Monitoring Nylon-6,6 Thermochemistry by Solid-State NMR

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ABSTRACT: Solid-state ^{13}C and ^{15}N NMR spectroscopy was used to study the structure and thermochemistry of nylon-6,6. Experiments were performed on samples of nylon-6,6 heated in the presence of labeled adipic acid and hexamethylenediamine (HMD) monomers as well as labeled bis(hexamethylenetriamine) (BHMT), a molecule previously implicated as a potential nylon cross-linker. The uptake and subsequent reaction of labeled materials were characterized by a variety of solid-state NMR techniques. Reaction of the central (α) nitrogen of BHMT to form an amide occurs very rapidly. With time, transamidation causes this position to become indistinguishable from the bulk amide nitrogen in nylon. Rotational-echo double resonance (REDOR), a solid-state NMR experiment that permits the quantitative measurement of ^{13}C−^{15}N labeled chemical bonds, was used to detect the formation and breaking of carbon−nitrogen bonds due to polymerization and transamidation. The reaction of adipic acid and hexamethylenediamine (HMD) and the transamidation reaction between the resulting oligomers and bulk nylon were studied by heating nylon-6,6 in the presence of [^{13}C]adipic acid and [^{15}N]HMD and characterizing the resulting polymers with REDOR. The combination of stable isotope labeling and NMR spectroscopy illustrated in this work should be applicable to the study of a wide variety of polymers.

Introduction

The thermochemistry of nylon-6,6 has been studied by numerous investigators, with the earliest studies dating back nearly 50 years.[1−3] An important finding common to many of these studies is the identification of degradation products that act as cross-linkers and promote gelation. Of the potential cross-linkages identified to date, most experimental evidence points to two species; amine-containing cyclopentanone (derived from cyclization of adipic acid) and bis(hexamethylenetriamine) (BHMT), as key cross-linkers.[4−6]

Cross-linking chemistries associated with amine-containing cyclopentanones and BHMT have been investigated with a variety of analytical methodologies,[7−10] but many mechanistic questions remain regarding the incorporation and distribution of cross-linkers formed during thermal degradation and the formation of other species via transamidation. New insight into both of these topics is provided in the present study via solid-state NMR characterization of nylon-6,6 thermally degraded in the presence of stable isotope-labeled reagents.

Solid-state NMR spectroscopy[11−13] is a powerful and versatile analytical technique for studying the structure and dynamics of polymers.[14−16] Solid-state NMR provides compositional information in polymers whose molecular weight and/or degree of cross-linking preclude analysis in solution. In the present study, solid-state NMR has the important advantage of being able to characterize thermally treated nylon reacted with cross-linker to beyond the polymer's gel point. Corresponding solution-state studies of thermal reaction products are limited to investigations of pregel, soluble nylon-6,6.

The bulk of the NMR work on polymers described in the literature has been performed at natural abundance. Natural-abundance studies of ^{13}C (1.1% natural abundance) and, to a lesser extent, ^{15}N (0.33% natural abundance) have yielded a wealth of information. These studies have the tremendous advantage that they can be performed on actual engineering polymers and do not require special sample preparation. At the same time, the requirement of natural abundance imposes limitations on the systems that can be studied and the types of information that can be derived from these studies.

^{13}C and/or ^{15}N isotopic enrichment, together with NMR detection, provides a particularly powerful combination for studying macromolecular systems. Stable isotope labels can provide both sensitivity and selectivity in these systems. In some cases, the signal(s) of interest may be weak and unobservable at natural abundance. In such situations, the boost in signal intensity provided by the stable isotope label can make the difference between success and failure. Isotopic enrichment can also provide the *selectivity* needed to study polymer systems by NMR. In many cases, especially in carbon-13 studies, there is sufficient *total* NMR signal. Due to the presence of many different natural-abundance signals, however, it may be impossible to distinguish the signals of interest in such samples. Selective isotopic enrichment can boost the signal of interest sufficiently so it can be distinguished from background natural-abundance signals.

