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^{13}C and ^{15}N CP/MAS NMR Characterization of Biuret-Rich 4,4′-Methylenebis(phenyl isocyanate) Based Resins

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ABSTRACT: A series of biuret resins was prepared under a variety of reaction conditions from 4,4′-methylenebis(phenyl isocyanate) (MDI) and formic acid. ^{13}C CP/MAS and CP/MAS/interrupted-decoupling results indicate that the concentration of biuret linkages is essentially constant in resins having the same formal HCO_2H/MDI molar ratio for curing temperatures between 120 and 160 °C but is larger for larger formal HCO_2H/MDI ratios for a given cure temperature. ^{13}C CP/MAS/interrupted-decoupling results indicate reduced concentrations of isocyanate groups in resin samples prepared from reaction mixtures with increased formal HCO_2H/MDI molar ratios for a given cure temperature. ^{15}N CP/MAS and CP/MAS/interrupted-decoupling results on an ^{15}N-enriched biuret resin provide additional insight into the chemical structures in these complex resin systems.

Introduction

Isocyanate-based polymer systems have been successfully modified with a wide variety of cross-link structures to obtain materials with improved physical properties.[1-4] Isocyanate-based polymerization reactions are often complicated by side reactions of the isocyanate groups with active hydrogen-containing moieties, reactions that can ultimately affect the chemical structure and physical properties of the desired polymer. For example, the most important reaction in polyurethane formation is the reaction between the isocyanate group and the OH group of a hydroxyl-containing compound:[5]

$$\mathrm{RNCO + R'OH \rightarrow RNHC(O)OR'} \tag{1}$$

An important side reaction in the preparation of polyurethanes is the reaction between isocyanate and water, resulting in substituted-urea linkages:[5]

$$\mathrm{RNCO + H_2O \rightarrow [RNHCO_2H] \rightarrow RNH_2 + CO_2} \tag{2a}$$

$$\mathrm{RNH_2 + R'NCO \rightarrow RNHC(O)NHR'} \tag{2b}$$

Other side reactions of isocyanate groups with the active-hydrogen sites of urethane and urea moieties result in the formation of allophanate (eq 3) and biuret (eq 4) linkages:[5]

$$\mathrm{RNCO + R'NHC(O)OR'' \rightarrow RNHC(O)NR'C(O)OR''} \tag{3}$$

$$\mathrm{RNCO + R'NHC(O)NHR'' \rightarrow R'NHC(O)NR''C(O)NHR} \tag{4}$$

Although certain cross-linking reactions like biuret formation can adversely affect the desired physical properties of a particular polyurethane resin, other isocyanate-based materials are specifically tailored to contain such cross-links. Biuret-type triisocyanate resins are commonly used in the coatings and related industries:[1,6]

$$\mathrm{3RNCO + H_2O \rightarrow RNHC(O)NRC(O)NHR + CO_2} \tag{5}$$

Other isocyanate-based biuret resins are formed from the reactions of diisocyanates with carboxylic acids.[7] These reactions are known to proceed in two principal ways:[8-10]

$$\mathrm{RNCO + R'COOH \rightarrow RNHC(O)R' + CO_2} \tag{6a}$$

$$\mathrm{2RNCO + 2R'COOH \rightarrow RNHC(O)NHR + R'C(O)OC(O)R' + CO_2} \tag{6b}$$

A mixture of products corresponding to these two pathways is usually obtained. Both reactions 6a and 6b have been shown to involve the formation of thermally unstable *N*-carboxyanhydrides of the general formula $\mathrm{RNHCO_2C(O)R'}$. Biuret linkage concentration is known to increase when the formal molar ratio of carboxylic acid to diisocyanate increases,[8] indicating that the formation of substituted-urea moieties via reaction 6b and the following condensation reaction between urea moieties and additional isocyanate groups (reaction 4) are probably the major pathways for biuret formation in these diisocyanate–carboxylic acid resin systems.

