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# Characterization of the Free-Radical Homopolymerization of *N*-Methylmaleimide[†]

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ABSTRACT: A hydrogen atom bombardment technique was employed at room temperature to initiate the free-radical homopolymerization of *N*-methylmaleimide (MMI), which can be considered a model compound for prepolymer resins containing the maleimide functional group. Several different radical species were observed and identified by electron spin resonance (ESR). The initial radical, which produced a spectrum having four major resonance lines, was formed by the addition of atomic hydrogen to the C–C double bond. This initial radical, which was too reactive to be observed in pure MMI, was stable for a few minutes in a photopolymerized MMI matrix containing trace amounts of MMI. The second radical species, which produced a three-line ESR spectrum, was identified as the propagating radical associated with the homopolymerization. At later stages of the polymerization reaction this propagating radical was replaced by a third radical species whose ESR spectrum consisted primarily of two intense lines near the center of the spectrum and two weaker extrema lines. This species is assigned to a vinyl radical and/or an internal backbone radical centered on a tertiary carbon.

## Introduction

Bis(maleimide) resins form a class of thermosetting polymers that are used as high-temperature matrices in high-performance composites. The mechanical properties of these materials depend on their network structures, which are controlled by the cure chemistry of the maleimide functional group. In several previous investigations electron spin resonance (ESR) spectroscopy has been used to examine the free-radical chemistry of the maleimide group. These studies have included the neat polycrystalline maleimides[1–5] as well as their solutions.[6–10] Typically, the free radicals have been generated by using UV irradiation or X- or $\gamma$-irradiation. Solution studies offer the advantage of spectral resolution (i.e., narrow ESR lines), but they also have the following disadvantages: (1) the radicals are less stable in solution than they are in the solid state, (2) the solvent can complicate the results by participating in the free-radical chemistry being investigated, and (3) the results cannot necessarily be extrapolated to the neat system. On the other hand, studies of polycrystalline systems have the disadvantage that the ESR lines are broadened because of hyperfine and $g$ anisotropy, making identification of the radicals by way of their resolved hyperfine structures difficult. With high-energy irradiation the situation is further complicated by the frequent superposition of spectra from several different radical species.[1,10]

Free radicals can also be generated thermally, both with and without the presence of added initiators. We have used this approach to induce free-radical homopolymerization in bis(maleimide)s and maleimide compounds.[11] In this study, both the types and the concentrations of free radicals associated with the cure process were monitored. While many radical species of interest were identified, this method of radical generation had some of the disadvantages of the irradiation methods referred to above. In particular, the observed ESR spectrum was often a superposition of three or more broad spectral components, which made it difficult to analyze the spectra.

In our present work on bis(maleimide) curing reactions, we have been able to simplify the ESR spectral analyses by using another technique, viz., hydrogen atom bombardment, to generate radicals in the model compound *N*-methylmaleimide (MMI) and in the related thermally and photochemically cured homopolymers. This technique has already been shown to be more selective than either X- or $\gamma$-irradiation for producing radicals in many organic materials, several of which have contained functional groups similar to those in MMI.[10,12–14] For example, it has been observed[12] that the hydrogen atoms preferentially add to certain C–C double bonds, that they are somewhat less likely to induce C–H bond scission by hydrogen-atom abstraction (with C–H bond scission in methyl groups being particularly unlikely), and that C–C

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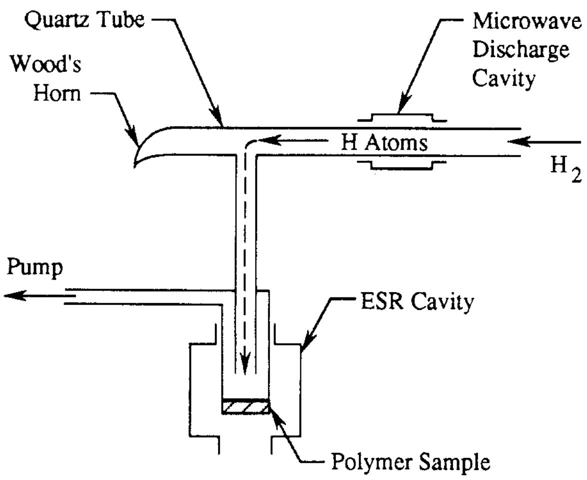

