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MECHANISMS OF ANTIOXIDANT ACTION: POLYMER GRAFTED ANTIOXIDANTS

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Abstract—It is shown that the antioxidant 3,5-di-*tert*-butyl-4-hydroxybenzyl acrylate, may be grafted to the surface of polymer artefacts. The antioxidant activity of the resulting "efficiently dispersed" antioxidant is very much higher than that of low molecular weight antioxidants containing the same functional group. Even after extraction with an effective solvent for the antioxidant–monomer and derived polymer, the oxidative stability of the polymer films is very much greater than that of polymer containing the antioxidant–monomer or antioxidant–polymer incorporated by a conventional melt technique without extraction. Optimum activity is believed to be associated with the formation of frequent short chain grafts in the surface of the polymer and is achieved by the use of a polymerization photo-activator such as benzophenone which also terminates kinetic chains.

Surface grafted antioxidants are also found to be effective u.v. stabilizers for polypropylene in contrast to the normal ineffectiveness of chain terminating antioxidants incorporated into the polymer by conventional techniques.

INTRODUCTION

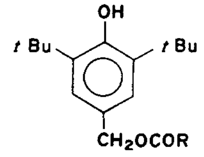
It has been suggested [1, 2] that three main factors determine the antioxidant behaviour of stabilizers for polypropylene under conditions of service.

(a) Intrinsic antioxidant behaviour which is determined primarily by the chemical structure of the antioxidant function and is readily determined by measuring the induction period in oxygen absorption in an oxidizable substrate in which the antioxidant is soluble.

(b) The microenvironment of the antioxidant in the polymer (e.g. compatibility, ease of migration, etc.). Oxygen absorption measurements in the polymer in a closed system measure the resultant effects of (a) and (b).

(c) The rate of loss of antioxidant from the polymer (e.g. by volatilization, extraction, etc.). The overall effect of all three factors can be measured by studying antioxidant behaviour in the form of a thin film in a rapid air stream. This kind of test, for example the torsion braid test [1], tends to accentuate the effect of physical loss from the polymer which can be important under conditions of service.

It has been shown that as the molecular weight of antioxidants with the same antioxidant function increases and hence volatility decreases, antioxidant effectiveness increases in an oven test [1]. However, it seems possible on theoretical grounds that there is a limit to antioxidant efficiency as molecular weight increases under these conditions due to mobility and compatibility limitations. The present study is concerned with an attempt to study these factors in a series of antioxidants containing the same antioxidant function (I) in which R varies from a low molecular weight alkyl group to a polymer chain.



(I)

Previous work has shown that a variety of antioxidants containing a vinyl group can be polymerized [3–5] and incorporated into the polymer in this form or co-polymerized with the polymer [6–9] to give a bound antioxidant system.

Graft co-polymerization of vinyl-containing antioxidants to preformed polymer artefacts has not been reported, however, and the purpose of the present study was to compare the effect of high surface concentrations of antioxidants by grafting them to thin films with that obtained by incorporating the same structure of varying molecular weight by conventional melt compounding.

It has previously been reported [10] that vinylpyridine can be grafted to polypropylene using u.v. light in the presence of benzophenone as photosensitizer. This technique was applied to the grafting of the vinyl antioxidant, 3,5-di-*tert*-butyl-4-hydroxybenzyl acrylate [DBBA; (I), R = vinyl]. It was also found that this monomer could be polymerized if oxygen was carefully excluded and this was used for comparison.

EXPERIMENTAL

Materials

2,6-Di-*tert*-butylphenol was a commercial product which was used without purification. Acrylic acid was obtained from Koch-Light and was distilled before use to remove stabilizers.

2,6-Di-*tert*-butyl-*p*-cresol (TBC) was obtained from I.C.I. Ltd. as Topanol OC. Polypropylene was unstabilized powder ex I.C.I. Ltd.; (HF 20/CV 170). Antioxidants were prepared as follows.

