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NATURAL ABUNDANCE <sup>15</sup>N CP/MAS NMR OF SOLID POLYAMIDES:  
A SENSITIVE TECHNIQUE FOR EXAMINING CRYSTALLINE COMPOSITION  
AND CONFORMATION IN THE SOLID STATE

by

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Submitted to

American Chemical Society

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A Sensitive Technique for Examining Crystalline  
Composition and Conformation in the Solid State

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ABSTRACT

High resolution solid state  $^{15}\text{N}$  NMR of several AB and AA-BB polyamides were obtained at the nitrogen natural abundance level. Resonances at 84 and 89 ppm (relative to solid glycine) clearly delineate  $\alpha$  and  $\gamma$  crystal forms, respectively. In addition, intermediate resonances are seen which have not been identified by x-ray or IR. These resonances are thought to belong to rigid noncrystalline or "amorphous" regions in these semicrystalline polymer samples. Amorphous nylons have also been examined using this technique and found to have a broad envelope of resonances indicative of random conformations of amide groups. The origin of the chemical shift difference is rationalized in terms of chain conformation about the plane of the amide group. Semi-empirical MO calculations of model amides show electron density variations which correlate with the shielding and deshielding of the nitrogen atom consistent with this interpretation. Based on these results,  $^{15}\text{N}$  solid state NMR is found to be a sensitive technique for examining local conformations in solid polyamides.

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## INTRODUCTION

Analysis of the morphology and composition of solid polymers is inherently more difficult than that of small molecule crystals and glasses. Thermal analysis and dynamic mechanical analysis have been used to evaluate molecular mobility, relaxation processes, and thermal transitions in solid polymers<sup>2</sup>. Spectroscopic techniques have included mainly x-ray diffraction and infrared for determining the type and degree of crystallinity and order in semi-crystalline polymers such as polyamides<sup>3,4</sup>. Recently, solid state NMR has been developing as a sensitive tool for measuring motion and order using both high-speed spinning and non-spinning methods, and focusing mainly on  $^{13}\text{C}$  CP/MAS,  $^2\text{H}$  wide-line and  $^1\text{H}$  multi-pulse techniques<sup>5-7</sup>.

We have been attempting to develop a two-pronged approach to new polymers and polymeric materials. On the one hand, we are employing new synthetic concepts combining polymer formation with processing to generate the desired product composition in a single step. For example, we have made several high performance polymers and molecular composites with controlled, *in situ* generation of the final structures<sup>8-11</sup>. On the other hand, we are exploring newly available spectral and physical analytical methods which allow molecular characterization of such materials. These methods give information relating as-obtained or end-use molecular composition and microscopic properties to macroscopic behavior. In the latter arena, we have begun examining the use of natural abundance  $^{15}\text{N}$  CP/MAS NMR for evaluating composition and morphology of a variety of aramids, polyamides, polyimides, urethanes and epoxies. We have communicated our initial results on the characteristic peaks seen in  $^{15}\text{N}$  CP/MAS spectra for the two main crystalline forms of nylon 6<sup>12</sup>, and on the multiple peaks seen in longer alkyl polyamides corresponding to two crystalline forms and several "amorphous" conformations of the amide groups<sup>13</sup>.

We report here the characteristic peaks for amide nitrogens in the two main crystalline forms found in a variety of aliphatic polyamides, generally called the  $\alpha$ - and  $\gamma$ -forms. We have also observed and further cataloged peaks which correspond to "amorphous" groups and/or amide units in intermediate or crystal-blended regions which have not been conclusively observed or identified by other techniques. In addition, we discuss the origin of polyamide chemical shifts in terms of conformationally dependent interaction between the plane of the amide group and the attached

methylene groups as demonstrated by semi-empirical molecular orbital calculations. In almost all cases, the  $^{15}\text{N}$  spectra are more complex than expected or predicted based on x-ray and FT-IR data.

### Experimental

Nylon 6 and nylon 6-6 polyamides were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. Zytel 330, APC-110, and APC-121 amorphous nylons were obtained from DuPont Chemical Co. (Parkersburg, West Virginia). Nylons 11, 12, 6-9, 6-10, 6-12 and 6-T were obtained from Scientific Polymer Products (Ontario, New York). Nylon 3 [poly( $\beta$ -alanine)] was prepared by the anionic polymerization of acrylamide. Glycine peptide oligomers and Gly- $\beta$ -Ala were obtained from Sigma Chemical Company (St. Louis, Missouri). The peptides were obtained as crystalline powders and used as received. Commercial polyamides were received as small pellets 1-2 mm in diameter.

The commercially-obtained polyamides were melt-pressed between layers of aluminum foil on a heated hydraulic press at 30,000 to 35,000 psi to give films of uniform thickness of approximately 0.1 mm. The press temperature was adjusted to 20°C or so above the observed melting temperature of each sample. Cooling rates of the molten samples were adjusted to give the desired crystal forms. Most of the polymers we synthesized were examined as precipitated powders, the remainder being melt-pressed films. The presence of  $\alpha$  and/or  $\gamma$  crystal forms was confirmed using IR (Nicolet 5DX FT-IR) and wide-angle x-ray (Phillips PW 1720 x ray unit using a wavelength of 0.154 nm) using methods previously described.<sup>3,4</sup>

Theoretical models were constructed using PCMODEL, a molecular mechanics package suitable for IBM-PC compatible computers.<sup>14</sup> The geometries of the model amides were first optimized using PCMODEL and the data prepared for molecular orbital calculations. Semi-empirical MO calculations were performed using AMPAC, a general purpose modeling package operating on a VAX 11/780 computer and utilizing the AM1 basis set.<sup>15</sup>

Solid state  $^{15}\text{N}$  CP/MAS NMR spectra were obtained on a Bruker MSL 200 spectrometer equipped with a Bruker MAS solids probe. A standard cross-polarization pulse sequence was used with a  $^1\text{H}$  90° pulse of 5  $\mu\text{s}$  and a contact pulse of 1-5 ms with a recycle delay of 3s between successive scans. From 1000 to 10,000 scans were collected for each sample. Spectral width was 25 KHz. The acquisition time was adjusted to give a digital resolution of 3.05 Hz/point. MAS rotor speeds were 3-5 KHz. All measurements were made at 300K. Chemical shifts are reported relative to solid glycine ( $\delta=0$  ppm) as an external reference. Literature  $^{15}\text{N}$  chemical shifts are converted to the glycine scale for comparison.

