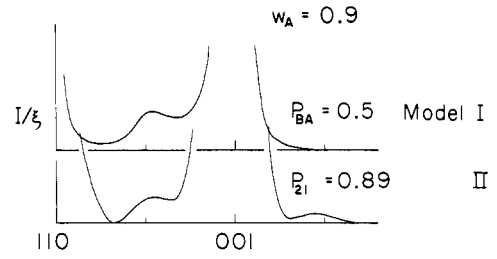

Figure 3. Calculated intensity distributions for models I and II.

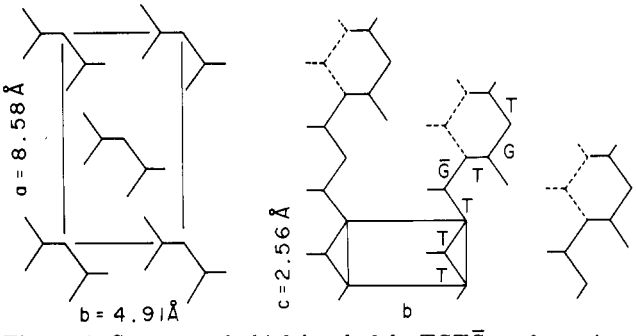

Figure 4. Structure of a kink band of the TGT$\bar{G}$ conformation.

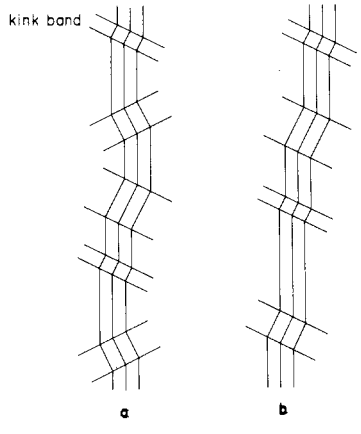

Figure 5. Schematic representation for two types of arrangements of the kink bands in a crystallite.

case of form I, two types of arrangements are also presumed to give different intensity distributions. Therefore, the arrangement assumed in the intensity calculation (Figure 5b) seems to be reasonable because the calculated intensity distributions reproduce the observed one well. This arrangement suggests that the formation of the kink bands is closely associated with a shear stress.

The diffuse streak scattering is observed generally on the fiber diagram of form I prepared by stretching unoriented form II. Accordingly, two mechanisms can be considered for the formation of the kink bands: (1) the TGT$\bar{G}$ conformation of form II remains, in part, after the transformation to form I and it forms a band in the crystallite of form I and (2) the kink bands are formed in the crystallite of form I by a shear stress after the transformation to form I. The kink bands in form II appear as an intermediate structure between forms II and III, arising from the flip-flop motion during the heat treatment.[3,8] However, it seems likely that the kink bands of the planar zigzag conformation also may be introduced into the crystallite of form II by a shear stress. Accordingly, the transformation from form II to form I is considered to be a kind of martensitic transformation. In other words, a shear stress forms the kink bands of the planar zigzag structure in the crystallite of form II, the kink bands grow in thickness, and, finally, form I results from the self-diffusion of the molecules into each stable position. From this consideration, the first mechanism seems to play an important role. In both mechanisms, the kink bands in form I result from a shear stress applied to the ends of the crystallite during the deformation process in contrast to the kink bands in form II. Furthermore, the formation of the kink bands may be associated with the transformation of form II to form I on stretching.

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Application of High-Resolution ^{13}C NMR Spectroscopy Using Magic Angle Spinning Techniques to the Direct Investigation of Solid Cured Phenolic Resins

Phenolic resins, formed from the reaction of phenol with formaldehyde, were among the very first completely synthetic polymers made[2] (Bakelite) and still find very wide commercial applications.[3]

The reaction is carried out under two general types of reaction conditions as indicated in Schemes I and II.

