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# Hydrogen Atom Bombardment of Monomers and Polymers: Maleimides, Bismaleimides, and Succinimide

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ABSTRACT: Electron spin resonance experiments are described which involve the bombardment of succinimide, substituted maleimides, and a substituted bismaleimide with hydrogen and deuterium atoms. Several different types of maleimide radicals, viz., the initial radical, the propagating radical, the penultimate radical, the backbone radical, and the vinyl radical, have been observed during and after termination of the microwave discharge used to generate the bombarding atomic species. These radicals have been identified by way of the hyperfine structure in their spectra observed under the appropriate experimental conditions. In some cases the spectral line widths decreased with time after the microwave discharge was terminated because radical concentrations close to the crystallite surfaces were reduced by hydrogen atom spatial diffusion and/or radical decomposition. In the hydrogen atom bombardment of aliphatic maleimides and bismaleimides, the radical reactions occurred exclusively at the maleimide double bond, whereas in aromatic maleimides and bismaleimides several types of cyclohexadienyl radicals were formed in addition to the maleimide radicals.

## Introduction

There have been several previous studies[1–8] of the free radicals generated by the bombardment of organic materials with hydrogen atoms. These studies include the bombardment of both low molecular weight solids[1–6] and polymeric solids.[7,8]

The experiments described here, involving the hydrogen/deuterium atom bombardment of monomers and polymers, were undertaken to better understand the free-radical cross-linking mechanisms in maleimide and bismaleimide polymers. We are using electron spin resonance (ESR) techniques to identify the free-radical intermediates involved in these cross-linking reactions and, in so doing, to verify our spectral assignments for the radicals that we have observed previously[9] in the hot-melt homopolymerizations of maleimides and bismaleimides. Also, the results described here will be compared and contrasted with our already reported[10] observations in the hydrogen atom bombardment of *N*-methylmaleimide.

The monomers included in this study were succinimide, maleimide, maleimide-2,3-$d_2$, 4,4′-bismaleimidodiphenylmethane (BDM), *N*-phenyl-2-bromomaleimide, 1,2-bismaleimidoethane (BMIE), and 1,2-bismaleimidohexane (BMIH). The structures of these monomers are shown in Figure 1. The polymers investigated were the thermal polymerization products of maleimide and maleimide-2,3-$d_2$.

## Experimental Section

The experimental arrangement for our ESR studies of polymers that have been bombarded with hydrogen atoms has been described previously.[10] The hydrogen atoms are generated in a microwave (2.5 GHz) cavity discharge, flow down a quartz tube, and are incident on the polymer sample located in the ESR cavity (9.5 GHz). A Woods horn is included to trap the UV and visible radiation emitted from the microwave discharge and to minimize the exposure of the sample to this radiation. One of the advantages of this experimental arrangement is that the radicals can be monitored by ESR, both with the discharge on and at various times following termination of the discharge, without exposing the samples to air. All ESR measurements were made at room temperature by using an X-band spectrometer (Bruker ER300) interfaced to a computer (Bruker 1600). The spectra could be added, subtracted, and scaled by using the available software. In the computer program[10,11] for the simulation of the ESR spectra, both anisotropic and isotropic coupling constants could be handled, and a Gaussian intrinsic line shape along with an intrinsic line-width parameter that was the same for all component lines was assumed.

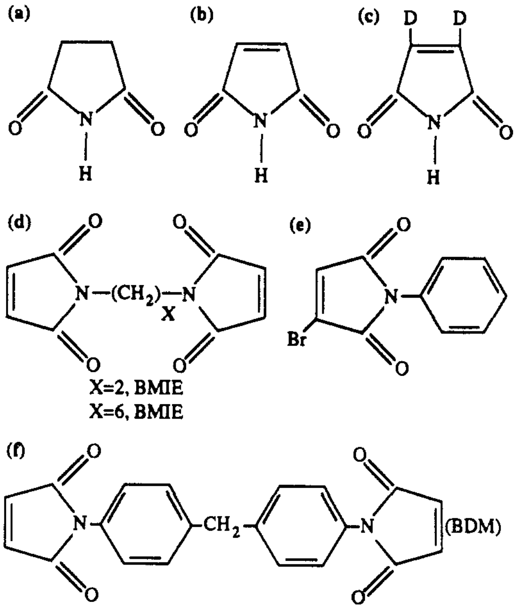

**Figure 1.** Monomers studied: (a) succinimide, (b) maleimide, (c) maleimide-2,3-$d_2$, (d) 1,6-bismaleimidoethane ($x = 2$); 1,6-bismaleimidohexane ($x = 6$), (e) *N*-phenyl-2-bromomaleimide, and (f) 4,4′-bismaleimidodiphenylmethane.

The maleimide-2,3-$d_2$ (95.5 atom % D) was obtained from Merck and Co., Montreal, Quebec. The 1,6-bismaleimidohexane and *N*-phenyl-2-bromomaleimide were purchased from ICN Biomedicals, Cambridge, MA. Maleic anhydride was obtained from Eastman Kodak Co., Rochester, NY. The other maleimides, 4,4′-bismaleimidodiphenylmethane, succinimide, and amines were obtained from Aldrich Chemical Co., Milwaukee, WI. All commercial monomers were better than 98% pure and were used without further purification.

