An electron spin resonance study of the thermal decomposition of poly(1,6-di-*N*-carbazolyl-2,4-hexadiyne)

F. P. Bradner and J. S. Shapiro*
School of Chemistry, Macquarie University, North Ryde, 2109, Australia

and D. Hunter and P. Pomery
Department of Chemistry, University of Queensland, Brisbane, 4057, Australia
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By monitoring the thermal decomposition of poly(1,6-di-*N*-carbazolyl-2,4-hexadiyne), through the use of an electron spin resonance (e.s.r.) spectrometer, it was possible to measure the spin concentrations associated with the decomposition process. Two types of experiments were conducted: in one the decomposition reaction was carried out within the e.s.r. unit, while in the second the decomposition was performed externally under an inert atmosphere, after which the decomposed material was examined. Both types of experiment yielded similar results, and these appeared to exclude a free-radical chain mechanism as the major mechanism of decomposition. The proposed mechanism involves side-group cleavage, followed by hydrogen abstraction by the carbazole radical, to form carbazole as the main reaction product.

(Keywords: electron spin resonance; thermal decomposition; polydiacetylenes; mechanism)

INTRODUCTION

As part of a study examining the thermal stability of polydiacetylenes, e.s.r. was used as a tool to monitor the decomposition process[1–4]. Previous studies of polydiacetylenes using e.s.r. have concentrated on the toluene sulfonate (TS) derivative[5–11]. Many of the initial results can be attributed to the group centred around Bloor[5–10]. In papers examining the e.s.r. spectrum of the TS derivative during polymerization, Stevens and Bloor[5,10] note that the polymer spin concentration and lineshape parameters follow the conversion *versus* time curve. They also noted the occurrence of increased spin concentration at high polymerization temperatures and conversions, and attributed the increase to thermal decomposition. The cause of these spins during polymerization was thought to be due to departure of the polymer chain from some ideal conformation. This result is reiterated in later papers[8,9], and the authors go on to conclude that not all the defects present are paramagnetic. Furthermore, no connection was found between the spins they observed in these studies and the triplet species reported as being a polymerization intermediate. However, the possible presence of these triplet species was suggested in another paper by this group[6]. The authors report the observation of spectra consistent with those proposed for triplet species, with high angular dependence. Carbene-type radicals were proposed. These spectra consisted of both low- and high-field components, the high-field lines being of higher angular dependence than the low-field lines, which were found to disappear at the end of the rapid polymerization period. The low-field absorption took somewhat longer to disappear, and was attributed to distorted polymer chains or trapped chain ends, which are capable of slow rearrangement to non-paramagnetic conformations. This was confirmed in another paper by Eichele *et al.*[7], where the triplet species was observed during polymerization while the singlet species was observed in fully polymerized crystals, which supported the presence of mobile defects.

Reviews by Sixl[11,12] summarized the results obtained by e.s.r. examination of the photo-product intermediates of the TS derivative. This work provided evidence to suggest that several reaction intermediates are present at the early stages of photopolymerization: diradicals, asymmetric carbenes and dicarbene intermediates were proposed.

We have previously reported the thermal decomposition of a specific polydiacetylene derivative, poly(1,6-di-*N*-carbazolyl-2,4-hexadiyne) or polyDCH[1–4]. These investigations concentrated on the determination of the kinetics and mechanism of decomposition, established using a plug-flow-type reactor, and also temperature-programmed and isothermal thermogravimetric analysis (t.g.a.). In conjunction with these studies, electron spin resonance (e.s.r.) was performed in order to determine whether paramagnetic species are formed during decomposition, and whether these are responsible for the autocatalytic behaviour observed during the decomposition reaction. The results of this study are reported here.

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* To whom correspondence should be addressed

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EXPERIMENTAL

The synthesis of the polyDCH has been reported elsewhere[13]. Monomer was polymerized using either γ-radiation (in varying doses) or by heating. The polymer was stored in the dark at 4°C under vacuum prior to decomposition. E.s.r. studies were performed on an ER 200D spectrometer fitted with a variable-temperature cavity (20–600°C). Data acquisition and manipulation were facilitated using the program SIMOPR[14]. An operating power of 40 dB was chosen and samples were referenced to Varian strong pitch $3\times10^{15}\pm15\%$ spins/cm^3.

Two types of decomposition studies were performed: (i) *in situ* decomposition within the e.s.r. cavity and (ii) decomposition in an external furnace. In the second instance, samples were decomposed to the desired conversions under vacuum and rapidly quenched in liquid nitrogen, and their e.s.r. spectrum was then analysed under vacuum at room temperature.

