largest remanent polarization.

(2) The true P_r obtained by frequency-dependent measurement rapidly decreases with increasing temperature.

(3) Although considerably high polarization is induced near T_c, most of it disappears through reversible randomization and irreversible switching-back of dipoles when the field is removed.

(4) The presence of an electric field results in a shift of T_c to higher temperature. The poled sample also exhibits a higher T_c than the unpoled one.

(5) Near T_c, the ϵ–E loop suggests a double-hysteresis nature.

(6) The shift of T_c and the double hysteresis indicate that the phase transition of this copolymer is of the first order.

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Nitroxide Spin Labeling of Epoxy Resins

I. M. Brown* and T. C. Sandreczki

McDonnell Douglas Research Laboratories, St. Louis, Missouri 63166.

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ABSTRACT: A description is given of the electron spin resonance results obtained from experiments dealing with the spin labeling of an uncured bifunctional and an uncured tetrafunctional epoxy resin. The labels were attached at the oxirane ring following an opening of the ring by primary, secondary, and tertiary amine nitroxides. Both neutral and zwitterion spin labels were identified. The former were either end labels or bridging-group labels; the latter formed a series of quaternary bases. Some of these quaternary bases can undergo a Hofmann elimination reaction to release a nitroxide spin probe.

Introduction

The spin label technique has been widely used with biological polymers but to a lesser extent with synthetic polymers.[1-5] This technique involves the use of electron spin resonance (ESR) spectroscopy to monitor a paramagnetic molecule, such as a nitroxide, that is bound at a known site in the polymer and serves as a probe of its environment. We are applying the spin label technique to amine-cured epoxy systems, a class of thermoset polymers employed as the matrix phase in fiber-reinforced composites. This paper describes one aspect of this work, the experiments dealing with spin labeling the uncured resins. Some of the results were briefly discussed in an earlier communication.[5]

The epoxy resins investigated were the diglycidyl ether of bisphenol A (DGEBA) in the form of the commercial resin DER332[6] and tetraglycidyl diaminodiphenylmethane (TGDDM) in the form of the commercial resin MY720.[7] These resins were spin labeled with the nitroxide amines 4-(methylamino)-2,2,6,6-tetramethylpiperidinyl-1-oxy (METAMIN), 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy (TAMIN), 4-(dimethylamino)-2,2,6,6-tetramethylpiperidinyl-1-oxy (DIMETAMIN), and 3-(*N*-methyl-*N*-(6-(methylamino)hexyl)carbamoyl)-2,2,5,5-tetramethylpyrrolinyl-1-oxy (PYRODDH). The molecular structures of the resins and the nitroxides are shown in Figure 1.

Sample Preparation

The resins were heated at $\sim$340 K for 1 h prior to use to melt any crystals that had formed (DGEBA) and to reduce the viscosity sufficiently to allow dissolution of the added nitroxide. The nitroxide amines METAMIN, TAMIN, and DIMETAMIN were obtained from a commercial source[8] and were used as received. The PYRODDH was synthesized in this laboratory in the following manner. First, the imidazole derivative of 3-carboxy-2,2,5,5-tetramethylpyrrolinyl-1-oxy (CPNO) was prepared as an intermediate product. This intermediate (IPNO) was made from CPNO and carbonyldiimidazole (CD) as follows: With stirring, 13.6 mequiv of CPNO was added to a solution of 26.1 mequiv of CD in 100 mL of chloroform. After additional stirring in a dry nitrogen atmosphere for 1 h, the mixture was extracted with water, dried with molecular sieves, and filtered. Following evaporation of solvent, the solid residue was recrystallized twice from methylcyclohexane to yield long, yellow needles, which were dried under vacuum.

PYRODDH was prepared from the IPNO intermediate using the reaction shown in Figure 2. A solution of 3 mequiv of IPNO in chloroform was added to 6 mequiv of *N*,*N*′-dimethyl-1,6-diaminohexane (DDH), and the mixture was stirred overnight to yield a product solution that contained approximately 50% PYRODDH, 25% PYRODDH biradical, and 25% unreacted DDH. The PYRODDH and DDH were separated from the solution by extraction with dilute aqueous HCl followed by addition of a NaOH solution to the aqueous layer and extraction with chloroform. The ESR spectrum of this chloroform layer revealed that no biradical contaminant was present. Evaporation of the chloroform yielded the mixture of PYRODDH and DDH that was used as the spin label.

