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Polymeric UV-Absorbers of 2-Hydroxybenzophenone Type. I. Polyesters on the Base of 2-Hydroxy-4-(2,3-epoxypropoxy)benzophenone

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Polymeric UV-Absorbers of 2-Hydroxybenzophenone Type. I. Polyesters on the Base of 2-Hydroxy-4-(2,3-epoxypropoxy)benzophenone*

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ABSTRACT

Some polyester light stabilizers were synthetized by the copolymerization of an equimolar mixture of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone with cyclic anhydrides of dicarboxylic acids. This synthesis was carried out in melt by using potassium benzoate or tert-amines as catalysts. The catalytic efficiency of potassium benzoate in heterogeneous phase increases with its surface area. In comparison with potassium benzoate, tert-amines show a higher catalytic effect in homogeneous medium. According to the UV spectra of the products, the 2-hydroxybenzophenone structural units of light stabilizers are not subject to destruction during the polymerization of an equimolar mixture of epoxide with anhydrides. The efficiency of UV stabilization of the stabilizers prepared in polypropylene is comparable with the efficiency of 2-hydroxy-4-n-octyloxybenzophenone with the exception of

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those samples which contain the structural units of maleinic anhydride and glycidyl-β-naphthyl ether. In contrast to 2-hydroxy-4-n-octyloxybenzophenone, the high molecular weight UV absorbers exhibit a lower extractibility from polypropylene sheets with trichloroethylene.

INTRODUCTION

The durability of polymers is often reduced by a gradual decrease in the content of low molecular weight UV absorbers. A loss of low molecular and more volatile stabilizers occurs even during thermal treatment of polymers. Besides the photolytic decomposition of light stabilizers, the atmospheric aging often involves a loss of stabilizers owing to their migration from polymers through extraction by water and various solvents. A decrease in the extractibility, volatility, and migration of UV absorbers may be achieved by using polymer stabilizers or by binding stabilizing structures into the polymer chain.

References in the field of polymer stabilizers involve the relatively ample group of UV absorbers of the hydroxybenzophenone type. There are the procedures for the polymerization of unsaturated derivatives of 2-hydroxybenzophenone (HBP) [1-7] and polycondensation of HBP derivatives with carbonyl compounds, most frequently with formaldehyde [8-10]; polycondensation of HBP carboxy derivatives [11-14]; condensation of HBP derivatives on phosphorylated polypropylene [15, 16]; the Fries rearrangement of polyesters [17-19]; and the polyaddition of diisocyanates with tri-(tetra)-hydroxybenzophenones [20].

This paper is concerned with the study of the preparation of higher molecular weight photostabilizers synthetized by the copolyaddition of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone alone or in a mixture with some epoxy compounds and cyclic anhydrides of dicarboxylic acids in the presence of alkaline salts and tert-amines as catalysts. The stabilization efficiency of some structurally different polymer UV absorbers in polypropylene was correlated with the efficiency of a low molecular weight photostabilizer (2-hydroxy-4-n-octyloxybenzophenone) during the photooxidation of polypropylene sheets at 60°C. The efficiency of UV absorbers was also evaluated by photooxidation after trichloroethylene extraction of polypropylene sheets.

EXPERIMENTAL

Materials

2-Hydroxy-4-(2,3-epoxypropoxy)benzophenone (HEPBP) was prepared by the slow addition of an aqueous alkaline solution of

2,4-dihydroxybenzophenone in an equimolar ratio with KOH to a five-fold molar excess of epichlorohydrin in a 2-hr period at 88°C. After shaking the reaction mixture with hot water several times, the separated reaction product was recrystallized from ethanol. The melting point of the product thus obtained was 98.5-99°C (99-100°C according to Ref. 21).

Glycidyl-β-naphtyl ether (GNE) was prepared from epichlorohydrin and β-naphtol under the same conditions as HEPBP. The melting point of the product was 81°C after vacuum distillation and crystallization.

Epichlorohydrin (ECH), cyclic anhydrides, alkaline salts, and tert-amines were commercial, analytical grade chemicals. Phthalic anhydride (PA) was purified by sublimation. After recrystallization from hot water, a part of the potassium benzoate (BzK) was crushed in a mortar while the remaining part was crushed in a laboratory vibration ball mill for 20 min at a vibration frequency 50 swings per second using stainless steel balls of 4 mm diameter.

The solvents were purified in the usual way.

