practical importance. For example, slow diffusion of RuO_4 could give a light stain even though the tetraoxide may be highly reactive on various polymers.

Detailed structural features of blends of PS/PMMA, ABS, and SAN/PS films and, in addition, the semicrystalline polymers HDPE and nylon 11 were significantly enhanced by RuO_4 staining before their examination in the TEM. The associated electron micrographs demonstrate that RuO_4 is extremely useful as a staining agent for many saturated and unsaturated polymers, improving image contrast in the TEM and stabilizing these films toward electron beam damage.

The staining technique makes available a method to observe phase behavior of polymer blends, the structure of spherulites, and the influence of solvent and temperature on the morphology and growth of phase-separated particles and spherulites.

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

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ABSTRACT: Experimental ^{13}C NMR data are presented for the cross polarization magic-angle spinning (CP/MAS) experiment applied to urea–formaldehyde polymers. The effect of static magnetic field is demonstrated with spectra presented at three magnetic field strengths—1.41, 2.35, and 4.70 T. The effect of residual dipolar coupling of ^{13}C to ^{14}N is largely suppressed at high fields, in contrast to the low-field case, allowing resolution of individual carbon types in these polymers. Spectra deconvolutions have been carried out on complex peaks, and tentative peak assignments and corresponding structural conclusions have been made on the basis of comparisons with solution data.

Introduction

The chemical shift in a ^{13}C NMR experiment is a sensitive probe of chemical structure, and the relatively large chemical shift range makes ^{13}C NMR an attractive tool for analyzing complicated materials such as those of synthetic polymers and resins. Limitations in solubility of many of these materials—especially cured resins—often preclude the use of liquid-state NMR. The technique of solid-state ^{13}C NMR with cross polarization and magic-angle spinning (CP/MAS)[1] provides a powerful technique to overcome

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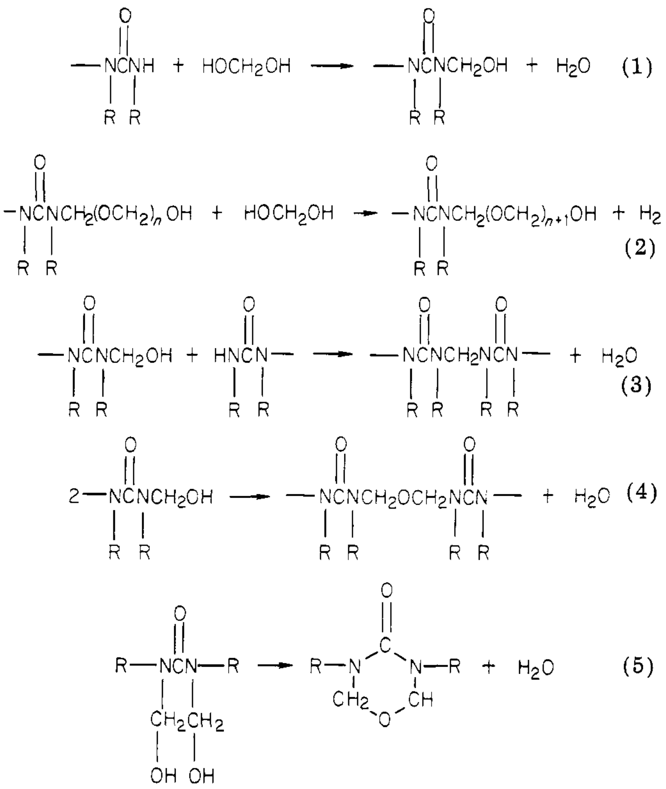
this limitation. A sample examined in the solid state has the highest possible concentration of ^{13}C and also makes the question of solubility unimportant. Furthermore, solid-state NMR eliminates structural uncertainties associated with the dissolution process. This relatively new approach has already been applied elegantly in the characterization of some synthetic polymer systems.[2] It is the application of ^{13}C CP/MAS NMR spectroscopy to a series of urea-formaldehyde (UF) polymers on which this paper is based.

Urea-formaldehyde polymers have great commercial importance, especially as adhesives for wood products. The conditions under which these materials are prepared and cured, however, have a pronounced effect on their final structure and on their physical and chemical properties. In particular, UF-bonded wood products suffer from poor durability in high-temperature, high-humidity environments and from the emission of formaldehyde gas into living areas; both limitations result to a considerable degree from the hydrolytic instability of the cured UF.[3] That instability, in turn, is believed to arise from differences in hydrolytic properties among the variety of chemical structures that may exist in the cured-product reactions of the type listed in Scheme I (R may be H or CH_2).[3] Consequently, to provide a rational basis for the improvement of chemical and physical properties, it is desirable to have a technique that can discriminate between different structural features in the cured resins.

