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On the Reported Intermediacy of Vinyl Radicals in Spontaneous Polymerization: An ESR-Spin Trapping Study and its Significance for the Bond Forming Initiation Theory

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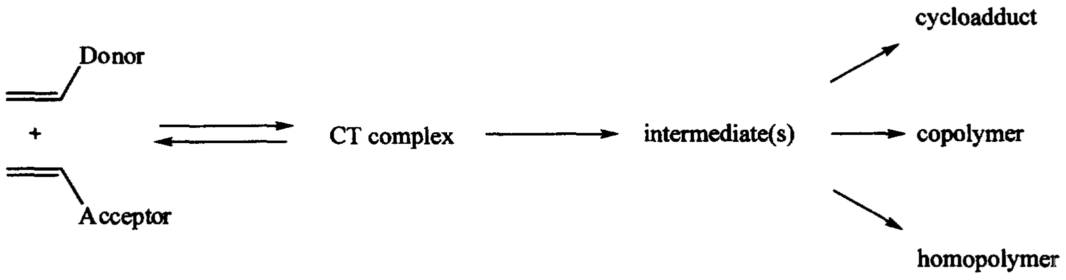
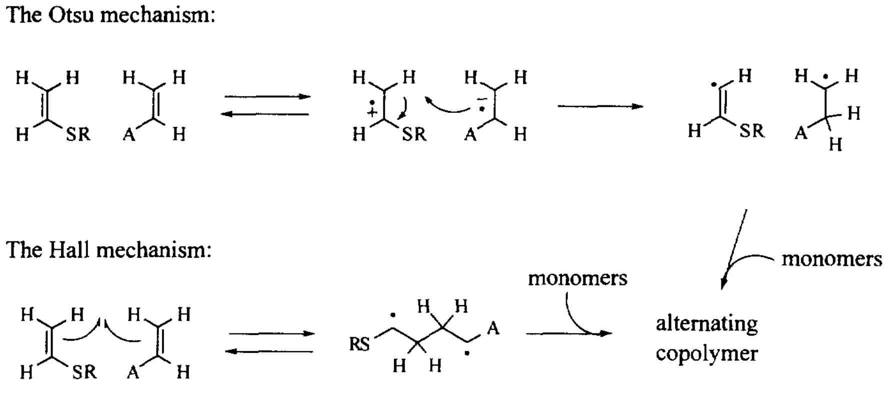
Abstract: Deuterated isopropyl vinyl sulfides and diethyl fumarate were synthesized and employed in a re-investigation of the mechanism of initiation of spontaneous polymerization of these co-monomers by means of spin-trapping/ESR spectroscopy. Previous radical spin-trapping studies had been interpreted as indicating the involvement of vinyl radicals. While our studies produced data substantially in agreement with the previous study, it must be noted that the data are not consistent with literature data for other vinyl radicals. Accordingly, results from both spin-trapping/ESR studies are inconsistent with involvement of vinyl radical intermediates, but are consistent with initiation by tetramethylene diradicals. © 1997 Elsevier Science Ltd.

Introduction

Electron-rich olefins can react with electron-poor olefins in several distinct ways. Spontaneous polymerizations can occur,[1] while cycloadditions and ene reactions have also been reported.[2] Polymerization can yield either alternating copolymers or homopolymers. These spontaneous polymerizations have been termed "charge transfer" (CT) polymerizations because a charge transfer complex, detectable by formation of a transient color, is frequently observed.



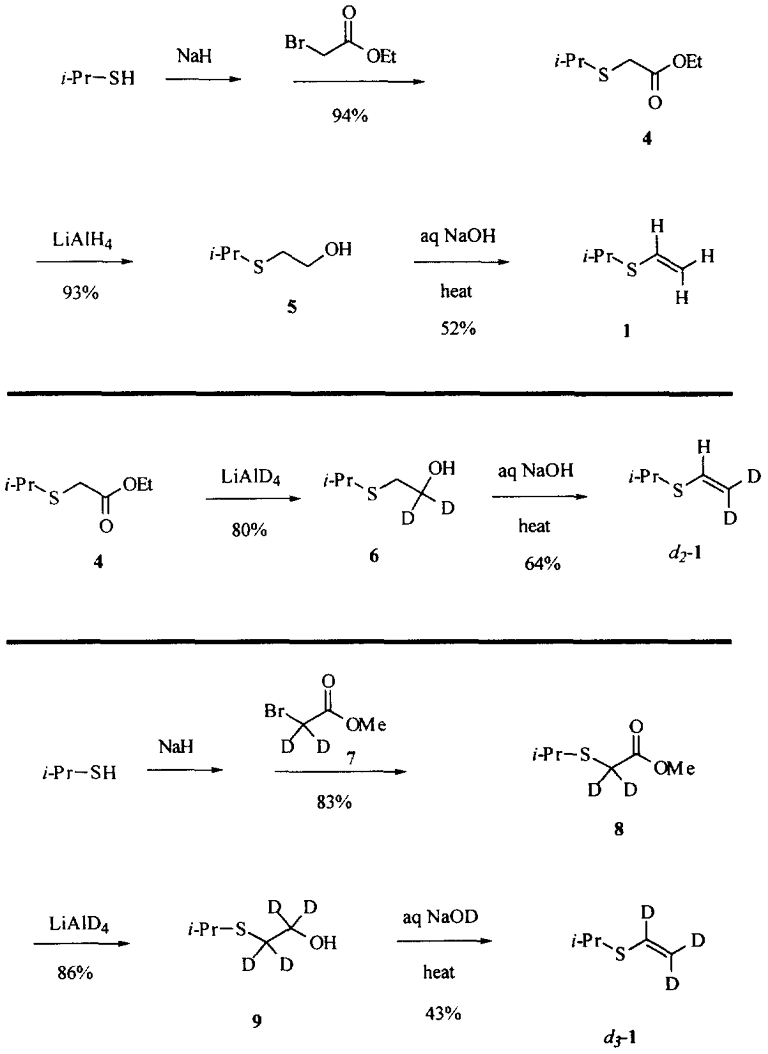
For nearly three decades, investigators have sought to delineate the initiation and propagation mechanism(s) of CT polymerizations.[1,3] Two mechanistic postulates have been advanced to account for initiation of spontaneous copolymerizations, represented in Scheme 1 by reaction of an alkyl vinyl sulfide with an acceptor-substituted ethylene. In the first mechanism, proposed by Otsu,[4] alkenes of opposite electronic structure form a CT complex, which leads to single electron transfer from the electron-rich to the electron-poor alkene. In the resulting tight radical ion pair, a proton is transferred from the radical cation to the radical anion to give one sp^3 carbon radical and one sp^2 carbon radical. It is presumed that one or both of these radicals serve to initiate copolymerization. Support for the Otsu mechanism comes principally from electron spin resonance (ESR) studies in which these and other radicals were purportedly trapped using 2-methyl-2-nitrosopropane (MNP).[4a] In the second mechanism, proposed by Hall,[3,5] alkenes of opposite electronic structure react directly to form a tetramethylene diradical. The Hall mechanism represents an extension of the chemistry of tetramethylene intermediates, which can possess zwitterionic as well as diradical character.[6] Tetramethylene zwitterions have been implicated in the initiation of homopolymerization, and are thought to lead as well to cyclobutane- and cyclohexane-containing small molecule products.[1a,7] It is presumed that the Hall tetramethylene diradical serves to initiate copolymerization. To date, this diradical has not been directly observed or trapped. As part of an effort to distinguish between these mechanisms, we have re-examined the spontaneous reaction(s) of the prototypical alkene co-monomers, isopropyl vinyl sulfide (IPVS, **1**) and diethyl fumarate (DEF, **2**), by means of spin-trapping/ESR spectroscopy using several deuterated analogs. In particular, we wished to confirm the identity of the Otsu vinyl radical by means of deuterium substitution, and to identify other radicals present in the course of initiation and/or propagation in this system.



Scheme 1. Proposed mechanisms for spontaneous initiation of copolymerization of electron-rich alkenes with electron-poor alkenes.

