Mechanisms of Antioxidant Action: Mechanochemical Transformation Products of 2,2,6,6–Tetramethyl-4–Hydroxypiperidinoxyl in Polypropylene

S. AL-MALAIKA, E. O. OMIKOREDE, and G. SCOTT, *Department of Molecular Sciences, Aston University, Aston Triangle, Birmingham B4 7ET, UK*

Synopsis

The effect of the processing operation on the nature and quantity of transformation products of 2,2,6,6-tetramethyl-4-hydroxypiperidinoxyl ($\rangle$NO˙) and its corresponding hydroxylamine ($\rangle$NOH) was investigated in polypropylene. It was found that both $\rangle$NO˙ and $\rangle$NOH are actively involved in a regenerative cycle and that this redox couple is responsible for the stability of the polymer whether the initial additive is $\rangle$NO˙ or $\rangle$NOH. The alkyl hydroxylamine ($\rangle$NOR), on the other hand, does not appear to play a significant role in the melt stabilization of the polymer. Quantitative measurements of $\rangle$NOH and $\rangle$NO˙ concentrations show that, under conditions of both restricted oxygen (CM) and oxygen excess (OM), the concentrations of both species change reciprocally throughout the processing operation. In a closed mixer (CM), the total overall concentration of $\rangle$NO˙ and $\rangle$NOH remains at a high constant level, whereas in an open mixer (OM), their total concentration decreases continuously to a low level, indicating the irreversible destruction of the redox couple ($\rangle$NO˙ and $\rangle$NOH). The photo-oxidative stability of the polymer was found to depend on the total concentration of the redox couple left in the system after processing in either CM or OM.

INTRODUCTION

Previous studies have shown[1-3] that the mechano- and photoantioxidant activities of the hindered piperidinoxyls (e.g., 2,2,6,6-tetramethyl-4-hydroxy-piperidinoxyl, $\rangle$NO˙) are due to their involvement in a catalytic cycle. Available evidence suggests that the hydroxylamine $\rangle$NOH and the nitroxyl $\rangle$NO˙ constitute a redox couple with the ability to deactivate a large number of kinetic chains in a redox process summarized in Scheme 1.

Scheme 1

where

$$>N = \text{HO}\!-\!\!\!\bigcirc\!\!\!<\!\!\!\begin{array}{c}CH_3\ CH_3\\N\\CH_3\ CH_3\end{array}$$
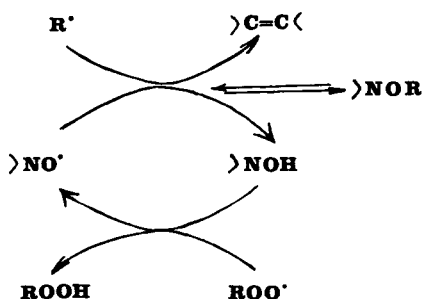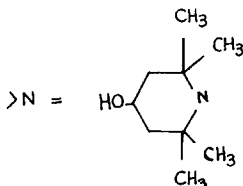
The nitroxyl concentration fluctuates rhythmically when polypropylene is processed in the presence of $>NO^{\cdot}$,[3] and in a preliminary communication we have shown[4] that the hydroxylamine, $>NOH$ also fluctuates reciprocally as demanded by Scheme 1.

The purpose of this paper is to investigate the role of oxygen in the mechanism outlined in Scheme 1 and to provide the experimental details upon which these conclusions are based.

EXPERIMENTAL

Materials

Unstabilized polypropylene (PP) was supplied by Imperial Chemical Industries, Ltd., as Propathene HF 20 CGV 170. The nitroxyl radical ($>NO^{\cdot}$) was purchased from Aldrich Chemical Co., Inc., and the corresponding hydroxylamine ($>NOH$) was prepared from this nitroxyl by the method of Rozantsev and Golubev[5] (melting point = 156°C, Literature 157°C).

Processing and Ultraviolet Irradiation

The additives were tumble mixed with PP at concentration of 1.16×10^{-5} mol g^{-1}, except where indicated, and processed in a Hampden-RAPRA torque rheometer at 180°C for different time intervals. The procedure was carried out in one of two ways. (1) In the normal way in a closed mixer with the chamber filled with the polymer, it was calculated that the maximum amount of oxygen available in the mixing chamber, when sealed, at the start of the mixing operation is 2.3×10^{-3} mol g^{-1}. Although the chamber is sealed by a hydraulic ram, there is evidence that slow diffusion of air does occur on prolonged mixing. (2) The procedure was also carried out under oxidative conditions in which the mixer was left open (OM) and was only half-full so that air could readily diffuse into the polymer during processing. On completion of mixing, the polymer samples were rapidly removed and quenched in cold water to prevent thermal oxidation. The polymer was then compression molded at 180°C for 3 min into sheets of thickness 200 μm using special high-temperature-grade cellophane as the mold release agent.

