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Aromatic secondary amines as antioxidants for polyolefins: Part 1—9,10-Dihydroacridine (acridan) derivatives

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A series of five acridan derivatives was studied as antioxidants in the thermoxidation of polypropylene. None induced major retardation in the polymer oxidation. Two of them, 9,9-diphenyl- and 9,9-dimethyl-acridans, showed synergism when used in the presence of dilauryl thiodipropionate (DLTP). In order to understand the role of the intermediate nitroxides during the oxidation, 9,9-diphenylacridan-1-oxyl was prepared and studied in the presence and in the absence of DLTP. The main reactivity of the nitroxide is explained through disproportionation and hydrogen abstraction reactions and formation of alkylated hydroxylamine, where the alkyl group is the polymer chain.

INTRODUCTION

Hindered secondary amines, mainly tetramethylpiperidine derivatives (HALS), and aromatic secondary amines are widely used in thermo- and in photostabilisation of polyolefins. The mechanism of their stabilisation is rather complicated and not yet completely elucidated, involving several species such as alkyl, alkylperoxy, alkoxy and nitroxide radicals. Many unclear aspects concern, in fact, the role of the last compounds.[1–5]

When high concentrations of alkylperoxy radicals are formed during the oxidation, secondary aromatic amines (DH) operate as chain-breaking donors (CB-D) according to the mechanism shown in eqn (1):

$$ROO^{\cdot} + DH \rightarrow ROOH + D^{\cdot} \qquad (1)$$

CB-D compounds, which donate a labile hydrogen to $ROO^{\cdot}$ giving rise to a stable (non-propagating) radical, are used as antioxidants. Radicals $D^{\cdot}$ must have a very low hydrogen abstraction power, in order to avoid the formation of new active radicals and must transform by disproportionation or recombination into non-reactive products. Experimental results demonstrate that radicals $D^{\cdot}$ coming from aromatic amines and alkylated phenols are converted to higher molecular weight products during their antioxidant action.[6–8]

For secondary aromatic amines and phenols, it has been demonstrated that their consumption rate during stabilisation is directly proportional to their concentration and the rate of oxygen absorption increases, during the induction period, in proportion to the antioxidant concentration. This means that a large quantity of the antioxidant is consumed in undesirable reactions.[7,9–11]

Secondary hindered amines are not effective as antioxidants when used at high temperature; however, when used at low or moderate temperature they behave as stabilisers, involving the formation of the corresponding nitroxides. The antioxidant activity of nitroxide radicals strongly depends on their molecular structure and on the conditions of oxidation,[12–14] and, it is commonly accepted that they work through the intermediate formation of the corresponding hydroxylamines or alkylated hydroxylamines. The hydroxylamines may readily regenerate the

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nitroxides by acting as very good hydrogen donors and, thus, as chain-breaking antioxidants. The evolution of the alkylated hydroxylamines is a more complicated task, in fact, they can be converted into the corresponding amines or nitroxides. Yasina *et al.*[14] showed that the real inhibitor in polypropylene thermoxidation is not the stable 2,2′,4,4′-tetramethoxydiphenyl nitroxide, but rather its precursor amine. For experiments carried out at 200°C, this radical converts into the corresponding amine, and the formation of one molecule of amine requires two molecules of nitroxide. This result could be easily explained through a disproportionation process where one molecule of amine and one molecule of quinoneimine *N*-oxide is formed.[15]

Hydroperoxides, which are the main chain-branching products formed during polymer oxidation, may be decomposed by aliphatic sulphides with formation of a negligible quantity of radicals. Sulphides give a synergistic effect when used in mixture with aromatic amines and phenols. However, they may be antagonists when used together with secondary hindered amines. The antagonism, in this case, may be attributed to the inhibition of the nitroxide formation since the hydroperoxides are decomposed by the sulphides.[16,17]

In the literature, there is little information on the antioxidant activity of 9,10-dihydroacridine derivatives (acridans) and their mixture with aliphatic sulphides. In the present paper the authors describe, by kinetics of oxygen absorption, the efficacy of a series of acridans and of 9,9′-diphenylacridan-1-oxyl in the thermoxidation of polypropylene, in the presence and in the absence of dilauryl thiodipropionate (DLTP), in the light of the above-mentioned literature reports.