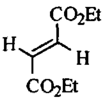
Synthesis of Monomers

Isopropyl vinyl sulfide (**1**) was synthesized by the method outlined in Scheme 2. Syntheses of d_2-**1** and d_3-**1** were accomplished similarly. Displacement of bromide from an alkyl α-bromoacetate by the sodium salt of 2-propanethiol produced the corresponding α-(1-methylethyl)thioacetate.[8] Following reduction with lithium aluminum hydride or lithium aluminum deuteride, the intermediate 2-(1-methylethyl)thioethanols were



Scheme 2. Syntheses of isopropyl vinyl sulfide monomers **1**, d_2-**1**, and d_3-**1**.

dehydrated by the method of Doumani[9] to give the desired 2-(ethenylthio)propane. In the case of d_3-**1**, exchange of the protons α to sulfur was observed when dehydration of **9** was carried out using sodium hydroxide in water, and so, following exchange of the hydroxyl proton using D_2O, dehydration of **9** was carried out using NaOD in D_2O. Fumaric-2,3-d_2 acid was converted to the corresponding ethyl ester, d_2-**2**, by acid-catalyzed esterification.



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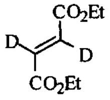


d_2-**2**

ESR Studies

In spin trapping experiments, detection of nitroxide radicals by ESR very much depends on the electronic and structural interactions of the radicals to be trapped and the spin trapping compound. Care must be taken when proposing reaction mechanisms based on the observed radical adducts, since side reactions unrelated to the process of interest may produce the most prominent signals in a composite ESR spectrum. In order to minimize such ambiguities, experiments similar to those described by Otsu[4] using 2-methyl-2-nitrosopropane (MNP) were performed, as were parallel experiments with the aromatic spin trap 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene, ND).

In most experiments strongly overlapping composite ESR spectra arising from several nitroxide radicals were obtained. The presence of several nitroxides of similar structure rendered accurate determination of their ESR hyperfine structures (hfs) extremely difficult. This was particularly true for the minor components due to overlap with the rather intense ^{13}C satellite lines of the major radicals. Therefore, ESR spectra were analyzed by spectral simulation with the aid of a fitting procedure (see Experimental). This sometimes led to somewhat different ESR hyperfine splitting constants (hfs) for the same radical species from spectra recorded at different stages of reaction. Also, the relative intensity ratios of the individual spectra exhibited some variation. These variations reflect the uncertainty of the ESR data.

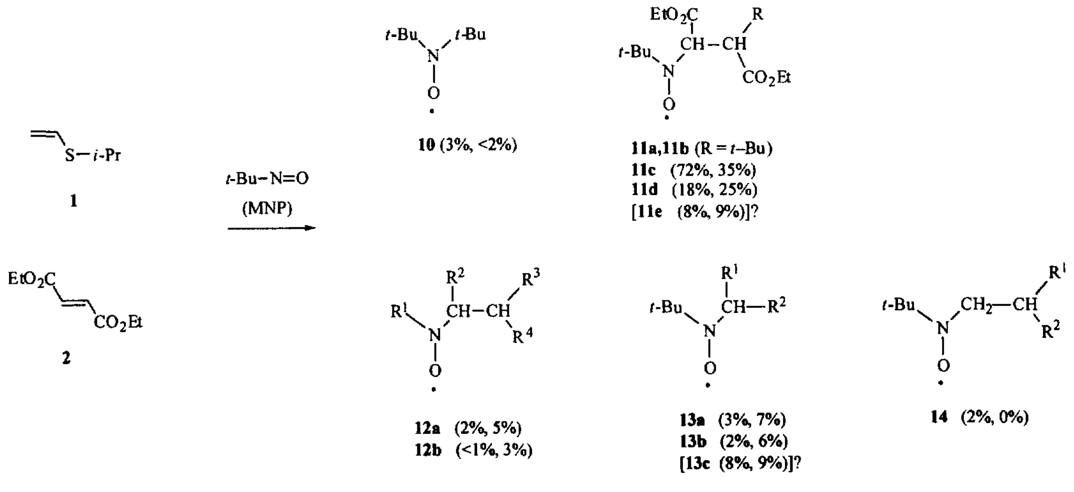
Spin-Trapping Experiments using 2-Methyl-2-nitrosopropane (MNP)

Control Experiments.

The interpretation of spin trapping experiments is often complicated by the detection of radicals due to impurities already present in the spin trap or to side reactions. This is especially true when nitroso compounds are employed as spin traps. Therefore, the individual reactants were first checked for radical formation in control experiments.

After dissolution of MNP in neat IPVS (**1**), the well-known spectrum of the di-*t*-butyl nitroxide radical (**10**, Scheme 3), which is commonly seen in MNP-based spin trapping studies, was observed. This species has been attributed to photolytic cleavage of MNP by ambient light and subsequent trapping of the *t*-butyl radical thus produced by MNP.[10] Radical **10** was also detected in solutions of MNP in inert hydrocarbon solvents (e.g., hexane). The intensity of the ESR signal due to **10** increased greatly upon extended exposure of the solution to white light. Thus, radical **10** most likely was produced during the preparation of the solutions, and not by a direct radical-forming reaction between IPVS and MNP.

After dissolution of MNP in neat DEF (**2**), a relatively weak 6-line ESR spectrum was observed which was unequivocally identified using deuterated DEF (*d_2*-**2**) as being due to nitroxide radicals **11**, the MNP adducts of secondary carbon-centered radicals which result from addition of radicals R to the olefinic double bond of DEF (Scheme 3). Spectral simulation indicated the superposition of two species of similar structure (**11a** and **11b**, Table 1) present in approximately a 4:1 ratio, along with some **10**. We tentatively attribute these signals, which decayed within a period of 5 hours, to a pair of diastereomers, though radicals with varying R cannot be excluded. Radical formation can again be attributed to photolytic cleavage of MNP by ambient light during sample preparation. Rapid addition of the nucleophilic *t*-butyl radical[11] to the electron-poor double bond of DEF, which is present in high concentration, might be expected, while its addition to the electron-rich double bond of IPVS should be, and apparently is, less favorable, even when IPVS is present in high concentration.



Scheme 3. Reactions of IPVS with DEF in the presence of MNP. The first percentage refers to *t* = 15 min and the second percentage refers to *t* = 28 h after mixing.

Reaction of IPVS (**1**) with DEF (**2**) in the presence of MNP.

Reaction of deoxygenated DEF with an equal volume of IPVS in the presence of MNP led to an immediate build-up of a composite ESR spectrum (Figure 1a) due to various nitroxide radicals **10–14**. The *g*-factors (Table 1), which were all in the range of 2.0060-2.0062, indicated that only dialkyl nitroxides were generated. The principal 6-line spectral component was again identified by deuterium labeling (see below) as deriving from DEF. From the time-dependent spectral changes and observations made in deuterium labeling experiments, the presence of several nitroxide radicals exhibiting just one small hydrogen hfs became evident. We obtained a best match of the simulated and experimental spectra by calculating a superposition of signals from three radicals (**11c, 11d,** and **11e** or **13c**) in the percentages given in Scheme 3 (the percentages refer to composition 15 minutes and ca. 28 hours after mixing). Since only very small differences in the hyperfine splitting constants were found for **11c** and **11d** compared to **11a** and **11b**, it is possible that these are the same species. However, the initial signal intensity was much higher than in the control experiment, and, contrary to the control experiment, increased continuously for several hours. While **11a** and **11b** certainly contribute to the composite ESR spectrum at t = 15 min (Figure 1a), radicals generated by the spontaneous reaction(s) of DEF with IPVS must certainly dominate the spectrum. No decision could be made as to whether the third component of the major 6-line signal also derived from DEF, viz. **11e**, or belonged to another nitroxide produced from IPVS, likely to be **13c**. Small β-H splittings of about 1.3-1.4 G are common for such types of nitroxides, e.g. the *i*-propyl adduct of MNP.[12]

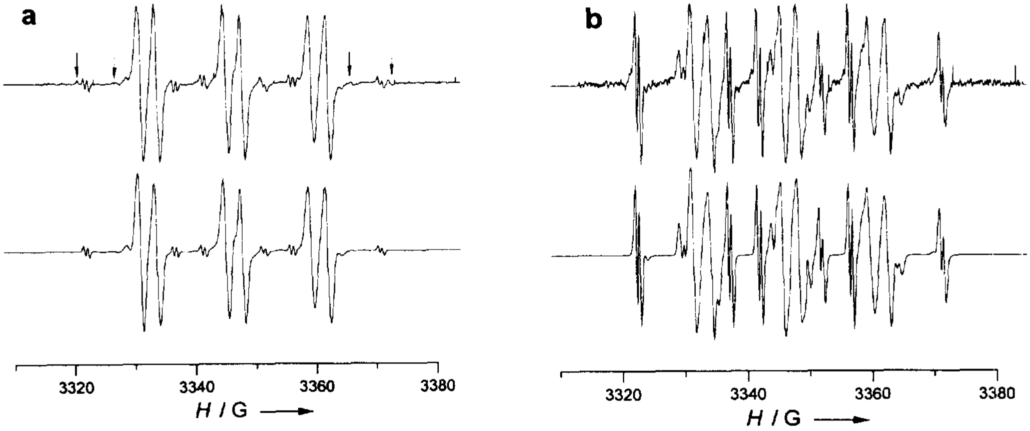


Fig. 1. ESR spectra obtained (a) 15 minutes and (b) 28 hours after addition of DEF to IPVS in the presence of MNP (top). Simulation using the relative intensities given in Scheme 1 (bottom).