Exhaustive extraction of polymer films was carried out by refluxing with hot dichloromethane under nitrogen atmosphere for 12 h using a Soxhlet apparatus, and the extracts were examined by electron spin resonance spectroscopy (ESR) for nitroxyl radical.

UV irradiation of polymer films was carried out in an accelerated weathering cabinet comprising two concentric cylinders. The outer cylinder houses 32

fluorescent lamps; 8 sunlamps, and 24 actinic blue lamps, which are arranged in symmetrical sequence on a 1 : 3 basis. The test samples are mounted on the inner cylinder, which rotates around the lamps at a distance from them of 15 cm. Measurement of the radiation output of the weathering cabinet, below 320 nm, was based on the use of polysulfone film, as described by Davis and Gardiner[6] as follows. A polysulfone film (35–40 μm thick) is prepared by casting a solution of the polymer (Union Carbide, Udel P1700) in chloroform (15%). The polysulfone film, which is sensitive to wavelengths below 320 nm,[6] is placed alongside the polymer samples being tested and irradiated in the UV cabinet. The increase in the 330 nm absorption of the polysulfone film (ΔA_{330}), measured on a Beckman DU7 microprocessor-controlled UV spectrophotometer, gives a measure of the incident radiation dose. The ΔA_{330} resulting from the exposure of the polysulfone film to the UV source is expressed in terms of an equivalent dose of 305 nm monochromatic radiation necessary to produce the same ΔA_{330} (a relation between the dose of 305 nm radiation and the resulting ΔA_{330} for polysulfone film is given by Davis and Gardiner[6]). It was also found[6] that the test temperature (-4 to 53°C) did not have any significant effect on the response of polysulfone. The measured average light intensity of the UV cabinet used in this work was 4.2 W m^{-2} (Intensities of the order of 4 W m^{-2} have been measured[6] outdoors with polysulfone with the sun directly overhead and clear sky conditions). Infrared spectra of the irradiated polymer films were recorded on a Perkin-Elmer 599 infrared spectrophotometer and the carbonyl index was calculated as $A_{1730 \text{ cm}^{-1}}/A_{2720 \text{ cm}^{-1}}$.

Testing Procedures

Melt Flow Index (MFI) Measurements

Processed PP samples were extruded in a Davenport melt flow indexer at 230°C and under a load of 2.16 kg. The weight of at least five samples extruded in a fixed time was recorded.

Measurement of Unsaturation in Polymer Films

Unsaturation in processed PP was measured chemically using the method of Gallo et al.,[7] as follows: 0.5 g of polymer films were swollen in 75 mL chloroform for 48 h; 5 mL of 20% trichloroacetic acid in chloroform was added, followed by 25 mL of 0.1 N iodine in chloroform. After 25 mL of 5% mercuric acetate in glacial acetic acid was added, the contents were swirled gently and stored in the dark for 20 h. After addition of 75 mL of 75% KI solution, the excess iodine was titrated against 0.1 N sodium thiosulfate solution in the presence of starch indicator. The same procedure was repeated without the polymer as a reference.

Measurement of Hydroperoxides in Polymer Films

Hydroperoxides in processed PP were measured chemically by a method based on those of Manasek et al.[8] and Geddes,[9] as follows: 0.5–1.0 g of polymer films (in small pieces) were added to 21.7 mL deaerated chloroform

and purged with nitrogen for 30 min. After the polymer was allowed to swell for 18 h, 3.3 mL of glacial acetic acid was added and the solution was purged with nitrogen for 3–5 min before and after the addition of 1–2 mL of freshly prepared deaerated 5% solution of sodium iodide in methanol. After storage for 2 h in the dark, for complete reaction, the liberated iodine was titrated against 0.01 N sodium thiosulfate.