EXPERIMENTAL

Melting points are uncorrected. UV spectra were recorded on a Perkin–Elmer spectrophotometer. IR spectra were recorded using a Nicolet Fourier Transform Infrared 20-SX spectrophotometer equipped with a Spec. Tech 'DRIFT' Collector (1% of sample in KBr). ^{1}H NMR spectra were recorded on a Gemini Varian 200 MHz spectrometer using TMS as internal standard. ESR spectra were recorded on a Varian E-4 spectrometer interfaced with a computer and with a ruby in the cavity as reference. Mass spectra were recorded on a Varian 112 S spectrometer.

Isotactic polypropylene powder (Profax 6501) was purchased from Himont. 9(10*H*)-Acridone **4**, its *N*-methyl derivative **5**, and Bu^{t}OOH were purchased from Aldrich. Dilauryl thiodipropionate was purchased from Enichem. Tetrahydrofuran (THF) and diethyl ether for Grignard reagents were dried according to the usual manner.[18]

Synthesis of 9,10-dihydro-9,9-diphenyl-acridine (1) and 9,9-dimethyl-acridine (2)

Compounds **1** and **2** were prepared following the reactions sequence described by Goldstein and Huser.[19] MeMgI, prepared according to the usual method under nitrogen, starting from 2·4 g (0·10 mol) of magnesium turnings and 21·3 g (0·15 mol) of MeI in diethyl ether (50 ml), was added to a stirred solution of methyl *N*-phenylanthranilate[20] (4·54 g, 0·02 mol in ml of THF) at room temperature in nitrogen. After 30 min the solution was refluxed for 1 h and then, after cooling at room temperature, poured into 10% aqueous NH_4Cl solution. The organic layer extracted with diethyl ether (3 × 100 ml) was dried on Na_2SO_4 and evaporated to dryness. The residue, containing the crude dimethyl-(*p*-aminophenyl)phenyl carbinol, was heated and stirred at 100°C for 30 min in acetic acid (30 ml) and *p*-toluensulfonic acid (0·10 g). The product precipitated after cooling was filtered off and washed with ligroin 60–80°C yielding 3·7 g of 9,9-dimethyl-acridan **2** (88% yield): m.p. 124–5°C from methanol (Ref. 21, 125–6°C); IR, ν (cm^{-1}), 3359 (NH), 1605, 1578; NMR, $CDCl_3$, δH, 1·66 (6H, s, 2 Me), 6·12 (1H, br s, NH), 6·69 (2H, d, arom), 6·9 (2H, d, arom), 6·9 (2H, t, arom), 7·11 (2H, pseudo-t, arom), 7·392 (2H, pseudo-q, arom); mass spectrum (*m/e*) for $C_{15}H_{15}N$: calculated: 209·28; found: 209 (M^+, 15%), 194 (100), 97 (15), 84 (16).

9,9-Diphenylacridan (**1**) was prepared in the same way, but using PhMgBr, prepared in THF, as Grignard reagent. Compound **1** was obtained in 74% yield, m.p. 245–6°C from ethanol (Ref. 22, 243–4°C); IR, ν (cm^{-1}), 3388 (NH), 1602, 1580; NMR, $CDCl_3$, δH, 6·28 (1H, br s, NH), 6·7–7·1 (9H, m, arom), 7·1–7·3 (9H, m, arom); mass spectrum (*m/e*) for $C_{25}H_{19}N$: calculated:

333·41; found: 333 (M^+ 24·5%), 257 (23), 256 (100).

Synthesis of 9,9-diphenyl-*N*-methylacridane (3)

Dimethyl sulphate (15 ml) was added over 30 min to 9,9-diphenylacridan (6·66 g, 0·02 mol) suspended in 40% aqueous NaOH (80 ml) at 60°C under vigorous stirring, and then heated at 100°C for 1 h. After cooling, water (300 ml) was added to the reaction mixture and the white precipate was filtered off. The separated product was dissolved into 20 ml of benzene and the solution, dried on Na_2SO_4, was chromatographed on a column of silica gel eluting with cyclohexane/ethyl acetate at a ratio of 9:1. From the first eluate compound **3** was isolated in 50·5% yield (3·5 g): m.p. 162–3°C; IR, ν (cm^{-1}), 1591; NMR, $CDCl_3$, $^\delta$H, 3·32 (3H, s, NMe), 6·8–7·0 (9H, m, arom), 7·18–7·35 (9H, m, arom). Mass spectrum (*m/e*) for $C_{26}H_{21}N$: calculated: 347·44; found: 347 (M^+, 47%), 270 (100), 254 (41), 135 (25). Analysis for $C_{26}H_{21}N$: calculated: C, 89·87; H, 6·1; N, 4·03: found: C, 89·85; H, 6·15; N, 4·01.

