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Stabilization of polypropylene against γ-initiated oxidation: Stabilizer attack during radiolysis*

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The destruction of additives in γ-irradiated polypropylene films has been measured by infrared and electron spin resonance spectroscopy immediately after irradiation. Hindered amine or hindered phenol additives containing the ester group [>CH—O—C(=O)—CH$_2$~] were found to undergo ester destruction. Hindered amines containing the >CH~O—C(=O)—C— group were not attacked. Phenols showed extensive loss of the phenolic —OH group, presumably by peroxyl radical attack. Irradiation under conditions where peroxyl radicals were not formed or were scavenged competitively by the presence of a phenol prevented or reduced attack on the reactive ester linkage in hindered amines. It is possible that peroxyl radical attack is occurring at the —CH$_2$— group α to the carbonyl, which is known to be activated towards oxidation.

INTRODUCTION

The use of γ-irradiation to sterilize plastic medical equipment is increasing in popularity with the reduction in the use of toxic and environmentally destructive ethylene oxide–chlorofluorocarbon mixtures in commercial and hospital sterilization systems. In addition food preservation by γ-irradiation is in limited use with some of the foodstuffs being packaged in plastics.[1] All plastics undergo some degradation as the result of γ-irradiation. Polypropylene (PP) medical equipment is particularly sensitive to radiolysis. In most applications, PP needs to be protected against oxidation triggered by the γ-sterilization process through the use of

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stabilizers.[2-6] Although phenolic antioxidants can prevent post γ-embrittlement, an unacceptable yellowing occurs. Hindered amine stabilizers, based on 2,2,6,6-tetramethylpiperidine, are extremely effective without discoloration.[4-6] During polymer oxidation, all of these antioxidants undergo conversions essential to their stabilization function. However some stabilizers have been reported to be changed during the radiolysis process.[1,4,6] In particular, distearyl 3,3′-thiodipropionate, a 2,6-di-*tert*-butyl phenol and tris(2,4-di-*tert*-butylphenyl) phosphite were extensively attacked, with the former no longer detectable by gas chromatographic analysis of extracts from PP samples, whereas hindered amines based on 2,2,6,6-tetramethylpiperidine were partially attacked.

In this study the decomposition of secondary and tertiary hindered amines and of a hindered phenolic antioxidant during the γ-irradiation in air of polypropylene is reported. Specifically, the

paper focuses on stabilizer decomposition during the actual radiolysis stage and an attempt to identify changes, which may be detrimental to the subsequent stabilizer action, as well as formation of intermediates important for the post-irradiation stabilization, is made.

EXPERIMENTAL

Films (~50 μm) were pressed under nitrogen from isotactic PP (Himont Profax 6501) containing calcium stearate (0·1 wt%) and various additives. Irradiations were performed in an AECL Gammacell 220 (^{60}CO irradiation at 0·7 Mrad/h dose rate). Irradiation and oxidation products in the polymer and from additives in the films were examined by Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer 1500 with DTGS detector or Nicolet 7199 with a cooled MCT detector) and by electron spin resonance (ESR, Varian E4 spectrometer) as described previously.[6,7] IR spectra of films were measured within one hour of removal from the Gammacell or were stored at −78°C to stop post-irradiation oxidation until spectra could be measured.

Additives were compounded into the polymer in a melt extruder and then pressed into film. The commercial additives studied are shown in Fig. 1. Additives **I** to **II** are produced by Ciba-Geigy as Tinuvin 770, bis(2,2,6,6-tetramethyl-4-piperidinyl)decanedioate, Tinuvin 765, bis(1,2,2,6,6-pentamethyl-4-piperidinyl)decanedioate and Tinuvin 622, poly-[(4-hydroxy-2,2,6,6-tetramethyl-1-piperidine-ethenyl) butanedioate]. Additives **IV**, bis(2,2,6,6-tetramethyl-4-piperidinyl) 1,5-dioxaspiro [5.5] undecane-3,3-dicarboxylate and **V**, bis(1,2,2,6,6-pentamethyl-4-piperidinyl) 1,5-dioxaspiro [5.5] undecane-3,3-dicarboxylate are produced by ICI Americas as Topanex 500 H and 516 H. Additive **VI**, 2-hydroxy-4-octoxybenzophenone, is produced by American Cyanamid as UV531 and additive **VII** tetrakis-[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-propionate] methane, by Ciba Geigy as Irganox 1010. Formulations that were extensively studied are shown in Table 1.

