

# Mechanisms of Antioxidant Action: C-Nitroso Compounds as UV Stabilizers for Polypropylene

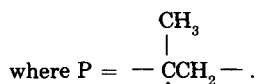
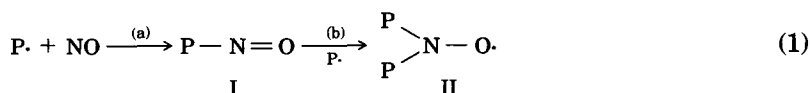
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## Synopsis

It is shown that nitroso-*tert*-alkanes are highly active UV stabilizers which become at least partially chemically attached to polypropylene during processing. The aromatic nitroso compounds are less effective as light stabilizers but are more effective than their alkyl analogues as thermal oxidative stabilizers. Mechanisms are proposed to account for the antioxidant activity of the nitroso compounds and their ability to cause crosslinking of the polymer during processing.

## INTRODUCTION

It has been shown<sup>1</sup> that N-nitrosoamines are highly effective stabilizers for polypropylene both at high temperatures in the polymer melt and under conditions of UV exposure. The evidence suggested that nitric oxide, formed by dissociation of the nitrosamine, was at least partially chemically combined with the polymer, since polymer bound nitroxyl radicals were detected in the extracted polymer. The mechanism proposed involved the initial formation of a macro nitrosoalkane, followed by further reaction of the latter with a second macroalkyl radical:



If this mechanism is correct, then it seems likely that *tert*-alkyl nitroso compounds should also be effective UV stabilizers for polypropylene and the purpose of the present work was to examine a variety of alkyl and aryl nitroso compounds as melt and UV stabilizers for PP.

## EXPERIMENTAL

### Synthesis of Nitroso Compounds

2-Methyl-2-nitrosopropane (tB-NO) and 2,4,4-trimethyl-2-nitrosopentane (tO-NO) were prepared for the corresponding amines by the method of Stowell<sup>2</sup> as follows: 0.5 mol amine + 40 g Na<sub>2</sub>NO<sub>4</sub> + 2H<sub>2</sub>O in 50 mL water were cooled in an ice bath. One mol (170 g 21%) H<sub>2</sub>O<sub>2</sub> was added dropwise

over 1–3 h at 15–20°C with stirring. After stirring for 30 min more at 20–25°C, 3 g of NaCl was added, and the blue organic layer was separated and dried over MgSO<sub>4</sub>. Distillation gave dark blue liquids which crystallized in ice. Characteristics are given in Table I.

Nitrosobenzene (B–NO) was prepared according to the literature.<sup>3</sup> 2,3,5,6-Tetramethyl nitrosobenzene (TMB–NO) and 2,3,4,5,6-pentamethyl nitrosobenzene (PMB–NO) were prepared from acetoxymercuritetramethyl benzene by the method of Smith and Taylor.<sup>4,5</sup> 2,4,6-Trichloronitrosobenzene (TCB–NO) was prepared by oxidation of trichloroaniline.<sup>6</sup> 4-Nitrosophenol (HB–NO) and 2-nitroso-1-naphthol (HN–NO) were prepared by the method of Vogel.<sup>7</sup> 2,6-Di-*tert*-butyl-4-nitrosophenol (HBB–NO) was prepared by the method of Barnes and Hickinbottom.<sup>8</sup>

**Materials.** Commercial polypropylene powder containing no additives was supplied by ICI (Plastics Division) as HF20.

**Processing.** The additives were tumble-mixed with polymer at the appropriate concentration and processed in a RAPRA-Hampden torque rheometer at 180°C for times indicated in the Results section. The procedure was carried out normally in a closed mixer with the chamber filled with polymer except where indicated. On completion of mixing, the samples were rapidly removed and quenched in cold water to prevent thermal oxidation. Films were compression molded at 180°C for 2 min to 0.008 in sheets using a special high temperature grade of cellophane as mould release agent. Melt-flow indices were determined in a Davenport polyethylene grader at 230°C.

**Testing Procedures.** Irradiation of the polymer films was carried out in an accelerated weathering cabinet in which eight fluorescent sunlamps (Westinghouse) and 24 actinic blue lamps were arranged in symmetrical sequence in the ratio 1:3. Infrared spectra of the polymer films were recorded in a Perkin-Elmer 599 IR Spectrophotometer. Carbonyl Index was calculated as  $A_{1730\text{ cm}^{-1}}/A_{2720\text{ cm}^{-1}}$ . Accelerated thermal oxidation of polymer films was carried out in a Wallace single-cell oven at 140°C. Each sample was placed in a separate cell, and the air flow through the cell was controlled at 2.5 ft<sup>3</sup>/h. Molecular mass distribution was measured on the processed samples by GPC by the RAPRA Polymer Supply and Characterisation Centre using *o*-dichlorobenzene as solvent at 138–140°C. Columns packed with styragel in series: 500, 10<sup>4</sup>, 10<sup>6</sup>, and 10<sup>7</sup>Å, using the Mark-Howink equation,  $[\eta] = 1.38 \times 10^{-4} M^{0.70}$  for calibration.

Chemical estimation of peroxide was carried out on the polymer films by the method of Manasek et al.<sup>9</sup> and Geddes<sup>10</sup> modified as described previously.<sup>11</sup> Chemical estimation of olefinic unsaturation was carried out on the polymer films after hot dichloromethane extraction for 50 h under nitrogen followed by vacuum drying for 24 h by the method of Gallo et al.<sup>12</sup>

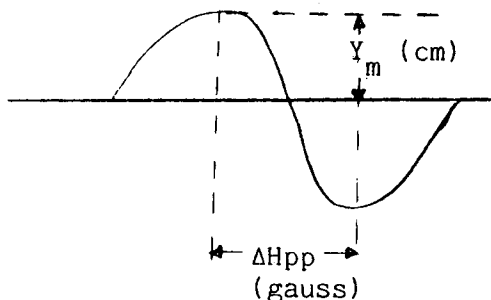
Free hydroxylamine was identified in the polymer by means of the diagnostic "oxine" reaction as follows: A CH<sub>2</sub>Cl<sub>2</sub> extract of the polymer was acidified with dilute HCl and treated with 1 mL of 1 w/v % of oxine (8-hydroxyquinoline) in ethyl alcohol, followed by 1 mL of 2*N* Na<sub>2</sub>CO<sub>3</sub> solution. On shaking the green coloration of indooxine<sup>13</sup> appeared immediately.

