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Functional Polymers. LIX. Synthesis and Polymerization of 2(2-Hydroxyphenyl)2*H*-benzotriazole-Based Glycidyl Methacrylate Derivatives

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FUNCTIONAL POLYMERS. LIX. SYNTHESIS AND POLYMERIZATION OF 2(2-HYDROXYPHENYL)2*H*-BENZOTRIAZOLE-BASED GLYCIDYL METHACRYLATE DERIVATIVES

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ABSTRACT

Three 2(2,4-dihydroxyphenyl)2*H*-benzotriazole derivatives were reacted with glycidyl methacrylate on the 4-hydroxyl group of the benzotriazole molecules to give the corresponding acrylic monomers. The new monomers were copolymerized with methyl methacrylate. In another approach, copolymers of methyl methacrylate and glycidyl methacrylate were allowed to react with the same three 2(2,4-dihydroxyphenyl)2*H*-benzotriazole derivatives and gave the corresponding 3-methacryloxy-2-hydroxypropyl derivatives. The monomers and polymers were characterized by the usual characterization techniques. The greatest emphasis was placed on the ultraviolet spectra in various solvents stressing the local proximity of the neighboring groups.

INTRODUCTION

The design of polymerizable 2(2-hydroxyphenyl)2*H*-benzotriazole ultraviolet stabilizers [1] has led to a number of 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives with various functional and polymerizable groups in the molecule. These 2(2-hydroxyphenyl)2*H*-benzotriazoles with vinyl- [2–4], (meth)acryloxy- [5], hydroxy- [6], acetoxy- [7], and carbomethoxy- [8] groups have been synthesized. The polymerizable groups allowed them to be incorporated into acrylic, styrenic addition polymers, into unsaturated polyesters [9] and ABS type polymers [10], and also into condensation polymers such as polyesters [11], polycarbonates [12], and polyamides [4].

Recently, a thorough study of the reactivity ratios of 2[2-hydroxy-5-vinyl-(isopropenyl)phenyl]2*H*-benzotriazole [2H5V(P)], respectively, in their copolymerization with styrene, methyl methacrylate, and *n*-butylacrylate has been published [13].

The incorporation of ultraviolet absorbers into polymers by free-radical-initiated grafting is another attractive alternative because it can be carried out on commercially available polymers [15, 16]. Once the stabilizer monomer has been grafted onto the polymer backbone, the grafted copolymer can be either molded to the end-use product or it can be added as a masterbatch to an unstabilized polymer so that the molar concentration of stabilizer is sufficient to protect the host polymer.

Grafting of vinyl monomers onto polymers with a hydrocarbon backbone chain of a polymer was first accomplished many years ago. More recently, polymerizable 2(2-hydroxy-5-vinylphenyl)2*H*-benzotriazole (2H5V) has been successfully grafted onto saturated aliphatic C—H groups of polymers. The results of such grafting reactions of 2H5V or 2H5P onto saturated aliphatic polymers were discussed [14].

More recently, the surface photografting of polymerizable 2(2-hydroxyphenyl)2*H*-benzotriazoles, such as 2(2-hydroxy-4-methacryloxyphenyl)2*H*-benzotriazole (BDHM), 2(2-hydroxy-4-acryloxyphenyl)2*H*-benzotriazole (BDHA), 2H5V or 2H5P, on thin films of low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP) was achieved [16]. The grafting efficiency was highest for LDPE films followed by the HDPE and PP films. Weather-O-Meter data suggested that the grafting had been efficient, and extraction data demonstrated that the grafted ultraviolet stabilizer was permanently incorporated onto the surface of the polymer to be stabilized. It was also shown that this type of stabilization was more effective in stabilizing the base polymers than the use of low molecular weight analogs.

It was our objective to incorporate 2(2-hydroxyphenyl)2*H*-benzotriazoles with aliphatic hydroxyl groups or with phenolic hydroxyl groups into polymers, particularly into acrylic or styrenic polymers by reacting the appropriate compounds with epoxy groups containing monomers [17]. The epoxy group could be provided by a low molecular weight polymerizable compound such as glycidyl methacrylate. The resulting monomer could be polymerized or copolymerized with the appropriate comonomers in desirable proportions. Alternatively, the hydroxylated 2(2-hydroxyphenyl)2*H*-benzotriazole could be reacted with a polymer that contained epoxy groups such as may be present in acrylic copolymers containing glycidyl methacrylate units. This approach would give polymers with 2(2-hydroxyphenyl)2*H*-benzotriazole groups as part of the polymer with aliphatic ester linkages which are known to be more resistant to hydrolysis than aromatic ester linkages.

Another alternative was to introduce 2(2-hydroxyphenyl)2*H*-benzotriazole derivatives with aliphatic hydroxy groups such as 2[2-hydroxy-5-(2′hydroxyethyl)-

phenyl]2*H*-benzotriazole (HHEPB) into methyl methacrylate (MMA) polymers by transesterification [18].

EXPERIMENTAL PART

Chemicals and Reagents

2(2,4-Dihydroxyphenyl)2*H*-benzotriazole (BDH), 2(2,4-dihydroxyphenyl)5-methoxy-2*H*-benzotriazole (MeBDH), and 2[2-hydroxy-5-(2′-hydroxyethyl)-phenyl)2*H*-benzotriazole (HHEPB) were synthesized previously [18].

For all reactions, the use of Aldrich anhydrous-grade solvents (Sure Seal bottles) was found to be adequate. All chemicals, unless otherwise stated, were used as received. Chloroform for the measurements of the absorption spectra was spectrograde and was used as received.

Azobisisobutyronitrile (AIBN) was recrystallized three times from dry methanol and dried 2 days at 0.05 mmHg at room temperature.

Methyl methacrylate was washed twice with aqueous 5% sodium hydroxide and twice with water; it was then dried over magnesium sulfate and distilled from calcium hydride under nitrogen at reduced pressure.

