

Mechanisms of Antioxidant Action: The Role of Nitroxyl Radicals in the Stabilization of PVC

J. B. ADENIYI, S. AL-MALAIKA, and G. SCOTT, *Department of
Molecular Sciences, University of Aston in Birmingham, Birmingham
B4 7ET, United Kingdom*

Synopsis

Hindered amines and their derived oxidation products, the hindered nitroxyls and hydroxylamines are processing stabilizers and photoantioxidants for poly(vinyl chloride). The evidence suggests that oxidation of the amines occurs very rapidly and completely during mechanooxidation and that the resulting redox couple operates by a catalytic mechanism as described previously for hydrocarbon polymers.

INTRODUCTION

It is now well established that the mechanism of action of the hindered piperidine light stabilizers in polyolefins involves their transformation during processing and in the early stages of photooxidation to the corresponding nitroxyl radicals.¹⁻⁸ The latter react with macroalkyl radicals in the polymer, with the concomitant formation of unsaturation.^{2,3,6-8}

Much less work has been carried out to investigate the UV stabilizing mechanism of the hindered piperidines and their derived nitroxyls in other polymers. It has been suggested^{9,10} that unsaturation is particularly important as an initiating species in the dehydrochlorination of PVC. If this is correct, then the formation of allylic groups by the mechanism proposed should result in the partial or complete reversal of the normal stabilization effect of nitroxyl radicals both during processing and in subsequent photooxidation. In the present study, two hindered piperidines, P—H and PS—H, were investigated as melt stabilizers and photoantioxidants of PVC together with their derived nitroxyls, P—O, PS—O, and hydroxylamines, P—OH and PS—OH.

EXPERIMENTAL

Materials

The PVC used was an unstabilized grade, Breon M90/50 (from British Petroleum). GPC analysis was carried out on the polymer by the RAPRA Characterization Centre and gave the following characteristics:

$$\begin{aligned} \bar{M}_n &= 30,740, & \bar{M}_w &= 74,120; & \bar{M}_z &= 187,900, \\ \bar{M}_v &= 67,500 & (\bar{M}_w/\bar{M}_n &= 2.41 & \text{ and } & \bar{M}_z/\bar{M}_n = 6.11) \end{aligned}$$

The density of the polymer was 1.4 g/cm³. The dibutyltinmaleate-based stabilizer (DBTM) was Irgastab T290 from Ciba Geigy. This is known to contain a small proportion of a hindered phenolic antioxidant. 2-Hydroxy-4-oxyloxybenzophenone (Cyasorb UV531) was used as supplied by American Cyanamid Corp. (mp = 47°C).

Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate (PS—H) was kindly provided by Ciba Geigy as Tinuvin 770 (mp = 82–85°C). Calcium stearate, supplied by Fisons Ltd., and Wax E by Hoechst AG, were used as lubricants; 2,2,6,6-tetramethyl-4-piperidinol (P—H) and its derived nitroxyl (P—O) were obtained from Aldrich Chemicals. 2,2,6,6-Tetramethyl-1,4-dihydropiperidine (P—OH) was made by reduction of 2,2,6,6-tetramethyl-4-hydroxy-piperidinoxyl (P—O) with hydrazine by the method of Rozantsev and Golubev¹¹ (mp = 157°C, lit. mp = 157°C).

Bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidinyl) sebacate (PS—O) was prepared by oxidation of the hindered amine (PS—H) by the method of Rozantsev et al.¹² [mp = 100–101°C (lit mp = 101°C¹²)].

Processing

The polymer was processed in a RAPRA-Hampden torque rheometer (MK11). The chamber was oil heated and thermostated. A processing temperature of 180°C and a rotor speed of 60 rpm was used throughout the present studies. Mixing was carried out with the chamber filled with the polymer formulation, air being essentially excluded by means of a sealing ram during the mixing procedure, although, in order to simulate commercial practice, no attempt was made to remove oxygen trapped or dissolved in the powder. The torque generated on the mixer rotors was monitored continuously during processing. At the end of a predetermined processing time, the processed polymer was rapidly withdrawn, chilled in water, dried, and stored in the form of lumps in sealed bags in a refrigerator.