## Results and Discussion

**Aliphatic Polyamides.** Several reports have appeared on  $^{15}\text{N}$  CP/MAS of synthetic and natural polypeptides showing strong dependence of chemical shift on composition, conformation and the presence of  $\beta$ -alkyl substituents.<sup>16-18</sup> Nylon 6 possesses both an all-coplanar and all-trans  $\alpha$ -form crystalline modification (Figure 1a), and a  $\gamma$ -form (Figure 1b) in which the amide groups are rotated approximately  $60^\circ$  out of the plane of the polymethylene zig-zag<sup>19,20</sup>. We earlier described the  $^{15}\text{N}$  CP/MAS results for nylon 6 and several block and random copolymers containing nylon 6 units<sup>12</sup>. Peaks were reported only for the  $\alpha$ - and  $\gamma$ -forms of this polymer (confirmed by IR and x-ray data) at 84.1 and 89.1  $\delta$  since these were by far the most intense peaks observed. Thus, a downfield shift with a  $\Delta\delta$  value of 5 ppm is observed going from the more thermodynamically stable  $\alpha$  to the  $\gamma$  form possessing the out-of-plane amide group.

Subsequent analysis was carried out on several nylons whose crystal structures had been previously determined.<sup>21</sup> We were surprised at the complexity of the spectra obtained, and concluded that peaks for various amide conformations in the "amorphous" regions were being observed.<sup>13</sup> We have now completed a survey of additionally available polyamides containing alkyl and alkyl-aryl groups in the backbone. Polyamide  $^{15}\text{N}$  chemical shifts are given in Tables 1 and 2 along with their predominant crystal form(s). While we have not yet been able to assign all peaks in the spectra obtained, we believe it important to present our results to promote additional study of the use of  $^{15}\text{N}$  CP/MAS NMR in the characterization of such polymers. Hopefully this will generate useful approaches to determining the relationships between chemical shifts observed and the molecular environment of the associated amide groups.

Table 1. Characteristic  $^{15}\text{N}$  NMR Peaks for Aliphatic A-B and AA-BR Polyamides. Underlined peaks are the most intense in each spectrum.

Sample	Treatment	Predominant Crystal Form	Chemical Shifts <sup>a</sup>					
Nylon 2 (Gly)	--	$\alpha$ -helix					<u>78.5</u> <sup>b</sup>	
Nylon 2 (Gly)	--	$\beta$ -sheet						<u>74.0</u> <sup>b</sup>
Gly-Gly	--	--					<u>83.9</u>	
Gly- $\beta$ -Ala	--	--					<u>83.7</u>	
Triglycine	--	--					77.6	75.5
Tetraglycine	--	--					76.9	71.6
Pentaglycine	--	--					77.5	76.1
Hexaglycine	--	--					76.7	74.8
Poly(Ala)	--	$\alpha$ -helix		<u>89.1</u> <sup>b</sup>				
Poly(Ala)	--	$\beta$ -sheet	<u>97.9</u> <sup>b</sup>					
Nylon 3 ( $\beta$ -Ala)	--	$\alpha^c$		<u>88.1</u>				
Nylon 6	slow/250°	$\alpha^d$					<u>84.0</u>	
Nylon 6	quench/250°	--		88.0			<u>84.3</u>	82.8
Nylon 6	KI/I <sub>2</sub> treat.	$\gamma^d$	92.1	<u>89.0</u>	87.0	85.4		
Nylon 7	slow/250°	$\alpha^e$			87.6 <sup>f</sup>	<u>86.5</u>	<u>85.4</u>	<u>84.1</u>
Nylon 11	slow/250°	$\alpha^e$			87.9	86.0	<u>84.0</u>	82.9 <sup>f</sup>
Nylon 12	slow/250°	$\gamma^g$	90.7 <sup>f</sup>	<u>88.9</u>		86.8 <sup>h</sup>		
Nylon 12	quench/250°	--	90.7 <sup>h</sup>	<u>88.3</u>		<u>86.5</u>	85.6 <sup>f</sup>	84.1 <sup>c</sup>
Nylon 6-6	slow/250°	$\alpha^e$	90.5 <sup>f</sup>		87.4 <sup>f</sup>		<u>84.0</u>	
Nylon 6-8	slow/250°	$\alpha^e$			87.5	86.0 <sup>f</sup>	<u>84.0</u>	
Nylon 6-9	slow/250°	$\alpha^e$	90.3 <sup>f</sup>	88.7	<u>87.6</u>	<u>86.6</u>	85.5	84.5
Nylon 6-10	slow/250°	$\alpha^e$		88.6			<u>85.8</u>	<u>83.8</u>
Nylon 6-10	quench/250°	--	91.2 <sup>h</sup>	89.1 <sup>f</sup>	<u>87.5</u>		<u>85.5</u>	84.0
Nylon 6-12	slow/250°	--		88.7 <sup>i</sup>	87.6 <sup>ii</sup>	86.3	<u>83.9</u>	79.7
Nylon 6-12	quenched	--			87.3	86.6	84.9	<u>83.7</u>

(a) in ppm downfield from glycine ( $\delta = 0$  ppm); (b) data taken from reference 17; (c) from reference 21c; (d) from reference 21d; (e) from reference 21e; (f) shoulder on main peak(s); (g) from reference 21f; (h) weak peak, comparable to noise intensity but appears real

Table 2. Characteristic  $^{15}\text{N}$  NMR Peaks for Amorphous Polyamides and Alkyl-Aryl Copolyamides. Underlined peaks are the most intense in each spectrum.

Polymer	Treatment/History	Chemical Shifts <sup>a</sup>								
A-N3/PBA	ppt rxn mix		<u>95.0</u>		<u>92.7</u>		91.1		89.1	72.7
			70.6		<u>68.4</u>		<u>63.5</u>			
A(N6/PBA)	ppt rxn mix		<u>101.6</u>							<u>80.9</u>
Nylon 6-T <sup>b</sup>	cool from 350°		88.9	<u>87.3</u>	<u>86.3</u>		<u>85.4</u>		83.6	
Zytel 330 <sup>c</sup>	cool from 350°	90.3 <sup>d</sup>	<u>89.7</u>	<u>87.7</u>		<u>83.0</u>	<u>82.0</u>	<u>78.1</u>	72.9 <sup>e</sup>	71.0 <sup>e</sup>
APC-121 <sup>c</sup>	slow cool from 350°	94.0 <sup>e</sup>	<u>88.0</u>		86.6	<u>80.1</u>	<u>77.1</u>	75.5		70.9
APC-110 <sup>c</sup>	commercial pellets	118.7	102.7	<u>100.6</u>	<u>95.9</u>	93.6	<u>91.5</u>			
		<u>90.4</u>	<u>88.4</u>		86.7					

<sup>a</sup>in ppm downfield from glycine ( $\delta = 0$ ppm)

<sup>b</sup>obtained from Specialty Sciences Polymers, Inc.

<sup>c</sup>obtained from E. I. duPont de Nemours, Co., Inc.

<sup>d</sup>shoulder on main peak

<sup>e</sup>peak intensity comparable to noise

Figure 2 gives representative spectra. The lowest trace (a) was observed for a nylon 6-10 sample that had been melt-pressed into a clear thin film and annealed to promote formation of the thermodynamically stable (for this polymer)  $\alpha$  crystalline form. The peak at 83.8  $\delta$  is relatively sharp with a peak-width at half-height of only 3.2 ppm. Trace b is the spectrum of the similarly-produced  $\gamma$ -form of nylon 12. The peak is located at 88.7  $\delta$  and has a peak-width of 4.1 ppm. These two spectra represent some of the cleanest examples we have seen to date of these two crystal forms.

