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Cross-Linking Reactions in Maleimide and Bis(maleimide) Polymers. An ESR Study

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ABSTRACT: The results of electron spin resonance (ESR) measurements on the homopolymerization reactions of two bis(maleimides) and several maleimide model compounds containing different amounts of radical initiators (0-10 wt %) are reported. Two types of radicals were identified: the propagating radical, which is an intermediate in the chain growth polymerization, and species such as the bis(maleimidophenyl)methyl radical and a substituted vinyl radical, both of which are the result of hydrogen atom abstraction reactions. The concentrations of the radicals observed in the hot-melt homopolymerization of one particular bis(maleimide) were determined as a function of cure time from the integrated ESR intensities. The similarity of the ESR results obtained in air-curing and in vacuum-curing suggests that hydroperoxides, which might be formed by reactions with ambient oxygen during the cure process, play no role as radical initiators. On the other hand, differential scanning calorimetry, along with ESR, suggests that trace amounts of impurities act as radical initiators; but, even in the absence of impurities, the bis(maleimides) will still homopolymerize by direct thermal homolysis. There is also evidence for thermal as well as thermooxidative degradation.

Introduction

Cured carbon fiber/bis(maleimide) composites are high-modulus, high-strength materials that are better than carbon fiber/epoxy composites in retaining their mechanical properties after hot-wet or hot-dry exposures at 525 K.[1-5] One undesirable property of bis(maleimide) matrices, however, is that they are brittle. Since the cross-link density of the network determines the strength and fracture toughness of the matrix, it is important to understand the mechanisms of the cross-linking reactions and to find ways of controlling these reactions. We are using electron spin resonance (ESR) spectroscopy to investigate these cross-linking reactions because they involve a free-radical mechanism. In this paper we report on our studies of the types and concentrations of radicals formed and trapped in the polymer matrix when bis(maleimide) monomers and selected maleimide model compounds undergo homopolymerization in the presence of different amounts of free-radical intitiator (0-10 wt %). The bis(maleimides) studied were 4,4′-bis(maleimidophenyl)methane (BDM) and the research-grade monomer 6-maleimido-1-(4′-maleimidophenyl)-1,3,3-trimethylindane (CIBA). The maleimides included in this study were *N*-phenylmaleimide, *N*-methylmaleimide, and maleimide. The structures are shown in Figure 1.

Experimental Section

The BDM monomer, the main bis(maleimide) used in many commercial resin formulations, was purified by recrystallization from hot mixtures of chloroform and methanol. Small quantities of the material were also purified with high-pressure liquid chromatography using a silica gel column as the stationary phase and methylene chloride containing 0.2% methanol as the mobile phase. The CIBA bis(maleimide) was used as received from the Ciba Geigy Chemical Co., Ardsley, NY. The BDM monomer and the maleimide monomers were obtained from the Aldrich Chemical Co., Milwaukee, WI. The latter were purified either by vacuum sublimation or by recrystallization from suitable solvents. The deuterated material *N*-phenyl-2,3-d_2-

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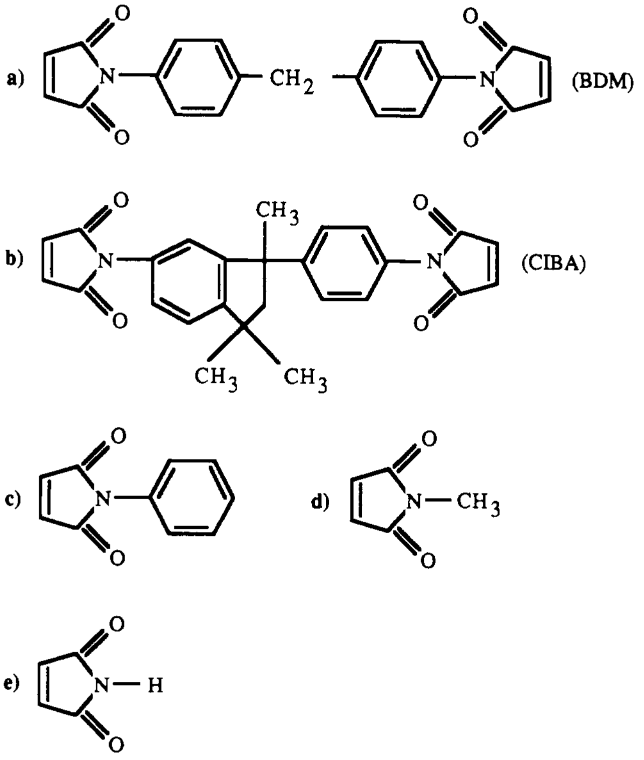


Figure 1. Bis(maleimides) and maleimides studied: (a) 4,4′-bis(maleimidophenyl)methane; (b) 6-maleimido-1-(4′-maleimidophenyl)-1,3,3-trimethylindane; (c) *N*-phenylmaleimide; (d) *N*-methylmaleimide; (e) maleimide.

maleimide was obtained from ICN Biomedicals, Cambridge, MA. The free-radical initiator, benzoyl peroxide (Aldrich), was used as received.