Scheme I
Reaction Scheme Leading to UF Polymers



^{13}C NMR studies have previously been reported on soluble model compounds and UF resins,[4] but this approach has not been successful on cured samples because of their insolubility. Initial CP/MAS experiments on solid UF resins in this laboratory were rather discouraging, because the spectra consisted largely of broad peaks, reminiscent of the spectra of coal; hence detailed information on individual chemical groups was not available.

The initial experiments were done at a low static magnetic field of 1.4 T (15-MHz ^{13}C and 60-MHz ^{1}H). Complications were expected from the presence of ^{14}N in these samples, as ^{14}N is known to inflict broadening on solid-state ^{13}C spectra.[5] The interpretation of an early ^{13}C CP/MAS study of UF samples at higher static magnetic field was precluded by the problem of spinning sidebands. A reexamination of these samples at higher magnetic field (4.7 T) was carried out when a method to overcome the spinning sideband problem became available.[6] The resulting spectra can be deconvoluted to give approximate relative concentrations of various functional moieties expected to be present in these types of polymers.

Experimental Section

NMR Spectra. ^{13}C CP/MAS spectra were obtained at 15.1 and 25.1 MHz on a home-built spectrometer that utilizes a Nicolet 1180 data system and a 1.4-T Varian HR-60 magnet or a Nalorac 4.7-T magnet operated at half field. The high-field experiments were performed at 4.70 T (50.3-MHz ^{13}C) on a modified wide-bore Nicolet NT-200 spectrometer. Spectra of the model compounds were obtained with a 3-ms contact time and an 8-s repetition time. Spectra of resins were obtained with a 1-ms contact time and repetition times of 1–1.3 s. Samples were spun at 1.9, 2.5, and 3.5 kHz (50-, 15-, and 25-MHz experiments, respectively) and 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.[7] Peak positions were determined relative to liquid tetramethylsilane (Me_4Si) by substitution and can be considered accurate to about ±1 ppm. Of course, relative peak positions within a given spectrum can be much more accurate, limited mainly by line width.

Sample spinning at 1.9 kHz on the 50.3-MHz instrument gave rise to several intense spinning sidebands, which complicate the interpretation of the resulting spectra. In order to overcome this problem the sideband supression method of Dixon[6] was utilized. In this method, four 180° ^{13}C pulses follow the contact period at specific times to produce an echo pattern in which the phases of the individual sidebands have been altered in a predictable manner. By the addition of individual spectra with the proper phase relationships, it is possible to reconstruct the center-band spectrum or the spectrum corresponding to a specific sideband. One can also recombine these various spectra to give a spectrum with "correct" intensities and free of sidebands. However, in the present work, only the carbonyl carbon resonance has a large enough chemical shift anisotropy to produce substantial spinning sidebands. Hence, except for the carbonyl resonance, the center-band spectra are nearly the same as recombined spectra, and the former were found to be suitable for the qualitative comparisons used in the spectral interpretations of this work. High spinner stability is required throughout the time of the Dixon experiment in order to suppress the sidebands effectively. In addition, accurate spinning speed measurements must be made in order to determine the proper spacing of the carbon pulse train. The ^{79}Br spectrum was used for this measurement, since 30–50 sidebands can be observed for KBr spinning at about 2 kHz at this field strength. The sample spinning rate was measured before and after each experiment and found to vary less than 0.2%. The total experimental time for obtaining a sideband-suppressed ^{13}C spectrum was typically 12–18 h.

The sideband-eliminated spectra were manually deconvoluted with standard Nicolet 1180 software (NTCCAP). Each spectrum was deconvoluted with a minimum number of resonances; for each resonance the chemical shift, line width, and intensity are variable parameters. After all the spectra were deconvoluted, the various simulation parameters were examined and each simulation was found to contain a set of nine unique chemical shifts. Structural assignments of all resonance positions were made by using the solution-state ^{13}C data of UF model systems and resins.[4]

Samples. The *N*,*N*′-dimethylolurea was prepared following Ludlum.[8] UF resins were prepared and treated as outlined in Scheme I and Table I. After preparation, all samples were vacuum-dried and stored cold, over desiccant.