Bismaleimidoethane (BMIE) was prepared by following the procedure of White et al.[12] Thus, maleic anhydride and distilled ethylenediamine were reacted in dry chloroform to obtain a suspension of the bisamic acid, which was filtered, rinsed and dried, and then imidized by refluxing in an acetone suspension containing nickel acetate, triethylamine, and acetic anhydride. Concentration of the decantate resulted in a brown precipitate, which was recrystallized from a 1:1 methanol–chloroform solution treated with decolorizing carbon to yield a white product.

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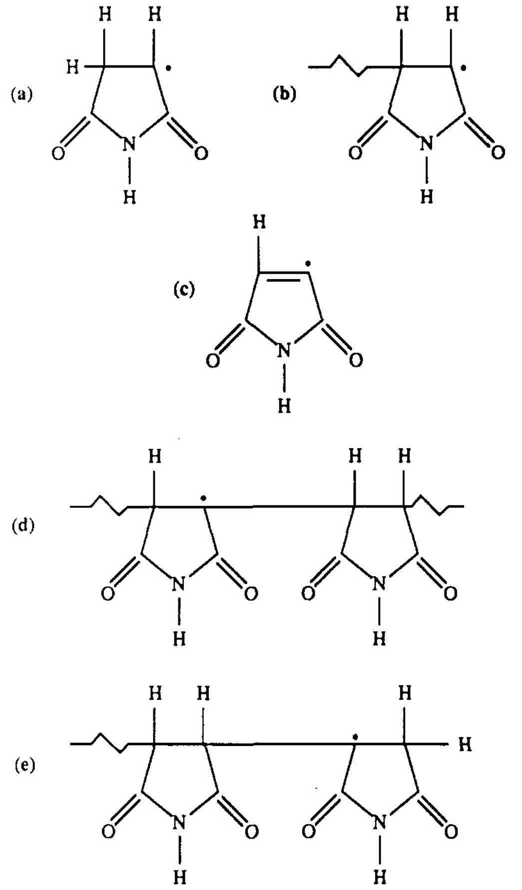

**Figure 2.** Radicals observed: (a) the initial radical, (b) the propagating radical, (c) the vinyl radical, (d) the backbone radical, and (e) the penultimate radical.

Polymerized maleimide and maleimide-*2,3*-$d_2$ samples were prepared by heating the respective sublimed monomer in a closed container to prevent evaporation. The maleimide was polymerized in the presence of air at 180 °C for 3 days followed by heating at 230 °C for 5 days. A single-line ESR spectrum observed from this sample prior to hydrogen atom bombardment was easily subtracted from the spectra obtained after bombardment. The deuterated maleimide was polymerized in vacuo at 180 °C for 16 h and then heated at 230 °C for 45 min.

## Results and Discussion

A succinimide sample was bombarded with hydrogen atoms to determine the hyperfine pattern of the spectrum of the initial radical, whose structure is shown in Figure 2. This radical is formed as a result of the hydrogen atom abstraction reaction indicated in Figure 3a. We have previously reported[10] the generation of a substituted version of this radical as a result of the reaction involving the hydrogen atom addition to the double bond of *N*-methylmaleimide after bombardment with hydrogen atoms. The initial radical was positively identified from its ESR spectrum, shown in Figure 4a, which consists of six main lines. Computer simulations of this spectrum indicate that the best fit shown in Figure 4b is obtained with the following spin Hamiltonian parameters: an isotropic coupling constant $A_0$ = 2.9 mT for the two $\beta$ protons; a nonaxially symmetric hyperfine tensor with $A_{xx}$ = 3.7 mT, $A_{yy}$ = 2.0 mT, and $A_{zz}$ = 0.7 mT for one $\alpha$ proton, $g_{xx}$ = 2.0045, $g_{yy}$ = 2.0023 and $g_{zz}$ = 2.0036, and a line-width parameter $W$ = 0.35 mT. These values are in agreement with those already reported[13,14] for the radicals formed after X-ray irradiations of single crystals of succinimide.

After prolonged (30 min) deuterium atom bombardment of the succinimide monomer, spectra such as that shown in Figure 5a were observed. This spectrum is similar to that shown in Figure 4a, which was obtained after hydrogen atom bombardment of succinimide. Only small differences at the center of each spectrum are noted. An appropriately scaled version of Figure 4a subtracted from Figure 5a yielded the three-line spectrum shown in Figure 5b. This spectrum is attributed to the deuterated radicals shown in Figure 3c. We believe that small amounts of these deuterated radicals are formed in the three steps depicted in parts a–c of Figure 3; these steps involve (1) hydrogen atom abstraction from a succinimide monomer, (2) deuterium atom addition to this radical, and (3) a further hydrogen atom abstraction from this deuterated monomer.

One notable feature in the spectra for the initial radical shown in Figure 6 is that the intrinsic line width decreases with time after the discharge is switched off. The initial widths are the result of spin–spin interactions with neighboring radicals because of high radical concentrations on and close to the surface of the succinimide monomer crystallites. After the discharge is switched off, these widths decrease because of decreases in the surface radical concentrations, which are brought about partly through hydrogen atom spatial diffusion in the form of the reactions shown in Figure 3d and partly through radical decomposition. This effect, involving reductions in the intrinsic line width with time following exposure to the hydrogen atom beam, has been observed and discussed previously.[4]

The main ESR spectrum exhibited by a powdered sample of maleimide, which has been bombarded with a beam of hydrogen atoms, is attributed to the propagating radical. Computer simulations of this radical, reported previously,[9] are similar to the three-line spectrum shown in Figure 7a, which was observed after a 5-min exposure of the maleimide sample to the hydrogen atom beam. Low-intensity lines, designated (S) in Figure 7a and having a magnetic field splitting between them of 9.5 mT, were also observed. As we will show below, the presence of these satellite lines can be interpreted in two ways.