Preparation and Photooxidation of Polymer Films

The processed polymer was comminuted to powder and compression molded between stainless steel glazing plates using 550 PU grade cellophane to separate the polymer from the steel plates. The polymer was preheated between the platens of an electrically heated press for 45 s at 170°C prior to the application of a pressure of 25 kg cm⁻² at 170°C for 3 min. Uniform films of standard thickness of 5×10^{-3} were produced by this procedure and were used for subsequent photooxidation studies. Photooxidation was carried out in a simulated sunlight cabinet consisting of a symmetrical array of 24 fluorescent Type C Phillips actinic blue lamps (05) and 8 Type A2 Westinghouse sunlamps (FS20). The fluorescent blue lamps gave a symmetrical distribution from 300–400 nm peaking at 374 nm while the fluorescent sunlamps gave a symmetrical distribution at 280–400 nm peaking at 217 nm. The lamps were arranged vertically and cylindrically around the samples which were attached to the outside surface of an inner rotating cylinder to even out the distribution of UV sources. The temperature inside the cabinet was standardized at

38°C ± 2 by means of a driven ventilator situated under the rotating frame. To eliminate the problem of decline in lamp intensity, a set of four lamps (three actinic and one sunlamp) was replaced sequentially at intervals of 2000 h.

Total Color Difference

Color formation in processed compression molded films was expressed as the difference relating to calibrated standard films containing the same formulation but which had been compression molded without processing. Measurement was carried out using a MEECO Colourmaster Model V in transmission. Readings were obtained using red, green, and blue filters and total color difference ΔT was calculated as follows:

$$\Delta T = (\Delta R^2 + \Delta G^2 + \Delta B^2)^{1/2}$$

where ΔR , ΔG , and ΔB are the differences between instrument readings of the test sample and the control sample using red, green, and blue filters, respectively.

Peroxide was measured by iodometric titration as follows: 0.5 g of powdered polymer was swollen in 75 cm³ of deaerated CHCl₃ for 12 h in a sealed flask. Deaerated glacial acetic acid (1 cm³) was added followed by 25 cm³ of freshly prepared 5% NaI. After standing for 4 h in the dark at room temperature, the liberated I₂ was titrated with 0.1N Na₂S₂O₃. Blank titration were carried out on the reagents for each set of experiments and the results adjusted accordingly.

Spectroscopic Measurements

Unsaturation was monitored by the IR absorbance at 2850 cm⁻¹ and was expressed as an index (UI) $A_{2850} \text{ cm}^{-1}/A_{2915} \text{ cm}^{-1}$, where the absorbance at 2915 cm⁻¹ is an invariant absorbance in the polymer. This method was found to correlate well both with the UV absorbance at 230 nm and with chemically measured monoenic unsaturation by the method of Martin.¹³

Nitroxyl Concentration was measured directly on the powdered polymer in the cavity of a JEOL-PE ESR spectrometer. The nitroxyl radical was seen as a broad singlet in the present experiments very similar to that observed previously in a similar study in polypropylene.^{14,15} The nitroxyl concentration was measured by comparing the height of the peak with that of a CuSO₄ reference sample measured simultaneously. The method of calculation has been given previously.¹⁴ Because of the very sharp fluctuations in nitroxyl radical concentration observed during processing (see Figs. 3 and 4), four mixing experiments were performed at each processing time and the bars shown in Figures 3 and 4 represent the spread of nitroxyl concentrations for four identically processed samples.