Other products formed from reactions 6a and 6b of diisocyanates and carboxylic acids can also react with isocyanate groups to form imide-type structures. Isocyanate groups might react with the amide product of reaction 6a to yield unsymmetrical imide linkages:

$$\mathrm{RNCO + R'NHC(O)R'' \rightarrow RNHC(O)NR'C(O)R''} \tag{7}$$

In addition, symmetrical imide linkages can be formed from the reaction of isocyanate groups with the anhydride product of reaction 6b:

$$\mathrm{RNCO + R'C(O)OC(O)R' \rightarrow R'C(O)NRC(O)R' + CO_2} \tag{8}$$

This paper addresses the ability of solid-state NMR spectroscopy with cross polarization (CP)[11] and magic-angle spinning (MAS)[12] to characterize cured HCO_2H/MDI-based resin systems tailored with a high concentration of biuret linkages. NMR characterization of biuret-containing systems has previously been limited to soluble oligomers or model compounds in liquid-solution studies[13,14] or model compounds in the solid state.[15] A solid-state NMR investigation of these types of systems should provide insight into the effect of reactant molar ratios and reaction temperature on the formation of various structures in HCO_2H/MDI-based biuret linkages. The biuret resins prepared for this investigation bear little resemblance to commercial materials. The NMR results presented here emphasize the ability of solid-state NMR to characterize chemical structural patterns, trends, and relationships and are not explored for correlation directly with specific physical properties or commercial products. The structural characterization strategies developed in this work should facilitate such correlations on materials of commercial interest.

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Experimental Section

NMR Measurements. ^{13}C CP/MAS spectra were obtained at 50.3 MHz on a modified wide-bore Nicolet NT-200 spectrometer. The NMR parameters used to accumulate the spectra are a 2-ms CP contact time and a 6-s repetition time. An interrupt time of 70 μs was used for the CP/MAS interrupted-decoupling (dipolar-dephasing) experiments.[16] Samples were spun at 6.0 kHz, using bullet-type spinners.[17] The magic angle was adjusted to ±0.1° by using the ^{79}Br spectrum of KBr placed in a spinner.[18]

^{15}N CP/MAS spectra of an ^{15}N-enriched resin are obtained at 20.3 MHz on the same modified NT-200 spectrometer. The NMR parameters used to accumulate the spectra presented here are a 4-ms contact time and a 6-s repetition time. An interrupt time of 70 μs was used for the CP/MAS interrupted-decoupling experiments. Samples were spun at 2.8–3.3 kHz, using bullet-type spinners; the magic angle was set by the KBr method.

Samples. 4,4′-Methylenebis(phenyl isocyanate) (MDI) was obtained from Eastman Kodak Co. and was purified by distillation through a Vigreux column at reduced pressure (142–145 °C at 0.15 Torr). ^{15}N-Enriched MDI (99.8% doubly labeled) was obtained from MSD Isotopes and was used without further purification to prevent loss of starting material. Anhydrous formic acid was obtained by refluxing 88% formic acid (Fisher Scientific Co.) over phthalic anhydride (99%; J. T. Baker Chemical Co.) for 12 h under a nitrogen atmosphere, followed by distillation (95–96 °C at 650 Torr). MDI-based biuret resins were prepared by adding various amounts of anhydrous formic acid to MDI and heating under a nitrogen atmosphere with stirring at various temperatures for various lengths of time.

