Monitoring the Thermal Degradation of an Isocyanurate-Rich MDI-Based Resin by ^{15}N and ^{13}C CP/MAS NMR

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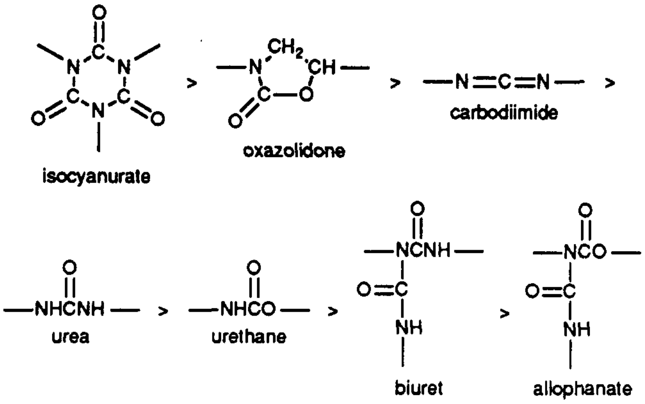
ABSTRACT: The thermal decomposition of an isocyanurate-rich resin based on 4,4′-diphenylmethane diisocyanate (MDI) was studied in successive heating experiments by ^{15}N and ^{13}C CP/MAS NMR. The thermal stabilities of the various MDI-derived linkages known to exist in the resin were found to fall into the following order: uretidione, biuret < urea < isocyanaurate < urea′, where the prime indicates that certain types of urea linkages, possibly formed from the complex thermal degradation chemistry of the sample, are more thermally stable than isocyanurate linkages. The ^{15}N CP/MAS results yield semiquantitative information on the concentrations of the various local nitrogen atom environments during the thermal decomposition process.

Introduction

Incorporation of isocyanurate linkages into polymer systems via the action of diisocyanate reactants has enjoyed widespread popularity as a chemical means of increasing thermal stability.[1-6] The thermal stabilities of the various nitrogen-containing linkages that are derived from diisocyanate species have been ranked previously and are shown below.[3,4,6-9]



The thermal degradation of the isocyanurate linkage has been studied by IR spectroscopy,[9-11] thermogravimetric analysis (TGA),[9,11] and liquid-solution proton NMR.[10] Thermogravimetry measures the formation of volatile products but is incapable of providing detailed structural information on the various degradation processes that occur in the bulk of the solid during the degradation. As a result, the nature of larger molecular weight fragments that are incapable of volatilization during the various stages of thermal de^{3}gradation are not well-characterized by TGA. Solid-state NMR spectroscopy, especially using cross-polarization (CP)[12] and magic-angle spinning (MAS),[13] has been used to study the thermal degradation of various macromolecular systems.[14-17] CP/MAS NMR can provide an excellent complement to IR spectroscopy for monitoring the thermal degradation of the insoluble bulk material in systems containing isocyanate-derived linkages. Solid-state NMR techniques are advantageous in that assignments of various resonances to specific chemical structures can often be confirmed by suitable variations of the pulse sequence.

This work addresses the thermal degradation of a cured isocyanurate-rich resin based on 4,4′-diphenylmethane diisocyanate (referred to here as MDI) via ^{15}N and ^{13}C CP/MAS NMR. This study further demonstrates the general applicability of solid-state NMR, especially ^{15}N CP/MAS, to isocyanate-derived, solid macromolecular systems. Recently developed large-volume MAS systems[18] render the natural-abundance ^{15}N solid-state NMR characterization of such systems almost "routine", although the particular work reported here is based on ^{15}N-enriched samples.

The MDI-based resin chosen for this study is known to contain a diverse array of chemical structures.[19] The work presented here emphasizes the changes in the structure of the *solid* resin as the temperature is increased under a nitrogen atmosphere and examines the ability of various solid-state NMR techniques to characterize these changes. Consecutive heating experiments were performed for examination of the degradation of the different types of linkages known to exist in these systems. The monitoring of volatile products has been reported previously[10] for the thermal decomposition of an isocyanurate system, and no attempt to monitor volatiles is presented here. This NMR study emphasizes chemical structural patterns and relationships in samples synthesized specifically to display those patterns and relationships clearly; no attempt was made to correlate these trends directly with physical properties or commercial products. The NMR patterns and strategies that emerge from this study can be used as the basis for such correlations in the future.

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 were a 4-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.[20] Samples were spun at 6.0 kHz, using bullet-type spinners.[21] The magic angle was adjusted to ±0.1° by using the ^{79}Br spectrum of KBr placed in a spinner.[22]

^{15}N CP/MAS spectra were obtained at 26.5 MHz on a Chemagnetics M-260 spectrometer. The NMR parameters used to accumulate the spectra were, unless otherwise noted, 0.5- and 6.0-ms contact times and a 6-s repetition time. An interrupt time of 100 μs was used for the CP/MAS interrupted-decoupling experiments. Samples were spun at 3.0 kHz, using spinners based on the Delft design,[23] and the magic angle was set by using the ^{35}Cl spectrum of NaCl placed in a spinner.