Isotopic enrichment has been used to study a wide variety of polymer systems. Numerous solid-state NMR studies of nylon-6,6 polymers have been reported,[17,18] including several employing ^{2}H, ^{13}C, and ^{15}N stable-isotope labeling.[19−22] In this manuscript, we describe two different studies of nylon-6,6 that combine stable isotope enrichment and solid-state NMR detection. In the first study, we describe solid-state ^{15}N NMR characterization of nylon-6,6 heated in the presence of [^{15}N]-BHMT, a molecule previously implicated in the formation of nylon gel.[4−6] These studies, designed to monitor the incorporation and subsequent reaction of BHMT in nylon-6,6, provide insights into the chemistry and reactivity of this triamine. In the second study, ^{13}C,^{15}N-REDOR NMR, a technique that can accurately count ^{13}C−^{15}N chemical bonds, is used to characterize samples of nylon-6,6 heated in the presence of both ^{13}C-enriched adipic acid and ^{15}N-enriched hexamethylenediamine.

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These studies provide insight into the formation of amide bonds between the adipic acid and HMD monomers as well as transamidation reactions between the resulting isotopically enriched nylon oligomers and bulk nylon.

Experimental Section

CPMAS NMR. Cross-polarization magic-angle spinning (CPMAS) ^{15}N NMR spectra were collected on a Monsanto-built instrument operating at a proton resonance frequency of 127.0 MHz. Samples were spun at the magic angle (54.7°) with respect to the static magnetic field at a rate of 3 kHz. CPMAS ^{15}N NMR spectra were obtained at 12.8 MHz following 2-ms matched, 37-kHz ^{1}H$-^{15}$N contacts. High-power proton dipolar decoupling ($H_1(H) = 65$ kHz) was used during data acquisition. In ^{15}N-delayed decoupling experiments,[23] a 100-μs delay was inserted after the cross-polarization period before applying the high-power dipolar decoupling field. Only signals from non-protonated nitrogens survive this 100-μs delay.

REDOR NMR. Rotational-echo double-resonance (REDOR) is a solid-state NMR technique sensitive to the through-space dipolar interaction between heteronuclear spin pairs (e.g., ^{13}C, ^{15}N).[24] The experiment has been used extensively to measure accurately the dipolar coupling, D_{CN}, between selectively ^{13}C- and ^{15}N-enriched sites.[25,26] From this dipolar coupling, the internuclear distance between the carbon and nitrogen spins can be easily calculated. By proper choice of experimental parameters, the REDOR experiment can be made sensitive to very short carbon$-$nitrogen distances (e.g., <2 Å) *only*, thus providing a convenient method for *quantitatively* measuring the formation and breaking of carbon$-$nitrogen chemical bonds. Data from these REDOR experiment are reported as the values $\Delta S/S$, representing the fraction of ^{13}C nuclei that are in chemical bonds with ^{15}N spins.

^{13}C-observe REDOR NMR experiments were performed following 2-ms matched, 50-kHz ^{1}H$-^{13}$C contacts. As with all ^{15}N NMR experiments, samples were spun at the magic-angle at a rate of 3 kHz. The ^{13}C$-^{15}$N dipolar decoupling was reintroduced during an 8 rotor-cycle evolution period (2.7 ms). The proton-decoupling field was 110 kHz during this evolution period and 80 kHz during data acquisition.

Preparation of Nylon Samples with Labeled Additives. A procedure referred to as the *wet method* was used to prepare all samples of unmodified nylon-6,6 polymer mixed with isotopically enriched BHMT, HMD, and/or adipic acid. This method depends on the fact that all of the labeled materials are fully soluble in water. In the *wet method*, the labeled materials were dissolved in water and the resulting solution was slurried with nylon. The slurry was then placed on a rotovac and the water removed under vacuum and heat (70 ± 10 °C). The final mass was broken up and dry-mixed to ensure uniformity and then dried overnight, normally in a desiccator over Drierite under 0.5 mmHg vacuum.

[α-^{15}N]BHMT (99 at. % ^{15}N) was purchased from Isotec (Miamisburg, OH) and was used as received. To prepare samples of nylon mixed with [^{15}N]BHMT, we dissolved 50.3 mg of labeled BHMT in 1.5 mL of water and transferred this solution to a flask with 2.30 g of cryoground nylon-6,6. The vial that contained the BHMT solution was rinsed with another 3 mL of water, which was also added to the ground nylon. The *wet method* was then used to prepare the final material for heating.

Samples of nylon-6,6 mixed with 20 mol % each adipic acid and hexamethylenediamine were prepared as follows. [^{13}C]-Adipic acid (0.4076 g) and 0.3253 g of [^{15}N]HMD were dissolved in 10 mL of deionized water. This solution, plus 2 mL of water as a wash, was added to 3.114 g of nylon-6,6 followed by application of the *wet method*. The resulting nylon particles were actually coated with adipic$-$HMD salt, since the labeled adipic acid and HMD were dissolved together in solution prior to being slurried with the nylon.