Trace c in Figure 2 was obtained on a nylon 6-10 sample which had been melt-pressed and rapidly quenched to room temperature. It shows a peak corresponding to residual  $\alpha$ -form at 84.3  $\delta$  and a small amount of  $\gamma$ -form at 89.3  $\delta$ . Most interesting are the additional peaks at 85.6 and 87.5  $\delta$ . These two peaks correspond closely to the two additional peaks seen in the spectrum (trace d) of predominantly  $\alpha$ -form nylon 11 with peaks at 83.7, 85.7 and 87.6  $\delta$ . We believe these two peaks correspond to hetero-crystalline domains in these samples in which the conformational, hydrogen-bonded environment of the specific groups represented by these peaks is intermediate to those of the  $\alpha$ - and  $\gamma$ -form environments.

It bears mentioning that polymers are not single crystals and correlations with single crystal models may be suspect.<sup>22</sup> What may in fact be displayed in the upper two spectra in Figure 2 are rigid interphase or transition zones between  $\alpha$  and  $\gamma$  regions as well, perhaps, as amorphous regions as shown schematically in Figure 3. In an elegant discussion on crystal forms of nylon-6, Parker and Lindenmeyer compared the unit cell dimensions published by several authors.<sup>23</sup> Despite many proposed "paracrystalline" forms, it appears that the  $\alpha$  and  $\gamma$  crystal forms predominate although the authors found a continuous variation in the unit cell between  $\alpha$  and  $\gamma$  nylon 6 rather than a sharp distinction. Also, it was shown that the x-ray patterns of samples containing both  $\alpha$ - and  $\gamma$ -forms could not be simulated by a simple mixture of pure  $\alpha$  and pure  $\gamma$ . Based on this discussion,

and on the NMR data reported in Tables 1 and 2, it appears that  $^{15}\text{N}$  CP/MAS NMR is effective in probing at the molecular level material that can only be poorly characterized by x-ray. Our hypothesis is further supported by the spectra in Figure 4 of Zytel 330, a completely amorphous nylon. This sample shows no crystallinity by IR and x-ray analysis. However, overlapping but distinct resonances are seen in the  $^{15}\text{N}$  NMR spectrum indicating distinct chemical environments in an overall amorphous polymer. That is, what is amorphous on a macroscopic level may not be "amorphous" or completely disordered on a molecular level.

The situation appears to correspond to that seen in the NMR analysis of vinyl polymer stereochemistry. Racemic and meso units composing diads, triads, and higher order sequences give individual peaks for many or all of the various combinations. Thus, even a non-stereoregular and non-crystalline vinyl polymer will show multiple peaks corresponding to specific repeat unit sequences. NMR sees these sequences at the molecular or repeat unit level rather than at the overall or average compositional level. On the other hand, x-ray diffraction requires ordered arrays of molecules or polymer sequences that extend far beyond individual repeat units. IR may see at both levels although the ability to resolve fragment differences is limited by the inherent peak width of polymer samples. Apparently what we have with  $^{15}\text{N}$  CP/MAS analysis of polyamides is sufficient spectral width and resolving power to allow observation of segments smaller than those required for obtaining x-ray active  $\alpha$ - or  $\gamma$ -crystalline domain.

These arguments are supported by a recent study of nylon 6 composites by  $^{13}\text{C}$  CP/MAS NMR<sup>23</sup>. The  $^{13}\text{C}$  CP/MAS spectra of most samples showed the presence of two crystalline phases plus an amorphous component. While the carbonyl carbon had an identical chemical shift for both samples (an observation we have confirmed), aliphatic carbons directly attached to the amide group were shifted significantly in the two crystalline forms. In the  $\alpha$ -form, the  $\text{CH}_2$ 's attached to the amide nitrogen and carbon were found at 42.8 and 36.8 ppm, respectively, while those of the  $\gamma$ -form were seen at 39.9 and 33.9. This 3 ppm difference was not observed for the other  $\text{CH}_2$ 's which showed at most a 0.5 ppm difference between the two forms. These researchers attempted to correlate peak intensity with crystalline composition. Quantitation was hampered by overlapping peaks and differences in relaxation rates which make it difficult to subtract amorphous contributions and make direct comparison of the  $\alpha$  and  $\gamma$  components. In addition, the  $^{15}\text{N}$  quadrupole coupling was not detected in the  $^{13}\text{C}$  spectra although (based on our experience) it should be present and lead to additional broadening of the peak for the  $\text{CH}_2$  attached to nitrogen. Careful work by these authors led to consistent quantitation, although correlation with x-ray results was poor. The argument was advanced that the two techniques probe composition at different levels; ie, solid state NMR (at least of crystalline domains) looks at crystallites (0.5-1 nm) that are considerably smaller than those seen by x-ray (5-10 nm). Thus, the NMR data gave consistently higher content values for a particular crystalline form than that calculated from x-ray diffraction data.

A further important conclusion from the  $^{13}\text{C}$  CP/MAS study of nylon 6 was that both extrusion and the presence of additives and fillers gave increased  $\gamma$  content. In fact, our initial report on the  $^{15}\text{N}$  CP/MAS of nylon 6 and its copolymers also showed that the presence of blocks of *p*-benzamide in nylon 6 copolymers induced formation of the normally less stable  $\gamma$  crystalline form<sup>12</sup>. Our results fully support the findings available through solid state carbon NMR. However, despite the fact that our approach may be considered by many to involve the more difficult nucleus to examine by solid state NMR, the method is easy, straightforward and appears to be quantitative. For example, the broad  $\alpha$  and  $\gamma$  resonances in the  $^{13}\text{C}$  alkyl region could only be resolved using peak deconvolution techniques while the  $^{15}\text{N}$  spectra reveal the two crystal forms explicitly. Use of the aliphatic carbon resonances for quantitative analysis is further complicated by the significant contribution of the amorphous fraction to the overlapping signals. Additional advantages include simpler spectra, greater peak separation and spectral width, direct observation of the atom of interest for hydrogen bonding and crystallinity differences, and (as will be shown below), a more sensitive chemical shift-conformation relationship for the range of dihedral angles involved.

**Polypeptides.** Natural and synthetic polypeptides are the only polyamides previously investigated by  $^{15}\text{N}$  CP/MAS NMR.<sup>17</sup> Of the nylon species shown in Table 1, the polypeptides nylon 2 (polyglycine) and  $\alpha$ -methyl nylon 2 (polyalanine) form two types of ordered structures. For nylon 2, the amide nitrogen chemical shift is upfield for the planar  $\beta$ -sheet (74.0) and downfield for the twisted  $\alpha$ -helix (78.5), consistent with our argument of conformationally dependent nitrogen chemical shifts. In fact, the  $\Delta\delta$  value of 4.5 ppm compares well with that of 4.5 ppm seen for the two main forms of nylons. The glycine-containing oligomers shown for comparison in Table 1 demonstrate the complexity of polymer crystallinity with increasing molecular weight. As the number of residues grows, more conformations are conceivable. However, they maintain similarities in their chemical shifts with resonances that fall between those reported for  $\alpha$ -helix and  $\beta$ -sheet (polyglycine).