The analytical samples were dried over P_2O_5 for 1 day at 50°C/0.01 mmHg.

Measurements

Infrared spectra were recorded on a Perkin-Elmer model 727 spectrophotometer and on a Shimadzu IR 435. Solid samples of low molecular weight compounds were measured in the form of potassium bromide pellets. Polymers were measured as films cast from chloroform solution onto sodium chloride plates and dried under nitrogen.

^{1}H-NMR spectra were determined on a Varian EM-390 90-MHz spectrometer, and chemical shift values are reported in ppm downfield from TMS.

Ultraviolet spectra were determined in chloroform on a Varian Cary 2300 spectrophotometer in a double-beam servo mode. Additional spectra of chloroform or methanol:phosphate buffer (24:75) solutions were kindly determined by Christine Smith and Joseph Falcetta at the Alcon Laboratories on a Varian DMS-100 spectrophotometer. The sample solutions were measured in quartz cells which had a 0.01-cm optical path length or a 1.0-cm optical path length.

Melting points were determined in open capillary tubes at a rate of temperature increase of 2°C/min on a Mel-temp melting point apparatus; they are uncorrected.

Column chromatographic separations were carried out on Merck silica-gel 60 (230–400 mesh).

Microanalyses (C, H, N, F) were carried out at Microlytics Laboratories, Deerfield, Massachusetts.

Molecular weight determinations [reported as daltons (da)] from K^+ ionization of desorbed species mass spectrometry (K^+IDS MS) measurements were performed on a modified Finnigan 4615B quadruple GC/MS system. The measurements were carried out at the laboratory of William J. Simonsick Jr. at the Marshall R&D Laboratory of E. I. du Pont de Nemours & Co.

Procedures

Synthesis of Monomers

Synthesis of 2(2-hydroxy-4-methacryloxy-2′-hydroxypropylphenyl)2H-benzotriazole (BDHG). A 100-mL round-bottom flask equipped with a reflux condenser, a flow control valve, and a magnetic stirring bar was charged with BDH (5.04 g, 22 mmol), glycidyl methacrylate (GMA) (3.4 mL, 25 mmol), tetrabutyl ammonium bromide (TBABr) (0.32 g, 1 mmol), benzene (30 mL), and hydroquinone (~10 mg). The flask was flushed with nitrogen and the mixture was then heated to reflux for 22 hours and allowed to cool to room temperature. The orange solution was transferred to a separatory funnel where it was diluted with 30 mL benzene, washed 3 times with water, and the organic phase dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure, leaving 9.8 g of dark orange oil. The oil was dissolved in ethanol (15 mL) and stored in a freezer at −20°C. After 2 weeks a yellow solid (5.0 g) had separated which was collected by filtration. Recrystallizations from ethanol gave 2.50 g (31%) of light yellow crystals (mp 118–120°C). The ultraviolet spectrum (chloroform) showed absorption maxima at 337.8 nm and at 296.7 nm (sh) with ϵ = 25,400 and 9636 L/mol·cm, respectively. The infrared spectrum (KBr) shows absorptions at 3500 cm^{-1} (OH stretch) and at 1715 cm^{-1} (ester C=O stretch). K^+IDS MS. Calculated: 369.3; Found: 369.

Analysis. Calculated for $C_{19}H_{19}N_3O_5$: C, 61.61; H, 5.17; N, 11.35%. Found: C, 61.66; H, 5.18; N, 11.40%.

Synthesis of 2(2-hydroxy-4-methacryloxy-2′-hydroxypropylphenyl)5-methoxy-2H-benzotriazole (MeBDHG). A 100-mL round-bottom flask equipped as described before was charged with 2(2,4-dihydroxyphenyl)5-methoxy-2*H*-benzotriazole (5.17 g, 20 mmol), glycidyl methacrylate (3.1 mL, 23 mmol), tetrabutyl ammonium bromide (0.32 g, 1 mmol), benzene (30 mL), and hydroquinone (~10 mg). After heating the mixture to reflux for 26 hours and work-up, 9.2 g of a dark orange oil was obtained which was dissolved in ethanol (30 mL), decolorized with charcoal, and stored in a freezer at −20°C. After 2 weeks a yellow solid had separated which was collected by filtration (5.2 g). Recrystallizations from ethanol gave 2.0 g (25%) of a pearly white product (mp 104–106°C). The ultraviolet spectrum (chloroform) shows an absorption maximum at 344 nm with ϵ = 28,570 L/mol·cm. The infrared spectrum shows absorptions at 3500 cm^{-1} (OH stretch) and at 1710 cm^{-1} (ester C=O stretch).

Analysis. Calculated for $C_{20}H_{21}N_3O_5$: C, 59.99; H, 5.29: N, 10.49%. Found: C, 59.88; H, 5.25; N, 10.37%.

Synthesis of 2(2-hydroxy-4-methacryloxy-2′-hydroxypropylphenyl)5-chloro-2H-benzotriazole (ClBDHG). To a 50-mL three-neck round-bottom flask as described before was charged ClBDH (5.24 g, 20 mol), GMA (3.0 mL, 22 mmol), TBABr (0.4 g, 1.2 mmol), toluene (30 mL), and about 10 mg hydroquinone. The mixture was heated to reflux for 12 hours. After the usual work-up there was 9.2 g of a yellow oil which was dissolved in ethanol (30 mL), decolorized with charcoal,

TABLE 1. Copolymerization of MMA with GMA with Varying Monomer Feed Ratios

Run	MMA (g, mmol)	GMA (g, mmol)	*n*MMA/*n*GMA	Yield (g)	η_{inh} (dL/g)
1	2.50, 25	3.55, 25	1	5.64	1.20
2	3.76, 37.6	1.78, 12.5	3	4.42	0.49
3	4.75, 47.5	0.36, 2.5	19	3.97	0.54

and stored in a freezer at −20°C. After 2 weeks a light orange solid [5.1 g (63%)] had deposited, and it was collected by filtration. Recrystallization from ethanol and purification by passing a concentrated THF solution of the solid through a silica-gel filled column using the solvent mixture THF:Hex gave 2.85 g (35%) of a fluffy solid, mp 113–114.5°C. The ultraviolet spectrum (chloroform) showed an absorption maximum at 349 nm with $\epsilon = 27{,}015$ L/mol·cm. The IR spectrum showed absorptions at 3490 cm^{-1} (O—H stretch) and at 1702 cm^{-1} (ester C=O stretch).