DBBA was prepared from acrylic acid and 3,5-di-*tert*-butyl-4-hydroxybenzylalcohol [11] by the method of Rocklin and Morris [12]. M.p. 67·5–69°. Infra-red spectrophotometry showed OH (phenolic), 3640 cm^{-1}; carbonyl (ester), 1830 cm^{-1}; vinyl, 1640 cm^{-1}. 3,5-Di-*tert*-butyl-4-hydroxybenzyl stearate was prepared from stearic acid and 3,5-di-*tert*-butyl-4-hydroxybenzyl alcohol by the method of Rocklin and Morris [11]. The melting point was 58° by differential thermal analysis. Infra-red data; OH (phenolic), 3640 cm^{-1}; carbonyl, 1750 cm^{-1}.

Poly-(3,5-di-*tert*-butyl-4-hydroxy benzylacrylate): 0·01 mol of the monomer was dissolved in 20 ml of benzene and 0·002 moles (0·03 g) of azobis*iso*butyronitrile (AZBN) added. The mixture was refluxed under nitrogen (white spot) for 8 hr. A further 0·015 g of AZBN was added and the polymerization allowed to proceed for a further 16 hr. On removal of the solvent, a white solid was obtained and i.r. examination showed the disappearance of the vinyl group. Additional NMR peaks appeared at 7·4–8·4 τ due to aliphatic polymer protons. Thermal gravitation analysis (TGA) showed that thermal weight loss occurred at 225° compared with 100° for the monomer. GPC analysis gave $\overline{M}_n = 9514$ and $\overline{M}_w/\overline{M}_n = 3{\cdot}64$.

Polypropylene film formation

Unstabilized polypropylene powder (100 g) was shaken with a solution of the antioxidant in dichloromethane (50–100 ml) sufficient to give 2×10^{-4} mole/100 g of powder. The solvent was removed by rotary evaporation at ambient temperature and the impregnated powder was stored in a refrigerator. Five grains of the powder was pressed between stainless steel plates (12 × 12 in.) at 180° for 3 min at 25 ton/in^2. The plattens were water cooled. Films of thickness 0·005 in. were selected for oxidation studies.

Films for grafting experiments were made in the same way with the omission of antioxidant.

Grafting of antioxidant to polypropylene

A typical experiment is as follows: 0·1 g of unstabilized polypropylene film (0·005 in.) was immersed in a benzene solution of the monomer ($\simeq$ 10 g/100 ml) and varying amounts of benzophenone were added. The solution and film were irradiated in a stoppered quartz tube containing air. The samples (up to six were irradiated simultaneously) were mounted on the circumference of a motor driven wheel in a cylindrical cabinet on the outside wall of which were mounted alternating fashion 15 × 20 W fluorescent sunlamps and 15 × 20 W blacklamps which combination emitted light from 270 nm upwards and approximated to sunlight [13]. These lamps were also used to study the u.v. stability of the polymer films.

Oxygen absorption measurements

A modified automated constant volume apparatus developed in this laboratory [14] was employed. The equipment is shown in Fig. 1. The reaction vessel A, containing solution or film as appropriate, was flushed with oxygen for several minutes and immersed in a thermostatted oil bath. The lagged reservoir (B) connected to the reaction vessel by capillary tubing (C) dipped into a beaker containing di-*n*-butylphthalate. The beaker was supported on a 6 × 2 × 1/16 in. steel plate which was rigidly fixed at one end, the flexible part bending under the weight of the filled beaker. Two strain gauges (Philips PR 9810F) were bonded to each side of the clamped plate with an epoxy adhesive. These were electrically connected to a recorder to form the four arms of a Wheatstone bridge circuit. As oxygen was absorbed by the sample in A, an equal volume of liquid was removed from the beaker into the reservoir, thus altering the resistance of the strain gauges. This was automatically recorded as an oxidation curve on a Leeds and Northrup "Speedomax" recorder. In all cases, the polymer films showed an induction period with negligible oxygen absorption during this time.

