

# Spin Trapping by 2-Methyl-2-nitrosopropane (MNP) in the Polymerization of Styrene or Substituted Styrenes and Maleic Anhydride

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**Dedicated to Professor Göran Bergson on the occasion of his 65th birthday**

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The copolymerization of styrene(s) and maleic anhydride in chloroform has been studied by the spin trapping technique, using 2-methyl-2-nitrosopropane (MNP) as the spin trap. Four types, A, B, C and D, of EPR spectra were recognized, among which three corresponded to trapping of the growing polymer chain at a centre originating from the styrene part or from two centres originating from the maleic anhydride part. The fourth EPR spectrum, denoted by D, had characteristics different from those of a spin adduct spectrum, in particular a large  $\alpha$ -H coupling of about 2 mT, suggesting that the oxygen-bonded nitrogen should be part of a ring structure. Such a structure might either be a cyclic five-membered aminoxyl or a six-membered 1,2-oxazine radical cation. It was also established that strong D spectra could be generated from styrene and MNP alone in the presence of a low concentration of zinc chloride. These findings were discussed in relation to the diradical mechanism of charge transfer polymerization.

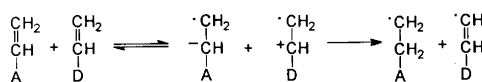
The copolymerization of styrene and diethyl fumarate gave rise to a similar set of spin adducts with MNP.

The copolymerization of a donor and acceptor type olefin has been the subject of extensive mechanistic discussion.<sup>1,2</sup> It was early suggested that electron transfer might take place between the reactants with formation of a radical ion pair, followed by transfer of a proton from the radical cation to the radical anion forming a pair of neutral radicals (Scheme 1; A denotes an electron-accepting group, D an electron-donating one). The actual initiator(s) of the polymerization process would be one or both of these radicals. Later, it was inferred that the olefin pair would first form a diradical which acts as the initiator (Scheme 1).

Spin trapping experiments, using 2-methyl-2-nitrosopropane (*t*-BuNO) as the trapping reagent, demonstrated the development of several aminoxyl radicals with characteristic EPR spectra during the polymerization of styrene or alkyl vinyl sulfides together with olefins activated by electron-withdrawing groups, like acrylonitrile, methyl acrylate, diethyl fumarate or maleic anhydride.<sup>3</sup> The aminoxyls were assumed to be the spin adducts of radicals either participating in the polymerization process

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The electron transfer mechanism



The diradical mechanism

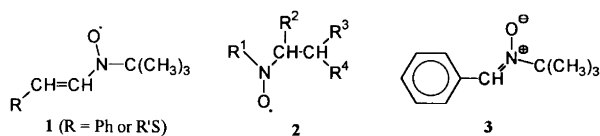


Scheme 1.

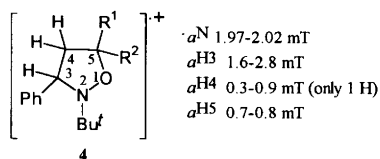
or formed in secondary reactions, such as Diels–Alder reactions between the donor and acceptor olefin.<sup>3b</sup>

Spectra of one type, to be denoted type D in the following, differed significantly from the spin adduct spectra. They had  $a^N$  around 1.5 mT and two hydrogen couplings, one of them with an unusually large  $a^H$  of about 2.0 mT and the second one  $< 0.1$  mT. These spectra were assigned by Sato *et al.* to vinyl spin adducts (**1**),<sup>3</sup> seemingly providing evidence for the electron transfer mechanism. However, a recent treatment of the problem<sup>4</sup> indicated that it is unlikely that **1** would be responsible for the

spectrum mentioned. No alternative structure was given, but it was surmised that the general structure **2**, possibly built into a ring system, should be the correct one.

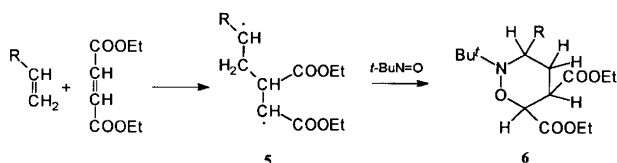


We<sup>5</sup> and others<sup>6</sup> have drawn attention to the fact that nitronium spin traps, such as *N-tert*-butyl- $\alpha$ -phenylnitronium (**3**, PBN) can participate in cycloaddition reactions with olefins or nitriles, an aspect of nitronium reactivity which has been utilized extensively for synthetic purposes.<sup>7</sup> Thus irradiation of an olefin and PBN in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) under oxidizing conditions led to the development of EPR spectra, assigned to isoxazolidine radical cations **4**<sup>+</sup> of cycloadducts **4**, with the observed ranges of coupling constants indicated.<sup>5</sup> The important features of these species in the present context are (i) the parent neutral compounds **4** are cyclic derivatives of hydroxylamine, and thus expected to be oxidized with ease to their radical cations (electrochemical studies place the peak potentials for the anodic oxidation of various acyclic hydroxylamines in the potential range 0.45–0.80 V vs. SCE),<sup>8</sup> and (ii) the hydrogen coupling constant at the carbon adjacent to the nitrogen atom is large, 1.6–2.8 mT.

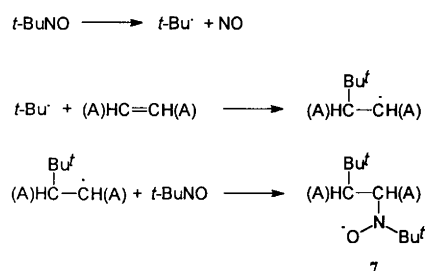


Similar species might be formed from *t*-BuNO under conditions of charge-transfer polymerization described above. If, for example, the suggested initiator radical, the diradical **5** formed from the two olefins,<sup>2</sup> is trapped by *t*-BuNO, the resulting spin adduct might undergo ring closure to give a perhydrooxazine derivative, as exemplified by the formation of **6** from a monoolefin as the donor and diethyl fumarate as the acceptor (Scheme 2). Such a compound would be easily oxidizable to its radical cation which might correspond to the D-type EPR spectra.

A recent finding<sup>4,9</sup> of relevance for the use of *t*-BuNO as a spin trap is a side-reaction in which the well known cleavage of *t*-BuNO by visible light leads to the formation of persistent *t*-Bu/*t*-BuNO adducts **7** from acceptor olefins (Scheme 3). Such adducts are formed even upon



Scheme 2.



Scheme 3.

very limited light exposure. The reaction depends on the kinetics of the addition of *t*-Bu $\cdot$  to the olefin:  $k_{\text{addition}}[\text{olefin}]$  must be higher than  $k_{\text{trap}}[t\text{-BuNO}]$  to give  $(t\text{-Bu})_2\text{NO}\cdot$ ,  $2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , a requirement met only by acceptor olefins of the type mentioned above.

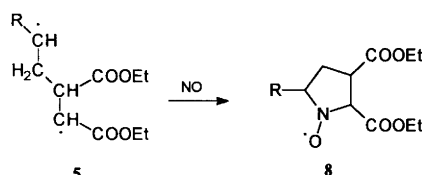
A problem introduced by Scheme 3 concerns the possible role of NO in the development of the D-type EPR spectra. As a hypothetical example, the diradical **5** might react with NO to give a species which might cyclize to **8** (Scheme 4), a kind of aminoxyl radical the EPR spectrum of which is known to show a large h.f.s. constant to an  $\alpha$ -hydrogen.<sup>10</sup>

Finally it was shown<sup>9</sup> that *t*-BuNO can undergo a formally one-electron reductive coupling with acceptor olefins, giving rise to aminoxyls **9** in a mechanistically less well understood reaction (Scheme 5).

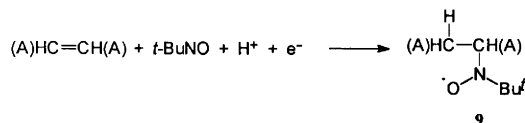
In what follows, we present a study of spin trapping in the maleic anhydride–styrene(s) reaction and propose structures to the radicals trapped. A limited investigation of the diethyl fumarate–styrene system was also performed.

## Results

*Reaction of styrene and maleic anhydride in the presence of t-BuNO. The origin of the D-type spectrum.* The EPR spectrum of a solution of styrene, maleic anhydride and *t*-BuNO in ethylbenzene,<sup>3b</sup> made up with normal precautions to exclude light and oxygen (preparation time of 2–3 min, argon deaeration of the sample immediately after mixing of the components, ordinary laboratory light) initially gave a mixture of two weak spectra, that

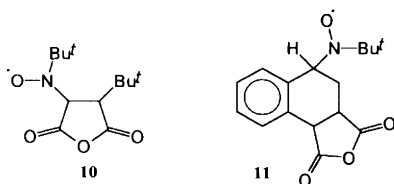


Scheme 4.



