Electron spin resonance study of the homopolymerization of aromatic bismaleimides

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Maleimide homopolymerization can be initiated by the maleimide monomer without the need for added initiator. This self-initiation is believed to occur through a donor–acceptor complex formed between maleimide groups. An in-situ electron spin resonance (e.s.r.) spectroscopic technique was used to study the free-radical homopolymerization of 1,1′-(methylenedi-4,1-phenylene)bismaleimide (MDP-BMI) over a range of temperatures. Total radical concentrations were measured as a function of time at polymerization temperatures from 180 to 230°C. By analysis of the e.s.r. spectra from different maleimide monomers, MDP-BMI, *N*-phenylmaleimide (NPM) and 1,1′-[methylenebis-(2,6-diethyl-4,1-phenylene)] bismaleimide (MDEP-BMI), with and without free-radical initiators, it was possible to identify the e.s.r. signals due to various radical species. Unreactive diphenylmethylene radicals were observed on the polymer chains formed from MDP-BMI. Additional spectral features are present that include the signal due to the propagating radical. Maleimides containing free-radical initiator also exhibited a broad doublet signal assigned to a vinyl radical formed by hydrogen abstraction from the maleimide double bond. From comparison of the spectra of NPM and MDEP-BMI monomers, both with and without free-radical initiators, it was shown that the maleimide propagating radical gives an unusually narrow, singlet e.s.r. peak quite different from the four-line signal previously reported. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Bismaleimides are capable of homopolymerizing, thermally, without the addition of a free-radical initiator. That the homopolymerization involves free radicals has been shown previously, as polymerization is affected by free-radical inhibitors[1,2]. Electron spin resonance (e.s.r.) spectroscopy can be used both to quantify the concentration of the free radicals, and to identify the radical species present. The work described in this paper was carried out by in-situ e.s.r. spectroscopy at various cure temperatures to study the homopolymerization of aromatic maleimides and bismaleimides.

Only a few papers have been published regarding e.s.r. studies of maleimide homopolymerization. Sato *et al.*[3] have published work on *n*-octadecyl maleimide polymerized with free-radical initiator in benzene, while Sandreczki and Brown[1,4,5] studied the homopolymerization of aromatic maleimides and bismaleimides, including systems with no added initiator. For the thermal polymerization of MDP-BMI, Sandreczki and Brown postulated that the initiation was via a biradical[1] formed by homolysis of the maleimide double bond They assigned other peaks in the e.s.r. spectra to the expected propagating radical (*Figure 1a*), analogous to that in other vinyl polymerizations. Finally, termination was determined to be by hydrogen abstraction at the benzylic methylene group to give a stable diphenylmethylene radical (*Figure 1b*).

The assignment of the mechanism for thermal initiation to a biradical does not, however, appear to be feasible. Homolysis of a double bond to give a biradical is not a favourable reaction, as was outlined by Flory[6]. Although the maleimide double bond is weaker than the styrene double bond due to the presence of the adjacent electron-withdrawing carbonyl groups in maleimides, it is still difficult to rationalise the existence of a biradical in the absence of any other evidence. Initiation is much more likely to occur via a donor–acceptor complex with the resulting formation of two separate radicals that can then undergo propagation reactions. This initiation scheme is indicated by *Figure 2*. Maleimide groups contain both donor and acceptor groups in the form of the carbonyl and electrophilic double bonds, respectively. It may be expected therefore that a donor–acceptor complex capable of initiating the polymerization will be readily formed.

MATERIALS AND METHODS

1,1′-(Methylenedi-4,1-phenylene)bismaleimide (MDP-BMI) from Aldrich and 1,1′-[methylenebis-(2,6-diethyl-4,1-phenylene)]bismaleimide (MDEP-BMI) were purified by column chromatography, using silica gel as the column support and eluting with chloroform. The elutant was reduced in volume on a rotary evaporator and the bismaleimide was then precipitated using methanol as the non-solvent.