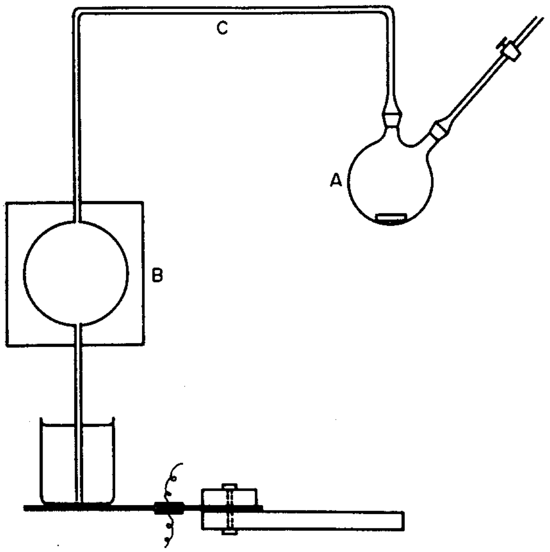


Fig. 1.

Extraction of stabilized films

Acetone was found to be an effective solvent for both DBBA and polyDBBA and Soxhlet extraction of the polypropylene films with acetone for 48 hr was found to remove all antioxidants except those bound to the polypropylene.

Antioxidant estimation

A calibration curve was plotted for poly DBBA in trichloroethylene using the u.v. absorbance at 282 nm. A good straight line was obtained. Grafted films were analysed by dissolving a known weight of the polypropylene film in trichloroethylene and estimating the antioxidant concentration using the above calibration graph.

Estimation of benzhydrol by GLC

Measurements were made on a Pye 104 gas chromatograph using a flame ionization detector. The column was a 5 ft carbowax 20 M operating at 240° and nitrogen was used as carrier gas. The retention time of benzhydrol in benzene was found to be 24 min. Benzpinacol was found to disproportionate to benzhydrol and benzophenone (R_t = 12 min) and was therefore estimated as benzhydrol. Since the yields of benzhydrol were low, the sensitivity of the instrument was increased by a factor of 20 in this estimation.

Determination of benzhydrol yield in the presence and absence of DBBA

Unstabilized polypropylene film (0·1 g, 0·005 in.) was suspended in 10 ml of benzene containing 0·1 g of benzophenone and irradiated for 90 hr. A sample of the liquid reaction product was removed for GLC analysis. A similar reaction was carried out but with the further addition of 0·5 g of DBBA and the analysis repeated. The peak height (R_t = 24) ratio was approximately 3:1 for the samples without and with monomer.

RESULTS

It was found that DBBA could be polymerized in the absence of oxygen to give a low molecular weight polymer ($\bar{M}_n \simeq 3000$) using AZBN as initiator. The effectiveness of this polymer as an antioxidant is compared with that of the monomer and the stearyl ester (DBBS; (I), R = $C_{18}H_{37}$) at equimolar isofunctional group concentration in decalin in Table 1.

Table 1. Induction periods of iso-functional antioxidants at equimolar isofunctional group concentration (2×10^{-4} mole/100 ml) at 120° in decalin

Antioxidant	Induction period (hr)
None	2
DBBA	102
Poly DBBA	100
DBBS	138
TBC	345

Within the limits of experimental error, the monomer and polymer are equally effective, and both are less effective than the long chain ester and the commercial antioxidant 2,6-di-*tert*-butyl-*p*-cresol (TBC) which is one of the most effective of the commercially available antioxidants in an oxygen absorption test.

When incorporated into polypropylene films at the same concentration by a conventional melt procedure, all the antioxidants except DBBS were found to be significantly less effective by oxygen absorption than in decalin at the same temperature (see Table 2). The position of DBBS and TBC were reversed and this is consistent with the theory developed earlier [2] that polymer compatibility and mobility factors become important in oxygen absorption tests in the polymer. The air oven test in which there is a continuous change of atmosphere over the surface of the polymer emphasizes the effect of antioxidant volatility and, as expected, TBC is relatively ineffective under these conditions [2]. Surprisingly, the polymeric antioxidant does not reflect its non-volatility under these conditions. The reason for this is not clear. It may result from its almost complete lack of solubility in the polymer under the conditions of melt incorporation used, since the melting point of the polymeric antioxidant (≃225°) is well above the temperature used for compression moulding of the polymer (180°). However, oxidative depolymerization of the antioxidant may also occur.