Table 1. ESR Parameters of MNP-Derived Nitroxide Radicals at 20 °C.

			hyperfine splittings[b] / G				
radical	source	g-factor[a]	$a(^{14}N)$	$a(H)$	$a(D)$	$a(^{13}C)$	$a(^{15}N)$
10	IPVS	2.00611	15.40			4.4 (6C) 4.0 (2C)	21.7
11a	DEF	2.00615	14.20	2.80		14.0 4.6 3.0 (4C)	19.6
11b	DEF	2.00617	14.65	2.35			
11c	DEF + IPVS	2.00616	14.20/14.22	2.77/2.69		13.6 4.6 3.0 (4C)	19.50
	DEF + d_2-IPVS	2.00617	14.21/14.08	2.74/2.76			
	DEF + d_3-IPVS	2.00615	14.21/14.60	2.74/2.80			
11d	DEF + IPVS	2.00613	14.25/14.15	2.32/2.57			
	DEF + d_2-IPVS	2.00613	14.16/13.90	2.30/2.70			
11e/13c	DEF + IPVS	2.00612	14.10/14.10	1.37/1.37			
	DEF + d_2-IPVS	2.00611	14.30/14.68	1.30/1.37			
	DEF + d_3-IPVS	2.00612	15.0	1.70			
11f	d_2-DEF + IPVS	2.00616	14.00/14.05		0.36/0.41	13.7 4.0 3.0 (4C)	20.0
	d_2-DEF + d_2-IPVS	2.00616	14.43		0.37	14.0 4.0 3.0 (4C)	19.80
	d_2-DEF + d_3-IPVS	2.00606	14.50/14.45		0.39/0.41	13.8 4.0 3.0 (4C)	19.90
11g	d_2-DEF + IPVS	2.00618	14.30/14.50		0.37/0.39		
	d_2-DEF + d_2-IPVS	2.00613	14.00		0.34		
	d_2-DEF + d_3-IPVS	2.00605	14.30/14.30		0.41/0.41		
12a	DEF + IPVS	2.00615	14.73/14.70	19.43/19.40 0.62/0.62			
12b	DEF + IPVS	2.00612	14.70/14.76	19.80/19.30 1.50/1.92			
12c	DEF + d_2-IPVS	2.00615	14.65	0.64	2.89		
12d	DEF + d_3-IPVS	2.00607	15.08	<0.1	2.82		
13a	DEF + IPVS	2.00615	14.85/14.67	5.20/5.86			
13b	DEF + IPVS	2.00615	14.68/14.68	4.60/4.58			
	DEF + d_2-IPVS	2.00615	14.66	4.25			
14[c]	DEF + IPVS	2.00610	15.2	5.8; 6.1; 8.8			

[a] estimated error ± 0.00003. [b] one nucleus, unless otherwise indicated; numbers separated by slash refer to the data evaluated for the reaction periods given in the legends of the Figures. [c] provisional data

The second characteristic feature of the composite ESR spectrum is a signal (ca. 2% relative intensity at $t = 15$ min) of twelve relatively sharp hyperfine lines. Such a hyperfine structure is consistent with a dialkyl nitroxide having just one β- and one γ-hydrogen atom interacting with the unpaired electron. It was this ESR signal—and similar signals in other experiments—which Otsu interpreted as being due to an IPVS-derived vinyl radical. Deuterium labeling experiments (see below) prove that the interacting β- and γ-hydrogen atoms were indeed initially attached to the unsubstituted and substituted olefinic carbon atoms, respectively, of IPVS. However, Otsu's assignment of this signal to the MNP adduct of an IPVS-derived vinyl radical appears doubtful (see Discussion Section). In fact, two very similar spectral components (**12a**, **12b**) were discernible which we tentatively assign to nitroxides of general structure **12**, although the β and γ hydrogens might not necessarily still be attached to the former olefinic carbons of the same molecule. Also, R^1 and R^2 might be part of a common ring system. In any case, R^1 should be a tertiary carbon substituent as the persistence of **12a**, **12b** strongly disfavors *both* hydrogen splittings being due to β hydrogens; i.e., a *sec,sec-* or *tert,prim*-nitroxide structure for **12a** and **12b** is unlikely.

Two other minor nitroxide structures, **13a**, and **13b**, were tentatively identified from their spectral features (Table 1). No satisfying analysis could be achieved for the tiny signals marked by arrows in Figure 1a. The overall width of this partial spectrum (51 G) and the perceptible line separations are consistent with a spin adduct of a primary carbon centered radical, such as **14**.

With the exception of **14**, the signal intensities of all radicals increased continuously for several hours, after which time a slow decay of all signals took place over several days. Radicals **11** appeared to be somewhat less persistent than most of the other nitroxides. After 28 hours a spectrum (Figure 1b) virtually identical to that previously published by Otsu[4] was recorded.

Reaction of IPVS (**1**) with d_2-DEF (d_2-**2**) in the presence of MNP.

Reaction of IPVS with d_2-DEF produced a much simpler ESR spectrum than was observed from undeuterated DEF (Figure 2). The lack of splitting of the three nitroxide hyperfine lines unequivocally proves that DEF was the source of radicals **11c** and **11d**. The initial spectrum (Figure 2a) could be satisfactorily analyzed in terms of a superposition of signals from two nitroxides, **11f** and **11g**, present in approximately a 5:1 ratio, and from di-*t*-butyl nitroxide **10** (ca. 5%). Deuterated **11e** or **13c** might also have been present. The signal intensity increased continuously for about a day with some change in the ratio of the components. After 2 days, the signal due to **10** had completely disappeared, leaving signals for **11f** and **11g** in a 2:1 ratio. These signals were still strong after 72 hours. Notably, the twelve-line spectrum assigned to structures **12** as well as signals from the other minor radicals (**13**-**14**) could not be detected at levels > 0.5% relative intensity (as deduced from the intensity of the ^{15}N satellite lines of **11f**/**11g**). The question as to whether **11e**/**13c** represents a product derived from DEF or IPVS could not be answered by this experiment, as a small percentage of undeuterated **13c** would have been covered by the wings of the major lines.

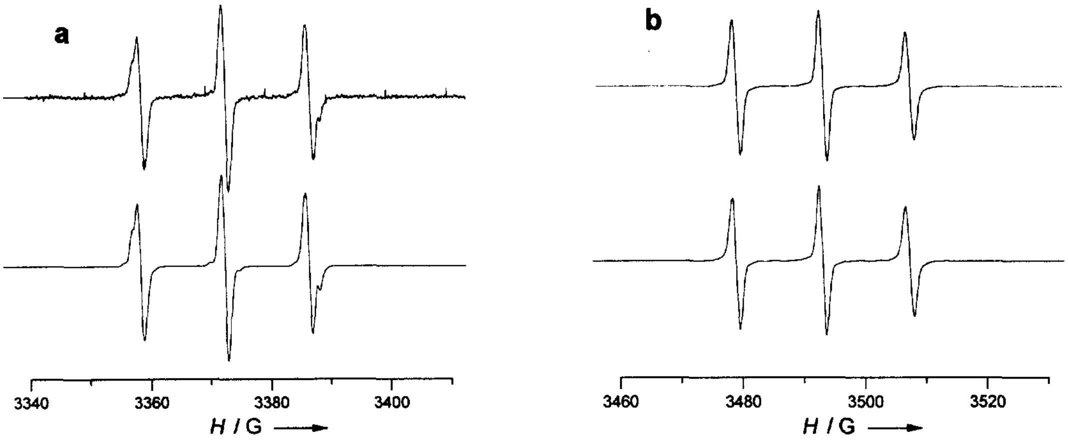
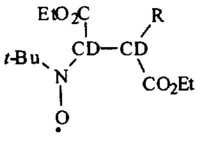


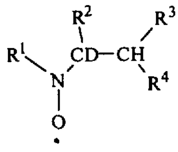
Fig. 2. ESR spectra obtained (a) 15 minutes and (b) 72 hours after addition of d_2-DEF to IPVS in the presence of MNP (top). Simulation (bottom).

Reaction of d_2-IPVS (d_2-**1**) with DEF (**2**) in the presence of MNP.