Polyalanine, however, shows the opposite effect. The twisted helix is now upfield (89.1 ppm) rather than downfield of the planar sheet (97.9 ppm). This must be due to a conformationally dependent substituent effect as described previously for  $^{15}\text{N}$  solution<sup>6,18</sup> and solid state<sup>17</sup> NMR of several poly(amino acids). An alkyl substituent in the  $\alpha$ -position causes a downfield shift of ca. 9-12 ppm. In solution, of course, the peak position is an average of the chemical shifts of the allowed conformations. Nonetheless, this reverse shielding effect appears to be peculiar to  $\alpha$ -substituted polypeptides. Complete understanding of the conformation dependency of  $^{15}\text{N}$  chemical shifts awaits appropriate studies with crystalline (for solid state behavior) and conformationally rigid models (for solution analysis).

Linear nylon 3 (poly  $\beta$ -alanine), although shown to exist only in the  $\alpha$  crystal form,<sup>21c,21e</sup> has a chemical shift (88.1 ppm) closer to that of the  $\gamma$  form seen in higher nylon analogues, a result for which we have no definitive explanation. This effect may be the opposite of that shown by nylon 2 and caused by the proximity of the carbonyl group to the amide. Through-space shielding for the nylon 2 nitrogen may result from the  $\pi$ -

cloud of carbonyl in the  $\alpha$  position in the next repeat unit, while for nylon 3 the nitrogen is somehow deshielded by the  $\beta$ -carbonyl through a through-bond or through-space mechanism. It is clear from the data in Table 1 that as the alkyl chain length between amide groups reaches 6 methylene units or beyond, secondary effects from adjacent amide units become less important and the chemical shifts depend only on amide conformation. The  $^{13}\text{C}$  CP/MAS chemical shift differences in peptides have been attributed to hydrogen-bonding, conformational effects, and helix formation.<sup>25</sup> Interactions that affect the  $^{15}\text{N}$  chemical shift should be similarly more complex in short chain nylon analogues than in nylons with longer alkyl chains.

### Conformational Effects on $^{15}\text{N}$ Chemical Shift

The origin of these chemical shift differences was originally unclear. It seemed reasonable at first that the chemical shift differences would be due to differences in hydrogen-bonding in the crystalline and amorphous domains. In amorphous polyamides, however, IR studies indicate that nylon-type polymers are completely hydrogen bonded making it improbable that the chemical shift change is due to some combination of "free" and "hydrogen-bonded" amide units.<sup>26</sup> In addition, x-ray studies show the hydrogen-bond length in both the  $\alpha$  and  $\gamma$  crystalline forms of nylon 6 to be identical to within 0.002 nm.<sup>19,27</sup> Figure 1 (showing the planar  $\alpha$  and twisted  $\gamma$  structures) suggests that the chemical shift difference may be due solely to conformationally-dependent changes about the amide bond. This interpretation is supported by  $^{15}\text{N}$  NMR solution spectra of N-substituted amides.<sup>28</sup> Simple E,Z isomerism about the amide C-N bond can be observed as two distinct resonances separated by 1-3 ppm.

This simple explanation is made more complex by substituent effects. In  $^{13}\text{C}$  NMR, replacement of hydrogens by other substituents, especially those  $\gamma$  to carbon nuclei, exerts a strong effect on chemical shifts (the " $\gamma$  gauche effect").<sup>29,30</sup>  $^{13}\text{C}$  CP/MAS NMR has thus been shown to be sensitive to secondary structure in peptides and  $\alpha$ -substituted nylons.<sup>31</sup> The  $^{13}\text{C}$  CP/MAS spectra of  $\alpha$  and  $\gamma$  nylon 6 (Figure 5), however, shows the carbonyl peaks to be identical within the limits of spectral resolution. The amide nitrogen is apparently more sensitive to conformation than are the carbonyl carbons. In more recent work involving the  $^{15}\text{N}$  CP/MAS spectra of peptides,<sup>16</sup> downfield shifts were observed in peptides with a carbon substituent  $\beta$  to the nitrogen in addition to shifts related to  $\alpha$ -helix and  $\beta$ -sheet conformations. A steric  $\gamma$  gauche-like effect for nitrogen may be responsible for the downfield chemical shift<sup>37</sup>.

To further explore the potential of  $^{15}\text{N}$  NMR to evaluate crystallinity and conformation requires additional NMR analysis coupled with molecular modeling. SCF-MO and valence shell theory have both been used to predict shielding of nuclei as a function of "effective nuclear charge" thus providing a method of correlating chemical shifts with local charge density.<sup>32,33</sup> More importantly, perturbations in charge density have been related to conformational geometry and steric strain.<sup>32</sup> Semiempirical calculations have been successful in reproducing experimental trends in magnetic shielding.<sup>34</sup>

Our initial efforts involving semiempirical calculations on a model system were encouraging. We have now calculated the heats of formations and electron distributions for the two conformations known to exist for the amide groups in the  $\alpha$ - and  $\gamma$ -forms of nylons. The models (Figure 6) consist of a central amide with two n-propyl fragments attached to the carbonyl and nitrogen atoms. The  $\alpha$ -form calculation was for an extended planar zig-zag (Figure 6a) of the methylene chains with the amide group lying in this plane. All bond lengths, bond angles, and dihedral angles for the  $\alpha$  model were fully optimized. The  $\gamma$ -form model (Figure 6b) had the amide plane rotated  $60^\circ$  from the two coplanar methylene chains attached to either side of the amide.<sup>19,20</sup> The amide plane dihedral angle with respect to the attached methylenes was fixed throughout the calculation. All other parameters were allowed to optimize.

The atom electron density is calculated according to the equation (1),<sup>35</sup>

$$q_{\text{atom}} = \sum_1^i n c_i^2 \quad (1)$$

where  $n$  is the number of electrons in an occupied orbital (2 for unperturbed ground state) and  $c_i$  is the  $i$ th coefficient of each secular equation describing a localized orbital. The net charge on each atom is defined in equation (2),

$$q_{\text{net}} = q_{\text{val}} - q_{\text{atom}} \quad (2)$$

where  $q_{\text{val}}$  is the normal atom valence. Table 3 lists the calculated charges for the amide nitrogens, carbons and oxygens in our model.

The  $\alpha$ -form nitrogen had higher electron density as indicated by the relative charge (-0.393, vs -0.378) than that of the  $\gamma$ -conformation, consistent with a more shielded, up-field chemical shift value for this nitrogen. Similarly, the oxygen of the  $\alpha$ -form was more electron poor than that of the  $\gamma$ -form but the difference was surprisingly small. The carbonyl and  $C_\alpha$  carbons showed little difference in charge, a fact correlating well with the observation of identical (although broad) peak envelopes and chemical shifts for nylon 6 (Figure 5) in the two main crystalline forms in  $^{13}\text{C}$  CP/MAS NMR.

