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Functional Polymers

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33:* 2[2-Hydroxy-4-Acryloxy(Methacryloxy-Phenyl]2H-4-Methoxybenzotriazole Monomers, Polymers and Copolymers

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ABSTRACT

2-(2,4-Dihydroxyphenyl)2H-4-methoxybenzotriazole was treated with acryloyl or methacryloyl chloride and gave 2[2-hydroxy-4-acryloxy(methacryloxy)phenyl]2H-4-methoxybenzotriazole. The two monomers were homopolymerized and copolymerized with styrene, methyl methacrylate and n-butyl acrylate with azobisisobutyronitrile as the initiator. The monomers, homopolymers and copolymers were characterized.

INTRODUCTION

2(2-Hydroxyphenyl)2H-benzotriazoles with vinyl- and isopropenyl group as polymerizable monomers have been prepared and their homopolymerization and/or copolymerization has been studied (1-4). 2(2-Hydroxyphenyl)2H-benzotriazoles with methoxy groups in the 4 position of the benzotriazole ring have also been prepared by reacting 4-methoxy-2-nitrobenzene-diazonium chloride with resorcinol or phloroglucinol followed by reductive cyclization to the benzotriazole derivatives (5).

It was the objective of this work to prepare 2(2,4-hydroxyphenyl)2H-4-methoxybenzotriazole and acrylate the 4-hydroxy position with acryloyl or methacryloyl chloride, to characterize the 2[2-hydroxy-4-acryloxy(methacryloxy)phenyl]2H-4-methoxybenzotriazole [MBDHA(M)] and to study their homo- and copolymerization.

EXPERIMENTAL

Materials

Chloroform (Fisher Scientific Co.) was purified as described previously. Methacryloyl chloride (Aldrich Chemical Co.), acryloyl chloride (Polysciences, Inc.), methyl methacrylate (MMA) (Eastman Kodak Co.) and n-butylacrylate (BA) (Polysciences, Inc.) were distilled twice under reduced pressure immediately before use. Styrene (St) (Aldrich Chemical Co.) was washed twice with 5% aqueous sodium hydroxide and twice with water to remove the inhibitor and, after drying over calcium sulfate, it was distilled in a nitrogen atmosphere.

Azobisisobutyronitrile (AIBN) (Aldrich Chemical Co.) was recrystallized three times from dry methanol and dried overnight at room temperature at 0.1 mm Hg.

N,N-Dimethylacetamide (DMAc), used as solvent for polymerization and for measurements of inherent viscosities of polymers, was reagent grade (Fisher Scientific Co.) and was used directly from freshly opened bottles.

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Measurements

Infrared spectra (Perkin-Elmer Spectrophotometer, Model 727), ^1H NMR spectra (60 MHz-24 Hitachi Perkin-Elmer Spectrometer), ^{13}C NMR spectra (Varian CFT-20 spectrometer), ultraviolet absorptions (Beckman MVI spectrometer) and elemental analyses were measured as previously described (3).

Preparations

2(2-Hydroxy-4-acryloxyphenyl)2H-4-methoxybenzotriazole (MBDHA). Into a 250 mL 3-neck roundbottom flask equipped with a mechanical stirrer and an addition funnel was placed MBDH (5) (3.86 g, 0.015 mol) and sodium hydroxide (1.2 g, 0.03 mol) in water (125 mL). The mixture was stirred at room temperature under nitrogen until the MBDH was completely dissolved. Acryloyl chloride (1.5 g, 0.016 mol) in chloroform (25 mL) was placed in the addition funnel and added in 1 hr. After the reaction was completed (1 hr) the organic solution was isolated, dried and evaporated; yield 3.3 g (71%). Recrystallization from ethanol gave pure MBDHA (white powder), m.p. 147-148° C. IR (KBr): 1720 cm^{-1} ($>C=O$). ^1H NMR: δ 3.93 ppm ($-OC\underline{H}_3$), 6.6 to 7.8 ppm (phenyl group), 6.35 ppm ($-C\underline{H}=$), 6.9 to 7.7 ppm (benzotriazole group), 6.13 ppm and 6.46 ppm ($=C\underline{H}_2$), 10.7 ppm ($-O\underline{H}$). ^{13}C NMR: δ 55.6 ppm ($-O\underline{C}H_3$), 127.4 ppm ($-\underline{C}H=CH_2$), 133.9 ppm ($-CH=\underline{C}H_2$) and 163.8 ppm ($-\underline{C}O-$).

Analysis: Calc. for $C_{16}H_{13}N_3O_4$: C 61.73%, H 4.20%, N 13.49%. Found: C 61.53%, H 4.02%, N 13.47%.

