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Solid-State NMR Investigation of Nylon 12

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ABSTRACT: Nylon 12 (polylauramide) was synthesized with >99% ^{15}N labeling at the amide nitrogen using ^{15}N-labeled potassium phthalimide in the Gabriel method. CP/MAS NMR was used to evaluate the crystal forms present in the samples which were either quenched from the melt in liquid nitrogen, annealed, or precipitated from a mixture of phenol and absolute ethanol (84:16 by weight). Commercially available nylon 12 was treated similarly to the synthesized polymer. Differences were observed in both the ^{15}N and the ^{13}C CP/MAS NMR spectra between the annealed, quenched, and precipitated samples consistent with the presence of γ, γ', and $\alpha + \gamma$ crystal forms. The ^{15}N spin–lattice relaxation times (T_{1N}) for the labeled samples were shown to increase in the following order consistent with decreasing mobility: $\gamma' < \gamma \leq \alpha$. The respective T_g's and T_m's for the γ (ca. 50 and 184 °C), γ' (ca. 45 and 177 °C), and α (ca. 40 and 169 °C) forms (measured by DSC) were consistent with literature values. Precipitated samples showed two melting endotherms for two crystal forms whose presence was confirmed by two peaks in the solid-state ^{15}N NMR spectrum at chemical shifts consistent with α and γ crystal forms. Comparison with two amide model compounds was also made with respect to ^{13}C chemical shifts for carbons α to the carbonyl (C_α) and the nitrogen (C_N).

Introduction

Nylon 12 has recently become important in replacing metals in applications such as automotive fuel lines. Its use is based on greater resistance to commercial fuel formulations than most commercial thermoplastics and other AB and AA–BB nylons.[1] Nylon 12 is thermoplastic, has excellent impact resistance, and possesses a lower moisture absorbance (about 1–2% when saturated with water) than many of the other commercially available nylons.[1] The increased use of plastics and engineering polymers in demanding applications suggests that a better understanding of their properties on both a microscopic and macroscopic level would be useful in evaluating ultimate performance.

As with most aliphatic polyamides, nylon 12 has been thoroughly characterized by X-ray, infrared, and differential scanning calorimetry.[2-10] The main crystal form obtained from the melt at atmospheric pressure is the γ-form, which has the amide plane twisted out of the polymethylene plane by ca. 60°.[11] The α-form can be obtained by precipitation from phenol–ethanol solution[6] or by slow crystallization from the melt at 500 MPa.[4] Both nylon 12 crystal forms have well-defined X-ray patterns, infrared absorptions, and thermogram traces. The amorphous region remains less well characterized, especially if the more ordered interphase is differentiated from the bulk amorphous domains.

Melt-quenched nylon 12 has been referred to as γ' to distinguish it from annealed, fully developed γ-form crystals,[4] although both have similar X-ray diffraction patterns. The γ'-form can be slowly annealed into the γ-form above 110 °C, while the α-form does not undergo this transformation. Both γ and γ' can be transformed into the α polymorph by precipitation from phenol–ethanol (84:16 by weight). However, the γ' can be converted to the α-form on treatment under high pressure and the γ cannot. It has also been shown that α and γ modifications can be used to prepare γ' by drawing above 70 °C and above 50 °C, respectively. The γ'-form may consist of small or poorly defined γ crystallites.

Recently, solid-state ^{13}C and ^{15}N NMR have been used by several groups to characterize bulk or film samples of nylons and aramids with and without ^{13}C or ^{15}N labels.[12-19] It has been shown with ^{15}N CP/MAS NMR that the predominant crystal forms (α and γ) for several nylons display clearly separate, sharp peaks with chemical shifts at ca. 84 and 89 ppm, respectively, relative to glycine at 0 ppm.[13,14,16,17] A broad amorphous resonance has been assigned at 86–87 ppm, which consists of at least two populations based on relaxation times.[14,16] ^{15}N chemical shift anisotropy (CSA) spectra have also facilitated characterization of ordered versus amorphous domains and allowed qualitative evaluation of motion and relaxation in both regions.[14,15] Characteristic differences in the ^{13}C CP/MAS NMR spectra of the α- and γ-forms of nylon 6, as well the amorphous (noncrystalline) material, have also been reported, with results similar to those obtained with ^{15}N CP/MAS NMR but complicated by multiple overlapping peaks.[18,19]

We report here our results on another member of the A–B family of nylons, polylauramide, including its synthesis with ^{15}N-labeling based on the Gabriel method, and the ^{15}N and ^{13}C solid-state NMR characterization of the resulting polymer in comparison with commercially available nylon 12. We also include the synthesis and solid-state NMR characterization of two amide compounds, *N*-(*n*-decyl)lauramide and *N*-(*n*-propyl)stearamide, as models for ^{13}C solid-state chemical shift assignments.

Experimental Section

Reagents and solvents were obtained from Aldrich Chemical Co. and used without further purification unless otherwise noted. FT-IR spectra were taken using a Perkin-Elmer 1600 FT-IR with KBr pellets, melt-pressed or solution-cast thin films, or neat samples cast on salt plates. Melting points were measured on an Electrotherm melting point apparatus and are uncorrected. DSC scans were taken on a Perkin-Elmer DSC 7 equipped with an IBM microcomputer. Solution ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker AC-300 at 300.17 and 75.468 MHz, respectively. Solid-state ^{13}C and ^{15}N spectra were recorded on a Bruker MSL-200 operating at 50.32 and 20.287 MHz, respectively. Shifts in the solid-state spectra for ^{13}C were referenced to adamantane (29.5 ppm) and for ^{15}N to glycine (0 ppm). Samples were placed in fused zirconia rotors fitted with Kel-F or ceramic caps and spun with dry air at 4–5 and 2–3 kHz for ^{13}C and ^{15}N, respectively. ^{13}C spectra were collected using a 3.75-μs ^{1}H 90° pulse, while ^{15}N spectra were collected using a 5.5-μs ^{1}H 90° pulse. A 10-ms contact time, 50-ms acquisition time, and 3-s recycle delay were used. Ringdown delays of 40 and 30 μs were used for ^{13}C and ^{15}N, respectively. ^{15}N spin–

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lattice relaxation times, $T_{1\mathrm{N}}$, were obtained using the method developed by Torchia.[20] ^{15}N spin–lattice relaxation times in the rotating frame, $T_{\mathrm{N}\rho}$, measurements were made with a radiofrequency (RF) field of 45–46 kHz. ^{15}N CSA spectra were collected using the parameters described above but with no spinning. The amorphous and crystalline peaks in the solid-state ^{15}N spectra were deconvoluted using LINESIM, a Bruker-supplied Pascal program for simulating NMR line shapes in solids as combinations of Gaussian line shapes. While peaks can be qualitatively identified with this method, quantitation requires using very long recycle times and high-power decoupling only (no cross-polarization). CSA spectra were deconvoluted using POWDER, another Bruker-supplied Pascal program. An Aspect 3000 computer was used to run both line-shape simulation programs.

Data was processed off-line using Spectra Calc[21] and SC NMR, an Array Basic program written in-house specifically for analyzing Bruker NMR data on microcomputers.