Measurement of Nitroxyl Radical Concentration

Nitroxyl radical concentrations in polymer films and in the oxidized extracts was determined using a JEOL (model JES-PE) electron spin resonance spectrometer. Well-resolved symmetrical triplet spectra with the characteristic g value of 2.0065 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 the g value was obtained by reference to the third and fourth lines of the MnO spectrum by means of the equation

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

(ΔH is the shift between the measured spectrum and the fourth line of the marker). Nitroxyl radical concentration in the polymer and extracts was measured by reference to a known weight of 0.1 M $CuSO_4$ solution placed in a capillary tube and fastened to the outside of the test sample tube. The ratio of $Y_m (\Delta H_{pp})^2$ for the test and the reference sample (see below) was taken as a relative measure of the concentration of radicals in the test sample relative to the reference sample.
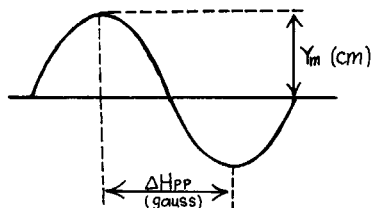
Measurement of the concentration of free hydroxylamine in the polymer samples was achieved by quantitatively converting $\rangle$NOH to the corresponding $\rangle$NO˙ and measuring the total nitroxyl concentration by ESR. This was done by exhaustive extraction of all the $\rangle$NOH and $\rangle$NO˙ from the polymer using hot dichloromethane under nitrogen in a Soxhlet apparatus. After complete extraction (normally around 12 h), no ESR signal could be measured in the polymer samples. After measuring the nitroxyl concentration in the extract (by ESR), the extract was treated with m-chloroperbenzoic acid to convert all $\rangle$NOH to $\rangle$NO˙ and the total concentration of $\rangle$NO˙ in the oxidized extract was finally measured by ESR. The presence of the free hydroxylamine ($\rangle$NOH) was also verified by means of the diagnostic "oxine" reaction,[10] as follows: a dichloromethane extract of the polymer was acidified with dilute HCl and treated with 1 mL of 1 w/v% of oxine (8-hydroxyquinoline) in

ethanol, followed by 1 mL of sodium carbonate solution. On shaking, the green coloration of indooxine appeared immediately.

RESULTS

Figure 1 compares changes in concentration of $\rangle NO\cdot$ and $\rangle NOH$ when PP is processed with $\rangle NO\cdot$ in the presence of excess oxygen (OM) and with re-
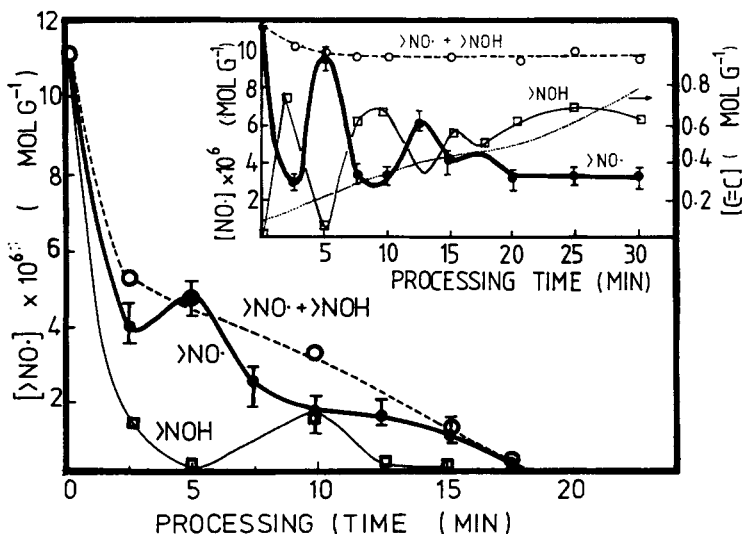

Fig. 1. Changes in [$\rangle NO\cdot$], [$\rangle NOH$], and [$\rangle NO\cdot + \rangle NOH$] concentrations during processing (OM) of PP containing $\rangle NO\cdot$. Inset shows the corresponding changes and the buildup of unsaturation in the polymer when processed (CM) with $\rangle NO\cdot$, (initial concentration of [$\rangle NO\cdot$] = 1.16×10^{-5} mol g^{-1}).
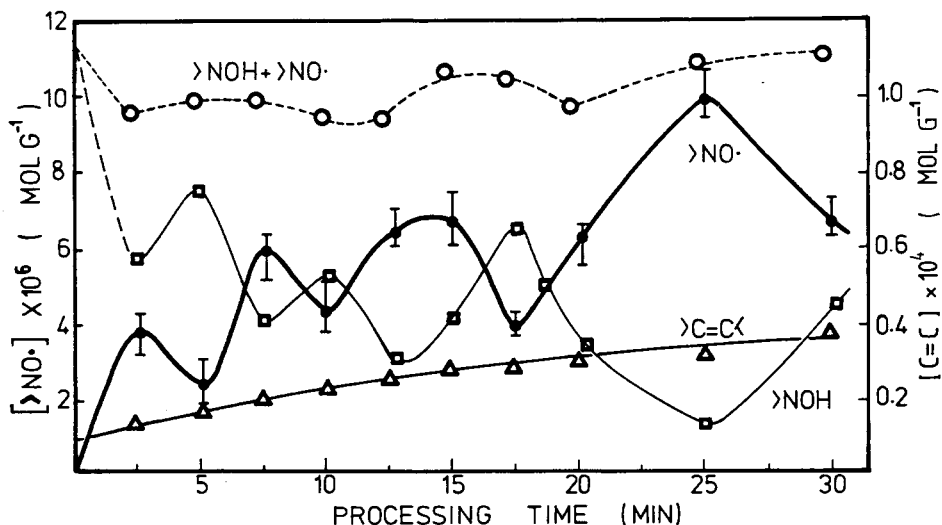
Fig. 2. Changes in [$\rangle NO\cdot$], [$\rangle NOH$], and [$\rangle NO\cdot + \rangle NOH$] concentrations and the buildup of unsaturation in PP containing $\rangle NOH$ when processed under CM conditions (initial concentration of [$\rangle NOH$] = 1.16×10^{-5} mol g^{-1}).