Results

Shown in Figure 1 is the static field dependence of the CP/MAS ^{13}C NMR spectrum of a urea-formaldehyde

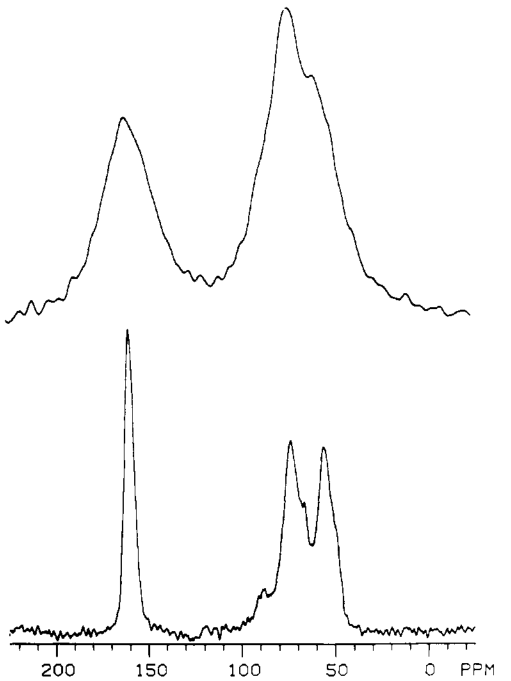


Figure 1. Static field dependence of the ^{13}C CP/MAS spectrum of sample I-3. For each spectrum a 1-ms contact time with a repetition rate of 1–1.3 s was used. The top spectrum was obtained at 1.40 T, accumulating 40 000 scans. The bottom spectrum was obtained at 4.70 T, using the sideband suppression method. Five 8000-scan spectra of different pitches were added to produce this sideband-suppressed spectrum.

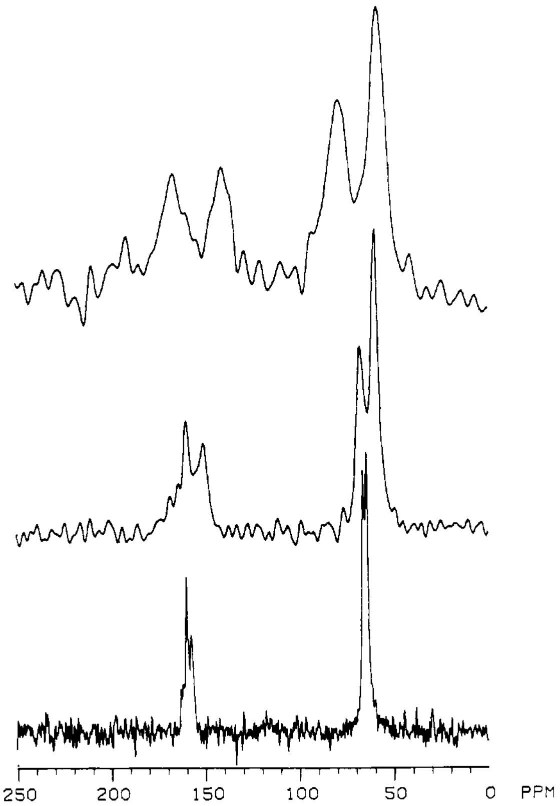


Figure 2. Static field dependence of the ^{13}C CP/MAS spectrum of N,N′-dimethylolurea ($HOCH_2NHCONHCH_2OH$). In each spectrum a 3-ms contact time was used, with an 8–10-s repetition rate, accumulating 10 000–35 000 scans. The top spectrum was obtained at 1.41 T, the middle spectrum at 2.35 T, and the bottom spectrum at 4.70 T, using the sideband suppression technique.

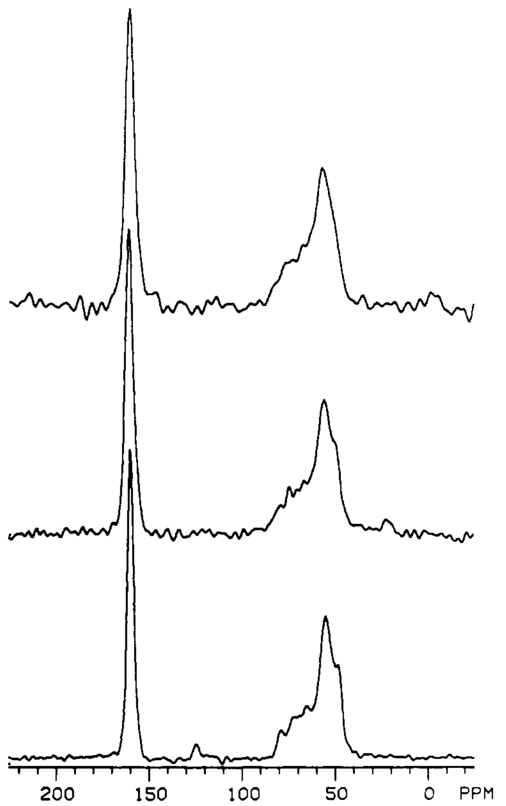


Figure 3. Static field dependence of the ^{13}C CP/MAS spectrum of a 99.7% ^{15}N-labeled urea–formaldehyde resin (sample III-2). For each spectrum a 1-ms contact time and 1–1.3-s repetition rate were used, accumulating 7 000–30 000 scans.

