Nitrogen-15 Solid State NMR Studies on the Cure and Degradation of Polyimide Films under Temperature and Humidity Stress

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ABSTRACT: An investigation of the thermal cure reactions and the hydrolysis reactions involved in the degradation of polyimide films under temperature and humidity stress using nitrogen-15 solids nuclear magnetic resonance (NMR) is herein reported. Nitrogen-15 labeling was used in combination with dipolar decoupled, cross polarization magic angle spinning (CPMAS) NMR techniques as a means of monitoring chemical reactions as these occur in solid state polyimide. The relative concentration of each nitrogen-containing functional group was calculated using standard NMR methods based on determination of the values of the cross polarization time constant, T_{HN}, the proton rotating frame time constant, $T_{1\rho\mathrm{H}}$, and observed spectral line intensities. The polyimides were derived from an oligomeric poly(amic acid) precursor [pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA)], a high molecular weight poly(amic acid ester) precursor (PMDA *m*-diacyl chloride diethyl ester and ODA), and a polyisoimide oligomer [3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) and 1,3-bis(3-aminophenoxy)benzene (APB) endcapped with (3-aminophenyl)acetylene (APA)]. The number of "defect sites" or imide-precursor groups where imidization does not occur was estimated to be between 6 and 9% of the total nitrogen and varies with the type of precursor used. The degree of imidization or cure was found to vary between 91 and 94% following a cure at 400 °C. Residual isoimide groups were detected after an extended 400 °C bake of the polyisoimide precursor. Cured films were subjected to temperature and humidity stress at 85 °C and 81% relative humidity for 450 h. Estimates of hydrolysis range from as little as 1% of total nitrogen for the BTDA–APB–APA derived material to approximately 13% for the PMDA–ODA poly(amic acid ester) precursor. About 30% of the amide acid groups formed during stress react with water in a second hydrolysis reaction with chain cleavage to yield a terminal diacid and a terminal amine group. Hydrolysis from temperature and humidity stress is almost completely reversed if the stressed polyimide is heated at 400 °C after stress. The data obtained in this study are consistent with previously reported macroscopic observations in which polymer properties degrade during temperature and humidity stress and are recovered after post temperature and humidity bakes.

Introduction

Polyimides are an important class of high-performance polymers noted for their exceptional thermal stability.[1-5] They are currently used in a wide variety of applications including composite matrix resins, wire enamels, films, electronic passivation coatings, and thin-film dielectric layers in electronic devices and packages. When used in electronic packaging applications, the desirable properties of polyimides include low dielectric constants, good mechanical strength and adhesion, high thermal stability and good solvent resistances, and more recently, photosensitivity.[2,3,5] One important consideration in the use of polyimides in microelectronic applications is the long term stability of such films in manufactured devices under field use conditions. In order to assure long term reliability of materials in hybrid devices, attempts are made to accelerate their failure mechanisms using accelerated stress testing. One such test that is often used for this purpose is exposure of the hybrid to elevated conditions of temperature and humidity (T & H stress). Failure rates calculated from T & H stress results can be used to project product lifetimes under use conditions and can serve as standards to ensure the use of the best manufacturing processes.

The hydrolysis reactions leading to the degradation of adhesion and mechanical properties of polyimide films under T & H stress conditions are of considerable interest in understanding the adhesive and/or mechanical failures that may be associated with polyimide films exposed to vigorous T & H stress conditions. In recent years, these hydrolysis reactions have been the subject of investigation.[3,6-8] One of the major problems in the work that has been reported has been consistent difficulty in obtaining quantitative chemical data on the extent of the hydrolysis reactions. Indeed, similar problems have plagued efforts to measure the extent of the thermal curing reactions of polyimide precursors. Direct chemical analysis using infrared spectroscopic methods,[9] while readily describing the curing reactions at extents of reaction ranging from 0 to 85–90%, fails at extents of reaction above 85–90%. Similarly, infrared experiments[8,13] which have sought to measure the degree of hydrolysis in thermally cured material after temperature and humidity stress have had difficulty in detecting the low concentrations of reaction products that are formed during hydrolysis. The current research attempts to clarify reactions at the imide functions of polyimide thin films during temperature and humidity stress by providing direct, quantitative chemical measurements.

A variety of analytical methods have been used to characterize the cure chemistry and degradation mechanisms of polyimides. A partial list of these methods includes infrared spectroscopy, a variety of thermal analysis techniques, mechanical testing, and carbon-13 nuclear magnetic resonance in solution and in the solid state. Due to the insoluble nature of most polyimides, the application of solution NMR methods in polyimide characterization has been limited to studies on their soluble precursors.[10] The carbon-13 solid state NMR spectra of a few polyimides have been reported.[9,11,12] Unfortunately, the line broadening encountered in the carbon-13 solids spectra is sufficiently severe as to render the aryl carbonyl

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region unsuitable for distinguishing and quantifying aryl carbonyl-containing functional groups. This is a serious problem, as the chemistry of interest involves reactions at these centers.

Reports have described the use of nitrogen-15 NMR in the characterization of polyamides,[14] and more recently, the polycondensation kinetics of the reaction of an aromatic diamine with an aromatic diacid in solution to yield a polyimide has been reported.[15] However, there have been no reports describing the characterization of the polyimide solid state through the use of nitrogen-15 as the probe nucleus in dipolar-decoupled, cross polarization magic angle spinning (DD-CPMAS) NMR experiments. The ^{15}N DD-CPMAS NMR method appears to be well suited for the chemical characterization of polyimides, since the chemical reactions encountered in the preparation and cure of these polymers involve reactions of nitrogen-containing groups, i.e. amines, amic acids, imides, and isoimides, where the nitrogen atoms are directly involved at the reaction sites. The ^{15}N solids spectra of polyimides should be simple compared to the corresponding ^{13}C spectra[9,11,12] and would be expected to show a large chemical shift dispersion among the different nitrogen-containing functional groups commonly found in polyimides and polyimide precursors. This combination of spectral simplicity and large chemical shift dispersion should allow for the development of quantitative algorithms for the determination of the relative amounts of each nitrogen containing group and hence a direct measure of the extent of cure. Such a method would be immediately useful in studies relating degree-of-cure to polymer physical properties and as a method for determining the degree of cure obtained by various curing methods (thermal, infrared, and microwave) and curing equipment. The extension of this technique to the study of degradation processes is yet another application. Finally, experimental methodology with the features described above would be useful in the study of other nitrogen-containing polymers and resins such as nylons, urethanes, and epoxies.

