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Monitoring Postcure Reaction Chemistry of Residual Isocyanate in 4,4′-Methylenebis(phenyl isocyanate) Based Isocyanurate Resins by ^{15}N and ^{13}C CP/MAS NMR

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ABSTRACT: The fate of residual isocyanate groups in three cured, ^{15}N-enriched isocyanurate-rich resins based on 4,4′-methylenebis(phenyl isocyanate) (MDI) was monitored by both ^{15}N and ^{13}C CP/MAS NMR. Data obtained on the samples immediately after curing are compared with results obtained after 7-month exposure to air. The consumption of isocyanate and the subsequent formation of urea linkages during this 7-month period are clearly identified from changes in the ^{13}C spectra. ^{15}N CP/MAS NMR results readily identify the consumption of isocyanate to form the amine as the product of isocyanate hydrolysis. In addition, the formation of urea condensation products from the reaction of amine and isocyanate groups is clearly shown. No significant reaction of urea linkages with isocyanate groups to form biuret linkages is observed in the ^{15}N spectra of air-exposed samples. Deconvolutions and integrations of the ^{15}N spectra yield estimates for the extent of isocyanate postcure reaction chemistry for each MDI-polyisocyanurate resin. ^{15}N spin-lattice relaxation times obtained on the samples exposed to air provide insight into the molecular motion of the various nitrogen environments. ^{15}N CP/MAS NMR is seen to be especially suited for monitoring the solid-state reaction chemistry of the isocyanate group.

Introduction

Monitoring solid-state reaction chemistry, including the degradation of polymeric materials, has enjoyed a sustained research effort in recent years.[1-4] The properties of a given polymeric material often degrade with time as a function of environmental exposure, extended use, or chemical reactions intrinsic to the material itself. Ideally, an analytical technique that is used to probe the degradation of a macromolecular structure should (a) identify pertinent chemical functionalities and linkages, (b) monitor their consumption to form the various degradation products, and (c) relate the elucidated chemical patterns to changes in physical properties of interest. Several different techniques are often employed to investigate degradation processes. Spectroscopic techniques are usually more informative in characterizing the reaction chemistry than methods primarily associated with mechanical properties. Spectroscopy can provide an excellent complement to mechanical methods by relating changes in chemical constituency to changes in physical properties. Solid-state CP/MAS NMR[5-7] has proved to be extremely useful in monitoring the reaction chemistry in solid polymers.[8-16]

For isocyanate-based polymer systems, postcure reactions of residual isocyanate groups are possible sources of sample degradation. The hydrolysis of an isocyanate group to form the amine and subsequent condensation between the amine and an additional isocyanate in the immediate vicinity to form a urea linkage is well-known:[17-21]

$$\mathrm{RNCO + H_2O \rightarrow [RNHCO_2H] \rightarrow RNH_2 + CO_2} \qquad \text{(1a)}$$

$$\mathrm{RNH_2 + R'NCO \rightarrow RNHC\underset{I}{O}NHR'} \qquad \text{(1b)}$$

An isocyanate group can then react via the active hydrogen atoms of urea linkages (I) to form biuret linkages (II):[17,18]

$$\mathrm{RNCO + R'NHCONHR'' \rightarrow R'NHCON\underset{II}{(R'')}CONHR} \qquad \text{(2)}$$

On the basis of the relative reactivities of the various reactants in the schemes above, it has been concluded that the hydrolysis of isocyanate to form the amine (eq 1a) and the condensation of amine with isocyanate to form the urea (eq 1b) should be the predominant postcure reactions.[19,21]

Previously, the hydrolysis of isocyanate and subsequent condensation chemistry of isocyanate-based polymers have been monitored by the decay of compressive strength and hardness,[20] FTIR,[22-24] and DSC.[25] One report[23] points to the potential of ^{13}C CP/MAS NMR for addressing the issue of postcure reaction chemistry of isocyanate groups but presents no results. No solid-state NMR investigations on the postcure reaction chemistry of isocyanate groups in polymer systems have been reported. Solid-state NMR has the advantage over other characterization methods by providing dynamical information in addition to structural information. The mobility of specific linkages and/or groups can be ascertained from measurements of various relaxation times, providing an enhanced overall understanding of the structure/dynamics. This information should be especially useful in understanding cross-linked resin systems in which a variety of linkages are known or suspected to exist.

The present paper summarizes the postcure reaction chemistry in three cured isocyanurate-rich resins based on 4,4′-methylenebis(phenyl isocyanate) (MDI) by means of ^{15}N and ^{13}C CP/MAS NMR. In addition, ^{15}N T_1 values obtained from the spectra of the samples exposed to air are discussed. The results presented here emphasize the reaction chemistry of isocyanurate-rich MDI-based resins and are not intended to be correlated explicitly with physical properties or specific commercial products.

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

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time of 70 ms was used for the CP/MAS interrupted-decoupling (dipolar-dephasing) experiments.[26] Samples were spun at 6.0 kHz, using bullet-type spinners.[27] The magic angle was adjusted to ±0.1° by using the ^{79}Br spectrum of KBr placed in a spinner.[28]

^{15}N CP/MAS spectra of samples run immediately after curing were obtained at 20.3 MHz on the same modified NT-200 spectrometer. The NMR parameters used to accumulate the spectra presented here were 0.4- and 6.0-ms contact times and a 6-s repetition time. Samples were spun at 2.8–3.3 kHz, using bullet-type spinners, and the magic angle was again set by the KBr method.

^{15}N CP/MAS spectra of the samples exposed to air for 7 months after curing were obtained at 26.4 MHz on a Chemagnetics M-260 spectrometer. The NMR parameters used to accumulate the spectra presented here were 0.4- and 6.0-ms contact times and a 6-s repetition time. Delay periods from 0.01 to 600 s were used for ^{15}N T_1 (T_{1N}) determinations, based on inversion–recovery experiments using cross polarization to prepare the nitrogen magnetization.[29] Samples were spun at 2.8–3.3 kHz, using Windmill-type spinners,[30] and the magic angle was set by using the ^{35}Cl spectrum of NaCl placed in a spinner.

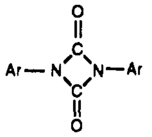
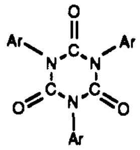
Samples. MDI-polyisocyanurate resins were initially prepared by adding 0.5% (by weight) stannous octoate to ^{15}N-enriched MDI (99.8% doubly labeled, MSD Isotopes) and heating under a nitrogen atmosphere with stirring at various temperatures for 2 h.[31] The samples were then cooled to room temperature under nitrogen and ground to approximately the same particle size (1–3 mm^3) in a drybox. After the initial NMR results were obtained, the samples were exposed to air for 7 months before the final results were obtained. No attempt was made to control the conditions (typically 635 Torr of air pressure and low relative humidity, 25–50%) to which the samples were exposed. The preparation of the MDI-based polyurea, poly[methylenebis(4-phenylurea)], is found elsewhere.[32]

Results and Discussion

In a previous paper[33] the effect of cure temperature on the formation of isocyanurate linkages in three ^{15}N-enriched MDI-polyisocyanurate resins was addressed in some detail. The predominant chemical structure in each of these resins was the isocyanurate linkage; varying degrees of isocyanurate cross-link density were observed. The isocyanurate cross-link density was found to be highest in the resin initially cured at 120 °C, followed by the samples cured at 160 and 100 °C, respectively. Correspondingly, the amount of residual isocyanate was highest for the sample initially cured at 100 °C, followed by the samples cured at 160 and 120 °C, respectively.