**Figure 1.** Hydrogen atom bombardment apparatus.

bond scission does not occur at all. In the work described in this paper, we have identified several radical species formed as a result of hydrogen atom bombardment, and we have monitored their development with time following termination of the discharge.

## Experimental Section

The *N*-methylmaleimide (MMI) was purchased from Aldrich Chemical Co., Milwaukee, WI, and had a nominal purity of 99%. In some cases this material was purified further by vacuum sublimation at 308 K. However, no significant differences were observed in the ESR spectra of the unpurified and purified samples. Polymerized MMI was prepared either thermally or photochemically. In the former case, sublimed MMI was sealed in an evacuated borosilicate glass tube and heated for 3 days at 453 K, followed by 5 days at 503 K; the glassy polymer obtained after this procedure was pulverized before being used in the ESR experiments. In the latter case, partially polymerized material was obtained by first grinding sublimed MMI to leave a thin layer of powder on the surface of the grinding vessel and then placing the vessel 10–15 cm from a 40-W fluorescent lamp for 48 h. The photopolymerized MMI obtained by this procedure was significantly less volatile than the nonpolymerized material, although subsequent ESR investigation indicated that a small amount of unreacted monomer was present.

Free radicals were generated in the MMI and polymerized MMI by hydrogen or deuterium atom bombardment by using the apparatus shown in Figure 1. The apparatus was designed to allow samples to be bombarded in the absence of air while they were within the ESR microwave cavity.[14,15] With this arrangement, spectra could be obtained either during or after the bombardment. Hydrogen or deuterium atoms were generated by a discharge maintained by a 2.45-GHz Evenson microwave cavity (OPTHOS Instruments, Rockville, MD) located ~20 cm from the sample. The hydrogen/deuterium flow rate (typically $5 \times 10^{-6}$ mol/s) was controlled by using a needle valve at the gas supply and by discharging into a 25 L/m rotary vacuum pump preceded by a liquid $N_2$ trap. The pump produced a vacuum of less than 10 μm when the supply valve was closed. Hydrogen atom concentrations at the sample, as measured relative to a strong-pitch reference, were as high as $1 \times 10^{15}$ atoms/cm$^3$. The use of He carrier gas improved this concentration insignificantly. The Wood's horn was included as a light trap to minimize the photogeneration of radicals in the samples.

The ESR spectrometer used in this study was a Bruker Model ESP300 instrument equipped with a $TE_{102}$ rectangular cavity and controlled by a Bruker 1600 computer. Spectra were typically acquired with a single scan period of 20 s; thus we were unable to observe any evolution of free-radical species that might have occurred over a shorter time period. Spectral simulations were performed by using the program FIBRE.[16]

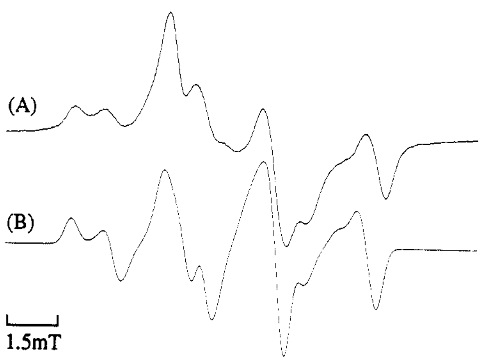

**Figure 2.** (A) Spectrum of the initial radical. The spectrum was recorded during hydrogen atom bombardment of photopolymerized MMI containing dilute MMI monomer. (B) Simulation of the initial radical spectrum assuming one α-hydrogen and two β-hydrogens.

