A similar situation is well-known in the field of thermotropic liquid crystals in which normal aliphatic acids even with a long alkyl chain are not nematogenic whereas in aliphatic diene acids a stable nematic mesophase is readily established.[21]

The analogy between molecules of para-aromatic polyamides and liquid crystalline systems may be extended further. As is clearly shown in Figure 7, PPPhTPhA molecules (and other similar polyamides) exhibit a highly organized intramolecular uniaxial orientational long-range order (along the x axis) as well as a coordination (transitional) long-range order along the x coordinate, whereas neither orientational nor translational long-range order is observed in the normal plane (yz). It is known that this type of ordering is characteristic of the smectic mesophase. Hence, we have many reasons to characterize PPBA molecules as molecules with an intramolecular quasi-smectic order. Para-aromatic polyamides clearly illustrate that the intramolecular structure and organization of the polymer not only determine its supermolecular structure but also ensure the principal properties of materials manufactured from them.[8]

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Functional Polymers. 4.[1] Polymers of 2,4-Dihydroxy-4′-vinylbenzophenone, New Polymeric Ultraviolet Absorbers

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ABSTRACT: The synthesis of 2,4-dihydroxy-4′-vinylbenzophenone was accomplished in five steps, with an overall yield of 15%, starting with *p*-ethylbenzoic acid. Pure 2,4-dihydroxy-4′-vinylbenzophenone was polymerized with azobis(isobutyro)nitrile as initiator; radical copolymerizations with methacrylic acid and styrene were also accomplished. In polymerizations with azobis(isobutyro)nitrile, no interference of the phenol groups of 2,4-dihydroxy-4′-vinylbenzophenone was observed. In copolymerization with styrene using benzoyl peroxide as initiator, the molecular weight of a copolymer containing 3 mol % 2,4-dihydroxy-4′-vinylbenzophenone was found to be significantly higher than that of styrene homopolymer prepared under identical conditions. This effect was also observed in the polymerization of styrene in the presence of a model compound, 2,4-dihydroxy-4′-ethylbenzophenone.

Polymers carrying reactive functional groups have been shown to be of value in a variety of uses. Among these polymers are materials which have ultraviolet-absorbing groups attached to the polymer chain.[2a] We have recently reported the synthesis of several 5-vinylsalicylic acid derivatives, which were homopolymerized and copolymerized with acrylic monomers.[2b] The present paper describes the synthesis and polymerization of another important UV absorber, 2,4-dihydroxy-4′-vinylbenzophenone.

In recent years a number of polymerizable 2-hydroxybenzophenones have been prepared. The most important route to these compounds utilizes the 4-hydroxyl group of 2,4-dihydroxybenzophenone to attach this unit to a reactive monomer capable of free-radical, coordination, or ring-opening polymerization. Acrylates, methacrylates, and unsaturated epoxide compounds have been employed as polymerizable substrates.[3-16] Allyl bromides, *p*-chloromethylstyrene, and epichlorohydrin have been used as substrates for displacement of halogen, yielding polymerizable ether derivatives of 2,4-dihydroxybenzophenone.[17-20] A Claisen rearrangement of 2-allyloxybenzophenone has been used to prepare 3-allyl-2-hydroxybenzophenone, which was copolymerized with ethylene with partial deactivation of the initiator (vanadium chloride and butyllithium).[21]

More recently, a first attempt to prepare 2-hydroxy-4′-vinylbenzophenone derivatives was made.[22,23] This type of monomer is very desirable because it may be expected to undergo copolymerization with acrylic monomers and with styrene derivatives, and because it contains no chemically sensitive linkages. The preparation of 2-methoxy-4′-vinyl-

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benzophenone and 2,4-dimethoxy-4′-vinylbenzophenone was achieved through the reaction of the corresponding methoxybenzaldehyde with *p*-styrylmagnesium chloride, followed by chromic acid oxidation of the alcohol to the ketone. These compounds could be homopolymerized and copolymerized with styrene with a radical initiator to give high molecular weight polymers. The reactivity ratios for these copolymerizations were reported to be: 2-methoxy-4′-vinylbenzophenone; 1.63, styrene, 0.28; and 2,4-dimethoxy-4′-vinylbenzophenone, 2.12; styrene, 0.41.

In order to convert these polymers to useful ultraviolet absorbers with a free 2-hydroxyl group, it was necessary to demethylate the 2 position. This reaction could be forced to essentially 100% conversion with $AlCl_3$ in nitrobenzene, but only at the expense of a substantial decrease in molecular weight.

Very recently, the results of another polymer–reaction approach to this problem were described.[24] Poly(4-vinylbenzoyl chloride) was allowed to react with resorcinol under Friedel–Crafts conditions, giving partial acylation and formation of a copolymer of 2,4-dihydroxy-4′-vinylbenzophenone and 4-vinylbenzoic acid. Substitution was limited to approximately 20% in this reaction. Also described in this paper was a Fries rearrangement of poly(3-methoxyphenyl vinylbenzoate), giving polymers containing up to 50 mol % 2-hydroxybenzoylphenyl groups.

Because of the difficulties encountered in the modification of polymers to produce poly(2,4-dihydroxy-4′-vinylbenzophenone), it was found desirable to prepare in a separate sequence of reactions pure 2,4-dihydroxy-4′-vinylbenzophenone and to study its homopolymerization and copolymerization behavior. The results of these studies are described in this paper.

Experimental Section

Materials. Acetic anhydride, AIBN, *N*-bromosuccinimide, chlorotrimethylsilane, ethylbenzene, methacrylic acid, tetraethylammonium chloride, tributylamine, and triethylamine were obtained from Eastman Organic Chemicals. Chloromethyl methyl ether and styrene were obtained from Aldrich Chemical Co. Lithium chloride was purchased from Fisher Scientific Co., boron trifluoride from Matheson Gas Products, and resorcinol from Matheson Coleman and Bell.

N,N-Dimethylacetamide (DMAc) was stirred overnight with P_2O_5 and distilled (bp 67 °C (17 mm)). Ethylbenzene was washed with concentrated H_2SO_4 until the washings were nearly colorless, then washed with water and 5% aqueous $NaHCO_3$, dried with $MgSO_4$, filtered, and distilled from sodium (bp 134–6 °C). Lithium chloride was dried for 3 h at 160 °C and cooled in a desiccator over P_2O_5. *N,N*-Dimethylformamide (DMF) was dried with magnesium sulfate, filtered, distilled (bp 87 °C (85 mm)), and used within 24 h of distillation. *N*-Bromosuccinimide was recrystallized from water and dried for 16 h at 60 °C (0.4 mm). Carbon tetrachloride was fractionally distilled. Styrene (bp 79 °C (85 mm)) and methacrylic acid were distilled (bp 80 °C (18 mm)) immediately before use.

Azobis(isobutyro)nitrile (AIBN) was recrystallized three times from dry methanol and dried at 0.1 mm for 16 h at room temperature. Benzoyl peroxide (BPO) was recrystallized twice from chloroform/methanol (1/2) and dried at 10^{-3} mm for 24 h at room temperature.

All distillations were done using a Vigreux fractionating column. Distillations at reduced pressure were carried out with magnetic stirring and a Claisen head; the pressure was stabilized with a manostat.

Measurements. Infrared spectra were recorded on Perkin-Elmer Model 727 or Model 283 spectrophotometers. Solid samples were measured as KBr pellets and liquid samples were measured between sodium chloride plates. The peak assignments were made to the nearest 5 cm^{-1}.

The ^1H NMR spectra of low molecular weight compounds were measured on a 60 MHz R-24 Hitachi Perkin-Elmer spectrometer. Polymer spectra were recorded on a 90 MHz R-32 Perkin-Elmer spectrometer.

Ultraviolet spectra were recorded on a Beckman MVI spectrometer in a double-beam servo mode. The maximum absorbance and corresponding wavelengths were determined by dialing in the wavelength and recording the absorbance value presented on the digital display.