Spin-Labeling Reactions of DGEBA with Nitroxide Amines

Following addition of a nitroxide amine to DGEBA, a sequence of ESR spectra was observed, each spectrum

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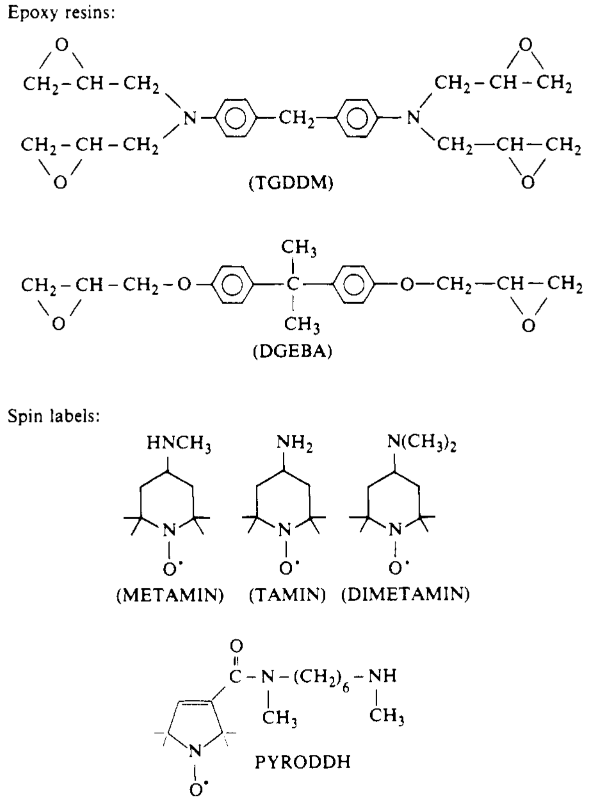

Figure 1. Epoxy resins and spin labels used.

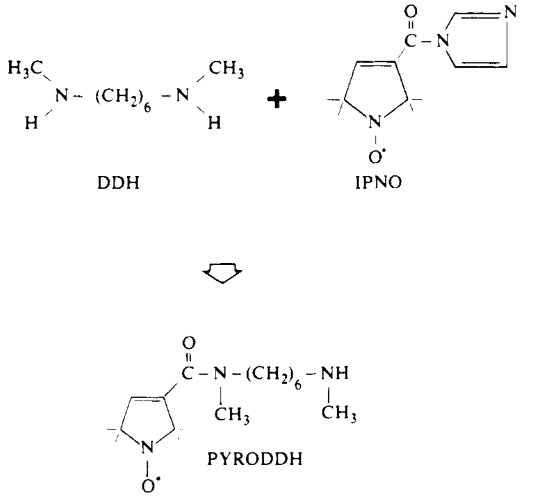

Figure 2. Synthesis of PYRODDH from DDH and IPNO.

corresponding to the appearance of a different nitroxide. For illustrative purposes, consider the results shown in Figures 3 and 4 obtained with the secondary amine METAMIN in DGEBA. Immediately after METAMIN was mixed with uncured DGEBA resin, the spectrum of the unreacted spin probe METAMIN was observed at 295 K (this spectrum is designated spectrum 1 in Figure 3). As the reaction proceeded at 295 K, the spectrum of a less mobile nitroxide developed (spectrum 2 in Figure 3) and increased in intensity as the intensity of spectrum 1 decreased. A typical sequence of spectra is shown in Figure 3. Following further heating at 360 K for ~24 h, a third spectrum (spectrum 3 in Figure 4) of an even more immobile species was observed. The third spectrum could be clearly distinguished from spectrum 2 only above 310 K. After prolonged heating of the solution at 360 K for ~70 h, yet another spectrum (spectrum 4 in Figure 4) consisting of three sharp lines superimposed on spectrum 3 was observed at 318 K.

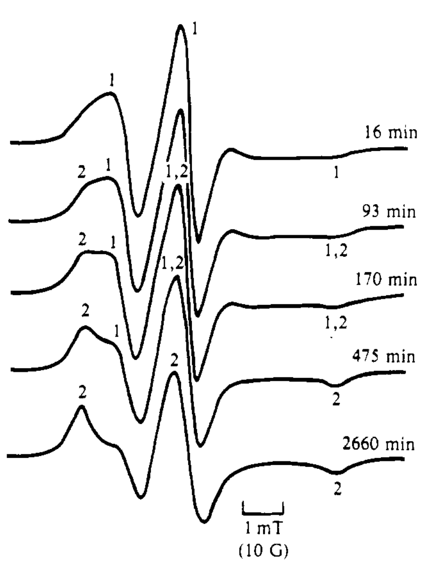

Figure 3. ESR spectra observed at 295 K for different times into the reaction of METAMIN with uncured DGEBA to form the end label (reaction temperature 295 K).

