurred through the 2- and 4-hydroxy groups of HBDH or HDBDH).

In conclusion, we have shown that 2(2-hydroxyphenyl)2H-benzotriazole units can be incorporated into polycarbonates by synthesis from Bisphenol A and the diphenyl carbonate as the derivative of the carbonic acid. The incorporation could also be accomplished by transesterification of the diacetyl derivatives of HDBDH (AcDBDH). As long as the ortho hydroxyl group remained unreacted (and this hydroxyl group is much less reactive because it is hydrogen bonded), the λ_{max} is at 340 nm.

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