

Functional Polymers

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34.* Benzotriazole-Substituted Undecenoates

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ABSTRACT

Selected 10-undecenoic acid esters were prepared from 10-undecenoic acid and four phenolic ultraviolet stabilizers: (1) 2(2-hydroxy-4-undecenoxyphenyl)2H-benzotriazole, (2) 2(2,6-dihydroxy-4-undecenoxyphenyl)2H-benzotriazole, (3) 2(2-hydroxy-4-undecenoxyphenyl)1,3-2H-dibenzotriazole, and (4) 2(2,6-dihydroxy-4-undecenoxyphenyl)1,3-2H-dibenzotriazole. The esterification was carried out by allowing 10-undecenoic acid to react with N,N'-carbonyldiimide followed by the addition of the phenol. The polymerizable ultraviolet absorbers were characterized.

INTRODUCTION

The synthesis of polymerizable stabilizers, particularly ultraviolet stabilizers, has resulted in the preparation of 2(2-hydroxyphenyl)2H-benzotriazole derivatives that have a vinyl or isopropenyl group attached to this ring system (1-5). Acryl, methacryl groups have also been attached to phenol or amino functionalities of the 2(2-hydroxyphenyl)2H-benzotriazole rings (6-10); the polymerizability of these monomers was demonstrated.

The use of spacer groups between the polymerizable group and the functional group has recently attracted considerable attention (11,12), and the placement of a number of methylene spacer groups between the ester functionality and the olefin double bond (13) has allowed polymerization of such functional olefins with Ziegler-Natta type initiators, not only for homo- but also for copolymerization (14). Of particular interest for the polymerization of functional olefins or epoxides were the derivatives of 10-undecenoic acid. For the preparation of some esters, the carboxylic acids (13,14) were allowed to react with N,N'-carbonyldiimidazole and then were treated with the alcohols or phenols to form the esters.

It was the objective of this part of the work to prepare 10-undecenoates of ultraviolet stabilizers and to characterize them. The study of their polymerization and copolymerization will then be done in a different context (Equation 1).

EXPERIMENTAL PART

A. Materials

10-Undecenoic acid (UA), N,N'-carbonyldiimidazole (CDI), and magnesium sulfate (Aldrich Chemical Co.) were used as received.

* Part XXXIII: F. Xi, W. Bassett, Jr., and O. Vogl, Polymer Bulletin 11(4), 329 (1984).

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Tetrahydrofuran (Aldrich Chemical Co.) (THF) was heated to reflux with lithium aluminum hydride (Alfa Products) (LAH) and distilled under a nitrogen atmosphere. Solvents such as benzene and ethanol were used without distillation.

B. Measurements

Infrared spectra were recorded on a Perkin-Elmer Spectrophotometer, Model 727, as KBr pellets (Figure 1 A-D). ^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; the spectra were measured in deuterated CDCl_3 in 15% or saturated solutions. Ultraviolet absorptions were measured in chloroform solution (Spectrograde, Fisher Scientific Co.) with a Beckman MVI spectrometer.

Melting points were determined on a MELT-TEMP Capillary melting point apparatus at a heating rate of $2^\circ\text{C}/\text{min}$. and are uncorrected. Microanalyses were carried out at the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Massachusetts.

C. Procedures

1. 2(2-Hydroxy-4-Undecenoxyphenyl)2H-Benzotriazole (BDHU)

In a dry 250-mL roundbottom flask under complete anhydrous conditions was placed 2(2,4-dihydroxyphenyl)2H-benzotriazole (17) (BDH) (2.27 g, 0.01 mol) and THF (100 mL). A dry 100-mL Erlenmeyer flask was charged with UA (1.93 g, 0.0105 mol) and THF (50 mL); CDI was slowly added with shaking to the UA solution (caution: vigorous carbon dioxide evolution); when the effervescence stopped, the 10-undecenoylimidazole solution was added to the roundbottom flask through a dropping funnel over a period of one hr at room temperature, and benzene (50 mL) was added. After washing with water, the organic phase was isolated, dried over magnesium sulfate overnight, and the solvent was removed on a rotating evaporator. The residue was purified by recrystallization from absolute ethanol; 2.1 g (53% yield); white flaky crystals, m.p. $104\text{--}105^\circ\text{C}$.

Anal. Calcd. for $\text{C}_{23}\text{H}_{27}\text{N}_3\text{O}_3$: C, 70.21%; H, 6.92%; N, 10.68%. Found: C, 69.99%; H, 6.82%; N, 10.71%.

