Mechanisms of Antioxidant Action: Photoantioxidant Activity of Polymer-Bound Hindered Amines. II. Bis Acrylates

S. AL-MALAIKA, A. Q. IBRAHIM,* M. J. RAO,† and G. SCOTT‡

Polymer Group, Department of Chemical Engineering and Applied Chemistry, Aston University, Aston Triangle, Birmingham, B4 7ET, U K

SYNOPSIS

1-Acryloyl-4-acryloyloxy-2,2,6,6-tetramethylpiperidine (AATP) has been covalently attached to polypropylene under conditions of reactive processing to give substantial concentrations of essentially 100% grafted antioxidant (AATP-B). Solution of the concentrates showed that at high concentration of grafted antioxidant some homopolymerized AATP was present and the polymer undergoes transient cross-linking during processing. Concentrates of bound AATP (AATB-B) when used as conventional additives for polypropylene are very effective photoantioxidants due to conversion to the related polymer-bound nitroxyl radicals by photosensitized oxidation. A typical commercial hindered phenol, Irganox 1076, when used at low concentration in combination with AATP-B also acts as a photosensitizer for nitroxyl formation. Unlike low molar mass-hindered piperidinoxyl, polymer-bound nitroxyls are effective thermal antioxidants that synergize very effectively with low concentrations of Irganox 1076.

INTRODUCTION

Antioxidants and UV stabilizers may be lost from polymers in the presence of extractive media that they contact in the course of their service life.[1,2] This is particularly significant in the case of packaging plastics in contact with oils and fats or in prostheses where bio-incompatible additives migrating into the body may cause severe toxicity problems.[3] A second reason why migration of antioxidants and stabilizers is important to their performance in polymers is that the physical loss of the protective agent from the polymeric component may substantially reduce its effectiveness. This is a cause of considerable concern in rubbers and plastics used in engineering components where extraction by mineral oils and synthetic fluids may reduce the lifetime of the article to that of the unprotected polymer.[4-6]

Polyolefin fibers and films are also susceptible to antioxidant and stabilizer loss, particularly when subjected to cleaning solvents and detergents, and these considerations have led in recent years[7] to considerable research activity directed to attaching antioxidants and UV stabilizers to polyolefins. One such approach has been described in an earlier communication[8] where it was shown that high levels of adduct formation can be achieved without homopolymerization by the use of bis-maleate esters of hindered piperidines. However, although levels of binding up to 70% can be achieved in this way without loss of photoantioxidant activity, the latter falls away at higher adduct yields. Although 70% adduct formation is quite satisfactory from a technological point of view for fibers and engineering polymers, it is not ideal for biomedical or packaging materials where it may be necessary in the future to show that no leaching of any additive can occur from the polymeric substrate.

It is known that acryloyl compounds graft to polymers to relatively low levels,[7] and the present

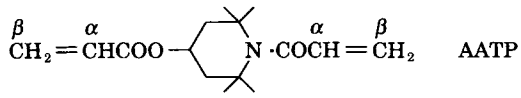
* Present address: Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.

† Present address: Albert Einstein College of Medicine, Yeshiva University, 1300 Morris Park Avenue, Bldg V, Rm 921, Bronx, NY 10461.

‡ To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 44, 1287–1296 (1992)
© 1992 John Wiley & Sons, Inc. CCC 0021-8995/92/071287-10$04.00

study is concerned with an alternative approach to substantivity that involves the attachment of the bifunctional hindered piperidine, 1-acryloyl-4-acryloyloxy-2,2,6,6-tetramethyl piperidine (AATP) to polypropylene under conditions of reactive processing:



AATP

EXPERIMENTAL

Materials

1-Acryloyl-4-acryloyoxy-2,2,6,6-tetramethyl piperidine (AATP) was prepared as follows[9]: 60 g of acryloylchloride in 800 dm^3 of dry toluene was added dropwise with stirring and ice cooling to 52 g of 2,2,6,6-tetramethylpiperidine and 70 g of triethylamine in benzene (1000 dm^3). The mixture was stirred for 1 h with ice cooling and then at room temperature for 8 h. Triethylamine hydrochloride was removed by filtration and the filtrate washed with aqueous sodium bicarbonate and dried over K_2CO_3. Toluene was removed under reduced pressure and the concentrate dissolved in hexane to precipitate byproduct impurities. The clear solution was evaporated, leaving a colorless, oily liquid.

Infrared analysis showed ester carbonyl at 1725 cm^{-1}, acrylamide carbonyl at 1640 cm^{-1}, and vinyl unsaturation at 1610 cm^{-1}. ^{1}H-NMR gave the following chemical shifts, δ (ppm): Acryloyl protons: α, 6.25–6.22(d); β, 6.20–6.14(d) and 6.5–6.42(d). Acrylamide: α, 5.90–5.72(d), β, 5.47–5.44(d) and 5.32–5.28(d). Methyl protons, 1.57(s), 1.54(s). Ring protons, (2) 2.30–2.20(d) and 2.06–1.90(t), (3) 5.32–5.20(t). ^{13}C (proton decoupled) NMR gave the following chemical shifts, δ (ppm): Acryloyl carbons: α, 125.7; β, 131.1. Acrylamide: α, 120.5; β, 128.2. Methyl carbons: 30 and 30.6. Ring carbons: (1) 55.6; (2) 43; (3) 66. Acryloyl carbonyl carbon: 167.1 and acrylamide carbonyl carbon, 163.5. Elemental analysis: C, 67.9 (67.7); H, 8.62(8.66), N, 520(5.27). Mass spectroscopy showed M^+, 265.9; M^+-15, 251, M^+-65, 210.9; M^+-88 (base), 178.0.