Ethyl 12-Bromododecanoate (1). 12-Bromododecanoic acid (4.19 g, 0.015 mol) and 25 mL of thionyl chloride were charged to a 50-mL round-bottomed flask. The flask was fitted with a reflux condenser and a drying tube, and the solution was heated under gentle reflux conditions for approximately 3 h. Excess thionyl chloride was removed under reduced pressure, and the resulting pale yellow oil was carefully poured into 100 mL of absolute ethanol. After the solution was stirred under ambient conditions overnight, the solvent was removed under reduced pressure. The resulting oil was taken up in diethyl ether, extracted with 3% (w/v) sodium carbonate, washed with water and saturated brine, and dried over anhydrous magnesium sulfate. Subsequent removal of the drying agent and the solvent gave a pale yellow oil, which was distilled under reduced pressure to give **1** as a colorless oil: bp 120–123 °C at 3–4 mmHg (3.86 g, 84% yield).

^{13}C NMR ($\mathrm{CDCl_3}$): δ 14.0 ($-C\mathrm{H_3}$); 24.9 ($-\mathrm{COCH_2}C\mathrm{H_2}-$); 27.9 ($\mathrm{BrCH_2CH_2}C\mathrm{H_2}-$); 29.5–29.9 ($-C\mathrm{H_2}-$); 30.1 ($-\mathrm{COCH_2CH_2}C\mathrm{H_2}-$); 32.6 ($\mathrm{BrCH_2}C\mathrm{H_2}-$); 33.4 ($-\mathrm{CO}C\mathrm{H_2}-$); 34.0 ($\mathrm{Br}C\mathrm{H_2}-$); 59.7 ($-\mathrm{O}C\mathrm{H_2}-$); 173.2 ($-C\mathrm{O}-$).

Ethyl 12-(Phthalimido)dodecanoate (2). ^{15}N-Labeled potassium phthalimide (1.86 g, 0.01 mol), **1** (3.06 g, 0.01 mol), and 30 mL of dry dimethylformamide (DMF) were charged to a dry 50-mL round-bottomed flask. A drying tube was connected to the flask, which was placed in a preheated oil bath at 100 °C for 12 h. After cooling to ambient temperature, the DMF mixture was poured into 200 mL of deionized water and extracted with diethyl ether. The ether solution was washed with water, dried over anhydrous magnesium sulfate, filtered to remove the drying agent, and concentrated to a pale yellow solid under reduced pressure. The resulting soft solid was recrystallized from methanol to give **2**: mp 46–48 °C (2.83 g, 76% yield).

^{13}C NMR ($\mathrm{CDCl_3}$): δ 13.8 ($-C\mathrm{H_3}$); 24.5 ($-\mathrm{COCH_2CH_2}-$); 26.4 ($>\mathrm{NCH_2}C\mathrm{H_2}-$); 28.1–29.0 ($-C\mathrm{H_2}-$); 33.8 ($-\mathrm{CO}C\mathrm{H_2}-$); 37.5 ($>\mathrm{N}C\mathrm{H_2}-$); 59.6 ($-\mathrm{O}C\mathrm{H_2}-$); 122.6 (ortho to the nearest imide CO); 131.7 (ipso to imide CO); 133.3 (meta to the nearest imide CO); 167.7 (imide CO); 173.1 (ester CO).

FT-IR (KBr): 3010 (ArH); 2913 and 2841 (aliphatic CH); 1769 and 1738 (imide CO); 1703 (ester CO); 1164 ($-\mathrm{OCH_2}-$); 718 and 713 cm^{-1} (ortho-disubstituted benzene).

12-Aminododecanoic Acid (3). Anhydrous hydrazine (0.54 g, 0.016 mol), **2** (3.00 g, 0.008 mol), and 25 mL of anhydrous methanol were charged to a 50-mL round-bottomed flask. The flask was fitted with a reflux condenser and heated under reflux conditions for 5 h. The methanol was removed under reduced pressure. The flask was charged with 25 mL of 6 N HCl and heated under reflux conditions for 3 h. The reaction mixture was suction-filtered hot, and the water and HCl were removed under reduced pressure. The resulting solid was taken up in deionized water and brought to neutrality with 3% (w/v) sodium carbonate. The precipitate was filtered and recrystallized from water (2 times) to give the free amino acid **3**; mp 185–186 °C (1.08 g, 62% yield).

^{13}C NMR (solid state): δ 30.3 and 33.5 ($-C\mathrm{H_2}-$); 40.0 ($-C\mathrm{H_2}$-$\mathrm{CO}-$); 42.4 ($-C\mathrm{H_2NH_2}$); 181.7 ($-C\mathrm{O}-$).

^{15}N NMR (solid state): δ 2.2 ($-\mathrm{CH_2}N\mathrm{H_2}$).

FT-IR (KBr): 3178 (NH); 2911 and 2844 (aliphatic CH); 1644 (CO); 1505 (NH wagging); 1389 ($\mathrm{CH_2}$ scissoring); 650 cm^{-1} (NH out-of-plane bending).

Polylauramide (4). A thick-walled test tube was charged with **3** (0.35 g, 1.6 mmol). After six vacuum–nitrogen purge cycles, the solid was heated to 210 °C for 5 h in an oil bath under constant nitrogen purge. Upon cooling to ambient temperature, the glass tube was wrapped in a cloth and carefully broken with a hammer. The near-colorless plug of polymer **4** was recovered quantitatively (0.32 g, 100% yield). Molecular weights and viscosities were not obtained since it was clear from the film-forming ability of all nylon polymers synthesized that adequate molecular weights for NMR studies were obtained. In fact, physical properties comparable to those of commercial nylons were displayed. Lack of observation of ^{15}N-labeled end groups (easily seen with >99% isotopic enrichment for concentrations of ca. 2–3%) confirm degrees of polymerization of ca. 20 000.

Polymer samples were melt-pressed at 250 °C (20 kpsi) between sheets of aluminum foil coated with a fluorinated mold release agent and either quenched with liquid nitrogen or annealed a few degrees below the melting point in the press. A separate sample was precipitated from a mixture of phenol and ethanol (84:16 by weight), washed with water, and dried under high vacuum at ambient temperature.

Approximately 27 000 transients (22.5 h) were taken on 200 mg of sample to get acceptable signal to noise at natural abundance levels. On ca. 20 mg of 99+% ^{15}N-labeled sample, however, only 256 transients (approximately 768 s) were required for very good signal to noise. While it is possible to obtain ^{15}N CP/MAS NMR spectra at the natural abundance level, the time required to achieve acceptable signal to noise is 2–3 orders of magnitude greater than that for labeled samples.

***N*-(*n*-Decyl)lauramide (5).** *n*-Decylamine (3.4 g, 0.02 mol) was stirred with 20 mL of 20% (w/v) potassium hydroxide and 10 mL of deionized water. Lauroyl chloride (4.7 g, 0.02 mol) was slowly added to the mixture in small portions with rapid stirring. After stirring for 15 min, the reaction mixture was poured into 50 mL of saturated brine. The resulting solid was filtered and recrystallized from alcohol to give **5** as a colorless solid: mp 75.5–77.5 °C (6.8 g, 91% yield).

^{13}C NMR ($\mathrm{CDCl_3}$): δ 13.9 ($-C\mathrm{H_3}$); 22.6 ($-C\mathrm{H_2CH_3}$); 25.8 ($-\mathrm{COCH_2}C\mathrm{H_2}-$); 26.9 ($-\mathrm{NHCH_2}C\mathrm{H_2}$); 29.2–29.5 ($-C\mathrm{H_2}-$); 31.8 ($-\mathrm{COCH_2CH_2}C\mathrm{H_2}-$); 36.7 ($-\mathrm{CO}C\mathrm{H_2}-$); 39.4 ($-\mathrm{NH}C\mathrm{H_2}-$); 173.1 ($-C\mathrm{O}-$).