Table 3 shows a large buildup of charge on  $C_N$  which should result in an upfield shift in the  $^{13}\text{C}$  NMR. As discussed earlier, this prediction was verified by Veeman and coworkers in their study of nylon 6 composites with  $^{13}\text{C}$  CP/MAS NMR.<sup>23</sup> The  $C_N$  resonance of the  $\gamma$  form was shifted upfield by almost 3 ppm from the  $\alpha$  crystal form. Nevertheless, the buildup of charge on  $C_N$  was unexpected. Redistribution of charge density from the nitrogen to oxygen via conjugated  $\pi$  orbitals in the amide group seemed more reasonable. Movement of charge from the nitrogen to  $C_N$  via a  $\sigma$  bond seemed unlikely. Another possible explanation was that protons on  $C_N$  were somehow influencing the charge distribution by through-space interaction with the

**Table 3.** Calculated Partial Charges for Planar and Twisted Conformations of N-Propyl Propionamide

Atom	Planar Form ( $\alpha$ )	Twisted Form ( $\gamma$ )	$\Delta q$
N	-0.393	-0.378	0.015
O	-0.369	-0.372	0.003
C (carbonyl)	0.298	0.298	0.000
C <sub><math>\alpha</math></sub>	-0.178	-0.177	0.001
C <sub><math>\beta</math></sub>	-0.019	-0.032	0.013

amide group. This hypothesis was supported by  $^1\text{H}$  and  $^{13}\text{C}$  NMR characterization of cyclic glycol peptides where the C-H coupling constant was found to be conformationally dependent, behavior which was rationalized as an interaction of the C-H bond with the nitrogen  $p_z$ -orbital.<sup>36</sup>

To test this hypothesis, we modeled several small molecules using AMPAC and varied the torsion angle of substituents with the plane of the amide group. Two possible interactions were contemplated: (1) the interaction of protons on the N-alkyl substituent with the nitrogen atom and (2) the interaction of protons on C <sub>$\alpha$</sub>  and C <sub>$\beta$</sub>  with amide  $\pi$ -orbitals. Figure 7 shows a plot of nitrogen charge versus the torsion angle for the methyl group of acetamide. A maximum is seen for the form in which the C <sub>$\alpha$</sub>  protons are gauche to nitrogen. This agrees qualitatively with the NMR data in that increased electron density results in nuclear shielding and corresponding upfield shifts. Similar results are obtained for N-methyl acetamide as depicted in Figure 8. Figure 9 shows a similar treatment of N-ethyl acetamide except now  $\gamma$ -protons are associated with the N-alkyl portion. The N-C <sub>$\alpha$</sub>  bond was rotated and the nitrogen electron density calculated. A more drastic decrease in electron density is seen than from previous models.

A series of model systems was generated and their atom partial charges calculated to test whether protons  $\gamma$  to the amide nitrogen could alter the nitrogen electron density. Table 4 shows the results of optimized AMPAC models. The calculated partial charge on the nitrogen atom is displayed as well the number of protons  $\gamma$  to the nitrogen. The  $^{15}\text{N}$  solution NMR chemical shifts are reported for comparison.<sup>37</sup> For convenience, arbitrary chemical shifts are listed relative to dimethyl formamide (DMF = 0 ppm) to allow most of the chemical shifts to be displayed as positive values.

Ideally, as partial negative charge increases or decreases on the nitrogen, there should be a corresponding upfield or downfield shift, respectively, in the  $^{15}\text{N}$  chemical shift. Since hydrogen bonding and solvent/concentration effects are ignored in gas phase AMPAC calculations, the AMPAC partial charges cannot predict chemical shifts quantitatively. For example, in comparing the primary amides with those having one N-methyl substituent, AMPAC predicts a large downfield shift upon alkylation of the nitrogen. The reported chemical shifts show almost no change. This suggests that hydrogen bonding and other intermolecular

**Table 4.** AM1 Calculation Results for Amide Model Compounds.

<u>Molecule</u>	<u>Charge on N</u>	<u>Chemical Shift</u>	
		<u>CH<sub>3</sub>NO<sub>2</sub> = 0 ppm<sup>a</sup></u>	<u>DMF = 0ppm</u>
Formamide	-0.448	-269.1 <sup>b</sup>	7.6
N-methyl formamide	-0.4023	-270.1 <sup>b</sup>	6.6
Acetamide	-0.440	-271.0 <sup>b</sup>	5.7
N-methyl acetamide	-0.391	-273.7 <sup>b</sup>	3.0
N-ethyl acetamide	-0.390	-254.8 <sup>b</sup>	21.9
N-n-propyl acetamide	-0.3807	-260.4 <sup>c</sup>	16.3
N-i-propyl acetamide	-0.3823	-244.1 <sup>c</sup>	32.6
N-t-butyl acetamide	-0.3803	-241.8 <sup>c</sup>	34.9
N-methyl propionamide	-0.3959	-276.5 <sup>b</sup>	0.2
N-methyl isobutanamide	-0.3890	-278.4 <sup>b</sup>	-1.7
N,N-dimethyl formamide	-0.3527	-276.7 <sup>d</sup>	0
N,N-diethyl formamide	-0.3473	-250.2 <sup>d</sup>	26.5
N,N-dimethyl acetamide	-0.3457	-281.0 <sup>d</sup>	-4.3
N,N-diethyl acetamide	-0.3404	-249.6 <sup>d</sup>	27.1

<sup>a</sup>Chemical shifts and experimental conditions reported in ref. 37

<sup>b</sup>neat liquid

<sup>c</sup>60% in CHCl<sub>3</sub>

<sup>d</sup>0.08 M Cr(acac)<sub>3</sub> added to neat liquid

interactions exert the major influence on chemical shifts in solution. In the higher alkyl homologues, especially the N-alkyl acetamides where substituents R on the nitrogen are varied, a reasonably consistent trend is observed. AMPAC predicts a decrease in nitrogen charge as R is varied from 3° < 2° < 1° < methyl. The chemical shifts reported for these amides follows approximately the same order with t-butyl acetamide having the largest downfield shift and lowest calculated nitrogen charge. AMPAC predicts little if any difference in nitrogen atom charge on increasing the chain length of the carbonyl substituent. The NMR data, however, shows an upfield trend for the series of N-methyl amides. While AMPAC appears to fail in its predictions for this series, it should be noted the  $\Delta\delta$  in this series is about 5ppm, well within a narrow range where experimental parameters could account for the discrepancy. The N-alkyl acetamides, on the other hand, show a total  $\Delta\delta$  of almost 30 ppm which can only be related to a substituent effect.

