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# Functional Polymers XLV.[†] Incorporation of Dihydroxy 2(2-Hydroxyphenyl)2*H*-Benzotriazole Derivatives into Polyesters

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ABSTRACT: 2(2,4-Dihydroxyphenyl)2*H*-4-hydroxybenzotriazole and 2(2,4-dihydroxyphenyl)2*H*-1,3-di(4-hydroxybenzotriazole) were incorporated in amounts of 1 to 10 mol% into examples of typical aliphatic or aromatic polyesters, either by direct synthesis from the monomers or by transesterification from already prepared polyesters. The polyesters showed UV spectra typical for the 2(2-hydroxyphenyl)2*H*-benzotriazole unit in amounts approximately corresponding to the feed composition. Some complications in the direct incorporation of dihydroxy-2(2-hydroxyphenyl)2*H*-benzotriazoles into polyesters were encountered when the diacid chloride method was used for the preparation of the polyesters; branched and crosslinked polyesters were obtained.

KEY WORDS Aliphatic and Aromatic Polyesters / Polymerizable Ultraviolet Stabilizers / Crosslinking / Acid Chlorides / Glycols / Transesterification /

2(2-Hydroxyphenyl)2*H*-benzotriazoles have become very important as ultraviolet screening stabilizers for polymeric materials.[1] Recently, a number of polymerizable ultraviolet stabilizers of the 2(2-hydroxyphenyl)2*H*-benzotriazole family have been reported[2-10]; they include vinyl and isopropenyl derivatives,[2-5] acrylates and methacrylates,[6-8] and some methoxy derivatives.[9,10] Some of these compounds were incorporated into polymers by copolymerization; others, for example 2(2-hydroxy-4-vinylphenyl)2*H*-benzotriazole (2H5V), by grafting [into polybutadiene[11] or onto the polymers with aliphatic carbon hydrogen bond such as polypropylene or poly(methyl methacrylate)[12]]; 2H5V was also incorporated into unsaturated polyesters[13] or other crosslinked polymers.[14] 2H5V was shown to have been placed firmly in the polymer matrix and remained in position even under severe degradation conditions.

2(2-Hydroxyphenyl)2*H*-benzotriazole derivatives were prepared with more than one benzotriazole ring in the molecule.[15,16] In addition, methoxysubstituted 2(2-hydroxyphenyl)-2*H*-benzotriazole derivatives have also been prepared.[9,10]

2(2-Dihydroxyphenyl)2*H*-4-hydroxybenzotriazole (HBDH), 2(2,4-dihydroxyphenyl)2*H*-1,3-di(4-hydroxybenzotriazole) (HDBDH), and their diacetoxy derivatives (AcBDH or AcDBDH) were considered as desirable ultraviolet stabilizers for polyesters.[17]

It was the objective of this work to prepare aliphatic and aromatic polyesters with HBDH and HDBDH incorporated into the polyester

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[†] Part XLIV: P. Grosso and O. Vogl, *Polym. Bull.*, **14**, 245 (1985).

[*] This paper is dedicated with warmest personal wishes to Professor Teiji Tsuruta on the occasion of his 65th birthday.

chain.

## EXPERIMENTAL

### *Materials*

The following solvents and reagents were distilled and stored over molecular sieve (all reagents were from the Aldrich Chemical Co.): butanediol-1,4 (at 20 mmHg), chloroform (washed with water and dried), ethylene glycol (at 20 mmHg), dichloromethane (from calcium hydride), dimethylacetamide (DMAc) (from calcium hydride at 20 mmHg), pyridine and tri-*n*-butylamine (from metallic sodium at 15 mmHg), hexanediol-1,6 (at 10 mmHg), and decanediol-1,10 (at 0.05 mmHg). The following reagents (Aldrich Chemical Co.) were recrystallized (and dried over phosphorus pentoxide at 0.15 mmHg for at least one day): isophthaloyl chloride and terephthaloyl chloride twice from *n*-hexane, dimethyl isophthalate from water. For spectral measurements, chloroform (spectral grade) or *s*-tetrachloroethane was used as the solvent.

All other solvents and reagents were used as received.

