Application of the J Cross-Polarization Technique to ^{15}N NMR of Polyamides in Solution

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ABSTRACT: We have utilized the J cross-polarization technique (JCP) to obtain natural-abundance ^{15}N NMR spectra of polyamides in solution. For polymers of DP $\sim$ 50 in 20% solutions, ^{15}N resonances of the amide nitrogens obtained in less than 1 h yielded signal-to-noise (S/N) ratios of about 4 using 5-mm sample tubes at room temperature with $H_0 = 2.3$ T. The JCP experiment provides a signal enhancement equal approximately to the ratio of the magnetogyric ratios ($\gamma_H/\gamma_N \sim 10$), which equates to a time savings of $\sim$100 compared to a conventional FT experiment without NOE. Additional time saving results from being able to repeat the pulse sequence at the proton T_1 rather than the usually longer nitrogen T_1. The ^{15}N chemical shifts of nylon 6,n polyamides can be differentiated for n = 6, 8, 10, and 12. In a nylon 6/6,12 copolyamide, the ^{15}N chemical shifts provide information about sequence distribution and, it appears, differential changes in conformation or solvation at elevated temperature. The ^{15}N shifts showed strong deshielding depending on the solvent used: sulfuric acid, trifluoroacetic acid, formic acid, and 1,1,1,3,3,3-hexafluoro-2-propanol. The deshielding increases with increasing acid strength (pK_a) of the solvent. The proton exchange rate at the NH of the amide increases in strong acids as the amide/acid ratio approaches 1/1 (increased nylon concentration). Variation in the ^{15}N shifts was greatest in the concentration study of nylon 66 in TFA. There was little dependence on temperature except for the ^{15}N chemical shifts of the nylon 6,12 component of the copolyamide.

Introduction

Nitrogen-15 chemical shift studies of polypeptides and polyamides by Kricheldorf and Hull[1] demonstrate that ^{15}N chemical shifts are substantially more sensitive to sequence lengths than are ^{13}C shifts. Unfortunately, the sensitivity of natural-abundance ^{15}N nuclear magnetic resonance (NMR) is low. The small magnetogyric ratio (γ) and low abundance yield a sensitivity some 50 times less than that of ^{13}C NMR; the long T_1's of ^{15}N aggravate the situation further. The nuclear Overhauser effect (NOE) can provide signal enhancements of up to $\sim$4 times for ^{15}N under optimum conditions, but because the magnetogyric ratio of ^{15}N is negative, signal intensity can be lost for ordinary proton-decoupled Fourier transform (FT) experiments when nondipolar mechanisms contribute to longitudinal relaxation.

In contrast, the J cross-polarization technique[2] (JCP) provides a signal enhancement of $\gamma_H/\gamma_N \sim 10$, which equates to a savings in time of $\sim$100 compared to a conventional FT experiment without NOE. Additional time saving results from being able to repeat the pulse sequence at the proton T_1 rather than the usually longer nitrogen T_1.

We have utilized the JCP technique to study the dependence of the ^{15}N chemical shifts of polyamides on solvent acidity, nylon concentration, and temperature. The full JCP signal enhancement obtained for the samples (with two exceptions) indicates that proton exchange at the amide nitrogen is slow compared to the time scale of the cross-polarization period of 8 ms.

Experimental Section

Samples. Nylons 6, 6,10, and 6,12 were obtained from Aldrich Chemical Co. Nylons 11, 12, 66, and 68 were from du Pont Co. du Pont also supplied a copolyamide of 85/15% nylon 6,12/6 (MW $\sim$ 5800). Nylon 66 had a molecular weight of $\sim$3700 while all others ranged from MW = 10 000 to MW = 20 000 with a polydispersity of $\sim$2.

The four solvents in the study were 98% sulfuric acid (H_2SO_4, pK_a = −3), trifluoroacetic acid (CF_3COOH, pK_a = 0.2), 98% formic acid (HCOOH, pK_a = 3.8), and 1,1,1,3,3,3-hexafluoro-2-propanol (($(CF_3)_2CHOH$, pK_a = 9.3).[3] The samples, which were prepared at du Pont, were 20% w/v solutions in each solvent except for the copolyamide, which was 24% w/v, and the nylon 66. Nylon 66 solutions were 11, 25, 39, and 44% w/v for the concentration study.