The glass transition temperatures of polymers were determined on a Perkin-Elmer DSC-1B differential scanning calorimeter at a scanning rate of 20 °C/min. The instrument was calibrated against salicylic acid, benzoic acid, nitrotoluene, and cyclohexane. Regular melting points were measured on a MEL-TEMP capillary melting point apparatus and are corrected. Thermal decomposition data were obtained using a Perkin-Elmer TGS-1 thermobalance at a heating rate of 20 °C.min under a flow of nitrogen gas.

Gel permeation chromatography was performed on a Waters Associates Model 201 liquid chromatograph, using a set of five MicroStyragel columns (500, 10^3, 10^4, 10^5, and 10^6 Å). Tetrahydrofuran was employed as solvent, at a flow rate of 1.5 mL/min. The columns were calibrated using a set of nine narrow-distribution polystyrenes obtained from Waters Associates.

Microanalyses were done by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst, Mass.

Preparations. 2,4-Dihydroxy-4′-ethylbenzophenone. In a 1-L three-necked round-bottomed flask was placed tetrachloroethane (90 mL), finely ground resorcinol (134 g, 1.22 mol), and *p*-ethylbenzoic acid (92.2 g, 0.61 mol). The flask was fitted with a mechanical stirrer, a gas inlet tube, and a reflux condenser with a calcium chloride drying tube.

The reaction mixture was vigorously stirred and heated to 80 °C with an oil bath, and boron trifluoride gas was rapidly bubbled into the mixture. After 15 min, the solution became deep red. The rate of boron trifluoride gas addition was gradually decreased over a period of 2 h. The solution was heated for an additional 2 h under a flow of nitrogen. The contents of the flask were then added to water and the mixture was neutralized with sodium bicarbonate. The organic layer was diluted in ether, washed with a 5% aqueous sodium bicarbonate solution and with water, dried with magnesium sulfate, and filtered. Ether was removed under reduced pressure in a rotary evaporator and the red oil was distilled (bp 195–200 °C (0.1 mm)) through a Claisen head fitted with a 10-cm Vigreux column (yield 129 g (88%)). The yellow, viscous oil crystallized from 750 mL of 50% aqueous acetic acid to yield 74 g (50% yield) of bright yellow crystals of 2,4-dihydroxy-4′-ethylbenzophenone. Additional product (13 g, 9%) was recovered by diluting the mother liquors with water.

2,4-Dihydroxy-4′-ethylbenzophenone melted at 111–113 °C. The infrared spectrum (KBr) showed absorptions at 2800 to 3500 cm^{-1} (OH stretching) and 1620 cm^{-1} (C=O stretching). The ^1H NMR spectrum ($CDCl_3$) showed δ 1.12 to 1.37 (CH_2CH_3, 3); 2.48 to 2.88 (CH_2CH_3, 2), 6.2 to 6.4 and 7.15 to 7.58 (aromatic protons and ArO*H*, 8), 12.68 (ArO*H*, 1). The UV spectrum (methanol) showed maxima at 326, 289, and 246 nm with molar extinction coefficients of 11.4×10^3, 14.6×10^3, and 9.40×10^3 L mol^{-1} cm^{-1}, respectively. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.49; H, 5.77.

2,4-Di(trimethylsilyloxy)-4′-ethylbenzophenone. A 100-mL round-bottomed flask which contained a magnetic stirring bar, 2,4-dihydroxy-4′-ethylbenzophenone (7.1 g, 29 mmol), and dry pyridine (50 mL) was fitted with a pressure-equalizing dropping funnel closed with a calcium chloride drying tube. Chlorotrimethylsilane (8.6 g, 79 mmol, 35% excess) was added via the dropping funnel over a period of 5 min while the flask was cooled by an ice–water bath. The contents of the flask were stirred for 10 min in the ice-bath, 110 min at room temperature, and 3 h at 50 °C. The mixture was cooled to 10 °C and filtered and the yellow filtrate was concentrated in a rotary evaporator under reduced pressure and gave 10.5 g (93%) of an orange oil. Distillation (132–136 °C, 0.01 mm) yielded 6.5 g (58%) of a slightly yellow oil. The infrared spectrum (neat) showed absorptions at 2975 cm^{-1} (CH stretching) and 1650 cm^{-1} (C=O stretching). The ^1H NMR spectrum ($CDCl_3$) showed δ 0.26 ($OSi(CH_3)_3$, 18), 1.07 to 1.35 (CH_2CH_3, 3), 2.50 to 2.85 (CH_2CH_3, 2), 6.30 to 7.80 (aromatic protons, 7). Anal. Calcd for $C_{21}H_{30}Si_2O_3$: C, 65.23; H, 7.82. Found: C, 65.50; H, 7.64.

A small amount of the compound was exposed to the atmosphere for 2 months and solidified to a yellow solid; the solid melted at 110.5–113 °C and was identified as 2,4-dihydroxy-4′-ethylbenzophenone (mp 111–113 °C).

2,4-Diacetoxy-4′-ethylbenzophenone. To a 125-mL Erlenmeyer flask which contained a solution of 2,4-dihydroxy-4′-ethylbenzophenone (10.5 g, 0.44 mol) and acetic anhydride (50 mL, 0.52 mol) was added concentrated sulfuric acid (5 drops). The flask was stoppered and left at room temperature for 18 h. The solution was then poured into cold water (400 ML) and an oil separated from the solution. The aqueous phase was neutralized with sodium carbonate and the product was extracted with chloroform (150 mL) and dried with

magnesium sulfate. The chloroform was removed under reduced pressure in a rotary evaporator. The residue, a light yellow oil (13.2 g, 94% yield), was distilled (bp 175–185 °C (0.006 mm)) and gave 10.8 g (77% yield) of 2,4-diacetoxy-4′-ethylbenzophenone. The infrared spectrum (neat) showed absorptions at 1660 and 1770 cm^{-1} (C=O stretching). The ^1H NMR spectrum ($CDCl_3$) showed δ 1.09 to 1.35 (CH_2CH_3, 3), 1.92 and 2.28 (CH_3CO_2, 6), 2.52 to 2.90 (CH_2CH_3, 2), 7.05 to 7.80 (aromatic protons, 7). Anal. Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found: C, 69.70; H, 5.34.

2,4-Diacetoxy-4′-(1-bromoethyl)benzophenone. Crude 2,4-diacetoxy-4′-ethylbenzophenone (82 g, 0.20 mol) was dissolved in carbon tetrachloride (285 mL) in a 1-L round-bottomed flask fitted with a reflux condenser. *N*-Bromosuccinimide (47.6 g, 0.27 mol) and AIBN (0.20 g) were added and the mixture was heated under a nitrogen atmosphere in an oil bath at 85 °C; after 10 min the reaction became very vigorous and was complete in 10 min. After 50 min, the mixture was cooled and filtered, and the solvent was removed under reduced pressure in a rotary evaporator. The yellow product was twice recrystallized from 95% ethanol. A 75% yield (77 g, mp 91–92 °C) of white needles was obtained. The infrared spectrum (KBr) of the product showed absorptions at 1745 and 1650 cm^{-1} (C=O stretching). The ^1H NMR spectrum ($CDCl_3$) showed δ 1.05, 2.25, and 1.92 to 2.05 (CH_3CO_2 and $CHBrCH_3$, 9), 5.00 to 5.37 ($CHBrCH_3$, 0.8), 7.00 to 7.15 and 7.37 to 7.82 (aromatic protons 2 and 5). Anal. Calcd for $C_{19}H_{17}O_5Br$: C, 56.31; H, 4.23. Found: C, 56.25; H, 4.24.

The compound decomposed to a dark oil when exposed to the atmosphere over a period of several weeks.

