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¹⁵N T₁ MEASUREMENTS OF SEMICRYSTALLINE NYLON 6

by

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Submitted to

Macromolecules

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^{15}N T_1 Measurements of Semicrystalline Nylon 6

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ABSTRACT

The solid state ^{15}N NMR characterization of nylon 6 is reported. Nylon 6 (20% ^{15}N enriched) was prepared by anionic polymerization of isotopically enriched caprolactam. The samples were prepared by three different treatments: quenched from the melt, slowly cooled and annealed, and artificially plasticized with excess caprolactam. CP/MAS spectra of the ^{15}N enriched samples showed a single sharp peak (α crystal form) at 84.2 ppm (relative to glycine) and a broader resonance at 87.2 ppm. Relaxation experiments were conducted to determine the spin lattice relaxation time T_{1N} for each sample at 300K. The crystalline resonance was found to have T_{1N} 's of 125-416s, consistent with a rigid, crystalline component. The downfield peak (87.2 ppm) had two measurable T_{1N} 's: a short component with T_1 of 1-3s and a second component with a longer T_1 of 19-29s. The two components for the non-crystalline peak are thought to belong to a liquid-like amorphous region (short T_1) and a more rigid "interphase" region (longer T_1) lying between the crystalline and amorphous regions. Comparison of relaxation data with sample crystallinity shows that T_{1N} values for the crystalline component increase with increasing percent crystallinity in the sample.

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INTRODUCTION

High resolution solid state NMR is becoming an important tool for characterizing polymer systems. Cross polarization and magic angle spinning (CP/MAS) along with high power decoupling allow acquisition of high resolution spectra of natural abundance ^{13}C nuclei with good sensitivity. Relaxation studies have identified non-crystalline regions poorly characterized by x-ray.¹ Recently, we have demonstrated that solid state CP/MAS NMR of natural abundance ^{15}N is readily obtainable on solid polyamides.^{2,3} In addition, ^{15}N CP/MAS peaks were shown to correlate with the two predominant crystal forms found in most solid polyamides; i. e. the α and γ crystal forms. Resonances were observed for other regions which could not be assigned to either crystal form. Further study by NMR and molecular modeling calculations showed nitrogen chemical shifts to be extremely sensitive to conformation about the amide group providing a tool for observing ordered region conformations in solid polyamides.⁴

Our interest in examining the previously unobserved non-crystalline and amorphous regions in polyamides by ^{15}N CP/MAS prompted us to prepare an isotopically enriched polyamide sample. We chose to prepare an ^{15}N enriched sample of nylon 6 because it is an important commercial polyamide which has been thoroughly characterized in the solid state by many techniques (DSC, IR, x-ray) including solid state ^{13}C NMR.^{5,6} Laboratory preparation of nylon 6 is relatively straight-forward. Isotopic enrichment was accomplished using commercially available hydroxylamine hydrochloride (99% ^{15}N) as shown in Figure 1. Details of the polymer synthesis will be reported in a future paper. Here we report preliminary ^{15}N NMR characterization of nylon 6 including the first report of ^{15}N T_1 values for a solid polyamide.

EXPERIMENTAL SECTION

^{15}N NMR. Spectra were obtained on a Bruker MSL-200 NMR spectrometer operating at a field strength of 4.7 T and equipped with a Bruker MAS probe. The ^{15}N resonance frequency was 20.287 MHz and that of the ^1H was 200.13 MHz. Samples were melt-pressed into films then placed in fused zirconia rotors fitted with Kel-F caps and spun at 3.0 to 3.2 KHz with dry air. Crystalline glycine was placed in the rotor with the samples as an internal chemical shift reference (0 ppm). CP/MAS spectra were obtained with a standard crosspolarization pulse sequence using a $3.5 \mu\text{s}$ ^1H 90° pulse and a mixing pulse of 2 ms. High power decoupling was used during a 50 ms acquisition time with a nutating field of 62-68 KHz. ^{15}N spin-lattice relaxation times ($T_{1\text{N}}$) were obtained using the CP-90- τ -90 pulse sequence of Torchia.⁷ Spectra without cross-polarization were obtained using a 90° ^{15}N pulse with broadband decoupling during acquisition. Peak deconvolution of the overlapping crystalline and amorphous resonances in the CP/MAS spectrum

was accomplished using TENSOR, a Bruker-supplied Pascal program for simulating overlapping NMR resonances as combinations of Lorentzian or Gaussian lineshapes.