The degassed samples of BDM were heated in a constant-temperature bath at 433 K while they were attached to a vacuum line (<1.0 Pa) for at least 30 min. These samples melted at 431 K to form a supercooled liquid, and they remained liquid during the degassing period so the oxygen diffusion and removal rates were high.

The ESR spectra were obtained as first or second derivatives of the imaginary part of the magnetic susceptibility by use of an X-band spectrometer (IBM Model 200D) interfaced to a computer (IBM Model 9001). The integrated ESR absorption intensities which were taken as a measure of the radical concentrations were evaluated from a double integration of the first-derivative spectra by use of the available software. Spectra were scaled and subtracted using the same software.

The differential scanning calorimetry measurements were made using a Du Pont 9900 instrument.

Summary of Results

Samples of BDM were heated at temperatures from 450 to 510 K either in air or, following careful degassing, in vacuo. All samples exhibited the first- and second-derivative ESR spectrum shown in Figure 2. Since this spectrum consists of two sets of quintets, i.e., a total of 10 lines (9 resolved), it is unequivocally assigned to the 4,4′-bis(maleimidophenyl)methyl radical[6] whose structure is shown in Figure 3a. The main splitting between the two central peaks in each quintet is 1.43 ± 0.04 mT, whereas the splitting between each peak in the quintets is 0.39 ± 0.03 mT. The former value is consistent with the reported isotropic coupling constants[7] for the methylene proton in substituted diarylmethyls, whereas the latter value is consistent with the isotropic coupling constants for the ortho-ring protons.[8]

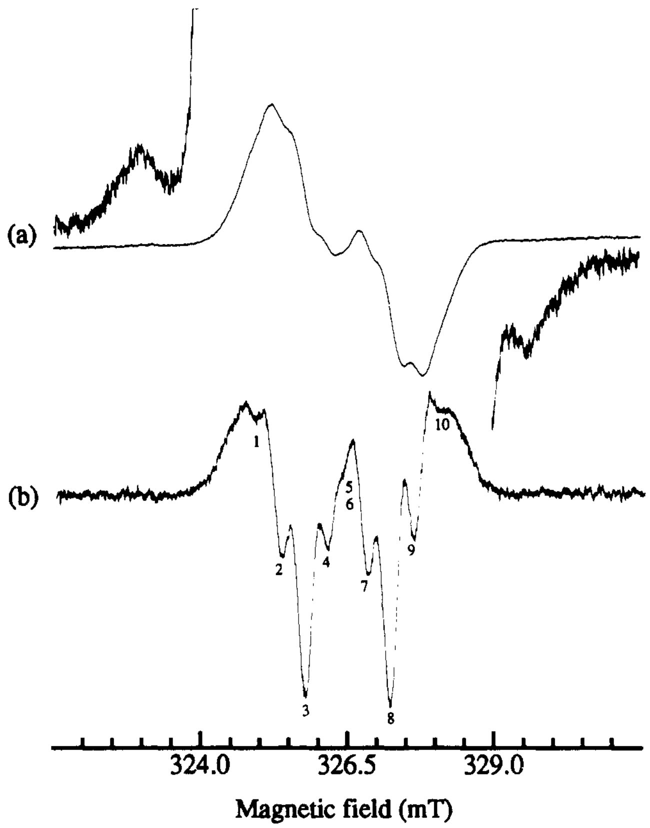


Figure 2. ESR spectra observed in BDM samples heated in vacuo at 503 K for 1 h: (a) first derivative; (b) second derivative.

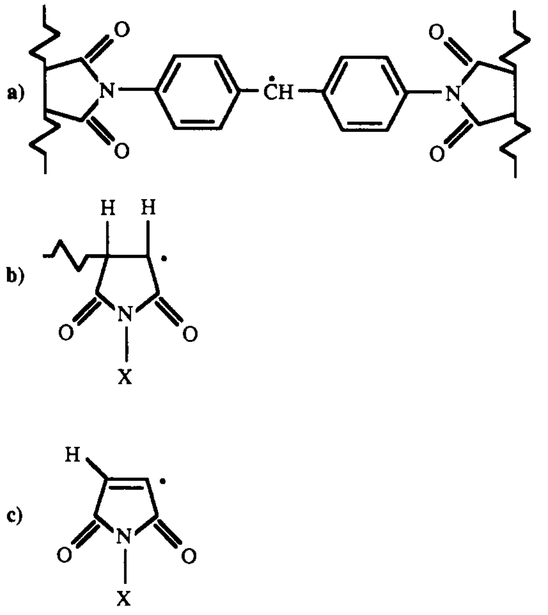


Figure 3. Radicals observed: (a) the bis(maleimidophenyl)methyl radical; (b) the propagating radical; (c) the vinyl radical.