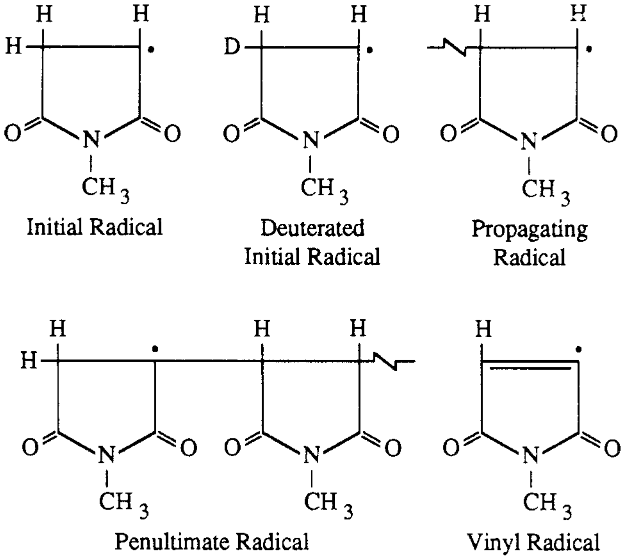

**Figure 3.** Structures of initial, deuterated initial, propagating, penultimate, and vinyl radicals.

## Results and Discussion

In separate experiments, samples of MMI monomer and polymer were placed in the apparatus shown in Figure 1 and were bombarded with hydrogen or deuterium atoms for times from 10 s to 2 h. The evolutions of the resulting radical species were monitored by way of their ESR spectra both during bombardment and for times up to 24 h following bombardment. The experimentally observed spectra were sometimes superpositions of different component spectra, and identification of the separate components was accomplished by referring to those cases in which a single component was dominant. Component spectra were assigned to particular radical species by comparison with results obtained previously from related compounds, e.g., succinimide, maleimide, *N*-phenylmaleimide, and *N*-(phenyl-2,3-$d_2$)-maleimide,[11,17] and by spectral simulation using hyperfine coupling constant values consistent with those reported by others.[18,19]

The ESR spectrum recorded from photochemically polymerized MMI during a 60-s hydrogen atom bombardment is shown in Figure 2A. The primary component of this spectrum is very similar to a spectrum we obtained previously from bombarded polycrystalline succinimide and that we identified as being from an initial radical similar to that shown in Figure 3.[17] Further evidence for the identification of spectrum A as the initial radical

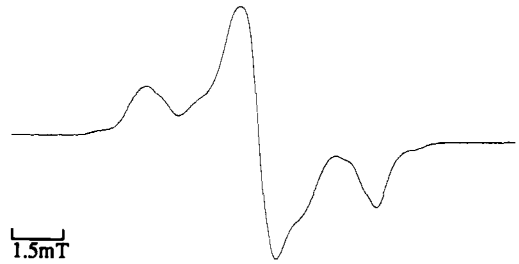

**Figure 4.** Spectrum of the deuterated initial radical. The spectrum was recorded during deuterium atom bombardment of photopolymerized MMI containing dilute MMI monomer.

is the simulation of this spectrum shown in Figure 2B. This simulation was calculated by assuming isotropic hyperfine couplings with two hydrogens (the hydrogens $\beta$ to the p-orbital containing the unpaired electron), an anisotropic coupling with one hydrogen (the $\alpha$-hydrogen), and a Gaussian line shape with a peak-to-peak width of 0.4 mT. The values used to produce the simulation in Figure 2B are the following: $A_0(\beta) = 2.9$ mT, $A_x(\alpha) = 3.7$ mT, $A_y(\alpha) = 2.0$ mT, $A_z(\alpha) = 0.7$ mT, $g_x = 2.0049$, $g_y = 2.0023$, and $g_z = 2.0036$. These values are approximately the same as the averaged values of Pace et al.[18] and Lund et al.[19] obtained from X-irradiated single crystals of succinimides.