2,4-Dihydroxy-4′-vinylbenzophenone. A 250-mL, three-necked, round-bottomed flask was charged with 10.0 g (24.6 mmol) of 2,4-diacetoxy-4′-(1-bromoethyl)benzophenone, 50 mL of DMAc, 60 mL (46.8 g, 0.252 mol) of tributylamine, and 0.50 g (2.1 mmol) of picric acid as polymerization inhibitor. The flask was quickly fitted with a reflux condenser and thermometer, flushed with dry nitrogen, and then placed in an oil bath at 140 °C while maintaining nitrogen flow. The mixture consisted of two phases below 65 °C but became homogeneous above that temperature. The reaction mixture darkened slightly during the reaction, becoming red-orange in color. After 80 min at 140 °C, the flask was removed from the bath and cooled to room temperature. The contents were poured into 500 mL of water, forming two liquid phases plus a red-brown solid. The liquid phases were extracted with two 100-mL portions of ether, and the combined extracts were washed with 100-mL portions of water, 3 N hydrochloric acid, water, 1 N hydrochloric acid, water, 5% $NaHCO_3$, and finally water again. The ether layer was dried over magnesium sulfate and filtered, and ether was removed at 20 mm at room temperature. After drying for 1 h at 10^{-3} mm at room temperature, the crude product was obtained as an orange oil (6.5 g, 81% yield). This crude product gave both a positive silver nitrate test and a positive Beilstein test, indicating contamination with unreacted starting material.

A 500-mL three-necked, round-bottomed flask was charged with crude 2,4-diacetoxy-4′-vinylbenzophenone (7.6 g, ca. 23 mmol), methanol (150 mL) and water (25 mL). The flask was fitted with a thermometer and reflux condenser and flushed with nitrogen. Sodium bicarbonate (7.6 g., 90 mmol) was added quickly, and the flask was immersed in an oil bath at 90 °C. The system was held at reflux for 1 h and then removed from the bath and cooled to room temperature. The contents of the flask were poured into 600 mL of distilled water, causing formation of an oily precipitate. The precipitate was extracted with 100 mL of ether, and the aqueous phase was washed with 100-mL portions of ether, chloroform (twice), and ether again. The combined organic phases were washed with water, dried with magnesium sulfate, and filtered, and the solvents were removed at 20 mm at room temperature to leave 4.2 g (75% yield) of crude 2,4-dihydroxy-4′-vinylbenzophenone as a sticky, orange solid. The yield of crude product based on 2,4-diacetoxy-4′-(1-bromoethyl)benzophenone was 61%. The ^1H NMR spectrum indicated that the crude product contained approximately 70% olefin, the remainder being primarily unreacted bromoethyl compound.

The sticky orange solid was chromatographed on silica gel, using the dry-column technique with 5:1 pentane:acetone as eluent, and gave 2.3 g (33%, based on 2,4-diacetoxy-4′-(1-bromomethyl)benzophenone) of pure 2,4-dihydroxy-4′-vinylbenzophenone, mp 96 °C dec (by DSC). The infrared spectrum (KBr) showed absorptions at 2800–3600 cm^{-1} (OH stretching), 1625 cm^{-1} (C=O stretching), plus 900 and 985 $cm.^{-1}$ (vinyl C–H bending). The ^1H NMR spectrum (DMSO-*d*) showed δ 5.5–7.9 (vinyl and aromatic protons and ArO*H*, 11) and 12.1 (broad, ArO*H*, 1). The UV spectrum (methanol) showed maxima at 329 and 291 nm, with molar extinction coefficients of 12.8 × 10^3 and 15.5 × 10^3 L mol^{-1} cm^{-1}, respectively. Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.98; H, 5.03. Found: C, 74.84; H, 4.77.

Polymerizations. Polymerization of 2,4-Dihydroxy-4′-vinylbenzophenone. A polymerization tube was charged with 2,4-dihydroxy-4′-vinylbenzophenone (0.250 g, 1.04 mmol), AIBN (1.0 mg, 6 × 10^{-3} mmol, 0.6 mol %), and freshly distilled DMF (1.5 mL). The tube was degassed by the freeze–thaw technique and sealed at 0.01 mm. After 30 h at 60 °C, the tube was opened, and the viscous contents were diluted with twice their volume of acetone. The acetone solution was added dropwise to 80 mL of rapidly stirred distilled water, and the polymer precipitated as an off-white, fluffy solid. The polymer was dried overnight at 30 mm at room temperature and then stirred with $CHCl_3$ to remove unreacted monomer; the yield of polymer was 0.149 g (60%). The polymer was purified by precipitation from methanol into an equal-volume mixture of hexane and anhydrous ether; the suspension was filtered after standing overnight, and the polymer was dried for 3 days at 56 °C (0.01 mm). The inherent viscosity of the polymer (0.5% in DMSO, 30 °C) was 0.57 dL/g. The infrared spectrum (KBr) showed an absorption at 1625 cm^{-1} (C=O stretching) plus a very broad O–H stretching band centered at 3360 cm^{-1}. The ^1H NMR spectrum (DMSO-*d*) showed δ 0.7–3.9 (CH–CH_2, DMSO), 5.3–8.3 (aromatic protons and ArO*H*), and 12.3 (ArO*H*). The UV spectrum (methanol) showed maxima at 324, 292, and 248 nm, with molar extinction coefficients of 9.10 × 10^3, 11.0 × 10^3, and 7.00 × 10^3 L mol^{-1} cm^{-1}, respectively. Anal. Calcd for $(C_{15}H_{12}O_3)_n$: C, 74.98; H, 5.03. Found: C, 75.01; H, 5.11.

Copolymerization of 2,4-Dihydroxy-4′-vinylbenzophenone with Methacrylic Acid. A polymerization tube was charged with 2,4-dihydroxy-4′-vinylbenzophenone (0.240 g, 1.00 mmol, 7.5 mol-% of monomer feed), freshly distilled methacrylic acid (1.06 g, 12.3 mmol, 92.5 mol % of monomer feed), AIBN (10.9 mg, 0.066 mol, 0.5 mol %), and DMF (1.0 mL). The tube was degassed by the freeze–thaw technique and sealed at 0.01 mm. After 6 h at 60 °C, the tube contents had solidified to form an opaque plug. The plug was dissolved in 30 mL of methanol, and the solution was added dropwise to 250 mL of $CHCl_3$. The polymer was collected by filtration, dried overnight at 30 mm at room temperature, ground finely, and then dried overnight at 0.01 mm at room temperature. The weight of recovered material was 1.26 g, indicating nearly quantitative yield of polymer. The copolymer was purified by precipitation from methanol solution into anhydrous ether and dried for 3 days at 56 °C (0.01 mm). The inherent viscosity of the copolymer (0.5% in DMSO, 30 °C) was 1.74 dL/g. The infrared spectrum (KBr) showed carbonyl absorptions at 1705 and 1625 cm^{-1}. The ^1H NMR spectrum (D_2O/NaOD) showed δ 0.0–2.2 [$CHCH_2$, $CH_2C(CH_3)$, 70], 6.8–7.3 (aromatic protons, 3). Independent ^1H NMR experiments established the positions of signals, as well as the fact that both phenol protons appear under the solvent peak. According to the ^1H NMR spectrum, the copolymer consisted of 3 mol % 2,4-dihydroxy-4′-vinylbenzophenone and 97 mol % methacrylic acid. The ultraviolet spectrum (methanol) showed absorptions at 325 (5.51 L g^{-1} cm^{-1}), 291 (6.83 L g^{-1} cm^{-1}), and 246 nm (3.59 L g^{-1} cm^{-1}). Anal. Calcd for $(-C_4H_6O_2-)_{97\%}$–$(-C_{12}H_{15}O_3-)_{3\%}$: C, 57.33; H, 6.87. Found: C, 57.43; H, 7.09.

A polymerization was carried out under similar conditions with 15 mol % of 2,4-dihydroxy-4′-vinylbenzophenone in the monomer feed. A 79% yield of copolymer with an inherent viscosity of 0.68 dL/g was obtained. The ^1H NMR spectrum indicated the presence of 6 mol % of 2,4-dihydroxy-4′-vinylbenzophenone in the copolymer. Anal. Calcd for $(-C_4H_6O_2-)_{92\%}$–$(-C_{12}H_{15}O_3-)_{8\%}$: C, 59.55; H, 6.64. Found: C, 59.60; H, 6.80.