Polypropylene (PP) was supplied as an unstabilized powder by ICI as Propathene HF22 and was stored in a freezer at −20°C. The hindered amine, 2,2,6,6-tetramethyl-4-piperidinol and bis-2,2,6,6-tetramethyl-4-piperidyl sebacate, Tinuvin 770, and Irganox 1076 [*n*-octadecyl-3-(3 5-di-*tert*-butyl-4-hydroxyphenyl) propionate], were kindly donated by Ciba-Geigy. Cyasorb UV 531 (2-hydroxy-4-octoxybenzophenone) was kindly donated by American Cyanamid. These commercial antioxidants were used as obtained from the manufacturers. Dicumyl peroxide was recrystallized from methanol. Di-*tert*-butyl peroxide (Akzo Chemie) was used as received.

Melt Reactions of PP with AATP

PP and AATP were processed in a closed chamber of a Hampden RAPRA torque rheometer at 60 rpm. Torque and temperature were continuously recorded. AATP and radical generators were tumble mixed with PP before processing. Concentrates of 5, 10, and 20% were processed for 10 min using different initiators/AAPT molar ratios as indicated in Table I. Temperature conditions were chosen (150–180°C) to ensure that the initiator was essentially decomposed. For subsequent testing of polymer samples, containing the required concentration of AATP, were compression molded (180°C/2 min) into films (250 μm thick) in an electric press between stainless-steel glazed plates.

Measurement of Binding

Polymer films of AATP concentrates were hot Soxhlet extracted with dichloromethane until their IR spectra showed no further change (Perkin-Elmer Fourior transform infrared, FTIR model 1710). Thermal aging was carried out in individual cells of a Wallace oven with an air throughput of 85 L/h. The sunlamp blacklamp (S/B) UV exposure cabinet has been described previously.[10] Embrittlement times for each formulation was measured in triplicate with an accuracy of ±5%. ESR measurements were carried out on samples of standard dimensions on a JEOL JE-PE spectrometer using MnO containing thermally diffused Mn^{2+} ions as a marker. The radical concentration was estimated as described previously.[11] Gel permeation chromatography was carried out by the RAPRA Polymer Characterisation Centre.

Table I Molar Ratio of DCP to AATP

0	A	B	C	D	E	F	G	H
0.0	0.003	0.004	0.005	0.01	0.02	0.05	0.1	0.2

RESULTS AND DISCUSSION

Grafting of AATP to PP by Reactive Processing in the Melt

Unstabilized PP was melt processed with various concentrations of AATP at different molar ratios of dicumyl peroxide (DCP) to AATP, as indicated in Table I, for 10 min at 180°C, and the resultant films were extracted with dichloromethane until no further change could be detected in the infrared spectrum of the film.

Figure 1 compares FTIR spectra of a 10% concentrate of AATP in PP processed in the absence (a) and presence (b) of DCP before and after Soxhlet extraction. Absorptions due to AATP (acrylamide carbonyl, 1640 cm^{-1}; C=C, 1610 cm^{-1}; ester carbonyl, 1725 cm^{-1}) decreased dramatically when AATP was used as a conventional additive (processed in the absence of peroxide). By contrast, the samples processed with a radical generator showed the absence of the unsaturation peak (at 1610 cm^{-1}), whereas the ester carbonyl and amide carbonyl absorptions remained unchanged in intensity even after exhaustive extraction [see Fig. 1(b)]. Almost identical spectra were obtained from samples processed at higher concentrations of AATP and replacement of DCP by *tert*-butyl peroxide (TBP) gave very similar results. Figure 2 shows the variation in torque in the mixer as a function of processing time for several different concentrations of AATP at ratio C (Table I). In each case, there is an increase in torque between 1 and 3 min at 180°C, which becomes more marked as the concentration of AATP is increased. It was not found possible to process the 30% sample at all. A powdery product was obtained that could not be melted or incorporated into PP. The effect of decreasing temperature was to displace the torque peak to longer times (2.5 min at 170°C; 3.5 min at 150°C for 20% concentrates), but behavior was otherwise identical.

It is evident from Figure 2 that both cross-linking and chain scission reactions are occurring concurrently during the processing of AATP in PP in the presence of DCP. The former dominates the early stages of processing, but the latter determines the ultimate viscosity of the polymer. Figure 3 shows that increasing [DCP]/[AATP] decreases both the height of the torque peak and the ultimate viscosity of the polymer. However, provided processing was continued well past the torque peak, no difficulty was experienced in incorporating the concentrates into unstabilized PP as additives (see below).