resin having a formaldehyde:urea (F:U) mole ratio of 1.7 and cured with H_3PO_4, pH 3.0, at 100 °C for 2 min (sample I-4). At 1.41 T the spectrum shows two broad resonances centered at 160 and 60 ppm. The disappointing aspect of this spectrum is the lack of resolution of the individual carbon moieties, at least partially expected because of the effect of ^{14}N.[5] Nevertheless, as relatively few structural types were expected in UF resins (in comparison, say, to coal), this low level of resolution was disappointing. At the higher fields of 2.35 and 4.70 T the spectrum does begin to show significant resolution. The peak at 160 ppm sharpens dramatically, while the broad peak at 60 ppm splits into two resonances, and at the highest field employed (4.70 T) this band shows additional resolution of two new peaks at 55 and 79 ppm. To our knowledge, this is the most dramatic field dependence of the ^{14}N effect that has been reported to date in the literature of ^{13}C CP/MAS NMR.

In order to characterize this field effect better, UF model compounds were also examined at different fields. Figure 2 shows the field dependence of the ^{13}C CP/MAS spectrum of N,N′-dimethylolurea. At a 1.4-T field the spectrum shows a broad asymmetric triplet centered at 160 ppm and a broad asymmetric doublet at 65 ppm. The splittings of 390 ± 10 and 310 ± 10 Hz, respectively, observed at 1.4 T are due to the interaction with the quadrupolar ^{14}N nuclei. This type of splitting has been observed for other nitrogen-containing compounds with large quadrupole coupling constants and in some cases has been predicted accurately by theory.[5] These splittings show a dramatic field dependence. As the static field increases, the magnitude of the splitting decreases, until at 4.70 T they reach 120 ± 5 and 105 ± 5 Hz. The width of each resonance also dramatically decreases at higher field.

To confirm that the large field effects are due to the residual dipolar interactions with ^{14}N nuclei, a UF resin sample in which 99.7% of the ^{14}N is replaced with ^{15}N (sample III-2) was examined at the three field strengths. The field dependence of the ^{13}C CP/MAS spectrum of this

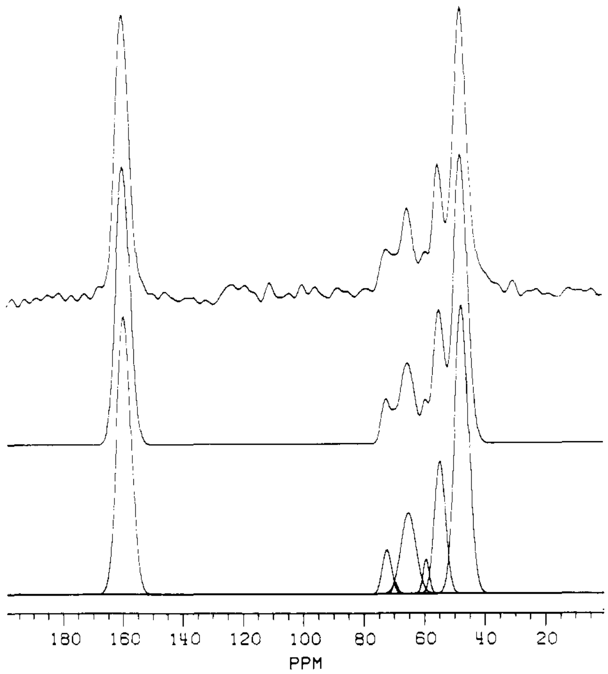


Figure 4. Deconvolution of ^{13}C spectrum of resin IV. Top, spectrum obtained at 4.70 T, using the sideband suppression method, 1-ms contact time and 1.3-s repetition rate; middle, simulation based on deconvoluted spectrum; botton, deconvoluted spectrum.

