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NATURAL ABUNDANCE ^{15}N CP/MAS OF NYLONS AND ARAMIDS.
A SENSITIVE TECHNIQUE FOR EXAMINING
CRYSTALLINE COMPOSITION AND CONFORMATION
IN SOLIDPOLYAMIDES

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) We have examined a variety of polyamides and aramids using natural abundance ¹⁵ N CP/MAS NMR. These have included commercially available A-B and AA-BB nylons, Kevlar and poly(p-benzamide) as well as a number of block and graft copolymers synthesized in our laboratory. Excellent correlation was observed between the type of crystalline form adopted by polyamides (and modifications) and the chemical shift of the rigid amide nitrogens. Values for the two form center around 84 ppm (relative to glycine at 0 ppm) and 88 ppm, respectively. For some samples, unexplained peaks between the two main crystalline peaks are tentatively assigned to rigid amide conformations that are not x-ray active but are seen by NMR. Aramids show similar complexity. Block and graft copolymers display characteristic peaks for composition (aryl vs alkyl nitrogen substituents) and for conformation and crystallinity.			
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Natural Abundance ^{15}N CP/MAS NMR of Nylons and Aramids.
A Sensitive Technique for Examining Crystalline
Composition and Conformation in Solid Polyamides

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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 polymers¹. Spectroscopic techniques have included mainly x-ray diffraction and infrared for determining the type and degree of crystallinity and order in semi-crystalline polymers, especially polyamides^{2,4}. Recently, solid state NMR has been developing as a sensitive tool for measuring motion and order using both high-speed spinning and non-spinning samples and focusing mainly on ^{13}C CP/MAS, ^2H wide-line and ^1H multi-pulse techniques⁵⁻⁷.

We have been attempting to develop a two-pronged approach to new polymers and polymeric materials. On the one hand, we are employing new concepts using synthesis to generate the desired product composition directly. For example, we have made several high performance polymers and molecular composites with controlled or in situ generation of the final structures⁸⁻¹¹. 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}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}N CP/MAS spectra for the two main crystalline forms of nylon 6¹², and on the multiple peaks seen in longer alkyl polyamides corresponding to two crystalline forms and several "amorphous" conformations of the amide groups¹³.

We report here our initial success in identifying the characteristic peaks for amide nitrogens in the two main crystalline forms found in nylons, generally called the α - and γ -forms. In addition, we have 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. We have also examined aramids, and aramid-nylon graft copolymers. In almost all cases, the ^{15}N spectra were more complex than expected or predicted based on x-ray and FT-IR data.

Experimental

Nylon 6 polyamide was obtained from Aldrich Chemical Company, Milwaukee, Wisconsin. Zytel 330 and APC-121 amorphous nylons were obtained from DuPont Chemical Co., Parkersburg, West Virginia. Kevlar aramid pulp and fibers were obtained from DuPont Chemical Co., Central Research and Development, Wilmington, Delaware. Nylons 11, 12, and 6-10, were obtained from Scientific Polymer Products, Ontario, New York. Commercial polyamides were received as small pellets 1-2 mm in diameter. Kevlar graft copolymers were synthesized in our laboratories as previously described.⁷

Kevlar fibers were used as received. Kevlar pulp was extracted for 24 hours with methylene chloride and dried *in vacuo* at 100°C. 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. The synthesized polymers described here were examined as melt-press 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, $\lambda = 0.154$ nm) using methods previously described.^{3,4} Molecular modeling calculations were performed using AMPAC¹⁴, a user-friendly quantum-mechanical modeling program operating on a VAX 11/780 computer.

Solid state ^{15}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 ^1H 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. ^{15}N chemical shifts reported in the literature are converted to the glycine scale and reported relative to glycine.

Results and Discussion

Several reports have appeared on ^{15}N CP/MAS of synthetic and natural polypeptides showing strong dependence of chemical shift on composition, conformation and the presence of β -alkyl substituents.¹⁵⁻¹⁷ Chemical shifts for polyglycine (nylon 2) amides in the all-trans crystalline conformation (the β -pleated sheet) and the twisted conformation of the α -helix were found at 74.0 and 78.5 δ , respectively.¹⁶ The out-of-plane twist caused a downfield shift of 4.5 δ .