Synthesis of 9,9-diphenylacridan-1-oxyl (6)

9,9-Diphenylacridan (1 g) dissolved in benzene (40 ml) and Bu^{t}OOH (1 g) dissolved in benzene/ethanol at a ratio of 1:1 were mixed at room temperature. PbO_2 (1 g) was then added with vigorous stirring. After 2h the lead salts were filtered off and the filtrate, reduced to a small volume, was chromatographed on a column of silica gel eluting with cyclohexane/ethyl acetate at a ratio of 9:1. From the orange fraction 370 mg (36% yield) of pure nitroxide **9** were obtained. This compound was identified by comparison with a sample obtained by oxidising acridan **1** with *m*-chloroperbenzoic acid. The present synthesis is more convenient than the one already described in the literature.[23]

Preparation of isotactic polypropylene for experiments

In order to eliminate traces of antioxidants, the commercial powder (see above) was washed with isopropanol (4 h) in a Soxhlet apparatus and then dried under vacuum.

Oxygen consumption measurements

The polymer powder was mixed with the appropriate quantity of antioxidant dissolved in ethanol or benzene, and the mixture was kept in air until dry. Oxygen consumption was monitored by evaluating the decrease in pressure during heating using a glass equipment of 12 ml in volume connected with an oil manometer. Volatile products were removed by solid KOH.

Analysis of the reaction products after thermoxidation

Antioxidants and their transformation products were extracted by heating the reaction mixture at 200°C under vacuum, using the principle of the sublimator. The trapping zone was cooled with solid carbon dioxide. The products of the separated mixture were isolated by TLC on silica gel eluting with benzene/heptane at a ratio of 3:1. The products were identified and their amounts determined by examining the ethanolic extracts by UV and gas–mass spectroscopies.

ESR measurements

The ESR spectrum of nitroxide **6** was recorded from benzene solution. The amount of nitroxide **6** in the polymer was determined at different times of thermoxidation by comparing the intensity of the ESR signal of the polymer powder with a calibration curve.

RESULTS AND DISCUSSION

The kinetics of oxygen consumption at 200°C by PP containing different antioxidants at the same initial concentration (0·05 mol/kg) are shown in Fig. 1. There is no major retardation in the polymer oxidation. The induction period of samples containing antioxidants is slightly higher than the control (Table 1). Acridans **1** and **2** are the most effective among the antioxidants studied, while nitroxide **6** has a very low stabilising effect. The low activity of compounds **3** and **5** could be ascribed to the fact that they cannot undergo hydrogen abstraction; however, it is more difficult to find a rational explanation for the behaviour of acridan **4**, which works like the corresponding *N*-methyl derivative **5** (Fig. 1,

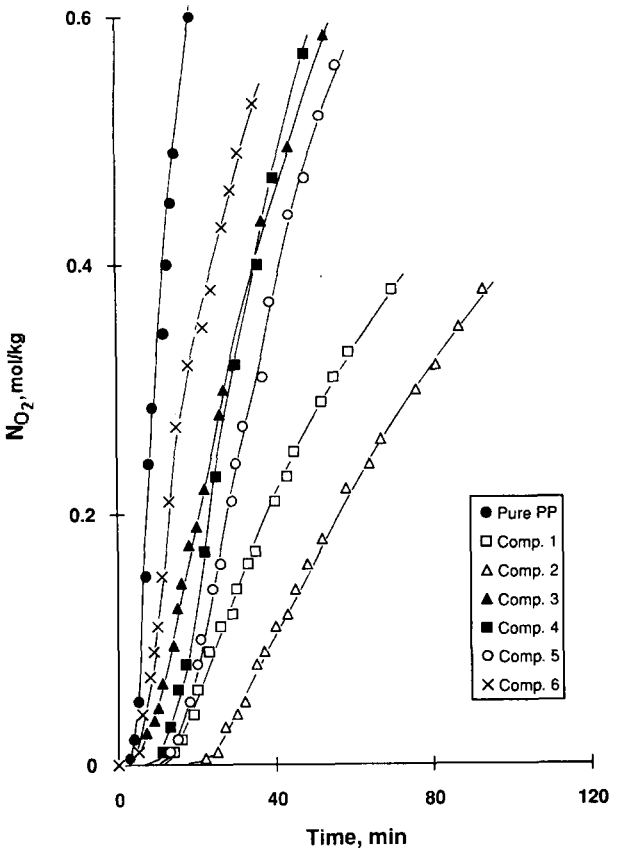


Fig. 1. Oxygen consumption versus time during PP thermoxidation at 200°C, $PO_2 = 300$ mm Hg, and initial concentration of antioxidants (i_0) = 0·05 mol/kg.