We also investigated how the ESR line shape changed with cure time. The samples were heated at 503 K either in evacuated, sealed sample tubes or in open sample tubes for times up to 10 000 min (166.7 h). The ESR measurements were made at room temperature. At certain times into the BDM homopolymerization reactions, weak satellite lines were detected on either side of the 10-line spectrum. Figure 2a shows the shapes and positions of these satellites with respect to the first-derivative 10-line spectrum observed in a BDM sample, which had been heated for 60 min at 503 K. After long times at 503 K (400 min for the evacuated samples and 1000 min for the samples exposed to air), a single line located at the center of the

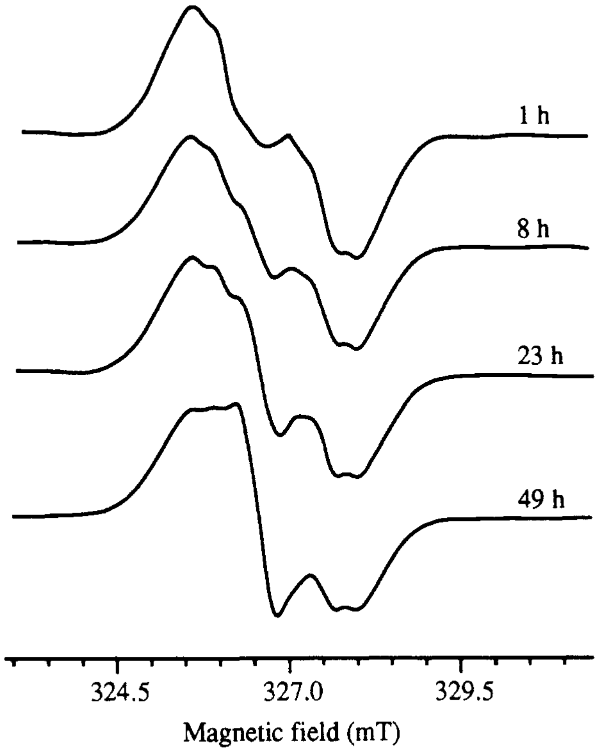


Figure 4. First-derivative ESR spectra observed in BDM samples after heating in vacuo at 503 K for the different times shown.

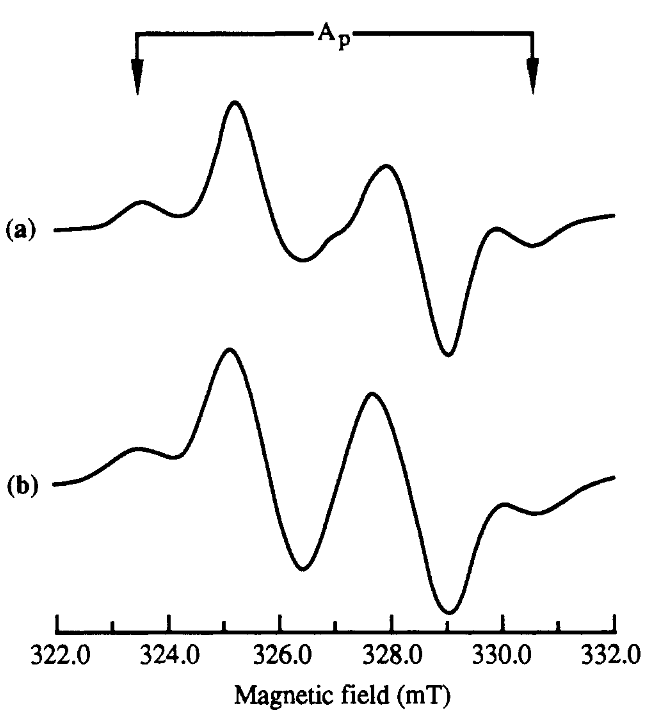


Figure 5. (a) ESR spectrum observed in samples of *N*-phenylmaleimide containing 10 wt % benzoyl peroxide after heating at 353 K for 50 min. A_p is the extrema splitting. (b) ESR line shape obtained as the weighted sum of the computer-simulated spectra for the propagating radical and the vinyl radical.

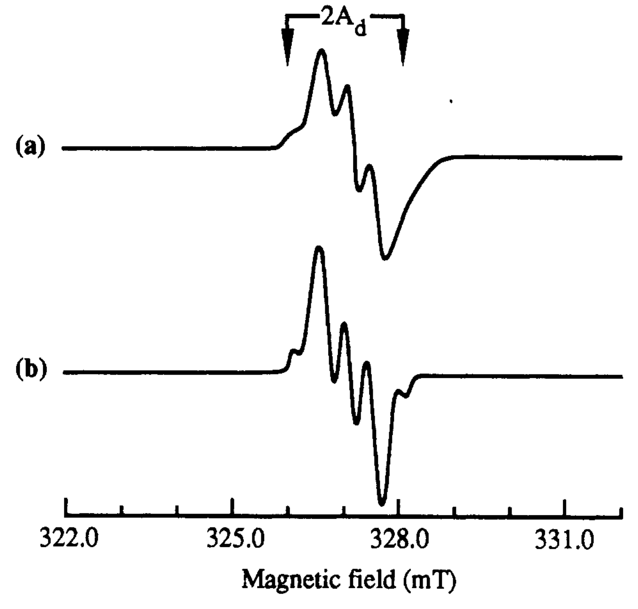


Figure 6. (a) ESR spectrum observed in samples of *N*-phenyl-2,3-d_2-maleimide containing benzoyl peroxide after heating at 353 K. $2A_d$ is the extrema splitting. (b) ESR line shape obtained as the weighted sum of the computer-simulated spectra for the deuterated propagating radical and the deuterated vinyl radical.

