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Preparation of Ultraviolet Stabilizing Polymers. I. Copolymerization of 2-Hydroxy-4-acryloyloxybenzophenone and Its Ultraviolet Stability

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Summary

To obtain ultraviolet stabilizing polymers, 2-hydroxy-4-acryloyloxybenzophenone was prepared from 2,4-dihydroxybenzophenone and copolymerized with styrene. Copolymers containing three different amounts of ultraviolet absorber were prepared. These copolymers, unstabilized pure polystyrene and a series of stabilized polystyrene, were exposed to ultraviolet, and the ultraviolet stability of these polymers was compared by the relative amount of infrared absorption around 1700 cm^{-1} due to the carbonyl group. Ultraviolet stability of the copolymers is very similar to that of blend polymers and is higher than that of unstabilized pure polystyrene.

INTRODUCTION

The stability of polymeric compounds to heat and light is of importance in practical use and various kinds of antioxidants or ultraviolet absorbers are added to the commercial materials. Unfortunately these additives migrate out from plastics on prolonged use, and so it is advantageous to attach ultraviolet absorbers permanently or covalently to polymeric compounds by introduction of reactive or polymerizable groups such as vinyl or allyl groups to ultraviolet absorbers (*1–3*).

The migration of dyes has been recognized in the field of the dyeing fibers, and one of the authors (Matsui) has extensively studied the preparation of various types of reactive or polymerizable dyes which in principle provide covalently bindable groups to dyes (*4*). It is, therefore, meaningful to study a series of preparations of ultraviolet-stabilizing polymeric compounds. This paper, the first of a series, deals with the copolymerization of 2-hydroxy-4-acryloyloxybenzophenone and styrene and with the stability of the copolymer to ultraviolet.

EXPERIMENTAL

Preparation of 2-Hydroxy-4-acryloyloxybenzophenone

Acryly chloride (9.5 g, 0.1 mole) was added dropwise to a mixture of 2,4-dihydroxybenzophenone (21.4 g, 0.1 mole), N,N-dimethylaniline (24.2 g, 0.2 mole) and hydroquinone (1 g), keeping the solution temperature at about 20°C for 30 min. The solution was heated at 50°C for 1 hour and left at room temperature overnight. The product mixture was poured into 150 ml of ice water and extracted with 200 ml of benzene. Benzene solution was washed with cold dilute hydrochloric acid three times to remove N,N-dimethyl-

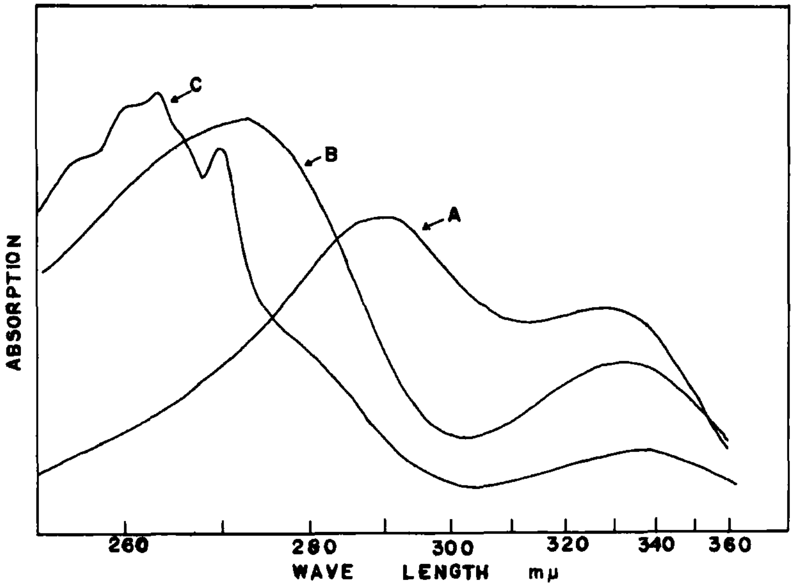

FIG. 1. Ultraviolet spectra. (A) 2,4-dihydroxybenzophenone; (B) 2-hydroxy-4-acryloyloxybenzophenone; (C) copolymer (No. 3).