Analysis. Calculated for $C_{19}H_{18}N_3O_5Cl$: C, 56.26; H, 4.49; N, 10.41%. Found: C, 56.39; H, 4.33; N, 10.35%.

Polymerizations and Reactions on Polymers

In a typical polymerization reaction, a 42-mL thick-walled pressure reaction bottle was charged with MMA (2.5 g, 25 mmol), AIBN (33 mg, 0.2 mmol), and dimethylacetamide (DMAc) (10 mL) followed by GMA (3.55 g, 25 mmol). The polymerization tube was capped with a silicone septum; helium gas was passed through the solution for 40 minutes and the tube was capped with a second silicone septum and placed in an oil bath of 50°C. After 20 hours the tube was opened, the highly viscous solution was diluted with DMAc (10 mL), and then it was precipitated by pouring the solution dropwise into methanol (400 mL). The polymer was collected by vacuum filtration, washed several times with fresh methanol, and dried overnight at 0.05 mmHg at room temperature. Yields are reported in Table 1 along with the inherent viscosities (dL/g) of the polymers obtained under the following conditions: 0.5% in DMAc, 30°C, for Run 1 and in toluene for the other two runs.

In a typical reaction of Table 2 (Run 1), a 250-mL round-bottom flask was

TABLE 2. Reaction of Poly(MMA-*co*-GMA) with BDH in the Presence of a Phase Transfer Catalyst

Run	*n*MMA: *n*GMA	Weight (g)	BDH (g)	Yield (g, %)	η_{inh} (dL/g)
1	1:1	1.21	1.23	0.86, 35	0.54
2	3:1	1.10	.057	1.03, 62	1.79
3	19:1	3.06	0.34	2.05, 60	0.65
4	19:1	2.26	0.22	1.91, 77	0.50

charged with the copolymer of *n*MMA:*n*GMA = 1:1 (1.21 g), toluene (150 mL) (or toluene/DMAc), followed by BDH (1.23 g, 5 mmol) and TBABr (0.1 g, 0.31 mmol). The reaction flask was flushed with nitrogen, fitted with a reflux condenser and heated to reflux for 20 hours (4 hours in the case of Run 3). The reaction mixture was then allowed to cool to room temperature and a small amount of insoluble material was removed by filtration. The orange solution was then added dropwise to methanol (2.0 L). The polymer precipitated, the suspension was filtered, and the filter-cake was washed several times with small portions of fresh methanol and dried overnight at 0.05 mmHg and room temperature to give 1.18 g (48%) of a cream colored polymer. The polymer was extracted (Soxhlet) with methanol for 6 hours, dissolved in the minimum amount of DMAc, reprecipitated in methanol, and dried at 0.05 mmHg and room temperature for 16 hours. It gave 0.86 g (35%) of a polymer with an inherent viscosity of 0.54 dL/g (0.2% in DMAc, 30°C).

Analysis. Calculated for $-(C_5H_8O_2)_{0.31}-(C_7H_{10}O_3)_{0.28}-(C_{19}H_{19}N_3O_5)_{0.41}-$: N, 4.65%. Found: N, 4.66%.

Copolymer with nMMA:nGMA = 3:1. Copolymer (1.10 g), toluene (80 mL), BDH (0.57 g, 2.5 mmol), and TBABr (0.05 g, 0.155 mmol).

Analysis. Calculated for $-(C_5H_8O_2)_{0.59}-(C_7H_{10}O_3)_{0.20}-(C_{19}H_{19}N_3O_5)_{0.21}-$: N, 2.32%. Found: N, 2.39%.

Copolymer with nMMA:nGMA = 19:1. Copolymer (3.06 g), DMAc:benzene = 1:1 (30 mL), BDH (0.34 g, 1.5 mmol), and TBABr (0.1 g, 0.31 mmol).

Analysis. Calculated for $-(C_5H_8O_2)_{0.91}-(C_7H_{10}O_3)_{0.06}-(C_{19}H_{19}N_3O_5)_{0.03}-$: N, 0.36%. Found: N, 0.35%.

Copolymer with nMMA: nGMA = 19.1. Copolymer (2.26 g), toluene (80 mL), BDH (0.22 g, 1 mmol), and TBABr (0.02 g, 6.2×10^{-5} mol).

Analysis. Calculated for $-(C_5H_8O_2)_{0.91}-(C_7H_{10}O_3)_{0.05}-(C_{19}H_{19}N_3O_5)_{0.04}-$: N, 0.40%. Found: N, 0.42%.

Poly(BDHG-co-MMA). A 42-mL thick-wall polymerization tube was charged with BDHG (0.35 g, 0.95 mmol), MMA (0.5 g, 5 mmol), AIBN (4 mg, 0.024 mmol), and DMAc (2 mL). The polymerization tube was then capped with a silicone septum, and after argon gas was passed through the solution for 40 minutes, the tube was capped with a second silicone septum and placed in an oil bath of 55°C. After 1 day the tube was opened, the viscous solution was diluted with 5 mL chloroform and added dropwise into methanol (100 mL). The polymer precipitated as a light yellow powder. It was collected by filtration, washed several times with fresh methanol, and dried overnight at 0.05 mmHg and room temperature. The polymer was extracted (Soxhlet) with ethanol for 3 hours, dissolved in the minimum amount of chloroform, and reprecipitated by pouring the solution into methanol. After isolation by filtration, the solid was dried at 0.05 mmHg and room temperature for 16 hours and gave 0.67 (79%) of a polymer with an inherent viscosity of 0.92 dL/g (0.5% in DMAc, 30°C). UV ($CHCl_3$): Found: N, 2.58% (for ϵ = 25,400 L/mol·cm).

