

Mechanisms of Antioxidant Action: The Effect of Spin Traps During the Processing and Photooxidation of PVC

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Synopsis

It is demonstrated by the use of spin traps that during the early stages of thermal processing of PVC considerable concentrations ($> 3 \times 10^{-6}$ mol g^{-1}) of free radicals are produced which are primarily responsible for the initial products (hydroperoxides, unsaturation, and hydrogen chloride) previously shown to be formed in the polymer. From a semiquantitative analysis of these products, it is estimated that more than 50% of the radicals are formed from hydroperoxides and the rest by mechanoscession of the polymer chain. The spin traps are effective processing stabilizers in combination with a tin maleate HCl scavenger. One of them (2-methyl-2-nitroso propane, MNP) has also been shown to be a photoantioxidant.

INTRODUCTION

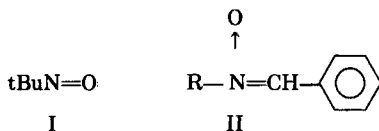
Previous studies¹⁻⁵ have demonstrated the chemical "damage" inflicted on PVC during normal mixing and compounding procedures is much more severe than that resulting from the introduction of structural abnormalities during the synthesis of the polymer. The initial stages of mechanooxidation in a shearing mixer lead to the formation of substantial concentrations of hydroperoxides, hydrogen chloride, and associated unsaturation, all of which are involved in the formation of polymeric unsaturation (and color) in the later stages of processing.¹⁻³ We have attributed the formation of these sensitising species to the reactions of initially formed macroalkyl radicals and the potent effect of HCl to a radical forming redox reaction between HCl and hydroperoxide⁵⁻⁷



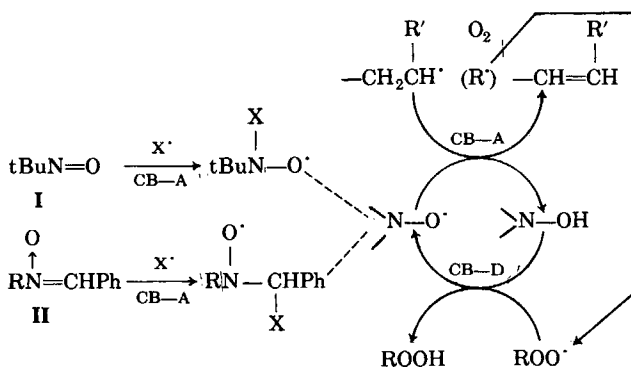
However, many workers still dispute the involvement of radical species during processing (see recent review by Hjertberg and Sörvik⁸) and invoke ionic catalysis by HCl to account for its catalytic effect on further HCl elimination. Evidence for participation of radicals during thermal processing of PVC has so far been based on the examination of the initially formed end products of their reaction and unlike the hydrocarbon polymers which have been extensively studied by ESR, the presence of macroradicals in PVC has not so far been unequivocally demonstrated. Results from this laboratory indicate that

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spin traps such as



2-Methyl-2-nitrosopropane I (MNP), diphenyl nitrone, II, R=Ph (DPN) and α -phenyl-*N*-methyl nitrone, II, R=Me (PMN) are able to trap radicals produced during the processing of polypropylene with the formation of the corresponding nitroxyl (see Scheme 1) whose concentration can be measured by ESR: The same procedure has now been investigated in PVC in an



Scheme 1. Formation and mechanism of antioxidant action of spin traps (ST) in polymers during mechanooxidation. X may be alkyl, alkoxy, hydroxyl, alkylperoxy, etc.

attempt to provide physical evidence for the free radical nature of PVC degradation during processing and for the participation of nitroxyl radicals in subsequent stabilization of PVC.

EXPERIMENTAL

Materials

PVC was unstabilized Breon M90/50 homopolymer supplied by British Petroleum Ltd ($\bar{M}_n = 30,740$; $M_w = 74,120$; $M_z = 187,900$, $\bar{M}_v = 675,500$). Calcium stearate was supplied by Fisons Ltd and Wax E by Hoechst AG. Dibutyl tin maleate (DBTM) was supplied by Ciba-Geigy Ltd. (mp 106°C). α -Phenyl-*N*-methylnitron (PMN) was prepared by the method of Beckman⁹ from *N*-methyl hydroxylamine and benzaldehyde, mp = 88°C (lit.^a 88–89°C). α , B-Diphenylnitron (DPN) was prepared in the same way from *N*-phenylhydroxylamine and benzaldehyde.¹⁰ Recrystallized from methane, mp 113°C (lit.¹⁰ 112–113°C).