ESR spectra of polymer films containing C–nitroso compounds were recorded using a JES-PF ESR Spectrometer. Well-resolved symmetrical triplet

spectra with the characteristic  $g$  values of nitroxyl radicals were obtained at low modulus width settings. Calibration was carried out using a marker sample consisting of MnO powder containing thermally diffused  $Mn^{2+}$  ions and  $g$  values were obtained by reference to the third and fourth lines of the MnO spectrum by means of the equation

$$g = \frac{6651}{3357 - \Delta H}$$

( $\Delta H$  is the shift between the measured spectrum and the 4th line of the marker). Nitroxyl radical concentrations in the polymer were measured by reference to a known weight of 0.1M  $CuSO_4$  solution fastened to the outside of the polymer sample tube in a capillary tube. The radical concentration was calculated at high modulus width settings in order to simplify the measurement. The ratio of  $Y_m(\Delta H_{pp})^2$  for the polymer and for the reference sample (see below) was taken as a relative measure of the concentration of radicals in the polymer sample relative to the reference sample.

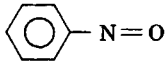
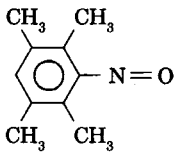
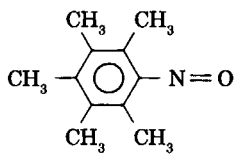
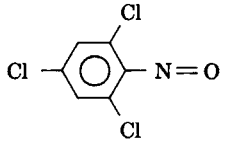
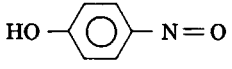
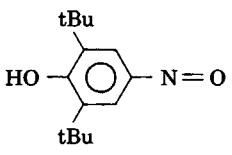
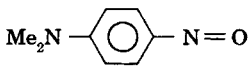
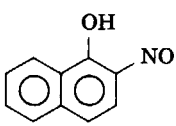


## RESULTS

### Melt Stabilization of PP by C-Nitroso Compounds

All the compounds listed in Table I were processed with PP at the same molar concentration ( $10^{-3}$  mol/100 g) at  $180^\circ C$  in a closed internal mixer (Hampden-RAPRA Torque Rheometer). Figure 1 shows that all the nitroso compounds were very effective melt stabilizers, the most effective of all being 4-nitrosophenol (HB-NO). Three compounds, tO-NO, PMB-NO, and DMA-NO, showed evidence of crosslinking similar to that described earlier for the N-nitrosamines.<sup>1</sup> The crosslinking reaction was confirmed by GPC examination of samples taken after processing for various times and is illustrated for tO-NO processed for 10 min in Figure 2, where the unstabilized, unprocessed polypropylene control is shown for comparison. PMB-NO behaved very similarly. It is clear that the molecular weight has increased but the distribution has remained similar. Peroxide formation was retarded by the nitroso compounds, and in the case of PMB-NO it was inhibited completely in a closed mixer (see Fig. 3). All the polypropylene samples were found to contain nitroxyl radicals after processing (see Table II). The growth of nitroxyl radical concentration with processing time is

TABLE I.  
 Chemical Characteristics of C-Nitroso Compounds

Structural formulas	Code	mp(°C)	Analysis (%)
$(\text{CH}_3)_3\text{C}-\text{N}=\text{O}$	tB-NO	80-81 (79-81 <sup>2</sup> )	C,54.9 (55.17) H,10.1 (10.34) N,16.2 (16.09)
$  \begin{array}{c}  \text{CH}_3 \\    \\  (\text{CH}_3)_3\text{CCH}_2\text{C}-\text{N}=\text{O} \\    \\  \text{CH}_3  \end{array}  $	tO-NO	63-65 (63-65 <sup>2</sup> )	C,66.8 (67.13) H,10.1 (10.34) N,10.0 (9.79)
	B-NO		C,67.0 (67.28) H,4.7 (4.67) N,15.6 (15.88)
	TMB-NO	158 (160 <sup>4</sup> )	C,73.4 (73.6) H,8.2 (8.0) N,7.6 (7.86)
	PMB-NO	157 (160 <sup>5</sup> )	C,74.0 (74.15) H,8.7 (8.98) N,7.6 (7.86)
	TCB-NO	142-143 (145-146 <sup>6</sup> )	C,34.9 (37.8) H,1.1 (1.0) N,6.9 (7.6)
	HB-NO		C,58.8 (58.53) H,4.0 (4.16) N,11.1 (11.38)
	HBB-NO	216 (218)	C,71 (71.48) H,8.8 (8.98) N,6.1 (5.95)
	DMA-NO	85-87	—
	HN-NO	103 (106 <sup>7</sup> )	C,69.5 (69.36) H,4.0 (4.04) N,7.9 (8.1)

shown for tB-NO and PMB-NO in Figure 4, and the formation of unsaturation in the polymer in the case of tB-NO is also shown in the same figure.