2(2-Hydroxy-4-methacryloxyphenyl)2H-4-methoxybenzotriazole (MBDHM). The synthesis of MBDHM followed essentially the same procedure as described for the synthesis of MBDHA except that methacryloyl chloride (1.73 g, 0.016 mol) was used as a starting material. The crude product of MBDHM was obtained in a yield of 3.0 g (61%). Recrystallization twice from ethanol gave pure MBDHM as a white powder, m.p. 141-143° C. IR (KBr): 1710 cm^{-1} ($>C=O$). ^1H NMR: δ 2.03 ppm ($-C(C\underline{H}_3)=CH_2$), 3.95 ppm ($-OC\underline{H}_3$), 6.6 to 7.7 ppm (phenyl group), 6.8 and 7.2 ppm (benzotriazole group), 5.80 ppm and 6.20 ppm ($=C\underline{H}_2$), 10.7 ppm ($-O\underline{H}$). ^{13}C NMR: δ 17.9 ppm ($-C(\underline{C}H_3)=CH_2$), 55.6 ppm ($-O\underline{C}H_3$), 128.0 ppm ($=\underline{C}H_2$), 135.1 ppm ($-\underline{C}(CH_3)=CH_2$), and 164.9 ppm ($-\underline{C}O$).

Analysis: Calc. for $C_{17}H_{15}N_3O_4$: C 62.76%, H 4.64%, N 12.91%. Found: C 62.33%, H 4.57%, N 12.53%.

Polymerizations and Copolymerizations of MBDHA and MBDHM. MBDHM (0.5 g) and AIBN (0.5 mg, 0.2 mol % based on monomer) were dissolved in 4 mL of DMAc and 2 mL of $CHCl_3$ and charged into a 10 mL Pyrex polymerization tube. The tube was degassed by three freeze-thaw cycles (liquid nitrogen) before it was sealed at 0.05 mm Hg and placed in a constant temperature bath at 50° C. After 3 days the tube was opened and the contents were poured into 200 mL of methanol. Poly-MBDHM precipitated, was collected by filtration, extracted with methanol and dried overnight at 65° C (0.1 mm Hg); the yield was 0.42 g (84%) and the inherent viscosity of the polymer was 1.02 dL/g (0.5% in DMAc, 30° C).

The polymerization of MBDHA and the copolymerizations of MBDHA or MBDHM with methyl methacrylate, n-butyl acrylate and styrene followed the same procedure as described for the homopolymerization of MBDHM. Details are summarized in Table 1.

RESULTS AND DISCUSSION

2(2,4-Dihydroxyphenyl)2H-4-methoxybenzotriazole was prepared as previously described (5). The compound was acrylated with acryloyl or methacryloyl chloride (Equation 1). MBDHA and MBDHM were homopolymerized and copolymerized with styrene, methyl methacrylate or n-butyl acrylate. The monomers were prepared from MBDH in 60-70% yield and gave the corresponding compounds

TABLE 1: Polymerization and Copolymerization of MBDHA and MBDHM a)

MBDHA (g)	Comonomer (g)	MBDHA in feed (mol %)	Yield (g)	Yield (%)	η_{inh} b)	N% (in polymer)	MBDHA found in polymer (mol %)
0.5	--	100	0.4	80	0.3	--	--
	n-butyl acrylate						
0.065	0.94	3	0.85	85	0.85	0.96	3.3
0.10	0.40	10	0.42	84	0.77	2.70	10.0
	methyl methacrylate						
0.088	0.91	3	0.89	89	0.85	1.24	3.2
0.13	0.37	10	0.45	90	0.79	3.53	10.2
	styrene						
0.085	0.92	3	0.40	40	0.40	2.68	7.6
0.13	0.38	10	0.30	60	0.49	5.20	17.3
MBDHM (g)		MBDHM in feed (mol %)					MBDHM found in polymer (mol %)
0.5	--	100	0.42	84	1.02	--	--
	n-butyl acrylate						
0.068	0.93	3	0.78	78	0.82	0.82	3.0
0.10	0.40	10	0.34	68	0.50	3.10	11.8
	methyl methacrylate						
0.091	0.91	3	0.86	86	1.07	1.02	2.6
0.13	0.37	10	0.43	86	0.60	3.13	9.0
	styrene						
0.088	0.91	3	0.40	40	0.41	2.32	6.5
0.13	0.37	10	0.25	50	0.27	5.29	18.2

a) Polymerization conditions: 50° C; 3 days; AIBN as initiator, 0.2 mol % based on monomers in feed.

b) 0.5% in DMAc, 30° C.

