# Surface photografting of polymerizable 2-(2-hydroxyphenyl)2*H*-benzotriazoles as ultra-violet stabilizers*

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Films of low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP) have been surface photografted with different polymerizable 2-(2-hydroxyphenyl)2*H*-benzotriazole monomers [2-(2-hydroxy-4-acryloxyphenyl)2*H*-benzotriazole (BDHA), 2-(2-hydroxy-4-methacryloxyphenyl)2*H*-benzotriazole (BDHM), 2-(2-hydroxy-5-vinylphenyl)2*H*-benzotriazole (2H5V) and 2-(2-hydroxy-5-isopropenylphenyl)2*H*-benzotriazole (2H5P)] in the presence of benzophenone as the photoinitiator using 254 nm ultra-violet irradiation. Photografted films of polyethylene (LDPE and HDPE) have much higher resistance towards photoageing (tested in a Weather-O-meter) than non-stabilized samples. Photografted films of polypropylene (PP) have a tendency to be photodegraded faster than non-grafted samples. This is interpreted as a result of destructive photo-oxidative degradation caused by traces of benzophenone that have not been completely removed from the grafted films by extraction.

**(Keywords: grafting; stabilization; photoinitiation; photodegradation)**

## INTRODUCTION

Polyolefins are notorious for their relatively poor stability when exposed to the environment. Polymer degradation due to ageing and weathering may cause the loss of physical, mechanical or surface properties. Consequently these polymers must be stabilized with antioxidants and photostabilizers. Photostabilization is of primary interest if outdoor use of an article made from polyolefins is anticipated.

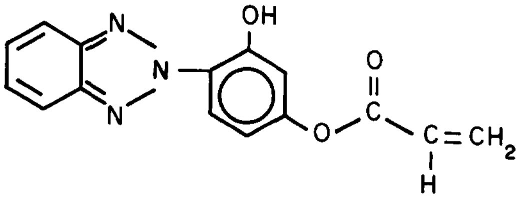
The mechanisms of photodegradation and photostabilization of polyolefins have been the subject of a number of intensive investigations during the past decade[1–4]. In spite of substantial efforts to protect polyolefins against photo-oxidative degradation by use of antioxidants and photostabilizers, the desired results have generally not been realized. For this reason, new concepts of polyolefin stabilization against light are under active investigation. One new concept is photostabilization of polyolefins by surface photografting with monomeric photostabilizers[5].

It has been shown before that a number of acrylic monomers can be photografted on polyolefins in the presence of benzophenone as a photoinitiator[6–10]. The most common method used was immersing the polymer film in a solution containing a photoinitiator and a monomer. After swelling, the polymer films were u.v. irradiated. This method, with some modifications, has been used in this paper for the photografting of monomers containing different 2-(2-hydroxyphenyl)-2*H*-benzotriazole groups onto polyethylene and polypropylene.

These monomers can be easily polymerized and are readily copolymerized with a number of different comonomers[11–13]. They have also been grafted by free-radical initiators onto a number of polymers[14–19]; however, photografting has not been reported. Covalent binding of the photostabilizers to the polymers has advantages and disadvantages, which will be discussed later.

## EXPERIMENTAL

The following 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers have been synthesized and used for photografting: 2-(2-hydroxy-4-acryloxyphenyl)-2*H*-benzotriazole (BDHA)[20], 2-(2-hydroxy-4-methacryloxphenyl)-2*H*-benzotriazole (BDHM)[20], 2-(2-hydroxy-5-vinylphenyl)-2*H*-benzotriazole (2H5V)[21] and 2-(2-hydroxy-5-isopropylphenyl)-2*H*-benzotriazole (2H5P)[21].



BDHA

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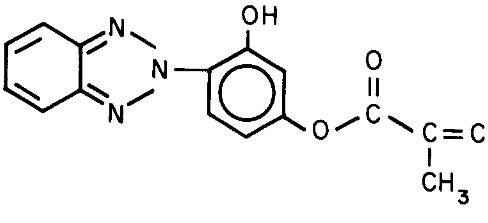
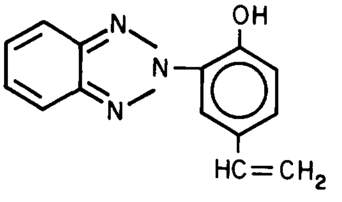
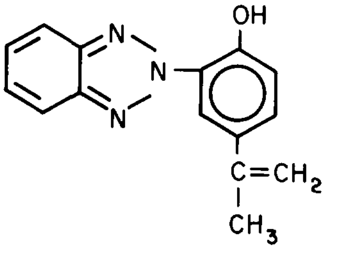


BDHM



2H5V



2H5P

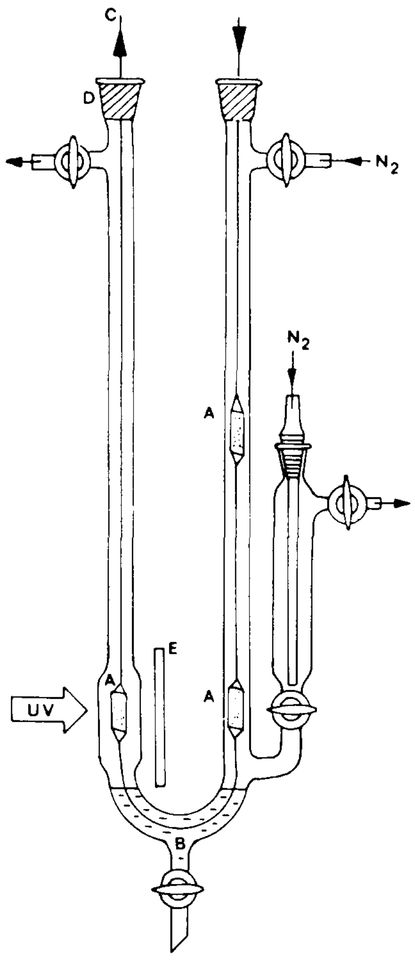


**Figure 1** Photoreactor used for grafting of polymer films

The monomer 2H5V had been stabilized against polymerization with picric acid, which was removed before use by gel chromatography using a column filled with Kieselgel 60 (Merck, Germany).