In both cases the final polymers are highly cross-linked, giving considerable mechanical strength to articles fabricated from them. Reaction under alkaline conditions yields a product which contains methylene bridges, dibenzyl ether linkages, and free methylol (CH_2OH) groups. Under acidic conditions the condensation product contains methylene bridges. However, conclusions regarding the structure of the final cured products are by inference only, as the high degree of cross-linking which gives them their useful mechanical properties also renders them completely insoluble in all solvents. Application of most analytical techniques to the determination of their structures is not practical, although IR spectroscopy has had limited success, being able to distinguish methylol from dibenzyl ether groupings from their C–O stretching frequencies.[4]

In recent years it has been shown that a combination of cross-polarization,[5] high-power decoupling, and magic angle spinning techniques[6] can be used to obtain high-resolution ^{13}C NMR spectra of solid materials, and a number of such studies have indicated the power and versatility of this technique.[7-9] The technique is particularly useful in the application to resins and other solid materials which are insoluble.[10] The present communication describes in outline the potential application of these techniques to the determination of the structures of solid phenolic resins and related compounds. Spectra were recorded on a Bruker CXP 100 spectrometer by using the

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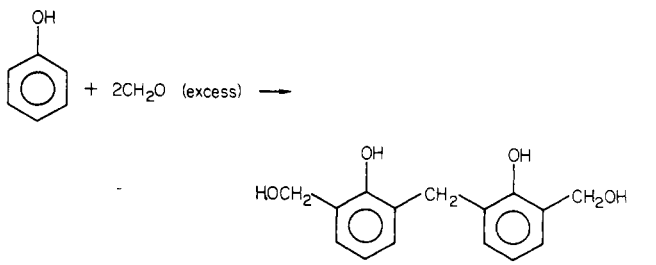
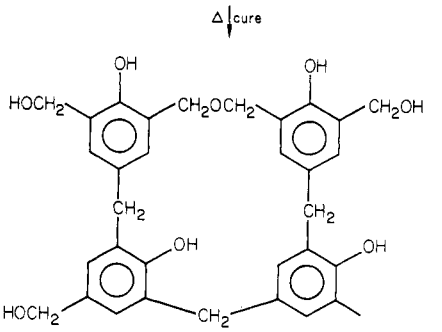
Scheme I

Alkaline Conditions

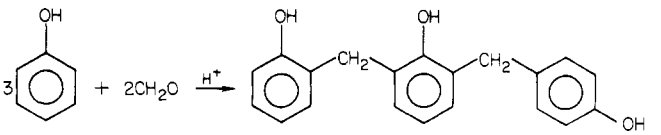


resol-type products

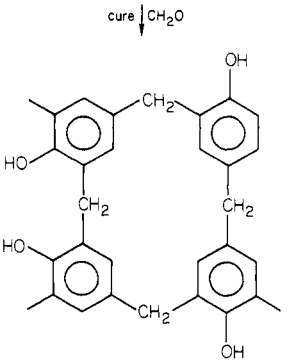


Scheme II

Acidic Conditions



novolac-type products



network polymer

spinning apparatus previously described.[11] The resins were cured at selected temperatures in an accurate mold into the appropriate shape for fast sample spinning.

The spectra obtained for a typical cured resol-type material prepared under alkaline conditions (phenol/formaldehyde/sodium hydroxide = 1/2/0.01, cured at 110 °C for 24 h) are shown in Figure 1. Figure 1A shows the ^{13}C spectrum of the solid resin without sample spinning. The peaks, particularly those due to the aromatic carbons, are considerably broadened due to the chemical shift anisotropy. This is removed on spinning at the magic angle (spinning rate ~3.5 kHz) as shown in Figure 1B; the considerable resolution obtained allows assignment of the resonances as given in the figure and these agree well with the shift values found from high-resolution ^{13}C NMR studies of stage-A resins in solution.[12] In particular, the resonances due to the phenol residues (Ar_1 is for the carbon bearing the phenol OH and Ar_2 for the remaining ring carbons) are well resolved from those assigned to the methylene groupings from the formaldehyde. The assignments are confirmed by the spectrum of the analogous polymeric material prepared under identical conditions but using formaldehyde enriched to ~5% with ^{13}C, as shown in Figure 1C. The methylene signals are assigned to free paraformaldehyde, to methylol groups, and to bridging methylenes as indicated. IR measurements show that there are no methylene ethers present which might contribute to the CH_2O peak. The spectra thus give a direct measure of the nature and the extent of the cross-linking in the polymer network and confirm by direct measurement the structure expected for cross-linked resols.