stricted oxygen diffusion (CM). Whereas the total concentration of the redox couple remains at a high constant level in CM (inset), it decreases rapidly to a very low level under oxidative conditions, in OM. This indicates that $\rangle$NO˙ is irreversibly destroyed much more rapidly under the latter conditions than under normal processing (CM) conditions. Under the latter conditions, alkylperoxyl radicals preferentially react with hydroxylamine with regeneration of $\rangle$NO˙.

In order to examine the role of the derived hydroxylamine formed in the polymer during processing with $\rangle$NO˙, a synthesized sample of $\rangle$NOH processed in PP under similar conditions was examined. Figure 2 shows that $\rangle$NO formed during processing (CM) of PP containing $\rangle$NOH fluctuates in a manner similar to that when $\rangle$NO˙ is the additive (Fig. 1, inset). Furthermore, the total concentration of the redox couple measured in the extracts is similar in both cases (see curves [$\rangle$NO˙ + $\rangle$NOH] in Fig. 1, inset, and Fig. 2). Similarly, the hydroxylamine concentration in the system (Fig. 2, curve $\rangle$NOH), reciprocates with [$\rangle$NO˙], and again resembles the behavior when $\rangle$NO˙ is the additive. Unsaturation builds up in both systems throughout the processing (see curves $\rangle$C=C$\langle$ in Fig. 1, inset, and Fig. 2).

Figure 3 compares the concentration of $\rangle$NO˙ during the processing of PP using $\rangle$NOH and $\rangle$NO˙ as additives under OM conditions. Under these conditions, the total concentration of the redox couple with $\rangle$NOH is higher than with $\rangle$NO˙ (see Fig. 4a). However, both compounds are good melt stabilizers (Fig. 4c), and hydroperoxide formation is inhibited in both systems

