Structurally Bound Stabilizers: Melt Grafting of UV Stabilizers onto Polypropylene, Polyethylene, and Polystyrene*

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Synopsis

Monomeric ultraviolet stabilizers, 2-hydroxy-4-methacryloyloxybenzophenone and 2-hydroxy-4-acryloyloxybenzophenone were synthesized by a modified process. These reactive UV stabilizers were grafted onto the backbone of polypropylene (PP), low-density polyethylene (LDPE), and polystyrene (PS) by melt processing in the mixer of Brabender Plasticorder. An infrared spectroscopic method was standardized for the quantitative determination of the extent grafting of these additives on the polymer backbone. Grafting of both the additives occurred in the order PS > LDPE > PP. Methacryloxy derivative of benzophenone was found to be more reactive towards the polymers studied than the acryloxy derivative.

INTRODUCTION

Antioxidants and stabilizers of low molecular weight tend to be lost from the polymer by evaporation, by degradation during the fabrication process, and by migration during the service life of the material.[1–4] Loss by evaporation during fabrication and migration during service life can be overcome by attaching the stabilizer to the polymer backbone by a chemical bond. Such reactive stabilizers contain a polymerizable group like vinyl or allyl in their side chain. Various workers have shown that under certain aggressive environments the synthetic polymers having chemically bound antioxidants are superior to polymers containing dispersed antioxidants.[5–7]

Polymeric UV stabilizers which are less prone to migration and leaching than the conventional low-molecular-weight compounds have been extensively studied.[8–15] In a recent study[16] it was shown that monomolecular 2-(2-hydroxyphenyl)benzotriazole completely leached from poly(methyl methacrylate) resin after an equivalent of 2 years exposure to rain whereas monomeric stabilizer 2-(5-vinyl-2-hydroxyphenyl)benzotriazole copolymerized with methyl methacrylate was unaffected.

Osawa and co-workers[17,18] prepared monomeric ultraviolet stabilizers, 2-hydroxy-4-acryloyloxybenzophenone and 2-hydroxy-4-methacryloyloxybenzophenone. The authors studied the photostabilizing efficiency of these reactive stabilizers for polystyrene by copolymerizing them with styrene and for polyethylene by blending their homopolymers with it.

In this study monomeric UV stabilizers, 2-hydroxy-4-acryloyloxybenzophenone and 2-hydroxy-4-methacryloyloxybenzophenone, have been prepared by

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modifying the method used by Osawa et al. The grafting of these stabilizers onto polyestyrene, polyethylene, and polypropylene during melt processing under N_2 atmosphere has been studied. An analytical method for the quantitative estimation of the extent of grafting has been developed. Photodegradation studies of UV-stabilizer-grafted polymer are in progress and will be reported later.

EXPERIMENTAL

Materials

Unstabilized isotatic polypropylene powder of MFI 1.5–2 g/10 min was obtained from our own polypropylene plant. The polymer was stored in the dark under N_2 atmosphere in a sealed polyethylene bag. Samples older than 1 week were not used in this study because of large amount of degradation in the unstabilized PP powder. Low-density polyethylene (Indothene 24FS040) made by IPCL was purified by solvent extraction.

Polystyrene used in this study was made in the laboratory by suspension polymerization using free-radical initiator. The average molecular weight was determined by viscosity and was 160,000.

Synthesis

Preparation of 2-hydroxy-4-acryloyloxybenzophenone (I): 2,4-Dihydroxybenzophenone (42.8 g; 0.2M) was dissolved in 5% aqueous sodium hydroxide solution (150 mL) in a three-necked round bottom flask having a dropping funnel. Benzene (300 mL) was added to the above solution, and the reaction mixture was stirred with a magnetic stirrer and its temperature was maintained at 20°C. Freshly distilled acryloyl chloride (15 mL) dissolved in benzene (100 mL) was slowly added to this reaction mixture through the dropping funnel during a period of 1 h. After complete addition, the reaction mass was stirred for additional 2 h, during which the yellow-colored product formed dissolved in benzene and the aqueous layer became colorless. The organic layer was separated, and the aqueous layer was extracted twice with benzene. All benzene extracts were mixed together and the solvent was removed on a rotary flash evaporator at about 40°C. Yield of the crude product was 54.0 g.