Analysis. Calculated for $-(C_5H_8O_2)_{0.77}-(C_{19}H_{19}N_3O_5)_{0.23}-$: N, 2.61%. Found: N, 2.61%.

Poly(MeDHG-co-MMA). MeBDHG (0.4 g, 1.0 mmol), MMA (0.5 g, 5.0 mmol), AIBN (4.0 mg), and DMAc (10 mL); polymer yield, 0.67 g (75%). Inherent viscosity: 0.42 dL/g (0.5% in DMAc, 30°C). UV ($CHCl_3$): Found: N, 3.1% (for $\epsilon = 28{,}570$ L/mol·cm).

Analysis. Calculated for $-(C_5H_8O_2)_{0.67}-(C_{20}H_{21}N_3O_6)_{0.33}-$: C, 59.97; H, 7.14; N, 3.46%. Found: C, 57.18; H, 6.85; N, 3.44%.

Poly(ClBDHG-co-MMA). ClBDHG (0.4 g, 1.0 mmol), MMA (0.5 g, 5.0 mmol), AIBN (4.0 mg), and DMAc (10 mL); polymer yield, 0.5 g (56%). Inherent viscosity: 0.32 dL/g (0.5% in DMAc, 30°C). UV ($CHCl_3$): Found: N, 3.6% (for $\epsilon = 27{,}015$ L/mol·cm).

Analysis. Calculated for $-(C_5H_8O_2)_{0.65}-(C_{19}H_{18}N_3O_5Cl)_{0.35}-$: N, 3.64%. Found: N, 3.62%.

Poly(HHEPBG-co-MMA). A 42-mL thick-wall polymerization tube was charged with HHEPBG (0.03 g, 0.76 mmol), MMA (3.8 g, 38 mmol), AIBN (42 mg, 0.25 mmol), and DMAc (15 mL). The polymerization tube was then capped with a silicone septum and helium gas was bubbled through the solution for 40 minutes. The tube was capped with a second silicone septum and placed into an oil bath of 60°C. After 3 days the tube was opened and the viscous solution was added dropwise to methanol (300 mL). The precipitated polymer was collected by filtration, washed several times with methanol, and dried overnight at 0.05 mmHg and room temperature; a light yellow polymer was obtained with a crude yield of 3.4 g (83%). The polymer was extracted (Soxhlet) with methanol for 6 hours, dissolved in the minimum amount of dichloromethane, and reprecipitated by pouring the solution into methanol. After isolation and drying at 0.05 mmHg and room temperature for 1 day, 2.9 g (70%) of a polymer with an inherent viscosity of 0.29 dL/g (0.5% in toluene, 30°C) was obtained.

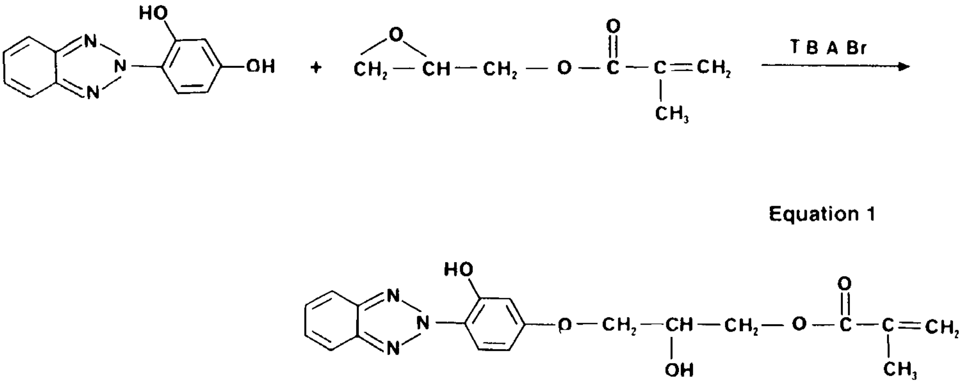
Analysis. Calculated for $-(C_5H_8O_2)_{0.95}-(C_{21}H_{23}N_3O_5)_{0.05}-$: C, 59.63; H, 7.87; N, 0.53%. Found: C, 60.04; H, 7.89; N, 0.57%.

Reaction of Poly(MMA-co-GMA) with HHEPB. A 200-mL round-bottom flask, equipped with a reflux condenser, was charged with poly(MMA-*co*-GMA) (*n*MMA:*n*GMA = 3:1, 1.1 g, 2.5 mmol GMA groups), HHEPB (0.97 g, 3.75 mmol), TBABr (0.05 g, 0.16 mmol), and toluene (80 mL). The reaction mixture was kept under a nitrogen atmosphere while it was heated to reflux. After 20 hours the yellow solution was cooled, a small amount of insoluble material was removed, and the filtrate was then added dropwise to methanol (0.4 L). The polymer precipitated, the suspension was filtered, the filter-cake washed several times with small portions of fresh methanol, and then air-dried at room temperature for 16 hours to give a cream-colored polymer. The polymer was suspended three times in methanol at 40°C, dissolved in the minimum amount of dichloromethane, reprecipitated in methanol, and dried at 0.05 mmHg and room temperature for 1 day to give 1.08 g (62%) of a polymer with an inherent viscosity of 1.0 dL/g (0.5% in DMAc, 30°C). The UV spectrum in chloroform solution showed an absorption maximum at 294 nm but none at 340 nm.

Analysis. Calculated for $-(C_5H_8O_2)_{0.75}-(C_7H_{10}O_3)_{0.22}-(C_{21}H_{23}O_5)_{0.03}-$: N, 1.16%. Found: N, 1.17%.