Benzophenone (BP) (Merck, Germany) was recrystallized twice from spectrally pure ethanol.

Films of three different polyolefins have been used as substrate for photografting low-density polyethylene (LDPE) (L-400, Statoil Co., Norway; film thickness 180 μm, 38% crystallinity), high-density polyethylene (HDPE) (Unifos, Sweden; film thickness 80 μm, 63% crystallinity) and polypropylene (PP) (Moplefan, Montedison, Italy; film thickness 20 μm).

The photografting of monomers on polyolefins has been carried out in a specially designed U-type photoreactor (*Figure 1*), where the polymer films were swollen with monomer and photoinitiator (BP) in chloroform solution in a syphon for specified times (from 1 to 10 min) and then u.v. irradiated at 254 nm with an HPK 125 W

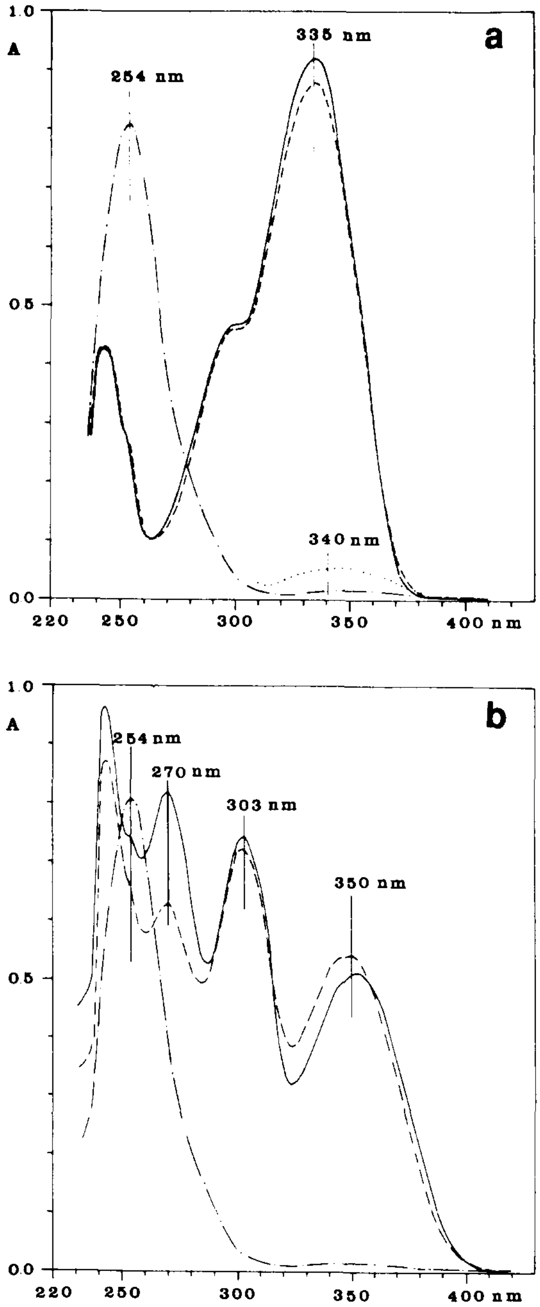


**Figure 2** Absorption spectra of 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers and benzophenone (BP) in chloroform solution ($3 \times 10^{-5}$ M). (a) (——) BDHA; (– – – –) BDHM; (—·—) BP; and (· · · ·) BP on larger scale ($A = 0.2$). (b) (——) 2H5V; (– – – –) 2H5P; and (—·—) BP

lamp (Philips, Netherlands) at a distance of 10 cm from the lamp. All operations were carried out under a nitrogen or air atmosphere. The monomer concentration was 0.1 M in all experiments, whereas the concentration of BP varied from 0.01 to 0.1 M. The polymer films were transported through the photoreactor by steel wire to which were attached aluminium frames. Photografted films were extracted with boiling chloroform for 24 h using a Soxhlet extractor.

Absorption spectra were measured by using a Perkin–Elmer 575 u.v./vis. spectrometer. I.r. spectra were recorded on a computerized Perkin–Elmer 580 *FT*i.r. spectrometer.

The grafting efficiency was determined in polymer films (extracted for 24 h in a Soxhlet extractor with boiling chloroform) by spectroscopic analysis using calibration curves for each monomer.

The best grafting results were obtained at a molar ratio of monomer to initiator of 1:1 and 10 min swelling time.

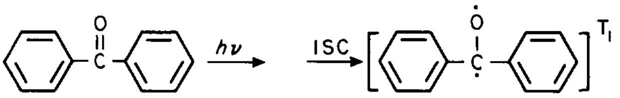
Electron microscope pictures of the film surfaces were made with a Super Mini SEM ISI microscope.

Photografted samples were exposed to the light (photoageing at 50°C in an Atlas Uvicon irradiator with four 40 W lamps ($\lambda \geq 300$ nm).

## RESULTS AND DISCUSSION

It is well known that benzophenone (BP) is an effective photoinitiator for the crosslinking of polyethylene[22] and for the photodegradation of polypropylene[23,24].

Benzophenone has two absorption bands, a strong band at 240–260 nm ($\varepsilon$ = 12 000–18 000, solvent-dependent) and a weak band at 345 nm ($\varepsilon$ = 120) (*Figure 2*). The triplet state of an excited BP molecule is capable of abstracting hydrogen from the polyolefin chain to form a benzophenone ketyl radical and a polymer alkyl radical[4] as illustrated below:



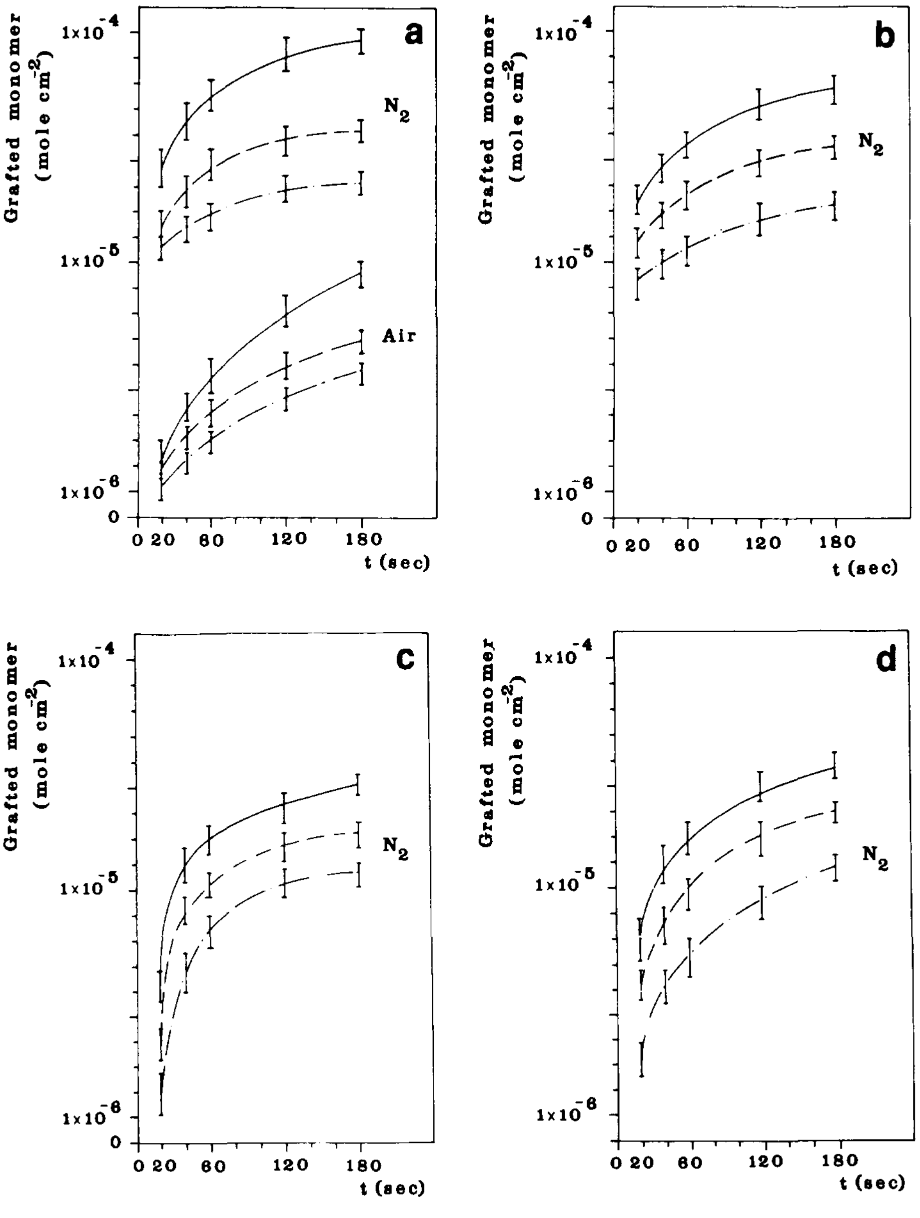
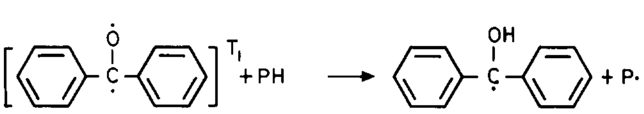


**Figure 3** Content of grafted 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers onto polyolefin surfaces: (——) on LDPE; (– – – –) on HDPE; and (—·—) on PP (10 min swelling time for all samples). (a) BDHA; (b) BDHM; (c) 2H5V; (d) 2H5P



Depending on the type of polyolefin used, the polymer alkyl radical formed can participate in a number of reactions such as oxidation to polymer peroxy radicals (in the presence of oxygen), chain scission and/or crosslinking reactions. The polymer alkyl radical formed can be used for grafting by addition of vinyl or acryl monomers:

$$P^{\cdot} + M \rightarrow PM^{\cdot} + M_n \rightarrow PM_nM^{\cdot}$$

This process was employed to graft different 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers (BDHA, BDHM, 2H5V and 2H5P) onto polyethylene (LDPE and HDPE) and polypropylene (PP). Because these 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers have strong absorption at 350–360 nm (*Figure 2*), it was impossible to use longer-wavelength ($\lambda > 300$ nm) radiation to excite benzophenone molecules required to photoinitiate grafting of these monomers. However, the application of u.v. irradiation at 254 nm, which is not absorbed by BDHA and BDHM (*Figure 2A*) and only partially absorbed by 2H5V and 2H5P (*Figure 2B*) gave excellent photografting results (*Figure 3*). The highest grafting efficiency was obtained for BDHA on LDPE ($1 \times 10^{-4}$ mol cm$^{-2}$). The lowest efficiency was observed for PP ($2 \times 10^{-5}$ mol cm$^{-1}$) (*Figure 3A*). The photografting efficiency is much higher when the reaction is carried out under nitrogen (*Figure 3A*). For that reason, all subsequent experiments were performed under a nitrogen atmosphere. The acrylic monomers (BDHA and BDHM) are photografted with higher efficiency than the vinyl monomers (2H5V and 2H5P) (*Figure 3*). The photografting efficiency for 2H5V