#### UV Stabilization by C-Nitroso Compounds

All the nitroso compounds were found to be effective UV stabilizers for polypropylene but the nitroso-*tert*-alkanes were outstandingly effective. Ta-

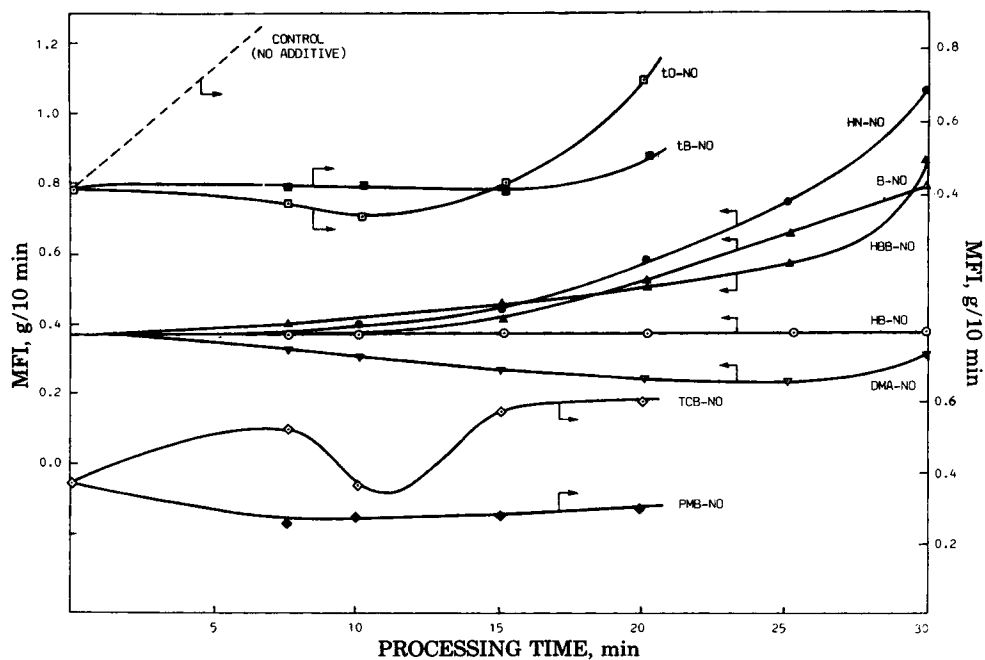


Fig. 1. Effectiveness of C-nitroso compounds as melt stabilizers for polypropylene (closed mixer at 180°C, 10<sup>-3</sup> mol/100 g).

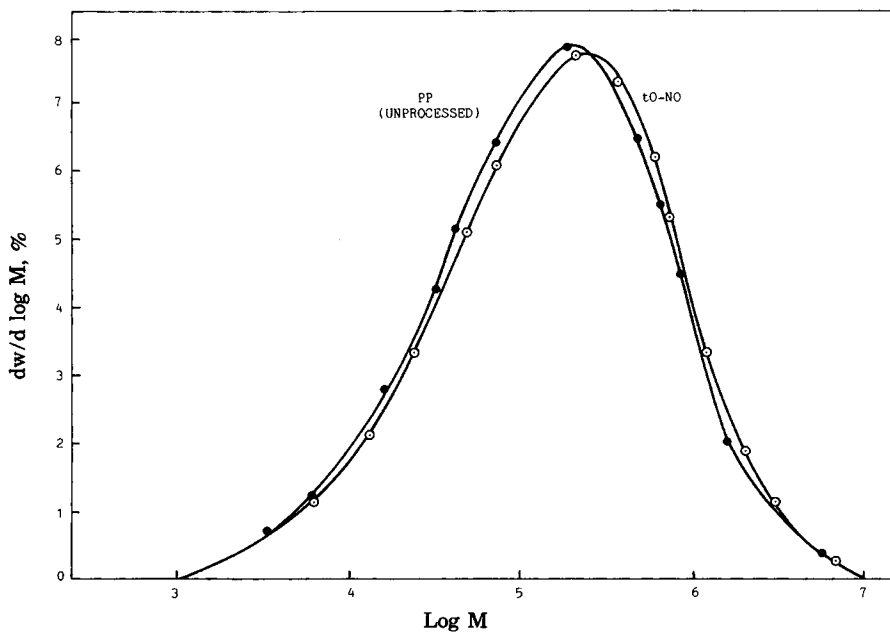


Fig. 2. Effect of tO-NO on the molecular weight distribution of PP processed for 10 min at 180°C (closed mixer).

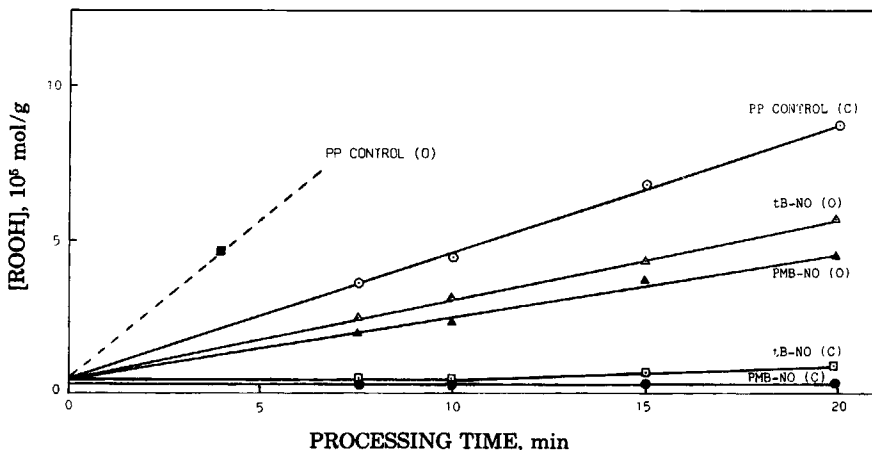


Fig. 3. Formation of hydroperoxide during processing of PP at 180°C in the presence of C-nitroso compounds ( $10^{-3}$  mol/100 g): (C) closed mixer; (O) open mixer.

ble III lists embrittlement times for polypropylene containing nitroso compounds after processing for varying times. Although not quite as effective as bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate (Tinuvin 770), a commercial UV stabilizer which also acts by generating nitroxyl, at the same molar concentration, tB-NO is very much more effective on a weight basis. (The figures in Table III correspond to  $\approx 0.1$  g/100 g and a concentration of Tinuvin 770 of  $\approx 0.3$  g/100 g is necessary to achieve the same level of stability under the same conditions.) All the nitroso compounds became more effective with processing time, reaching a maximum at 10–15 min. Figure 5 shows typical carbonyl formation curves for tB-NO at different processing times.