The isocyanurate linkage is thermolytically and hydrolytically stable and is not expected to degrade appreciably after curing.[34,35] However, other structures readily identifiable from the ^{15}N or ^{13}C CP/MAS spectra, such as biuret linkages, urea linkages, amine groups, and residual isocyanate groups, might undergo substantial changes in concentration during the postcure reactions indicated in reactions 1 and 2. Although the primary aspects of the reaction chemistry in reactions 1 and 2 are thought to be well understood on the basis of solution-state studies,[17,19,21] understanding of this kind of chemistry for solid, polymeric materials has been lacking in sufficient detail. In the case of a cured, cross-linked isocyanate-based resin, the hydrolysis of residual isocyanate groups depends on the diffusion of water vapor into the sample to form the amine (reaction 1a). The formation of urea linkages depends on this kind of generation of amine groups and the proximity and availability of additional isocyanate groups for reaction according to reaction 1b. The reaction of isocyanate groups with urea linkages to form biuret structures (reaction 2) also depends on the availability of both isocyanate groups and urea linkages and their mutual proximity. Other considerations being equal, one would expect that MDI-polyisocyanurate resins that contain higher concentrations of residual isocyanate groups will undergo more significant hydrolysis, condensation, and biuret formation chemistry than resins containing lower concentrations of residual isocyanate groups.

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

name	structure	^{15}N chem shift,[b] ppm
isocyanate	ArNCO	46
amine	$ArNH_2$	53
urea	ArNHC(O)NHAr	104
biuret	ArNHC(O)N(Ar)C(O)NHAr	114 (NH) 141 (N)
uretidione		145
isocyanurate		149

[a] MDI-based resins and chemical shifts originally reported in ref 33. [b] Nitrogen chemical shifts referenced to liquid NH_3 at 0 ppm.

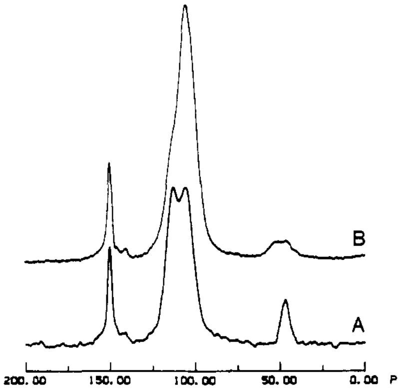


Figure 1. (A) 20.3-MHz ^{15}N CP/MAS spectrum (τ = 0.4 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 100 °C. (B) 26.4-MHz ^{15}N CP/MAS spectrum (τ = 0.4 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 100 °C after 7-month exposure to air.

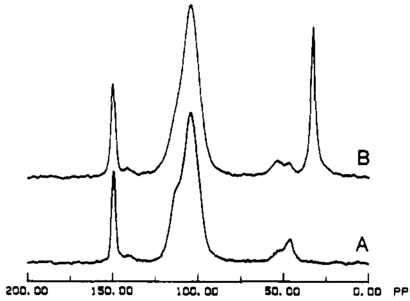


Figure 2. (A) 20.3-MHz ^{15}N CP/MAS spectrum (τ = 0.4 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 120 °C. (B) 26.4-MHz ^{15}N CP/MAS spectrum (τ = 0.4 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 120 °C after 7-month exposure to air.

As described earlier,[33] ^{15}N CP/MAS NMR is a powerful structure elucidation technique for these particular systems. Accordingly, ^{15}N CP/MAS experiments, including variable contact time experiments, were carried out to provide more insight into the postcure reaction chemistry of unreacted isocyanate groups. The ^{15}N chemical shifts

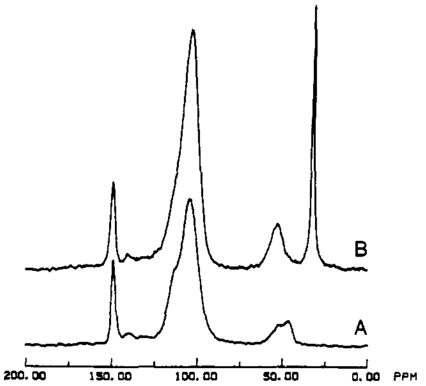


Figure 3. (A) 20.3-MHz ^{15}N CP/MAS spectrum (τ = 0.4 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 160 °C. (B) 26.4-MHz ^{15}N CP/MAS spectrum (τ = 0.4 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 160 °C after 7-month exposure to air.

of pertinent resin moieties and model compounds were reported previously.[33] ^{15}N and ^{13}C chemical shift assignments of the most relevant structures are summarized in Table I. Figures 1–3 show ^{15}N CP/MAS spectra obtained initially after curing (part A of each figure) and after 7-month exposure to air (part B of each figure) on the three ^{15}N-enriched MDI-polyisocyanurate resins initially cured at 100, 120, and 160 °C, respectively. The spectra shown were obtained under conditions (0.4-ms CP contact time) that optimize the detection of nitrogens tightly coupled to hydrogens, i.e., amine (~53 ppm), amide (~114 ppm), and urea (~104 ppm) nitrogens. The additional resonance at 32 ppm in two of the spectra corresponds to ^{15}N-enriched glycine added as an "internal" reference in those two cases.

If significant postcure reaction chemistry of isocyanate has occurred in the samples represented in Figures 1–3, this condition should manifest itself as follows in three regions of the ^{15}N CP/MAS B spectra (7-month exposure) relative to A spectra (immediately after initial cure): (1) decreased intensity of the isocyanate nitrogen resonance at 46 ppm, (2) increased intensity of the amine nitrogen resonance at 53 ppm, and (3) increased intensity of the urea nitrogen resonance at 104 ppm. All three regions show the expected changes, but to different extents for the three samples. If significant reaction between isocyanate and urea linkages has occurred to form biuret moieties, it should manifest itself as follows in three regions of the ^{15}N CP/MAS spectra: (1) decreased intensity at 46 ppm, (2) increased intensity of the biuret amide resonance at 114 ppm, and (3) increased intensity of the biuret imide resonance at 141 ppm. No significant intensity differences in the 114 or 141 ppm regions of the ^{15}N CP/MAS spectra are observed when B spectra are compared to A spectra in Figures 1–3. Experiments favoring the observation of the biuret imide nitrogens (results discussed below) also indicate no significant differences in biuret formation between B samples and A samples. Thus, it appears that the postcure reaction of residual isocyanate groups with urea linkages (reaction 2) is negligible compared with the isocyanate hydrolysis and subsequent condensation chemistry (reactions 1a and 1b) in these cured MDI-polyisocyanurate resins. The concentration of biuret linkages is discussed in more detail below.

Figures 4–6 show ^{15}N CP/MAS spectra obtained initially after curing (A parts of these figures) and after exposure to air (B parts) for the same samples covered in Figures 1–3; Figures 4–6 were obtained under conditions (6-ms CP contant time) for which the observation of nitrogens bearing no directly attached hydrogens, i.e., isocyanurate, uretidione, imide, and isocyanate nitrogens, is optimized. The intensities of the isocyanurate, biuret imide, and uretidione resonances do not appear to differ significantly in Figures 4–6, when comparing the spectra obtained after exposure to air (B spectra) with the spectra obtained initially after curing (A spectra). However, decreases in residual isocyanate concentrations are more obvious in these B spectra than in the corresponding B spectra in

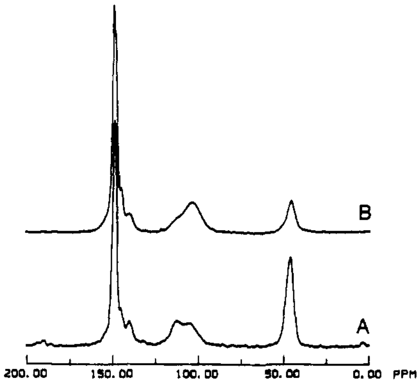


Figure 4. (A) 20.3-MHz ^{15}N CP/MAS spectrum (τ = 6.0 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 100 °C. (B) 26.4-MHz ^{15}N CP/MAS spectrum (τ = 6.0 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 100 °C after 7-month exposure to air.