This was purified by recrystallization in ethanol, mp 76–77°C. 2-Hydroxy-4-acryloyloxybenzophenone was characterized by microanalysis and spectroscopic methods.

ANAL. Calcd: C, 71.70%; H, 4.51%. Found: C, 72.25%; H, 5.01%.

Preparation of 2-hydroxy-4-methacryloyloxybenzophenone (II): This was prepared in exactly the same way as the acryloxy derivative except that, instead

of acryloyl chloride, methacryloyl chloride was used.   The product was recrystallized from ethanol, mp 76–77°C, and characterized.

ANAL. Calcd: C, 72.3%; H, 4.96%. Found: C, 72.65%; H, 5.25%.

Melt Grafting

The polymer was first solvent-blended with 5% of the additive in a rotary flash evaporator.   The solvents used were benzene for PP, acetone for LDPE, and methanol:hexane (1:9) mixture for PS.   The dry powdery mass obtained after removal of solvent was then melt-mixed in the Brabender Plasticorder Model PLV-151 under N_2 atmosphere (300 mL/min) at 45 rpm for 45 min.   The mixing temperature for polypropylene and polystyrene was 175°C whereas for LDPE it was 150°C.

Estimation of Extent of Grafting

The extent of grafting was estimated by an infrared spectroscopic method on a Beckman instrument model 4220.   Polymer films of 0.2 mm thickness made by compression moulding were used for the analysis.

For each polymer–additive pair characteristic peaks, a polymer peak in the region in which the additive was transparent and an additive peak in the region in which the polymer was transparent were identified.   The ratio of these peaks was used as an index for estimation of degree of grafting.   A calibration curve was made for each set of polymer–additive mixtures by solution-blending the additive in the polymer in different concentrations and recording the infrared spectrum.   The curve of additive concentration vs. absorbence ratio of the peaks selected was plotted.