RESULTS AND DISCUSSION

All of the hindered amines and the phenol stabilizer contain ester linkages (Fig. 1). These
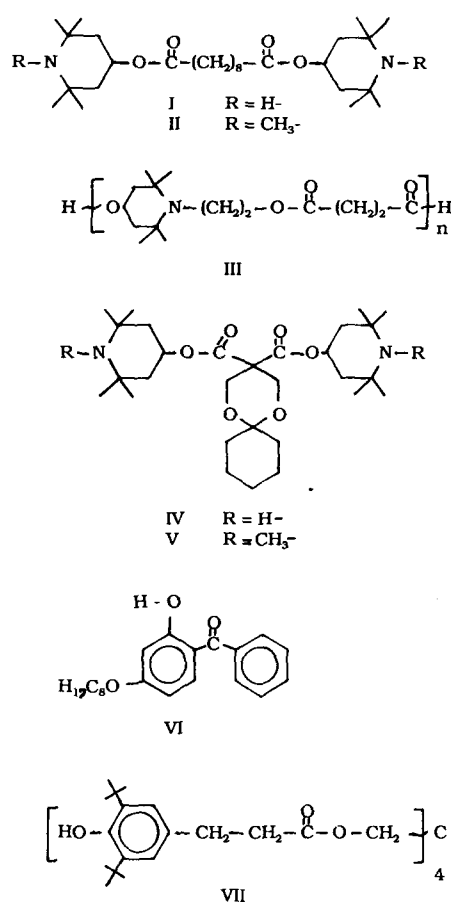
Fig. 1. Structures of additives.

ester groups can be readily identified and quantified at ~1740 cm^{-1} from FTIR difference spectra (Fig. 2, curves A and B).

Unstabilized and stabilized films were exposed to a normal γ-irradiation sterilization dose, 2·5 Mrad in air at ambient temperature (~40°C in the Gammacell). Immediately after irradiation, FTIR spectra of all samples showed an increase in both —OH species (~3400 cm^{-1} absorbance not shown) and carbonyl species (~1715 cm^{-1}, Fig. 2, curves C to G) as compared with the initial, non-irradiated samples. Amine stabilizers **I** to **V** and phenol **VII** all cause the same reduction in oxidation product formation as compared with additive-free control sample. In addition, all hindered amine formulations strongly suppressed the subsequent oxidation of the PP samples during storage at room temperature or accelerated ageing at 60°C (control brittle at ~5 days, amine samples at >200 days) without yellowing of the polymer.[4-6] All formulations containing the phenol **VII** yellowed noticeably.

IR and ESR spectroscopies indicated immediate changes in the additives themselves as a result

Table 1. Stabilized polypropylene film samples (stabilizer concentration)

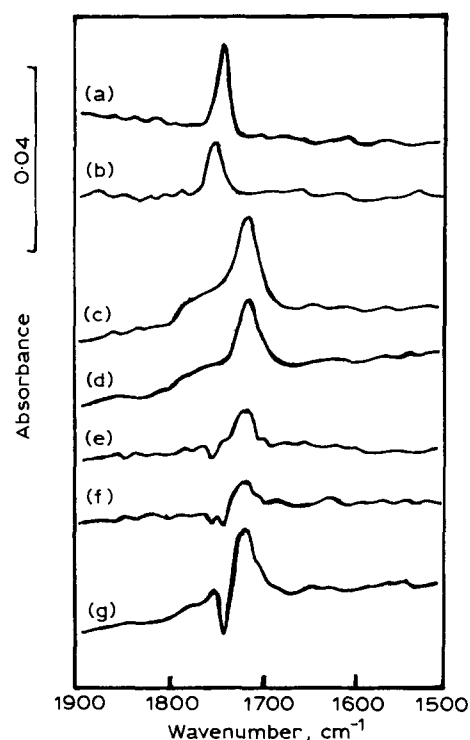| Additive[a]	1	2	3	4	5	6	7	8	9	10	11
I (770)		0·12					0·12		0·12		
II (765)			0·12							0·12	
III (622)				0·12							
IV (500)					0·12						0·12
V (516)						0·12					
VI (UV531)							0·12				
VII (1010)								0·12	0·12	0·12	0·12

[a] Structures are given in Fig. 1.

Fig. 2. IR changes upon γ-irradiation. FTIR spectra measured immediately after 2·5 Mrad γ-irradiation in air at 40°C. Spectra shown were obtained by spectral subtraction of the spectrum of each non-irradiated sample. Spectra not corrected for modest thickness variations (±20%). For sample description refer to Table 1. A, (Sample 2, non-oxidized) – (sample 1, non-oxidized); B, (sample 8, non-oxidized) – (sample 1, non-oxidized); C, (sample 1, 2·5 Mrad γ, air RT) – (sample 1, non-oxidized); D, (samples 5 or 6, 2·5 Mrad γ, air RT) – (samples 5 or 6, non-oxidized); E, (sample 8, 2·5 Mrad γ, air RT) – (sample 8, non-oxidized); F, (samples 9 or 10, 2·5 Mrad γ, air RT) – (sample 9 or 10, non-oxidized); G, (sample 2, 3, 4 or 7, 2·5 Mrad γ, air RT) – (sample 2, 3, 4 or 7, non-oxidized).