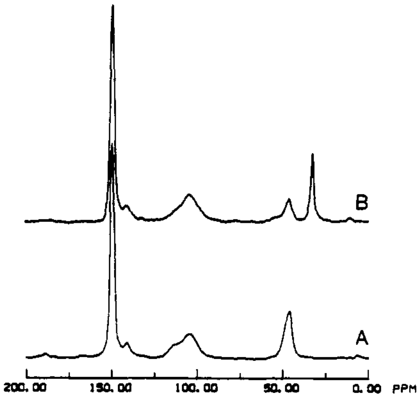


Figure 5. (A) 20.3-MHz ^{15}N CP/MAS spectrum (τ = 6.0 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 120 °C. (B) 26.4-MHz ^{15}N CP/MAS spectrum (τ = 6.0 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 120 °C after 7-month exposure to air.

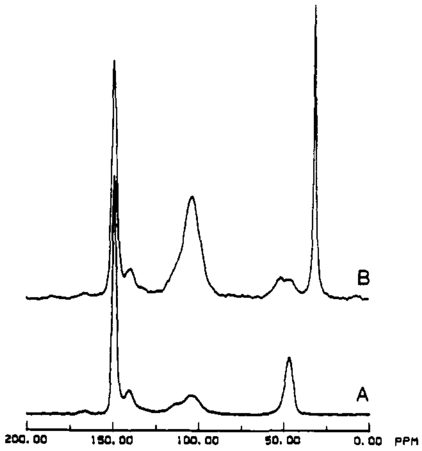


Figure 6. (A) 20.3-MHz ^{15}N CP/MAS spectrum (τ = 6.0 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 160 °C. (B) 26.4-MHz ^{15}N CP/MAS spectrum (τ = 6.0 ms; t_d = 6 s) of MDI-polyisocyanurate resin initially cured at 160 °C after 7-month exposure to air.

Figures 1–3. In addition, intensity increases for the amine group (53 ppm) and the urea linkage (104 ppm) are observed in the B spectra of Figures 4–6 compared to the corresponding A spectra, even though the experimental conditions used to obtain these spectra are not optimized for the observation for hydrogen-bearing nitrogen environments.

The observed changes in spectral intensity for the isocyanate, amine, and urea nitrogens and the apparent lack of change in spectral intensity for the biuret, uretidione, and isocyanurate nitrogens in the spectra represented in Figures 1–6 can up to this point be discussed only qualitatively. However, these intensity patterns must be evaluated quantitatively, if the postcure reaction chemistry in the three resins is to be characterized satisfactorily. Quantitative results were obtained previously[33] on the extent of cross linking via isocyanurate ring formation by comparing integrated intensities (corrected for CP dynamics) of isocyanurate and isocyanurate nitrogen resonances. In that case, the resonances were well resolved and a straightforward integration was possible. However, the spectra in Figures 1–6 are complicated by overlapping resonances, specifically, the isocyanate resonance (~46 ppm) overlapping with the amine resonance (~53 ppm) and the urea resonance (~104 ppm) overlapping with the biuret amide resonance (~114 ppm). The relative intensity patterns can nevertheless be extracted from partially overlapping resonances by deconvolution and subsequent integration of the contributing peaks. In any case, these resonance patterns are quantitatively useful only if the individual peak intensities corresponding to the individual types of nitrogen environments displayed in a given spectrum can be related quantitatively to each other. If one knows the values of the pertinent NMR relaxation parameters, T_{NH} (the ^{1}H–^{15}N cross polarization time constant), $T_{1\rho H}$ (the rotating-frame ^{1}H spin–lattice relaxation time), and T_{1H} (the ^{1}H spin–lattice relaxation time), this issue of quantitativeness can be evaluated and the appropriate corrections can be made. By fitting the variable contact time (τ) results to the following equation, one can determine values of T_{NH} and $T_{1\rho H}$:[33,36]

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

In this equation, $I(\tau)$ is the nitrogen magnetization for a given CP contact time (τ), t_d is the repetition delay, and I^* is the nitrogen magnetization one would obtain if cross polarization were instantaneous and rotating-frame relaxation were infinitely slow. For a given value of t_d, the factor $I^*/I(\tau)$, calculated from eq 3 for the contact time used in a given experiment, is the factor one should apply to the directly measured spectral intensity $I(\tau)$ in order to obtain analytically useful numbers for comparisons. A repetition time of 6 s was chosen for all the ^{15}N CP/MAS experiments represented in Figures 1–6 to ensure complete proton spin–lattice relaxation. Six seconds is more than 4 times the largest T_{1H} value encountered for the resins of this study (displayed in Tables II and III); hence the last factor in parentheses in eq 3 is essentially unity.

Table II contains the ^{15}N cross-polarization parameters obtained on the various ^{15}N resonances in the A spectra of Figures 1–3 from variable contact time experiments on MDI-based isocyanurate-rich resins immediately after curing.[33] Table III summarizes results on the corresponding parameters obtained on the same samples after 7-month exposure to air; these results correspond to spectra B in Figures 1–3. Each of the spectra shown in Figures 1–3 were analyzed according to eq 3, using the T_{NH} and $T_{1\rho H}$ parameters in Tables II and III obtained by computer fit according to eq 3 of the variable contact time data. Although ^{15}N nuclei in the residual isocyanate, isocyanurate, biuret imide, and uretidione structures are not optimally cross polarized under the experimental conditions represented by Figures 1–3, one can correct the intensities for a given contact time by using eq 3 to obtain the corresponding corrected, CP-enhanced intensities. The

Table II
^{15}N Cross-Polarization Parameters Obtained on MDI-Polyisocyanurate Resins after Initial Curing

peak,[a] ppm	T_{NH},[b,c] ms	$T_{1\rho H}$,[b,d] ms	I^*/I(0.4 ms)[e]	T_{1H},[f] s
		100 °C Resin		
46	3.3	17	9.7	1.1
104	0.2	5.0	1.2	1.1
114	0.2	5.0	1.2	1.1
141	2.4	14	6.5	1.1
145	3.0	26	8.1	1.1
150	3.0	17	7.9	1.1
		120 °C Resin		
46	3.3	14	9.4	1.2
53	0.2	3.8	1.3	1.2
104	0.1	4.6	1.1	1.2
114	0.1	5.5	1.1	1.2
141	2.3	9.7	6.5	1.2
150	2.8	15	7.5	1.2
		160 °C Resin		
46	2.6	12	8.2	1.1
53	0.2	4.0	1.2	1.1
104	0.1	4.4	1.1	1.1
114	0.1	4.8	1.1	1.1
141	3.3	8.1	7.7	1.1
150	2.5	10	7.1	1.1

[a] Chemical shifts of ^{15}N resonances referenced to liquid NH_3 at 0 ppm. [b] Obtained from variable contact time experiments. [c] Uncertainty ranged from ±3 to ±11%. [d] Uncertainty ranged from ±2 to ±11%. [e] Calculated from eq 3. [f] Obtained via cross polarization.