Results and Discussion

^{13}C and ^{15}N chemical shift assignments used in this study are based on solution and/or solid-state chemical shifts of model compounds presented previously.[15] Figure 1 shows the 50.3-MHz ^{13}C CP/MAS spectra (left side of figure) and the corresponding ^{13}C CP/MAS/interrupted-decoupling spectra (right side of figure) obtained on a series of HCO_2H/MDI-based biuret resins cured for 3 h at 120, 140, and 160 °C. For each cure temperature, three resin samples were prepared from reaction mixtures having formal HCO_2H/MDI molar ratios of 0.4/1, 0.8/1, and 1.3/1.[19] The spectra in Figure 1 show the entire ^{13}C chemical shift range relevant to these systems, except for the methylene carbon resonance at 41 ppm. The ^{13}C CP/MAS and CP/MAS/interrupted-decoupling spectra of HCO_2H/MDI-based biuret resins in Figure 1 are characterized by seven peaks or regions of spectral intensity associated with the following types of carbon structural situations:[15] a resonance centered at 120 ppm corresponding to aromatic carbons ortho to amide nitrogens; a resonance centered at 125 ppm corresponding to isocyanate carbonyl carbons and aromatic carbons ortho to isocyanate nitrogens; a peak centered at 132 ppm corresponding to various unsubstituted aromatic carbons meta to amide and imide nitrogens and to isocyanate-substituted aromatic carbons; a peak centered at 138 ppm corresponding to imide-substituted and amide-substituted aromatic carbons and to methylene-substituted aromatic carbons para to isocyanate groups; a resonance centered at 141 ppm corresponding to various methylene-substituted aromatic carbons; a resonance centered at 155 ppm corresponding to amide and imide carbonyl carbons; and a peak centered at 165 ppm corresponding to the carbonyl carbon of formic acid.

There are several observable differences in the ^{13}C CP/MAS spectra of Figure 1 when one compares the spectra of resin samples prepared from reaction mixtures with different formal HCO_2H/MDI molar ratios and cured at the same temperature. The ^{13}C CP/MAS spectra of resins prepared from mixtures with the same formal HCO_2H/MDI molar ratio and cured at different temperatures do not exhibit discernible differences. For each curing temperature, the gross resolution of peaks centered at 120, 125, and 137 ppm in the ^{13}C CP/MAS spectra in Figure 1 is better for spectra obtained on resins corresponding to a formal HCO_2H/MDI molar ratio of 1.3/1 or 0.8/1 relative to the spectra obtained on resins corresponding to a formal HCO_2H/MDI molar ratio of 0.4/1. For a given curing temperature, the ^{13}C CP/MAS spectra of samples corresponding to formal HCO_2H/MDI molar ratios of 1.3/1 and 0.8/1 are very similar.