Polymerization

The polymerization was carried out in the melt state. The melt was placed in sealed glass ampoules with a nitrogen atmosphere. The reaction mixture of the initial powdered substances was homogenized into ampoules before weighing if potassium benzoate was used as a catalyst. If tert-amines were used as catalysts, they were added to the weighed and homogenized reactants and, after replacing the air by nitrogen, the ampoules were sealed. The ampoules were heated to the reaction temperature in an oil bath which was accurately thermostated to ±0.2°C. The reaction mixture was homogenized again after melting by shaking the ampoules. In the course of the investigation of polymerization the ampoules were removed from the bath at fixed time intervals and the polymerization product was withdrawn and crushed in a mortar. Hydrolysis of nonconsumed phthalic anhydride was performed with hot water in a portion of the product, and the free acid content was determined by titration with an aqueous 0.01 N solution of KOH with phenolphthalein as the indicator. After extraction with hot ethanol the polymers were purified by precipitating the acetone solutions with water. After drying, white or slightly yellowish products were obtained.

The molecular weights of polymers were determined by the VPO method using benzene as the solvent. The IR spectra were recorded with UR 20, Carl Zeiss, Jena, while the UV spectra were obtained with a Unicam SP 700 A.

Evaluation of the Efficiency of Photostabilization

The UV absorbers and antioxidants were added to the powdered and nonstabilized polypropylene, and the mixture was homogenized in a plastograph (Brabender) for 10 min in a nitrogen atmosphere at 190°C.

The molar concentration of polymer photostabilizers in polypropylene was equivalent to 0.5 wt% of 2-hydroxy-4-n-octyloxybenzophenone stabilizer. Topanol CA (0.2 wt%) and dilauryl thiodipropionate (0.3 wt%) were used as thermooxidation stabilizers. The polypropylene sheets were prepared by molding at 200°C. Extractions of the polypropylene sheets with trichloroethylene were carried out for 1 hr at 25°C.

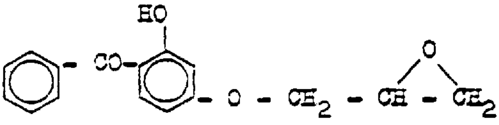
The efficiency of photostabilization of polymer UV absorbers in a mixture with the stabilizers of thermooxidation was estimated volumetrically. This method is based on the measurement of the timed consumption of oxygen during the photooxidation of polypropylene sheets by means of a modified apparatus [13]. A polypropylene sheet (4 cm^2), placed in a cylindrical cell of Sial glass with the volume V_1, was irradiated in an oxygen atmosphere by a medium pressure mercury arc (Tesla THK-101). This cell was placed in an air thermostat heated to 60 ± 0.15°C. The volume of oxygen consumed, V_t, was indicated by the shift of the silicon drop situated at one end of the measuring capillary. The measuring capillary (1.55 mm diameter) was situated in a horizontal position and its other end was connected to an oxygen-filled vessel of volume V_2 and thermostated together with the measuring capillary in an air bath accurate to ±0.1°C. The number of moles of oxygen consumed was calculated from

$$n_t = \frac{p_0}{RT}\left(V_1 - \frac{V_1 - V_t}{1 + \frac{V_t}{V_2}}\right)$$

The starting pressure in the apparatus was adjusted to the atmospheric pressure p_0. The photooxidation apparatus was placed in a constant-temperature room (±1°C).

RESULTS AND DISCUSSION

2-Hydroxy-4-(2,3-epoxypropoxy)benzophenone contains a reactive oxirane end-ring and therefore has capabilities for the preparation



of polymer UV absorbers. The polymerization of terminal epoxides with cyclic anhydrides of dicarboxylic acids is well known [22-29]. In comparison with a polycondensation reaction, the high rate of the reaction without low molecular weight products is quite advantageous. Fischer [22] found that the polymerization catalyzed by tert-amines afforded an alternating copolymer, and Tanaka and Haung [29] proved that the polyester with the highest molecular weight was formed in the highest yield if the reactants were used in equimolar proportion.

In the synthesis of polymer UV absorbers, HEPBP was polymerized with cyclic anhydrides of dicarboxylic acids. Also prepared were some copolymers in which a part of the HEPBP was replaced by other epoxide compounds (ECH and GNE, Table 1). The largest part of the experiments was, however, carried out by using a pair of monomers, namely HEPBP and PA.