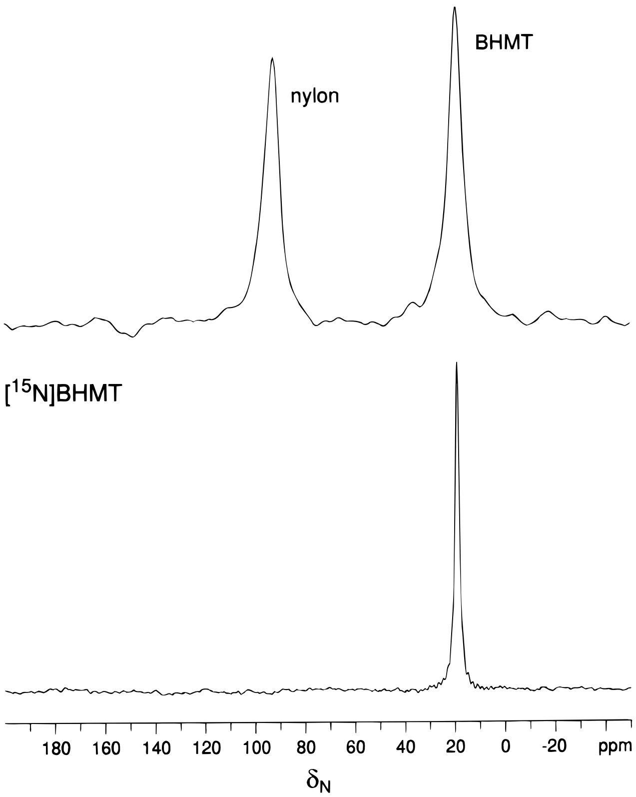

Figure 1. Cross-polarization magic-angle spinning (CPMAS) ^{15}N NMR spectra: (bottom) [^{15}N]BHMT; (top) [^{15}N]BHMT mixed with nylon-6,6.

Static Reactor Design and Use. All of the heated samples were prepared by heating the samples in a static reactor. The reactor itself was a 2-L, round-bottom flask equipped with seven 24/40 female joints mounted vertically on the top. One joint was in the middle of the flask and the other six were in a ring on the outside of its upper surface. The middle joint was connected to a nitrogen bubbler to keep the 280 °C oil under a nitrogen blanket and to provide pressure relief. The flask was filled with Therminol 66 heat-transfer fluid (Solutia, Inc.), which was warmed by a heating mantle connected to a temperature controller. The upper part of the outside of the flask was wrapped with glass wool for thermal insulation. A magnetic stirrer placed under the heating mantle was used to stir the oil.

Materials to be heated were sealed under vacuum ($(1-2) \times 10^{-2}$ mmHg) in $^{1}/_{4}$ in. o.d. × 11 in., medium-wall glass tubes using a propane torch. The contents of the tubes were cooled with dry ice during the sealing process. The bottom 4.5 in. of each glass tube, which contained the nylon mixture, was sealed off, but not separated from, the top (6.5 in.) portion of the tube. The upper end of the tube was then placed in a glass adapter composed of a 24/40 male joint on the bottom and an Ace Glass O-ring thread on the top. When the male end of this adapter was placed in the female 24/40 joint of the static reactor, the bottom of the glass tube, containing the material to be heated, was suspended in the oil bath. The height of the glass tube was adjusted so all of the space below the seal was immersed in the oil, thereby preventing steam and/or organics from condensing at a cool surface.

Sample Preparation for Analysis. Glass tubes, whose contents had been heated for the desired time, were removed from the oil bath and cooled to room temperature in a vertical position. Tubes were scored with a file just above the top of the solid nylon sample and broken so the samples could be removed. Samples were then cryoground under liquid nitrogen conditions in a commercial device designed for that purpose.