N-*phenylmaleimide (NPM)*

Into a three-necked flask was placed 9.99 g (0.11 mol) of maleic anhydride and 200 mL of dry ether. The solution was

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cooled in an ice-bath and stirred under nitrogen until the maleic anhydride was dissolved. Then 10 mL (0.11 mol) of aniline was added dropwise with stirring. A thick, creamy suspension formed immediately. After 1 h at room temperature the *N*-phenylmaleanilinic acid was collected by vacuum filtration as a fine, off-white powder in quantitative yield (98%).

18.5 g (0.097 mol) of the *N*-phenylmaleanilinic acid was added to a solution of 3 g of anhydrous sodium acetate in 30 mL acetic anhydride. The reaction mixture was heated with stirring to 60–70°C for 3 h. After cooling to room temperature, the solution was poured into *ca*. 500 mL of ice water. The precipitate was collected by vacuum filtration and washed three times with water and once with hexane. The crude product was then recrystallized from cyclohexane to give *N*-phenylmaleimide as bright yellow needles.

Melting point 92°C (by d.s.c.) Lit. 91°C [7]

[1]H n.m.r. (CDCl$_3$) δ 6.82 ppm (s, 2H), δ 7.3–7.5 ppm (mult., 5H)

[13]C n.m.r. (CDCl$_3$) δ 126.0, 127.9, 129.1, 131.5 (aromatic) 134.2 (vinyl), 169.5 ppm (carbonyl)

Sample preparation

The e.s.r. samples were prepared by the following method. The purified monomers were dried in a vacuum oven at 60–70°C for at least 24 h, before being loaded into Spectrosil quality quartz tubes. All samples were degassed under high vacuum (< 0.1 Pa) for 12 h and sealed either under high vacuum or after backfilling to approximately 50 kPa with nitrogen.

E.s.r. spectroscopy spectra were obtained on a Bruker ER200D spectrometer operating in the X-band, at 9.28 GHz. A variable temperature insert was used, which enabled the control of the sample temperature up to about 250°C with an accuracy of $\pm 1°C$ over the long reaction times of up to 8 h.

Generally, four scans were co-added for each spectrum to give a reasonable signal-to-noise ratio in the shortest possible time. The spectra were displayed as the first derivative of the absorption peak to aid resolution of the fine structure[8]. Radical concentrations were calculated against a calibration standard of strong pitch (Varian) of 3×10^{15}
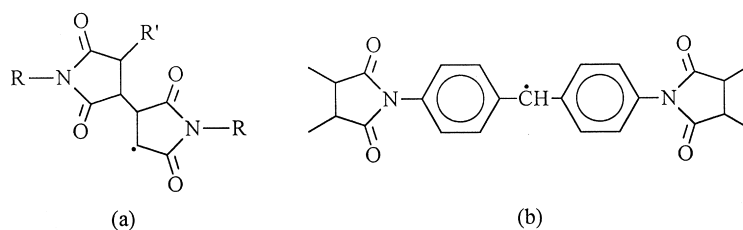

Figure 1 Main radical species present during homopolymerization of MDP-BMI, the propagating radical (a) and a diphenylmethylene radical (b)
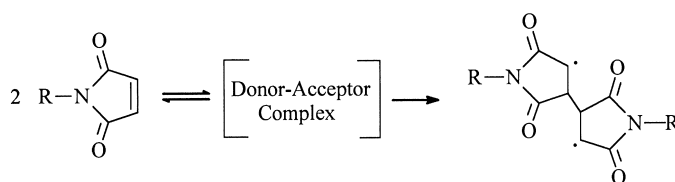