Scheme 5.

of the *t*-Bu *t*-BuNO adduct **10** and a  $3 \times 2$  line spectrum of broad lines,  $a^N = 1.47$ ,  $a^H = 0.45$  mT, the latter being denoted a type C spectrum (Fig. 1a). In a parallel, similar experiment more stringent precautions to exclude light (semi-dark room) led to the complete removal of the spectrum of **10**. Upon standing of either sample in the dark, the same spectrum developed as that observed by Sato *et al.*<sup>3b</sup> (Figs. 1b and 1c), although more slowly (of the order of 20 h, compared to 15 min) while the C spectrum remained at the same level. Based on indirect evidence, these authors assigned this spectrum to an aminoxyl derived from a rearranged Diels Alder adduct of styrene and maleic anhydride (**11**).<sup>11</sup>



The spectrum of Fig. 1c upon closer examination was best analyzed in terms of at least three components, namely the previously mentioned type C spectrum, a  $3 \times 2 \times 2$  line spectrum (type B,  $a^N = 1.45$ ,  $a^H = 0.167$ ,  $a^H = 0.056$  mT) and a  $3 \times 2 \times 2 \times 2 \times 2$  line spectrum (type A,  $a^N = 1.505$ ,  $a^H = 0.172$ ,  $a^H = 0.169$ ,  $a^H = 0.100$ ,  $a^H = 0.057$  mT). The basis for this analysis is discussed below. A simulated spectrum is shown in Fig. 1d. The type-D spectrum mentioned in the beginning was not detectable.

Since there was some previous indication that the D spectrum was more intense in chloroform,<sup>3b</sup> the experiment was repeated in this solvent. Also the concentration of *t*-BuNO was kept at a higher level, as in previous investigations.<sup>3b,4</sup> Apart from an almost identical ABC combination of spectra, a weak D spectrum ( $a^N = 1.50$ ,  $a^H = 2.00$ ,  $a^H = 0.063$  mT) appeared, again after considerable time (10 h instead of 15 min stated in the original publication). Its intensity was of the order of 0.5–2% of the ABC spectrum. Since the D spectrum appeared erratically and with low intensity in most cases studied below, in seeming contrast to published observations,<sup>3b,c</sup> we suspected that it might be the result of difficultly controllable factors connected with the sample preparation. The most obvious candidate for causing side-reactions is NO, formed by accidental photolysis of *t*-BuNO, and its presence is most easily recognized by the appearance of the spectrum of **10**. This spectrum always appeared immediately after sample preparation, unless the light conditions were controlled at a level of semi-darkness (see above).

That NO might be involved in the development of the D spectrum was indicated by, for example, the following experiment. The ABC spectrum obtained from a solution of 4-fluorostyrene, maleic anhydride and *t*-BuNO in chloroform was not accompanied by the D spectrum after 20 h of reaction at 23 °C. Irradiation of the sample tube for 3 min by diffuse daylight immediately superim-

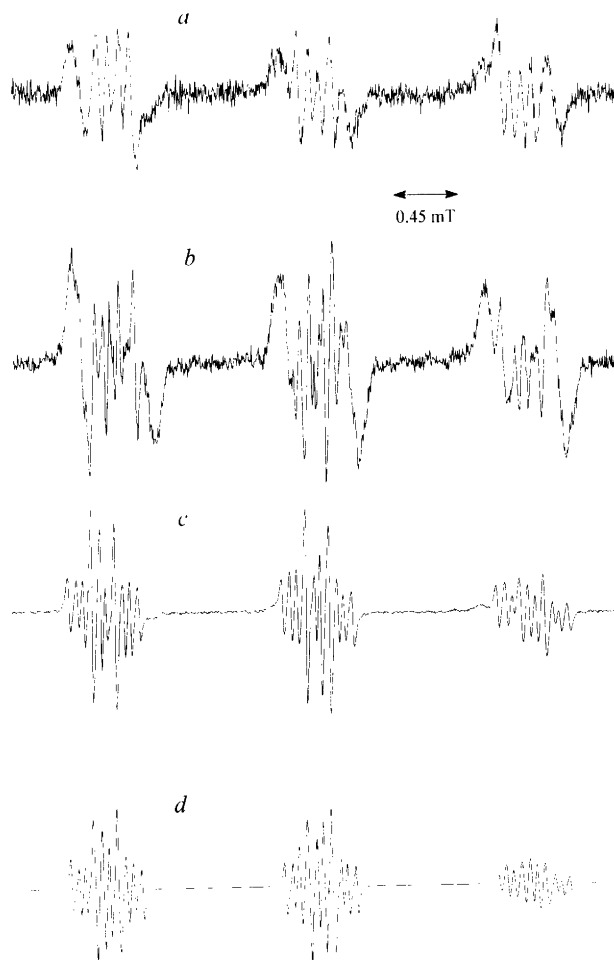


Fig. 1. EPR spectra recorded from a solution of *t*-BuNO (ca. 30 mmol dm<sup>-3</sup>), styrene (ca. 4.1 mol dm<sup>-3</sup>) and maleic anhydride (ca. 0.5 mol dm<sup>-3</sup>) in ethylbenzene after (a) 15 min, (b) 5 h and (c) 50 h in the dark. Spectrum (d) is a simulation based on the data given in Table 2, the *g* displacement of the A and C spectra being 0.029 and -0.010 mT in relation to the B spectrum.

posed a strong spectrum of **10** upon the ABC spectrum, and after 0.5–1 h a weak D spectrum had developed and the ABC spectrum had begun to reappear. However, the relative intensity of the D spectrum still was low (ca. 1.5% of the ABC combination), suggesting that yet another factor might be involved. Dioxygen is a second candidate for causing problems during sample preparation, and in this case a combination of light and dioxygen will have the capacity to produce some NO<sub>2</sub>, a one-electron oxidant with the redox potential required for oxidizing e.g., cyclic hydroxylamines to their radical cations.

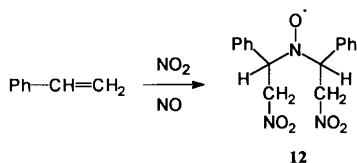
Several tests of this hypothesis of combined NO–dioxygen intervention were performed, but no really convincing evidence for its correctness was obtained. If a combination of NO and dioxygen is necessary for the formation of the D spectrum, their interplay and reactions with the other reaction components must be complex. It also must be recognized that the D spectrum was

controlled by relatively fast kinetics of formation and disappearance. The corresponding species appeared and decayed over a period of at most 100 h, while the species corresponding to the B and C spectra persisted at high and almost constant concentrations for at least 700–800 h.

As a control experiment to see if NO by itself might cause radical formation, a solution of NO, styrene and maleic anhydride without any *t*-BuNO present was prepared. It immediately developed a weak EPR spectrum of a pair of diastereomeric aminoxyls **12** [ $a^N=1.51$ ,  $a^H=1.19$  (2 H),  $a^H=0.069$  (2 H) mT;  $a^N=1.44$ ,  $a^H=0.72$  (2 H) mT] known<sup>12</sup> to result from the interaction between NO, NO<sub>2</sub> and styrene (Scheme 6). Even if the sample was prepared under Ar protection, there was evidently still dioxygen present to produce some NO<sub>2</sub>. These radicals disappeared after 20 h in the dark, and no radicals of the ABCD type appeared at any time.

A similar styrene–maleic anhydride–NO experiment in chloroform, but with *t*-BuNO present, was then performed. The first EPR spectrum taken after mixing (Fig. 2a) showed the same set of radicals as in the experiment without *t*-BuNO. After the sample had been warmed to 45 °C for 30 min in the dark (warming can be employed<sup>3</sup> to speed up the reaction), a strong 3 × 2 line spectrum ( $a^N=1.48$ ,  $a^H=0.49$  mT; these values are close to those of what has been denoted the C spectrum and the spectrum will therefore be considered as such) had developed (Fig. 2b). In the middle of each group of lines small peaks reflect the presence of weak AB spectra, but no D component was seen. After 2.5 h at 23 °C the AB component had grown relative to the 3 × 2 spectrum, and the outer doublet of a weak D spectrum had become visible (Fig. 2c). After 20 h the AB spectra dominated over the weak C and D components (Fig. 2d).

It is known that a Lewis acid, like zinc chloride, has a catalyzing effect upon the copolymerization of a mixture of a donor and acceptor olefin. Spin trapping experiments in styrene mixtures with methyl methacrylate, methyl acrylate, methacrylonitrile or acrylonitrile in the presence of zinc chloride gave rise to strong D-type spectra in addition to the usual aminoxyl spectra.<sup>3a</sup> In the styrene–maleic anhydride system, the addition of zinc chloride for the first time reproducibly gave D spectra (Table 1), now of higher intensity, maximally about 10% of the combined ABC spectrum. The D spectrum built up more rapidly than in the absence of zinc chloride, a plateau of constant intensity being reached after 5 h (Fig. 3) and lasting for at least 24 h. The ABC spectrum grew linearly during this period.



Scheme 6.

