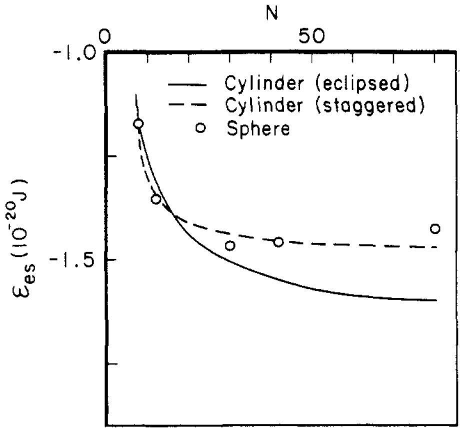

Figure 3. Ground-state electrostatic energy as a function of cluster size for cylindrical and spherical clusters.

spherical clusters. We see that the electrostatic energy does not vary significantly from one geometry to another.

3.3. Discussion. In order to have a complete theory of ionic clustering, or self-organization in ionomers, the first-principles treatment of the electrostatic term presented above has to be combined with a model for the deformation of polymer chains on clustering that contributes an elastic term to the Hamiltonian. Models for the elastic term that have been presented by us[5] and by other authors[1-4] either model polymer chains as a Gaussian random walk or else use concepts of bulk elasticity. While both approaches are reasonable as a starting point, neither is satisfactory as a theory of ionic clustering. We have therefore not attempted to combine the above model with an approximate elastic model but hope to present a more fundamental model for the elastic term based on self-avoiding random walks[14] in the near future.

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Nitrogen-15 Nuclear Magnetic Resonance of Cured Urea–Formaldehyde Resins Using Cross Polarization and Magic-Angle Spinning

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ABSTRACT: ^{15}N NMR spectra have been obtained on two urea–formaldehyde (UF) resins that were prepared with ^{15}N enriched to 99% and on model compounds with ^{15}N in natural abundance. Solid-sample techniques were used, with cross polarization (CP) and magic-angle spinning (MAS). The spectra consist largely of peaks in two partially overlapping regions. Distinctions between secondary and tertiary amide nitrogens are made partly on the basis of chemical shift differences and partly on the basis of interrupted-decoupling experiments. Overall, a lower level of structural detail is obtained than what is provided by corresponding ^{13}C CP/MAS experiments, but ^{15}N data should provide a useful supplement to ^{13}C data in the elucidation of structure in cured UF resins.

Introduction

Urea–formaldehyde (UF) resins are important binder products, especially for the manufacture of composition board, but emission of formaldehyde from UF-bonded particle board has generated concern in the particleboard industry.[1-8] For cured UF resins, both poor durability in high-temperature, high-humidity environments and the emission of formaldehyde are due to a considerable degree to hydrolytic instability,[2,9-12] which in turn is determined by the structural moieties present in the resins. Therefore, it is of considerable importance to have reliable spectroscopic techniques for determining the correlations between molecular structures and macroscopic properties of cured resins.

Four potentially reactive centers (atomic sites) in urea and two in formaldehyde are responsible for the large variety of likely structural moieties in UF resins. The following reactions are believed to occur to varying extents

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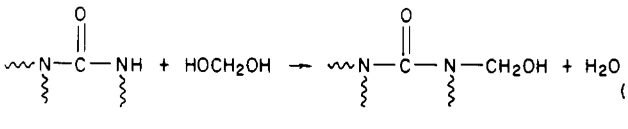
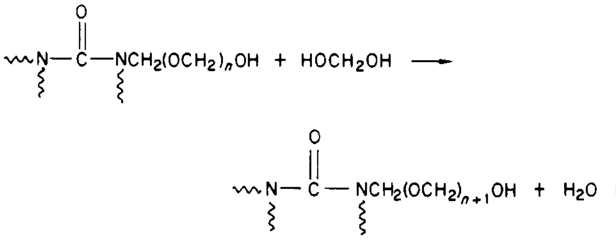
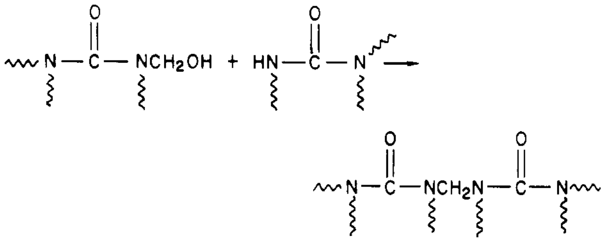
in the formation of a UF resin:[2,11]