Reaction of d_2-IPVS with DEF initially produced an intense ESR spectrum (Figure 3a) which consisted of signals due to radicals **11c** and **11d** (80%), **11e**/**13c** (12%), and very likely small amounts of **13a** and **13b**. The maximum signal intensity was reached at 4 h. After 18 h the percentages of **11c**, **11d**, and **11e**/**13c** had changed to about 40, 18, and 20%, respectively, and other signals had become apparent (Figure 3b). Simulation revealed the formation of **12c** (16%), the monodeuterated derivative of **12a**, and species **13b** (6%).



11f,11g



12c

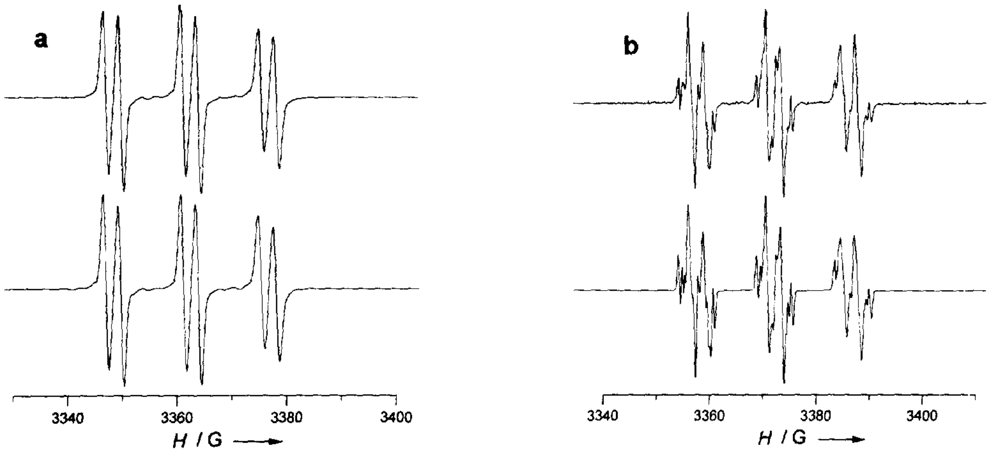
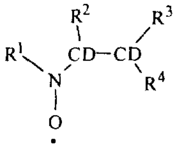


Fig. 3. ESR spectra obtained (a) 15 minutes and (b) 18 hours after addition of DEF to d_2-IPVS in the presence of MNP (top). Simulation (bottom).

Reaction of d_3-IPVS (d_3-**1**) with DEF (**2**) in the presence of MNP.

The origination of the species **12** from IPVS was further corroborated by reaction of DEF with d_3-IPVS. Initially, only signals from **11c** and **11e**/**13c** (simulated as a 9:1 ratio), and probably some **10**, were observed (Figure 4a). After 19 h, the spectrum (Figure 4b) indicated the formation of the dideuterated nitroxide **12d** (ca. 13%) and **11e**/**13c** (7%). Nitroxides **13a,b** could not be identified with certainty.



12d

Reaction of d_2-IPVS (d_2-**1**) with d_2-DEF (d_2-**2**) in the presence of MNP.

The reaction of d_2-DEF with d_2-IPVS was similar to the reaction of d_2-DEF with undeuterated IPVS and led to the immediate formation of nitroxides **11f** and **11g**. The recorded ESR spectrum was virtually identical to that shown in Figure 2a. Except for a strong increase in intensity, and probably the formation of a small amount of **13b** (ca. 1%), no change was observed in the ESR spectrum after 27 hours.

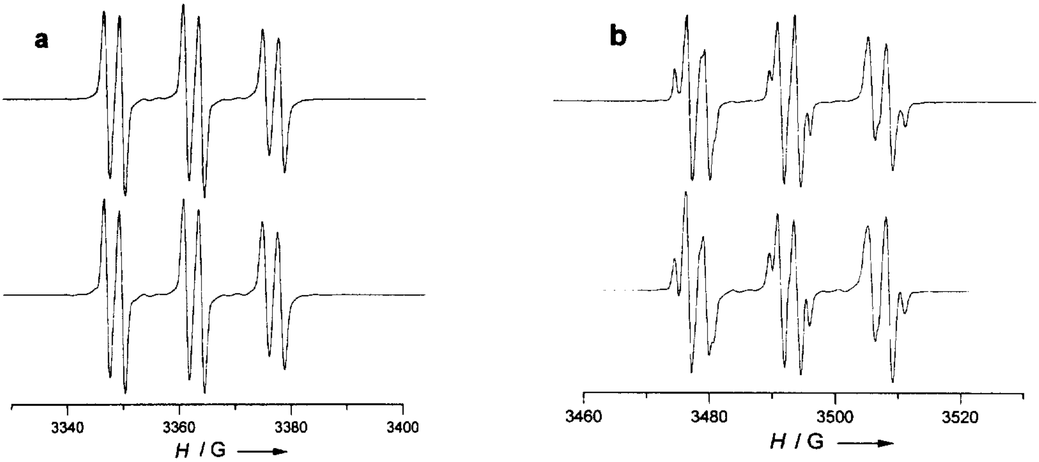


Fig. 4. ESR spectra obtained (a) 30 minutes and (b) 19 hours after addition of DEF to d_3-IPVS in the presence of MNP (top). Simulation (bottom).

Reaction of d_3-IPVS (d_3-**1**) with d_2-DEF (d_2-**2**) in the presence of MNP.

The only signals initially observed from the reaction of d_2-DEF and d_3-IPVS were again those due to **11f** and **11g** (Figure 5a). In contrast to the preceding experiment, new signals grew in within 48 h (Figure 5b), which were assigned to nitroxides **12d** (14%) and **11e/13c** (7%). Smaller signals due to nitroxide species with hydrogen splittings in the 3-5 G range, e. g. **13a** and **13b**, also might have been present but could not be satisfactorily resolved.

Spin Trapping Experiments using Nitrosodurene (ND)

Control Experiments.

As previously discussed, MNP is photolytically unstable and sensitive to oxygen. Use of this spin trap introduces a source of *t*-butyl radicals that may compromise the study of radicals produced by interactions of the monomers. Nitrosodurene (ND) has greater thermal and photochemical stability than MNP. No ESR signals were detected in control experiments with ND in neat DEF and IPVS over a 24 hour period. Unfortunately, the ESR spectra obtained using ND as a spin trap were generally much weaker and exhibited broader, less resolved lines than those produced using MNP. Therefore, the ESR spectra from studies with ND could only be analyzed in terms of the major radicals present, and with less numerical accuracy.

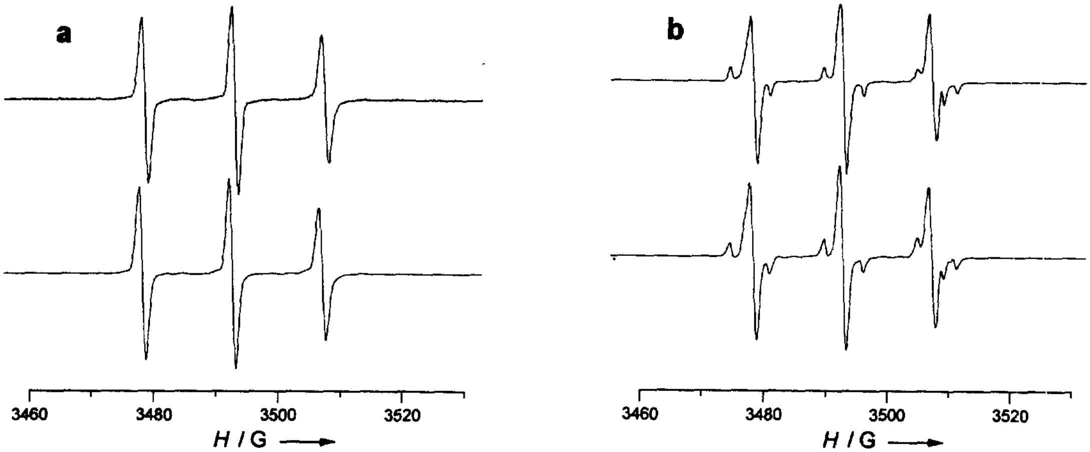
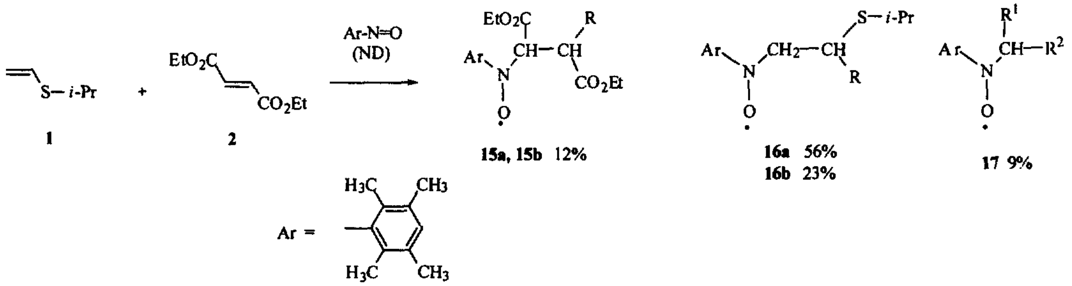


Fig. 5. ESR spectra obtained (a) 15 minutes and (b) 48 hours after addition of d_7-DEF to d_3-IPVS in the presence of MNP (top). Simulation (bottom).