Spectrum 1 is assigned to the unreacted spin probe METAMIN, spectrum 2 to a DGEBA monomer end labeled with METAMIN, spectrum 3 to a spin-labeled quaternary base in which two DGEBA molecules are attached to a METAMIN molecule, and spectrum 4 to the spin probe TEMPENE. The structures of these nitroxides are shown in Figure 4. These spectral assignments have been confirmed in the following manner.

TEMPENE was synthesized from the iodide salt of 4-(trimethylammonio)-2,2,6,6-tetramethylpiperidinyl-1-oxy (TRIMETAMIN iodide) to verify that spectrum 4 could be conclusively assigned to the nitroxide TEMPENE. The TRIMETAMIN iodide was reacted with sodium isopropoxide to yield the TRIMETAMIN isopropoxide salt, which was thermally converted to TEMPENE at 410 K in an evacuated container. The TEMPENE was recovered on a cold-finger condenser by vacuum sublimation. TEMPENE was also purchased commercially,[8] where it was synthesized in a second manner. The starting material was 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (TANOL) in the form of its methanesulfonic acid ester. The latter was reacted with alcoholic potassium hydroxide to produce TEMPENE by elimination. The ESR spectra of both sources of TEMPENE were obtained in DGEBA. These spectra were virtually identical with one another and also with spectrum 4 at 318 K both in the splitting between the three hyperfine lines and in the relative heights of the three lines; i.e., the isotropic nitrogen hyperfine coupling constants and the motional correlation times were the same. Indeed, above 318 K these parameters were so distinctive that no nitroxide (including METAMIN, TAMIN, DIMETAMIN, and TANOL) other than TEMPENE fitted spectrum 4.

The TEMPENE forms as the result of a Hofmann elimination reaction[9-11] that involves a scission of the carbon–nitrogen bond in a spin-labeled quaternary base. Hence, the identification of the spin probe TEMPENE is an indication that its precursor, a spin-labeled quaternary base, can be assigned to spectrum 3.

Although we have not identified the exact mechanism for this elimination reaction, we have considered the possibilities of it proceeding through conformations that permit syn or anti orientations of the relevant β hydrogen with respect to the quaternary nitrogen.[10,11] In the case of the syn orientation that occurs in the energetically un-

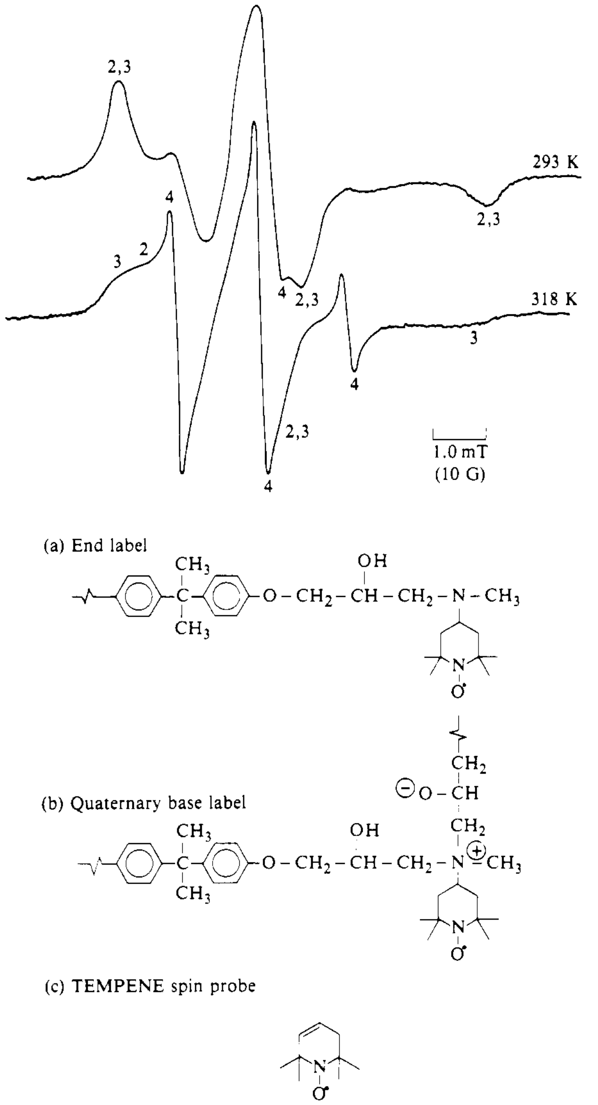

Figure 4. Spectra observed at 293 and 318 K after 72 h into the reaction of METAMIN with uncured DGEBA. Spectrum 2 denotes the spectrum of DGEBA end labeled with METAMIN. Spectrum 3 denotes the spectrum of the quaternary base. Spectrum 4 denotes the spectrum of TEMPENE. Structures of nitroxide species resulting from the reaction of DGEBA with METAMIN: (a) end-labeled DGEBA; (b) quaternary base; (c) TEMPENE spin probe.