RESULTS AND DISCUSSION

Synthesis of 2-hydroxy-4-acryloyloxybenzophenone and 2-hydroxy-4-methacryloyloxybenzophenone has been reported by Osawa and co-workers. The modified method used by us is simple and the course of the reaction is easy to follow.   Initially the sodium salt of 2,4-dihydroxybenzophenone is soluble in aqueous medium, and, as its reaction with acrylolyl chloride or methacryloyl chloride proceeds, the product becomes soluble in benzene.   The organic layer develops color whereas the aqueous layer becomes colorless.   The products were purified by double crystallization and were identified by spectroscopic techniques.   Osawa et al. have recorded the IR and UV spectra of the monomeric stabilizers and reported their characteristic frequencies.   NMR spectra (Fig. 1) of these compounds have been recorded on JEOL FX-100 in $CDCl_3$ solvent, with TMS as internal standard.   Chemical shifts are expressed in units and are accurate up to ±0.001 ppm.
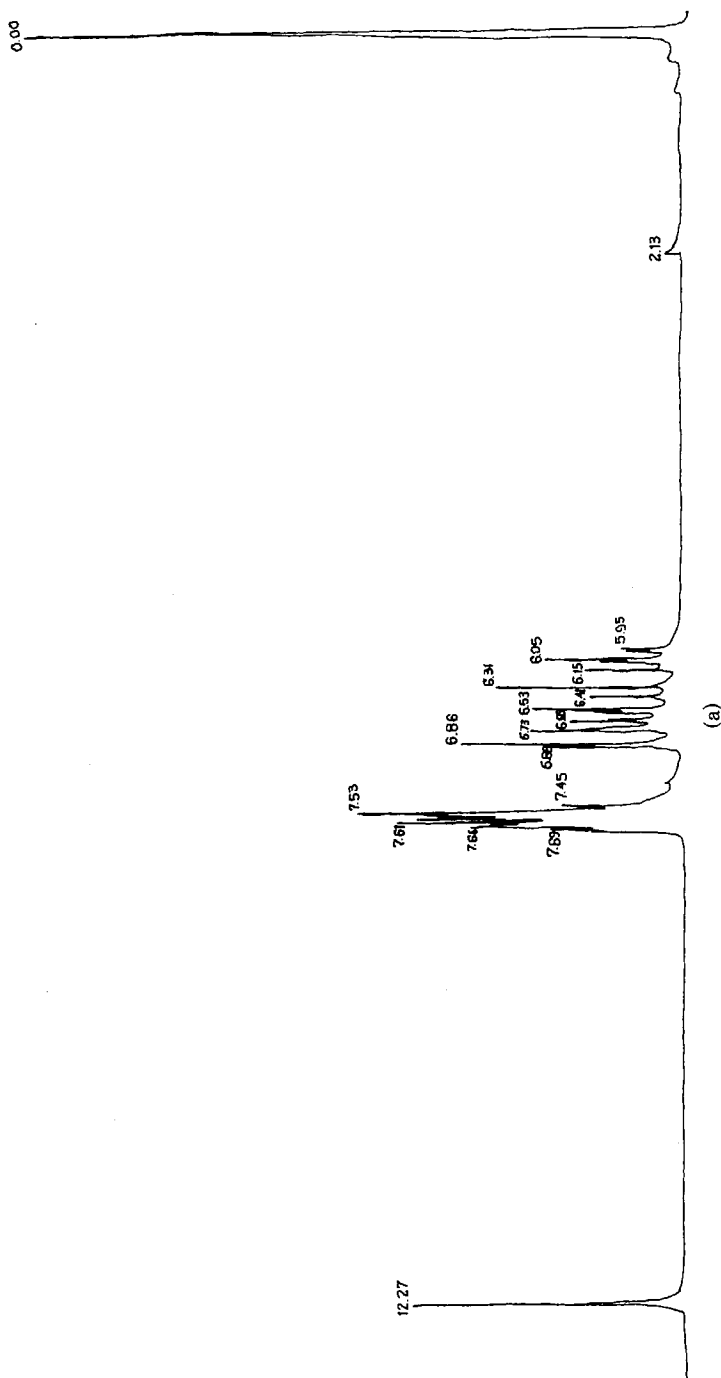
Fig. 1. (a) ^{1}H NMR spectrum of 2-hydroxy-4-acryloyloxybenzophenone; (b) ^{1}H NMR spectrum of 2-hydroxy-4-methacryloyloxybenzophenone.
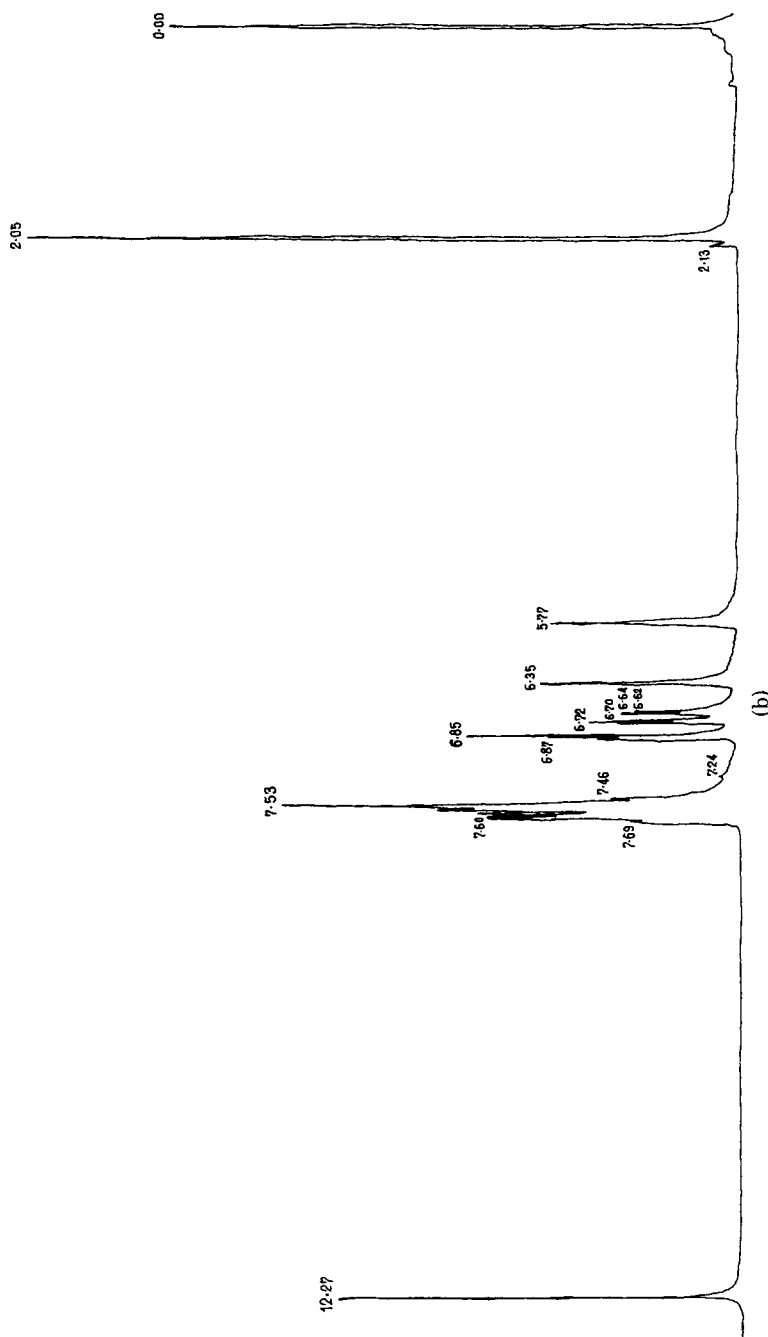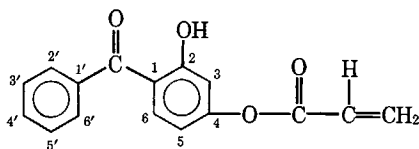
Fig. 1. *(Continued from previous page.)*