Reaction of IPVS (**1**) with DEF (**2**) in the presence of ND.

After mixing equal volumes of DEF and IPVS with a few mg of ND, the slow build-up of a composite ESR spectrum was observed (Figure 6). According to simulation (Table 2) and deuterium labeling studies (see below), nitroxide radicals of types **15** and **16** (Scheme 4) were produced. The superpositions of (at least) two species of both structures were indicated, though a reliable evaluation of the individual spectral data was only possible for **16**. A small contribution by species **17** is also likely. The signal intensity increased slowly with time, somewhat faster for **16a** and **16b** than for **15a** and **15b**. A maximum was reached after about 24 h. As is generally observed for nitroxide adducts of primary carbon-centered radicals, **16a** and **16b** appeared to be less persistent than **15a** and **15b**, but could still be detected after 55 h. Importantly, an ESR signal analogous to **12**, which might indicate the trapping of a vinyl-type radical, could not be detected.



Scheme 4. Reactions of IPVS with DEF in the presence of ND. The percentages refer to Fig. 6.

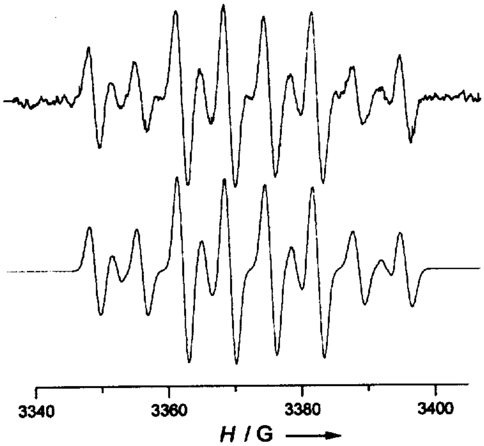


Fig. 6. ESR spectrum obtained 24 hours after addition of DEF to IPVS in the presence of ND (top). Simulation (bottom).

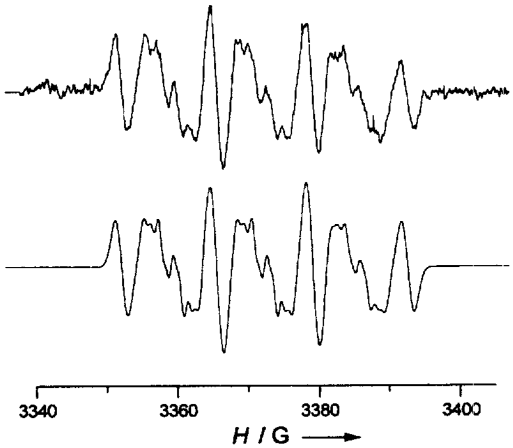
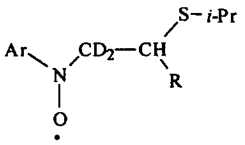


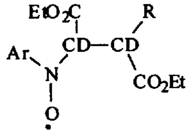
Fig. 7. ESR spectrum obtained 27 hours after addition of DEFto d_2-IPVS in the presence of of ND (top). Simulation (bottom).

Reaction of IPVS (d_2-**1**) with DEF (**2**) in the presence of ND.

Reaction of DEF and d_2-IPVS produced an ESR spectrum (Figure 7) which unequivocally proved that the major nitroxide radicals, **16c** and **16d** (ca. 75 and 13% relative intensity) were derived via radical addition to the substituted olefinic carbon of IPVS. Radicals **15a** and **15b** were also present in amounts (6% each) similar to the preceding experiment. Reliable detection of a small percentage of **17** (or its deuterated analogue) was hampered by the strong spectral overlap.



16c, 16d



15c, 15d

Reaction of d_2-IPVS (d_2-**1**) with d_2-DEF (d_2-**2**) in the presence of ND.

The ESR spectrum recorded 3 hours after mixing d_2-DEF and d_2-IPVS is displayed in Figure 8. The prominent, small 1:1:1 triplet splitting confirms the formation of **15c** and **15d** (24%). The major components were again the d_2-IPVS-derived nitroxides **16c** and **16d** (60 and 15%, respectively). Some **17** (ca. 1%) was also detected. After 53 hours, most of **16c** and **16d** had decayed, leaving **15c** and **15d** as the major spectral constituents (70%).

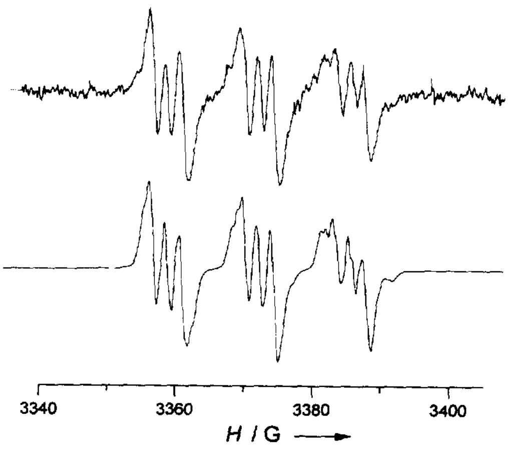
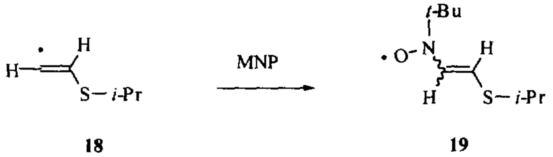


Fig. 8. ESR spectrum obtained 3 hours after addition of d_2-DEF to d_2-IPVS in the presence of ND (top). Simulation (bottom).

Discussion

A key element in the Otsu mechanism for spontaneous copolymerization of electron-poor and electron-rich olefins (Scheme 1) is the formation of an intermediate vinyl-type radical, e.g. **18**, via deprotonation of the radical cation formed initially from IPVS. Support for this mechanism rests upon the observation of a particular type of nitroxide radicals in spin trapping studies using MNP as the spin trapping agent. The ESR signals of these species exhibit one large (ca. 19-21 G) and one small (< 1 G) hydrogen splitting and were assigned to vinyl nitroxide radicals, e.g. **19**.[4] This interpretation was apparently



corroborated by detection of similar ESR signals in experiments designed to generate vinyl radicals via halogen abstraction from vinyl halides by silyl or tin radicals.[4] Deuterium labeling experiments (see above) confirm that the protons interacting with the unpaired electron in this species originate from the vicinal olefinic positions of IPVS, the larger hyperfine splitting being due to one of the hydrogen atoms at the terminal carbon (C2) and the small splitting being due to the single hydrogen at the substituted carbon (C1). The absence of an apparent splitting by the second hydrogen at C2 would seem to be consistent with the trapping of an IPVS-

Table 2. ESR Parameters of ND-Derived Nitroxide Radicals at 20 °C.

radical	source	g-factor[a]	hyperfine splittings[b] / G		
			$a(^{14}N)$	a(H)	a(D)
15a + **15b**[c]	DEF + IPVS	2.0062	13.59	13.10 0.75	
15a	DEF + d_2-IPVS	2.0062	13.51	12.90 0.79	
15b	DEF + d_2-IPVS	2.0062	13.41	14.47 0.64	
15c	d_2-DEF + d_2-IPVS	2.0062	13.52		2.08 0.14
15d	d_2-DEF + d_2-IPVS	2.0062	13.34		2.08 0.11
16a	DEF + IPVS	2.0061	13.26	12.76 7.14 0.76	
16b	DEF + IPVS	2.0061	13.29	14.29 6.71 0.81	
16c	DEF + d_2-IPVS	2.0062	13.18	0.90	1.96 1.09
	d_2-DEF + d_2-IPVS	2.0062	13.33	1.08	2.02 1.08
16d	DEF + d_2-IPVS	2.0062	13.24	0.60	2.25 1.04
	d_2-DEF + d_2-IPVS	2.0062	13.50	0.69	2.37 0.81
17	DEF + IPVS	2.0062	13.38	3.5	
	d_2-DEF + d_2-IPVS	2.0062	13.32	3.6	

[a] estimated error ± 0.0001. [b] one nucleus. [c] average data for two species.