The three-line spectrum shown in Figure 7a remains unchanged for times as long as 15 h after the discharge is terminated. Thus, there is no positive indication that the trapped propagating radical is being converted to another type of radical during or after the hydrogen atom bombardment of the maleimide monomer. This conclusion is in marked contrast to the behavior observed in a similar experiment with *N*-methylmaleimide monomer where a predominantly two-line spectrum, associated with either the backbone radical, and/or the vinyl radical developed following the appearance of the propagating radical. The only explanation we can offer for this lack of appearance of the two-line spectrum is that the atomic arrangement in the maleimide crystals is not conducive to the hydrogen atom abstraction reactions, shown in Figure 8c,d, which are necessary for the formation of the backbone and vinyl radical, respectively.

The five-line spectrum shown in Figure 7b was observed after deuterium atom bombardment of maleimide monomer. We can simulate this line shape by the superposition of the three-line spectrum from the propagating radical (i.e., Figure 7a) and a two-line spectrum associated with a deuterated radical. In addition, the 9.5-mT lines (the S lines in Figure 7a) observed in the hydrogen bombardment of maleimide are absent in the deuterium bombardment of maleimide (Figure 7b).

Any interpretation of the spectra in Figure 7a must also be consistent with that of Figure 7b. We can explain the features in these spectra in either of the following two ways. The three lines in Figure 7a are assigned to the propagating

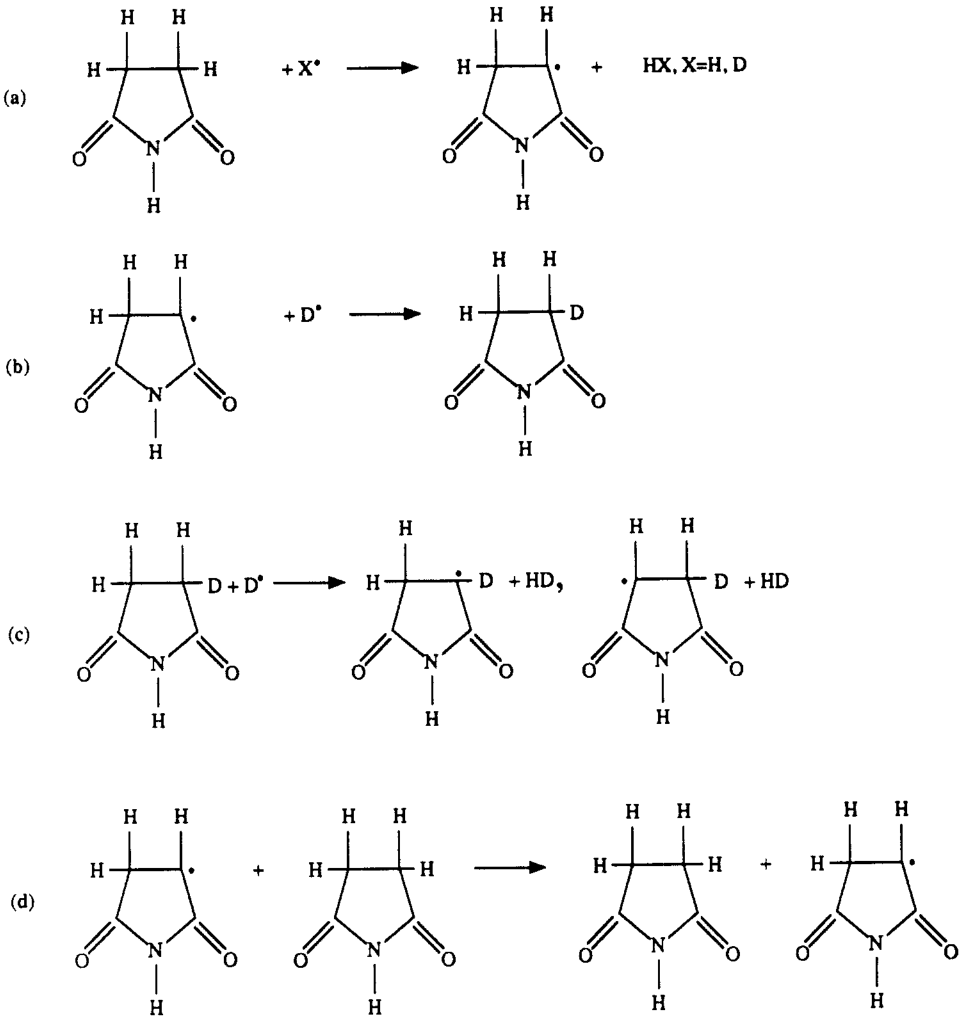

Figure 3. Reactions identified as occurring during and after the hydrogen-deuterium bombardment of succinimide.