Figure 2 Thermal initiation of free-radical homopolymerization in maleimides
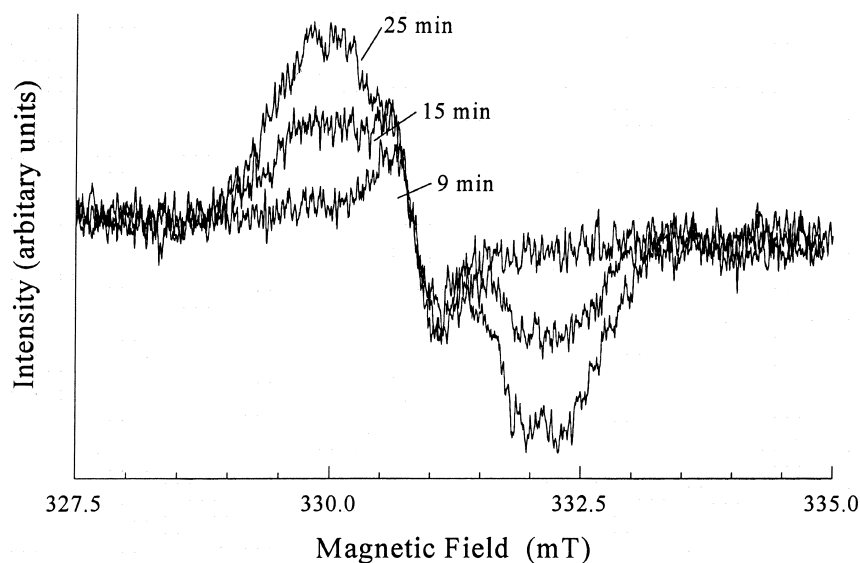

Figure 3 E.s.r. spectra at various times for MDP-BMI cured in situ at 220°C

spins per cm. The *g*-value is a parameter analogous to the chemical shift of an n.m.r. line and is used as an aid to characterize different radicals[8].

RESULTS AND DISCUSSION

The e.s.r. spectra observed from MDP-BMI samples change greatly during the course of the polymerization. In *Figure 3*, e.s.r. spectra collected during the first 30 min of cure at 220°C are overlayed. Initially, only a small singlet peak centred at $g = 2.0028$ is observed with what is possibly some extra fine structure in the wings. As the polymerization proceeds, the radical concentration starts to increase rapidly with a broader radical signal observed.

E.s.r. spectroscopy will give the concentration of radicals in the thermoset during cure. *Figure 4* is a plot of the total radical concentration during cure at different temperatures for pure samples of MDP-BMI. The general trend is for the radical concentration to increase slowly at first, then the rate of radical formation accelerates, until at longer cure times the rate of formation decreases again and the concentration of radicals appears to approach a limiting value. The time prior to the rapid rise in radical concentration decreases with increasing temperature.

From *Figure 3* we could note a large change in the e.s.r. spectra during cure. The change in the lineshape of the e.s.r. spectrum over the cure demonstrates that there are at least two radical species present. An e.s.r. spectrum from MDP-BMI at 230°C is plotted as *Figure 5*. This spectrum was obtained after polymerization has effectively ceased, due to gelation and vitrification of the resin. Here the spectrum appears to consist of a broad doublet with some extra, unresolved peaks (marked by the arrows). The spectrum was reproducible from run to run and was independent of the orientation of the sample in the magnetic field, indicating that the unresolved peaks were not due to anisotropic effects arising from vitrification of the resin. The broad doublet most likely arises from a relatively stable radical on the polymer chain that builds up in concentration once the polymerization has reached a certain extent of reaction. This feature has been previously assigned to a radical of diphenylmethylene type[1] (*Figure 1b*). This radical species is formed by hydrogen abstraction by the propagating radical and is relatively stable inside the polymer network, which accounts for it only appearing at longer cure times (higher conversion).