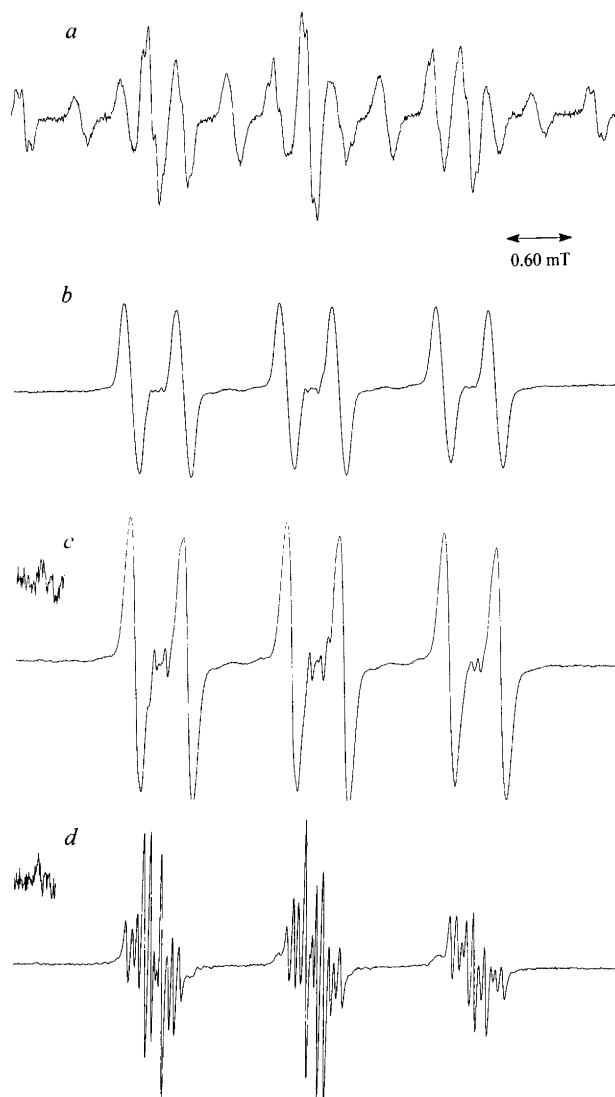


Fig. 2. EPR spectra recorded from a solution of *t*-BuNO (ca. 150 mmol dm<sup>-3</sup>), styrene (ca. 2.5 mol dm<sup>-3</sup>) and maleic anhydride (ca. 0.5 mol dm<sup>-3</sup>) in (<sup>2</sup>H)chloroform which had been bubbled by NO for 20 s. Spectra were taken after successively (a) 15 min from mixing, (b) 30 min at 45 °C in the dark, (c) 2.5 h at 23 °C in the dark and (d) 20 h at 23 °C in the dark.

A critical fact was established when the zinc chloride experiment was performed with styrene and *t*-BuNO alone in chloroform. This led to the development of an intense D spectrum (Table 1) together with an aminoxyl spectrum with 3 × 2 broad lines,  $a^N=1.51$ ,  $a^H=0.37$  mT, and a weak triplet from *t*-Bu<sub>2</sub>NO,  $a^N=1.59$  mT (Fig. 4). After 24 h, a second, weaker D spectrum with  $a^N=1.50$ ,  $a^H=1.84$  and  $a^H=0.078$  mT had developed, and the 3 × 2 line spectrum had evolved into a more complex pattern. Under these conditions, the D spectrum appeared with styrene in as low a concentration as 20 mmol dm<sup>-3</sup>.

Reaction of styrene and maleic anhydride in the presence of *t*-BuNO-(<sup>2</sup>H)<sub>9</sub>. Fully deuteriated *t*-BuNO has been

Table 1. EPR spectra of type D, obtained from a solution of a donor and an acceptor olefin, or donor olefin alone, and *t*-BuNO with or without zinc chloride present.

Donor olefin	Acceptor olefin	Solvent	$a^N$ /mT	$a^H$ /mT	$a^H$ /mT	Ref.
PhCH=CH <sub>2</sub>	Maleic anhydride	CDCl <sub>3</sub>	1.50	2.00	0.063	This work
PhCH=CH <sub>2</sub>	None	CDCl <sub>3</sub> /ZnCl <sub>2</sub>	1.513	2.033	0.067	This work
PhCH=CH <sub>2</sub>	Maleic anhydride	CHCl <sub>3</sub>	1.51	2.02	0.07	3b
PhCH=CH <sub>2</sub>	Me acrylate	Neat/ZnCl <sub>2</sub>	1.49	2.02	0.07	3a
PhCH=CH <sub>2</sub>	Me methacrylate	Neat/ZnCl <sub>2</sub>	1.49	1.98	0.07	3a
PhCH=CH <sub>2</sub>	2-Me-acrylonitrile	Neat/ZnCl <sub>2</sub>	1.49	1.97	0.07	3a
PhCH=CH <sub>2</sub>	Acrylonitrile	Neat/ZnCl <sub>2</sub>	1.49	2.02	0.07	3a
PhCH=CD <sub>2</sub>	Maleic anhydride	CDCl <sub>3</sub>	1.50	0.305 (D)	0.075	This work
PhCH=CD <sub>2</sub>	None	CDCl <sub>3</sub> /ZnCl <sub>2</sub>	1.510	0.306 (D)	0.066	This work
4-Me-styrene	Maleic anhydride	CDCl <sub>3</sub>	1.48	2.08	0.077	This work
4-Me-styrene	None	CDCl <sub>3</sub> /ZnCl <sub>2</sub>	1.510	2.030	0.067	This work
4-MeO-styrene	Maleic anhydride	CDCl <sub>3</sub> <sup>a</sup>	1.51	1.94	0.076	This work
4-MeO-styrene	None	CDCl <sub>3</sub> /ZnCl <sub>2</sub>	1.511	1.933	0.082	This work
4-AcO-styrene	Maleic anhydride	CDCl <sub>3</sub>	1.49	2.03	0.073	This work
4-AcO-styrene	None	CDCl <sub>3</sub> /ZnCl <sub>2</sub>	1.510	2.045	0.068	This work
4-Cl-styrene	Maleic anhydride	CDCl <sub>3</sub>	1.51	2.02	0.072	This work
4-Cl-styrene	None	CDCl <sub>3</sub> /ZnCl <sub>2</sub>	1.505	2.050	0.066	This work
3-Cl-styrene	Maleic anhydride	CDCl <sub>3</sub> <sup>a</sup>	1.50	2.06	0.068	This work
3-Cl-styrene	None	CDCl <sub>3</sub> /ZnCl <sub>2</sub>	1.505	2.043	0.066	This work
4-F-styrene	Maleic anhydride	CDCl <sub>3</sub> <sup>b</sup>	1.51	2.05	0.066	This work
4-F-styrene	None	CDCl <sub>3</sub> /ZnCl <sub>2</sub>	1.503	2.039	0.066	This work
PhC(CH <sub>3</sub> )=CH <sub>2</sub>	Maleic anhydride	CDCl <sub>3</sub>	1.51	1.77	Broad singlet	This work
PhC(CH <sub>3</sub> )=CH <sub>2</sub>	None	CDCl <sub>3</sub> /ZnCl <sub>2</sub>	1.512	1.768	Broad singlet	This work
PhC(CH <sub>3</sub> )=CH <sub>2</sub>	Me acrylate	Neat ZnCl <sub>2</sub>	1.44	1.64	Singlet	3a
PhCH=CH <sub>2</sub>	Diethyl fumarate	CDCl <sub>3</sub>	1.50	2.00	0.071	This work
			1.58	2.36	0.055	
PhCH=CD <sub>2</sub>	Diethyl fumarate	CDCl <sub>3</sub>	1.50	0.307 (D)	0.075	This work
			1.58	0.363 (D)	0.055	
isoPrSCH=CH <sub>2</sub>	Diethyl fumarate	Neat	1.45	1.94	0.07	3c
isoPrSCH=CH <sub>2</sub>	Diethyl fumarate	Neat	1.47	1.94	0.062	4
			1.47	1.98	0.150	
isoPrSCH=CD <sub>2</sub>	Diethyl fumarate	Neat	1.465	0.289 (D)	0.064	4
isoPrSCD=CD <sub>2</sub>	Diethyl fumarate	Neat	1.508	0.282 (D)	<0.01	4

<sup>a</sup>The D spectrum was only detected in the presence of ca. 20 mmol dm<sup>-3</sup> ZnCl<sub>2</sub>. <sup>b</sup>The D spectrum was only detected in the presence of ca. 20 mmol dm<sup>-3</sup> ZnCl<sub>2</sub> or after short illumination (see text).

used to improve the resolution of the EPR spectra of spin adducts due to the decrease in h.f.s. constants caused by coupling to the *tert*-butyl hydrogens.<sup>13</sup> In the case dealt with here, the spectrum of **10** appearing in the beginning of the reaction showed significant line narrowing ( $\Delta H_{pp}$  changing from 0.052 to 0.025 mT; note, however, that the coupling constant affected is not the one from the *N*-*t*-Bu group), but the change of  $\Delta H_{pp}$  in the AB spectra was much smaller (<0.005 mT), indicating that the coupling to the *tert*-butyl group at nitrogen is almost negligible. The D spectrum did not appear in this experiment, presumably because of the low concentration of *t*-BuNO-(<sup>2</sup>H<sub>0</sub>) employed, ca. 10 mM.