Photopolymerized MMI was bombarded with deuterium atoms for 60 s, during which time the ESR spectrum shown in Figure 4 was obtained. This spectrum has only three resonance lines, indicating a hyperfine interaction with only two hydrogens. We assign this spectrum to the deuterated initial radical shown in Figure 3, which has one $\alpha$- and one $\beta$-hydrogen. Simulation of this spectrum yields coupling constants for these two hydrogens that are equal to those for the nondeuterated initial radical described above. No resolved hyperfine structure was observed from the $\beta$-deuterium.

In the photopolymerized MMI the monomer concentration was low, as evidenced by the low vapor pressure of the photopolymerized MMI (<10 $\mu$m) compared to that of pure monomeric MMI (190 $\mu$m) in the bombardment apparatus. As described below, it was this low monomer concentration that stabilized the initial radical in the photopolymerized MMI and enabled acquisition of spectra due primarily to the initial radical (i.e., Figures 2A and 4). In a previous study, certain peaks of multicomponent spectra were correctly attributed to the initial radical.[1] However, to date, spectra due primarily to initial radicals have not been observed in solid maleimides.

A series of spectra acquired from a sample of sublimed MMI monomer following hydrogen atom bombardment for 12 s is shown in Figure 5. It might be expected that the most intense spectral component obtained immediately following bombardment would be from the initial radical, as was observed in the photopolymerized MMI sample. This was not the case. Instead, the most intense component was the three-line component designated as P in Figure 5A. A similar three-line spectrum has been observed previously[1-3,5] in irradiated maleimides, and Zott et al.[1] have assigned it to the propagating radical shown in Figure 3. Peaks P in Figure 5A are assigned to the propagating radical for the following reasons: (1) The intensities of the three lines are approximately in the ratio 1:2:1, suggesting that component P is produced by a radical in which its unpaired electron is delocalized over two hydrogen nuclei with nearly the same coupling constants (i.e., the $\alpha$- and the $\beta$-hydrogens); and (2) the spectrum is similar to that of the deuterated initial radical (Figure 4), which also has one $\alpha$- and one $\beta$-hydrogen.

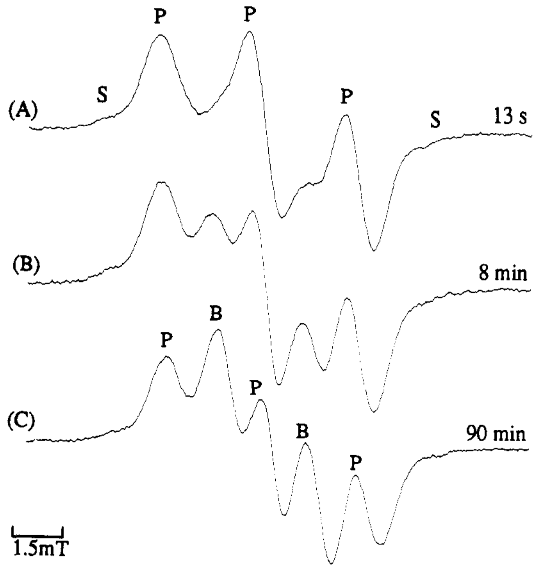

**Figure 5.** Time evolution of MMI monomer following hydrogen atom bombardment for 12 s. Amplitudes of spectra A, B, and C, have been multiplied by 1.0, 1.7, and 2.5, respectively.

There are smaller peaks (designated as S) in Figure 5A that occur at the same field positions as the extreme high- and low-field peaks in the initial radical spectrum shown in Figure 2. Therefore, the peaks designated S suggest the presence of small amounts of initial radical. The more intense center-field peaks of the initial radical are not observed in Figure 5; however, their apparent absence is probably the result of overlap with the more intense P peaks.