Table 1). A more detailed investigation on compounds **1** and **3** shows that an increase in the initial concentration of these antioxidants produces a decrease in the rate of oxidation without affecting the oxidation induction period (see Figs 2 and 3). This result could be reasonably explained by assuming an interaction of PP-hydroperoxides with acridans producing a decrease in the chain-branching rate.

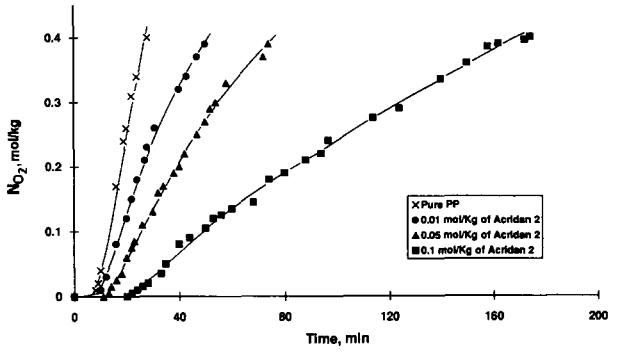


Fig. 2. Oxygen consumption versus time during PP thermoxidation at 200°C and $PO_2 = 300$ mmHg using different initial concentrations of acridan **2**.

In contrast, the ability of secondary amines to react with hydroperoxides is well documented.[24] In order to confirm this supposition, the decomposition of PP-hydroperoxides at 100°C with and without acridan **2** was studied. These experiments were carried out using a pre-oxidised PP powder containing 0·1 mol/kg of

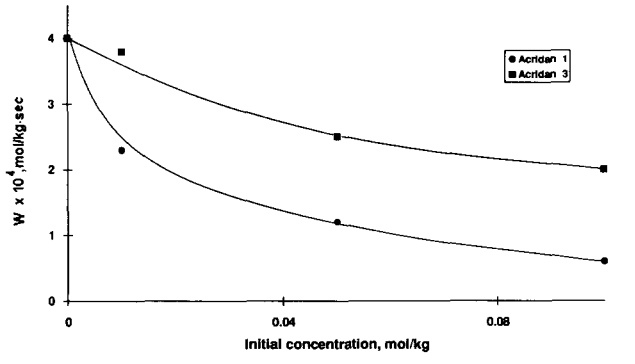
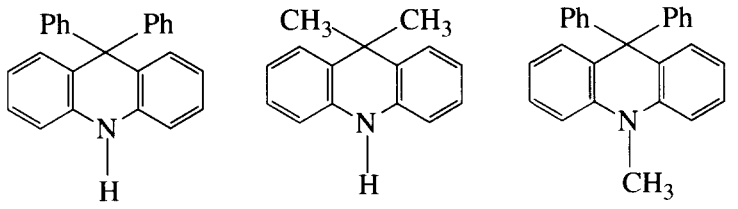


Fig. 3. Initial rate of oxygen consumption versus initial concentration of acridans **1** and **3** at 200°C and $PO_2 = 300$ mmHg.

Table 1. Induction period of PP oxidation in the presence of 0·05 mol/kg of antioxidant at 200°C, $pO_2 = 300$ mmHg

Compound	Without DLTP		With DLTP[a]
	Induction period (min)	W × 10^4 (mol/kg s)	Induction period (min)
Pure PP	8	3·9	40
1	13	1·2	560
2	23	1·0	560
3	7–8	2·5	40
4	13	3·5	120
5	15	2·8	—
6	8–10	2·5	—

[a] i_0 (DLTP) = 0·01 mol/kg.