Copolymerization of 2,4-Dihydroxy-4′-vinylbenzophenone with Styrene. Polymerizations were performed in duplicate. The same solutions of styrene and initiator in DMF were used for the homopolymerization of styrene and for the preparation of copolymerization mixtures. Homopolymerizations and copolymerizations were performed simultaneously and under identical conditions. The copolymerization of 2,4-dihydroxy-4′-vinylbenzophenone with styrene, with AIBN as initiator, illustrates the procedure.

A polymerization tube was charged with 2,4-dihydroxy-4′-vinylbenzophenone (0.042 g, 0.174 mmol, 2 mol %), freshly distilled styrene (0.91 g, 8.74 mmol, 98 mol %), AIBN (7.2 mg, 0.043 mmol, 0.4 mol %), and DMF (0.5 mL). The tube was degassed by the freeze–thaw technique and sealed at 0.01 mm. After 18 h at 60 °C, the viscous tube contents were diluted to 15 mL with benzene, and the polymer was precipitated via dropwise addition of the solution to 100 mL of rapidly stirred methanol. After two additional reprecipitations, the yield of fluffy, white polymer was 0.30 g (31%). The inherent viscosity of the polymer (0.5% in THF, 25 °C) was 0.356 dL/g, and the average molecular weights obtained from gel permeation chromatography were $\overline{M}_n$ = 48 200 and $\overline{M}_w$ = 83 000. The infrared spectrum (KBr) showed a weak carbonyl absorption at 1625 cm^{-1}, as well as bands at 1275 and 1115 cm^{-1} which are prominent in the spectrum of poly(2,4-dihy-

droxy-4′-vinylbenzophenone). The ultraviolet spectrum (THF) showed an absorption at 326 nm (1.76 L g^{-1} cm^{-1}). Anal. Calcd for $(-C_8H_8-)_{97\%}-(-C_{12}H_{15}O_3-)_{3\%}$: C, 91.13; H, 7.53. Found: C, 91.06, 90.63; H, 7.35, 7.30.

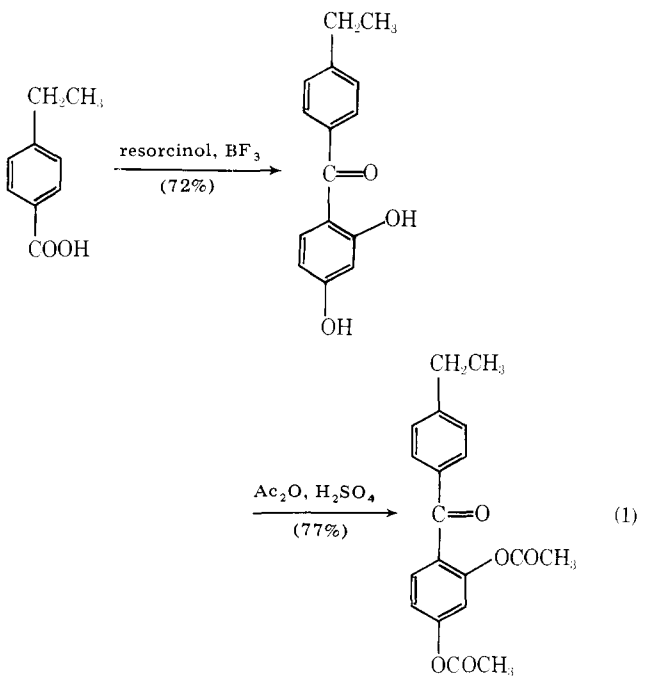
Experiments with benzoyl peroxide were performed under similar conditions, except that the initiator was 0.5 mol % of the comonomer mixture, and the reaction time was 27 h. Elemental analysis of the copolymers indicated that 3 mol % of 2,4-dihydroxy-4′-vinylbenzophenone was incorporated into the copolymer. Anal. Calcd for $(-C_8H_8-)_{97\%}-(-C_{12}H_{15}O_3-)_{3\%}$: C, 91.13; H, 7.53. Found: C, 91.01, 91.36; H, 7.35, 7.62.

Polymerization of Styrene in the Presence of 2,4-Dihydroxy-4′-ethylbenzophenone. A solution of freshly distilled styrene (10 mL, 9.1 g, 87.4 mmol), benzoyl peroxide (0.1060 g, 0.438 mmol, 0.5 mol %), and DMF (5 mL) was prepared in a flask capped with a serum stopper under a flow of dry nitrogen. When the solution was homogeneous, 1.5 mL of solution were transferred to each of eight polymerization tubes, each of which contained the desired quantity (see Table II) of 2,4-dihydroxy-4′-ethylbenzophenone. The tubes were degassed by three freeze–thaw cycles at 10^{-3} mm and then sealed at 10^{-3} mm and placed in a constant temperature bath at 60 °C. After 27 h at 60 °C, the tubes were removed from the bath and cooled to room temperature. Each tube was opened, the contents were diluted with 10 mL of benzene, and the resulting solution was added dropwise to 100 mL of rapidly stirred methanol to precipitate the polymer. The precipitated polymer was stirred for 1–2 h in methanol, collected by filtration, and dried overnight at room temperature at 10^{-3} mm. Yields ranged from 54 to 60%. The peak molecular weights of the polymers were determined by gel permeation chromatography, and inherent viscosities were measured at 25 °C in THF.

Results and Discussion

Pure 2,4-dihydroxy-4′-vinylbenzophenone was prepared in a five-step synthesis, starting with *p*-ethylbenzoic acid [eq 1 and 2]. The behavior of this compound in free-radical homopolymerization and copolymerization was investigated with the objective of preparing novel polymeric ultraviolet absorbers. Special emphasis was given to the determination of the molecular weights of the resulting polymers. The effect of the model compound, 2,4-dihydroxy-4′-ethylbenzophenone, on styrene polymerization was also determined.

Synthesis of 2,4-Dihydroxy-4′-vinylbenzophenone. The starting material for the synthesis of 2,4-dihydroxy-4′-vinylbenzophenone was *p*-ethylbenzoic acid. The compound is commercially available but was conveniently prepared in the laboratory in two steps from ethylbenzene. 4-Ethylacetophenone[25] (free of 2-ethylacetophenone and 2,4-diethylacetophenone) was obtained by a low-temperature (5–25 °C) acetylation of ethylbenzene with acetyl chloride by the Perrier modification of the Friedel–Crafts reaction. The Perrier modification, in which acetyl chloride and aluminum chloride were first allowed to react and the ethylbenzene was added last, was recommended by Pearson[26] to avoid alkyl position isomerization and disproportionation.



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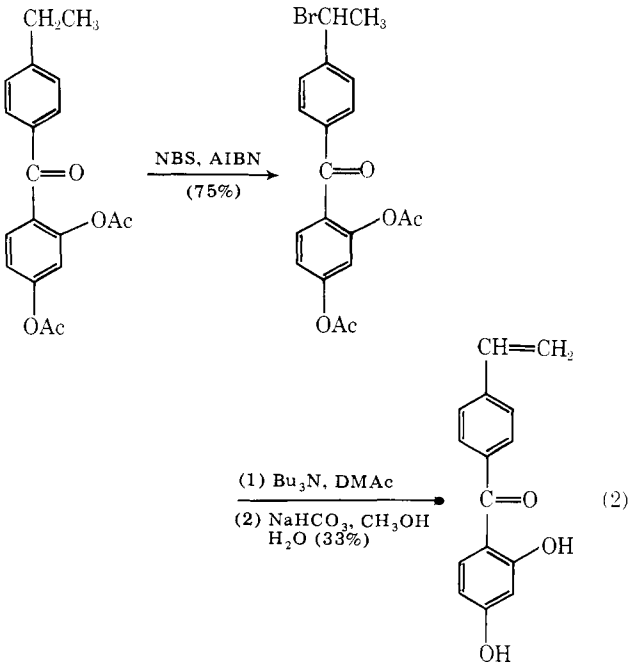

(2)

The next step in the reaction sequence was the oxidation of 4-ethylacetophenone with sodium hydroxide and bromine (sodium hypobromite) to form 4-ethylbenzoic acid.[27] The oxidation was not complicated by formation of terephthalic acid, as has been reported in the sodium hypochlorite oxidation of *p*-ethylacetophenone.[28] 4-Ethylbenzoic acid was thus obtained in an overall yield of 68%.