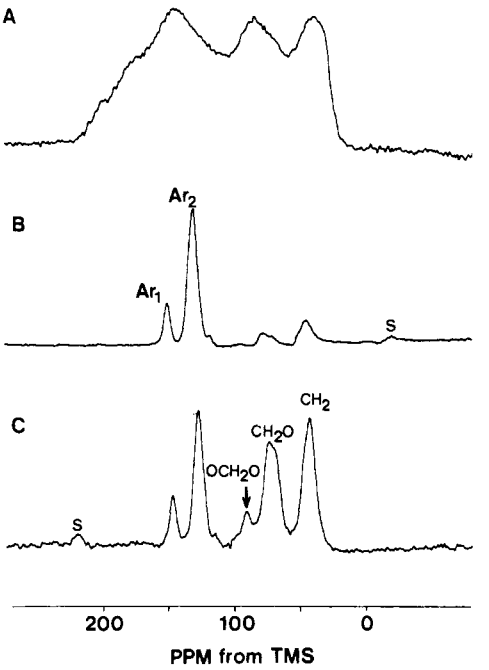


Figure 1. Solid-state ^{13}C NMR spectra obtained at 22.6 MHz from a solid rotor of a cured resol-type material (phenol/formaldehyde/sodium hydroxide = 1/2/0.01, cured at 110 °C for 24 h) using matched spin-lock cross polarization with radio-frequency fields of 40 kHz: (A) static sample, 1-ms cross-polarization time, 2-s recycle time, 3000 FID's; (B) magic angle spinning at 3.6 kHz, 1-ms cross-polarization time, 2-s recycle time, 2000 FID's; (C) conditions as in B except that 500 FID's were averaged and the sample was prepared by using formaldehyde ^{13}C enriched to ~5%. The small peaks marked s denote spinning side bands.

Although the use of magic angle spinning gives a marked improvement in spectral resolution as indicated in Figure 1, the peak widths are still 150–250 Hz, which is much greater than those observed for crystalline organic materials (~20 Hz) and glassy polymers (~60 Hz) at these frequencies. There are thought to be two sources of broadening in these resins: first, as shown by high-resolution solution NMR studies of the prepolymers, there are a whole variety of closely related isomeric forms of a given type of carbon unit, depending on the number and type of linkings in the immediate area and their points of attachment to the phenolic residues; second, there will be a residual chemical shift dispersion in each one of these signals due to variation of the spatial arrangement of the surrounding groups in the disordered three-dimensional network. From these considerations, limited resolution may be expected to be characteristic of cross-linked, two-component resins in general.

It is also possible to differentiate those carbons which have protons directly bonded to them, giving additional information on the number and positions of substitution on the benzene ring. The pulse sequence for making such measurements was recently described by Opella[13] and consists of the normal cross-polarization sequence with a short delay (~50–100 μs) inserted between the cross-po-