RESULTS AND DISCUSSION

Three 2(2,4-hydroxyphenyl)2*H*-benzotriazole derivatives were reacted with the epoxy group of gycidyl methacrylate (GMA) to form BDH, MeBDH, and ClBDH. BDH, MeBDH, and ClBDH were also allowed to react with the epoxy group of acrylic copolymers having glycidyl methacrylate units in the copolymers. The reaction of BDH with GMA (12% excess) was successfully carried out using TBABr as a phase-transfer catalyst (Eq. 1). The reaction of GMA with another ultraviolet absorber, 2,4-dihydroxybenzophenone, in the presence of ammonium nitrate as the catalyst was described by Fertig [20].



Equation 1

Synthesis of BDHG, MeBDHG, and ClBDHG

Our reaction was carried out in refluxing benzene in the presence of a small amount of hydroquinone to prevent radical polymerization of the acrylic monomers GMA and BDHG. A dark oil which was difficult to isolate was obtained, but it was ultimately obtained from methanol from which it could also be recrystallized to give light yellow crystals, mp 118–120°C. The ultraviolet spectrum of the compound taken in chloroform solution (Fig. 1a) gave a double maximum, one at 338 nm with a molar extinction coefficient of 25,400 L/mol·cm and the other at 297 nm and ϵ = 9640 L/mol·cm. The ultraviolet spectrum of BDHG was also measured in a methanol:phosphate buffer and showed a maximum at 323 nm and a shoulder at 291 nm with molar extinction coefficients of 14,275 and 12,182 L/mol·cm, respectively (Fig. 1b). The polar effect of this solvent mixture caused a hypsochromic shift of the band to shorter wavelength.

The infrared and ^{1}H-NMR spectra and the elemental analysis of BDHG were consistent with the expected structure. The infrared spectrum showed a strong absorption peak due to the ester carbonyl group at 1715 cm^{-1} and an absorption peak centered at 3500 cm^{-1} due to hydroxyl groups.

The ^{1}H-NMR spectrum consisted of sharp singlets at 2.1 ppm due to the methyl protons of the methacrylate, a slightly broadened singlet at 3.1 ppm due to the protons of the secondary hydroxyl group, two distorted triplets at 4.2 $(ArO{-}C\underline{H}_2{-})$ and at 4.4 ppm $({-}C\underline{H}_2{-}O(O){-})$, two singlets at 5.7 and 6.3 ppm due to the geminal hydrogens of the methacrylate group, multiplets at 6.6 and 6.8 ppm due to the aromatic protons, and the aromatic hydroxyl group which gave a sharp singlet at 11.6 ppm.

The K$^+$IDS spectrum of BDHG showed a pseudomolecular ion peak [M]K$^+$

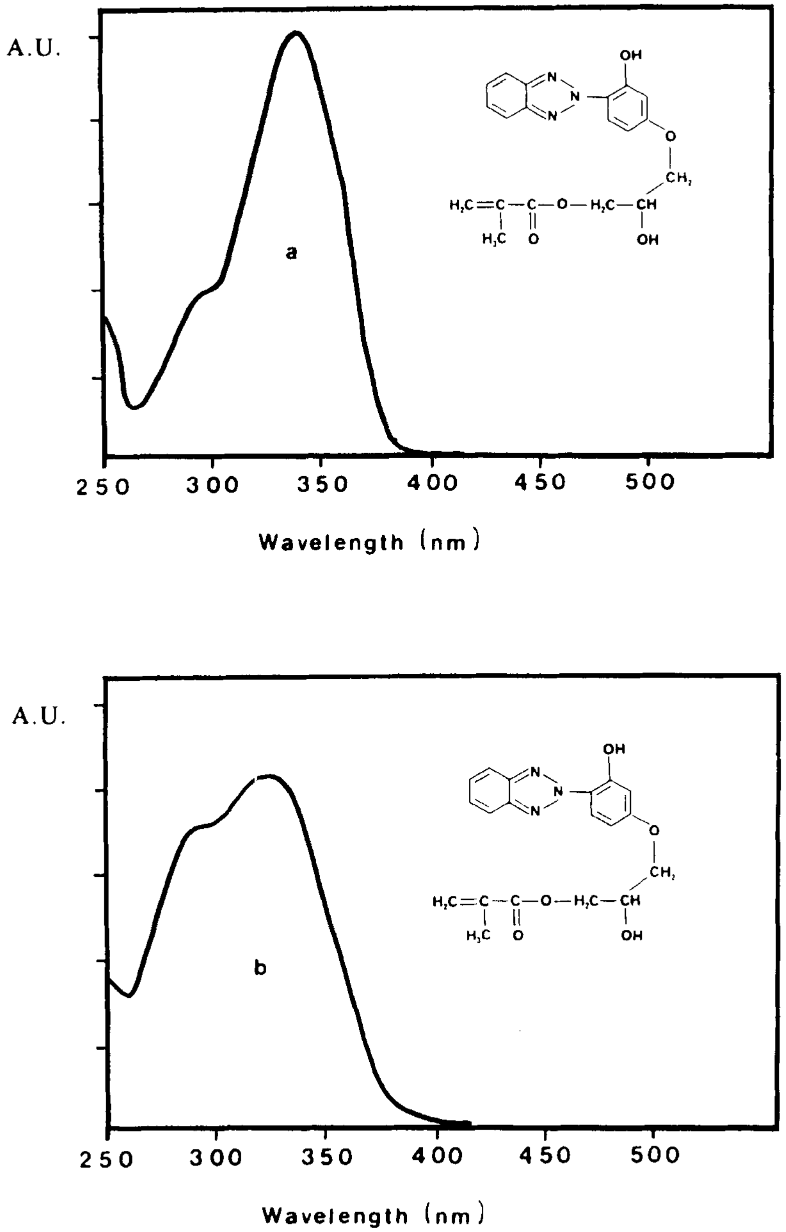


FIG. 1. Ultraviolet spectrum of BDHG. (a) In chloroform. (b) In methanol:phosphate buffer.

at 408 Daltons (da). When one subtracts the mass of the potassium ion, 39.1 da, the molecular weight of BDHG is 368.9 da; the calculated molecular weight is 369.4 da. Isotope satellite peaks were found where expected. Another small peak was found at 476 da. This peak corresponds to a species with a second methacryloxy group, probably from substitution also on the hindered 2-hydroxy group of BDH.