Distillations were carried out through a 30-cm Vigreux column equipped with a variable reflux ratio distillation head. Reduced pressure distillations were carried out with a magnetic stirrer and a Cartesian-type diver manostat. HBDH and HDBDH were prepared according to a previously described method.[9,10,17]

Silicon oil baths were used for heating the reactions up to 250°C. The following vapor baths were used for higher temperatures: phenylacetic acid, 265°C; dimethyl pathalate, 283°C; diethyl phthalate, 298°C.

### *Measurements*

Infrared spectra were recorded on a Perkin–Elmer spectrometer, Model 727, and $^1$H NMR (90 MHz) spectra on a JEOL FX-90 multinuclear FT NMR spectrometer; TMS was used as the internal standard. Ultraviolet absorptions were measured in chloroform or in 60/40 phenol/*s*-tetrachloroethane solutions using a Varian Cary 15 or a Varian Cary 2300 spectrophotometer in a double-beam servo mode (1.0 cm optical path length).

Melting points were determined on a MELT-TEMP capillary melting point apparatus and are uncorrected.

Microanalyses were carried out at the Microlytic Laboratory in South Deerfield, Massachusetts.

### *Procedures*

*Preparation of Poly(butylene isophthalate) in Solution by the Acid Chloride Method*: Into a dry 250 ml three-neck flask equipped with magnetic stirrer, reflux condenser and dropping funnel was placed butanediol-1,4 (2.25 g, 25 mmol) and tri-*n*-butylamine (9.3 g, 11.9 ml, 50 mmol) in dichloromethane (15 ml). The content of the flask were kept under a nitrogen atmosphere, and isophthaloyl chloride (5.1 g, 25 mmol) dissolved in dichloromethane (20 ml) was added dropwise over a 10-min period. A vigorous exothermic reaction took place and a white suspension formed immediately. Stirring was continued overnight at room temperature before the contents of the flask were poured into a beaker of rapidly stirred methanol (400 ml) to precipitate the white polymer. The polymer was washed with methanol (100 ml), water (100 ml), and finally with more methanol and dried at 1.5 mmHg; yield 3.95 g (72%).

*Preparation of Poly(butylene isophthalate) with 3 mol% of HBDH Incorporated*: The above procedure was repeated with butanediol-1,4 (2.16 g, 24 mmol), HBDH (0.38 g, 1.5 mmol) (dissolved in dichloromethane), and isophthaloyl chloride (5.07 g, 50 mmol). After work-up and drying, a yield of 4.51 g (80%) of white polymer was obtained. Analysis of the polymer for its nitrogen content gave:

*Elemental Analysis*. Calcd for 3 mol% HBDH in poly(butylene isophthalate) assuming the yield as quantitative: N, 1.39%. Found: N, 1.49%. No viscosity measurements were made as the polymer was found to be insoluble

**Table I.** Characterization of polyesters with 1.5 mol% HBDH; synthesis from diacid chlorides and glycols ([$\eta$] in dl g$^{-1}$)

| | Poly(sebacate) | Poly(isophthalate) | Poly(terephthalate) |
|---|---|---|---|
| Ethylene glycol | 0.05[a,c] | 0.18[b,c] | insoluble |
| Butanediol-1,4 | 0.11[a,c] | 0.15[b,c] | insoluble |
| Hexanediol-1,6 | 0.12[a] | insoluble | insoluble |
| Decanediol-1,10 | 0.14[a] | insoluble | insoluble |
| 2,2-Dimethylpropanediol | 0.10[a] | insoluble | insoluble |
| *trans*-Cyclohexane-1,4-dimethanol | 0.09[a] | insoluble | insoluble |

[a] Inherent viscosity measured in 1,2-dichloroethane at 30°C.

[b] Inherent viscosity measured in phenol/*s*-tetrachloroethane (60/40).

[c] UV spectra measured in chloroform at a concentration of $2 \times 10^{-5}$ l mol$^{-1}$ cm$^{-1}$, $\lambda_{max} = 307$ nm.