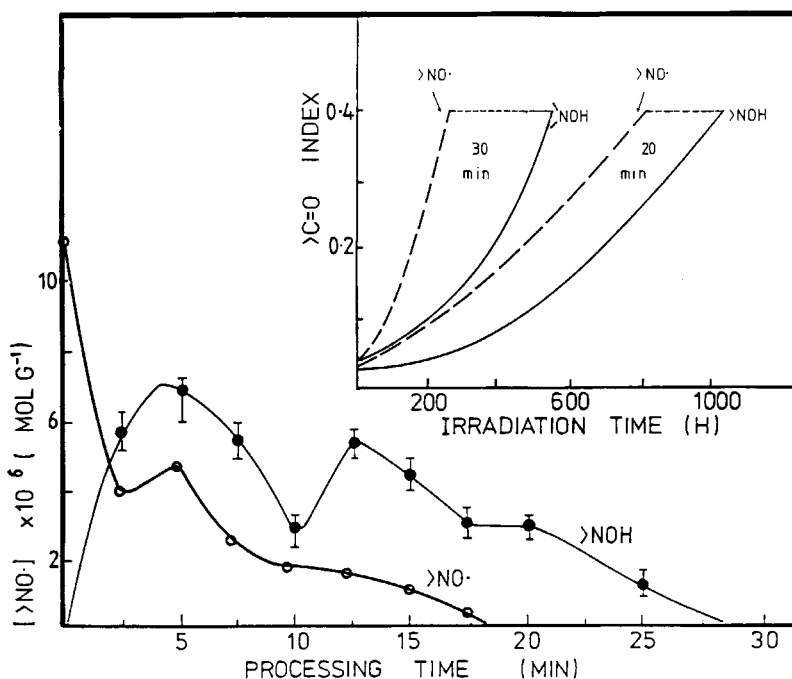Fig. 3. Changes in concentration of $\rangle$NO˙ during processing (OM) of PP with $\rangle$NO˙ and $\rangle$NOH as additives (initial concentration of additives = 1.16×10^{-5} mol g^{-1}). Inset compares photostabilizing effectiveness of $\rangle$NO˙ and $\rangle$NOH when processed (OM) in PP for 20 and 30 min.
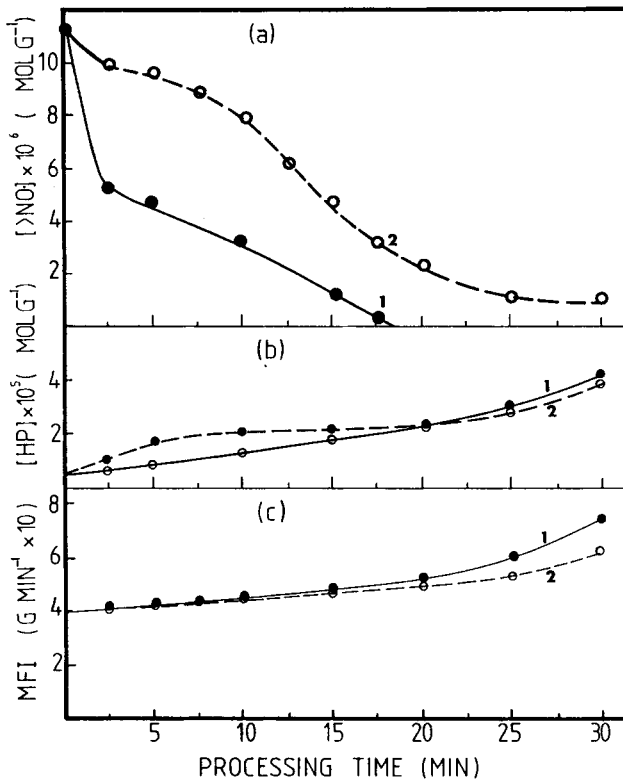
Fig. 4. (a) Changes in total concentration of [)NO˙ +)NOH], (b) hydroperoxide concentration, and (c) melt flow index of PP processed (OM) with)NO˙ (1 (-●-) and)NOH (2 (-○-) as additives (initial concentration of [)NO˙] and [)NOH] = 1.16×10^{-5} mol g^{-1}).
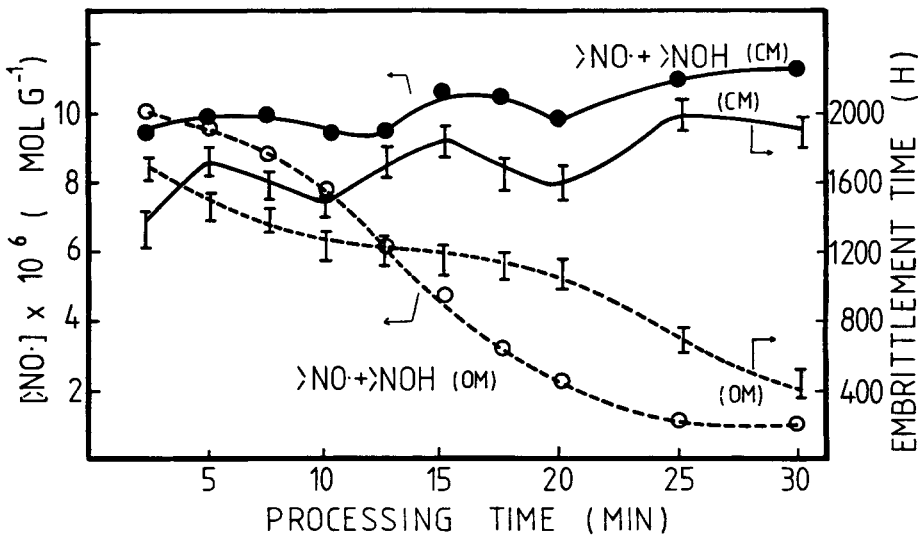

