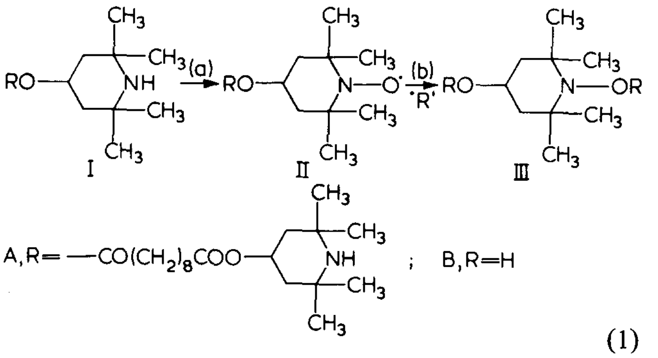
Mechanisms of antioxidant action—behaviour of hindered piperidines during photo-oxidation of polypropylene

Khirud B. Chakraborty and Gerald Scott
Department of Chemistry, University of Aston, Gosta Green, Birmingham B4 7ET, UK

(Received 20 January 1980)

Hindered piperidines with structure I effectively stabilize polyolefins against photo-oxidation[1–4].

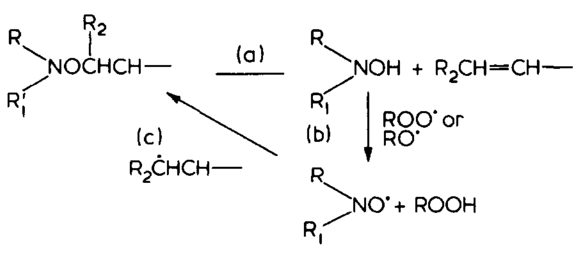


(1)

However, they are known to be converted rapidly to the corresponding nitroxyl radicals (II) under oxidizing conditions[1,5], which include commercial processing operations[4]. Nitroxyl radicals are effective traps for alkyl and macroalkyl radicals (reaction (1b))[6–8], but the evidence suggests[9–11] that reaction (1b) is not itself sufficient to account for the effectiveness of nitroxyl radicals as antioxidants and an additional process (2) has been proposed to account for the continuous regeneration of II[9]:

$$\mathrm{III} \xrightarrow{R''OO^{\bullet}} R''OOR' + \mathrm{II} \qquad (2)$$

This suggestion is not entirely satisfactory since it has been shown that the rate of reaction (2) is not high enough to account for the observed facts[10]. An alternative regenerative mechanism, reaction (3), has been shown to operate during thermal[12] and mechano-oxidation[13] of substrates with the appropriate structures:



(3)

N,N-disubstituted hydroxylamines are known to be very effective antioxidants[14] (reaction (3b)) and this communication reports evidence for the occurrence of reaction (3) during the photo-oxidation of polypropylene containing I and II.

Figure 1 shows, by i.r. spectrophotometry, the formation of carbonyl (1715 cm^{-1}) and unsaturation (1640 cm^{-1}) in polypropylene containing a commercial hindered piperidine, Tinuvin 770 (IA) and a related nitroxyl radical (IIB). The carbonyl induction period correlates closely with the embrittlement time of the polymer but there is a steady build-up of unsaturation in the polymer during the induction period. E.s.r. studies showed the formation of a nitroxyl radical from the piperidine in an auto-accelerating process; after reaching a maximum concentration, this species decayed to a lower stationary concentration until the end of the carbonyl induction period. *Figure 2* shows the results of a similar study in 1-methylcyclohexane containing IA. *Figure*