Table III
^{15}N Cross-Polarization Parameters and T_{1N} Values Obtained on MDI-Polyisocyanurate Resins after 7-Month Exposure to Air

peak,[a] ppm	T_{NH},[b,c] ms	$T_{1\rho H}$,[b,d] ms	T_{1N},[e] s	I^*/I(0.4 ms)[f]	T_{1H},[g] s
		100 °C Resin			
46	2.8	11	121	7.7	1.2
53	0.2	4.4	32	1.4	1.2
104	0.1	4.0	83	1.1	1.2
114	0.1	4.0	83	1.1	1.2
141	2.3	8.3	86	6.4	1.2
145	3.5	16	184	9.4	1.2
150	3.9	9.7	140	9.5	1.2
		120 °C Resin			
46	2.6	12	109	7.1	1.3
53	0.3	4.6	24	1.6	1.3
104	0.1	4.8	78	1.1	1.3
114	0.1	4.8	78	1.1	1.3
141	2.4	7.3	75	6.7	1.3
150	3.4	10	132	9.1	1.3
		160 °C Resin			
46	2.1	13	102	6.0	1.3
53	0.2	4.5	20	1.2	1.3
104	0.2	5.8	61	1.2	1.3
114	0.2	5.8	61	1.2	1.3
141	2.4	9.4	68	6.7	1.3
150	3.0	13	116	8.2	1.3

[a] Chemical shifts for ^{15}N resonances referenced to liquid NH_3 at 0 ppm. [b] Obtained from variable contact time experiments. [c] Uncertainty ranged from ±3 to ±11%. [d] Uncertainty ranged from ±2 to ±11%. [e] Obtained from inversion–recovery (CP preparation) experiments. Uncertainty ranged from ±5 to ±18%. [f] Calculated from eq 1. [g] Obtained via cross polarization.

Table IV
Data Obtained from the ^{15}N Spectra of MDI-Polyisocyanurate Resins before and after 7-Month Exposure to Air Indicating the Percentages of Contributing Resonances Present in Each Resin

	after initial cure		after exposure to air	
peak, ppm	rel I, %	cor rel I,[a] %	rel I, %	cor rel I,[a] %
		100 °C Resin		
46	5.7	22	3.1	11
53	0	0	3.4	2.2
104	47	22	60	32
114	33	15	24	13
141	1.9	4.7	1.1	3.4
145	0.7	2.3	0.8	3.6
150	11	34	7.8	35
		120 °C Resin		
46	3.5	15	2.5	8.5
53	3.6	2.1	4.4	3.4
104	63	32	67	35
114	16	8.1	15	8.0
141	1.3	3.9	1.5	4.9
150	12	39	9.2	40
		160 °C Resin		
46	5.2	16	0.7	2.2
53	4.1	2.3	10	6.6
104	59	29	67	43
114	18	8.8	12	7.7
141	1.5	5.9	1.3	4.4
150	12	38	8.3	36

[a] Corrected intensity = (uncorrected intensity) × (I^*/I(0.4 ms)) × (100%)/(total corrected intensity).

resulting corrected intensities are given in Table IV.

Isocyanurate cross-link formation was found to be the most extensive in the resin initially cured at 120 °C, followed by the samples cured at 160 and 100 °C, respectively.[33] Comparing corrected intensities of A spectra with those of the corresponding B spectra in Figures 1–3 (see Table IV), one sees that the relative concentration of the isocyanurate moieties in the three samples is not significantly different between corresponding pairs of these two (A and B) sets, indicating that the isocyanurate linkages are hydrolytically stable under the conditions specified in this study.

Varying intensity decreases for the isocyanate resonance (46 ppm) in the B spectra relative to the corresponding A spectra are observed for the three resins represented in Figures 1–3. Referring to Table IV, one can see that the residual isocyanate concentration in the sample initially cured at 120 °C drops from 15% to 8.5% upon prolonged exposure to air. Thus, ca. 43% of the isocyanate groups after the initial cure are consumed to form the postcure reaction products. Similarly, 50% of the isocyanate content present to the sample immediately after the initial cure at 100 °C is consumed during the 7-month exposure to air; this indicates that, although the amount of residual isocyanate present immediately after the initial cure was significantly larger for the 100 °C case than for the 120 °C case, the *percentage* of residual isocyanate that underwent postcure reaction chemistry upon exposure to air is roughly comparable for these two samples. However, in the sample initially cured at 160 °C, ca. 86% of the residual isocyanate is consumed to form postcure reaction products during the air exposure. Thus, although the resin initially cured at 100 °C had significantly more residual isocyanate than the sample initially cured at 160 °C, postcure reaction chemistry from prolonged air exposure occurred to a larger fractional extent in the latter, indicating a difference in the overall isocyanate reactivities between the two samples. This reactivity difference is presumably associated with a difference in the average structural/dynamical environment in the isocyanate moieties in the two samples. Macroscopic water penetration into the samples should have occurred with roughly the same efficiencies unless significant differences in the morphology of the two samples existed after the initial cure. Hence, the observed difference in the postcure isocyanate reactivities is probably due to structural differences (chemical and/or morphological) associated with the initial curing behavior of the two samples.

For the sample initially cured at 160 °C, solidification occurred significantly earlier in the curing process than was the case with the other samples, cured at lower temperatures.[37] The more rapid solidification results in a more irregular, cross-linked resin, in which larger pockets or regions of unreacted MDI monomer might be trapped or occluded in the solid matrix. This more irregular structure may also result in a large number of voids or imperfections in the cured product; such voids could possibly facilitate the diffusion of water vapor into the sample initially cured at 160 °C relative to the samples cured at lower temperatures.

Polymeric materials undergoing a more inhomogeneous curing process are known to undergo accelerated degradation relative to materials undergoing a more homogeneous curing process because of such voids and imperfections.[38–40] For the samples initially cured at 100 and 120 °C, solidification occurred much later in the curing process, permitting a cross-linked network to form that may be more thermodynamically determined and more homogeneous relative to the sample cured at 160 °C. According to this view, a more homogeneous curing process occurs at the lower cure temperatures, possibly producing smaller regions of unreacted monomer and fewer voids and imperfections than in the higher temperature cure case. This postulated increase in water diffusion efficiency for the more inhomogeneous samples (160 °C initial cure) is consistent with the dramatic decrease in residual isocyanate concentration and increases in amine and urea concentrations seen for the 7-month air exposure in Figure 3B relative to 3A. Although the terms homogeneous and inhomogeneous are used here to discuss the curing process, we recognize that all of these cross-linked resins are very heterogeneous systems, compared to an organic solid that is a pure substance. Thus, the above discussion regarding the degree of homogeneous vs inhomogeneous character of the curing process of the three resins reflects relative patterns. The extent to which unreacted MDI monomer and/or voids and imperfections in the resins immediately after curing affects the postcure reaction chemistry of isocyanate groups upon prolonged exposure to air is addressed in more detail below.

Alternatively, the apparently higher residual isocyanate reactivity in the higher temperature product could be due to starburst dendrimer characteristics.[41] The more highly strained isocyanate groups on the perimeter of the starburst limit of the higher temperature resin product could be intrinsically more reactive than residual isocyanates on the smaller dendrimers of a lower temperature preparation.

Among the resin samples not subjected to 7-month air exposure, the residual isocyanate groups were the least extensive and the isocyanurate cross-link network most extensive in the sample initially cured at 120 °C, rendering this sample the most unlikely candidate for significant isocyanate postcure chemistry of the three samples studied. A modest decrease in isocyanate concentration and modest increases in amine and urea concentrations were observed for this sample upon exposure to air, as seen by inspection of Table IV. The relatively small residual isocyanate concentration that accompanies a homogeneous curing process precludes a substantial reaction between amine and isocyanate groups to form urea linkages during the 7-month air exposure in the samples initially cured at 120 °C. The sample initially cured at 100 °C was shown previously to have the highest concentration of residual isocyanate groups among the samples initially investigated.[33] Although the *percentage* of residual isocyanate groups that undergo postcure chemistry during 7-month air exposure was comparable for the samples initially cured at 100 and 120 °C, the *absolute amount* of isocyanate converted to hydrolysis/condensation products is considerably larger (see Table IV) for the 100 °C cure case (11%) than for the 120 °C cure case (6.5%).