10-line spectrum was observed. As is shown in Figure 4, the intensity of this single line increased with heating time.

Several ESR studies were carried out on the substituted maleimide model compounds, *N*-methylmaleimide, *N*-phenylmaleimide, and *N*-phenyl-2,3-d_2-maleimide in an attempt to identify the radical giving rise to the satellite lines. The four-line spectrum shown in Figure 5a was observed from a degassed sample of *N*-phenylmaleimide containing benzoyl peroxide (5 wt %), which had been heated for 50 min at 353 K. We have considered assigning this spectrum to one radical, but, in view of the results of the following experiments, we have abandoned this interpretation and now believe that the four-line spectrum is the superposition of two spectra from different radicals. Samples of *N*-methylmaleimide and maleimide containing benzoyl peroxide exhibited an additional single line superimposed on the same four-line spectrum.

The experimental line shape shown in Figure 5a resembles the "Pake-doublet"[9] that can be expected from the dipolar interaction present in some biradicals.[10] To rule out this interpretation, we repeated the experiment by heating a sample of *N*-phenyl-2,3-d_2-maleimide and benzoyl peroxide and observed the five-line spectrum shown in Figure 6a. The ratio of the extrema splittings A_p to A_d defined in Figures 5a and 6a, respectively, is $A_p/A_d = 6.5$, which is the ratio of the gyromagnetic ratios for the proton and deuteron. This result suggests that the four-line spectrum and the five-line spectrum arise from hyperfine interactions of the unpaired electron with the hydrogen (deuterium) nuclei located on the 2 and 3 positions of the maleimide ring, and not, for example, from an interaction with the imide nitrogen.

The results obtained in the following experiment support this conclusion and provide information on the extent of delocalization of the unpaired electron. We coprecipitated *N*-phenylmaleimide and *N*-phenyl-2,3-d_2-maleimide from solution to form crystals in which these monomers were mixed at a molecular level. These mixed crystalline monomers were then thermally homopolymerized with benzoyl peroxide in the same manner as described above. The resulting ESR spectrum consisted of a superposition of the spectra shown in Figures 5a and 6a. No additional lines were observed. These ESR results suggest that the unpaired electron has resolvable hyperfine interactions with only the nuclei on a single monomer. Otherwise, since the monomers are incorporated randomly into the growing polymer and there is a nonvan-

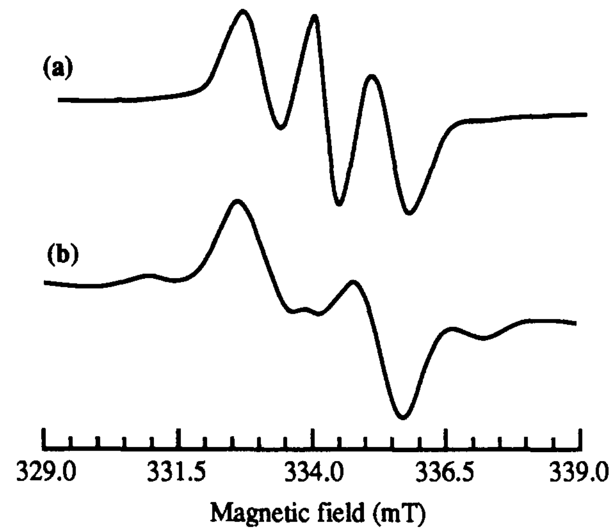


Figure 7. (a) ESR spectrum observed in samples of CIBA bis(maleimide) containing benzoyl peroxide after heating at 348 K for 75 min. (b) ESR spectrum from same sample after 65 min additional heating at 378 K.

ishing probability for deuterated and protonated monomers being adjoining monomers, additional lines would be observed arising from interactions with protons or deuterons located on these adjoining monomers.

There is further direct experimental evidence that the line shape in Figure 5a is the superposition of two spectra. We have found that the relative intensities of the outer shoulders and the inner lines can vary markedly with different resins or with the same resin that has undergone different heat treatments. The spectra observed from samples of CIBA bis(maleimide) containing benzoyl peroxide show such a behavior. For example, in the spectrum shown in Figure 7a, the intensities of the outer shoulders are small whereas, as is shown in Figure 7b, on additional heating of the same sample at 378 K the intensities of the outer shoulders have been restored.

