Polymer photostabilization by HALS derivatives: the role of piperidine–hydroperoxide association

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Hindered amine light stabilizers (HALS), namely those based on 2,2,6,6-tetramethylpiperidine, belong to a class of powerful stabilizers whose performance is superior to classical light screeners[1]. Originally, their effectiveness was attributed to the presence of nitroxide – an efficient radical trap – which is formed by the oxidation of parent amine[2]. Carlsson[3] has pointed out that other species, such as O-substituted hydroxylamines formed by the transformation of original piperidine, may also participate actively in the photostabilization cycle. However, Grattan *et al.*[4] have shown that the overall stabilizing effect exhibited by HALS in practice far exceeds that calculated theoretically considering only radical trapping by the nitroxide and substituted hydroxylamine. It was suggested that other stabilizing processes should be considered. One of the possibilities they suggested is the formation of associates between the nitroxide and hydroperoxide present in the polymer. This process would lead to a strong local concentration of the stabilizing species in the vulnerable oxidized regions rich in –OOH groups. Moreover, these authors have reported the value of the equilibrium constant for such associate formation to be 26 M^{-1} using the e.s.r. ^{14}N hyperfine coupling constant data. We have recently observed[5] that not only nitroxide but also the parent piperidine is capable of forming associates with hydroperoxides. The formation of stable, well-defined associates between hydroperoxides and various non-hindered amines was first reported by Oswald *et al.*[6] who termed these compounds alkylammonium hydroperoxide salts.

We have prepared various HALS–ROOH associates by mixing pentane solutions of the components in equimolar quantities, using both t-butylhydroperoxide (TBHP) and cumenehydroperoxide (CHP), while 2,2,6,6-tetramethylpiperidine (I), 2,2,6,6-tetramethyl-4-oxo-piperidine (II) and bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate (III) were used as the representatives of HALS. Either solid crystals (in the case of associates derived from amines II and III) or an oily liquid (in the case of amine I) resulted following evaporation of the solvent.

Inspection of the i.r. spectra of the pure compounds reveals that pronounced changes occur within the region 3700–2100 cm^{-1}. *Figure 1* shows the spectrum of the I–TBHP associate where a typical broad band extending from 3700–2100 cm^{-1} is present. Moreover, new absorptions at 3100 and 2800 cm^{-1} superimposed on this band are characteristic also for the associate formation, the strong hydroperoxide dimer absorption at 3400 cm^{-1} being suppressed. *Table 1* shows the i.r. spectral characteristics for other HALS–ROOH derivatives.

When these spectra are compared with those belonging to purely ionic ammonium salts (e.g. 2,2,6,6-tetramethylpiperidinium benzoate) it can be seen that the discrete structure of the 'ammonium band' (2700–2250 cm^{-1}) is missing. Also the scissoring vibrations of NH_2^+ at 1620 and 1550 cm^{-1} present in the benzoate salt are absent in all our HALS–ROOH associates.

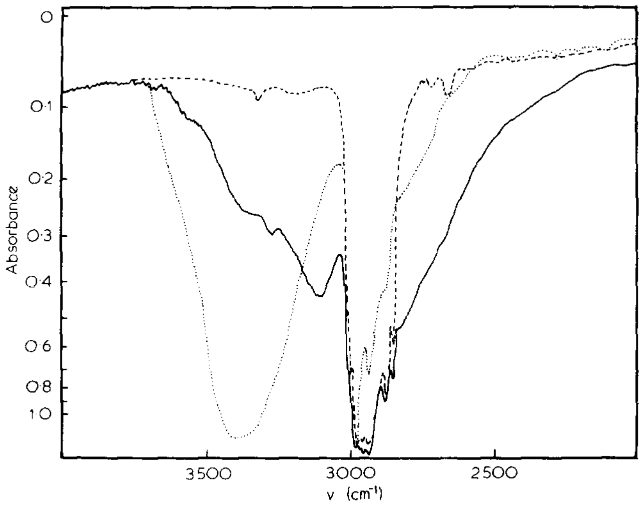

Figure 1 I.r. spectral changes observed during HALS–ROOH association. – – –, 2,2,6,6-tetramethylpiperidine (I); ...., t-butylhydroperoxide (TBHP); ———, (I–TBHP) associate 1:1 mol. Spectra of pure materials taken in a 0.025 mm AgBr cell