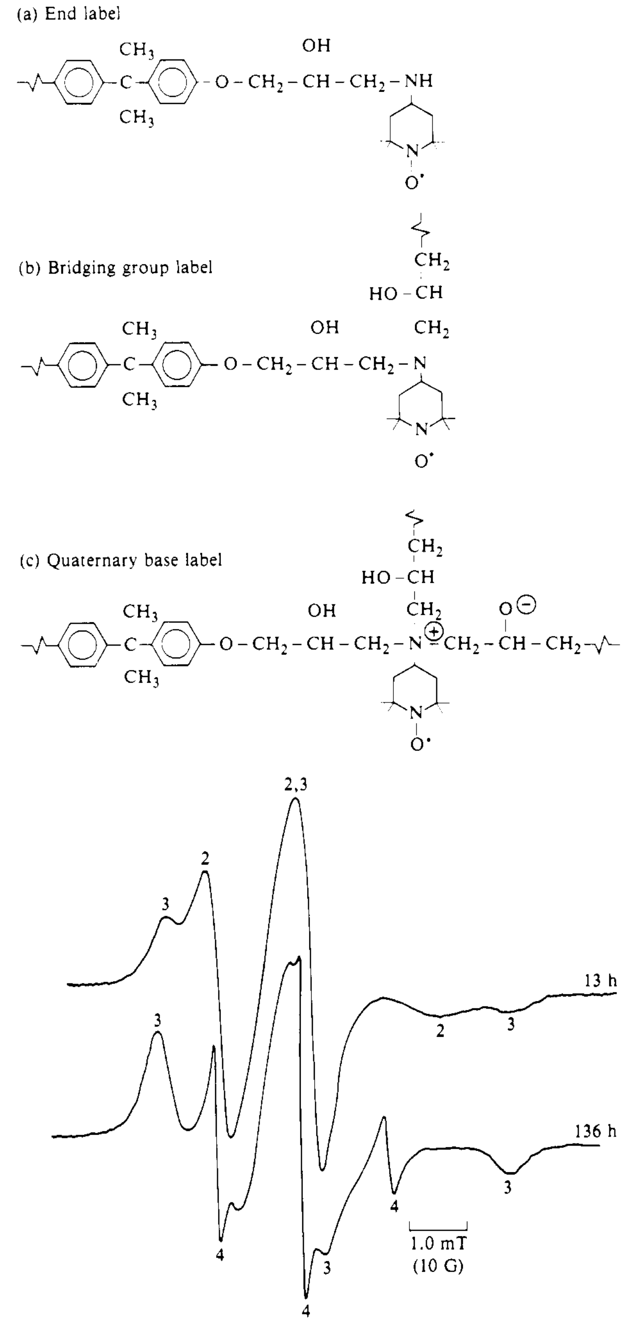

Figure 5. Structures of nitroxide species resulting from the reaction of DGEBA with TAMIN: (a) end-labeled DGEBA; (b) bridging group; (c) quaternary base. Spectra observed at 318 K after 13 and 136 h into the reaction of TAMIN with uncured DGEBA. Spectrum 2 denotes the spectrum of DGEBA end-labeled with TAMIN. Spectrum 3 denotes the spectrum of the bridging group and/or the quaternary base. Spectrum 4 denotes the spectrum of the TEMPENE spin probe.

favorable boat conformation of the piperidine ring, the O^- group associated with the quaternary nitrogen can interact easily with the β hydrogen. The contribution of this mechanism to TEMPENE formation is limited by the relative population of the boat conformation of the piperidine ring. On the other hand, in the case of the anti orientation that occurs in the chair conformation of the piperidine ring, molecular models show that the O^- group can interact with the β hydrogen only with difficulty.[12] However, the O^- group can also participate in a single homopolymerization reaction step (vide infra) by reacting with another epoxy group to produce a new O^- group that is an additional three bonds distant from the quaternary nitrogen (this would correspond to $n = 1$ in Figure 6 for the case of the DIMETAMIN reactions in DGEBA). This mechanism is probably more important than the syn elimination mechanism because the new O^- group has ample motional freedom to interact with the anti-oriented β hydrogen. Anti elimination involving an RO^- group that is located on an adjacent DGEBA molecule or originates from a trace amount of resin impurity (water or residual sodium hydroxide) is also possible. However, the importance of this mechanism cannot be estimated because of the difficulty in measuring the low RO^- concentration in the DGEBA resin.