TABLE I
Characteristic Peaks of Each Polymer–Additive System

Polymer	Additive	Polymer peak (cm^{-1})	Additive peak (cm^{-1})
PP	Acryloxy—	2720	700
PP	Methacryloxy—	2720	700
LDPE	Acryloxy—	2000	1750
LDPE	Methacryloxy—	2000	1750
PS	Acryloxy—	1870	1630
PS	Methacryloxy—	1870	1630

Chemical shifts for acryloyloxy derivative:

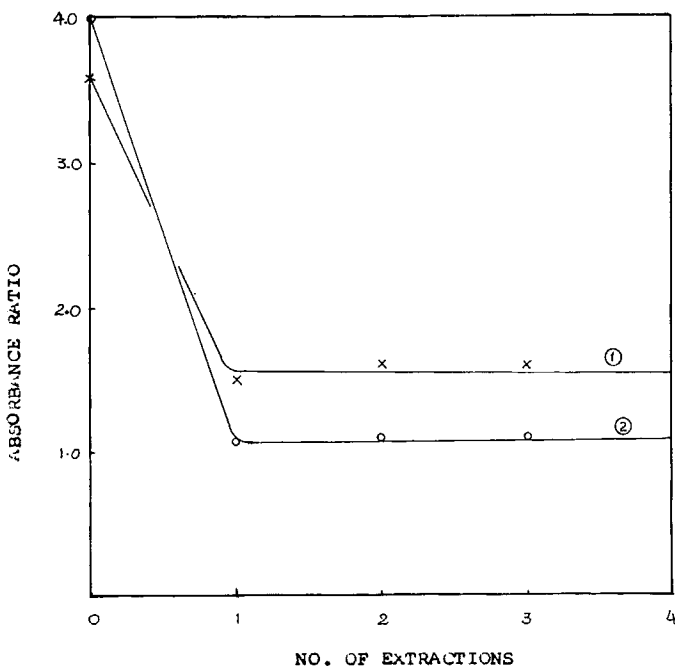| 5.95–6.56	—C$\underline{H}$ = C$\underline{H}_2$
6.68	5$\underline{H}$
6.87	3$\underline{H}$
7.45–7.69	2′–6′$\underline{H}$,6$\underline{H}$
12.37	O–$\underline{H}$