Table 1 I.r. spectral characteristics of various 1:1 molar HALS–ROOH associates

$TBHP^{a,f}$	$CHP^{b,f}$	$I^{c,f}$	$II^{d,f}$	$III^{e,g}$	$(I–TBHP)^f$	$(II–TBHP)^f$	$(III–TBHP)^g$	$(I–CHP)^f$	$(II–CHP)^f$	$(III–CHP)^g$
3550^h	3570^h									
3400^{vs}	3430^{vs}			3425^{w-m}			3425^{vw}			3425^{vw}
		3330^{vw}	3338^m	3330^m	3270^{vw}	3300^m	3295^m	3285^w	3300^m	3300^m
					3100^m	3130^m	3080^m	3070^w	3080^m	3080^m
					2830^{vw}	2840^w	2818^m	2800^w	2840^w	2820^m
		2670^w	2720^w	2718^w						
			1710^{vs}	1724^{vs}		1710^{vs}	1720^{vs}		1705^{vs}	1718^{vs}
1630^m	1605^m							1605^m	1605^m	1605^w

[a] t-butylhydroperoxide; [b] cumenehydroperoxide; [c] 2,2,6,6-tetramethylpiperidine; [d] 2,2,6,6-tetramethyl-4-oxo-piperidine; [e] bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate; [f] as such in a 0.025 mm AgBr cell; [g] in a KBr pellet; [h] hydroperoxide monomer peak (visible upon dilution); [s], strong; [m], medium; [w], weak; [v], very

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The i.r. spectral measurements of TBHP at various concentrations (0.02–0.5 M) have enabled us to calculate the equilibrium constant of ROOH dimerization K_D

$$2\ \mathrm{ROOH} \rightleftharpoons (\mathrm{ROOH})_2$$

$$K_D = \frac{[(\mathrm{ROOH})_2]}{[\mathrm{ROOH}]} \qquad (1)$$

The values of K_D at 27°C were found to be 2.3 and 3.4 M^{-1} for CCl_4 and cyclohexane, respectively. The value measured at 30°C in CCl_4 by Walling[7] has been reported to be 1.9 M^{-1} which correlates well with our observation. In dilute hydroperoxide solution, in which hydroperoxide monomer predominates, it was thus possible to measure the amine I–TBHP association constant K_N without having to consider equilibrium (1)

$$\mathrm{ROOH} + \text{amine I} \rightleftharpoons \mathrm{ROOH}\cdots\text{amine I}$$

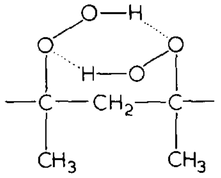
$$K_N = \frac{[\mathrm{ROOH}\cdots\text{amine I}]}{[\mathrm{ROOH}]\ [\text{amine I}]} \qquad (2)$$

The value of K_N was obtained by following the concentration of TBHP monomer $[\mathrm{ROOH}]_0 = 0.025$ M) while varying the concentration of amine I ($[\text{amine I}]_0 = 0.025$–1.25 M). Increasing the concentration of amine I suppresses the 3550 cm^{-1} hydroperoxide monomer peak while new absorptions at 3100 and 2740 cm^{-1} due to the associate appear in compensated spectra. The values of K_N at 27°C were found to be 23 ± 2 and 29 ± 1 M^{-1} for CCl_4 and cyclohexane, respectively. Equilibrium (2) may be changed reversibly with temperature. The temperature dependence of K_N has enabled us to calculate $-\Delta H$ of the association process at 22.6 ± 0.8 kJ mol^{-1} (5.4 ± 0.2 kcal mol^{-1}).

^1H n.m.r. spectra of the HALS–ROOH associates exhibit a pronounced upfield shift of the OH proton on increasing the temperature, e.g. in the case of the amine I-CHP associate, the value of $\delta = 5.57$ ppm observed at 23°C was shifted to 5.23 ppm upon increasing temperature to 60°C.