Results and Discussion

CPMAS ^{15}N NMR: [^{15}N]BHMT. Figure 1 (bottom) shows the CPMAS ^{15}N NMR spectrum of [^{15}N]BHMT,

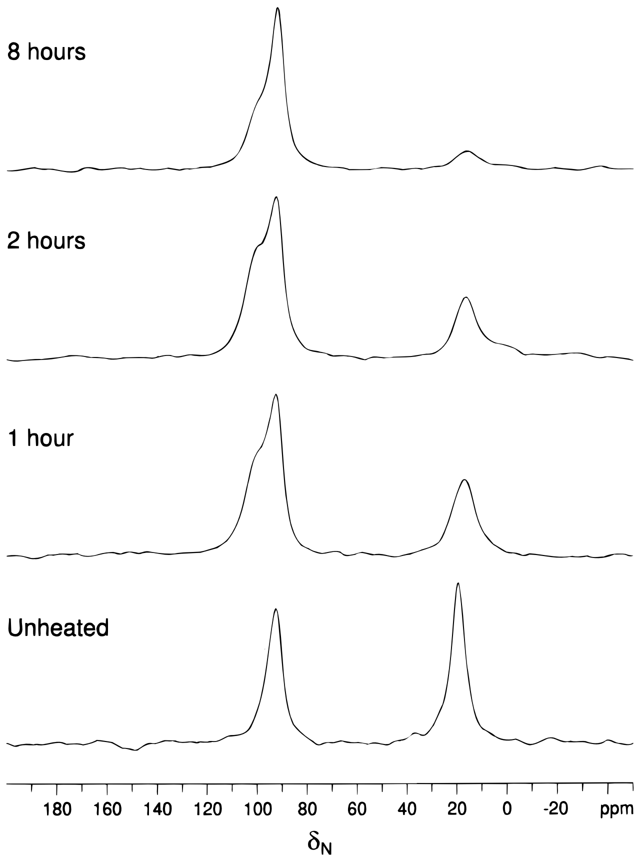

Figure 2. CPMAS ^{15}N NMR spectra of [^{15}N]BHMT mixed with nylon-6,6 following heating at 280 °C for up to 8 h.

while the spectrum of this enriched BHMT mixed with nylon-6,6 is shown in Figure 1 (top). As expected, the spectrum of [^{15}N]BHMT consists of a single sharp line at a chemical shift ($\delta_N = 20$ ppm) characteristic of amine nitrogen. The ^{15}N NMR spectrum of the nylon-6,6/[^{15}N]-BHMT sample shows two resonances, corresponding to amine nitrogen ($\delta_N = 20$ ppm; labeled BHMT) and amide nitrogen ($\delta_N = 90$ ppm; natural-abundance nylon backbone), respectively. The broad lines in the nylon-6,6 spectrum reflect the relatively disordered, heterogeneous nature of this sample compared with crystalline BHMT.

Solid-state ^{15}N NMR spectra of samples of nylon-6,6/[^{15}N]BHMT heated for times ranging from 0 to 141 h are shown in Figures 2 and 3. Upon heating, the amine resonance from [^{15}N]BHMT is rapidly converted to an amide signal and after 24 h of heating, the BHMT amine signal has nearly completely disappeared. Concomitant with the disappearance of the amine signal is the appearance of a second amide nitrogen signal ($\delta_N = 100$ ppm).

Further insights into this 100 ppm signal are provided by performing a *delayed-decoupling* experiment, the data of which are displayed in Figure 4. In this experiment, the proton decoupling was turned *off* during the first 100 μs of data acquisition. As a result, signals from protonated nitrogens rapidly dephase and disappear from the delayed-decoupling spectrum, while signals from nonprotonated nitrogens remain. Figure 4 (bottom) is the conventional CPMAS ^{15}N NMR spectrum of a nylon-6,6/[^{15}N]BHMT sample after 8 h of heating, while the delayed-decoupling spectrum is shown in Figure 4 (top). These spectra clearly demonstrate that the amide signal at 100 ppm, which appears as the amine signal disappears, is due to nonprotonated amide nitrogens. As expected, signals due to [^{15}N]BHMT amine nitrogens and amide nitrogens in the nylon backbone disappear from the delayed-decoupling spectrum, since both of these species are protonated. We interpret these results to indicate [^{15}N]BHMT is rapidly