2-Methyl-2-nitrosopropane (MNP) was made by oxidation of *tert*-butylamine as follows: *Tert*-butylamine (52.3 mL) and Na₂WO₄·H₂O (4 g) in 50 mL H₂O cooled in ice/salt and H₂O₂ (16.7 mL, 21% w/v) added dropwise over 2 h

with stirring at $< 20^{\circ}\text{C}$. Blue organic layer separated, washed with dil. HCl and dried over MgSO_4 . Distillation gave dark blue nitroso compound, bp $50\text{--}55^{\circ}\text{C}$ transforming to colorless crystals on cooling to 0°C , mp $69\text{--}70^{\circ}\text{C}$.

ELEMENTAL ANAL: C, 55.4 (55.2%); H, 4,10.2 (10.3%); N, 16.1 (16.1)%.

Processing was carried out on a Hampden-RAPRA torque rheometer, as described previously.¹¹ Dibutyl tin maleate (DBTM) was added to all formulations containing the spin traps to scavenge HCl which was otherwise found to destroy the spin traps. A temperature of 180°C and rotor speed of 60 rpm was used throughout. Films for UV irradiation were prepared by compression molding at $170^{\circ}\text{C}/3$ min between cellophane sheets (550 PU grade), as described previously.¹¹

The estimation of nitroxyl radicals concentration by ESR has been described previously¹¹ using 0.1 M CuSO_4 solution as a reference.

The measurement of olefinic unsaturation and hydroperoxide by mercuric acetate catalyzed iodination and KI reduction, respectively, have been described previously.³

RESULTS

Figure 1 shows the concentration of nitroxyl ($> \text{NO} \cdot$) measured in PVC containing DBTM by ESR after processing with 2×10^{-5} mol/g of MNP (I) for various times. It is clear that the maximum nitroxyl concentration occurs earlier than at 5 min, but it was difficult to measure this concentration reproducibly. DPN and PMN behave similarly and the effect of increasing the initial concentration of the spin traps on the concentration of $> \text{NO} \cdot$ measured at 6 min is shown in Figure 2. In each case the nitroxyl concentration approaches a limiting value in the region of 3×10^{-6} mol/g.

The olefinic unsaturation formed in PVC after processing at 180°C for 6 min under the same conditions as in Figure 2 was found to be 10^{-6} mol/g for

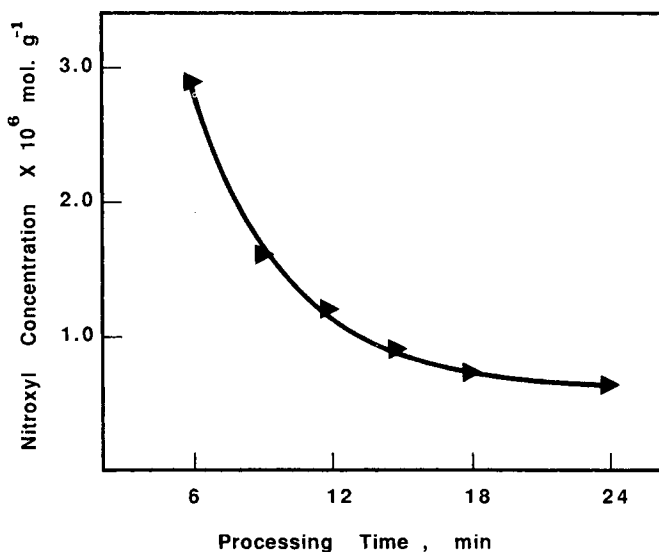


Fig. 1. Decay of nitroxyl radical in PVC containing MNP (initial concentration 2×10^{-5} mol g^{-1} after processing at various times. All samples contain 7.2×10^{-5} mol g^{-1} DBTM.

