# Ultraviolet Stabilizing Monomers and Polymers. II. Synthesis and Polymerization of Acrylate and Methacrylate Derivatives of 2,4-Dihydroxybenzophenone*

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Synopsis

In the addition of stabilizing agents to plastic materials, problems such as incompatibility, migration, volatility, and/or solvent extraction of the additive frequently arise. With a view toward overcoming such problems in the use of ultraviolet absorbing stabilizers, acrylate and methacrylate derivatives containing the 2-hydroxy-4-alkoxybenzophenone moiety have been synthesized. The ultraviolet absorbing monomers were synthesized by reaction of 2,4-dihydroxybenzophenone with glycidyl acrylate and glycidyl methacrylate. They were homopolymerized and blended with poly(vinyl chloride), poly(vinylidene chloride), polystyrene, and poly(methyl methacrylate). They were also copolymerized with the corresponding monomers. The polymer blends and copolymers were investigated for ultraviolet stability versus corresponding controls. Effective ultraviolet stabilization was observed. Differences in the stability of some blends as compared to corresponding copolymers is thought to be due to incompatibility.

In recent years there has been increasing interest in the synthesis of ethylenically unsaturated ultraviolet absorbers which could be copolymerized, thereby permanently incorporating a stabilizing moiety into a polymer. This approach would minimize problems such as incompatibility, migration, volatility, and solvent extraction. The patent literature

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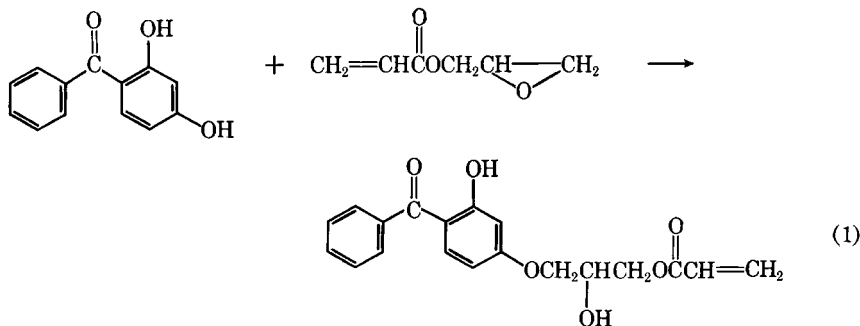
* For Part I see Fertig et al.[1]

describes the synthesis and copolymerization of monomeric salicylates,[2,3] benzophenones,[4-7] and benzotriazoles.[8,9]

In the work described here, acrylate and methacrylate derivatives of 2,4-dihydroxybenzophenone have been prepared by very simple organic reactions [eq. (1)]. These monomers may be readily homopolymerized and copolymerized with a wide range of other vinyl monomers, giving good yields of polymer with high molecular weight.

MONOMER SYNTHESIS

2,4-Dihydroxybenzophenone was heated with glycidyl acrylate or glycidyl methacrylate in the presence of a salt catalyst. Fission of the epoxide group by the phenolic hydroxyl at the 4-position gave 2-hydroxy-4-(3-acryloxy-2-hydroxypropoxy)benzophenone or 4(3-methacryloxypropoxy)benzophenone [eq. (1)]. It is possible that some isomeric 2-acryloxy-3-hydroxy derivative is formed in small amounts.[10] For the sake of brevity we refer to these monomers as benzophenone methacrylate and benzophenone acrylate (BPMA and BPA, respectively). The monomers were washed with dilute sulfuric acid to remove excess glycidyl acrylate or glycidyl methacrylate and extracted with benzene. The monomers are viscous yellow liquids soluble in a wide range of organic solvents. They polymerized on attempted distillation at low pressure.

The ultraviolet spectra of 2,4-dihydroxybenzophenone, BPA, and BPMA are similar, as can be seen from Figure 1. The percentage transmission ordinates in Figure 1 have been separated to show the similarity since otherwise the curves would be almost superimposed.

POLYMERIZATION

Most of the work was carried out with the methacrylate, since this monomer is easier to prepare and to handle. Although these monomers contain a phenolic hydroxyl group, there is no significant inhibition of polymerization. This is probably due to the *ortho* carbonyl group which ties up the phenolic hydrogen by hydrogen bonding and therefore prevents it from interfering in the polymerization.