A different bismaleimide, 1,1′-(methylenedi-2,6-diethyl-4,1-phenylene) bismaleimide (MDEP-BMI) exhibited very
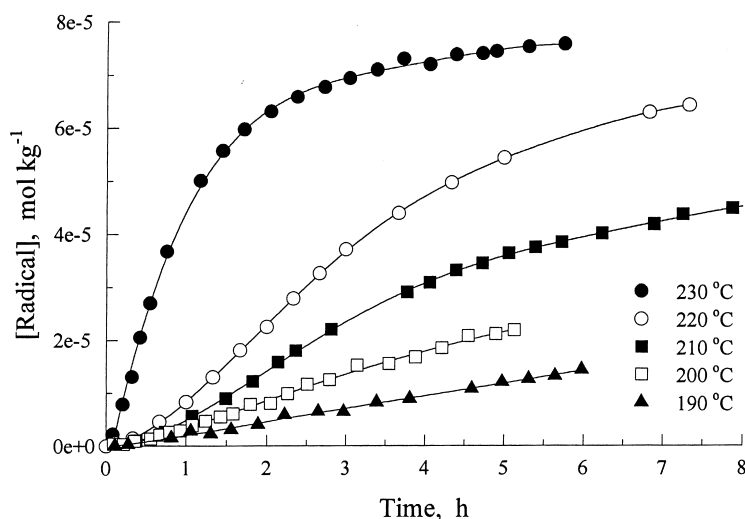
Figure 4 Total radical concentration as a function of cure temperature for MDP-BMI
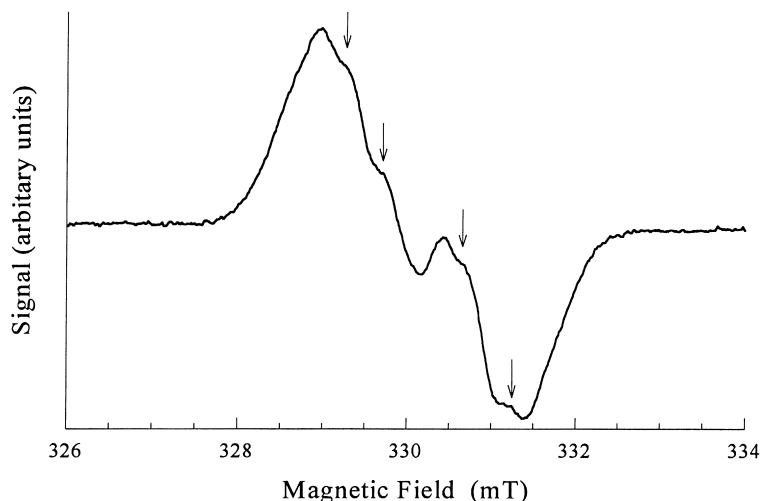
Figure 5 E.s.r. spectrum of MDP-BMI after curing in vacuum at 230°C for 5.5 h. Additional fine structure is indicated by the arrows

different behaviour when measured in situ at similar temperatures. The radical concentration slowly increased, then decreased slightly at long times, but was at all times very low compared with MDP-BMI. The e.s.r. spectra observed throughout the cure appeared as a single line centred at $g = 2.0029$ (see *Figure 6*) without the broad doublet observed in MDP-BMI samples. The lack of diphenylmethylene radicals in MDEP-BMI is presumably due to the presence of the ethyl groups. It is possible that steric hindrance prevents formation of the diphenylmethylene radical, or else, that any such radicals formed are quickly scavenged by H-abstraction from the mobile aliphatic side-groups and terminated by the main combination or disproportionation pathway.

N-phenylmaleimide homopolymerized only to a small extent at 200°C in the absence of added initiator. The e.s.r. spectrum for *N*-phenylmaleimide does, however, show a small radical signal very similar to that observed for MDEP-BMI.

Simulation of e.s.r. spectra

From a qualitative analysis of the e.s.r. signal during thermal homopolymerization of MDP-BMI, there appear to be at least two, and possibly three, radical species present in the system. These are the propagating radical, a diphenylmethylene radical on the polymer backbone and possibly also a radical from thermal degradation of the polymer, which was observed to increase over long cure times[1].

It should be possible to simulate the observed e.s.r. spectra by assigning appropriate parameters to the radicals. A computer program, SIMOPR, developed at the University of Queensland[9] was used to collect, manipulate and simulate isotropic e.s.r. spectra.