Samples. The MDI-polyisocyanurate resin was initially prepared by adding 0.5% (by weight) stannous octoate to ^{15}N-

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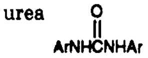
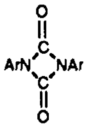
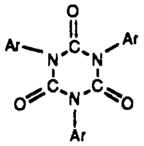
Table I
Structures and ^{15}N Chemical Shifts Pertinent to MDI-Based Resins[a]

structure	^{15}N chemical shift,[b] ppm
isocyanate ArNCO	46
amine $ArNH_2$	53
urea  $\mathrm{ArNH\overset{O}{\overset{\|}{C}}NHAr}$	104
biuret 	NH 114 N 141
uretidione 	145
isocyanurate 	149

[a] MDI-based resins and chemical shifts originally reported in ref 19. [b] Nitrogen chemical shifts referenced to liquid NH_3 at 0 ppm.

enriched MDI (99.8% doubly labeled, MSD Isotopes) and heating under a nitrogen atmosphere with stirring at 100 °C for 2 h.[1] The sample was then cooled to room temperature under nitrogen, and the resulting solid was ground in a drybox to obtain particles 1–3 mm^3 in size. The sample had been exposed to air in a vial for 18 months before the consecutive heating experiments were undertaken. Heating experiments were accomplished by placing the sample in a Sybron Thermolyne tube furnace equipped with an Omega Engineering, Inc., Model 660 type K thermocouple thermometer. The sample was exposed to various temperatures indicated in the figures and text (±2 °C) for 30 min under a nitrogen atmosphere. After heating at each temperature, the sample was cooled under nitrogen, weighed and packed in a spinner.

Results and Discussion

^{15}N and ^{13}C chemical shift assignments used in this study are based on solution and/or solid-state chemical shifts of model compounds presented previously.[19] Table I summarizes these assignments for the most relevant types of structures. ^{15}N CP/MAS has provided valuable information for the structure elucidation of nitrogen-containing macromolecular resins.[19,24,25] Therefore, because the nitrogen site is involved with all the common reaction chemistry of the isocyanate group, the thermal degradation of the kinds of MDI–isocyanate-derived linkages indicated above should be amenable to study by ^{15}N solid-state NMR technqiues.

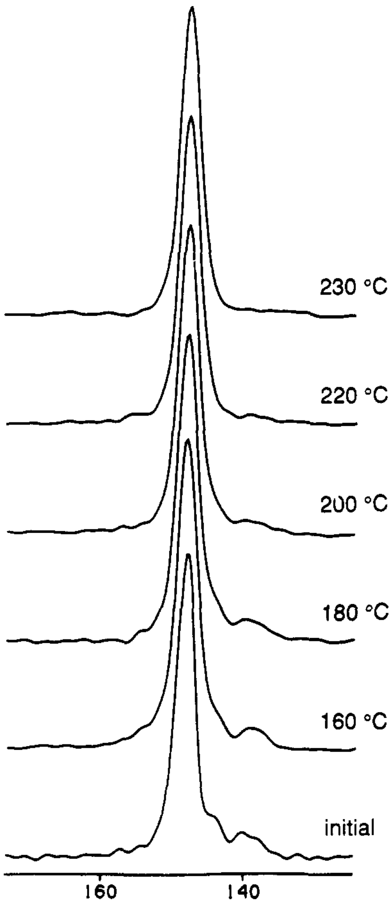


Figure 1. 180–120 ppm region of the 26.5-MHz ^{15}N CP/MAS spectra (CP contact time = τ = 6 ms; repeition delay = t_d = 6 s) of a MDI-based resin initially cured with stannous octoate for 2 h at 100 °C and exposed to air for 18 months, after heating the sample for 30 min at the temperatures indicated in the figure.

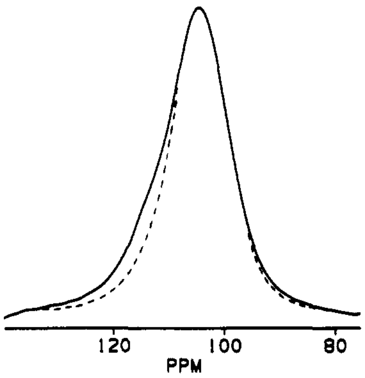


Figure 2. 140–80 ppm region of the 26.5-MHz ^{15}N CP/MAS spectra (τ = 0.5 ms; t_d = 6 s) of MDI-based resins corresponding to "initial" conditions (solid line) and after exposure to 230 °C (dashed line).

Figures 1–4 show ^{15}N CP/MAS results on the thermal degradation of a ^{15}N-enriched isocyanurate-rich MDI-based resin initially cured at 100 °C. The initial sample had been exposed to air for 18 months prior to the consecutive heating experiments; results obtained on the corresponding resin sample immediately after curing, as well as after prolonged exposure to air, are presented elsewhere.[19,26] In Figure 1, the spectra are displayed in a format to emphasize the spectral region containing resonances due to the MDI-based biuret imide (141 ppm), uretidione (145 ppm shoulder), and isocyanurate (150 ppm) moieties.[19] These spectra were obtained under conditions (6-ms CP contact time) that favor the observation of nitrogen atoms without directly attached hydrogens relative to what one would observe with a very short CP contact time (vide infra). On the basis of information on cross-polarization dynamics presented below, we can estimate that for a 6-ms contact time the intensities of non-proton-bearing nitrogens are disfavored by a factor of only about 2 relative to the intensities of proton-bearing nitrogens. Of course, the interrupted-decoupling (dipolar-dephasing) technique discriminates very effectively in favor of nitrogen nuclei to which hydrogen is not directly attached (vide infra).

As the temperature to which the resin is subjected is increased from 160 to 230 °C, the ^{15}N spectral intensity corresponding to biuret imide (141 ppm) and uretidione

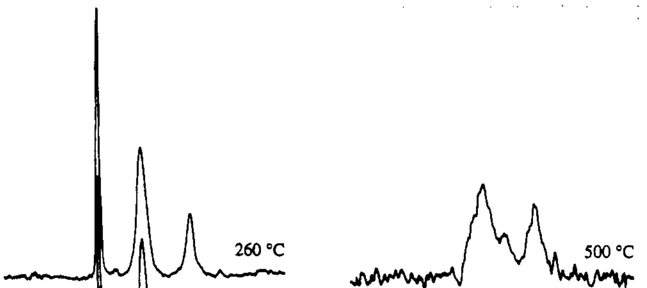


Figure 3. 26.5-MHz ^{15}N CP/MAS spectra (τ = 6 ms; t_d = 6 s) of the isocyanurate-rich MDI-based resin heated at the temperatures indicated.