*Reaction of styrene- $\beta,\beta$ -(<sup>2</sup>H<sub>2</sub>) and maleic anhydride in the presence of *t*-BuNO.* When styrene- $\beta,\beta$ -(<sup>2</sup>H<sub>2</sub>) replaced styrene in the reaction with maleic anhydride in the presence of *t*-BuNO in chloroform, the large  $a^H$  of 2.00 mT in the D spectrum was replaced by an  $a^{2H}$  of 0.305 (calcd. 0.307) mT while the B and C spectra remained unchanged. The A spectrum could only be simulated (Fig. 5) by assuming that the hydrogens corresponding to the two smallest  $a^H$  of 0.100 and 0.067 mT had been replaced by deuteriums.

*Reaction of substituted styrenes and maleic anhydride in the presence of *t*-BuNO.* Various X-substituted styrenes reacted with maleic anhydride with *t*-BuNO present to give ABC spectra with the A component predominating (Table 2) and a weak D spectrum (Table 1) for the case of X=4-Me, 4-AcO, 4-Cl or  $\alpha$ -Me. In the case of 4-MeO-, 4-F-, or 3-Cl-styrene, the D spectrum appeared only in the presence of ZnCl<sub>2</sub>.

The case of 4-acetoxystyrene was critical for the analysis of all other spectra, since it consisted only of the A component as far as could be established within the limits of the analytical technique. This made possible (Fig. 6) the assignment of four hydrogen coupling constants which well simulated the experimental spectrum. Slight variations of the two largest coupling constants then were sufficient for the simulation of the variable features which were visible in the other A spectra.

A second critical case was provided by the spectrum from 3-chlorostyrene which clearly was dominated by an aminoxyl spectrum (B') with three couplings to hydrogen, superimposed upon a weak A spectrum, the identifiable characteristics of which were almost identical to other A spectra (Fig. 7). The fact that the B' spectrum from 3-chlorostyrene had three hydrogen couplings led us to

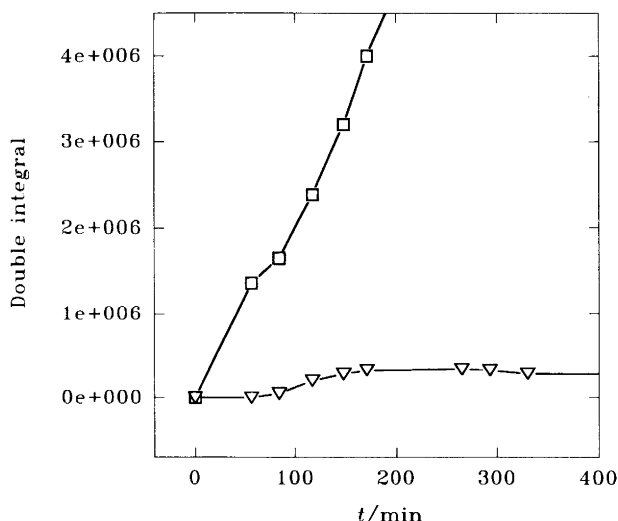


Fig. 3. Time dependence of the doubly integrated D and A+B+C spectra in a solution of *t*-BuNO (ca. 150 mmol dm<sup>-3</sup>), styrene (ca. 2.5 mol dm<sup>-3</sup>), maleic anhydride (ca. 0.5 mol dm<sup>-3</sup>) and zinc chloride (ca. 20 mmol dm<sup>-3</sup>) in (<sup>2</sup>H)chloroform. Triangles, D spectrum; squares, A+B+C spectrum. The D spectrum kept at a constant level for at least 24 h, while the A+B+C spectrum grew linearly with the same slope during this time.

scrutinize all AB spectral combinations with the same assumption for the B component, but in all cases a B spectrum with only two hydrogen couplings was sufficient. It was checked that the B' spectrum from 3-chlorostyrene could not be due to a combination of one chlorine and one hydrogen coupling.

It was established that strong D spectra were obtained in all cases from the donor olefin and *t*-BuNO alone in the presence of zinc chloride (Table 1).

*Reaction of styrene or styrene-β,β-(<sup>2</sup>H<sub>2</sub>) and diethyl fumarate in the presence of t-BuNO.* The trapping of radicals in the reaction between diethyl fumarate and a typical donor olefin, isopropyl vinyl sulfide, was recently described in detail,<sup>4</sup> and the styrene–diethyl fumarate reaction was therefore only briefly studied for a comparison. As for *t*-BuNO–maleic anhydride, the light-induced reaction between *t*-BuNO and diethyl fumarate yields a

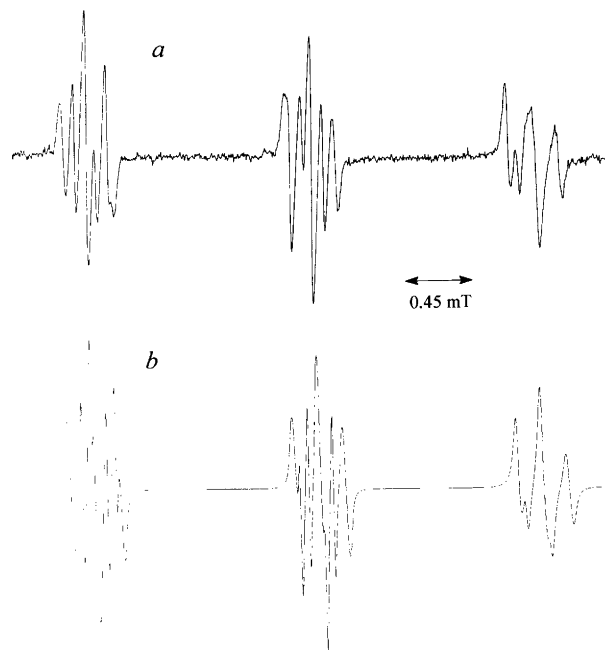
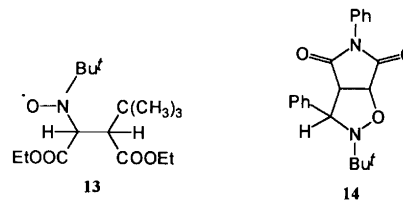


Fig. 5. (a) EPR spectrum recorded from a solution of *t*-BuNO (ca. 150 mmol dm<sup>-3</sup>), styrene-β,β-(<sup>2</sup>H<sub>2</sub>) (ca. 5 mol dm<sup>-3</sup>) and maleic anhydride (ca. 0.5 mol dm<sup>-3</sup>) in (<sup>2</sup>H)chloroform after keeping the sample for about 250 h in the dark to allow for the disappearance of the C spectrum. (b) Simulation based upon the data given in Table 2, the *g* displacement of the A spectrum being 0.029 mT in relation to the B spectrum.

characteristic adduct (**13**) which usually is seen as a 3+2 line spectrum of six broad lines but can be resolved further under favourable conditions:  $a^N = 1.45$ ,  $a^H = 0.266$ ,  $a^{H'} = 0.062$ ,  $a^{H''} = 0.024$  (4 H) mT.<sup>9</sup>



The reaction between styrene, diethyl fumarate and *t*-BuNO in chloroform immediately gave rise to a 3 × 2

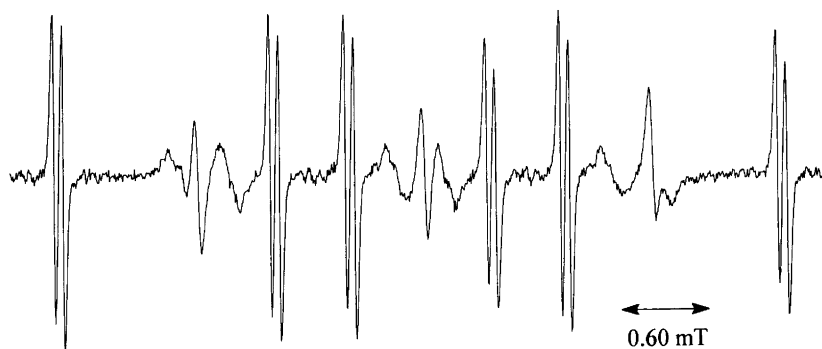


Fig. 4. EPR spectrum recorded from a solution of *t*-BuNO (ca. 150 mmol dm<sup>-3</sup>), styrene (ca. 1.2 mol dm<sup>-3</sup>) and zinc chloride (10–20 mmol dm<sup>-3</sup>) in (<sup>2</sup>H)chloroform after being kept in the dark for 20 min at 40 °C.

Table 2. EPR spectra of type ABC, obtained in the dark from reactions of styrene or substituted styrenes with maleic anhydride in chloroform, unless otherwise stated.