Nylon 6 also possesses an all-trans α -form crystalline modification (Figure 1a) and a γ -form (Figure 1b) in which the amide groups are rotated approximately 60° out of the plane of the polymethylene zig-zag.^{18,19} We earlier described the ^{15}N CP/MAS results for nylon 6 and several block and random copolymers containing nylon 6 units.¹² Peaks were reported only for the α - and γ -forms of this polymer (confirmed by IR and x-ray data) at 84.1 and 89.1 δ since these were by far the most intense peaks observed. Again a downfield shift is observed for the out-of-plane amide group with a $\Delta\delta$ value of 5 δ in this case.

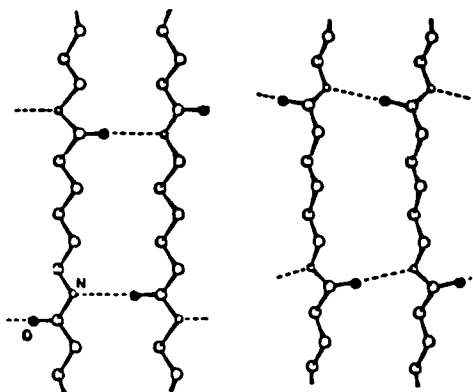


FIGURE 1: a) Alpha structure (left) and b) gamma structure of Nylon 6 homopolymer. (From ref. 19)

Subsequent analysis was carried out on several nylons whose crystal structures had been previously determined.^{20,21} 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. We have now completed an initial survey of available polyamides containing alkyl, aryl and both alkyl-aryl groups in the backbone. 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 interest in the use of ^{15}N CP/MAS NMR characterization of polymers, and perhaps generate approaches to determining the relationships between chemical shifts observed and the molecular environment of the associated amide groups.

The 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 α crystalline form. The peak at 83.8 δ is relatively sharp with a peak-width at half-height of only 3.2 ppm. Trace b is the spectrum of the similarly-produced γ -form of nylon 12. The peak is located at 88.7 δ and has a peak-width of 4.1 ppm. These two spectra represent the cleanest examples we have seen to date of these two crystal forms.

Trace c in the Figure 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 α -form at 84.3 δ and a small amount of γ -form at 89.3 δ . Most interesting are the additional peaks at 85.6 and 87.5 δ . These two peaks correspond closely to the

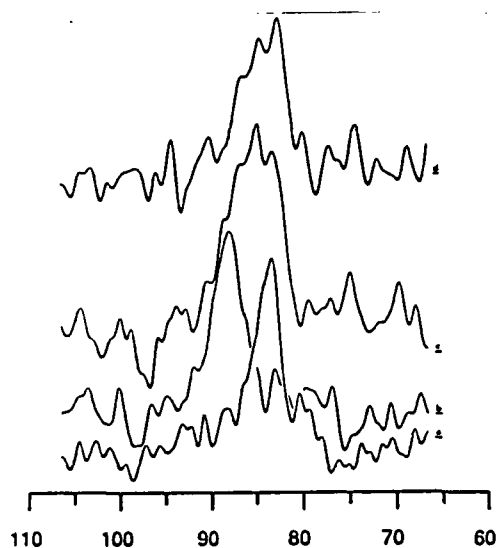


FIGURE 2. ^{15}N CP/MAS spectra of aliphatic nylons.