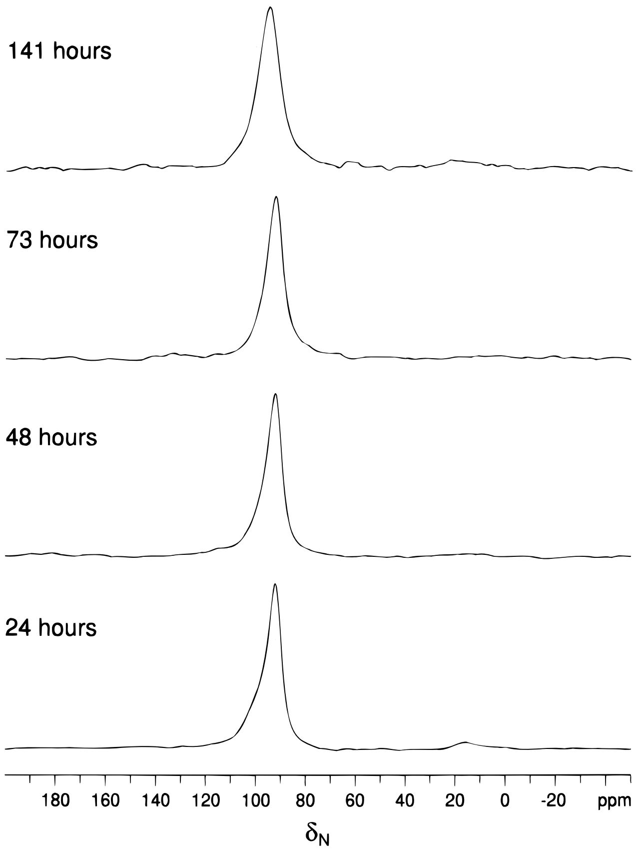

Figure 3. CPMAS ^{15}N NMR spectra of [^{15}N]BHMT mixed with nylon-6,6 following heating at 280 °C for 24 (bottom) to 141 (top) hours.

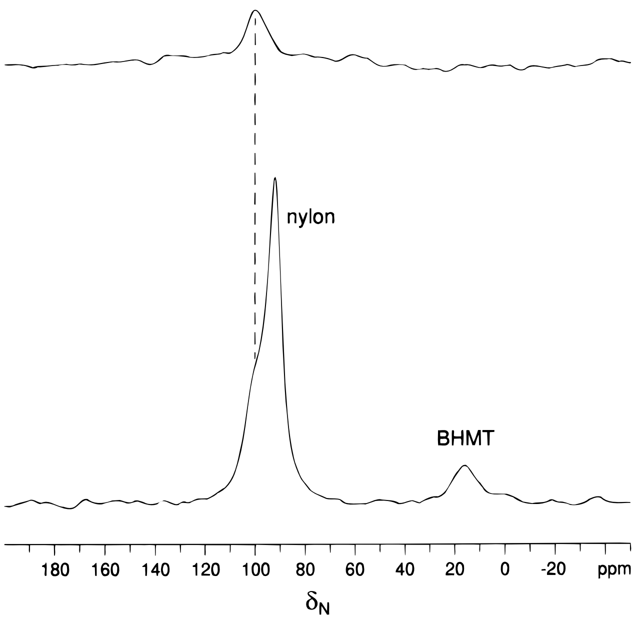

Figure 4. Solid-state ^{15}N NMR spectra of [^{15}N]BHMT mixed with nylon-6,6 following heating at 280 °C for 8 h: (bottom) CPMAS; (top) delayed decoupling, in which the proton decoupler is turned off during the first 100 μs of data acquisition. Only signal from nonprotonated nitrogens is observed in the delayed decoupling spectrum.

incorporated into nylon-6,6 through the formation of amide bonds to BHMT's central nitrogen.

Upon further heating, an interesting effect is observed. With time, the amide-nitrogen signal near 100 ppm disappears and the solid-state ^{15}N NMR spectra of samples heated for long times consist of a single resonance at 90 ppm, the chemical shift observed for main-chain amide nitrogens in nylon-6,6 itself. In other words, with increased heating, the labeled amide nitrogens become indistinguishable from the bulk amides in the nylon backbone. Delayed-decoupling experiments (data not shown) confirm that for long heating times, all of the observed amide nitrogens are protonated. This change in character of the labeled amide nitrogens reflects transamidation, scrambling, and/or cracking reactions, which result in the labeled BHMT nitrogen being incorporated into the nylon main chains as protonated amides. We know of no other way to accurately monitor the transamidation process that occurs as the BHMT reacts.