It is not clear from the results reported above whether the additive is unextractable from the polymer because it is covalently bound or whether it is present as a polymerized but separate phase. This is important because it has been previously shown that macromolecular antioxidants made by the vinyl polymerization route are much less effective than are conventional additives containing the same functional group due to phase separation.[12]

Figure 4 shows a gel permeation chromatograph of DCP-treated PP in the presence and absence of AATP. In the presence of AATP and DCP (ratio C), the molecular weight distribution is sharpened compared to unprocessed PP, indicating some chain scission of the longer molecules. There was no evidence of a separate phase: DCP alone reduces M_w (see Table II) and sharpens M_w/M_n.

Solutions of 5, 10, and 20% AATP concentrates in xylene showed that there was a small amount of xylene insoluble material in the higher concentrates (see Table III). This material had similar properties to homopolymerized AATP (see below), and after filtration and repeated recrystallization of the PP, over 80% of the hindered amine was retained in the polymer as indicated from its IR spectrum (see Table III).

To investigate the mechanism of the grafting process, AATP was reacted with an equimolar quantity of methylcyclohexane (MCH) with DCP at ratio C in a sealed ampule at 180°C. Within seconds, the originally clear solution became a white solid. Heating of the solid in a vacuum oven at 80°C/10 h led to no loss of weight, indicating that all the MCH had reacted with the vinyl compound. Polymers with identical appearance and behavior were obtained using isooctane and dodecane as substrates. The polymer obtained was in all cases completely insoluble in the common organic solvents and decomposed at 350°C without melting. The reaction with MCH was repeated at 95°C/24 h. Low molar mass materials remained and were removed by hexane washing. About 15% of this product was found to be soluble in DCM, and GPC examination in THF indicated that the M_n was 8000. The product obtained at 180°C is clearly highly cross-linked and is chemically attached to the hydrocarbon substrate. The AATP–MCH reaction product was incorporated into PP by a conventional processing operation. After dissolving the polymer in xylene as described above, 80% of the additive was recovered as an insoluble residue and only 5% of the AATP moiety was found in the recrystallized PP.

It seems clear from the processing and model experiments that the acrylate polymer is essentially attached to the hydrocarbon substrates. Moreover, it is clear that all the hindered amine is attached