In evaluating these model systems, it is important to remember they represent gas phase behavior and ignore dipolar interactions, hydrogen bonding, and other non-ideal situations present in both the solid state and in solution. It must also be remembered that the solution chemical shifts given in the table represent conformationally averaged values while the calculated values are for only a single conformation. Semi-empirical MO methods have been remarkably successful in the past in predicting properties for which they were not parameterized.<sup>38</sup> As previously mentioned, quantum chemical calculations have shown the <sup>13</sup>C CP/MAS chemical shift of peptides to be affected by both hydrogen bonding and conformation.<sup>25</sup> The hydrogen bond contribution to <sup>13</sup>C chemical shifts is reported to be dominant for N--O bond lengths less than 0.26 nm.<sup>27</sup> For both  $\alpha$  and  $\gamma$  nylons, the N--O bond length is greater than 0.28 nm.<sup>27</sup> At these distances, hydrogen bond strength drops off rapidly leaving conformational interactions to dominate the chemical shift in <sup>13</sup>C CP/MAS NMR. <sup>15</sup>N CP/MAS chemical shifts appear to be similarly influenced.

Although hydrogen bonding is not accounted for in these quantum chemical models, the electronic structures simulate  $\alpha$  and  $\gamma$  nylon chemical shift trends remarkably well. If the total nitrogen shielding  $\sigma$  for each of the conformations is represented by the equations

$$\sigma_{\alpha} = \sigma_{E\alpha} + \sigma_{H\alpha} \quad (3)$$

$$\sigma_{\gamma} = \sigma_{E\gamma} + \sigma_{H\gamma} \quad (4)$$

where  $\sigma_E$  is the sum of local electronic contributions and  $\sigma_H$  is the shielding induced by hydrogen bond perturbation of the system, the terms  $\sigma_H$  may be eliminated provided  $\sigma_{H\alpha} = \sigma_{H\gamma}$ . The assumption of  $\sigma_{H\alpha} = \sigma_{H\gamma}$  is probably valid since the hydrogen bond lengths and orientations are nearly equivalent for the  $\alpha$  and  $\gamma$  crystal forms.<sup>27</sup> An alternative explanation may be that the  $\alpha$  and  $\gamma$  structures lie in the domain of long hydrogen bond length where conformation, not hydrogen bonding, exerts the major influence on the chemical shift.<sup>27</sup> In this case,  $\sigma_H$  in eqn. (3) and (4) can be effectively ignored. Either case implies that the total shieldings, and ultimately the chemical shifts, are due to local electronic contributions principally affected by conformation.

## Conclusion

We conclude that natural abundance  $^{15}\text{N}$  CP/MAS NMR analysis of nitrogen-containing polymers is not only feasible but is sensitive to composition, conformation and crystalline form. Amorphous polyamides as well crystalline forms can be characterized with this technique. We believe the origin of the chemical shift differences is due to conformation as well as substituent effects similar to the " $\gamma$  gauche effect" previously observed in  $^{13}\text{C}$  NMR. This conclusion is supported qualitatively with semi-empirical MO calculations which correlate with the experimental data. We hope to continue the NMR studies and molecular modeling of these and related synthetic polymers.