Fig. 2. Grafting of UV stabilizers on polystyrene ($A_R = A_{1630\ cm^{-1}}/A_{1870\ cm^{-1}}$): (1) methacryloxy derivative; (2) acryloxy derivative.
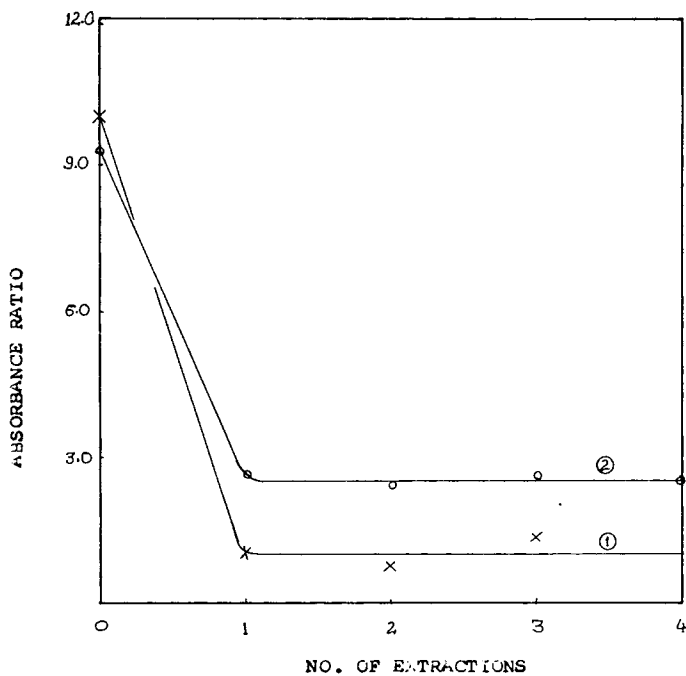
Fig. 3. Grafting of UV stabilizers on LDPE ($A_R = A_{1750 \text{ cm}^{-1}}/A_{2000 \text{ cm}^{-1}}$): (1) acryloxy derivative; (2) methacryloxy derivative.
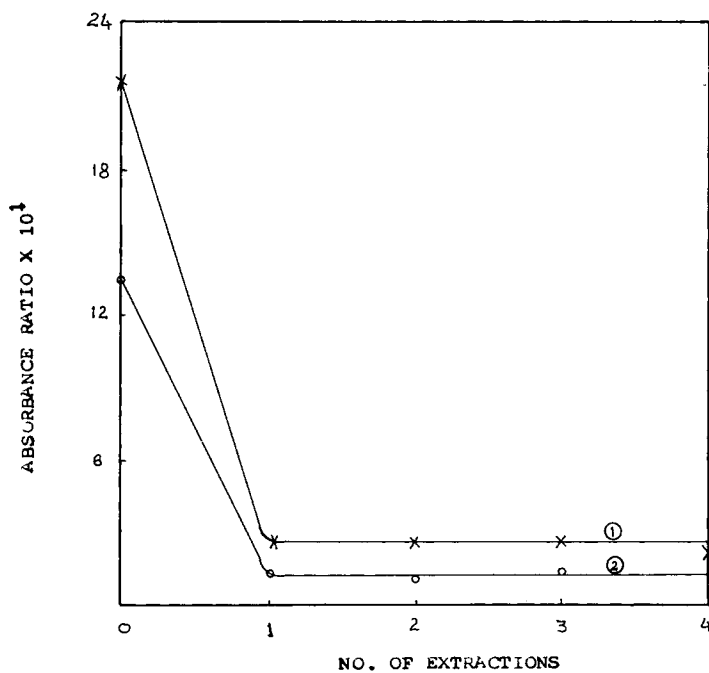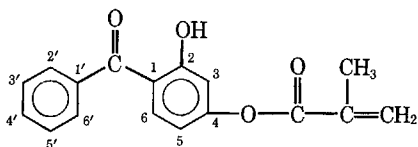