**Table II.** Polyesters prepared from the diesters and glycols with 1 mol% HBDH or HDBDH[a]

| | Type of stabilizer (1 mol%) | Yield | [$\eta$] | $\lambda_{max}$ |
|---|---|---|---|---|
| | | % | dl g$^{-1}$ | nm |
| Poly(ethylene sebacate) | HDBDH | 87 | 0.52 | 345 (broad) |
| Poly(butylene sebacate) | HBDH | 80 | 0.20 | 345 |
| Poly(ethylene isophthalate) | HBDH | 83 | 0.15 | 350 |
| Poly(ethylene isophthalate) | HDBDH | 87 | 0.18 | 340 |
| Poly(butylene isophthalate) | HBDH | 91 | 0.33 | 345 |
| Poly(butylene isophthalate) | HDBDH | 90 | 0.29 | 345 |
| Poly(ethylene terephthalate) | HBDH | 97 | insol. | insol. |
| Poly(ethylene terephthalate) | HDBDH | 94 | insol. | insol. |
| Poly(butylene terephthalate) | HBDH | 94 | insol. | insol. |

[a] All viscosity and UV measurements were made in phenol/*s*-tetrachloroethane (60/40).

in the 60/40 phenol/*s*-tetrachloroethane mixture.

*Preparation of Poly(butylene isophthalate) with* 10 mol% *HDBDH Incorporated*: Using the above procedure, the following reactants were used: butanediol-1,4 (0.36 g, 4 mmol), HDBDH (0.38 g, 1 mmol), tri-*n*-butylamine (1.86 g, 10 mmol), and isophthaloyl chloride (1.02 g, 5 mmol). Dry DMAc (2 ml) was used to dissolve HDBDH which was insoluble in dichloromethane. After work-up and drying, a yield of 0.98 g (76%) of off-white polymer was obtained.

Elemental Analysis calculated for 10 mol% HDBDH in poly(butylene isophthalate), assuming quantitative yield: N, 8.80%. Found: N, 8.26%.

Both samples of poly(butylene isophthalate) with 3 mol% HBDH or with 10 mol% HDBDH (2 g each) were extracted in a Soxhlet extractor with *n*-hexane (50 ml) for one day. In both cases, not a trace of HBDH or HDBDH was detected when the *n*-hexane extracts were evaporated and the residue subjected to TLC analysis.

Using the acid chloride procedure outlined for the preparation of poly(butylene isophthalate) with the intended incorporation of HBDH or HDBDH, the following polyesters were prepared, starting with 25 mmol of acid chloride, 25 mmol of the mixture of glycol and 1.5 mol% of the 2(2,4-dihydroxyphenyl)2*H*-benzotriazole compounds, HBDH or HDBDH (Table I).

*Preparation of Polyesters in the Melt from the Dimethylesters with HBDH or HDBDH*: *Poly*(*butylene sebacate*) *with* 1 mol% *HBDH*: A polymerization tube with a side-arm and nitrogen inlet with capillary needle was charged with a mixture of butanediol-1,4 (4.5 g, 50 mmol), dimethyl sebacate (11.5 g, 50 mmol), HBDH (2.43 g, 1 mmol), lead oxide (0.1 g), and calcium acetate dihydrate (0.1 g) as catalysts. The mixture was heated to 170—180°C at atmospheric pressure under nitrogen for 3 h; the pressure was then lowered to 20 mmHg and the temperature was raised to 190—200°C; after 2 h at 210—220°C the pressure was reduced to 1.5 mmHg and the melt held for 1.5 h at 280°C (1.5 mmHg). The highly viscous melt was cooled, the polymer dissolved in dichloromethane and precipitated by pouring the solution into methanol (400 ml); an off-white solid was obtained in a yield of 10.5 g (80%).

The inherent viscosity [$\eta$] in 1,2-dichloroethane was 0.3 dl g$^{-1}$. The UV spectrum (chloroform) showed $\lambda_{\max}$ at 345 nm ($\varepsilon = 2.6 \times 10^4$ l mol$^{-1}$ cm$^{-1}$) and 307 nm ($\varepsilon = 1.1 \times 10^4$ l mol$^{-1}$ cm$^{-1}$). Using the procedure outlined for the preparation of poly(butylene sebacate) in the melt with 1 mol% of HBDH, the following polyesters were prepared from the dimethylesters and the corresponding glycols (Table II).