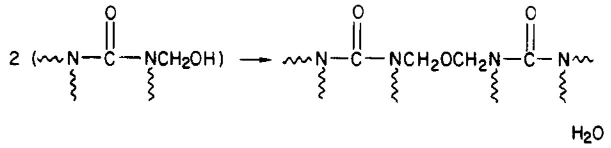
$$\sim N-\overset{O}{\overset{\|}{C}}-NH + HOCH_2OH \rightarrow \sim N-\overset{O}{\overset{\|}{C}}-N-CH_2OH + H_2O \quad (1)$$



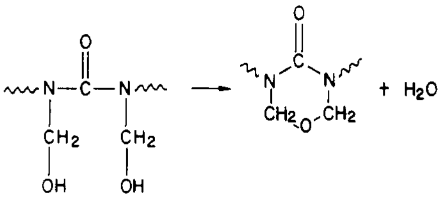
$$\sim N-\overset{O}{\overset{\|}{C}}-NCH_2(OCH_2)_nOH + HOCH_2OH \rightarrow \sim N-\overset{O}{\overset{\|}{C}}-NCH_2(OCH_2)_{n+1}OH + H_2O \quad (2)$$



$$\sim N-\overset{O}{\overset{\|}{C}}-NCH_2OH + HN-\overset{O}{\overset{\|}{C}}-N\sim \rightarrow \sim N-\overset{O}{\overset{\|}{C}}-NCH_2N-\overset{O}{\overset{\|}{C}}-N\sim \quad (3)$$



$$2\,(\sim N-\overset{O}{\overset{\|}{C}}-NCH_2OH) \rightarrow \sim N-\overset{O}{\overset{\|}{C}}-NCH_2OCH_2N-\overset{O}{\overset{\|}{C}}-N\sim + H_2O \quad (4)$$



(5)

In the past 7 years or so, liquid-solution ^{13}C NMR[13-17] has emerged as a powerful technique for studying UF resins in their early stages of formation, and the most complete information available on the structures of such UF resins is now provided by ^{13}C NMR spectra. The ^{13}C NMR spectra indicate specifically that branching occurs already in the initial stages of the condensation and that the content of branches increases with reaction time. However, high-resolution liquid-state NMR techniques can be useful only in the early stages of polymerization, while the resin still remains soluble.

While much information has been published on the kinetics and synthetic pathways of the initial reactions of the UF resin system, little is known concerning how these reactions proceed during the condensation of high molecular weight intermediates. Even though they are very important in determining the properties and performances of UF resins, the details of the structure of the cured resin and the curing process are still obscure in many respects. Apart from the complexity of these reactions, the insolubility of the products in many solvents provides a formidable barrier to characterization by conventional means. As was found in ^{13}C NMR studies on furfuryl alcohol resins[18] and phenol–formaldehyde resins,[19] the curing process of UF resins may not necessarily be just the extension of those reactions occurring in the early stages.

Limitations in solubility of many resins, especially cured resins, can be overcome by using solid-sample ^{13}C NMR techniques with cross-polarization and magic-angle spinning (CP/MAS).[20] A sample examined in the solid state has the highest possible concentration and this approach also eliminates structural uncertainties associated with the dissolution process. Although the initial ^{13}C NMR CP/MAS experiments[21] carried out on UF resins in this laboratory at a low static magnetic field of 1.41 T (15 MHz for ^{13}C) were rather discouraging because of complications due to effects of the ^{14}N present in these samples,[22] a reexamination of these samples at higher magnetic field (4.70 T), using sideband suppression methods,[23] yielded structurally informative spectra.[21] The ^{13}C NMR spectra obtained at higher field were deconvoluted to give approximate relative concentrations of various functional moieties, providing some information about the structural differences between different resins and on the structural changes that accompany the curing of a UF resin. Nevertheless, due to severe overlap for those peaks in the ^{13}C NMR CP/MAS spectra corresponding to non-carbonyl carbons, the desired level of structural detail was not achieved.