^{13}C NMR (solid state): δ 15.7 ($-C\mathrm{H_3}$); 25.7 ($-C\mathrm{H_2CH_3}$); 27.3 ($-\mathrm{COCH_2}C\mathrm{H_2}-$); 33.8–34.1 ($-C\mathrm{H_2}-$); 35.6 ($-\mathrm{CO}C\mathrm{H_2}-$); 41.7 ($-\mathrm{NH}C\mathrm{H_2}-$); 172.7 ($-C\mathrm{O}-$).

^{15}N NMR (solid state): δ 83.3 ($-\mathrm{CO}N\mathrm{HCH_2}-$).

***N*-(*n*-Propyl)stearamide (6).** Stearoyl chloride (2.00 g, 0.007 mol) and 25 mL of methylene chloride were charged to a flask. The flask was then cooled to 5 °C in an ice bath. *N*-Propylamine (0.78 g, 0.013 mol) and triethylamine (1.47 g, 0.01 mol) were then added to the flask sequentially. The ice bath was removed, and the flask was allowed to stir at ambient temperature overnight. The resulting light yellow solution was washed with 10% (w/v) HCl and then twice with deionized water. The solvent was removed under reduced pressure, and the resulting solid was recrystallized from carbon tetrachloride to give **6**; mp 82 °C (1.8 g, 75% yield).

^{13}C NMR ($\mathrm{CDCl_3}$): δ 11.2 (propyl $C\mathrm{H_3}-$); 14.0 ($C\mathrm{H_3}-$); 22.6 (propyl $\mathrm{CH_3}C\mathrm{H_2}-$); 22.8 ($\mathrm{CH_3}C\mathrm{H_2}-$); 25.8 ($-C\mathrm{H_2CH_2CO}-$); 29.3–29.6 ($-C\mathrm{H_2}$-s); 31.8 ($-\mathrm{CH_2CH_2CH_2CO}-$); 36.8 ($-C\mathrm{H_2CO}-$); 41.1 ($-C\mathrm{H_2NHCO}-$); 173.1 ($-C\mathrm{O}-$).

^{13}C NMR (solid state): δ 12.3 (propyl $C\mathrm{H_3}-$); 15.2 ($C\mathrm{H_3}-$); 24.4 (propyl $\mathrm{CH_3}C\mathrm{H_2}-$); 24.6 ($\mathrm{CH_3}C\mathrm{H_2}-$); 28.0 ($-C\mathrm{H_2CH_2CO}-$); 30.8–33.0 ($-C\mathrm{H_2}$-s); 34.4 ($-C\mathrm{H_2CH_2CH_2CO}-$); 36.5 ($-C\mathrm{H_2CONH}-$); 41.9 ($-C\mathrm{H_2NHCO}-$); 173.8 ($-C\mathrm{O}-$).

^{15}N NMR (solid state): δ 92.3 ($-\mathrm{CO}N\mathrm{HCH_2}-$).

Results and Discussion

Synthesis. ^{15}N-Labeled 12-aminododecanoic acid was successfully prepared in good yield using the Gabriel method. The amino acid was then melt-polymerized in quantitative yield to give the corresponding polyamide with >99% ^{15}N labeling at the amide nitrogen. Care must

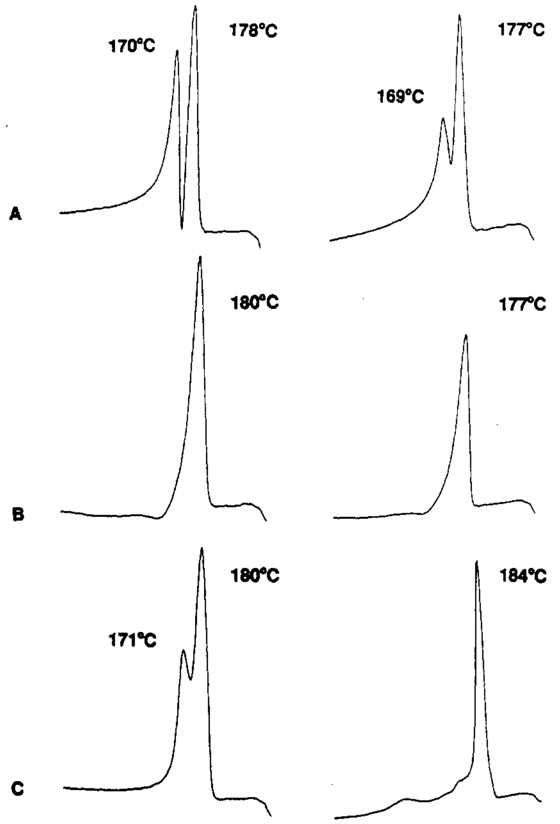

Figure 1. DSC thermograms of commercial (left column) and ^{15}N-labeled (right column) nylon 12: (A) α- plus γ-forms, (B) γ′-form, and (C) γ-form.

be taken to exclude oxygen during polymerization or discoloration and degradation will occur. Films of good integrity were melt-pressed, treated in various ways, and used for NMR evaluation. This work extends our previous efforts using this efficient method of preparing ^{15}N-labeled nylons starting with ^{15}N-labeled potassium phthalimide. Overall yields were good, and polymers with reasonable molecular weight and properties have so far been obtained for nylon 6, 11, and 12.

Figure 1 contains the DSC thermograms of commercial and ^{15}N-labeled nylon 12 at a heating rate of 10 °C/min. Both traces (A) for the α + γ mixture precipitated from 84:16 phenol–ethanol (by weight) show two melting endotherms, indicating the presence of two polymorphs, with the melting temperatures of each respective polymorph being similar. However, a crystallization exotherm can be seen superimposed on the endotherms in trace A for the commercial material as suggested by the deep valley between the two peaks. If the superimposed exotherm is present in the ^{15}N-labeled sample, it is not as noticeable. Perhaps the crystallites in the commercial sample are small enough to melt completely and then recrystallize into the γ-form before they melt, while the crystallites in the ^{15}N-labeled sample are too large to undergo complete melting and recrystallization before the γ crystals melt. Trace B for the quenched samples (γ′-form) shows a single melting endotherm. The peak shapes are similar, and the melting temperatures are in close agreement. The thermograms for the annealed samples are seen in trace C, with the γ melting temperatures being in good agreement with each other. The commercial material shows two melting endotherms, suggesting that the sample is a mixture of α- and γ-forms. However, the ^{13}C and ^{15}N solid-state NMR spectra do not show the presence of two crystal forms. We have no explanation for this at the present time.