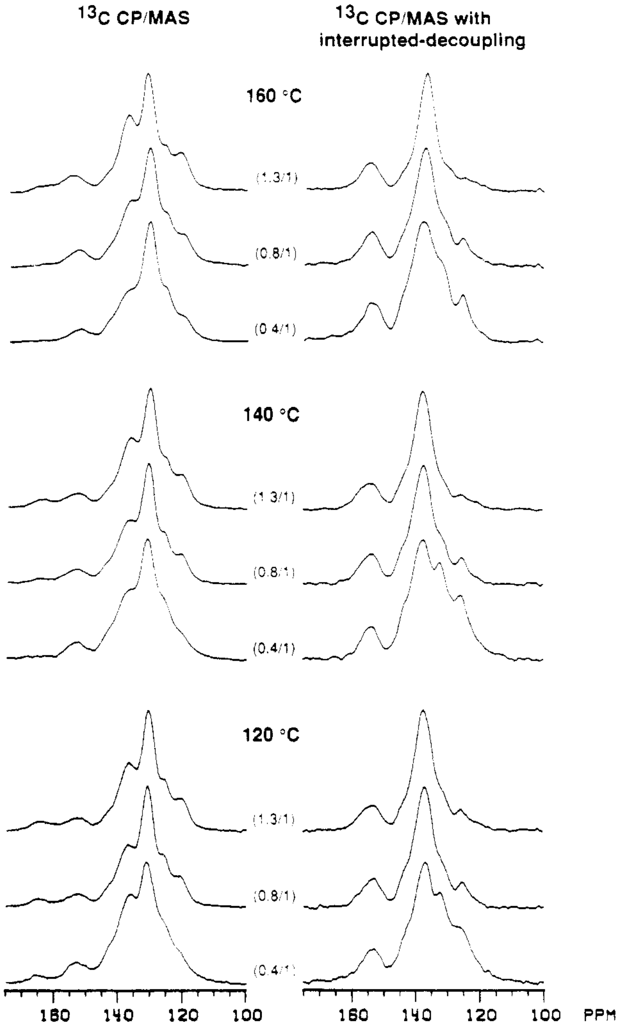


Figure 1. 50.3-MHz ^{13}C CP/MAS spectra (CP contact time = τ = 2 ms; repetition delay = t_d = 6 s) and ^{13}C CP/MAS/interrupted-decoupling spectra (τ = 2 ms; t_d = 6 s; interrupt time = 70 μs) of HCO_2H/MDI-based biuret resins cured for 3 h at the temperatures indicated. The fraction in parentheses indicates the formal HCO_2H/MDI molar ratio of the reactants.

To help identify some of the structures responsible for the observed intensity changes in the 120–145 ppm region of the ^{13}C CP/MAS spectra, dipolar-dephasing (interrupted-decoupling)[16] experiments were carried out on each of the samples represented by the spectra on the left side of Figure 1. In these experiments, a delay period of 70 μs was inserted between the CP contact period and the beginning of data acquisition, during which the ^{1}H decoupler is turned off and ^{13}C magnetization due to ^{13}C's that have strong dipolar interactions with protons is attenuated by dephasing associated with ^{13}C–^{1}H dipolar interactions. As a result, ^{13}C signal intensity persists for carbons that do not directly bear hydrogens and methyl carbons (for which ^{13}C–^{1}H dipolar interactions are strongly attenuated by rapid rotation), while signal intensities from methylene and methine carbons are dramatically reduced.

Because the dipolar-dephasing experiment relies on the largely incoherent ^{13}C spin behavior under $^{13}C-^{1}H$ and $^{1}H-^{1}H$ dipolar interactions, intensities in the resulting spectrum typically cannot be treated in a quantitative manner, especially when overlapping resonances are present. Individual carbons that bear hydrogens can dephase differently because of differing strengths of the $^{13}C-^{1}H$ dipolar interactions and differing rates of $^{1}H-^{1}H$ flip flops. Results from these experiments are shown on the right side of Figure 1.

The removal of intensity in the interrupted-decoupling spectra of Figure 1 in the 120 ppm region (corresponding to unsubstituted aromatic carbons ortho to amide nitrogens) and the 132 ppm region (corresponding to various unsubstituted aromatic carbons meta to amide and imide nitrogens) improves the resolution of certain substituted aromatic carbon resonances in those spectra relative to the corresponding "normal" CP/MAS spectra. Isocyanate carbonyl carbons (125 ppm), isocyanate-substituted aromatic carbons (132 ppm), and various nitrogen-substituted and methylene-substituted aromatic carbons (about 137 ppm) are more easily identified in the interrupted-decoupling spectra than in the normal ^{13}C CP/MAS spectra.

Peaks pertaining to isocyanate moieties are of particular interest, since monitoring these peaks gives information on the extent of isocyanate reaction to form various cross-links, e.g., biuret linkages. For resins cured at a specific temperature, the intensity of the isocyanate carbonyl resonance (125 ppm) is clearly smaller in the interrupted-decoupling spectra in Figure 1 for a larger HCO_2H/MDI molar ratio. However, for resins prepared from reaction mixtures corresponding to a given formal HCO_2H/MDI molar ratio, the intensity of this peak does not vary significantly in the interrupted-decoupling spectra in Figure 1 for resins cured at different temperatures. These results would suggest that increasing the HCO_2H/MDI ratio results in an increased consumption of isocyanate groups, presumably to form biuret linkages, and that over the temperature range investigated, the cure temperature has little effect on the consumption of isocyanate groups to form biuret linkages.