Results and Discussion

Polyimides have been prepared from a variety of precursors.[1-5] The polyimide precursors used in this study were poly(amic acids), poly(amic acid esters), and polyisoimides. The precursors are converted to polyimides by intramolecular cyclization with elimination of water in the case of poly(amic acids), by elimination of an alcohol in the case of poly(amic acid esters), or by isomerization as in the polyisoimides. In this work, spectral data were obtained on an oligomeric poly(amic acid) (PAA) prepared by the condensation of pyromellitic dianhydride (PMDA) with 4,4′-oxydianiline (ODA), on a poly(amic acid ethyl ester) (PAE) prepared by the polymerization of PMDA *m*-diacyl chloride diethyl ester with ODA and on an acetylene terminated polyisoimide (PISI) obtained by condensation of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) with 1,3-bis(3-aminophenoxy)benzene (APB) followed by endcapping with (3-aminophenyl)acetylene (APA) and final dehydration to yield the polyisoimide.[12,16] These materials are depicted in Figure 1.

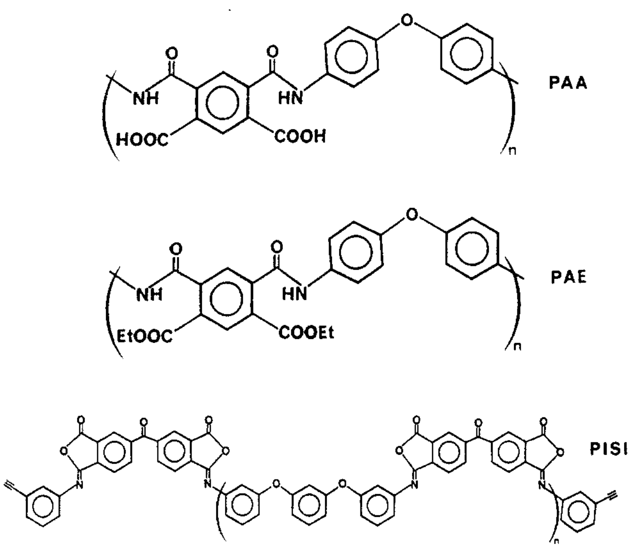

Figure 1. Structures of the polyimide precursors used in this study.

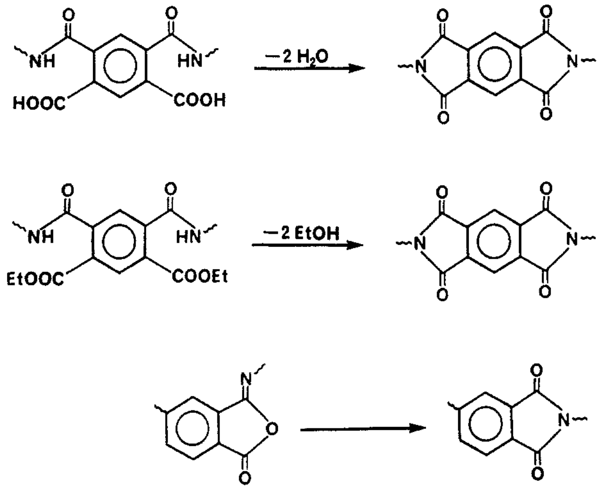

Figure 2. Curing reactions for the poly(amic acid), poly(amic acid) ethyl ester, and the polyisoimide materials.

Measurement of the ^{15}N-CPMAS Spectra of Oligomeric PMDA–ODA Polyimide. Because of the low natural abundance of ^{15}N (0.37 atom %) and the relative insensitivity of the ^{15}N nucleus compared to the ^{13}C nucleus as well as the low atom % of nitrogen in most polyimides (7.3 atom % per polymer repeat unit for PMDA–ODA polyimide), we began our studies using an oligomeric PMDA–ODA poly(amic acid) containing 99 atom % ^{15}N at both ODA amine positions. The low molecular weight oligomeric material was prepared to ensure that all likely nitrogen resonances including terminal amine groups would be available in sufficient quantity for detection. The level of enrichment used in this study results in a calculated sensitivity increase of 270× compared to the natural abundance material. Consequently, data acquisition times are shortened, detection limits are improved, CPMAS experimental parameters are easier to optimize, and the task of extracting relaxation times, in particular the cross polarization time constant, T_{HN}, and the proton rotating frame time constant, $T_{1\rho\mathrm{H}}$, is uncomplicated by problems of long data acquisition times and instrument stability. As the following discussion will show, accurate measurements of T_{HN} and $T_{1\rho\mathrm{H}}$ are essential to spectral interpretation.

As shown in Figure 2, poly(amic acids) cure by thermal cyclodehydration. This cure reaction involves the cyclodehydration of two *o*-amide acid functions per polymer repeat unit to yield a bis(imide) repeat unit and two molecules of water.

Parts A–F of Figure 3 show a series of ^{15}N DD-CPMAS spectra obtained under identical experimental NMR conditions from samples of oligomeric PAA cured at different temperatures and for different times. The cross polarization contact time (T_{CP}) used was 2.00 ms. After thermal curing at 150 °C for 30 min, the PAA has been

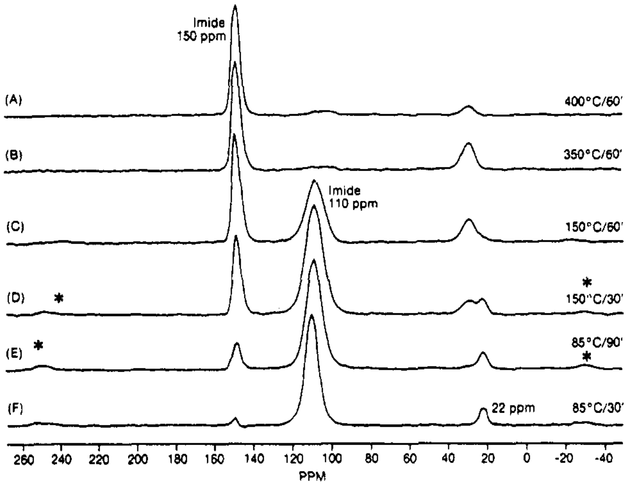

Figure 3. ^{15}N CPMAS spectra of PMDA–ODA poly(amic acid) (PAA) thermally cured at different temperatures and times. Chemical shifts are referenced to external ammonium sulfate. The cure temperatures and times are on the right axis. * = spinning sidebands.

partially cyclized to the imide. Four prominent NMR resonances were observed at 150, 110, 28, and 22 ppm with respect to a reference of solid ammonium sulfate which is assigned 0 ppm (Figure 3D). The 150 ppm resonance is assigned to the imide nitrogen, the 110 ppm resonance is assigned to the amide nitrogen, the 28 ppm resonance arises from the terminal imide/ODA amine nitrogen, and the 22 ppm resonance arises from the terminal amic acid/ODA amine nitrogen. These assignments were made on the basis of the results of dipolar dephasing experiments, previously reported values of ^{15}N chemical shifts,[17] and the changing intensity of the lines as the polymer cure reaction proceeds with increasing temperature or with increasing time at temperature.