If Figure 5a is the superposition of two different spectra,[11] what two types of radical can we expect to be present? The conventional picture[12] of the role of radical initiators in the thermal polymerization of maleimides is outlined in Figure 8a. The three radicals that appear are the initiator radical $(R^\bullet)$, the propagating radical, and the initial radical. In the case of benzoyl peroxide, the initiator radical is never observed, presumably, because it is too reactive. On the other hand, the initial radical should show a spectrum indistinguishable from that of the propagating radical. We can therefore expect to observe only one spectrum, a three-line spectrum characteristic of the propagating radical, as a result of the radicals generated by the scheme shown in Figure 8a. Moreover, it is well-known that benzoyl peroxide exhibits a tendency to abstract hydrogen atoms.[12] In the specific cases of the substituted maleimides, this abstraction could result in the formation of the vinyl radical[13,14] shown in Figure 8b.

Spectra for the vinyl radical and the propagating radical were computer simulated, assuming appropriate values[15] for the isotropic hyperfine coupling constants (A), a line-width parameter (W), and the g-value (g). In the case of the vinyl radical, a two-line spectrum was generated with the parameters A = 2.6 mT (i.e., one proton), W = 1.3 mT, and g = 2.003. In the case of the propagating radical a three-line spectrum was generated with the parameters A = 3.2 and 2.7 mT (i.e., two nonequivalent protons), W = 1.3 mT, and g = 2.003. The two-line spectrum was weighted with a factor of 4.5 and added to the three-line spectrum to obtain the spectrum shown in Figure 5b. This line shape is in good agreement with the experimentally observed spectrum shown in Figure 5a.

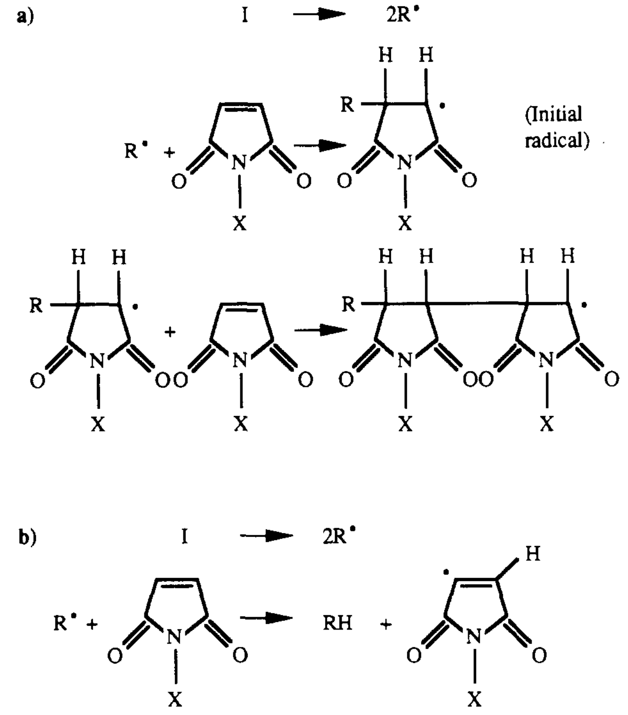


Figure 8. (a) Conventional scheme for the thermal polymerization of maleimides involving radical initiators (I) decomposing to form initiating radicals $(R^\bullet)$, the initial radical, and the propagating radical. (b) Reactions involved in hydrogen atom abstraction from maleimides by the initiating radicals $(R^\bullet)$.

The corresponding spectra for the deuterated radicals were simulated by dividing the proton coupling constants used to generate Figure 5b by 6.5, the ratio of the gyromagnetic ratios for the proton and the deuteron. Thus, for the deuterated vinyl radical, a three-line spectrum was generated with the parameters A = 0.40 mT (one deuteron), W = 0.35 mT, and g = 2.003. In the case of the deuterated propagating radical, a five-line spectrum was generated with the parameters A = 0.49 and 0.42 mT (two nonequivalent deuterons), W = 0.35 mT, and g = 2.003. The three-line spectrum was weighted with a factor of 4.5 and added to the five-line spectrum to obtain the resultant spectrum shown in Figure 6b. Not only is this line shape in excellent agreement with the experimental spectrum shown in Figure 6a but it is also consistent with the spectra shown in Figure 5. From these studies we have concluded that the outer shoulders in Figure 5a, and hence the satellite lines in Figure 2, can be assigned to the propagating radical.[16]

The concentrations of the diphenylmethyl radical, the propagating radical, and the radical species associated with the single line shown in Figure 4 were measured in a sample of BDM that had been carefully degassed. These measurements were made at room temperature in a sample of BDM that had been heated at 503 K for different times up to 10 000 min (166.7 h). The concentrations of these three radicals measured as a function of cure time are shown in Figure 9. The same measurements were made on a sample of BDM that had been heated at 503 K in air for different periods of time. The results for these measurements are shown in Figure 10. The main difference between the data in Figures 9 and 10 is that