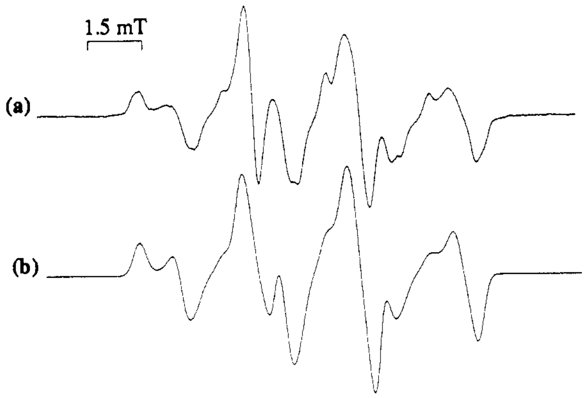

**Figure 4.** (a) Spectrum observed after the hydrogen atom bombardment of succinimide. The discharge was on 3 min and off 240 min. (b) Computer simulation of the spectrum for the initial radical. The spin Hamiltonian parameters used were $g_{xx} = 2.0045$, $g_{yy} = 2.0023$, and $g_{zz} = 2.0036$, $A_0 = 2.9$ mT for two $\beta$ protons and $A_{xx} = 3.7$ mT, $A_{yy} = 2.0$ mT, and $A_{zz} = 0.7$ mT for one $\alpha$ proton, the line-width parameter $W = 0.35$ mT.

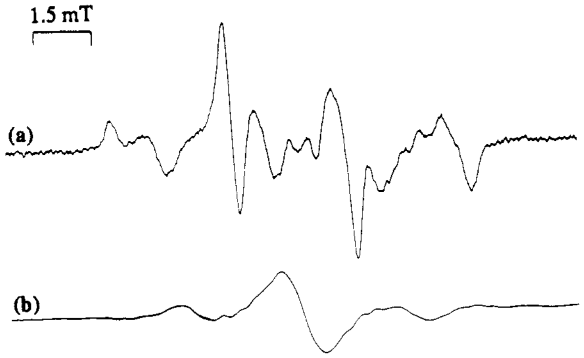

**Figure 5.** (a) Spectrum observed after the bombardment of succinimide with deuterium atoms. The discharge was on 30 min and off 30 min. (b) Difference spectrum obtained by subtracting the spectrum in Figure 4a from that in Figure 5a.

radical, and the S lines are the two outer lines belonging to the spectrum for trapped initial radical. The rest of the spectrum from the initial radical is not observed because of the overlap with the much more intense lines of the propagating radical. In the deuterium atom bombardment, the propagating radical, exhibiting a three-line spectrum, will still be present. However, deuterated propagating radicals, whose structures are similar to those shown in Figure 3c, will also be formed as a result of hydrogen-deuterium exchange and will produce the extra two lines in Figure 7b. The two outer lines (separated by 9.5 mT) of the initial radical will not be present because the deuterated initial radical has hyperfine components from only two protons.

Alternatively, the S lines in Figure 7a can be assigned to the penultimate radical shown in Figure 2e. The unpaired electron will be coupled to three $\beta$ protons, and if they are equivalent, with an isotropic coupling constant $A_0 = 3.15$ mT, then the spectrum will consist of four lines with two outer lines having a 9.5-mT separation. It is likely, however, that because of a distribution of different main-chain conformations, the observed spectrum will consist of these four lines superimposed on three lines (i.e., two interacting protons), which are indistinguishable from

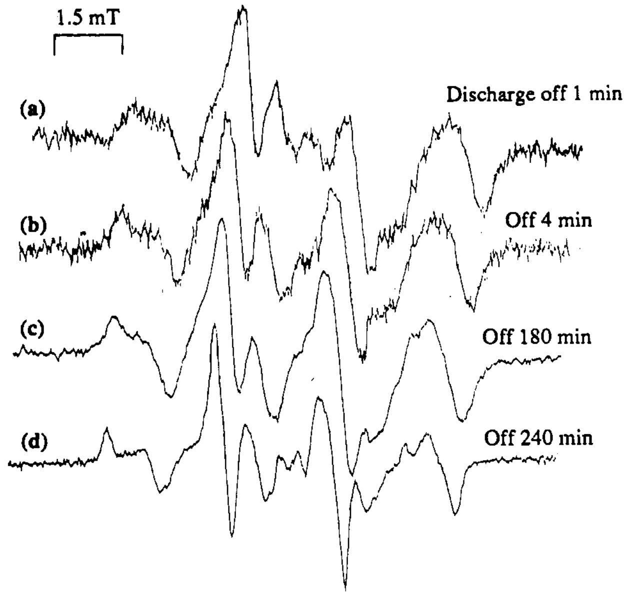

**Figure 6.** Series of spectra observed in the bombardment of succinimide with hydrogen atoms when the discharge has been off (a) 1 min, (b) 4 min, (c) 180 min, and (d) 240 min.