The dipolar dephasing experiment is useful for identifying rigid or nearby nitrogen–hydrogen interactions.[18,19] When rigid or nearby interactions are present, NMR signals dephase quite rapidly as a function of dephasing time, leading to a loss in observed intensity as the dephasing time increases. Under the same conditions, nonrigid or distant interactions show little loss in signal intensity. In the case of amide compared to imide nitrogen, one expects rapid dephasing of the mobile amide nitrogen–hydrogen interaction but no loss in the rigid imide intensity. The results of a dipolar dephasing experiment performed on a PAA sample cured at 150 °C for 60 min are shown in Figure 4. The top spectrum (4A) was obtained using standard instrument parameters and the bottom spectrum (4B) was obtained using dephasing with bilevel excitation/decoupling.[18] The line at 110 ppm loses intensity while the line at 150 ppm is not affected. This result supports the assignment of the line at 110 ppm as amide and the line at 150 ppm as imide. As expected from the presence of near nitrogen–hydrogen interactions, the amine lines at 28 and 22 ppm also show dephasing behavior but to a lesser degree than the amide line. The dephasing behavior of the amine lines suggests that these resonances have cross polarization time constants, T_{HN}, and proton rotating frame time constants, $T_{1\rho H}$, that are very different from those of the amide resonance and therefore dephase on a different time scale. The discussion that follows will show that this is indeed the case.

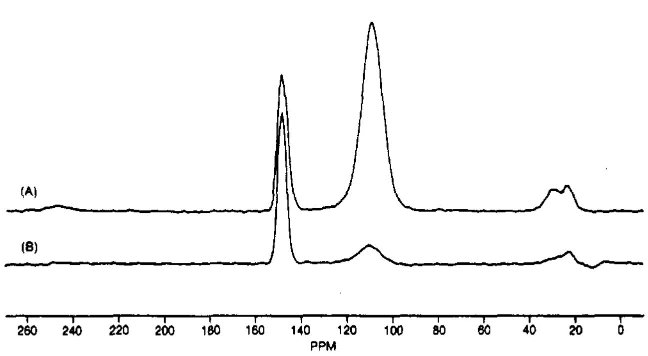

Figure 4. Dipolar dephased spectrum of PAA partially cured at 150 °C for 30 min. Spectrum 4A shows the spectrum before dephasing and spectrum 4B shows the result of dephasing. Note the marked attenuation of the amide line at 110 ppm and the essentially unchanged imide line at 150 ppm.

Returning to Figure 3, the sample cured at 85 °C for 30 min (Figure 3F) shows only a small amount of imide. When the cure time at 85 °C was increased to 90 min (Figure 3E), the imide line intensity increased and a noticeable low-field shoulder was present in the amine resonance. One explanation for the identity of the low-field shoulder is an amine salt. However, it is not possible to distinguish an amine salt from the free base using the spectral data. This is because the difference in chemical shift between the aromatic amines and their conjugate acid salts is small. For example, a chemical shift difference of only 4 ppm is observed between the nitrogens of aniline and anilinium hydrochloride.[11] When the cure temperature was raised to 150 °C and held for 30 min, the spectrum (Figure 3D) showed a prominent imide line whose intensity increased at the expense of the amide line as expected. Interestingly, the amine line at 22 ppm is now accompanied by an adjacent line at 28 ppm. Since there has been appreciable conversion of amide to imide and since the oligomer is amine terminal, our conclusion is that the resonance at 28 ppm is due to terminal 1,4-oxydianiline amine groups whose polymer bound amide nitrogen has been converted to imide nitrogen. Increasing the cure time at 150 °C from 30 to 60 min (Figure 3C) results in increased imide intensity, and the amine intensity at 22 ppm has been reduced to a high-field shoulder on the amine line at 28 ppm. The change observed in the amine intensities in Figure 3C compared to Figure 3D clearly supports the conclusion reached above on the chemical structure of the species associated with the 28 ppm amine line. Continued heating at 350 °C for 60 min (Figure 3B) results in almost complete conversion of amide to imide nitrogen and sharpens the terminal amine resonance. However, a small amount of residual amide is still present as a broad signal just above the spectral baseline. Raising the cure temperature to 400 °C and holding at that temperature for 60 min yields a sample whose spectrum (Figure 3A) shows a decrease in the terminal amine resonance and in the amide resonance. However, the terminal amine and amide resonances were still present even after 1 h of curing at 400 °C. Retention of the amine resonance after curing at 400 °C is not unexpected, as the sample was prepared using a stoichiometric excess of amine groups in the poly(amic acid) polycondensation. However, the residual amide signal clearly shows that the curing reaction is not yet complete.

Quantitative Analysis. Before further discussions, it is useful to analyze the ^{15}N NMR spectrum of the PAA oligomer for what quantitative information may be extracted. Referring to Figure 3A–F, the small signals labeled with an asterisk (*) are spinning sidebands which are generated by the incomplete motion-averaging of the orientational dispersion of resonances (chemical shift anisotropy) that occurs in the solid state. The sidebands occur as integral multiples of the rotor speed and are spaced symmetrically about the central resonance. If magic angle