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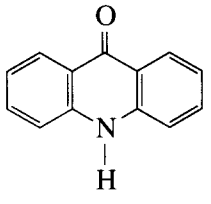

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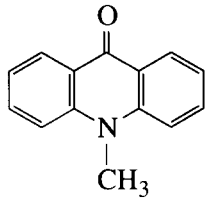

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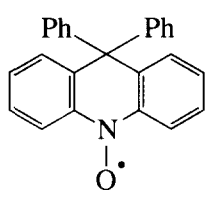

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Table 2. Hydroperoxide decomposition in PP at 100°C

Time (min)	Concentration of PPOOH (mol/kg)	
	Without **2**	In the presence of **2**
0	0·10	0·10
30	0·065	0·062
80	0·051	0·034
100	0·048	0·028

PPOOH. The results, summarised in Table 2, clearly demonstrate that the acridan favours the PP-hydroperoxides' decomposition. The reaction was performed under vacuum in sealed tubes; after an appropriate time the PP powder was washed with ethanol in order to remove the unreacted acridan **2** and other low-molecular-weight compounds. The residual concentration of PPOOH as well as the initial one, was measured by the iodometric method described in the literature.[7]

The studied acridans have no critical concentration and possess a weak antioxidant power according to the proposed classification.[7] DLTP when added to PP in the presence of acridans **1**, **2** and **4** causes a considerable increase in the induction period and similar results were obtained for PP in the presence of nitroxide **6**. This synergism was not observed in the case of *N*-methyl acridan **3** (Table 1).

Figures 4 and 5 show the oxygen consumption against time during the PP oxidation at 200°C using a constant concentration of DLTP (0·01 mol/kg) and varying the concentration of acridan **1** and nitroxide **6**, respectively. The curves in both figures have a very similar shape showing at the beginning, a very low increase in oxygen consumption, which is quite stable for a certain period and then a drastic increase at the end of the induction period. It is also noteworthy that the absorbed oxygen is higher the longer the induction period.

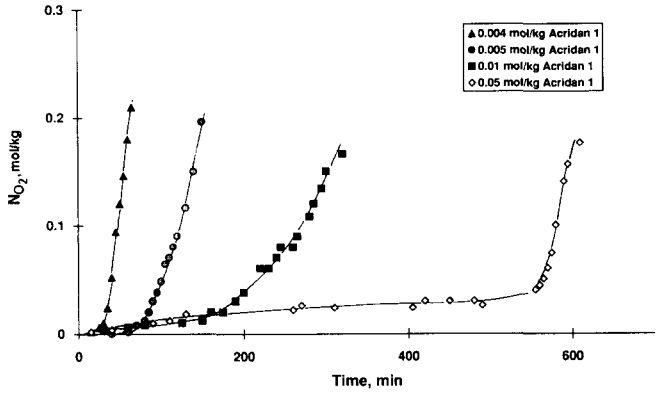


Fig. 4. Oxygen consumption versus time during PP thermoxidation at 200°C and $PO_2 = 300$ mmHg using different initial concentrations of acridan **1** in the presence of DLTP ($i_0 = 0{\cdot}01$ mol/kg).

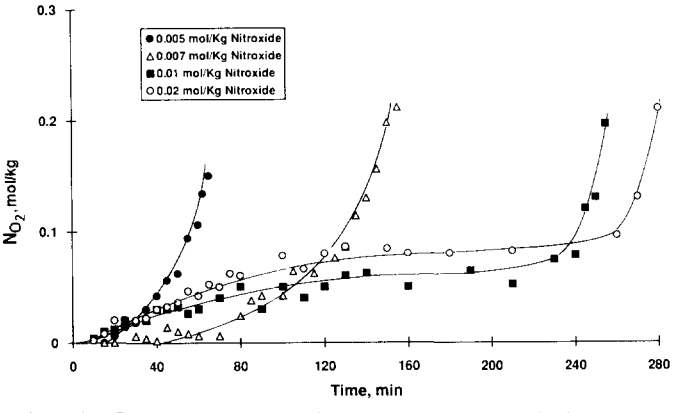


Fig. 5. Oxygen consumption versus time during PP thermoxidation at 200°C and $PO_2 = 300$ mmHg using different initial concentrations of nitroxide **6** in the presence of DLTP ($i_0 = 0{\cdot}01$ mol/kg).

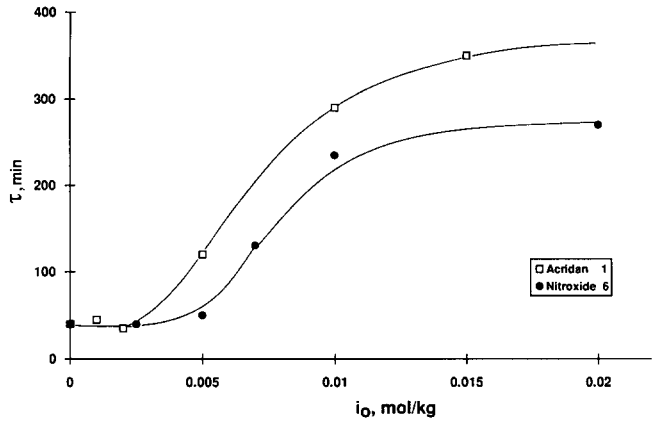


Fig. 6. Induction period versus initial concentration of acridan **1** and nitroxide **6** during PP thermoxidation at 200°C and $PO_2 = 300$ mmHg in the presence of DLTP ($i_0 = 0{\cdot}01$ mol/kg).