RESULTS

An initial study was performed to examine the effect of polymerization dose on the e.s.r. spectrum. E.s.r. parameters determined for various polymerization doses in such experiments are shown in *Table 1*. In addition, in *Table 1* are displayed the parameters obtained for thermally polymerized polyDCH and for DCH monomer. In both types of polymer, broad singlets were obtained. *Table 1* indicates that, as the polymerization dose increases, so does the spin concentration. However, very little change is observed in ΔH_{pp} (the peak width at inflection), which was found to be approximately equal to 20 G. *Table 1* also indicates that ΔH_{pp} for the thermally polymerized sample is almost half the value for the radiation-polymerized material, and is found to be equal to 11.1 G. The g value observed for the thermally polymerized material is also somewhat larger than that obtained for the radiation-polymerized material, 2.0033 as opposed to 2.0025, respectively. The spin density and peak width observed for the thermally polymerized polyDCH were found to be similar to the values obtained by Stevens and Bloor for the thermally polymerized polyTS derivative[5]. In their study these authors observed approximately 2×10^{16} spins/g, while ΔH_{pp} was found to be equal to 7 G for polyTS polymerized at temperatures between 60 and 80°C.

Table 1 Summary of e.s.r. parameters obtained for thermally polymerized polyDCH and γ-radiation-polymerized polyDCH produced with varying polymerization doses

Sample	ΔH_{pp} (G)[a]	g value	Spins/g
110.0 Mrad[b]	22.5	2.0025	7.53×10^{17}
70.0 Mrad	20.5	2.0025	5.72×10^{17}
30.0 Mrad	20.3	2.0026	3.95×10^{17}
21.7 Mrad	22.0	2.0025	3.36×10^{17}
8.7 Mrad	22.0	2.0026	1.21×10^{17}
6.7 Mrad	22.0	2.0028	0.81×10^{17}
TP[c]	11.1	2.0033	0.85×10^{17}
Monomer[d]	–	–	$<10^{13}$

[a] ΔH_{pp} is the peak width at inflection point of e.s.r. absorbance spectrum
[b] Indicates the dose used to polymerize the sample
[c] TP represents thermally polymerized sample, 150°C for 100 h
[d] Indicates that monomer was freshly prepared prior to e.s.r. examination

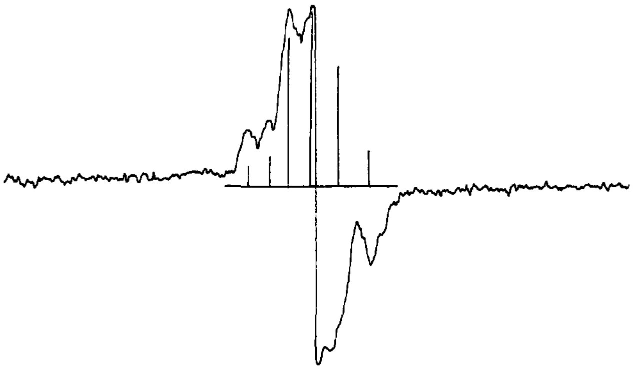

Figure 1 E.s.r. spectrum of monomer that was stored in a vacuum in the dark for 3 months

Table 1 indicates that the spin density present in freshly prepared monomer is below detection level. However, it was found that monomer that had been stored for 3 months (and has a light blue coloration) exhibited a very weak sextet, shown in *Figure 1*. Since it is likely that only extremely low levels of polymer are present at this stage, it is suggested that this spectrum is somehow related to the polymerization process. The disappearance of this spectrum on polymerization, either by radiation or by thermal means, is believed to be due to the swamping of this signal by other signals generated by either polymerization process. This aspect will be discussed in more detail later in this paper. Stevens and Bloor reported the observation of carbene-like resonances or triplet species at around $g=2$ in polyTS single crystals[5]. The triplet they observed has low angular dependence but is quite well resolved. They suggest that the absorbance may be attributed to distortion of the polymer chain double bond, giving unpaired electrons on adjacent sites. Alternatively, they suggested that the cause may be trapped chain ends behaving as weakly coupled diradicals, with one electron localized at the chain end and the other delocalized into the adjacent polymer chain. This second alternative is very unlikely in the case of low-conversion DCH monomer, as trapping of chain ends would not be occurring to any great extent. In any case, it is not clear what the cause of the sextet is in the case of aged DCH monomer, and further work is required to resolve this matter.