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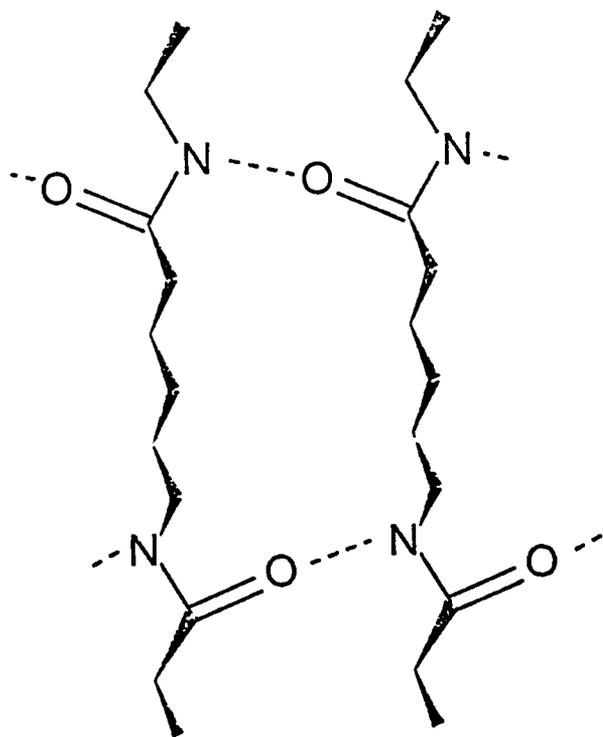
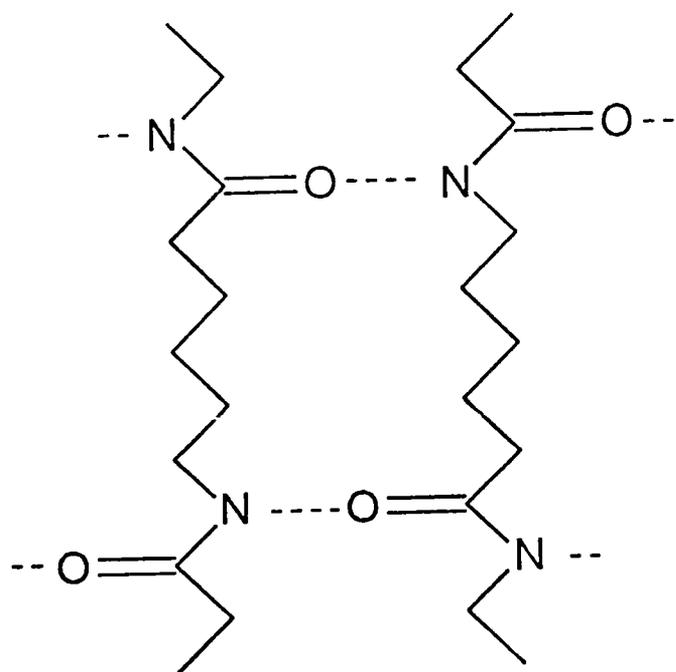
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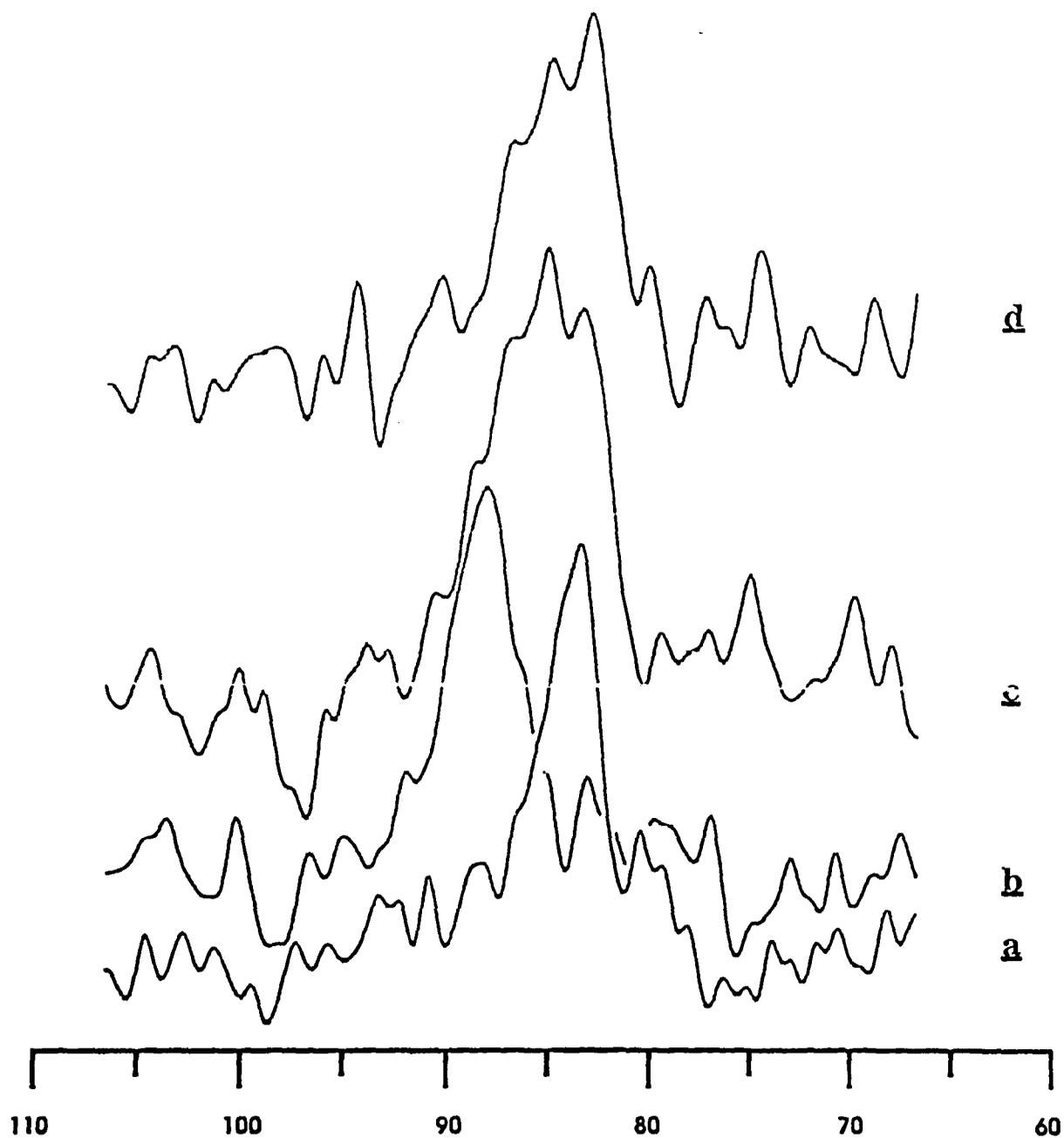
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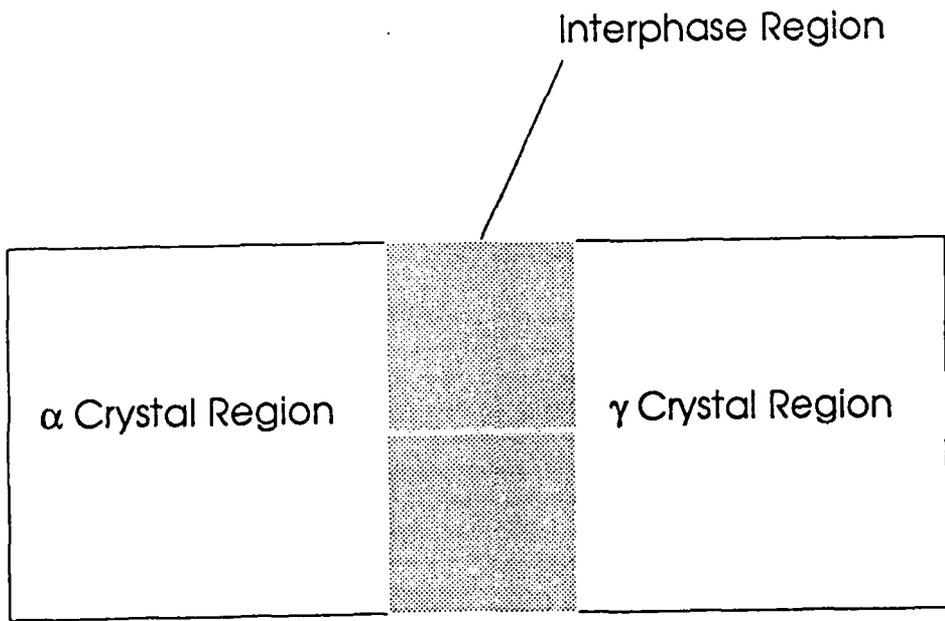
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**$^{15}\text{N}$  CP/MAS NMR spectra of Aliphatic Nylons: a) nylon 6-10  $\alpha$ -form; b) nylon 12  $\gamma$ -form; c) nylon 6-10 and d) nylon 11 quenched from the melt showing intermediate "amorphous" peaks.**