Soxhlet extraction of the films with acetone completely removed all antioxidants and their stability reverted to that of the unstabilized polypropylene.

As expected, DBBA grafted on to the surface of polypropylene film imparted a very much improved oxidation resistance after acetone extraction compared with that given by either antioxidant–monomer or polymer incorporated conventionally (see Table 3). The antioxidant effectiveness at optimum irradiation time is better by an order of magnitude than when introduced into the polymer melt.

Table 3. Induction periods of polypropylene films (0·1 g, thickness 0·005 in.) grafted with DBBA (5 per cent) in the presence of benzophenone (1 per cent) in benzene (100 ml) at 120° after acetone extraction

Irradiation time (hr)	Induction period (hr)
24	50
36	73
45	110
70	140
90	366
126	87

An experiment carried out at the optimum grafting time but in the presence of nitrogen rather than air (see Table 4) indicated that oxygen has a beneficial effect on the grafting process.

Table 2. Induction periods at 120° of polypropylene films (0·005 in.) containing 2×10^{-4} mol/100 g of antioxidants

Antioxidant	Oxygen absorption (hr) Before extraction	After acetone extraction	Air oven
None	2	2	7
DBBA	28	2	20
Poly DBBA	35	2	18
DBBS	130	2	244
TBC	115	2	11

Table 4. Effect of air in the benzophenone initiated u.v. grafting of DBBA to polypropylene. (Monomer: benzophenone ratio = 3·14) after acetone extraction

Atmosphere	Induction period (hr)
Air	366
Nitrogen	172

The effect of varying the monomer to benzophenone ratio in the grafting solution was examined at the previously found optimum irradiation time. When the monomer concentration was held constant and the benzophenone concentration was varied, a very marked optimum antioxidant activity was observed (see Fig. 2) at a monomer to benzophenone ratio of 2. A similar result was obtained when the benzophenone concentration was held constant and the monomer concentration was varied. Using the u.v. method to determine antioxidant concentration, the actual concentration of grafted antioxidant in the polymer was not found to be appreciably different in films which exhibited very different stabilities (see Table 5).

The very much greater effectiveness of the grafted antioxidant at similar concentration after acetone extraction can be seen by comparing Tables 2 and 5.

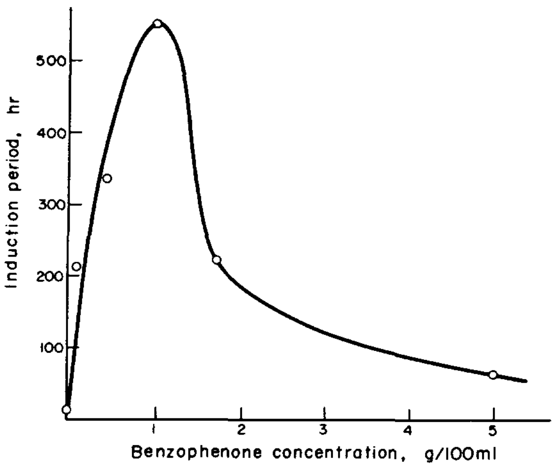


Fig. 2.

Table 6. Effect of grafted and acetone extracted DBBA on u.v. stability of polypropylene film (irradiated for 90 hr in benzene in the presence of air)

	Embrittlement time (hr)
P.P. alone	63
PP + 1% BP	18
PP + 1% BP + 2·5% DBBA	158

Grafted DBBA was also found to be an effective u.v. stabilizer, as shown in Table 6 which also demonstrates that polypropylene irradiated with u.v. in the presence of benzophenone but in the absence of DBBA is effectively activated to u.v. degradation after acetone extraction.