Donor olefin	Spectrum type	$a^N/\text{mT}$	$a^H/\text{mT}$	$a^{H'}/\text{mT}$	$a^{H''}/\text{mT}$	$a^{H'''}/\text{mT}$	Proportion
PhCH=CH <sub>2</sub>	A	1.520	0.172	0.169	0.100	0.057	80
	B	1.460	0.167	0.056	—	—	15
	C	1.47	0.45	—	—	—	5
PhCH=CH <sub>2</sub> in ethylbenzene	A	1.505	0.172	0.169	0.100	0.057	70
	B	1.450	0.167	0.056	—	—	15
	C	1.47	0.45	—	—	—	15
PhCH=CD <sub>2</sub>	A	1.528	0.172	0.169	0.015 (D)	0.009 (D)	70
	B	1.480	0.167	0.056	—	—	30
4-Me-styrene	A	1.525	0.179	0.162	0.102	0.060	80
	B	1.468	0.162	0.052	—	—	20
	C	1.47	0.52	—	—	—	<sup>a</sup>
2,4,6-Me <sub>3</sub> -styrene	C	1.50	0.47	0.17	—	—	<sup>b</sup>
4-MeO-styrene	A	1.525	0.179	0.162	0.102	0.060	80
	B	1.468	0.162	0.052	—	—	10
	C	1.48	0.45	—	—	—	10
4-AcO-styrene	A	1.519	0.167	0.156	0.107	0.062	100
4-Cl-styrene	A	1.518	0.179	0.154	0.100	0.060	85
	B	1.460	0.163	0.061	—	—	15
	C	1.48	0.45	—	—	—	<2
3-Cl-styrene	A	1.518	0.179	0.154	0.100	0.057	10
	B	1.446	0.129	0.096	0.060	—	90
4-F-styrene	A	1.523	0.179	0.153	0.102	0.061	70
	B	1.456	0.162	0.052	—	—	30
PhC(CH <sub>3</sub> )=CH <sub>2</sub>		1.552	0.123	0.059	0.018 (4 H)		

<sup>a</sup>Only seen in the beginning of the reaction. <sup>b</sup>The dominant part, 80%, of the spectrum was that of **10** [ $a^N$  1.436;  $a^H$  0.167, 0.079, 0.015 (9 H) mT].

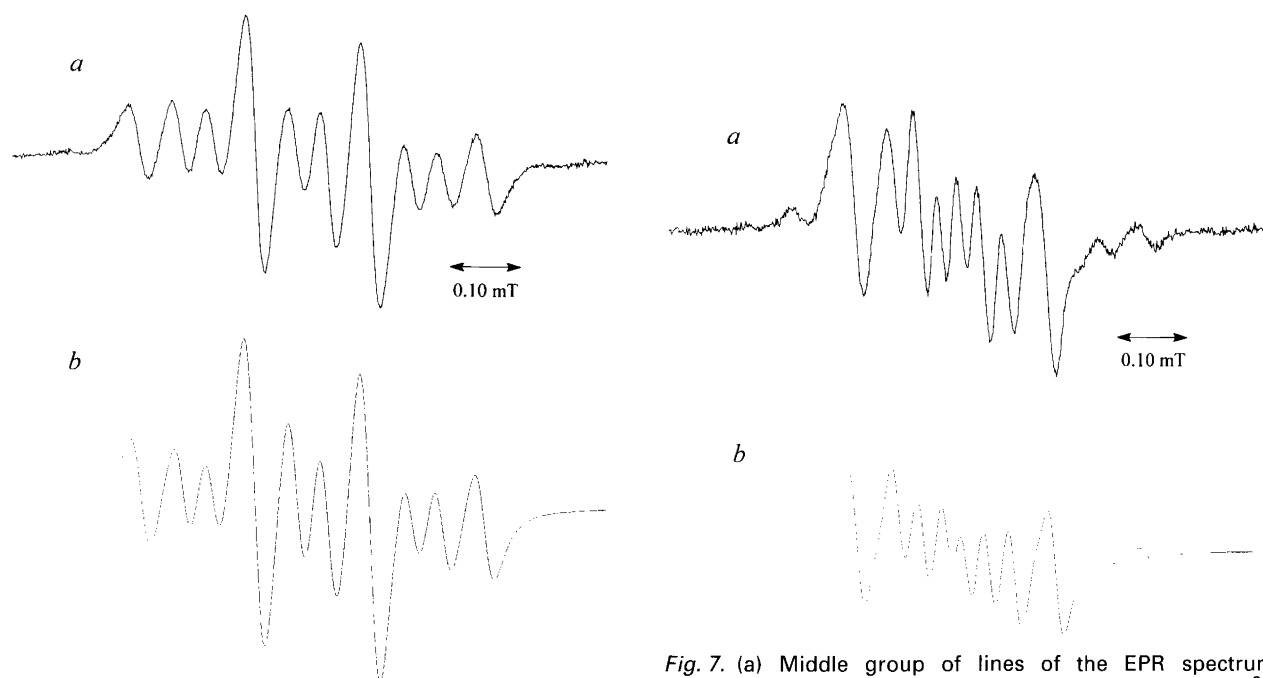


Fig. 6. (a) Middle group of lines of the EPR spectrum recorded from a solution of *t*-BuNO (ca. 150 mmol dm<sup>-3</sup>), 4-acetoxystyrene (ca. 1.8 mol dm<sup>-3</sup>) and maleic anhydride (ca. 0.5 mol dm<sup>-3</sup>) in (<sup>2</sup>H)chloroform after keeping the sample for about 200 h in the dark. (b) Simulation based upon the data given in Table 2.

Fig. 7. (a) Middle group of lines of the EPR spectrum recorded from a solution of *t*-BuNO (ca. 150 mmol dm<sup>-3</sup>), 3-chlorostyrene (ca. 1.9 mol dm<sup>-3</sup>) and maleic anhydride (ca. 0.5 mol dm<sup>-3</sup>) in (<sup>2</sup>H)chloroform after keeping the sample for about 200 h in the dark. (b) Simulation based upon the data given in Table 2, the *g* displacement of the A spectrum being 0.029 mT in relation to the B spectrum. The visible lines of the A spectrum are indicated by arrows.

line spectrum of six broad lines, initially with  $a^N=1.47$ ,  $a^H=0.29$  mT, which increased in intensity and slightly increased its  $a^H$  over 20 h in the dark,  $a^N=1.47$ ,  $a^H=0.32$  mT. There was also noticeable an emerging  $3 \times 2$  line spectrum of  $a^N=1.47$ ,  $a^H=0.60$  mT. In the same period, two D-type spectra in an intensity of about 10% of the  $3 \times 2$  line spectrum appeared (h.f.s. constants, see Table 1). This combination of spectra increased slowly in intensity over the next 50 h and then decayed. At the end, when almost all paramagnetic activity had disappeared, a short light exposure restored the EPR spectrum of **13**.

With styrene- $\beta,\beta$ -( $^2\text{H}_2$ ) instead of styrene the same sequence of spectra appeared, the D spectra now with the large  $a^H$  converted into a deuterium coupling (Table 1). The two other spectra remained unchanged, except that the  $a^N=1.47$ ,  $a^H=0.60$  mT spectrum was more intense at the end of the experiment (about 150 h).

*Redox behaviour of the cycloadduct 14 between PBN and N-phenylmaleimide.* As an additional model of **5**, the PBN-*N*-phenylmaleimide cycloadduct (**14**)<sup>9</sup> was chosen. The attempted preparation of cycloadducts of simple alkenes and PBN failed owing to the extremely low reaction rate under normal reactions conditions.<sup>14</sup>

Cyclic voltammetry of **14** in dichloromethane- $\text{Bu}_4\text{NPF}_6$  showed a chemically reversible redox couple at  $E_{\text{rev}}=1.31$  V vs. Ag/AgCl with a peak separation of about 75 mV, reversibility being observed at sweep rates down to at least  $0.025$  V  $\text{s}^{-1}$ . This behaviour suggested that its EPR spectrum should be obtainable in HFP,<sup>5,15</sup> using  $\text{Tl}^{\text{III}}$  trifluoroacetate as the oxidant. Mixing these components in HFP in the dark gave a reddish-coloured solution displaying an EPR spectrum with  $a^N=2.06$ ,  $a^H(1\text{H})=2.22$  and  $a^H(1\text{H})=0.52$  mT. The spectrum disappeared within 15 min. With the weaker oxidant, 4-tolyl- $\text{Tl}^{\text{III}}$  bis(trifluoroacetate), there was no thermal reaction with **14**, but UV irradiation slowly built up the same EPR spectrum as above [ $a^N=2.04$ ,  $a^H(1\text{H})=2.23$  and  $a^H(1\text{H})=0.53$  mT].

## Discussion

*The diradical and electron-transfer mechanisms.* A consistent mechanistic picture of what is denoted charge-transfer polymerization of a donor and an acceptor olefin has been given by Hall.<sup>2</sup> This mechanism takes into account not only the polymerization reaction, but also explains the concurrent formation of low-molecular-weight products by cycloaddition reactions. Hall discarded the electron transfer (ET) mechanism, simply because electron-transfer is not possible in the situations discussed. Instead, Hall favoured a mechanism where the initiating radical species is a diradical formed by reaction of the two olefins in a tail-to-tail fashion, like the one exemplified above (**5**). The two mechanisms are shown in Scheme 1 in the Introduction.