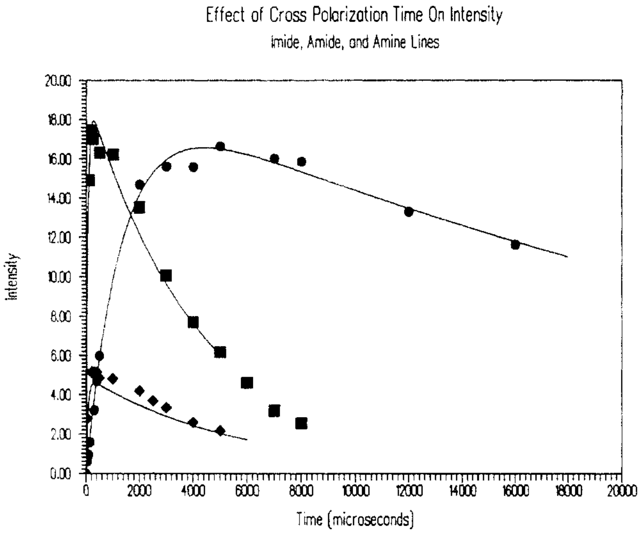

Figure 5. Plots of normalized spectral line intensity as a function of cross polarization time, T_{CP}, in microseconds for the major ^{15}N resonances observed in the PAA sample cured at 150 °C for 30 min. The solid lines show the best fit of the data to eq 1 and the filled circles, filled squares, and filled diamonds represent data obtained for the imide line at 150 ppm, the amide line at 110 ppm, and the amine line at 28 ppm.

spinning speeds considerably larger than the 5 kHz or 300 000 rpm used in this work were available, such satellites would be shifted out of the spectral region of interest and would become attenuated to invisibility. However, when sidebands are present and when quantitative information is desired, the sideband intensity must be added to the intensity of the parent line.

To obtain quantitative estimates of the concentrations of the various nitrogen-containing functional groups, two important magnetic dipolar effects[14] must be considered which can result in different relaxation rates for different nitrogens. The first factor is the heteronuclear cross polarization rate or T_{HN} for transfer of magnetic polarization between the hydrogen spin ensemble or bath (labeled H) and a given nitrogen (labeled N); the second factor is the rate of relaxation of the hydrogen spin bath or $T_{1\rho H}$. The relationship of the observed NMR intensity I_t at cross polarization contact time t for a given nitrogen has been successfully approximated[19] by the relationship shown in eq 1. Equation 1 shows that the observed signal intensity increases with T_{HN} and decreases with $T_{1\rho H}$.

$$I_t = I_0(1 - e(-t/T_{HN}))e(-t/T_{1\rho H}) \qquad (1)$$

Experimentally determined values of T_{HN} and $T_{1\rho H}$ vary with many factors including instrument settings and are usually measured experimentally under typical instrumental operating conditions. If good estimates of these constants are available, then the observed intensities I_t at a given contact time t can be extrapolated to their theoretical value I_0. It is the I_0's of each nitrogen type that are used to estimate relative concentrations. This is accomplished by multiplying the observed signal intensity of a given spectral line by the I_0 value and expressing the result as a percentage of the total corrected signal intensity for all nitrogens.

Figure 5 shows a plot of the observed intensity values versus cross polarization contact time obtained from a sample of PAA cured at 150 °C for 30 min (Figure 1C). Results are shown for the imide line at 150 ppm, for the amide line at 110 ppm, and for the amine line at 28 ppm. The data were fitted to eq 1 to yield the time constants shown in Table 1. As both Figure 5 and Table 1 show, the observed nitrogen resonances all have different time scales associated with their T_{HN} and $T_{1\rho H}$ values. For example, given a cross polarization contact time of 2.00 ms as was used in most of the spectra reported here, the plot shown in Figure 5 describes a sample in which the observed signal intensity due to both the amide and amine nitrogens is decreasing according to $T_{1\rho H}$ while the intensity of the imide signal is increasing to a maximum according to T_{HN}. Thus, none of the observed lines have reached their maximum intensity value at T_{cp} = 2.00 ms and direct integration of the signal areas will lead to erroneous conclusions about the relative amount of each nitrogen-containing functional group in the sample. Applying the time constants from Table 1 and eq 1 to the observed spectral intensities, including sideband contributions, of the PAA oligomer spectrum shown in Figure 3C yields calculated concentrations of 31% imide, 61% amic acid, and 8% amine.

Table 1. Compilation of the T_{HN} and $T_{1\rho H}$ Values in Milliseconds for the Nitrogen Species Shown in Figure 1C[a]

^{15}N type	chemical shift	T_{HN}	$T_{1\rho H}$
imide	150	1.23	17.5
amide	110	0.064	3.02
amine	28	0.22	3.64
amine	22	0.25	2.12

[a] The chemical shifts are reported with respect to a reference of solid ammonium sulfate.

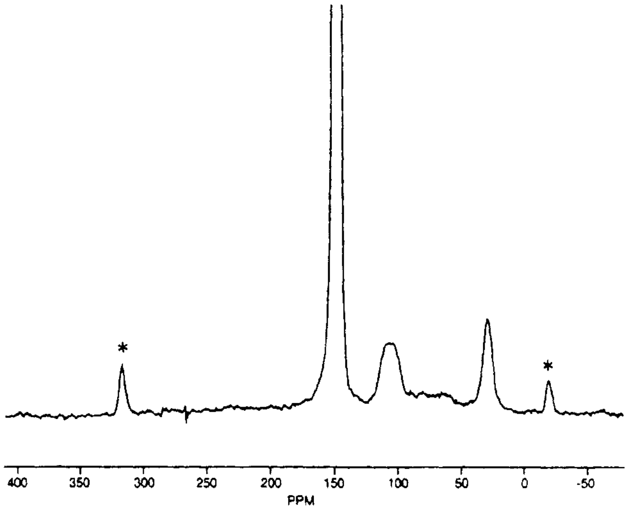

Figure 6. ^{15}N-CPMAS spectrum of PAA cured at 400 °C for 60 min.

Calculation of the Extent of Cure. The extent of conversion of the amide acid, amide ester, or isoimide to the imide or the "degree of imidization" of the precursor, whether poly(amic acid), poly(amic acid) ester, or poly-isoimide has also been an area of considerable interest.[1-5] The ^{15}N spectra obtained here provide a direct, quantitative measurement of the number of unreacted precursor groups or "defect sites" in the polyimide backbone. This is a result that has been difficult, if not impossible, to achieve using infrared spectroscopy,[8,13] especially on samples having a high degree of conversion of amide to imide.