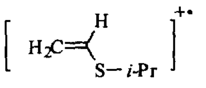
derived vinyl radical. However, as detailed below, there are several problems with assignment of a vinyl structure to the pertinent nitroxide ESR signal.

(i) From data tabulated in the Landolt-Börnstein collection,[13] it can be seen that assignment of structure **19** to Otsu's radical would be inconsistent with the observed ^{14}N splitting and hydrogen splittings. Conjugative interaction of the double bond with the nitroxide group should lead to a preferred geometry in which the olefinic hydrogens are in the plane of the nitroxide, i.e., orthogonal to the singly-occupied orbital. This orientation should give rise to rather small hydrogen splittings, with the γ-H hfs somewhat larger (5-8 G) than the β-H hfs (2-4 G). Spin delocalization also strongly reduces the spin density at nitrogen and should result in significantly smaller ^{14}N hyperfine splittings (5-10 G) than were observed.

(ii) We observed relatively broad ESR hyperfine lines (0.4-1 G linewidths) for all MNP-derived nitroxides, likely due to the unresolved hfs of the *t*-butyl group. By way of contrast, the signal for Otsu's radical exhibits relatively sharp lines (ca. 0.2-0.4 G linewidth). Thus, the second (tertiary) substituent at nitrogen is probably not *t*-butyl, implying that this species is not **19** and is not formed via a direct route from intact MNP.

(iii) α-Unsubstituted vinyl radicals are highly reactive and exhibit high rate constants for both hydrogen abstraction and addition to unsaturated systems.[14] Given the high monomer concentrations (ca. 8 $mol \cdot L^{-1}$) relative to the spin trap (ca. 0.03 $mol \cdot L^{-1}$), competitive formation of a vinyl spin adduct might not be expected. Vinyl radicals similar to **18** have been reported to decay rapidly, with rate constants in the range of 10^5 s^{-1}, by *intra*molecular hydrogen abstraction from the S-alkyl group.[15] This should further reduce the likelihood of trapping by MNP.

(iv) The formation of a freely diffusing vinyl radical **18** by proton loss from the IPVS-derived radical cation **20** is also unlikely on thermochemical and structural grounds. It has been reported that radical cations of vinyl sulfides adopt a cyclic structure (e.g., **21**) rather than a linear structure.[16,17] Trapping of such a radical cation, or the corresponding thiacyclopropenyl radical that would be formed after loss of a proton, would produce ESR spectra inconsistent with the observed hyperfine structure. Significantly, vinyl radical formation from such radical cations was not reported.[16] It has also been shown that alkenyl radical cations generated in cyclohexane solution react by rapid hydrogen abstraction from the solvent (*k* ca. 10^5 M^{-1} s^{-1})[17] rather than by deprotonation.



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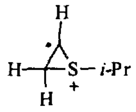

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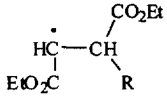
In the reaction of *deuterated* DEF with *undeuterated* IPVS, the ESR signal for the Otsu radical could not be detected (see Figure 2 and accompanying discussion). This observation is difficult to explain if the Otsu mechanism is operative since under such circumstances formation of the postulated vinyl radical and its addition to MNP should not be influenced by a deuterium isotope effect. On the other hand, when *deuterated* IPVS was employed, deuterated species **12c** and **12d** were detected, but their growth was markedly retarded. Hence, a hydrogen transfer step seems to play a central role in the formation of radicals **12**, but it is unlikely to be the deprotonation of **20** (to give **18**).

While we can dismiss structure **18**, we cannot give a definitive structure for the Otsu nitroxide, or account for the origin of the corresponding radical. As similar species were not detected in experiments with the spin trap ND, the formation of nitroxide radicals **12** is probably related to the specific properties of MNP. It is conceivable that the Otsu nitroxide was formed from minor, as yet unidentified decomposition products of MNP or related nitroxides, or that MNP undergoes a characteristic reaction with certain species present in this system. The ^{14}N splitting and the *g*-factor of the Otsu nitroxide are typical values for dialkyl nitroxides, i.e, **12a**. Large β-hydrogen splittings of around 20 G are characteristic of five-membered cyclic nitroxides, e.g. pyrrolinyl-1-oxyl radicals.[18] A rigid cyclic structure would also account for the narrow width of the hfs lines observed for this nitroxide radical.

The question as to whether the ESR data are consistent with the Hall initiation mechanism remains. According to this mechanism, DEF radical adduct **22** and IPVS radical adduct **23** might be trapped following initiation. However, these species are presumed to be intermediates in the polymerization process as well. Given the relative concentrations of spin trap to monomer (ca. 1:300), addition of monomer would be favored even if trapping of the initiating species were faster by from one to two orders of magnitude. Despite this limitation, the results of this study are most instructive.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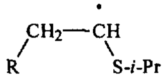
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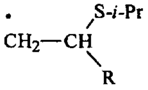
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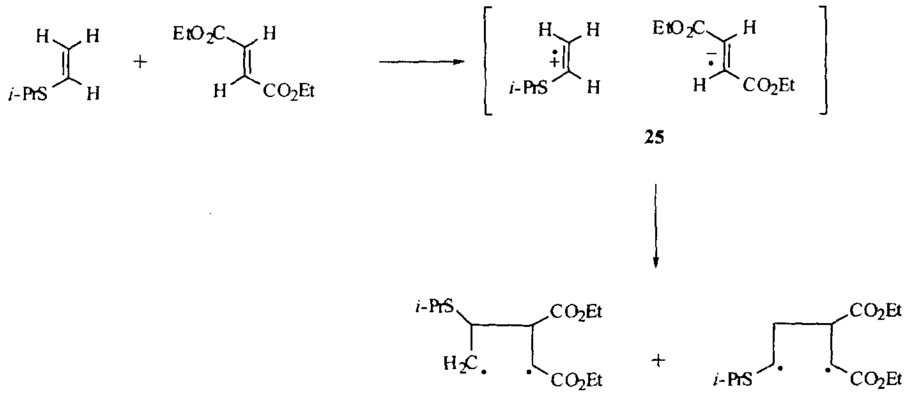
In experiments using both MNP and ND radical traps, the formation of DEF adduct radicals **11** and **15** (Schemes 3 and 4) was unequivocally proven by deuterium labeling. However, correspondence of the observed MNP-derived minor nitroxide components **13a-c** with the IPVS adduct radicals **23** and of minor nitroxide component **14** with the regioisomeric IPVS adduct radical **24** is uncertain. The hyperfine structures of **13a-c** are in agreement with trapping of radicals **23**, and the overall spectral width, the low initial yield, and the comparatively short lifetime of nitroxide **14** (marked by arrows in Figure 1a) are consistent with trapping of radicals **24**. The identity of **13b** with the expected nitroxide spin adduct of **23** is very probable, as the hyperfine splitting by a single hydrogen, definitely detected in the DEF + d_2-IPVS reaction (and probably in the d_2-DEF + d_2-IPVS reaction), was not observed in the DEF + d_3-IPVS and d_2-DEF + d_3-IPVS reactions. However, the question remains as to why radicals **13** and **14** could not be detected in the d_2-DEF + IPVS experiment (and probably the d_2-DEF + d_2-IPVS experiment). It seems unlikely that radical addition to IPVS, giving **23** and/or **24**, would be that much affected, kinetically or thermodynamically, by deuterium substitution at DEF.

In the ND spin trapping experiments, the detection of nitroxides **16** convincingly proves that radicals **24** are indeed true intermediates in the IPVS/DEF system. Nitroxides **16** were the major components in the composite ESR spectra (Figures 6-8), despite the fact that such primary alkyl nitroxides are less persistent than secondary or tertiary alkyl nitroxides. The existence of the isomeric IPVS adducts **23** related to nitroxides **17** is also likely, though the low ESR signal intensity prevented an unambiguous identification. However, the relative signal intensities of nitroxides **15-17** do not necessarily reflect the actual ratios of the related radicals

22-24. The competitive rates of reaction of these radicals with monomer and the spin trap, which are governed by steric and electronic factors, can limit the build-up of the corresponding ESR signals, as can concentration.