Figure 4 shows that the nitroxyl concentration reaches a maximum between 10 and 15 min processing time, and it is therefore of interest to relate embrittlement time to nitroxyl concentration. This is shown in Figure 6, curve A, from where it can be seen that the effectiveness of tB-NO is related to the initial nitroxyl radical concentration in the polymer, although this relationship is not linear.

TABLE II  
Nitroxyl Radical Concentrations and  $g$  Values in Polypropylene after Processing<sup>a</sup>

Nitroso compound	Nitroxyl concentration, $10^5$ mol/100 g				$g$ value
	10 min		15 min		
	Unextracted	Extracted	Unextracted		
tB-NO	3.9	2.1	4.2		2.0059
tO-NO	1.9	1.1	2.1		2.0067
B-NO	4.1	1.4	4.1		2.0071
PMB-NO	2.5	0.9	2.4		2.0065
TMB-NO	2.3	1.2	2.1		2.0062

<sup>a</sup> Initial concentration  $10^{-3}$  mol/100 g.

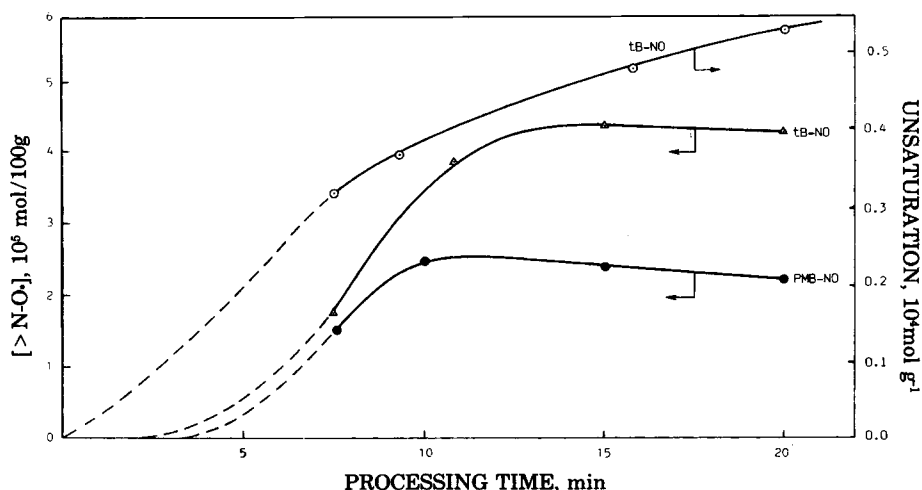


Fig. 4. Formation of nitroxyl [ $-\text{N}-\text{O}\cdot$ ] and unsaturation in PP during processing at  $180^\circ\text{C}$  in a closed mixer (concentration of additive,  $10^{-3}$  mol/100 g).

In a separate series of experiments the nitroxyl concentrations corresponding to different initial tB-NO concentrations were correlated with the embrittlement times of the polymer films, and these are also plotted in Figure 6 (curve B). There is again a nonlinear increase in effectiveness with nitroxyl concentration.

A film containing tB-NO ( $1.5 \times 10^{-3}$  mol/100 g) which was processed to give the maximum nitroxyl concentration (15 min at  $180^\circ\text{C}$ , see Fig. 4) was irradiated and the nitroxyl concentration and the unsaturation index were measured at intervals by ESR. The results are summarized in Figure 7. The behavior is characteristic of nitroxyl radicals in polypropylene during UV irradiation.<sup>1,14</sup> After an initial sharp drop in concentration during the first 100 h the concentration remained constant until shortly before the sample embrittled (870 h), when the signal became too weak to measure quantitatively.

TABLE III  
Photooxidative Embrittlement Times for Polypropylene Stabilized with Nitroso Compounds ( $10^{-3}$  mol/100 g)<sup>a</sup>

Nitroso compound	Embrittlement time (h)			
	Processing time (min)			
	7.5	10	15	20
Control (no additive)	85	85	75	—
tB-NO <sup>b</sup>	660	770	875	800
tO-NO	660	690	650	630
B-NO	330	330	280	240
PMB-NO	—	200	—	—
TCB-NO	180	200	180	160
HB-NO	—	170	—	—
HBB-NO	—	160	185	200
DMA-NO	230	260	210	190
HN-NO	—	150	—	—

<sup>a</sup> Processed at  $180^\circ\text{C}$  in a closed mixer.

<sup>b</sup>  $1.5 \times 10^{-3}$  mol/100 g.

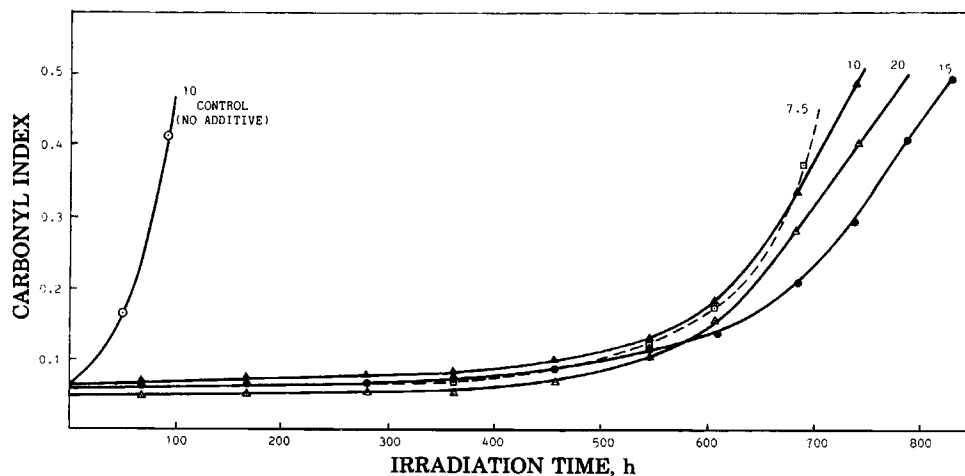


Fig. 5. Effect of processing (CM, 180°C) on the photooxidation of PP containing tB-NO ( $1.5 \times 10^{-3}$  mol/100 g). Numbers on curves are processing times (min).