of γ-irradiation. However, it became apparent that additives were not being attacked in the anticipated ways. For example, nitroxides are key products formed from both secondary and tertiary hindered amines.[8] No nitroxide was detected by ESR immediately after irradiation

(< 1% of piperidyl groups oxidized). However, nitroxide did accumulate progressively over a 4–5 day period during oven ageing at 60°C, reaching ~50% and ~25% of the initial secondary and tertiary amine groups respectively.

Immediately after γ-irradiation, in air, FTIR difference spectra of samples 2–4 (additives I–III) showed a consistent negative absorption at about 1740 cm^{-1}, indicating some loss of the ester groups (Fig. 2, curve G). Samples 5 and 6 (additives IV and V) showed no loss in ester absorption (Fig. 2, curve D). Based upon experimental IR extinction coefficients, ester loss and percentage changes from the initial concentration were calculated and are listed in Table 2. No new products from ester scission could be identified by FTIR spectroscopy. This may result from the presence of the PP oxidation products masking any absorption of the additive decomposition products.

Various hindered amine stabilizer formulations for additives I, II, IV and V from 0·05 to 0·5 wt% were studied briefly. All showed the same ester loss (I and II) or retention (IV and V) as found at 0·12 wt%.

As expected, the phenol VII underwent extensive attack at the phenolic —OH site during irradiation as shown by the loss of its IR absorption at 3649 cm^{-1} (phenolic —OH), only 42% remaining immediately after γ-irradiation. No phenoxyl radicals were detected by ESR. However ester loss was also observed (Table 2, curve E). The ester group in VII absorbs at 1746 cm^{-1} and so its loss can be observed together with 1737 cm^{-1} loss upon γ-irradiation in air of samples containing both phenol VII and hindered amines I and II.

To explore the origin of ester loss from additives I–III, films were γ-irradiated under various conditions. The presence of the 2-hydroxybenzophenone (additive VI, sample 7)

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Table 2. Additive ester group loss[a]

Sample	Additive(s)	γ-Exposure conditions	Additive concentration mmol/kg	Ester group IR extinction coefficient in additive (cm^{-1} l mol^{-1})	$\underset{\parallel}{\overset{O}{-C-O-}}$ Loss	
					m. equiv/kg	%
2	I		2·4	498(1738)	2·4	50
3	II		2·35	548(1737)	2·7	57
4	III	2·5 Mrad, RT, air	4·4	420(1737)	3·9	89
7	I		2·4	498(1738)	2·4	50
	and VI		+3·7	—	—	—
5	IV	2·5 Mrad, RT, air	2·3	306(1734)	0	0
6	V		2·2	292(1734)	0	0
2	I	2·5 Mrad vacuum at −78°C or RT	2·4	498(1738)	0	0
3	II		2·35	548(1737)	0	0
4	III	+3 day RT vacuum	4·4	420(1737)	0	0
7	I		2·4	498(1738)	0	0
	and VI		+3·7	—	0	0
2	I	2·5 Mrad, vacuum −78°C	2·4	498(1738)	1·7	35
3	II	+ immediate air, RT	2·35	548(1737)	1·9	40
4	III	exposure	4·4	420(1737)	1·1	25
7	I		2·4	498(1738)	2·3	48
	and VI		+3·7	—	—	—
8	VII		1·02	448(1746)	1·7[b]	40[b]
9	I	2·5 Mrad, RT, air	2·4	498(1738)	1·9[c]	40[c]
	and VII		+1·02	448(1746)	1·2[b]	28[b]
10	II		2·35	548(1737)	1·3[c]	28[c]
	and VII		+1·02	448(1746)	1·0[b]	24[b]
11	I		2·30	306(1734)	0[c]	0[c]
	and VII		+1·02	448(1746)	2·1[b]	50[b]

[a] Initial additive concentration 0·12 wt%.
[b] Of ester function of phenol VII.
[c] Of ester function of the hindered amine.

failed to prevent loss of the ester functionality of additive I (Fig. 2, Table 1) although this combination is an extremely effective stabilizer for γ-irradiated PP.[6] γ-Irradiation under vacuum at −78°C or room temperature of samples containing additives I–III caused negligible loss of the ester absorption provided that these samples were stored for 3 days or longer under vacuum at room temperature after irradiation to allow the decay of PP macroalkyl radicals before admission of air. In contrast, admission of oxygen immediately after irradiation under vacuum at −78°C or 22°C caused a partial loss of ester (Table 2).