In any case, it is of great interest to note the significant formation of primary radicals **24**. The regioselectivity of radical addition to unsymmetrically substituted alkenes is primarily determined by steric factors.[11] In the present case, there is additionally a stereoelectronic preference for generation of the α-thio substituted radical.[19] Thus, addition at the terminal methylene carbon of IPVS should predominate over addition at the methine carbon to produce **23** in the course of propagation. To account for the formation of nitroxides related to radicals **24**, one might hypothesize that during propagation regioselectivity is not absolute. Occasionally a primary radical is formed and is efficiently trapped by the spin trapping agent. ND is known to react faster with carbon-centered radicals than does MNP.[20] Alternatively, radicals **23** and **24** may be generated in different stages of the reaction. Assuming that, following CT complex formation, the first step of the initiation mechanism is an electron transfer from IPVS to DEF, then the caged radical ion pair **25** might be expected to preferably collapse to biradical **26** rather than to **27**. A possible reason for preferred bond formation through the methine carbon of IPVS, despite the unfavorable steric repulsion, would be a higher positive charge density at this carbon, which is predicted by quantum-chemical calculations.[21] Nitroxides **16** might then be attributed to trapping of the initiating species, while nitroxides **17** would be attributed to trapping of the propagating species.



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Conclusion

The radicals detected in the present spin trapping study, while consistent with the previous study by Otsu, do not support the intermediacy of vinyl radicals in the initiation of the spontaneous polymerization of IPVS and DEF. Results are consistent with the major tennents of the Hall bond-forming initiation mechanism, but do not allow discrimination between trapping of the postulated tetramethylene diradicals and propagating radicals, since both would give rise to nitroxides which would exhibit virtually identical ESR spectra.

EXPERIMENTAL SECTION

All reactions were performed in flame-dried glassware under argon. Reaction mixtures were stirred magnetically. Diethyl ether ("ether") and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl. Dichloromethane (CH_2Cl_2) was distilled from CaH_2. Ethyl bromoacetate, lithium aluminum deuteride (98 atom % D), and 2-propanethiol were purchased from Aldrich, diethyl fumarate was obtained from Fluka, and fumaric-2,3-d_2 acid was purchased from CDN Isotopes (99.24 atom % D). Analytical thin-layer chromatography was performed on Merck glass-backed pre-coated plates (0.25 mm, silica gel 60, F-254). Visualization of spots was effected by treatment of the plate with a 7.5% solution of phosphomolybdic acid in 95% ethanol followed by charring on a hot plate. Gravity-driven column chromatography was performed on Merck silica gel 60 (70-230 mesh). Proton NMR spectra were recorded in $CDCl_3$ solution at 250.1 MHz using tetramethylsilane (0 ppm) as an internal standard. Mass spectrometric analyses were performed by the Nebraska Center for Mass Spectrometry, Lincoln, NE. Elemental analyses were performed by Desert Analytics, Tucson, Arizona.

ESR Spectroscopic Measurements. All ESR experiments were performed at room temperature under identical conditions and with careful exclusion of oxygen. ESR samples were prepared by injecting the deoxygenated reactants (0.25 ml each) into dry, septum-capped, argon-flushed 4-mm quartz tubes, preloaded with 4 mg of a spin trap compound, either MNP or ND. Samples were kept in the dark after mixing of the reagents. ESR spectra were recorded on a Bruker ER-420 X-band spectrometer equipped with a microwave frequency counter and a gaussmeter and connected to a home-built data acquisition system. ESR hyperfine splittings were evaluated by least-squares fitting of the the digitized experimental spectra to computer-simulated spectra using the WinSIM program.[12]

Diethyl Fumarate-d_2 (d_2-2). To a well stirred solution of absolute ethanol (50 mL, 860 mmol) and sulfuric acid (0.10 mL, 18 M, 1.8 mmol) under argon was added fumaric acid-d_2 (4.96 g, 42 mmol). The solution was heated to reflux for 2 h and the ethanol-water azeotrope was distilled from the mixture. This process was repeated a second and a third time. The mixture was then poured into sat aq $NaHCO_3$ soln (100 mL) and extracted with CH_2Cl_2 (2 x 100 mL). The organic extracts were combined, dried ($MgSO_4$), and filtered. Volatiles were removed *in vacuo*, and the colorless oil was purified via column chromatography on silica gel 60 (70-230 mesh) eluted with 20% ethyl acetate/hexanes to yield the pure diester (6.51 g, 37 mmol, 89%). IR (neat) cm^{-1} 2995, 2211, 1727, 1625, 1455, 1378, 1055; ^1H NMR δ 1.35 (6, t, J = 9.8 Hz), 4.27 (4, q, J = 9.8 Hz); MS (CI) *m/z* (relative intensity) 175 (100), 147 (26), 129 (27), 128 (7), 101 (7), 89 (3), 61 (3), 41 (35); HRMS (CI) calcd for $C_8H_{11}D_2O_4$ (M + H^+): 175.0939, found 175.0937.

Anal. Calcd for $C_8H_{10}D_2O_4$: C, 55.16; H, 6.94. Found: C, 55.09; H, 7.09.

Ethyl 2-[(1-Methyl)ethylthio]acetate (4). To a well stirred solution of sodium hydride (80% in oil, 5.90 g, 197 mmol) in THF (300 mL) under argon was added a solution of 2-propanethiol (16.8 mL, 181 mmol) in THF (250 mL) dropwise. The solution was heated to reflux for 1 h, then cooled to room temperature. To this mixture was added a solution of ethyl bromoacetate (20 mL, 180 mmol) in THF (60 mL) dropwise. The mixture was stirred for 0.5 h and water (500 mL) was then added. The layers were separated and the aqueous phase was extracted with ether (3 x 250 mL). The organic extracts were combined, dried ($MgSO_4$), and filtered. Volatiles were removed by simple distillation to yield the product as a pale yellow oil (27.6 g, 170 mmol, 94%). IR (neat) cm^{-1} 2961, 2926, 2867, 1732, 1460, 1410, 1383, 1365, 1272, 1217, 1132, 1054, 1031; ^1H NMR δ 1.29 (6, d, $J = 6.6$ Hz), 1.29 (3, t, $J = 7.2$ Hz), 3.08 (1, heptet, $J = 6.7$ Hz), 3.26 (2, s), 4.19 (2, q, $J = 7.2$ Hz).

Anal. Calcd for $C_7H_{14}O_2S$: C, 51.82; H, 8.70. Found: C, 51.65; H, 8.90.

2-[(1-Methyl)ethylthio]ethanol (5).[22] To a well stirred solution of $LiAlH_4$ (5.14 g, 135 mmol) in ether (360 mL) under argon was added a solution of **4** (25.6 g, 158 mmol) in ether (360 mL) dropwise. After 0.5 h the mixture was cooled to 0 °C and the reaction quenched by addition of water (5.1 mL), aq NaOH soln (4 M, 5.1 mL), and water (77 mL) (CAUTION! dropwise addition with stirring). The white aluminum salts were removed by filtration and extracted continuously with ether overnight. The organic extracts were combined, washed with brine (1 L), dried ($MgSO_4$), and filtered. Volatiles were removed by simple distillation to yield the product as a pale yellow oil (17.6 g, 146 mmol, 93%). IR (neat) cm^{-1} 3395, 2954, 2925, 2865, 1457, 1449, 1418, 1381, 1363, 1244, 1154, 1043, 1010, 669; ^1H NMR δ 1.25 (6, d, $J = 6.8$ Hz), 2.16 (1, s), 2.74 (2, t, $J = 6.0$ Hz), 2.93 (1, heptet, $J = 6.8$ Hz), 3.69 (2, t, $J = 6.0$ Hz).

2-(Ethenylthio)propane (1).[23] In a round-bottomed flask fitted for downward distillation were placed **5** (17.54 g, 146 mmol) and KOH pellets (16.51 g, 292 mmol) under argon. The mixture was stirred and heated in an oil bath at 230 °C. The crude product was distilled along with water from the reaction mixture at about 105 °C. The distillate was diluted with ether (20 mL) and filtered through a column containing 4Å sieves. The product (7.81 g, 76 mmol, 52%) was obtained via distillation at ambient pressure, bp 103-105 °C, lit[20] bp 105-108 °C. IR (neat) cm^{-1} 3087, 2959, 2924, 2865, 1582, 1460, 1450, 1382, 1365, 1241, 1156, 1056, 1024, 958, 881, 725, 707; ^1H NMR δ 1.29 (6, d, $J = 6.8$ Hz), 3.13 (1, heptet, $J = 6.8$ Hz), 5.17 (1, d, $J = 16.8$ Hz), 5.19 (1, d, $J = 10.2$ Hz), 6.35 (1, dd, $J = 16.8$ Hz, 10.2 Hz.