A second species that could produce the extreme high- and low-field peaks in Figure 5A is the penultimate radical shown in Figure 3. This radical would result from abstraction of the hydrogen located on the second backbone carbon of the polymer chain. Energetically, the penultimate radical is easy to produce because it is centered on a tertiary carbon. As is the case for the initial radical, the hyperfine interaction in the penultimate radical involves three hydrogens. A four-line spectrum with extrema lines separated by ~9.0 mT is produced if the adjoining monomer unit is rotated such that overlap of the closest hydrogen with the p-orbital containing the unpaired electron is favorable (see below).

Several minutes after hydrogen atom bombardment of MMI, the intensities of the lines designated P in Figure 5 decrease, and the intensities of two new lines, designated B, increase. After 1.5 h, the five-line spectrum in Figure 5C was observed. This spectrum changed only slightly over a period of 24 h. Previously, spectra similar to Figure 5C have been assigned by others to single species such as a nitrogen-centered radical[1] or a methylated initial radical formed by the addition of methyl radical to the C–C double bond of the MMI.[4] These assignments are inappropriate here. We have shown in a previous study of thermally polymerized deuterated *N*-phenylmaleimide[11] that spectra similar to that in Figure 5C result not from hyperfine interaction with the nitrogen nucleus but from hyperfine interactions with hydrogen nuclei. We can also exclude the methylated initial radical because hydrogen atom bombardment is unlikely to induce the C–N bond scission that produces the methyl radical precursor.[4,10,12]

An alternative interpretation for the spectrum of Figure 5C is that it is a superposition of a three-line component from trapped propagating radicals and a two-

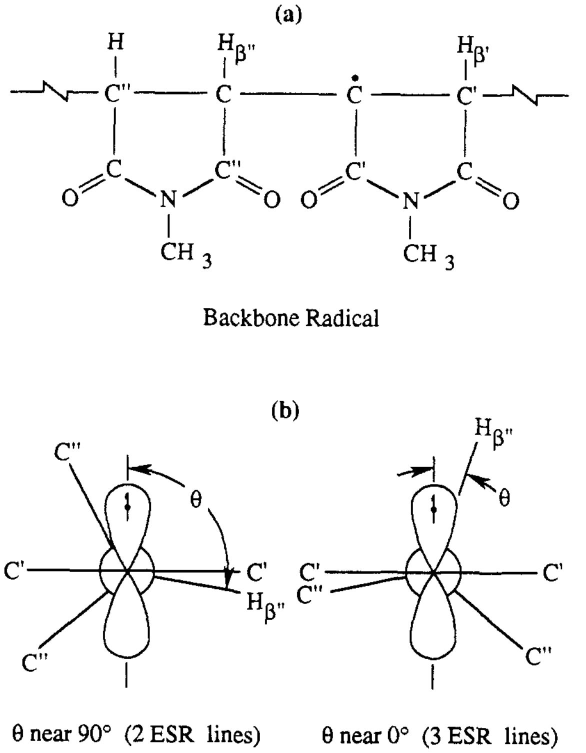

**Figure 6.** (A) Structure of the backbone radical. (B) Newman projections of the backbone radical. Carbon atoms are less eclipsed when $\theta$ is near 90°, making conformations with $\theta$ near this value more favorable energetically.

line (or predominantly two line) component having a hyperfine splitting of 2.8 mT.

One species that might produce the two-line spectrum is the vinyl radical shown in Figure 3, although the relative instability of vinyl radicals as a class makes assignment of the two-line spectrum to this radical uncertain. This vinyl radical would result from the abstraction of a hydrogen atom from MMI monomer. The 2.8-mT splitting of the two-line component in Figure 5 is in reasonable agreement with typical vinyl radical coupling constants of 3.3–3.4 mT,[20,21] considering the electron-withdrawing effect of the carbonyl groups of the MMI vinyl radical. This electron-withdrawing effect may also help stabilize both the MMI vinyl radical and the MMI propagating radical. However, just as an unsubstituted vinyl radical is less stable than an unsubstituted ethyl radical, the MMI vinyl radical should be less stable than the MMI propagating radical. Therefore, while we cannot completely rule out the formation of the MMI vinyl radical, conversion of the propagating radical to this species seems unlikely.