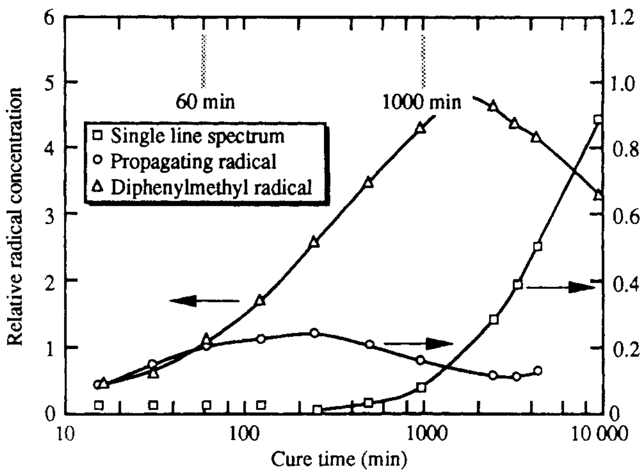


Figure 9. Concentrations of the bis(maleimidophenyl)methyl radical, the propagating radical, and the radical associated with the single line measured in BDM as a function of cure time. The homopolymerizations were carried out in vacuo at 503 K. The actual concentrations of the propagating radical are ≈1/50 of those shown.

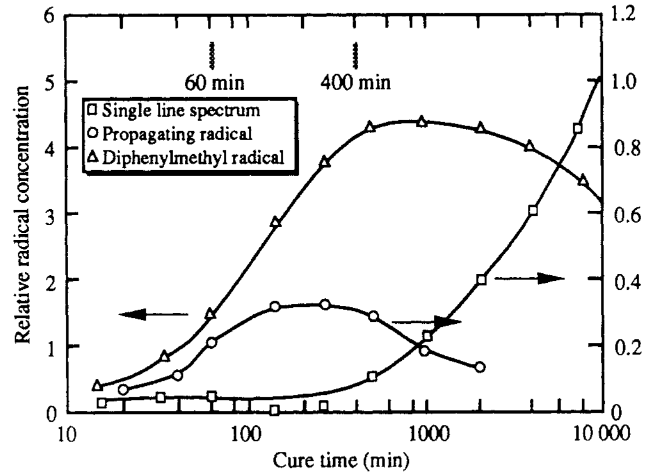


Figure 10. Concentrations of the bis(maleimidophenyl)methyl radical, the propagating radical, and the radical associated with the single line measured in BDM as a function of cure time. The homopolymerizations were carried out in air at 503 K. The actual concentrations of the propagating radical are ≈1/50 of those shown.

the single-line spectrum could be detected at an earlier time (400 min instead of 1000 min) in the samples exposed to air. Thus the stabilities as well as the formation rates of the radicals in the polymer matrix are affected only slightly by the sample exposure to air. Extrapolations of the exotherm data obtained from differential scanning calorimetry (DSC) measurements indicate that, for samples of BDM heated at 503 K, the cure is complete in 60 min,[17] whereas, as is shown in Figures 9 and 10, the radical reactions proceed long after this time. Part of the explanation for this discrepancy lies in the fact that unreacted maleimide groups are trapped in the polymer matrix. Infrared data[18] for some bis(maleimide) formulations indicate that, after heating at 510 K for 5 h, as much as 25% of the maleimide groups remain unreacted. Moreover, ^{13}C NMR measurements[19] in BDM samples show that after 2 h of heating at 493 K, 50% of the maleimide groups remain unreacted in the matrix, whereas after 65 h, only 20% are unreacted.

Table I
DSC Exotherm Temperatures

resin	exotherm temp, K
CIBA	573
CIBA + 5 wt % BPO	373
BDM (as received)	491
BDM + 1 wt % BHT	526
BDM + 5 wt % BHT	543
BDM + 10 wt % BHT	544
BDM (ultrapure)	558

DSC measurements were made on samples of the CIBA resin with and without the radical initiator BPO and also on samples of BDM with and without the radical scavenger butylated hydroxytoluene (BHT). The temperatures of the exotherm peaks are summarized in Table I. In the pure CIBA resin, the exotherm occurred at 573 K, whereas in the samples containing BPO the exotherm was lowered to 373 K. This result demonstrated that homopolymerization of the bis(maleimide) resin involves a free-radical mechanism. As Table I shows, in the BDM samples containing the radical scavenger BHT, the exotherm appeared at 526, 543, and 544 K depending on the amount of scavenger added rather than at 491 K for the as-received samples or 558 K for the ultrapure sample. These results not only corroborate the presence of a free-radical mechanism in the homopolymerization of BDM but also indicate that the impurities in the as-received monomers act as radical initiators.

Discussion

All the radicals observed in this study have been trapped in some form of solid matrix, and there is evidence that the rigidity of the surrounding matrix has an important role in determining the stability of the radical. Thus, in measuring the radical concentrations as a function of cure time, i.e., as in the data shown in Figures 9 and 10, the measured concentrations do not increase monotonically from time zero. No diphenylmethyl radicals were detected after the first 15 min of heating. This result is understandable if a certain matrix rigidity is required for radical stability, so that polymerization has to proceed to near vitrification or beyond before the radical concentrations are high enough to be detected by their ESR spectra. Matrix rigidity also reduces the rate of molecular oxygen diffusion in the polymer. This might explain why the radical stabilities are unaffected by the exposure of the samples to oxygen during the cure.