Homopolymerization

The homopolymer of BPMA was prepared by polymerization of the monomer in tetrahydrofuran with the use of azobisisobutyronitrile as initiator. The polymer was isolated as a light yellow powder by precipitation from methanol. The properties of the polymer are shown in Table I. The ultraviolet spectrum of poly (BPMA) is also shown in Figure 1.

The use of poly(BPMA) as a high molecular weight ultraviolet absorber was investigated. Due to its molecular weight, migration and volatility
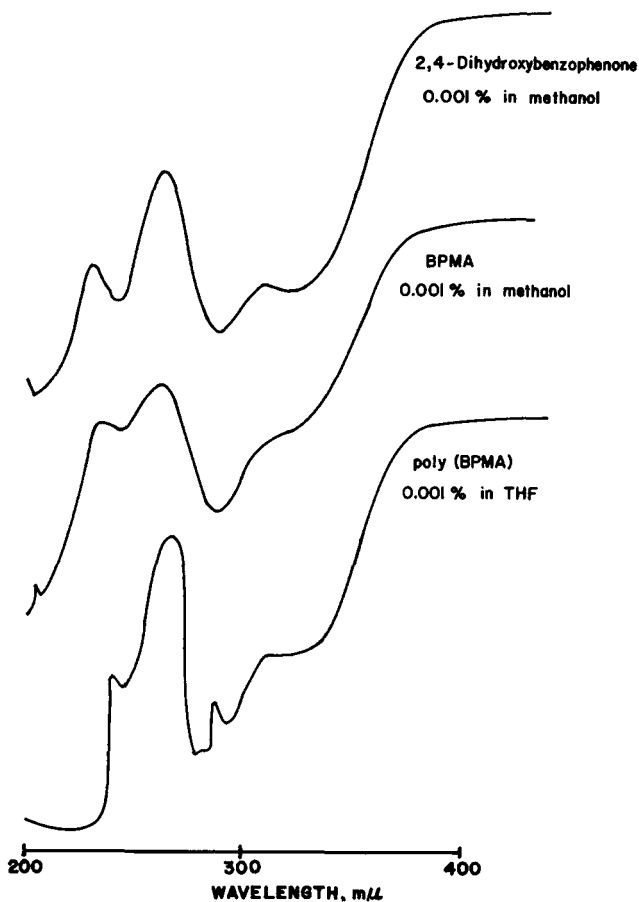
Fig. 1. Ultraviolet spectra of 2,4-dihydroxybenzophenone and derivatives.

problems would be minimized, though, of course, the polymeric nature limits compatibility with the polymers to be stabilized.   In fact, it appears that good compatibility is necessary for efficient stabilization (see below). To screen the stabilizing effect of poly(BPMA), it was blended at the 1%

TABLE I

	Poly(BPMA)
Intrinsic viscosity in THF	0.20
T_g, °C.	59
Solubility	Soluble in acetone, tetrahydrofuran, dioxane
	Insoluble in methanol, benzene, ethyl acetate, perchloroethylene

level with various polymers and copolymers. Films of these blends were then exposed to a GE UA-11B lamp, and changes in molecular weight or insolubles were followed with exposure time. These artificial exposure conditions would not show up the long-term advantages of the permanently
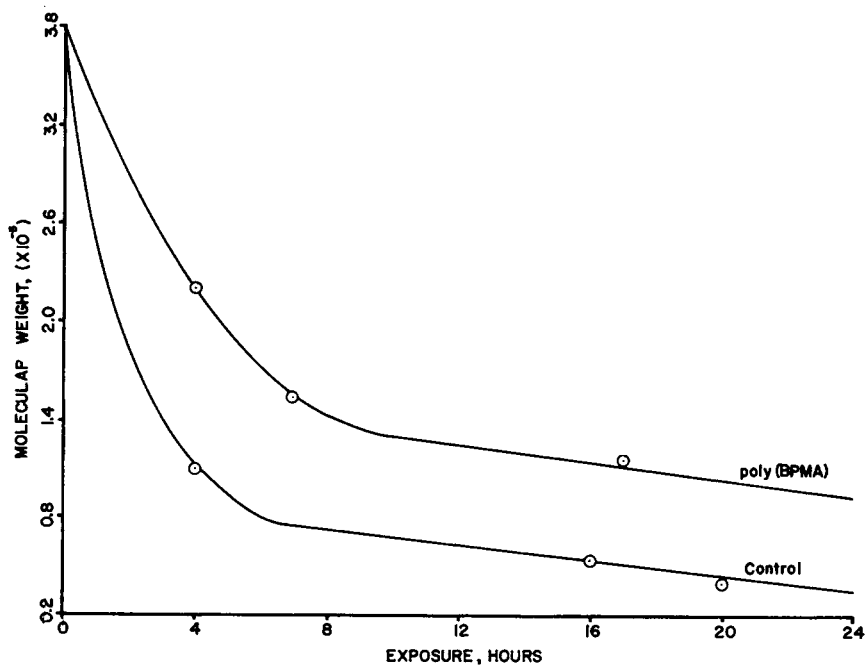

