$(2)^{-2n}l_{mn} \to 0$ as $n \to \infty$ for all m. Consequently, Q_n is zero and we have, finally

$$P_1 = KP_0 = \frac{1 - (1 - 4\beta\delta)^{1/2}}{2\delta}P_0 \qquad \text{(A24)}$$

We can now use eq A3 to express P_2 in terms of P_1

$$P_2 = \beta P_1 + \delta P_3 \qquad \text{(A4')}$$

$$= \beta P_1 + \beta\delta P_2 + \delta^2 P_4 \qquad \text{(A5')}$$

$$= (\beta + \delta\beta^2)P_1 + 2\delta^2\beta P_3 + \delta^3 P_5 \qquad \text{(A6')}$$

etc.

Following the procedure outlined above, we find

$$P_2 = KP_1 = \frac{1 - (1 - 4\beta\delta)^{1/2}}{2\delta}P_1$$

Repeating the whole process for P_3, we find $P_3 = KP_2 = K^2P_1 = K^3P_0$, and, in general, $P_n = K^nP_0$, which is the desired result.

References and Notes

(1) K. F. O'Driscoll and F. P. Gasparro, *J. Macromol. Sci., Chem.* **A1**, 643 (1967). K. F. O'Driscoll and J. R. Dickinson, *Ibid.*, **A2**, 449 (1968). J. A. Howell, M. Izu, and K. F. O'Driscoll, *J. Polym. Sci., Polym. Chem. Ed.*, **8**, 699 (1970). M. Izu and K. F. O'Driscoll, *Ibid.*, **8**, 1675, 1687 (1970). M. Izu and K. F. O'Driscoll, *Polym. J.*, **1**, 27 (1970). M. Izu, K. F. O'Driscoll, R. J. Hill, M. J. Quinn, and H. J. Harwood, *Macromolecules*, **5**, 90 (1972). B. K. Kang, K. F. O'Driscoll, and J. A. Howell, *J. Polym. Sci.*, **10**, 2349 (1972). B. K. Kang and K. F. O'Driscoll, *Macromolecules*, **7**, 886 (1974). B. K. Kang and K. F. O'Driscoll, *J. Macromol. Sci., Chem.*, **A7**, 1197 (1973).

(2) P. Wittmer, in "Multicomponent Polymer Systems", American Chemical Society, Washington, D.C., 1971; Adv. Chem. Ser. No. 99, pp 140–174.

(3) G. G. Lowry, *J. Polym. Sci.*, **42**, 463 (1960).

(4) A. C. Hindmarsh, Program LSODES (Livermore Solver for Ordinary Differential Equations), Livermore, CA, 1980.

(5) G. G. Lowry, "Markov Chains and Monte Carlo Calculations in Polymer Science", Marcel Dekker, New York, 1970.

(6) W. Bruns, I. Motoe, and K. F. O'Driscoll, "Monte Carlo Applications in Polymer Science" (Lecture Notes in Chemistry), Springer-Verlag, New York, 1981.

(7) Numerical Algorithms Group Program G05CAF. This subroutine has been tested for uniform distribution over the range $0 < r < 1$ and for absence of correlations between subsequent pseudo random number. It has been found to give satisfactory results in a wide variety of Monte Carlo simulations.

(8) S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943).

(9) This result can be proven more rigorously by noting that

$$l_{mn} = \frac{(2n-1)!}{(m+n-1)!(n-m)!}\left(\frac{2m}{m+n}\right) = \frac{2n!}{(m+n)!(n-m)!}\left(\frac{m}{n}\right)$$

or

$$l_{mn} = \frac{m}{n}\binom{2n}{n-m}$$

From this result we find that

$$\frac{l_{(m+1)n}}{l_{mn}} = \frac{(n-m)(m+1)}{m(m+n+1)}$$

and the maximum value for l_{mn} occurs at $m \approx (n/2)^{1/2}$ for large n. Since the maximum value of $\binom{2n}{n-m}$ is found at $m = 0$ and the maximum value of $(m/n)\binom{2n}{n-m}$ is found at $m \approx (n/2)^{1/2}$

