Polymer Bulletin 12, 237-243 (1984)

Polymer Bulletin

Functional Polymers.
29. Polymerizable Acrylic Ultraviolet Absorbers with Two Benzotriazole Groups in the Molecules

Shanjun Li[a], Amitava Gupta[b], Ann Christine Albertsson[a], Walter Bassett, Jr.[c], and Otto Vogl[a]**

[a] Polytechnic Institute of New York, 333 Jay Street, Brooklyn, NY 11201, USA

[b] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA

[c] Polymer Science and Engineering Department, University of Massachusetts, Amherst, MA 01003, USA

---

* Part 28: O. Vogl, Functional Polymers, Macromol. Chem., in press.

** To whom all inquiries should be addressed.

ABSTRACT

Acrylates and methacrylates of 1,3(2,4-dihydroxyphenyl)-di(2H-benzotriazole) and 1,3(2,4,6-trihydroxyphenyl)-di(2H-benzotriazole) have been prepared by treating acrylic acid or methacrylic acid with N,N'-dicyclohexyl carbodiimide and then allowing this mixture to react with the phenolic ultraviolet absorbers to give 1,3[2-hydroxy-4-acryloxy(methacryloxy)phenyl]-di(2H-benzotriazole) and 1,3[2,6-dihydroxy-4-acryloxy(methacryloxy)phenyl]-di(2H-benzotriazole). The yield of the esters was from 10 to 30%; they were characterized by their infrared, ^1H, and ^{13}C NMR spectra; their polymerizability was demonstrated. The compounds had λ_{max} of 330 to 335 nm with extinction coefficients ranging from 3.0 to 3.5 x 10^4 L/mol•cm.

INTRODUCTION

Polymerizable ultraviolet absorbers of 2(2-hydroxyphenyl)2H-benzotriazole have been studied extensively in recent years. Two different types of polymerizable groups have been introduced into the 2(2-hydroxyphenyl)2H-benzotriazole ring. Vinyl or isopropyl groups in the 5 position of the phenyl ring (1-4) or in the 4 position of the benzotriazole ring (5,6) resulted in the synthesis of styrene-type monomers. Acryl(methacryl) or acrylamide(methacrylamide) groups were also introduced into the benzotriazole ring by utilizing a 4-hydroxy-group in the benzotriazole ring (7). The unhindered 4-hydroxy-group of 2(2,4-dihydroxyphenyl)2H-benzotriazole (8) was also esterified (9,10) with acryloyl or methacryloyl groups, similar to the well-known esterification of the unhindered 4-hydroxy-group in 2,4-dihydroxybenzophenone (11).

With the recent finding that resorcinol or phloroglucinol can react readily, especially in basic solution, with more than two mols of 2-nitrobenzenediazonium chloride to give after reductive cyclization di- and tribenzotriazolized di- and trihydroxybenzenes (12,13), the initial interest in making polymerizable acryloyl or methacryloyl derivative of these compounds became a definite possibility.

Initial attempts with more classical methods of esterification, such as the use of the acid chlorides under various reaction conditions, failed.

Esterification methods for phenols and alcohols that are esterified with difficulty have recently been developed (14-16); they allow the preparation of esters under mild conditions at neutral pH and at room temperature.

It was the objective of this work to prepare acrylates and methacrylates of hindered phenolic ultraviolet stabilizers, to characterize them, especially by their ultraviolet spectra, and possibly to demonstrate their polymerizability.

EXPERIMENTAL PART

A. Materials

Acrylic acid (AA), methacrylic acid (MA), 4-pyrrolidinopyridine (4-PP), N,N′-dicyclohexylcarbodiimide (DCC), and magnesium sulfate (all Aldrich Chemical Co.) were used as received.

Tetrahydrofuran (Aldrich Chemical Co.) (THF) was heated to reflux with lithium aluminum hydride (Alfa Products) (LAH) and distilled under nitrogen atmosphere.