Brown and Sandreczki[1] assigned the diphenylmethylene radical to a ten-line spectrum by coupling of the radical both to the methylene proton with a hyperfine splitting (h.f.s.) of 1.43 ± 0.04 mT, and to the ortho-ring protons, with a h.f.s. of 0.39 ± 0.03 mT. These parameters seem to be reasonable, but it could not be determined whether there is actually a pair of quintets present in the spectrum as the linewidth is greater than the splitting involved. A simple doublet, or even a pair of triplets, could be expected for the diphenylmethylene radical, depending on the actual conformation of the radical and whether there is a through-space interaction with the aromatic protons. As the linewidth (ΔH_{pp}) is larger than the hyperfine splitting, this radical will appear as a doublet regardless. However, a simulation of the spectrum using the above parameters gave an e.s.r. signal significantly wider than that actually observed, necessitating that the correct parameters be determined for the spectra.

During most of the polymerization of MDP-BMI, the concentration of propagating radicals is expected to be relatively constant. As the concentration of the diphenylmethylene radical is increasing in the same region, spectral subtraction should isolate the lineshape due to that radical
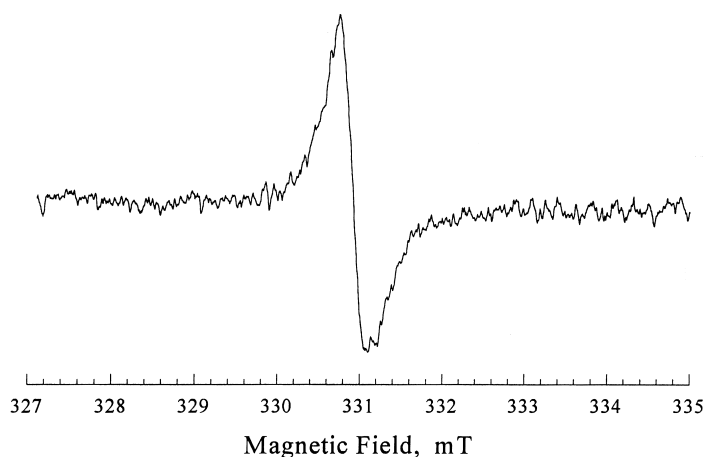
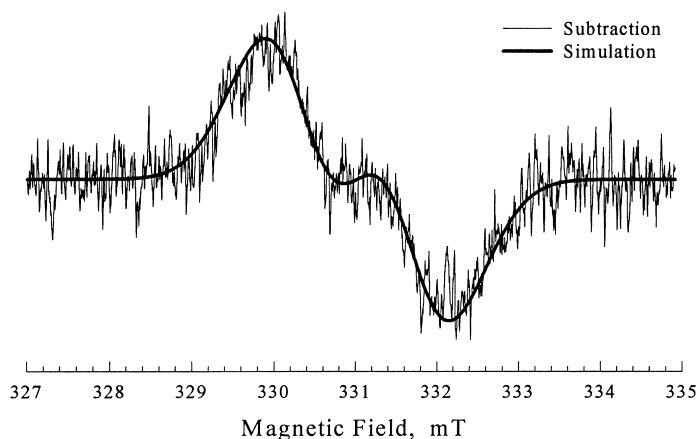**Figure 6** E.s.r. spectrum of MDEP-BMI after 2 h at 200°C

Figure 7 Subtraction e.s.r. spectrum for MDP-BMI at 220°C showing the lineshape of the diphenylmethylene radical. The simulation used a h.f.s. of 1.2 mT (a-H) and ΔH_{pp} of 1.15 mT

alone. A representative subtraction spectrum is presented in *Figure 7* from between 40 and 60 min cure of MDP-BMI at 220°C. This e.s.r. lineshape is characteristic of a doublet where the linewidth is of similar magnitude to the hyperfine splitting. Simulation of this radical lineshape suggested that the observed signal can be sensibly simulated by a doublet where ΔH_{pp} is 1.2 ± 0.1 mT and the h.f.s. is 1.2 ± 0.1 mT.