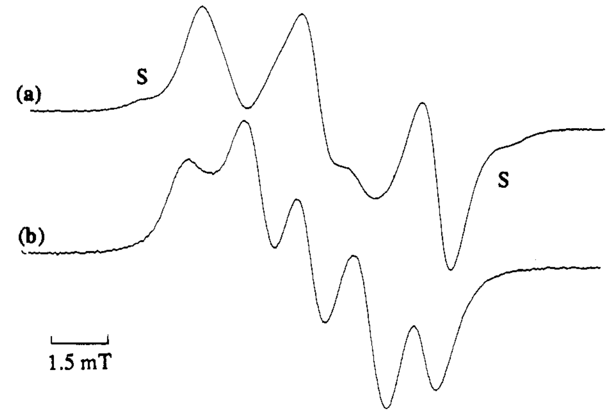

**Figure 7.** (a) Spectrum observed after the bombardment of maleimide with hydrogen atoms. The discharge was on 5 min and off 190 min. (b) Spectrum observed after the bombardment of maleimide with deuterium atoms. The discharge was on 5 min and off 150 min.

the three lines of the propagating radical. A fuller discussion of the spectra that can be expected from distributions in main-chain conformations has been given previously.[10] In the case of a deuterated penultimate radical, the superposition of the spectra from a distribution of main-chain conformations can result in five lines (three lines + two lines), three of which overlap with the propagating radical spectrum. In fact, a weighted sum of the computer-simulated spectra for all conformations of the deuterated penultimate radical has a line shape similar to the observed one shown in Figure 7b.

The relatively low concentration of initial radical observed after hydrogen atom bombardment of the maleimide monomer is undoubtedly due to its rapid conversion to the propagating radical by way of reaction (b) in Figure 8. This reaction is fast because the monomer concentration is high. Therefore, to stabilize the initial radical, we thermally polymerized samples of maleimide, thereby reducing the concentration of residual monomer and the rate of chain propagation. The spectrum observed after a 150-min hydrogen atom bombardment of a powdered sample of this polymerized maleimide is shown in Figure 9a. It can be concluded that the peaks marked I belong to the initial radical since they can be identified with lines in the spectrum for the initial radical generated in the hydrogen bombardment of succinimide (shown in Figure 4a), thermally polymerized *N*-methylmaleimide,[10] and also photolytically polymerized *N*-methylmaleimide.[10]

A sample of the powdered, thermally polymerized maleimide was heated at 200 °C under vacuum for 33 h to further reduce the amount of residual unreacted monomer. The spectrum shown in Figure 9b, which was observed after prolonged hydrogen atom bombardment of this sample, consists of the superposition of the initial radical spectrum and another multiline spectrum. The difference spectrum that was obtained by computer subtraction of the spectrum shown in Figure 9a from that in Figure 9b, resulted in the five-line spectrum shown in Figure 9c. We assign this five-line spectrum to a backbone radical of the type shown in Figure 2d. As we have discussed previously,[10] the five lines are a superposition of a two-line spectrum and a three-line spectrum, which correspond to the two extreme conformations that these backbone radicals can adopt.

We have verified the assignment of the three-line spectrum in Figure 7a to the propagating radical in our investigations of the deuterated monomer, maleimide-*2,3*-$d_2$. The spectrum shown in Figure 10a was observed from a sample that had been bombarded with deuterium atoms for 2 h and then exposed to air for 24 h. A computer simulation of the spectrum for the deuterated propagating radical shown in Figure 10b was calculated by using the following spin Hamiltonian parameters: $g_{xx}$ = 2.0045, $g_{yy}$ = 2.0023, and $g_{zz}$ = 2.0036, and isotropic hyperfine coupling constant $A_0$ = 0.44 mT for one $\beta$ deuteron, and a nonaxially symmetric hyperfine tensor with the principal values $A_{xx}$ = 0.56 mT, $A_{yy}$ = 0.31 mT, and $A_{zz}$ = 0.10 mT for one $\alpha$ deuteron. These principal values of the **g**-tensor were the same as those used above for the initial radical, i.e., to simulate the spectrum shown in Figure 4b. The hyperfine coupling constants were obtained by taking the values for the $\alpha$ and $\beta$ protons of the initial radical and scaling them down by a factor of 6.5, the ratio of the gyromagnetic ratios for the proton and the deuteron. As can be seen in Figure 10, there is excellent agreement with the experimental spectrum, which verifies that it can be assigned to the propagating radical. The additional lines denoted by H in Figure 10a can be assigned to propagating radicals in which the terminal monomer unit contains one proton and one deuteron since their relative intensities are consistent with the isotopic purity of the as-received maleimide-*2,3*-$d_2$ (95.5 atom %). The stabilities of both the deuterated and protonated propagating radicals to atmospheric oxygen suggest that they are trapped several layers deep within the crystals.[15]

The spectrum shown in Figure 11 was observed after bombardment of the deuterated maleimide monomer with hydrogen atoms. There are four lines (the Q and R lines) in addition to the partially resolved deuterated propagating radical. The Q lines are significantly more intense than the H lines in Figure 10a, which were observed after deuterium atom bombardment and air exposure. This increased intensity would indicate that the Q lines can be assigned to a protonated radical species where the protons have come from the hydrogen atom beam. Such a radical would be the initial radical containing one proton (a two-line spectrum), which is formed as the result of a hydrogen addition to the deuterated monomer. This initial radical is in some way trapped within the crystal and prevented from undergoing chain propagation. The R lines are attributed to the initial radical, which originates from the protonated monomer impurity. Thus, this radical contains two protons and should show three hyperfine lines with