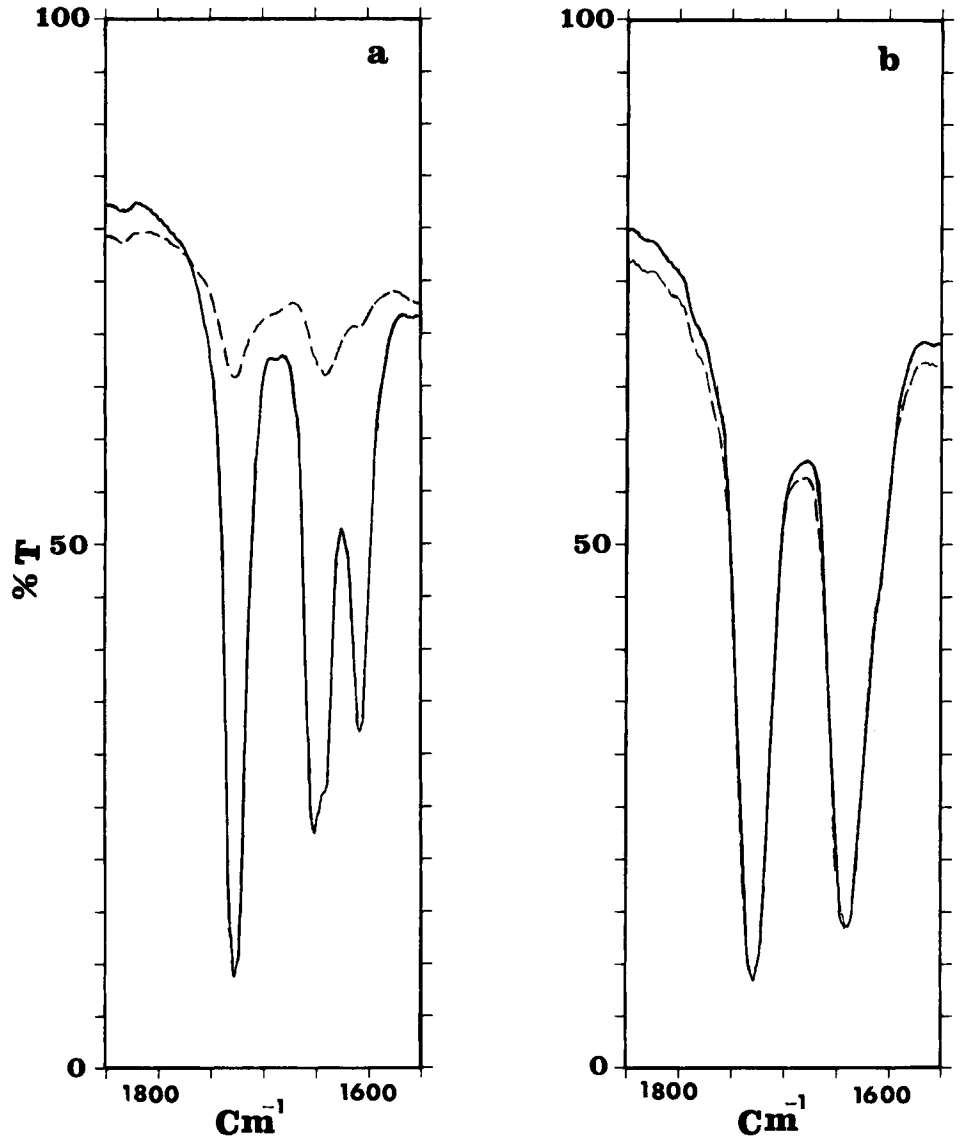


Figure 1 Fourier transform infrared spectra in the region 1850–1550 cm^{-1} of AATP concentrate (10%) in PP in the absence (a) and the presence (b) of DCP (molar ratio of DCP/AATP = 0.005) before (——) and after (– – –) exhaustive Soxhlet extraction.

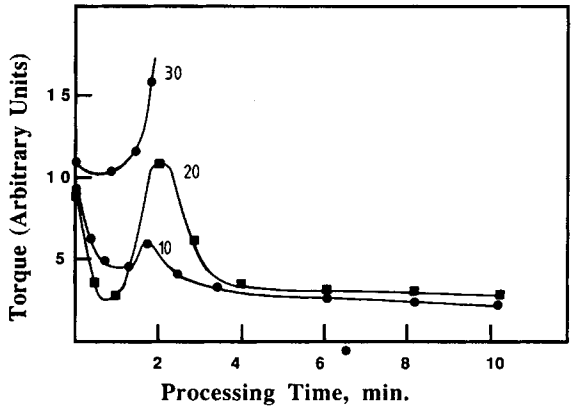


Figure 2 Effect of concentration of AATP (numbers on curves, in %) on the torque developed during melt processing of PP in the presence of DCP (molar ratio of DCP/AATP = 0.005) at 180°C.

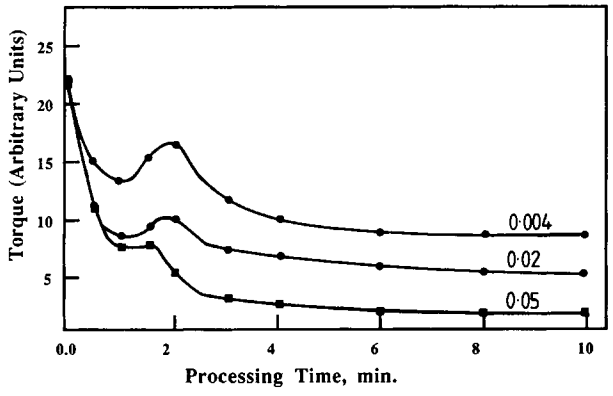


Figure 3 Effect of concentration of DCP (numbers on curves expressed as molar ratio of DCP/AATP) on torque developed during melt processing of PP in the presence of 10% AATP at 180°C.

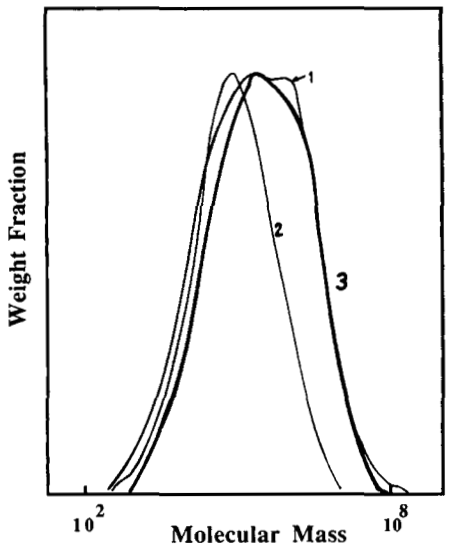


Figure 4 Molecular mass distribution of PP samples: (1) unprocessed PP, (2) PP processed in the presence of 1.5×10^{-4} mol/100 g DCP, and (3) PP processed in the presence of 10% AATP in the presence of DCP (molar ratio of DCP/AATP = 0.005).

through one or other of the vinyl groups and that the remaining vinyl group is involved partly in graft polymerization and partly in cross-linking of PP, since a negligible amount of unsaturation remained in the polymer after the reaction. On average, then, more than one AATP vinyl group is attached to the polymer, thus accounting for the torque peak during processing. The effect of processing beyond the torque peak is to reduce the M_w/M_n by preferentially breaking the high molar mass cross-linked polymer. In the work described in the next section, no problems were encountered in incorporating the concentrates as additives in unstabilized polypropylene provided the torque returned to the lower stationary level during its preparation.