E.s.r. spectra for the propagating radical of *N*-octadecyl-maleimide in benzene with 2,2′-azoisobutyronitrile (AIBN) as the initiator have been reported by Sato[3]. Brown and Sandreczki[1] also acquired similar spectra from a different bismaleimide, 6-maleimido-1-(4′-maleimidophenyl)-1,3,3-trimethylindane, in the presence of benzoyl peroxide (BPO). In both cases a three-line spectrum was observed that was assigned to the propagating radical. A four-line spectrum— a doublet of doublets—is expected from coupling with the two non-equivalent protons. The explanation for a three-line rather than a four-line spectrum involves overlap of the inner peaks. However, a different spectrum was reported in the literature for NPM with BPO initiator[1]. Therefore, in order to determine whether the literature assignments of the propagating radical were correct, computer simulations were performed, as well as e.s.r. experiments on the different monomers with and without free-radical initiators.

Propagating radicals in vinyl polymerization usually have hyperfine splitting parameters of around 2.0 and 3.4 mT for the α and β hydrogens irrespective of the nature of the R-group[10]. Brown and Sandreczki[1] used parameters of 3.2 and 2.7 mT to simulate the three-line spectrum. However, the observed spectral width for the maleimides is only about 5.0 mT, which means that the hyperfine splitting must be significantly less than is usual in vinyl radicals. This narrowing of the hyperfine splitting is quite reasonable due to electron delocalization into the imide ring.

An experiment was performed with *N*-phenylmaleimide using free-radical initiators. Dicumyl peroxide was used as the initiator in order to carry out the polymerization at a temperature well above the melting point of the monomer. The half-life, $t_{1/2}$ for dicumyl peroxide is 125 min at 120°C[11]. The e.s.r. spectrum obtained after 1 h at 120°C is given in *Figure 8*. This spectrum appears to be similar to those shown in the work by Sato[3] for solution polymerization of *N*-octadecylmaleimide with AIBN, but it is different to the spectrum obtained from NPM polymerized with BPO at 90°C[1]. There are minor, additional lines in the wings of the e.s.r. spectra for NPM polymerized with dicumyl peroxide. These were also observed in NPM polymerized with BPO and are therefore assigned to secondary initiator radicals.

The presence of the three-line e.s.r. signal from the propagating radical could not be discerned directly from thermally polymerized MDP-BMI because of the low signal-to-noise ratio and the strong overlapping signal due to diphenylmethylene radicals. In NPM no diphenylmethylene radical is possible, neither was this radical observed in MDEP-BMI. Instead, the e.s.r. spectra for thermally
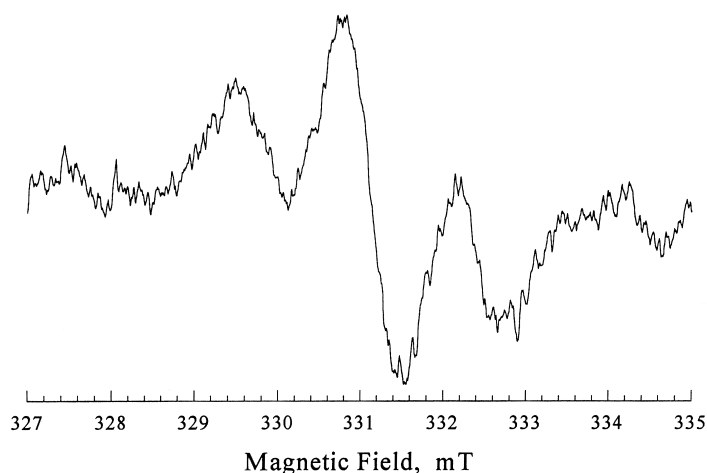

Figure 8 E.s.r. signal for NPM with 10% dicumyl peroxide after 1 h at 120°C
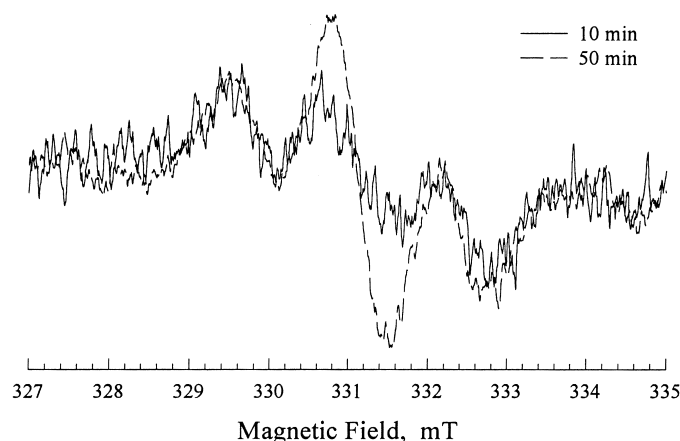