^{15}N NMR. The JCP experiments were run at 2.3 T on a modified Varian HA-100 with external fluorine lock. Experimental conditions were as follows: 5-mm spinning sample, 25 °C, 8-ms cross-polarization time, broad-band proton decoupling, 1000 accumulations at 3-s intervals (experiment time, 48 min), 1200-Hz sweep width/quadrature detection, 2K data points, and 2-Hz exponential line broadening. A signal-to-noise ratio (S/N) of 3–4 was typical. Two thousand accumulations were done on the copolyamide. Chemical shifts were measured against an external standard of ^{15}N-enriched acetamide in water (saturated solution). These values were referenced to external 15 M aqueous acidified $^{15}NH_4NO_3$ (=0 ppm):

$$\delta_{^{15}NH_4^+} = 89.5 + \delta_{(CH_3CO^{15}NH_2)}$$

In the temperature study of nylons 6 and 6,12 and the copolyamide, the ^{15}N shift of enriched acetamide solution was measured at each temperature prior to and following the collection of data.

Results and Discussion

Kricheldorf et al.[1,4,5] have done ^{15}N NMR studies of polypeptides containing glycylglycine units and polyamides in various acid solutions (CF_3COOH, HCOOH, 2,2,2-trifluoroethanol, and fluorosulfonic acid). In these studies, 1.5 g of sample was used to prepare solutions in 20-mm sample tubes and data collection times were 0.5–2 h at 2.1 T. A favorable NOE contributed to the S/N.

Utilizing the JCP technique,[2] we obtained comparable S/N ratios with solutions containing 0.15 g of sample in 5-mm sample tubes and data collection times of 0.4–1.6 h (majority of experiments were 0.8 h). These comparable data collection times for a sample one-tenth that employed in the above FT experiments[1,4,5] equate to a 100-fold savings in time for the JCP experiment. Ideally, if our sample coil had been able to accommodate a tube containing 1.5 g of polyamide in solution, a data collection time of $\sim$30 s would have sufficed.

Kricheldorf has determined[6] that the ^{15}N NOE approaches −1 for many polymers in high magnetic fields (e.g., NOE = −1.1 for polyglycine in CF_3COOH (TFA) at

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Table I
^{15}N Chemical Shifts of Nylons in Solution[a]

nylon	H_2SO_4	TFA	HCOOH	$(CF_3)_2$-CHOH
6	124.0	118.0 (118.0)[b]	106.5 (105.0)[d]	102.2
11	124.9	120.8		
12	125.0	120.8 (121.1)[b]		
66	125.5	118.2 (117.9)[c]	106.6	103.3
68	124.2	119.7 (119.8)[c]	107.1	103.1
6,10	124.1	119.1 (119.6)[c]	107.7	102.7
6,12	124.2	119.9	108.4	102.2

[a] All chemical shift data referenced to $^{15}NH_4^+ = 0$ ppm (see text). (Chemical shift data ±0.1 ppm (±0.2 ppm in $(CF_3)_2CHOH$)). [b] Reference 4. [c] Reference 7. [d] Reference 5.

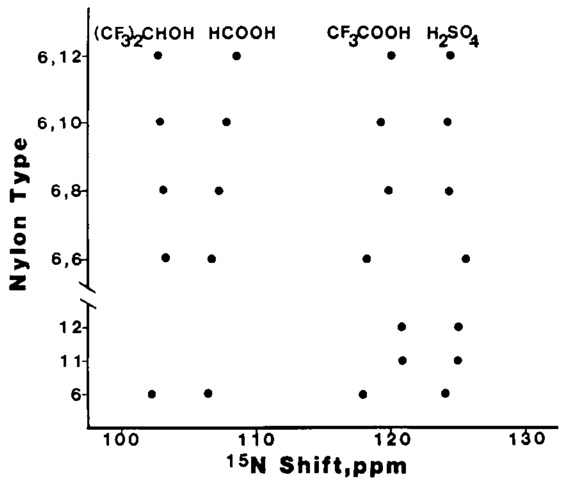

Figure 1. ^{15}N chemical shifts of polyamides in 1,1,1,3,3,3-hexafluoro-2-propanol, formic acid, trifluoroacetic acid, and sulfuric acid.

9.2 T and 32 °C). In the cross-polarization experiment, however, the signal enhancement depends only on the ratio of the magnetogyric ratios (γ_H/γ_N) and not on their signs. Therefore, rather remarkable sensitivity could be achieved for ^{15}N (and other low-γ nuclei) through the combination of cross-polarization techniques, high magnetic field strengths, and, when available, large samples. The caveat for cross-polarization experiments is that the low-γ and high-γ species must couple. The practical lower limit for this coupling in our present JCP spectrometer is a few hertz.

Table I lists the ^{15}N chemical shifts we obtained for nylon *n* and nylon 6,*n* sequences in the various solvents. Corresponding literature data[4,5,7] for common solvents are also included. The latter, which were referenced to $^{15}NO_3^-$, were converted relative to $^{15}NH_4^+$ using the relation

$$\delta_{^{15}NH_4^+} = 354.2 - \delta_{^{15}NO_3^-}$$

such that nylon 6/TFA is equal in both sets of data. The chemical shift data are in good agreement for the nylon/solvent combinations common to both studies.