Fig. 5. Changes in total concentration of [)NO˙ +)NOH] during processing (CM and OM) of PP with)NOH as additive (initial [)NOH] = 1.16×10^{-5} mol g^{-1}). Changes in UV embrittlement time of the same samples are also shown.
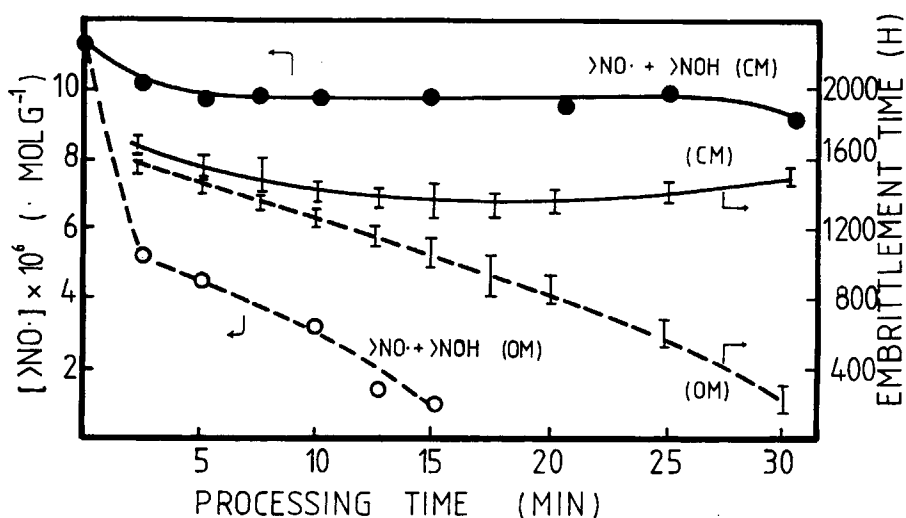
Fig. 6.   Changes in total concentration of [$>$NO$^\cdot$ + $>$NOH] during processing (CM and OM) of PP with $>$NO$^\cdot$ as additive (initial [$>$NO$^\cdot$] = 1.16 × 10^{-5} mol g^{-1}). Changes in UV embrittlement time of the same samples are also shown.
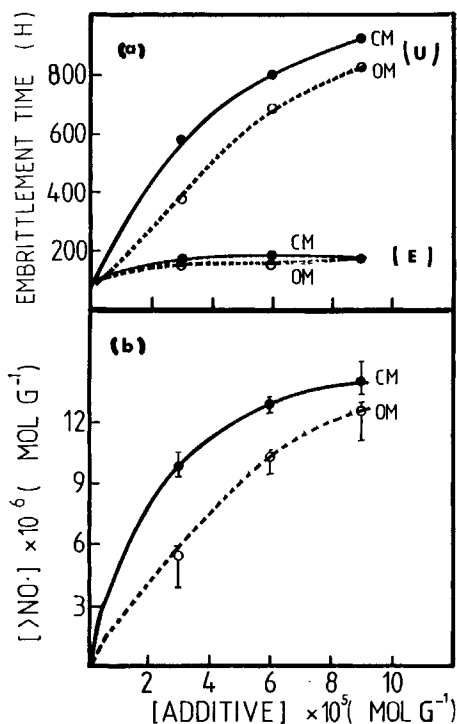

Fig. 7.   (a) Effect of solvent extraction on UV embrittlement time of PP containing different concentrations of $>$NO$^\cdot$ processed in closed (CM) and open mixer (OM); E (extracted samples), U unextracted samples). (b) The concentration of [$>$NO$^\cdot$] left in the polymer after processing and before UV irradiation in the above samples.

(Fig. 4b). The slightly better melt stability of polymer samples containing $\rangle$NOH at the later stages of processing in OM (Fig. 4c) appears to reflect the higher levels of the redox couple left in this system (see Fig. 4a). This is also reflected in the lower rate of photo-oxidation, as shown by the lower values of carbonyl indices at any given time in the $\rangle$NOH processed samples compared with those processed with $\rangle$NO˙ (inset, Fig. 3). There is a general relation between the total concentration of the redox couple (i.e., $\rangle$NO˙ + $\rangle$NOH) and the UV embrittlement time. However, this is more evident under CM conditions that in OM (see Figs. 5 and 6). When PP is processed with $\rangle$NO˙, the UV lifetime of the polymer is always higher when processing is carried out in CM compared with OM conditions, and this corresponds to higher levels of $\rangle$NO˙ (Fig. 7). Exhaustive extraction of polymer films led to the complete removal of nitroxyl and the the reduction in UV lifetime to a level approaching that of the control without antioxidant (Fig. 7). The residual UV stability of the extracted films could be due to a very small stationary concentration of unextractable polymer-bound alkyl hydroxylamine formed in the system.