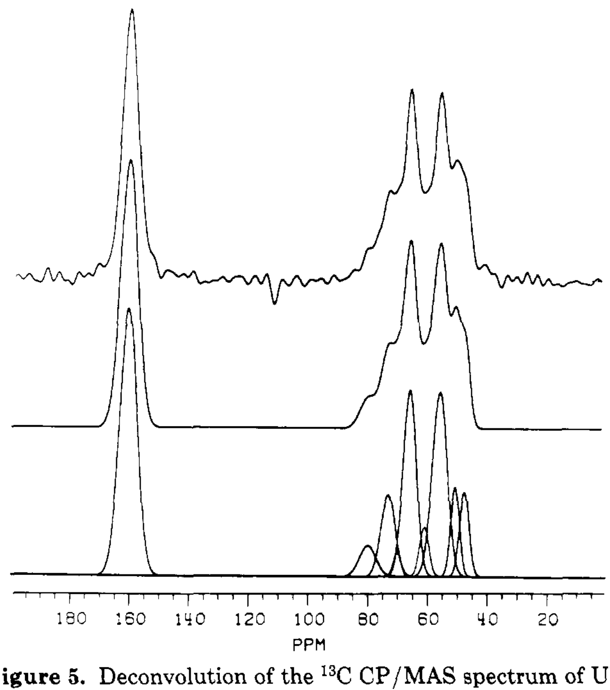


Figure 5. Deconvolution of the ^{13}C CP/MAS spectrum of UF resin II. Top, spectrum obtained from 40 000 scans at 4.70 T, using a 1-ms contact time, a 1.3-s repetition rate and the sideband suppression technique; middle, simulation based on deconvoluted spectrum; botton, deconvoluted spectrum.

^{15}N-labeled UF resin is shown in Figure 3 and is seen to be much less pronounced than with the ^{14}N counterpart. However, a careful examination of spectra for this ^{15}N-labeled compound shows that hints of resolution present at 1.4 T are more clearly defined at 4.70 T.

The ^{13}C CP/MAS spectra of several different urea–formaldehyde resins are shown in Figures 4–7. Each spectrum was obtained at 4.70 T, using the Dixon method of sideband suppression.[6] In each case the spectra were deconvoluted, using Nicolet 1180 software. The center-band spectra, rather than recombined spectra, are shown in the figures and were used in the deconvolutions. The general quality of the former was found to be better suited to the deconvolution procedure, which, except for carbonyl resonances, yielded qualitatively the same results for center-band and recombined spectra.

It was found that the spectra for all four resin samples of Figures 4–7 could be simulated accurately by using a set of nine different chemical shift positions. These pos-

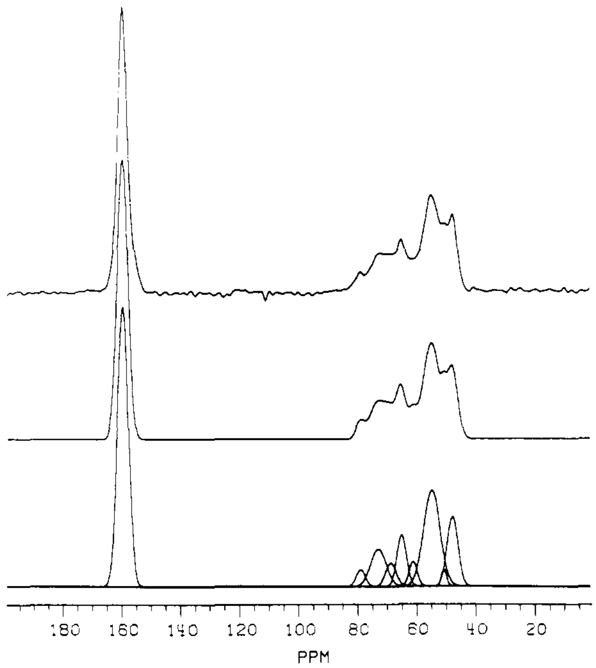


Figure 6. Deconvolution of the ^{13}C CP/MAS spectrum of a 99.7% ^{15}N-labeled resin (sample III-1). Top, spectrum obtained at 4.70 T, using a 1-ms contact time, a 1.3-s repetition rate, and sideband suppression; middle; simulation based on deconvoluted spectrum; bottom, deconvoluted spectrum.

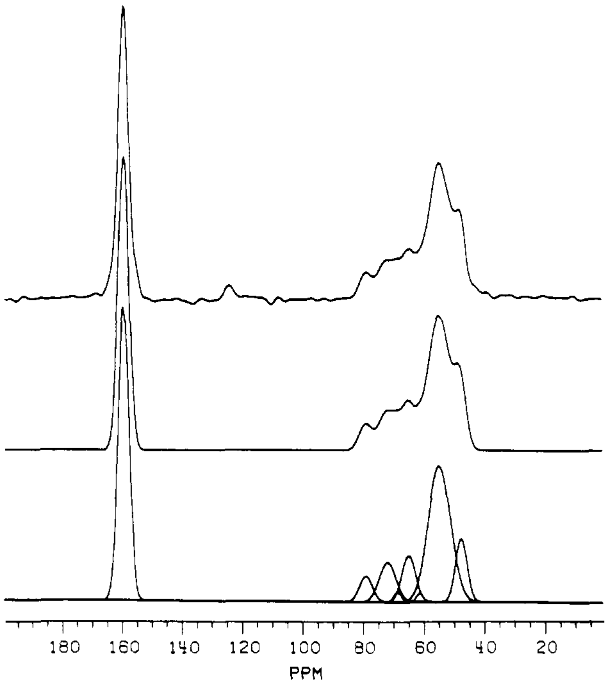


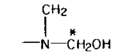
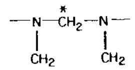
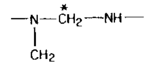
Figure 7. Deconvolution of the ^{13}C CP/MAS of a cured urea–formaldehyde resin, III-2. (This ^{15}N-labeled resin is identical with the sample in Figure 6, except it has been cured at 100 °C for 20 min. Top, spectrum obtained at 4.70 T using 1-ms contact time, a 1.3-s repetition time, and sideband suppression; middle, simulation based on deconvoluted spectrum; bottom, deconvoluted spectrum.