*Preparation of 2*(*2,4-dihydroxypheny*)*2H-1,3-Di*(*4-acetoxybenzotriazole*) (*AcDBDH*): In a 100 ml three-neck flask equipped with condenser and magnetic stirrer under a nitrogen atmosphere, a mixture of triphenylphosphite (23.1 g, 75 mmol), acetic acid (4.5 g, 75 mmol), and pyridine (30 ml) was stirred for 20 min at ~40°C. HDBDH (5.64 g, 15 mmol) was then added to this solution and stirring continued for 1 h; the solution was held for 3 h at 70—75°C, then cooled, diluted with chloroform (100 ml), washed with water (75 ml), diluted HCl (1 : 1) (4 × 50 ml), water (75 ml), and then dried over magnesium sulfate. After evaporation of the solvent, this residue, a yellow oil, was subjected to chromatography on silica (TLC grade, 250 g) using chloroform as eluent; from the oil, AcDBDH crystallized out as a light-yellow solid, which was obtained in 34% yield (2.4 g), mp 171—172°C.

*Elemental Analysis*. Calcd for $C_{22}H_{16}O_6N_6$: C, 57.39%; H, 3.48%; N, 18.26%. Found: C, 57.80%; H, 3.69%; N, 17.90%.

IR ($CHCl_3$): 3550 cm$^{-1}$ (OH), 1710 cm$^{-1}$ (C=O). $^1$H NMR (90 MHz, $CDCl_3$), $\delta$ in ppm: 8.0—8.6 (benzylic, 8), 2.35 ($-\overset{\overset{O}{\|}}{C}-C\underline{H}_3$, 6), 12.3 (–OH). UV spectrum ($2 \times 10^{-5}$ mol l$^{-1}$ in chloroform): $\lambda_{\max} = 335$ nm ($\varepsilon = 4.2 \times 10^4$ l mol$^{-1}$ cm$^{-1}$).

*Transesterification of AcDBDH with Poly*(*butylene isophthalate*): A sample of previously prepared poly(butylene isophthalate) (2 g; [$\eta$] = 0.31 dl g$^{-1}$, 0.5% in phenol/*s*-tetrachloroethane), AcDBDH (25 mg, $5.4 \times 10^{-5}$ mol) and zinc oxide (3 mg), were placed in a polymerization tube which was equipped with a side-arm and an inlet tube for nitrogen capillary. The tube was heated to 298°C for 1.5 h while nitrogen passed through the molten liquid. The pressure was reduced to 1.5 mmHg over a 10-min period and the melt maintained for 5 h at this temperature. The tube was then cooled, the glassy solid dissolved in *s*-tetrachloroethane and precipitated into methanol (250 ml). The off-white solid was washed with methanol and dried to give 1.65 g of poly(butylene isophthalate) with HDBDH incorporated.

The UV spectrum of this sample ($2 \times 10^{-5}$ mol l$^{-1}$) of stabilizer concentration as calculated from the feed ratio of AcDBDH) in phenol/*s*-tetrachloroethane (60/40) showed $\lambda_{\max}$ at 328 nm. The viscosity, measured on 0.5% concn of the polymer in the same solvent system was: [$\eta$] = 0.29 dl g$^{-1}$.

## RESULTS AND DISCUSSION

Several aliphatic and aromatic polyesters have been prepared that have HBDH or HDBDH incorporated in the polymer backbone chain. The amounts of HBDH or HDBDH in the polyester varied from 1 to 10 mol%. Most of the work was done at the practical level of 1 to 1.5 mol%, but the incorporation of higher amounts was also demonstrated to be feasible. For example, 3 mol% of HBDH or HDBDH was incorporated into poly(butylene isophthalate), and even 10 mol% of HDBDH was incorporated into poly(butylene isophthalate) (eq 1). The preparation of "homopolymers" of HBDH or HDBDH with dicarboxylic acid was not investigated.

The polyesters were prepared from three typical dicarboxylic acids: sebacic acid, isophthalic acid, and terephthalic acid. The glycols used were: ethylene glycol, butanediol-1,4, hexanediol-1,6, decanediol-1,10, 2,2-dimethylpropanediol, and *trans*-cyclohexane-1,4-dimethanol.

We have used basically three techniques for the incorporation of HBDH or HDBDH: (a) solution synthesis of the polyester from the diacid chloride and the glycol (with the appropriate stoichiometric amount of glycol replaced by the bisphenols HBDH or HDBDH), (b) melt synthesis of the polyester from the diester and the glycol, and (c) transesterification of the already prepared polyester with HBDH or HDBDH, or better with AcDBDH.