I.r. and n.m.r. spectral evidence, together with the value of $-\Delta H$ for the association process, suggest the existence of a strong hydrogen bond in HALS–ROOH associates rather than ionic bonding.

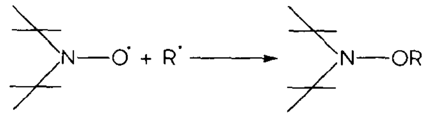
The observed affinity of HALS towards ROOH supports the hypothesis of a considerable local increase in piperidine concentration around the hydroperoxidized sites in the polymer. Grattan *et al.*[4] have attempted to express the phenomenon quantitatively for the case of nitroxide free radical association with TBHP, where the association constant was found to be almost the same as measured by us for piperidine I. Their estimate, however, would hold only for an isolated (monomeric) hydroperoxide. Polypropylene hydroperoxide is known to exist in the form of a 'fence' hydroperoxide with a predominating dimeric 1,3-dihydroperoxide structure[8].



(3)

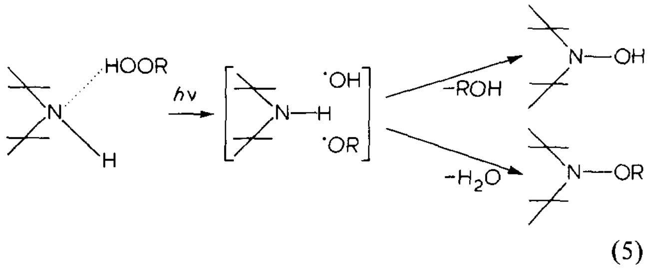
Thus the piperidine in the proximity of such a hydroperoxide will have to compete with equilibrium hydroperoxide monomer–dimer (3). The equilibrium constant K_D, measured for TBHP, is of no value in this case since it reflects intermolecular dimerization which will be far less probable in the polymer phase than the topologically preferred intramolecular dimerization of polypropylene 1,3-dihydroperoxide. Alternatively, the initial concentration of HALS in the polymer exceeds that of hydroperoxide by several orders of magnitude. Therefore, it is justifiable to assume that in the polymer phase the HALS–ROOH associates exist, although the quantification of this phenomenon is still difficult.

In view of these results, it is possible to offer an explanation for some of the already observed phenomena concerning polypropylene stabilized by HALS, e.g. Carlsson[3] reported that the parent piperidine was rapidly converted to an O-substituted hydroxylamine in the polymer being photooxidized. The process is considered generally to proceed via nitroxide free radicals which trap polymeric radicals ($R^\bullet$)



(4)

It was shown, however, that in the presence of oxygen this reaction is not favourable since $R^\bullet$ radicals are rapidly peroxidized[3,5]. Assuming the existence of HALS–ROOH associates the formation of an $\gtrsim$N–OR compound may readily be accounted for by the reaction



(5)

This reaction will be enhanced because of the proximity of the stabilizer near the peroxide being photolysed. The $\gtrsim$N–OR species can then fulfil their stabilizing role as previously suggested by Denisov[9]. The hydroxylamine $\gtrsim$N–OH, a more reactive compound, has not yet been detected in these systems. This is not surprising, because its stationary concentration will be very low. Facile loss of hydrogen in the presence of free radicals will effect rapid conversion to nitroxide.

The formation of HALS–ROOH associates would also account for the phenomenon observed by Chakraborty and Scott[10], who reported the increased efficiency of HALS in severely processed polypropylene (i.e. rich in ROOH content).

The HALS–ROOH associate formation, precluded at elevated temperatures (see above), will not occur during thermooxidation; this might be one of the reasons why HALS exhibit a rather poor efficiency as antioxidants.

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E.p.r. study of polyacetylene films

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Doped polyacetylene is a material which many laboratories research, and experiments concerning its transport[1–3] and magnetic properties[4–6] have been performed.