REDOR NMR: [$^{13}C_2$]Adipic Acid and [$^{15}N_2$]Hexamethylenediamine. The results obtained using [^{15}N]-BHMT clearly demonstrate the power of combining stable isotope enrichment and solid-state NMR detection for monitoring *in situ* chemistry in intact polymers. The change in nitrogen chemical shift and subsequent loss of an attached proton allow the incorporation and reaction of BHMT in nylon-6,6 to be inferred. We now describe a series of experiments that allow the direct visualization of ^{13}C−^{15}N chemical bonds in nylon-6,6 polymers. As described earlier, ^{13}C,^{15}N-REDOR NMR provides a means for quantitatively monitoring the formation and/or breaking of carbon−nitrogen chemical bonds. To demonstrate the power of the technique, we describe the results of a preliminary REDOR NMR study of nylon heated in the presence of [$^{13}C_2$]adipic acid and [$^{15}N_2$]hexamethylenediamine (HMD), which demonstrate these methods are well suited for studying amide-bond formation and transamidation reactions in labeled nylon.

In performing these experiments, it was important to work with well-characterized materials. Unfortunately, our attempts to produce nylon on a small (i.e., 500 mg) scale yielded polymers of widely varying molecular weight that were often discolored. Instead, we prepared model, labeled polymers by coating samples of nylon-6,6 with a mixture of [$^{13}C_2$]adipic acid and [$^{15}N_2$]-hexamethylenediamine (20 mol %, each), heated these for variable lengths of time at 280 °C, and monitored first the formation and then the subsequent breaking of ^{13}C−^{15}N chemical bonds with REDOR NMR.

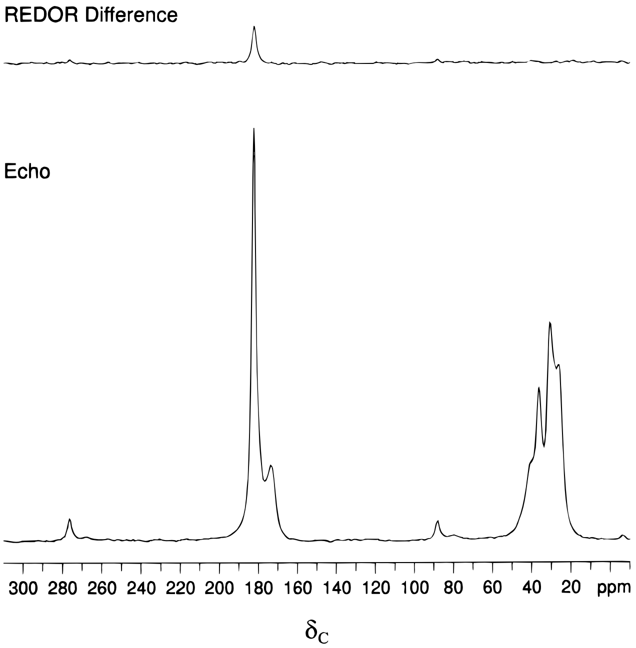

Figure 5. Rotational-echo double-resonance (REDOR) ^{13}C NMR of nylon-6,6 plus [$^{15}N_2$]HMD and [$^{13}C_2$]adipic acid, 20 mol % each, prior to heating.

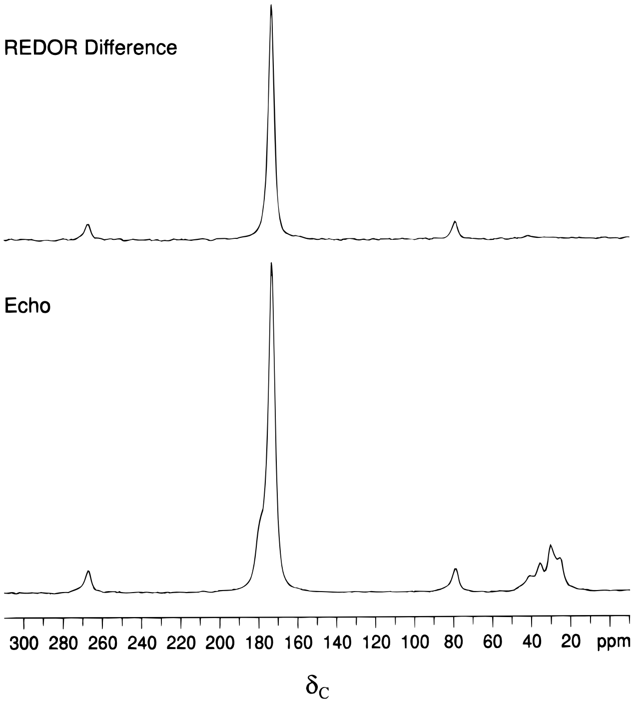

Figure 6. REDOR ^{13}C NMR of nylon-6,6 plus [$^{15}N_2$]HMD and [$^{13}C_2$]adipic acid, 20 mol % each, heated to 280 °C for 1.5 min.