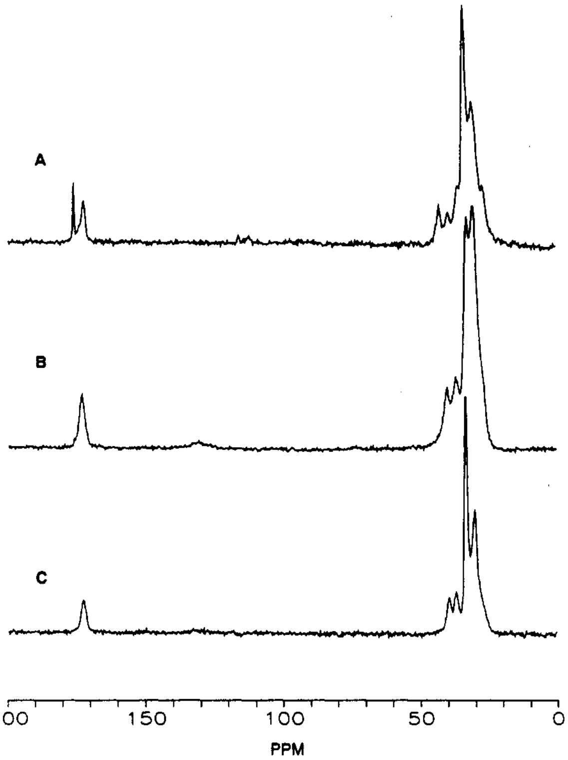

Figure 2. ^{13}C CP/MAS NMR spectra of ^{15}N-labeled nylon 12: (A) α- plus γ-forms, (B) γ′-form, and (C) γ-form.

^{13}C CP/MAS NMR. Figure 2 contains the ^{13}C CP/MAS NMR spectra of the various samples of nylon 12 synthesized here, while Table I summarizes the chemical shifts for these polymers and two model amides. Clear differences can be seen in peak intensity, positions, and sharpness. The preferred thermodynamic crystal form for nylon 12 crystallized from the melt is the γ-form, which has the amide plane twisted out of the plane of the methylenes by about 60°.[11] The kinetically stable α-form has been reported to form upon precipitation from phenol–ethanol.[6] The difference between the amide and zigzag polymethylene chain plane orientation is reflected in differences in the chemical shift values in both the ^{13}C and ^{15}N CP/MAS NMR spectra for the different crystal forms.

The main peak in trace C for the annealed sample is seen at 33.6 ppm and is assigned to methylene units in the all-trans conformation, similar to the main peak value for the all-trans methylenes in side-chain comb polymers.[22] The peak upfield from the main peak (at 30.3 ppm) is assigned to the methylene groups in the gauche conformation. The peak at 33.6 ppm is the more intense, indicating a larger population of all-trans methylenes in material that has been annealed (γ-form). Its sharpness further indicates that well-ordered domains exist down to the molecular level.

For the sample quenched from the melt in liquid nitrogen (γ′-form), the main peak is at 30.8 ppm (trace B), which arises from γ-gauce contributions to the methylene unit shifts. The peak at 33.1 ppm is present in this sample, but it is obvious that the relative intensity ratio of the two peaks is very different from that of similar peaks in trace C. Interestingly, the main peak for the all-trans methylene units in trace A (α-form) is shifted downfield (to 34.2 ppm) relative to the peak in traces B and C. Even though both polymorphs of nylon 12 crystallize in the monoclinic unit cell,[23] the greater downfield shift seen for the peak corresponding to the all-trans methylene units may be a result of deshielding brought about by differences in

Table I
^{13}C CP/MAS NMR Data in ppm for Synthesized Nylon 12 (Commercial), Model Amides, and Nylon 6[a]

sample	C_β	CH_2 gauche	CH_2 trans	C_α	C_N	CO
α	27.1 (27.3)	30.9 (31.2)	34.2 (34.3)	38.9 (38.7)	43.0 (42.4)	172.9 (172.8)
γ'	ca. 27 (27)	30.8 (30.8)	33.1 (33.2)	37.0 (37.0)	40.3 (40.6)	173.6 (173.7)
γ	ca. 28 (28)	30.3 (30.6)	33.6 (33.5)	37.3 (37.1)	39.8 (40.0)	173.6 (173.7)
model lauramide	27.3		34.2	35.6	41.2	172.7
model stearamide	27.9		33.0	36.4	41.8	173.7
α nylon 6	30.1			37.8	43.6	173.4
γ nylon 6	26.5			36.7	39.9	173.0

[a] Data taken from ref 17.

intermolecular interactions due to crystal-packing effects. The all-trans methylenes in the lauramide model compound also appear at 34.2 ppm, similar to α nylon 12, while the main peak for the stearamide model appears at 33.0 ppm, close to the peaks for annealed and quenched nylon 12. The differences in the ^{13}C chemical shifts of 1 ppm or less have been shown to correlate with changes in packing and molecular motion for polyethylene[24] and well-ordered linear alkanes in the range C_{19}–C_{60}.[25]

The carbon β to the carbonyl (C_β) for the α-form is seen clearly at 27.1 ppm. This peak is not as well-resolved in the spectra for the γ' and γ-forms. A shoulder upfield from the main peak can be seen centered near 28 ppm in traces B and C. In contrast, the carbon α to the carbonyl (C_α) for the γ and γ' crystal forms appears at 37 ppm, while it appears near 39 ppm for the α-form. We feel this downfield shift on going from the thermodynamically stable γ-form to the kinetically generated α-form is due to deshielding by the amide NH in its coplanar orientation with the methylene unit next to the carbonyl. A similar effect is seen at the carbon adjacent to the nitrogen (C_N), which appears at 39.8 ppm in the annealed material and 43.0 ppm in the solution-precipitated sample, although for this carbon it is apparently the coplanar C=O group which deshields.

Downfield shifts observed on going from γ to α (labeled samples) for C_α and C_N are 1.6 and 3.2 ppm, respectively. The C_β was not observable because of overlapping signals from other carbons. Semiempirical MO calculations based on *N*-ethylpropanamide have suggested a decrease in partial atomic charge for C_α and C_N on going from the γ to the α nylon polymorph.[26] Others have seen analogous behavior for the various crystal forms of nylon 6 by ^{13}C CP/MAS NMR.[17,18] The C_N was shifted downfield on going from the γ to α by 3.7 ppm, and the C_α showed a downfield shift of 1.1 ppm. The C_β shifted 3.6 ppm downfield on going from γ to α.

The nylon 12 carbonyl chemical shift was observed to change only slightly with crystal form as shown by data in Table I. The α-form showed the most shielded carbonyl at 172.9 ppm, while it was at 173.1 and 173.6 ppm for the annealed and quenched materials, respectively. The carbonyl peak shows similar behavior in the various crystal forms of nylon 6 with values of 173.4 and 173.0 ppm for the α- and γ-forms, respectively, which are within experimental error. The carbonyl group for amorphous nylon 6 is seen at 174.5 ppm, downfield from the other nylon 6 crystal forms[17] and consistent with nylon 12 behavior. These small differences are difficult to measure reliably and are probably of little diagnostic value.

The ^{15}N chemical shifts of the model amides (discussed below) suggest that the lauramide adopts an α-like conformation while the stearamide assumes a γ-like structure. In fact, the relative peak positions for the all-trans methylenes, C_β, and the carbonyl all are consistent with these two conformations. The C_α and C_N peaks show relative chemical shifts opposite to the others, although the fact that their absolute values are so far from those of the nylon 12 samples may indicate that an additional through-space or through-bond effect is influencing these two positions.