A similar sequence of spectra was observed when TAMIN reacted with DGEBA. The situation is complicated by the fact that TAMIN can form an end label (Figure 5a), a bridging group (Figure 5b), and a quaternary base (Figure 5c). Spectra could be unambiguously identified with the spin probe TAMIN and the end label. However, only one spectrum could be associated with either the bridging-group label or the quaternary base. Yet, the positive identification of TEMPENE in the TAMIN/DGEBA reactions indicates that its precursor, the quaternary base, had indeed formed. Examples of the spectra observed at different times into the reaction of TAMIN with DGEBA are shown in Figure 5. These spectra indicate that after 13 h into the reaction at 353 K, the spectra of the end label and either the bridging group and/or the quaternary base are observed at 318 K, whereas after 136 h the spectrum of TEMPENE appeared along with the spectrum of the quaternary base.

The results of the reaction of DIMETAMIN with DGEBA are consistent with the above assignments of nitroxide species with the observed spectra. Thus, only three distinct spectra were observed following the mixing of DIMETAMIN and DGEBA. These spectra are associated with the DIMETAMIN spin probe, the spin-labeled quaternary base, and TEMPENE. The latter was not observed even after 14 days in samples that were kept below 300 K; on the other hand, at temperatures above 363 K, the TEMPENE appeared even before the complete disappearance of the spin probe DIMETAMIN. This behavior is indicative of a large activation energy for the Hofmann elimination reaction.

Spectral discrimination was essential for identification of the different spin labels and spin probes in the uncured resin when two or more radicals were simultaneously present. The principal values of the **g** tensor and nitrogen hyperfine tensor for all the nitroxide species investigated are similar enough that if two are present and both are undergoing slow tumbling, then their spectra are indistinguishable. Spectral discrimination was, however, achieved in many cases because the different nitroxide species had different motional correlation times.

If the molecular rotational motion is assumed to be that of a rigid sphere with radius a rotating in a liquid with viscosity η at temperature T, the motional correlation time τ_c is given by the Stokes–Einstein equation

$$\tau_c = \frac{4}{3}\frac{\pi\eta a^3}{kT} \qquad (1)$$

where k is the Boltzmann constant. Thus, differences in molecular size can provide the necessary spectral discrimination to allow species identification. Moreover, spectral discrimination can be optimized if the observation temperature is adjusted so that the resin viscosity is such that the rotational motion of the smaller nitroxide species is in the fast regime (i.e., $\tau_c < 3 \times 10^{-9}$ s) yet the motion of the larger species remains in the slow regime (i.e., $\tau_c > 3 \times 10^{-9}$ s). This feature is illustrated by the results shown in Figure 4. At 293 K it is not obvious that more than one spectrum is presesnt, whereas at 318 K three spectra associated with the end label, the quaternary base, and TEMPENE can be resolved.

There is evidence that there are parallel reactions to the Hofmann elimination. These reactions are of the type shown in Figure 6 involving the formation of a series of quaternary bases in which charge separation has been brought about by the stepwise addition of DGEBA molecules following oxirane ring opening by the O^- group.

The evidence presented for the existence of these different quaternary bases with different degrees of charge separation is contained in the temperature dependence of the ESR spectra. Figure 7 shows the temperature dependence of the collapse of the extrema splitting for two samples of DGEBA containing DIMETAMIN. One sample, a, which had been heated at 363 K for 6 h, contained the spin-labeled quaternary base only; the other sample, b, which had been heated at 363 K for 4 days, contained the spin-labeled quaternary base and a large amount of TEMPENE (the area under the TEMPENE spectrum was ~18% of the area under the total spectrum). As shown in Figure 7, the motional collapse of the extrema splitting for the spin-labeled quaternary base in sample b occurred