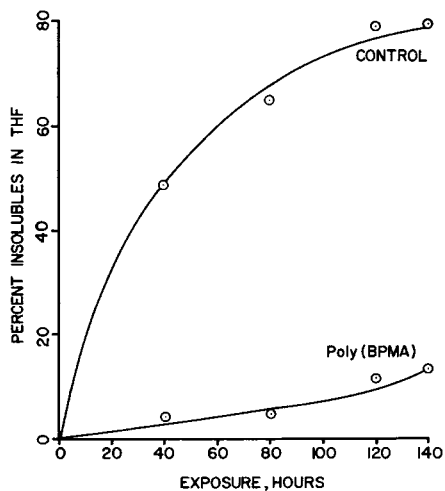Fig. 2. Ultraviolet exposure of poly(methyl methacrylate) blended with poly(BPMA).

Fig. 3. Ultraviolet exposure of poly(vinyl chloride) blended with poly(BPMA).
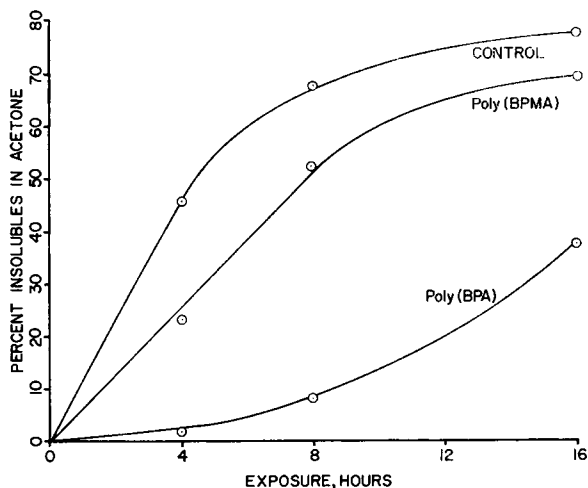
Fig. 4. Ultraviolet exposure of poly(vinylidene chloride/acrylonitrile) blended with poly(BPMA) and poly(BPA).
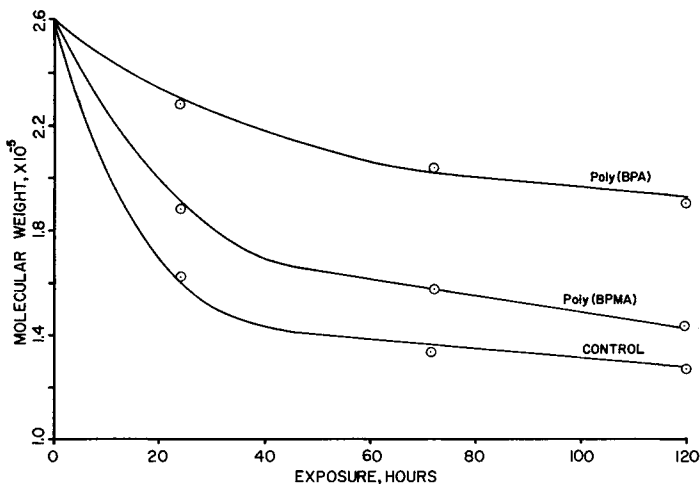

Fig. 5. Ultraviolet exposure of polystyrene blended with poly(BPMA) and poly(BPA).

attached moieties. However, the purpose here was to confirm that the chemical modifications of the hydroxybenzophenone and subsequent polymerization did not detract from its efficiency as an ultraviolet light absorber. Figures 2–5 show the results. It can be seen that protection is achieved in all cases. Poly(BPMA) showed marked incompatibility with the vinylidene chloride/acrylonitrile copolymer (Fig. 4) and polystyrene (Fig. 5), and here poly(BPA) was also screened. It was found to be compatible and appears to perform significantly better than poly(BPMA) as a stabilizer.