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

2. 2(2,6-Dihydroxy-4-Undecenoxyphenyl)2H-Benzotriazole (BTHU)

The synthesis of BTHU followed essentially the same procedure as described for the synthesis of BDHU, but 2(2,4,6-trihydroxyphenyl)2H-benzotriazole (17) (BTH) (2.43 g, 0.01 mol) in THF (100 mL) was added to UA (1.93 g, 0.0105 mol) and CDI (1.62 g, 0.01 mol) in THF (50 mL). After work-up, BTU (1.4 g, 34%) (white needles) was obtained by recrystallization from absolute ethanol, m.p. $93\text{--}94^\circ\text{C}$.

Anal. Calcd. for $\text{C}_{23}\text{H}_{27}\text{N}_3\text{O}_4$: C, 67.46%; H, 6.64%; N, 10.26%. Found: C, 67.26%; H, 6.47%; N, 10.28%.

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

3. 2(2-Hydroxy-4-Undecenoxyphenyl)1,3-di(2H-Benzotriazole) (DBDHU)

The synthesis of DBDHU followed the same procedure as outlined for DBHU. To a stirred solution of 2(2,4-dihydroxyphenyl)1,3-di(2H-benzotriazole) (DBDH) (3.44 g, 0.01 mol) in THF (100 mL) was added dropwise a

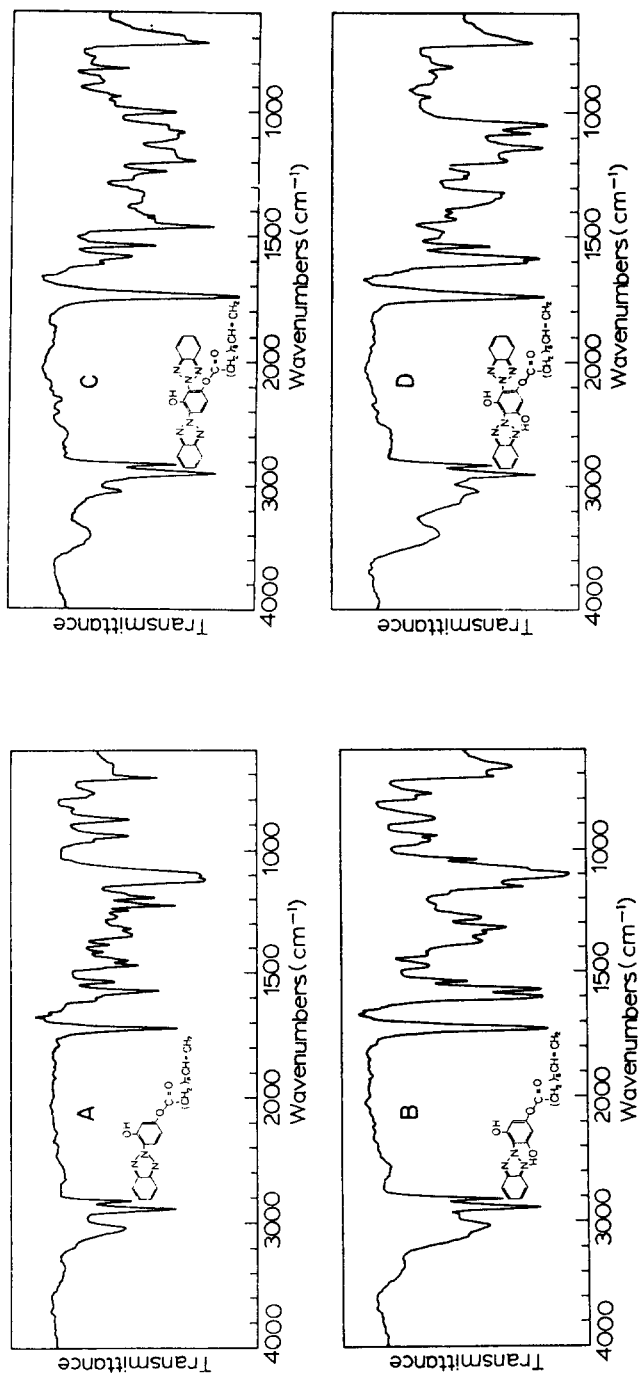
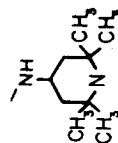
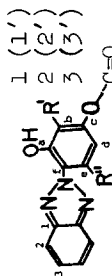


FIGURE 1. Infrared Spectra of: A) 2(2-Hydroxy-4-undecenoxyphenyl)2H-Benzotriazole (BDHU); B) 2(2,6-Dihydroxy-4-undecenoxyphenyl)1,3,5-Benzotriazole (BTHU); C) 2(2-Hydroxy-4-undecenoxyphenyl)1,3-Di(2H-benzotriazole) (DEDHU); D) 2(2,6-Dihydroxy-4-undecenoxyphenyl)1,3,5-Di(2H-benzotriazole) (DETHU).