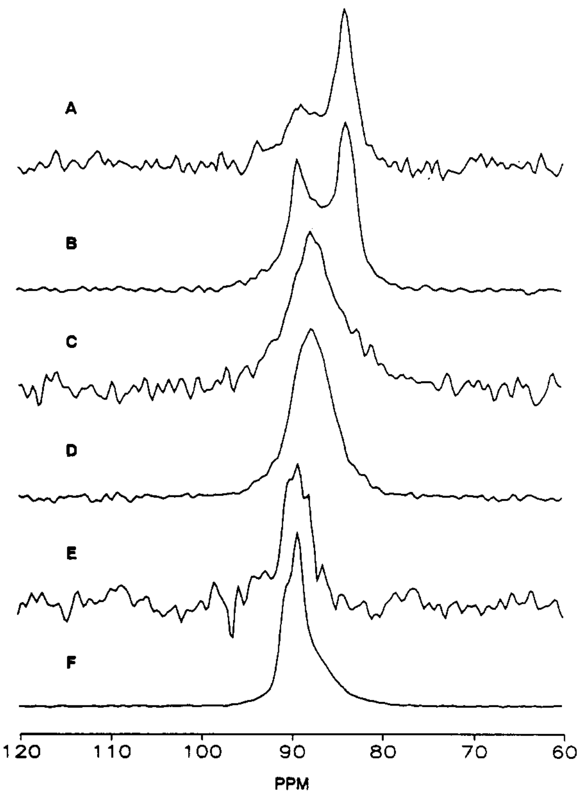

Figure 3. ^{15}N CP/MAS NMR spectra of ^{15}N-labeled (l) and commercially available (c) nylon 12: (A) α- plus γ-forms (c), (B) α- plus γ-forms (l), (C) γ-form (c), (D) γ'-form (l), (E) γ-form (c), and (F) γ-form (l).

^{15}N CP/MAS NMR. Figure 3 contains the ^{15}N CP/MAS NMR spectra for the ^{15}N-labeled and unlabeled polymers. While evaluation of ^{13}C CP/MAS NMR spectra is complicated by multiple overlapping resonances for various backbone carbons, analysis of the ^{15}N CP/MAS NMR spectra is straightforward. Trace F is for the labeled sample annealed >50 h and containing γ-form and noncrystalline regions. The main peak at 89.3 ppm is assigned to the γ crystal form while the amorphous peak is a broad shoulder at 86.6 ppm. Trace E for the annealed commercial sample shows identical chemical shifts but somewhat different peak shapes and poor signal to noise. A shoulder appearing at 90.3 ppm in the spectrum of the labeled γ-rich material has been seen before at the natural abundance level but has not been assigned.[26] This peak may belong to material epitaxially crystallized on the surface of γ crystallites or to an ordered interphase region. While its exact identity is unclear, the fact that it has a T_{1N} similar to that of the γ-form indicates a rigid, highly ordered environment.

The spectrum for the quenched labeled sample is seen in trace D. The corresponding spectrum of commercially available material is trace C. While they are very similar in shape, the base of trace C is broader than that of trace D. Residual monomer (lauryllactam) may be acting as plasticizer and increasing the size or conformational mobility of the amorphous region. Upon annealing a sample of commercial nylon 12, a sublimate formed which was readily soluble in $CDCl_3$. The proton NMR spectrum agreed with the proton NMR spectrum of lauryllactam.[27] Similar plasticizing behavior was seen before with nylon 6 prepared from caprolactam.[16]

The main peaks of spectra C and D are shifted slightly upfield compared to those of traces E and F. This may be due to a larger size distribution of smaller crystallites in the former, resulting in a slight shielding effect. Wide-angle X-ray diffraction (WAXD) patterns of the γ and γ' crystal forms were very similar,[4] although the pattern for the annealed γ-form sample was sharper than that of the quenched material. The γ'-form can be easily transformed into the γ-form by simply annealing the material at ambient pressure at temperatures near but below the melting point of the polymer. Like the WAXD patterns, the γ-form spectrum shows the sharpest peaks. Annealing increases crystalline content and crystallite size while narrowing the size distribution, and these increases should be manifested in sharper spectral lines.

The most interesting of the spectra in Figure 3 are traces A and B for mixtures of α and γ crystal forms in commercial and synthesized materials, respectively. This is the first observation that we know of peaks for the two crystal forms being so cleanly separated in the ^{15}N CP/MAS NMR spectra. The downfield resonance occurs at exactly the same chemical shift (89.3 ppm) as that of the sample prepared with mainly the γ-form. The peak at 84.1 ppm for the α-form is in agreement with that observed for α nylon 11 and nylon 6.[16,17] The amorphous resonances lie between, and partially overlap, these two extremes. The difference in the relative peak intensities between the samples is puzzling. Sample preparation and treatment were identical, yet the commercially available material shows a greater α content (based on peak intensities) perhaps due to the small amounts of residual monomer acting as plasticizer to aid in the formation of the kinetically formed α crystallites. The method reported in the literature to prepare a sample high in α content was claimed to give 100% α-form when analyzed by X-ray[7] diffraction methods. This suggests that the amount of each form present is very sensitive to the sample preparation method and that the differences observed here are not significant. However, the ability of solid-state ^{15}N NMR to observe all phases simultaneously is an important development.

Magic-angle spinning (MAS) without cross-polarization was used to selectively look at and remove the mobile (amorphous) region peak of the labeled materials. Figures 4–6 each show CP/MAS, MAS, and difference spectra for nylon 12 α, γ', and γ crystal forms, respectively. Each of the MAS spectra gives a broad peak approximately 7 ppm wide at half-height. In Figure 4, subtraction of this peak from the CP/MAS spectrum clearly shows base-line-resolved peaks for the α- and γ-forms at 84.2 and 89.1 ppm with peak widths at half-height of 2.4 and 2.1 ppm, respectively. This difference spectrum is identical to that obtained using a long recycle delay (60 s) during which the magnetization of the fast-relaxing amorphous material decays away leaving only peaks for the rigid, slow-relaxing components.

Similarly, Figure 5 shows the CP/MAS, MAS, and difference spectra for the quenched or γ'-form. Peak width at half-height of trace A is 4.5 ppm, while that of the difference spectrum (trace C) is 3.9 ppm. The peak appears at 88.9 ppm, slightly upfield from the main resonance for the γ-form, and may reflect differences in crystallite size between the γ- and γ'-forms. Figure 6 shows the corresponding spectra for the annealed sample γ-form. The

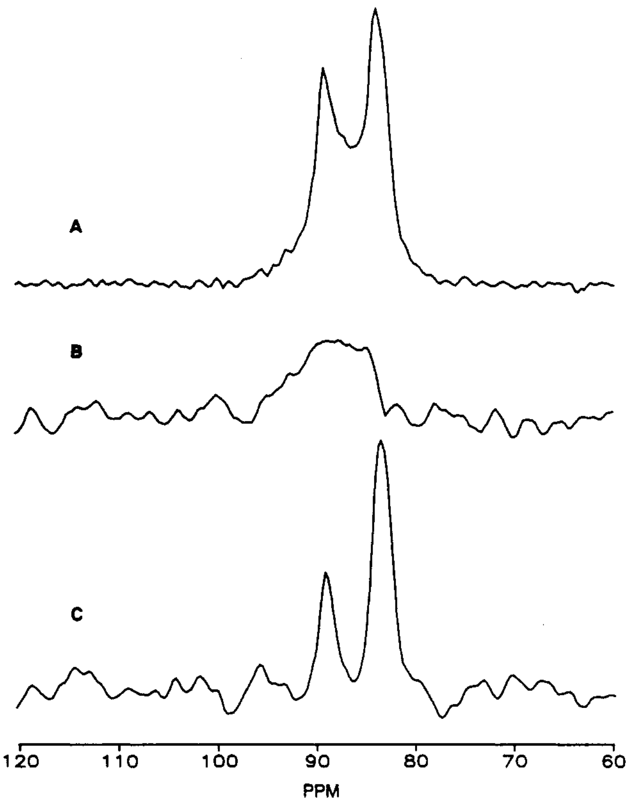

Figure 4. ^{15}N NMR spectra of ^{15}N-labeled $\alpha + \gamma$ nylon 12: (A) CP/MAS, (B) MAS (no cross-polarization), and (C) subtraction of B from A.