The experimental results reported here provide some information about the mechanism involved in the first step of the homopolymerization reaction. Although direct, thermally induced homolysis of vinyl-type or maleimide monomers can occur, it is known that, in most cases of thermally induced chain growth polymerization, trace impurities present behave as radical initiators to polymerize the monomers in the way outlined in Figure 8. Peroxy radicals and hydroperoxides can form continuously in some thermally induced polymerizations carried out in the presence of oxygen. If these hydroperoxides form in this way in bis(maleimides), they can decompose on heating to produce an alkoxy radical and in turn a maleimido radical initiator (M$^\bullet$), as is shown in Figure 11. Since the results in Figures 9 and 10 show that molecular oxygen has almost no effect on radical formation, these results also imply that neither hydroperoxides nor alkoxy and peroxy radicals act as initiators in the later stages of the BDM homopolymerization.

Furthermore, the trend of the exotherm temperatures listed in Table I is evidence that the chain initiation can be induced by direct thermal homolysis. If the chain-initiation mechanism involves radical initiator impurities, then the large amounts of BHT added (10 wt %)

$$\begin{array}{rcl} \mathrm{I} & \longrightarrow & 2\mathrm{R}^\bullet \\ \mathrm{R}^\bullet + \mathrm{O}_2 & \longrightarrow & \mathrm{ROO}^\bullet \\ \mathrm{ROO}^\bullet + \mathrm{MH} & \longrightarrow & \mathrm{ROOH} + \mathrm{M}^\bullet \\ \mathrm{ROOH} & \longrightarrow & \mathrm{RO}^\bullet + {}^\bullet\mathrm{OH} \\ \mathrm{RO}^\bullet + \mathrm{MH} & \longrightarrow & \mathrm{ROH} + \mathrm{M}^\bullet \\ {}^\bullet\mathrm{OH} + \mathrm{MH} & \longrightarrow & \mathrm{H_2O} + \mathrm{M}^\bullet \end{array}$$

Figure 11. Reaction scheme for thermal polymerizations in air involving radical initiators (I), initiating radicals ($R^\bullet$), peroxyradicals, alkoxyradicals, maleimidoradicals ($M^\bullet$), and hydroperoxides.

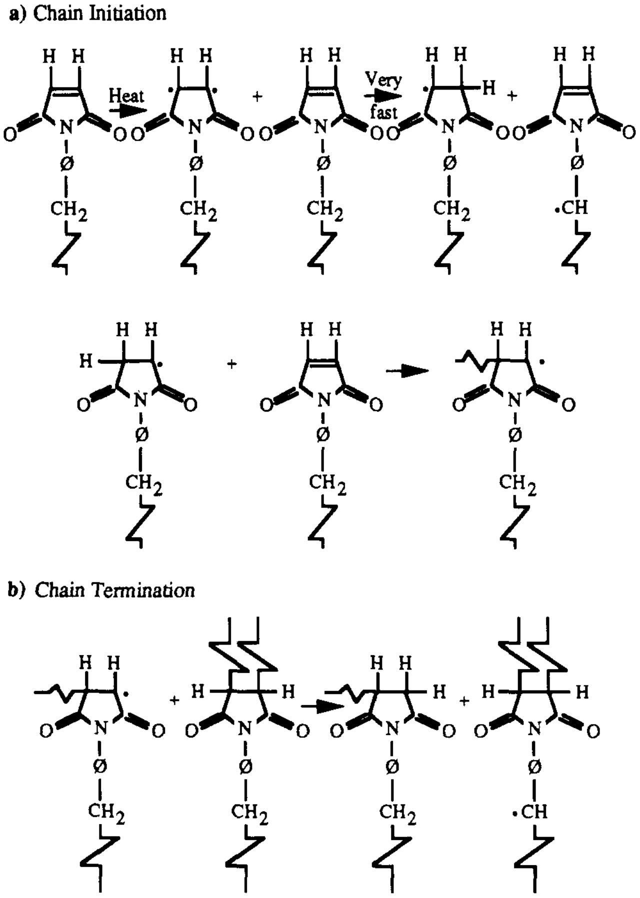
would scavenge the trace amounts of radical initiators to completely suppress the homopolymerization. On the other hand, a mechanism involving direct, thermally induced homolysis would result in the formation of many radicals that would eventually overcome the BHT scavenger and, at this stage, homopolymerization involving a radical mechanism would take place. This appears to be the situation in the samples containing greater than 5 wt % BHT, where the homopolymerization is suppressed, but nevertheless occurs, at 543 K.

We have other reasons to doubt that the initiator mechanism involves an impurity. During the pregel polymerization phase, the radicals formed by dissociation of the initiator impurity have enough mobility to attack the maleimide groups. However, it is difficult to see how these initiator radicals or the propagating radicals could have enough mobility to react with the trapped unreacted maleimide groups at times well after matrix vitrification (say, 1000 min) when the matrix is very rigid. Furthermore, the ESR measurements in samples of BDM containing large amounts of BHT scavenger indicate that the diphenylmethyl radical concentrations were approximately the same as in the unscavenged samples. This result suggests that radical initiator impurities are not necessary for the generation of diphenylmethyl radicals. We therefore conclude that the initiation step in the homopolymerization of pure BDM can involve a thermally induced homolytic cleavage at the double bond, as is shown in Figure 12.