As nitrogen is another element that is comparable in occurrence to carbon in UF resins, we decided to explore the utility of ^{15}N CP/MAS NMR on these systems to see if this approach would add some structural information not readily obtainable from the ^{13}C CP/MAS spectra. It was anticipated, for example, that by employing interrupted-decoupling techniques[24] it should be possible to distinguish tertiary amides from secondary amides and primary amides. This type of information would be very important with regard to cross-linking in the resin structure, and it cannot be obtained readily by the ^{13}C CP/MAS method. Since the natural abundance of ^{15}N is only 0.37%, the use of ^{15}N-enriched materials was necessary. Previous reports of ^{15}N CP/MAS studies have been promising, especially for protein systems[25] and for surface-adsorbed species.[26] This paper is a preliminary report of our solid-state ^{15}N CP/MAS experiments on ^{15}N-enriched urea–formaldehyde resins.

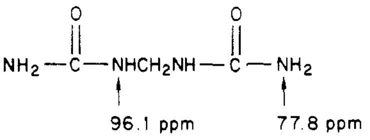
Experimental Section

A. Samples. The preparations of model compounds and the ^{15}N-enriched UF resins have been described previously.[21,27] The former include *N,N'*-dimethylolurea ($HOCH_2NHCONHCH_2OH$), methylenediurea ($NH_2CONHCH_2NHCONH_2$), and dimethylolurea dimethyl ether ($CH_3OCH_2NHCONHCH_2OCH_3$). Resins UF-10-1 and UF-10-2 represent two different extents of curing. Resin UF-10 was acidified to pH 3.0, and one portion (UF-10-1) was immediately vacuum-dried at ambient temperatures, while another portion (UF-10-2) was heated for 20 min at 100 °C before vacuum-drying.

B. NMR Measurements. ^{15}N CP/MAS spectra were obtained at 20.3 MHz on a Nicolet NT-200 spectrometer, modified in-house for solid-sample work and using a modified "windmill" spinner. Spectra of model compounds were obtained with a 1-ms contact time and a 1-s repetition time. Spectra of ^{15}N-enriched resins were obtained with a variable contact time running from 100 μs to 10 ms and with a repetition time of 1 s. Spectra of resins were also taken with the interrupted-decoupling CP/MAS technique,[24] with interrupted-decoupling times of 50, 75, 100, and 120 μs under the condition of 1-ms contact time and 1-s repetition time. Peak positions were determined by substitution relative to liquid ammonia and are reported with higher chemical shifts corresponding to lower shieldings. Structural assignments of resonance positions were made tentatively by using solution-state ^{15}N data[28] and some CP/MAS ^{15}N data that we obtained on UF model systems. For the latter purpose ^{15}N CP/MAS NMR spectra were obtained on ^{15}N-enriched urea and in natural abundance on *N,N'*-dimethylolurea, methylenediurea, and dimethylolurea-dimethylether.

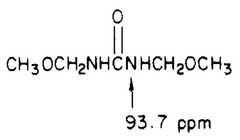
Results

The chemical shifts obtained by CP/MAS for four solid model compounds are shown below:



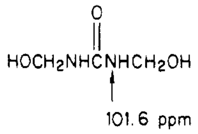
$\mathrm{NH_2{-}\overset{O}{\overset{\|}{C}}{-}NHCH_2NH{-}\overset{O}{\overset{\|}{C}}{-}NH_2}$

methylenediurea



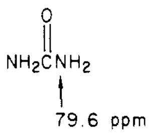
$\mathrm{CH_3OCH_2NH\overset{O}{\overset{\|}{C}}NHCH_2OCH_3}$

dimethylolureadimethylether



$\mathrm{HOCH_2NH\overset{O}{\overset{\|}{C}}NHCH_2OH}$

dimethylolurea



$\mathrm{NH_2\overset{O}{\overset{\|}{C}}NH_2}$

^{15}N-enriched urea

Figures 1 and 2 show the ^{15}N spectra of two ^{15}N-labeled UF resins (UF-10-1 and UF-10-2) obtained in normal CP/MAS experiments and with various interrupted-decoupling times. The spectra of both UF-10-1 and UF-10-2 obtained at a 1-ms contact time show two main peaks, at 114 and 94 ppm. Figure 3 shows the spectra of UF-10-2 at different contact times. From these results and analogous data on UF-10-1 one can estimate that the CP relaxation times are about 1.5 and 0.5–1 ms for the peaks centered at 114 and 94 ppm, respectively. The proton $T_{1\rho}$ values for these systems appear to be roughly 3 ms. For UF-10-2 there is also a very weak peak around 50 ppm. Due to the complexity and variety of the UF-resin structure, we expected more than two main peaks in the ^{15}N spectra. However, attempts to deconvolute the spectra into a larger number of contributing peaks (say, five) yielded only ambiguous results.

When one examines the possible (expected) UF-resin structures according to their ^{15}N chemical shifts, one finds the following groupings: (a) tertiary amide attached to methylol, 113 ppm; (b) tertiary amide not attached to methylol (but attached to a methylene linkage, to a methyl ether moiety, or to a dimethylene ether linkage), 104–106 ppm; (c) secondary amide attached to methylol, 102–108 ppm; (d) secondary amide not attached to methylol, 94–96 ppm; (e) primary amide, 78 ppm; (f) amine, 50 ppm. Within the ability of the ^{15}N CP/MAS approach to resolve lines and within the related constraints of achievable peak widths, there is severe overlap of peak positions for some of the structural types of interest for UF resins. Hence, ^{15}N CP/MAS does not provide a straightforward, easy approach to a treasury of valuable structural detail for UF resins prepared from high F/U ratio. However, some potentially significant relationships are apparent.

One sees by comparing Figures 1 (top) and 2 (top) that the lower shielding peak around 104–116 ppm is more pronounced (relative to the larger 94-ppm peak) for the more highly cured resin, UF-10-2, than it is for the less cured resin, UF-10-1. This argues in favor of a predominant conversion during cure of structures of type d into structures of type a and/or b and against a predominant curing conversion of structures of type c to structures of type d. The interrupted-decoupling or diplar dephasing experiment[24] should be capable of providing additional information on these points.

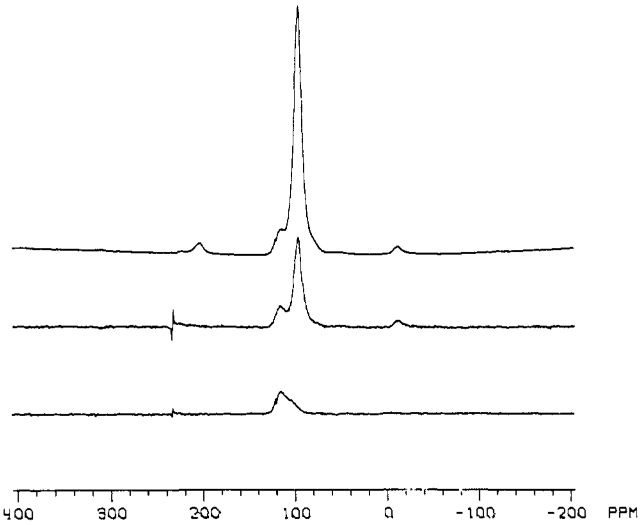


Figure 1. ^{15}N CP/MAS spectra of UF-10-1 with and without an interrupted-decoupling period (1-ms CP contact time): top, no interrupt period; middle, 50-μs interrupt period; bottom, 120-μs interrupt period.