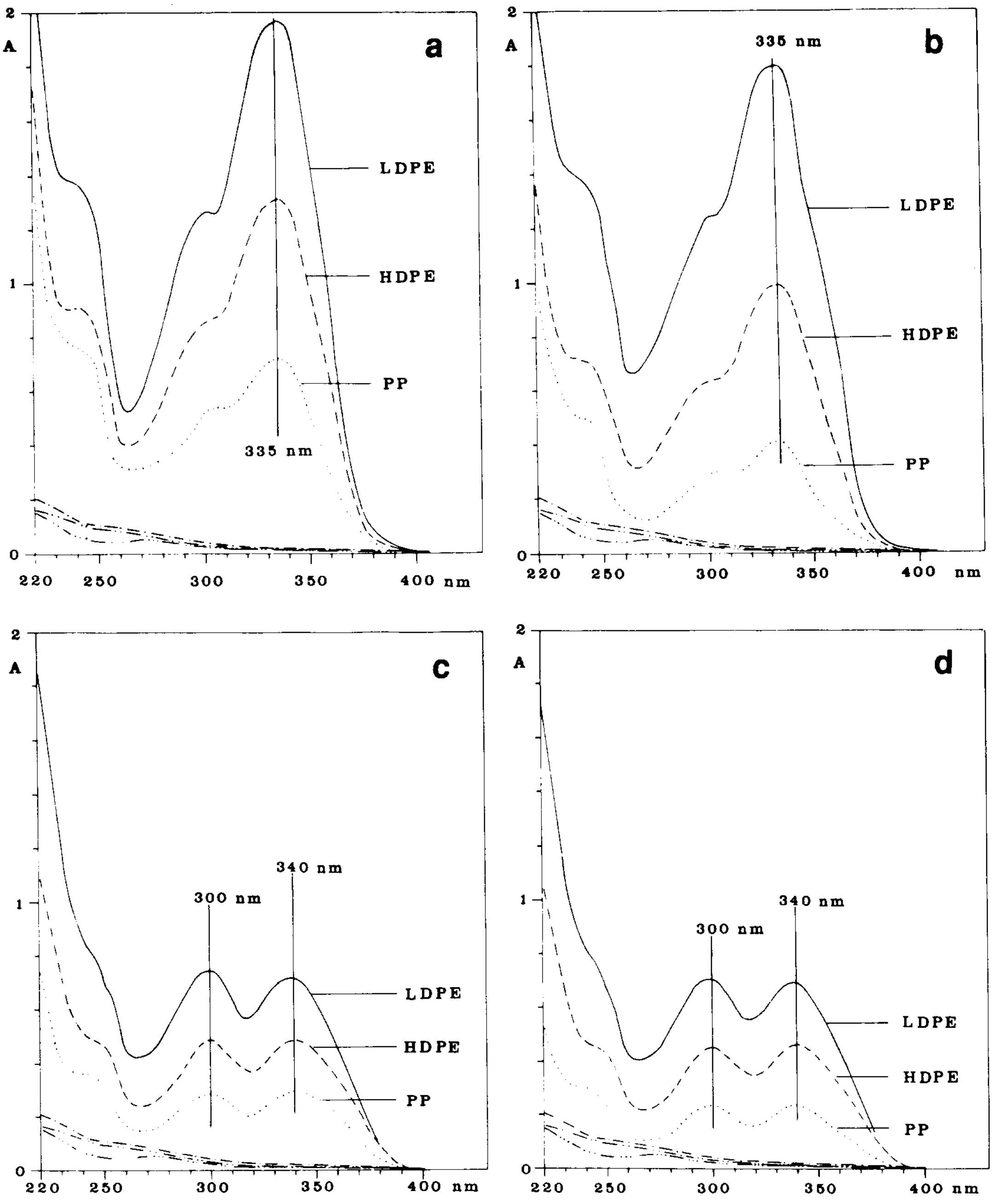


**Figure 4** Absorption spectra of polymer film samples grafted for 60 s with different 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers after 10 min swelling time. (a) BDHA; (b) BDHM; (c) 2H5V; (d) 2H5P