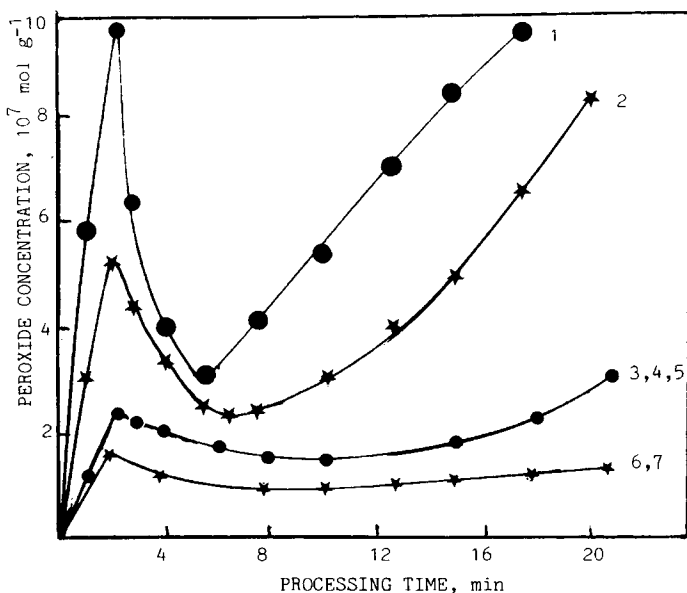


Fig. 1. Effect of processing time on the formation of hydroperoxide during processing of PVC at 180°C in a closed mixer: (1) without additives; (2) DBTM (2.9×10^{-3} mol/100 g) and lubricants (0.65 g/100 g Wax E + 0.8 g/100 g CaSt); (3) DBTM, lubricants [as in (2)] and P—H (2×10^{-3} mol/100 g); (4) DBTM, lubricants [as in (2)] and P—O (2×10^{-3} mol/100 g); (5) DBTM, lubricants [as in (2)] and P—OH (2×10^{-3} mol/100 g); (6) DBTM, lubricants [as in (2)] and PS—H (1×10^{-3} mol/100 g); (7) DBTM, lubricants [as in (2)] and PS—O (1×10^{-3} mol/100 g).

RESULTS AND DISCUSSION

Hindered Piperidines and Their Oxidation Products as Antioxidants

In preliminary experiments it was found that, in the absence of metal carboxylates, neither the hindered piperidines nor their derived nitroxyls had any significant retarding effect on the degradation of PVC during processing as evidenced by color formation. It has been shown previously that hydroperoxide and solvent-insoluble gel formation is a concomitant of dehydrochlorination and color formation during processing.¹⁶ The extent of these changes is reduced by a tin carboxylate stabilizer¹⁷ as shown typically in Figure 1 for dibutyl tin maleate (DBTM). The further addition of the hindered piperidines P—H and PS—H and their oxidation products caused a further synergistic stabilizing effect (see Fig. 1). The bispiperidine (PS—H) and its nitroxyl (PS—O) were particularly effective and unlike polypropylene where the nitroxyls and hydroxylamines are more effective than the parent amine, little distinction was evident in the present instance. A similar inhibiting pattern was observed in gel formation.

The hindered piperidines and their derivatives were also photoantioxidants in combination with DBTM. The nitroxyls and hydroxylamines were only marginally more effective than the parent amines (see Table 1) but the bis

TABLE I
Photoantioxidant Activities of a Hindered Piperidine and
Its Derivatives in PVC Containing DBTM^a (7.2×10^{-3} mol/100 g)

Photoantioxidant	UV embrittlement time (h)				
	0	1 ^b	2 ^b	5 ^b	10 ^b
P—H	986	1144	1260	1338	1350
P—O [•]	986	1180	1272	1344	1355
P—OH	986	1190	1284	1352	1360

^aControl without additives, 658 h.

^bConcentration of photoantioxidant (10^4 mol/100 g).

series was substantially more effective than the lower molecular mass analogues in inhibiting carbonyl and unsaturation formation. This is shown typically for visible color formation in Figure 2. A similar pattern of activity was observed with combinations of the hindered piperidines and the UV absorber, Cyasorb UV531 (see Table II).

Transformation of Hindered Piperidine Derivatives during Processing

The results shown above indicate that the parent amines are equally as effective as their oxidation products as processing antioxidants and photoantioxidants. This behavior is different from the effects of the same compounds in