TABLE 1: ^{13}C NMR Chemical Shift Data for: A) 2-(2-Hydroxy-4-Undecenoxyphenyl)-2H-Benzotriazole (BDHU); B) 2-(2,6-Dihydroxy-4-Undecenoxyphenyl)-2H-Benzotriazole (BTHU); C) 2-(2-Hydroxy-4-Undecenoxyphenyl)-1,3-Di(2H-Benzotriazole) (DBDHU); D) 2-(2,6-Dihydroxy-4-Undecenoxyphenyl)-1,3-Di(2H-Benzotriazole) (DBTHU).

R', R''	H	H OH	Btr H	Btr OH	
a	150.1	151.8	147.9	148.2	-
b	112.1	103.1	*	*	-
c	152.1	152.3	147.7	148.5	-
d	113.6	103.1	114.6	104.3	-
e	121.9	151.8	122.6	152.3	-
f	123.2	111.7	123.9	111.7	-
1 (1')	142.8	140.4	142.8/145.0	140.3/144.9	-
2 (2')	117.6	116.9	117.7/118.6	116.9/118.6	-
3 (3')	127.8	128.5	127.2/128.4	127.0/129.1	-
C=O	171.8	171.6	170.9	170.5	172.3
CH ₂	34.4	34.4	34.0	34.0	35.0
CH ₂	24.9	24.9	24.6	24.6	25.8
(CH ₂) ₅	{ 28.9/29.1	28.9/29.1/29.2	28.9/29.0	28.9/29.0	{ 28.5/28.9 29.1/29.3
CH ₂	33.8	33.8	33.8	33.8	33.7
CH	139.1	139.2	139.2	139.2	139.2
CH ₂	114.2	114.2	114.2	114.2	114.2



*Peak obscured by larger signal.

TABLE 2: Ultraviolet Absorption Data of Benzotriazole-Substituted Undecenoates

Compound	λ_{max} , nm	ϵ , L/mol·cm $\times 10^{-4}$	λ_{max} , nm	ϵ , L/mol·cm $\times 10^{-4}$
BDHU	247	1.19	334	2.39
BTHU*	247	0.75	335	2.76
DBDHU**	247	1.57	335	3.26
DBTHU*	247	1.31	327	3.16

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

*Shoulder at 290 nm. ** λ_{max} 290 nm; ϵ , L/mol·cm $\times 10^{-4}$.

solution of UA (1.93 g, 0.0105 mol) and CDI (1.62 g, 0.01 mol) in THF (50 mL). Crude DBDHU (1.0 g, 20% yield) was purified by recrystallization from absolute ethanol and gave white crystals, m.p. 113-115°C.

Anal. Calcd. for $C_{29}H_{30}N_6O_3$: C, 68.21%; H, 5.92%; N, 16.45%. Found: C, 68.02%; H, 5.96%; N, 16.33%.

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

4. 2(2,6-Dihydroxy-4-Undecenoxyphenyl)1,3-di(2H-Benzotriazole) (DBTHU).

DBTH was esterified as described for the synthesis of DBDHU. To a solution of 2(2,4,6-trihydroxyphenyl)1,3-di(2H-benzotriazole) (DBTH) (3.6 g, 0.01 mol) in THF (100 mL) was added a solution of UA (1.93 g, 0.0105 mol) and CDI (1.62 g, 0.01 mol) in THF (50 mL). Crude DBTHU (1.3 g, 25% yield) was recrystallized from ethanol:benzene (5:1) and gave white crystals, m.p. 155-156°C.

Anal. Calcd. for $C_{29}H_{30}N_6O_4$: C, 66.15%; H, 5.74%; N, 15.96%. Found: C, 65.90%; H, 5.65%; N, 16.03%.