CP/MAS and T_{1N} of Crystalline and Amorphous Nylon 6.

The CP/MAS spectrum of nylon 6 is shown in Figure 2, upper trace. The spectrum shown is similar to natural abundance ^{15}N spectra we previously reported.^{2,3} The main strong peak clearly overlaps a broader resonance at lower field. The overlapping peaks were fit with a composite lineshape (Figure 2) and the individual components deconvoluted as shown. From the deconvoluted components, the upfield resonance is located at 84.2 ppm with a linewidth at half height of 2.4 ppm. This peak was previously correlated with the α crystal form of nylon 6.^{2,3} The broader downfield resonance is centered at 87.2 ppm and possesses a linewidth at half height of 6.3 ppm. This resonance had not been observed in our previous work with polyamides at the ^{15}N natural abundance level. We believe this to be the signal from the non-crystalline or "amorphous" fraction of the nylon sample since its chemical shift appears midway between the α and γ resonances typically observed for nylon 6 and other nylons³. (The γ form gives a sharp resonance at 88.5 ppm).²

To conclusively identify the downfield resonance as that of the amorphous region, relaxation experiments were conducted to evaluate the mobility of each region by monitoring spin-lattice relaxation times (T_{1N}). Using the method of Torchia⁷, relaxation times T_{1N} were obtained at 300K for resonances at 84.2 ppm (α crystal resonance) and 87.2 ppm (approximate position of the amorphous resonance) for several samples. Figure 3 shows a plot of magnetization decay for the crystalline component of the annealed sample. The crystalline component had a T_{1N} of 416s. Figure 4 shows the two component decay of the amorphous fraction of the same sample with a T_{1N} of 29.6s and an additional component with T_{1N} of 1.9s. The two shorter T_1 's for the 87.2 ppm peak is consistent with an amorphous fraction with much greater mobility than the crystalline portion of the sample. In addition, the detection of two T_{1N} 's may indicate two types of non-crystalline regions: a bulk amorphous fraction with liquid-like mobility and a non-crystalline "interphase" region with restricted motion. Similar phase morphology is observed in polyethylene where the crystalline and the non-crystalline "interphase" region are clearly delineated by their T_{1C} relaxation times.¹ To our knowledge, this is the first report of NMR observation of an interphase region in a semicrystalline polyamide as well as the first relaxation measurements of crystalline and amorphous regions by ^{15}N CP/MAS.

We took advantage of the difference in spin lattice relaxation times T_{1N} between the two phases to directly observe the amorphous fraction. An MAS spectrum of the ^{15}N labeled nylon 6 was obtained without

cross-polarization. By using a recycle delay of 5 to 10 seconds, the ^{15}N magnetization in the crystalline regions is quickly saturated. The nuclei in the amorphous region with shorter $T_{1\text{N}}$ can then be observed directly. Using this method, the spectrum of the amorphous region was obtained (Figure 5, lower trace). This spectrum is nearly identical to the deconvoluted peak from the CP/MAS spectrum shown in Figure 4; i. e., the resonance is broad and downfield of the α crystal peak but upfield from the observed position of the γ crystal peak. Spectral subtraction gives the center trace in Figure 8. Now the resonance for the α crystal form is clearly seen as a symmetrical Lorentzian line with contributions from the non-crystalline region removed.

^{15}N T_1 measurements are also reported in the Table for the in situ prepared sample as well as methanol extracted samples that were quenched from the melt. The amorphous regions in all samples have shorter relaxation times than the crystalline regions, a fact consistent with ^{13}C relaxation studies of these materials.⁵ In addition, the in situ prepared samples have shorter $T_{1\text{N}}$ values than any of the methanol extracted samples. Since the $T_{1\text{N}}$ values are associated with motions of the polymers, a shorter $T_{1\text{N}}$ value for the in situ sample indicates more rapid motion, due either to plasticization by residual caprolactam in the sample or differences in the crystalline regions. We are continuing our relaxation studies to confirm the proposed phase morphology and correlate the effects of plasticizers and thermal history on ^{15}N relaxation times.