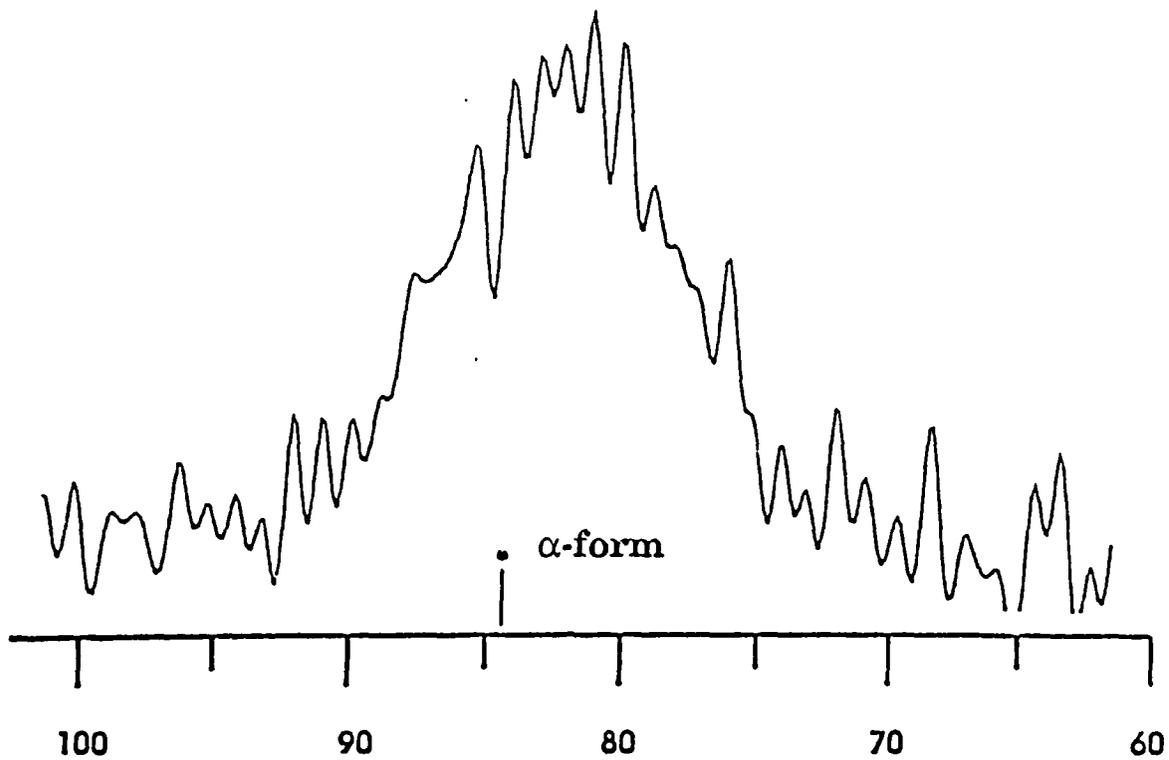


Interphase Region

$\alpha$  Crystal Region

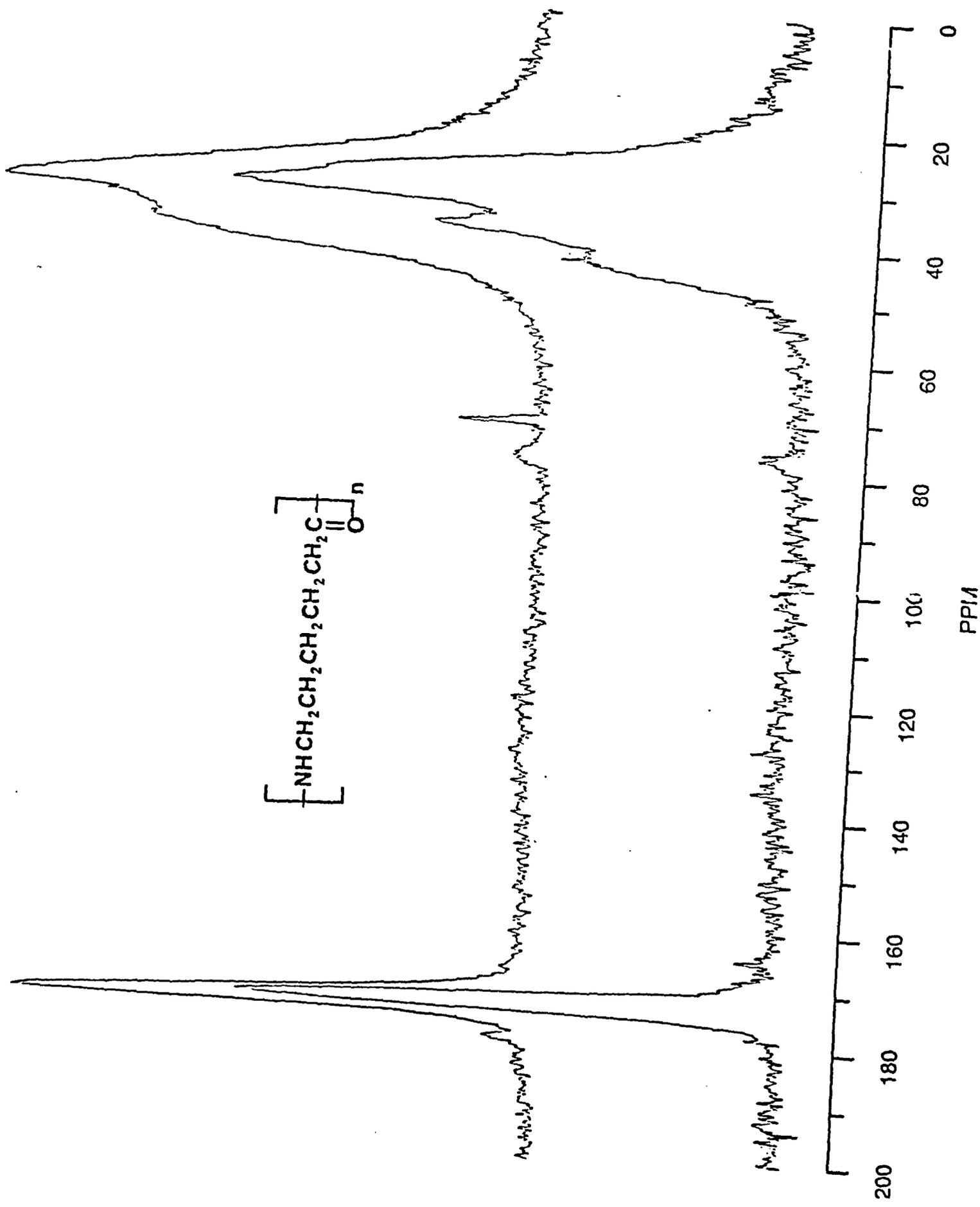
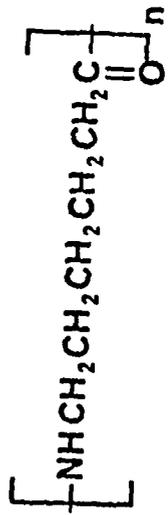
$\gamma$  Crystal Region

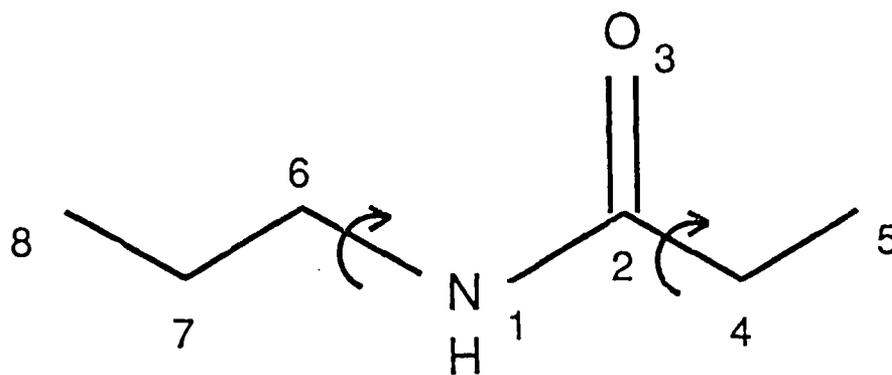
Amorphous Region



**<sup>15</sup>N CP/MAS NMR spectrum of ZYTEL 330<sup>\*</sup> brand of amorphous nylon showing multiple peaks. Relative position of α crystal form is shown for comparison.**

**<sup>\*</sup>Trademark of Dupont Chemical Co., Inc.**





$\alpha$  form: Dihedral 7,6,1,2 = 1,2,4,5 =  $180^\circ$

$\gamma$  form: Dihedral 7,6,4,2 =  $120^\circ$ ; Dihedral 1,2,4,5 =  $240^\circ$