A more plausible assignment for the two-line spectrum B is a radical whose unpaired electron is located on one of the internal maleimide groups of a polymer chain (Figure 6A). The formation of this backbone radical depends not only on the stability of this radical (which is high since the unpaired electron is centered on a tertiary carbon) but also on the concentration of polymer molecules in the bombarded MMI. In the hydrogen atom bombardment technique most of the free-radical chemistry occurs near the sample surface. Local surface concentrations of polymer could therefore be high although the average concentration in the bulk is low. Moreover, the backbone radical could form by an intramolecular transfer in which the propagating radical would bend back on itself to abstract an internal hydrogen atom.

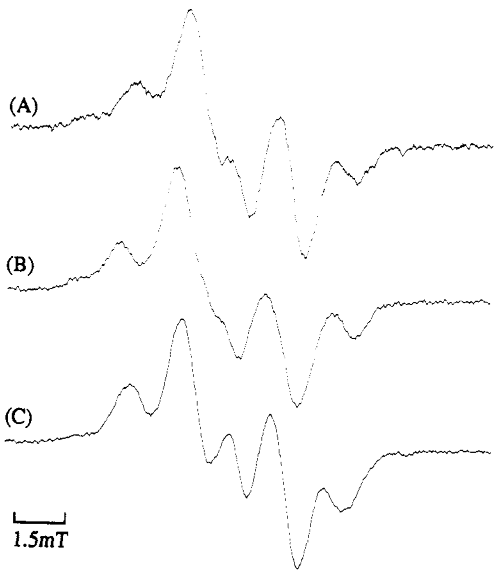

**Figure 7.** (A) Spectrum from thermally polymerized MMI recorded 20 min after a hydrogen atom bombardment lasting 6 min. (B) Spectrum from photochemically polymerized MMI recorded 28 min after a hydrogen atom bombardment lasting 78 s. (C) Difference spectrum for MMI obtained by subtracting Figure 5A from Figure 5C.

To assess the likelihood of formation of the backbone radical in polymer-rich regions of the MMI, we subjected samples of photochemically polymerized MMI and thermally polymerized MMI to hydrogen atom bombardment. Samples containing reduced concentrations of monomer were prepared by baking the polymers at 373 K or higher under vacuum for 15 h. The samples were then typically bombarded for times from 10 s to 6 min. The spectra recorded immediately after bombardment included contributions from the initial radical; however, within several minutes these initial radical components disappeared, leaving spectra like those shown in Figure 7A,B. Spectral components due to the propagating radical were never apparent, indicating that reaction of the initial radical with MMI monomer did not occur to any significant extent. These results suggest that the spectra in Figure 7A,B are associated with a radical formed either by direct reaction of the initial radical with a neighboring polymer chain or by reaction of the polymer with a bombarding hydrogen atom. Both reactions would involve hydrogen atom abstraction.

A spectrum similar in appearance to those in Figure 7A,B can also be obtained for the case of the MMI monomer by subtraction of an appropriately scaled version of the propagating-radical spectrum (Figure 5A) from the spectrum observed 90 min after bombardment (Figure 5C). This difference spectrum is shown in Figure 7C.

Of the three possible radicals resulting from hydrogen atom abstraction, the backbone, penultimate, and propagating radicals (see Figures 3 and 6), only the backbone radical is capable of producing the two dominant center-field lines in Figure 7.[22] In the backbone radical the unpaired electron interacts with both the hydrogen on its own monomer unit (the $\beta'$-hydrogen in Figure 6A) and the hydrogen on the adjoining monomer unit (the $\beta''$-hydrogen). The strength of the interaction with the $\beta''$-hydrogen depends on the conformation of the polymer chain,[23] and the spectrum associated with the backbone radical can have two, three, or four lines, depending on the orientation of this hydrogen relative to the axis of the p-orbital containing the unpaired electron. In particular, a two-line spectrum is produced when this hydrogen is rotated into the plane perpendicular to the p-orbital.