Photostabilization of PP with AATP-Bound (AATP-B) Concentrates

A 10% concentrate of AATP-B in polypropylene made using [TBP]/[AATP] ratio C was diluted to 0.4 g/100 g in unstabilized PP. Part of the film was exhaustively extracted, and as indicated above, no significant amount of hindered amine was extracted. When the films were exposed to UV light, the unextracted sample embrittled at 2150 h, whereas the extracted sample embrittled in 400 h (see Table IV). AATP as an additive is significantly inferior to AATP-B before extraction, but on extraction, which removed the additive almost completely, it was similar to the unstabilized control. Poly(AATP) had little activity as a photoantioxidant even without extraction. The very low activity of the exhaustively extracted AATP-B sample is surprising in the light of the fact that the AATP is not lost from the polymer by extraction. It is known[13-16] that hindered piperidines themselves are not photoantioxidants, but, rather, the derived nitroxyl radicals formed by oxidation. It seemed important, therefore, to compare the rate of nitroxyl radical formation in the samples listed in Table IV during photooxidation. Figure 5 shows that when AATP is used as an additive, nitroxyl radical generation begins very quickly and is very substantial within the unstabilized lifetime of the film (90 h). AATP-B(U) behaves similarly but the nitroxyl concentration rises to a higher level. In the case of AATP-B(E) and poly(AATP), nitroxyl generation is much slower. It seems clear then that extraction has removed a necessary reagent for the formation of nitroxyl. The possibility that this might be a small amount of unreacted AATP was investigated by adding a small molar proportion (5 mol %) of AATP to the fully extracted masterbatch. The results, given in Table V, show clearly that a very small amount of AATP does fulfill the function envisaged.

AATP was incorporated into PP as an additive and exposed to UV with concomitant formation of

Table III Gel Content of AATP Concentrates in PP

AATP Added to PP (%)	Gel Content (%)	AATP Retained in PP After Recrystallization
5	0	> 90
10	5	90
20	12	80

Table II GPC Characteristics of DCP-Treated PP

Sample	$10^{-4} M_n$	$10^{-5} M_w$	$10^{-6} M_z$	M_W/M_n
Unprocessed PP	4.27	4.48	2.63	10.48
DCP at ratio C	4.4	1.80	0.70	4.1
10% AATP, DCP at ratio C	6.52	4.84	2.26	7.43

Table IV UV Embrittlement Times of PP Films Containing 1.51×10^{-3} mol/100 g (0.4 g/100 g) of Hindered Piperidines

Sample	Embrittlement Time (h)
Control, no additive	90
AATP additive, U	1900
AATP additive, E	150
AATP-B, U	2150
AATP-B, E	400
Poly(AATP), U	250
Tinuvin 770	1400

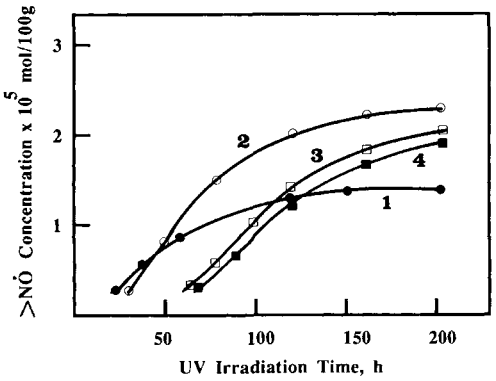


Figure 5 Effect of UV irradiation on nitroxyl radical development in PP samples containing 0.4% AATP diluted from 10% AATP concentrate processed in the presence of 0.005 DCP/AATP molar ratio, 1 PP processed with 0.4% AATP as an additive, 2 AATP-B(U), 3 AATP-B(E), 4 Poly(AATP).

nitroxyl in the first 5 h of UV exposure. Kurumada et al.[17] have reported that 1-acryloyl-4-benzoyl 2,2,6,6-tetramethylpiperidine is almost twice as effective as a UV stabilizer than is the 1-acetyl analog. They suggest that the saturated amides are converted to nitroxyl by reaction with "oxyl" radicals derived from hydroperoxides. This would account for the slower formation of nitroxyl shown in Figure 5. The mechanism of this process is being investigated and will be reported in a later communication.

Synergism between AATP-B and Conventional UV Stabilizers and Antioxidants

Table VI reports the cooperative photoantioxidant effects observed between a fully extracted AATP-B concentrate and a typical UV absorber, UV531, and a hindered phenol, Irganox 1076, thermal antioxidant. It is clear that both antioxidants synergize powerfully with the fully bound AATP. Particularly surprising is the effect of the hindered phenol, Irganox 1076. At concentrations where it has no UV stabilizing effect alone, it increases the effectiveness of AATP-B by over one order of magnitude. This does not appear to be normal synergism since the optimal amount of thermal synergist required is quite extraordinarily low. Figure 6 shows that the concentration of nitroxyl in the sample increases most rapidly and to a higher level in the PP film

Table V UV Embrittlement Times of PP Films Containing AATP in Bound and Unbound Form

Sample	Concentration (g/100 g)	Embrittlement Time (h)
AATP additive	0.02	320
AATP-B, E	0.4	400
AATP-B, E + AATP additive	0.4 + 0.02	1850
Poly(AATP) + AATP additive	0.4 + 0.02	550

Table VI Photoantioxidant Synergism between AATP-B and Conventional Stabilizers

Sample	Concn (g/100 g)	UV Embrittlement Time (h)
No additive	—	90
AATP-B(E)	0.4	150
AATP-B(E) + Irganox 1076	0.4 + 0.04	1980
AATP-B(E) + Irganox 1076	0.4 + 0.1	1600
AATP-B(E) + Irganox 1076	0.1 + 0.4	650
AATP-B(E) + UV531	0.4 + 0.1	2050
Irganox 1076	0.1	160
Irganox 1076	0.04	100
UV531	0.1	350