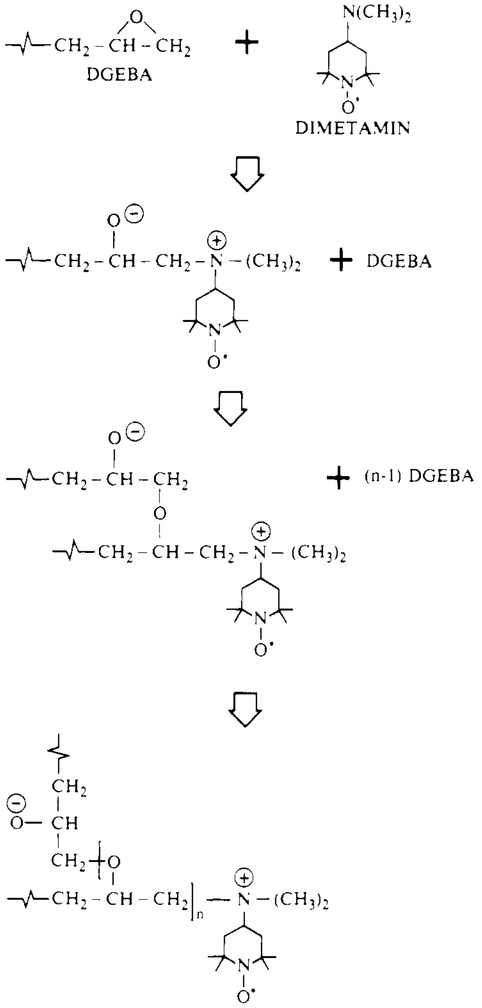

Figure 6. Reaction scheme for the formation of the different spin-labeled quaternary bases involved in the homopolymerization of DGEBA with DIMETAMIN as the initiator.

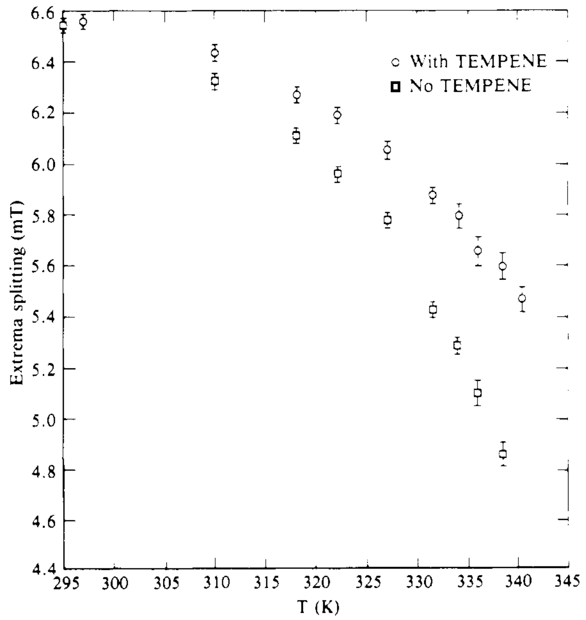

Figure 7. Temperature dependence of the extrema splitting for a sample of DIMETAMIN in DGEBA that had been heated for 4 days at 363 K (with TEMPENE) and also a sample that had been heated for 6 h at 363 K (no TEMPENE).

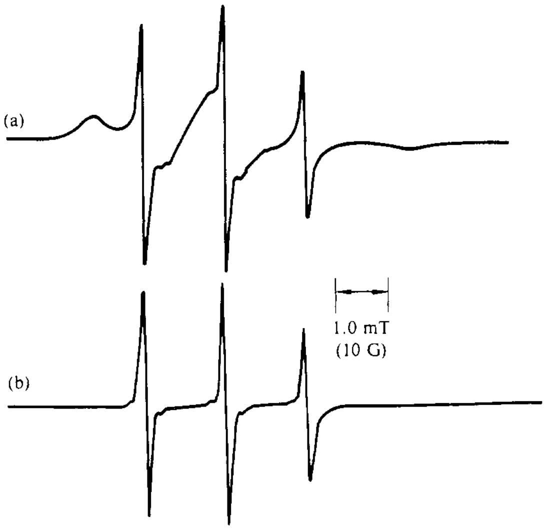

Figure 8. Spectra observed from (a) the reactions of DIMETAMIN with DGEBA and (b) TEMPENE in DGEBA.