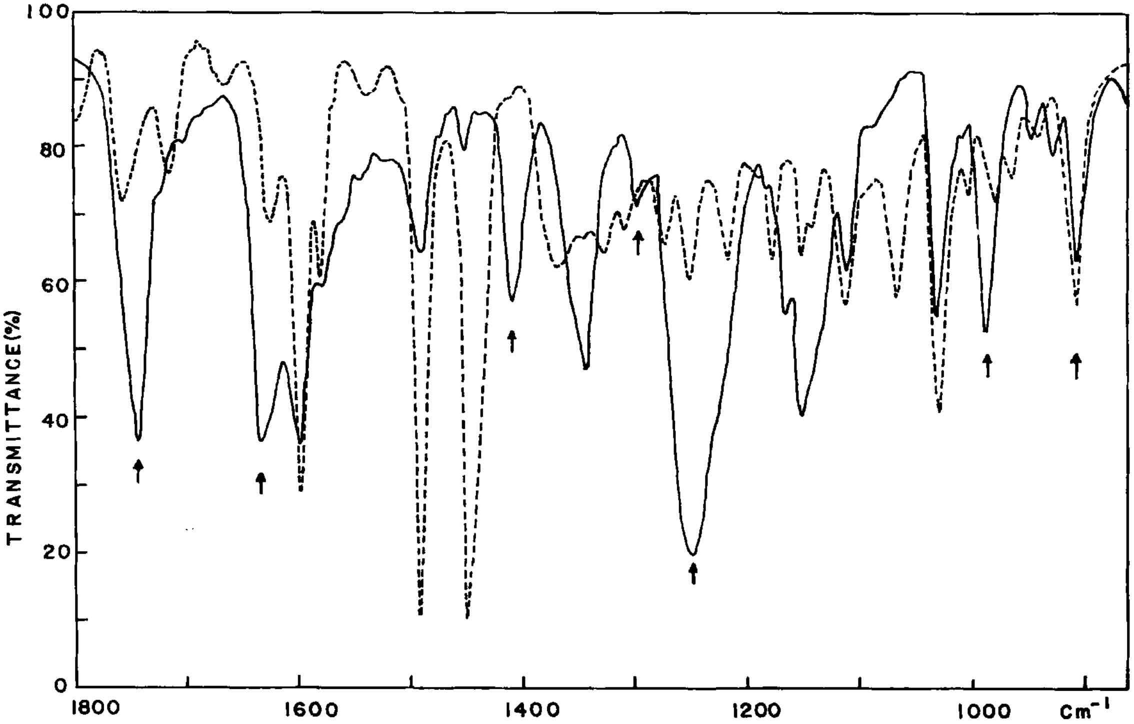

FIG. 2. Infrared spectra of monomer and copolymer. Solid line, monomer; dashed line, copolymer (No. 3).

aniline and finally washed with water, and then it was purified by column chromatography using active alumina. After the middle part cut from the column chromatograph on alumina was recrystallized with pure ethanol, the material was analyzed. Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.70%; H, 4.51%; found: C, 71.86%; H, 4.76%; m.p., 80 to 81°C.

The ultraviolet spectra of 2-hydroxy-4-acryloyloxybenzophenone shown in Fig. 1 indicate that the absorption band at 333 mμ due to $n \rightarrow \pi^*$ transition is essentially the same as that of 2,4-dihydroxybenzophenone, but a hypsochromic shift of $\pi \rightarrow \pi^*$ transition is observed.

In the infrared spectra shown in Fig. 2, the absorption bands at 905, 985, 1295, and 1410 cm^{-1} are assigned to the out-of-plane deformation of the hydrogens of $=CH_2$, the out-of-plane deformation mode of $-CH=$, the in-plane deformation of the hydrogen of $-CH=$, and the in-plane deformation of the hydrogens of $=CH_2$, respectively. The absorption bands at 1745, 1635, and 1250 cm^{-1} are also assigned to the C=O stretching vibrations in ester, the C=O stretching vibrations in ketone, and C—O stretching vibrations in ester groups.

Copolymerization of 2-Hydroxy-4-acryloyloxybenzophenone and Styrene

Copolymerization of 2-hydroxy-4-acryloyloxybenzophenone and styrene was carried out with benzoylperoxide in toluene in a sealed

TABLE 1

Radical Copolymerization of 2-Hydroxy-4-acryloyloxybenzophenone with Styrene at 70°C[a]

Expt.	Mole ratio of 2-H-4-AB[b]/St	Yield, %	Time, hr	Intrinsic viscosity [η]	2-H-4-AB in copolymer[c] (molar ratio to 100 moles St unit)
1	0/100	94.6	35	0.27	0
2	0.5/100	92.8	35	0.31	0.47
3	1.0/100	87.1	35	0.40	0.76
4	3.0/100	37.8	3.5	1.05	6.82

[a] The volume of toluene used as a solvent was the same as that of styrene, and the initiator was BPO (benzoyl peroxide) (31.7 mg).

[b] 2-Hydroxy-4-acryloyloxybenzophenone.