Table I. Resin Sample Preparation

sample	synthesis procedure	postsynthesis treatment
I	1.9/7.7[a] → 1.9/4.7 → 1.7/5.4 → 1.7/7.5	
I-1		pH 3.0/dried
I-2		pH 3.0/100 °C/0.5 min/dried
I-3		pH 3.0/100 °C/1 min/dried
I-4		pH 3.0/100 °C/2 min/dried
I-5		pH 3.0/100 °C/3 min/dried
I-6		pH 3.0/100 °C/5 min/dried
I-7		pH 3.0/100 °C/10 min/dried
I-8		pH 3.0/100 °C/60 min/dried
II	1.9/7.7 → 1.9/4.5 → 1.7/5.5 → 1.5/6.3 → 1.5/7.7	dried
III[b]	as with II	
III-1		pH 3.0/dried
III-2		pH 3.0/100 °C/20 min/dried
IV	formalin (12% CH_3OH) at pH 3.0 added dropwise slowly to urea in H_2O to a final F:U molar ratio of 1.7; pH adjusted to 7.0 (white precipitate collected)	

[a] F:U molar ratio/pH. Each arrow represents 30 min at 88-90 °C. Formalin contained 6% CH_3OH. [b] Used 99% ^{15}N-enriched urea.

Table II. Results of Spectral Deconvolution

resonance	probable chemical group[a]	name of group	ppm[b] range	line width (Hz) for sample[c]				intensity (%) for sample[d]			
				IV (Figure 4)	II (Figure 5)	III-1 (Figure 6)	III-2 (Figure 7)	IV (Figure 4)	II (Figure 5)	III-1 (Figure 6)	III-2 (Figure 7)
A	$\overset{*}{C}{=}O$	urea residue carbonyl	159.3-169.6	276	342	214	214	*e*	*e*	*e*	*e*
B	$\text{-N(R)}\overset{*}{C}H_2OCH_3$ $\text{-}\overset{*}{C}H_2\text{- ir uron}$	methoxymethylol on secondary or tertiary N cyclic methylene ether	78.7-78.7		328	181	254	0	6	3	6
C	 $\text{-N(CH}_2\text{)-}\overset{*}{C}H_2OH$	methylol on tertiary N	71.6-72.8	176	282	209	322	6	12	14	13
D	$\text{-N(}\overset{*}{C}H_2OH)_2$ $\text{-NH}\overset{*}{C}H_2OCH_2OH$ $\text{uron-}\overset{*}{C}H_2OH$	dimethylol methylene of hemiformal methylol on uron N	68.3-69.9	98	151	210	155	1	2	5	2
E	$\text{-NH}\overset{*}{C}H_2OH$	methylol on secondary N	64.5-65.2	287	262	190	265	17	27	12	11
F	 $\text{-N(CH}_2\text{)-}\overset{*}{C}H_2\text{-N(CH}_2\text{)-}$	methylene between tertiary N's	59.4-61.0	121	187	161	134	3	5	5	2
G	 $\text{-N(CH}_2\text{)-}\overset{*}{C}H_2\text{-NH-}$	methylene between tertiary and secondary N	54.5-54.8	216	293	333	435	20	30	40	55
H	$\overset{*}{C}H_3OH$	methanol	49.5-50.2		172	105		0	9	2	0
I	$\text{-NH}\overset{*}{C}H_2NH\text{-}$	methylene between secondary N's	46.3-47.4	265	189	220	228	53	9	19	13

[a] N always attached to carbonyl; R = H or CH_2. [b] Position of peak maxima used in deconvolution. [c] Line widths used in deconvolution. [d] Relative integrated intensity (percent) used in deconvolution, based on all peaks except the A peak. [e] Intensities not given because of intensity distortions due to sideband-suppression procedure. [f] Uron is the cyclic reaction product of reaction 5, Scheme I.

itions are labeled A–I in Table II, which lists the deconvolution parameters for each spectrum. In Figures 4–7, the top spectrum is the experimental sideband-suppressed spectrum, the bottom plot shows the separated Gaussian contributions obtained by deconvolution, and the middle plot is the simulated spectrum obtained by combining the Gaussian contributions of the lower plot. In each case it is seen that there is an excellent fit between the experimental and simulated spectra. Using the solution-state ^{13}C NMR data for chemical shifts,[4] we make the assignments for the resonance positions listed in Table II.