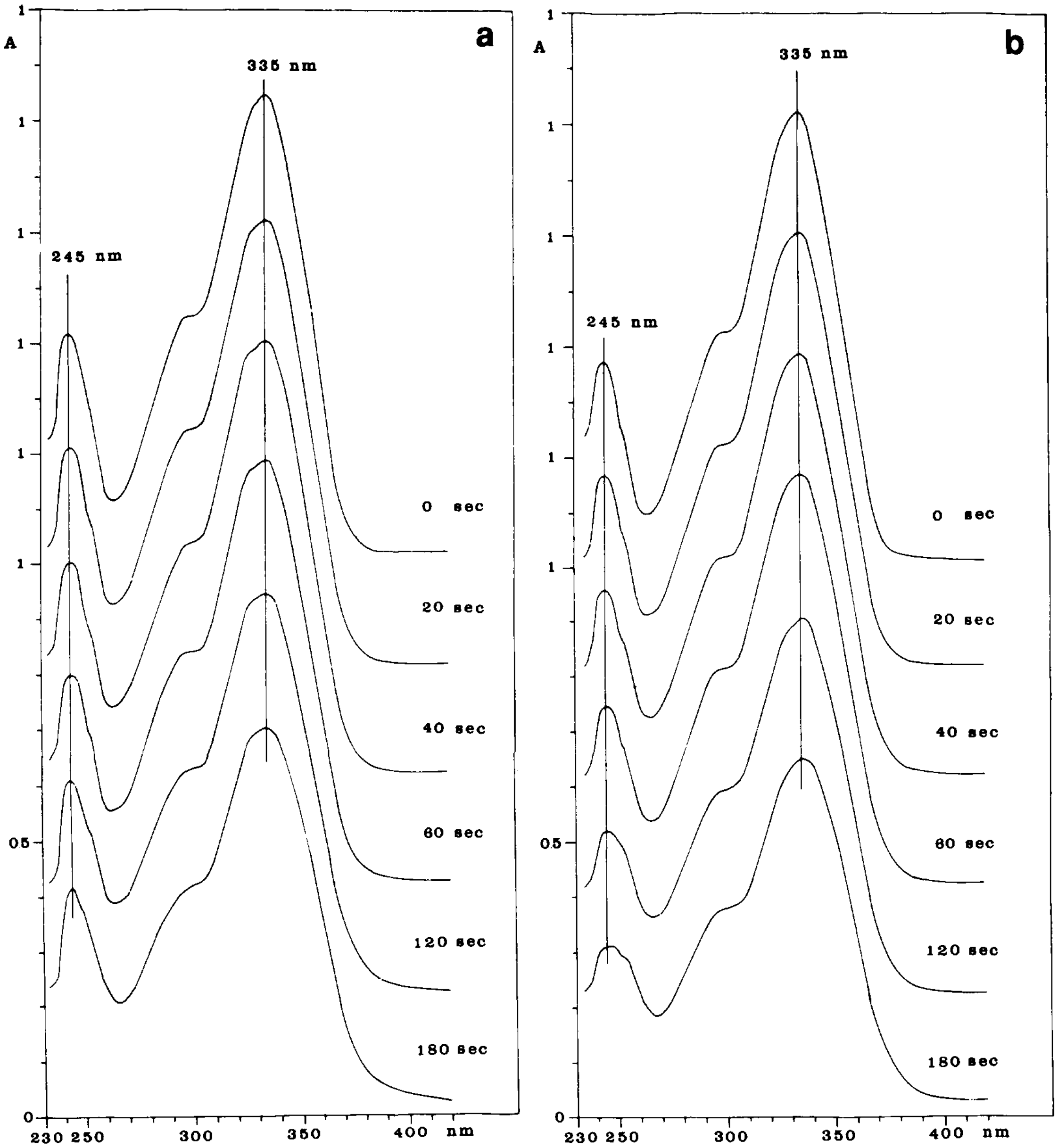


Figure 5 Absorption spectra of 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers in chloroform solution ($3\times10^{-5}$ M) after different times of u.v. irradiation at 254 nm. (c) BDHA; (b) BDHM

and 2H5P is extremely low ($(1-3)\times10^{-9}$ mol cm$^{-2}$) for a short time of u.v. irradiation (20 s) compared with results for BDHA and BDHM (*Figure 3*). In all cases, 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers were more efficiently photografted onto LDPE than onto HDPE in this order (*Figure 3*). Irradiation times over 180 s do not increase photografting efficiency very much and may lead to side-reactions such as photocrosslinking and/or photodegradation. All experiments that were carried out at the optimum grafting time in the presence of nitrogen rather than in air indicate that nitrogen blanketing is essential for the photografting process. It seems likely that the hydroperoxide formed during photo-oxidation in the presence of air leads to a less effective grafting of 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers.

The photografted polyolefin films (after 24 h extraction in boiling chloroform) exhibit the characteristic absorption of the pure 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers (*Figure 4*). For the photografted monomers BDHA and BDHM the absorption band (335 nm) does not change in comparison with that of the pure monomers (*Figure 2A*). For the monomers 2H5V and 2H5P, there is a clear shift of the absorption band from 350 nm of the pure monomers (*Figure 2B*) towards 340 nm for monomers grafted onto polymer films (*Figures 4C* and *4D*). This shift of absorption bands at 350 nm is also observed during the photolysis of 2H5V and 2H5P at 254 nm (see *Figures 6A* and *6B*), which may be due to the formation of homopolymers from these monomers. This result suggests that grafted chains of 2H5V and 2H5P should be in the form of long chains in comparison to rather short chains in the case of grafted BDHA and BDHM monomers, which do not exhibit any shift in the u.v. frequency. At this stage of the experiments, we could not determine the length of the grafted chains. However, it may be concluded that shorter and more frequent photostabilizer chains attached to the polyolefin surfaces are more effective as photostabilizers than long and less frequent chains.

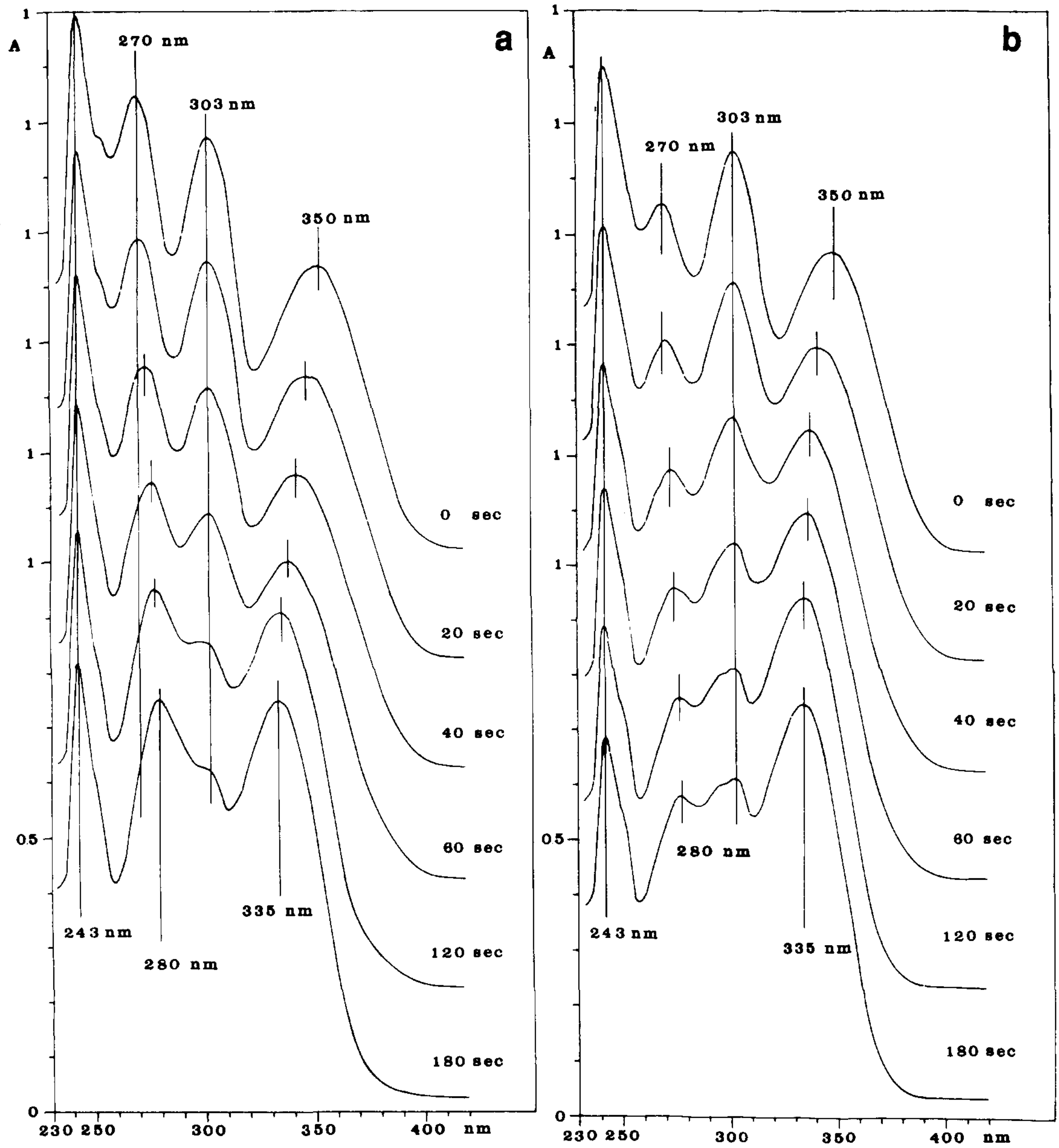


**Figure 6** Absorption spectra of 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers in chloroform solution ($3 \times 10^{-5}$ M) after different times of u.v. irradiation at 254 nm. (c) 2H5V; (b) 2H5P