$$l_{mn} \lesssim \binom{2n}{n}\left(\frac{1}{2n}\right)^{1/2}$$

and

$$(2)^{-2n}l_{mn} \lesssim (2)^{-2n}\binom{2n}{n}\left(\frac{1}{2n}\right)^{1/2}$$

using this result together with the fact that $\binom{2n}{n} < (2)^{2n}$, we find that $(2)^{-2n}l_{mn} \lesssim (1/2n)^{1/2}$ or $\lim_{n\to\infty}((2)^{-2n}l_{mn}) = 0$.

---

^{13}C NMR Studies of Solid Phenolic Resins Using Cross Polarization and Magic-Angle Spinning

Richard L. Bryson,[†] Galen R. Hatfield, Thomas A. Early, Allen R. Palmer, and Gary E. Maciel*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

Received February 2, 1983

ABSTRACT: ^{13}C NMR data are presented for the cross polarization/magic-angle spinning experiment applied to phenol/formaldehyde resins of the Novolak type. Spectra were obtained at three magnetic field strengths, 1.41, 2.35, and 4.70 T. Although sensitivity is better at higher fields, there is no real gain in resolution at higher field. Spectral deconvolutions were carried out and tentative peak assignments made. The results confirm the view that the curing process involves cross-linking in each of the resins studied.

Introduction

The chemical shift in a ^{13}C NMR experiment is a powerful tool for structural elucidation in macromolecules such as polymers and resins. Due to the limited solubility of many of these materials, especially cured resins, the use of solid-state ^{13}C NMR with cross polarization (CP) and magic-angle spinning (MAS) is very valuable.[1-3] This approach renders the question of solubility irrelevant and eliminates structural uncertainties associated with dissolution. The ^{13}C CP/MAS approach has been applied to several synthetic polymer systems but only sparingly to resins.[4-7] It is the application of this technique to two phenol/formaldehyde resins of the Novolak type on which this paper is based.

Phenol/formaldehyde resins have important commerical applications.[8] Details of the curing process are responsible for many of the important physical and mechanical characteristics of these materials. Thus, the development of tools that can provide structural information relevant to the curing process is important for understanding and improving the synthetic process.

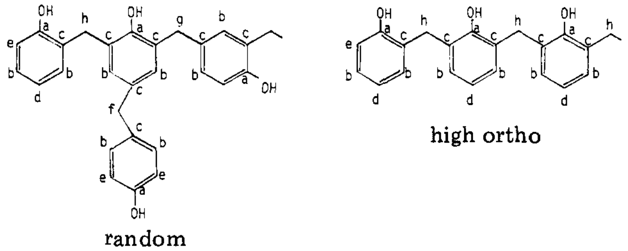
Extensive ^{13}C NMR studies on phenol/formaldehyde resins have been carried out in the liquid state,[9-12] but

---

[†] Deceased.

0024-9297/83/2216-1669$01.50/0

Table I
^{13}C Peak Assignments Based on Solution-State ^{13}C Data[9-12] of Phenol/Formaldehyde Model Systems and Resins



carbon	region, ppm[a]	description[b]
a	150	hydroxy-substituted carbons
b	130	unsubstituted meta aromatic carbons
c	125	methylene-substituted aromatic carbons
d	120	unsubstituted para aromatic carbons
e	115	unsubstituted ortho aromatic carbons
f	40	para-para methylene bridge
g	35	ortho-para methylene bridge
h	30	ortho-ortho methylene bridge

[a] Relative to tetramethylsilane. [b] Ortho, meta, and para designations are relative to the hydroxy-substituted carbon.

solid-state studies have been extremely limited.[4]