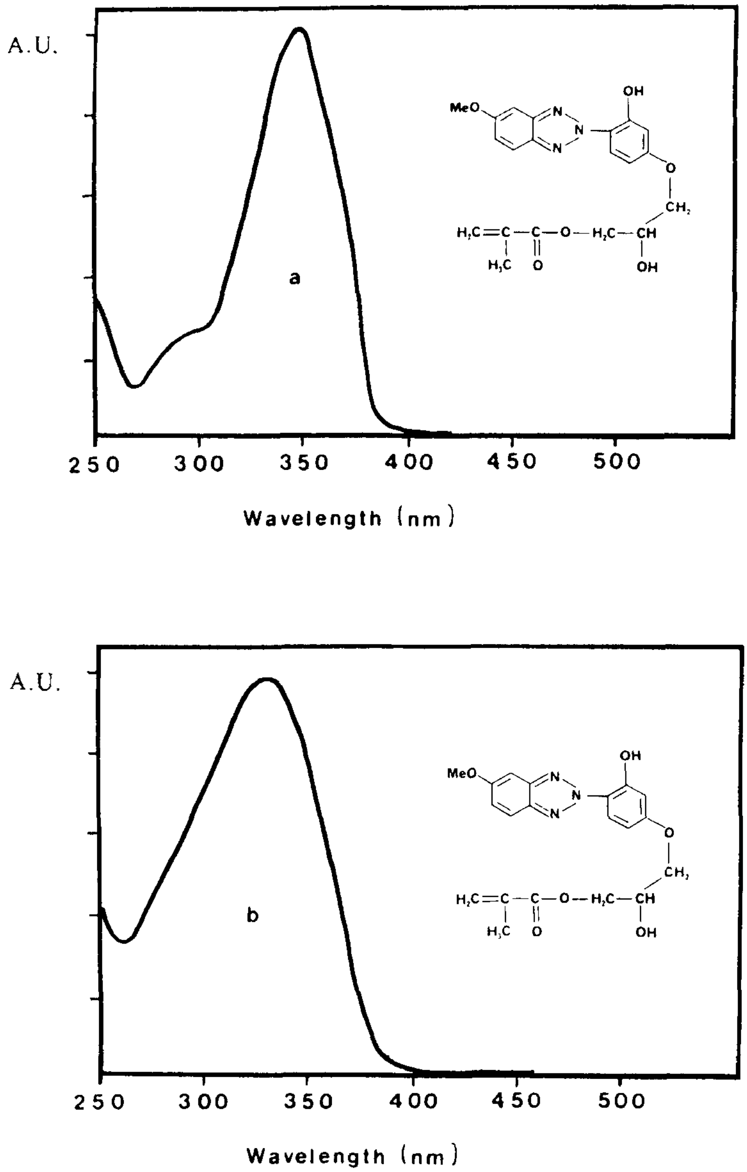


FIG. 2. Ultraviolet spectrum of MeBDHG. (a) In chloroform. (b) In methanol:phosphate buffer.

The synthesis of MeBDHG followed the same procedure as described above for BDHG, with MeBDH reacted with GMA in 15% excess. After isolating the compound from the dark oil by crystallizing from methanol, yellow crystals were obtained in about 25% yield with a melting point of 104–106°C.

The ultraviolet spectrum of the compound in chloroform showed an absorption maximum at 344 nm and a molar extinction coefficient of 28,570 L/mol·cm and a shoulder at about 298 nm (Fig. 2a). The ultraviolet spectrum measured in a methanol:phosphate buffer showed a maximum at 330 nm with a molar extinction coefficient of 15,340 L/mol·cm, a hypsochromic shift such as had been seen for BDHG (Fig. 2b). The molar extinction coefficient of MeBDHG and BDHG in both kinds of solutions at 400 nm was practically zero.

The infrared spectrum and the ^{1}H-NMR spectrum of MeBDHG were essentially the same as that of BDHG. The small differences are based on the methoxy substituent. The methoxy protons were found at 3.9 ppm, and the singlet of the aromatic 2-hydroxy group had its chemical shift slightly downfield, shifted to 11.4 ppm.

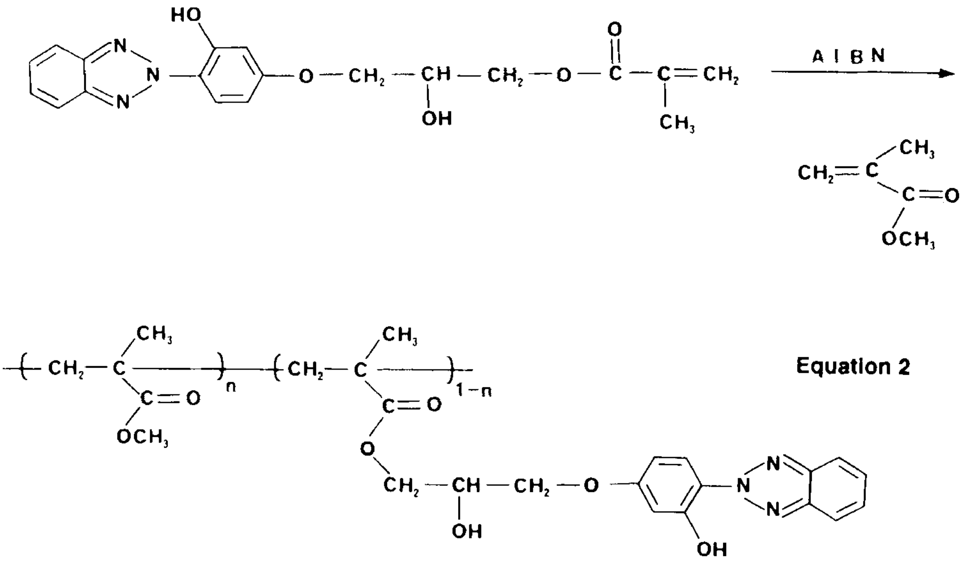
The synthesis of ClBDHG was accomplished similarly to the procedure used for the other two compounds. The oil obtained from the reaction was dark orange and could be crystallized from methanol. Final purification was done by column chromatography. A fluffy white solid was obtained in 35% yield with a melting point of 113–114.5°C. The ultraviolet spectrum of the compound in chloroform solution showed absorption maxima at 349 and 295 nm, with molar extinction coefficients of 27,015 and 11,750 L/mol·cm, respectively (Fig. 3).