Additional evidence for the increased consumption of isocyanate groups in resins prepared from mixtures with higher formal HCO_2H/MDI molar ratios is provided by inspection of the 132 ppm region of the interrupted-decoupling spectra in Figure 1. Although certain hydrogen-bearing aromatic carbons have chemical shifts in this spectral region (vide supra), only intensity corresponding to isocyanate-substituted aromatic carbons should survive appreciably under interrupted-decoupling conditions in these experiments. Accordingly, the trend of decreasing intensity for the isocyanate carbonyl peak (125 ppm) corresponding to resins cured at a given temperature with increasing HCO_2H/MDI molar ratios is also observed for the isocyanate-substituted aromatic carbons at 132 ppm in the interrupted-decoupling spectra of Figure 1.

Deconvolutions (not shown) of the interrupted-decoupling spectra in Figure 1 were carried out, and the resulting relative peak areas of the contributing resonances are summarized in Table I. Although the relative areas obtained directly in this way from deconvolutions of the ^{13}C CP/MAS/interrupted-decoupling spectra should not be considered quantitative because they have not been corrected in terms of spin dynamics in any way, they can nevertheless aid in the qualitative examination of a given spectrum, if one has a reasonable knowledge of the contributing resonances. The results shown in Table I support the general trends discussed above for the interrupted-decoupling spectra in Figure 1. For the resins cured at a given temperature, intensity decreases can be noted in Table I for peaks centered at 125 and 132 ppm in spectra obtained in resins prepared with increasing HCO_2H/MDI molar ratios. Although the ^{13}C CP/MAS/interrupted-decoupling spectra of the various HCO_2H/MDI-based biuret resins reveal certain valuable qualitative patterns, a true estimate of the amount of biuret linkages formed or the amount of isocyanate remaining is made difficult because of the largely qualitative nature of the interrupted-decoupling experiment and the relatively complex nature of the ^{13}C spectra, with overlapping resonances.

Table I
Relative Peak Areas (Arbitrary Units) in the Interrupted-Decoupling ^{13}C CP/MAS Spectra of MDI-Based Biuret Resins[a]

^{13}C chem shifts,[b] ppm					
155	141	138	132	125	120
		(0.4/1; 120 °C)[c]			
14	8.9	40	12	22	3.4
		(0.8/1; 120 °C)			
14	6.8	61	8.1	8.0	2.5
		(1.3/1; 120 °C)			
15	6.4	64	5.8	6.2	3.2
		(0.4/1; 140 °C)			
11	8.8	39	14	23	4.0
		(0.8/1; 140 °C)			
16	11	54	9.5	7.5	2.5
		(1.3/1; 140 °C)			
16	10	59	8.0	4.4	2.7
		(0.4/1; 160 °C)			
15	5.3	53	14	10	3.1
		(0.8/1; 160 °C)			
17	7.4	57	10	6.6	2.9
		(1.3/1; 160 °C)			
17	6.9	63	6.9	2.9	3.0

[a] Relative integrated peak intensities obtained by deconvolution of 50.3-MHz spectra, uncorrected for spin dynamics in any way. [b] Chemical shifts of ^{13}C resonances referenced to TMS at 0 ppm. [c] Numbers in parentheses correspond to the formal HCO_2H/MDI molar ratio and cure temperature.

A HCO_2H/MDI-based biuret resin was prepared from ^{15}N-enriched MDI (99.8% doubly labeled) in a reaction mixture having a formal HCO_2H/MDI molar ratio of 0.4/1 and cured at 140 °C for 3 h. The ^{13}C CP/MAS spectrum (A) and the CP/MAS/interrupted-decoupling spectrum (B) of this resin are shown in Figure 2. These spectra display the same general features of the corresponding spectra in Figure 1 obtained on resins containing nitrogen isotopes in natural abundance (0.4% ^{15}N and 99.6% ^{14}N) and prepared at the same temperature and from a reaction mixture with the same formal HCO_2H/MDI molar ratio. This shows that the residual effects of $^{14}N-^{13}C$ dipolar interactions on the ^{13}C CP/MAS spectra[20] are not substantial in the spectra of Figure 1.