Experimental Section

NMR Measurements. The 15.1-MHz ^{13}C CP/MAS spectra were obtained on a JEOL FX-60 spectrometer modified for work with solids. The 25.1-MHz spectra were obtained on a home-built spectrometer that utilizes a Nicolet 1180 data system and a Nalorac 4.7-T magnet operated at half field. The 50.3-MHz experiments were performed on a modified wide-bore Nicolet NT-200 spectrometer. Spectra were obtained with 1-, 2-, and 4-ms contact times; the relative peak intensities showed no contact-time dependence. Spectra in which other parameters were varied were obtained with a 2-ms contact time and a 1-s repetition time. Samples were spun at 2.2, 3.3, and 1.7 kHz for the 15-, 25-, and 50-MHz experiments, respectively, using bullet spinners.[13] The magic angle was adjusted to within 0.1° by using the ^{79}Br spectrum of a small sample of KBr placed in the spinner.[14]

Sample spinning in the high-field experiments gave rise to several intense spinning sidebands. The Dixon method[15-17] of sideband suppression was utilized to eliminate sideband interference in the interpretation of spectra. The accurate knowledge of spinning speeds and the high spinner stability required by this method called for measurement of spinning rate before and after each experiment. The speed was found to vary less than 0.2%. The total experimental time for obtaining a sideband-suppressed ^{13}C spectrum was typically several hours.

All spectra were deconvoluted, using standard Nicolet 1180 software (NTCCAP). Deconvolutions were carried out with the minimum number of resonances necessary to provide a reasonable fit of the experimental spectrum.

Samples. The samples were Novolak phenolic resins prepared at the Durez Division of the Occidental Chemical Corp. One sample was prepared under conditions believed to produce a "high-ortho" resin, and the other, a "random" resin. Resins were cured by heating a mixure of 90% resin + 10% hexamethylenetetramine (HMTA) at 135 °C for a specified time.

Results

Peaks in the ^{13}C CP/MAS NMR spectra obtained in this study were assigned on the basis of comparisons with solution-state ^{13}C NMR data in the literature. A summary of the structure/shift relationships used in these assignments is given in Table I.

Shown in Figure 1 is the static-field dependence of the CP/MAS ^{13}C NMR spectrum of a phenolic resin cured with HMTA at 135 °C for 1 h. One can see that the sensitivity of aromatic carbons improves with higher field strengths; however, there is no corresponding gain in resolution with increasing field strength. In fact, a loss in intensity in the region of 32 ppm occurred in the 50-MHz spectra. This loss is often associated with the sideband-suppression technique, which systematically tends to decrease the intensity of regions with smaller T_2 values and can discriminate against carbons with tightly coupled protons (e.g., because of insufficient decoupling or insufficient mismatch during the 180° ^{13}C pulses).[15] Without the use of the sideband-suppression technique, the 50-MHz spectra would be severely complicated by spinning sidebands, especially those due to the aromatic carbon resonances. Several T_2 measurements were performed, using the CP spin-echo method,[18] to examine the extent to which differences in intensity could be assigned to structural differences (e.g., curing effects), rather than deficiencies in technique. The T_2 values were found to be 0.03–0.06 s for the aromatic carbons and around 0.015 s for the aliphatic carbons. The T_2 values were found to remain approximately constant with curing. This large difference in efficiency of transverse relaxation for the aromatic and aliphatic carbons partially explains why the intensity in the aliphatic carbon region is depleted in the sideband-suppressed 50-MHz ^{13}C spectra. In any case, as some uncertainties were introduced in the sideband-suppression experiments and as there appeared to be no real gain in resolution in the higher field experiments (4.7 T), it was decided to focus on results obtained at 2.35 T, for which sideband suppression is not necessary. The 2.35-T ^{13}C CP/MAS spectra of the two phenolic resins, together with their deconvolutions, are shown in Figures 2 and 3.