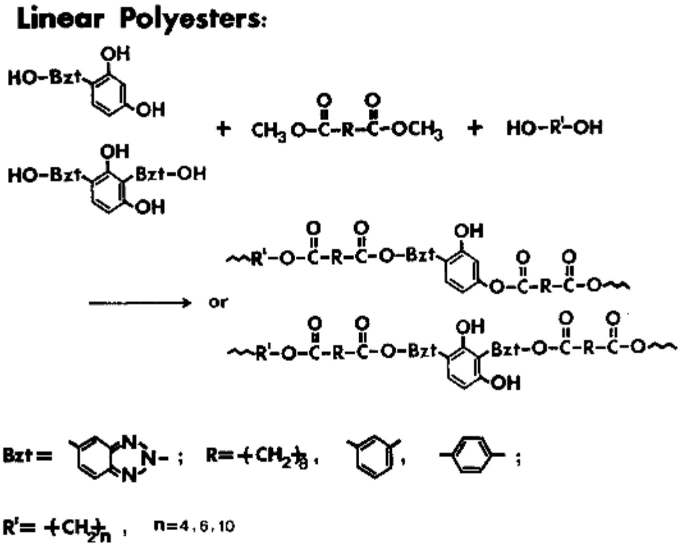
Synthesis (a) produced polyesters of relatively low molecular weight for the poly(sebacate) series and two soluble polyesters of the poly(isophthalate) series. The remainder of the poly(isophthalate) series and the poly(terephthalate) series was insoluble (Table I).

Investigation of the UV spectra of the four soluble polyesters of sebacic and isophthalic acid with ethylene glycol and butanediol-1,4 indicated that the $\lambda_{\max}$ of the polyester was at 307 nm. Knowing that the "normal" UV spectra of 2(2-hydroxyphenyl)2*H*-benzotriazoles have their $\lambda_{\max}$ at or near 340 nm and that the 2-acetylated compounds do not have a 340 nm $\lambda_{\max}$ but the $\lambda_{\max}$ at 305 to 310 nm, we concluded that these polyesters are branched. This means that polyesters prepared by the acid-chloride method have branched and cross-linked structures by virtue of the high reactivity of the acid chloride toward all hydroxyl groups available; even the hydrogen-bonded 2-hydroxy group in the 2(2-hydroxyphenyl)2*H*-benzotriazole system was reactive (eq 2). Figures 1 and 2 show the UV spectra of selected polyesters with HBDH and HDBDH incorporated to 1 mol%.

Polyesters prepared by synthesis route (b) are generally soluble, have $[\eta]$ of 0.2 to 0.5 $\mathrm{dl\,g^{-1}}$, and show absorption maxima in the 340 to 350 nm range, indicating that the 2-hydroxy group of the 2(2-hydroxyphenyl)2*H*-benzotriazole system remains free and consequently should provide the good UV protection known for 2(2-hydroxyphenyl)2*H*-benzotriazoles.

Since it is known that incorporation of bisphenols into polyesters by replacement of some of the glycol units is most effectively done by using the diacetate of the bisphenol, we prepared the diacetate of HDBDH, where only the unhindered 4-hydroxy groups of the phenyl ring of the two benzotriazole groups were acetylated, but the 2,4-dihydroxy groups were left unreacted. Within the experimental errors of our measurements, the $\lambda_{\max}$ of AcDBDH, the polyesters with 1 mol% HDBDH prepared according to system (b) and the polyesters prepared by transesterification (system c) with AcDBDH were very similar, indicating that transesterification with the diacetate AcDBDH also produced a linear polyester with the HDBDH units incorporated in the polyester chains. (For UV spectrum, see Figure 3.)

In conclusion, we have prepared polyesters with UV-absorbing units of the 2(2-hydroxyphenyl)2*H*-benzotriazole family incorporated into the polymer backbone by direct polyester



(1)