When the spin concentrations stated in *Table 1* are plotted against polymerization dose, as shown in *Figure 2*, two linear regions are clearly observed, with a change in slope occurring at approximately 20–25 Mrad. The fact that the change in slope occurs at approximately 20–25 Mrad is significant because this is precisely the dose required to form polymer of high conversion (>95%). Thus the steeper slope is associated with the rapid polymerization regime. (The polymerization of polydiacetylenes usually has associated with it both rapid and slow polymerization regimes. This has to do with the fact that the polymerization occurs in the solid state and is mediated by strain.) However, one cannot presume that the above-mentioned spins are directly associated with the polymerization process, especially since carbene-type diradicals are the accepted polymerization intermediate.

In order to determine whether the broad singlet observed in radiation-polymerized material is directly attributable to radiation damage, a sample of thermally polymerized polyDCH was subjected to a γ-radiation

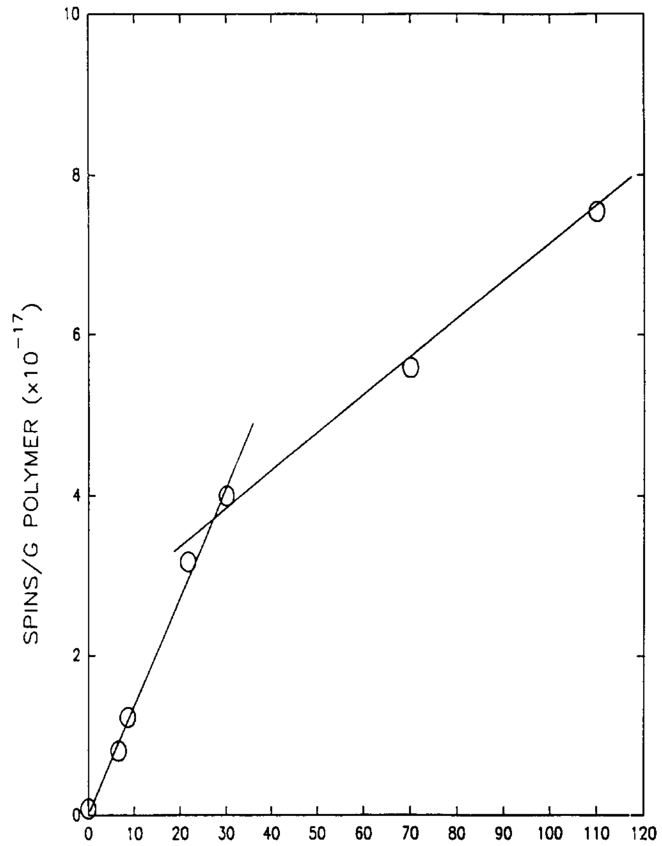

Figure 2 A plot of the dependence of spin concentration on polymerization dose (Mrad)

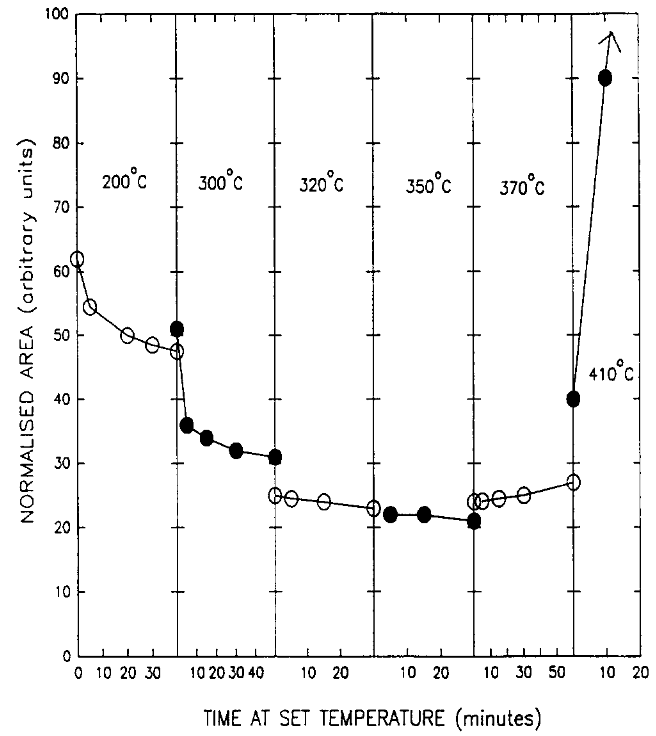

Figure 3 A plot of relative spin concentration *versus* time at various temperatures. Decomposition was performed in an external oven. Sample used was γ-radiation-polymerized, dose 30 Mrad