Since the nitrogen site is involved with all the common reaction chemistry of the isocyanate group, the formation of biuret cross-links and other isocyanate-derived moieties should be amenable to ^{15}N solid-state NMR techniques. ^{15}N CP/MAS has provided valuable information for the structure elucidation of isocyanate-based macromolecular resins.[15,21] Recently developed large-volume MAS systems[22] render the natural-abundance solid-state ^{15}N NMR characterization of such systems almost "routine", in favorable cases, although the particular work reported

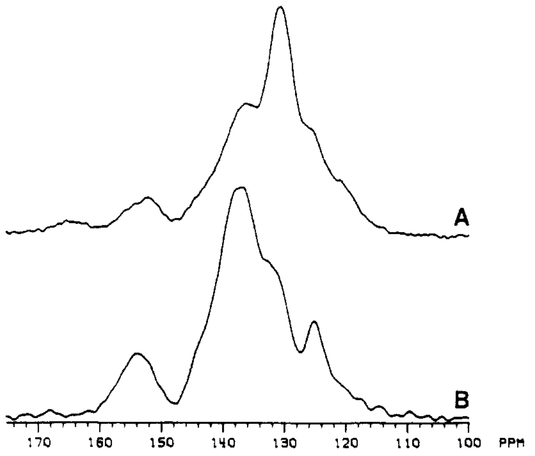


Figure 2. 50.3-MHz ^{13}C CP/MAS spectra of ^{15}N-enriched HCO_2H/MDI resin prepared from a reaction mixture having a formal HCO_2H/MDI molar ratio of 0.4/1 and cured at 140 °C for 3 h: (A) τ = 2 ms; t_d = 6 s; (B) interrupted-decoupling spectrum; τ = 2 ms; t_d = 6 s; interrupt time = 70 μs.

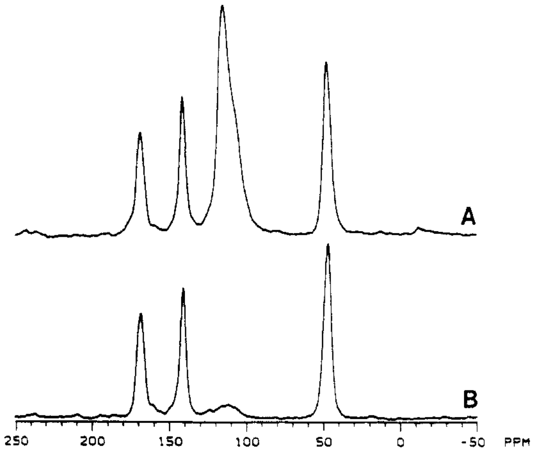


Figure 3. 20.3-MHz ^{15}N CP/MAS spectra of resin represented in Figure 2: (A) τ = 4 ms; t_d = 6 s; (B) interrupted-decoupling spectrum; τ = 4 ms; t_d = 6 s; interrupt time = 70 μs.

here is based on an ^{15}N-enriched sample.

Figure 3 shows the ^{15}N CP/MAS spectrum (A) and the interrupted-decoupling spectrum (B) of the same ^{15}N-enriched resin represented in Figure 2. Comparison of the A and B spectra in Figure 3 indicates that both the resonances centered at 104 ppm and at 114 ppm correspond to nitrogen environments tightly coupled to protons, i.e., nitrogen atoms with directly attached hydrogen atoms, since intensity in these regions is strongly attenuated under interrupted-decoupling experimental conditions (spectrum B) compared to the normal CP/MAS results (spectrum A). The peaks at 46, 141, and 168 ppm in spectrum A of Figure 3, which survive strongly under interrupted-decoupling conditions, can all be attributed to nitrogen environments that do not bear directly attached hydrogen atoms. On the basis of these data and ^{15}N liquid-solution results previously reported on pertinent model compounds,[15] the ^{15}N CP/MAS spectrum A is characterized by five peaks or regions of spectral intensity arising from the following types of nitrogen structural situations: a peak at 46 ppm corresponding to isocyanate nitrogens; a resonance centered at 104 ppm corresponding to urea-type nitrogens; the predominant peak at 114 ppm corresponding to biuret amide nitrogens; a peak at 141 ppm corresponding to biuret imide nitrogens; and a peak at 168 ppm corresponding to some different imide nitrogen environment. The assignment of the 168 ppm peak to a particular nitrogen structure has not yet been made unambiguously. A likely possibility that might correspond to this peak is discussed below.