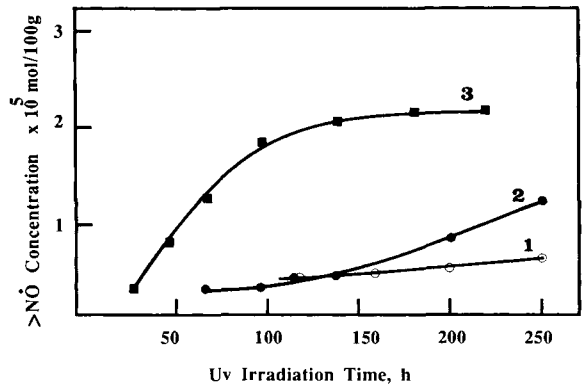
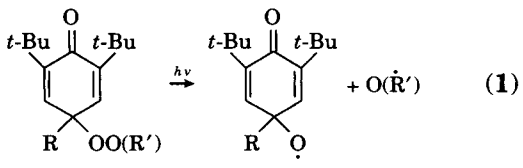


Figure 6 Effect of UV irradiation on nitroxyl radical development in PP samples; processed with Irg. 1076 + AATP-B at ratio of 0.25 (curve 1); UV531 + AATP-B at ratio of 0.25 (curve 2), and Irg.1076 + AATP-B at ratio of 0.1 (curve 3).

with the lowest [1076]/[AATP-B] ratio, and, indeed, no nitroxyl signal was recorded up to 250 h of UV exposure at a [1076]/[AATP-B] ratio of 4. The growth of nitroxyl in the sample containing 0.04 g Irganox 1076 (curve 1) is very similar to that of unextracted AATP-B in Figure 5. The hindered phenol at very low concentration thus appears to sensitize the oxidation of AATP to nitroxyl. The mechanism of this process is not at present fully understood, but it is clear that at higher concentration Irganox 1076 is actually retarding the same process. It is known that oxidation products of hindered phenols are potent sensitizers for photooxidation. Of these, the peroxydienone (**I**) is an early oxidation product[18] and the radicals produced by phytolysis (reaction 1) are clearly potential initiators for the oxidative transformation of the *N*-acyl piperidine to the corresponding nitroxyl discussed above:



(I) (1)

where R = alkyl or H.

Figure 6 shows that UV531, like the hindered phenol at the same concentration, actually retards nitroxyl formation. It seems likely that the main function of UV531 is to extend the lifetime of the polymer long enough for the critical concentration[19] of nitroxyl to develop by hydroperoxide photolysis. Table VI shows that the embrittlement time of PP containing 0.1% of UV531 alone was 350 h, and this is much longer than the time necessary for the formation of a substantial nitroxyl concentration in the polymer (see Fig. 6).

AATP-B as a Thermal Antioxidant

AATP-B, like low molar mass hindered piperdines, has no activity as a thermal antioxidant for polypropylene (air oven at 140°C) (see Table VIII), but preaging in air at 85°C was found to considerably improve high-temperature thermal aging. Table VII shows that this is associated with the formation of nitroxyl radicals in the polymer. In view of the profound synergism observed between AATP-B and a hindered phenol in photooxidation, it was of some interest to see whether a similar effect was observed in thermal oxidation. Table VIII compares the antioxidant activity of Irganox 1076 and AATP-B both alone and in combination. It is clear that at relatively low concentration the phenolic antioxidant converts AATP-B to a very powerful thermal antioxidant. The synergistic effect (the difference between the actual effect and the sum of the effects of the individual components[20]) in the case of the lowest [1076]/[AATP-B] ratios is well over 1000%. Although much of this activity is lost on solvent extraction due to removal of the Irganox 1076, preaging at 85°C restores a proportion of it, suggesting that a small amount of AATP-B is converted to antioxidant under these conditions.

The development of nitroxyl radicals during oven aging at 140°C is shown in Figure 7 for two of the combinations in Table VIII. Nitroxyl was observed earlier ($\approx$ 200 h) in the sample with the higher (0.1/0.2) [1076]/[AAPT-B] ratio, but the highest antioxidant activity and most effective synergism was obtained from the sample with the lower ratio (0.1/0.4). It is clear, then, that AATP-B is a reservoir from which the effective antioxidant, the nitroxyl radical, is formed by oxidation. The phenolic antioxidant performs two conflicting roles. In the first place, it protects the polymer long enough for the critical concentration of nitroxyl to develop, but at the same time it inhibits the formation of nitroxyl by scavenging the reactive species (e.g., oxyl radicals) that bring this about. Optimal synergism therefore occurs at low hindered phenol/AATP ratios.