Figure 5 shows ^{13}C,^{15}N-REDOR NMR data for a sample of nylon-6,6 coated with 20% [$^{13}C_2$]adipic and [$^{15}N_2$]HMD prior to heating. The small carbonyl signal at 170 ppm in Figure 5 (bottom) is due to natural-abundance carbon in the nylon backbone, while the large signal near 180 ppm is due to labeled adipic acid. The integrated intensity of the adipic acid carbonyl signal is ∼3.5× that of the nylon carbonyl signal, significantly less than the factor of 17× expected on the basis of the molecular composition of this sample. Because the spin−lattice relaxation time (T_1) of adipic acid is longer than that of nylon, the data in Figure 5 were collected with a longer recycle delay (10 s between scans) than were the subsequent data on heated nylon samples (1 s between scans). Nonetheless, the significant under-representation of the adipic acid signal in Figure 5 (bottom) indicates that, even after 10 s, the adipic acid was not fully relaxed. The small REDOR difference signal associated with the isotopically enriched adipic acid (Figure 5, top) arises from ^{15}N sites in [^{15}N]HMD, which are physically near, but not actually bonded to, the adipic acid, and is consistent with the presence of adipic−HMD salt in this sample.

Figure 6 shows ^{13}C,^{15}N-REDOR NMR data for a nylon-6,6/[^{13}C]adipic acid/[^{15}N]HMD sample following heating at 280 °C for 1.5 min. The majority of the labeled [^{13}C]adipic acid signal has moved upfield and appears at the same chemical shift as the backbone

Table 1. Nylon-6,6 + 20 mol % Each [1,6-$^{13}C_2$]Adipic Acid and [$^{15}N_2$]HMD

heating duration @ 280 °C	$\Delta S/S^a$
6 min	0.64
15 min	0.60
2 h	0.38
12 h	0.25
40 h	0.25
56 h	0.26
72 h	0.23
120 h	0.23

[a] Fraction of carbonyl carbons (nylon + nylon-like oligomers) that are chemically bonded to ^{15}N spins.

carbonyls in nylon. The REDOR difference signal associated with the resonance at this chemical shift has increased markedly. We interpret these data to indicate that amide bonds form very rapidly between [^{13}C]adipic acid and [^{15}N]HMD, yielding nylon oligomers containing highly isotopically enriched amide bonds. Residual [^{13}C]-adipic acid can be seen in Figure 6 (bottom) as a small, downfield shoulder on the main carbonyl carbon peak. Because these data were collected with a 1 s recycle delay, the residual adipic acid may be under-represented in this spectrum, as in Figure 5.

The results of a REDOR study on a series of heated nylon samples are presented in Table 1. After 6 min of heating, nearly two-thirds of the carbonyl carbons are bonded to ^{15}N spins, reflecting the formation of amide bonds between [^{13}C]adipic acid and [^{15}N]HMD. With increasing time, the REDOR difference signal is reduced, as transamidation between ^{13}C−^{15}N-labeled oligomers and bulk nylon-6,6 dilutes the fraction of ^{13}C−^{15}N labeled amide bonds. We do not attempt a more detailed interpretation of these data at this time but simply point out the REDOR method provides a powerful way to monitor *in situ* chemistry in polymers. A number of NMR experiments have been recently described for detecting and measuring ^{13}C−^{13}C dipolar couplings.[27−32] By employing these techniques, we can extend the types of experiments shown here to study the formation and breaking of carbon−carbon bonds in intact polymer systems.

In summary, the combination of stable-isotope labeling and solid-state ^{13}C and ^{15}N NMR spectroscopy has permitted the study of cross-linker incorporation into nylon-6,6 and the characterization of amide-bond formation and transamidation reactions at a level of detail not reported previously for nylon polymers. The ability to profile these reactions, in depth, demonstrates the general applicability of this methodology for characterizing reactions between polymers and low molecular weight compounds occurring in polymer melts.

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