Copolymerization

BPMA may be copolymerized without difficulty with a wide range of vinyl monomers.   BPMA at the 1% level, was copolymerized with styrene, vinyl acetate, vinyl chloride, and vinylidene chloride.   For ease of preparation and evaluation the chloride polymers were prepared with 10% ethyl acrylate.   Control polymers without BPMA were also prepared.

The copolymers and controls were then exposed to ultraviolet exposure from a GE UA-11B lamp and changes in molecular weight and color difference were measured.   Figures 6–10 show the results.   It can be seen that some protection is achieved in all cases.   Copolymerization of monomeric BPMA with styrene and vinylidene chloride results in significant
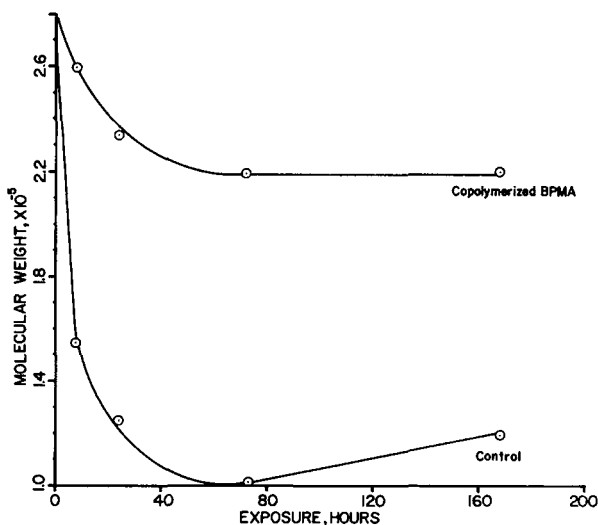

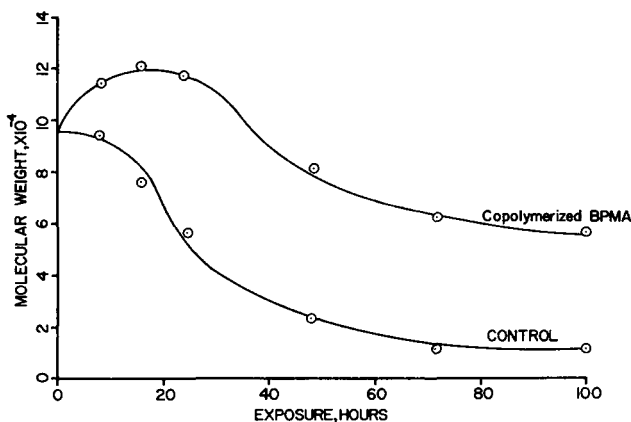Fig. 6. Ultraviolet exposure of polystyrene with copolymerized BPMA.

Fig. 7. Ultraviolet exposure of poly(vinyl acetate) with copolymerized BPMA.
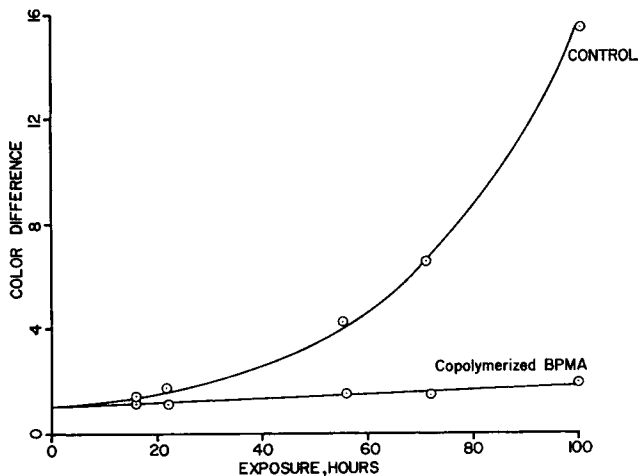
Fig. 8. Ultraviolet exposure of poly(vinyl chloride) with copolymerized BPMA.
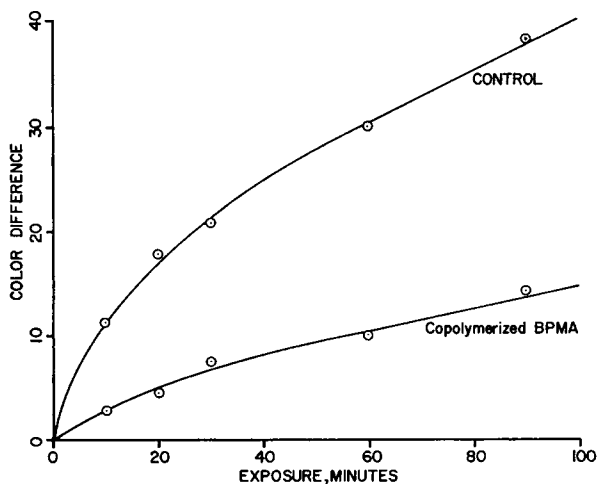