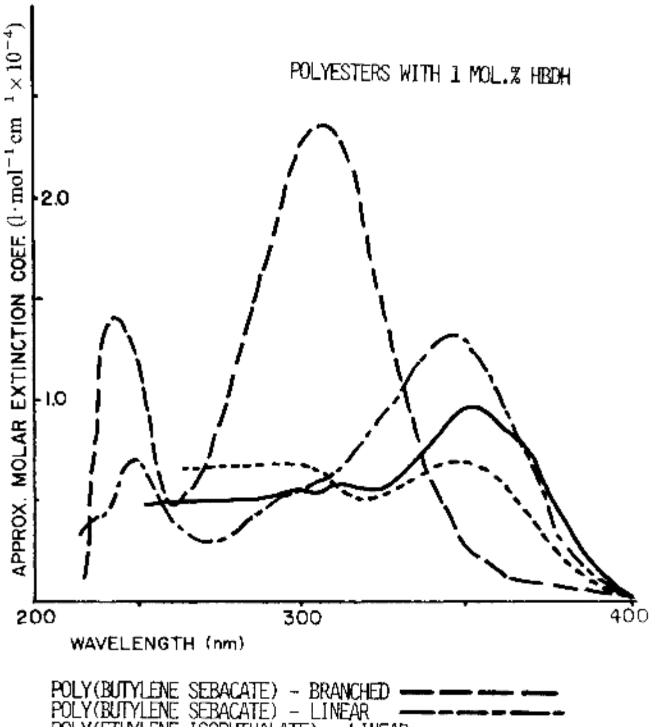


**Figure 1.** UV spectra of polyesters with 1 mol% HBDH.

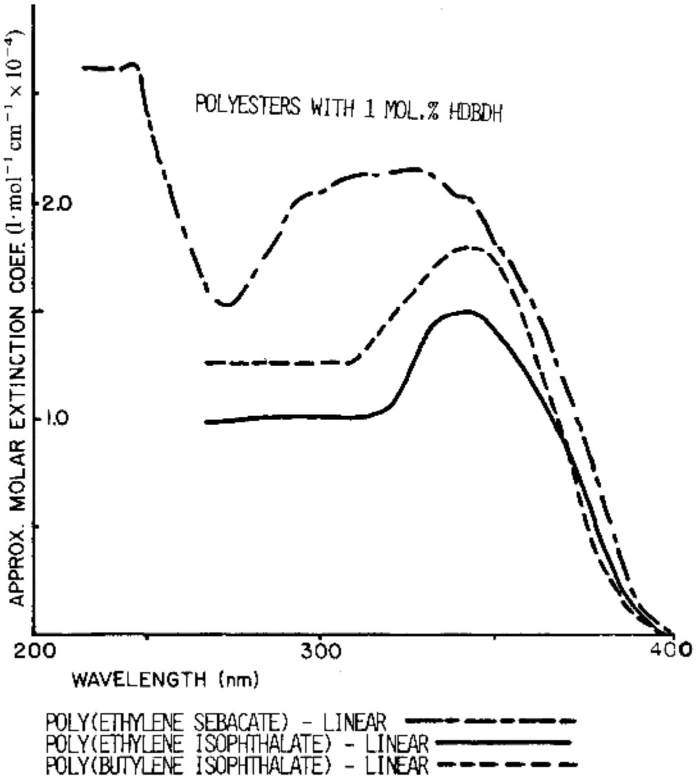
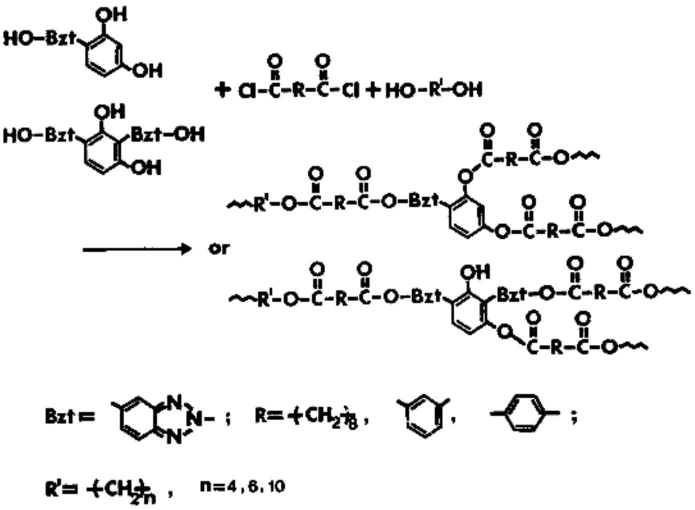