Other nitrogen environments, such as biuret and uretidione structures, experienced small air-exposure changes in concentration, as seen in Table IV. For the samples initially cured at 100 and 160 °C, both the amide and imide nitrogens of biuret moieties show small decreases in concentration upon 7-month exposure to air. Biuret linkages are known to undergo hydrolysis, but the rate of hydrolysis should be much faster for isocyanate groups than for biuret linkages.[21] The sample initially cured at 120 °C actually shows a small *increase* in biuret imide concentration upon exposure to air. An increase in biuret linkage concentration in the sample initially cured at 120 °C upon 7-month exposure to air could occur from the reaction of residual isocyanate with urea linkages according to reaction 2. However, the magnitude of the air-exposure changes observed in biuret amide and imide concentrations for the three samples in Table IV is quite small; consequently no claims for significant changes in biuret concentration upon exposure to air are made here for any of the three samples.

The relative concentration of uretidione linkages appears to increase slightly upon 7-month exposure to air for the sample initially cured at 100 °C. MDI is known to form the uretidione dimer upon standing at room temperature.[17,18] Results obtained on the three samples immediately after the initial cure indicate that the significant formation of uretidione structures was observed only in the sample cured at 100 °C.[33] Perhaps this lowest temperature curing process generated structures that thermodynamically or kinetically favor the continued formation of uretidione structures after the initial cure.

Residual isocyanate in these MDI-polyisocyanurate resins can exist in the form of (a) unreacted MDI monomer or (b) "half-reacted" MDI, i.e., a system in which one of the original isocyanate groups of MDI remains intact and one has reacted to form either a monomeric species or an oligomeric or polymeric species. Gel permeation chromatography (GPC) has been used to determine the relative amounts of MDI monomer, trimer (isocyanurate), and larger isocyanurate oligomers during the catalyzed reaction of neat MDI at different temperatures.[42] The GPC results showed that, as the MDI monomer concentration decreased, MDI trimer molecules were generated, followed by the formation of MDI pentamer, heptamer, and nonomer. A MDI pentamer corresponds to a structure containing two isocyanurate moieties, a heptamer contains three isocyanurate moieties, etc. In this GPC study, between 26% and 31% of the total isocyanate content at the "final" reaction time was due to MDI monomer. The "final" reaction time corresponded to 40–70 min for low-viscosity samples cured between 50 and 130 °C and indicated that the MDI monomer concentration was still decreasing at the final time for which data were obtained (solidification). However, no determination of the concentration of the corresponding isocyanate-based structures was made for the *solid* resin, because GPC cannot be used for insoluble cross-linked resins.

If one assumes that the *solid* resins cured for 2 h in the preparation of samples of this study contained considerably less MDI monomer than the low-viscosity samples in the GPC study mentioned above, say, 20% of the total isocyanate content after the initial cure, a rough approximation for the percentage of MDI monomer contributing to the isocyanate resonance in the A spectra of Figure 1–3 can be made from the results shown in Table IV. These percentages of the *total* corrected ^{15}N CP/MAS intensity (all derived from the initial MDI monomer) corresponding to remaining MDI monomer are 4%, 3%, and 3% for the resins resulting from initial curing at 100, 120, and 160 °C, respectively. These kinds of small differences in the amount of MDI monomer present for the three initially cured samples cannot *alone* account for the dramatic differences observed in the ^{15}N spectra upon 7-month exposure to air for the sample initially at 160 °C compared with the samples initially cured at 100 and 120 °C. That is, the apparent differences in postcure reaction chemistry of the isocyanate groups in these samples cannot be based mainly on arguments of significantly different residual MDI monomer concentrations in the initially cured resins. This effectively precludes a dominant role that larger MDI pockets or regions might play in the increased postcure isocyanate reaction chemistry observed for the sample initially cured at 160 °C relative to the samples initially cured at 100 and 120 °C. These results would suggest that the postulated increase in the number of voids and imperfections in the sample initially cured at 160 °C, relative to the samples initially cured at 100 and 120 °C, and the corresponding more facile access of water molecules to unreacted isocyanate groups and/or the alternate dendrimer issue outlined above are probably the predominant factors determining the observed differences in postcure chemistry for the samples.

Although the terminal isocyanate groups of a rigid isocyanurate structure and the MDI monomer isocyanate groups are not distinguishable on the basis of chemical shift in the solid-state ^{15}N NMR spectra, these different types of isocyanate environments should manifest different NMR relaxation behavior. $T_{1\rho H}$ values have been used to establish homogeneity and inhomogeneity in polymer systems.[43,44] $T_{1\rho H}$ values can be obtained via ^{15}N signals in ^{15}N CP/MAS experiments by applying a rf pulse to the protons and spin-locking the protons for some period τ before cross polarization from protons to nitrogens.[43] In such an experiment, the proton spin-locking period is systematically varied for a given CP contact time to determine the rate of decay of proton magnetization in the rotating frame, as measured from the ^{15}N magnetization. This decay is characterized by the rate constant $1/T_{1\rho H}$. If this decay for a given ^{15}N resonance is described by a simple monoexponential, then most of the ^{1}H nuclei giving rise to the corresponding ^{15}N magnetization manifest similar proton relaxation behavior in the rotating frame. This behavior is a result of efficient proton rotating-frame spin diffusion in homogeneous systems.[43,44] If a given peak has two major components with substantially different reorientational mobilities, such as the terminal isocyanate groups in "partially cured" isocyanurate-rich oligomers and the isocyanate groups of unreacted MDI in the present context, the rate of decay of proton magnetization in the rotating frame should exhibit biexponential behavior (or, for more than two components, multiexponential behavior), indicating the presence of the dissimilar environments. A "direct" ^{15}N-monitored $T_{1\rho H}$ experiment[43] was performed on a freshly cured MDI-polyisocyanurate resin tailored to have a high concentration of residual isocyanate groups[45] to establish the presence or absence of a significant concentration of unreacted MDI monomer in these types of systems. The results indicate that the isocyanate peak was well characterized by a single exponential, giving a $T_{1\rho H}$ value of 5.2 ms. In addition, the isocyanurate resonance was also characterized by a single exponential, with essentially the same $T_{1\rho H}$ value (5.1 ms). These data would suggest that the isocyanate environments in this sample are homogeneous and are closely associated with the isocyanurate structures, i.e., terminal isocyanates of isocyanurate moieties.

Additional evidence for the close association of residual isocyanate groups and isocyanurate structures comes from the $T_{1\rho H}$ values summarized in Tables II and III and obtained from a computer fit of variable contact time ^{15}N CP/MAS curves according to eq 3. These $T_{1\rho H}$ values are less "direct" measures of $T_{1\rho H}$ than the values obtained by spin-locking the protons for a variable time before cross polarization.[46] When one compares $T_{1\rho H}$ values for a given sample in Tables II and III, the isocyanurate and isocyanate peaks are seen to be similar. However, large differences are observed between values obtained for the isocyanate and isocyanurate moieties and those obtained for the urea, biuret, and amine moieties. These differences are observed for both sets of data, i.e., data obtained initially after curing (Table II) and after prolonged exposure to air (Table III). These data would suggest that the urea biuret, and amine environments are somehow physically separated from the isocyanate and isocyanurate environments, which display characteristically different NMR relaxation behavior. Similar $T_{1\rho H}$ values in Tables II and III for the isocyanurate and isocyanate moieties within a given sample suggest that the structural/chemical environments of these moieties are physically not substantially separated from each other. T_{1N} values (vide infra) obtained on these samples after 7-month exposure to air also suggest that the isocyanate groups are closely associated with the isocyanurate moieties.