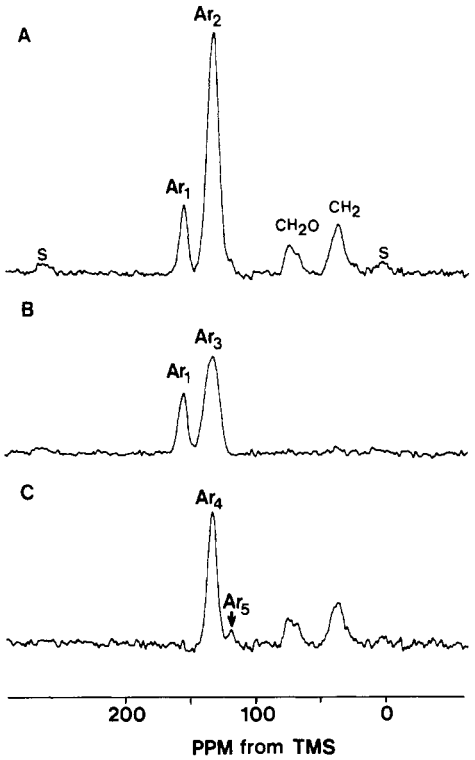


Figure 2. Solid-state ^{13}C NMR spectra of a solid rotor of a cured resol-type material similar to that used for Figure 1 obtained under the following experimental conditions: (A) magic angle spinning, 1-ms cross-polarization time, 2-s recycle time, 500 FID's (cf. Figure 1B); (B) conditions as in A except that during the 50-μs dwell before acquisition, the proton decoupler was gated off for the first 40 μs;[13] (C) result of subtracting 1.15 times spectrum B from spectrum A. The small peaks marked s denote spinning side bands.

larization/spin-locking step and the data acquisition during which time both carbon and proton radio-frequency fields are turned off. The magnetization of those carbons with directly bonded protons is rapidly destroyed due to the large proton–carbon dipolar interactions, while that of those carbons with no attached protons is relatively unaffected. The net result is that signals are observed for only the latter carbons.[13,14]

In the case of the solid phenolic resins, the experiment may be used to investigate the substitution pattern in the phenol ring. Figure 2 shows the results from such an experiment on a cured resol sample similar to that used to obtain the spectra shown in Figure 1. Figure 2A shows the normal cross-polarization spectrum, and Figure 2B the spectrum of only those carbons with no protons attached. The peaks are due to the aromatic carbon to which the OH is attached (Ar_1) and the ortho- and para-substituted ring carbons (Ar_3) as indicated in the figure. A comparison of the intensities of these two peaks gives the total substitution in the ring. Figure 2C is the difference between the upper two spectra and thus corresponds to those carbons with directly bonded protons. The largest peak at low field corresponds to the meta ring carbons where no substitution has taken place (Ar_4) and the small peak to unsubstituted ortho and para carbons (Ar_5), indicating a high overall degree of substitution. The two high-field peaks are due to methylol and methylene groups as before.

Similar measurements to those above made on a series of solid, cured resins of increasing degree of cure indicate qualitatively that the curing process involves the conversion of methylol residues to methylene bridges. Preliminary relaxation time measurements indicate that it should be possible to relate quantitatively the peak areas to the relative proportions of the different moieties present and to use these spectra in conjunction with IR both for quantitative analysis and also to quantify the energetics of the curing process.

Spectra of similar resolution to those described above are obtained for novolac-type resins and preliminary results indicate that other formaldehyde resins such as urea–formaldehyde and melamine–formaldehyde are also amenable to study by these techniques.[15]

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Role of the Triplet State in the Deactivation of Carbazole Exciplex Systems

By following the deactivation of the exciplex formed between several carbazole-containing polymers and dimethyl terephthalate (DMT) and comparing it to the same process in the monomeric *N*-isopropylcarbazole (NIPC)–DMT system, we have found that a major nonradiative decay route for exciplex deactivation involves a transition to the carbazole triplet state in the monomeric system but not in the poly(*N*-vinylcarbazole) (PVCz)–DMT system. Optically excited PVCz and NIPC interact with DMT and form an exciplex which is manifested by quenching of the PVCz or NIPC fluorescence and appearance of a new red-shifted emission band.[1-6] In a recent

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