The results of polymerizations, the components used, the reaction conditions, and some characteristics of the polymer UV absorbers prepared are presented in Table 1, while the UV spectra of selected polyester photostabilizers are shown in Fig. 1. These spectra are characterized by two absorption bands, i.e., at $\lambda_{1\ \mathrm{max}} = 287$ nm and $\lambda_{2\ \mathrm{max}} = 328$ nm. The absorbance at 400 nm is practically zero. The spectra are, therefore, analogous to the spectra of low molecular weight HBP derivatives. The absorption band at the longer wavelength (in the region of high sensitivity of different polymers to photodegradation [30]), which is attributed to the intramolecular hydrogen bond in the o-hydroxybenzophenone molecule [31], remains preserved. In the series of UV spectra of polyester UV absorbers prepared, the copolyesters consisting of PA-HEPBP-GNE (No. 7) and PA-HEPBP-ECH (No. 8) prepared under the conditions given in Table 1 exhibit different values of absorbance (Fig. 1). The weight of copolyesters used for spectral analysis in UV were chosen according to the molar content of HEPBP in the polymerizing batch. According to the absorbance values, the molar concentration of the HEPBP structural units is smaller in copolymer No. 7 than in the polymerizing batch, which means that HEPBP is a less reactive component than GNE in the reaction system containing PA. Conversely, the proportion of the HEPBP component is higher in copolymer No. 8 than in the polymerizing batch. A higher reactivity of HEPBP with respect to ECH in the three-component system containing PA is also indicated by a lower chlorine content. Analysis has shown that the chlorine content

TABLE 1. Copolymerization of Epoxy Compounds with Cyclic Anhydrides Using Potassium Benzoate as a Catalyst[a]

	Epoxide		Anhydride						
Experiment	Type	Amount (mmole)	Type	Amount (mmole)	Amount of BzK (mole %)	Polymerization time (hr)	Polymerization temperature	mp (°C)	M_n[b]
1	HEPBP	12.2	PA	12.2	0.72	4	135	103-10	1600
2	HEPBP	20	PA Maleic anhydride	10 10	1.4	3.5	130	78-86	1225
3	HEPBP	10	Hexahydrophthalic anhydride	10	2	4	100	74-89	-
4	HEPBP	10	Tetrahydrophthalic anhydride	10	2	4	100	69-75	-
5	HEPBP	10	3-Chlorotetrahydrophthalic anhydride	10	2	4	100	48-59	-
6	HEPBP	10	Succinic anhydride	10	2	4	100	75-87	-
7	HEPBP GNE	10 10	PA	20	1.4	3	130	70-78	965
8	HEPBP ECH	20 200	PA	220	0.72	3.5	110	70-75	1150

[a] HEPBP, 2-hydroxy-4-/2,3-epoxypropoxy/benzophenone; PA, phthalic anhydride; GNE, glycidyl-β-naphtyl ether; ECH, epichlorohydrin; BzK, potassium benzoate.

[b] Measured by the VPO method with benzene as solvent.

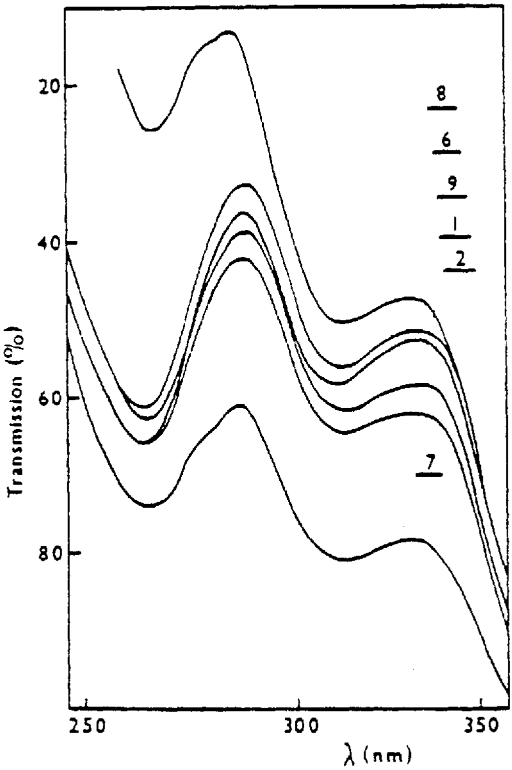


FIG. 1. Spectra of polymer photostabilizers in the near-UV region. Samples 1, 2, 6, 7, and 8 are the same as in Table 1; No. 9 corresponds to 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone. The spectrum of Sample 3 is the same as the spectrum of the Sample 6, and the spectra of Samples 4 and 5 are the same as the spectrum of Sample 1. They have been recorded with an Unicam SP 700 A in chloroform, d = 0.5 cm, c = 5×10^{-5} mole/liter.

(Cl = 11.4%) corresponds to the ratio ECH/HEPBP ≅ 6 whereas this value is equal to 10 for the polymerizing batch. The absorptivity value thus characterizes the average composition of copolymers with respect to the HEPBP component content.