DISCUSSION

The very high antioxidant activity of nitroxyl radicals reported in this study has not been previously

Table VII Effect of Low-Temperature Preaging on the High-Temperature Heat Stability of PP-containing AATP-B (1 g/100 g)

	Time of Preaging at 85°C (h)				
	0	100	200	400	500
Embrittlement time at 140°C (h)	0.5	3	8	15	15
[N—O·]generated in sample by preaging (10^6 mol/100 g)	Too low to measure quantitatively			3	3.4

Table VIII Synergism between AATP-B and Irganox 1076 in PP at 140°C

Antioxidant	Concentration (g/100 g)	Time to Embrittlement (h)			Synergism[20] (%)
		Unextracted	Extracted	Extracted After Preaging 48 h/85°C	
None	—	0.5	0.5	—	—
1076	0.02	5.0	1.5	—	—
1076	0.1	95	2	2	—
1076	0.2	160	2	3	—
1076	0.4	260	2	3	—
1076	1.0	500	2	4	—
AATP	0.4	0.5	0.5	—	—
AATP-B	0.2	0.5	0.5	—	—
AATP-B	0.4	0.5	0.5	—	—
Tinuvin 770	0.4	0.5	0.5	—	—
AATP-B + 1076	0.2 + 0.02	50	1.5	3	1200
AATP-B + 1076	0.2 + 0.1	650	5.5	15	787
AATP-B + 1076	0.2 + 0.2	750	4.4	35	570
AATP-B + 1076	0.4 + 0.1	950	—	30	1051
AATP-B + 1076	0.4 + 0.2	1200	—	65	850
AATP-B + 1076	0.4 + 0.4	1300	—	20	600
AATP-B + 1076	0.4 + 1.0	1500	—	5	400

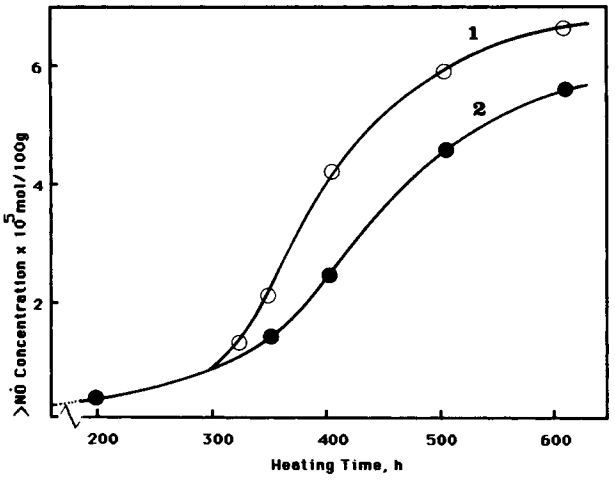
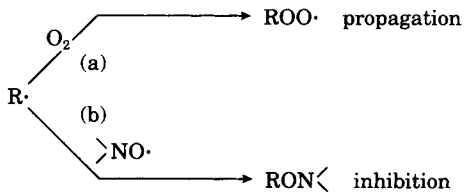


Figure 7 Effect of oven aging (at 140°C) on nitroxyl radical development in PP samples processed with 0.4% AATP-B + 0.1% Irg.1076 (curve 1) and 0.2% AATP-B + 0.1% Irg.1076 (curve 2).

noted in the literature of the low molar mass hindered amines. Thus, for example, bis-(2,2,6,-tetramethyl-4-piperidinyl) sebacate (Tinuvin 770) has virtually no thermal antioxidant or melt-stabilizing activity in the saturated hydrocarbon polymers.[14,21] The explanation normally advanced to account for the lack of activity of the derived nitroxyl radicals as thermal antioxidants in a high-temperature air oven test is that, under these conditions, the alkylperoxyl radical concentration is high and the alkyl radical concentration relatively low. However, alkylperoxyl is not trapped by nitroxyl, and in liquid hydrocarbons, the concentration of alkylperoxyl remains unchanged when nitroxyl is introduced.[22] An alternative way of looking at this is that when nitroxyl reacts with an alkyl radical it does so in competition with oxygen, and since the rate constant for reaction (2a) is generally higher than that for (2b),[22,23] inhibition will occur only at low oxygen pressures or when the alkyl radical is particularly stable, as in the case of olefinic polymers[21,22]:



(2)

However, Denisov[24] has pointed out that in solid polymers the concentration of oxygen is not only intrinsically lower than in liquid hydrocarbons, but under steady-state conditions in an autoxidizing polymer, it is limited by the rate of diffusion of oxygen through the polymer, again a much slower process than in liquid hydrocarbons. It is not surprising, then, that at high temperatures, as under photooxidative conditions, when the rate of initiation is high, the oxygen concentration will be low and reaction (2b) will be able to compete with (2a).[21] It must be concluded, then, that the lack of thermal antioxidant activity of the low molar mass hindered amines in an air oven results from the physical loss of the additives and of their derived nitroxyls from the polymer by volatilization under these conditions. Chemical attachment of nitroxyl precursors to the polymer backbone then appears to be a desirable objective not only from the standpoint of removing the hazard of migration of the potentially toxic materials into foodstuffs and directly or indirectly into biological processes, but also because it allows the antioxidant to achieve its full potential as a catalytic chain-breaking antioxidant.[25]