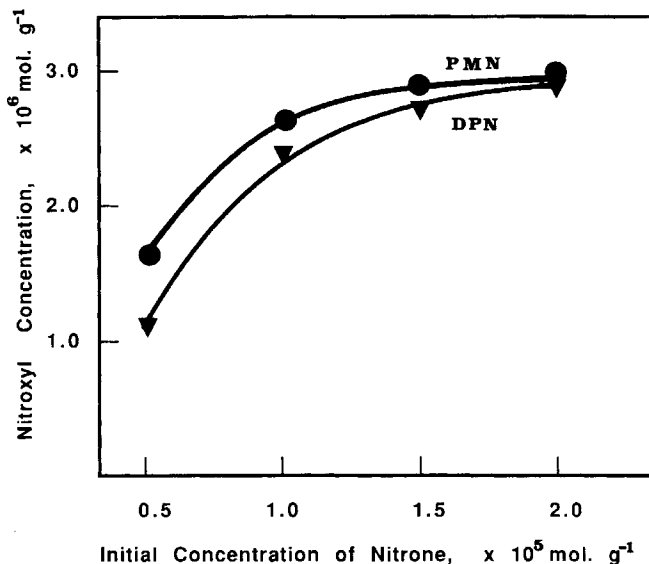


Fig. 2. Effect of increasing the initial concentration of nitron spin traps in PVC on the amount of the corresponding nitroxyl formed after processing for 6 min. All samples contain $7.2 \times 10^{-5} \text{ mol g}^{-1}$ DBTM.

the unstabilized control and $0.7 \times 10^{-6} \text{ mol/g}$ for PVC containing the spin traps.

Figure 3 compares the rates of hydroperoxide formation during processing at 180°C for MNP and PMN compared with the control without stabilizer (DPN was almost identical to PMN). It is clear that the spin traps reduce

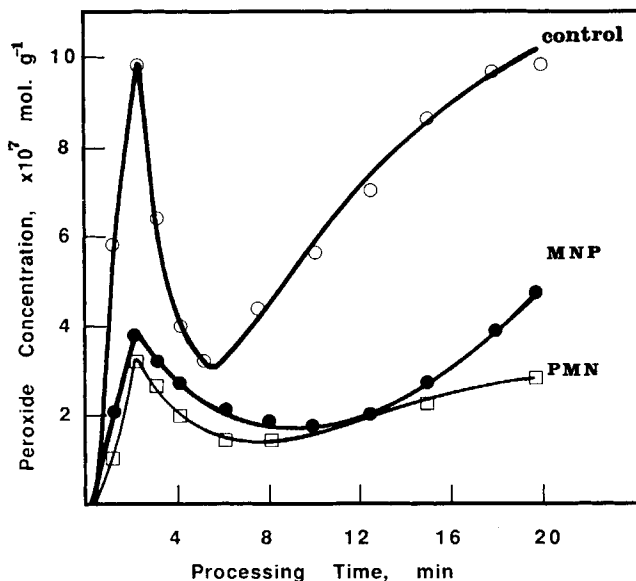


Fig. 3. The development of peroxides in unstabilized (control) and stabilized (with the spin traps MNP and PMN) PVC during processing. All samples contain a $2.9 \times 10^{-5} \text{ mol g}^{-1}$ DBTM.

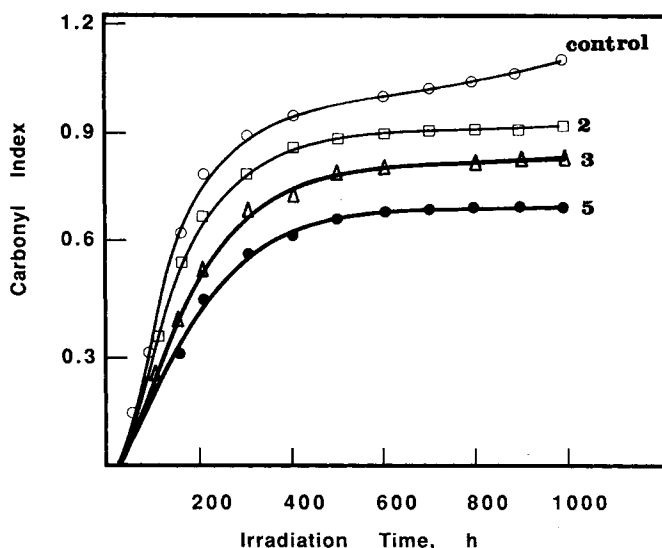


Fig. 4. Photooxidative stability of PVC in the absence (control) and presence of different concentrations of MNP. Numbers on curves are concentrations of MNP $\times 10^{-5}$ mol g $^{-1}$. All samples contain 2.9×10^{-5} mol g $^{-1}$ DBTM.

both the initial rate of peroxide formation and the maximum initial concentration achieved (0.38 and 0.34×10^{-6} mol/g, respectively, compared with 10^{-6} mol/g for the control). The formation of peroxidic gel³ during the first 5 min of processing follows exactly the same pattern.