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

B. Measurements

Infrared spectra were recorded on a Perkin-Elmer Spectrophotometer, Model 727, on solid samples as potassium bromide pellets.

^1H 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 as 15% or saturated solutions in $CDCl_3$ (for details, see Ref. 2).

Ultraviolet absorptions were measured in chloroform solution (Spectrograde, Fisher Scientific Co.).

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

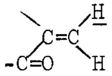
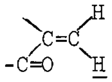
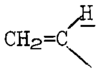
1. 1,3(2-Hydroxy-4-methacryloxyphenyl)-di(2H-benzotriazole) (DBDHM): A dry 250-mL roundbottom flask equipped with a magnetic stirrer, dropping funnel, a nitrogen inlet and an exit tube, connected to a paraffin oil bubbler was charged with 1,3(2,4-dihydroxyphenyl)-di(2H-benzotriazole) (DBDH) (3.44 g, 0.01 mol), 4-PP (0.15 g, 0.001 mol), dissolved in THF (100 mL), and the flask was placed in a glove box. A dry 100-mL Erlenmeyer flask was placed in a glove box and charged with MA (0.86 g, 0.01 mol), DCC (2.27 g, 0.011 mol), and THF (50 mL). The mixture was allowed to stand at room temperature for 30 min, until white crystals of N,N′-dicyclohexylurea (DCU) began to precipitate; the solution was then decanted into a dropping funnel. This solution was added dropwise to the DBDH solution with stirring over a period of one hr at room temperature; the reaction was allowed to proceed for 12 hr. Benzene (50 mL) was then added, white crystals of DCU were filtered, and the filtrate washed with water (3 x 50 mL), 5% acetic acid solution (3 x 50 mL), and again with water (3 x 50 mL). The solution was dried over magnesium sulfate, the solvent evaporated on a rotary evaporator; the crude ester was purified by recrystallization from absolute ethanol and benzene (5:1). White crystals (1.1 g, 27% yield) were obtained, m.p. 216-218°C.

Anal. Calcd. for $C_{22}H_{16}N_6O_3$: C, 64.07%; H, 3.91%; N, 20.38%. Found: C, 63.84%; H, 3.96%; N, 20.39%.

IR (KBr): 1760 and 1730 cm^{-1} ($\nu_{C=O}$ stretching). The ^1H and ^{13}C NMR chemical shift data are presented in Tables 1 and 2. The numerical values of the ultraviolet absorption spectrum are presented in Table 3, the IR spectrum in Figure 1 and the ultraviolet spectrum in Figure 2.

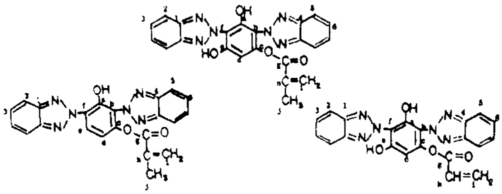
2. 1,3(2-Hydroxy-4-acryloxyphenyl)-di(2H-benzotriazole) (DBDHA): The synthesis of DBDHA followed essentially the same procedure as described

TABLE 1: ^1H NMR Chemical Shift Data for DBDHM[a)], DBTHM[b)], and DBTHA[c)]

Chemical shift[d)] assignment	DBDHM	DBTHM	DBTHA
$-CH_3$	1.8	1.7	–
	5.5	5.5	6.0
	5.9	5.9	6.4
	–	–	6.2
Aromatic	7.2, 8.6	6.9	7.0
Benzotriazole ring	7.4, 7.9	7.5, 8.0	7.6, 8.1
OH	12.2	11.9, 12.3	12.0, 12.4

a) 1,3(2-Hydroxy-4-methacryloxyphenyl)di(2H-benzotriazole).
b) 2,4(1,3-Dihydroxy-5-methacryloxyphenyl)di(2H-benzotriazole).
c) 2,4(1,3-Dihydroxy-5-acryloxyphenyl)di(2H-benzotriazole).
d) Observed data (ppm from internal TMS, samples in $CDCl_3$).