^{15}N spin-lattice relaxation times (T_{1N}) of polymers have not been reported until recently,[47] primarily because of the low natural abundance of ^{15}N. The determination of individual T_{1N} values in these complex, cured MDI resins might lead to an increased understanding of the overall structure by providing information on the relative mobilities of the different groups. Table III summarizes the various T_{1N} values measured on the three MDI-polyisocyanurate resins after 7-month exposure to air. Unfortunately, no corresponding data were obtained on the resin samples immediately after curing.

The T_{1N} values given in Table III show large variations among the individual chemical structures within a given sample. Variations between samples for a given structural moiety are not as substantial. With the one exception of the uretidione nitrogen in the sample initially cured at 100 °C, the largest T_{1N} value for each of the samples was observed for the isocyanurate nitrogen, indicating that these cross-link sites, with no directly attached hydrogens, are part of the most rigid environments in each sample. Also exhibiting large T_{1N} values in these samples are the peaks due to isocyanate nitrogens. The isocyanate peaks in these samples were checked for biexponential or multiexponential T_{1N} behavior to establish the presence or absence of significant MDI monomer. In each case, the data were fit satisfactorily by a single exponential, indicating that substantial MDI monomer probably does not exist. The similarity in T_{1N} values of isocyanate and isocyanurate moieties within a given sample, like the $T_{1\rho H}$ results discussed above, suggests that the majority of residual isocyanate groups remaining after 7-month exposure to air are closely associated with the isocyanurate moieties, i.e., terminal isocyanate groups of isocyanurate-rich oligomeric structures.

The T_{1N} results shown in Table III might be viewed as indicating that the urea and biuret nitrogen environments are considerably more mobile than the isocyanurate or isocyanate environments. However, since the urea and biuret amide nitrogens bear directly attached protons, the ^{15}N–^{1}H dipolar interaction should induce more efficient T_{1N} relaxation compared to that in the isocyanurate and isocyanate nitrogens, which have no directly attached protons. As a result, the smaller T_{1N} values observed for hydrogen-bearing nitrogen moieties are not necessarily an indication of increased motion relative to nitrogen moieties not bearing hydrogens but may reflect the dominance of the ^{15}N–^{1}H dipolar interaction as the major relaxation mechanism.

Inspection of Table III reveals that the T_{1N} values of the amine resonances are significantly smaller than the corresponding values of the urea and biuret resonances. The nitrogen atom of an amine group bears two directly attached protons and therefore can be more efficiently relaxed by ^{15}N–^{1}H dipolar interactions than nitrogens bearing one or no directly attached protons. In addition, rapid motion of the amino groups might be providing an efficient relaxation mechanism for these environments. ^{15}N CP/MAS interrupted-decoupling experiments suggest that the ^{15}N–^{1}H interactions in the amino groups of these resins are substantially time dependent, behaving like methyl groups in ^{13}C CP/MAS interrupted-decoupling experiments; considerable spectral intensity persists in both cases after interrupt times of 120 μs.[48] Hydrogen-bonding patterns might be expected to reduce the mobility of an amino group, especially in regions of high amine concentration. However, with the amino group concentration so low in the samples after prolonged exposure to air (2–7% of the total corrected ^{15}N intensity; see Table IV), it is unlikely that extensive hydrogen bonding between amino groups exists. Hydrogen bonding is also possible from the amino hydrogens to the carbonyl oxygens of various moieties in these resins. In any case, it would appear that the effective relaxation of the amino group nitrogens, as reflected in their smaller T_{1N} values relative to the other nitrogen moieties, is dominated by modulation of the ^{15}N–^{1}H dipolar interaction due to the motion of the amino group and/or proton exchange.

Although the structural trends that one can recognize in the ^{13}C CP/MAS and CP/MAS/interrupted-decoupling spectra are not as straightforward or compelling as in the corresponding ^{15}N spectra (vide supra), the main features of these spectra are nevertheless consistent with the interpretations discussed above for the ^{15}N NMR data. The ^{13}C chemical shifts of pertinent model compounds were reported previously.[33] The previously reported 50.3-MHz ^{13}C CP/MAS spectra of three ^{15}N-enriched MDI-polyisocyanurate resins prepared at different cure temperatures are given in Figure 7, where they are presented in a format to display the entire chemical shift range relevant to these systems, except for the methylene carbon resonances at 41 ppm. These spectra are characterized by six resonances, or spectral regions, associated with the following types of carbon structural situations: a shoulder

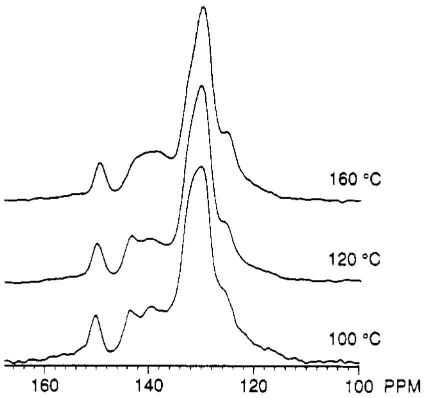


Figure 7. 50.3-MHz ^{13}C CP/MAS spectra (CP contact time = τ = 4 ms; repetition delay = t_d = 6 s) of three ^{15}N-enriched MDI-polyisocyanurate resins prepared at different cure temperatures (indicated) and obtained immediately after curing.

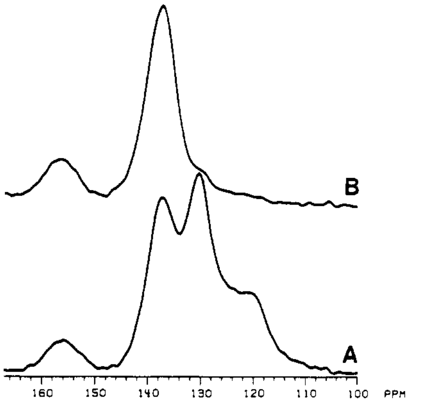


Figure 8. 50.3-MHz ^{13}C CP/MAS spectra of MDI-based polyurea poly[methylenebis(4-phenylurea)]: (A) τ = 4 ms, t_d = 6 s; (B) interrupted-decoupling spectrum, τ = 4 ms, interrupt time = 70 μs, t_d = 6 s.

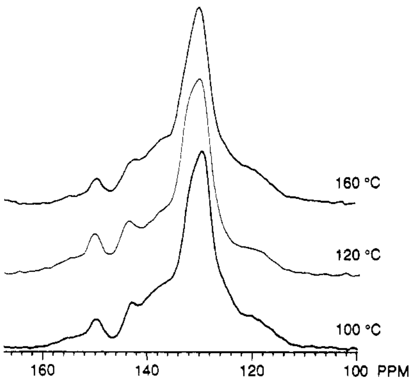


Figure 9. 50.3-MHz ^{13}C CP/MAS spectra (τ = 4 ms; t_d = 6 s) of three ^{15}N-enriched MDI-polyisocyanurate resins, initially prepared at different cure temperatures, obtained after 7-month exposure to air.

at 125 ppm due to isocyanate carbonyl carbons and aromatic carbons ortho to isocyanate functionalities; the predominant resonance at 130 ppm due to various hydrogen-bearing aromatic carbons; the region centered about 138 ppm due to benzyl-substituted aromatic carbons para to isocyanate functionalities; the region centered about 143 ppm due to benzyl-substituted aromatic carbons para to isocyanurate moieties; a resonance at 150 ppm due to isocyanurate carbonyl carbons; and a region centered at 155 ppm corresponding to urea carbonyl carbons. Differences among the spectra of Figure 7 were discussed earlier.[33]

The 50.3-MHz ^{13}C CP/MAS and CP/MAS/interrupted-decoupling[26] spectra of the MDI-based polyurea are shown in Figure 8. The normal CP/MAS spectrum (Figure 8A) is characterized by four major resonances, arising from the following types of carbon structural situations: a broad resonance at 119 ppm corresponding to unsubstituted aromatic carbons ortho to urea nitrogens; the resonance at 130 ppm corresponding to unsubstituted aromatic carbons meta to urea nitrogens; the resonance centered at 137 ppm corresponding to nitrogen-substituted aromatic carbons and benzyl-substituted aromatic carbons para to urea nitrogens; and the resonance centered at 155 ppm corresponding to urea carbonyl carbons. Note that in the interrupted-decoupling spectrum (Figure 8B) signal intensity is seen only for the substituted aromatic carbons centered at 137 ppm and for the urea carbonyl carbons at 155 ppm.