Since the ET mechanism between a donor and acceptor

olefin is often discussed and even subjected to extensive experimental tests,<sup>16</sup> we deemed it of interest to perform a thermochemical analysis of the ET step involved in some typical cases.<sup>17</sup> The free energy change of an electron-transfer step establishes a lower limit of the free energy of activation, and thus gives an idea of the maximally possible rate constant.<sup>18</sup> For an electron-transfer process of the type discussed here, taking place between two neutral species and giving two oppositely monocharged species in a low dielectric constant environment, the electrostatic correction is  $-331.2/(Dr_{12})$  in the expression for the free energy change [eqn. (1), where  $E(\text{D}/\text{D}^{\cdot+})$  and  $E(\text{A}/\text{A}^{\cdot-})$  are the redox potentials in V of the donor and acceptor olefin, respectively,  $D$  is the dielectric constant and  $r_{12}$  is the distance in Å between the reactants in the precursor complex] will be fairly large and uncomfortably close to the limit where one cannot be sure that this correction represents a physical reality. In the particular reaction discussed here, we have used a  $D$  value of 5 (for chloroform) and assume that this value is representative for the cases where neat components have been used. With  $r_{12}=6$  Å, the electrostatic correction term becomes  $-11$  kcal  $\text{mol}^{-1}$ , a fairly respectable quantity and certainly not negligible.

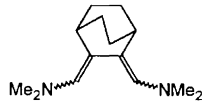
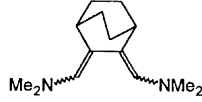
$$\Delta G^{\circ} = 23.06 \times [E(\text{D}/\text{D}^{\cdot+}) - E(\text{A}/\text{A}^{\cdot-})] - 331.2/(Dr_{12}) \quad (1)$$

Table 3 shows cases typical of the rare situations where ET between a pair of olefins has been experimentally established to occur, and cases where other mechanisms take precedence. It is seen that the borderline between non-ET and ET processes is located somewhere in the  $\Delta G^{\circ}$  region between 8 and  $-12$  kcal  $\text{mol}^{-1}$ . This is not a very precise assignment, but of course mirrors both the lack of data and the uncertainty by which this region can be defined. Note also how dominant the electrostatic interaction becomes in this region. The main point here is quite well seen: none of the polymerization reactions studied by spin trapping can proceed via electron transfer. Therefore, the spin trapping experiments reported above will be analyzed in terms of Hall's suggestion that a diradical is the initiating species.

*The possible origin of the D spectrum.* The best way to obtain a strong D spectrum was to allow the donor olefin and *t*-BuNO alone to react in the presence of zinc chloride. This fact by itself shows that the species corresponding to the D spectrum cannot be derived from a radical involved in the copolymerization process. D spectra were also obtained reproducibly and in reasonably high intensity from styrene(s)-maleic anhydride-*t*-BuNO with zinc chloride present. Without this additive, the results were erratic, and any D spectra actually appearing were weak. The experiments with NO present did not conclusively establish that NO is involved, although it cannot be excluded that  $\text{NO}_2$  is formed by oxidation of NO by traces of oxygen. It therefore seems as if electrophilic catalysis of a reaction between *t*-BuNO



Table 3. Thermochemical data for electron transfer (ET) between donor and acceptor olefins.<sup>2,16-18,26,27</sup>

Acceptor olefin, A	Donor olefin, D	$E(A/A^{\cdot-})/$ V	$E(D/D^{\cdot+})/$ V SCE	$e^2/Dr_{12}/$ kcal mol <sup>-1</sup> <sup>a</sup>	$\Delta G^{\circ\prime}/$ kcal mol <sup>-1</sup> <sup>b</sup>	Outcome
TCNE	PhSCH=CH <sub>2</sub>	0.24	1.35	11.0	14.6	No ET
TCNE	4-MeOPhSCH=CH <sub>2</sub>	0.24	1.09	11.0	8.6	No ET
TCNE	<i>N</i> -Vinylcarbazole	0.24	1.08	11.0	8.4	No ET
TCNE	( <i>E,E</i> )-1,4-bis(Me <sub>2</sub> N)-1,3-butadiene	0.24	-0.32	11.0	-23.9	ET
TCNE		0.24	-0.20	11.0	-21.0	ET
Dimethyl dicyanofumarate	( <i>E,E</i> )-1,4-bis(Me <sub>2</sub> N)-1,3-butadiene	-0.27	-0.32	11.0	-12.1	ET
Fumaronitrile	( <i>E,E</i> )-1,4-bis(Me <sub>2</sub> N)-1,3-butadiene	-1.29	-0.32	11.0	11.4	No ET
Maleic anhydride	PhCH=CH <sub>2</sub>	-0.50	2.05	11.0	47.8	No ET
Diethyl fumarate	PhCH=CH <sub>2</sub>	-1.54	2.05	11.0	71.8	No ET
Me fumarate		-1.5	-0.20	11.0	19.0	No ET
Acrylonitrile	PhCH=CH <sub>2</sub>	-2.17	2.05	11.0	86.3	No ET
Maleic anhydride	4-MeO-styrene	-0.50	1.49	11.0	34.9	No ET

<sup>a</sup>The dielectric constant  $D$  was assumed to be 5 and the distance  $r_{12}$  between the reactants in the precursor complex  $6 \text{ \AA}$ .

<sup>b</sup>See eqn. (1).

and the donor olefin is needed for generating the species corresponding to the D spectrum at a rate high enough for EPR spectral observation to be feasible. Alternatively phrased, runs without any deliberately added electrophilic catalyst might show slow kinetics due to the inhibiting effect of some nucleophilic impurity. Under such conditions, the D spectrum might become too weak for observation.

A thorough analysis of the proposal that a vinylaminoxyl, like **1**, R=Ph, would be the species corresponding to the D spectrum was performed by Mash *et al.*<sup>4</sup> The suggestion was deemed unlikely, and it can only be added here that a consideration of the known properties of vinylaminoxyl radicals further reinforces this conclusion: their EPR spectra show a higher coupling constant in the  $\beta$  than in the  $\alpha$  position, 0.8 vs. 0.1–0.2 mT, with a concomitant high reactivity for coupling in the  $\beta$  position.<sup>19</sup> Mash *et al.*<sup>4</sup> proposed that a cyclic aminoxyl might be a more likely alternative structure, since h.f.s. coupling constants to an  $\alpha$  hydrogen  $\geq 2$  mT only have been found in spectra of cyclic aminoxyls.

Since there was some indication that NO might be involved in the development of the D spectrum one can speculate that the donor olefin might form a diradical, of which three are possible for a monosubstituted olefin (**15**–**17**). Reaction with NO might then give aminoxyls **18**–**20**. Of these, **18** is ruled out by the results obtained

with the  $\beta,\beta$ -*d*<sub>2</sub>-styrene, whereas **19** is expected to show large couplings to three hydrogens in its EPR spectrum, and **20** to four hydrogens.

A second role of NO would be to react with residual oxygen to give NO<sub>2</sub>, an oxidant and/or a Lewis acid capable of inducing the development of the D spectrum in the same way as zinc chloride. The concentration of NO<sub>2</sub> will then have to be low enough so as to preclude the formation of aminoxyls **12**. As discussed above, weakly oxidizing species would be capable of generating radical cations from cyclic hydroxylamines. EPR spectra of some pertinent radical cations are given in Table 4. These spectra have  $a^N$  around 2 mT and  $a^H\alpha$  between 1.5 and 2.8 mT, depending how closely the  $\alpha$  C–H bond is oriented in parallel with the N–O system. Note the small or absent bridgehead hydrogen splittings in **23**<sup>+</sup> and **24**<sup>+</sup>, where the rigid structure places the C–H bonds in the nodal plane of the N–O  $\pi$  system.

Starting from diradicals **16** and **17** (**15** needs not to be considered for the same reason as above), additive cyclization with *t*-BuNO would give regioisomers **25**–**27** as potential precursors for formation of radical cations. The radical cation of **25** would have the critical CH<sub>2</sub> group attached to oxygen which demands that one and only one of the hydrogens  $\alpha$  to oxygen couples with the same large h.f.s. constant as if the hydrogen had been placed  $\alpha$  to nitrogen, not likely in view of the spin density

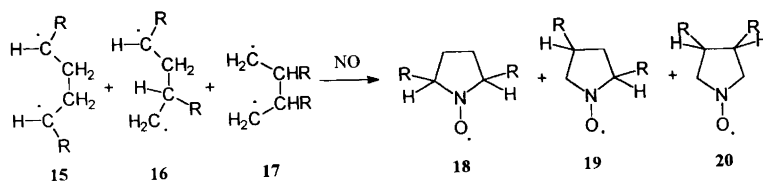
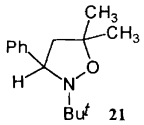
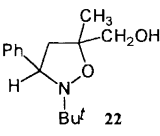
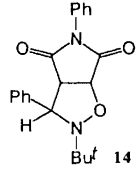
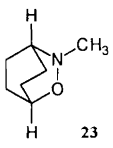
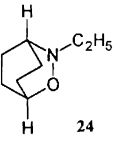
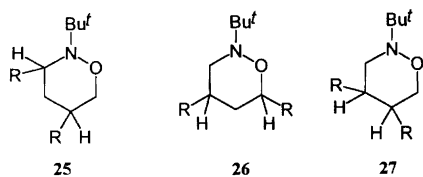


Table 4. EPR spectral parameters for radical cations of some cyclic hydroxylamines.