Figure 9 E.s.r. spectra of NPM with 10% dicumyl peroxide. Spectra shown are those after 10 and 50 min reaction at 120°C

homopolymerized MDEP-BMI appeared as in *Figure 6*. This spectrum is quite unlike the spectrum observed for NPM with dicumyl peroxide, with only a single line observed instead of three lines, but with approximately the same apparent *g* value.

The spectrum for MDEP-BMI without free-radical initiator is also similar to that initially observed during cure in MDP-BMI before the diphenylmethylene radicals appear and is identical to that observed in NPM without added free-radical initiators. This raises the question of whether the three-line spectrum is actually due to the propagating radical. Indeed, closer analysis of the *N*-phenylmaleimide spectra when polymerized with free-radical initiator indicated that, contrary to the previously published studies, this three-line spectrum arises from two other radicals. Proof of this is given in *Figure 9*, as over time, the ratio of the intensity of the inner line compared

with the outer line changes. This change in relative intensity can only be explained by a change in the relative concentration of two different radicals.

Spectral subtraction of the e.s.r. spectra for NPM between 10 and 50 min of cure gave the spectrum in *Figure 10*. Again, this component has the same spectral width and *g*-value as the spectra observed in both NPM and MDEP-BMI without free-radical initiators, which strongly suggests that it is associated with the propagating radical.

The outer two lines in *Figure 9* only occur in maleimide systems polymerized using free-radical initiators, therefore they must be due to either primary or secondary initiator radicals. It is proposed that this doublet arises from vinyl radicals formed by hydrogen abstraction by initiator radicals from the maleimide double bond. The pathway for this is indicated in *Figure 11* and has been previously proposed to occur in maleimide systems[1,5].
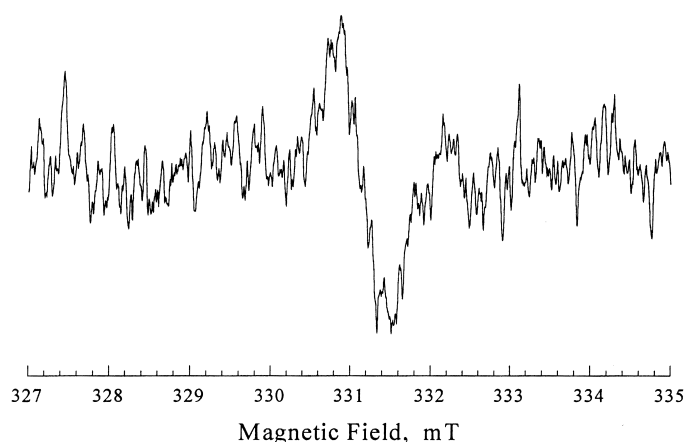

Figure 10 Subtraction of the initial spectrum of NPM cured with dicumyl peroxide from the spectrum after 50 min reaction at 120°C
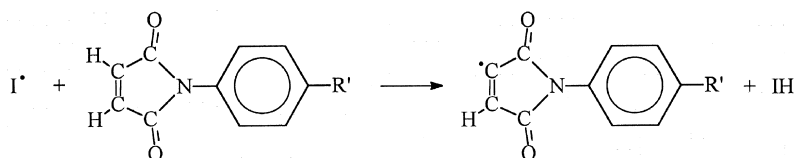