TABLE 2: ^{13}C NMR Chemical Shift Data for DBDHM, DBTHM, and DBTHA



Assignment	Chemical shift	DBDHM, in ppm	DBTHM, in ppm	DBTHA, in ppm
Phenoxy group	a	147.4	148.4	148.4
	b	a)	116.1	116.2
	c	147.4	148.4	148.4
	d	114.4	104.4	104.1
	e	122.6	152.3	152.3
	f	124.0	111.6	111.7
Benzotriazole group	1	142.8	140.3	140.3
	2	117.7	116.9	116.8
	3	128.4	129.1	129.1
	4	145.0	144.9	144.9
	5	118.6	118.6	118.6
	6	127.2	127.0	127.0
Substituent	g	164.4	164.1	162.8
	h	134.8	134.8	126.7
	i	b)	128.2	133.6
	j	18.0	18.0	–

a) Obscured by peak ~126 ppm. b) Obscured by peak ~128 ppm.

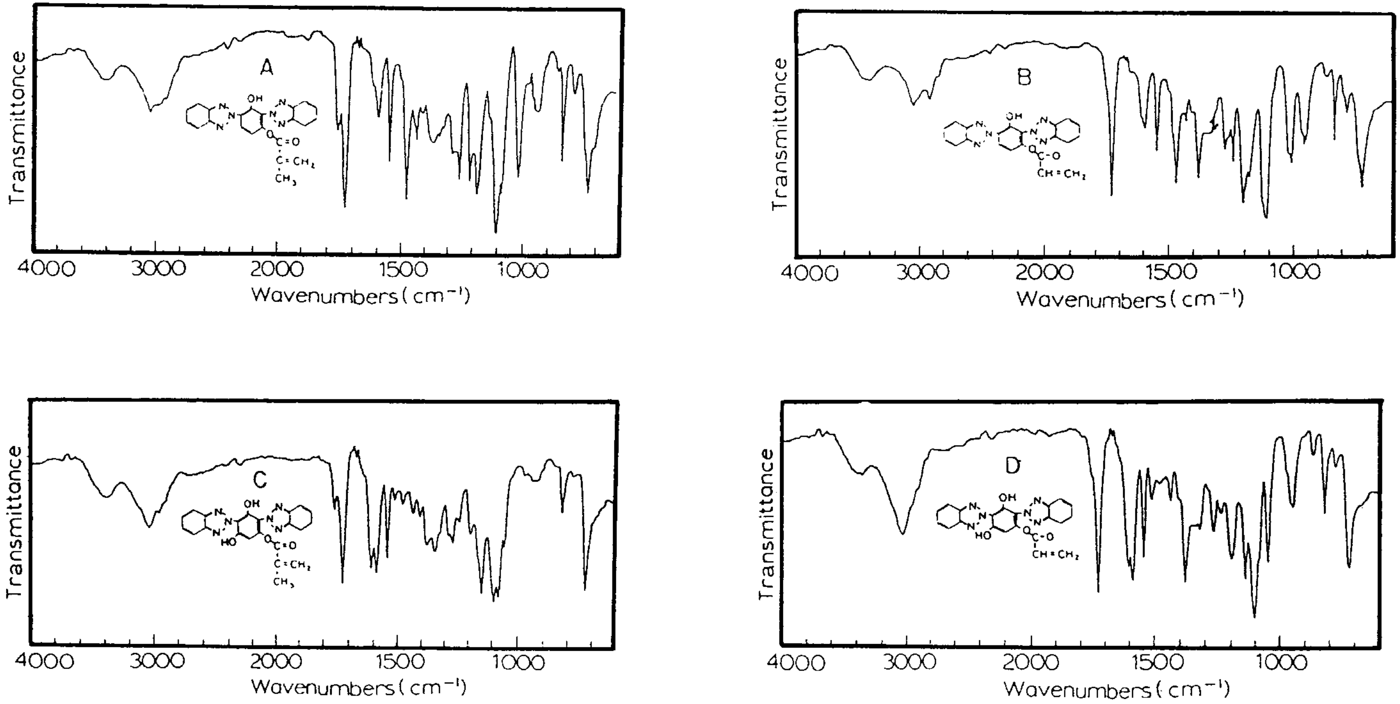


FIGURE 1: Infrared spectra of:
A) 1,3(2-Hydroxy-4-methacryloxyphenyl)-di(2H-benzotriazole) (DBDHM).
B) 1,3(2-Hydroxy-4-acryloxyphenyl)-di(2H-benzotriazole) (DBDHA).
C) 1,3(2,6-Dihydroxy-4-methacryloxyphenyl)-di(2H-benzotriazole) (DBTHM).
D) 1,3(2,6-Dihydroxy-4-acryloxyphenyl)-di(2H-benzotriazole) (DBTHA).