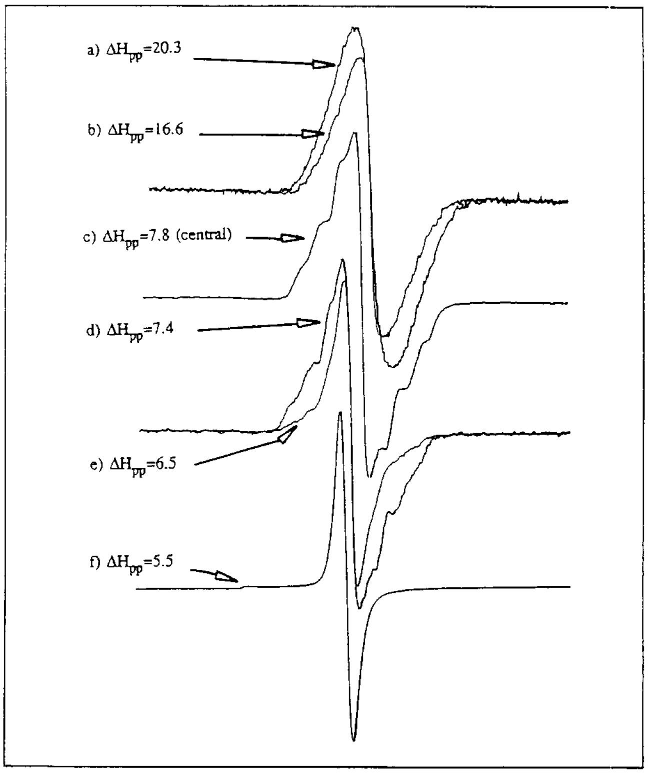

Figure 4 E.s.r. spectra obtained after radiation-polymerized polyDCH was decomposed according to the treatment shown in *Figure 3*: namely, (a) 300°C for 5 min, (b) 300°C for 50 min, (c) 320°C for 20 min, (d) 350°C for 20 min, (e) 370°C for 60 min and (f) 410°C for 10 min

dose of 14 Mrad, leading to quite unexpected results. Although there was a three-fold increase in the spin concentration after irradiation, ΔH_{pp} remained at the value observed for the thermally polymerized crystals (11 G), and did not increase to the expected value of approximately 22 G. Clearly, then, ΔH_{pp} is not related to the radiation defect, but to the original polymerization condition.

Decomposition studies

In the case where polyDCH samples were decomposed in the e.s.r. tube externally, the samples were subsequently cooled and analysed by e.s.r. A plot of relative area (spin concentration) *versus* time recorded at various decomposition temperatures is shown in *Figure 3*. Starting from 200°C, the relative spin concentration initially decreases, reaching a minimum at approximately 350°C. Upon further heating the spin concentration increases, first slowly, and then rapidly above 400°C. During the change in spin concentration shown in *Figure 3*, the linewidth was found to decrease with increasing temperature from 21 to 5 G. *Figure 4* displays some of the e.s.r. spectra that were obtained at different temperatures for a sample that was polymerized using a total dose of 30 Mrad. Initially, the spectrum consists of a broad singlet (*Figure 4a*), but after the heat treatment described in *Figure 3* a very sharp singlet develops (*Figure 4f*). At approximately 350°C, the spectrum assumes the form of a poorly resolved septet. This septet disappears on heating to higher temperatures. It was found that initial polymerization dose has no effect on the e.s.r. spectra obtained during decomposition.

Thermally polymerized polyDCH was also examined in a similar fashion to that described above for the 30 Mrad sample. *Figure 5* shows how normalized area (spin concentration) varies with time at various temperatures. Initially, the spin concentration increases slowly. However, as the temperature is increased to 350°C, the spin concentration begins to increase very rapidly. The linewidth was observed to narrow from 11 to 6 G after decomposition at 400°C. No evidence of the septet observed during the decomposition of the radiation-polymerized sample is found during the decomposition of thermally polymerized polyDCH.