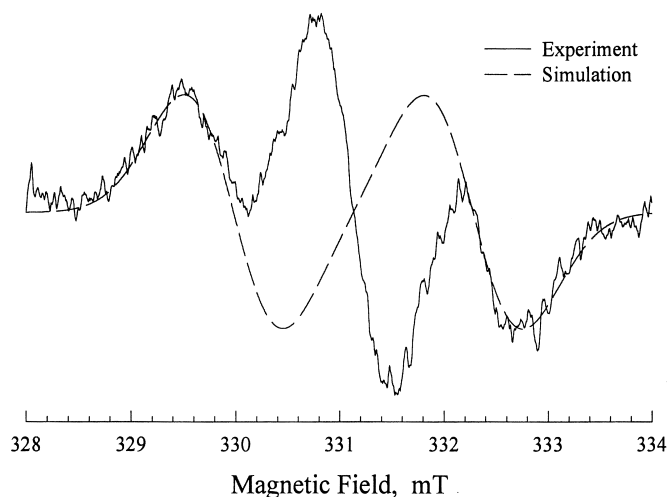**Figure 11** Formation of the vinyl radical from initiator radical and maleimide

Figure 12 E.s.r. signal for NPM reacted with dicumyl peroxide and a simulation of the e.s.r. signal for the vinyl radical component
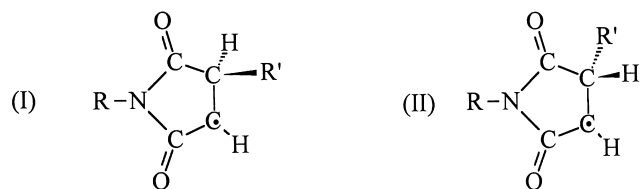
Figure 13 Structure of the maleimide propagating radical, showing two possible conformations, where R′ indicates the polymer chain
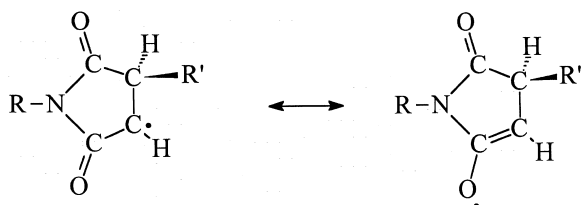

Figure 14 Possible resonance structures of the maleimide propagating radical

Although vinyl radicals are not usually observed in other vinyl polymerizations, it can be argued that this is reasonable in the maleimides. The electron-deficient nature of the maleimide double bond might be expected to increase the susceptibility of the vinyl bond to hydrogen abstraction compared with normal vinyl bonds. Peroxide initiators are known to readily undergo hydrogen abstraction reactions[12]. These vinyl radicals, if present, would be expected to have h.f.s. of about 2.6 mT[13]. The outer pair of lines in the three-line spectrum in the presence of free-radical initiator can be simulated with a h.f.s. of 2.3 mT and ΔH_{pp} of 0.95 mT (*Figure 12*).

From *Figure 13* it is apparent that the β-carbon is sp^3 hybridized, while the α-carbon is sp^2 hybridized. Therefore, there are two possible conformations resulting from addition of the polymer radical to the monomer. These conformations are not readily interchangeable as a result of the rigid imide and aromatic side group. When the end group is in conformation (I), there is no interaction between the free radical, which is in an orbital perpendicular to the plane of the maleimide ring, and the β-proton. Conformation (II) allows interaction between the unpaired electron and the β-proton; however, this conformation may be much less favourable due to steric hindrance.

Interaction with the α-proton would still be expected to occur in either conformation. However, it is possible that there is an additional factor that may be responsible for the extremely small hyperfine splitting parameters. That is why there may be expected to be a large degree of delocalization of the free-radical onto the carbonyl of the maleimide ring. Large electron delocalization has been observed previously in maleic anhydride radicals[14] and so this is expected to occur also in maleimide radicals. *Figure 14* represents the alternative structures of the propagating radical that may exist through electron delocalization. One possibility is that there is a release of ring strain associated with delocalization in these maleimide radicals which may act as a driving force for the delocalization.

Contrary to the assignments in previously published work[3,4], the e.s.r. signal for the maleimide propagating radical has therefore been assigned to this single line spectrum.

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