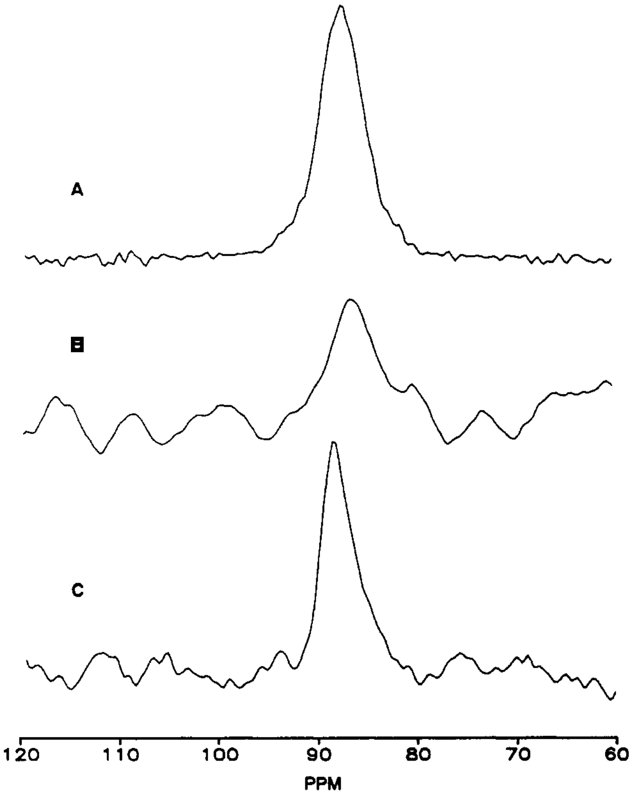

Figure 5. ^{15}N NMR spectra of ^{15}N-labeled γ' nylon 12: (A) CP/MAS, (B) MAS (no cross-polarization), and (C) subtraction of B from A.

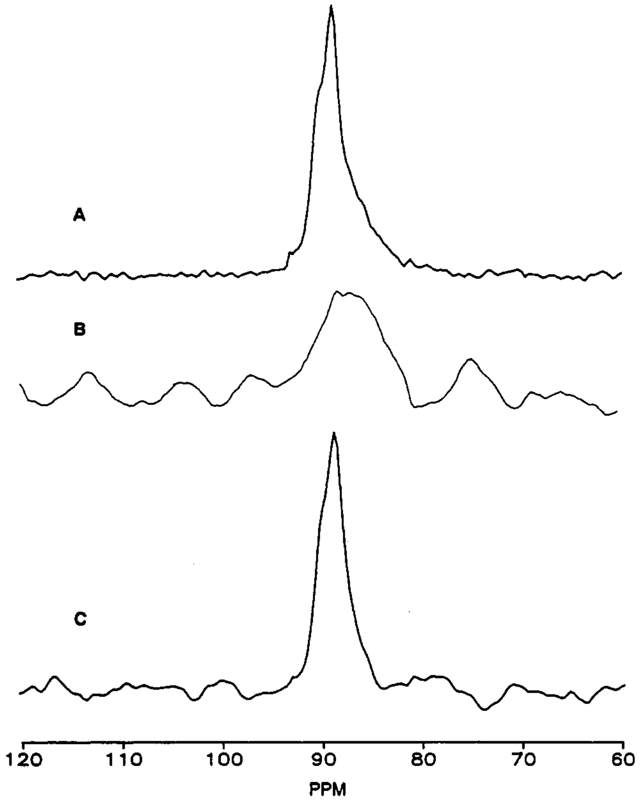

Figure 6. ^{15}N NMR spectra of ^{15}N-labeled γ nylon 12: (A) CP/MAS, (B) MAS (no cross polarization), and (C) subtraction of B from A.

peak width at half-height is 3.3 ppm for trace A and 3.0 ppm for trace C. The shoulder seen downfield at 90.3 ppm remains after spectral subtraction of the amorphous component. This suggests that the shoulder is not due to some amorphous conformation but results from some other rigid or crystalline component with an amide bond twist of more than 60°. We have no proof or supporting evidence for this possibility at the present time. However, spectral subtraction of the γ-form from the mixture of α and γ clearly shows a peak at 84.1 ppm for the α polymorph with a broad peak centered near 87 ppm for the amorphous component and a negative peak at about 91 ppm (see Figure 7). The negative peak at 91 ppm confirms that it represents a unique component of the γ nylon 12 sample.

The ^{15}N chemical shifts of the model amides are consistent with the α and γ modifications for nylons. *N*-(*n*-Decyl)lauramide, α-form model, has a sharp peak at 83.3 ppm which is ca. 1 ppm in width at half-height. *N*-(*n*-Propyl)stearamide, γ-form model, has a sharp peak at 92.3 ppm which is ca. 1 ppm at half-height. The amide nitrogen for the lauramide compound is shielded slightly more than the amide nitrogen of α nylon 12, while that of the stearamide model is deshielded slightly more than the amide nitrogen of γ nylon 12. These differences may be due to additional crystal-packing effects or crystallite perfection not present in the polymer crystallites; the latter is supported by the peak width for these materials, which is about half the width of the crystalline peaks of the polymer samples.

^{15}N T_{1N} and $T_{N\rho}$ Measurements. The results from ^{15}N spin-lattice relaxation time determinations in the laboratory and the rotating frame are summarized in Table II. It is clear that the γ-rich samples have at least three components, a fast-relaxing component (with T_{1N} on the order of a few seconds), an intermediate-relaxing component (tens of seconds), and a slow-relaxing component (hundreds of seconds). The slow-relaxing component of the γ-form is obviously material in the rigid crystalline domains while the fast-relaxing material is in amorphous domains. Similar behavior has been observed for nylon 6,[16] nylon 11,[14] and polyethylene.[24] The intermediate time is attributed to a more ordered interphase region joining the two. This component may be epitaxially crystallized material near the surface of a crystallite or polymer chains extending from the crystallite surfaces into the amorphous region in an ordered array that is neither crystalline nor liquidlike amorphous. Such interphase regions may be too small to be detected by X-ray or DSC but still be observable by solid-state NMR.