[c] Determined by photometry.

tube. The resulting polymers were purified by repeated (three times) precipitations with chloroform(solvent)–methanol(precipitant) and by washing until constant ultraviolet absorption was obtained. All samples were dried for a few days at room temperature and at about 100 mm Hg pressure prior to analysis. The results obtained are shown in Table 1.

Ultraviolet Stability Test

The ultraviolet-stability test was carried out with a Toshiba Model H-400 ultraviolet generator. Films (0.06 ± 0.01 mm) of copolymers, a series of blend polymers, and unstabilized pure polystyrene were exposed to ultraviolet 10 cm distant from the light source and the change of oxygenated groups was determined by infrared spectra at intervals of 1, 3, 5, 10, 15, 20, 25, and 50 hr.

RESULTS AND DISCUSSION

The monomer is readily copolymerized with styrene and copolymers have a slightly yellowish color which increases with an increase in the amount of 2-hydroxy-4-acryloyloxybenzophenone. The ultraviolet spectrum of the copolymer in Fig. 1 is essentially equal to that of monomer or original absorber in the $n \rightarrow \pi^*$ transition region; the difference is observed in $\pi \rightarrow \pi^*$ transition region. Further investigation of this point is required.

It is well known that in thermal and or photochemical oxidation of polymeric compounds oxygenated groups such as aldehyde, carboxylic acid, peroxide, etc., are generated, and it is a good practice to determine the change of these groups during oxidation of polymeric compounds. Therefore the copolymers, blend polymers, and unstabilized pure polystyrene were exposed to ultraviolet and the spectral changes of the samples were compared. In general, the absorption bands at about 1700 and 1750 cm^{-1} due to aldehyde or carboxylic groups and to ester groups, respectively, have been found to increase their intensities, and their regions became broad in the course of the oxidation of polymers (5) (see Fig. 3).

To analyze these spectral changes quantitatively, the absorption ratios of the bands at 1720 and 1750 cm^{-1} to the 1802 cm^{-1} band were obtained. The results are shown in Figs. 4 and 5. In each curve the original values are substrated to show the change of the oxygenated groups only. As shown in Fig. 4, the change of the ab-

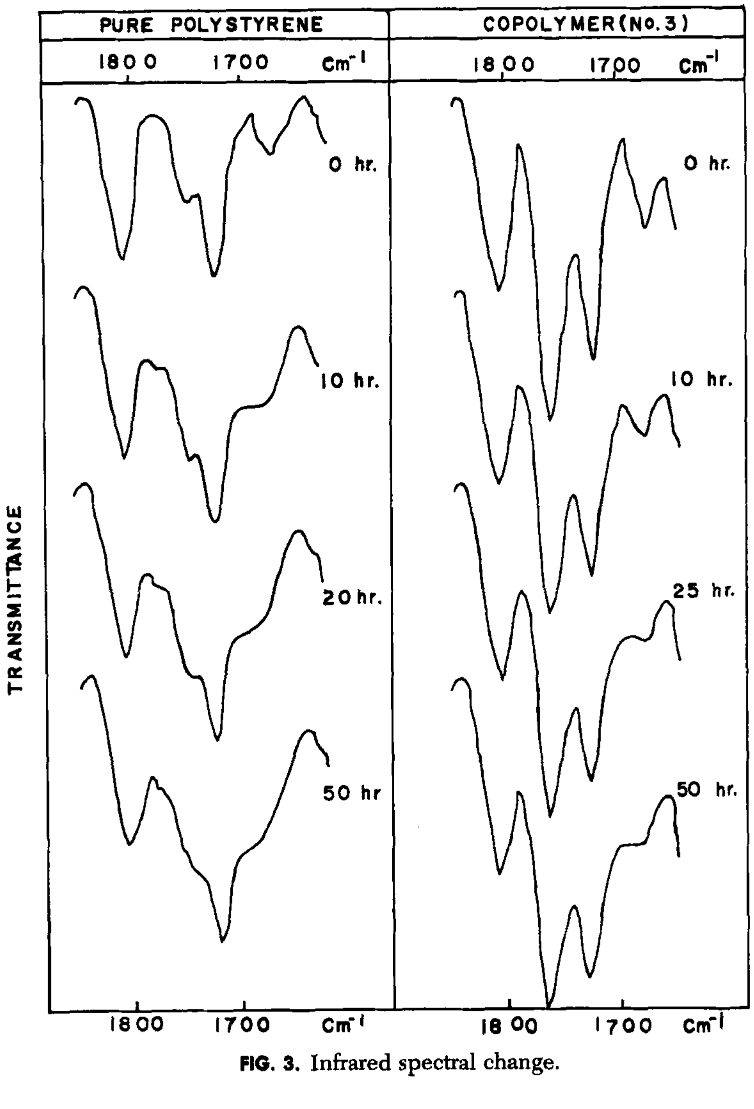

FIG. 3. Infrared spectral change.