DISCUSSION

The concentrations of $\rangle$NO˙ and $\rangle$NOH in PP fluctuate reciprocally during processing (Figs. 1 and 2). Under limited oxygen access (CM), the total concentration of $\rangle$NO˙ and $\rangle$NOH in both systems remains at a high constant level throughout the processing operation, confirming the previously suggested reversible redox reaction between nitroxyls and hydroxylamines (see reaction Scheme 1). This behavior is remarkably similar to that described previously for the galvinoxyl-hydrogalvinoxyl couple.[11] The reciprocal alternation of the concentrations of [$\rangle$NO˙] and [$\rangle$NOH], whether the initial additive is $\rangle$NO˙ or $\rangle$NOH (Figs. 1 and 2), indicates that the conditions in the mixing chamber are continuously changing. The almost constant concentration of the redox couple when the polymer is processed in CM implies that the mechanochemically formed macroalkyl radicals are able to reduce $\rangle$NO˙ to $\rangle$NOH quantitatively. Concomitantly, $\rangle$NOH is reoxidized back to $\rangle$NO˙ either by ROO˙ or by ROOH. When the oxygen initially present in the system is substantially depleted, $\rangle$NO˙ will again be able to compete efficiently with oxygen for macroalkyl radicals to form $\rangle$NOH.

Although a quantitative kinetic treatment is not possible on the basis of the available data, the rythmic complementary fluctuation of [$\rangle$NO˙] and [$\rangle$NOH] can be understood on the basis of the following reasoning. After the initial very high shear conditions, when the viscosity of the polymer in the mixer has been reduced to an essentially constant value and the oxygen concentration in the mixer is low and limited by the rate of diffusion into the chamber, the following conditions will hold. First, at high [$\rangle$NO˙], reaction (1) is the predominant process:
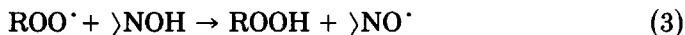
$$\rangle NO˙ + R˙ \rightarrow \rangle NOH + \rangle C{=}C\langle \tag{1}$$
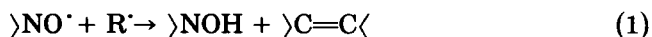
Under these conditions, [R˙] and hence [ROO˙] will be low. Second, as $\rangle$NO˙ is converted to $\rangle$NOH, the rate of reaction (1) decreases and oxygen, whose concentration has been increasing, is able to compete for R˙ with $\rangle$NO˙

[reaction (2)]:

$$R\dot{} + O_2 \rightarrow ROO\dot{} \qquad (2)$$

As [$\rangle$NOH] increases, reaction (3) becomes dominant, followed by (4) and (5):

$$ROO\dot{} + \rangle NOH \rightarrow ROOH + \rangle NO\dot{} \qquad (3)$$

$$ROOH + \rangle NOH \rightarrow \rangle NO\dot{} + RO\dot{} + H_2O \qquad (4)$$

$$RO\dot{} + \rangle NOH \rightarrow ROH + \rangle NO\dot{} \qquad (5)$$

Since there is no evidence that hydroperoxide undergoes cyclic concentration changes (see Fig. 4b), it seems likely that reactions (4) and (5) can be ignored and that reaction (3) is primarily responsible for nitroxyl regeneration. Reaction (2) then depletes oxygen in the system, resulting in an increase in [R$\dot{}$], and reaction (3) increases [$\rangle$NO$\dot{}$] so that the cycle begins again. The ability of the redox couple to deactivate both alkyl and alkylperoxyl radicals present in PP during processing also leads to subsequent high photo-oxidative stability of the polymer (Figs. 5 and 6, curves CM).

When the polymer is processed with either $\rangle$NO$\dot{}$ or $\rangle$NOH under OM conditions, the total concentration of the redox couple reduces much more rapidly than when the polymer is processed in a closed mixer. Under these