The infrared spectrum, the ^{1}H-NMR spectrum, and the elemental analysis were consistent with the expected structure. The aromatic hydrogen-bonded 2-hydroxyl group gave a sharp singlet at 11.2 ppm.

The K$^+$IDS mass spectrum of ClBDH gave a pseudomolecular peak [M]K$^+$ at 442 da, which corresponds to a molecular weight for ClBDH of 402.9 da; Isotope peaks, especially those assignable to the chlorine isotopes, are also noticeable.

Copolymerization of BDHG, MeBDHG, and ClBDHG

BDHG was copolymerized with MMA on a 41 wt% basis, using AIBN as the initiator and DMAc as the solvent (Eq. 2).



Equation 2

DMAc was selected as the solvent to keep the reactants and final products in solution throughout the progress of polymerization. The inherent viscosity of the copolymer was 0.92 dL/g. As a comparison, the inherent viscosities of commercially available PMMA samples with molecular weights of 90,000 and 400,000 da were determined to be 0.29 and 0.80 dL/g, respectively.

The ultraviolet spectrum of a chloroform solution of the polymer gave a nitrogen value of 2.58 wt%. This value was arrived at by considering that the absorbing moiety is the BDHG unit for which the molar extinction coefficient is 25,400 dL/mol·cm (vide supra). This value is in excellent agreement to the nitrogen value found by chemical analysis (2.61%). From this result it was calculated that the polymer consisted of 23 wt% (7.5 mol%) BDHG. Since the monomer feed had 41 wt% BDHG, it is evident that the copolymer is richer in MMA than the monomer feed, which indicates that MMA polymerizes preferentially. However, earlier work on the copolymerization of MMA and 2(2-hydroxy-4-methacryloxyphenyl)-2*H*-benzotriazole (BDHM) showed that BDHM was incorporated preferentially over MMA in the copolymer.

MeBDHG was also copolymerized with MMA on a 44 wt% basis, using AIBN as the radical initiator and in DMAc as the solvent. The copolymer was obtained in good yield, and the inherent viscosity of the copolymer was found to be 0.42 dL/g, indicating a high molecular weight polymer. The copolymer was again analyzed by its ultraviolet spectrum for the comonomer composition and gave a nitrogen value of 3.1 wt%, using the extinction coefficient of the monomer MeBDHG as the standard. The nitrogen value from elemental analysis was 3.44 wt%. The incorporation of MeBDHG into the copolymer is consequently 33 wt% or 11 mol%. Since

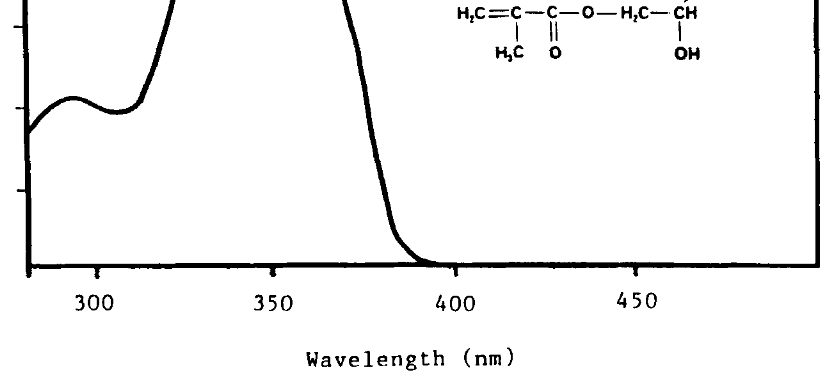


FIG. 3. Ultraviolet spectrum of ClBDHG in chloroform.

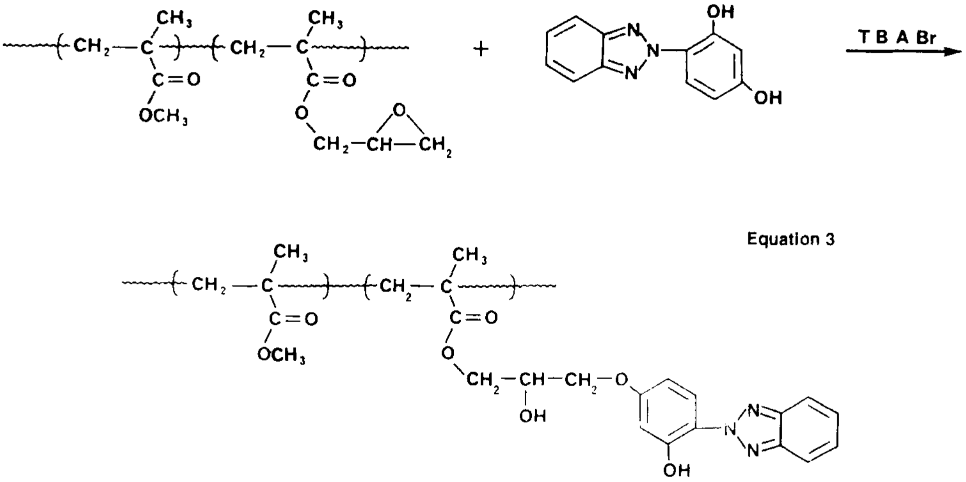
the monomer feed had 44% MeBDHG, it must be concluded that the copolymer is richer in MMA than the monomer feed, which indicates that MMA polymerized preferentially over MeBDHG.