The 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers were photolysed during u.v. irradiation at 254 nm (*Figures 5* and *6*). In the case of photolysis of BDHA and BDHM, there is no change in absorption band positions (*Figure 5*) as compared with pure monomers (*Figure 2*). In the case of monomers 2H5V and 2H5P, the absorption spectra showed a shift of absorption maxima from 270 nm to 280 nm and from 350 nm to 335 nm (*Figure 6*), which is a result of the formation of homopolymers from these monomers. Benzophenone did not increase the rate of photolysis of the 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers in solution of $CHCl_3$ (*Figure 7*). After 180 s of u.v. irradiation, ~15 wt% of monomers BDHA and BDHM and ~20 wt% of monomers 2H5V and 2H5P were photolysed. For this reason, the application of shorter u.v. irradiation times for grafting of these monomers was preferred in order to minimize the photolysis reaction.

The electron micrograph of polyethylene (LDPE) photografted with BDHA monomer showed changes of surface morphology in comparison with ungrafted film (*Figure 8*). The photografted surface was very rough, which suggests that photografting was not uniform and the amount of photografted material was unevenly distributed. The electron microscope pictures for other monomers showed the same image of the photografted surfaces.

Photographed films were tested for photostability in the Uvicon Weather-O-meter. Depending on the amount of monomers grafted onto the polymer films (photografted for different times: 20, 40 and 60 s), the kinetics of formation of carbonyl groups (at 1714 $cm^{-1}$) differ remarkably (*Figure 9*). The best photostabilizing properties are obtained for samples photografted under 60 s of u.v. irradiation, for both LDPE and HDPE. BDHA and BDHM give better photostabilizing properties than the two other monomers, 2H5V and 2H5P (*Figure 10*). During photoageing of grafted polyethylene films with

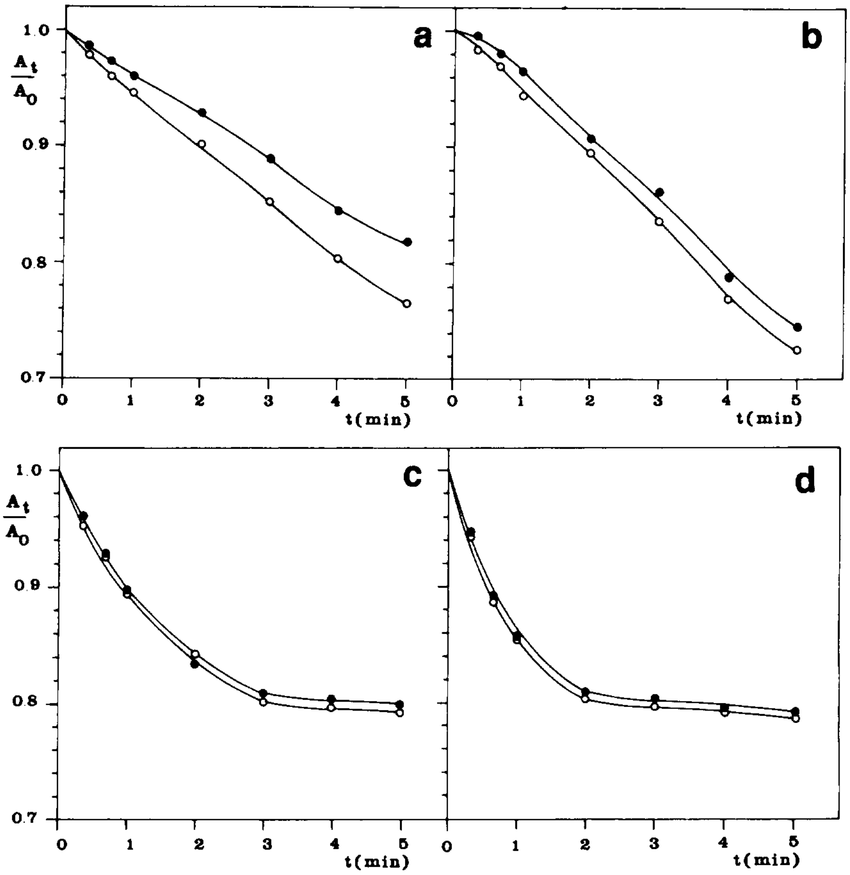


**Figure 7** Kinetics of photolysis of 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers in pure form (—○—) and in the presence of benzophenone (BP) (—●—) in chloroform solution ($3 \times 10^{-5}$ M). Molar ratio of 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomers to BP = 1:1. (a) BDHA; (b) BDHM; (c) 2H5V; (d) 2H5P