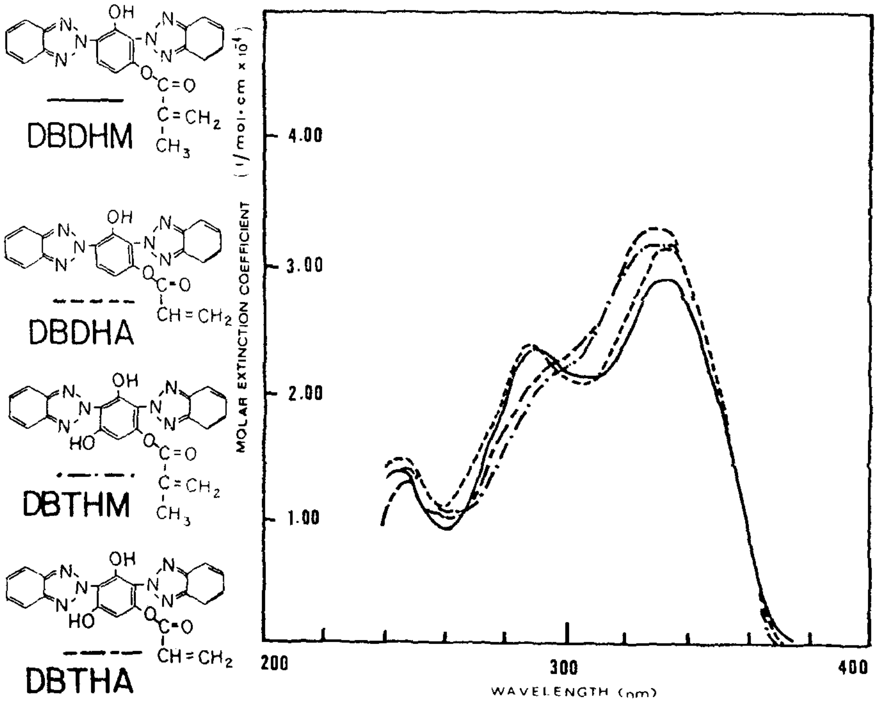


FIGURE 2: Ultraviolet spectra of:
A) 1,3(2-Hydroxy-4-methacryloxyphenyl)-di(2H-benzotriazole) (DBDHM).
B) 1,3(2-Hydroxy-4-acryloxyphenyl)-di(2H-benzotriazole) (DBDHA).
C) 1,3(2,6-Dihydroxy-4-methacryloxy)-di(2H-benzotriazole) (DBTHM).
D) 1,3(2,6-Dihydroxy-4-acryloxyphenyl)-di(2H-benzotriazole) (DBTHA).

TABLE 3: Ultraviolet Absorption Data for 2(2-Hydroxyphenyl)2H-benzotriazole-Substituted Meth(Acrylates)

Compound	λ_{max}, nm	ε L/mol · cm x 10^{4}	λ_{max}, nm	ε L/mol · cm x 10^{4}	λ_{max}, nm	ε L/mol · cm x 10^{4}
DBDHM	247	1.40	290	2.37	329	2.94
DBHA	248	1.50	289	2.41	330	3.15
DBTHM	247	1.34			332	3.34
DBTHA	249	1.42			334	3.19

Absorptions determined in solutions of chloroform.
Concentrations: 2 x 10^{-5} mol/L.

for the synthesis of DBDHM, except that AA (0.72 g, 0.01 mol) was used as the acrylating agent.