Radical cation of	$a^N/mT$	$a^{H\alpha(N)}/mT$	$a^{H\alpha(O)}/mT$	Others	Ref.
 21	2.01	2.76	—		9
 22	2.02	2.68	—	0.346 (1 H in CH <sub>2</sub> group)	9
 14	2.06	2.22	0.52		This study
 23	1.99	1.99 (3 H), 0.0	0.090	0.43 (2 H), 0.165 (2 H), 0.103 (2 H) to bridge hydrogens	20
 24	1.994	1.543 (2 H), 0.0	0.074	0.44 (2 H), 0.170 (2 H), 0.099 (2 H) to bridge hydrogens	20

distribution on the N–O function,  $\rho_N=0.75$  and  $\rho_O=0.18$ .<sup>20</sup> In  $26^{+\cdot}$  or  $27^{+\cdot}$  the same critical CH<sub>2</sub> group is attached to nitrogen, and thus either of these might be responsible for the D spectrum, provided that the conformation around the C–N bond is such that only one large coupling to one of the hydrogens exists.



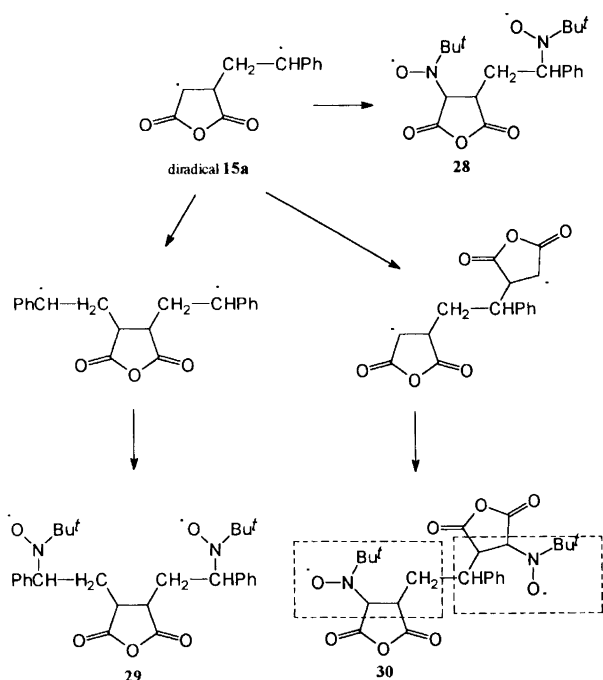
Thus among radical cations originating from a diradical formed from two molecules of the monoolefin, only  $26^{+\cdot}$  or  $27^{+\cdot}$  would pass the deuterium substitution test and correspond to a credible EPR spectrum. It should again be noted that  $26^{+\cdot}$  or  $27^{+\cdot}$  is derived from the ‘wrong’ diradical and that it is required that only one of the  $\alpha$  hydrogens is involved in coupling. Two diastereomers of  $26^{+\cdot}$  are possible, and the late development of a second D-type spectrum therefore is compatible with this structure.

The suggestion that  $26^{+\cdot}$  might be the species corresponding to the D spectrum is presently a speculative one. The fact that the system of donor olefin alone, together with *t*-BuNO and zinc chloride, not only gives

the D spectrum in high intensity, but also gives rise to a second D spectrum and possibly several spectra of conventional aminoxyl appearance, suggests other possibilities, and will be the subject of further work.

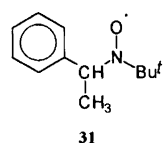
*The possible origin of the A, B and C spectra.* The assignment of the ABC spectra (Table 2) to species directly or indirectly emanating from a diradical **15**, the initiating radical proposed by Hall, is complicated by several factors. Starting from the relevant diradical from styrene and maleic anhydride, **15a**, and assuming that alternate copolymerization takes place, species with the radical centre located at the succinic anhydride or styrene part will appear and have a possibility to be trapped by *t*-BuNO. Scheme 7 shows the type of aminoxyl environments which are created by trapping at both radical centres (bis-adduct **28**) of **15a** and the species formed after the first step of the polymer growth process by either adding a styrene or maleic anhydride monomer to **15a**. Bis-adducts **29** and **30** are representative of the aminoxyl environments generated by trapping of growing polymer chains: in **29** we can see that all trapped styrene centres will have the same regiochemistry with respect to the succinic anhydride moiety, whereas in **30** two regiochemically different trapped succinic anhydride ends can be recognized.

What kind of EPR spectra would be expected from a

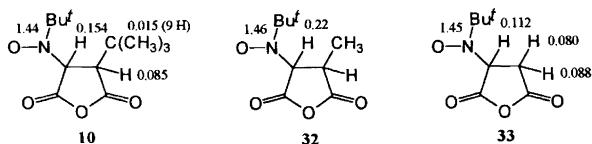


Scheme 7.

consideration of species **29** and **30**, remembering that they are only the first members of a series of oligomeric analogous species with one or two aminoxyl groups? The simplest representative of a trapped styrene centre is **31**,



which has been reported to have an EPR spectrum with  $a^N = 1.48$  mT and  $a^H = 0.38$  mT in benzene.<sup>21</sup> Aminoxyl **31** is actually identical to the spin adduct obtained from PBN (**3**) and methyl radical and has been obtained in several methyl radical reactions.<sup>10</sup> The lines were broad, presumably due to the unresolved coupling from the methyl group. The same spectrum was obtained here by allowing ethylbenzene to react with nickel peroxide<sup>22</sup> in the presence of *t*-BuNO:  $a^N = 1.49$  mT,  $a^H = 0.37$  and  $a^H = 0.059$  (3 H) mT, the latter h.f.s. constant being extracted by a forward-back Fourier transform routine. The simplest models of trapped succinic anhydride are available in spin adducts **10**, **32** and **33**, showing<sup>9</sup> the following h.f.s. couplings in their EPR spectra.



Thus, if the radical centres of the growing polymer chains are trapped by *t*-BuNO, one would expect that styrene centres would give rise to an EPR spectrum of

several overlapping spectra of  $3 \times 2$  broad lines and with  $a^N$  about 1.48 mT and  $a^H$  about 0.4 mT, and the succinic anhydride centres a similarly composite EPR spectrum of  $3 \times 2$  or  $3 \times 2 \times 2$  broad lines,  $a^N$  being about 1.45 mT and  $a^H$  and  $a^H$  about 0.1–0.2 and 0.1 mT.

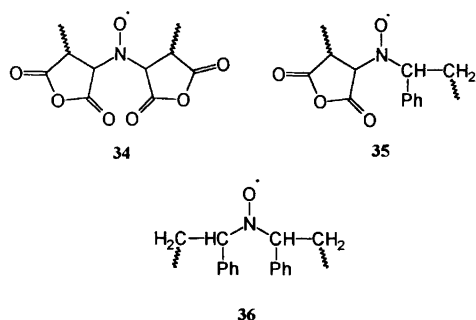
The C spectra from maleic anhydride and a variety of styrenes, except 3-chlorostyrene and 2,4,6-trimethylstyrene, were of the  $3 \times 2$  line type,  $a^N = 1.47$ –1.48 mT and  $a^H = 0.45$ –0.49 mT. The lines were broad ( $\Delta H_{pp} = 0.10$ –0.11 mT) and their shape indicative of further unresolved lines. In comparison with the spectra expected for trapping of styrene centres, the similarity is good enough to allow the proposal that spectrum C corresponds to species with the structural characteristics of species **29**.

The B spectra from maleic anhydride and a variety of styrenes, except 3-chlorostyrene ( $3 \times 2 \times 2 \times 2$  lines) and 2,4,6-trimethylstyrene (no B spectrum seen), were of the  $3 \times 2 \times 2$  line variety,  $a^N$  being about 1.47 mT and  $a^H$  and  $a^H$  about 0.16 and 0.06 mT. In principle, this description would qualify well for a spectrum of a trapped succinic anhydride radical centre, most likely the one in the right box of **30**, were it not for a problem of signal width. The lines of the B spectra are relatively narrow, 0.025–0.03 mT, and as discussed above, the effect of replacing *t*-BuNO with (<sup>2</sup>H<sub>9</sub>)-*t*-BuNO was small and not in agreement with expectations based on earlier findings.<sup>13</sup> We are therefore faced with the difficulty of explaining why these lines are relatively narrow, yet should represent overlapping spectra of several structurally similar species. In addition, we have to assume that the couplings from the *t*-Bu group are very small in this type of aminoxyls.

Similar considerations apply to the more complex A spectrum. In principle, it could emanate from one of the trapped succinic anhydride radical centres of **30**, most likely the one in the left box, but the narrow lines present the same problem as above.