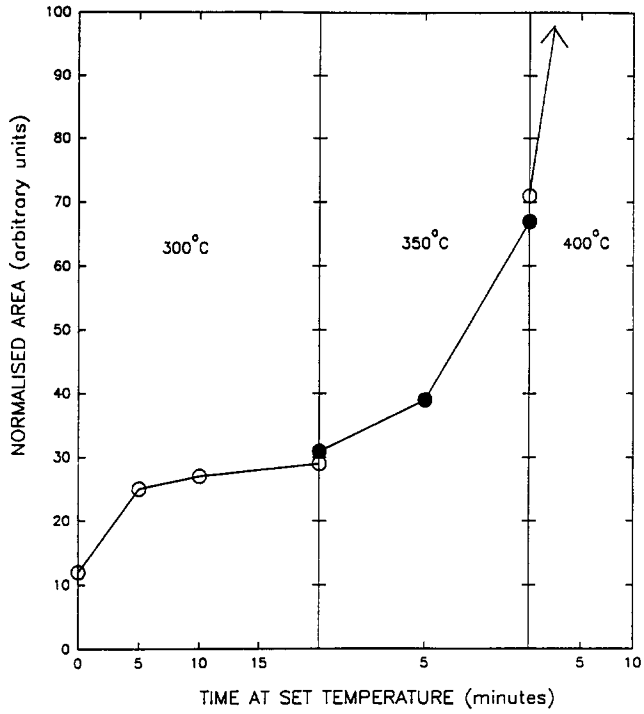

Figure 5 A plot of spin concentration *versus* time at various temperatures for thermally polymerized polyDCH. Decomposition was performed in an external oven

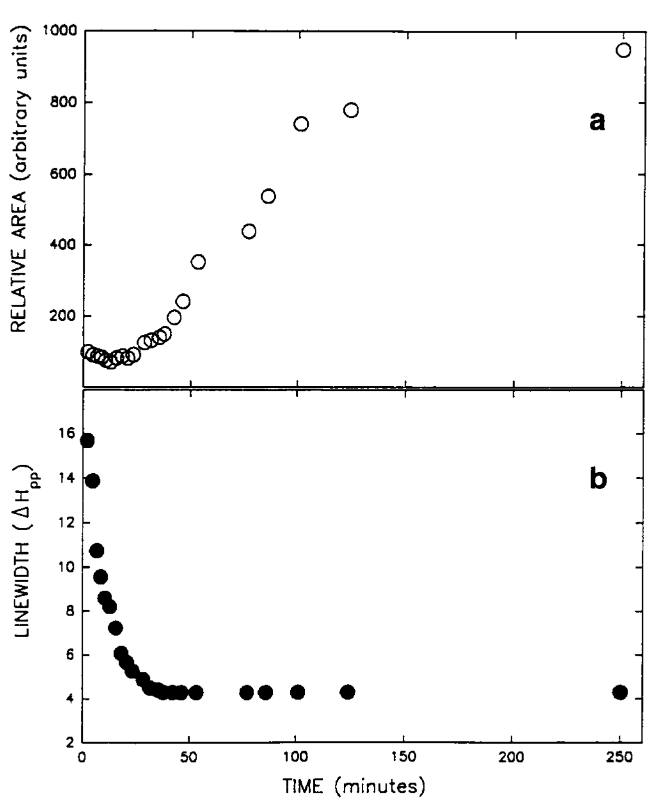

Figure 6 (a) Plot of variation of spin concentration with time, and (b) plot of variation in linewidth with time. Sample used was γ-radiation-polymerized (dose 30 Mrad) and decomposed isothermally at 409°C in the e.s.r. cavity

In situ decomposition of polymer in the e.s.r. cavity was performed in order to monitor the e.s.r. parameters more frequently. In this way, the generation of radicals could be compared to the rate of formation of products *versus* time data obtained from flow system experiments (published elsewhere[1–3]). In this way it was hoped to establish whether the bimodal rate *versus* time behaviour observed previously is also reproduced in the form of radical concentration *versus* time. However, since e.s.r. spectra were not obtained at room temperature, the results are only comparative owing to differences in population states that result from heating the polymer. *Figure 6* demonstrates the results obtained for the thermal decomposition of a radiation polymerized sample of polyDCH (dose 30 Mrad), decomposed isothermally at 409°C. While *Figure 6a* indicates how spin concentration varies with time, *Figure 6b* describes the change of linewidth with time. The results obtained in these *in situ* experiments are similar to those obtained for samples decomposed externally, cooled and then analysed using e.s.r.