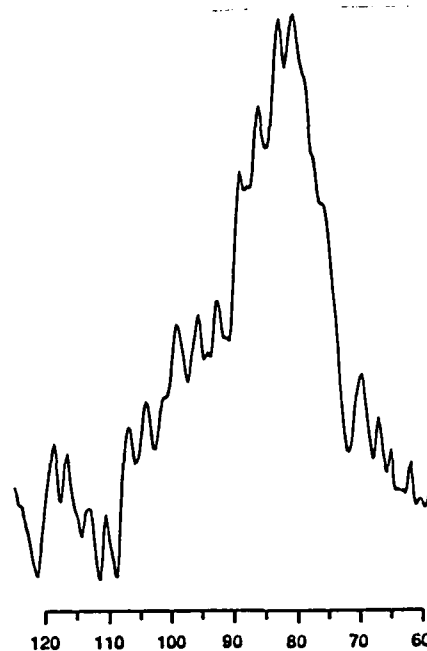


FIGURE 3. Amorphous nylons APC-121 (above) and Zytel-330 (at left) showing multiple resonances.

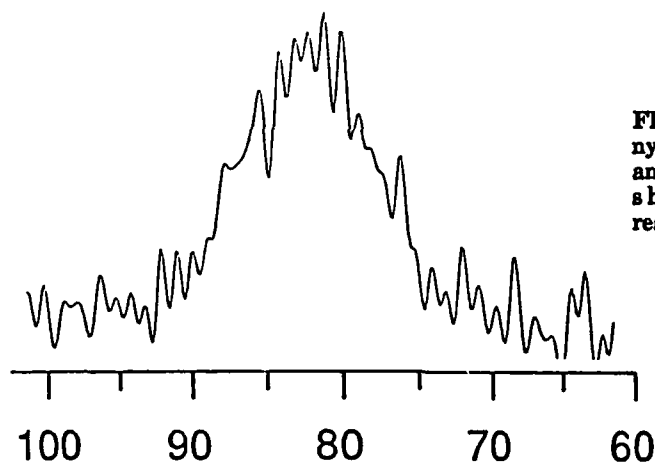
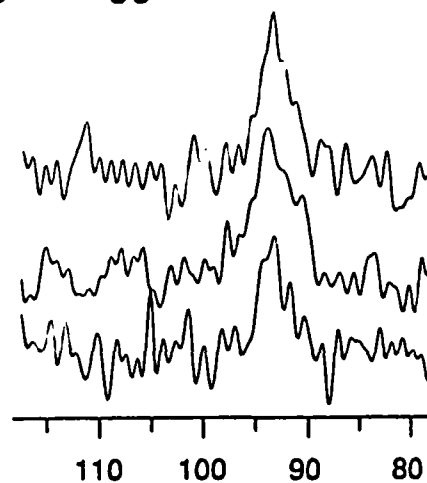


FIGURE 4. ^{15}N CP/MAS spectra (right) of Kevlar (PPTA) aramid: Lower trace, precipitated pulp; upper trace, fibers; middle trace, pulp annealed at 500°C .



two additional peaks seen in the spectrum (trace d) of predominantly α -form nylon 11; peak positions 83.7, 85.7 and 87.6 δ . We believe these two peaks correspond to amorphous or hetero-crystalline domains in these samples in which the conformational and hydrogen-bonding environment of the specific groups represented by these peaks is intermediate to those of the α - and γ -form environments. The situation appears to correspond to that seen in the NMR analysis of vinyl polymer stereochemistry. Both racemic and meso 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. That is, NMR sees at the molecular or repeat unit level rather than at the overall or average compositional level. Similarly, x-ray diffraction requires ordered arrays of molecules or polymer sequences that extend 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}N CP/MAS analysis of polyamides is sufficient spectral width and resolving power to allow observation of segments smaller than those required for obtaining an x-ray active α - or γ -crystalline domain. This hypothesis is supported by the spectra in Figure 3 of two amorphous nylons. Neither show crystallinity in IR and x-ray analysis. However, broad but distinct resonances are seen in the ^{15}N NMR indicating distinct chemical environments existent in a presumably amorphous polymer.

Figure 4 displays the ^{15}N CP/MAS spectra of poly(phenylene terephthalamide) (Kevlar) processed under various conditions. The lower trace shows the spectrum of Kevlar pulp. Trace b above shows the pulp after annealing at 500 $^{\circ}\text{C}$ for 8 hours. Trace c shows the spectrum of the oriented fiber. In all three spectra, a single resonance is seen with two other peaks upfield. The presence of two crystal forms of Kevlar has been postulated and evaluated by x-ray.^{22,23} The spectral and chemical shift differences indicate ^{15}N CP/MAS may be useful in identifying distinct crystal forms of aramids.

