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Investigation of the Curing of Phenolic Resins by ^2H NMR Spectroscopy

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Received September 11, 1984

ABSTRACT: The curing of specifically deuterated phenol/formaldehyde resins has been studied by ^2H quadrupole echo NMR. The ^2H NMR spectra of the cured resins are characterized by quadrupole patterns with a rigid limit quadrupole splitting, indicating that the resin is rigid on a time scale of 10^5 Hz. The ^2H NMR spin–lattice relaxation times, which reflect motional processes in the materials, show a rapid increase with curing time followed by a leveling off. This increase in T_1 parallels the increase in the number of cross-links, as reflected by the increase in the methylene/methylol ratio, detected by ^{13}C solid-state CP MAS NMR. Resins prepared with deuterated formaldehyde also show the presence of C^2H_3 groups when they are cured at 120 °C for 4 h or more, indicating that degradation of the resin is occurring.

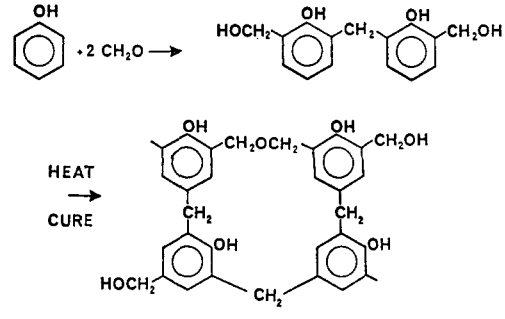
Introduction

The reaction of phenol with formaldehyde to give phenolic resins is of significant commercial importance. The cured resin, commonly called Bakelite, is highly cross-linked, giving it considerable mechanical strength and good ablative properties.

If the polymerization reaction is performed under basic conditions a resol-type product (prepolymer) is formed. Curing of the resol gives a polymer with free methylol groups but cross-linked with methylene bridges and benzyl ether linkages (Scheme I). The solid-state curing of the resin has been studied extensively by ^{13}C solid-state CP MAS NMR.[1-4] The combined[5] use of cross polarization (CP),[6] high-power decoupling, and magic angle spinning (MAS)[7] has enabled high-resolution ^{13}C spectra of the solid polymers to be obtained. The curing process is characterized by a decrease in the intensity of the resonance attributed to free methylols and benzyl ether linkages, both of which are also detected by IR.[8] As this resonance decreases, there is a concomitant increase in the intensity of the peak assigned to bridging methylene groups. This variation in the methylene/methylol peak area has been used to monitor the curing process of phenol/formaldehyde resins at a variety of temperatures.[2,3]

In the present study, the curing process has been studied by ^2H NMR. Since deuterium has a spin $I = 1$ the deuterium nucleus has a quadrupole moment, which arises from the nonspherical charge distribution inside the nucleus. In the solid state, the ^2H NMR spectrum is completely dominated by the interaction of this quadrupole moment with the electric field gradient generated by the C–^2H bonding electrons. For a single crystal containing only one type of deuteron the ^2H NMR spectrum will show two lines, for the two allowed transitions, with a spacing ($\Delta\nu$) equal to the strength of the quadrupole interaction

Scheme I



(the quadrupole coupling constant) modulated by the orientation of the C–^2H bond with respect to the external magnetic field. The magnitude of this quadrupole interaction is shown in eq 1, where θ is the angle between the C–^2H bond vector and the magnetic field and e^2qQ/h is the quadrupole coupling constant.

$$\Delta\nu = \frac{3}{4}\frac{e^2qQ}{h}(3\cos^2\theta - 1) \quad (1)$$

However, since the cured phenolic resin is amorphous, all possible orientations of the C–^2H bond can occur. The resulting spectrum is a Pake doublet with the singularities (the $\theta = 90°$ orientations and indicated by the arrows in Figure 2B) separated by the quadrupole splitting, $\Delta\nu_Q$.

$$\Delta\nu_Q = \frac{3}{4}\frac{e^2qQ}{h} \quad (2)$$

For aliphatic deuterons the coupling constant generally takes a value of ≈167 kHz while aromatic deuterons have a value of ≈176 kHz. This leads to quadrupole splittings of ≈125 kHz for rigid aliphatic deuterons and ≈132 kHz

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for rigid aromatic deuterons.