Exhaustive extraction of processed polypropylene films containing tB-NO, tO-NO, and B-NO (Table IV) was found to reduce their UV stability but not to that of the control film without additive. It is clear that the chemically combined nitroxyl which can still be measured by ESR has a positive UV stabilizing role, but it seems likely that nonnitroxyl products are also removed by the extraction since examination of the extract by the "oxine" test for hydroxylamine showed the presence of this elimination product.

#### Thermal Antioxidant (Oven Aging) Activity of C-Nitroso Compounds

Table V compares the effectiveness of the nitroso compounds as thermal antioxidants at 140°C. It is clear (cf. Table III) that there is in general an inverse correlation between thermal and UV stabilizing effectiveness. Increasing processing time does not improve the performance of the nitrosoalkanes, but it has quite a marked effect on the nitrosobenzenes. Table VI shows that the more effective nitrosobenzene derivatives show an almost linear concentration/activity relationship. An important difference between the active and inactive nitroso compounds is that the former generally impart color to the polypropylene whereas the latter do not (see Table V). Nitrosobenzene is an exception to this generalization. In the case of PMB-NO ( $10^{-3}$  mol/100 g), processed for 10 min, the nitroxyl concentration was found to decrease rapidly during oven aging and was only about 1% of the concentration of PMB-NO initially added to the polymer when the sample embrittled (11.5 h).

#### Model Compound Studies

It is known that nitroxyl radicals react rapidly with alkyl radicals at temperatures below 100°C to give alkyl hydroxylamines.<sup>15,16</sup> Consequently,



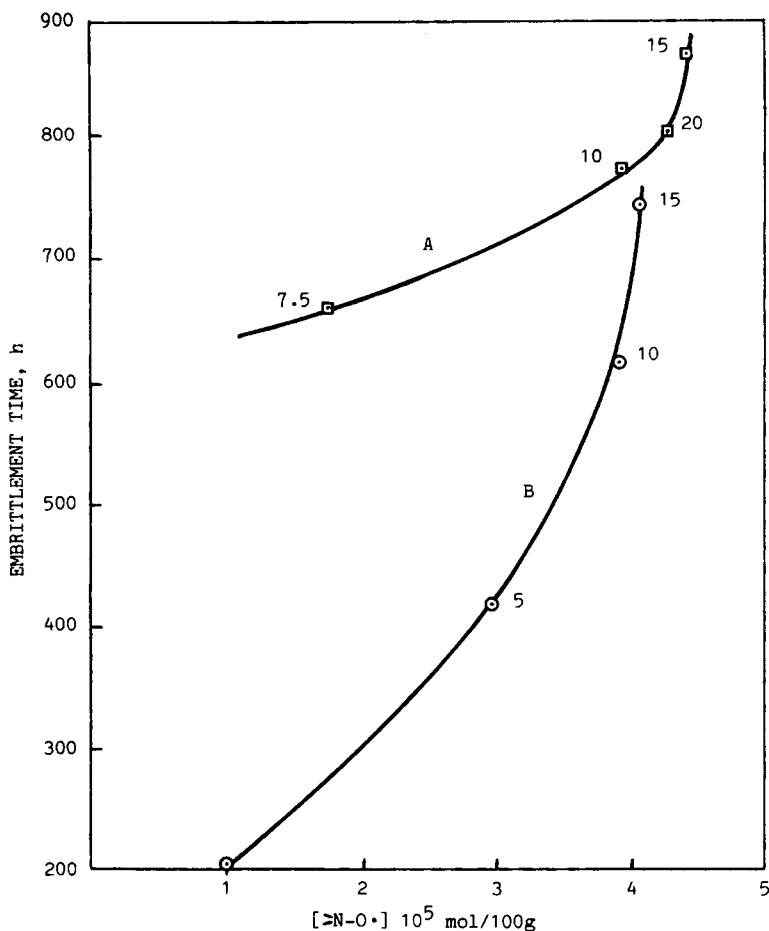
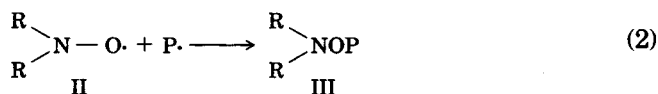


Fig. 6. Relationship between nitroxyl radical concentration  $[N-O\cdot]$  and embrittlement time for PP films containing tB-NO. (A) tB-NO ( $1.5 \times 10^{-3} \text{ mol}/100 \text{ g}$ ) processed for different times; numbers on curves are processing times (min); (B) tB-NO at different concentrations; numbers on curves are concentrations ( $10^4 \text{ mol}/100 \text{ g}$ ), processed for 10 min in a closed mixer.

reaction (2) will lead to the removal of nitroxyl radicals as they are formed by reaction (1).



tO-NO was allowed to react with a 50% molar excess of AIBN (i.e., a 3:1  $[R\cdot]/[tO-NO]$  molar ratio) in *p*-xylene at 110°C and 130°C and the nitroxyl radical concentration was followed by removing samples at intervals and examining by ESR in the usual way. The results are summarized in Figure 8. 80% of the theoretically possible concentration of nitroxyl radicals was produced in the first 5 min at 130°C (slightly less at 110°C). The concentration fell away very sharply to a minimum at about 8 min and then slowly began