A 72% yield of pure 2,4-dihydroxy-4′-ethylbenzophenone was then obtained by the acylation of resorcinol by 4-ethylbenzoic acid, with boron trifluoride as catalyst. The crude red produce was first distilled and then recrystallized from aqueous acetic acid to yield bright yellow crystals, mp 111–113 °C.

The UV spectrum of the 2,4-dihydroxy-4′-ethylbenzophenone and the ^1H NMR spectrum of a derivative of 2,4-dihydroxy-4′-ethylbenzophenone (2-hydroxy-4-methoxymethoxy-4′-ethylbenzophenone) showed that the product was the 2,4 isomer and not 2,6-dihydroxy-4′-ethylbenzophenone, which would have been obtained by acylation between the two hydroxyl groups of resorcinol. The UV spectrum of the product had three absorptions (246, 289, and 326 nm) which are characteristic of 2,4-dihydroxybenzophenones (245–255, 280–290, 335–345 nm).[29] The spectrum was not similar to the UV spectrum of 2,6-dihydroxybenzophenone which has only two absorptions (250 and 280 nm).[29] The ^1H NMR spectrum of 2-hydroxy-4-methoxymethoxy-4′-ethylbenzophenone showed clear, sharp signals, which was not the case with the ^1H NMR spectrum of 2,4-dihydroxy-4′-ethylbenzophenone, and it was therefore more useful in the determination of the position of substitution. The chemical shifts and coupling constants of the aromatic protons were consistent with the structure of the 2,4 isomer but not with that of the 2,6 isomer. The synthesis of 2-hydroxy-4-methoxymethoxy-4′-ethylbenzophenone from 2,4-dihydroxy-4′-ethylbenzophenone and chloromethyl methyl ether is discussed below.

At this stage, an unsuccessful attempt was made to brominate the ethyl group of 2,4-dihydroxy-4′-ethylbenzophenone. The radical side chain bromination did not take place, but

rather an aromatic substitution reaction on the ring containing the phenol groups occurred. The ^1H NMR spectrum of the crude product showed that three phenol proton signals were present in the 12.5- to 13.3-ppm range and that the integrated signal intensity of the aromatic protons had decreased from 7 to 6. The ^1H NMR spectrum also indicated that the ethyl group was unaffected by the reaction since its quartet and triplet were still present. No attempts were made to isolate or further characterize the reaction product.

Bromination of the hydroxyl-substituted aromatic ring of 2,4-dihydroxy-4′-ethylbenzophenone thus apparently took precedence over the radical side chain bromination of the ethyl group with NBS. Evidently, the resonance donating phenol groups activated the aromatic ring to aromatic electrophilic bromination and may have also inhibited the radical side chain bromination. Aromatic bromination with NBS is not unusual. For example, reaction of NBS with resorcinol, 4-hydroxybenzoic acid, and 1,3-dimethoxybenzene reportedly gave 2,4,6-tribromoresorcinol, 3,5-dibromo-4-hydroxybenzoic acid, and 4-bromo-1,3-dimethoxybenzene, respectively.[30]

In order to prevent electrophilic ring bromination, several different methods of blocking of the phenol were investigated. 2,4-Diacetoxy-4′-ethylbenzophenone was successfully brominated on the side chain with NBS to yield 2,4-diacetoxy-4′-(1-bromomethyl)benzophenone. Evidently, acetylation of the phenol groups decreased their resonance donating ability and/or sterically hindered substitution on the aromatic ring since side chain bromination occurred rather than ring bromination. 2,4-Dihydroxy-4′-ethylbenzophenone was easily converted to 2,4-diacetoxy-4′-ethylbenzophenone with acetic anhydride in the presence of a small amount of sulfuric acid. After distillation, the yield of 2,4-diacetoxy-4′-ethylbenzophenone was 77%. Bromination with NBS, using AIBN as activator, then afforded a 75% yield of 2,4-diacetoxy-4′-(1-bromoethyl)benzophenone as white needles, mp 91–2 °C.

Two other blocking groups were also employed, with less success. An attempt was made to synthesize 2,4-dimethoxymethoxy-4′-ethylbenzophenone, since it was expected that the methoxymethoxy group would be an effective base stable protecting group[31] for the anticipated dehydrobromination of 2,4-dimethoxymethoxy-4′-(1-bromoethyl)benzophenone. However, the ^1H NMR spectrum of the product, which was isolated after the reaction of 2,4-dihydroxy-4′-ethylbenzophenone and chloromethyl methyl ether, showed that it was 2-hydroxy-4-methoxymethoxy-4′-ethylbenzophenone and not the expected 2,4-dimethoxymethoxy-4′-ethylbenzophenone. An attempted side chain bromination of 2-hydroxy-4-methoxymethoxy-4′-ethylbenzophenone with NBS resulted in bromination of the aromatic ring and formation of a mixture of isomers as determined by ^1H NMR spectroscopy.

Use of the trimethylsilyl group was similarly unsuccessful. Treatment of 2,4-di(trimethylsilyloxy)-4′-ethylbenzophenone with NBS failed to afford any brominated products. It had been expected that the base stable trimethylsilyloxy protecting groups would sterically hinder bromination of the aromatic ring and could be left on the molecule during the subsequent dehydrobromination reaction of 2,4-di(trimethylsilyloxy)-4′-benzophenone and radical polymerization of 2,4-di(trimethylsilyloxy)-4′-vinylbenzophenone. The protecting groups could then have been easily removed under slightly acidic conditions in the presence of water.[32]

The overall yield of 2,4-diacetoxy-4′-(1-bromoethyl)benzophenone, based on analytically pure products at each stage, was 42%, and a higher yield would undoubtedly have been obtained without thorough purification of each new compound. The final stages of the preparation proved to be substantially more difficult. Dehydrobromination of 2,4-diacetoxy-4′-(1-bromoethyl) was accomplished by treatment with tri-*n*-butylamine in DMAc at 140 °C; an 81% yield of crude 2,4-diacetoxy-4′-vinylbenzophenone was obtained. The product was not purified but was treated with sodium bicarbonate in aqueous methanol to unblock the phenol groups. After purification by dry-column chromatography and recrystallization, a 33% yield of pure 2,4-dihydroxy-4′-vinylbenzophenone was obtained.

Several other dehydrohalogenation agents were investigated for the elimination of hydrogen bromide from 2,4-diacetoxy-4′-(1-bromomethyl)benzophenone. Strong bases such as NaOH, KOH, and sodium and potassium *tert*-butoxides were investigated, in protic solvents and in aprotic solvents, with little success. In general tarry products were obtained, with the ^1H NMR spectra indicating very low yields of olefin. Weak bases, such as lithium chloride and tetraethylammonium chloride (in DMAc or DMF), afforded only low conversion to the olefin, even after 36 h at 100 °C. Silver nitrate in aqueous alcohol, although reacting rapidly with the benzylic bromide to produce a solid precipitate, produced little olefin in 17 h in the dark at room temperature. Several tertiary amines were then investigated, with mixed results. Collidine produced no reaction even in 45 h at 100 °C, while the use of quinoline at the same temperature caused complete disappearance of starting material within 1 h (with formation of little or no olefin). Pyridine and triethylamine were similarly ineffective.