From the above data, it is clear that there is no evidence that the radical concentration follows the same behaviour observed for product evolution in flow system experiments[1–3]. As the e.s.r. spectra were monitored at 2 min intervals, it is unlikely that sudden variation in spin concentration would be missed.

DISCUSSION

It was initially suspected that the paramagnetic species observed to occur in the γ-radiation-polymerized sample was due entirely to radiation damage. However, the results summarized in *Figure 2* suggest that radiation damage may not be the only mechanism operating. The fact that the change in slope in *Figure 2* occurs approximately at the end of the fast polymerization regime indicates that the first linear region may be related to some defect generated during the polymerization process. The structure of the radical responsible for the appearance of this signal is not clear. These spectra are, however, not characteristic of the triplet species that have been identified during the polymerization of many diacetylene crystals[6,7,11,12]. It is not uncommon to observe broad singlets in polymers that have been subjected to high levels of radiation[15]. It has been suggested that allylic radicals of the type $-CH_2-\dot{C}H-(CH=CH)_n-CH_2-$ are generally responsible for these broad singlets. However, in the polymers reported by the above authors, radiation damage results in the formation of polyene sequences, whereas in the case of polydiacetylenes, conjugation is already present. It is possible that the radiation damage causes a break in the conjugation, creating a series of conjugated species of varying length. However, it seems unlikely that the conjugation length would be short. As the polymer samples are heated, the signal is observed to narrow. Some of this narrowing is probably attributable to motional narrowing, in which the electron becomes further delocalized as the temperature of the system provides enough energy for the radicals to overcome the energy barrier that may 'pin' the electron.

Lack of hyperfine splitting could indicate that either (i) there are many different radicals present, all being subjected to different magnetic environments and, therefore, the singlet is really a superposition of many hyperfine lines, or (ii) the free electron is oscillating back and forth along the conjugated sequence, spending very little time adjacent to a hydrogen atom, thus not resulting in any resolved splitting. The first option is possible, as Lawton *et al.*[16] have suggested. However, the second option is also possible, especially in the case of the polymer examined in this study, because it has so few protons present. It is unlikely that the signal is due to radiation damage of the methylene carbazole side group, as some hyperfine structure would be expected[18], and a g value of 2.0026 is generally too low for a radical in the presence of a nitrogen atom[19].

It seems most likely that the radicals producing both linear regions found in *Figure 2* are identical. During rapid polymerization, it is likely that the growing polymer is more susceptible to radiation damage than polymer that has undergone a very high level of conversion. This may be associated with the configuration of the growing chain end, which may be more susceptible to radiation damage, and is more abundant at low degrees of polymerization. The source of the signal in both the low- and high-slope regimes are probably the same, as all signals, even at the lowest doses, are broad singlets with similar e.s.r. parameters. It is therefore likely that radiation damage is the source of these signals. Sandman *et al.*[20] also observed a broad singlet, $\Delta H_{pp} = 20$ G, in a single crystal that was radiation-polymerized. The authors attributed their paramagnetic species to radiation damage that occurred during the polymerization process. Finally, the observation that the thermally polymerized sample exhibits a completely different resonance also supports the hypothesis that the broad singlet is due to radiation damage.

The origin of the spin species observed in the thermally polymerized samples is not clear. However, this signal is very similar to that observed by Stevens *et al.*[5] for the polyTS derivative, which was also thermally polymerized. The above authors suggest several reasons why paramagnetism may occur in the polyTS derivative. These are: (a) structural or skeletal bond rupture, (b) structural bond alternation defects, (c) unpaired electron sites remaining on the polymer chain after side-group loss and (d) daughter defects associated with a parent radical responsible for chain propagation. It is possible that any one or a combination of these defects are responsible for the paramagnetism observed in thermally polymerized samples of polyDCH in this study.

Both the *in situ* and the decomposition experiments conducted outside the e.s.r. spectrometer provided similar results. Both experiments indicated that three different radicals (or spin regimes) are present during the decomposition of γ-radiation-polymerized polyDCH. The first is the one that results in the broad singlet, which narrows and then decreases in concentration as the temperature increases. This species is attributed to radiation damage caused by the high total polymerization doses employed. A second radical species is observed as a septet when the total spin concentration is at a minimum. This multiple line spectrum was observed in both external decomposition experiments and *in situ* decomposition experiments. During *in situ* experiments this signal was observed on initial heating to 409°C, and disappeared very rapidly. As no visual evidence was apparent when that decomposition had commenced (white precipitate formation indicates the evolution of carbazole), this septet may provide some insight into the early stages of decomposition. It seems that the only reason that the septet was observed at all is because the broad singlet concentration, described above, is at a minimum, and the creation of the new spin species due to the decomposition of the polymer has not yet begun. Reports of the thermal decomposition occurring in the TS derivative at the latter stages of polymerization and at higher polymerization temperatures are well documented[5,10]. No such decomposition was observed in the case of the DCH derivative, which is not surprising considering its greater thermal stability[1–4,12].