Crude DBDHA was recrystallized from absolute ethanol and benzene (5:1) and gave 1.0 g (25% yield) of white crystals, m.p. 230-232° C.

Anal. Calcd. for $C_{21}H_{14}N_6O_3$: C, 63.31%; H, 3.54%; N, 21.10%. Found: C, 63.25%; H, 3.81%; N, 21.30%.

IR (KBr): 1740 cm^{-1} ($\nu_{C=O}$ stretching). The ^1H and ^{13}C NMR chemical shift values are presented in Tables 1 and 2, the numerical values of the ultraviolet absorption spectrum are presented in Table 3, the IR spectrum in Figure 1 and the ultraviolet spectrum in Figure 2.

3. 1,3(2,6-Dihydroxy-4-methacryloxyphenyl)-di(2H-benzotriazole) (DBTHM): The synthesis of DBTHM followed the same procedure as outlined for the synthesis of DBDHM, but with 1,3(2,4,6-trihydroxyphenyl)-di(2H-benzotriazole) (DBTH) (3.60 g, 0.01 mol) as the starting material. Crude DBTHM was purified by recrystallization from absolute ethanol and benzene (5:1), yielding 0.5 g (12%) of pale yellow crystals, m.p. 191-192° C.

Anal. Calcd. for $C_{22}H_{16}N_6O_4$: C, 61.68%; H, 3.76%; N, 19.62%. Found: C, 61.70%; H, 3.67%; N, 19.55%.

IR (KBr): 1760 and 1730 cm^{-1} (ν_{C-O} stretching). The ^1H and ^{13}C NMR chemical shift data are presented in Tables 1 and 2. The numerical values of the ultraviolet absorption spectrum are presented in Table 3, the IR spectrum in Figure 1 and the ultraviolet spectrum in Figure 2.

4. 1,3(2,4-Dihydroxy-4-acryloxyphenyl)-di(2H-benzotriazole) (DBTHA): The procedure for the synthesis of DBTHA was essentially the same as that described for the synthesis of DBDHM, except that DBTH (3.60 g, 0.01 mol) was used instead of DBDH, and AA (0.72 g, 0.01 mol) instead of MA was used as the starting material. After recrystallization from absolute alcohol and benzene (5:1), 0.5 g (12% yield) of white crystals was obtained, m.p. 214-216° C.

Anal. Calcd. for $C_{21}H_{14}N_6O_4$: C, 60.87%; H, 3.41%; N, 20.28%. Found: C, 61.19%; H, 3.49%; N, 19.89%.

IR (KBr): 1740 cm^{-1} ($\nu_{C=O}$ stretching). The ^1H and ^{13}C NMR chemical shift data are presented in Tables 1 and 2. The numerical values of the ultraviolet absorption spectrum are presented in Table 3, the IR spectrum in Figure 1 and the ultraviolet spectrum in Figure 2.

RESULTS AND DISCUSSION

Acrylate and methacrylate esters of DBDH and DBTH were prepared in moderate yields. The less hindered DBDH was esterified more readily, and DBDHA or DBDHM were obtained in about 25% yield of purified compounds. DBTH was esterified with more difficulty, and yields of the esters DBTHA or DBTHM ranged from 10 to 15%. The esterifications were carried out by allowing AA or MA to react with DCC and then allowing the mixture to react with DBDH or DBTH.

More traditional esterification methods, for example the reaction of acryloyl or methacryloyl chloride with DBDH or DBTH, did not give pure compounds, but rather mixtures of mono- and diesters which could not be separated. These acid chloride esterifications had been carried out in solution or in a two-phase system of the Schotten-Baumann type. Esterification of AA or MA and DBDH or DBTH with N,N′-diimidazole carbonyl(DIC) did also not give the desirable phenol esters. The DIC method has later been found to be the method of choice for the synthesis of 10-undecenoic acid esters of some 2(2-hydroxyphenyl)2H-benzotriazole derivatives.