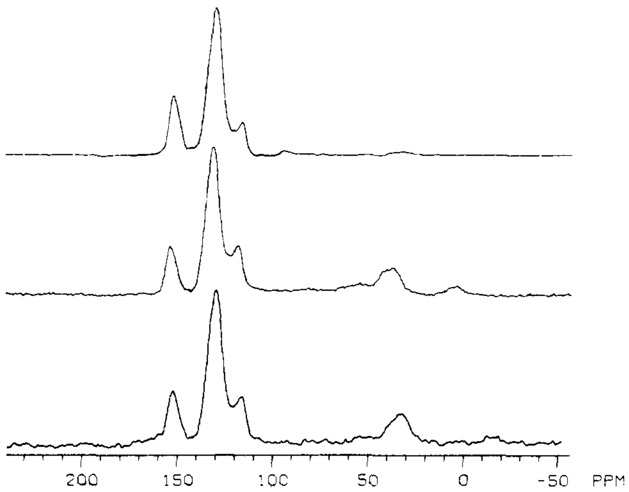


Figure 1. Static-field dependence of the ^{13}C CP/MAS spectrum of the "random" resin. Each spectrum was obtained with a 2-ms contact time and a 1-s repetition time. The bottom spectrum, obtained at 1.41 T, and the middle spectrum, obtained at 2.35 T, were each accumulated with 9000 scans. The top spectrum was obtained at 4.70 T, using the sideband-suppression technique. Five 3200-scan spectra of different pitches were added to produce this sideband-suppressed spectrum.

An interrupted decoupling experiment[19] was also carried out on each of the resins. In this experiment a delay period (say 40–100 μs) is inserted between the CP contact period and data acquisition. During this delay period, the ^{1}H decoupler is turned off, and ^{13}C magnetization due to ^{13}C's with strong dipolar interactions with protons is attenuated by dephasing. Results from the interrupted decoupling experiments on each resin, together with their deconvolutions, are presented in Figures 4 and 5. Each spectrum was obtained at 2.35 T.

The spectra of the random resin (Figures 2 and 4) could be simulated accurately by using a set of six peaks, each

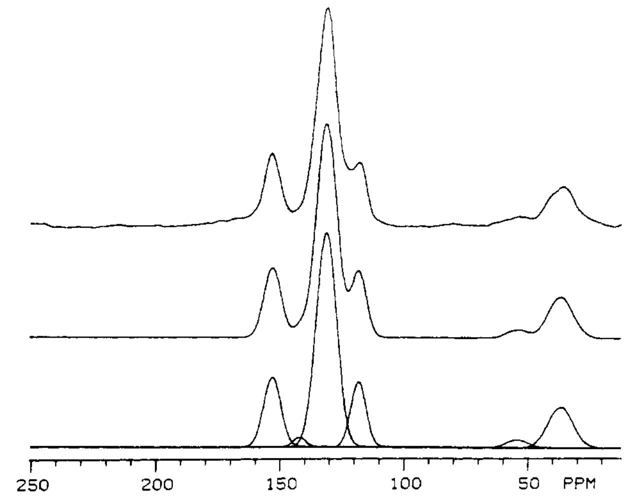


Figure 2. Deconvolution of the ^{13}C spectrum of the "random" resin cured for 1 h, obtained at 2.35 T. Top, 2-ms contact time and 1-s repetition time. Middle, simulation based on deconvoluted spectrum. Bottom, deconvoluted spectrum.