DISCUSSION

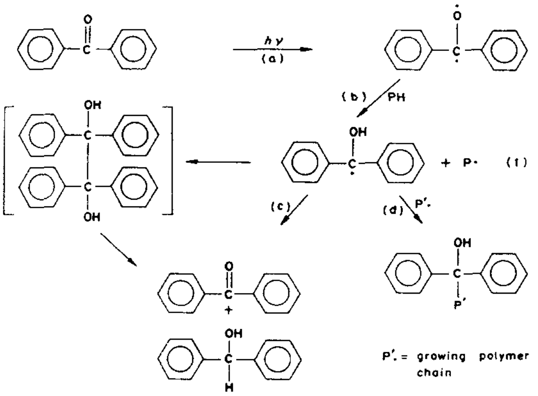
The results confirm the conclusions reached earlier [1, 2] that antioxidants with the same functional group behave similarly in a model system when studied by oxygen absorption, but that in a polymer artefact with high surface area to volume ratio antioxidant volatility is dominating. The acetone extraction process simulates and accentuates the loss of antioxidant from the polymer under certain kinds of service conditions (for example, in the presence of solvents, oils or detergents) and it is clear that antioxidants which are chemically bound to the polymer are, under certain conditions, very much more effective than low molecular weight antioxidants or even polymeric antioxidants.

The most interesting feature of the polymer grafted antioxidant is the observed optimum activity which depends on the ratio of monomer to benzophenone and not on the absolute concentration of benzophenone in the monomer solution. It has previously been suggested [10] that when benzophenone or a substituted benzophenone are used to photo-initiate either oxidation or polymerization, the diphenylhydroxymethyl radical formed inhibits the radical chain process. In the homopolymerization of vinyl pyridine, the extent of polymerization is inversely related to the benzophenone concentration [10]. In the present system, the same process has been found to occur. Irradiation of benzophenone in benzene in the presence of poly-

Table 5. Induction periods of polypropylene films grafted in air at varying DBBA/BP ratios (BP concentration = 1 g/100 ml concentration time = 90 hr) after acetone extraction

DBBA concentration (g/100 ml)	DBBA/BP molar ratio	I.P. (hr)	Grafted antioxidant concn (mole/100 g PP)
10	6·28	342	$3{\cdot}02 \times 10^{-4}$
5	3·14	366	—
2·5	1·57	555	$3{\cdot}18 \times 10^{-4}$

propylene gave benzhydrol as the major reaction product 1(c). Any benzpinacol formed in the reaction would have disproportionated to give benzhydrol and benzophenone, and therefore benzhydrol yield is a measure of the formation of diphenylhydroxymethyl not involved in termination reactions. In the presence of DBBA under the same conditions, only about 30 per cent of the expected benzhydrol was obtained due to competition from the termination reaction, 1(d).



The effect of increasing initiation and termination rates is to produce shorter but more numerous grafts. It must be concluded that shorter and more frequent antioxidant chains attached to the polymer backbone are more effective than long chains. This implies that the ability of a bound antioxidant to exert its influence must be limited by spatial considerations and this will be severely restricted in polymers above their *Tg*.

However, the ability of polymer-bound antioxidants to function in polymers above their *Tg* if adequately dispersed is clearly demonstrated. Rather more surprising, however, is the ability of surface grafted antioxidants to behave as u.v. stabilizers (see Table 5), since phenolic antioxidants are not normally considered to be effective u.v. stabilizers. This must be a consequence of the high concentration of radical scavenging species in the surface layers of the polymer.

It is evident from Table 6 that in the absence of an antioxidant, benzophenone is an effective activator for the photo-oxidation of polypropylene. However, this is not primarily a function of the presence of benzophenone, since this is removed by acetone treatment, but of the introduction of hydroperoxide into the polymer which is known to behave as an effective photo-oxidation initiator [15, 16]. It seems likely that hydroperoxide is also involved in the vinyl initiation process [10] and this is consistent with the fact that the absence of air during grafting leads to a less effective antioxidant graft.

$$P\cdot + O_2 \longrightarrow PO_2\cdot \xrightarrow{PH} PO_2H + P. \qquad (2)$$

Table 3 shows that there is a very sharp optimum in antioxidant behaviour with increasing grafting time in the presence of air. In the light of the above discussion, this is clearly due to the fact that destructive oxidative reactions initiated by benzophenone are in competition with the desired grafting process. In the presence of substantial amounts of hydroperoxide found by reactions 1(b) and (2), the antioxidant will be rapidly destroyed.