**Figure 2.** UV spectra of polyesters with 1 mol% HDBDH.

## Branched or Crosslinked Polyesters:



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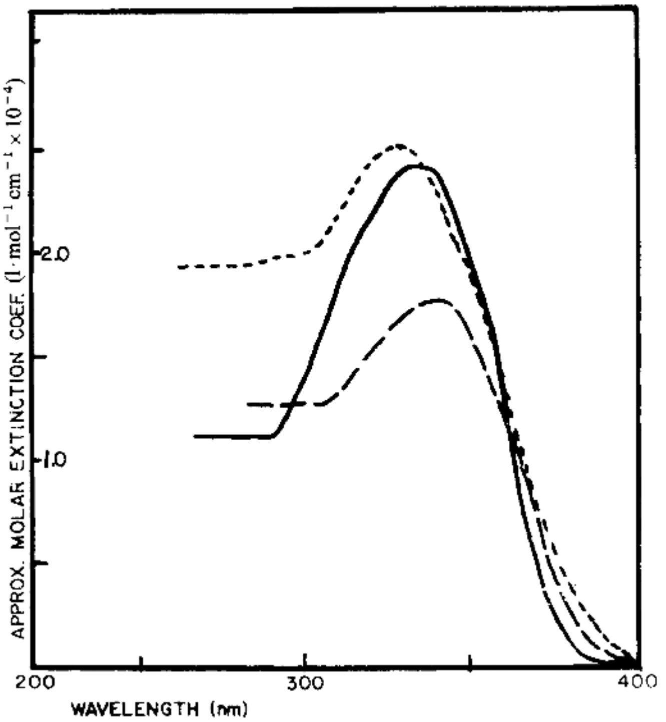

——, AcDBDH; — — —, POLYESTER WITH 1 MOL% HDBDH; ----, POLYESTER TRANSESTERIFIED WITH AcDBDH

**Figure 3.** UV spectra of AcDBH, polyesters with 1 mol% HDBDH, and polyesters transesterified with AcDBDH.

synthesis from the diesters or by transesterification using HBDH and HDBDH. By the diacid chloride polyester synthesis, branched and crosslinked polyesters were obtained.

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## REFERENCES

1. O. Vogl, A. C. Albertsson, and Z. Janovic, *Polymer*, **26**, 1288 (1985).
2. S. Yoshida and O. Vogl, *Makromol. Chem.*, **183**, 259 (1982).
3. A. Gupta, G. Scott, and O. Vogl, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **23**, 219 (1982).
4. Z. Nir, A. Gupta, and O. Vogl, *J. Polym. Chem., Polym. Chem. Ed.*, **20**, 2735 (1982).
5. S. K. Fu, A. Gupta, A. C. Albertsson, and O. Vogl, "New Trends in the Photochemistry of Polymers," Norman S. Allen and Jan F. Rabek, Ed., Elsevier Applied Science Publishers, London, 1985, p 247.
6. S. J. Li, A. C. Albertsson, A. Gupta, W. Bassett, and O. Vogl, *Monatsh. Chem.*, **115**, 853 (1984).
7. S. J. Li, A. Gupta, A. C. Albertsson, W. Bassett, and O. Vogl, *Polym. Bull.*, **12**, 237 (1984).
8. F. Xi, W. Bassett, and O. Vogl, *Polym. Bull.*, **11**, 329 (1984).
9. F. Xi, W. Bassett, and O. Vogl, *Makromol. Chem.*, **185**, 2497 (1984).

10. S. K. Fu and O. Vogl, *Montash. Chem.*, in press.
11. M. Kitayama and O. Vogl, *Polym. J.*, **14**, 537 (1982).
12. W. Pradellok, A. Gupta, and O. Vogl, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 3307 (1981).
13. Z. J. Song, B. Ranby, A. Gupta, E. Brosig, and O. Vogl, *Polym. Bull.*, **12**, 245 (1984).
14. W. Dickstein and O. Vogl, *J. Macromol. Sci., Chem.*, **A22**, 387 (1985).
15. S. J. Li, A. Gupta, and O. Vogl, *Monatsh. Chem.*, **114**, 937 (1983).
16. S. J. Li, W. Bassett, A. Gupta, and O. Vogl, *J. Macromol. Sci., Chem.*, **A20**, 309 (1983).
17. P. M. Gomez, S. K. Fu, A. Gupta, and O. Vogl, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **26**, 100 (1985).