(145 ppm shoulder) in Figure 1 steadily decreases until it is virtually absent from the spectrum corresponding to a heating temperature of 230 °C. From these data, the biuret and uretidione linkages appear to be less thermolytically stable than the isocyanurate linkages, a result consistant with the conclusions of previous investigations.[9,27] The biuret amide moieties (114 ppm)[19] should also thermally degrade by 230 °C, since these structures cannot exist without the simultaneous existence of biuret imide moieties; this issue is addressed in Figure 2, which shows the 140–80 ppm region of the ^{15}N spectra of the initial cured resin (solid line) and the resin after exposure to 230 °C (dashed line). These spectra are displayed in a format to emphasize the MDI-based urea (104 ppm) and biuret amide (114 ppm) nitrogen structures. The results in Figure 2 were obtained under experimental conditions (0.5-ms CP contact time) that favor the observation of nitrogens that bear directly attached hydrogens. On the basis of CP dynamics data presented below, we can estimate that the intensities for nitrogens with directly attached hydrogen(s) are favored by about a factor of 5 under these CP conditions, relative to nitrogens with no directly attached hydrogen. Clearly, a substantial spectral intensity associated with biuret amide nitrogens (114 ppm lower shielding shoulder on the major resonance at 104 ppm) has disappeared upon 230 °C treatment, confirming the degradation of biuret linkages indicated in Figure 1. These data would suggest that biuret linkages are, along with uretidione linkages, less thermolytically stable than the urea linkages, again agreeing with previous conclusions.[6,27] A priori, subtle changes in line shape could result from changes in sample morphology, but we believe that the character of the changes in these spectra reflect the chemical–structural transformations indicated above.

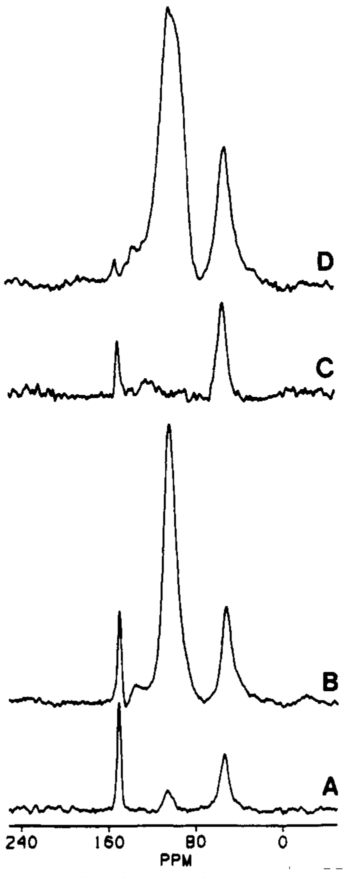
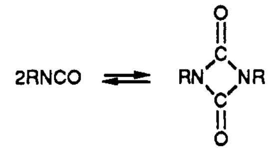


Figure 4. 26.5-MHz ^{15}N CP/MAS spectra. (A) Interrupted-decoupling spectrum (τ = 2 ms; interrupt time = 100 μs; t_d = 6 s) of MDI-based resin after heating at 300 °C. (B) Normal spectrum (τ = 2 ms; t_d = 6 s) of MDI-based resin after heating at 300 °C. (C) Interrupted-decoupling spectrum (τ = 1 ms; interrupt time = 100 μs; t_d = 6 s) of MDI-based resin after heating at 340 °C. (D) Normal spectrum (τ = 1 ms; t_d = 6 s) of MDI-based resin after heating at 340 °C.

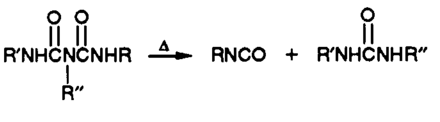
Uretidione structures are known to exist in equilibrium with isocyanate structures even at room temperature:



(1)

As the temperature of such a system is increased, the uretidione structures revert back to the isocyanate.[27,28] The decrease in uretidione intensity (145 ppm) in the spectra of Figure 1 for increased temperature is consistent with this view. The intensity of the isocyanate moiety, however, does not increase upon increased heating temperature (vide infra), indicating that the isocyanate may quickly react to form other structures. This subject is addressed in more detail below.

Biuret linkages are known to decompose thermally, yielding urea and isocyanate structures:[29]



$$\mathrm{R'NH}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\underset{\underset{\mathrm{R''}}{|}}{\mathrm{N}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHR} \xrightarrow{\Delta} \mathrm{RNCO} + \mathrm{R'NH}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{NHR''} \qquad (2)$$

This is probably the major pathway for the decrease in biuret structures with increasing temperature indicated in Figures 1 and 2. In addition, increases in urea linkage concentration (vide infra) are also observed in spectra that show decreases in biuret concentration. The fate of isocyanate groups generated from reaction (2) is reserved for a later discussion.

The spectra corresponding to heating temperatures of 180–240 °C in Figure 3 clearly contain two additional peaks in spectral regions not included in Figures 1 and 2; these two peaks arise from the MDI-based isocyanate nitrogens (46 ppm) and the amine nitrogens of the corresponding substituted anilines (53 ppm). The spectra in Figure 3 were obtained under experimental conditions (6-ms CP contact time) that optimize the observation of nitrogen structures bearing no directly attached hydrogens; note, however, that urea linkages (104 ppm) are dominant in most of the spectra of Figure 3.