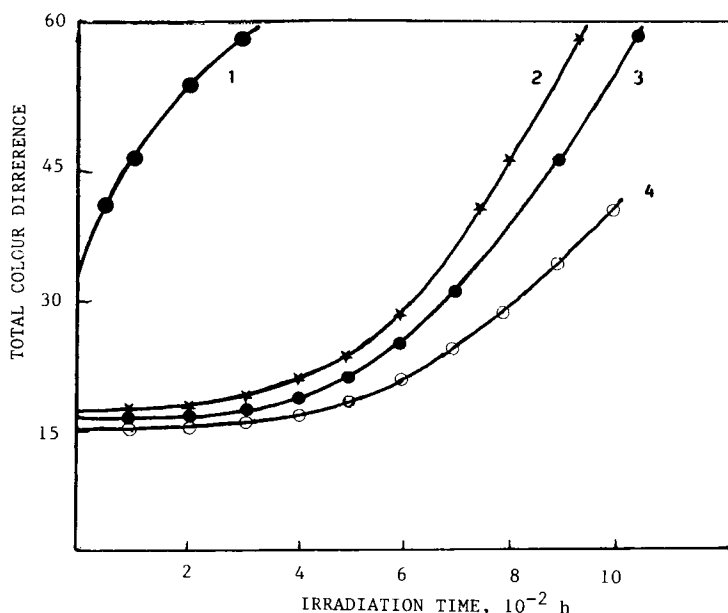


Fig. 2. Effect of photoantioxidants (2×10^{-3} mol/100 g) on colour formation in PVC during UV irradiation (all formulations contained DBTM and lubricants as in Fig. 1 and were processed at $180^{\circ}\text{C}/5$ min): (1) no photoantioxidant; (2) P—H; (3) Cyasorb UV531; (4) PS—H.

TABLE II
 Combination Effects of Hindered Piperidines and Their
 Derivatives (0.25 g/100 g) with Cyasorb UV 531 (0.25 g/100 g)^a

Photoantioxidant	UV embrittlement time (h)	
	2.0 ^b	2.5 ^b
P—H	1595	1618
P—O [•]	1610	1633
P—OH	1622	1640
PS—H	1656	1787
PS—O [•]	1770	1783
UV531 alone	1256	1372

^aAll formulations contained DBTM (at the concentrations indicated) and were processed for 5 min at 180°C in a closed mixer.

^bConcentration of DBTM (g/100 g).

polypropylene, where the hindered nitroxyls and hydroxylamines are much more effective than the hindered amines as melt stabilizers and as photoantioxidants.

It is known from previous studies in polyolefins that the nitroxyl radical/hydroxylamine couple is the effective stabilizing system both during processing and in photooxidation^{5,6,18} and that the end of the induction period corresponds to the irreversible removal of the redox couple from the oxidizing medium. Figure 3 shows that a very similar phenomenon occurs in PVC. The

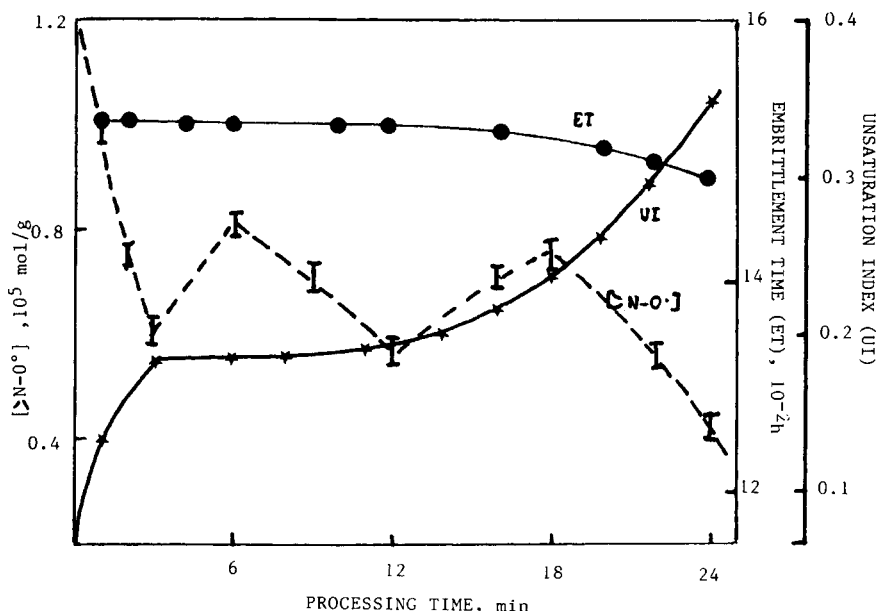


Fig. 3. Effect of processing time (180°C/closed mixer) on nitroxyl concentration [$>N-\dot{O}$] olefinic unsaturation (UI) and UV embrittlement time (ET). All formulation contain DBTM and lubricants concentrations as in Figure 1 and PS—O (2×10^{-3} mol/100 g).