The diphenylmethyl radical can be the result of a hydrogen atom abstraction from the parent molecule by the reactive biradical shown in Figure 12. Alternatively, if the propagating radical is involved, these hydrogen atom abstractions are chain-terminating reactions which limit the chain length and result in a polymer network that is less extensively cross-linked than it would be in their absence. Over the period 1000–10 000 min, the decrease in the concentration of diphenylmethyl radicals (1.4 units for both the vacuum and the air data) is almost the same as the increase in concentration of the radical associated with the single-line spectrum (0.9 units for the vacuum data and 1.0 units for the air data). Thus, most of the loss in the diphenylmethyl radical concentration may arise because of its conversion to another radical as a result of a thermal degradation reaction. Moreover, the earlier appearance (400 instead of 1000 min) of the single-line spectrum for samples heated in air indicate the additional presence of a radical produced as the result of thermooxidative degradation.

Summary of Conclusions

ESR studies of the homopolymerization reactions of bis(maleimides) and maleimides reveal the presence of two types of radicals: the propagating radical, which is an intermediate in the chain growth polymerization, and species that are the result of hydrogen atom abstraction reactions, such as the bis(maleimidophenyl)methyl radical and a substituted vinyl radical. Samples that have been polymerized in the hot-melt form in air show the same dependence of the radical concentrations on cure time as samples that have been carefully degassed. We therefore concluded that hydroperoxides, which might be generated through exposure of the hot-melt samples to air, play little, if any, role as radical initiators. Both the DSC and ESR results indicate that impurities in the as-received samples of BDM act as radical initiators. However, even if these impurities are removed, the bis(maleimide) will still polymerize through a thermally induced homolysis of the double bond. The appearance of a single ESR line data in the cure of samples that have been degassed and in samples that have been exposed to air suggests the occurrence of thermal and thermooxidative degradation.



a) Chain Initiation

b) Chain Termination

Figure 12. Reactions involving the generation of bis(maleimidophenyl)methyl radicals (a) in a chain-initiation step and (b) in a chain-termination step.

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Registry No. BDM, 13676-54-5; CIBA, 123811-63-2; *N*-phenylmaleimide, 941-69-5; *N*-methylmaleimide, 930-88-1; maleimide, 541-59-3.

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Chirality of Polyvinyl Compounds. 10.[1] Asymmetric Perturbation of Side-Chain Chromophores Caused by the Main-Chain Configuration of Optically Active Vinyl Polymers

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ABSTRACT: After removal of the D-mannitol template, copolymers of 3,4-*O*-cyclohexylidene-D-mannitol 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] (1) with comonomers having aromatic chromophores obtained by free radical polymerization were investigated for their chiroptical properties. As comonomers, usually those containing aromatic systems of benzene, naphthalene, biphenyl, and stilbene with a varying distance of the chromophores from the polymerizable group were used. The copolymers are optically active due to the chirality of the configuration of the main chain. While the (*S*,*S*)-(4-vinylphenyl)boronic acid diads cause a strong negative Cotton effect at 233 nm, the aromatic comonomeric units generally bring about a positive Cotton effect at higher wavelength. Depending on the extent to which these two influences are operating, optical rotations varying from strongly negative to strongly positive were observed for the copolymers of different comonomers. The aromatic comonomeric unit shows the highest influence on the chiroptical properties if it is present as an isolated entity directly bound to the main chain. The asymmetry of the aromatic chromophore is caused by a conformational perturbation through the neighboring (*S*,*S*) diads.

Introduction

Much of the interest in optically active polymers stems from the potential of these materials for several specialized uses, viz., (i) chiral matrices for asymmetric synthesis, (ii) chiral stationary phases for the resolution of racemates, (iii) synthetic molecular receptors, and (iv) chiral liquid crystals for ferroelectric and nonlinear optical applications.[2-5] This has stimulated a considerable amount of research directed toward designing improved synthetic procedures for obtaining optically active polymers with well-defined molecular and supermolecular structural ordering of the polymer chain and the functional groups.

Based on molecular symmetry considerations, we have recently developed a novel synthetic strategy for obtaining optically active vinyl polymers whose chirality arises from the configurational relationships in the main chain. Our approach toward constructing such a chiral polymer chain involves stereoregular placement of two monomeric units in a defined absolute configuration (asymmetric diads), which are separated from one another by one or more nonstereoregular comonomer units.[2,6] Hence by polymerization of the appropriate template monomer 1 with another comonomer such as styrene, methacrylonitrile, etc. and subsequent removal of the chiral template units, one is furnished with polymers showing appreciable optical activity.[7] Our detailed synthetic and mechanistic investigations revealed the absolute configuration of the asymmetric diad units to be (*S*,*S*), showing negative optical rotations.[8] Furthermore, since the asymmetric configurations and hence the optical activity are mainly

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