Several changes are observed with increased heating temperature in the spectra of Figure 3, reflecting the chemistry of the thermal degradation processes of the resin. As demonstrated previously,[19] quantitative results can be obtained from ^{15}N CP/MAS spectra, if appropriate variable contact time experiments are performed. To adopt this approach with each sample is unreasonable in the present context because of the number of samples and the associated time requirements. However, a variable contact time experiment was performed on the MDI-based resin that had been heated to 360 °C. A repetition time of 6 s was chosen for the variable contact time ^{15}N CP/MAS experiments to ensure complete proton spin–lattice relaxation. Six seconds was more than 4 times the largest T_{1H} value obtained previously on this sample.[19] From the resulting data, values for T_{NH} (the ^{1}H–^{15}N cross-polarization time constant) and $T_{1\rho H}$ (the rotating-frame proton spin–lattice relaxation time) were obtained by fitting the variable contact time data to eq 3.[30] In this equation, $I(\tau)$

$$I(\tau) = I^*[T_{1\rho H}/(T_{1\rho H} - T_{NH})](e^{-\tau/T_{1\rho H}} - e^{-\tau/T_{NH}}) \quad (3)$$

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. A useful quantity, $I^*/I(\tau)$, the correction factor used to obtain analytically useful intensities, can be calculated from eq 3.

Table II summarizes the ^{15}N cross-polarization parameters obtained from the variable contact time experiment performed on the MDI-based resin after heating at 360 °C. Values of I^*/I(6 ms), the uncorrected relative intensities, and the corrected relative intensities for each resonance are given in Table II. The values found for T_{NH}, $T_{1\rho H}$, and I^*/I(6 ms) are not dramatically different from those (given in parentheses in Table II) obtained on the "initial" MDI–polyisocyanurate resin (i.e., the resin resulting from 7-months exposure to air).[26] The corrected relative intensities (given in parentheses in Table II) obtained "indirectly", i.e., using T_{NH} and $T_{1\rho H}$ values corresponding to the "initial" resin and the uncorrected relative intensities corresponding to the resin after heating to 360 °C, are also similar to the results obtained "directly" for the resin after heating to 360 °C. As a result, T_{NH} and $T_{1\rho H}$ values obtained from the variable-contact experiment on the "initial" sample (after 7-months exposure to air) were used in eq 3 to estimate the percentages of specific nitrogen structures contributing to each spectrum in Figure 3. The authors recognize that this method of determining relative concentrations of specific structures is approximate and that some of these results are therefore semiquantitative.

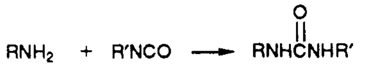
Table II
^{15}N Relaxation Parameters and Relative Intensities of MDI-Based Resin Obtained after Heating to 360 °C

				rel intens (I), %	
peak,[a] ppm	T_{NH}, ms	$T_{1\rho H}$, ms	I^*/I(6 ms)	uncorrd	corrd[b]
53	0.2	6.5	3	23	22
	(0.2)[c]	(4.4)	(3)		(21)[d]
104	0.3	5.7	3	71	75
	(0.1)	(4.0)	(4)		(76)
150	3.8	23	2	6	3
	(3.9)	(10)	(2)		(3)

[a] Chemical shifts of ^{15}N resonances referenced to liquid NH_3 at 0 ppm. [b] Corrected relative intensity = (uncorrected relative intensity) × (I^*/I(6 ms))(100%)/(total corrected intensity). [c] Values obtained on the "initial" resin (i.e., after 7-month exposure to air but before heating). [d] Corrected relative intensities obtained "indirectly", i.e., using T_{NH} and $T_{1\rho H}$ values corresponding to the "initial" resin and the uncorrected relative intensities corresponding to the resin after heating to 360 °C.

Table III contains the intensities corrected by using the factor I^*/I(6 ms) calculated from eq 3 for the major resonances in each spectrum in Figure 3. No attempt was made to estimate contributions from biuret amide (114 ppm) and uretidione (145 ppm) structures, because changes in concentration of these structures are relatively insignificant compared to changes observed in other structures (vide infra) in the spectra of Figure 3. Nevertheless, as noted above, the spectra in Figure 3 clearly show the disappearance of spectral intensity associated with uretidione and biuret structures as the sample is exposed to higher temperatures.

Inspection of Table III and Figure 3 reveals that residual isocyanate groups (46 ppm) decrease, with the concomitant increase of amine groups (53 ppm), as the heating temperature is increased. By 240 °C, only a trace of isocyanate groups remains, while the amine groups concentration continues to increase as the heating temperature is increased. Although biuret amide linkages (114 ppm) appear to be depleted as the heating temperature is increased to 240 °C (vide supra), the overall intensity in the large peak centered at 104 ppm increases, according to the results in Table III. It appears that urea linkage formation is increased in the resins heated to lower temperatures (i.e., 180 and 220 °C) relative to the "initial" spectrum in Figure 3. This increase in urea concentration is probably associated in part with the degradation of biuret linkages indicated in reaction (2). In addition, residual (initially unreacted) isocyanate groups and isocyanate groups originating from the decomposition of uretidione structures (reaction 1), both present in the resin during the lowest temperature treatments, might react with amine groups to form additional area linkages:[28]



$$RNH_2 + R'NCO \longrightarrow RNH\overset{O}{\overset{\|}{C}}NHR' \quad (4)$$

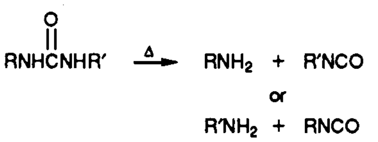
The results in Figure 3 and Table III indicate that the concentration of urea linkages is decreased upon heating at higher temperatures (i.e., going from 220 to 260 °C), indicating the degradation of a significant portion of the urea linkages. This change is most dramatic in progressing from a 250 to a 260 °C heating temperature.