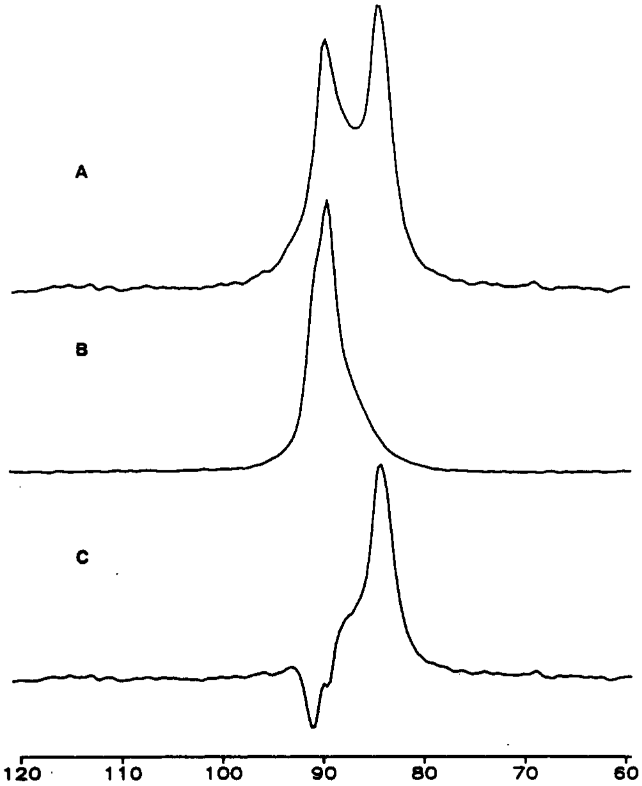

Figure 7. ^{15}N CP/MAS NMR spectra of ^{15}N-labeled nylon 12: (A) α- plus γ-forms, (B) γ-form, and (C) subtraction of B from A.

The broad upfield peak (87 ppm) in the γ crystal form spectrum (trace F, Figure 2) was conclusively identified as amorphous based on T_{1N} measurements. The two-component decay rates (4 and 41 s) were both fast compared to those of the γ crystal peak at 89.3 ppm (20 and 314 s). The peak at 89.3 ppm is in a rigid environment with highly restricted motion based on T_{1N} data. The decay rates of the shoulder at 90.3 ppm (10 and 319 s) are approximately the same as those for the main peak, indicating that the residues associated with this peak are probably in as rigid an environment as the γ crystalline material itself. The γ′ sample (melt-quenched) has relaxation values less than those of the annealed sample, consistent with less ordered chain segments and/or smaller crystallites than the annealed material.

While the motion in the amorphous region of all the samples seems to be less restricted than that of the rigid crystalline domains, it does not appear to be as unrestricted as that of the amorphous region of poly(oxymethylene) that has a T_{1C} on the order of 75 ms.[28] The amide units of nylons are anchored in hydrogen-bonded assays that tie down the polymer chains and restrict their motion, unlike poly(oxymethylene), which has much greater mo-

Table II
^{15}N T_{1N} and $T_{N\rho}$ Data for the Crystal Forms of the Nylon 12 Synthesized Here

	quenched		annealed			precipitated		
	γ'	amor	shoulder	γ	amor	γ	amor	α
	88.8	86.6	90.3	89.3	86.6	89.3	86.6	84.2
T_{1N}, s	3/34	4/79	10/319	20/314	4/41	9/160	2/107	2/323
$T_{N\rho}$ ms	34.0/0.6	33.3/1.77	8.9/1.15	10.5/2.16	14.2/2.07	22.2/1.95	59.3/12.3	25.3/9.32

tional freedom. The presence of more than one fast-relaxing amorphous component may be due to a very mobile liquidlike region plus a more ordered interphase that consists of a distribution of domain sizes whose spin–lattice relaxation times vary with crystal thickness.[29] Alternatively, the interphase region may consist of a gradient ranging from highly ordered near the crystallite surface to very mobile near the liquidlike amorphous regions. The latter is supported by the fast-relaxing components of the peaks at ca. 84, 89, and 91 ppm, which may correspond to amorphous material possessing the same conformation (and therefore chemical shift) as the crystalline residues but with sufficient mobility to display short T_{1N} values. Both possibilities (domain size variation or interphase gradient) are consistent with broad envelopes of chemical shifts and relaxation times representing a distribution of relatively rigid (compared to other polymers or even segments in the same polymer) conformational environments for amorphous amide units.

The relaxation behavior of the solution-precipitated sample containing both α- and γ-forms appears to be essentially the same as the thermally treated material with both fast- and slow-relaxing components observed. However, the relaxation times for the two crystal forms are comparable to each other and to that of the annealed sample. If solution precipitation gives a kinetically stable α-form which can be converted to the γ-form upon heating, it might be expected that the domain sizes of γ crystallites generated during precipitation at ambient temperature would be much smaller than those formed during thermal annealing. Thus, the T_{1N} spin–lattice relaxation times of the solution-generated γ domains would be shorter than those of the annealed sample. That this is not the case seems to indicate comparable crystallite sizes with a high degree of regularity. Similarly, comparable times for the α- and γ-forms in the same sample indicate that the difference in their thermodynamic stability is low so that under conditions which allow formation of both, extended arrays with few defects form. In fact, the sharpness and separation of the ^{15}N NMR peaks for the two crystal forms is consistent with physically separated and well-defined crystallites of each.

Spin–lattice relaxations for ^{15}N in the rotating frame ($T_{N\rho}$) for all samples are similar in that they are adequately fit using two components. The calculated values are shown in Table II along with the T_{1N} values. Within the respective samples, both short and long values for all components are similar, suggesting that similar motions (in the kilohertz range[30]) occur throughout each sample.

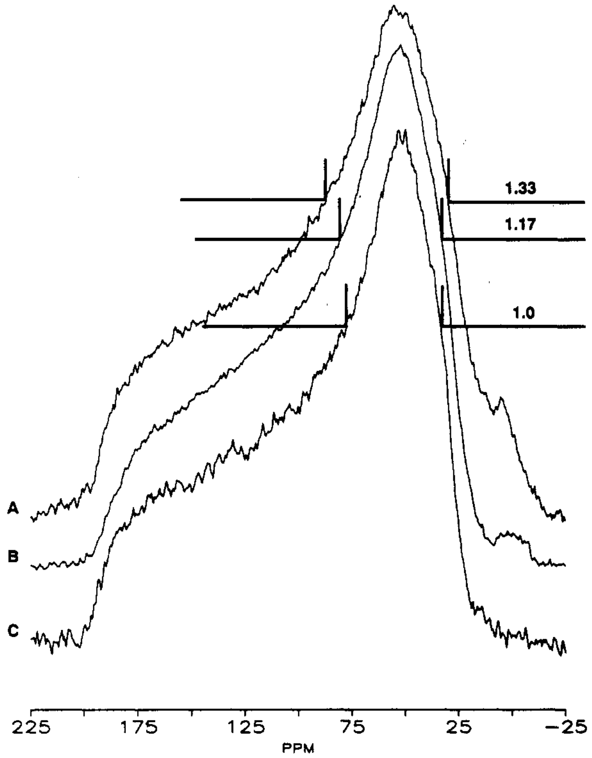

Figure 8. ^{15}N chemical shift anisotropy spectra of ^{15}N-labeled nylon 12, cross-polarization without magic-angle spinning: (A) α- plus γ-forms, (B) γ'-form, and (C) γ-form.

Table III
^{15}N Chemical Shift Anisotropy Data for ^{15}N-Labeled Nylon 12 Polymorphs

sample	σ_{11}, ppm	σ_{22}, ppm	σ_{33}, ppm	σ_{iso},[a] ppm calc	σ_{iso},[a] ppm found	$\Delta\sigma$[b], ppm	η[c]
$\alpha + \gamma$	22	54	188	88.0	84.2/89.3	150.0	0.32
γ'	29	54	185	89.3	88.8	143.5	0.26
γ	28	52	188	89.5	89.3	148.0	0.24

[a] Isotropic chemical shift = $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$. [b] Anisotropy = $\Delta\sigma = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2$. [c] Asymmetry = $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{iso})$.