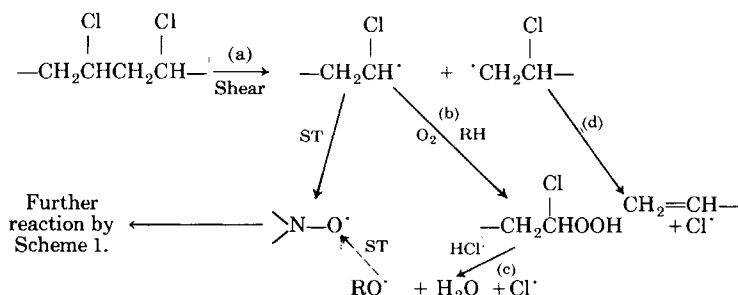
Figure 4 shows that MNP retards the photooxidation of PVC compared with a control containing a thermal stabiliser (DBTM). Table I lists the UV embrittlement times as a function of processing time at the concentration levels normally used in industrial practice. It is evident that the stabilizing effectiveness of the MNP does not decrease in parallel with the decrease in nitroxyl concentration in the system. Figure 1 shows that the nitroxyl concentration decreases by more than 50% between 6 and 10 min processing, but Table I indicates almost no significant reduction in the UV stability of the polymer over the same processing interval.

TABLE I
Effect of Processing Time (180°C) on the UV Embrittlement
Time of PVC Containing MNP (0.25 g/100 g) and DBTM (2.5 g/100 g).

Processing time (min)	Embrittlement time (h)		
	Control no addition	DBTM alone	DBTM + MNP
5	658	986	1250
10	600	972	1246
15	537	925	1188
20	562	925	1133

DISCUSSION

If the theories outlined in the introduction are correct, then there are two main ways in which radicals can be produced in a shearing mixer during the processing of PVC. The first is the chain scission process itself, Scheme 2, reaction (a) and the second is the reaction of the secondary product, the hydroperoxide with HCl, Scheme 2, reaction (c):



Scheme 2. Radical mechanisms involved in the mechanooxidation of PVC during thermal processing.

Some indication of what proportion of the radicals arise from each process can be gauged from the concentration of the secondary products during the first few minutes of processing. The maximum concentration of hydroperoxides that can be measured during this period in unstabilized PVC is about 10^{-6} mol/g. This does not represent the total amount that has been formed, since it is rapidly decomposed in the presence of hydrogen chloride which is formed in about the same amount in a radical generating reaction [Scheme 2, reaction (c)]. However, the fact that unsaturation [by reaction (d)] and hydroperoxide [by reaction (b)] are formed in more or less equivalent amounts (10^{-6} mol/g¹⁰) indicates that reactions (b) and (d) in Scheme 2 contribute equally to the consumption of macroalkyl radicals during the initial stages and thus account for $\approx 2 \times 10^{-6}$ mol/g of the 3×10^{-6} mol/g of radicals trapped by the spin traps. However, as evidenced by hydroperoxide formation not all the radicals are trapped by the spin traps; about 25% are converted to hydroperoxides (see Fig. 3). Hence, assuming the formation of a similar amount of unsaturation, the total radical concentration produced is probably nearer 5×10^{-6} mol/g. Consequently, about 40% of the radicals are produced by direct chain scission and the rest by secondary reactions.

The molar ratio of unsaturation to peroxides is actually higher in the presence of a spin trap (1.43) than in its absence (1.0). This suggests that another reaction is leading to the formation of unsaturation. It seems probable that some unsaturation results from oxidation of macroalkyl by nitroxyl in a further chain-breaking acceptor antioxidant process (Scheme 1) as previously described for the hindered piperidinoxyls.¹¹ This reaction would explain the rapid decay of nitroxyl during processing (Fig. 1) and would also account for the fact that, in spite of the considerable reduction in nitroxyl concentration, the polymer remains relatively stable to UV light even after 20 min processing. Studies in polypropylene have shown¹² that hydroxylamines (>NOH) have similar activity to the nitroxyls from which they are derived.

CONCLUSIONS

1. The incorporation of spin traps into PVC during processing indicates the formation of $> 3 \times 10^{-6}$ mol/g of radicals during the first 6 min, of which secondary reaction of hydroperoxide with HCl accounts for more than 50%.

2. It is concluded that radical reactions are primarily responsible for the degradation of PVC during thermal processing and subsequent photooxidation and that spin traps which remove macroalkyl radicals are effective stabilizers for the polymer in both environments.

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