sorption at about 1720 cm^{-1} in pure polystyrene (No. 1) is much larger than that of copolymers (Nos. 2, 3, 4) and blend polymers (Nos. 2′, 3′, 4′), and copolymers and blend polymers have essentially equal ultraviolet stability. In other words, the ultraviolet stability increases with an increase in the amount of the absorbing materials in the polymers. The absorption band at 1750 cm^{-1} due

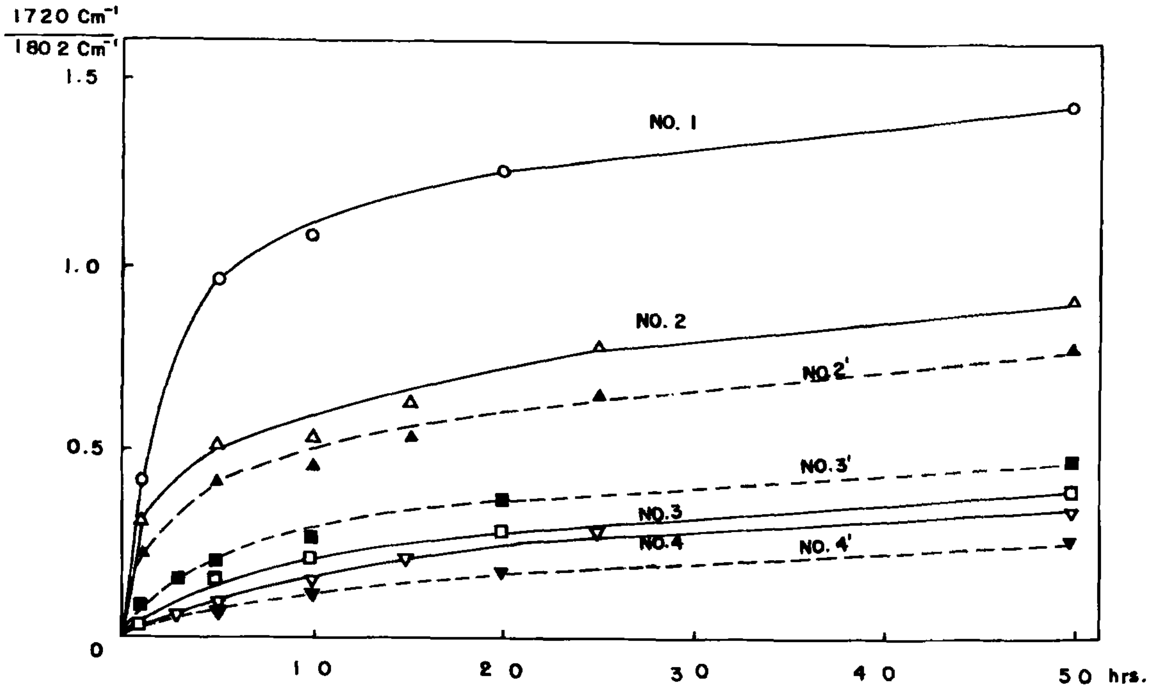

FIG. 4. Change in 1720-cm^{-1} absorption. No. 1, pure polystyrene; No. 2, copolymer (0.4% of 2-H-4-AB), No. 3, copolymer (0.76% of 2-H-4-AB); No. 4, copolymer (6.82% of 2-H-4-AB): No. 2′, blend polymer (0.45% of 2-H-4-AB); No. 3′, blend polymer (0.75% of 2-H-4-AB); No. 4′, blend polymer (6.50% of 2-H-4-AB).