The usefulness of ^{15}N CP/MAS NMR is further demonstrated in Figure 5 of Kevlar with grafts of nylon-3. X-ray analysis of this composite, after annealing, revealed only PPTA crystal form I⁶. The NMR spectrum reveals much more information. In addition to characteristic peaks for nylon-3 and the alkylated nitrogen, the group of peaks in the region from -247 to -253 suggests reduced PPTA crystallinity and possible "amorphous" regions induced in the typically highly crystalline polymer. The amorphous and semicrystalline behavior of N-alkyl aramids has been previously established.^{24,25} ^{15}N CP/MAS offers the potential for investigating these irregular forms which are not amenable to conventional x-ray analysis.

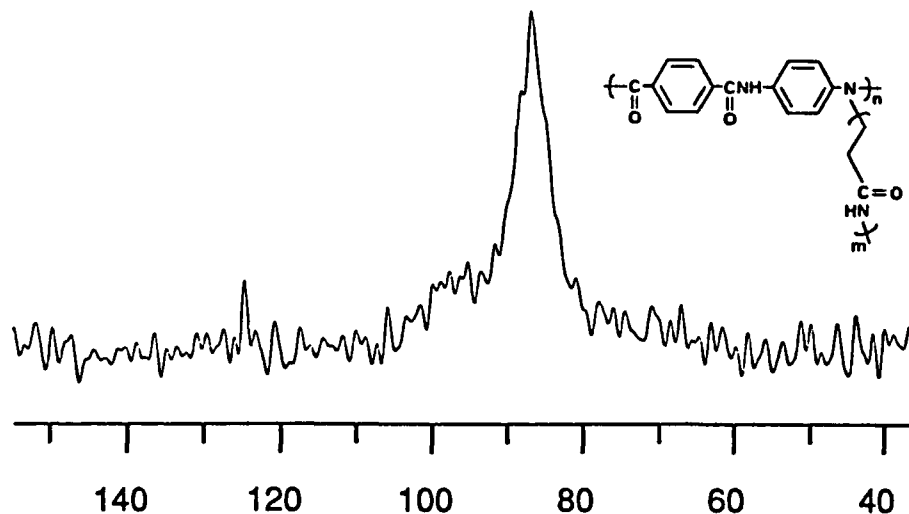


FIGURE 5: Kevlar-nylon 3 graft copolymer showing graft site and multiple resonances for aramid nitrogens.

To further explore the potential of ^{15}N NMR to evaluate crystallinity and conformation requires additional NMR analysis coupled with molecular modeling.¹⁷ Initial results in applying the latter to understand the former are encouraging. We have calculated the energetics and electron distributions for the two conformations known to exist for the amide groups in the α - and γ -forms of nylons. The model consisted of a central amide with two n-hexane fragments attached to the carbonyl and nitrogen atoms. The α -form calculation was for an extended planar zig-zag of the methylene chains with the amide group lying in this plane. The γ -form calculation had the amide plane rotated 60° from the two coplanar methylene chains on attached to the amide. Essentially identical heats of formation were obtained for both. Most interesting is the electron densities calculated for the amide nitrogens, carbons and oxygens. The α -form nitrogen had significantly higher electron density (0.4 vs 0.32) than that of the γ -conformation, consistent with the more shielded chemical shift value for this nitrogen. Similarly, the oxygen of the α -form was more electron poor than that of the γ -form. Not surprisingly, the carbonyl carbons showed little difference in electron density, a fact correlating well with the observation of identical although broad peak envelopes and chemical shifts for nylons in the two main crystalline forms in ^{13}C CP/MAS NMR.

We conclude that natural abundance ^{15}N CP/MAS NMR analysis of nitrogen-containing polymers is not only feasible but is sensitive to composition, conformation and crystalline form. We are continuing our NMR studies and molecular modeling of these and related synthetic polymers.

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