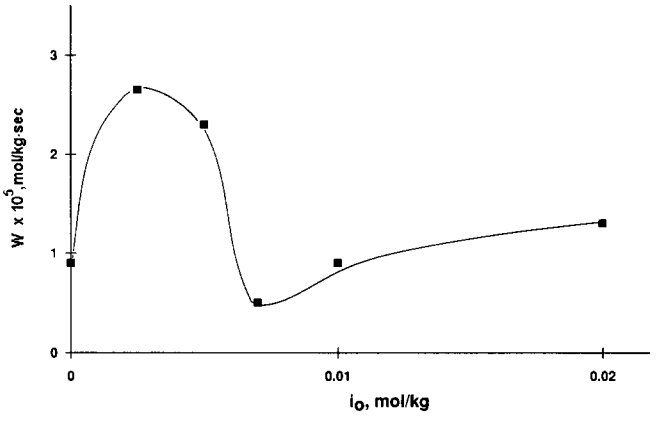


Fig. 8. The maximum rate of oxygen consumption during the induction period of PP thermoxidation versus initial concentration of nitroxide **6** at 200°C and $PO_2 = 300$ mmHg in the presence of DLTP ($i_0 = 0{\cdot}01$ mol/kg).

The induction period of PP oxidation increases with increasing acridan **1** and nitroxide **6** initial concentrations (Fig. 6). A comparison between acridan **1** and the corresponding nitroxide **6**, reported in Fig. 6, shows that at all concentrations acridan **1** is more efficient than nitroxide **6**. Their critical concentrations are $2{\cdot}0–2{\cdot}5 \times 10^{-3}$ and 5×10^{-3} mol/kg, respectively, i.e. the effectiveness of nitroxide **6** is roughly half that of acridan **1**.

The variation of the maximum oxygen consumption rate during the induction period of PP thermoxidation with the initial concentration of acridan **1** and nitroxide **6** is respectively described by Figs 7 and 8, which show a higher oxygen consumption rate for nitroxide **6** in comparison to that of acridan **1**, even if the behaviour of the curves is similar in both cases.

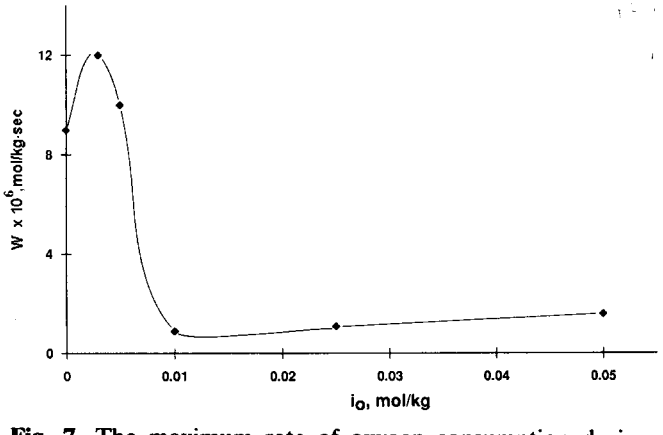
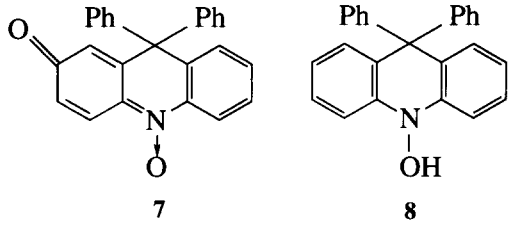


Fig. 7. The maximum rate of oxygen consumption during the induction period of PP thermoxidation versus initial concentration of acridan **1** at 200°C and $PO_2 = 300$ mmHg in the presence of DLTP ($i_0 = 0{\cdot}01$ mol/kg).

Furthermore, the rate of oxygen consumption increases at low and high concentrations of antioxidant demonstrating a prooxidant effect of the studied compounds. An increasing oxygen consumption rate was previously observed for 2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenol)[9] and 2,2′-di-(8-formyl-1,6,7-trihydroxy-5-*iso*-propyl-3-methyl-naphtyl),[10] when used at high concentration in PP stabilisation. This phenomenon was explained by a direct reaction of phenols with oxygen. In the present case, the increase in oxygen absorption rate at low concentrations may be attributed to the initiation of oxidation by antioxidant at concentrations lower than the critical one.