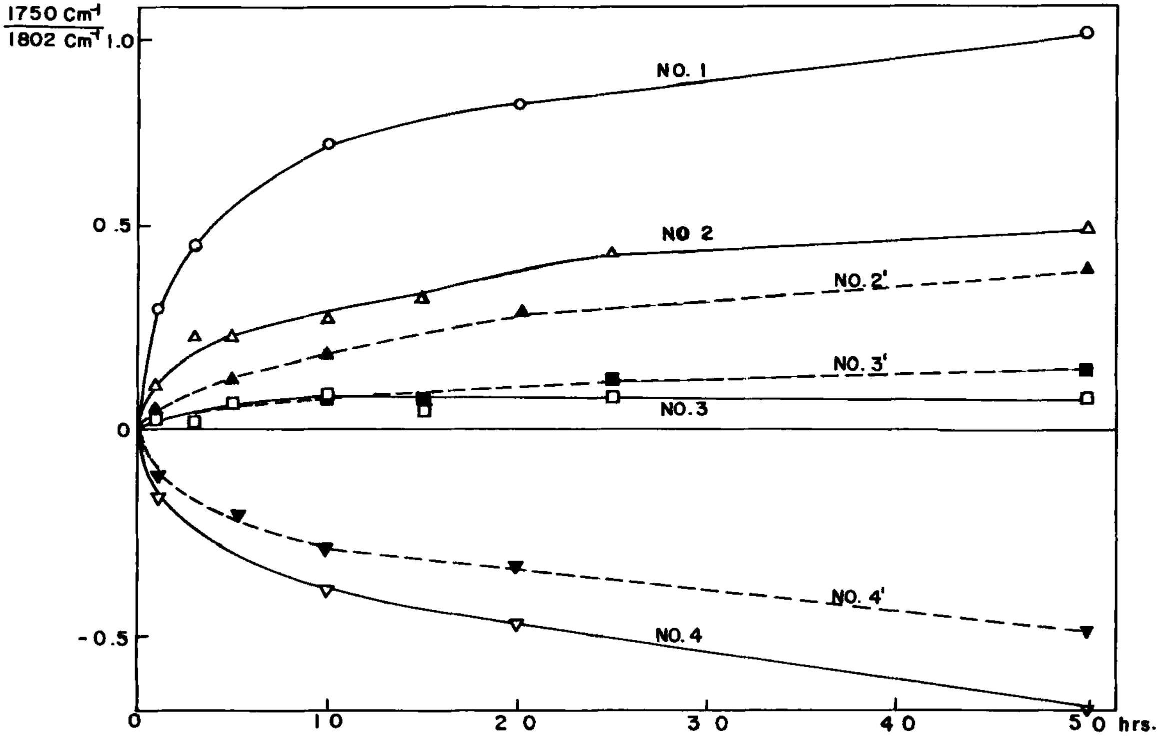

FIG. 5. Change in 1750-cm^{-1} absorption. No. 1, pure polystyrene; No. 2, copolymer (0.47% of 2-H-4-AB); No. 3, copolymer (0.76% of 2-H-4-AB); No. 4, copolymer (6.82% of 2-H-4-AB); No. 2′, blend polymer (0.45% of 2-H-4-AB); No. 3′, blend polymer (0.75% of 2-H-4-AB); No. 4′, blend polymer (6.5% of 2-H-4-AB).

to the ester groups also shows a good parameter of ultraviolet stability. As shown in Fig. 5, the intensity change of the absorption band at 1750 cm^{-1} for pure polystyrene is much larger than that of copolymers and blend polymers. In the case of a high concentration of absorber, decrease in ester groups is observed. This is probably due to the occurrence of the Fries rearrangement of the ester groups by ultraviolet irradiation (6–9).

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Zusammenfassung

Zur Darstellung von UV stabilisierten Polymeren wurde 2-Hydroxy-4-acryloyloxybenzophenon aus 2,4-Dihydroxybenzophenon dargestellt und mit Styrol copolymerisiert. Copolymere mit verschiedenen Gehalten an UV-Absorber wurden dargestellt. Diese Copolymeren, unstabilisiertes reines Polystyrol und eine Reihe von stabilisierten Polystyrolproben wurden UV-Strahlung ausgesetzt, und die UV-Stabilität dieser Polymeren mit der relativen IR Absorbtion bei 1700 cm^{-1} (Carbonylgruppe) verglichen. Die UV-Stabilität des Copolymeren ist fast genau die gleiche wie die von Polymergemischen, jedoch besser als die von unstabilisiertem reinen Polystyrol.

Résumé

On a preparé la hydroxy-2-acryloxy-4-benzophenone à partir de la dihydroxy-2,4-benzophenone et copolymerisé avec le styrène dans le but d'obtenir des polymères stabilisant l'ultraviolet. On a aussi preparé des copolymères contenant trois taux differents d'absorbeurs d'ultraviolet. Ces copolymères, polystyrène pur nonstabilisé et une série de polystyrènes stabilisés, sont exposés à l'ultraviolet, et leur stabilité ultraviolette comparée par le montant relatif d'absorption dans l'infrarouge à 1700 cm^{-1} due au groupement carbonyle. La stabilité ultraviolette de ces copolymères est prèsque semblable à celle des polymères mélangés et superieure à la stabilité du styrène nonstabilisé.