The thermal degradation of urea linkages is believed to result in the formation of isocyanate and amine moieties:[29,31]

Table III
Data Obtained from the ^{15}N Spectra in Figure 3 Indicating the Percentages of Contributing Resonances for Each Thermal Decomposition Temperature

	peak,[a] ppm	rel *I*, %	corr *I*,[b] %		peak,[a] ppm	rel *I*, %	corr *I*,[b] %
initial	46	6.4	3.3	280 °C	53	20	20
	104	57	77		104	65	73
	141	3.0	1.6		150	15	7
180 °C	46	4.6	2.1	300 °C	53	21	20
	104	67	83		104	67	74
	141	1.7	0.9		150	12	5.9
	150	27	14				
220 °C	46	2.4	1.1	340 °C	53	26	24
	53	1.2	1.3		104	66	72
	104	69	84		150	7.4	3.4
	150	27	14				
240 °C	46	1.1	0.7	380 °C	53	18	16
	53	4.5	4.7		104	79	82
	104	65	80		150	3.6	1.6
	150	29	15				
250 °C	53	12	12	440 °C	53	32	29
	104	63	75		104	67	71
	150	25	13		150	1	0.4
260 °C	53	19	21	500 °C	53	32	28
	104	49	62		104	68	72
	150	32	17				

[a] Chemical shifts for ^{15}N resonances referenced to liquid NH_3 at 0 ppm. [b] Corrected relative intensity = (uncorrected relative intensity) × (I^*/I(6 ms))(100%)/(total corrected intensity).

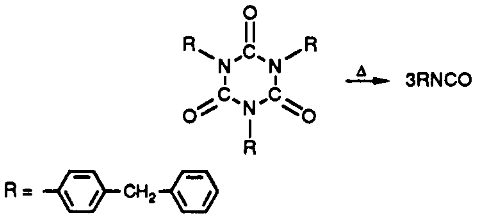


$$\mathrm{RNH\overset{O}{\overset{\|}{C}}NHR'} \xrightarrow{\Delta} \mathrm{RNH_2 + R'NCO} \text{ or } \mathrm{R'NH_2 + RNCO} \quad (5)$$

As indicated by the results in Figure 3 and Table III, a significant amount of amine groups (53 ppm) is present after heating the sample to 240 °C and this amount increases to about 21% of the total observed ^{15}N intensity after heating the sample to 260 °C. With the amine group concentration so high in the resin after heating to temperatures above 240 °C, the condensation reaction (4) between isocyanate and amine to yield urea linkages might be significant.[28] With urea linkages being formed from reaction (4) and degraded according to reaction (5), the thermal degradation chemistry of the urea linkages is not easily described for this chemical system.

The isocyanurate nitrogen intensity (150 ppm) does not change significantly in the spectra of Figure 3 until the sample is subjected to temperatures above 260 °C. The spectrum obtained after heating at 280 °C has significantly less intensity at 150 ppm than the spectrum obtained after heating the resin at 260 °C. This isocyanurate resonance decreases steadily with temperature increases above 260 °C until 440 °C, where only a trace of spectral intensity at 150 ppm is observed. From these results, it appears that the isocyanurate linkage is more thermally stable than *some*, but not *all*, of the urea linkages.

A previous IR spectroscopy study of the thermal decomposition of an isocyanurate model, 1,3,5-tris(4-benzylphenyl)triazine-2,4,6-trione, at 400 °C indicated that the parent isocyanate is the major thermal decomposition product:[10]


(6)

However, there is no evidence for an increase in concentration of isocyanate groups (46 ppm) with increased heating temperature from the results in Figure 3 and Table III. Since significant ^{15}N intensity centered at 104 ppm persists in the spectra corresponding to little or no isocyanurate structures (heating above 360 °C), some of these urea linkages persisting after the degradation of most or all of the isocyanurate linkages might be urea condensation products from reaction (4). With the amine group (53 ppm) concentration so high in the resin, especially after heating to 240 °C, any isocyanate formed from the thermal degradation of isocyanurate linkages might quickly react with the abundant amine to reform other urea linkages. We recognize that the thermal decomposition chemistry of simple model compounds might not adequately reflect the chemistry of the thermal decomposition of the complex MDI-based resin studied here. The MDI-based resin is known to have several types of nitrogen-containing linkages, which should complicate the thermal degradation chemistry significantly in comparison to that of a model compound that contains only one or two types of nitrogen-containing moieties.

A dramatic difference is seen in the spectral region corresponding to urea linkages (104 ppm) in the spectra of Figure 3 between heating temperatures of 300 and 340 °C. This peak broadens significantly with a shift of intensity to increased shielding, when the heating temperature is raised from 300 to 340 °C. The increased broadening is most likely due to a large increase in the number of different chemical–structural environments for the urea linkages, i.e., inhomogeneous broadening. The complex recombination chemistry to form urea linkages described above may lead to an increased chemical shift dispersion for the urea resonance.

The broadening of the urea linkage resonance (104 ppm) upon heating to 340 °C may also contain a contribution due to the formation of carbodiimide linkages. Previous work[10] was done on the thermal decomposition of 2-ethoxyethanol/MDI trimer, a MDI-based isocyanurate model compound bearing three urethane linkages (i.e., a MDI–isocyanurate moiety whose terminal isocyanate groups have been converted to simple urethane groups). That study revealed the presence of both isocyanate and carbodiimide structures at 295 and 320 °C, with the latter predominating as the major thermal decomposition product at these temperatures. Carbodiimide linkages can be formed at elevated temperatures from the reaction of two isocyanate groups:[10,32]

$$2\mathrm{RNCO} \xrightarrow{\Delta} \mathrm{RN{=}C{=}NR} + \mathrm{CO_2} \qquad (7)$$