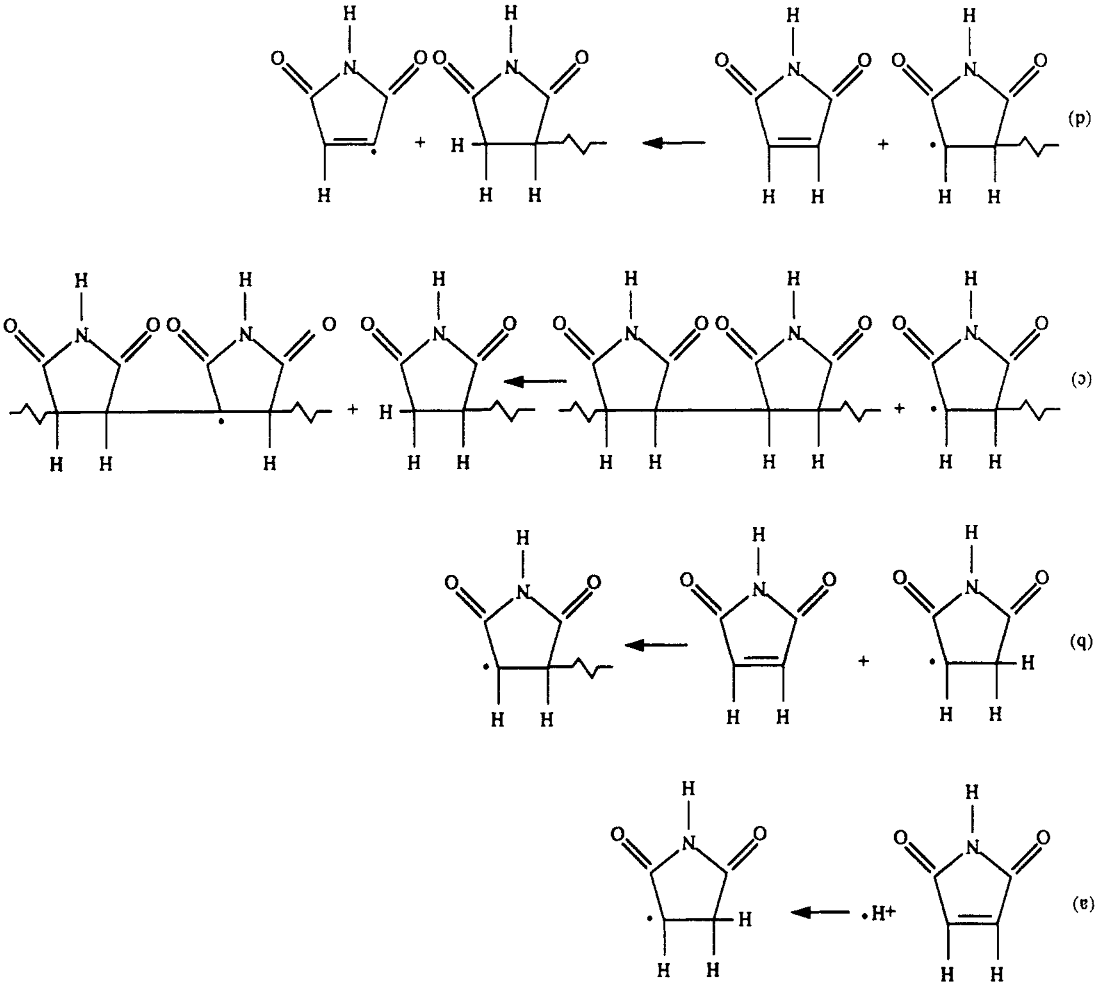

**Figure 8.** Reactions identified as occurring during and after the bombardment of maleimide monomer and/or polymer with hydrogen atoms.

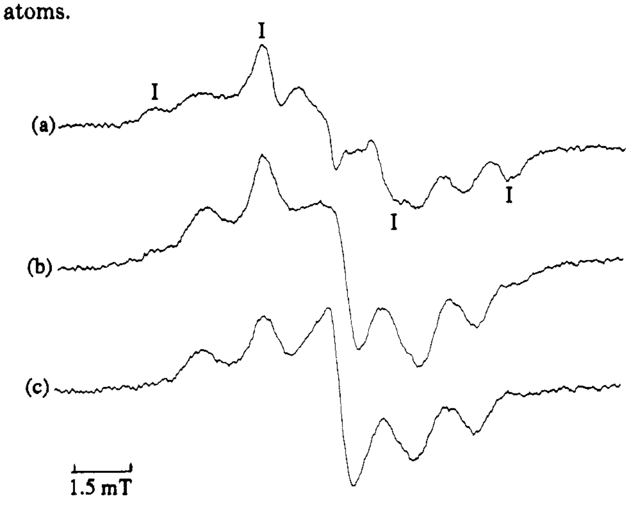

**Figure 9.** Spectra observed during the bombardment of thermally polymerized maleimide with hydrogen atoms (a) after the discharge had been on 150 min, (b) after the sample had an additional 33 h baking at 200 °C in vacuo and the discharge had been on 140 min, and (c) the difference spectrum resulting from (b) − (a).