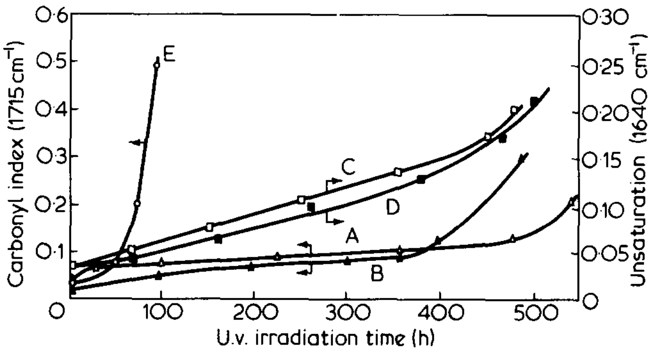


Figure 1 Effect of Tinuvin 770 (IA) and 4-hydroxy-2,2,6,6-tetramethyl piperidinoxyl (IIB) on carbonyl (1715 cm^{-1}) and unsaturation (1640 cm^{-1}) during the photo-oxidation of polypropylene. (Concentrations of additives, 3 x 10^{-4} mol 100 g^{-1}). A, carbonyl formation, IA; B, carbonyl formation, IIB; C, unsaturation formation, IA; D, unsaturation formation, IIB; E, control. A underwent embrittlement at 540 h; B, at 455 h

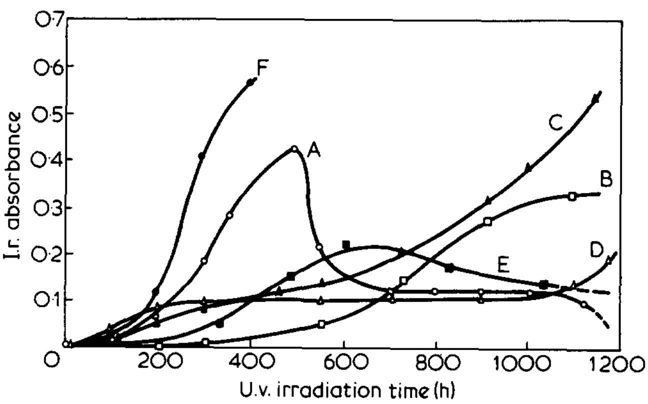


Figure 2 Effect of Tinuvin 770 (IA) on the photo-oxidation of methyl cyclohexane (concentration 10^{-2} M). A, growth and decay of nitroxyl IIB (1340 cm^{-1}); B, formation of vinylene (965 cm^{-1}); C, formation of vinylidene (895–900 cm^{-1}); D, formation of carbonyl (1715 cm^{-1}); E, growth and decay of hydroxylamine (2760–70 cm^{-1}); F, carbonyl control

0032–3861/80/030252–02$02.00

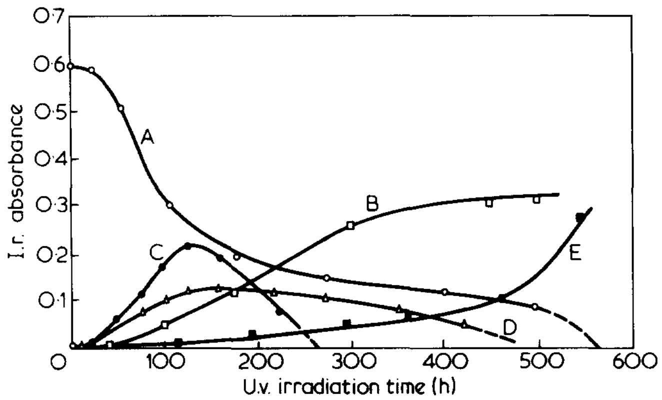


Figure 3 Effect of nitroxyl IIB (10^{-2} M) on the photo-oxidation of methyl cyclohexane. A, decay of nitroxyl, IIB; B, formation of vinylene (965 cm^{-1}); C, growth and decay of hydroxylamine (2760–70 cm^{-1}); D, growth and decay of N–O (in NOR where R=H or alkyl) (1300 cm^{-1}); E, formation of carbonyl (1715 cm^{-1})

3 compares the behaviour of nitroxyl IIB in the same substrate. The free hydroxylamine (2760–70 cm^{-1}) and associated unsaturation (965, 895 cm^{-1}) are formed in both cases at the expense of the nitroxyl radical, confirming the validity of the regenerative mechanism (reaction 3). It seems clear that the hydroxylamines act as reservoirs for the nitroxyl and the exceptional efficiency of the regenerative mechanism results from the participation of the complementary chain-breaking donor (CB–D) and chain-breaking acceptor (CB–A) antioxidant mechanisms[13].