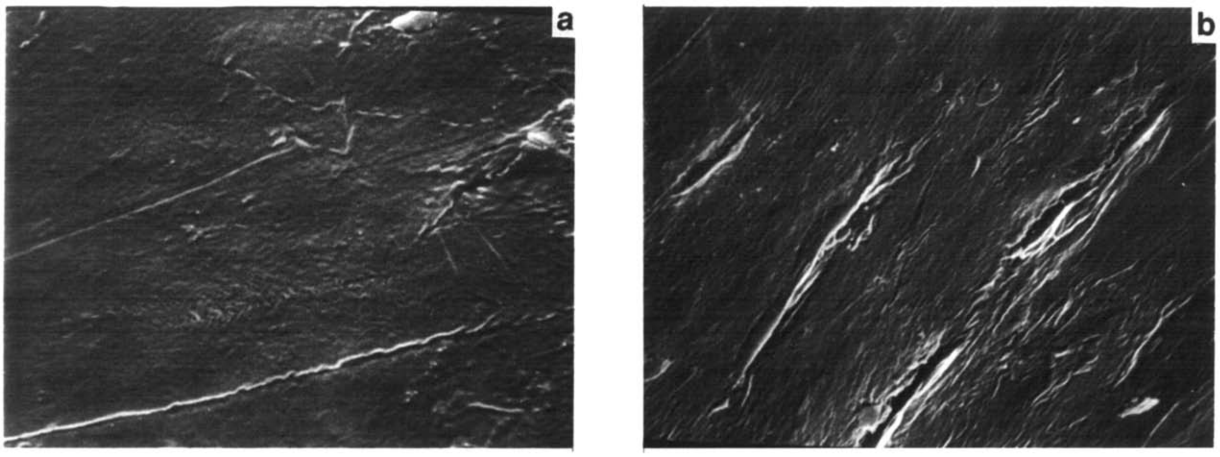


**Figure 8** Electron microscope pictures of (a) ungrafted LDPE and (b) LDPE grafted with 2-(2-hydroxyphenyl)-2*H*-benzotriazole monomer (BDHA)

different monomers, it has been observed that after 700 h most grafted monomeric chains were photolysed (*Figure 11*): 20–25 wt% of BDHA and BDHM remained on the grafted polymer surface and only 5–10 wt% of 2H5V and 2H5P. From the ageing results, it is evident that photografting of BDHA and BDHM monomers onto the surface of polyethylene (LDPE and HDPE) increased their photostability towards photoageing.

E.s.c.a. studies of surface photo-oxidation of poly[2-(2-hydroxy-3-vinyl-4-methylphenyl)-2*H*-benzotriazole][25] and its copolymers[26] indicate that these polymers were rapidly photo-oxidized and were unsuitable for use as photostabilizers on a polymer surface. Oxygen uptake on the surface was more rapid for the copolymers and was related to the benzotriazole content of the surface. The behaviour of these photostabilizers at the surface was indicative of photosensitization and not photostabilization.

Photoageing of photografted polypropylene shows that this polymer has a much higher tendency to be photodegraded than non-grafted polymer films. Benzo-

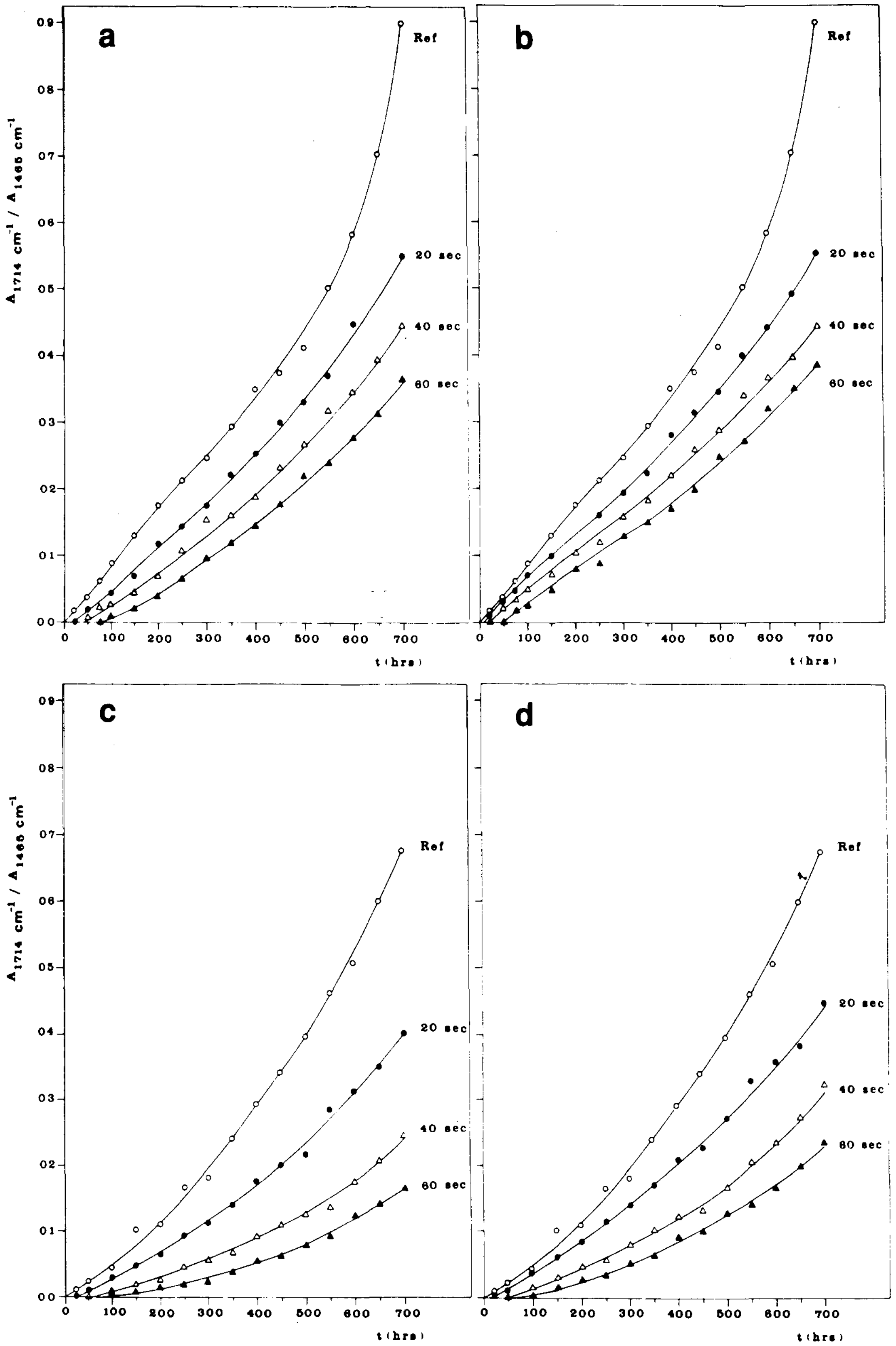


**Figure 9** Kinetics of carbonyl group formation in photografted polyethylene films after 10 min swelling time and different times for the grafting reaction (20, 40 and 60 s) during ageing in Uvicon Weather-O-meter at 50°C. (a) BDHA on LDPE; (b) BDHM on LDPE; (c) BDHA on HDPE; (d) BDHM on HDPE

phenone is an effective activator for the photo-oxidative degradation of polypropylene[23,24]. Traces of benzophenone that have not been removed by extraction after photografting are probably responsible for the rapid photodegradation of this polymer. It is clear that destructive oxidative photodegradation initiated by benzophenone is competing with the desired grafting process. Thus, another type of photoinitiator for grafting of polypropylene films should probably be used.