The characteristic absorption band corresponding to the vibrations of carbonyl group of o-hydroxybenzophenone at 1625 cm^{-1} remains preserved in the IR spectra (Fig. 2). The absorption bands which belong to phthalic anhydride (1779, 1785, and 1853 cm^{-1}) disappear and a new band at ν = 1735 cm^{-1}, which corresponds to a newly formed esteric bond, appears when the polymer has been prepared.

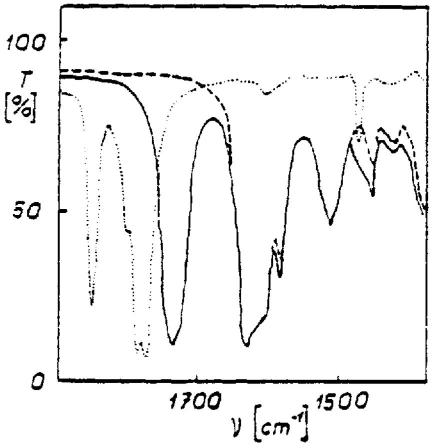


FIG. 2. Infrared spectrum of the polymer UV-absorber of the HEPBP-PA type (——), phthalic anhydride (..), and HEPBP (--). The spectra were recorded with an UR-20, Carl Zeiss, Jena, in the mixture o-xylene—chloroform (1:4) in NaCl cells, d = 0.16 mm, and c = 0.1 mole/liter.

The course of polymerization of the equimolar PA-HEPBP mixture catalyzed by 2 mole % potassium benzoate (Fig. 3) illustrates the effect of temperature on the rate of polymerization as well as the influence of the surface of catalyst which has been treated either by coarse crushing in a mortar (Curve 1) or by grinding in a laboratory vibration ball mill (Curve 2). The grinding of catalyst in a ball mill strongly affected the polymerization system by approximately doubling the reaction rate in the region of 10-60% conversion. Polymer yield increases exponentially with the concentration of potassium benzoate finely ground in a vibration mill (Fig. 4) according the empirical relation

$$\text{conversion } \% = a\text{BzK}^b$$

where a = 39 and b = 0.46.

Under the conditions of polymerization the catalyst was not completely soluble in the polymerization system and gradually settled down. A more uniform dispersion of heterogeneous catalyst was achieved by shaking the reaction mixture. In this way the equilibrium solubility of catalyst in the polymerization system could be reached.

If the polymerization is carried out in the homogeneous phase in the

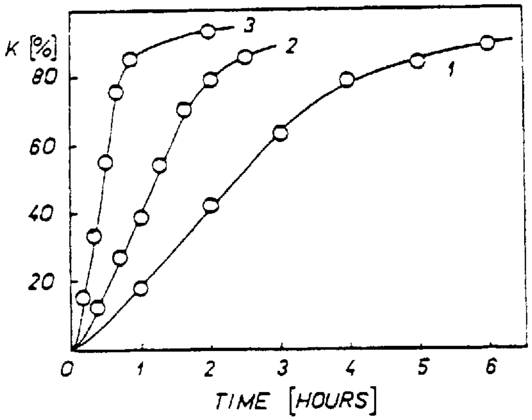


FIG. 3. Dependence of conversion on the polymerization time of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone with phthalic anhydride (molar ratio 1:1) at a 2% concentration of the catalyst (potassium benzoate). (1) 105°C, (2) 105°C (potassium benzoate was ground for 20 min in a vibration ball mill), and (3) 135°C.

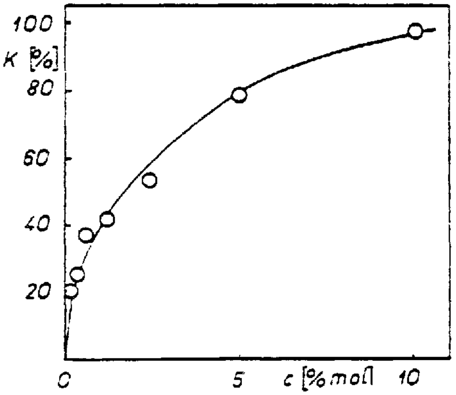


FIG. 4. Effect of potassium benzoate concentration on conversion in the polymerization of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone with phthalic anhydride at 135°C for a constant time of polymerization (30 min). The catalyst was ground in a vibration mill.

presence of soluble catalysts (for instance, tert-amines), the polymerization rates are higher than those achieved by heterogeneous catalysis with potassium benzoate (Fig. 3) as is evident from the experimental values in Fig. 5. Provided tri-n-hexylamine and methyldibuthylamine are used as catalysts, the polymerization rate is obviously smaller in the initial stage of reaction than in the region of 20-60% conversion. Tanaka and Kakiuchi [23c] explain this fact by a progressive increase in the concentration of the catalytic centers of the type (NR_3...HOX), while the compounds with hydroxyl groups may arise directly from a compound with an epoxy end-group in the presence of trialkylamine as a catalyst. With regard to the fast course of the reaction at 105 and 120°C (Fig. 5), it is obvious that the reaction proceeds at a nonstationary temperature in the initial stage so that the effect of the progressive growth of catalytic centers as well as the increase in the initiation rate is partially concealed because of temperature inconsistency in the reaction mixture.