The ^{15}N chemical shift of diphenyl carbodiimide (R = C_6H_5) is 106 ppm, based on liquid-solution data.[33] Carbodiimide ^{15}N resonances should survive under interrupted-decoupling conditions, since these nitrogens bear no directly attached hydrogens. Consequently, interrupted-decoupling experiments were performed on the resin sample heated at 300 °C (Figure 4A) and 340 °C (Figure 4C). The ^{15}N CP/MAS/interrupted-decoupling spectra (A and C) and the normal ^{15}N CP/MAS spectra (B and D) are shown for both heating temperatures for comparison. For both samples, ^{15}N intensity centered at 104 ppm is strongly attenuated in the interrupted-decoupling spectra compared to the corresponding "normal" spectra, indicating that the nitrogen structures contributing to this spectral region are tightly coupled to hydrgens, i.e., nitrogen structures bearing directly attached hydrogens. If a significant formation of carbodiimide structures were responsible for the observed broadening of the urea resonance at 104 ppm in the spectra of Figure 3 for samples heated at 340 °C or higher, the ^{15}N intensities arising from these structures would survive interrupted-decoupling conditions.

The absence of significant carbodiimide linkage formation in this MDI-based resin is probably due to preferential reaction of the available isocyanate groups with amine moieties to yield urea linkages (reaction 4). In simple model compounds such as phenyl isocyanate[32] and 2-ethoxyethanol/MDI trimer,[10] the thermal decomposition/reversion to parent isocyanate allows for carbodiimide formation, since the concentration of isocyanate groups is high. However, in the MDI-based resin described here, a typical isocyanate group readily encounters amine groups more frequently than other isocyanate groups, thereby more rapidly forming urea linkages. These differences in thermal degradation chemistry between the simpler model compounds studied previously[10,32] and the complex MDI resin of this study are not unexpected, if one considers the differences in chemical constituencies in the materials.

Another possible source of broadening for the urea peak in resins heated above 300 °C could be the significant formation of free radicals at these temperatures. Paramagnetic species are known to broaden resonances in solid-state NMR spectra due to the dipolar and scalar interactions between paramagnetic centers and the observed nuclei.[33-35] ESR experiments on similarly prepared resins were conducted on the samples after heating at 300, 340, and 440 °C to establish the existence and concentration (N_e) of paramagnetic species, i.e., free radicals. No free radicals were detected in the sample heated at 300 °C. However, free radicals (N_e = (2–5) × 10^{17} spins/g) were found in the sample subjected to 340 °C, and the concentration increased (to N_e = (5–10) × 10^{18} spins/g) in the sample heated at 400 °C. Using $N_e = 5 \times 10^{17}$ spins/g as the number of free radicals present in the sample after heating at 340 °C, one can estimate an average distance $R \sim 80$ Å between free radicals, assuming a resin density of 1 g/cm.[36] Assuming that the ^{15}N resonances of only nitrogen nuclei within 15 Å of a paramagnetic center can be broadened or shifted substantially, one can crudely estimate the maximum percentage of nitrogen signal intensity lost or broadened due to the paramagnetic centers. A simple calculation leads to the conclusion that this percentage is less than about 20%, indicating that the observed broadening of the 104 ppm peak in the spectrum obtained after heating at 340 °C (relative to the spectrum obtained after heating at 300 °C) in Figure 3 cannot be due mainly to free-radical generation. Hence, it seems likely that increased chemical shift dispersion resulting from the complex thermal decomposition/recombination chemistry of the urea moieties discussed above is probably the dominant factor in the observed "broadening" of the urea resonance in Figure 3.

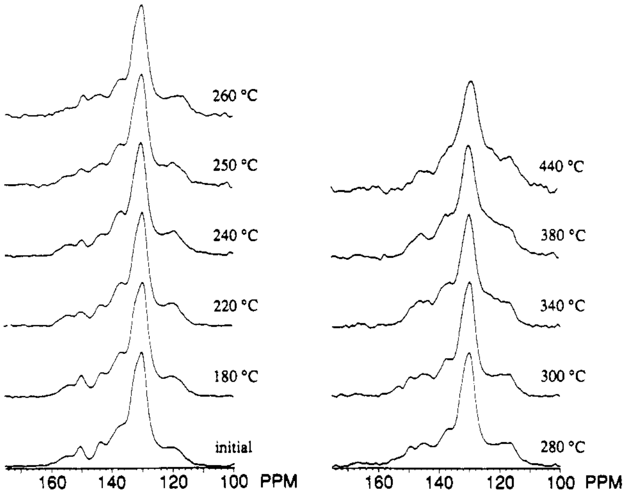


Figure 5. 50.3-MHz ^{13}C CP/MAS spectra (τ = 4 ms; t_d = 6 s) of the heated MDI-based resins represented in Figure 3.

A significant decrease in the total integrated ^{15}N NMR intensity (normalized to a given level of base-line noise and a specific number of scans) is observed in the spectra in Figure 3 that correspond to heating temperatures above 380 °C. As indicated above, paramagnetic species are known to cause S/N decreases in solid-state NMR experiments, because strong dipolar interactions between electrons and nuclei can shift and/or broaden NMR signals beyond detection.[34,35] A decrease in normalized S/N of roughly 25% is observed for the spectrum obtained after heating at 440 °C relative to the spectrum obtained after heating at 340 °C. Using $N_e = 5 \times 10^{18}$ spins/g for the number of free radicals generated after heating at 440 °C, the average distance R between free radicals is about 60 Å. On the basis of the same simple model and approximations indicated above, we can estimate the maximum percentage of ^{15}N NMR intensity that would be lost due to paramagnetic centers in this case; this estimate is about 38%, which is in reasonable qualitative agreement with the experimentally observed decrease in S/N. In addition, changes in ^{1}H T_1 values for the samples subjected to high-temperature treatment may be a contributing factor to the observed decreased in S/N.