If significant postcure reaction chemistry of residual isocyanate occurs according to reactions 1a and 1b in the MDI-polyisocyanurate resins, it should be manifest in the ^{13}C CP/MAS and ^{13}C CP/MAS interrupted-decoupling spectra as increases in spectral regions corresponding to amine and urea structures and decreases in spectral regions corresponding to isocyanate structures. Intensity increases in the 119, 137, and 155 ppm regions in the spectra of the MDI-polyisocyanurate resins exposed to air and decreases in the 125 ppm region relative to the spectra of the MDI-polyisocyanurate resins obtained initially after curing should accompany any significant postcure isocyanate chemistry. Both the MDI-polyisocyanurate and the MDI-based polyurea resins have ^{13}C resonances centered at 130 ppm,[33] making this region difficult to analyze by solid-state ^{13}C NMR.

Figure 9 shows the 50.3-MHz ^{13}C CP/MAS results for the same MDI-polyisocyanurate resins represented in Figure 7 after 7-month exposure to air. There are several dramatic changes in these spectra compared to those of the initially cured resins presented in Figure 7. The shoulder centered at 125 ppm in the spectra of Figure 7, corresponding to isocyanate carbonyl carbons and aromatic carbons ortho to isocyanate groups, is absent or much lower in intensity in the spectra of Figure 9. In addition, this spectral region is complicated by an increase in spectral intensity centered at 119 ppm (due to aromatic carbons ortho to urea nitrogens), making the 115–125 ppm region difficult to interpret in spectra obtained under "normal" CP/MAS conditions. A decrease in spectral intensity in the 125 ppm region of the spectra in Figure 9 relative to the spectra of Figure 7 reflects the consumption of unreacted isocyanate groups, presumably to form hydrolysis and condensation products, especially urea linkages. This presumption is supported by the increased intensity centered at 119 ppm in the spectra of Figure 9 relative to the spectra of Figure 7. For this particular resonance, the normal ^{13}C CP/MAS spectra are more informative for monitoring the urea condensation product than are the interrupted-decoupling spectra (discussed below), since the hydrogen-bearing aromatic carbons ortho to urea nitrogens are strongly attenuated under dipolar-dephasing NMR conditions. Intensity in the spectral region centered at 137 ppm, corresponding to urea-substituted aromatic carbons and benzyl-substituted aromatic carbons para to urea nitrogens, is also larger in the spectra of Figure 9 than in the spectra of Figure 7. There is also information on the concentration of urea carbonyl carbons from the relatively broad, featureless spectral region centered at 155 ppm in the spectra of Figure 9. This region is virtually devoid of intensity in the spectra of Figure 7.

^{13}C CP/MAS/interrupted-decoupling experiments were also carried out on each of the MDI-polyisocyanurate

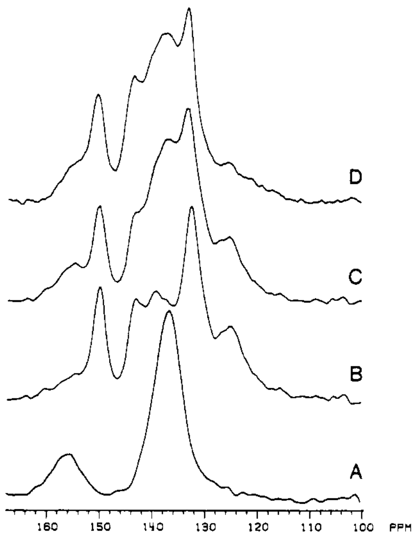


Figure 10. 50.3-MHz ^{13}C CP/MAS interrupted-decoupling spectra (τ = 4 ms, interrupt time = 70 μs; t_d = 6 s) of (A) MDI-based polyurea, (B) MDI-polyisocyanurate resin initially cured at 100 °C, (C) addition of (0.24) (A) plus (0.76) (B), and (D) MDI-polyisocyanurate resin initially cured at 100 °C and exposed to air for 7 months.

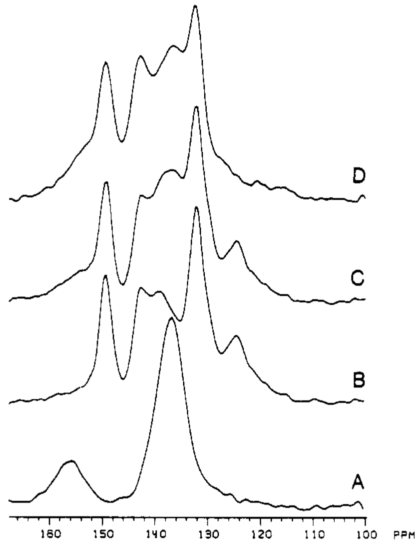


Figure 11. 50.3-MHz ^{13}C CP/MAS interrupted-decoupling spectra (τ = 4 ms, interrupt time = 70 μs; t_d = 6 s) of (A) MDI-based polyurea, (B) MDI-polyisocyanurate resin initially cured at 120 °C, (C) addition of (0.10) (A) plus (0.90) (B), and (D) MDI-polyisocyanurate resin initially cured at 120 °C and exposed to air for 7 months.

resins, both immediately following the initial cure[33] and after a 7-month exposure to air. The interrupted-decoupling experiment removes spectral intensity associated with those carbons experiencing strong ^1H–^{13}C dipolar couplings, e.g., methylene and methine carbons, simplifying the spectra and making spectral interpretation more straightforward. Figures 10–12 show the ^{13}C CP/MAS/interrupted-decoupling results on MDI-polyisocyanurate resins cured at 100, 120, and 160 °C, respectively. One can see dramatic differences in several spectral regions between the spectra obtained on the resins after prolonged exposure to air (Figures 10D, 11D, and 12D) and the corresponding spectra obtained immediately after curing (Figures 10B, 11B, and 12B). Deconvolutions (not shown) of spectra B and D in Figures 10–12 were carried out, and the resulting relative peak areas of the contributing resonances for both sets of spectra are summarized in Table V.

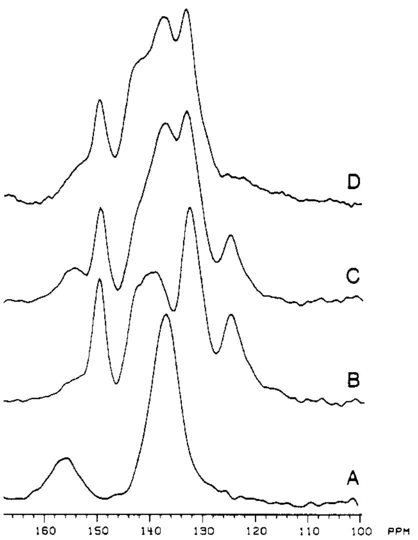


Figure 12. 50.3-MHz ^{13}C CP/MAS interrupted-decoupling spectra (τ = 4 ms, interrupt time = 70 μs; t_d = 6 s) of (A) MDI-based polyurea, (B) MDI-polyisocyanurate resin initially cured at 160 °C, (C) addition of (0.30 (A) plus (0.70) (B), and (D) MDI-polyisocyanurate resin initially cured at 160 °C and exposed to air for 7 months.