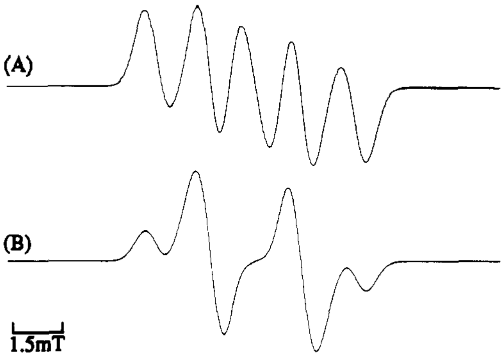

**Figure 8.** (A) Simulation of the backbone radical spectrum, assuming all angles $\theta$ equally probable. (B) Simulation of backbone radical spectrum with 2.5× weighting of angles $\theta$ near 90°.

A computer simulation of the spectrum for the backbone radical is shown in Figure 8A. This simulation is the superposition of equal amounts of ten, single-component spectra, each corresponding to a different orientation (defined by dihedral angle $\theta$ in Figure 6B) of the $\beta''$-hydrogen relative to the p-orbital containing the unpaired electron. In producing this simulated spectrum, values of $\theta$ from 0° to 90°, in 10° steps, were used in the formula

$$A(\beta'') = 3.5(\cos\theta)^2\ \mathrm{mT}$$

to calculate values for the $\beta''$ coupling constant.[23] A constant value of 2.7 mT was used for the $\beta'$ coupling constant. The simulated spectrum in Figure 8A looks like a simple superposition of a two-line component and a three-line component and is therefore in qualitative agreement with the experimental spectra in Figure 7. However, the relative intensities of the two- and three-line components are incorrect. These intensities depend on the values of $\theta$ used in the simulation, and an increased intensity of the two-line component requires that most values of $\theta$ be near 90°. Considerations of local steric effects, as depicted by the Newman projections in Figure 6B, suggest that $\theta$ values near 90° are indeed more likely than those near 0°. Figure 8B is a simulation made by assuming that conformations in which $\theta$ is greater than 45° are 2.5 times more probable than those in which $\theta$ is less than 45°. The relative intensity of the two-line component is enhanced, resulting in good agreement with the experimental spectra in Figure 7.

Considering the agreement of the simulated spectrum in Figure 8B with the spectra in Figure 7 and the relative stability of the backbone radical (a tertiary radical), we attribute the spectra in Figure 7 primarily to this radical.

We note that in addition to the spectral components in Figure 7 discussed above there is a component having two, weak extrema lines separated by ~9.0 mT. These two lines could be either from trace amounts of initial radical trapped in the polymer matrix or from the penultimate radical, a species present in lower concentration than the backbone radical for degrees of polymerization greater than three. For the penultimate radical to produce the four-line spectrum having these two extrema lines, its unpaired electron must interact with three $\beta$-hydrogens, which corresponds to a conformation in which $\theta$ is near 0°.

## Summary

The hydrogen atom bombardment technique has enabled us to characterize the sequence of reactions involved in the homopolymerization of *N*-methylmaleimide (MMI). The reactions identified in this study have included the following: (1) the addition of atomic hydrogen (deuterium) to the C–C double bond of MMI to form an initial radical, (2) the reaction of the initial radical with MMI to form a polymer chain terminated with a propagating radical, and (3) the abstraction of hydrogen by the initial and propagating radicals from monomeric MMI to form a vinyl radical and/or from polymerized MMI to form internal and penultimate backbone radicals centered on tertiary carbons.

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**Registry No.** MMI, 930-88-1; MMI (homopolymer), 26714-86-3; H, 12385-13-6; D, 16873-17-9.