Figure 6 shows the ^{15}N NMR spectrum of the PAA oligomer after curing at 400 °C for 60 min. Cyclization to the imide is still incomplete, and the amide resonance is prominent and centered at 110 ppm and is calculated to be 12% of the total nitrogen. The percentages of imide and amine in the sample were calculated to be 80% and 8%, respectively. Thus, a significant fraction of the available amide groups were not cyclized after heating at

400 °C for 60 min. This is an important result, as many of the commonly used thermal regimes used for curing poly(amic acids) do not exceed temperatures of 400 °C and therefore an incomplete cure of the material will result. Other unidentified nitrogen resonances are also seen near the baseline of this spectrum as a broad signal ranging from 100 to 50 ppm. These may be due to amine degradation products or to reaction products with the solvent.

Spectra of the PAE material after cure at 400 °C for 60 min show that approximately 9% amide remains after cure. Significantly, an amine resonance was not detected in the PAE derived polyimide after cure, indicating that the ethanol that is evolved during cure does not react with the amide group to yield a terminal amine and a terminal diester. While not shown here, the spectra of the cured PAE material are equivalent to the spectrum shown in Figure 8B. The spectrum of the uncured PAE polymer showed only amide nitrogen at 110 ppm.

The extent of conversion of the PAE polyimide was 91% compared to the PAA derived polyimide conversion of 80%. The PAA material has an average chain length of about 6 repeat units, as calculated from NMR end-group analysis, and would therefore not be expected to be affected by steric hindrance as much as the PAE, which has an average chain length of about 80 repeat units (calculated from the light scattering molecular weight data) provided that the glass transition temperatures behave similarly during cure. It appears that the glass transition temperature may rise to meet the cure temperature in the PAA material very quickly and restrict the chain motions more than in the longer PAE. This is consistent with both FTIR measurements[13] and mass spectrometric measurements[21] which show that PAE requires a cure temperature 50–70 °C higher than PAA to reach a 50% degree of imidization and that the onset of PAE imidization occurs at 210 °C. Thermogravimetric methods have shown the imidization of PMDA–ODA poly(amic acid) to be rapid over the temperature range 150–220 °C.[21] In the thermogravimetric study, the imidization rate of the poly(amide acid) was measured under isothermal conditions and was observed to become very slow immediately after the isothermal reaction temperature was reached. Moreover, the temperature at which poly(amic acid) imidization reached a maximum value was directly related to the polyimide glass transition temperature.

A spectrum of the PISI resin powder is shown in Figure 7. The isoimide line is prominent and is centered at 225 ppm. As expected, the isoimide line is well separated from the smaller imide and amide lines at 150 and 110 ppm, respectively. The isoimide spinning sidebands are especially prominent and indicate that the isoimide nitrogen has more chemical shift anisotropy than either the imide or amide nitrogens. The observed large anisotropy of the isoimide line is thought to be due to the presence of all possible regioisomeric orientations of the isoimide group in the sample. Since the isoimide nitrogen is rigidly bound to the isoimide ring through an exocyclic imine bond, the regioisomeric effect on chemical shift anisotropy should be much larger in the isoimide case than in the case of the freely rotatable regioisomeric amide bonds found in the PAA or PAE sample. The small broad signal centered at 260 ppm present in the polyisoimide powder spectrum, is attributed to BTDA residues having an isoimide linkage on one side and an imide linkage on the other side. This structural assignment is supported by the observation that the imide line at 150 ppm is 8% of the total nitrogen and that the 260 ppm line represents 8% of the total isoimide intensity.

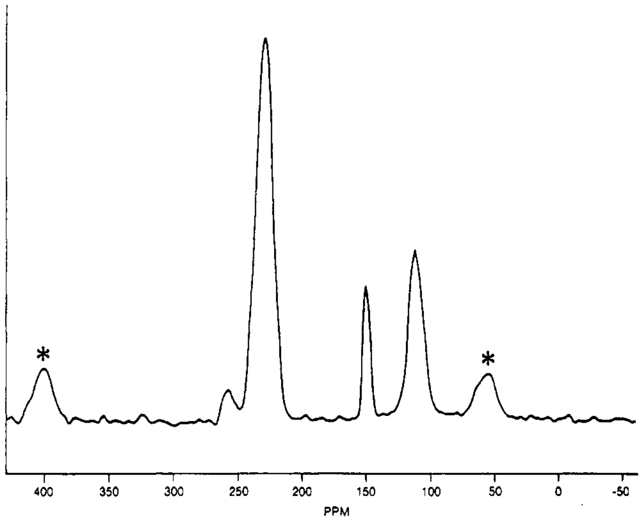

Figure 7. ^{15}N-CPMAS spectrum of the PISI powder prior to cure. The isoimide nitrogen resonance is the large line at 230 ppm. The sample also contains imide (150 ppm) and amide (110 ppm) nitrogen.

Spectra of the PISI derived polyimide after cure at 400 °C for 1 h and workup of the data resulted in the finding that 6% of the nitrogen was not imidized with 2.9% accounted for as isoimide nitrogen and 3.1% as amide nitrogen. It is somewhat surprising to detect the presence of the reactive isoimide group in the spectrum of the cured PISI material following a 400 °C cure, especially since the glass transition in this material occurs at 230 °C.[22] However, the steric requirements of the isomerization in the solid state may be sufficiently great as to limit the thermodynamically favored isomerization of the isoimide to the imide. An alternative explanation is that the isoimide to imide isomerization is subject to acid–base catalysis and occurs readily in solution[23] while removal of solvent and the corresponding loss of catalyst forces the isomerization to occur by an uncatalyzed, sterically encumbered thermal process. It should be noted at this point that the polyisoimide solutions used in this work contain both imide and amide nitrogens, and therefore, amide acid groups are present in the polyisoimide backbone prior to cure. Typical amide acid levels in the casting solution may be as high as 10% to 20% of total nitrogen. These are higher than in the solid precursor due to the rapid hydrolysis of isoimide to amide that occurs when isoimide solutions in NMP solvent are exposed to atmospheric moisture. The presence of the amide acid groups in the precursor solution may account for the residual amide acid signal observed in cured material. Finally, it should be noted that residual amounts of isoimide groups were not detected in the polyimides obtained from either the PAA or PAE precursors during thermal curing. This result directly contradicts earlier reports[24] which estimated the isoimide content in thermally cured PAA material as about 5% of total nitrogen.

Typically, polyimides are cured to 400 °C in some stepwise fashion under an inert atmosphere. The temperature steps are selected at points of rapid imidization, solvent outgassing, and so on. Most authors seem to agree that above 300 °C, the degree of imidization is greater than 90%.[1,2,13] The estimates obtained here of from 91 to 94% following a 400 °C bake are consistent with these estimates but are believed to be more accurate.