Because of the low natural abundance of the deuterium isotope it is necessary, for the NMR experiment, to synthetically increase the deuterium levels. While this requires extra effort, it does result in a deuteron placed specifically at one location in the molecule. This enables a study to be made of only the motions which are occurring at the site of the deuterium label. Further, because ^2H is a nonperturbing probe (unlike a spin label) it presents a cleaner picture of the motions occurring at the molecular level.

The presence of motions which are fast compared to the quadrupole interaction ($>1 \times 10^5$ s^{-1}) will modulate the electric field gradient tensor and narrow the spectrum.[9,10] Since the electric field gradient is axially symmetric, the effect of anisotropic motions on the observed NMR line shapes will often be predictable. Because of this, the influence of molecular motions on the spectra of deuterated polymers has recently become an area of interest.[10]

For a quadrupole nucleus such as deuterium, the spin–lattice relaxation process, which is characterized by a spin–lattice relaxation time, T_1, is dominated by fluctuations of the quadrupole interaction.[11] Since the quadrupole interaction is entirely intramolecular in nature, the T_1 values can give information on the rates of molecular motions. In particular, T_1 is sensitive to rates of motions with frequencies of the order of the deuterium NMR frequency. That is, the ^2H T_1 values will be sensitive to the density of motions with frequencies near 30 MHz.

Experimental Section

The deuterated formaldehyde, ^{13}C-enriched formaldehyde, and perdeuterated phenol were obtained from MSD Isotopes, Quebec. The [3,5-$^2H_2$]phenol was prepared from perdeuterated phenol by base-catalyzed exchange in water in order to remove the deuterons from the 2, 4, and 6 positions.[12] Mass spectral analysis of the [3,5-$^2H_2$]phenol indicated less than 2% residual deuterium at the "protonated" 2, 4, and 6 positions.

The resin samples were prepared by condensing phenol and formaldehyde in the presence of base (phenol/formaldehyde/NaOH = 1/2/0.01) and then vacuum distilling off the excess water.[13] Two separate sets of resin samples were prepared: the first contained deuterated formaldehyde with unlabeled phenol and the second used [3,5-$^2H_2$]phenol with 5% ^{13}C-enriched formaldehyde. The prepolymers were analyzed by high-resolution ^{13}C solution NMR and three selected for the experiments presented in this paper. They were one sample prepared with specifically deuterated phenol having a methylene/methylol ratio (indicative of the degree of curing) of 0.35 and two samples prepared from deuterated formaldehyde having methylene/methylol ratios of 0.30 and 0.44. The samples were then cured as thin films, between two hot plates, at 75 or 120 °C, for varying times.

The ^2H NMR spectra were obtained on a Bruker CXP-200 operating at 30.72 MHz. Spectra were acquired by using the quadrupole echo sequence,[14] with full phase cycling of the 90° (4.5 μs) pulses and with 50-μs pulse spacings. Spectra were often acquired with 45° (2.25 μs) pulses in order to obtain better line shapes by minimizing the effects of pulse roll-off.[15] The spin–lattice relaxation times were determined by using a modified saturation–recovery sequence. The center of the quadrupole pattern and the two peaks were first saturated with a DANTE pulse sequence.[16] The DANTE sequence uses a train of short pulses with a fixed pulse spacing to create a condition where only a narrow spectral window, centered on the resonance frequency, is excited. As well, excitation also occurs in sidebands which are separated from the center by ±1/pulse spacing. By using a large number of short, carefully spaced pulses, three saturating holes were burned in the quadrupole pattern (at the center and at the two singularities). Typically 1000 pulses of duration 0.35 μs (≈7°) were used with a pulse spacing of 15.9 μs for the formaldehyde-deuterated samples and 15.2 μs for the phenol-deuterated samples. A variable delay was then introduced to allow the sample to partially relax and the spectrum was acquired with the quadrupole echo sequence. Typically, 10–12 delays were used and the data were fitted to a straight line.