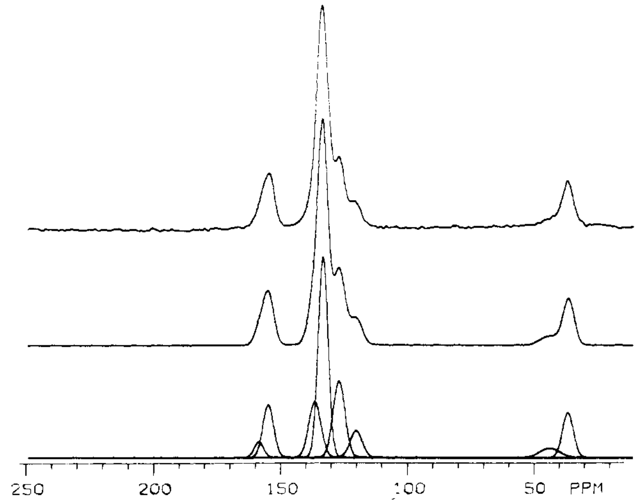


Figure 3. Deconvolution of the ^{13}C spectrum of the "high-ortho" resin cured for 1 h, obtained at 2.35 T. Top, 2-ms contact time and 1-s repetition time. Middle, simulation based on deconvoluted spectrum. Bottom, deconvoluted spectrum.

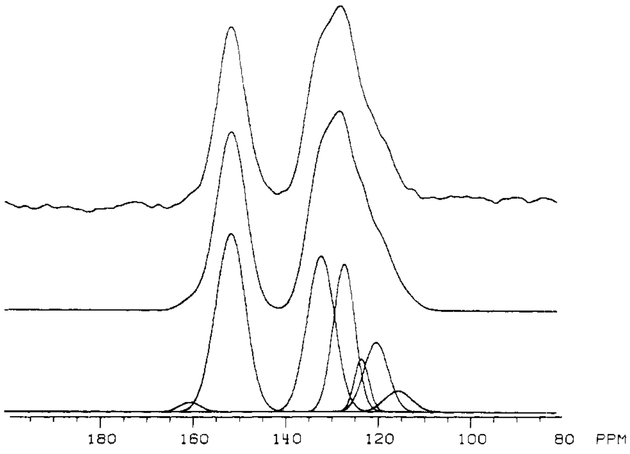


Figure 4. Deconvolution of the ^{13}C spectrum for the interrupted decoupling experiment of the "random" resin cured for 1 h. Spectra were obtained at 2.35 T with a 70-μs interrupt time. Top, 2-ms contact time and a 1-s repetition time. Middle, simulation based on deconvoluted spectrum. Bottom, deconvoluted spectrum.

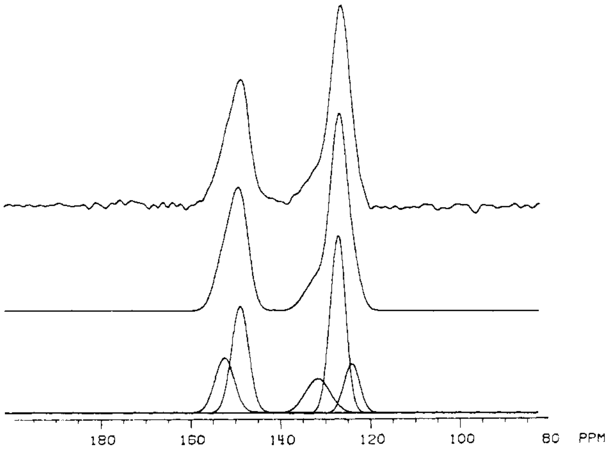


Figure 5. Deconvolution of the ^{13}C spectrum for the interrupted decoupling experiment of the "high-ortho" resin cured for 1 h. Spectra were obtained at 2.35 T with a 70-μs interrupt time. Top, 2-ms contact time and a 1-s repetition time. Middle, simulation based on deconvoluted spectrum. Bottom, deconvoluted spectrum.