Much less work has been done on nondoped samples. Nevertheless, such research can yield interesting information about the origin and nature of the electrons which contribute to the observed electrical conductivity and magnetic susceptibility of nondoped as well as doped samples. We present here an experimental e.p.r. study to check whether unpaired electrons exist in a pure *cis*–(CH)$_x$ polyacetylene isomer and remain during the thermal isomerization from *cis* to *trans*.

Using the method described by Ito *et al.*[7], polyacetylene has been directly prepared at –78°C in the e.p.r. tube which was sealed under vacuum just after termination of polymerization. Using a Bruker ER 10 spectrometer with a variable temperature apparatus, the e.p.r. spectra were immediately recorded at the temperature of polymerization. *Figure 1a* shows that, if there is a very broad, large signal, due in particular to Ti^{3+} ions contained in the catalyst system and centred near $g = 1.95$, no signal exists at the free electron g value 2.0023. The catalyst e.p.r. spectrum, which has been extensively studied[8,9], is known to depend strongly on the characteristics of the catalytic melt (particularly the molar ratio of the constituents (C$_2$H$_5$)$_3$ Al and (n-C$_4$H$_9$O)$_4$ Ti, and on the temperature. Our observations are in agreement with other work[8,9].

Increasing the temperature to –18°C drastically changes the form of the spectrum centered at $g = 1.95$ but at the same time a small symmetric signal appears at $g = 2.0023$ (*Figure 1b*). Its width (defined as the distance in gauss between the two peaks of the absorption derivative), which is difficult to measure with accuracy, is of the order of 10 gauss.

A further increase in temperature to 25°C again changes the catalyst signal while the signals in the spectrum near $g = 2.0023$ continues to grow without any significative change in line-width and position (*Figure 1c*). After 15 min at this

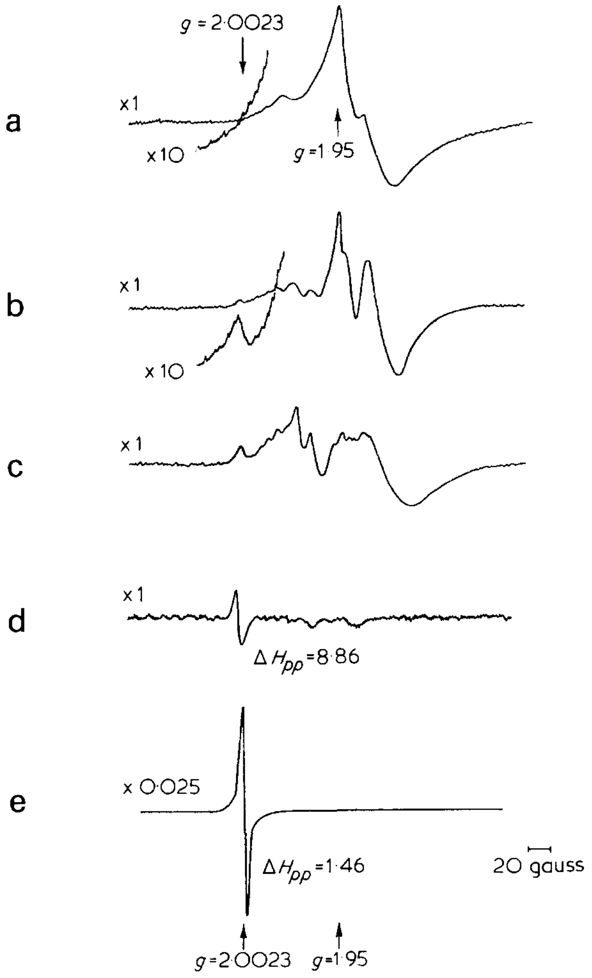

Figure 1 Recorded e.p.r. spectra on polyacetylene and its catalytic system from the temperature at which it has been polymerized to room temperature. While the catalyst signal at $g = 1.95$ disappears by thermal treatment and oxidation, the signal coming from the polyacetylene at $g = 2.0023$ builds up. Its linewidth decreases when the system is heated to 200°C. (a), –78°C; (b), –18°C; (c), 25°C; (d), 25°C, 20 min exposure to air pressure; (e), 25°C, after 1 min heat treatment at 200°C

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