The general formula for nylon *n* is $-[(CH_2)_xCONH]_y-$, where $x = n - 1$. As the length of the aliphatic chain increases, the amide signal shifts downfield (increasing δ). This downfield shift has been attributed to the increase in basicity of the amide group as the chain length increases and, thus, an increase in the extent of protonation of the amide.[1,7]

The general formula of nylon 6,*n* is $-[(CH_2)_3NHCO(CH_2)_xCONH(CH_2)_3]_y-$, where $x = n - 2$. Figure 1 is a plot of ^{15}N chemical shifts of the various nylons with respect to the four solvents used in this study. A previous study of nylons 6,*n* in TFA has been reported.[7] The large downfield shifts are attributed to deshielding of the amide nitrogen by the presence of hydrogen bonding and/or protonation at the amide carbonyl.[2,5] The deshielding increases with increasing acid strength ($(CF_3)_2CHOH$ < HCOOH < TFA < H_2SO_4). The ^{15}N shifts in HCOOH solutions show the most sensitivity to sequence length variation in the 6,*n* nylons, presumably because of the smaller size of formic acid and, thus, its ability to better solvate the chain.

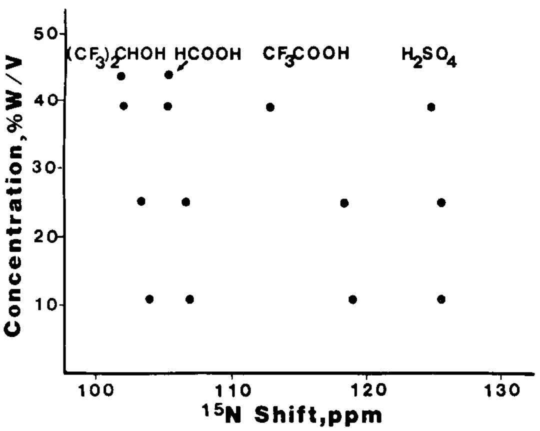

Figure 2. ^{15}N chemical shifts of nylon 66 vs. concentration in 1,1,1,3,3,3-hexafluoro-2-propanol, formic acid, trifluoroacetic acid, and sulfuric acid.

Table II
^{15}N Chemical Shifts[a] vs. Temperature

			copolyamide	
T,[b] °C	nylon 6[c]	nylon 6,12[d]	nylon 6[c]	nylon 6,12[e]
32	118.0	119.8	118.4	118.9
36	117.9	119.8	118.1	118.9
42	117.7	119.8	117.9	118.7
49	117.6	119.7	117.9	118.7
56	117.4	119.6	117.7	118.1

[a] Solvent is trifluoroacetic acid; all chemical shift data referenced to $^{15}NH_4^+ = 0$ ppm. [b] All temperatures ±1 °C. [c] Data ±0.2 ppm. [d] Data ±0.1 ppm. [e] Data ±0.4 ppm.

Figure 2 is a plot of ^{15}N chemical shifts of nylon 66 in the four solvents at various concentrations (11, 25, 39, and 44% w/v). No signal was obtained from the 44% solutions of nylon 66 in H_2SO_4 or TFA. The concentration dependence (11–39%) of the shift in TFA was 6.2 ppm, changing by 5.5 ppm between 25% and 39%. In H_2SO_4 the corresponding shift with concentration was less than 1 ppm though the signal intensity of the 39% solution decreased. The concentration dependence of the ^{15}N shift of the nylon in HCOOH and $(CF_3)_2CHOH$ was less then 2 ppm, with no significant decrease in signal intensity.

In a study of small amides in TFA–chloroform solutions, Stewart et al.[9] found that fast proton exchange occurs at the NH proton when the amide/TFA ratio is approximately 1/1. The ratio of amide group to TFA in our study is ~1/8 at 11% and ~1/2 at 39%. In the case of fast proton exchange at the NH, JCP would be ineffective and result in loss of signal as observed for the 44% solutions in TFA and H_2SO_4, where the amide/acid ratio approaches 1/1. The upfield shift of the ^{15}N signal of 39% nylon 66/TFA solution may be associated with the formation of the postulated cyclic hydrogen-bonded complex between amide and solvent.[9]

Because of the large concentration dependence of nylon 66 in TFA, it was chosen as the solvent in which to study