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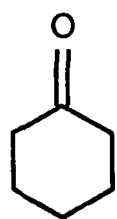
TABLE

<u>Sample</u>	<u>% xtal</u>	<u>Parameter</u>	<u>Amorphous Phase (87.2 ppm)</u>		<u>Crystalline Phase (84.2 ppm)</u>
In situ	23	T _{1N}	----- ^a	26s	111s
Melt Quenched	29	T _{1N}	2.7s	19s	230s
Annealed (160 °C)	45	T _{1N}	1.9s	29.1s	416s

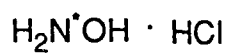
^aThe short T₁ component was not observed for this sample.

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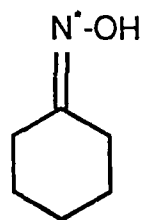
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EtOH/Py



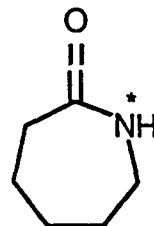
reflux



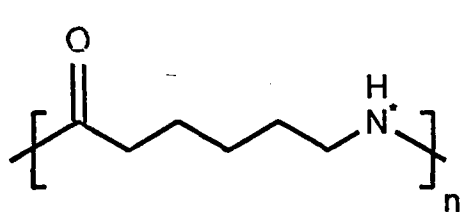
80%

polyphosphoric
acid

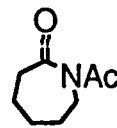
40°C / 18 Hrs.