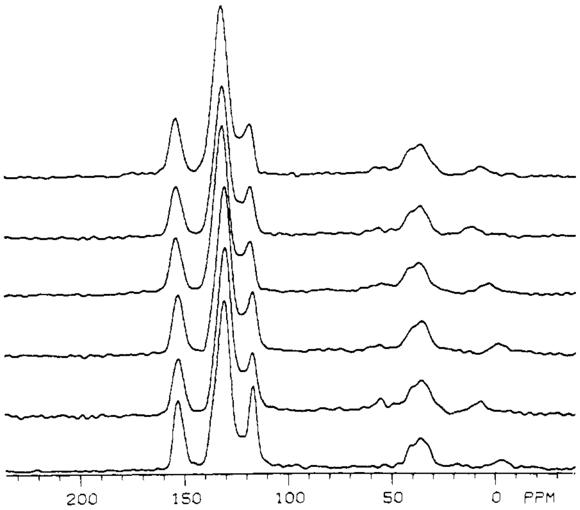


Figure 6. Effect of cure time on the ^{13}C CP/MAS spectrum of the "random" resin. Cure times from bottom to top are 0, 0.25, 0.5, 1, 4, and 24 h. All spectra were obtained at 2.35 T with a contact time of 2 ms and a 1-s repetition time.

with its own chemical shift position and Gaussian line width. However, the interrupted decoupling experiment (Figure 4) revealed that the major resonance at 132 ppm should be resolved into four resonances, centered at 132, 128, 124, and 121 ppm.

The high-ortho resin (Figures 3 and 5) could be simulated accurately by using a set of eight peaks. A resonance at 125 ppm is clearly observable in the normal CP/MAS spectrum, in contrast to that of the random resin, for which this peak was resolvable only in the interrupted decoupling experiment. Some of the peaks in the spectra of the high-ortho resin were generally narrower than the corresponding peaks for the random resin.

The ^{13}C CP/MAS spectra of each resin as a function of curing time are presented in Figures 6 and 7. All spectra were obtained at 2.35 T. For the random resin in Figure 6 the intensity in the region from +5 to −10 ppm is due to a spinning sideband. The most significant changes were observed to occur in the first 15 min of curing. Close inspection, including deconvolution, reveals that a new region of intensity appears at roughly 60 ppm upon curing, especially for the random resin. It is clear from deconvolutions (not shown) that, as curing time increases, there is a significant decrease in integrated intensity in the regions of 117 and 140 ppm; deconvolution also reveals an increase in the line width of the peak at 117 ppm.

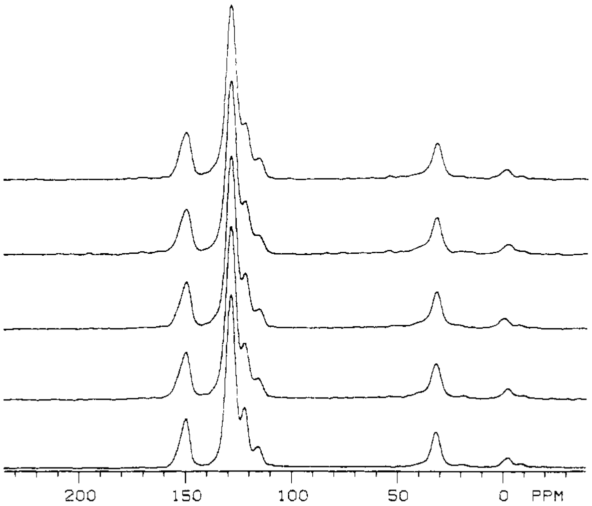


Figure 7. Effect of cure time on the ^{13}C CP/MAS spectrum of the "high-ortho" resin. Cure times from bottom to top are 0, 0.25, 0.5, 1, and 4 h. All spectra were obtained at 2.35 T with a contact time of 2 ms and a 1-s repetition time.

Discussion

It was shown that for the ^{13}C CP/MAS spectra of both resins, there was a shift in intensity within the region 115–130 ppm with curing. This region represents the unsubstituted ortho, meta, and para aromatic carbons, which are potential sites for cross-linking, as well as the methylene-substituted aromatics. If the curing process involved cross-linking, we would expect the regions due to the unsubstituted aromatic carbons to lose intensity and the region due to the methylene-substituted aromatics to gain intensity. Examination of the normal CP/MAS spectra reveals a shift in intensity within this region involving an observable decrease in intensity in the regions of 115 and 130 ppm, corresponding to unsubstituted ortho and meta aromatic carbons. A detailed analysis of the region at 125 ppm, corresponding to the methylene-substituted aromatics, is impossible using only the normal CP/MAS spectra. This region is more addressable in the interrupted decoupling experiment, where the 115–130-ppm region becomes more resolvable. Deconvolutions of the interrupted decoupling spectra reveal an increase in intensity around 125 ppm with curing. Thus, the ^{13}C spectra confirm the view that cross-linking occurs during the curing process.