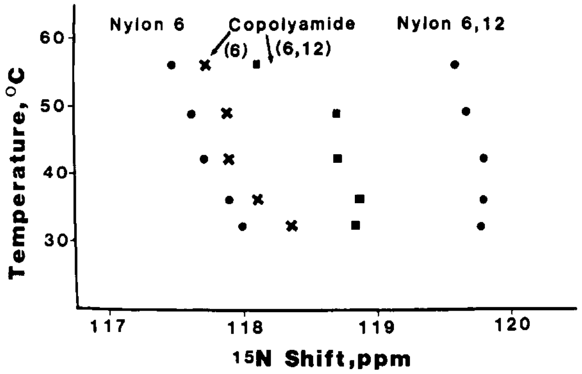

Figure 3. ^{15}N chemical shifts of polyamides in trifluoroacetic acid vs. temperature. The nylon 6,12 component of the copolymer shifts upfield at higher temperatures.

temperature dependence of a copolyamide and its two components, 6 and 6,12. Figure 3 is a plot of temperature vs. ^{15}N chemical shifts of nylons 6 and 6,12 and of the copolyamide (85% 6,12/15% 6) in TFA. Nylons 6 and 6,12 as well as the 6 component of the copolymer showed little temperature dependence from 31 to 56 °C. The 6,12 component showed little dependence up to 49 °C and then shifted upfield at 56 °C, approaching the 6 component. The chemical shift differences ($\Delta\delta$) for nylon 6 and the 6 component were 0.6–0.7 ppm while $\Delta\delta$ for nylon 6,12 was 0.2 ppm from 31 to 56 °C (Table II). For the 6,12 component of the copolymer, $\Delta\delta$ was 0.2 ppm over the 31–49 °C temperature range; from 49 to 56 °C, however, $\Delta\delta$ for the 6,12 component was 0.6 ppm. The large shift seems to indicate a conformational change as opposed to a degradation since data collected following the high-temperature measurements were in very good agreement with data collected prior to elevation of temperature to 56 °C. The change apparently decreases the extent of protonation and/or decreases the basicity of the amide groups since the amide signal of the 6,12 component shifts upfield toward the signal of the shorter chain, less basic 6 component of the copolyamide. Since there was no appreciable change in the ratio of peak intensities for the copolyamide, there should not have been an appreciable increase in the rate of proton exchange at the NH of the amide. Further temperature studies may reveal whether TFA acts as the Θ solvent for the copolyamide at elevated temperatures.

Conclusions

Utilizing the J cross-polarization technique in liquids has allowed us to undertake experiments formerly impractical for ^{15}N NMR: a decrease in experimental time by a factor of 100 was demonstrated. We have differentiated the ^{15}N chemical shifts of a copolyamide and extended the measurements of ^{15}N chemical shifts in nylon *n* and nylon 6,*n* polyamides. We have determined solvent and concentration dependences of nylon ^{15}N chemical shifts and studied the effect of temperature on a copolyamide and its component nylons.

Our data imply that, in the presence of excess acid, protonation and/or hydrogen bonding takes place at the oxygen of the amide carbonyl. As a result, the nitrogen is deshielded and the ^{15}N signal shifts downfield with increasing acid strength. As the amide/acid ratio approaches 1/1 in strong acids, however, our results show an increase in the rate of proton exchange at the NH of the amide and an upfield shift of ^{15}N signal in the nylon 66/TFA solution.

The amount of information which can be gained relating to nitrogen chemistry would be a boon not only for nylons and other industrial products but in the field of biochemistry as well, where nitrogen is a most common element and samples are often small. In the case of fast proton exchange, the system could be cooled and observed in the region of slow exchange as necessary.

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Determination of Short-Chain Branching in Polyethylenes by Pyrolysis–Hydrogenation Glass Capillary Gas Chromatography

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ABSTRACT: Pyrolysis–hydrogenation glass capillary gas chromatography was applied to the determination of the short branches in low-density polyethylenes (LDPE). The relative peak intensities of characteristic key isoalkanes in the C_{11} region such as 4-methyl-C_{10} for methyl branches, 3-methyl-C_{10} for ethyl branches, and 5-methyl-C_{10} for butyl branches were correlated with the associated short branch contents in LDPE's by comparing the data of reference model ethylene–α-olefin copolymers with known short branch contents. As a whole, butyl branches are most abundant, ethyl branches occur less frequently, and methyl branches are only a minor structural feature along the polymer chain of LDPE's. The estimated total branch contents for various LDPE's were in fairly good agreement with those obtained by the conventional IR method. The possibility of estimating amyl branch contents was also discussed.

Since the first report on the branches along the polymer chain in polyethylene (PE) by Fox and Martin[1] in 1940, various analytical methods have been adopted for characterization of chain branching. Among these are IR,[2-5] ^{1}H NMR,[6] ^{13}C NMR,[7-10] γ radiolysis,[2,11,12] and pyrolysis–hydrogenation gas chromatography (PHGC).[13-22]

Earlier work with a packed separation column[13,14] showed that PHGC was a very promising technique for

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