Table V
Interrupted-Decoupling ^{13}C CP/MAS Intensities of MDI-Polyisocyanurate Resins before and after 7-Month Exposure to Air[a]

	relative peak areas	
peak,[b] ppm	after initial cure	after exposure to air
	Initial Cure Temperature: 100 °C	
125	13.8	7.7
137	2.5	17.3
155	3.6	9.7
	Initial Cure Temperature: 120 °C	
125	13.8	7.0
137	1.8	15.1
155	1.1	10.8
	Initial Cure Temperature: 160 °C	
125	15.9	5.0
137	5.0	19.0
155	2.0	8.0

[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.

Although the relative areas obtained directly from deconvolutions of the ^{13}C CP/MAS/interrupted-decoupling spectra (Table V) 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. There is a visible decrease in the spectral intensity in the region corresponding to the isocyanate carbonyl carbons centered at 125 ppm for the spectra D relative to the corresponding spectra B in Figures 10–12. The deconvolution data support this observation, revealing a B → D decrease of approximately a factor of 2 or more for the intensity of this resonance. Accompanying this observed B → D isocyanate decrease are B → D intensity increases corresponding to formation of the MDI-polyurea linkages. Large intensity increases centered at 137 and 155 ppm are observed in the D spectra compared to the B spectra of Figures 10–12. Both the observed decrease in intensity at 125 ppm and the increases in spectral intensity for the 137 and 155 ppm regions are more obvious in the interrupted-decoupling spectra of Figures 10–12 than in the corresponding normal CP/MAS spectra of Figures 7 and 9.

To further demonstrate that the hydrolysis of unreacted isocyanate groups in the MDI-polyisocyanurate resins results in the formation of MDI-polyurea linkages, weighted spectral additions of A and B were carried out for each of the Figures 10–12, resulting in the corresponding addition spectra, C. Comparing in each of the Figures 10–12 the addition spectrum C with the direct experimental spectrum D, one can see that the addition procedure reasonably reproduces the expected intensity changes. For each C spectrum in Figures 10–12, intensity increases relative to the corresponding A spectrum are accounted in the 137 and 155 ppm regions.

Close examination of the spectra in Figures 10–12 reveals several important features that correspond to differing degrees of postcure isocyanate chemistry in the three resin samples. Spectra 10D and 12D show larger intensity increases upon exposure to air in the 137 ppm region (corresponding to aromatic carbons in urea-substituted aromatic rings) relative to spectrum 11D. This result is not unexpected, since the sample represented in Figure 11 was shown to have the least residual isocyanate concentration after the initial cure at 120 °C.[33] The sample initially cured at 160 °C, represented by Figure 12B, was shown to contain less residual isocyanate than the sample initially cured at 100 °C, represented by Figure 10B. However, upon comparison of spectra 10D and 12D together with interrupted-decoupling spectra of the corresponding resins before exposure to air (Figures 10B and 12B), it appears that atmospheric hydrolysis and subsequent condensation have occurred to a greater extent in the resin initially cured at 160 °C (Figure 12). The intensity of the 137 ppm resonance is larger in spectrum 12D than in spectrum 10D and the intensity of the residual isocyanate (125 ppm) is correspondingly smaller in spectrum 12D. Although intensity for the urea carbonyl carbons (155 ppm) appears in this qualitative assessment to be comparable for all the D spectra in Figures 10–12, these data would suggest that isocyanate postcure chemistry has occurred to the greatest extent for the sample initially cured at 160 °C, followed by the samples initially cured at 100 and 120 °C, in that order.

Evidence for the isocyanate hydrolysis product shown in reaction 1a, the amine, is indicated by the increased relative intensity on the high-shielding side ($\sim$146 ppm) of the isocyanurate peak (150 ppm) in the D spectra of Figures 10–12 compared to the corresponding B spectra. This effect appears to be most pronounced in Figure 12, corresponding to the sample initially cured at 160 °C. The increased intensity centered at 146 ppm in the D spectra of Figures 10–12 relative to the corresponding B spectra in Figures 10–12 corresponds to amino-substituted aromatic carbons.[33] The ^{13}C chemical shift of aromatic carbons ortho to amino groups is ca. 115 ppm. The spectra in Figure 9 may include an intensity increase in this region relative to the corresponding spectra in Figure 7, but this region is complicated by the presence of aromatic carbons ortho to urea-substituted carbons at 119 ppm.

In any case, one should keep in mind that, due to the intensity uncertainties associated with uncorrected CP/MAS data, especially in the interrupted-decoupling experiment, these ^{13}C NMR results should be considered only in a qualitative manner. Nevertheless, the general trends and changes observed in the ^{13}C results when one compares spectra obtained immediately after curing with spectra obtained after 7-month exposure to air support the corresponding, more definitive ^{15}N results presented above.

Summary and Conclusions

The solid-state, postcure reaction chemistry in three MDI-based, isocyanurate-rich resins exposed to air for 7 months was elucidated by means ^{15}N and ^{13}C CP/MAS NMR methods. It was established that this chemistry is essentially that originating from residual isocyanate groups still present after the initial cure. ^{13}C CP/MAS results are able to identify decreases in isocyanate concentrations and increases in urea linkages, when data obtained initially after curing are compared with data obtained after 7-month exposure to air. However, the ^{13}C results are only qualitative in nature, and the different extents of hydrolysis for the three samples could not be readily determined by ^{13}C CP/MAS. ^{15}N CP/MAS results were able to identify clearly the product of isocyanate hydrolysis, namely, the amine, as well as the urea-linkage condensation product from the reaction of amine with isocyanate. In addition, ^{15}N CP/MAS was able to quantify the extents of these postcure reactions for each sample by measuring concentrations of isocyanate, amine, and urea groups both before and after prolonged exposure to air. The different extents to which hydrolysis occurred in the three samples can be interpreted in terms of the cure conditions. The sample initially cured at 160 °C, having undergone a more "inhomogeneous" curing process, was found to undergo the most extensive isocyanate postcure reaction chemistry, followed by the samples initially cured at 100 and 120 °C, respectively. The presence of substantial MDI monomer concentration in these resins was not observed, indicating that perhaps an enhancement in water diffusion efficiency (possibly associated with voids and imperfections from inhomogeneous curing) or dendrimer size in the sample initially cured at 160 °C is responsible for the observed increase in postcure chemistry of this sample relative to samples initially cured at 100 and 120 °C. The postcure reaction of isocyanate with urea linkages to form biuret linkages was found to be insignificant compared to the hydrolysis and subsequent condensation reactions to form urea linkages. Evidence for the possible existence of chemically and structurally distinct domains was provided by significant differences in $T_{1\rho H}$ values for individual nitrogen structures in these MDI-based resins. Evidence for the close association of residual isocyanate groups and isocyanurate moieties was provided by similar $T_{1\rho H}$ and T_{1N} values for the two structures. In addition, T_{1N} values might provide insight into the motion of the different linkages and groups. ^{15}N CP/MAS NMR provides a powerful analytical tool for probing the structure, chemistry, and dynamics of isocyanate-based macromolecular systems.

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