The purification of 2,4-dihydroxy-4′-vinylbenzophenone was found to be surprisingly difficult. Although the elimination reaction was run at high temperature, the crude product of the reaction contained substantial starting material, as evidenced by spectral data and by qualitative analyses for bromine (see Experimental Section). The high molecular weight of 2,4-dihydroxy-4′-vinylbenzophenone precluded distillation at a temperature at which the double bond is stable with respect to polymerization, and contamination with the bromide thwarted numerous attempts at crystallization. Similarly, dry-column chromatography was complicated by the presence of the bromide, since the chromatographic behavior of these compounds is dominated by the 2,4-dihydroxybenzophenone structure, with the side chain contributing very little to the adsorption process. After many unsuccesful attempts, however, chromatography on silica gel with a 5/1 pentane/acetone solvent system produced a material capable of crystallization. Recrystallization from 2/1 pentane/chloroform then afforded pure 2,4-dihydroxy-4′-vinylbenzophenone as needles or platelets, depending on the rate of cooling. The compound polymerized at (or below) its melting point; differential scanning calorimetry at 20 °C/min showed no melting endotherm but rather a substantial exotherm beginning at 96 °C and with a maximum at ca. 120 °C.

Preparation and Characterization of Polymers of 2,4-Dihydroxy-4′-vinylbenzophenone. 2,4-Dihydroxy-4′-vinylbenzophenone was successfully polymerized in solution in DMF with AIBN as initiator to give poly(2,4-dihydroxy-4′-vinylbenzophenone) with an inherent viscosity of 0.57 dL/g [eq 3]. The polymer was obtained in 60% yield after 30 h at 60

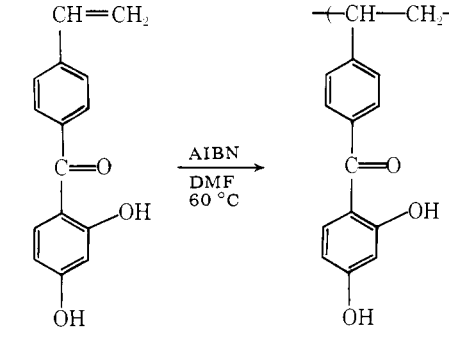

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Table I
Copolymerization of 2,4-Dihydroxy-4′-vinylbenzophenone with Styrene

Initiator	[2,4-DHVB] mol %	η_{inh},[a] dL/g	M_w	M_n	M_w/M_n
AIBN	1.9	0.36	83 000	48 000	1.73
AIBN	0	0.33	77 000	44 000	1.75
BPO	1.9	0.40	104 000	58 000	1.79
BPO	0	0.33	69 000	39 000	1.77

[a] 25 °C, 0.5 wt % in THF.

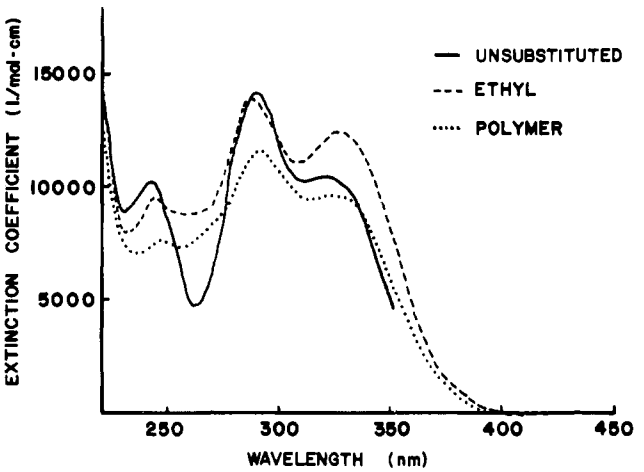


Figure 1. Ultraviolet spectra of 2,4-dihydroxybenzophenone derivatives.

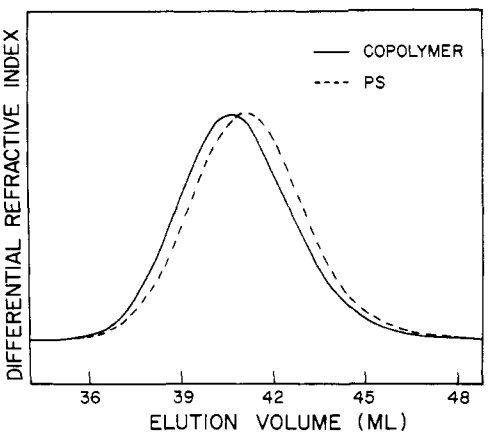
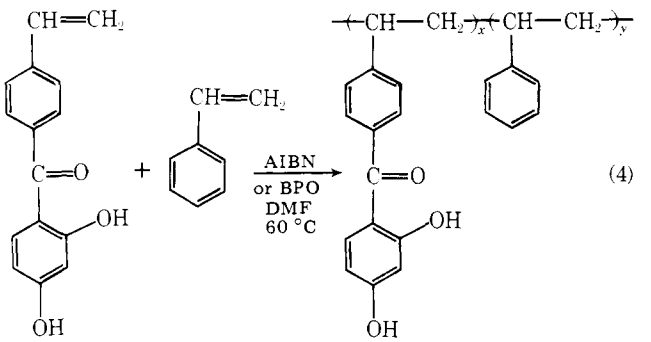


Figure 2. Gel permeation chromatography of polystyrene and of copolymer of styrene with 2,4-dihydroxy-4′-vinylbenzophenone; AIBN as initiator.

°C in a sealed tube. The UV spectrum showed the three absorption maxima characteristic of the 2,4-dihydroxybenzophenones (at 324, 292, and 248 nm), indicating that the polymer structure is that given in eq 3 (i.e., a substantially linear vinyl polymer structure). The extinction coefficient of the polymer is, however, significantly lower than those of model compounds throughout the ultraviolet spectral region (Figure 1). This hypochromic effect is not surprising in view of earlier work on the ultraviolet spectra of vinyl polymers;[33] for example, Gallo and Russo[34] and Stutzel, Miyamoto, and Cantow[35] have described hypochromic effects in styrene–methyl methacrylate copolymers, and Gibson[36] has reported a similar phenomenon in polymers containing carbazole chromophores.

Poly(2,4-dihydroxy-4′-vinylbenzophenone) exhibited no detectable glass transition in the differential scanning calorimeter between room temperature and 400 °C at a heating rate of 20 °C/min. Differential thermogravimetric analysis indicated a maximum degradation rate at 385–400 °C, at a heating rate of 20 °C/min, under nitrogen. The thermogravimetric spectrum was extremely broad, and a residue of 57% of the sample weight remained, even after heating to 510 °C. This is in accord with the recently published work of Still and Whitehead[37] on the degradation of poly(*p*-hydroxystyrene). These authors found a residue of approximately 30% of the sample weight on heating to 480 °C, in contrast to poly(*p*-methoxystyrene) and conventional polystyrene, each of which produced 100% volatile products at temperatures below 450 °C. A carbonization reaction in poly(*p*-hydroxystyrene) was demonstrated, both in thermogravimetric analysis and in vacuum pyrolysis experiments and was believed to account for the increased residue formation. A similar reaction may explain the substantial residue formed in degradation of poly(2,4-dihydroxy-4′-vinylbenzophenone); we have made no attempt to investigate this phenomenon.

Copolymerization of 2,4-Dihydroxy-4′-vinylbenzophenone with Styrene. Although the infrared, ^{1}H NMR, and ultraviolet spectra of poly(2,4-dihydroxy-4′-vinylbenzophenone) gave no indication of substantial branching in the polymer, the presence of two phenol groups in the structure of the monomer caused us to be concerned about the potential of branching and/or chain transfer in the free-radical polymerization of this monomer. In order to investigate these possibilities, the copolymerization of 2,4-dihydroxy-4′-vinylbenzophenone with styrene was examined [eq 4]. The



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analysis of styrene-rich copolymers by gel permeation chromatography was used to detect possible interference of the phenol groups in the polymerization, since significant branching and chain transfer would produce measurable changes in the molecular weight and molecular weight distribution of the polymer. Polymerization experiments were performed in sealed tubes in DMF, with either AIBN or benzoyl peroxide (BPO) as initiator. Styrene homopolymers were prepared simultaneously, under identical conditions, and all experiments were performed in duplicate. 2,4-Dihydroxy-4′-vinylbenzophenone constituted 2 mol % of the monomer feed, and the initiator concentration was 0.4–0.5 mol %. Figures 2 and 3 show GPC traces for copolymers prepared at 60 °C; the molecular weight data are shown in Table I. In each case, elemental analysis of the copolymers indicated incorporation of 3 mol % of 2,4-dihydroxy-4′-vinylbenzophenone units.