Effect of T & H Stress. With respect to the PAE derived polyimide spectrum shown in Figure 8, three

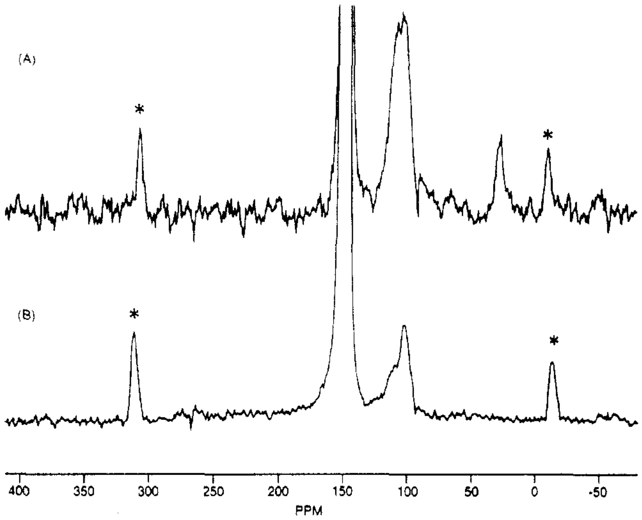

Figure 8. Spectrum of PAE after temperature and humidity stress (8A) compared to the spectrum of PAE following a 400 °C/1 h post-stress bake.

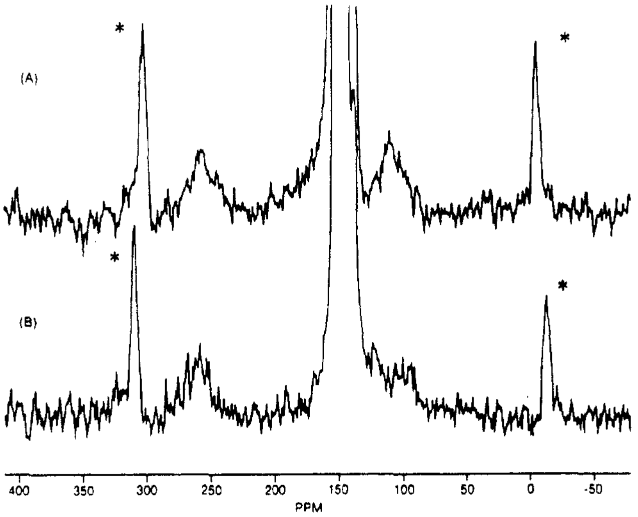

Figure 9. Spectrum of PISI after temperature and humidity stress (9A) compared to the spectrum of PISI following a 400 °C/1 h post-stress bake.

resonances are prominent after T & H stress at 85 °C and 81% relative humidity for 450 h (Figure 8A). The imide resonance is at 150 ppm, the amic acid/ester resonance is at 110 ppm and the terminal amine groups are at approximately 30 ppm. Following a post T & H bake at 400 °C for 1 h (Figure 8B), the amide group concentration was observed to decrease and the terminal amine resonance was not detected.

The spectrum of the PISI material after T & H stress is shown in Figure 9A. The spectrum shows a broad isoimide resonance at 260–270 ppm, the imide resonance is 150 ppm, the amic acid resonance is at approximately 110 ppm, and a weak amine resonance occurs at about 30 ppm. Since residual isoimide functions in the cured material are present at low concentrations, it is expected that the signal that is observed would be the isoimide–imide line at 260 ppm rather than the isoimide–isoimide line at 230 ppm. As in the spectra of the cured PISI material discussed above, it is surprising to detect the reactive isoimide function in a sample exposed to sufficient T & H stress to hydrolyze imide groups to amides and amines. In a separate experiment, the polyisoimide oligomer when treated with water in NMP or DMSO solution reacts in less than 24 h to yield an amide acid. It may be that the same steric barrier that apparently prevents complete isomerization of the isoimide to the imide also acts to suppress the hydrolysis reaction. Following a 400 °C post T & H bake for 1 h, the bottom spectrum (Figure 9B) shows that the isoimide resonance has changed very little, that the amic acid resonance has decreased slightly, and that the very weak amine resonance has decreased below detection. A summary of the relative percentages of the various nitrogen functions present before T & H stress, after T & H stress, and after the post T & H stress bake is given in Table 2. The values shown in Table 2 have been corrected for the contributions of spinning sideband intensities and for the T_{HN} and $T_{1\rho H}$ relaxations, as discussed above. The PAE material showed a 12.7% increase in the number of amide acid groups after an 85 °C/81% TH stress for 450 h. However, the PISI material showed only a 1.1% increase in amide groups. Thus, polyimides vary in their susceptibility to degradation under T & H stress conditions. Such variation in hydrolytic susceptibility has been observed by other workers.[8,25] Both polyimides show formation of terminal amine groups following temperature and humidity stress. This reaction, while prominent in the PAE material, occurs to a much lesser extent in the PISI sample. Stepwise hydrolysis of imide functions will yield the amide acid followed by a second hydrolysis of yield terminal amine and acid functions with concomitant scission of the polymer backbone. It is this chain scission reaction that is largely responsible for the degradation in mechanical properties that has been observed[6,26] when the PMDA-ODA polyimide film is exposed to elevated humidity.

Table 2. Summary of the Nitrogen Functional Group Composition in Polyimide Samples after Cure at 400 °C, after Exposure to 85% Relative Humidity at 81 °C, and after a Post-Stress Bake at 400 °C

	nitrogen functional group composition			
polyimide sample	% isoimide	% imide	% amide	% amine
	Polyisoimide (PISI)			
400 °C cure	2.9	94.0	3.1	0
450 h T/H	2.7	93.0	4.1	0.30
400 °C post T & H bake	3.3	93.7	3.0	0
	Poly(amide ester) (PAE)			
400 °C cure	0.0	91.0	9.0	0
450 h T/H	0.0	74.8	21.7	3.5
400 °C post T & H bake	0.0	90.9	9.1	0

The hydrolysis reactions of the polyimides that occur during temperature and humidity stress are substantially reversed by heating the sample at 400 °C. This result is not surprising because the hydrolyzed groups probably remain situated in an orientation favorable for condensation reactions and because primary aromatic amines are aggressive nucleophiles, especially at elevated temperatures. Most of the chemical degradation that occurs during T & H stress may be reversed with a post T & H bake at an appropriate elevated temperature and for a sufficient time. The reversal of the hydrolysis reaction observed here is in agreement with similar behavior observed by DeIasi.[27]

Summary

The results obtained in this study clearly demonstrate the effectiveness of the ^{15}N CP-DDMAS experiment in providing quantitative information on the curing reactions involved with polyimide precursors. The technique is particularly valuable in the detection of nitrogen functional groups at levels of less than 10% of total nitrogen. The experiment is also a powerful means of obtaining quantitative information on the extent of degradation reactions. The results demonstrate the need for obtaining quantitative estimates of the values of the relaxation parameters of each type of nitrogen so that quantitative measurement of the amount of each nitrogen species in a sample can be obtained. The results show that different polyimide backbone structures are quantitatively different in the amount of hydrolysis they undergo during temperature and humidity stress.