Quantitative ^{13}C MAS spectra were obtained at 22.6 MHz with a Bruker CXP-100 spectrometer. A home-built probe with an Andrew–Beams spinning apparatus was used to spin Kel-F spinners at ≈3 kHz. Quantitative ^{13}C spectra were obtained by MAS, with high-power decoupling during acquisition and a 120-s recycle time.

Results and Discussion

In order to probe both the cross-linking bridges and the aromatic rings, it is necessary to have separate samples which are labeled at only one of the sites. As well, for the phenol it is necessary to ensure that the deuterons are only at the 3 and 5 positions. Since the cross-linking occurs at the 2, 4, and 6 positions (see Scheme I), the presence of deuterons at these positions would result in their loss from the ring and possible incorporation elsewhere in the polymer.

The use of specific deuterium labeling makes it possible to very directly and unambiguously probe the dynamic structures of specific points in an organic molecule. However, in the case of polymers and other complex molecules, a problem exists in that it is difficult to prepare a series of specifically labeled samples which are *identical* in all other respects given the number of compositional variables (for example, composition, sequence, tacticity, molecular weight, and degree of curing) except for the position of the label. Thus, there is ambiguity in that spectral changes observed in the deuterium spectra may reflect differences in the different samples rather than differing mobilities of different positions in the polymer.

In the present work where the major variable is the degree of curing this problem has been circumvented by characterizing the phenol-deuterated material in terms of composition and degree of curing (measured by the methylene/methylol ratio) by high-resolution ^{13}C solution NMR. Several samples of formaldehyde-deuterated material were then prepared and two chosen of identical composition to the phenol-deuterated material but with slightly higher and lower degrees of curing. The results on the cured samples indicated that differences in the prepolymers were not a contributing factor to the spectral changes.

Prepolymer. The prepolymers formed from the reaction of phenol with formaldehyde are viscous liquids whose high-resolution, ^{13}C solution spectra show some cross-linking to have occurred.[2] The quadrupole echo ^2H NMR spectra of the neat, specifically deuterated prepolymers are shown in Figure 1. The spectrum of the [3,5-$^2H_2$]-phenol containing resol (methylene/methylol = 0.35) consists of two components. The first is a large isotropic line and the second a broad quadrupole pattern (Pake doublet) with a quadrupole splitting of $\Delta\nu_Q$ = 130 kHz. The presence of two components indicates that while some of the prepolymer is sufficiently mobile to give a narrow line, a large portion (≈50%) of the prepolymer is already so extensively cross-linked that it is rigid at a local level on the NMR time scale.

For the [$^2H_2$]formaldehyde containing prepolymer of methylene/methylol ratio = 0.30, the ^2H NMR spectrum shows only a narrow line, indicating a very mobile prepolymer. The ^2H NMR spectrum of the slightly more cross-linked material (methylene/methylol = 0.44) indicates the presence of some rigid moieties, presumably due to the slightly higher degree of curing, but spectra obtained on both samples after further curing are identical, as are their relaxation times, indicating that these small differences in the prepolymers do not play a significant role in

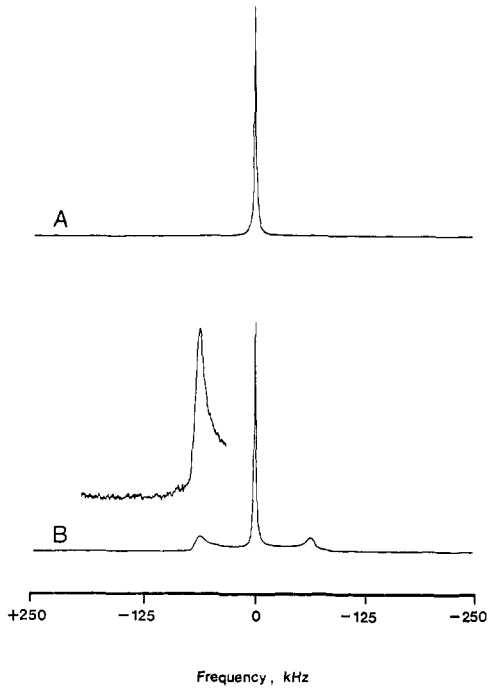


Figure 1. ^2H NMR spectra of the two phenol/formaldehyde prepolymers: (A) [$^2H_2$]formaldehyde-containing prepolymer (methylene/methylol = 0.30); (B) spectrum of [3,5-$^2H_2$]phenol-containing prepolymer (methylene/methylol = 0.35).