Table II
Relaxation Parameters and Relative Intensities Obtained from ^{15}N CP/MAS Experiments on ^{15}N-Enriched HCO_2H/MDI-Based Biuret Resin[a]

peak,[b] ppm	T_{1H},[c] s	T_{NH},[d] ms	$T_{1\rho H}$,[d] ms	$I^*/I(4\ ms)$[e]	rel int (I), % uncor	rel int (I), % cor[f]
46	1.1	2.1	15	1.4	22	15
104	1.1	0.14	3.9	2.7	12	15
114	1.1	0.14	3.8	2.7	38	50
141	1.1	1.9	8.0	1.6	14	10
168	1.1	1.5	7.2	1.6	14	10

[a] Resin prepared from ^{15}N-enriched MDI in a reaction mixture having a formal HCO_2H/MDI molar ratio of 0.4/1 and cured at 140 °C for 3 h. [b] Chemical shifts of ^{15}N resonances referenced to liquid NH_3 at 0 ppm. [c] Obtained via cross polarization. [d] Obtained from variable contact time experiments. [e] Calculated from eq 9. [f] Corrected relative intensity = (uncorrected relative intensity) × (I^*/I(4 ms))/(total corrected intensity).

It can readily be seen by comparing the ^{15}N CP/MAS spectrum A in Figure 3 with ^{13}C CP/MAS spectra in Figures 1 and 2 that quantitative treatment of the ^{15}N spectrum should be more straightforward than for any of the ^{13}C spectra. This difference arises because ^{15}N has a larger chemical shift range than ^{13}C for the structural situations present in these systems and there are fewer chemically distinct types of nitrogen moieties than carbon moieties in such systems. Both factors lead to simpler ^{15}N spectra and a correspondingly smaller likelihood of overlapping resonances. Determining the relative concentrations of the various MDI-derived nitrogen structures should lead to an increased understanding of these complex resin systems. As demonstrated previously,[15] quantitative results can be obtained from ^{15}N CP/MAS spectra if appropriate variable contact time experiments are performed. Table II summarizes the ^{15}N cross-polarization parameters obtained from a variable contact time experiment performed on the ^{15}N-enriched HCO_2H/MDI-based biuret resin. A repetition time of 6 s was chosen for this experiment to ensure complete proton spin-lattice relaxation. Six seconds is more than 5 times the largest T_{1H} value displayed in Table II; these values were obtained by ^{15}N-detected (CP-based) ^1H inversion-recovery experiments.[23]

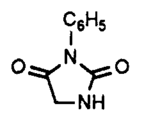
From the variable contact time data, values for T_{NH} (the ^1H–^{15}N cross-polarization time constant) and $T_{1\rho H}$ (the rotating-frame proton spin-lattice relaxation time) were obtained by fitting the measured intensity, $I(\tau)$, to eq 9:[24]

$$I(\tau) = I^*[T_{1\rho H}/(T_{1\rho H} - T_{NH})](e^{-\tau/T_{1\rho H}} - e^{-\tau/T_{NH}}) \quad (9)$$

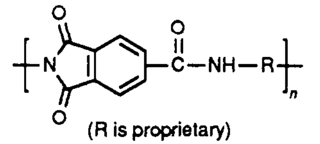
In this equation, $I(\tau)$ is the nitrogen magnetization observed for a given CP contact time (τ), and I^* is the nitrogen magnetization one would obtain if cross polarization were instantaneous and rotating-frame relaxation were infinitely slow. The quantity $I^*/I(\tau)$ calculated from eq 9 is the correction factor used to obtain analytically useful intensities. Values of the uncorrected relative intensities, $I(\tau)$, the correction factors, I^*/I(4 ms), and the corrected relative intensities for each resonance, I^*, are given in Table II.