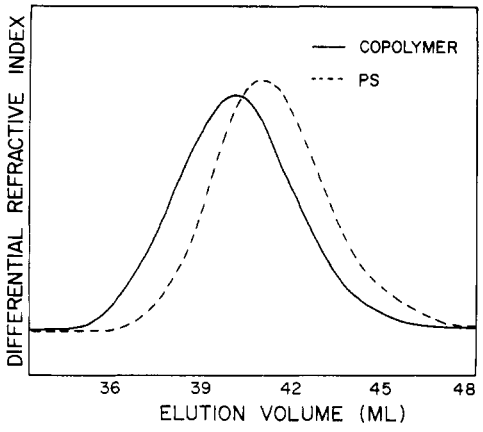
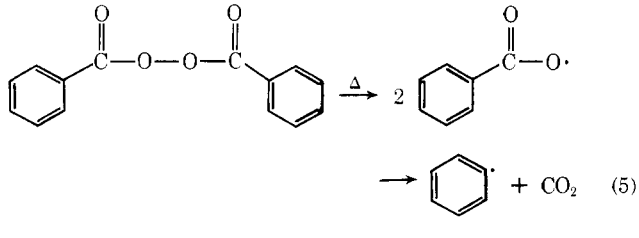


Figure 3. Gel permeation chromatography of polystyrene and of copolymer of styrene with 2,4-dihydroxy-4′-vinylbenzophenone; benzoyl peroxide as initiator.

It is apparent that the presence of 2,4-dihydroxy-4′-vinylbenzophenone affected the polymer molecular weight and molecular weight distribution very little when AIBN was used as the initiator (Figure 2); in fact, the number-average and weight-average molecular weights of the copolymer and styrene homopolymer may be regarded as identical within the precision of the experiment. In contrast, addition of the compound to the peroxide-initiated system results in a significant *increase* in molecular weight, again without substantial broadening of the distribution (Figure 3). The weight-average molecular weight of the copolymer is 104 000 vs. 69 000 for the styrene homopolymer, with a polydispersity index of 1.8 in each case. (Actually, a polydispersity index closer to 2.0 might be expected in these polymerizations. The figures given here are based on calibration by nine narrow-distribution polystyrenes obtained from Waters Associates but are otherwise uncorrected. Conclusions drawn from these comparative studies are not dependent upon the absolute value of the polydispersity index.)

The increased molecular weight of the copolymer suggests two possibilities: First, the copolymer may have aggregated in the GPC analysis (in THF), for example, through hydrogen bonding of the phenol groups. The apparent molecular weight increase would then have been an artifact, merely a result of an increase in the effective size of the polymer molecule in solution. The second possibility is that the effect was genuine, i.e., that the presence of 2,4-dihydroxy-4′-vinylbenzophenone did indeed result in an increased molecular weight of the copolymer with styrene, at least when benzoyl peroxide was used as the initiator. The difference in behavior between the AIBN system and the benzoyl peroxide system suggests that this effect resulted from a reaction involving the initiator or initiator fragments, rather than with the end of the growing chain. Should this be the case, it is not surprising that the behavior of benzoyl peroxide as initiator for the polymerization differed from that of AIBN.

Benzoyl peroxide initially decomposes by homolytic scission of the peroxide bond and may then further decompose to yield the phenyl radical and carbon dioxide [eq 5]. The result is that the polymerization is initiated by a mixture of benzoyloxy



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radicals, in which the unpaired spin is borne by the oxygen atom, and phenyl radicals, which are resonance-stabilized carbon radicals. This scheme is well-known, and Bevington and Ho[38] have done quantitative radiotracer studies of labeled benzoyl peroxide as initiator for styrene polymerization in DMF at 60 °C, proving that there are indeed both benzoyloxy and phenyl end groups in polystyrene prepared under these conditions. The difference in the behavior of the initiators in our experiments may thus result from a difference in the character of the initiator fragments, the benzoyloxy radical from benzoyl peroxide vs. the resonance-stabilized carbon radical from AIBN.

Recent work by Kato[39] and by Pacifici and Browning[40] has shown that these two types of radicals do indeed behave differently, in a very important manner. In a study of the vinyl polymerization of hindered phenol compounds, Kato found that these compounds polymerized normally with AIBN as initiator, but not with benzoyl peroxide, cumene hydroperoxide, or tetraethylthiuram disulfide. It was suggested that the resonance-stabilized carbon radical derived from AIBN preferentially underwent addition to the double bond, while the other species abstracted the phenolic hydrogen atom, resulting in inhibition of polymerization. Pacifici and Browning found that this preference for addition vs. abstraction was great enough to allow the use of α-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N*-*tert*-butylnitrone for the differentiation of oxy radicals and carbon radicals. Oxy radicals abstracted the phenolic hydrogen atom of this compound, giving a stable phenoxyl radical, whereas carbon radicals preferentially added to the α carbon of the nitrone to yield a stable nitroxide. The ESR spectra of these stable species were easily differentiated. Experiments using AIBN and benzoyl peroxide were found to be consistent with the discussion given above, i.e., AIBN gave only the nitroxide signal, and benzoyl peroxide gave both nitroxide and phenoxyl signals. The implications of this behavior in our experiments are clear: one would expect AIBN to undergo addition to the vinyl double bond, even in the presence of the phenol groups of 2,4-dihydroxy-4′-vinylbenzophenone, and the molecular weight should be affected very little. Benzoyl peroxide, on the other hand, produces benzoyloxy radicals which are prone to abstraction of the phenolic hydrogen atom; this may result in a decrease in initiator efficiency (f) and an increase in molecular weight, since the kinetic chain length is, ideally, proportional to $f^{-1/2}$.[41] Chain transfer, and a resultant decrease in molecular weight, would not be expected in either system, since the active center of the polymerization is itself a resonance-stabilized carbon radical, with little tendency to undergo the abstraction reaction.

2,4-Dihydroxy-4′-ethylbenzophenone in Styrene Polymerization. The results of the copolymerization experiments are thus understandable in terms of the reactivities of the radical species involved in the chain growth. In order to rule out the possibility of artifacts in the GPC analysis, a second experiment was conducted. Homopolymerization of styrene in the presence of the model compound, 2,4-dihydroxy-4′-ethylbenzophenone, was performed, with the concentration of model compound varying from 0 to 10 mol %. The reactivity of the ethyl-substituted compound was expected to be similar to that of the vinyl compound, but the polymers obtained were pure polystyrenes, making the chromatographic analysis unambiguous.

The polymerizations were run at 60 °C in DMF, in sealed tubes, with benzoyl peroxide as 0.5 mol % of the monomer/initiator mixture. The appropriate amount of 2,4-dihydroxy-4′-ethylbenzophenone was added to each polymerization tube, followed by the monomer/initiator mixture in DMF; the same solution was used for all tubes, in order to be certain that the monomer/initiator ratio was constant. After completion of the polymerization, the polymers were analyzed by

Table II
Polymerization of Styrene with Added 2,4-Dihydroxy-4′-ethylbenzophenone

[2,4-DHEB], mol %	η_{inh},[a] dL/g	Peak mol wt in GPC
0	0.362	59,000
0.43	0.376	64,000
1.08	0.379	66,000
2.01	0.376	67,000
2.88	0.374	67,000
4.72	0.397	72,000
9.01	0.408	77,000

[a] 25 °C, 0.5 wt % in THF.