Scheme 2
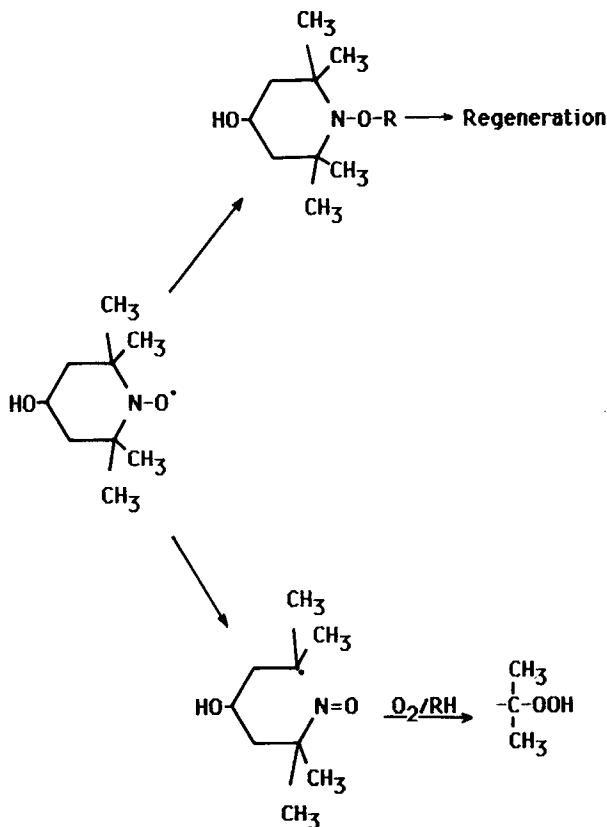
conditions, $\rangle$NOH is very rapidly converted to $\rangle$NO˙ by alkylperoxyl radicals or hydroperoxides. This is supported by the fact that in OM the comparative nitroxyl concentration is higher in the case of $\rangle$NOH than in the case of $\rangle$NO˙ (Fig. 4a). The nitroxyl is presumably irreversibly destroyed by reaction with oxygen or alkylperoxyl radicals (Scheme 2) and hence the antioxidant cycle (Scheme 1) cannot operate efficiently and the melt stability of the polymer starts to decrease (see Fig. 4). There is no doubt, then, that the alkyl hydroxylamine, $\rangle$NOR, does not play a very significant part as a reservoir for nitroxyl radical in the melt stabilization of PP. The low stationary concentration[4] suggests that it is either formed reversibly at the high temperatures encountered during processing (Scheme 3b) or it undergoes thermal elimination via the Cope elimination (Scheme 3a).
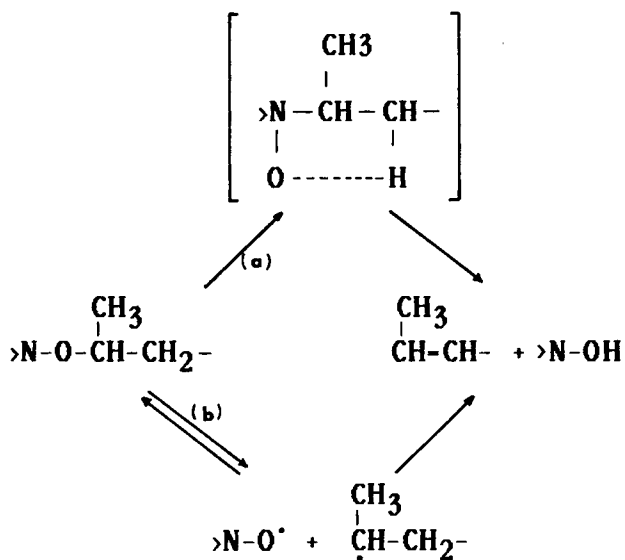
Scheme 3

In either event, free hydroxylamine represents the main reservoir for nitroxyl radicals.

References

1. K. B. Chakraborty and G. Scott, *Polymer*, **21**, 252 (1980).
2. R. Bagheri, K. B. Chakraborty, and G. Scott, *Polym. Deg. Stab.*, **4**, 1 (1982).
3. R. Bagheri, K. B. Chakraborty, and G. Scott, *J. Polym. Sci.*, **22**, 1573 (1984).
4. S. Al-Malaika, E. O. Omikorede, and G. Scott, *Polym. Commun.*, **27**, 173 (1986).
5. E. G. Rozantsev and V. A. Golubev, *Bull. Akad. Sci.*, USSR, 852 (1966).
6. A. Davis and D. Gardiner, *Polym. Deg. Stab.*, **4**, 145 (1982).
7. S. G. Gallo, H. K. Wiese, and J. F. Nelson, *Ind. Eng. Chem.*, **40**, 1277 (1984).
8. Z. Manasek, D. Berek, M. Micko, M. Lazer, and J. Parlinec, *Rubber Chem. Technol.*, **36**, 532 (1963).
9. W. C. Geddes, *Eur. Polym. J.*, **3**, 733 (1964).
10. R. G. W. Hollingshead, *Oxin and Its Derivatives*, Vol. IV, Butterworths, London, 1956, p. 991.
11. K. B. Chakraborty and G. Scott, *Polym. Deg. Stab.*, **5**, 145 (1983).