The corrected relative intensities of the five different nitrogen environments in Table II indicate that most of the MDI isocyanate groups (~85%) are consumed to form the urea, biuret amide, and various imide-type moieties discussed above. The most abundant HCO_2H/MDI-based structures are the biuret amide linkages (114 ppm), accounting for nearly half of the total corrected nitrogen intensity in this sample. A high concentration of MDI-based urea linkages (104 ppm) also exists in this resin, indicating that reaction 6b and/or reaction 2b is/are probably the major initial reaction(s) in these systems, since biuret linkage formation can result only from reaction of additional isocyanate groups and urea linkages according to reaction 4 above.

The peak at 168 ppm corresponding to an imide-type nitrogen environment accounts for about 10% of the total corrected nitrogen intensity (see Table II) in the ^{15}N-enriched resin. Since biuret amide, biuret imide, and urea linkages constitute about 75% of the total corrected nitrogen content in this sample, it would appear that reaction 6b is the predominant between MDI and formic acid. If reaction 6a were a significant reaction, two additional nitrogen environments should be formed: (1) the *N*-formyl product from reaction 6a (R′ = H) and (2) the nitrogen-substituted *N*-formyl product resulting from reaction 7 between isocyanate groups and the *N*-formyl product (R″ = H). These two environments would be expected to display ^{15}N chemical shifts of about 136 ppm[25] and about 165–172 ppm,[26] respectively. Since only one peak is seen in the spectra of Figure 3 that does not correspond to isocyanate groups, urea linkages, or biuret linkages, this probably precludes the significance of reaction 6a for this particular resin. Since reaction 6b appears to be the predominant reaction between MDI and formic acid, a significant concentration of formic anhydride should be generated (see reaction 6b). Reaction between this anhydride moiety and isocyanate groups would lead to a diformyl imide linkage according to reaction 8. The ^{15}N chemical shifts of some imide-type linkages are shown below:



$\delta_{NC_6H_5}$ = 164 ppm
(ref 26)



(R is proprietary)
Torlon
δ_N = 172 ppm
(ref 22)

These imide-type environments have ^{15}N chemical shifts that are in the same region as the 168 ppm peak in the spectra of Figure 3. Hence, the ^{15}N chemical shift assignment of this peak tentatively to a diformyl imide product is in reasonable agreement with structures having similar imide-type structures.

Summary and Conclusions

^{13}C CP/MAS and CP/MAS/interrupted-decoupling results on a series of HCO_2H/MDI-based biuret resins establish the fact that the biuret linkage concentration is increased when the formal HCO_2H/MDI molar ratio is increased for a given cure temperature. The ^{13}C solid-state NMR results indicate that cure temperature, over a temperature range of 120–160 °C, does not have a significant effect on the amount of biuret linkages formed in these particular resins. The ^{15}N CP/MAS and CP/MAS/interrupted-decoupling results obtained on a ^{15}N-enriched HCO_2H/MDI-based biuret resin yield simpler solid-state NMR spectra than their corresponding ^{13}C counterparts, allowing for a quantitative determination of the relative concentrations of the different nitrogen structures in that resin. From the solid-state ^{15}N spectra, it appears that the major reaction between MDI and formic acid is the formation of MDI-based urea linkages and formic anhydride, which react further with isocyanate groups to yield biuret linkages and perhaps diformyl imide moieties under the conditions specified.

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