^{15}N Chemical Shift Anisotropy. Figure 8 contains the ^{15}N chemical shift anisotropy spectra of the ^{15}N-labeled nylon 12 samples, and Table III summarizes the calculated tensor elements and associated parameters. The gross appearance of the powder patterns is the same, each being a composite of spectra from crystalline and amorphous domains. Their width is approximately 180 ppm, similar to that seen for nylon 11,[14] nylon 6,[15] and poly(amino acids),[31] although the spectrum of the sample with both α- and γ-forms is slightly wider. This is probably due to the overlap of the α powder pattern (displaced slightly upfield) with the γ powder pattern, as suggested by the value of the calculated σ_{11} component (see Table III), and the width of the spectrum at 60% relative intensity (see Figure 8). Trace A (mixture of α and γ) is ca. 30% wider the that of the γ-rich sample due to overlap of the σ_{22} tensor element from both α and γ contributions. The increased width (ca. 17%) of trace B over trace C at 60% intensity may be due to a greater distribution of conformational environments, causing line broadening similar to that seen in the ^{15}N CP/MAS NMR spectrum of the γ'-form.

The anisotropy ($\Delta\sigma$) and asymmetry (η) parameters calculated from the chemical shift tensors are affected by the three-dimensional distribution of electron density around the nucleus. These values are similar for the annealed and quenched samples since their overall chemical bonding and electron distributions are not much affected by crystal packing and small changes in conformation.

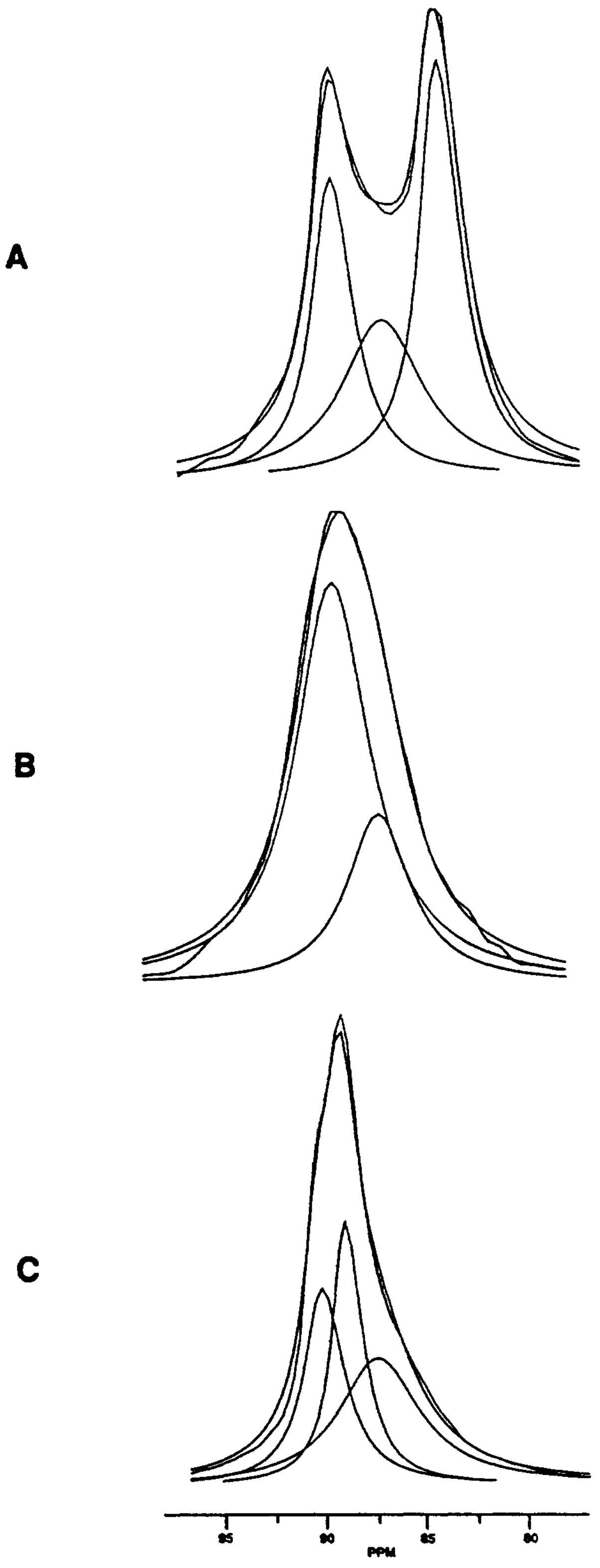

Figure 9. Experimental spectra, simulated individual peaks, and composite spectra for ^{15}N-labeled nylon 12: (A) α- plus γ-forms, (B) γ'-form, and (C) γ-form.

Spectral Simulations. It is useful to use computer-generated peaks to fit experimentally obtained spectra in order to better observe possible components contributing to the composite spectrum. Figure 9 contains composite totals and individual peak simulations along with experimental spectra for the nylon 12 samples examined. Each experimental spectrum can be fit well with two or more components. The simulated peak near 87 ppm is common to all of the spectra and is attributed to the amorphous mobile phase present in these semicrystalline materials. By adding peaks that correspond to the well-defined crystal forms to the amorphous peak, good composite spectra can be obtained for each sample spectrum. All three samples contain major amorphous peak contributions. The composite spectrum of the γ' sample (middle) is most consistent with a γ-like peak overlapping the amorphous peak. Finally, the 90.3 ppm peak is clearly due to a major component of the sample.

Conclusions

Nylon 12 with >99% ^{15}N labeling of the amide nitrogen was synthesized and used to prepare samples rich in the γ-form (by thermal annealing), γ'-form (quenched from the melt), and α-form (precipitated from phenol–ethanol 84:16 by weight). Solid-state ^{13}C and ^{15}N NMR techniques were used to characterize the polymer samples. Clear differences were seen in both the ^{13}C and ^{15}N CP/MAS NMR spectra for the samples. The peaks in the ^{15}N NMR spectra agree very well with the chemical shifts seen for other nylons possessing similar crystal forms and with the spectra of the model amides. A low-field shoulder (90.3 ppm) present in the γ-rich annealed sample was found to have a T_{1N} of ca. 300 s, which is comparable to that of the γ and α crystal forms although its identity is unknown at this time. Spin–lattice relaxation measurements for ^{15}N showed that the relative mobility increased in the order $\alpha \simeq \gamma < \gamma'$. ^{15}N chemical shift anisotropy powder patterns for all of the samples were similar, while the powder pattern for the $\alpha + \gamma$ sample was slightly wider than that for the other samples due to the overlapping spectra (α and γ). ^{15}N CP/MAS NMR results for natural abundance samples were similar in overall information despite a large decrease in sensitivity and confirm the *practical* use of ^{15}N solid-state NMR characterization of unlabeled materials.

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Registry No. 1, 72338-48-8; **2**, 136116-02-4; **2**-^{15}N, 136116-01-3; **3**, 693-57-2; **3** (homopolymer), 25768-33-6; **3** (SRU), 24937-16-4; **3**-^{15}N, 136116-03-5; **3**-^{15}N (homopolymer), 136116-08-0; **3**-^{15}N (SRU), 136144-72-4; **5**, 22205-13-6; **6**, 129392-93-4; 12-bromododecanoic acid, 73367-80-3; ^{15}N-potassium phthalimide, 1074-82-4; *n*-decylamine, 2016-57-1; lauroyl chloride, 112-16-3; stearoyl chloride, 112-76-5; *N*-propylamine, 107-10-8; nylon 12, 25038-74-8.