This new species, which is attributed to the decomposition reaction, is the third spin species, which increases in concentration and narrows rapidly as decomposition commences. The actual value of the spin concentration due to this narrow component is probably larger than reported here. This is because the decomposition reaction results in loss of mass, which would result in a decrease in density of material, from which the spin concentration is determined. The narrow component is still increasing in concentration when all visual evidence of rapid decomposition has disappeared. Although the spin concentration continues to increase even though the rate of the decomposition reaction has slowed, the linewidth remains constant at $\Delta H_{pp} = 4.3$ G. Such a narrow signal has been observed during the decomposition of many organic molecules (for example, the decomposition of poly(vinyl chloride), PVC[19]. It is usually attributed to a carbon radical, which often results during cyclization and polyaromatization of decomposing organic materials. The precise nature of the radical depends on the starting material, but the outcome is usually a carbon radical that is extremely mobile. Probably the best example of this kind of radical is strong pitch, which provides an extremely narrow signal and is used to calibrate the e.s.r. spectrometer. This and other evidence such as solid-state ^{13}C n.m.r. and i.r. studies indicate that, at higher conversions, cyclization and polyaromatization are occurring during the decomposition of polyDCH.

As has been described in the earlier publications[1,2], the decomposition of polyDCH proceeds via side-group cleavage, which is initiated and propagated via mechanical means. Thus loss of the carbazole side groups probably results in the septet. Proposed reaction schemes reported in a previous publication suggest that homolytic side-group cleavage occurs as indicated in *Figure 7a.* Carbazole radicals shown in *Figure 7a* could then further react by abstracting a hydrogen atom from a nearby chain. This abstraction would result in the formation of allylic-type radicals as shown in *Figure 7b.* This allylic radical may be trapped for some time, until (a) it has become thermally activated and, as shown in *Figure 7b,* can be resonance stabilized, or (b) it can recombine with a nearby radical. Other possible sources of the septet have been examined, and these were eliminated. It was suggested that this resonance may be due to carbazole radicals, which either form because of radiation damage or form during the decomposition reaction as suggested in *Figure 7a.* Both possibilities were eliminated after performing irradiation experiments on carbazole, which indicated that the radicals formed did not have the same hyperfine splitting as the septet. There is also the possibility that the septet is due to radiation damage of the backbone, but then one would expect the radical to be observable at lower temperatures. Therefore, the hypothesis that the septet is due to allylic-type radicals is quite reasonable.