Fig. 4. Grafting of UV stabilizers on polypropylene ($A_R = A_{700 \text{ cm}^{-1}}/A_{2720 \text{ cm}^{-1}}$): (1) acryloxy derivative; (2) methacryloxy derivative.

Chemical shifts for methacryloyloxy derivative:

2.05	—C$\underline{H}_3$
5.77,6.35	—C = C$\underline{H}_2$
6.67	5$\underline{H}$
6.86	3$\underline{H}$
7.46	2'-6'$\underline{H}$,6$\underline{H}$
12.27	O—$\underline{H}$

In order to find out the extent of grafting, the infrared spectrophotometric method was employed. The different frequencies for additive and polymer selected for each polymer–additive system are given in Table I.

During melt-grafting a fairly large amount of these additives (5% by weight) was used. Since complete grafting of these additives is not expected, the ungrafted additives were extracted from the polymer by dissolving it in a solvent and then reprecipitating in a nonsolvent in which the additives were soluble. In Figures 2–4 the absorbence ratio of additive to polymer peak is plotted against the number of extraction treatments the polymer was subjected to. The plateaux of the plots signify the complete removal of the ungrafted additive. It is evident from the plots that one extraction treatment is sufficient to remove the ungrafted additive. The amount of additive grafted on the polymer backbone for each pair of the polymer–additive system determined from the respective calibration curve is given in Table II. Results show that for both the additives the grafting on the polymers occurs in the order

PS > LDPE > PP

It is expected that in case of polystyrene the extent of grafting would be maximum, because the tertiary C—H bond would require minimum energy due to resonance stabilization of the resulting radical for its rupture. Keeping this in view, it is expected that grafting on PP backbone should be higher than LDPE; however, the results obtained are to the contrary. Lower grafting on PP can be attributed to the faster rate of radical generation because of the higher mixing temperature. Thus it appears that the formation of the homopolymer of the additive is greater. The low-molecular-weight homopolymer gets leached out of the polymer matrix during the extraction process. This could also be due to higher stereo regularity in PP chains.

It has been observed that methacryloxy derivative is more reactive than the acryloxy one with respect to the three polymers studied. In both the cases the free radicals formed are resonance stabilized by the neighboring carbonyl group. The higher grafting efficiency in case of methacryloxy derivative compared to the acryloxy one may be due to additional stabilization of the radical formed

TABLE II
Extent of Grafting of Stabilizers

Polymer	% grafting acryloxy	% grafting methacryloxy	Processing temp (°C)
Polyestyrene	1.500	2.500	175
Polyethylene	0.275	0.750	150
Polypropylene	0.175	0.750	175

from methacryloxy derivative because of hyperconjugation with the methyl group as shown by:
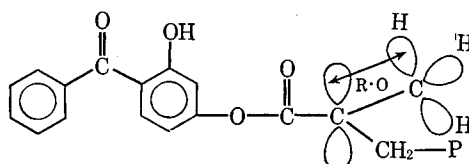
The investigations on accelerated weathering tests are under progress and will be reported in a separate communication.

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