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

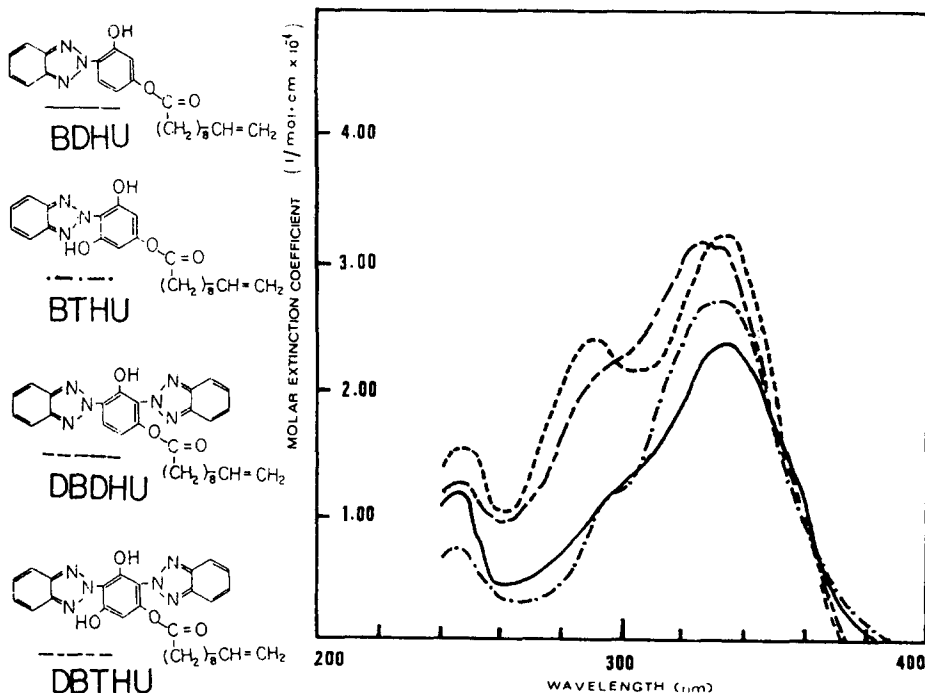
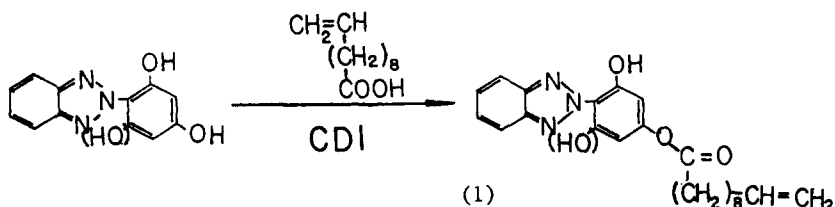


FIGURE 2: Ultraviolet Spectra of: A) 2(2-Hydroxy-4-undecenoxyphenyl)-2H-Benzotriazole (BDHU); B) 2(2,6-Dihydroxy-4-undecenoxyphenyl)1,3-2H-Benzotriazole (BTHU); C) 2(2-Hydroxy-4-undecenoxyphenyl)1,3-Di(2H-benzotriazole) (DBDHU); D) 2(2,6-Dihydroxy-4-undecenoxyphenyl)1,3-Di(2H-benzotriazole) (DBTHU).

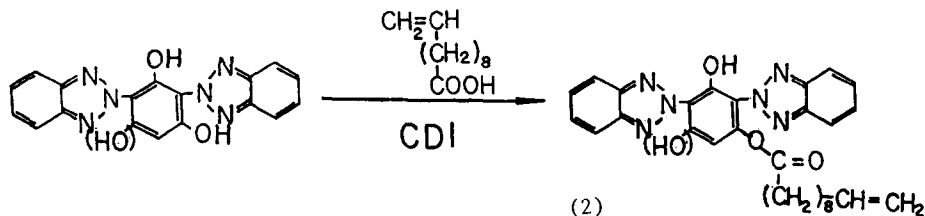
RESULTS AND DISCUSSION

Several new polymerizable ultraviolet stabilizers, esters of UA, have been prepared. For convenience in the laboratory, the esterification was done with the imidazolyl derivative of UA, easily accessible by the reaction of CDI with UA and used without isolation. The mild esterification technique avoided, or at least minimized, the esterification on more than one hydroxyl group of the ultraviolet absorbers.

The yield of the acylation was moderate to good, better with BDH and BTH because reaction occurred only at the unhindered 4-hydroxy position. A yield of only about 20% of the UA ester was obtained with DEBH and DETH (Equation 1,2). This relatively low yield is undoubtedly caused by the lower reactivity of the hindered hydroxyl group, but even more importantly by some loss in the purification of the compounds by crystallization.



All four compounds show melting points around or slightly above 100°C. The position of attachment of the 10-undecenoxy group was established beyond any reasonable doubt by careful evaluation of the chemical shift values of the ¹³C NMR spectra.



The ultraviolet spectra were found to be slightly but not very significantly altered from that of the starting material or the methacrylate ester. It might be recalled that in the case of the attempted esterification of BTH with acryloyl chloride only the corresponding dihydrocoumarin, obtained by an internal Michael's addition of the initially formed acrylate ester with the carbon atom in ortho position in the benzene ring, could be isolated. 4-(10-Undecylamido)-2,2,6,6-tetramethylpiperidine was also prepared by this method (see Table 1).

In a single set of experiments, we had shown (13) that an aromatic compound with free hydroxyl groups could be incorporated into a polyolefin by coordination polymerization using Ziegler/Natta type initiating systems when the functional monomer is heavily complexed, for example, with diethyl aluminum chloride. We had also shown that a spacer group of at least five methylene groups between the olefin double bond to be polymerized and a functional carboxylate group is necessary for such a complexed functional group not to interfere with the olefin polymerization by coordination initiators.

We believe that the monomers described in this work (after suitable complexation) should easily be incorporated into olefin polymers and copolymers providing a polymer which has the stabilizer permanently incorporated into the polymer chain.

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