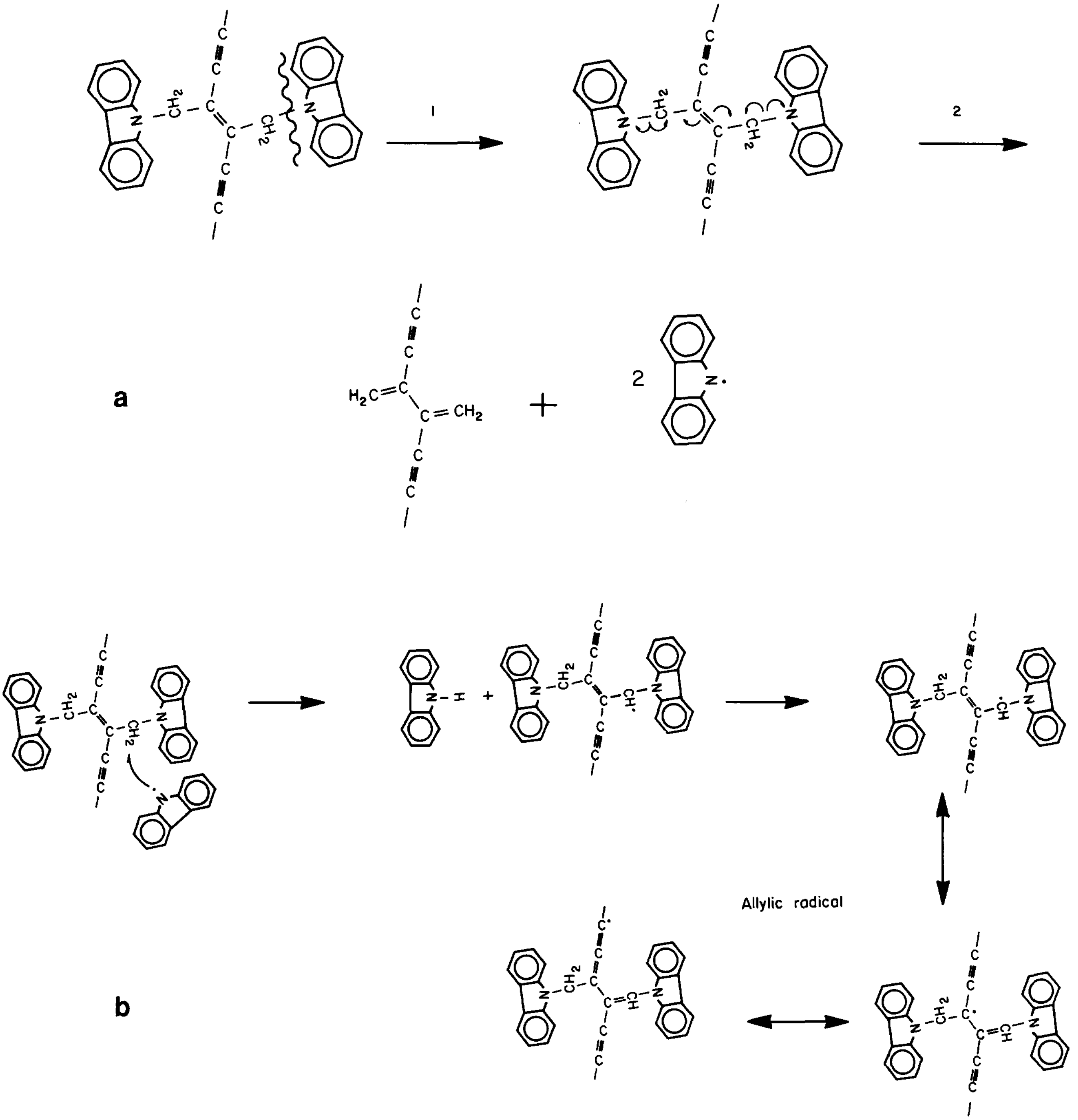

Figure 7 (a) A possible radical non-chain mechanism describing the decomposition of polyDCH. (b) A possible mechanism describing how the carbazole radicals formed during side-group cleavage may abstract a hydrogen atom and result in allylic-type radicals

Decomposition of thermally polymerized polyDCH provided similar results to those obtained for the decomposition of radiation-polymerized polyDCH except that the radical concentration began to increase at lower temperatures, and there was no sign of the septet observed in radiation-polymerized polyDCH. It is likely, however, that the reason the septet was not observed in the case of thermally polymerized materials is because the spin concentration due to the narrow singlet increases so rapidly, even at lower temperatures, that this signal swamps that of the septet. The emergence of this narrow singlet at lower temperatures is in line with t.g.a. and flow system studies[1,2], which indicate that the thermally polymerized material decomposes at approximately 40°C lower than the radiation-polymerized material.

CONCLUSIONS

Resulting from the study of the decomposition of polyDCH performed while using e.s.r. to monitor spin concentrations, it was found that the γ-radiation polymerization process itself results in some radiation damage to the polymer. However, since the change in slope of the radical yield plot corresponds to the end of the rapid polymerization period, it appears likely that during rapid polymerization the polymer/monomer matrix is more susceptible to radiation damage than at higher conversions. Thermally polymerized polyDCH also exhibits unpaired spins, but these were found in a much lower concentration and of different type than those found for γ-radiation-polymerized polyDCH. It was suggested that some conformational defect is the cause of this signal.

The decomposition of γ-radiation-polymerized polyDCH results initially in a reduction of spin concentration and a narrowing of the peak-to-peak width. This was proposed to be due to motional narrowing, as thermal excitation results in delocalization of the spin species. When the spin concentration was at a minimum and just prior to the visual confirmation that decomposition had commenced, a multi-line septet was observed, and this has been attributed to allylic-type radicals. Finally, as decomposition proceeds, a narrow line singlet emerges as the predominant signal, which is attributed to a carbon radical commonly found during the latter stages of decomposition of many organic materials.

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