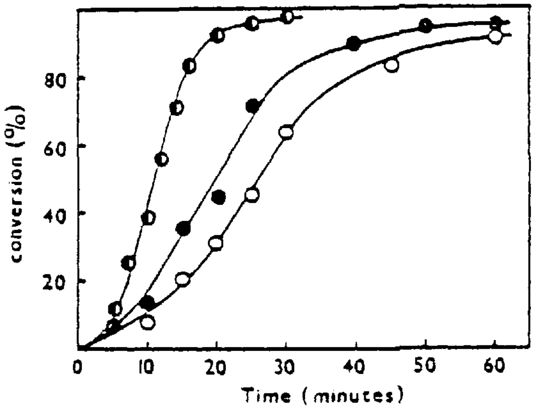


FIG. 5. Dependence of conversion on the polymerization time of 2-hydroxy-4-(2,3-epoxypropoxy)benzophenone with phthalic anhydride in the presence of tert-amines functioning as catalyst. (○) Tri-n-hexylamine, c = 0.85 mole %, 105°C. (●) Methyldibutylamine, c = 1.1 mole %, 105°C. (◐) Tri-n-hexylamine, c = 0.85 mole %, 120°C.

Some of the polyester UV absorbers prepared were added to polypropylene as described previously and exposed to accelerated aging. It is obvious from Fig. 6 that the efficiency of photostabilization of a polymer UV absorber prepared by polymerizing HEPBP with PA (Polymer 1, Table 1) may be compared in the stabilized system containing polypropylene with the efficiency of a low molecular weight stabilizer, Cyasorb UV 531, provided the molar concentration of o-hydroxybenzophenone structures is equal in both cases. On the other hand, the extraction of sheets with trichloroethylene for 1 hr at 25°C results in the removal of the photostabilizer Cyasorb UV 531 from polypropylene (Fig. 6). This is evident from a decreased polymer stability. The resistance to photooxidation of the extracted sheets containing a polymer UV absorber of the HEPBP-PA type is decreased to a substantially lesser extent than that of one of the extracted sheets

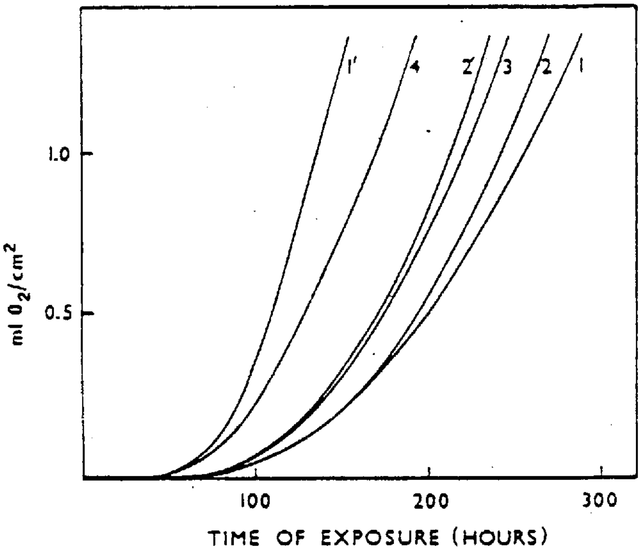


FIG. 6. Time dependence of the consumption of oxygen in the photooxidation of polypropylene sheets stabilized with Topanol CA (0.2 wt%), dilauryl thiodipropionate (0.3 wt%) and UV-absorber. Curve 1 is 2-hydroxy-4-n-octyloxybenzophenone (0.5 wt%), the Curves 2, 3, and 4 correspond to Samples 1, 2, and 7, respectively of Table 1. Curves 1' and 2' are after 1 hr extraction in trichloroethylene at 25°C. Sheets 2, 3, and 4 contain the same molar content of UV-absorbers as Sample 1.

containing a low molecular weight stabilizer, which gives evidence of the lower extractibility of the former. Lower extractibility is also confirmed for the other polymer stabilizers, but in the case of these polyesters (Fig. 6) the presence of structural units of maleic acid and naphthalene reduce the effect of stabilization.

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