Fig. 9. Ultraviolet exposure of poly(vinylidene chloride) with copolymerized BPMA.

protection of the resulting copolymers (Figs. 6 and 9).   This is in contrast to the poor protection afforded by blending poly(BPMA) into the homopolymers (Figs. 4 and 5).   Presumably, the improved stability of the copolymers is due to the better homogeneity achieved by copolymerization as opposed to blending in a polymeric system where the polymeric ultraviolet absorber has limited compatibility.

   In certain systems, such as those involving Ziegler catalysts, copolymerization is technically difficult.   In such a case the monomer may be incorporated at the polymer processing stage along with other additives. In some such cases, the processing temperature is high enough to cause thermal polymerization of the monomer within the polymer substrate.
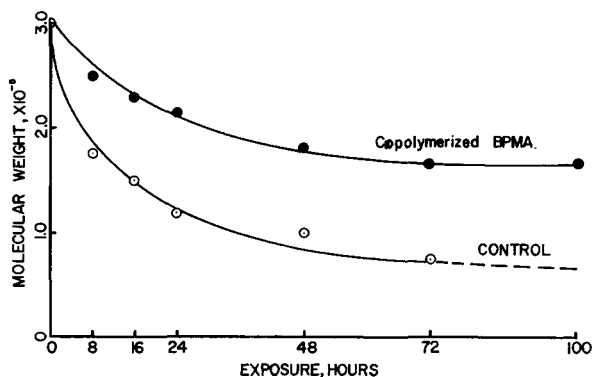
Fig. 10. Ultraviolet exposure of poly(methyl methacrylate) with copolymerized BPMA.

This is indicated by methanol (Soxhlet) and perchloroethylene extraction studies on polypropylene blended with 0.2% BPMA as shown in Table II.

Films of these blends were exposed to General Electric RS 4 sunlamps, and time to embrittlement is shown in Table III.

TABLE II

| | % Extracted by | |
Ultraviolet absorber	Methanol	Perchloro- ethylene
BPMA	5	3
2-Hydroxy-4-octoxybenzophenone	70	20

TABLE III

Absorber	Time to embrittlement, days
BPMA	18
2-Hydroxy-4-octoxybenzophenone	19
Control	4

These data show that the ultraviolet absorbing monomer BPMA may be incorporated into polymeric systems by copolymerization or blending of the homopolymer and provide effective ultraviolet stability to the system.

EXPERIMENTAL

Preparation of 2-Hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)-benzophenone (BPMA)

A mixture of glycidyl methacrylate (156 g., 1.10 mole), 2,4-dihydroxybenzophenone (214 g., 1.00 mole), and the catalyst (ammonium nitrate, 3 g.) were heated with stirring for 7 hr. at 80°C. under a nitrogen atmos-

phere.   The reaction was slightly exothermic during the initial stages.
The resulting product, 2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)-
benzophenone (BPMA), a viscous yellow liquid, was dissolved in benzene
(500 ml.) and washed with a 1% sulfuric acid solution to remove residual
glycidyl methacrylate by hydrolysis to glycol and also to remove the salt
catalyst.   After drying the benzene solution over magnesium sulfate for
20 hr., the solvent was removed under reduced pressure, leaving the mono-
mer product (350 g.) in a yield of 98.3% based on dihydroxybenzophenone.
Saponification indicated 98+% purity.   The monomer contained less
than 1% residual 2,4-dihydroxybenzophenone by aqueous base titration
in benzene–methanol with phenolphthalein as indicator.

After chromatography on silica gel the material was analyzed.