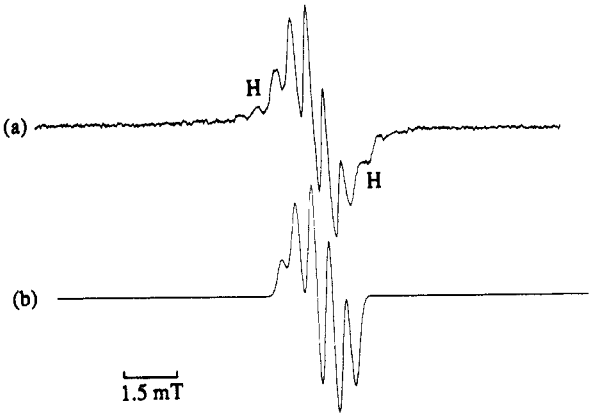

**Figure 10.** (a) Spectrum observed after the bombardment of maleimide-2,3-$d_2$ monomer by deuterium atoms. The sample had been bombarded for 2 h and then exposed to air for 24 h. (b) Computer simulation of the propagating radical for maleimide-2,3-$d_2$.

an overall splitting of approximately 6.0 mT, which is consistent with the splitting between the S lines in Figure 11 (6.3 mT).

A sample of thermally polymerized maleimide-2,3-$d_2$ that had been heated at 200 °C for 15 h in a vacuum oven was also studied. The spectra shown in Figure 12 were observed from this sample during a 9-min bombardment with hydrogen atoms. The intensities of the peaks designated Q in Figure 12a are larger than those of the corresponding Q peaks in Figure 11 (by a factor 3). This result can be expected since much, but not all, of the deuterated monomer has been removed from the thermally polymerized sample so that the chain propagation rate should be substantially reduced. As is shown in Figure 12b,c, at long times following bombardment, the Q peaks decrease with time following termination of the bombardment, indicating that the initial radical is reactive and converts to a more stable species, e.g., the backbone radical.

As the spectra in Figure 13 indicate, a series of radicals

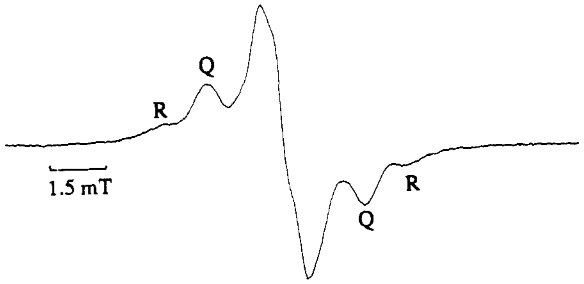

**Figure 11.** Spectrum observed after the bombardment of maleimide-2,3-$d_2$ monomer with hydrogen atoms. The discharge had been on 46 s and off 42 h.

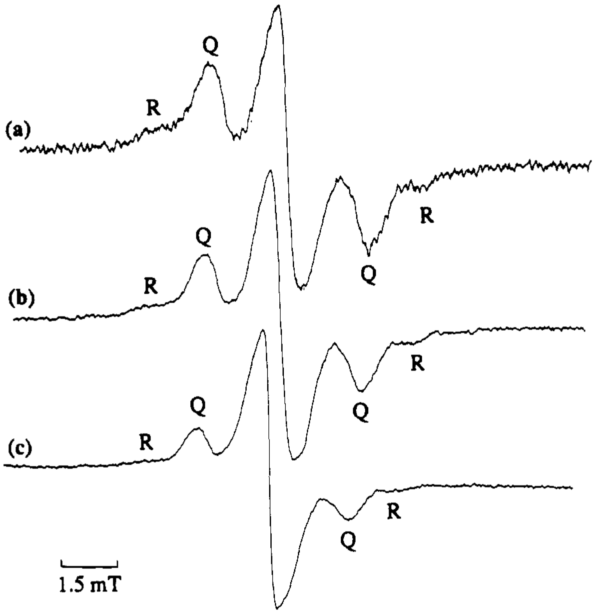

**Figure 12.** Spectra observed during and after the hydrogen atom bombardment of a sample of thermally polymerized maleimide-2,3-$d_2$ that been baked in vacuo at 200 °C for 15 h: (a) during a 9-min bombardment; (b) 41 min after discharge was off; (c) 22 h after discharge was off.

are formed following hydrogen atom bombardment of the 1,2-bismaleimidoethane (BMIE) monomer. Spectrum a, recorded immediately after the discharge is switched off, is composed primarily of propagating radical, although the presence of a small amount of another radical is indicated by the extreme high- and low-field peaks (designated S). As is described above in the results for the maleimide monomer, these S peaks can be assigned to the initial radical and/or the penultimate radical. Again, the reason for the low concentration of initial radical is the rapid conversion to the propagating radical by way of reaction (b) in Figure 8. At longer times following bombardment, the spectra b–d in Figure 13 indicate that other, different radicals are being formed. These radicals are backbone radicals and/or the vinyl radical. Our previous studies[10] in *N*-methylmaleimide have shown that because of distributions in main-chain conformations, these backbone radicals can exhibit a spectrum that looks like a simple superposition of a two-line spectrum on a three-line spectrum and hence resemble the spectra shown in Figure 13b–d. Samples of another aliphatic bismaleimide, 1,6-bismaleimidohexane (BMIH), were also bombarded with hydrogen atoms. A series of spectra similar to those shown in Figure 13a–d, were observed at increasing times after the termination of the discharge. An example of one of these spectra is shown in Figure 13e.