Figure 5 shows the ^{13}C CP/MAS results obtained on the same set of thermal-degradation samples represented in Figures 1–4. Figure 6 shows the corresponding ^{13}C CP/MAS interrupted-decoupling[20] results. The spectra shown in Figure 5 and 6 are presented in a format to display the entire chemical shift range relevant to these systems, except for the methylene carbon resonance at 41 ppm. This particular resonance was uninformative in terms of the present context because it showed no significant changes upon thermal degradation of the sample. Although the trends that one can recognize in the spectra shown in Figures 5 and 6 are not as straightforward or compelling as those in the corresponding ^{15}N spectra (vide

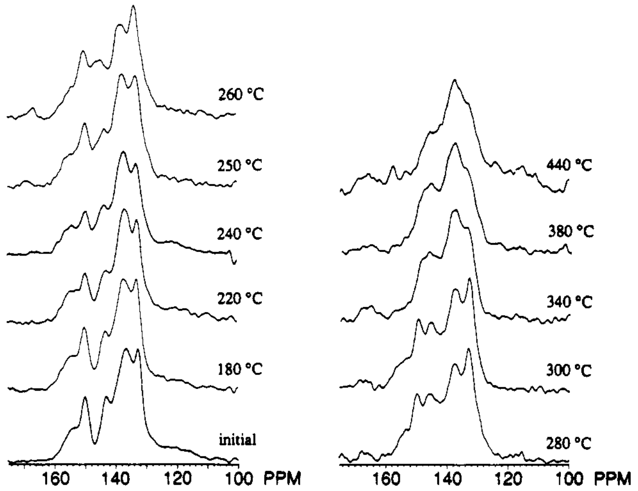


Figure 6. 50.3-MHz ^{13}C CP/MAS interrupted-decoupling spectra (τ = 4 ms, interrupt time = 70 μs; t_d = 6 s) of the heated MDI-based resins represented in Figure 3.

supra), the main features of these spectra are consistent with the above interpretations and are discussed here briefly.

The ^{13}C spectra corresponding to the "initial" conditions, i.e., before any postcure heating had taken place, are characterized by eight distinct peaks or pertinent spectral regions associated with the following types of carbon structural situations:[19] a resonance centered at 119 ppm corresponding to unsubstituted aromatic carbons ortho to urea-substituted carbons; the intensity at 125 ppm corresponding to isocyanate carbonyl carbons and aromatic carbons ortho to isocyanate-substituted carbons; the peak at 130 ppm corresponding to unsubstituted aromatic carbons meta to isocyanurate-substituted and urea-substituted carbons and to unsubstituted aromatic carbons ortho to isocyanurate-substituted carbons; the resonance at 133 ppm corresponding to isocyanurate-substituted aromatic carbons; the intensity at 137 ppm corresponding to urea-substituted aromatic carbons and benzyl-substituted aromatic carbons para to urea-substituted aromatic carbons; the resonance at 143 ppm corresponding to benzyl-substituted aromatic carbons para to isocyanurate-substituted carbons; the resonance at 150 ppm corresponding to isocyanurate carbonyl carbons; and the region centered at 155 ppm corresponding to urea carbonyl carbons. Other chemical structures could be identified in this sample and other samples by means of ^{15}N CP/MAS NMR methods,[19] even if unambiguous identification from ^{13}C CP/MAS and CP/MAS/interrupted-decoupling NMR spectra was not possible.

Certain regions in the spectra of Figures 5 and 6 undergo dramatic changes when the resin is subjected to increased temperatures. Spectral intensity increases are seen in the 137 ppm region as the sample is heated to 240 °C. In addition, the broad resonance centered at 119 ppm in the spectra of Figure 5 appears to increase in intensity as the sample is heated to 240 °C. Intensity increases in both of these regions relative to the "initial" spectra in Figures 5 and 6 correspond to an increased concentration of urea linkages (vide supra). However, as the sample is subjected to even higher temperatures, e.g., at 250, 260, and 280 °C, spectral intensity in the region centered at 137 ppm, along with intensity at 155 ppm, appears to decrease relative to the spectra obtained for the sample subjected to 240 °C.

As the temperature imposed on the sample is increased above 240 °C, the peak at 119 ppm in the spectra of Figure 5 undergoes a shift to higher shielding, moving to about 116 ppm at the higher temperatures. As the temperature is increased above 240 °C, there is an increase in intensity in the region centered at 146 ppm in the spectra of Figures 5 and 6. The intensity increase at 146 ppm is more obvious in the ^{13}C CP/MAS interrupted-decoupling spectra of Figure 6 than that in the corresponding "normal" CP/MAS spectra of Figure 5. Resolution on the high-shielding side of the isocyanurate carbonyl resonance (150 ppm) decreases in the spectra of Figure 6 as the heating temperature is increased above 240 °C. Intensity increases in both the 116 and 146 ppm regions of the spectra in Figures 5 and 6 corresponding to increased heating temperatures above 240 °C are associated with increases in amino group concentrations. The spectral intensity centered at 116 ppm does not survive under interrupted-decoupling experimental conditions (see spectra in Figure 6) and is therefore associated with an aromatic carbon atom bearing hydrogen. On the basis of liquid-solution models compounds,[19] this resonance is attributed to aromatic carbons ortho to amino-substituted carbons. The spectral intensity centered at 146 ppm persists under interrupted-decoupling experimental conditions and is attributed to amino-substituted aromatic carbons. Other ^{13}C resonances associated with aromatic structures with attached amino groups are difficult to delineate unambiguously because their chemical shifts are coincident with the chemical shifts of aromatic structures containing isocyanurate and urea moieties.