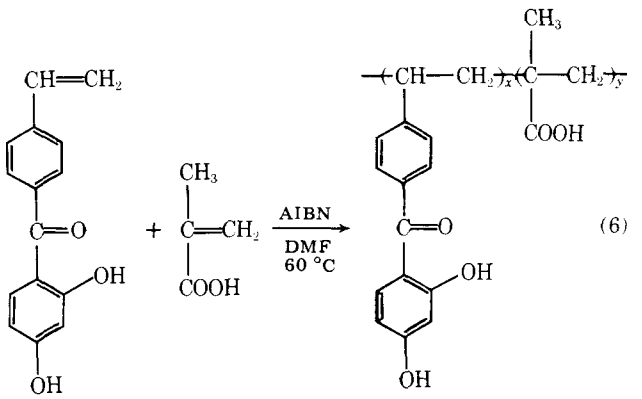
GPC and by inherent viscosity measurements; these results are summarized in Table II. Addition of 2,4-dihydroxy-4′-ethylbenzophenone did not significantly affect the yield of polymer; yields varied only from 54 to 60%.

Although the effect is not large, the GPC data in Table II clearly indicate an increase in the molecular weight of the polymer with increasing concentration of 2,4-dihydroxy-4′-ethylbenzophenone. This is supported by inherent viscosity measurements, with the polymer prepared in the presence of 9 mol % of the additive exhibiting an inherent viscosity of 0.408 dL/g vs. 0.362 dL/g for the control polymer. The ethyl compound is apparently not as active as the vinyl derivative in influencing the molecular weight, but nevertheless, the effect is measurable and is consistent with the behavior of 2,4-dihydroxy-4′-vinylbenzophenone in copolymerization with styrene. The results obtained in the copolymerization studies clearly cannot be solely ascribed to artifacts in the chromatographic analysis. Further, more detailed, studies of this effect are planned.

Thermal Analysis of Copolymers. The thermal behavior of styrene/2,4-dihydroxy-4′-vinylbenzophenone copolymers was examined, via differential scanning calorimetry and thermogravimetric analysis. The copolymers were prepared with 2 mol % of 2,4-dihydroxy-4′-vinylbenzophenone in the monomer feed and were shown by elemental analysis to contain 3 mol % of these units. The glass transition temperature of the copolymers (measured at a heating rate of 20 °C/min) was found to be slightly higher than that of styrene homopolymer; a value of 104–5 °C was found for copolymers prepared with either AIBN or BPO as initiator vs. 101–2 °C for styrene homopolymer. A slight loss in chain fleixibility may occur as a result of association of the dihydroxybenzophenone units in the polystyrene matrix.

Thermogravimetric analysis showed little difference between the copolymers and styrene homopolymer; the only effect of the comonomer appeared to be formation of a small amount (1–2 wt %) of char, which was to be expected in view of the previously discussed degradation behavior of the 2,4-dihydroxy-4′-vinylbenzophenone homopolymer.

Copolymerization of 2,4-Dihydroxy-4′-vinylbenzophenone with Methacrylic Acid. 2,4-Dihydroxy-4′-vinylbenzophenone was also copolymerized with methacrylic acid, using AIBN as the initiator [eq 6]. The copolymers were found to be enriched in methacrylic acid with respect to the monomer feed, indicating that the 2,4-dihydroxybenzoyl group probably behaved as an electron-withdrawing substituent, reducing the electron density at the double bond. With 15 mol % of 2,4-dihydroxy-4′-vinylbenzophenone in the feed, a reaction time of 6 h at 60 °C afforded a copolymer containing 7 mol % of these units, with an inherent viscosity of 0.68 dL/g (30 °C, 0.5 % in DMSO). Under similar conditions with 7.5 mol % in the feed, a copolymer containing 3 mol % 2,4-dihydroxy-4′-vinylbenzophenone units, with an inherent viscosity of 1.74 dL/g, was obtained.



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Detailed studies of the ultraviolet absorption properties of these new polymers of 2,4-dihydroxy-4′-vinylbenzophenone will be reported in a future paper in this series.

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Soluble Functional Polymers. 2. Utilization of Water-Insoluble Chromophores in Water-Soluble Polymeric Dyes[1]

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ABSTRACT: Two simple and practical routes have been developed for the preparation of water-soluble polymers having water-insoluble anthraquinone chromophores incorporated into their structure. Bonding of chromophore to polymer backbone was attained in both cases via copper(I)-catalyzed nucleophilic substitution of bromoanthraquinones by polymeric amines. The first route involved treating poly(vinylamine) with 0.5 equiv of bromoanthraquinone, followed by converting unreacted backbone amines into water-solubilizing sulfamate groups (Me_3N–SO_3 treatment). The second route employed a 60:40 vinylamine–vinylsulfonate copolymer for the direct preparation of water-soluble products. The copolymer was prepared by copolymerization of *N*-vinylacetamide and sodium vinylsulfonate, followed by acid hydrolysis. The copolymer exhibited an upper limit for chromophore attachment of 50–55% available amines. The reasons for this are discussed in terms of monomer sequencing.

Synthetic polymers have long been employed advantageously for their physical–mechanical properties rather than their chemical properties. Chemical modifications of polymers (unlike the chemistry of their preparation) were little studied until the 1950's. During recent years, however, the development and utilization of specifically functionalized polymers has received attention from chemists in a variety of fields.[2-4] Research has shown, for example, that polymeric reagents,[5] which consist of reactive functionality bound to an insoluble support, are particularly useful and valuable because of their nonpolluting and recyclable nature,[6] and because of the mechanical and operational advantages inherent in solid–liquid systems. Biologically active molecules, such as drugs,[7] enzymes,[8] hormones,[9] and insect sex attractants,[10] have been immobilized on polymers for a number of uses.[11] Polymeric organometallics have been shown to have excellent semiconducting properties.[12] Functionalized resins have found numerous applications as insolubilized chelating agents,[13] supports for organic synthesis,[14] protecting groups,[15] agents for ion exchange[16] and affinity chromatography,[17] catalysts,[18] and immobilizing media for the detection of unstable reaction intermediates.[19]

Much less attention has been focused on *soluble* functionalized polymers even though materials of this type suggest advantages in a variety of applications. Polymeric water-soluble dyes, which are of considerable biological and technological interest because of their various properties,[20] are examples of materials in this class which have been little investigated.[21] One reason for this is that the vast majority of chromophores are not available in a water-soluble (e.g., sulfonated) form,[22] and thus cannot be converted into water-soluble materials by the polymerization of easily prepared monomers. In order to prepare water-soluble polymeric dyes constructed of fundamentally water-insoluble chromophores, the chromophore must somehow be attached to, or be made a part of, a polymeric system which otherwise contains the required solubilizing functionality.

Nucleophilic polymeric amines provide two straightforward synthetic approaches to materials of this type. One route involves preparing an amine homopolymer, utilizing a portion of the amines for chromophore attachment, and converting the remainder into solubilizing groups. An equally viable method involves preparing a copolymer of both amine and sulfonate containing monomers and attaching chromophores to the amines. We report here the successful implementation of both of these routes for the preparation of water-soluble polymeric dyes using water-insoluble anthraquinone chromophores.

Homopolymer Route

Chromophore Attachment. Halogen atoms appropriately positioned on an anthraquinone nucleus undergo a facile copper(I)-catalyzed nucleophilic displacement by amines (Ullmann condensation).[23] A representative number of bromoanthraquinones were selected for reaction with poly(vinylamine hydrochloride) (1) in such a manner that residual amines would be available for conversion into water-solubilizing groups by sulfamation. This polymeric amine was chosen as the nucleophilic backbone for chromophore attachment because it is an easily prepared and characterized, homogeneous, linear polymer possessing a high density of reactive primary amines.[1,24]

The first step in the homopolymer route to water-soluble polymeric dyes involved an Ullmann condensation between 1 and 0.5 equiv of a bromoanthraquinone (Scheme I). The six water-insoluble bromoanthraquinones employed are listed

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