at higher temperatures than those for the quaternary base in sample a. This result implies that at a given temperature the motional correlation time for the quaternary base in sample b is longer than that in sample a. If eq 1 is valid, the reason for the difference in correlation time is either an increase in the molecular size of the quaternary base or an increase in the viscosity of the resin because of extensive cross-linking resulting from catalytic homopolymerization. The latter effect was shown to be negligible since only small amounts of DIMETAMIN were used (these samples contained <0.08 wt % DIMETAMIN). Thus, a sample of DGEBA containing only TEMPENE exhibited a three-line spectrum with the same relative intensities as the spectrum exhibited by TEMPENE produced in the DIMETAMIN reaction with DGEBA (see Figure 8). The identical spectra indicate the same value of the motional correlation time for TEMPENE in both samples, thus proving that the resin viscosity was unaffected by the presence of the quaternary base. Hence the data in Figure 7 imply that there is an increase in the molecular size of the quaternary base with time, presumably because of reactions of the type shown in Figure 6. Indeed, if there is enough DIMETAMIN present as an initiator, quaternary base reactions of the type shown in Figure 6 can lead to homopolymerization of the DGEBA, as evidenced by our preparation of a cured rigid sample of DGEBA containing only ~5 wt % DIMETAMIN as the curing agent.

The reactions of PYRODDH with the epoxy DGEBA were also investigated by studying the ESR line shapes as a function of time. The amine functionality of PYRODDH should be similar to that of DDH. The PYRODDH spin label was therefore of interest since it could be considered as a model compound for DDH in its reactions with DGEBA. Furthermore, since the nitroxide group in PYRODDH is at the end of a flexible chain, fast rotational motions (i.e., $\tau_c < 3 \times 10^{-9}$ s) should occur at lower temperatures for the PYRODDH spin label than for the more rigidly attached labels such as TAMIN or METAMIN. This difference could be advantageous for spin-label studies where it is necessary to evaluate the motional correlation times from the EPR line shapes using the theory of Kivelson.[13]

When PYRODDH was allowed to react with DGEBA, the ESR spectrum observed at 313 K indicated that the PYRODDH became increasingly immobilized as the reactions progressed. These reactions appeared to be complete after 18 h at 363 K since longer heating produced no additional spectral changes. By analogy with the METAMIN/epoxy reactions at 360 K, it seems likely that PYRODDH forms both the end label and the quaternary base. Unfortunately, it was not possible to verify the formation of both these spin-labeled products since only two EPR spectra could be identified (i.e., one spectrum for the PYRODDH spin probe and one for a spin label). This observation implies that both spin labels have approximately the same value for the motional correlation time at all temperatures. Furthermore, since no mobile Hofmann elimination product analogous to TEMPENE was observed after prolonged heating, the presence of a quaternary base could not be conclusively demonstrated.

The results of the spin labeling of TGDDM with METAMIN, TAMIN, or DIMETAMIN are similar to the results with DGEBA in that an end label, a spin-labeled quaternary base, and the Hofmann elimination product TEMPENE were identified. For illustrative purposes, the temperature dependence of the spectra observed at an early stage (after 15 min at 363 K) in the reaction of DIMETAMIN with MY720 is shown in Figure 9a. Above 330 K the spectrum of the quaternary base (designated Q in Figure 9a) can be distinguished from that of the unreacted spin probe DIMETAMIN (designated P). The temperature dependence of the spectra observed at a later stage (after 90 min at 363 K) in the same reaction is shown in Figure 9b. Above 340 K the spectrum of the spin probe TEMPENE (the peaks are designated T in Figure 9b) can be clearly distinguished from that of the quaternary base (designated Q).

As the reactions of the nitroxide amines with MY720 proceeded, the total integrated ESR intensity decreased with time because the nitroxide decomposed to form diamagnetic products. After ~8 h into the reactions at 363 K, this decrease was so great (over 1 order of magnitude) that achieving an adequate signal-to-noise ratio became a problem. It was therefore necessary to signal average the spectra using a data acquisition system (Varian E-900) for samples that had been heated longer than 4 h. Most of these spectra were the result of 25 scans, so that an improvement in signal-to-noise ratio of 5 was realized.

Infrared Measurements in the Uncured Epoxy Containing TAMIN

The reaction of TAMIN with uncured DGEBA was monitored with infrared spectroscopy to obtain additional or new information supporting the conclusions of the ESR results. In particular, it was hoped that it would be possible to distinguish between the binding of TAMIN to one, two, or more DGEBA molecules.

Both the DGEBA and TAMIN were dried over P_2O_5 at 335 and 298 K, respectively, using a drying pistol. These materials were then mixed under a dry-nitrogen atmosphere and monitored with an infrared spectrometer (Perkin-Elmer Model 457). Standard solution cells with potassium bromide windows and a 0.1-mm path length were used. The absorption bands at 3.03 and 2.97 μm, identified with TAMIN NH stretching vibrations, decreased in intensity with time, and a strong, broad absorption band, presumably attributable to alcoholic OH stretching vibrations, appeared at 2.93 μm. This new absorption band is consistent with the reaction of an amine with an epoxy whereby OH groups are produced as a result of an opening of the oxirane ring.