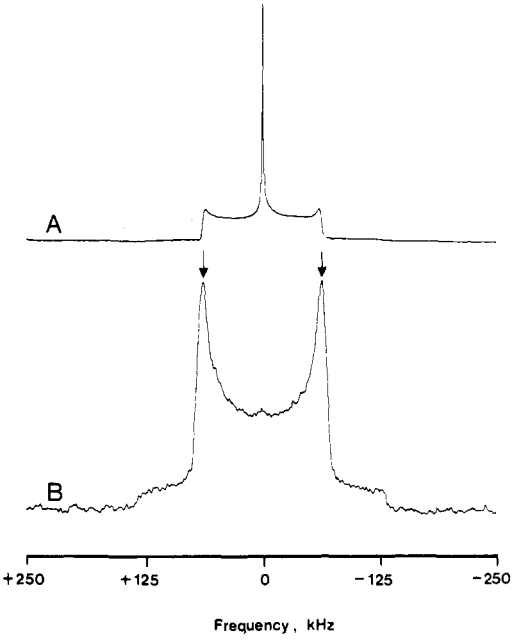
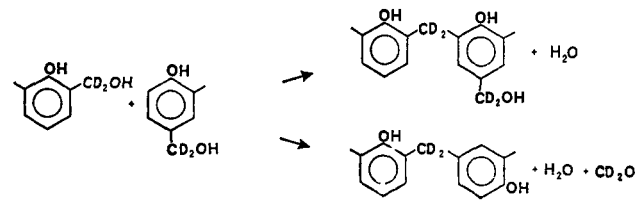


Figure 2. ^2H NMR spectra of the two phenol/formaldehyde resins cured at 75 °C for 180 min: (A) [$^2H_2$]formaldehyde-containing resin; (B) [3,5-$^2H_2$]phenol-containing resin. The arrows indicate singularities in the spectrum referred to in the text.

determining the dynamic structures of the cured materials.

Influence of Curing on the ^2H NMR Line Shape. Curing of the phenolic resins is known to substantially increase the extent of cross-linking.[2-4] This is reflected in the ^2H NMR spectra by a very rapid increase in the intensity of the rigid quadrupole pattern at the expense of the narrow, isotropic component. Figure 2 shows the ^2H NMR spectra of the two labeled resins after 3 h of curing at 75 °C. For the [3,5-$^2H_2$]phenol containing resin, the spectrum consists of only a rigid quadrupole pattern with $\Delta\nu_Q \approx 133$ kHz. The lack of any remaining isotropic component indicates that the phenyl rings are completely

Scheme II



rigid, due presumably to cross-links through the 2, 4, and 6 positions of the ring. This rigid line shape is seen for all of the resins with deuterium at the meta positions.

For the resin made from [$^2H_2$]formaldehyde, the spectrum shows a quadrupole pattern with $\Delta\nu_Q = 122$ kHz. There is, however, considerable spectral intensity in the center of the pattern compared to the completely rigid pattern shown in Figure 2B indicative of a substantial contribution from intermediate degrees of motion. In addition, the spectrum still shows a very narrow central line, although considerably reduced in intensity. Further curing of this sample for as much as 21 h at 75 °C did not substantially change this ratio. For [$^2H_2$]formaldehyde-containing samples cured at temperatures of 120 °C there was no evidence for this narrow line.