TABLE 2: Ultraviolet Absorption of Monomer, Polymer and Copolymers of MBDHA and MBDHM in $CHCl_3$ ($C = 2 \cdot 10^{-5}$ mol/L)

Compound	λ_{max}* (nm)	$\epsilon \cdot 10^{-4}$ (L/mol • cm)
MBDHA	344	2.83
Poly(MBDHA)	338	2.62
Poly(MMA-co-MBDHA)	344	3.27
Poly(n-BA-co-MBDHA	344	2.84
MBDHM	344	2.78
Poly(MBDHM)	340	3.18
Poly(MMA-co-MBDHM)	344	2.62
Poly(n-BA-co-MBDHM)	344	3.09

*Shoulder at λ_{max} = 290 nm.

m.p. 147°C and m.p. 141°C, respectively. The compounds were characterized by their infrared, ^1H, and ^{13}C NMR spectra.

The monomers MBDHA and MBDHM were homopolymerized with AIBN as the initiator in a mixture of DMAc and chloroform as the solvent. The polymers were obtained with an η_{inh} of 0.3 or 1.0 dL/g, respectively (Table 1). Their ultraviolet spectra had a λ_{max} of 344 nm and an ϵ of 2.6×10^4 and 2.8×10^4 L/mol • cm; shoulders were detected at 290 nm (Table 2 and Figure 1).

Copolymerization with n-butyl acrylate, methyl methacrylate in copolymer compositions of 3 and 10 mol % of MBDHA or MBDHM gave copolymers mixtures similar in composition to the feed composition as judged by nitrogen analysis. The copolymers of MBDHA and MBDHM with methyl methacrylate or n-butyl acrylate gave a yield of 70 to 90% with an η_{inh} of 0.8 to 1.0 dL/g.

Copolymers with styrene had substantially higher amounts of MBDHA or MBDHM incorporated in the copolymers; the yields of the copolymers with styrene were between 40 and 60%, and the η_{inh} was 0.3 to 0.4 dL/g. Slight variation could be detected in the extinction coefficient value of the copolymers at λ_{max} of 344 nm. The data were within 10% of each other and could very well be caused by the possible inaccuracy of the determination of the copolymer composition by elemental analysis. The values of nitrogen varied from 1% to slightly over 5% and the nitrogen analysis is normally accurate to ±0.2%.

In conclusion, MBDHA and MBDHM were prepared, homopolymerized and copolymerized; monomer and polymers were characterized. Similar to BDMA and BDHM, MBDHA and MBDHM are potentially interesting monomers as polymerizable ultraviolet stabilizers.

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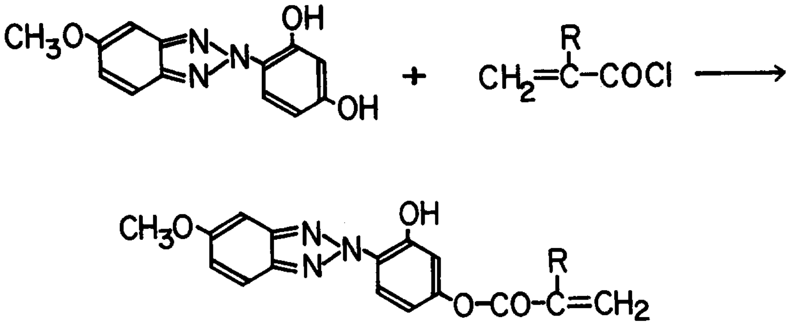
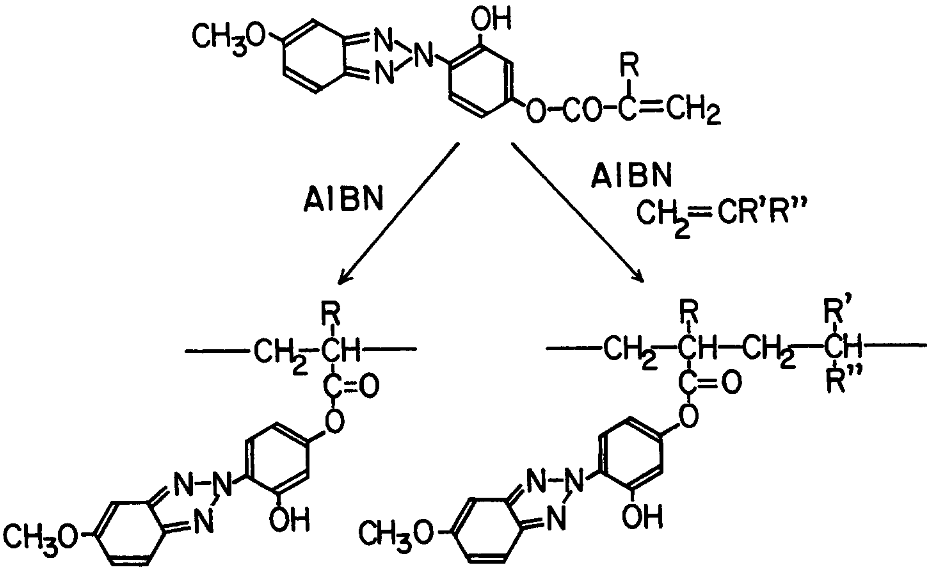