There are six major resonance positions that account for more than 85% of the intensity in the spectra of all the samples. In addition to these six resonance contributions, three minor components are needed to complete the deconvolution (D, F, and H).

Some points should be emphasized in regard to the deconvolution of the various spectra. Only resonance A (carbonyl) has appreciable sideband intensity and, since the sideband-suppressed spectra were used for the deconvolution, the measured intensity for peak A will be underestimated, typically by roughly 50%. For the other peaks, while absolute intensities may be in question, the qualitative comparions of *relative* intensities used in the Discussion can be considered reliable. Gaussian line shapes were used for the deconvolution and may not represent the true line shapes. The true line shapes of individual chemical groups may have some different, more complex dispersion due to the heterogeneity of the samples. For example, the fact that no intensity at resonance positions G and I was needed for the fit of Figure 7 does not necessarily mean that the corresponding chemical groups are totally absent in the resin. Examination of the line width for resonance H of this spectrum (416 Hz) shows it to overlap badly with the resonance at position G. In fact, it might be reasonable to assume that nearest-neighbor effects and other factors might cause a small dispersion of chemical shifts of methylene resonances between resonances G and H, which in some samples may be overlapped in a manner to preclude an accurate deconvolution. Therefore the intensity ratios of only the six major components (resonances A, B, C, E, G, and I) are reasonable to use to characterize the various samples. It is clear from this study that measurements at an even higher static magnetic field than 4.70 T are warranted. Such measurements may provide greater spectral dispersion directly and should also provide improved signal-to-noise ratios, which will permit the use of various resolution-enhancement methods.

In an attempt to understand better the chemistry of the curing process, resin I was subjected to various cure times from 0 to 60 min. The results of this experiment are shown in Figure 8. The anomalous peak at 30 ppm is probably due to acetone introduced in the washing of those samples. Because of the severe overlap of resonances in these spectra, a deconvolution was not attempted. Nevertheless, it is clear that as the curing time increases, carbon intensity is being depleted at about 65 ppm and concurrently growing in at about 55 ppm. That is, loss of intensity occurs at resonance positions corresponding to moieties B, C, and E, whereas resonance positions of G and I gain intensity.

Discussion

The ^{14}N–^{13}C dipolar interaction has been studied from the theoretical as well as experimental point of view and has been found to be dependent on the quadrupolar coupling tensor of the ^{14}N nucleus and the orientation of the electric field gradient with respect to the dipolar interaction axis.[5] It has been shown that, in order to calculate the ^{14}N–^{13}C dipolar interaction, ^{14}N spin functions have to include both Zeeman and quadrupolar spin parts. This ^{14}N influence is field dependent. As the static field is increased, the quadrupolar interaction becomes smaller compared to the Zeeman interaction, and at high enough fields the ^{13}C–^{14}N dipole–dipole interaction will nearly be removed by MAS. For smaller static fields, the quadrupolar coupling constant becomes comparable to the Zeeman interaction, and the Zeeman ^{14}N wavefunctions are no longer good eigenfunctions; that is, the nitrogen nuclei are not necessarily quantized along the static magnetic field axis. This makes spinning about the magic angle ineffective in averaging the ^{14}N–^{13}C dipolar couplings. This effect is well illustrated in the field dependence shown in the spectra of Figures 1 and 2. With a sample that contains ^{15}N, the largest ^{13}C–^{15}N dipolar interaction is 1.1 kHz, if one assumes a 1.4-Å bond length. A broadening influence of this magnitude should be eliminated by MAS, as no quadrupolar interactions are involved, and results in spectra that are nearly independent of field, as illustrated in Figure 3.

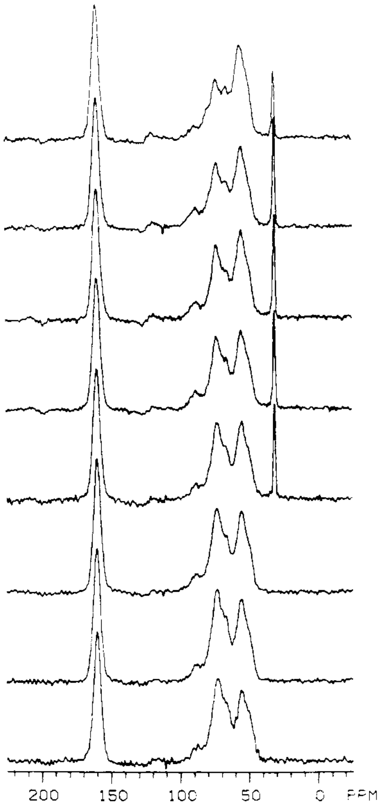


Figure 8. Effect of cure time on the ^{13}C CP/MAS spectrum of resin I (samples I-1 through I-8). Cure times from bottom to top are 0, 0.5, 1, 2, 3, 5, 10, and 60 min. All the spectra were obtained at 4.70 T using the sideband-suppression method, a contact time of 1 ms, and a repetition rate of 1.3 s. Resins were cured at 100 °C with H_3PO_4 at pH 3.