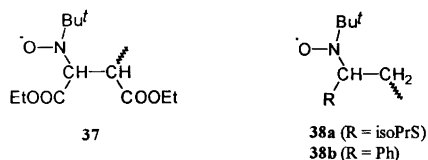
We have contemplated possible ways of obtaining aminoxyls with no attached *N*-*t*-Bu group, but none of them appears tenable. As an example, one route would be to assume coupling of a radical centre, for example of diradical **15a**, with NO, which might be present at least in the beginning of the reaction due to accidental photolysis of *t*-BuNO during preparation of the sample. The resulting nitroso compound would act as a spin trap toward other radicals and eventually give rise to non-cyclic aminoxyls **34**–**36**. The problem with such a mechanism is that it requires a non-photochemical reaction for the generation of NO in order to explain the long-term growth of the AB spectra in darkness.

Against this background, we conclude that the narrow linewidths of the AB spectra and their insensitivity to deuterium labelling of the *tert*-butyl group probably are best explained by the assumption that the coupling constant to the *t*-Bu hydrogens is very small. It should be noted that similarly narrow linewidths were found in



the EPR spectra of aminoxyls **8a**, especially when cyclic olefins were employed.<sup>9</sup>

*Spin trapping in the styrene–diethyl fumarate system.* Mash *et al.*<sup>4</sup> performed a very thorough study of spin trapping by *t*-BuNO in the isopropyl vinyl sulfide–diethyl fumarate system, including the use of selectively deuteriated isotopomers of both precursors. The main  $3 \times 2$  line spectrum observed,  $a^N = 1.42$ ,  $a^H = 0.27$  mT, was conclusively assigned to trapped centres located at the diethyl succinate part (**37**), and a weaker spectrum of  $a^N = 1.49$  and  $a^H = 0.52$ – $0.59$  mT tentatively to trapped centres at the isopropyl vinyl sulfide part (**38a**). With styrene as the donor olefin, we obtained a main spectrum of  $a^N = 1.47$ ,  $a^H = 0.29$ – $0.32$  mT and a minor spectrum of  $a^N = 1.47$ ,  $a^H = 0.60$  mT. The similarities between the two sets of experiments are striking, and we therefore assign the styrene–diethyl fumarate–*t*-BuNO spectra to structures **37** and **38b**. As for the pair of D spectra obtained in both systems, their spectral parameters are similar (Table 1), and therefore their origins are presumably identical.



## Conclusions

This study has aimed at testing the diradical mechanism suggested by Hall.<sup>2</sup> The possibility that a diradical might add across the N=O bond of *t*-BuNO and give a cyclic hydroxylamine, the radical cation of which might correspond to the D spectrum, has been explored. However, the hypothesis was falsified by the fact that the D spectrum was shown to be derived from an electrophilically promoted reaction between *t*-BuNO and the donor olefin alone. We conclude that the species corresponding to the D spectrum cannot be involved in the spontaneous copolymerization reaction of donor+acceptor olefin. Further work is needed to elucidate the nature of this radical.

The other spin adduct spectra observed (ABC type) agree reasonably well with the assumption that radicals containing one type of styrene radical centre (**29**) and two types of succinic anhydride centres (**30**) are trapped.

## Experimental

*Materials.* The substituted styrenes were purchased from either Aldrich or Lancaster in the highest quality available, and used as received. Styrene (Kebo, >99.5%) was distilled to remove the inhibitor, and stored at  $-20^\circ\text{C}$ . Styrene- $\beta,\beta$ -( $^2\text{H}_2$ ) and ( $^2\text{H}$ )chloroform were purchased from Dr. Glaser AG, Switzerland. Diethyl fumarate was 98% (Eastman), and maleic anhydride was from BDH (>99.5%). *t*-BuNO was purchased from Aldrich, and ( $^2\text{H}_9$ )-*t*-BuNO was synthesized according to a published procedure.<sup>23</sup> The cycloadduct **14** was available from an earlier study.<sup>9</sup> Dichloromethane was of Suprasolv<sup>®</sup> and HFP of UVASOL<sup>®</sup> quality (Merck AG). Tetrabutylammonium hexafluorophosphate (Aldrich) was recrystallized twice from cyclohexane–ethyl acetate (70:30). Nitrogen oxide was from Alfax, Sweden. All other chemicals were of the highest commercial quality available.

*Instruments and methods.* Cyclic voltammetry was performed by the BAS-100 instrument, using an Ag/AgCl electrode as the reference, and with *iR* compensation. Potentials given and discussed in the text are given with the SCE as reference. EPR spectra were recorded by the Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer. The EPR experiments were performed as described earlier (100 kHz modulation frequency, microwave effect 0.4–1.25 mW, modulation amplitude 0.01–0.04 mT).<sup>9</sup> Simulations were carried out by the public domain programme WINSIM<sup>24</sup> or Simfonia<sup>®</sup> from Bruker AG.

*Reactions between styrene(s), maleic anhydride and t-BuNO in chloroform.* *t*-BuNO (10 mg, about  $150 \text{ mol dm}^{-3}$ ), the styrene ( $200 \mu\text{l}$ ,  $1.9$ – $2.5 \text{ mol dm}^{-3}$ ) and maleic anhydride ( $30$ – $40 \text{ mg}$ ,  $0.4$ – $0.6 \text{ mol dm}^{-3}$ ) were dissolved in ( $^2\text{H}$ )chloroform ( $500 \mu\text{l}$ ; used to avoid the ethanol present as inhibitor in chloroform) under conditions of ordinary laboratory light. The solution was bubbled with argon in a quartz EPR tube for 2 min and then the tube was sealed. The total time for exposure to laboratory light was at most 4 min. In general, this procedure gave a sample which initially contained radical **10** according to its characteristic EPR spectrum. As the reaction proceeded, this spectrum was replaced by the ABC combination of spectra within 3–4 h of keeping the sample in the dark. Samples were kept in the dark at all times, unless otherwise stated.

The development of the EPR spectrum of **10** can be completely avoided by conducting the sample preparation in a semi-darkened room. Since this spectrum does not seem to affect the development of the spectra of interest and also is a useful diagnostic of the initial reaction conditions, most reactions were performed under conditions of ordinary laboratory light. Exposure to daylight from a north-facing window had a strong promoting effect on the formation of **10**, as pointed out before.<sup>9</sup>

Whenever added, the concentration of zinc chloride was ca. 20 mmol dm<sup>-3</sup>.

*Reactions between styrene(s) and t-BuNO in chloroform.* *t*-BuNO (10 mg, about 150 mmol dm<sup>-3</sup>) and the styrene (200 μl, 1.9–2.5 mol dm<sup>-3</sup>) were dissolved in (<sup>2</sup>H)chloroform (500 μl) under conditions of ordinary laboratory light. Zinc chloride (ca. 1 mg) was added. The solution was bubbled with argon in a quartz EPR tube for 2 min and then the tube was sealed. The tube was kept in the dark at 40 °C for 30 min before the first EPR spectrum was recorded. With styrene itself, reactions were also performed at [styrene]=200 and 20 mmol dm<sup>-3</sup>.

*Reaction between styrene, maleic anhydride and t-BuNO in ethylbenzene.* This reaction was performed on a solution made up from *t*-BuNO (2.1 mg, 30 mmol dm<sup>-3</sup>), styrene (350 μl, 4.1 mol dm<sup>-3</sup>) and maleic anhydride (34 mg, 0.5 mol dm<sup>-3</sup>) in ethylbenzene (350 μl), approximately the same composition as that used previously.<sup>3b</sup>

*Reaction between styrene, maleic anhydride and NO in chloroform.* A solution of styrene (200 μl, about 2.5 mol dm<sup>-3</sup>) and maleic anhydride (30–40 mg, 0.4–0.6 mol dm<sup>-3</sup>) in (<sup>2</sup>H)chloroform (500 μl) was deaerated by Ar bubbling from 2 min. NO was then bubbled into the solution for 20 s, and the tube was sealed.

*Reaction between styrene, maleic anhydride, t-BuNO and NO in chloroform.* A solution of styrene (200 μl, about 2.5 mol dm<sup>-3</sup>), maleic anhydride (30–40 mg, 0.4–0.6 mol dm<sup>-3</sup>) and *t*-BuNO (10 mg, 150 mmol dm<sup>-3</sup>) in (<sup>2</sup>H)chloroform (500 μl) was deaerated by Ar bubbling from 2 min. NO was then bubbled into the solution for 20 s, the tube sealed and the solution monitored by EPR spectroscopy at intervals.

*Reactions between styrene, diethyl fumarate and t-BuNO in chloroform.* A solution of styrene (200 μl, about 1.9 mol dm<sup>-3</sup>), diethyl fumarate (200 μl, about 1.1 mol dm<sup>-3</sup>) and *t*-BuNO (10 mg, 130 mmol dm<sup>-3</sup>) in (<sup>2</sup>H)chloroform (500 μl) was deaerated by Ar bubbling from 2 min. The tube was sealed and the solution monitored by EPR spectroscopy at intervals.

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