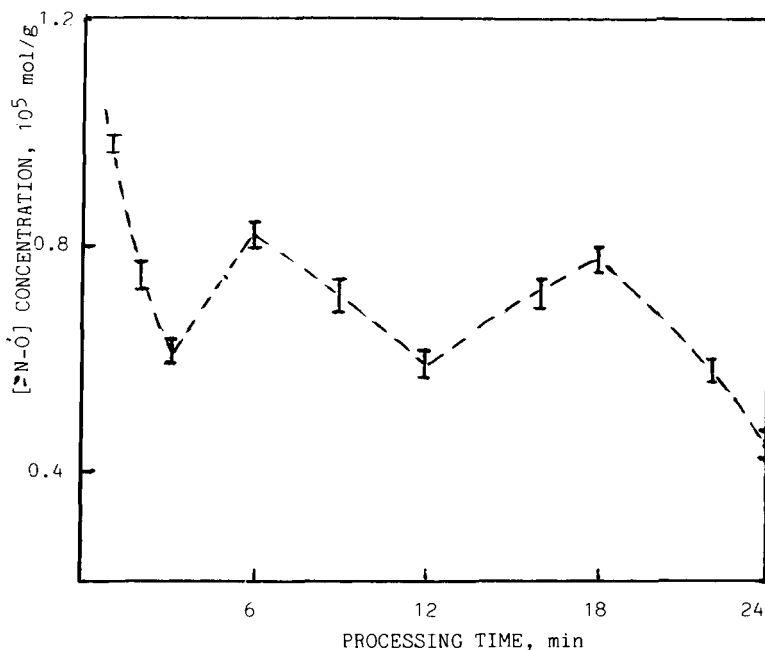
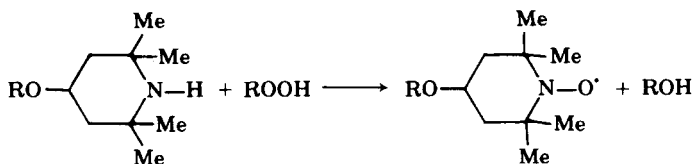


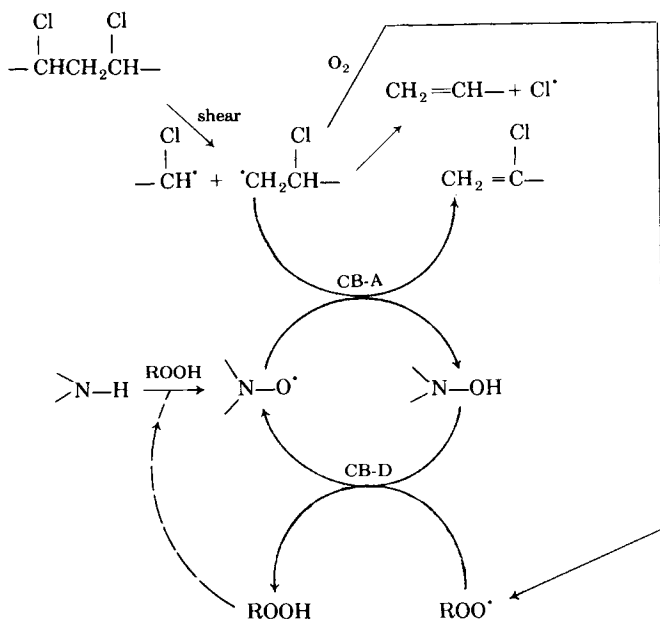
Fig. 4. Effect of processing time (180°C/closed mixer) on nitroxyl concentration [$>N-\dot{O}$] formed from PS-H (2×10^{-3} mol/100 g) during processing in PVC. Formulation contains DBTM and lubricants (at the concentrations given in Fig. 1).