At −78°C, PP peroxyl radicals have been shown to be indefinitely stable by ESR spectroscopy, peroxyl radicals accumulating during irradiation but neither propagating nor terminating at this temperature.[7] When stabilized samples were irradiated at −78°C in air or oxygen and then suddenly warmed to room temperature, ester loss still occurred for additives I to III but to a lower degree than for samples irradiated at ambient temperature in air (*cf.* values shown in Table 2).

Although γ-induced reactions are normally statistically distributed through thin polymer samples, specific decomposition has been reported for alcohol and halide groups dispersed in hydrocarbons.[9] The absence of ester loss during γ-irradiation under vacuum precludes specific decomposition processes, such as reactions with electrons, ions, excited species or alkyl radicals.[10]

The absence of ester attack under vacuum irradiation and the lower loss when all peroxyl radicals were allowed to react simultaneously after accumulation at −78°C are consistent with peroxyl radical attack causing ester loss rather than attack by other radicals or excited species. If ester loss does result from peroxyl radical attack, no ester loss should result if peroxyl radicals can be competitively scavenged before ester attack can occur. It has been previously shown that peroxyl radicals are formed by γ-irradiation in air at −78°C, but can then be deactivated by subsequent reaction with nitric oxide gas at −78°C to give nitrates before they can propagate or terminate.[11] Although peroxyl conversion to nitrate occurred under these conditions, NO itself was found to attack all ester groups under

the long reaction conditions (24 h at −78°C) and so the results were ambiguous.

Hindered phenols are known to be highly effective peroxyl radical scavengers in oxidizing liquids and polymers.[12,13] This is consistent with the loss of the phenolic —OH ($3649\,cm^{-1}$ absorption) during irradiation. Samples containing the amines I or II together with phenol VII showed a reduction in the loss of the ester linkage absorbing at ∼$1738\,cm^{-1}$ in I and II (Fig. 2 and Table 2). In addition the ester linkage in VII absorbing at $1746\,cm^{-1}$ is partially protected by the presence of I and II but not by IV. Continuing studies with other proprietary phenols have shown an even more dramatic suppression of ester loss of amines I and II than when phenol VII was used.

From the results shown in Fig. 2 and Table 2, ester loss is consistent with PP peroxyl attack upon C—H groups adjacent to the carbonyl moiety of the ester group. This could then be followed by an oxidative scission reaction (reaction 1), although there is no evidence as to the nature of the scission products.

$$ \text{(1)} $$
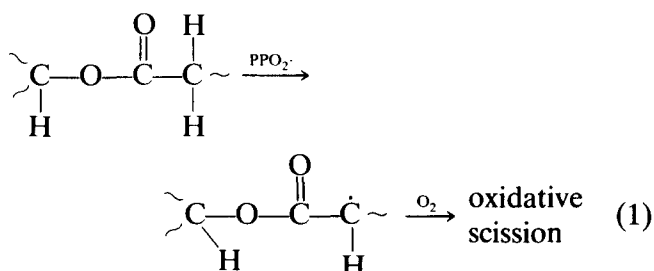
For additives IV and V, no abstractable CH groups exist α to the carbonyl moiety

$$ \text{(2)} $$
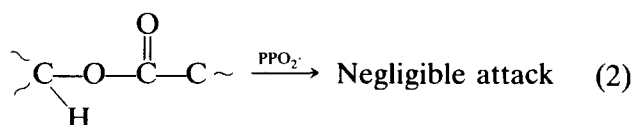
and ester loss could not occur by this proposed mechanism (reaction 2). This suggestion is consistent with the reported reactivity of CH groups adjacent to the ester function. The CH adjacent to the C(=O) moiety has been shown to be ∼5 times more reactive to attack by the same peroxyl radical (*tert*-butyl peroxyl radical) than is the CH bonded through oxygen to this moiety.[14] However, it is surprising that peroxyl

attack should occur on this ester site in the presence of a large excess of reactive *tert*- C—H sites in the polymer.

The percentage loss of the ester groups in additives I and VII is in fair agreement with the data of Horng and Klemchuk who measured overall additive disappearance at $0.5\,wt\%$.[4] From the work of Allen *et al.*, additive loss is concentration dependent, percentage loss increasing with decreasing additive level.[1] From the data on the additive VII presented here, this phenol apparently undergoes attack by peroxyl radicals at both the —OH sites (58% destruction) and the ester site (40% destruction).

Although ester loss occurs in γ-irradiated PP samples containing additives I–III, all of the hindered amine additives studied were highly effective in suppressing post-γ-irradiation oxidation in air at 60°C. Competing effects (such as additive scission at the ester link followed by grafting of these fragments to the polymer) presumably account for the sustained stabilization by additives I, II and III.

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