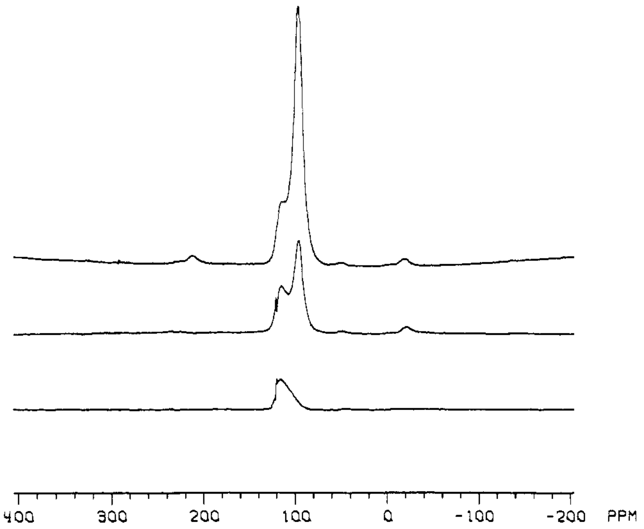


Figure 2. ^{15}N CP/MAS spectra of UF-10-2 with and without interrupt decoupling period (1-ms CP contact time): top, no interrupt period; middle, 50-μs interrupt period; bottom, 120-μs interrupt period.

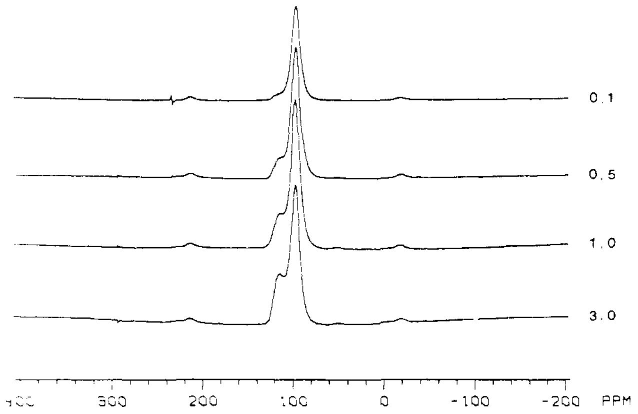


Figure 3. ^{15}N CP/MAS spectra of UF-10-2 as a function of CP contact time (as indicated in milliseconds).

During the interrupt period of the dipolar dephasing experiment the nuclear spin magnetization associated with a ^{15}N spin with a directly attached proton (as in a secondary amide) is dephased more rapidly by the proton dipolar interaction than would be the ^{15}N magnetization of a ^{15}N spin with no directly attached proton (as in a tertiary amide). However, examination of spectra in Figures 1 and 2 reveals that an unambiguous conclusion is not warranted, due to the severe overlap of signals of type b with those of type c. A straightforward interpretation would also be compromised by the long period of storage of these resins between the time of preparation and the time of the ^{15}N NMR experiments. In the spectra of resin UF-10-2 there appears a small but unambiguous peak around 50 ppm; it is tentatively assigned to amine resulting from the hydrolysis of amide at high temperature.[6,29]

More definitive conclusions are desirable and might be expected from a combination of intensive ^{13}C and ^{15}N NMR studies on freshly prepared ^{15}N-enriched samples in which the U/F ratio and curing time are varied systematically, especially for UF resins prepared from lower F/U ratios. Also in this context, it should be of interest to apply an ^{15}N analogue of the technique recently developed by Terao, Miura, and Saika[30] for distinguishing carbon resonances of CH$_n$ for $n = 0$–2. Such experiments are planned. In the meantime, it seems appropriate to make the following generalization: Currently ^{13}C CP/MAS spectra are overall more useful than ^{15}N CP/MAS spectra in providing structural detail on UF resins, but ^{15}N data will provide a useful supplement.

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Registry No. NH_2-CO-$NHCH_2NH$-CO-NH_2, 13547-17-6; $CH_3OCH_2NHCONHCH_2OCH_3$, 141-07-1; $HOCH_2NHCONHCH_2OH$, 140-95-4; NH_2CONH_2, 57-13-6; (urea)·(formaldehyde) (copolymer), 9011-05-6.

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