As expected, photografting monomers onto the surfaces of polyethylene films (LDPE and HDPE) imparts a much improved photodegradation resistance compared with

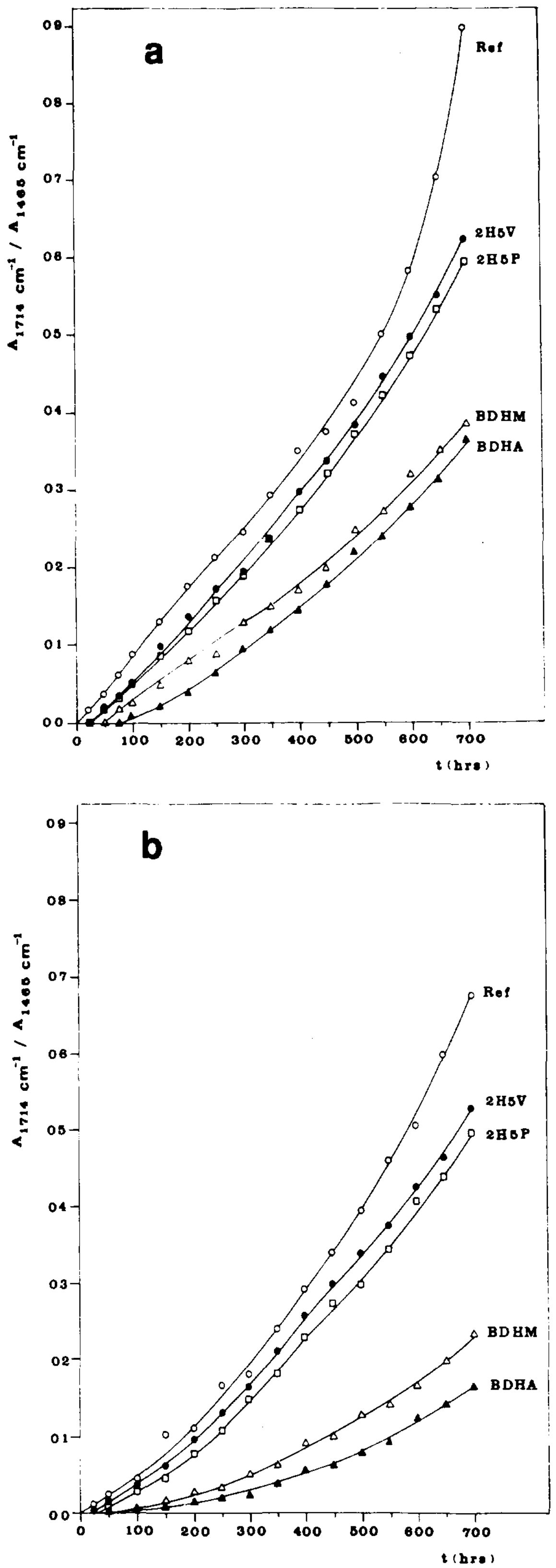


**Figure 10** Kinetics of carbonyl group formation in photografted polyethylene films after 10 min swelling time and 60 s for the grafting during ageing in Uvicon Weather-O-meter at 50°C (a) LDPE; (b) HDPE

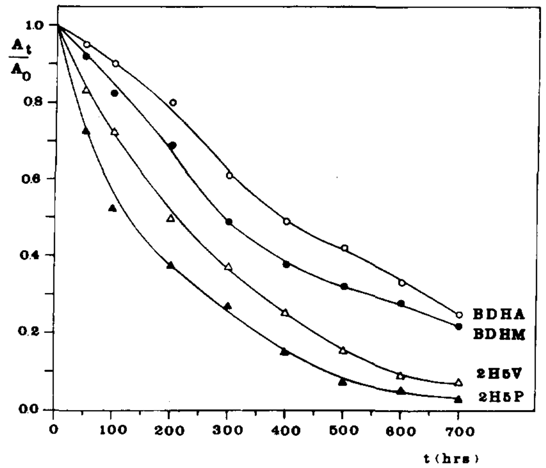


**Figure 11** Kinetics of photolysis of grafted 2-(2-hydroxyphenyl)-2*H*-benzotriazole photostabilizers onto LDPE film surface during ageing in Uvicon Weather-O-meter at 50°C

non-stabilized films. The grafted photostabilizers have a number of advantages in comparison with polymer-bound additives, which have a limited mobility related to chain segment motion in the amorphous regions of the polymer. Since the surface of a polymer is considered to be most susceptible to photo-oxidative degradation, the surface grafting of a photostabilizer is expected to be the most effective method for protection of the polymer against degradation.

Grafted photostabilizers may also exhibit synergistic activity in combination with other additives. In the case of polymeric additives in the polymer matrix, concentration of these additives in the amorphous part of a semicrystalline polymer implies that these regions will contain all the additives whereas the crystalline regions will have none. The mobility (diffusion) of additives in a polymer matrix is important for stabilizing activity.

In the case of polymer-bound additives, diffusion in a polymer matrix is somewhat limited. Grafted photostabilizers, in turn, are not readily extracted or evaporated from the surface (in the presence of solvents, oils, etc.). It is clear that grafted photostabilizers, when located at a polymer surface, are more effective than low-molecular-weight photostabilizers or even polymer-bound photostabilizers that are incorporated in the polymer matrix.

The grafting of photostabilizers onto polymer surfaces needs to be examined in greater detail if industrial applications are to be considered. Further efforts in this area are currently in progress.

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