(1)

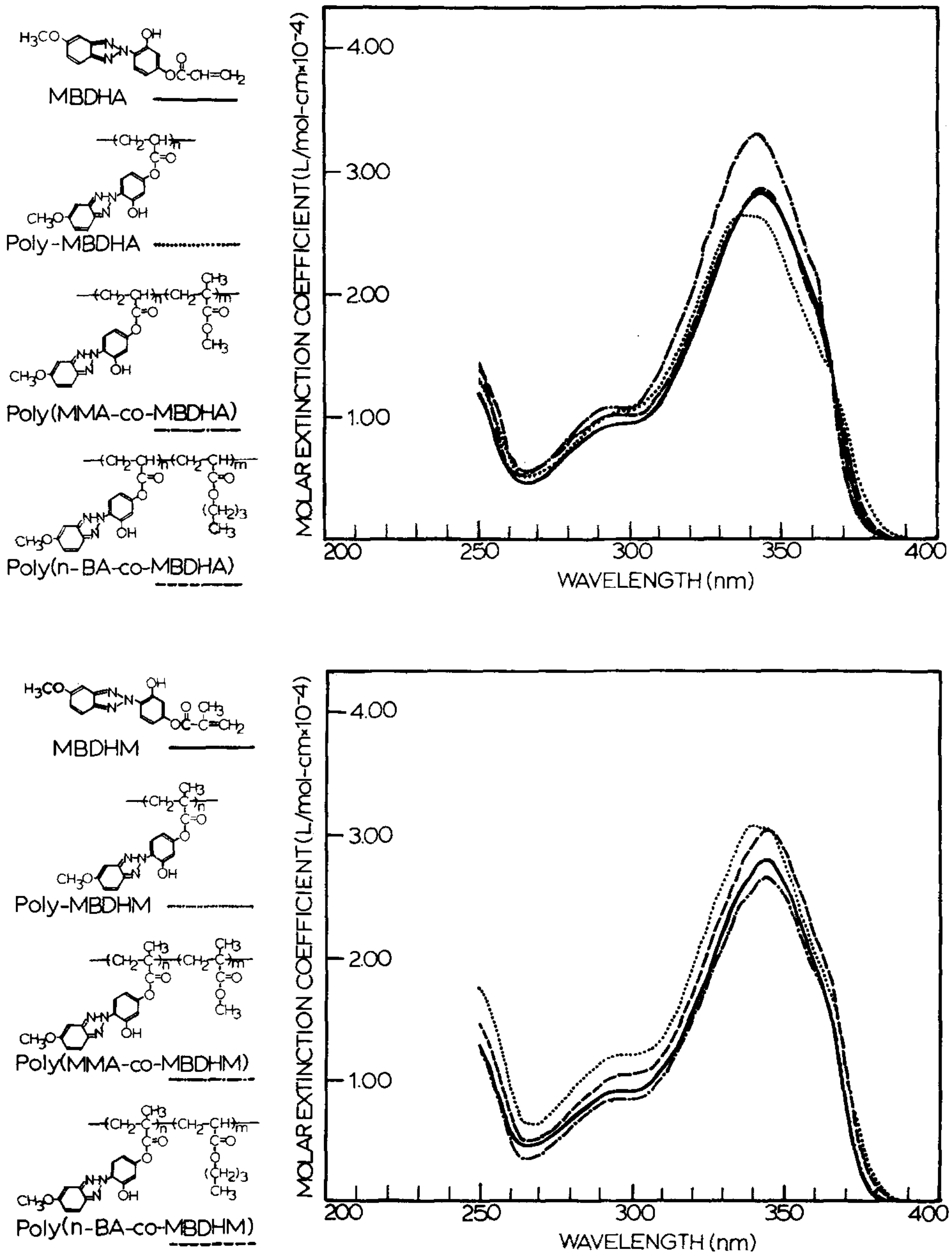
R = H, CH_3



(2)

R = H, CH_3
R' = H, CH_3
R'' = C_6H_5, $COOCH_3$, $COOC_4H_9$

FIGURE 1: Ultraviolet Spectra of MBDHA and MBDHM, their Homo- and Copolymers.



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