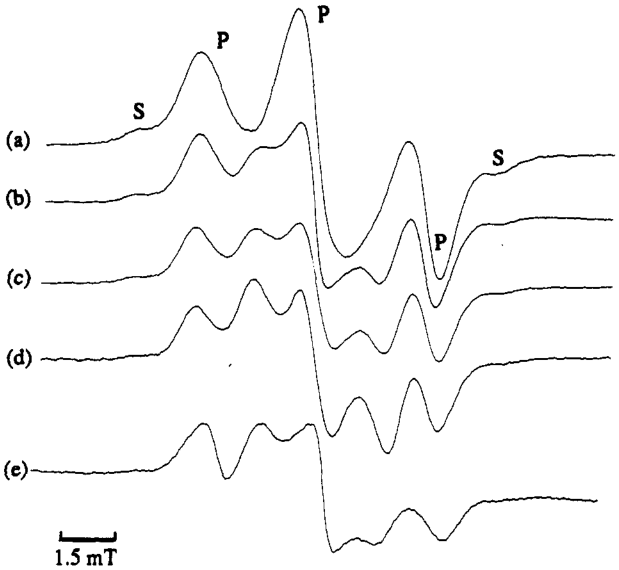

**Figure 13.** Spectra observed after the bombardment of BMIE and BMIH with hydrogen atoms. The BMIE spectra were observed (a) 0 h, (b) 3 h, (c) 7 h, and (d) 47 h after the discharge was off, whereas the BMIH spectrum was observed (e) 15 min after the discharge was off.

All the results in the aliphatic bismaleimides show that the radical reactions following hydrogen atom bombardment occur exclusively at the double bond in the maleimide group. On the other hand, in the hydrogen atom bombardment of maleimide or bismaleimide monomers containing an aromatic ring substituent, the results are more complicated. Several such compounds such as *N*-phenyl-2-bromomaleimide and 4,4′-bismaleimidodiphenylmethane were investigated. In all cases the spectra were almost featureless,[16] presumably because the apparent line widths associated with the hyperfine components are much larger than those observed in the spectra from *N*-methylmaleimide, maleimide, or the aliphatic bismaleimides. We conclude that this apparent broadening is actually the result of a superposition of spectra from several different types of radicals. These species would include the cyclohexadienyl-type radicals,[3] formed by the addition of hydrogen atoms at the double bonds in the aromatic rings, as well as the maleimido-type radicals.

## Conclusions

The ESR results obtained in succinimide illustrate that hydrogen atom bombardment is an irradiation technique that in some circumstances will generate radicals selectively in solids. Thus, the observed ESR line shape indicates the presence of one radical species that is formed as the result of a hydrogen atom abstraction, whereas the results in X-irradiated succinimide[13,14] indicate the presence of several different types of radicals formed as the result of chain scissions at carbon–carbon as well as carbon–hydrogen bonds.

After bombardment with hydrogen atoms, maleimide and bismaleimide polymers containing aliphatic substituents usually show the formation of several different types of radicals, viz., the initial radical, the propagating radical, the penultimate radical, the backbone radical, and the vinyl radical. With the appropriate experimental conditions, each of these radicals can be identified by the hyperfine structure in its ESR spectrum. However, radical assignment is not always unique because of spectral overlap. Thus, after bombardment of maleimide with hydrogen atoms, two outer lines with a splitting of 9.5 mT can be assigned to either the initial radical or the penultimate radical. Again, after bombardment of aliphatic bismaleimides, two lines with a splitting of 2.8 mT indicate the presence of either backbone radicals or vinyl radicals.

In the presence of high monomer concentration the initial radical is usually too reactive to be observed, as it is consumed quickly in the chain-extension process to form the propagating radical. Vinyl radicals are also usually unstable, but in maleimides their increased stability may be the result of the presence of the carbonyl groups. The exact reason for the absence of secondary radicals, such as the vinyl radical or a backbone radical, in the hydrogen bombardment of maleimide monomer is unclear; however, a possible explanation is that the molecular arrangement in the crystal structure is unsuitable for the hydrogen atom abstraction necessary to form either of these radicals. The observation of the initial radical in thermally polymerized maleimide is consistent with the conclusion that the initial step after hydrogen atom bombardment of the maleimide or aliphatic bismaleimide is an opening of the maleimide double bond and a hydrogen atom attachment in the way shown in Figure 8a.

We have concluded that the broad lines observed following hydrogen atom bombardment of the maleimides and bismaleimides containing aromatic substituents are the result of a superposition of spectra from several different types of cyclohexadienyl radicals as well as the maleimido radicals.

The results described in this paper are relevant to our previous study[9] of the free radicals involved in the thermally induced cross-linking reactions in bismaleimides and maleimides. Thus, the spectra associated here with the propagating radical and the vinyl radical show that our previous assignments were correct and hence verify that these species were present in the hot-melt homopolymerization reactions.

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(15) The absence of initial radical in samples that have been exposed to air is not surprising. Since the initial radical is a primary radical, it will be confined mainly to surface sites where it will be vulnerable to attack by oxygen.
(16) In some aromatic maleimides and bismaleimides, four shoulders are just resolvable, but, in all cases, the observed line widths are significantly greater than those in the spectra of aliphatic maleimides and bismaleimides.

**Registry No.** BDM, 13676-54-5; BMIE ($x = 2$), 5132-30-9; BMIE ($x = 6$), 4856-87-5; succinimide, 123-56-8; maleimide, 541-59-3; maleimide-*2,3*-$d_2$, 57876-23-0; *N*-phenyl-2-bromomaleimide, 72000-67-0; (maleimide)(maleimide-*2,3*-$d_2$) (copolymer), 129570-31-6.