Experimental Section

Reagent Chemicals. Isotopically enriched (99 atom % ^{15}N) 4,4′-oxydianiline (ODA) was obtained from the MSD Division of Merck, Inc. The pyromellitic dianhydride (PMDA) used was the zone-refined material available from Aldrich Chemical Co. The acetylene terminated polyisoimide oligomer was purchased from the National Starch and Chemical Corp. and was prepared using 100% ^{15}N-enriched 1,3-bis(3-aminophenoxy)benzene (APB) obtained from Isotec, Inc., and had a number average degree of polymerization of 15 and number average molecular weight estimated by NMR acetylene end-group analysis to be 10 000. The synthetic details on the polyisoimide material are not available.

Preparation of ^{15}N-Labeled PMDA–ODA Poly(amic acid) (PAA). PMDA and labeled ODA were polymerized in *N*-methyl-2-pyrrolidone (NMP) solvent according to previously described procedures[7] using a diamine to dianhydride ratio of 1.081. The labeled poly(amic acid) was obtained as a 15% solid solution in NMP and had η_{inh} = 0.43 dL/g at a poly(amide acid) concentration of 0.50 g/dL at 25 °C.

Synthesis of ^{15}N-Labeled PMDA–ODA Poly(amic acid) *Meta* Ethyl Ester (PAE). All HPLC analyses were performed on a Hewlet-Packard 1090 liquid chromatograph with a Hewlett-Packard 9000–300 Chem Station at ambient temperature using the conditions described below. The polymer intrinsic viscosity was determined by measuring the relative and specific viscosities of at least four NMP/polymer solutions between the concentrations of 0.5 and 2.0 wt % with a Cannon-Ubbelohde suspended-level viscometer, size 100. Both the specific viscosity vs concentration (Huggins equation) and inherent viscosity vs concentration (Kraemers equation) functions were plotted and extrapolated to zero concentration to give the intrinsic viscosity.

HPLC Analysis of PMDA Derivatives. A Hewlett-Packard 60 × 4.6 mm Hypersil ODS 3 micron P/N 79916OD-344 (C_{18} reversed-phase) column was used. Ultraviolet detection was performed at a wavelength of 230 nm. A binary mobile phase was used consisting of acetonitrile as one phase and a buffer solution prepared from 50 g of 0.15 M phosphate buffer (pH 2.7), 79 g of methanol, and 850 g of water as the second phase. The phosphate buffer was prepared from 0.1 mol of sodium dihydrogen phosphate and 0.05 mol of phosphoric acid, diluted up to 1 L with deionized water. The flow rate was 0.5 mL/min. The solvent program was initially 10% acetonitrile in buffer, changing linearly to 100% acetonitrile over 9 min and then being held at 100% acetonitrile for 8 min, and was then returned 10% acetonitrile over 3 min and held at 10% acetonitrile for a least 5 min before the next run. Samples were injected as 2-μL aliquots of approximately 0.1% w/w sample solutions.

The PMDA diacid diester was prepared for analysis by dissolving a solid sample in 1:1:2 methanol:0.15 M phosphate buffer (pH 2.7):acetonitrile at a concentration of 1 mg/mL. PMDA and the diester diacyl chloride were derivatized for analysis by adding 10 mg of solid sample or 4 drops of ethyl acetate reaction mixture to a screw top vial containing 1.0 g of 10% bis(*n*-propyl)amine in acetonitrile. The vial was shaken and allowed to stand for 2 min. The contents were then diluted with 9 g of 1:1 methanol:0.15 M pH 2.7 phosphate buffer and shaken until clear.

Preparation of 4,6-Dicarbethoxyisophthalic Acid (*Meta* Diester Diacid of PMDA, *M*-DADE). A 250-mL flask equipped with a stirrer, reflux condenser, and heating mantle was charged with 150 mL of dry ethanol. PMDA (52.3 g, 0.24 mol) was then added as a solid. The reaction mixture was stirred under argon for 4 h with gentle heating, during which time the temperature rose to approximately 60 °C and the mixture became homogeneous. When the reaction temperature started to decline, 50 mL of ethyl acetate was added and the mixture was allowed to cool with stirring overnight. The resulting slurry was filtered under vacuum to give crop 1 as a white crystalline solid. The solid was washed once with 15 mL of ethyl acetate and the combined filtrate and wash were slowly evaporated at reduced pressure until turbidity ensued. The suspension was heated to dissolution and then allowed to cool slowly to room temperature with stirring. The resulting white crystalline solid was recovered on a filter (crop 2) and washed once with 15 mL of ethyl acetate, and the combined filtrate and wash were treated as before. The white crystalline precipitate was filtered (crop 3) and washed with 15 mL of 1:1 ethyl acetate:hexane and 15 mL of hexane. The combined filtrate and washings were once again treated as before. The resulting slurry was filtered (crop 4) and washed with 15 mL of hexane. The remaining filtrate was discarded. All crops were dried in a vacuum oven overnight at 50 °C (0.2 Torr). HPLC analysis revealed that crops 1 and 2 were primarily the *para* diacid diester and crops 3 and 4 were primarily the *meta* isomer. The desired composition of the final product is approximately 95% *meta* and 5% *para*, which is obtained by combining the appropriate crops above in the appropriate quantities.