Interestingly enough, the esterification method of AA or MA with 2(2-hydroxyphenyl)2H-benzotriazoles using DCC gave readily the esters DBDHA, DBDHM, DBTHA, and DBTHM. With other alcohols, for example (2,2,6,6-tetramethylpiperidinol-4), acryl and methacryl derivatives of N,N'-dicyclohexylurea were obtained as the only reaction products instead of the esters.

The NMR numerical values of the compounds are represented in Table 1 for the ^{1}H NMR spectra and in Table 2 for the ^{13}C NMR spectra. The data are in full agreement with the proposed structures as are the infrared spectra which are shown in Figure 1.

The ultraviolet spectra represented in Figure 2, whose numeric values are tabulated in Table 3, show the main absorption λ_{max} shifted to 330 nm for the DBDH derivatives and to 334 nm for the DBTH derivatives, λ_{max} 10 to 15 nm lower than the parent compounds DBDH or DBTH. The extinction coefficients are also slightly lower by about 20% to 3.0-3.2 L/mol•cm x 10^4 for the DBDH derivatives and 3.2-3.4 L/mol•cm x 10^4 for the DBTH derivatives. DBDHA and DBDHM have another λ_{max} at 290 nm and one at 247 nm, while DBTHA and DBTHM have only a shoulder near 300 nm and a peak at 248 nm.

The four acrylate and methacrylate derivatives of DBDH and DBTH provide additional interesting examples of polymerizable ultraviolet stabilizers of the 2(2-hydroxyphenyl)2H-benzotriazole family with very high extinction coefficients.

ACKNOWLEDGMENTS

This work was supported by Grant No. 956413 from the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California. S.L. would like to thank Fudan University, Shanghai, P.R.C., for granting him a leave of absence to work at the Polytechnic Institute of New York. A.C.A. would like to express her appreciation to the Royal Institute of Technology, Stockholm, Sweden, for granting her a leave of absence and to the National Swedish Board for Technical Development (STU) for financial assistance.

REFERENCES

1. O. Vogl and S. Yoshida, Rev. Roum. de Chimie 7, 1123 (1980).
2. S. Yoshida and O. Vogl, Makromol. Chem. 183, 259 (1982).
3. Z. Nir, A. Gupta and O. Vogl, J. Polym. Sci., Polym. Chem. Ed. 20, 2735 (1982).
4. W. Pradellok, A. Gupta and O. Vogl, J. Polym. Sci., Polym. Chem. Ed. 19, 3307 (1981).
5. S. Yoshida, C.P. Lillya and O. Vogl, J. Polym. Sci., Polym. Chem. Ed. 20(8), 2215 (1982).
6. S. Yoshida and O. Vogl, U.S. Pat. 4,380,643 (1983).
7. J. Belusa, Z. Janousek and H. Knoflickova, Chem. Zvesti 28(5), 673 (1974).
8. K. Elbs, J. Prakt. Chem. 108, 209 (1924).
9. S.J. Li, A.C. Albertsson, W. Bassett, Jr. and O. Vogl, Monatsh. Chem., in press.
10. F. Xi, W. Bassett, Jr. and O. Vogl, in press.
11. S. Tocker, U.S. Pat. 3,107,199 (1963); CA 57, 10861 (1962).
12. S.J. Li, A. Gupta and O. Vogl, Monatsh. Chem. 114, 93 (1983).
13. F. Xi, W. Bassett, Jr. and O. Vogl, Polymer Bulletin, in press.
14. A. Hassner and V. Alexanian, Tetrahedron Letters 46, 4475 (1978).
15. F. Kurzer and K. Douraghi-Zadeh, Chemical Rev. 67(2), 107 (1967).
16. H.G. Khorana, Chemical Rev. 53, 145 (1953).

Accepted August 14, 1984