7 **8**

In order to clarify the role of nitroxides in the retardation of polymer oxidation by using acridine derivatives, we studied the reaction of acridan **1** with peroxy radicals formed by treating *tert*-butyl peroxide with lead dioxide in heptane solution.[25] The reaction mainly affords nitroxide **6** (Fig. 9) and the quinoneimine *N*-oxide **7**,[23] which were identified by comparison with authentic samples.

Using acridan **1** as stabiliser, the expected formation of nitroxide **6** during PP thermoxida-

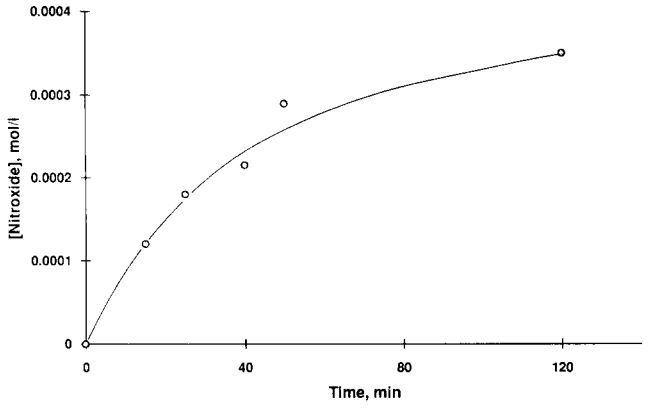


Fig. 9. Concentration of formed nitroxide **6** versus time during the reaction of acridan **1** with *tert*-butyl peroxy radicals in solution at room temperature.

tion at 130 and 200°C did not take place. In order to understand this behaviour, PP powder with pure nitroxide **6** was heated at 130°C for 2 h under a nitrogen atmosphere. After heating, the sample did not contain traces of nitroxide, but only the acridan **1**, at a concentration lower than that of the initial nitroxide **6**, and traces of quinoneimine *N*-oxide **7** (Table 3). The authors also performed experiments with nitroxide **6** in the presence of DLTP. In this case a decrease in nitroxide concentration and formation of acridan were also observed (see Table 3).

The behaviour of acridan **1** and nitroxide **6** in the oxidation of PP in the presence of DLTP at 200°C is reported in Fig. 10. The samples of PP containing 0·01 mol/kg of acridan **1** and 0·01 mol/kg of DLTP were oxidised at different times and the decrease in the concentration of acridan **1** is evidenced by curve 1 of Fig. 10(a), and its logarithm by the curve 1 of Fig. 10(b). Other samples of PP containing nitroxide **6** (0·01 mol/kg) and DLTP (0·01 mol/kg) were also oxidised in the same conditions. The preliminary heating of the samples with nitroxide at 200°C (15 min) without oxygen causes the transformation of 70% of nitroxide **6** into acridan **1**: final

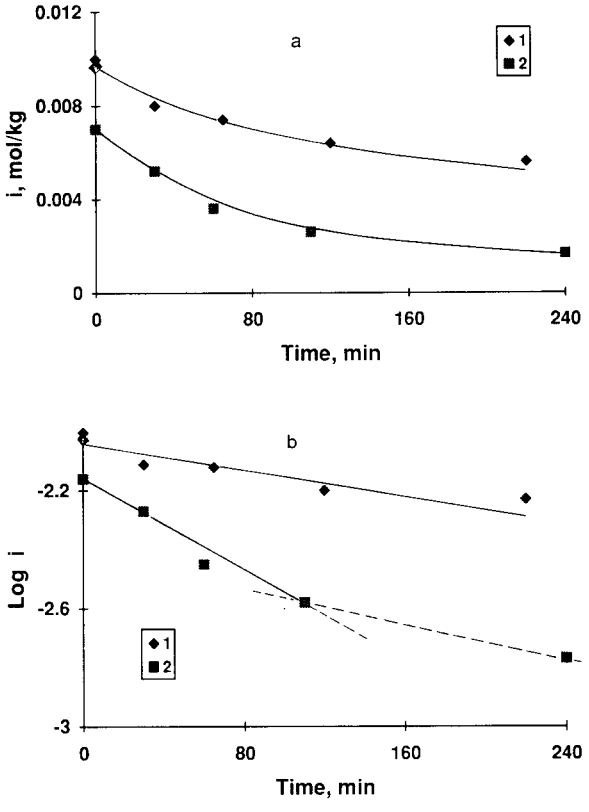
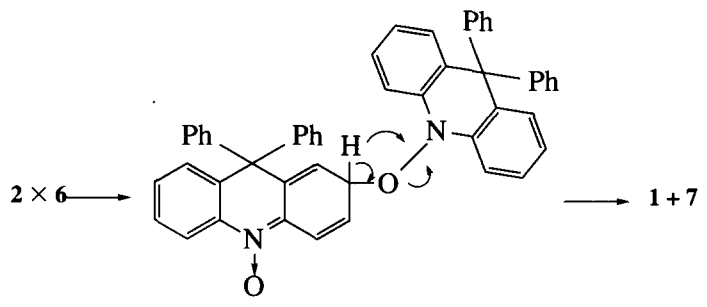