References

1 Carlsson, D. J., Grattan, D. W., Suprunchuk, T. and Wiles, D. M. *J. App. Polym. Sci.* 1978, **22**, 2217
2 Ustilon, J. J. and Patel, A. R. *Am. Chem. Soc. Polym. Prepr.* 1977, **18**, 393
3 Allen, N. S. and McKellar, J. F. *Br. Polym. J.* 1977, **9**, 302
4 Chakraborty, K. B. and Scott, G. *Chem. Ind.* 1978, 237
5 Shlyapintokh, V. Y. *et al. Dokl. Akad. Nauk. SSSR*, 1975, **225**, 1132
6 Murayama, K., Morimura, S. and Yoshioda, T. *Bull. Chem. Soc. Jpn.* 1969, **42**, 1640
7 Howard, J. A. *Advances in Free Radical Chemistry* 1972, **4**, 49
8 Murayama, K., *J. Synth. Chem. Jpn.* 1971, **29**, No 4
9 Shilov, V. B. and Denisov, E. T. *Vysokomol. Soed. A.* **16**, 2313; Sudnik, M. V., Rozantsev, M. F., Shapiro, A. B. and Rozantsev, E. G. *Bull. Akad. Sci. USSR* 1976, 2706
10 Carlsson, D. J., Garton, A. and Wiles, D. M. 'Developments in Polymer Stabilization' (Ed. G. Scott), App. Sci. Pub. 1979, 219
11 Carlsson, D. J., Gratton, D. W. and Wiles, D. M. *Polym. Degrad. Stability*, 1979, **1**, 69
12 Bolsman, T. A. B. M., Blok, A. P. and Frijns, J. H. G. *Rec. Trav. Chim Pays-Bas*, 1978, **97**, 313
13 Scott, G. *J. S. African Chem. Soc.* in press, Katbab, A. and Scott, G. *Chem. Ind.* in press
14 Brownie, I. T. and Ingold, K. U. *Can. J. Chem.* 1967, **45**, 2427

Copolymerization of acrylic acid with sulphur dioxide

Christos P. Tsonis
Chemistry Department, University of Petroleum & Minerals, Dhahran, Saudi Arabia
and Wallace M. Pasika
Chemistry Department, Laurentian University, Sudbury, Ontario, Canada
(Received 5 December 1979)

Numerous copolymerizations of simple aliphatic alkene monomers with liquid sulphur dioxide have been documented and established as proceeding by a free radical mechanism[1–4]. Regardless of the polymerization feed ratio, the composition of these polysulphones is that of an alternating copolymer.

In contrast, there is an overwhelming tendency for alkenes with positive values of *e* (Alfrey–Price *Q*–*e* values), to be reluctant to copolymerize with sulphur dioxide and to prefer to homopolymerize[3,5–8]. Nevertheless, acrylamide, which would be placed into the latter category, has been copolymerized with sulphur dioxide using a variety of free radical initiators[9,10]. In this communication we report the first example of the copolymerization of acrylic acid (AA) with sulphur dioxide.

Experimental

Materials. Acrylic acid (J. T. Baker Chemical Co.) was purified on a high vacuum line. Anhydrous sulphur dioxide (Union Carbide) was condensed into a jacketed burette (through which an aqueous ethylene glycol solution at –33°C was circulated) and run into the reaction vessels as needed and in the amount required. The t-butyl hydroperoxide (Aldrich Chemical Co.) was used as received. Methanol was purified by distillation. All other solvents were used as received.

Table 1 Effect of temperature on copolymerization

	Copolymer composition			
Temperature (°C)	wt% S	wt% AA	wt% SO_2	AA:SO_2 mole ratio
24	1.97	96.1	3.9	21.8
–33	2.02	96.0	4.0	21.3
–42	2.64	94.7	5.3	15.8
–52	4.20	91.6	8.4	9.7
–60	5.50	89.0	11.0	7.2

Conditions: 1 ml AA; 10 ml SO_2; 0.1 ml $(CH_3)_3COOH$; 5 min

0032–3861/80/030253–03$02.00