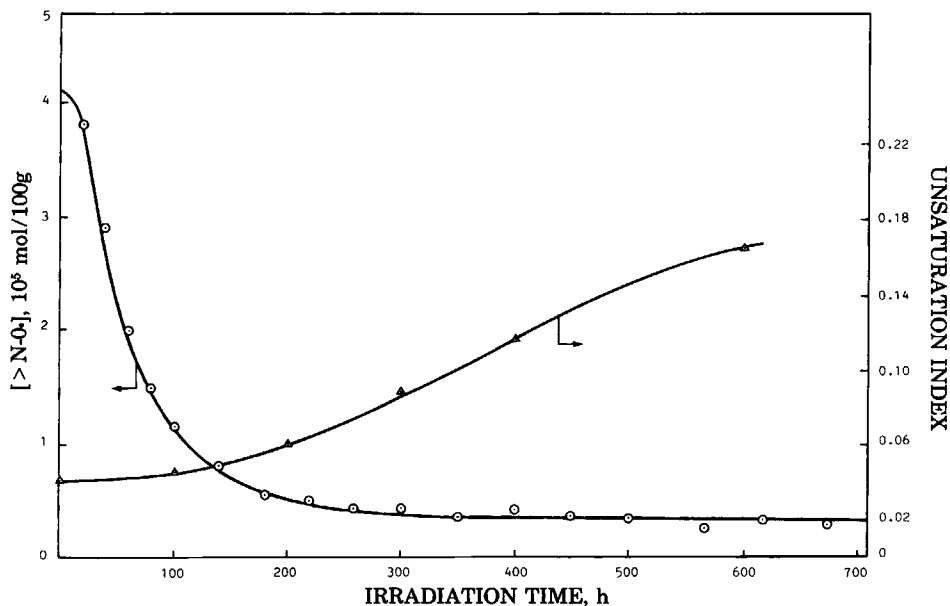


Fig. 7. Decay of nitroxyl radical concentration and formation of unsaturation in PP containing tB-NO ( $1.5 \times 10^{-3}$  mol/100 g).

to increase again. TLC examination of the products at this point showed the presence of methacrylonitrile, due to elimination from the alkyl hydroxylamine (reaction 3):

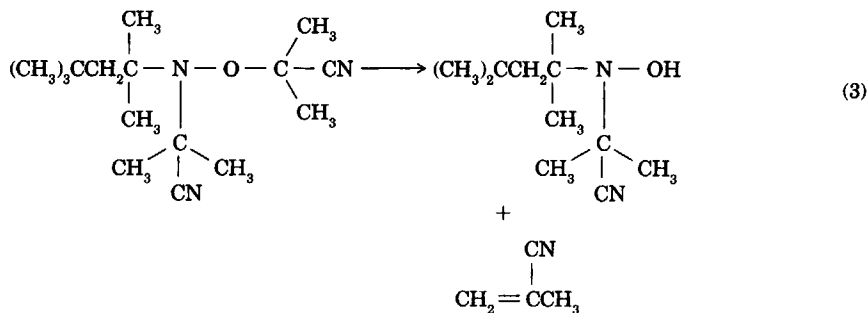


TABLE IV  
Effect of Solvent ( $\text{CH}_2\text{Cl}_2$ ) Extraction on the Effectiveness of Nitroso Compounds as UV Stabilizers<sup>a</sup>

Compound	Embrittlement time (h)			
	Processing time (min)			
	10		15	
	Unextracted <sup>b</sup>	Extracted <sup>b</sup>	Unextracted	Extracted
tB-NO	770 (3.9)	195 (2.1)	875	255
tO-NO	690 (1.9)	210 (1.1)	650	170
B-NO <sup>c</sup>	330 (4.1)	125 (1.4)	280	125

<sup>a</sup> Concentration  $1.5 \times 10^{-3}$  mol/100 g.

<sup>b</sup> Figures in parenthesis are nitroxyl concentrations taken from Table II.

<sup>c</sup>  $10^{-3}$  mol/100 g.

TABLE V  
Thermal Antioxidant Activity (Air Oven at 140°C) of Nitroso Compounds<sup>a</sup>

Nitroso compound	Color	Embrittlement time (h)			
		Processing time (min)			
		7.5	10	15	20
<i>Aliphatic</i>					
tB-NO	Colorless	1.0	1.0	0.5	0.5
tO-NO	Colorless	1.0	1.0	0.7	0.7
<i>Aromatic</i>					
B-NO	Colorless	—	7.0	—	—
TMB-NO	Yellow	9.0	12.0	11.0	6.5
PMB-NO	Yellow	9.5	11.5	20.5	19.0
TCB-NO	Yellow	3.5	4.5	3.5	3.0
HB-NO	Brown	—	5.0	—	—
HBB-NO	Yellow	14.0	21.0	18.5	16.0
DMA-NO	Brown	—	11.0	—	—
HN-NO	Brown	—	8.5	—	—

<sup>a</sup>  $10^{-3}$  mol/100 g; processed at 180°C.

Under the conditions considered (excess air) the reaction is almost certainly more complex than reaction (3) due to the additional presence of both alkylperoxyl and alkoxy radicals.

## DISCUSSION

The thesis proposed in the introduction has been confirmed experimentally. The C-nitrosoalkanes which are the primary products of the reaction of alkyl radicals with NO are shown to be as effective as the hindered piperidines as UV stabilizers on a molar basis, and are much more effective on a weight basis. Unlike the hindered piperidines but like the N-nitrosamines, the nitrosoalkanes are also effective melt stabilizers for polypropylene, and they show a similar ability to the latter to repair broken chains as evidenced by the MFI decrease.

It is not at first sight obvious why nitroso compounds should initially lead to the relinking of broken chains, since this implies the ability to scavenge at least two macroradicals. Although this is in principle possible through a combination of reactions 1 and 2, it has been shown above (Fig.

TABLE VI  
Effect of Concentration on the Antioxidant Activity of Substituted Nitroso Benzenes at 140°C (Air Oven)<sup>a</sup>

Nitroso compound	Thermal embrittlement time (h)		
	1 <sup>b</sup>	5 <sup>b</sup>	10 <sup>b</sup>
TMB-NO	1.0	4.0	12.0
PMB-NO	1.0	4.5	11.5
TLB-NO	1.0	2.0	4.5
HBB-NO	1.7	16.0	21.0
DMA-NO	2.0	8.5	11.0

<sup>a</sup> Processed at 180°C/10 min.