The rate of decrease of the peaks attributed to TAMIN NH stretching and bending vibrations, 2.97 and 14.7 μm, respectively, indicate that DGEBA reacts with TAMIN at a rate that is consistent with the reaction rates indicated

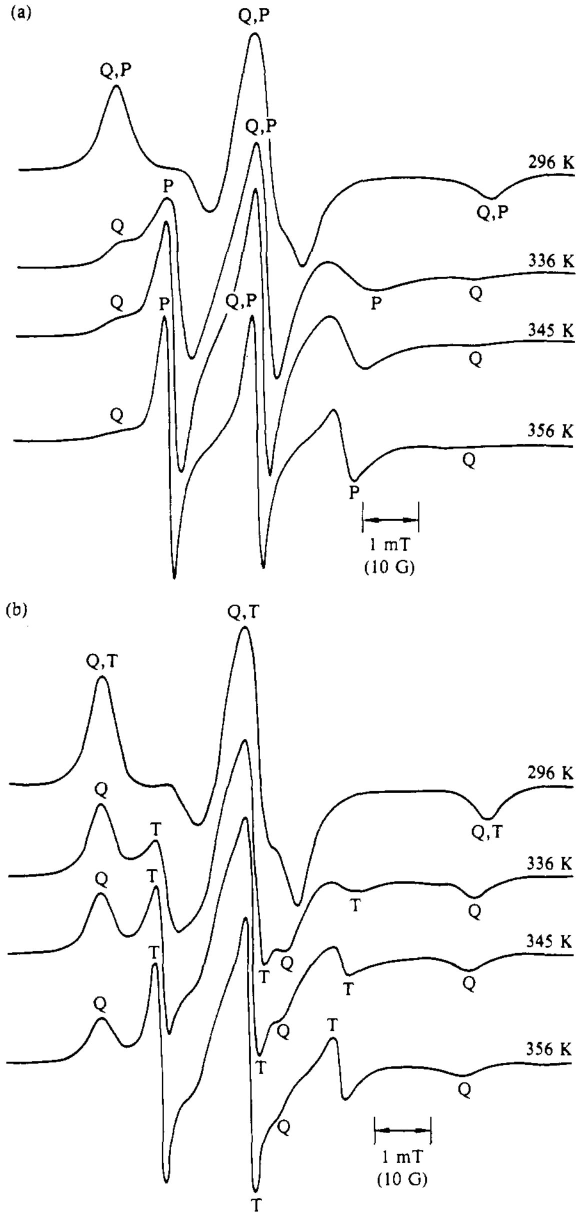

Figure 9. ESR spectra observed at the temperatures shown from a sample of MY720 containing DIMETAMIN after heating at 363 K for (a) 15 min and (b) 90 min. The derivative peaks associated with the unreacted DIMETAMIN spin probe, the quaternary base, and TEMPENE are designated P, Q, and T, respectively.

from the ESR results; the reaction at 300 K was essentially complete in ~8 h. However, in contrast to the detailed conclusions inferred from the ESR results where it was possible to positively identify an end label, a quaternary base, and the spin probe TEMPENE, it was not possible to conclude from the infrared spectra the number of DGEBA molecules bound to TAMIN.

Conclusions

In the reactions of the nitroxide amines with the DGEBA resin, the spectral discrimination between the different spin-labeled products is distinct enough and the reaction rates are sufficiently slow to allow a spectroscopic monitoring of the initial addition products. Thus, ESR spectroscopy was used to monitor the addition of nitroxide amines to one, two, three, and more DGEBA molecules and also to detect the presence of the spin probe TEMPENE which is the product of a Hofmann elimination reaction. Moreover, the ESR spin-labeling method would appear to be the only spectroscopic method capable of providing such details of the reactions between an epoxy and a nitroxide amine. The nitroxide amines can be viewed as model compounds for aliphatic amines, so that the reactions that have been identified in the spin-labeling experiments should provide some insight into analogous reactions that occur when epoxy resins are cured with conventional amine curing agents.

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Registry No. TAMIN, 14691-88-4; PYRODDH, 87655-74-1; TGDDM, 31305-94-9; DGEBA, 25085-99-8; DDH, 13093-04-4; IPNO, 26405-33-4; METAMIN, 42585-33-1; DIMETAMIN, 71335-68-7.

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