The weights and *meta:para* ratio (normalized to a combined 100%) of a typical set of four crops is summarized as follows:

crop	weight (g)	meta/para ratio
1	25.4	6.4/93.6
2	6.8	3.0/97.0
3	17.5	96.1/3.9
4	22.1	84.1/15.9

Preparation of PMDA *M*-Diacyl Chloride Diester. A 250-mL flask equipped with a stirrer, chilled water reflux condenser, addition funnel, and heating mantle was charged with the diester diacid of PMDA (DADE) (23.3 g, 0.075 mol, 95:5 *meta:para* isomer ratio) obtained from part 1 (above). Ethyl acetate (100 mL) was then added, and the reaction mixture was heated to 55–58 °C. Oxalyl chloride (27.3 g, 18.7 mL, 0.215 mol) was slowly added to the reaction mixture (subsurface) over 3–4 h. There was a significant amount of offgassing throughout the addition which was bubbled through a caustic scrubber.

The reaction temperature was maintained at 55–58 °C for an additional 12 h. When the reaction was judged complete (HPLC, reactive samples), the batch was cooled, a vacuum was applied to the reactor, and the excess oxalyl chloride was removed (along with ethyl acetate) by vacuum distillation (32–55 °C at 26 in. Hg). The batch was distilled to a thick syrup, fresh dry ethyl acetate (100 mL) was added via vacuum transfer, and the resulting solution was again distilled to a thick syrup.

At this point, all of the residual oxalyl chloride had been removed (as determined by the accompanying HPLC method) and the total volume of the batch was adjusted to 70 mL by addition of ethyl acetate. The batch was kept under nitrogen and below 25 °C until it was ready to be used in part 3 of the procedure, preferably within a few hours.

Preparation of ^{15}N-Enriched PMDA–ODA Poly(amic acid *M*-Ethyl Ester) (PAE). A 500-mL flask equipped with a stirrer, addition funnel, and cooling capability was charged with oxydianiline (ODA) (15.4 g, 0.074 mol, 50% ^{15}N-enriched), *N*-methyl-2-pyrrolidinone (NMP) (130 mL, anhydrous, Aldrich Chemical) and pyridine (13.6 mL, 13.2 g, 0.16 mol). The reaction was stirred under argon to dissolve the ODA and cooled to 0–3 °C (ice/acetone bath). To the reaction was slowly charged the ethyl acetate solution containing the *meta* diacid chloride. The rate of addition was such that the temperature of the reaction never exceeded 10 °C. There was a substantial exotherm upon addition. The addition usually took about 2 h in order to maintain a maximum temperature of 10 °C.

When the addition was complete, 10 mL of NMP was used to rinse the remnants of the diacid chloride into the polymerization reactor. The batch was stirred at ambient temperature overnight. The product was precipitated by slowly adding the batch to deionized water (10 volumes), while stirring with high shear agitation (Waring blender). The poly(amic acid ethyl ester) was isolated by vacuum filtration on a Buchner funnel. The polymer was slurried and filtered once from 500 mL of a 10% solution of 2-propanol in deionized water, twice from 500 mL of deionized water, once from 500 mL of neat 2-propanol, and once from 500 mL of ethyl acetate and then dried under vacuum (0.2 Torr) at 50 °C to yield 35.2 g of ^{15}N-enriched PMDA-ODA poly(amic acid *m*-ethyl ester) with a measured intrinsic viscosity of 0.385 dL/g and a molecular weight (light scattering) of 31.5K.

Preparation of Films and NMR Samples. Film casting solutions were prepared from the poly(amic acid ethyl ester) (PAE) and polyisoimide (PSIS) materials by combining the dry polymer and NMP solvent in high density polypropylene bottles and mixing on a bottle rolling mixer. A concentration of 20 wt % resin was used. The poly(amic acid) solution was used directly as synthesized.

Films were cast on $6 \times 6 \times {}^3/_8$ in. borosilicate glass plates using a Gardener casting knife set to a gap of 10 mils. This gap yielded film thicknesses of 1–1.5 mils after cure at 400 °C.

The wet poly(amic acid) (PAA) draw-downs were cured using a step-cure sequence consisting of successive stages at 85, 150, 350, and 400 °C. The cures at 85 and 150 °C were done on hot plates in ambient air and the cures at 350 and 400 °C were done in a three-zone, 4-in. bore, Lindberg tube furnace purged with dry nitrogen flowing at 5 L/min.

The wet poly(amic acid diethyl ester) (PAE) draw-downs were cured at 150 °C/30 min, 230 °C/30 min, 300 °C/30 min, and 400 °C/40 min using a programmable Blue M convection oven. The wet polyisoimide draw-downs were cured at 150 °C C/60 min, 230 °C/60 min, 300 °C/90 min, and 400 °C/2 h in a programmable Blue M convection oven. All cures in the Blue M convection oven were done using a nitrogen ambient maintained at an oven pressure of 0.5 psi.

Temperature and humidity stressing was done in a Blue M temperature/humidity chamber regulated at 85 °C and 81% relative humidity. All post temperature and humidity stress bakes were done in the Blue M oven using an ambient to 400 °C ramp at 2 °C/min.

The cured films were recovered by mechanical peeling for films cured at 85 and 150 °C or by immersion in hot (95 °C) deionized water for films cured at 350 and 400 °C. The films recovered in hot water were dried at 110 °C for 24–36 h. The film samples were prepared for NMR analysis by grinding them to fine powders in a SPEX 6700 Freezer Mill cooled with liquid nitrogen. The grinding step is necessary to produce balanced rotors that spin properly.

Solid State NMR Measurements. NMR measurements were recorded with an IBM Instruments solids accessory and a Bruker NR-300AF spectrometer with a 7-T Oxford superconducting magnet. A Doty 7-mm CP/MAS NMR probe was used for sample excitation and rotation. NMR spectra were recorded at 30.4 MHz for the ^{15}N resonance. Proton decoupling was at 300.13 MHz. For solid state studies, the CP contact time was 2 ms and the relaxation delay was 3. For the PSIS powder spectrum, a contact time of 10 ms was used. Matched Hartmann–Hahn fields were 20–40 kHz and MAS rotor speeds were from 4.5 to 5 kHz. At the spinning speeds used, spinning sidebands were small and mainly from the imide resonance at 150 ppm and the amide acid resonance at 105 ppm. The isoimide resonance had exceptionally large sidebands which are indicative of large chemical shift anisotropy. The chemical shifts are reported with respect to the ammonium cation of an external reference of solid ammonium sulfate (MSD Isotopes). Other spectral parameters were as follows: spectral width SW = 25000 Hz, FT size SI = 4096, delay DE = 5.0, digital resolution DR = 12, and line broadening LB = 30 Hz.

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