CONCLUSIONS

1. 1-Acryloyl-4-acryloyloxy-2,2,6,6-tetramethyl piperidine (AATP) can be chemically attached to polypropylene by reactive processing to give antioxidant concentrates from which the antioxidant cannot be physically removed.
2. Concentrates obtained in this way are effective photoantioxidants for polypropylene in unextracted form. However, extraction appears to remove a small amount of a sensitizer (possibly an *N*-acrylate) that facilitates the formation of nitroxyl by oxidation of AATP-B.
3. A hindered phenol (Irganox 1076) also sensitizes the photooxidation AAPT-B to nitroxyl and acts as a powerful synergist in photoinhibition.
4. A UV absorber (UV531) synergizes with AATP-B, but it seems likely that this is due to its ability to extend the life of the polymer until nitroxyl is present in a critical concentration.
5. AATP-B, like the low molar mass hindered piperidines, has no thermal antioxidant activity, but unlike the latter, it is converted to a powerful thermal antioxidant by thermal oxidation in the presence of a very small amount of hindered phenol. The latter probably protects the polymer from thermal oxidative degradation until the critical concen-

tration of polymer-bound nitroxyl has been formed.

We are grateful to the Federal Government of Nigeria and the Bauchi State Government for financial support to one of us (A. Q. I.). We are also grateful to Ciba-Geigy SA for providing samples of Tinuvin 770 and Irganox 1076 and to American Cyanamid for donating a sample of Cyasorb UV531.

REFERENCES

1. D. K. Thomas, *Developments in Polymer Stabilisation-1,* G. Scott, Ed., Applied Science, London, 1979, p. 137 *et seq.*
2. G. Scott, *Developments in Polymer Stabilisation-4,* G. Scott, Ed., Applied Science, London, 1981, p. 181 *et seq.*
3. D. F. Williams, *Biocompatability of Orthopaedic Implants,* Vols. I and II, CRC Press, Boca Raton, FL, 1982.
4. O. Ajiboye and G. Scott, *Polym. Deg. Stab.,* **4,** 397 (1982).
5. K. B. Chakraborty, G. Scott, and S. M. Tavakoli, *Advances in Elastomers and Rubber Elasticity,* J. Lal and J. E. Mark, Eds., Plenum Press, New York, 1986, p. 189.
6. G. Scott and S. M. Tavakoli, *Polym. Deg. Stab.,* **19,** 43 (1987).
7. D. Munteanu, *Developments in Polymer Stabilisation-8,* G. Scott, Ed., Elsevier Applied Science, London, 1987, p. 179 *et seq.*
8. S. Al-Malaika, A. Q. Ibrahim, and G. Scott, *Polym. Deg. Stab.,* **22,** 233 (1988).
9. Sankyo, Br. Pat. 1,296,245 (1970).
10. S. Al-Malaika, E. O. Omikorede, and G. Scott, *J. App. Polym. Sci.,* **33,** 703 (1987).
11. R. Bagheri, K. B. Chakraborty, and G. Scott, *Polym. Deg. Stab.,* **4,** 1 (1982).
12. B. W. Evans and G. Scott, *Eur. Polym. J.,* **10,** 453 (1974).
13. V. Ya Shlyapentokh, V. B. Ivanov, O. M. Khoostach, A. B. Shapiro, and E. G. Rozantsev, *Kunst Fortschr.,* **B2,** 25 (1975).
14. K. B. Chakraborty and G. Scott, *Polymer,* **21,** 252 (1980); R. Bagheri, K. B. Chakraborty, and G. Scott, *Polym. Deg. Stab.,* **4,** 1 (1982).
15. D. J. Carlsson, A. Garton, and D. M. Wiles, *Developments in Polymer Stabilisation-1,* G. Scott, Ed., Applied Science, London, 1979, p. 246 *et seq.*
16. N. S. Allen, *Polym. Photochem.,* **1,** 43 (1981).
17. T. Kurumada, H. Ohsawa, T. Fujita, T. Toda, and T. Yoshioka, *J. Polym. Sci. Polym. Chem. Ed.,* **23,** 2747 (1985).
18. J. Pospisil, *Developments in Polymer Stabilisation-1,* G. Scott, Ed., Applied Science, London, 1979, Chap. 1.
19. Y. A. Shlyapnikov, *Developments in Polymer Stabilisation-5,* G. Scott, Ed., Applied Science, London, 1982, Chap. 1.
20. G. Scott and M. F. Yusoff, *Polym. Deg. Stab.,* **2,** 309 (1980).
21. G. Scott, *Developments in Polymer Stabilisation-7,* G. Scott, Ed., Elsevier Applied Science, London, 1984, Chap. 2.
22. S. A. Maslov and G. E. Zaikov, *Developments in Polymer Stabilisation-8,* G. Scott, Ed., Elsevier Applied Science, London, 1987, Chap. 1.
23. V. Ya Shlyapintokh and V. B. Ivanov, *Developments in Polymer Stabilisation-5,* G. Scott, Ed., Applied Science, London, 1982, Chap. 3.
24. E. T. Denisov, *Developments in Polymer Stabilisation-5,* G. Scott, Ed., Applied Science, London, 1982, Chap. 2.
25. S. Al-Malaika, A. Q. Ibrahim, and G. Scott, Br. Pat. Appl. pending.

Received October 18, 1989
Accepted January 1, 1990