Fig. 10. Consumption of acridan **1** (curve 1), and acridan **1** formed from nitroxide **6** (curve 2) during PP thermoxidation at 200°C and $PO_2 = 300$ mmHg, in the presence of DLTP ($i_0 = 0{\cdot}01$ mol/kg); (a) in coordinates i versus time; (b) in coordinates log i versus time.

concentration of acridan **1** is 0·007 mol/kg (see Fig. 10(a), curve 2). The variation of the concentration of acridan **1**, coming from nitroxide **6**, during oxidation is shown in Fig. 10(a), curve 2, and its logarithm in Fig. 10(b), curve 2. These experiments explain the differences in the critical concentrations of acridan **1** and nitroxide **6** observed in Fig. 6. In fact, these differences agree with the different initial concentration of acridan for the samples described in Fig. 10(a). In addition, Fig. 10 shows that the rate of consumption of acridan **1** is higher in samples initially containing nitroxide **6**.

Table 3. Transformation of nitroxide (6) after 2 h heating at 130°C in nitrogen atmosphere in PP in the absence and in the presence of DLTP

Before heating		After heating	
i_0(**6**) (mol/kg)	i_0(DLTP) (mol/kg)	Concentration of **6** (mol/kg)	Concentration of **1** (mol/kg)
0·0071	0	0	0·0049
0·0093	0·01	0·003	0·0031



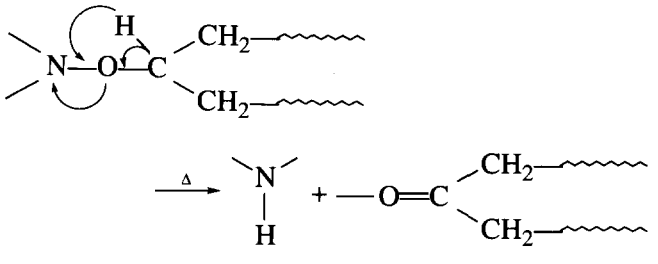
Scheme 1.

The effective rate constants calculated considering the first order law of acridan consumption during the induction period are 6×10^{-5} and $1{\cdot}6 \times 10^{-4}$/s for acridan **1** and acridan **1** produced from nitroxide **6**, respectively.

It is well known that nitroxides have good hydrogen abstraction power, thus the behaviour of samples of curve 2 of Fig. 10(b) is probably due to this feature. Figure 10(b) also shows that curve 1 and curve 2 become parallel in time. This behaviour could be due to the disappearance of a product that can initiate oxidation, but at present the results are not sufficient to explain this behaviour.

The results, presented in this paper could be interpreted by suggesting that nitroxide **6**, having the nitroxide function in a conjugated position with a π-system, may (i) undergo a disproportionation reaction to form acridan **1** and the quinoneimine *N*-oxide **7** (Scheme 1);[15] (ii) be reduced to the corresponding hydroxylamine **8**; (iii) be transformed into the hydroxylamine bonded to the polymer chain (>N—OPP).

A high concentration of acridan **1** found in the experiments with nitroxide **6**, clearly demonstrates that not only the disproportionation reaction takes place (in this case the quinoneimine *N*-oxide **7** and acridan **1** are formed in a 1:1 molar ratio), but other reactions such as that reported in Scheme 2 should be taken into account. A more detailed investigation is under study in order to clarify the mechanism reported in Scheme 2; however, studies carried out on alkylated hydroxylamines, chosen as a model, support the authors' proposal (Carloni, P., *et al.*, unpublished results).



Scheme 2.

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