<sup>b</sup> Concentration,  $10^4$  mol/100 g.

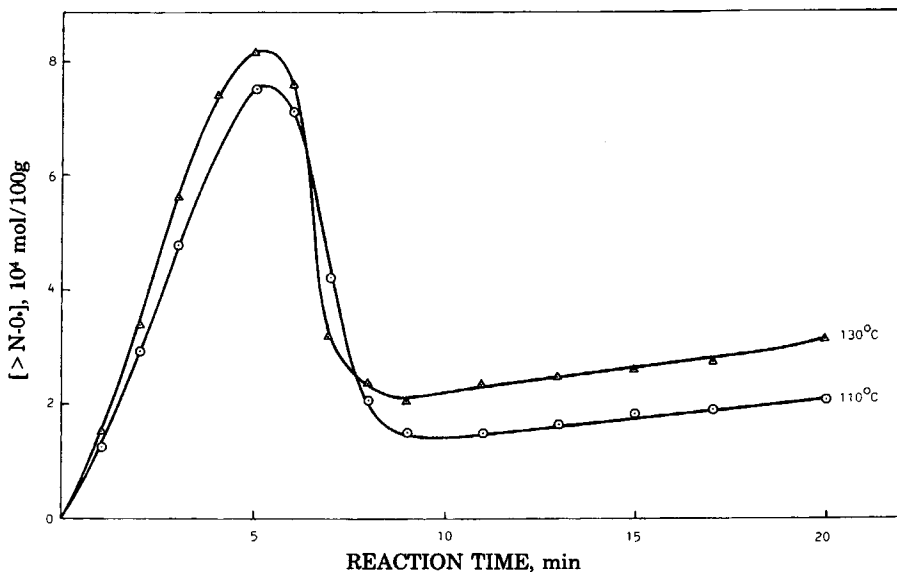


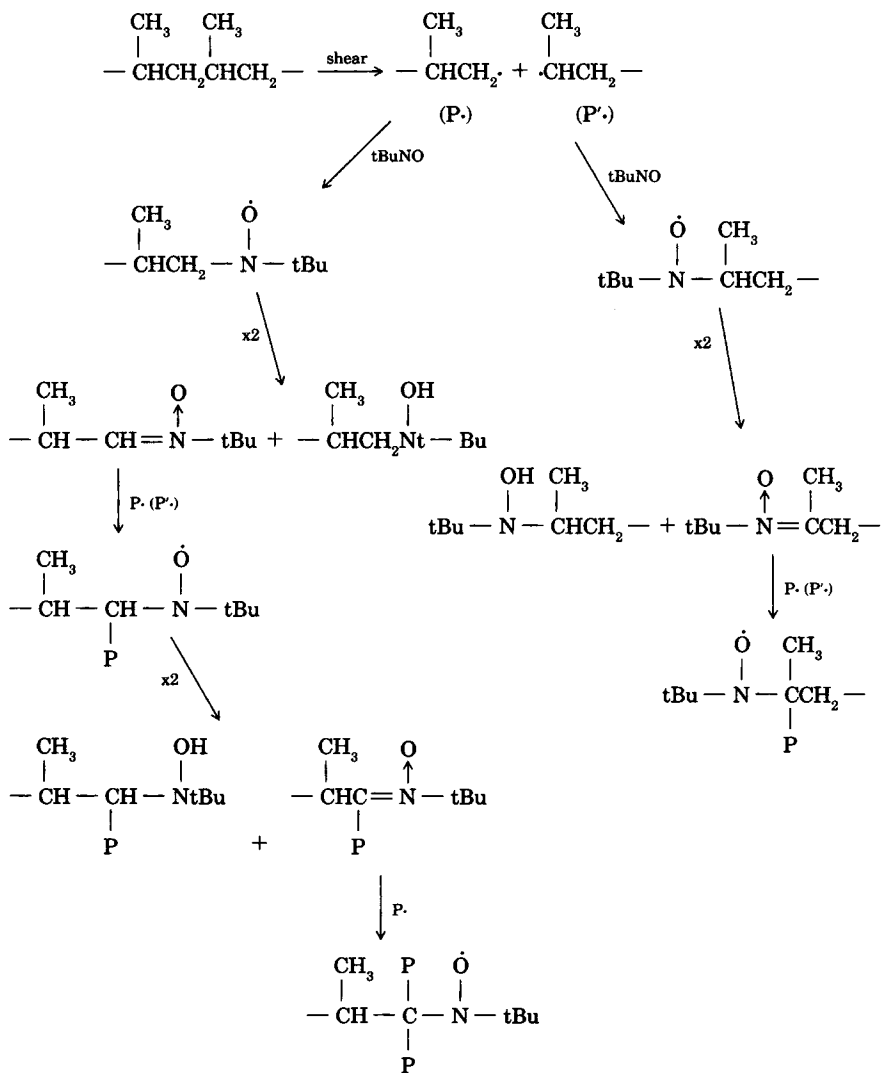
Fig. 8. Formation and decay of nitroxyl during the reaction of AIBN ( $1.5 \times 10^{-3} \text{ mol}/100 \text{ g}$ ) with tO-NO ( $1 \times 10^{-3} \text{ mol}/100 \text{ g}$ ) in *p*-xylene in air at two temperatures.

8) that the alkyl hydroxylamines (III) have only transitory existence at  $130^\circ\text{C}$ <sup>17</sup> (see also Ref. 16), and they could not survive at processing temperatures.