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Résumé—On montre que l'antioxydant acrylate de 3,5-di-*tert*-butyl-4-hydroxybenzyle, peut être greffé à la surface des polymères synthétiques. Les propriétés antioxydantes de ce composé "efficacement dispersé" sont largement supérieures à celles des composés de faible poids moléculaire contenant le même groupe fonctionnel. Même après extraction avec un bon solvant de l'antioxydant–monomère et du polymère dérivé, la stabilité des films de polymère à l'oxydation est bien plus grande que celle du polymère contenant l'antioxydant–monomère ou un polymère auquel on a incorporé un antioxydant par un procédé de fusion classique sans extraction. On suppose que l'activité optimale est due à la formation d'un grand nombre de courts greffons à la surface du polymère, obtenus par polymérisation à l'aide d'un photo-activateur tel que la benzophénone, qui agit également comme agent de terminaison des chaînes cinétiques.

Les antioxydants greffés superficiellement sont également des stabilisants efficaces à l'u.v. pour le polypropylène, alors que les antioxydants en bout de chaîne, incorporés dans le polymère par les techniques classiques, sont connus pour leur inefficacité.

Sommario—Si mostra che l'antiossidante 3,5-di-*tert*-butil-4-idrossibenzil-acrilato può venir innestato sulla superficie di artefatti in polimeri. L'attività antiossidante del risultante antiossidante "efficientemente disperso" è molto più elevata di quella di antiossidanti di basso peso molecolare contenenti i medesimi gruppi funzionali. Perfino dopo estrazione con un efficace solvente per il monomero antiossidante e polimero derivato, la stabilità all'ossidazione della pellicola di polimero è molto più grande di quella del polimero contenente il monomero antiossidante oppure polimero antiossidante incorporato mediante tecniche convenzionali di fusione senza estrazione. Si pensa che l'attività ottimale sia da collegarsi alla formazopne di frequenti innesti a catena corta nella superficie del polimero e la si ottiene mediante l'impiego di un fotoattivatore di polimerizzazuone del tipo benzofenone il quale termina pure le catene cinetiche. Si è pure trovato che gli antiossidanti innestati su superficie sono efficaci stabilizzatori per raggi formazione di frequenti innesti a catena corta nella superficie del polimero e la si ottiene mediante l'impiego di un fotoattivatore di polimerizzazione del tipo benzofenone il quale termina pure le catene cinetiche.

Si è pure trovato che gli antiossidanti innestati su superficie sono efficaci stabilizzatori per raggi ultravioletti per il polipropilene, a contrasto della normale inefficacia di antiossidanti terminatori di catena che vengono incorporati nel polimero con tecniche convenzionali.

Zusammenfassung—Es wird gezeigt, daß das Antioxidans 3,5-Di-*tert*.-butyl-4-hydroxibenzylacrylat auf die Oberfläche von Polymerteilchen aufgepfropft werden kann. Die Aktivität dieses "wirkungsvoll dispergierten" ("efficiently dispersed") Antioxidans ist wesentlich größer als die niedermolekularer Antioxidantien mit denselben funktionellen Gruppen. Selbst nach Extraktion des Pfropfcopolymeren mit einem Lösungsmittel für das monomere Antioxidans ist die Stabilität von Polymerfilmen gegenüber Oxidation wesentlich größer als die eines Polymeren, das das monomere Antioxidans oder dessen Polymeres in einer konventionellen Schmelztechnik ohne Extraktion beigemengt bekam. Ein Optimum an Aktivität wird zurückgeführt auf die Bildung kurzkettiger Pfröpflinge auf der Oberfläche des Polymeren. Dies wird erreicht durch Zusatz eines Photoaktivators für die Polymerisation wie z.B. Benzophenon, der die kinetische Kette beendet.

Diese an der Oberfläche gepfropften Antioxidantien sind auch wirksame u.v.-Stabilisatoren für Polypropylen im Gegensatz zu der normalen Unwirksamkeit kettenabbrechender Antioxidantien, die über die übliche Technik einem Polymeren zugemischt werden.