2-[(1-Methyl)ethylthio]ethanol-1,1-d_2 (6). To a well stirred suspension of $LiAlD_4$ (5.39 g, 128 mmol) in ether (500 mL) under argon was added a solution of **4** (27.6 g, 170 mmol) in ether (300 mL) dropwise. The reaction was stirred 0.5 h, then cooled to 0 °C. Water (5.4 mL), aq NaOH (4 M, 5.4 mL), and water (80 mL) were added sequentially to the reaction mixture with stirring (CAUTION! dropwise addition). The white aluminum salts were removed by filtration and extracted continuously with ether overnight. The organic extracts were combined, washed with brine (500 mL), dried ($MgSO_4$), and filtered. Volatiles were removed by simple distillation to yield the product as a pale yellow oil (16.7 g, 137 mmol, 80%). IR (neat) cm^{-1} 3377, 2959, 2923, 2865, 2208, 2104, 1458, 1449, 1424, 1381, 1364, 1240, 1205, 1155, 1124, 1087, 1053, 970, 942; ^{1}H NMR δ 1.28 (6, d, J = 6.7 Hz), 2.42 (1, s), 2.75 (2, s), 2.96 (1, heptet, J = 6.7 Hz); MS (EI) *m/z* (relative intensity) 122 (98), 119 (10), 107 (20), 89 (100), 75 (35), 74 (19), 69 (35), 63 (20), 62 (48), 61 (19), 59 (12), 55 (35), 48 (20), 47 (52), 46 (13), 45 (20), 43 (95), 41 (51), 39 (20); HRMS (EI) calcd for $C_5H_{10}D_2OS$: 122.0734, found 122.0728.

Anal. Calcd for $C_5H_{10}D_2OS$: C, 49.14; H, 9.89. Found: C, 48.80; H, 10.09.

2-(Ethenylthio)propane-2',2'-d_2 (d_2-1). In a round-bottomed flask fitted for downward distillation were placed **6** (16.7 g, 137 mmol) and KOH pellets (15.4 g, 273 mmol) under argon. The mixture was stirred and heated in an oil bath at 230 °C. The crude product distilled from the reaction mixture at about 105 °C. The distillate was diluted with ether (35 mL) and filtered through a column containing 4Å sieves. The product (9.1 g, 87 mmol, 64%) was obtained via distillation at ambient pressure, bp 103-105 °C. IR (neat) cm^{-1} 2960, 2925, 2865, 2321, 1553, 1530, 1459, 1448, 1382, 1365, 1261, 1238, 1156, 1054, 894; ^{1}H NMR δ 1.26 (6, d, J = 6.7 Hz), 3.11 (1, heptet, J = 6.7 Hz), 6.32 (1, br s); MS (EI) *m/z* (relative intensity) 105 (100), 104 (12), 91(8), 90 (6), 89 (7), 88 (12), 63 (20), 43 (27), 41 (10).

Anal. Calcd for $C_5H_8D_2S$: C, 57.63; H, 9.67. Found: C, 57.13; H, 9.65.

Methyl Bromoacetate-2,2-d_2 (7). To a well-stirred solution of acetic-d_3 acid-d_1 (10.0 g, 156 mmol) in $CHCl_3$ (15 mL) was added thionyl choride (13.5 mL, 187 mmol). Solution was heated to reflux for 0.5 h, then cooled to room temperature. To this mixture was added *N*-bromosuccinimide (34 g, 190 mmol), 75 mL $CHCl_3$, and 48% aq HBr (11 drops). The dark red solution was heated to reflux for 1 h, then cooled to rt and poured into cold methanol (400 mL). This yellow solution was poured into water (1.5 L) and the mixture was extracted with ether (2 x 500 mL). The organic extracts were combined, washed with sat aq $NaHCO_3$ soln (500 mL) and brine (500 mL), dried ($MgSO_4$), and filtered. Volatiles were removed by simple distillation and the product obtained by distillation at ambient pressure, bp 139-141 °C, as a colorless oil (8.4 g, 54 mmol, 35%). IR (neat) cm^{-1} 3003, 2953, 2843, 2294, 2272, 2192, 1732, 1646, 1505, 1498, 1436, 1366, 1253, 1153, 1060, 1005, 913, 862, 825, 734, 628; ^{1}H NMR δ 3.65 (3, s).

Methyl 2-[(1-Methyl)ethylthio]acetate-2,2-d_2 (8). To a well stirred suspension of sodium hydride (80% in oil, 1.6 g, 54 mmol) in THF (75 mL) under argon was added a solution of 2-propanethiol (4.6 mL, 49.5

mmol) in THF (75 mL) dropwise. The mixture was heated to reflux for 1 h, then cooled to room temperature. To this mixture was added **7** (7.69 g, 49.6 mmol) in THF (15 mL) dropwise. The reaction mixture was stirred for 0.5 h, and then water (125 mL) was added. The phases were separated and the aqueous phase extracted with ether (3 x 75 mL). The organic extracts were combined, dried ($MgSO_4$), and filtered. Volatiles were removed via simple distillation to yield the product as a yellow oil (6.2 g, 41 mmol, 83%). IR (neat) cm^{-1} 2955, 2925, 2865, 2245, 2168, 1732, 1457, 1433, 1252, 1155, 1064, 1009; ^{1}H NMR δ 1.17 (6, d, J = 6.6 Hz), 2.95 (1, heptet, J = 6.7 Hz), 3.62 (3, s).

2-[(1-Methyl)ethylthio]ethanol-1,1,2,2-d_4 (9). To a well stirred solution of $LiAlD_4$ (1.24 g, 29.5 mmol) in ether (125 mL) under argon was added a solution of **8** (5.91 g, 39.3 mmol) in ether (125 mL) dropwise. The reaction was stirred for 0.5 h, then cooled to 0 °C. Water (1.25 mL), aq NaOH (4 M, 1.25 mL), and water (18 mL) were added sequentially to the reaction mixture with stirring (CAUTION! dropwise addition). The white aluminum salts were removed by filtration and extracted continuously with ether overnight. The organic extracts were combined, washed with brine (250 mL), dried ($MgSO_4$), and filtered. Volatiles were removed by simple distillation to yield the product as a pale yellow oil (4.2 g, 34 mmol, 86%). IR (neat) cm^{-1} 3367, 2958, 2923, 2864, 2224, 2164, 2136, 2091, 1460, 1450, 1381, 1364, 1310, 1245, 1155, 1106, 1053, 1032, 976, 898, 669; ^{1}H NMR δ 1.28 (6, d, J = 6.7 Hz), 2.52 (1, br s), 2.96 (1, heptet, J = 6.7 Hz).

2-(Ethenylthio)propane-1',2',2'-d_3 (d_3-1). In a round-bottomed flask was placed **9** (2.70 g, 21.7 mmol) and D_2O (1 mL). The mixture was stirred for 15 min and the D_2O layer was removed. This deuterium-proton exchange was repeated 2 times. To the organic oil was added NaOD (4.5 mL, 44 mmol, 40% in D_2O) and the flask was fitted for downward distillation under argon. The mixture was stirred and heated in an oil bath at 230 °C, and the crude product distilled from the reaction mixture (bp 100-105 °C). The distillate was extracted with pentane (3 x 5 mL), the extracts dried ($MgSO_4$), and filtered. Volatiles were removed by simple distillation to yield a colorless oil (1.0 g, 9.4 mmol, 43%). IR (neat) cm^{-1} 2961, 2927, 2868, 2221, 2102, 1463, 1166, 970; ^{1}H NMR δ 1.28 (6, d, J = 6.7 Hz), 2.95 (1, heptet, J = 6.7 Hz.

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19. The Q and e values for IPVS are 0.31 and -1.20, respectively, while the values for DEF are 0.25 and 2.26; taken from Young, L. J. Tabulation of Q-e Values, in *Polymer Handbook*, 2nd ed.; Brandrup, J.; Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975; Ch. II, pp. 387-404.
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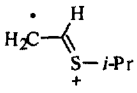
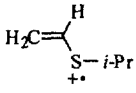
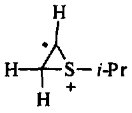
21. Density-functional-theory (DFT) calculations at the UB3LYP/6-31G** level and charge analysis by the Natural Population Analysis (NPA) method indicate that the IPVS radical cation is best described by two resonance structures (**20**-*i* and **20**-*ii*). The spin is almost equally distributed on S (0.59) and on the terminal carbon (0.51), while the charge resides principally at S (+0.71). Interestingly, calculations place the cyclic cation radical **21** approximately 32 kcal/mol higher in energy than 20.



20-*i*



20-*ii*



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