85%

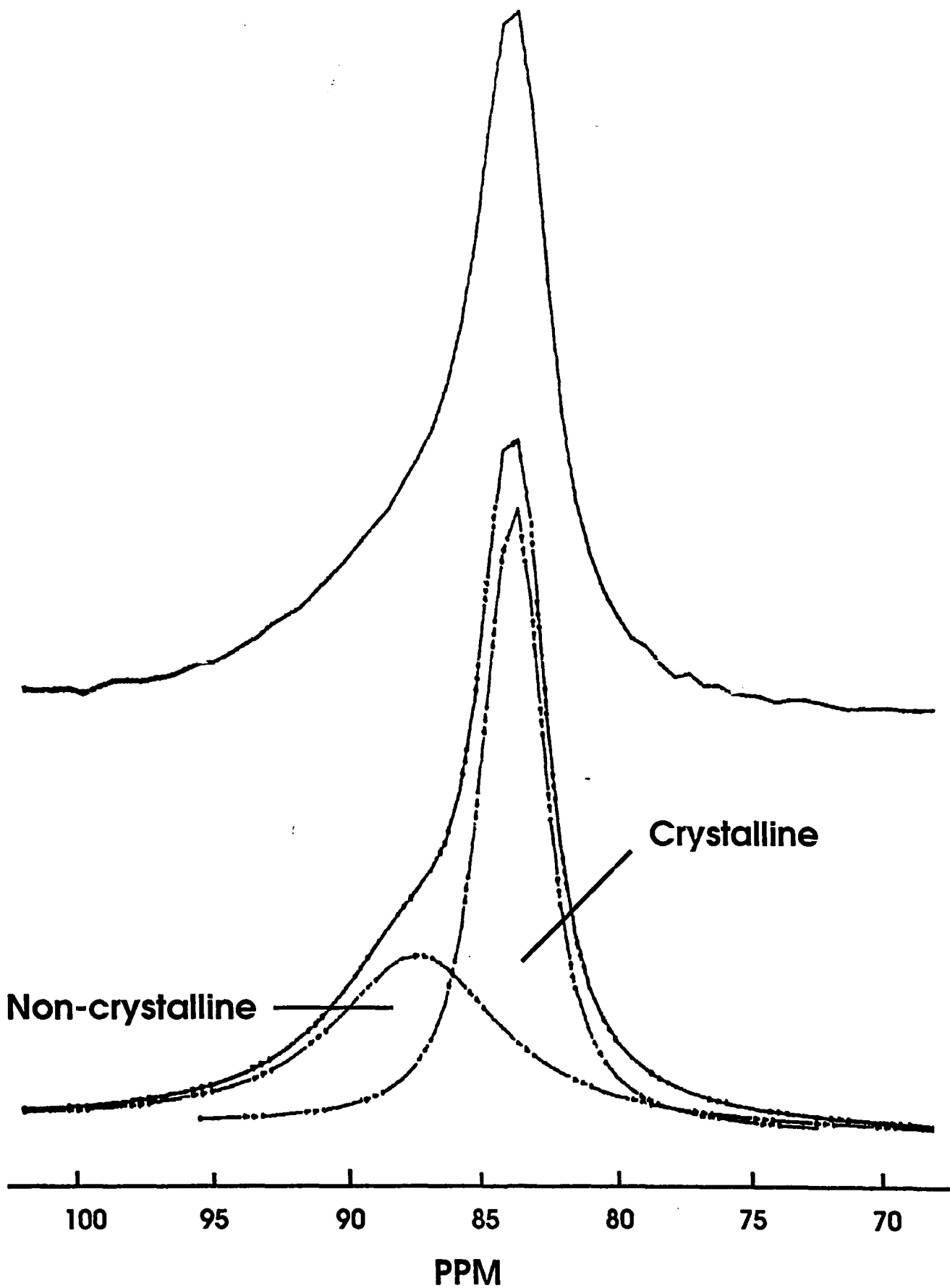


NaH/

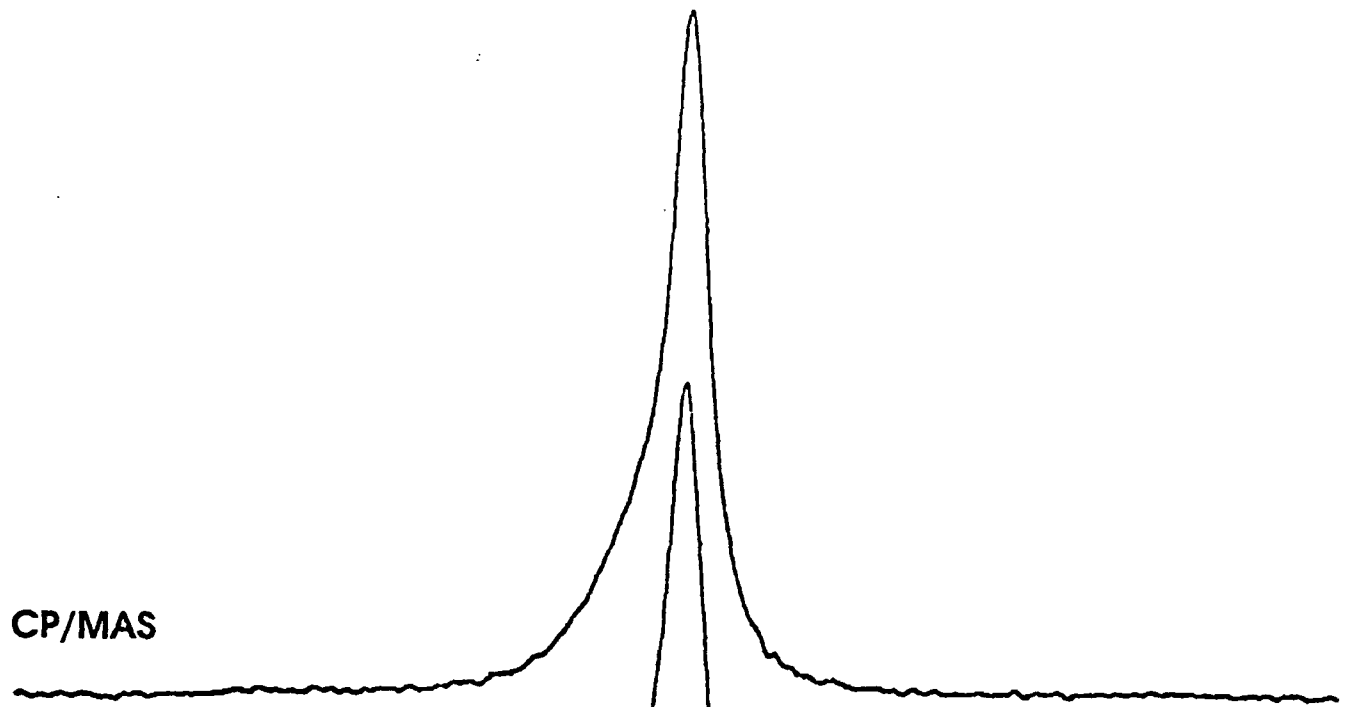


160°C





CP/MAS



Difference Spectrum



90° pulse with MAS



120

110

100

90

80

70

60

50

PPM