ClBDHG was also copolymerized with MMA on a 44 wt% basis using AIBN as the polymerization initiator. The copolymer had an inherent viscosity of 0.32 dL/g. The ultraviolet spectrum showed absorption intensities equivalent to a nitrogen value of 3.6%. This value is close to the value obtained by elemental analysis (3.62%) and shows 35 wt% or 12 mol% of ClBDHG in the copolymer, also slightly less than the monomer feed.

Reactions on Polymers

Copolymers of MMA and GMA were synthesized with the purpose of subsequently carrying out reactions on the reactive glycidyl group. The copolymerizations were carried out in DMAc in molar ratios of MMA to GMA of 1, 3, and 19. The copolymers were of high molecular weight as evidenced by their inherent viscosities.

Each copolymer was dissolved in toluene, and BDH was added to the solution with TBABr as the phase transfer catalyst (Eq. 3). In each case, after reacting for 1 day, the mixture was added with rapid stirring to a nonsolvent such as methanol to precipitate the polymer.



Equation 3

The reaction of BDH with the glycidyl group was found to be incomplete. Consequently the polymers were terpolymers of MMA, GMA, and BDHG. In the experimental part of the chemical composition of the copolymers was reported as weight percent for each component in the polymer chain. If the composition was reported as mole percent of each component in the terpolymer, the following would be the percentages: for Run 1, $\mathrm{MMA}_{0.05}$-$\mathrm{GMA}_{0.32}$-$\mathrm{BDHG}_{0.18}$; for Run 2, $\mathrm{MMA}_{0.75}$-$\mathrm{GMA}_{0.18}$-$\mathrm{BDHG}_{0.07}$; for Run 3, $\mathrm{MMA}_{0.95}$-$\mathrm{GMA}_{0.04}$-$\mathrm{BDHG}_{0.01}$; and for Run 4, $\mathrm{MMA}_{0.95}$-$\mathrm{GMA}_{0.04}$-$\mathrm{BDHG}_{0.01}$. The percentage of MMA in each polymer is assumed to be essentially the same as is its percentage in the MMA/GMA comonomer feed. It appears that the extent of the reaction decreased as the concentration of GMA in the copolymer decreased; in other words, as the molar ratio MMA/GMA decreased from 1 to 3 to 19, the mole percent of BDHG in the terpolymer decreased from

36% to 28% to 20%, respectively. This seems to have to do with the availability of the glycidyl groups for reaction with BDH.

The K^+IDS spectrum for copolymer sample 1 was obtained; it showed a base peak at 551 da. This mass would correspond with a unit consisting of one part of GMA and one of BDHG. The peak at 429 da cannot be interpreted at this time. The peak at 449 da (~32%) corresponds to the mass of $[BDHG]K^+$.

HHEPBG was synthesized by the reaction of HHEPB with GMA in the presence of TBABr as a phase transfer catalyst.

MMA was copolymerized with 7.3 wt% of HHEPBG, using AIBN as the polymerization initiator. The final yield of copolymer after work-up was 70% and its inherent viscosity in toluene was 0.29 dL/g. The copolymer had 5 wt% (1.4 mol%) of HHEPB incorporated into the copolymer.

The ultraviolet spectrum of the copolymer showed absorption maxima at 338 and 295 nm with a ratio of Abs(338)/AB(295) = 0.95. The ultraviolet spectrum of HHEPB showed two absorption maxima at 335 and 296 nm. In this case the absorbance ratio is 1.22.

One can consider that in chloroform solution the copolymer is in a coiled conformation and the HHEPB moiety is surrounded by its nearest neighbors, the methacrylate esters, effectively creating a polar environment. A similar "solvent" effect by comonomer units has been found and reported recently [21] for styrene and MMA copolymers of BDHM. This polar environment interferes in part with hydrogen bond formation between the proton of the 2-hydroxy group in the ortho position of the phenyl group and the 2-nitrogen atom of the benzotriazole ring.

An interesting observation is that the 2-hydroxy-3-methacryloxy)propyl ethyl ester group in the 5-position of the phenyl group can be considered as an electron donating group. It has been reported recently [22] that when an electron donating group, such as an ethyl group, is placed in the 5-position, the capability of the hydrogen atom of the ortho hydroxyl group to form an intramolecular hydrogen bond is decreased, in which case the authors observed a ratio of extinction coefficients of 0.60. However, this ratio of less than 1 is not observed, as has been noted above for HHEPB.

The reaction of HHEPB with poly(MMA-*co*-GMA) was also carried out under reaction conditions similar to those described for the reaction of poly(MMA-*co*-GMA) with BDH. The copolymer used for this reaction was Run 2 from Table 1 of the Experimental Part. It was dissolved in toluene to which a 50% molar excess of HHEPB with respect to the GMA unit was added. TBABr was used as the phase transfer catalyst, and the reaction was carried out under reflux conditions for 1 day. Work-up gave a polymer that was isolated in 62% yield and had an inherent viscosity of 1.0 dL/g (the starting polymer had an inherent viscosity of 1.79 dL/g). Elemental analysis showed that there were 30 mol% or 10 wt% of HHEPB incorporated into the copolymer.

A rather big surprise came when the ultraviolet spectrum of the copolymer was inspected. The spectrum showed a strong absorption maximum at 294 nm but none at 340 nm, the typical maximum of 2(2-hydroxyphenyl)2*H*-benzotriazoles. This can be interpreted to mean that HHEPB had reacted with the phenolic hydroxy group. This indicates that under our reaction conditions, the normally unreactive phenolic hydrogen-bonded hydroxyl group also reacted with the glycidyl groups.

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