The presence of a narrow isotropic line in the ^2H NMR spectrum is indicative of a rapidly reorienting species. Its observation in the prepolymer indicates that a large portion of the formaldehyde-derived functionalities in the prepolymer is still mobile. However, its observation in the cured samples is likely a result of small deuterium-containing molecules given off in the curing process. The conversion of C^2H_2OH to C^2H_2 groups could liberate $C^2H_2{=}O$ as shown in Scheme II.[2,3] Support for this explanation comes from the completely rigid ^2H NMR spectrum observed for the [3,5-$^2H_2$]phenol containing resin cured at the same temperature. Since this resin is labeled at only the meta positions of the phenol, none of the deuterons will be lost as small molecules, as occurs for deuterons introduced with formaldehyde. Finally, if the [$^2H_2$]formaldehyde-containing resin is cured at 120 °C, no narrow line is observed. It is likely therefore that any small molecules, for example $C^2H_2{=}O$, are driven off from the resin at these higher temperatures.

Curing of the [$^2H_2$]formaldehyde-containing resins at 120 °C for periods of at least 4 h results in the introduction of a new spectral feature (Figure 3A). The new feature is a quadrupole pattern with a quadrupole splitting of $\Delta\nu_Q = 40$ kHz. A splitting of 40 kHz is typically found for deuterated methyl groups, which are able to undergo rapid rotation about their C_3 axis.[9,10] Figure 3B shows the spectrum of the [3,5-$^2H_2$]phenol containing resin after a similar curing, where no C^2H_3 groups are observed.

Influence of Curing on T_1. The most noticeable effect of increased curing on the deuterium-containing resins was an increase in the measured spin–lattice relaxation times. Because of the difficulty in completely inverting the total quadrupole pattern with the 9-μs, $\pi/2$ pulses available on our spectrometer, an exact determination of the T_1 by inversion–recovery methods was impractical. Instead, a DANTE pulse sequence[16] was used to saturate portions of the quadrupole pattern and the recovery of these "holes" to equilibrium was then monitored.

The T_1 was determined for each of the three labeled resins, at 75 °C and 120 °C, for a variety of curing times. Figure 4 shows the results presented as plots of the T_1 vs. curing time. The close agreement in the relaxation properties of the two C^2H_2O-labeled systems confirms that the small differences in the degrees of cross-linking of the

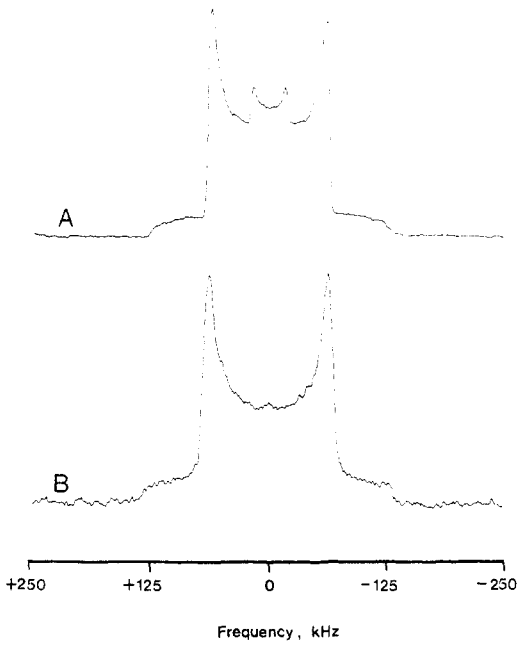


Figure 3. ^2H NMR spectra of the two resins cured at 120 °C for 4 h showing the formation of C^2H_3 groups in (A) [$^2H_2$]formaldehyde-containing resin and (B) [3,5-$^2H_2$]phenol-containing resin.