Cross-linking also increases the number of different conformations and configurations available to the aromatic carbon. This may broaden lines because of chemical shift dispersion, which can account for the increased peak width that was observed to accompany curing. We might also expect the resonances in the simpler high-ortho resin to be generally narrower than corresponding resonances in the random resin, if it is mainly cross-linking that occurs during curing. Inspection of Figures 6 and 7 reveals that such line width differences exist for the largest aromatic and aliphatic peaks; Figures 4 and 5 show a corresponding difference in the interrupted decoupling results. The variable cure time study demonstrated that the early stage of the curing time is when a large percentage of the the cross-linking occurs.

The variable field study demonstrated no overall advantage to studying these resins at higher fields. Studies at high field (4.7 T) require greater experimental effort and produce no resolution or sensitivity advantage. At present, spinning speed is the limiting factor, and spectra should be obtained at a field strength for which one can conveniently spin out chemical shift anisotropy.

Acknowledgment. We gratefully acknowledge partial support of this work by the Durez Division of the Occidental Chemical Corp. and helpful discussions of Dr. S. A. Sojka of Durez.

Registry No. Hexamethylenetetramine, 100-97-0; phenol–formaldehyde copolymer, 9003-35-4.

References and Notes

(1) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
(2) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031.
(3) Schaefer, J.; Stejskal, E. O. "Topics in Carbon-13 NMR Spectroscopy"; Levy, G. C., Ed.; Wiley: New York, 1979; Vol. I.
(4) Fyfe, C. A.; Rudin, A.; Tchir, W. *Macromolecules* **1980**, *13*, 1322.
(5) Maciel, G. E.; Szeverenyi, N. M.; Early, T. A.; Myers, G. E. *Macromolecules* **1983**, *16*, 598.
(6) Maciel, G. E.; Chuang, I.; Meyers, G. E. *Macromolecules* **1982**, *15*, 1218.
(7) Sefcik, M. D.; Stejskal, E. O.; McKay, R. A.; Schaefer, J. *Macromolecules* **1979**, *12*, 423.
(8) Knop, A.; Scheib, W. "Chemistry and Application of Phenolic Resins"; Springer-Verlag: New York, 1979.
(9) Dradi, E.; Casiraghi, G.; Casnati, G. *Chem. Ind.* (*London*) **1978**, Aug 19, 627.
(10) Siling, M. E.; Urman, Y. G.; Adorova, I. V.; Alekseyeva, S. G.; Matyukhina, O. S.; Slonim, I. Y. *J. Polym. Sci.* **1977**, 358.
(11) Sojka, S. A.; Wolfe, R. A.; Deitz, E. A.; Dannels, B. F. *Macromolecules* **1979**, *12*, 767.
(12) Kim, M. G.; Tiedeman, G. T.; Amons, L. W. "Weyerhauser Science Symposium", Vol 2, 1981.
(13) Bartuska, V. J.; Maciel, G. E. *J. Magn. Reson.* **1981**, *42*, 312.
(14) Frye, J. S.; Maciel, G. E. *J. Magn. Reson.* **1982**, *48*, 125.
(15) Dixon, W. T. *J. Magn. Reson.* **1981**, *44*, 220.
(16) Dixon, W. T.; Schaefer, J.; Sefcik, M. D.; Stejskal, E. O.; McKay, R. A. *J. Magn. Reson.* **1981**, *45*, 173.
(17) Dixon, W. T. *J. Chem. Phys.* **1982**, *77*, 1800.
(18) Earl, W. L.; VanderHart, D. L. *Macromolecules* **1979**, *12*, 762.
(19) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.