ANAL.   Calculated for $C_{20}H_{20}O_6$:   C, 67.41%; H, 5.66%.   Found: C, 67.50%; H,
5.91%; n_D^{25} 1.596.

Preparation of Poly(BPMA)

Homopolymerization.   A solution of 30 g. BPMA and 0.15 g. azobisiso-
butyronitrile in 70 g. tetrahydrofuran was refluxed for 6 hr. at 70°C.   The
polymeric product was precipitated from methanol as a light yellow pow-
der, 21 g., yield 71%; intrinsic viscosity in tetrahydrofuran 0.2; T_g 59°C.
Blends of poly(BPMA) with other polymers were prepared by dissolving the
materials in tetrahydrofuran and then casting films.

Copolymerization.   Vinyl acetate polymers were prepared by solution
polymerization at 60% solids in ethyl acetate with azobisisobutyronitrile
as initiator.   Styrene polymers were prepared by bulk polymerization also
with azobisisobutyronitrile.   The vinyl chloride/ethyl acrylate and vinyli-
dene chloride/ethyl acrylate polymers were prepared by latex polymeriza-
tion in anionic surfactant systems with ammonium persulfate as initiator.

Ultraviolet exposures were carried out on 1 mil dry films with the use of
GE UA-11B lamp at a distance of 2 ft. in a parabolic reflector over a 2-ft.
diameter rotating turn-table at 40–42°C.   A modified reflectance photom-
eter (Photovolt 610) was used to measure discolorations.

Molecular weights were calculated from intrinsic viscosities by using the
Staudinger equations.

The polypropylene blends were prepared by milling Hercules Profax
6513 resin, heat-stabilized but not light-stabilized, with the BPMA for 8
min. at 174°C. and molding into 6 mil films for 2 min. at 190°C.   These
were exposed to a GE RS-4 sunlamp at a distance of 5 in. at 54°C.

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Résumé

Outre l'addition d'agents stabilisants à des matériaux plastiques, les problèmes tels que l'incompatibilité, la migration, la volatilité et l'extraction de solvants de ces additifs se posent fréquemment. En vue de surmonter de tels problèmes au cours de l'utilisation de stabilisants adsorbants dans l'ultraviolet, des dérivés acryliques et métacryliques contenant des groupes benzophénone-2-hydroxy-4-alkoxylés ont été synthétisés. Les monomères absorbant dans l'ultraviolet ont été synthétisés par réaction de 2,4-dihydroxybenzophénone avec l'acrylate de glycidyle et le méthacrylate de glycidyle. Ils ont été homopolymérisés et mélangés à du chlorure de polyvinyle, du chlorure de polyvinylidène, du polystyrène et du polyméthacrylate de méthyle. Ils ont également été homopolymérises avec le monomère correspondant. Les mélanges de polymères et copolymères ont été étudiés du point de vue de la stabilité ultraviolette en fonction des différentes méthodes de contrôle. Une stabilisation effective a l'égard de l'ultraviolet a été observée. Les différences de stabilité de certains mélanges comparées aux copolymères correspondants sont vraisemblablement dues à des phénomènes d'incompatibilité.

Zusammenfassung

Beim Zusatz von Stabilisatoren zu Plastomeren treten häufig Probleme wie Unverträglichkeit, Wanderung, Flüchtigkeit und Lösungsmittelextraktion des Additivs auf. In dem Bestreben, solche Probleme bei der Verwendung von Ultraviolettabsorptionsstabilisatoren zu lösen, wurden Acrylat- und Methacrylatderivate mit dem 2-Hydroxy-4-alkoxybenzophenonbaustein synthetisiert. Die ultraviolettabsorbierenden Monomeren wurden durch Reaktion von 2,4-Dihydroxybenzophenon mit Glycidylacrylat und Glycidylmethacrylat synthetisiert. Sie wurden homopolymerisiert und mit Polyvinylchlorid, Polyvinylidenchlorid, Polystyrol und Polymethylmethacrylat vermischt. Weiters wurden sie auch mit den entsprechenden Monomeren kopolymerisiert. Die Polymermischung und die Kopolymeren wurden auf ihre UV-Stabilität im Vergleich zu entsprechenden Kontrollproben untersucht. Es wurden eine wirksame UV-Stabilisierung beobachtet. Stabilitätsunterschiede zwischen gewissen Mischungen und den entsprechenden Kopolymeren werden auf Unverträglichkeit zurückgeführt.