A possible explanation of this phenomenon may lie in the instability of the initially formed nitroxyl radicals resulting from reaction of the PP macroalkyl radicals ( $P\cdot$ ) with tB-NO, since it has been shown that these disproportionate readily.<sup>18</sup> Scheme 1 summarizes the chemistry of this process. It is clear that reaction of the primary alkyl radical ( $P\cdot$ ) with nitrosobutane (tB-NO) may lead to the trapping of two further macroalkyl radicals and reaction of tB-NO with the secondary radical ( $P\cdot'$ ) to the trapping of one additional macroalkyl. Unlike trialkyl hydroxylamines, these adducts, these adducts, since they involve carbon-carbon bonds, might be expected to be reasonably stable at processing temperatures, and the fact that a considerable proportion of the free nitroxyl radicals in the polymer are chemically combined is consistent with this conclusion.

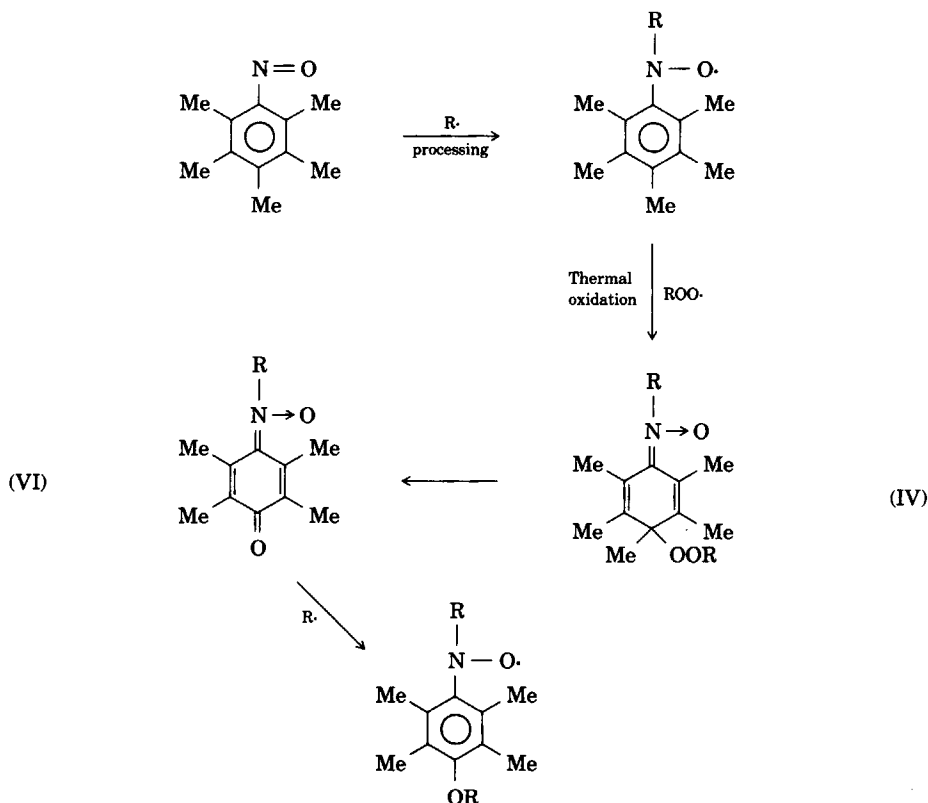
Both bound and unbound nitroxyl radicals appear to be effective UV stabilizers, and, as in earlier studies,<sup>14</sup> photostabilizing activity is found to be related to nitroxyl radical concentration (Fig. 6). However, the relationship is nonlinear, indicating that the products other than nitroxyl are involved in the UV stabilizing activity. It has been shown earlier<sup>14</sup> that alkyl hydroxylamines and free hydroxylamines together act as a reservoir for nitroxyl radicals by oxidation by alkylperoxy and hydroperoxides, and the same explanation can be invoked here.

The general similarity in behavior of the N-nitroso compounds reported earlier<sup>1</sup> and the nitrosoalkanes reported in the present study is striking. Both show an increase in nitroxyl concentration with increasing processing time, rising to a maximum at about 10 min, and both show a decrease in nitroxyl concentration during UV exposure, reaching a stationary concentration after several hundred hours of UV irradiation. Again, only the



Scheme 1. Possible reactions involved in the crosslinking of PP with nitrosoalkanes.

aromatic compounds show thermal antioxidant activity (see Table V). It is not surprising that the nitroso benzene derivatives which contain a chain-breaking electron donor (CB-D) function (amine or phenol) should show activity as heat stabilisers for PP, but it is somewhat surprising that the methyl- and chlorine-substituted nitrosobenzenes (TMB-NO, PMP-NO and TCB-NO) should be so effective. The thermal antioxidant activity of these compounds (Table V) shows a marked optimum (10–15 min) with processing time, suggesting that again nitroxyl radicals are involved, but in this case they must trap alkylperoxyl, not alkyl, radicals since the former are the predominant species during thermal oxidation whereas alkyl radicals are relatively more important during photooxidation.<sup>19,20</sup> It is known<sup>21</sup> that aromatic nitroxyl radicals can scavenge alkylperoxyl whereas alkyl nitroxyls cannot. The probable chemistry is outlined in Scheme 2.



Scheme 2. Mechanism of thermal antioxidant activity of a nitroso benzene.

The formation of colored products associated with all the thermally effective nitroso compounds (Table V) supports this mechanism since nitrones and their quinonoid breakdown products (VI) contain conjugated unsaturation. The relative ineffectiveness of the nitrosobenzene derivatives as UV stabilizers is probably due to the same reason, since aromatic nitroxyl compounds are known to be photo-unstable<sup>22</sup> and the derived quinonoid products may also be photosensitizers for polypropylene.<sup>23</sup>

The mechanism shown in Scheme 2 also provides an explanation for the cross-linking reaction that occurs with the aromatic nitroso compounds (see Table II). If only one alkyl radical were trapped, crosslinking would not occur. However, the quinonoid nitron (VI) would be expected to be reactive toward alkyl radicals and the radical trapping process could in principle be repeated several times.

The possible role of nitrones in the stabilization of polypropylene will be discussed in a later paper.

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