With the superior ^{13}C CP/MAS resolution available at higher fields, it is possible to characterize more fully the chemical structures present in a solid urea–formaldehyde resin. Individual chemical groups can be quantified with a single high-field CP/MAS spectrum. Within the present limits of that quantification process, the results (Table II) of the analysis on the resin samples in Figures 4–7 are generally consistent with chemical expectations. For example, we expect the following:

(i) The synthesis conditions of resin IV (acid, excess urea) should have minimized ether groups (low intensity of resonances B and D), producing a linear chain with little tertiary nitrogen (high I and low C, F, and G). The moderate level of methylol on secondary nitrogen is consistent with the low F:U ratio (1.7) and absence of any cure treatment.

(ii) Samples II, III-1, and III-2 should be similar except that the degree of cure should be in the order III-2 ≫ III-1 > II. Thus, the methylols on secondary nitrogens (resonance E) should increase in that same order and the concentration of branching tertiary nitrogens (resonance G) should decrease.

A comparison of carbonyl line widths (resonance A) shows the peaks of the two ^{15}N-containing polymers to be sharper than those of the corresponding ^{14}N-containing resins. (A comparison of other line widths may be less meaningful, because of overlaps of resonances.) This is consistent with the ^{14}N effects discussed above.

Finally, the CP/MAS ^{13}C NMR technique provides a convenient, direct way to follow the chemistry of the curing process, as shown in Figure 8. In this example, intensity is decreasing from the region about 65 ppm, while it is concurrently increasing in the 55-ppm region as curing progresses. Thus, methylol end groups (resonance E)—and possible ether groups (resonance D)—decrease with cure while branching tertiary nitrogens (resonance G) increase.

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Registry No. Urea–formaldehyde copolymer, 9011-05-6.

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Stereosequence-Dependent ^{13}C NMR Chemical Shifts in Polystyrene

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ABSTRACT: ^{13}C NMR chemical shifts are calculated for the various stereosequences present in atactic polystyrene. Calculated chemical shifts are obtained by quantitatively accounting for the number of γ interactions, or gauche arrangements, between carbon atoms separated by three bonds, i.e., carbons γ to each other. The effects of magnetic shielding produced by the ring currents from phenyl groups that are first and second neighbors along the chain in either direction from a given carbon atom are also considered. ^{13}C NMR chemical shifts calculated to the hexad level of stereosequence are presented for the methylene carbons and to the heptad and pentad levels for the C(1) and C(4) carbons of the phenyl groups. The overall spreads (~4 ppm for CH_2, ~1 ppm for C(1), and ~0.5 ppm for C(4)) and ordering of the resonances observed in the ^{13}C NMR spectra of atactic polystyrene are generally reproduced by the calculated chemical shifts. This agreement aids the analysis of polystyrene stereosequence via ^{13}C NMR.

The connections between stereosequences and ^{13}C NMR spectra have been drawn[1-4] numerous times for many different vinyl polymers. However, for polystyrene, determination of its stereoregularity by ^{13}C NMR spectroscopy has proved elusive.[3,5-11] Long-range sensitivity to stereosequence (hexads for CH_2 and heptads for C(1) carbons) and some sensitivity to solvent of the observed ^{13}C NMR resonances in polystyrene have both contributed to the difficulty in their complete assignment.

Recently renewed experimental efforts have been made to assign the ^{13}C NMR spectra of atactic polystyrene. Jasse et al.[7] synthesized and separated the stereoisomers of several polystyrene oligomers, including 2,4,6,8-tetraphenylnonane (2,4,6,8-TPN). They recorded the ^{13}C NMR spectra of each and attempted a pentad assignment of polystyrene based on the ^{13}C chemical shifts observed for C(1) belonging to the internal phenyl groups. However, as noted by the authors, 2,4,6,8-TPN is not an oligomeric model compound for polystyrene C(1) pentad structure.

Harwood and co-workers[9] have measured the ^{13}C NMR spectra of partially epimerized isotactic polystyrenes. They interpreted the spectra by comparison with stereosequence distributions that were calculated by Monte Carlo simulation of the epimerization process. As an example, they concluded that the mm triad resonance of the methine carbon comes ~0.2 ppm downfield from the (mr and rm) and rr triads, with the latter separated by less than 0.05 ppm.

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