nitroxyl concentration is reduced to about one third of its initial concentration during the first 2 min of processing at 180°C. There is rapid formation of unsaturation during this time followed by a much slower increase. Characteristic oscillation of the nitroxyl concentration was also observed, but, in spite of this, the UV embrittlement times of the compression-molded samples did not show a similar fluctuation but declined in an autoaccelerating fashion. This is entirely consistent with the view proposed earlier that the nitroxyl/hydroxylamine couple is the effective UV stabilizer and not the parent amine. It is also borne out by the fact that the nitroxyl concentration is almost the same throughout the processing operation irrespective of whether the nitroxyl or the parent amine is added to the polymer (cf. Figs. 3 and 4). This implies that the amine is oxidized to the nitroxyl extremely rapidly in the initial stages of processing. In the absence of amine the hydroperoxide concentration is very much higher (see Fig. 1), suggesting that the amine, which is not an antioxidant,¹³ is rapidly oxidized by hydroperoxide to nitroxyl, possibly catalyzed by the tin stabilizer;



CONCLUSIONS

Hindered amines are oxidized to nitroxyl radicals very rapidly in PVC during thermal processing almost certainly by hydroperoxide formed by mechanooxidation. The thermal and photostabilizing effects observed are due to the derived nitroxyl/hydroxylamine couple which acts as an antioxidant by the cyclical mechanism described previously⁶ and outlined for PVC in Scheme 1:



CB-A = chain breaking electron acceptor

CB-D = chain breaking electron donor

Scheme 1. Role of nitroxyl radicals in the stabilization of PVC.

It seems evident that the CB-A step in the above reaction is able to compete with the chlorine atom elimination which normally occurs.¹⁶ Although olefinic unsaturation more than doubles during the first 3 min of processing, this does not lead to decrease in photooxidative stability of the resulting films. An important function of the hindered piperidines is to decrease the amount of hydroperoxide formed during processing, and the light stability of the films is commensurately increased. This is consistent with the earlier conclusion that hydroperoxide rather than unsaturation is the most important photoinitiator during the photooxidation of processed PVC.^{19,20}

References

1. K. B. Chakraborty and G. Scott, *Chem Ind.*, 237 (1979).
2. K. B. Chakraborty and G. Scott, *Polymer*, **21**, 252 (1980).
3. R. Bagheri, K. B. Chakraborty, and G. Scott, *Polym. Deg. Stabi.*, **4**, 1 (1982).
4. G. Scott, *Pure Appl. Chem.*, **55**, 1615 (1983).

5. K. B. Chakraborty and G. Scott, *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 553 (1984).
6. G. Scott, *Developments in Polymer Stabilisation—7*, G. Scott, Ed., Elsevier, London, 1984, P. 65.
7. G. Scott, *Br. Polym. J.*, **16**, 271 (1984).
8. G. Scott, *Polym. Deg. Stabil.*, **10**, 97 (1985).
9. L. D. Loan and F. H. Winslow, *Polymer Stabilisation*, W. L. Hawkins, Ed., Wiley-Interscience, New York, 1977, p. 117.
10. G. Ayrey and R. C. Poller, *Developments in Polymer Stabilisation—2*, G. Scott, Ed., Applied Science, London, 1980, p. 1.
11. F. G. Rozantsev and V. A. Golubev, *Bull. Akad. Sci., Div. Chem. Sci., USSR*, 852 (1966).
12. E. G. Rozantsev, V. A. Golubev., M. B. Neiman, and Y. V. Kokhanov, *Bull. Akad. Sci., Div. Chem. Sci., USSR*, 559 (1965).
13. R. W. Martin, *Anal. Chem.*, **21**, 921 (1949).
14. R. Bagheri, K. B. Chakraborty, and G. Scott, *Polym. Deg. Stabil.*, **4**, 1 (1982).
15. R. Bagheri, K. B. Chakraborty, and G. Scott, *J. Polym. Sci.*, **22**, 1573 (1984).
16. G. Scott, M. Tahan, and J. Vyvoda, *Eur. Polym. J.*, **14**, 377 (1978).
17. G. Scott, M. Tahan, and J. Vyvoda, *Eur. Polym. J.*, **14**, 913 (1978).
18. S. Al-Malaika, O. E. Omikorede, and G. Scott, *J. Polym. Sci.*, to appear.
19. B. B. Cooray and G. Scott, *Polym. Deg. Stabil.*, **3**, 127 (1980–1981).
20. B. B. Cooray and G. Scott, *Developments in Polymer Stabilisation—2*, G. Scott, Ed., Applied Science, London, 1980, p. 53.

Received March 19, 1986

Accepted March 21, 1986