As the resin heating temperature is increased above 300 °C, the spectra in Figures 5 and 6 become quite complex, indicating significant degradation of the material by 340 °C. Four broad spectral regions characterize the spectra obtained on the sample heated at 340 °C in Figure 5: (1) a broad region centered between 116 and 119 ppm corresponding primarily to aromatic carbons ortho to amino-substituted and urea-substituted carbons, (2) the predominant resonance centered at 130 ppm corresponding to various unsubstituted aromatic carbons of rings bearing amine, urea, and isocyanurate moieties, (3) a region centered at 137 ppm corresponding primarily to structures associated with urea structures (vide supra), and (4) a region centered at 146 ppm corresponding to amino-substituted aromatic carbons. The isocyanurate carbonyl resonance (150 ppm) appears to decrease in intensity in the spectra of Figures 5 and 6 in progressing from 300 to 340 °C. Other ^{13}C resonances attributed to isocyanurate structures, e.g., isocyanurate-substituted aromatic carbons (133 ppm) and benzyl-substituted aromatic carbons para to isocyanurate-substituted carbons (143 ppm), are not clearly identified in the 340 °C spectrum of Figure 5. The corresponding interrupted-decoupling spectra of Figure 6 provide more convincing evidence for the significant decrease of isocyanurate structures upon heating from 300 to 340 °C. The intensity of the isocyanurate-substituted aromatic carbon resonance at 133 ppm in Figure 6 is clearly smaller for the sample heated to 340 °C than for the sample heated to 300 °C. This resonance appears as a higher shielding shoulder on the dominant 137 ppm peak in the 340 °C spectrum in Figure 6. However, even with the aid of the interrupted-decoupling results, identification of the other carbon resonances (143 and 150 ppm) associated with isocyanurate structures was not achieved because of the complexity and overlap patterns in the spectra obtained on the sample heated at 340 °C.

It would be very difficult to relate the observed spectral changes to the thermal degradation of specific MDI-based linkages on the sole basis of the ^{13} CP/MAS and CP/MAS/interrupted-decoupling results presented in Figures

5 and 6. Nevertheless, these spectra provide some evidence for an increase in urea linkage concentration (137 ppm) up to a sample heating temperature of 240 °C. Above this temperature, some urea linkages have degraded, as apparent intensity decreases in the 137 and 155 ppm regions of the spectra in Figures 5 and 6 would appear to suggest. The concentrations of structures associated with amine groups in Figures 5 and 6 (116 and 146 ppm spectral regions) appear to rise steadily as the sample is subjected to increasing temperatures. Some of the spectral regions associated with the isocyanurate structures (133 and 150 ppm) do not change dramatically until the sample is heated above 300 °C. For heating temperatures of 340 °C and above, it appears from the spectra of Figures 5 and 6 that ^{13}C intensity in the spectral regions associated with isocyanurate structures continues to decrease and regions corresponding to urea (119, 130, and 137 ppm) and amine (116, 130, and 146 ppm) structures start to predominate.

In general, the ^{13}C CP/MAS and CP/MAS/interrupted-decoupling spectra shown in Figures 5 and 6 contain overlapping resonances that prevent unambiguous identification of less predominant structures known to exist in these MDI-based resins. As a result, the solid-state ^{13}C NMR results presented here are only *qualitatively* suggestive, providing little detailed information on the relative thermal stabilities of the various types of linkages in these MDI-based resins.

Summary and Conclusions

The ^{15}N CP/MAS and CP/MAS/interrupted-decoupling results yield simpler spectra than their ^{13}C CP/MAS counterparts. Even structures in low concentration, such as biuret and uretidione linkages, are clearly identified in the ^{15}N spectra. The following changes in the chemical structure and constituency of the resin upon increasing heating temperature were observable from the ^{15}N CP/MAS results: (1) the degradation of biuret and uretidione linkages by 230 °C, (2) a decrease in residual isocyanate groups at heating temperatures up to 240 °C, (3) an increase in concentration of urea linkages in samples heated up to 240 °C and the dramatic decrease in concentration of urea linkages between 250 and 260 °C, (4) a steady increase in amine group concentration and (5) decreases in isocyanurate concentration for heating temperatures of 280 °C and above. In addition, ^{15}N CP/MAS and CP/MAS/interrupted-decoupling experiments verify that the increased line width of the urea peak (104 ppm) upon heating at temperatures of 340 °C or above is *not* due to carbodiimide structures. ESR results on similarly prepared MDI-based resins indicate that the concentration of free radicals after heating to 340 °C is not high enough to account for the significant "broadening" observed in the ^{15}N spectrum corresponding to a sample heated at this temperature. This "broadening" is probably due to an increased chemical shift dispersion for the urea resonances (due to increased structural diversity resulting from the complex condensation and degradation chemistry).

The ^{15}N NMR results yields semiquantitative information on the relative concentrations of the major components known to exist in the resin during the thermal degradation process. The results of this study support some of the conclusions of previous investigations in terms of a ranking of thermal stabilities of the various MDI-based linkages known to exist in this resin: biuret, uretidione < urea < isocyanurate < urea′, where the prime indicates that certain urea linkages are more thermolytically stable than even isocyanurate linkages. Urea and amine moieties were found to be the most thermolytically stable nitrogen-containing structures in the resin. ^{13}C CP/MAS and CP/MAS/interrupted-decoupling NMR monitoring of the thermal degradation of a MDI-based resin provide some evidence for the initial increase in urea structures corresponding to temperature exposures up to 240 °C. The solid-state ^{13}C NMR results also provide evidence for the steady increase in concentration of amine structures upon increased resin heating temperature and possible evidence for the thermal degradation of some urea linkages (between 250 and 260 °C) and isocyanurate linkages (between 300 and 340 °C). However, the spectra obtained by using these techniques are complex, and the results could be interpreted in only a qualitative manner.

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