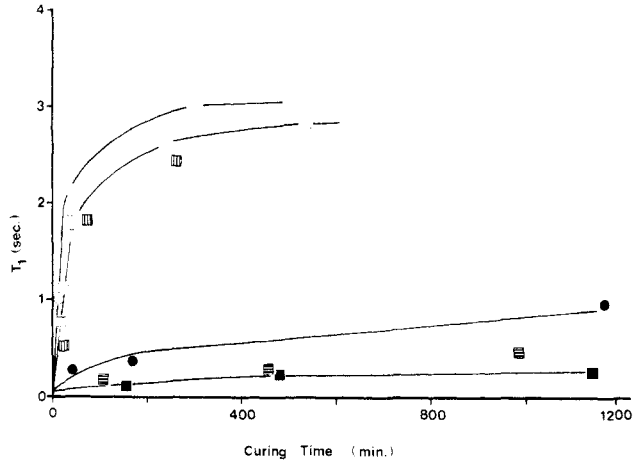


Figure 4. Plot of the spin–lattice relaxation time vs. the curing times for various deuterated phenolic resins: (■) [$^2H_2$]formaldehyde resin (methylene/methylol = 0.30) cured at 75 °C; (▣) [$^2H_2$]formaldehyde resin (methylene/methylol = 0.44) cured at 75 °C; (●) [3,5-$^2H_2$]phenol resin (methylene/methylol = 0.35) cured at 75 °C; (□) [$^2H_2$]formaldehyde resin (methylene/methylol = 0.30) cured at 120 °C; (▣) [$^2H_2$]formaldehyde resin (methylene/methylol = 0.44) cured at 120 °C; (○) [3,5-$^2H_2$]phenol resin (methylene/methylol = 0.35) cured at 120 °C.

prepolymers do not make a significant contribution to the dynamical properties of the cured systems. It is worth noting that the data for each T_1 could be fit very well with a single-exponential relaxation. This indicates that for the [$^2H_2$]formaldehyde-labeled resins, the methylene and methylols have essentially the same T_1's. Similarly, although the aromatic rings will be cross-linked to different extents, the T_1's of the meta positions must be very similar in all of the isomeric cases.

The T_1 curves are characterized by a rapid increase during the initial stages of the curing process followed by a more gradual leveling off. For samples cured at 120 °C the early curing stage was most dramatic, with the T_1's rising quickly from ≈50 ms for the prepolymer to over 2 s before leveling off. However, the samples cured at 75 °C did not rise over 400 ms in this early curing period.

The increase in the ^2H T_1's with increasing curing results from a decrease in the density of motions near the deuterium NMR frequency. This loss of motion results from an increase in the number of cross-links which occurs with curing. As the sample becomes more extensively cross-linked, the polymer becomes more efficiently tied down, eliminating many of the possible motions.

The increase in cross-linking with curing has also been studied by solid-state ^{13}C NMR.[1-4] These studies have shown an increase in the methylene/methylol ratio which parallels the ^2H T_1 changes reported in this study. As an internal check, the [3,5-$^2H_2$]phenol-containing resin was prepared with the formaldehyde enriched with ^{13}C. Quantitative ^{13}C MAS NMR showed a rapid increase in the methylene/methylol ratio as the sample was cured, followed by a gradual leveling off. After 20 h of curing at 75 °C the methylene/methylol ratio reached 1.3, from 0.35 in the prepolymer. For samples cured at 120 °C this ratio reached 2.2 before leveling off.

Conclusions

The application of wide-line ^2H NMR to the study of phenolic resins provides a new look at the curing process. The ^2H NMR spectra of specifically deuterated, cured resins consist of a rigid limit quadrupole splitting. This indicates that the resins undergo no large-scale motions on a time scale of $>10^5$ s^{-1}. The spectra of [$^2H_2$]formaldehyde-containing resins, cured at 120 °C for 4 h, exhibit spectra consistent with the formation of C^2H_3 groups, which are a known degradation product.[13]

The ^2H spin–lattice relaxation times exhibit a rapid increase in the initial stages of the curing followed by a gradual leveling off. This trend parallels and, indeed, is likely a consequence of the increase in the methylene/methylol ratio, which results from the cross-linking process.

Acknowledgment. We acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada in the form of an operating grant (C.A.F.) and a Graduate Fellowship (M.S.M.) and the Province of Ontario for a BILD matching grant (C.A.F.). We also thank the South Western Ontario High Field NMR Centre.

Registry No. (Phenol)·(formaldehyde) (copolymer), 9003-35-4.

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